Hydrogen Energy: Production, Storage, Transportation and Safety

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Lecture - 23
Electrolysis of Water for Hydrogen Production

In the last class we have seen hydrogen production by means of thermo chemical cycles, where the required energy for water splitting can come from any of the thermal means, whether it is from nuclear energy or from solar thermal. And the hydrogen is being produced by splitting up of water by means of cycles, where certain chemicals they undergo a series of steps finally, producing hydrogen and oxygen.

Today we will look at Electrolysis of Water; this is again a method where we can split water to produce hydrogen and oxygen.

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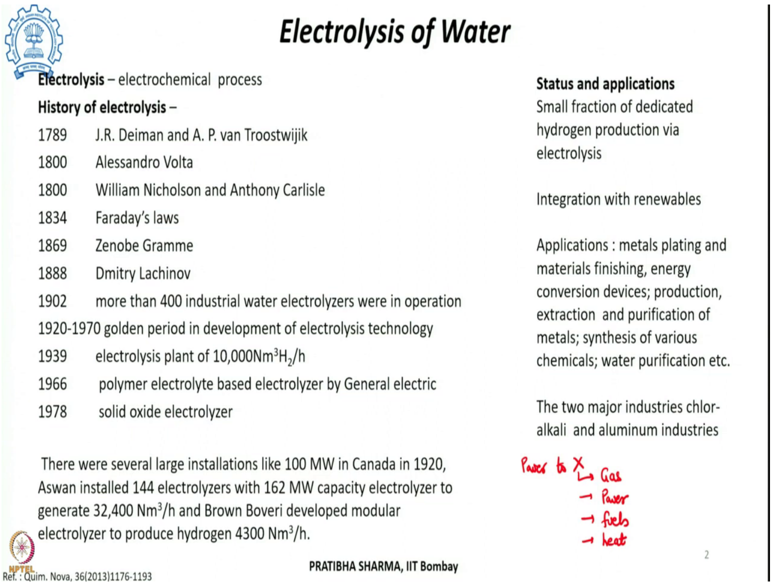

Electrolysis of Water

Electrolysis – electrochemical process

History of electrolysis –

1789	J.R. Deiman and A. P. van Troostwijik
1800	Alessandro Volta
1800	William Nicholson and Anthony Carlisle
1834	Faraday's laws
1869	Zenobe Gramme
1888	Dmitry Lachinov
1902	more than 400 industrial water electrolyzers were in operation
1920-1970	golden period in development of electrolysis technology
1939	electrolysis plant of 10,000Nm^{3}H$_2$/h
1966	polymer electrolyte based electrolyzer by General electric
1978	solid oxide electrolyzer

There were several large installations like 100 MW in Canada in 1920, Aswan installed 144 electrolyzers with 162 MW capacity electrolyzer to generate 32,400 Nm^3/h and Brown Boveri developed modular electrolyzer to produce hydrogen 4300 Nm^3/h.

Status and applications

Small fraction of dedicated hydrogen production via electrolysis

Integration with renewables

Applications : metals plating and materials finishing, energy conversion devices; production, extraction and purification of metals; synthesis of various chemicals; water purification etc.

The two major industries chlor-alkali and aluminum industries

Power to X
↳ Gas
→ Power
→ fuels
→ heat

Ref. : Quim. Nova, 36(2013)1176-1193

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This is an electrochemical process and it is important in the sense because, hydrogen being produced by means of electrolysis is pure, it can be about 99.999 percent pure, as well depending upon the technology used and it is a major technology.

It offers several advantages, like we can we know that the renewable power is penetration is increasing. The renewable power cost is decreasing, at the same time the renewable energy systems they have a supply demand mismatch because of the intermittency. Whether it is solar or wind water electrolysis can be integrated here such that the excess of electricity whenever being produced can be stored in the form of hydrogen produced by means of electrolysis and then it can be used as required.

So, it provides a sort of flexibility with the renewable energy system by either providing options like power to X, where this X can be either gas. So, the renewable based electricity can be used to produce hydrogen and that can be converted to gas, that is hydrogen or can be used for producing methane, which can be used for various application or it can be for power to power.

So, the hydrogen which is being produced can be used in a fuel cell to produce power again, it can be power to fuels where the hydrogen produced can be used for producing liquid fuels or it can be for hydrogen to power to heat, power used to produce hydrogen to produce heat. So, it offers a wide variety of possibilities when integrated with renewable energy systems.

The electrolysis technology it is not a new technology, it is since last more than 200 years the development have been there. If you look at the history of electrolysis in the year as early as 1789 J R Deiman and A P Van Troostwijik, they for the first time observed gases being released when they inserted 2 gold wire into a tube filled with water and subjected to electricity.

This after that in 1800 Alessandro Volta, he invented the Voltaic pile, a week after this invention William Nicholson and Anthony Carlisle they have in fact, identified they have performed the electrolysis and producing gases. Later these gases evolved were identified as hydrogen and oxygen.

The explanation to the process was first provided with the Faradays law coming up in the year of 1834, when it was explained that the amount of gases being produced is related to the amount of charge being fed in the process. In the year 1869 Zenobe Gramme, he in came up with the Gramme machine and this was for the first time economical hydrogen production by means of this route.

In the year 1888 Dmitry Lachinov, for the first time he came up with the industrial scale hydrogen production using an electrolyzer and this was about by 1902, that more than 400 industrial water electrolyzers were in operation.

So, it is said that the 1920 to 1970 was a sort of golden period in the development of electrolysis technology, where the most of the components, most of the technology they were invented and they evolved during this period, their components they came into picture in this particular duration.

In 1939, the first large scale electrolysis plant it was commissioned and this had a capacity of 10000 normal meter cube of hydrogen produced per hour. In 1948, the first alkaline water electrolysis was performed by the Lurgi plant came into picture, then 1966 the polymer electrolyte membrane based electrolyzer, this was first being commissioned by the general electric. And it was in 1978, the solid oxide electrolyzers they were being considered for electrolysis of water.

So, there were several large scale installations even as early as 1900, early 1900s like about 100 megawatt in Canada up electrolyzer plant was installed, then as one they installed 144 electrolyzers with a capacity of 162 megawatt and that could generate 32400 normal meter cube of hydrogen per hour. ABB the Asian Bound Boveri they developed modular electrolyzers that could produce hydrogen of capacity 4300 normal meter cube per hour.

So, the technology ways back to more than 200 years, but it was when the production of hydrogen started from hydrocarbons like steam reforming or coal gasification. Then this process of electrolysis was the interest in it declined. The reason was the process from hydrocarbons, hydrogen production that was economical was energy efficient. So, the current status is out of the total global hydrogen production a small fraction is by means of water electrolysis, roughly 0.03 percent of it is by water electrolysis.

There are two major industries which are performing electrolysis like Chloralkali industry where hydrogen comes out as a byproduct. So, on electrolysis of an aqueous solution of brine get NaOH, chlorine and hydrogen as a byproduct. Also aluminum electro winding industry uses electrolysis technique; there are various applications of electrolysis of water.

Other than these like metal plating and metal finishing, it is being integrated with energy conversion devices, production extraction purification of metals, synthesis of various chemicals, water purification systems. So, there are various still the applications of electrolysis of water. Now, in order to understand the electrolysis of water, let us look at the basics of it.

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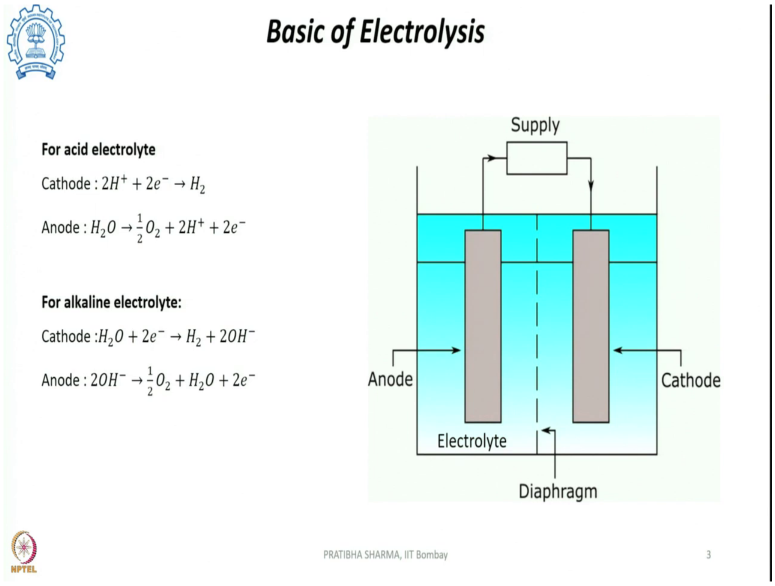

Basic of Electrolysis

For acid electrolyte

Cathode : $2H^+ + 2e^- \rightarrow H_2$

Anode : $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$

For alkaline electrolyte:

Cathode :$H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Anode : $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

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If we look at a simple electrochemical cell which is the smallest unit of an electrolyzer, when combined in different ways forms an electrolyzer; that how we can combine those electrolytic cells we will see in the later part of the in the late in the other classes.

So, this is an electrochemical cell having two electrodes an anode and a cathode being separated by means of a separator or a diaphragm. When an electric current is passed through it then the reactions occurs in such a way that the electrons flows through the outer circuit and ions within the electrolyte from one electrode to another.

Now, depending upon which electrolyte it is, whether it is an acidic electrolyte H^+ ion flows, if it is alkaline electrolyte then OH^- ions flows. The ions flow in such a manner that H^+ in case of acid electrolyte they reach at the cathode combined with the 2 electron and hydrogen is evolved at the cathode side.

Similarly, water gets splitted and H^+ ions are released, which pass through this electrolyte through this separator across the electrolyte to reach to cathode and oxygen in this process is evolved at the anode side. So, the oxygen evolves at anode and hydrogen evolves at the cathode side. So, this is how the basic electrolytic cell works.

In order to get an idea about the various reactions that occurs, what is the thermodynamics behind the process involved, electrochemical process of the electrolysis, what is the kinetics involved, how the cell performs what is the efficiency, we will start with the basic understanding of the process.

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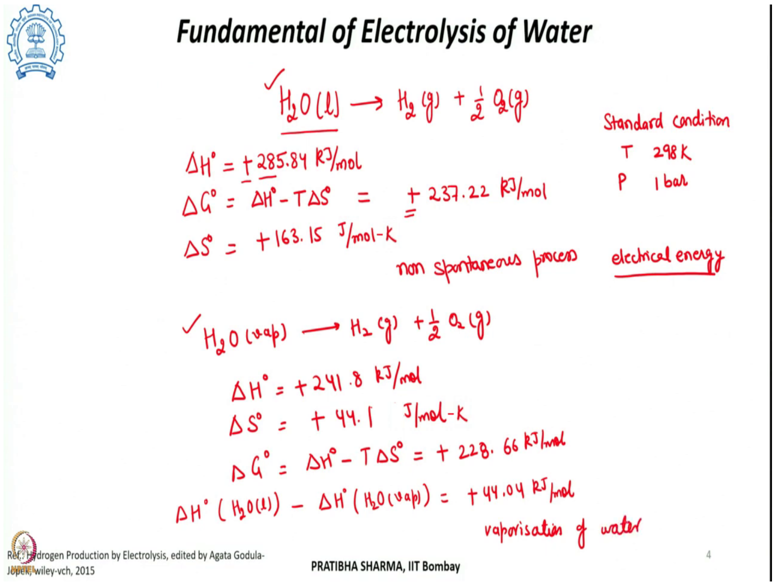

Fundamental of Electrolysis of Water

$$\checkmark\ \underline{H_2O(l)} \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

$$\Delta H^\circ = \underline{+}\,\underline{285}.84\ kJ/mol$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \ = \ \underline{\underline{+}}\,237.22\ kJ/mol$$

$$\Delta S^\circ = +163.15\ J/mol\text{-}K$$

non spontaneous process

Standard condition

T 298 K

P 1 bar

<u>electrical energy</u>

$$\checkmark\ H_2O(vap) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$$

$$\Delta H^\circ = +241.8\ kJ/mol$$

$$\Delta S^\circ = +44.1\ J/mol\text{-}K$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = +228.66\ kJ/mol$$

$$\Delta H^\circ(H_2O(l)) - \Delta H^\circ(H_2O(vap)) = +44.04\ kJ/mol$$

vaporisation of water

Ref.: Hydrogen Production by Electrolysis, edited by Agata Godula-Jopek, wiley-vch, 2015

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So, fundamentals of electrolysis of water so, the basic reaction we can write is that water in its liquid state dissociates to give hydrogen, gas and oxygen. Now, in this step the liquid water which undergoes the dissociation, the enthalpy change of the process is 285.84 kilojoule per mole. Now, this is highly endothermic. The Gibb's free energy change in the process under standard conditions is (delta H - T delta x S), where delta S is given by 163.15, this is 163.15 joule per mole kelvin.

So, we can find out the delta G for this process and this comes out to be 237.22 kilojoule per mole, these are under standard conditions. By standard conditions we mean temperature of 298 K and a pressure of 1 bar which is approximately 1.01 atmosphere.

Now, we can see that the enthalpy change is highly endothermic as such the delta G is positive, thus it is in it is a non spontaneous process and it requires certain amount of energy, which needs to be fed for the splitting up of water. And that required energy comes in the form of electrical energy in the process.

So, when we supply this electrical energy in that case the water splits into hydrogen and oxygen, the constituents. Now, this is when the splitting up of water occurs when it is in liquid state. Now, if it is in vapor state, it splits to give hydrogen and oxygen. For this particular process, the value of delta H^0 is 241.8 kilojoule per mole, delta S^0 for this process is 44.1 joule per mole kelvin and delta G^0 can be found from this at the standard temperature pressure conditions that comes out to be 228.66 kilojoule per mole.

So, this is when the starting water is in liquid state or if it is in vapor state. The difference between the delta H values for the two states, when water is in liquid state to when water is in vapor state and that equals to 44.04 kilojoule per mole. And this is nothing but the required enthalpy for vaporization of water.

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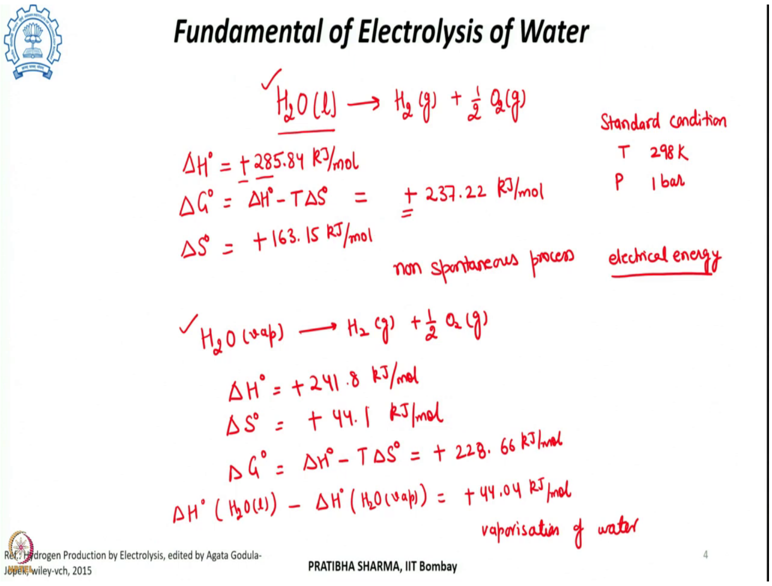

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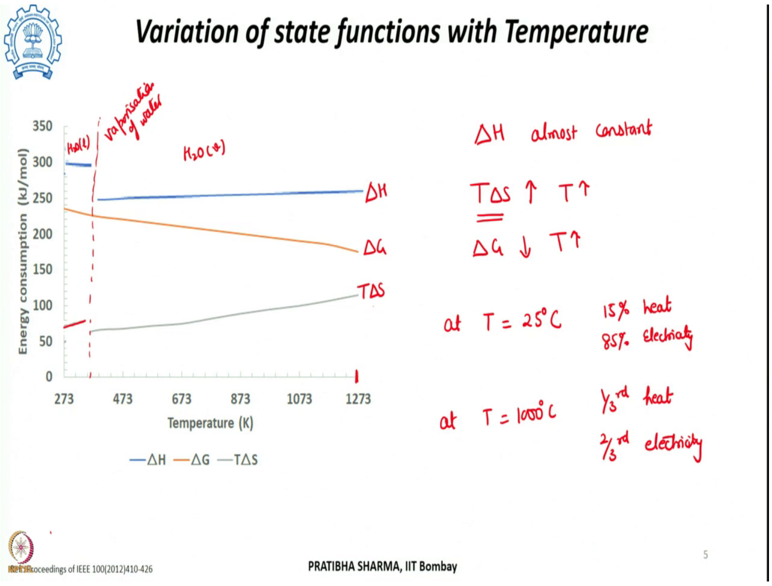

Variation of state functions with Temperature

ΔH almost constant

TΔS ↑ T↑

ΔG ↓ T↑

at T = 25°C 15% heat
85% electricity

at T = 1000°C 1/3rd heat
2/3rd electricity

Ref.: Proceedings of IEEE 100(2012)410-426

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Now, if we look at the temperature dependence of these thermodynamic functions, these state functions and if we plot these functions, then we can see that at 100 degree centigrade, approximately at 100 degree centigrade there is a disconnect between the lines and this corresponds to the vaporization of water. So, prior to that it is in liquid state and thereafter it is in vapor state.

So, if we see the values, this is the delta H value the change in the enthalpy of the reaction it remains almost constant in the entire temperature range of study. So, the enthalpy change which is required for splitting up of 1 mole of water to produce its constituent hydrogen and oxygen this is almost constant, throughout the temperature range as the temperature increases till even the 1000 degree centigrade.

If we see the value for (T x delta S), again there is a discontinuity in the beginning that is corresponding to the vapor phase and then this discontinuity this corresponds to the vaporization of water. But (T x delta S) we can see that it increases as the temperature of operation increases.

The change in delta S is nominally small, but the product (T x delta S) it increases. At the same time the value of delta G it decreases as the temperature increases in the process. At a temperature of 25 degree centigrade, it is observed that 15 percent of the requirement is of heat or the thermal energy. The contribution of which comes from (T x delta S).

And the remaining 85 percent is by means of electricity, which changes at 1000 degree centigrade; however, the situation changes that one-third of the energy requirement is in the form of heat or the thermal energy requirement and two-third of it is in the form of electricity in the process.

Now, these equations which we have mentioned, they have a temperature dependence.

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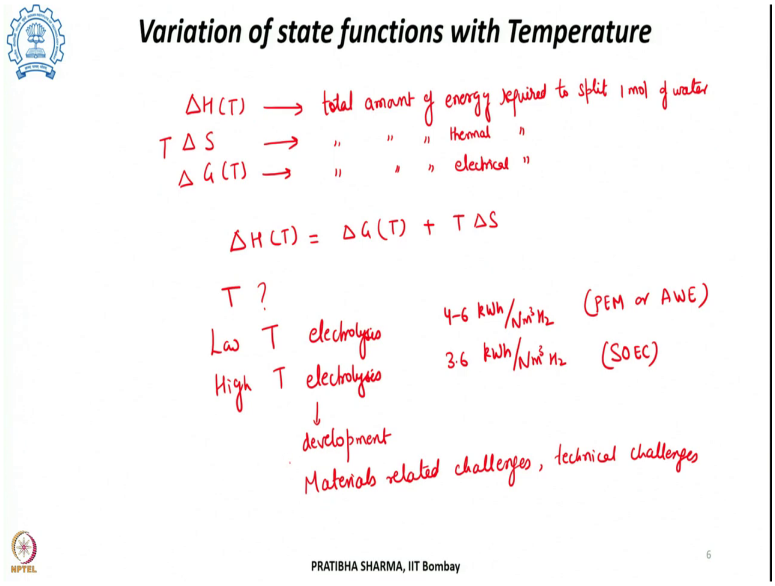

Variation of state functions with Temperature

$\Delta H(T) \longrightarrow$ total amount of energy required to split 1 mol of water

$T\Delta S \longrightarrow$ " " " thermal "

$\Delta G(T) \longrightarrow$ " " " electrical "

$$\Delta H(T) = \Delta G(T) + T\Delta S$$

T ?

Low T electrolysis 4-6 kWh/Nm^3 H_2 (PEM or AWE)

High T electrolysis 3.6 kWh/Nm^3 H_2 (SOEC)

↓

development

Materials related challenges, technical challenges

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So, all these state functions whether it is delta H, whether it is delta S or whether it is delta G they have a sort of temperature dependence. The term (T x delta S) it has temperature dependence and this delta H represents the total amount of energy required to split one mole of water. In the process (T x delta S) term requires the total amount of energy the thermal energy or heat energy which is required in the process. While delta G represents the total amount of electrical energy required to split 1 mole of water.

So, the total energy wherein certain contribution is from electrical energy and the remaining contribution is from thermal energy. Now, what temperature is best for performance of electrolysis, can be decided by means of the electrical energy input, how much is the energy consumed, what is the cost which is required for producing hydrogen. So, if we look at the low temperature processes, low temperature electrolysis like the polymer electrolyte membrane, based electrolysis or alkaline water electrolysis that we will see in more detail later.

For low temperature electrolysis, roughly the energy requirement is about 4 to 6 kilowatt hour per normal meter cube of hydrogen being produced, this is for PEM or water alkaline water electrolyzers.. While for high temperature electrolysis this energy demand is about 3.6 kilowatt hour per normal meter cube of hydrogen being produced, so, this is for solid oxide electrolyzer.

So, we can see that high temperature electrolysis has advantage of lower electricity requirement, at the same time the thermal energy requirement can also be fed by means of the waste heat which is available from the industrial processes or from other processes.

But the major disadvantage is that the high temperature electrolysis are still under development. And there are challenges, there are materials related challenges, operation at such high temperatures and there are certain technical challenges like when we are using pressurized water then the associated leaks with it.

So, there are several other challenges that still needs to be considered before the high temperature electrolysis or solid oxide electrolysis could be commercialized. Now, let us look at the cell voltages the reversible and the thermo neutral cell voltages.

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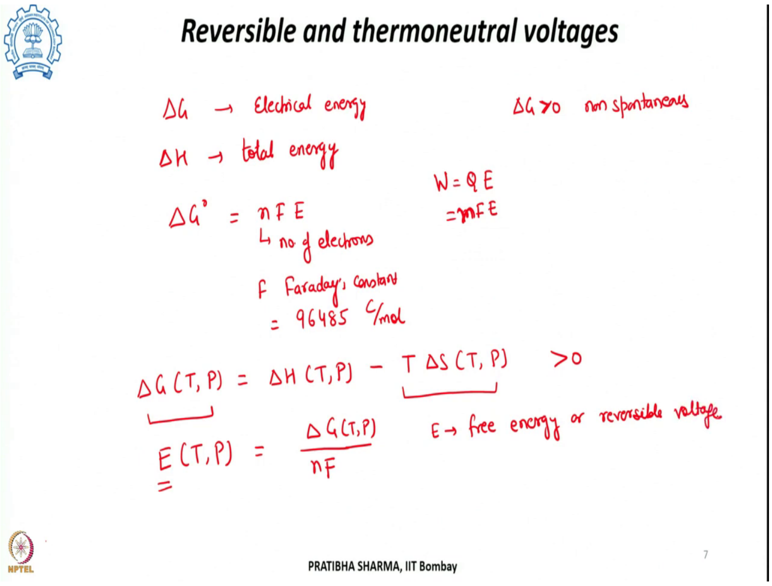

Reversible and thermoneutral voltages

$\Delta G \rightarrow$ Electrical energy

$\Delta G > 0$ non spontaneous

$\Delta H \rightarrow$ total energy

$W = QE$

$= nFE$

$\Delta G^{\circ} = nFE$

↳ no of electrons

F Faraday's constant

$= 96485$ C/mol

$$\underbrace{\Delta G(T,P)} = \Delta H(T,P) - \underbrace{T\,\Delta S(T,P)} \quad > 0$$

$$\underline{\underline{E}}(T,P) = \frac{\Delta G(T,P)}{nF}$$

$E \rightarrow$ free energy or reversible voltage

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Now, we have seen that delta G, delta H they are the required total energy at the same time the delta G is the electrical energy requirement and delta H is the total energy required for water splitting. Certain percentage of it is coming from (T x delta S) term.

Now, the process as we have seen delta G is greater than 0, in case of electrolysis. So, the process is non-spontaneous and we have to supply the required energy in order to accomplish the decomposition. Now, if we see the delta G value under standard conditions this is nFE. Now, we know that the work done in order to carry a charge Q across a potential difference E is given by (Q × E) and that can be written as nFE, where n is the number of charges involved.

So, here it is the number of electrons involved in the process, number of electrons transferred occurring during 1 mole of water splitting, F is the Faraday's constant. This value of Faraday constant is 96485 coulomb per mole, this is the charge on electron per mole and delta G is the free energy change associated with the reaction.

Now, for this particular transformation, if we see the delta G change as a function of temperature and pressure this is change in the enthalpy as a function of temperature and pressure minus the (T × delta S) term and this is greater than 0 for the process. So, if this transformation occurs at a temperature T and P and pressure P, then this is the related equation.

So, this is the net electrical energy input, this is the net heat required for the process. And then we can write the corresponding voltage as it is (ΔG/nF). This thermodynamic voltage E is also known as free energy voltage or reversible voltage.

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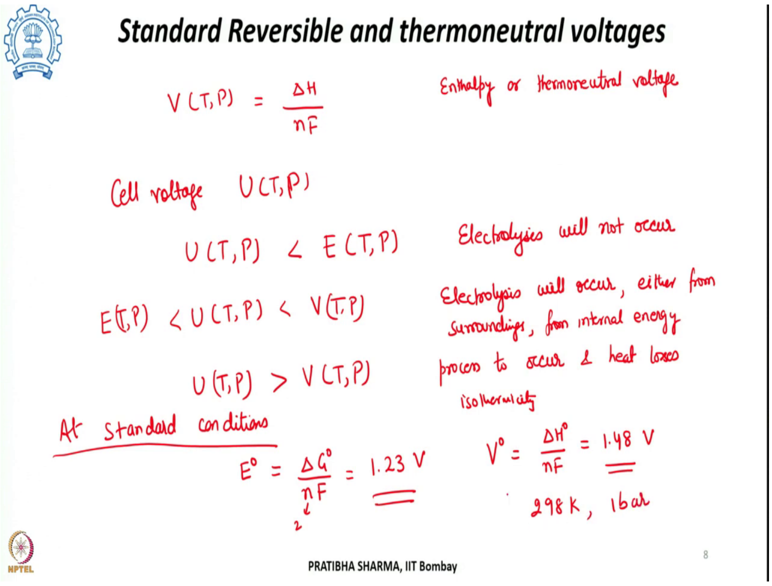

Standard Reversible and thermoneutral voltages

$V(T,P) = \frac{\Delta H}{nF}$ Enthalpy or thermoneutral voltage

Cell voltage $U(T,P)$

$U(T,P) < E(T,P)$ Electrolysis will not occur

$E(T,P) < U(T,P) < V(T,P)$ Electrolysis will occur, either from surroundings, from internal energy

$U(T,P) > V(T,P)$ process to occur & heat losses isothermality

At standard conditions

$E^\circ = \frac{\Delta G^\circ}{\underset{2}{n}F} = 1.23\ V$

$V^\circ = \frac{\Delta H^\circ}{nF} = 1.48\ V$

298 K, 1 bar

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Similarly, we can write in terms of enthalpy voltage. So, this is (ΔH/nF), this is enthalpy voltage or known as thermoneutral voltage.

Now, if we represent the cell voltage for an electrochemical cell by U, then in that case it has if we relate that with E and V. So, if this is the cell voltage, if the cell voltage is less than the reversible voltage or the free energy voltage, in that case the electrolysis will not occur, as the system will not have the required energy for the process to take place. If it the cell voltage is higher than the free energy voltage, but it is lower than the enthalpy voltage, electrolysis process will occur.

But it will require certain amount of thermal energy and that can be taken from either from the surroundings or from the internal energy of the cell and this is not a desired state and as such a cell is not operated under such conditions, because the economics does not favor.

So, the current density will be very low and it is not desirable to operate in this region; however, when the cell voltage is higher than this voltage V, which is thermoneutral voltage or enthalpy voltage, in that case the electrolysis will occur and sufficient current will flow for the process to occur.

And at the same time, there will be certain heat losses involved. So, the process will start and the heat losses will be there. So, it cannot maintain the isothermicity in the process. Let us even calculate the values for these thermodynamic voltages under standard conditions. Now, if we look at the standard conditions the value of reversible voltage under standard conditions is represented by E^0 and that can be given by ($\Delta G^0/nF$), the number of electrons transferred that is 2 and the Faraday's constant.

And finally, we can put in these values to find out the reversible cell voltage which comes out to be 1.23 volt. The thermoneutral voltage V^0 can be found by putting in the values for ($\Delta H^0/nF$) and that is approximately 1.48 volt. So, these are under standard conditions of temperature 298 K and 1 bar pressure;.

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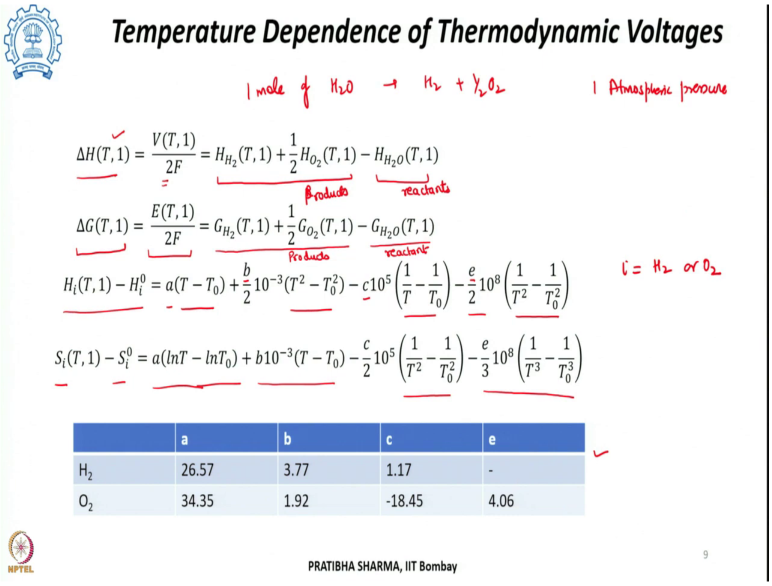

Temperature Dependence of Thermodynamic Voltages

1 mole of $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ 1 Atmospheric pressure

$$\Delta H(T,1) = \frac{V(T,1)}{2F} = \underbrace{H_{H_2}(T,1) + \frac{1}{2}H_{O_2}(T,1)}_{\text{Products}} - \underbrace{H_{H_2O}(T,1)}_{\text{reactants}}$$

$$\Delta G(T,1) = \frac{E(T,1)}{2F} = \underbrace{G_{H_2}(T,1) + \frac{1}{2}G_{O_2}(T,1)}_{\text{Products}} - \underbrace{G_{H_2O}(T,1)}_{\text{reactant}}$$

$$H_i(T,1) - H_i^0 = a(T - T_0) + \frac{b}{2}10^{-3}(T^2 - T_0^2) - c10^5\left(\frac{1}{T} - \frac{1}{T_0}\right) - \frac{e}{2}10^8\left(\frac{1}{T^2} - \frac{1}{T_0^2}\right)$$

$i = H_2$ or O_2

$$S_i(T,1) - S_i^0 = a(lnT - lnT_0) + b10^{-3}(T - T_0) - \frac{c}{2}10^5\left(\frac{1}{T^2} - \frac{1}{T_0^2}\right) - \frac{e}{3}10^8\left(\frac{1}{T^3} - \frac{1}{T_0^3}\right)$$

	a	b	c	e
H_2	26.57	3.77	1.17	-
O_2	34.35	1.92	-18.45	4.06

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Now, if you want to see how does these vary with temperature and pressure, how does the efficiency changes understanding that we will be able to understand the performance of the electrochemical cell. So, if we look at the temperature dependence of the process for 1 mole of water being split to get hydrogen and oxygen. In that process the change in the ΔH and at say 1 atmospheric pressure can be obtained as ΔH at a temperature of T pressure 1 is given by the enthalpy voltage V/2F, where 2 is for n the number of electrons transferred.

And this is given by the change in the enthalpy by subtracting the products from the reactant side enthalpy so, the enthalpy for hydrogen under the same condition for oxygen minus that for water. Same can be done for finding out ΔG value, which is the reversible cell voltage or the free energy voltage divide by 2F and this is again subtracting Gibb's free energy of products minus that of reactant which is water here.

This change in enthalpy for species I, where this species can be hydrogen or it can be oxygen, can be obtained as there are certain constants a, b, c and e which are given by this table. The coefficients multiplied by difference in temperatures, $(T – T^0)$, $(T^2 - (T^0)^2)$, another factor $(1/T – 1/T^0)$. And similarly, $(1/T^2 - (T^0)^2)$ with different coefficients.

Now, there are different correlations available. Similarly the change in the entropy can be written. $a\times(\ln(T) – \ln(T^0) + b\times(10^{-3}\times(T – T^0) – (c/2)\times10^5\times(1/T^2 – 1/(T^0)^2) – (e/3)\times10^8 \times(1/T^3 – 1/(T^0)^3)$. T^0 is the reference temperature being considered and this is the table for these coefficients a, b, c and e.

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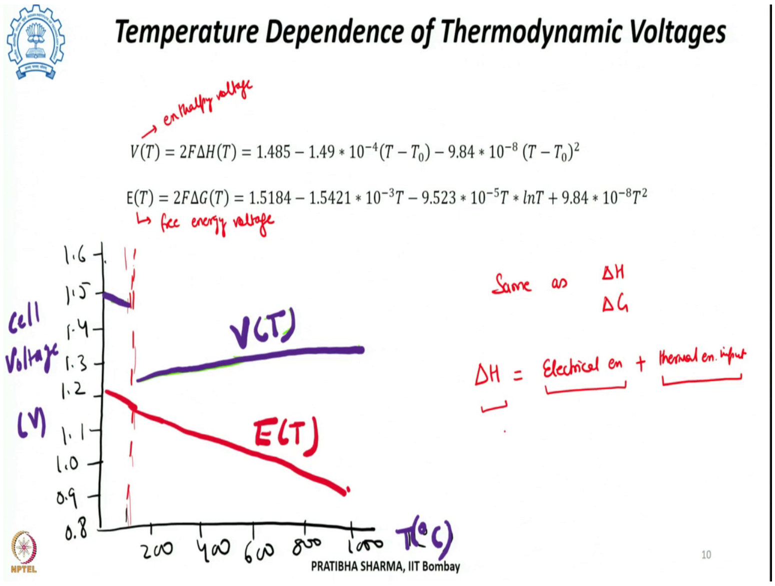

Temperature Dependence of Thermodynamic Voltages

→ enthalpy voltage

$$V(T) = 2F\Delta H(T) = 1.485 - 1.49 * 10^{-4}(T - T_0) - 9.84 * 10^{-8}\,(T - T_0)^2$$

$$E(T) = 2F\Delta G(T) = 1.5184 - 1.5421 * 10^{-3}T - 9.523 * 10^{-5}T * lnT + 9.84 * 10^{-8}T^2$$

↳ free energy voltage

Same as ΔH ΔG

$$\underbrace{\Delta H}_{} = \underbrace{\text{Electrical en}}_{} + \underbrace{\text{thermal en. input}}_{}$$

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So, there are different correlations available and if we substitute all these values we can get the value for the enthalpy voltage, substituting the value of a, b, c and d. Similarly we can get the value for the free energy voltage. This is a curve showing how these voltages vary for different temperatures.

Now, again there is a discontinuity observed in case of the enthalpy voltage corresponding to the vaporization of water at 100 degree centigrade. After that these changes in the voltage these are similar to what we have seen the changes in the thermodynamic potentials. And these are correspondingly similar as the variations in the ΔH and ΔG with temperature that we have seen earlier.

So, if we see here the V(T), it is almost remaining constant; however, the E(T) that changes as the temperature of the cell changes. As such the total required energy which is sum of the Gibbs free energy or the electrical energy input and the required thermal energy input remains almost constant. However, if certain amount of energy is fed by means of the thermal energy, by the term TΔS then the required electrical energy input reduces as such still the total energy input requires same.

This actually has a benefit, when we look at the high temperature electrolysis.

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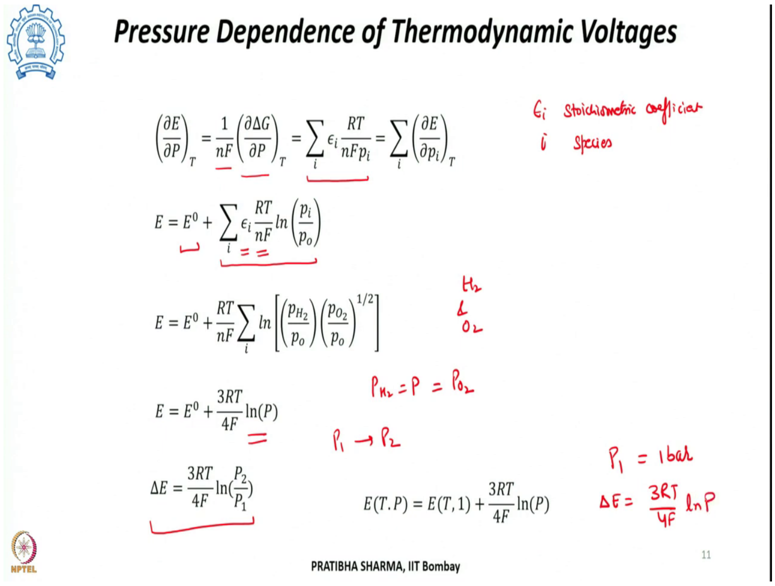

Pressure Dependence of Thermodynamic Voltages

$$\left(\frac{\partial E}{\partial P}\right)_T = \frac{1}{nF}\left(\frac{\partial \Delta G}{\partial P}\right)_T = \sum_i \epsilon_i \frac{RT}{nFp_i} = \sum_i \left(\frac{\partial E}{\partial p_i}\right)_T$$

ϵ_i Stoichiometric coefficient

i Species

$$E = E^0 + \sum_i \epsilon_i \frac{RT}{nF} ln\left(\frac{p_i}{p_o}\right)$$

$$E = E^0 + \frac{RT}{nF}\sum_i ln\left[\left(\frac{p_{H_2}}{p_o}\right)\left(\frac{p_{O_2}}{p_o}\right)^{1/2}\right]$$

H_2 & O_2

$$E = E^0 + \frac{3RT}{4F}\ln(P)$$

$P_{H_2} = P = P_{O_2}$

$P_1 \rightarrow P_2$

$$\Delta E = \frac{3RT}{4F}\ln(\frac{P_2}{P_1})$$

$$E(T.P) = E(T,1) + \frac{3RT}{4F}\ln(P)$$

$P_1 = 1$ bar

$$\Delta E = \frac{3RT}{4F} \ln P$$

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Now, if we also see the pressure dependence of the thermodynamic voltage, then (del E/del P), that is the thermodynamic voltage variation with pressure at a constant temperature is given by (1/nF) (del ΔG/ del P) and this can be written in terms of the stoichiometric coefficient (epsilon$_i$ × (RT/nF×p$_i$) whether it is hydrogen or oxygen.

And this can be summed up for the different species, whether it is hydrogen or oxygen. So, i is the individual species involved in the process. So, (del E/del p$_i$) at a constant temperature. Now, this can be integrated such that E = E^0 + Σ over the species i, stoichiometric term RT/nF; R, is the gas constant ideal gas constant at a temperature T upon nF × ln(pi/p$_0$).

Now, when we consider the different species involved both hydrogen and oxygen in the process. So, E = E^0 + (RT/nF) summed over i ln(partial pressure of hydrogen (p$_{H2}$)/p$_0$) and the stoichiometric coefficient is half; so, (p$_{O2}$/p$_0$)$^{1/2}$.

Now, in this case let us say if the pressure of hydrogen is P and that is also the pressure of oxygen. So, we can rewrite this expression as E = E^0 + 3RT/ 4F × ln(P). However, if in the process the pressure changes from P1 to P2, then we can write the change in the voltage thermodynamic voltage as 3RT/4F ln(P2/P1). And if let us say the initial pressure P1 is 1 bar, then we can write the ΔE = 3RT/4F × ln(P).

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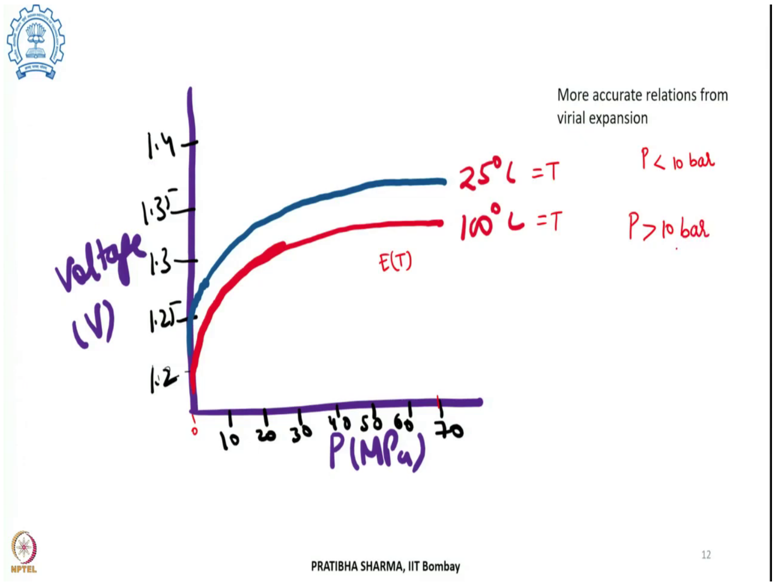

More accurate relations from virial expansion

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This can be plotted as the variation at different temperatures, let us say if the temperature being considered at 25 degree or 100 degrees centigrade. We can plot this E(T) as a function of pressure, till 70 MPa or 700 bar, we can see that with the increase in temperature the voltage reduces.

Now, these expressions that we have derived, we have considered the ideal gas equation. We can apply ideal gas equation for pressures usually less than 10 bar. However, to get more accurate expressions the state equations needs to be considered and these state equations needs to be applied for higher pressures, than 10 bar and then we can get the accurate relationships for the variation of pressure.

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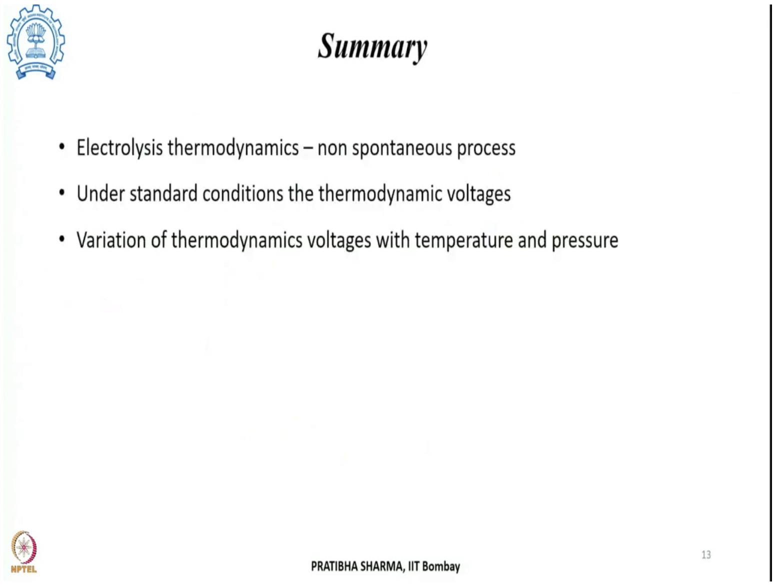

Summary

- Electrolysis thermodynamics – non spontaneous process
- Under standard conditions the thermodynamic voltages
- Variation of thermodynamics voltages with temperature and pressure

To summarize this part, we have seen the thermodynamics associated with electrolysis, we have seen that the process of electrolysis is a non-spontaneous process, where the energy is required for the process to take place, which can be supplied by means of electricity. Under standard conditions we have seen what are the different thermodynamic voltages and we have also seen how these thermodynamic voltages they vary with temperature and pressure.

In the next class we will see what are the different components involved in the electrolyzer, what are the different barriers to the flow of current and how that affects the efficiency of the electrolyzer.

Thank you.