Electrochemical Energy Storage
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Module - 01
Introduction to electrochemical energy storage and conversion
Lecture - 04
Concepts of Thermodynamics Pertinent to Electrochemical Cells

Welcome to my course Electrochemical Energy Storage. And today we are in module number-1, where I am introducing the basic principles of the chemical energy storage and conversion. And in last three lectures, I have covered basics of electrochemistry, then introduction of primary and secondary batteries, and super capacitor in general.

And in this particular lecture which is lecture number-4, I will cover the concepts of thermodynamics which are pertinent to electrochemical cell. As you can understand this topic is large and the intention is not to exactly talk about the thermodynamics at length, but whatever is necessary for you to understand the electrochemical energy storage concepts.

So, first I will start with the topic of entropy, concept of enthalpy and free energies. Then we will talk about free energy and its relation to chemical potential, conditions of equilibrium, and mass action expressions. Then, we will talk about electrochemical potential, the charge interface and associated Debye lengths.

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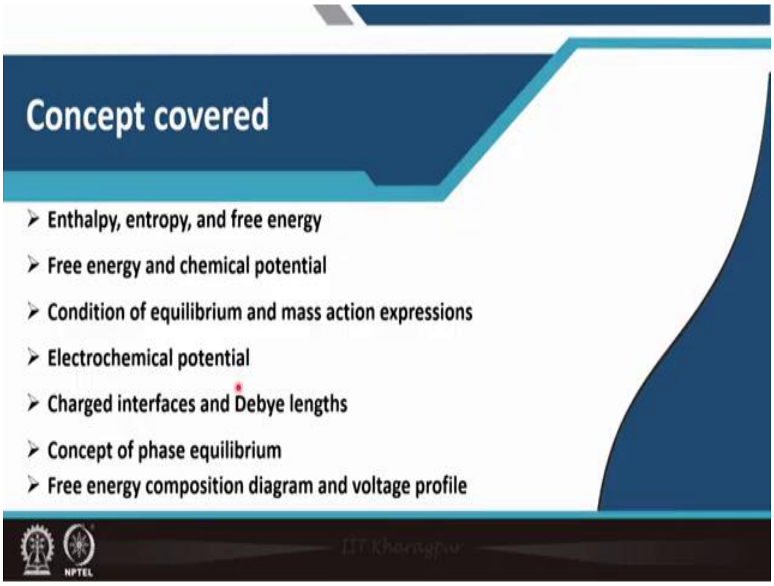

Concept covered

- Enthalpy, entropy, and free energy
- Free energy and chemical potential
- Condition of equilibrium and mass action expressions
- Electrochemical potential
- Charged interfaces and Debye lengths
- Concept of phase equilibrium
- Free energy composition diagram and voltage profile

I will also cover the concept of phase, and concept of phase which are in equilibrium state in an electrochemical cell. And finally I will cover the free energy composition diagram and how it is related to the voltage profile.

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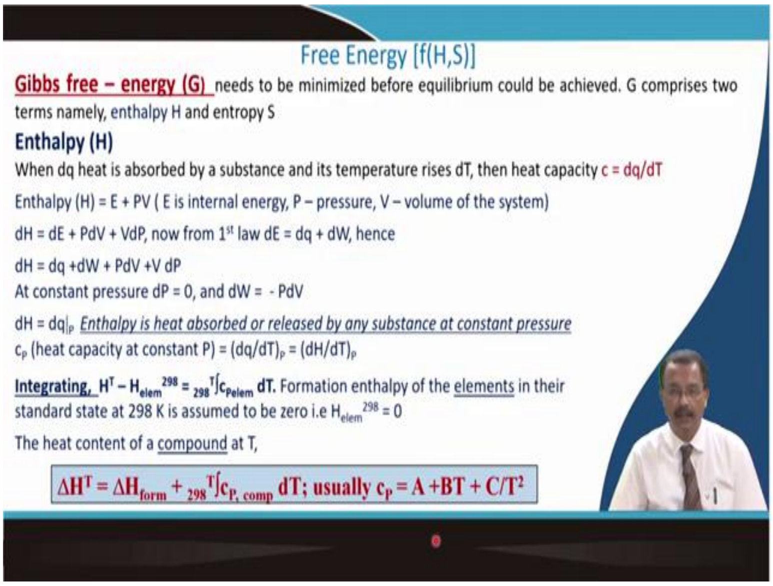

Free Energy [f(H,S)]

Gibbs free – energy (G) needs to be minimized before equilibrium could be achieved. G comprises two terms namely, enthalpy H and entropy S

Enthalpy (H)

When dq heat is absorbed by a substance and its temperature rises dT, then heat capacity $c = dq/dT$

Enthalpy (H) = E + PV (E is internal energy, P – pressure, V – volume of the system)

$dH = dE + PdV + VdP$, now from 1st law $dE = dq + dW$, hence

$dH = dq + dW + PdV + V\,dP$

At constant pressure $dP = 0$, and $dW = -PdV$

$dH = dq|_P$ *Enthalpy is heat absorbed or released by any substance at constant pressure*

c_P (heat capacity at constant P) $= (dq/dT)_P = (dH/dT)_P$

Integrating, $H^T - H_{elem}^{298} = {}_{298}{}^{T}\!\int c_{P_{elem}}\, dT$. Formation enthalpy of the elements in their standard state at 298 K is assumed to be zero i.e $H_{elem}^{298} = 0$

The heat content of a compound at T,

$$\boxed{\Delta H^T = \Delta H_{form} + {}_{298}{}^{T}\!\int c_{P,\,comp}\, dT;\ \text{usually } c_P = A + BT + C/T^2}$$

Now, as you know first let us talk about the free energy which is a function of enthalpy and entropy. So, the Gibbs free energy needs to be minimized before equilibrium could be achieved. So, this free energy G that comprises two term – one is enthalpy this H, and another one is entropy.

So, in case of enthalpy we know that when dq amount of heat is absorbed by a substance and its temperature say is raised by dT, then we can define the heat capacity (which is denoted by this small c) is the differential of the heat that is being absorbed per unit temperature rise.

$c = dq/dT$

Now, this enthalpy term can be written in terms of internal energy, pressure of the system and volume of the system.

Enthalpy (H) = E + PV (E is internal energy, P – pressure, V – volume of the system)

So, if you differentiate that, you will get this expression.

$dH = dE + PdV + VdP$

And from 1st law you can obtain the following expression for this change in internal energy which is equal to the absorbed heat plus the amount of work that is being done.

$dE = dq + dW$

$dH = dq + dW + PdV + V\,dP$

If you consider a constant pressure, then this $dP=0$. Therefore,

$dW = - PdV$

$dH = dq_P$

So, dH at constant P is equal to dq, which means enthalpy is the heat absorbed or released by any substance at constant pressure.

c_P (heat capacity at constant P) = $(dq/dT)_P = (dH/dT)_P$

$H^T - H_{elem}^{298} = {}_{298}{}^{T}\int c_{Pelem}\, dT$.

So, the formation enthalpy of the elements in their standard state at temperature of 298 Kelvin is 0. So, elemental enthalpy is 0. Now, if you consider a compound at a particular temperature, then this enthalpy change this can be given by this relation.

$\Delta H^T = \Delta H_{form} + {}_{298}{}^{T}\int c_{P,\ comp}\, dT$

And usually the expression for c_p is taken as a power series

$c_P = A + BT + C/T^2$

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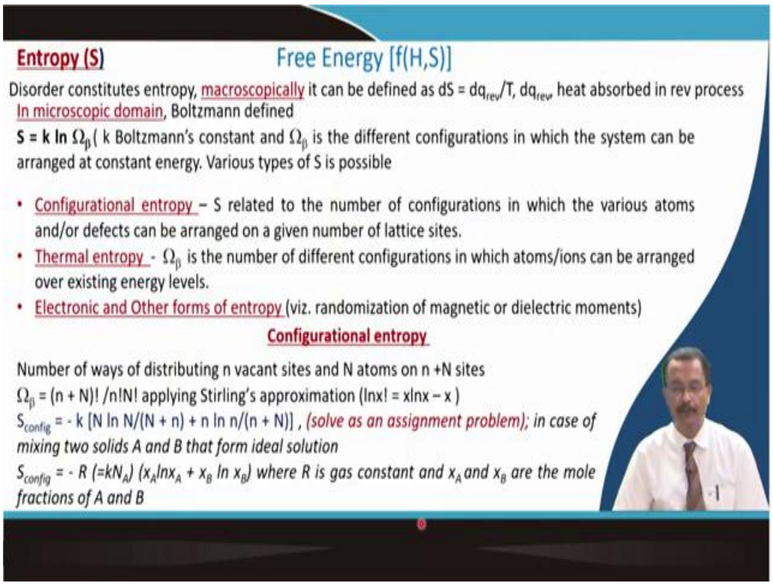

Entropy (S) Free Energy [f(H,S)]

Disorder constitutes entropy, macroscopically it can be defined as $dS = dq_{rev}/T$, dq_{rev}, heat absorbed in rev process

In microscopic domain, Boltzmann defined

$S = k \ln \Omega_\beta$ (k Boltzmann's constant and Ω_β is the different configurations in which the system can be arranged at constant energy. Various types of S is possible

- Configurational entropy – S related to the number of configurations in which the various atoms and/or defects can be arranged on a given number of lattice sites.
- Thermal entropy - Ω_β is the number of different configurations in which atoms/ions can be arranged over existing energy levels.
- Electronic and Other forms of entropy (viz. randomization of magnetic or dielectric moments)

Configurational entropy

Number of ways of distributing n vacant sites and N atoms on n +N sites

$\Omega_\beta = (n + N)! / n!N!$ applying Stirling's approximation ($\ln x! = x\ln x - x$)

$S_{config} = - k [N \ln N/(N + n) + n \ln n/(n + N)]$, *(solve as an assignment problem); in case of mixing two solids A and B that form ideal solution*

$S_{config} = - R (=kN_A) (x_A \ln x_A + x_B \ln x_B)$ where R is gas constant and x_A and x_B are the mole fractions of A and B

Now, we will talk about entropy. Disorder constitutes entropy macroscopically which can be defined as

$dS = dq_{rev}/T$

Boltzmann defined entropy as

$S = k \ln \Omega_\beta$

where omega beta is the term for different configuration in which the system can be arranged at constant energy.

Various types of entropy are possible. Configurational entropy relates the number of configuration in which various atoms or defects that can be arranged on a given number of the lattice site. We have another term which is thermal entropy, and that is actually number of different configuration in which the atoms or ions can be arranged over an existing energy level. We will talk more about it. And electronic entropy and other forms of entropy are also important that is dependent on, for example, randomization of magnetic or dielectric moments in certain materials.

So, the expression for configurational entropy can be derived by distributing the number of n vacant sites and N atoms.

$\Omega_\beta = (n + N)! /n!N!$

Applying Stirling's approximation

$\ln x! = x\ln x - x$

$S_{config} = - k [N \ln N/(N + n) + n \ln n/(n + N)]$

So, you can work it out and as a part of your assignment. This is relevant when we mix two solids A and B in the form of an ideal solution. So, configurational entropy for the ideal solution is given by this relation

$S_{config} = - R (x_A \ln x_A + x_B \ln x_B)$

where R is gas constant and x_A and x_B are the mole fractions of A and B

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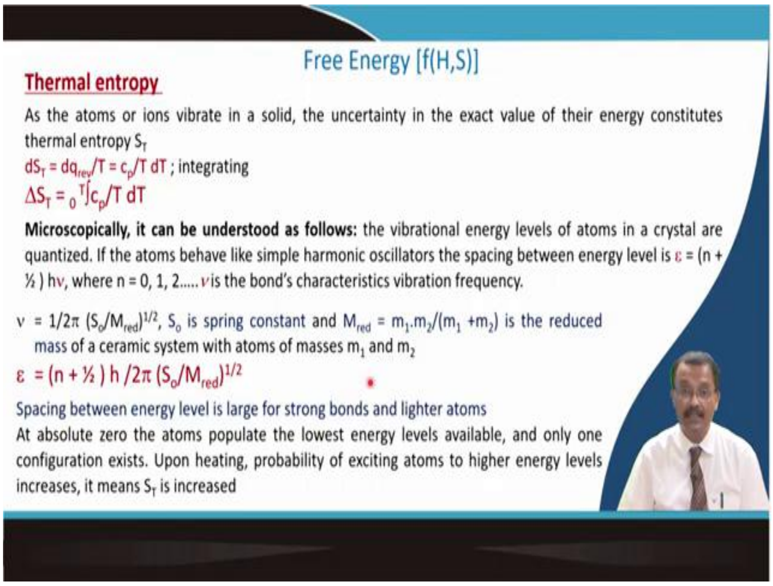

Free Energy [f(H,S)]

Thermal entropy

As the atoms or ions vibrate in a solid, the uncertainty in the exact value of their energy constitutes thermal entropy S_T

$dS_T = dq_{rev}/T = c_p/T\ dT$; integrating

$\Delta S_T = {}_0{}^T\int c_p/T\ dT$

Microscopically, it can be understood as follows: the vibrational energy levels of atoms in a crystal are quantized. If the atoms behave like simple harmonic oscillators the spacing between energy level is $\varepsilon = (n + ½)\ h\nu$, where $n = 0, 1, 2.....$ ν is the bond's characteristics vibration frequency.

$\nu = 1/2\pi\ (S_o/M_{red})^{1/2}$, S_o is spring constant and $M_{red} = m_1.m_2/(m_1 + m_2)$ is the reduced mass of a ceramic system with atoms of masses m_1 and m_2

$\varepsilon = (n + ½)\ h/2\pi\ (S_o/M_{red})^{1/2}$

Spacing between energy level is large for strong bonds and lighter atoms

At absolute zero the atoms populate the lowest energy levels available, and only one configuration exists. Upon heating, probability of exciting atoms to higher energy levels increases, it means S_T is increased

Now, thermal entropy is related to the atom or ion vibration in a solid, and the uncertainty in the exact value of their energy constitutes thermal entropy

$dS_T = dq_{rev}/T = (c_p/T)\ dT$

$\Delta S_T = {}_0{}^T\int (c_p/T)\ dT$

So, microscopically, it can be understood as follows. The vibration energy levels of atom in a crystal are actually quantized. And if atoms behave like simple harmonic oscillators, then the spacing between the energy level can be defined as

$\varepsilon = (n + ½)\ h\nu$, where $n = 0, 1, 2.....$ ν is the bond's characteristics vibration frequency.

$\nu = 1/2\pi\ (S_o/M_{red})^{1/2}$, S_o is spring constant and $M_{red} = m_1.m_2/(m_1 + m_2)$ is the reduced mass of a ceramic system with atoms of masses m_1 and m_2

$\varepsilon = (n + ½)\ h/2\pi\ (S_o/M_{red})^{1/2}$

So, it can tell you that spacing between the energy level is large for the strong bond and lighter atoms. So, when you are at absolute 0 K temperatures, the atom populates at the lower energy levels which are available, and only one kind of configuration exists. When you heat the material, probability of exciting atoms to higher energy levels increases with S_T also increasing.

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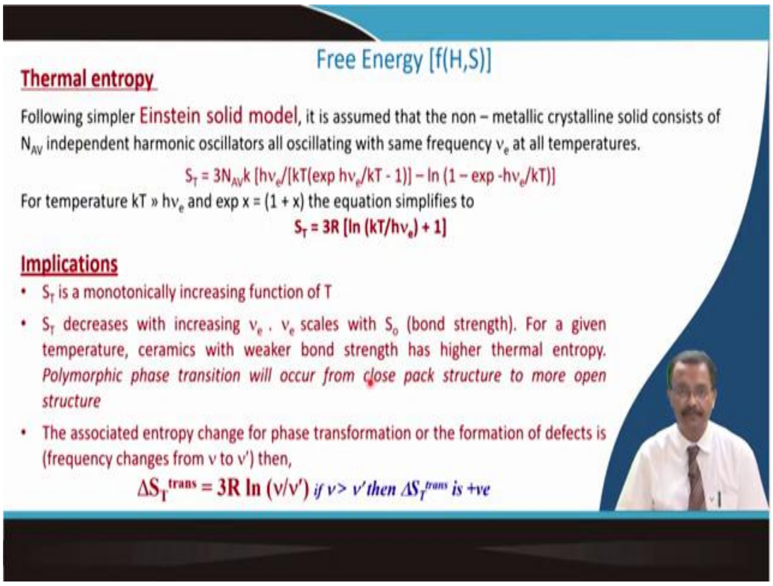

Free Energy [f(H,S)]

Thermal entropy

Following simpler **Einstein solid model**, it is assumed that the non – metallic crystalline solid consists of N_{AV} independent harmonic oscillators all oscillating with same frequency ν_e at all temperatures.

$$S_T = 3N_{AV}k\,[h\nu_e/[kT(\exp h\nu_e/kT - 1)] - \ln(1 - \exp -h\nu_e/kT)]$$

For temperature $kT \gg h\nu_e$ and $\exp x = (1 + x)$ the equation simplifies to

$$S_T = 3R\,[\ln(kT/h\nu_e) + 1]$$

Implications

- S_T is a monotonically increasing function of T
- S_T decreases with increasing ν_e . ν_e scales with S_0 (bond strength). For a given temperature, ceramics with weaker bond strength has higher thermal entropy. *Polymorphic phase transition will occur from close pack structure to more open structure*
- The associated entropy change for phase transformation or the formation of defects is (frequency changes from ν to ν') then,

$$\Delta S_T^{trans} = 3R\ln(\nu/\nu') \quad \textit{if } \nu > \nu' \textit{ then } \Delta S_T^{trans} \textit{ is +ve}$$

So, Einstein simplifies this. So, in Einstein solid model, it is assumed that the non – metallic crystalline solid consists of N_{AV} (Avogadro number) independent harmonic oscillators all oscillating with same frequency ν_e at all temperatures.

So, we can have a simplified equation of the thermal entropy.

$$S_T = 3N_{AV}k\,[h\nu_e/[kT(\exp h\nu_e/kT - 1)] - \ln(1 - \exp -h\nu_e/kT)]$$

For temperature $kT \gg h\nu_e$ and $\exp x = (1 + x)$ the equation simplifies to

$$S_T = 3R\,[\ln(kT/h\nu_e) + 1]$$

So, this relation tells you that thermal entropy monotonically increases with a function of temperature, and it decreases with increasing frequency ν_e. And in fact, ν_e scales with the bond strength. For given temperature, ceramic which are having weaker bond strength has higher thermal entropy. So, you know the polymorphic phase transformation will occur from one crystal structure to another crystal structure without changing their composition. Usually, it occurs from a closed pack structure to more open structure. So, in case of zirconia monoclinic to tetragonal that kind of phase transformation occurs. The associated entropy change for phase transformation or the formation of defect particularly for the frequency change from say ν to ν' is given as:

$\Delta S_T^{trans} = 3R \ln (\nu/\nu')$ *if* $\nu > \nu'$ *then* ΔS_T^{trans} *is +ve*

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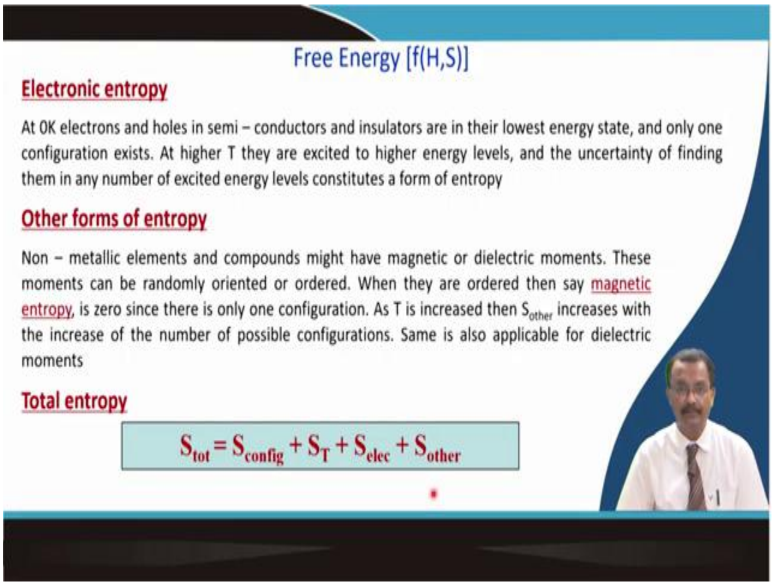

Free Energy [f(H,S)]

Electronic entropy

At 0K electrons and holes in semi – conductors and insulators are in their lowest energy state, and only one configuration exists. At higher T they are excited to higher energy levels, and the uncertainty of finding them in any number of excited energy levels constitutes a form of entropy

Other forms of entropy

Non – metallic elements and compounds might have magnetic or dielectric moments. These moments can be randomly oriented or ordered. When they are ordered then say magnetic entropy, is zero since there is only one configuration. As T is increased then S_{other} increases with the increase of the number of possible configurations. Same is also applicable for dielectric moments

Total entropy

$$S_{tot} = S_{config} + S_T + S_{elec} + S_{other}$$

Apart from this we have electronic entropy at 0 degree Kelvin; electrons and holes (particularly in semiconductors and insulators) are at the lowest energy state, and only one configuration exists. At higher temperature, they are excited to higher energy level, and the uncertainty of the finding of them in any number of the excited energy level constitutes the form of entropy.

There are other forms of entropy, such as magnetic or dielectric moment. These moments can be randomly oriented or ordered. When they are ordered they say magnetic entropy, is zero since there is only one configuration.

As temperature increases, then S increases with the increased number of possible configuration. And same thing is applicable to dielectric moment as well dielectric polarization that can also be arranged under certain condition. And with the increase in temperature, they can be completely random particularly for a ferroelectric to paraelectric kind of phase transition.

So, the total entropy constitutes configurational entropy, thermal entropy, electronic entropy, and the other entropy which is the magnetic and dipole moment.

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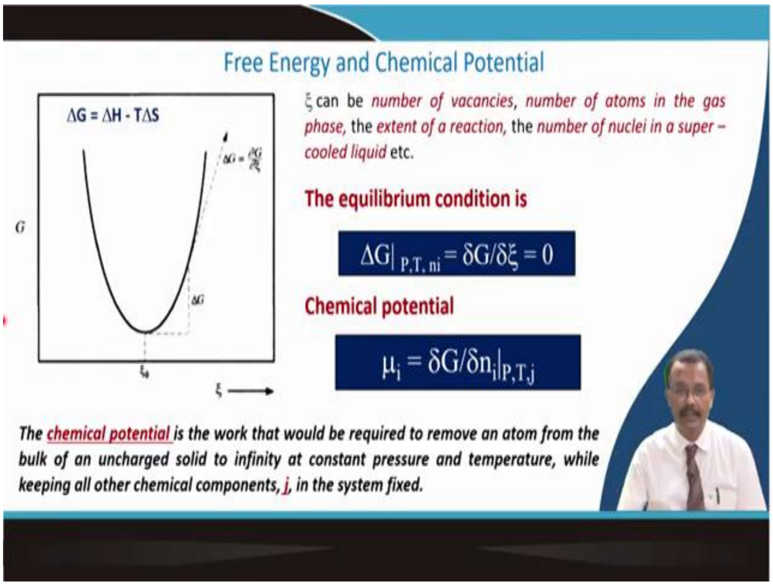

Free Energy and Chemical Potential

ξ can be *number of vacancies*, *number of atoms in the gas phase*, the *extent of a reaction*, the *number of nuclei in a super – cooled liquid* etc.

The equilibrium condition is

$\Delta G|_{P,T,\,ni} = \delta G/\delta\xi = 0$

Chemical potential

$\mu_i = \delta G/\delta n_i|_{P,T,j}$

The chemical potential is the work that would be required to remove an atom from the bulk of an uncharged solid to infinity at constant pressure and temperature, while keeping all other chemical components, j, in the system fixed.

Now, if you plot this free energy as a function of a parameter which is x_i. The x_i can be various types of thing not all relevant to your electrochemical energy storage, but in general there can be number of vacancies, number of atoms in a gas phase, the extent of a reaction the number of nuclei in a super cooled liquid when it is being crystallized. So, various types of this x_i is possible.

So, at equilibrium condition

$$\Delta G|_{P,T,\,ni} = \delta G/\delta\xi = 0$$

$$\mu_i = \delta G/\delta n_i|_{P,T,j}$$

.

So, physically the chemical potential is a work that would be required to remove an atom from the bulk of an uncharged solid to infinity at a constant pressure and temperature while keeping other chemical components which is defined as j in the system fixed. So, I guess that you could understand now the significance of this chemical potential.

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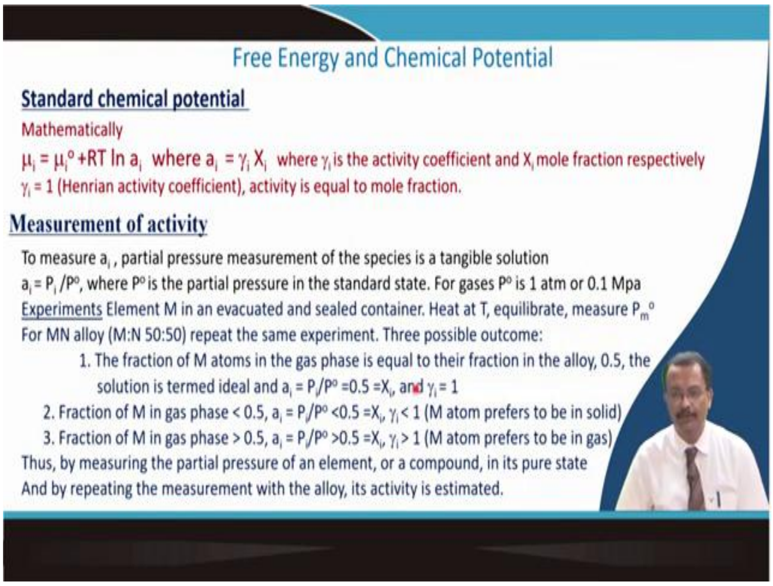

Free Energy and Chemical Potential

Standard chemical potential

Mathematically

$\mu_i = \mu_i^o + RT \ln a_i$ where $a_i = \gamma_i X_i$ where γ_i is the activity coefficient and X_i mole fraction respectively

$\gamma_i = 1$ (Henrian activity coefficient), activity is equal to mole fraction.

Measurement of activity

To measure a_i, partial pressure measurement of the species is a tangible solution

$a_i = P_i / P^o$, where P^o is the partial pressure in the standard state. For gases P^o is 1 atm or 0.1 Mpa

Experiments Element M in an evacuated and sealed container. Heat at T, equilibrate, measure P_m^o

For MN alloy (M:N 50:50) repeat the same experiment. Three possible outcome:

1. The fraction of M atoms in the gas phase is equal to their fraction in the alloy, 0.5, the solution is termed ideal and $a_i = P_i/P^o = 0.5 = X_i$, and $\gamma_i = 1$
2. Fraction of M in gas phase < 0.5, $a_i = P_i/P^o < 0.5 = X_i$, $\gamma_i < 1$ (M atom prefers to be in solid)
3. Fraction of M in gas phase > 0.5, $a_i = P_i/P^o > 0.5 = X_i$, $\gamma_i > 1$ (M atom prefers to be in gas)

Thus, by measuring the partial pressure of an element, or a compound, in its pure state

And by repeating the measurement with the alloy, its activity is estimated.

So, standard chemical potential is defined mathematically as μ_i^o

$\mu_i = \mu_i^o + RT \ln a_i$ where $a_i = \gamma_i X_i$ where γ_i is the activity coefficient and X_i mole fraction respectively

$\gamma_i = 1$ (Henrian activity coefficient), activity is equal to mole fraction.

This μ_i is constitutes two parts – one is at standard state and then it depends on gas constant and temperature, and ln of the activity part. So, this activity is defined as γ_i into X_i where, γ_i is the activity coefficient and X_i is the mole fraction that is there in the system.

So, usually γ_i is taken as one and we call it Henrian activity coefficient. So, the measurement of activity is not very relevant for this lecture, but still I will just go through it. So, you can measure it.

To measure a_i , partial pressure measurement of the species is a tangible solution

$a_i = P_i / P^o$, where P^o is the partial pressure in the standard state. For gases P^o is 1 atm or 0.1 Mpa

So, the experiment that is done is you take an element M and evacuate a sealed container which is there in a sealed container heat at a temperature T, and then equilibrate it and measure the value of P_m that partial pressure of the metal at standard state.

Now, you consider an alloy of MN say you have taken 50-50, and repeat the same experiment. So, you can have three possible outcomes. The first outcome is the fraction of M in the gas phase is equal to their fraction in the alloy which was 0.5. Then the solution is term ideal. So, a_i is P_i by P_0 that is 0.5 that is equal to the mole fraction and gamma is equal to 1. Likewise, the fraction of M in gas phase could be less than 0.5.

So, γ_i is coming less than 1, so that means, physically that M atom prefers to be in the solid. And when γ_i is more than 1, then M atom that prefers to be in the gaseous state. So, you measure the partial pressure of an element or a compound in its pure state and by repeating the measurement with alloy its activity can be estimated.

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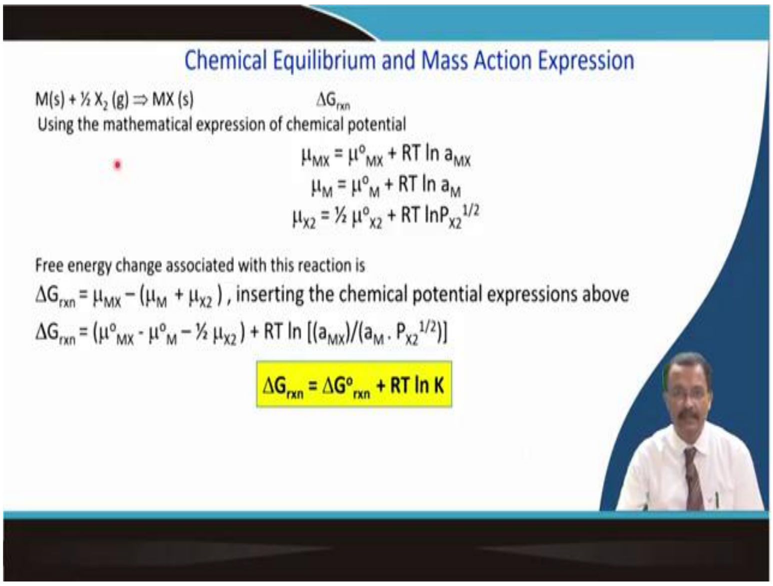

Chemical Equilibrium and Mass Action Expression

$M(s) + ½ X_2 (g) \Rightarrow MX (s)$ ΔG_{rxn}

Using the mathematical expression of chemical potential

$$\mu_{MX} = \mu^o_{MX} + RT \ln a_{MX}$$
$$\mu_M = \mu^o_M + RT \ln a_M$$
$$\mu_{X2} = ½ \mu^o_{X2} + RT \ln P_{X2}^{1/2}$$

Free energy change associated with this reaction is

$\Delta G_{rxn} = \mu_{MX} - (\mu_M + \mu_{X2})$, inserting the chemical potential expressions above

$\Delta G_{rxn} = (\mu^o_{MX} - \mu^o_M - ½ \mu_{X2}) + RT \ln [(a_{MX})/(a_M . P_{X2}^{1/2})]$

$$\boxed{\Delta G_{rxn} = \Delta G^o_{rxn} + RT \ln K}$$

So, if I take a simple equation like a solid is reacting with a gas component to form another solid and the free energy change can be related to this chemical equilibrium and mass action expression. So, the mathematical expression is

$\mu_{MX} = \mu^o_{MX} + RT \ln a_{MX}$

$\mu_{M} = \mu^o_{M} + RT \ln a_{M}$

$\mu_{X2} = ½\, \mu^o_{X2} + RT \ln P_{X2}^{1/2}$

So, your free energy change del G reaction that is given by this relation.

$\Delta G_{rxn} = \mu_{MX} – (\mu_{M} + \mu_{X2})$, inserting the chemical potential expressions above

$\Delta G_{rxn} = (\mu^o_{MX} - \mu^o_{M} – ½\, \mu_{X2}) + RT \ln [(a_{MX})/(a_{M} . P_{X2}^{1/2})]$

$\Delta G_{rxn} = \Delta G^o_{rxn} + RT \ln K$

We will be using the above relation you can achieve from chemical potentials through mass action expression.

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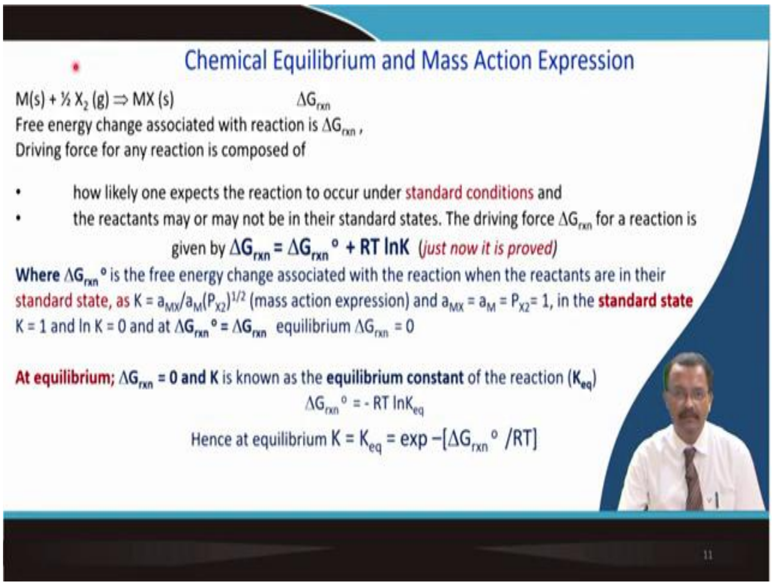

Chemical Equilibrium and Mass Action Expression

$M(s) + ½\, X_2\, (g) \Rightarrow MX\, (s)$ ΔG_{rxn}

Free energy change associated with reaction is ΔG_{rxn} ,

Driving force for any reaction is composed of

- how likely one expects the reaction to occur under standard conditions and
- the reactants may or may not be in their standard states. The driving force ΔG_{rxn} for a reaction is given by $\Delta G_{rxn} = \Delta G_{rxn}{}^o + RT \ln K$ *(just now it is proved)*

Where $\Delta G_{rxn}{}^o$ is the free energy change associated with the reaction when the reactants are in their standard state, as $K = a_{MX}/a_M(P_{X2})^{1/2}$ (mass action expression) and $a_{MX} = a_M = P_{X2} = 1$, in the **standard state** $K = 1$ and $\ln K = 0$ and at $\Delta G_{rxn}{}^o = \Delta G_{rxn}$ equilibrium $\Delta G_{rxn} = 0$

At equilibrium; $\Delta G_{rxn} = 0$ **and K** is known as the **equilibrium constant** of the reaction (K_{eq})

$$\Delta G_{rxn}{}^o = - RT \ln K_{eq}$$

Hence at equilibrium $K = K_{eq} = \exp -[\Delta G_{rxn}{}^o /RT]$

So, again we go back to the same equation. And free energy change associated with this relation is ΔG_{rxn}. So, the driving force for any reaction that is basically composed of two things. One is how likely one expects in the reaction to occur under standard condition. Second the reactants may or may not be in their standard states.

So, the driving force del G rxn for a reaction then is given by this relation which just now I have proved. So, this is in the non-standard case. Now, this value ΔG_{rxn}^0 is the free energy change associated with the reaction when the reactants in their standard state. Now, what is this standard state?

When the reactants are in their standard state, $K = a_{MX}/a_M(P_{X2})^{1/2}$ (mass action expression) and $a_{MX} = a_M = P_{X2} = 1$

In the **standard state** K = 1 and ln K = 0 and at $\mathbf{\Delta G_{rxn}^{o} = \Delta G_{rxn}}$

At equilibrium $\mathbf{\Delta G_{rxn} = 0}$

$\Delta G_{rxn}^{o} = - RT \ln K_{eq}$

Hence at equilibrium $K = K_{eq} = \exp -[\Delta G_{rxn}^{o} /RT]$

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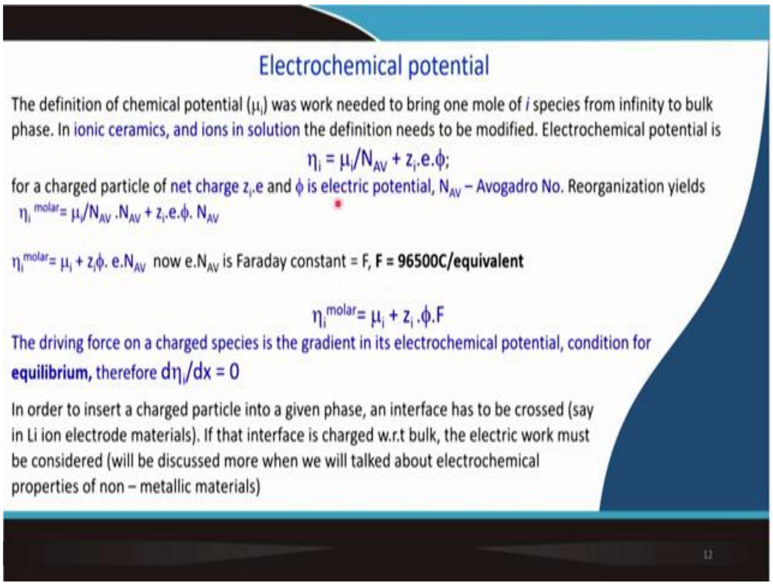

Electrochemical potential

The definition of chemical potential (μ_i) was work needed to bring one mole of *i* species from infinity to bulk phase. In ionic ceramics, and ions in solution the definition needs to be modified. Electrochemical potential is

$$\eta_i = \mu_i/N_{AV} + z_i.e.\phi;$$

for a charged particle of net charge $z_i.e$ and ϕ is electric potential, N_{AV} – Avogadro No. Reorganization yields

$\eta_i^{molar} = \mu_i/N_{AV} .N_{AV} + z_i.e.\phi. N_{AV}$

$\eta_i^{molar} = \mu_i + z_i\phi. e.N_{AV}$ now $e.N_{AV}$ is Faraday constant = F, **F = 96500C/equivalent**

$$\eta_i^{molar} = \mu_i + z_i .\phi.F$$

The driving force on a charged species is the gradient in its electrochemical potential, condition for **equilibrium,** therefore $d\eta_i/dx = 0$

In order to insert a charged particle into a given phase, an interface has to be crossed (say in Li ion electrode materials). If that interface is charged w.r.t bulk, the electric work must be considered (will be discussed more when we will talked about electrochemical properties of non – metallic materials)

Now, electrochemical potential is the work that is needed to bring one mole of i species (any species) from infinity to the bulk phase. So, in ionic ceramics, this is important; and for ion in solution, the definition needs to be modified. So, electrochemical potential is given by the following relation

$\eta_i = \mu_i/N_{AV} + z_i e\phi$

So, if you reorganize that yields, this molar electrochemical potential gives the relation.

$\eta_i^{molar} = \mu_i/N_{AV} .N_{AV} + z_i.e.\phi. N_{AV}$

$\eta_i^{molar} = \mu_i + z_i .\phi.F$

So, this product e and Avogadro number is nothing but Faraday constant, which is 96500 coulomb per equivalent.

The driving force on a charged species is the gradient in its electrochemical potential. At the condition for **equilibrium,** $d\eta_i/dx = 0$

In order to insert a charged particle into a given phase, an interface has to be crossed (say in Li ion electrode materials). If that interface is charged w.r.t bulk, the electric work must be considered

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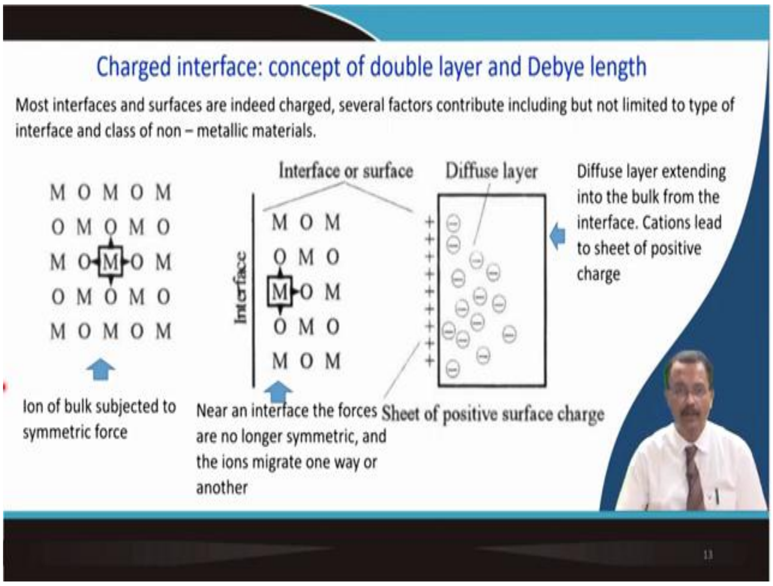

Charged interface: concept of double layer and Debye length

Most interfaces and surfaces are indeed charged, several factors contribute including but not limited to type of interface and class of non – metallic materials.

Ion of bulk subjected to symmetric force

Near an interface the forces are no longer symmetric, and the ions migrate one way or another

Sheet of positive surface charge

Diffuse layer extending into the bulk from the interface. Cations lead to sheet of positive charge

So, now most interface and surface they are indeed charged, the several factors that contribute include the type of the interface and class of the ceramic material in the non-metallic type of materials. So, you can see that ion in a bulk, they are subjected to a symmetric force by the anions and this cation bond. Now, near the interface, the forces are no longer symmetric and ions migrate one way or another. So, migration is possible.

So, if you dip this in an electrolyte which is having salt, then depending on this charged surface which is shown the sheet of positive charge here at the interface from the electrolyte the negative anion they get attracted and forms a stern layer here at the first interface.

But once you move into the solution, you will see that the concentration of this negative ions balance the sheet of the positive ions to form an electric double layer.

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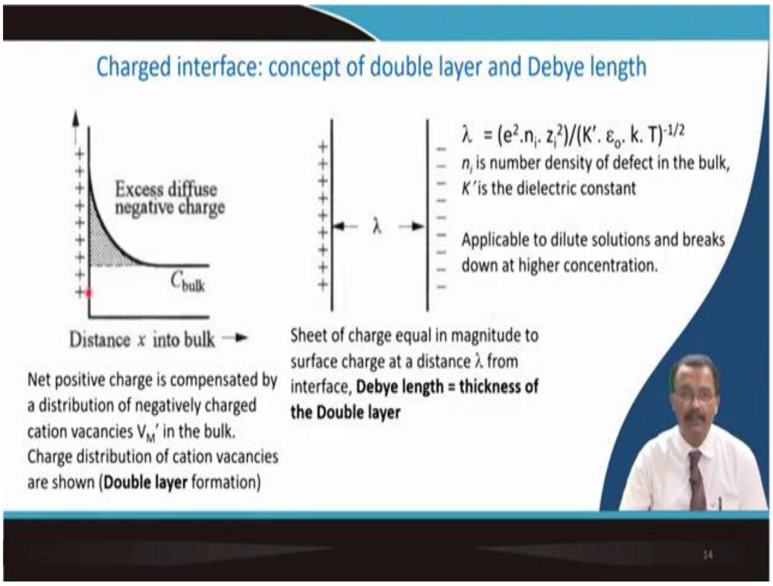

Charged interface: concept of double layer and Debye length

λ = (e^2.n$_i$. z$_i$^{2})/(K′. ε$_o$. k. T)$^{-1/2}$
n_i is number density of defect in the bulk, K' is the dielectric constant

Applicable to dilute solutions and breaks down at higher concentration.

Net positive charge is compensated by a distribution of negatively charged cation vacancies V_M' in the bulk. Charge distribution of cation vacancies are shown (**Double layer** formation)

Sheet of charge equal in magnitude to surface charge at a distance λ from interface, **Debye length = thickness of the Double layer**

So, this is the type of electric double layer that is formed. And as I told that the net positive charge is compensated by a distribution of negatively charged cation vacancies in the bulk. And charge distribution of cation vacancies they lead to the double layer formation. So, you can estimate the value of double layer by this simple expression, which constitutes the number of defect in the bulk.

$$\lambda = (e^2.n_i.\ z_i^2)/(K'.\ \varepsilon_o.\ k.\ T)^{-1/2}$$

n_i is number density of defect in the bulk, K' is the dielectric constant

So, this material is not perfect. It depends on the dielectric constant of the electrolyte and the other parameter like temperature, charge associated with the cation and so on. So, this is only applicable to a dilute solution. And at higher concentration, it breaks down. So, this is called the Debye length wherein the sheet of charge equal in magnitude to the surface charge at a distance of lambda from the interface. And this Debye length is actually the thickness of the double layer.

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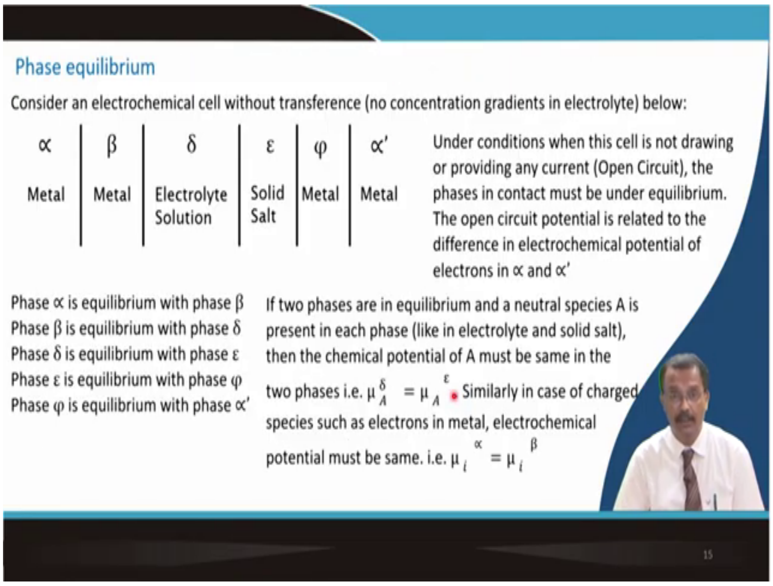

Phase equilibrium

Consider an electrochemical cell without transference (no concentration gradients in electrolyte) below:

∝	β	δ	ε	φ	∝’
Metal	Metal	Electrolyte Solution	Solid Salt	Metal	Metal

Under conditions when this cell is not drawing or providing any current (Open Circuit), the phases in contact must be under equilibrium. The open circuit potential is related to the difference in electrochemical potential of electrons in ∝ and ∝’

Phase ∝ is equilibrium with phase β
Phase β is equilibrium with phase δ
Phase δ is equilibrium with phase ε
Phase ε is equilibrium with phase φ
Phase φ is equilibrium with phase ∝’

If two phases are in equilibrium and a neutral species A is present in each phase (like in electrolyte and solid salt), then the chemical potential of A must be same in the two phases i.e. $\mu_A^{\delta} = \mu_A^{\varepsilon}$. Similarly in case of charged species such as electrons in metal, electrochemical potential must be same. i.e. $\mu_i^{\propto} = \mu_i^{\beta}$

Now, we will talk about the phase that is there inside the material. So, you can see in an electrochemical chain you have metal which is current collector. Then you may have another metal like copper, then you have electrolyte solution. Then you have inside the electrolyte solution a solid salt. Then you have another metal and then you have the final current collector.

So, you can assume there is no concentration gradient in the electrolyte under condition when the cell is not drawing any power. We call it is an open circuit condition. And this must be under equilibrium. So, open circuit potential is related to the difference in their electrochemical potential of electrons which is there in alpha and alpha dash.

So, as I said this phase ∝ is in equilibrium with β, that is in equilibrium with δ, then ε and then finally, ϕ. So, you can write under equilibrium condition

$$\mu_A^{\delta} = \mu_A^{\varepsilon}$$

Similarly, in case of charge species such as electron in metal, the electrochemical potential must be same.

$$\mu_i^{\propto} = \mu_i^{\beta}$$

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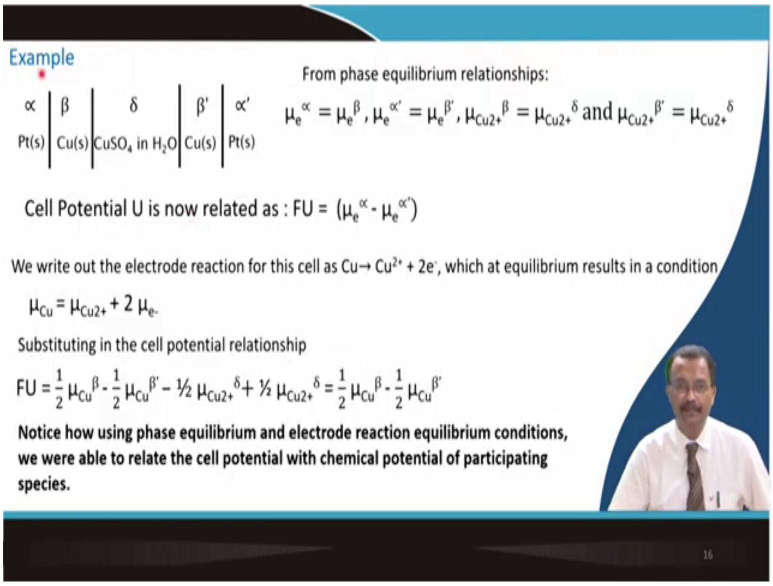

Example

$\propto$	β	δ	β'	$\propto'$
Pt(s)	Cu(s)	$CuSO_4$ in H_2O	Cu(s)	Pt(s)

From phase equilibrium relationships:

$\mu_e^{\propto} = \mu_e^{\beta}$, $\mu_e^{\propto'} = \mu_e^{\beta'}$, $\mu_{Cu2+}^{\beta} = \mu_{Cu2+}^{\delta}$ and $\mu_{Cu2+}^{\beta'} = \mu_{Cu2+}^{\delta}$

Cell Potential U is now related as : $FU = (\mu_e^{\propto} - \mu_e^{\propto'})$

We write out the electrode reaction for this cell as $Cu \rightarrow Cu^{2+} + 2e^-$, which at equilibrium results in a condition

$\mu_{Cu} = \mu_{Cu2+} + 2\,\mu_{e-}$

Substituting in the cell potential relationship

$FU = \frac{1}{2}\mu_{Cu}^{\beta} - \frac{1}{2}\mu_{Cu}^{\beta'} - ½\,\mu_{Cu2+}^{\delta} + ½\,\mu_{Cu2+}^{\delta} = \frac{1}{2}\mu_{Cu}^{\beta} - \frac{1}{2}\mu_{Cu}^{\beta'}$

Notice how using phase equilibrium and electrode reaction equilibrium conditions, we were able to relate the cell potential with chemical potential of participating species.

I will cite one example. So, this is the chain platinum – one metal, then copper, then copper sulfate in H_2O, then you have another copper metal, and then you have a current collector. So, from our definition, phase equilibrium relationship this equation is valid.

$\mu_e^{\propto} = \mu_e^{\beta}$, $\mu_e^{\propto'} = \mu_e^{\beta'}$, $\mu_{Cu2+}^{\beta} = \mu_{Cu2+}^{\delta}$ and $\mu_{Cu2+}^{\beta'} = \mu_{Cu2+}^{\delta}$

So, I have already told you that you can calculate the cell potential, where the Faraday constant is multiplied by equilibrium potential voltage at open circuit to get the chemical potential of electron in alpha minus chemical potential of electron in alpha dash.

$FU = (\mu_e^{\propto} - \mu_e^{\propto'})$

We write out the electrode reaction for this cell as $Cu \rightarrow Cu^{2+} + 2e^-$, which at equilibrium results in a condition

$\mu_{Cu} = \mu_{Cu2+} + 2\,\mu_{e-}$

Substituting in the cell potential relationship

$FU = \frac{1}{2}\mu_{Cu}^{\beta} - \frac{1}{2}\mu_{Cu}^{\beta'} - ½\,\mu_{Cu2+}^{\delta} + ½\,\mu_{Cu2+}^{\delta} = \frac{1}{2}\mu_{Cu}^{\beta} - \frac{1}{2}\mu_{Cu}^{\beta'}$

Notice how using phase equilibrium and electrode reaction equilibrium conditions, we were able to relate the cell potential with chemical potential of participating species.

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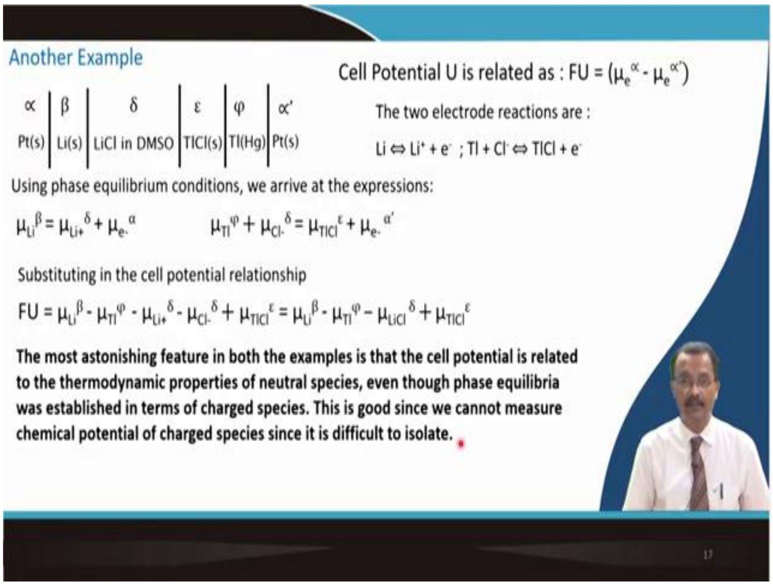

Another Example

Cell Potential U is related as : $FU = (\mu_e^{\alpha} - \mu_e^{\alpha'})$

α	β	δ	ε	φ	α'
Pt(s)	Li(s)	LiCl in DMSO	TlCl(s)	Tl(Hg)	Pt(s)

The two electrode reactions are :

$Li \Leftrightarrow Li^+ + e^-$; $Tl + Cl^- \Leftrightarrow TlCl + e^-$

Using phase equilibrium conditions, we arrive at the expressions:

$\mu_{Li}^{\beta} = \mu_{Li+}^{\delta} + \mu_{e-}^{\alpha}$ $\qquad$ $\mu_{Tl}^{\varphi} + \mu_{Cl-}^{\delta} = \mu_{TlCl}^{\varepsilon} + \mu_{e-}^{\alpha'}$

Substituting in the cell potential relationship

$FU = \mu_{Li}^{\beta} - \mu_{Tl}^{\varphi} - \mu_{Li+}^{\delta} - \mu_{Cl-}^{\delta} + \mu_{TlCl}^{\varepsilon} = \mu_{Li}^{\beta} - \mu_{Tl}^{\varphi} - \mu_{LiCl}^{\delta} + \mu_{TlCl}^{\varepsilon}$

The most astonishing feature in both the examples is that the cell potential is related to the thermodynamic properties of neutral species, even though phase equilibria was established in terms of charged species. This is good since we cannot measure chemical potential of charged species since it is difficult to isolate.

I have given here another example, the same kind of electronic chain. And I leave it on you to calculate this value, the electron chemical potential in alpha and electron chemical potential in alpha dash. Now, here you must remember that it is not a single phase relation here I have put lithium. So, lithium is getting oxidized and you have also titanium chloride salt here.

Cell Potential U is related as : $FU = (\mu_e^{\alpha} - \mu_e^{\alpha'})$

The two electrode reactions are :

$Li \Leftrightarrow Li^+ + e^-$; $Tl + Cl^- \Leftrightarrow TlCl + e^-$

Using phase equilibrium conditions, we arrive at the expressions:

$\mu_{Tl}^{\varphi} + \mu_{Cl-}^{\delta} = \mu_{TlCl}^{\varepsilon} + \mu_{e-}^{\alpha}$

$\mu_{Li}^{\beta} = \mu_{Li+}^{\delta} + \mu_{e-}^{\alpha}$

Substituting in the cell potential relationship

$FU = \mu_{Li}^{\beta} - \mu_{Tl}^{\varphi} - \mu_{Li+}^{\delta} - \mu_{Cl-}^{\delta} + \mu_{TlCl}^{\varepsilon} = \mu_{Li}^{\beta} - \mu_{Tl}^{\varphi} - \mu_{LiCl}^{\delta} + \mu_{TlCl}^{\varepsilon}$

And you can see this is a nice example that shows the cell potential is related to the thermodynamic properties of the neutral species because the charged species is somehow it gets cancelled. So, only neutral species that is there. And this is good because we cannot measure exactly the chemical potential of the charged species since it is difficult to isolate. So, if our voltage term constitutes only the neutral species that is making our life easier.

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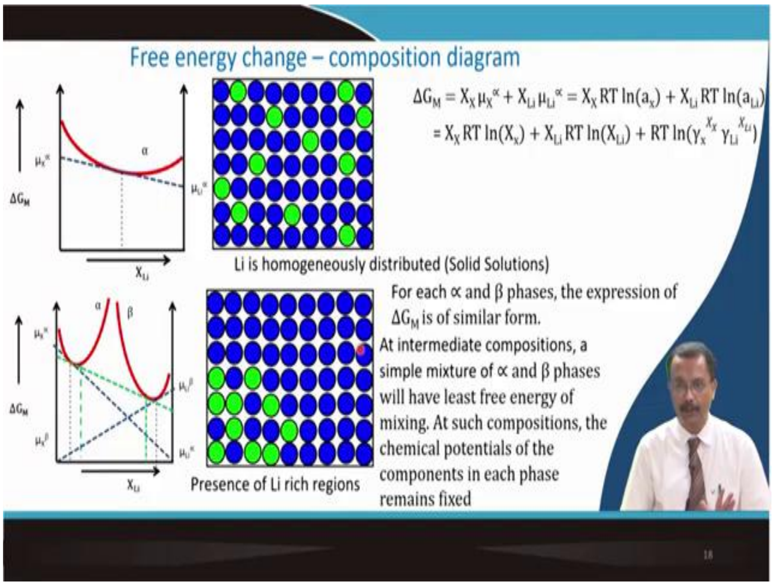

Free energy change – composition diagram

$$\Delta G_M = X_X \mu_X^{\alpha} + X_{Li} \mu_{Li}^{\alpha} = X_X RT \ln(a_X) + X_{Li} RT \ln(a_{Li})$$
$$= X_X RT \ln(X_X) + X_{Li} RT \ln(X_{Li}) + RT \ln(\gamma_X^{X_X} \gamma_{Li}^{X_{Li}})$$

Li is homogeneously distributed (Solid Solutions)

For each ∝ and β phases, the expression of ΔG_M is of similar form.

At intermediate compositions, a simple mixture of ∝ and β phases will have least free energy of mixing. At such compositions, the chemical potentials of the components in each phase remains fixed

Presence of Li rich regions

Finally, this I will not elaborate in this lecture because I will elaborate in other lectures, but just to maintain the continuity you know that in a two phase mixture of two different types of atoms say this green and blue. So, always you can derive the free energy change after the mixing.

And this relation is with the mole fraction and the chemical potential of x and the other component which is the in this case is lithium. And then you can write this relation, and eventually you can plot the free energy diagram. So, in this case, it is a solid solution because one component is homogeneously mixed with others.

$\Delta G_M = X_X \mu_X^{\propto} + X_{Li} \mu_{Li}^{\propto} = X_X RT \ln(a_x) + X_{Li} RT \ln(a_{Li}) = X_X RT \ln(X_x) + X_{Li} RT \ln(X_{Li}) + RT \ln(\gamma_x X_X \gamma_{Li} X_{Li})$

And in this case, this is a two phase mixture although I have shown that this is affluent in green, and this is affluent in blue, but one or two green also you assume that that is there. So, it is a clear cut mixture of two. So, in case of a solid solution, you can actually estimate I will show later part of your assignment problem that how to get this one. And in case of a mixture of two phase, you get two ΔG_M minima here.

Now, the important part here is that at any composition of lithium if you can draw a tangent, then wherever it cuts this axis where lithium is maximum that will give you the chemical potential of lithium. For the other phase, the chemical potential you can get from here. Same thing applies here.

So, if you draw at this particular composition a tangent, it will come here; for this one it will come here. And if you have a common tangent that indicates that the phase mixture here this phase mixture they are having the minimum free energy condition. So, this is just the implication of the free energy change and composition diagram.

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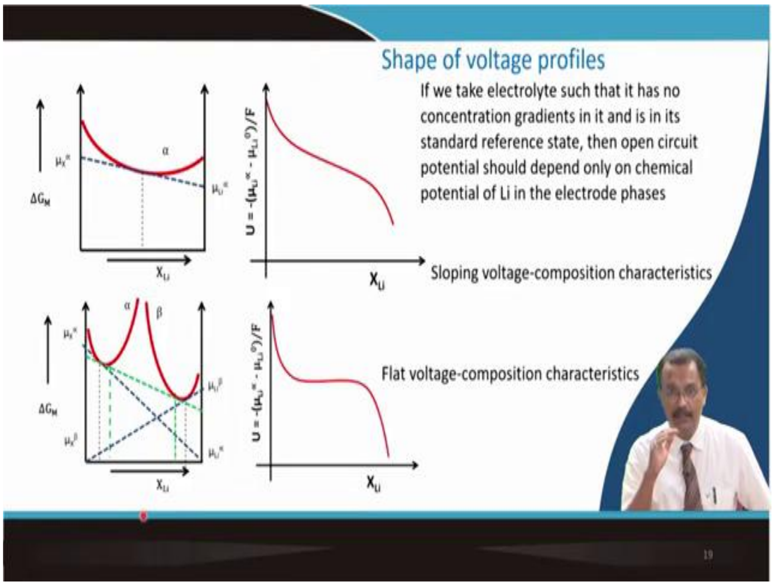

Shape of voltage profiles

If we take electrolyte such that it has no concentration gradients in it and is in its standard reference state, then open circuit potential should depend only on chemical potential of Li in the electrode phases

Sloping voltage-composition characteristics

Flat voltage-composition characteristics

What is more important is that once you have this chemical potential known from this composition then you can relate it with the equation that I have shown

$$U = -(\mu_{Li}^{\alpha} - \mu_{Li}^{0})/F$$

And you can see that if you have a solid solution, then you have a sloping voltage profile. As you put more lithium during your discharge into the cathode, then you will see that this kind of sloping voltage. But instead if you have a two phase mixture, then we will prove later that it will give you a constant kind of thing, and then it will fall here and here. So, shape of the voltage profile that can be related with the free energy versus composition diagram.

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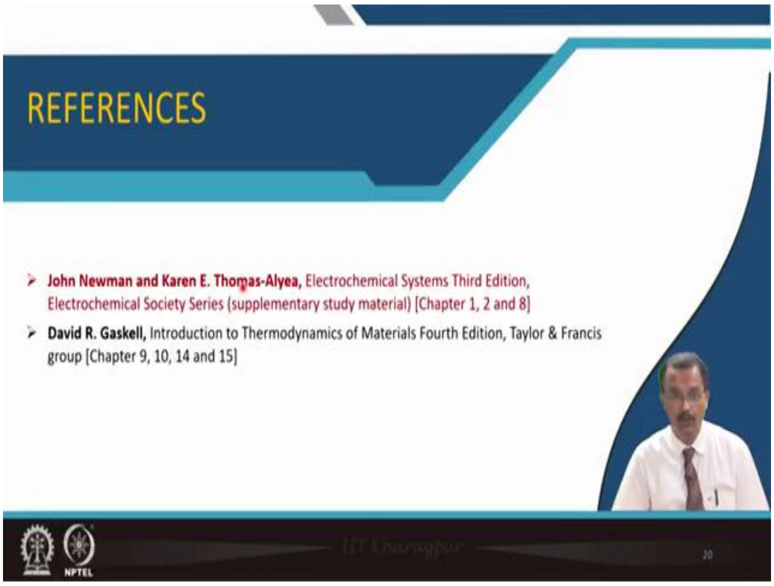

REFERENCES

- **John Newman and Karen E. Thomas-Alyea,** Electrochemical Systems Third Edition, Electrochemical Society Series (supplementary study material) [Chapter 1, 2 and 8]
- **David R. Gaskell,** Introduction to Thermodynamics of Materials Fourth Edition, Taylor & Francis group [Chapter 9, 10, 14 and 15]

So, references are these two nice books. As I have said I have not covered everything, but whatever is needed for you to understand the topics that I will be describing in future. So, these two books are important.

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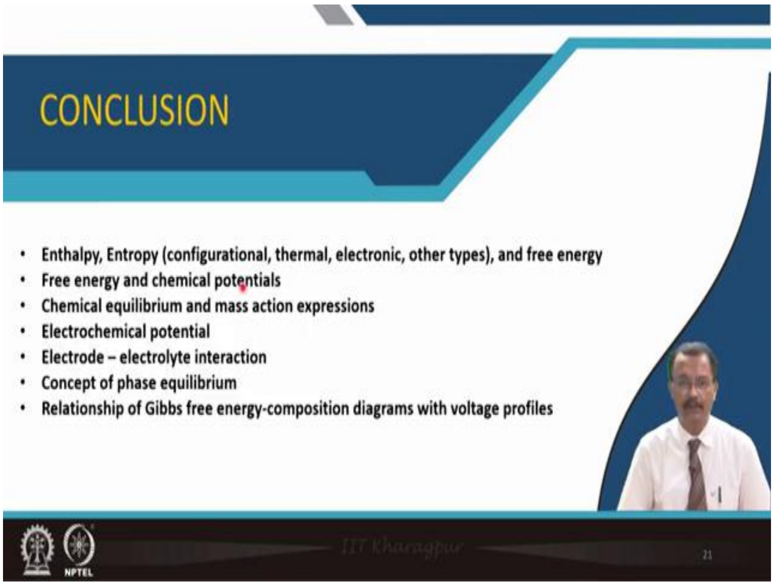

CONCLUSION

- Enthalpy, Entropy (configurational, thermal, electronic, other types), and free energy
- Free energy and chemical potentials
- Chemical equilibrium and mass action expressions
- Electrochemical potential
- Electrode – electrolyte interaction
- Concept of phase equilibrium
- Relationship of Gibbs free energy-composition diagrams with voltage profiles

So, in this particular lecture, we have introduced enthalpy, entropy, configurational, thermal, electronic, and other types, then free energy, then free energy, and chemical potential, then chemical equilibrium and mass action expressions. Then we introduce the term electrochemical potential.

Then electrode electrolyte interaction, concept of phase equilibrium at least in the equilibrium state, and how you can estimate the open circuit potential under equilibrium and then finally, I have touched the Gibbs free energy composition diagram with voltage profile.

Thank you for your interest.