Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 52
Electrolytes

Welcome back!

We are looking at module number 6, which is on Reaction Equilibria. We had looked at the conditions for reaction equilibria, and then, the equilibrium constants, the temperature/pressure dependence of the equilibrium constant. And then, we worked out a few problems with which we reviewed or we are brought back to memory, if you can call it so, whatever has been learnt in the earlier classes starting with higher secondary.

Today is pretty much the last class on module 6. The next class will be a review for the entire course.

In this class, let us look at a formalism for handling electrolytes. Why do we need to look at electrolytes at all?

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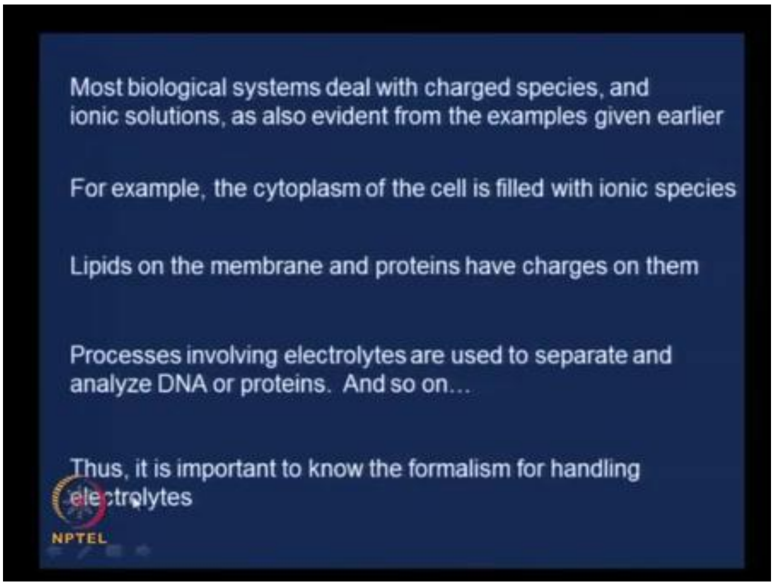

Most biological systems deal with charged species, and ionic solutions, as also evident from the examples given earlier

For example, the cytoplasm of the cell is filled with ionic species

Lipids on the membrane and proteins have charges on them

Processes involving electrolytes are used to separate and analyze DNA or proteins. And so on…

Thus, it is important to know the formalism for handling electrolytes

Why are we looking at electrolytes at all? Because, most biological systems deal with charged species and ionic solutions. Even if you go back to the three examples that we considered one after another in the last couple of classes, you would have seen the occurrence of ionic species all over there. There was ATP, the NADH was a charged species, we talked about half reactions, reduction potentials, and so on, and so forth.

And if you look around, and see many reactions that occur in the cell, you would see the occurrence of ionic species in them. Not just that; the cytoplasm itself – … the cell envelope and what is inside apart from the organelles is the cytoplasm – it is filled with ionic species. If you look at some of the major biomolecules … you know there are four major types of biomolecules, as you can recall – carbohydrates, proteins, lipids and nucleic acids. And out of these, if you look at lipids and proteins predominantly, and even the other types in some specialized cases, they all have charges on them.

For example, lipids – as you know, the lipid bilayer is the one that is essential, for the functionality of the cell membrane. And what exactly is a lipid? It is a charged species; it has these tails, the hydrophobic tails, and the hydrophilic head; the hydrophilic head has a charge on it. … You would have heard examples of lipids on the membrane, and most of them are charged species, and that kind of a structure is necessary for its function. Similarly, proteins … amino acids that make up the proteins, have charged side groups on them.

And even some of the other groups could be charged depending on the pH at which they operate. … If you put a sequence of amino acids together, as in the case of a protein, the protein molecule is definitely charged. Nucleic acids are charged. And some carbohydrates are certainly charged. Therefore, you find charges in all these basic constituents of bio systems, the biomolecules. Therefore, we certainly need to look at the charges. If you want even further motivation, the processes involving electrolytes are used to separate and analyze DNA or proteins.

… We typically run gels, in which we separate out the various paths of the DNA analyze them, various proteins in a protein mixture analyze them and so on, and so forth. So, all these are electrically active processes, involving electrolytes. Therefore, it is important to know the formalism for handling electrolytes, from a thermodynamics view point also. This is a slight extension of what you would find in your text book. In fact, you will not find electrolytes in Smith, Van Ness and Abbott.

Nevertheless, I thought since this is the last class, I will take the liberty of introducing you to something slightly beyond your syllabus. It certainly falls into the scope of the course. And it will be good to know.

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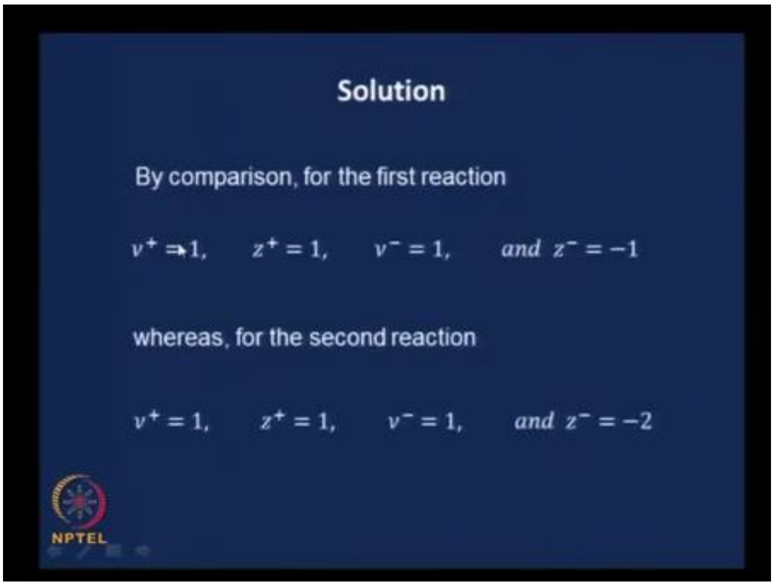


Solution

By comparison, for the first reaction

$v^+ = 1, \quad z^+ = 1, \quad v^- = 1, \quad and\ z^- = -1$

whereas, for the second reaction

$v^+ = 1, \quad z^+ = 1, \quad v^- = 1, \quad and\ z^- = -2$

Let us consider the electrolyte – as you know, electrolyte is any species that is charged – and let us represent the electrolytes as $M_{\nu+}A_{\nu-}$ (M nu plus A nu minus). M could be the positively charged species, A could be the negatively charged species. nu plus is the number of positive charges associated with M. nu minus is the number of … negative charges, associated with A, and together they could be an uncharged species, also. Not necessarily, but they could uncharged also.

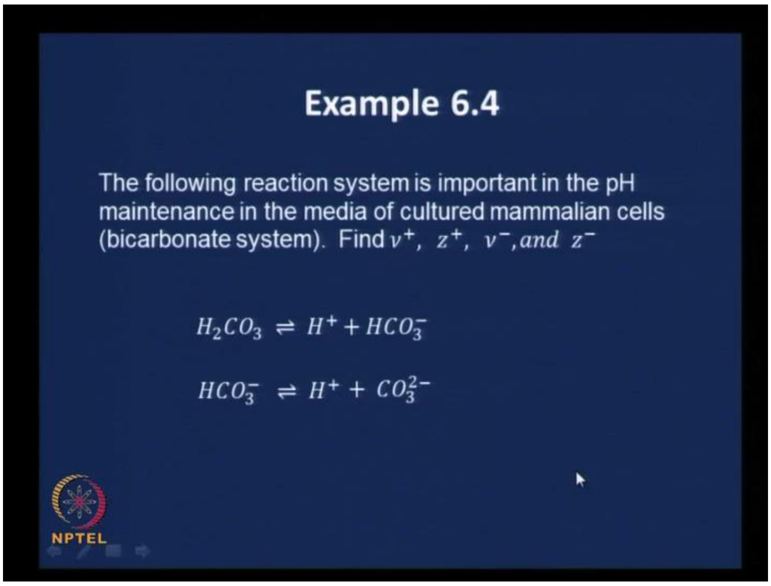
So, this, when it is a dropped into a solution for example, when it is taken in a solution form, it dissociates as follows to give you nu plus molecules or if you take one molecule of M nu plus A nu minus, it will dissociate in an aqueous solution, for example, to give you nu plus molecules of M z plus and nu minus molecules of A z minus by the stoichiometry of the whole thing; this is nothing but material balance, …. So, if you extend that to moles – …we talked of molecules, an Avogadro number of molecules is a mole.

And therefore, one mole of M nu plus A nu minus gives you nu plus moles of M z plus, the positively charged species in the electrolyte, and nu minus moles of the negatively charged species in the electrolyte. We will get a little more comfortable with this terminology in a little while. Please wait till then. It is good to introduce it in a generic form here.

$$M_{\nu+}A_{\nu-} \rightleftharpoons \nu^+M^{z+} + \nu^-A^{z-}$$

Let us call this equation 6.51. … For completeness, nu plus and nu minus are the numbers of positive and negative ions, respectively, from one molecule of the parent electrolyte.

z plus and z minus are the number of ionic charges. … Of course, as you will see soon, this nu plus and z plus need not always be equal. Similarly, nu minus and z minus need not always be equal. Nu is the stoichiometric part, and z is a number of charges associated with each molecule.



Example 6.4

The following reaction system is important in the pH maintenance in the media of cultured mammalian cells (bicarbonate system). Find ν^+, z^+, ν^-, and z^-

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

To understand the terminology a little better, let us work out an example, in the same fashion that we have been doing so far. For that, let us consider a relevant system here. The following reaction system is important in the pH maintenance in the media of cultured mammalian cells, the bicarbonate system. For example, you may have come across mammalian cell culture. Mammalian cells are cultured in … many different vessels for example, they are passaged in what is called a T flask, a tissue culture flask, which is typically placed inside a carbon dioxide incubator.

You have a supply of carbon dioxide to that incubator. Incubator is something that maintains the temperature, humidity conditions, and in this case, carbon dioxide is also supplied to the incubator. Why is it supplied because, that is essential for maintaining the pH of the solution to be in a very narrow range of, let us say 6.8 to 7.2, or even finer. That is the wide range over which many mammalian cells are even alive. Below 6.8, they are all gone, and above 7.4 they are gone. Typically, the bicarbonate system, which involves the equilibrium of a bicarbonate salt in the medium with the carbon dioxide that is supplied in a gas form, is necessary to maintain the pH of the solution.

I will show you the reactions, and then I will let you figure out how the pH is maintained on your own. You just need to go and look at the bicarbonate buffer system, for mammalian cell culture. You can do a search; you can look at any books on mammalian cell culture – that is one of the first things that will be covered there. The question here is relevant to whatever we are doing here. It is to find nu plus z plus nu minus and z minus. The reactions are

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

These, in fact, are the reactions … that play a role to maintain the pH in the mammalian cell medium in a narrow range. … Because, when the mammalian cells are going to grow, … they are going to produce lactic acid. Lactic acid is … going to move from the inside of the cell to outside of the cell, into the medium. If there is acidification due to lactic acid, the pH is going to drop. Therefore, the medium should be able to withstand at least a reasonable acidification or the addition of acidic ions, lactic acid H plus ions, to the medium, and that is done this way.

Similarly, on the other side … if the pH goes up … due to some means, then this medium must be able to handle that. I am not getting into the mechanism of the bicarbonate buffer itself. That, … I am leaving to you as some additional reading. You can go ahead and do it. … For now, please find nu plus, z plus, nu minus, and z minus. Take about 10 minutes to do it. Go ahead, please.

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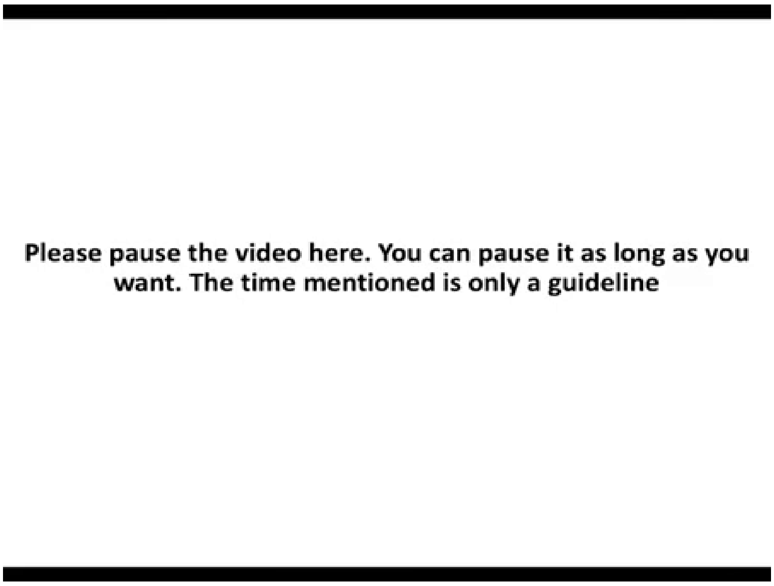

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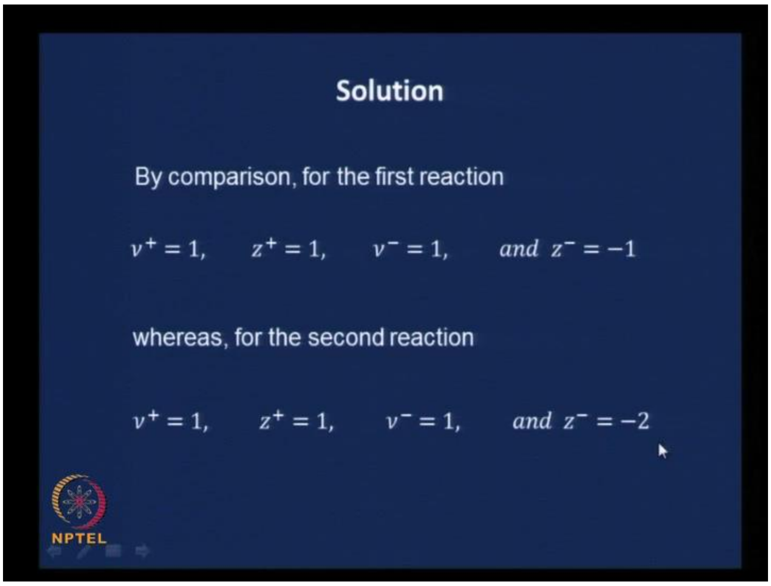
It is essentially an exercise to get comfortable with the terminology, the stoichiometric coefficients, as well as the number of charges that are associated with these molecules. The reactions that we are considering here are H2CO3 going to H plus and HCO3 minus; that is the first reaction. So, for that, you need to write nu plus, z plus, nu minus, z minus. You would have done that. And, do the same for the second reaction.



Solution

By comparison, for the first reaction

$\nu^+ = 1, \quad z^+ = 1, \quad \nu^- = 1, \quad and \;\; z^- = -1$

whereas, for the second reaction

$\nu^+ = 1, \quad z^+ = 1, \quad \nu^- = 1, \quad and \;\; z^- = -2$

The solution is reasonably straight forward. Just by comparison, you can see that

$\nu^+ = 1,\ z^+ = 1,\ \nu^- = 1,\ and\ z^- = -1$

If you wondering … where this came from, for the first reaction … nu plus is the stoichiometric coefficient of the positively charged species, that is 1 here. Therefore, nu plus is 1. There is one charge associated with the positively charged species. Therefore, z plus is 1. nu minus is again 1 here, the stoichiometric coefficient of the negatively charge species. And, z minus – there is one negative charge associated here. Therefore, z minus is 1.

In contrast, here … z minus is minus 1 because … that is the convention we follow; we add the sign also to the number. Therefore, z minus is taken as minus 1 here. In contrast here, z minus would become minus 2 as we will see in the solution given. For the second reaction please go ahead, and check. You would have already gotten this;

$\nu^+ = 1,\ \ z^+ = 1,\ \ \nu^- = 1,\ and\ z^- = -2$

by the same logic as a first reaction, but z minus is actually minus 2.

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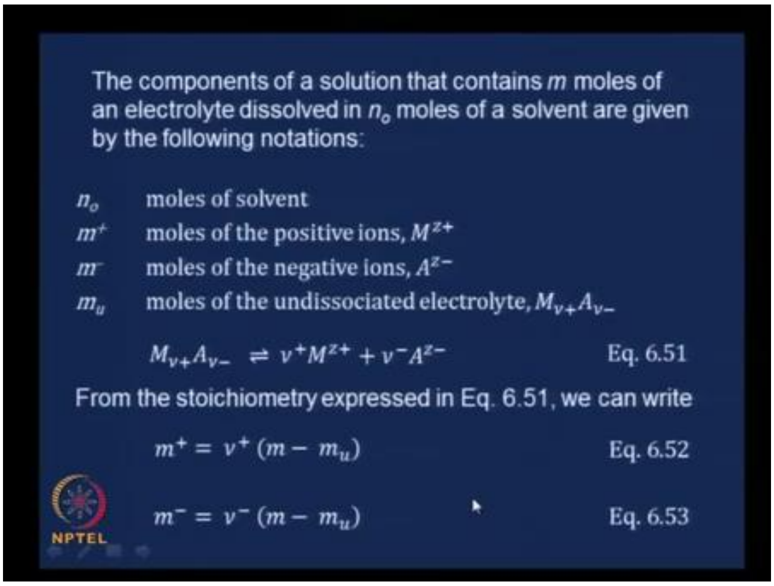

The components of a solution that contains m moles of an electrolyte dissolved in n_o moles of a solvent are given by the following notations:

n_o	moles of solvent
m^+	moles of the positive ions, M^{z+}
m^-	moles of the negative ions, A^{z-}
m_u	moles of the undissociated electrolyte, $M_{\nu+}A_{\nu-}$

$$M_{\nu+}A_{\nu-} \rightleftharpoons \nu^+M^{z+} + \nu^-A^{z-} \qquad \text{Eq. 6.51}$$

From the stoichiometry expressed in Eq. 6.51, we can write

$$m^+ = \nu^+ (m - m_u) \qquad \text{Eq. 6.52}$$

$$m^- = \nu^- (m - m_u) \qquad \text{Eq. 6.53}$$

Now, the components of the solution – that is what we are going to look at – that the solution, let us say, contains M moles of the electrolyte … you know how we represent our electrolyte – M plus nu plus A minus nu minus – electrolyte dissolved in n 0 moles of the solvent. If this is the situation, this is how we will represent things, electrolytes and our formulations. n moles of an electrolyte dissolved in n 0 moles of the solvent.

If that is so, then the notation is n 0 is the moles of the solvent, that is as given here. m plus is taken to represent the moles of the positive ions, M z plus. m minus is taken to represent the moles of the negative ions, A z minus, and m u is the moles of the un dissociated electrolyte, M nu plus A nu minus. Now, the reaction that we saw earlier,

$$M_{\nu+}A_{\nu-} \rightleftharpoons \nu^{+}M^{z+} + \nu^{-}A^{z-}$$

The number of moles of this that exist at equilibrium, when the dissociation has taken place is called m u. And this results from adding m moles of an electrolyte, which could be of course, different from m u, to n 0 moles of the solvent. That is the system that we are considering.

Now, from the stoichiometry as given here, it is quite easy to see that the number of moles of positive ion as represented by M plus is nothing but, nu plus because, one mole of this results in nu moles of the positive ion; nu plus times m, m is the total number of moles with a electrolyte, minus the moles of the un dissociated electrolyte. … If m u is what is remaining here, m minus m u must have converted to this. … One mole of this gives you nu plus moles of this, and therefore, m plus equals nu plus into m minus m u. Similarly, m minus would be nu minus into m minus m u;

$$m^{+} = \nu^{+}\,(m - m_u)$$
$$m^{-} = \nu^{-}\,(m - m_u)$$

equations 6.52 and 6.53.

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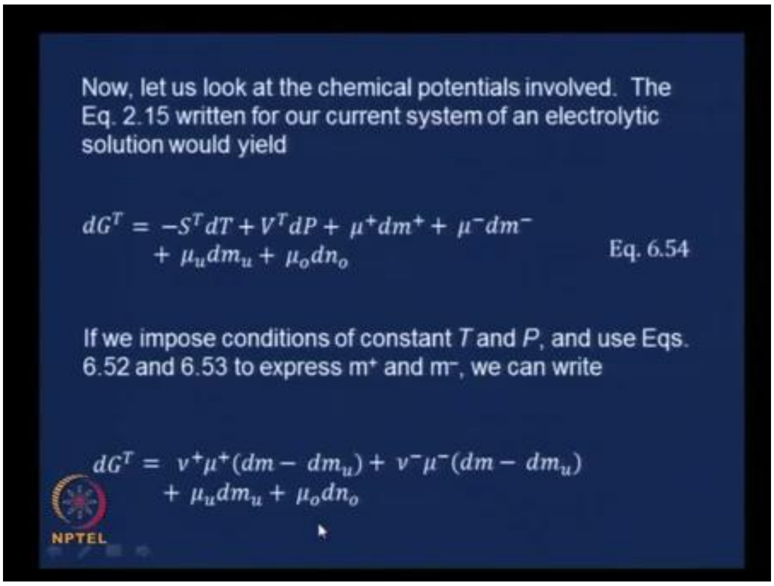

Now, let us look at the chemical potentials involved. The Eq. 2.15 written for our current system of an electrolytic solution would yield

$$dG^T = -S^T dT + V^T dP + \mu^+ dm^+ + \mu^- dm^- + \mu_u dm_u + \mu_o dn_o \qquad \text{Eq. 6.54}$$

If we impose conditions of constant *T* and *P*, and use Eqs. 6.52 and 6.53 to express m⁺ and m⁻, we can write

$$dG^T = \nu^+\mu^+(dm - dm_u) + \nu^-\mu^-(dm - dm_u) + \mu_u dm_u + \mu_o dn_o$$

Now, let us get to a thermodynamics thing. Let us look at the chemical potentials involved. Equation 2.15, one of the basic equations … you will remember that when you see that written here. If you write equation 2.15 which involves Gibbs free energy, total Gibbs free energy written for our current system of an electrolytic solution, would be d G T equals – yeah, now it is coming back to you – minus S T d T plus V T d p plus sum over i mu i d n i.

Going by our terminology, and writing each one of those terms separately, we get

$$dG^T = -S^T dT + V^T dP + \mu^+ dm^+ + \mu^- dm^- + \mu_u dm_u + \mu_o dn_o$$

We will call this equation 6.54. Now, if we impose conditions of constant temperature, and pressure, the first two terms are going to go to 0, d T is 0, d P is 0.

$$dG^T = \nu^+\mu^+(dm - dm_u) + \nu^-\mu^-(dm - dm_u) + \mu_u dm_u + \mu_o dn_o$$

And, if we use equation 6.52 and 6.53 to express m plus and m minus … remember, we express m plus in terms of the number of moles of the electrolyte added, and the number of moles of the un dissociated electrolyte; just the two equations before this. Let me write it and it will come back to you. If we do use these two expressions, equations 6.52 and 6.53 to express m plus and m minus, we get d G T, the first two terms have gone to 0 already, equals mu plus which is here, and d m plus is nothing but nu plus into (d m minus d m u) quite easy to see this. Similarly, you have a mu minus here, and d m minus is nu minus into d m minus d m u, plus, of course, mu u d m u plus mu 0 d n 0 the number of moles of the solvent.

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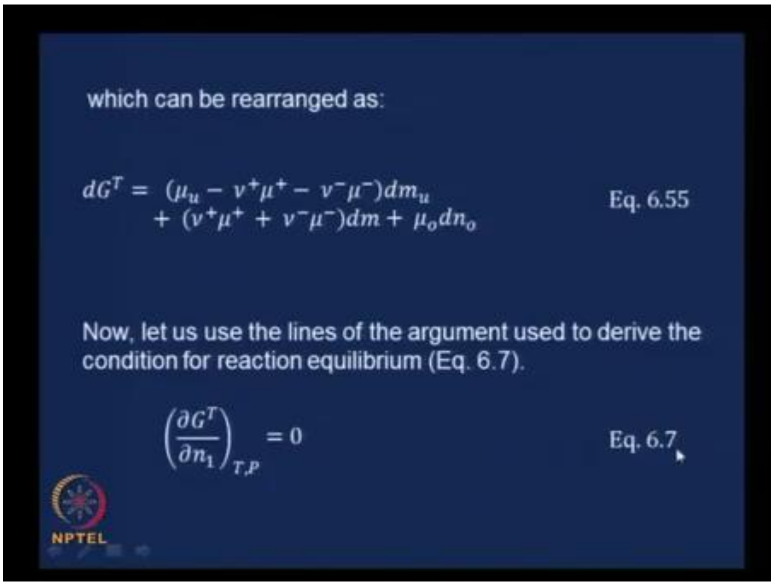

which can be rearranged as:

$$dG^T = (\mu_u - \nu^+\mu^+ - \nu^-\mu^-)dm_u + (\nu^+\mu^+ + \nu^-\mu^-)dm + \mu_o dn_o \qquad \text{Eq. 6.55}$$

Now, let us use the lines of the argument used to derive the condition for reaction equilibrium (Eq. 6.7).

$$\left(\frac{\partial G^T}{\partial n_1}\right)_{T,P} = 0 \qquad \text{Eq. 6.7}$$

And we can rearrange this as d G T … I have essentially collected all terms with a d m u together, mu u minus nu plus mu plus minus nu minus mu minus d m u. You know, from here there is a d m u here, there is a d m u here and there is a d m u here; I just have collected the coefficients of those, … and collated them in terms of d m u, d m, and d n 0. And so, the first term was mu u minus nu plus mu plus minus nu minus mu minus d m u. The second term, I have collected in terms of d m, nu plus mu plus plus nu minus mu minus d m, plus mu 0 d n 0;

$$dG^T = (\mu_u - \nu^+\mu^+ - \nu^-\mu^-)dm_u + (\nu^+\mu^+ + \nu^-\mu^-)dm + \mu_o dn_o$$

equation 6.55.

And now, let us use the lines of the argument used to derive the condition for reaction equilibrium. … If you call the lines of argument, it was that we had free energy, and the free energy changes with the reaction coordinate or the number of moles. And therefore, if you take the partial derivative of that with respect to the reaction coordinate, under certain constant conditions, then since this the minimum at equilibrium, the slope of this curve … you know …the free energy versus reaction coordinate or the number of moles, the slope of that curve would be 0. We will use the same lines of argument here;

$$\left(\frac{\partial G^T}{\partial n_1}\right)_{T,\,P} = 0$$

This is the condition for equilibrium, which is carried on from our early courses even. This also formalizes equation 6.7 in this module.

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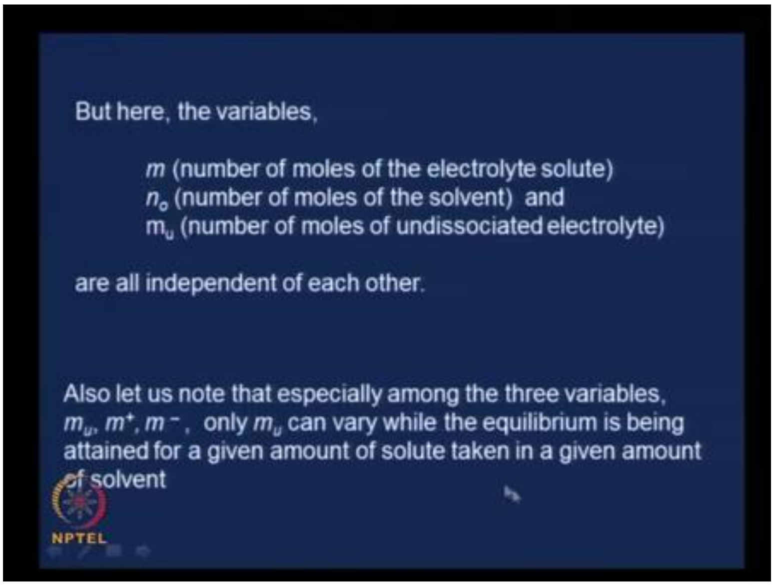

But here, the variables,

m (number of moles of the electrolyte solute)
n_o (number of moles of the solvent) and
m_u (number of moles of undissociated electrolyte)

are all independent of each other.

Also let us note that especially among the three variables, m_u, m^+, m^-, only m_u can vary while the equilibrium is being attained for a given amount of solute taken in a given amount of solvent

But here, the variables … you know … m is the number of moles of the electrolyte solute, which is dropped into n 0 moles of the solvent, and it results in m u number of moles of un-dissociated electrolyte; all these three are independent of each other. You could take some number of moles of the electrolyte solute in some number of moles of the solvent, and depending on the conditions, some number of moles of the un-dissociated electrolyte will remain. The rest would have dissociated.

In other words, these are not dependent on each other. That is only point that I am trying to make here. These are independent of each other. Whereas, if you consider these three variables, m u, the number of moles of un dissociated electrolyte, the number of moles of positively charged electrolyte, the number of moles of negatively charged electrolyte, these are related by the equilibrium distribution. You know, at a certain point in the dissociation, it can dissociate only to a certain number of moles of m u plus and … a certain number of moles of the positive species, and certain number of moles of the negative species, that is governed by equilibrium.

Therefore, only one of them can be considered to be independent, whereas, the other two will depend on that based on the equilibrium conditions. Therefore, only m u can vary while the equilibrium is being attained, for a given number of moles of solute m taken in a certain number of moles of the solvent n 0. Once we are clear about these things, it’s quite easy write the functionality dependences.

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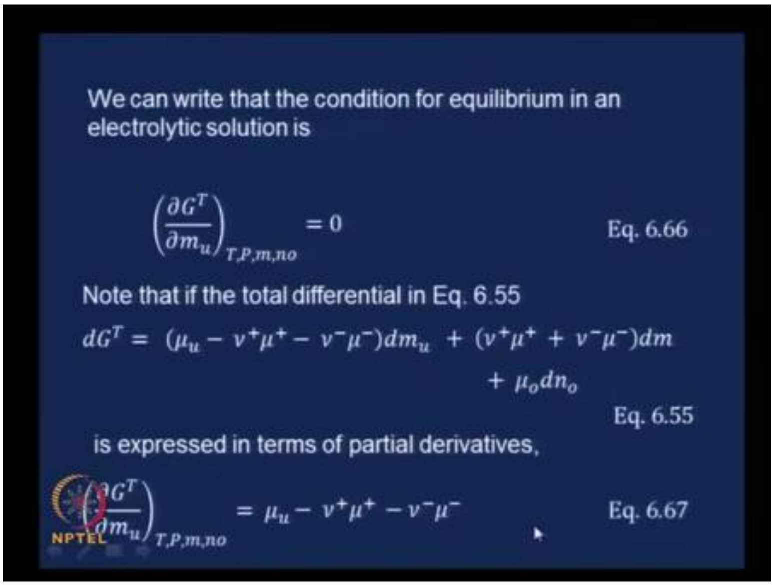

We can write that the condition for equilibrium in an electrolytic solution is

$$\left(\frac{\partial G^T}{\partial m_u}\right)_{T,P,m,no} = 0 \qquad \text{Eq. 6.66}$$

Note that if the total differential in Eq. 6.55

$$dG^T = (\mu_u - v^+\mu^+ - v^-\mu^-)dm_u + (v^+\mu^+ + v^-\mu^-)dm + \mu_o dn_o \qquad \text{Eq. 6.55}$$

is expressed in terms of partial derivatives,

$$\left(\frac{\partial G^T}{\partial m_u}\right)_{T,P,m,no} = \mu_u - v^+\mu^+ - v^-\mu^- \qquad \text{Eq. 6.67}$$

We can write the condition for equilibrium in an electrolytic solution as dou G T dou m u, you know … we are just taking it with respect to one independent variable, the number of moles of the un-dissociated electrolyte, at constant T, P, m and n 0, the number of moles of all other species, and the number of moles of the solvent, this is 0.

$$\left(\frac{\partial G^T}{\partial m_u}\right)_{T,P,m,no} = 0$$

This is the condition for equilibrium, equation 6.66. … Note if the total differential is considered in 6.55, d G T equals under constant conditions of temperature and pressure, was nothing but

$$dG^T = (\mu_u - \nu^+\mu^+ - \nu^-\mu^-)dm_u + (\nu^+\mu^+ + \nu^-\mu^-)dm + \mu_o dn_o$$

This if we write in terms of partial differentials, it is easy to see … this is d G T; therefore, this would be dou G T dou m u at constant other things, I am not going to mention the constants here, dou G T dou m u d m u, dou G T dou m d m, dou G T dou n 0 d n 0. Therefore, dou G T dou m u at constant T, P, m, n 0 is nothing but this term, mu u minus nu plus mu plus minus nu minus mu minus.

$$\left(\frac{\partial G^T}{\partial m_u}\right)_{T, P, m, no} = \mu_u - \nu^+\mu^+ - \nu^-\mu^-$$

Let us call this equation 6.67. Now we know where we are getting at. This is equal to 0, so we are going to equate this to 0.

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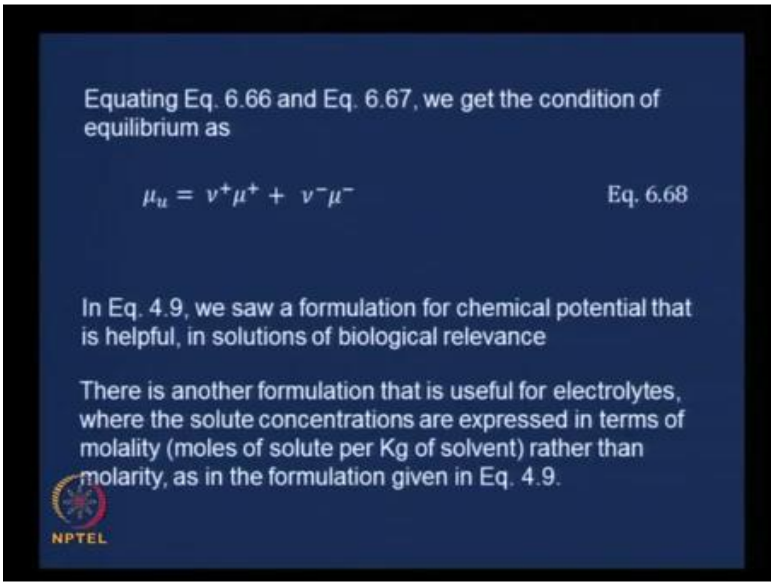

Equating Eq. 6.66 and Eq. 6.67, we get the condition of equilibrium as

$$\mu_u = \nu^+\mu^+ + \nu^-\mu^- \quad \text{Eq. 6.68}$$

In Eq. 4.9, we saw a formulation for chemical potential that is helpful, in solutions of biological relevance

There is another formulation that is useful for electrolytes, where the solute concentrations are expressed in terms of molality (moles of solute per Kg of solvent) rather than molarity, as in the formulation given in Eq. 4.9.

If we do that, we get

$$\mu_u = \nu^+\mu^+ + \nu^-\mu^-$$

In other words, the chemical potential of the un-dissociated species must equal the sum of the chemical potentials of the charged species weighed by its stoichiometric coefficients; equation 6.68. Now, in equation 4.9, we saw a formulation for chemical species that is helpful, in solutions of biological relevance. … This was a solution … which makes it convenient, and so on, and so forth.

Similarly, there is a another formulation that is used for electrolytes, where the solute concentrations are expressed in terms of molality … l, l instead of r … molality, which is moles of solute per kilo gram of solvent. It is not moles of solute per volume of the solvent, it is moles of solute per unit mass of the solvent. … molarity of course, you know, is moles of the solute per liter of the solution whereas, here it is moles of the solute per kilogram of the solvent.

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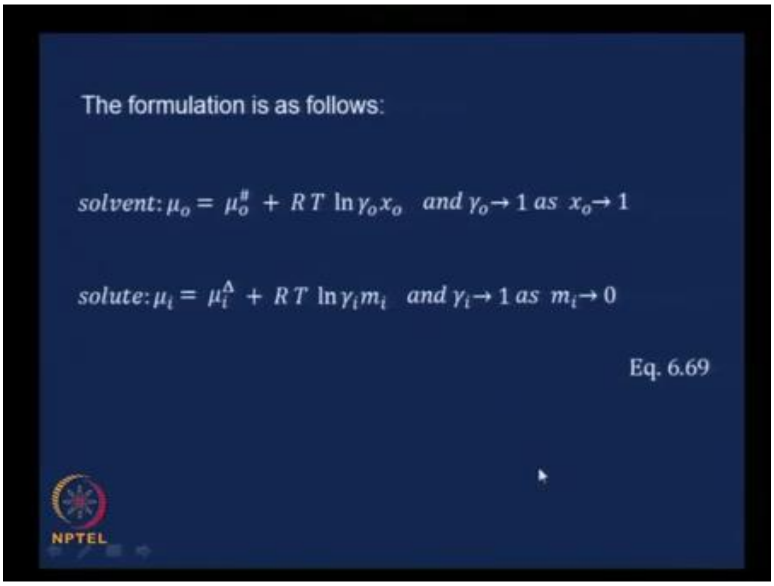

The formulation is as follows:

solvent: $\mu_o = \mu_o^{\#} + R\,T \ln \gamma_o x_o$ and $\gamma_o \to 1$ as $x_o \to 1$

solute: $\mu_i = \mu_i^{\Delta} + R\,T \ln \gamma_i m_i$ and $\gamma_i \to 1$ as $m_i \to 0$

Eq. 6.69

If we use this formulation, then we get, for the solvent

$$solvent: \qquad \mu_o = \mu_o^{\#} + R\,T\ ln\gamma_o x_o \qquad and\, \gamma_o \to 1\ \ as\ x_o \to 1$$

$$solute: \qquad \mu_i = \mu_i^{\Delta} + R\,T\ ln\gamma_i m_i \qquad and\, \gamma_i \to 1\ \ as\ m_i \to 0$$

For the solute, we have mu i equals mu i triangle, if we want to call it that – this is based on molality, moles of the solute by the mass of the solvent, plus R T ln gamma i m i, this is in molal units, moles of the solute by the mass of the solvent. The activity coefficient gamma i tends to 1 as m i, the molality, tends to 0. Let us call this equation 6.69.

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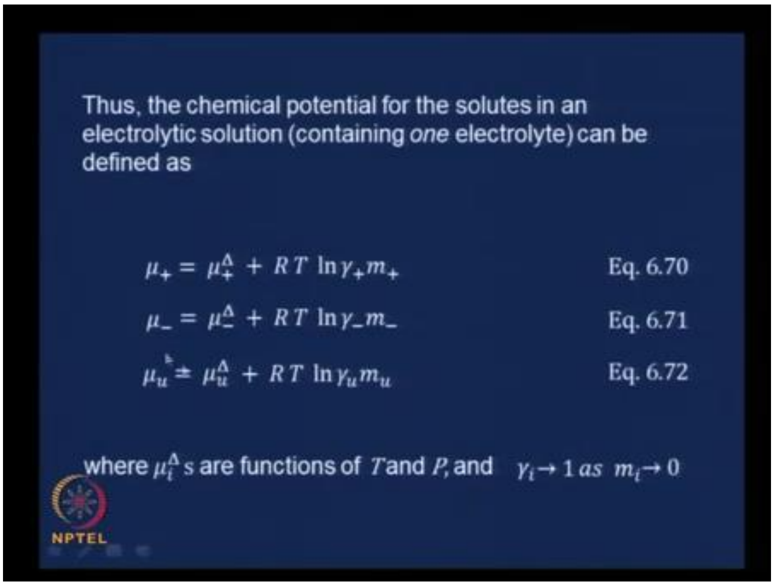

Thus, the chemical potential for the solutes in an electrolytic solution (containing *one* electrolyte) can be defined as

$\mu_+ = \mu_+^\Delta + R\,T\,\ln \gamma_+ m_+$ Eq. 6.70

$\mu_- = \mu_-^\Delta + R\,T\,\ln \gamma_- m_-$ Eq. 6.71

$\mu_u = \mu_u^\Delta + R\,T\,\ln \gamma_u m_u$ Eq. 6.72

where μ_i^Δ s are functions of T and P, and $\gamma_i \to 1$ as $m_i \to 0$

Therefore, the chemical potential for the solutes in an electrolytic solution, let us say it contains only one electrolyte to begin with, we will deal only with one electrolyte in this course. This is anyway an extension to you, and if it gets more complicated, you can get into a research mode, and find out how it is handled. It has already been done in papers and so on. This can be defined as …

$$\mu_+ = \mu_+^\Delta + R\,T\,ln\,\gamma_+ m_+$$

Let us call this equation 6.70.

And, I am just writing the chemical potential for each of these species separately.

$$\mu_- = \mu_-^\Delta + R\,T\,ln\,\gamma_- m_-$$

equation 6.71. And, mu u the chemical potential of the un-dissociated species, is nothing but

$$\mu_u = \mu_u^\Delta + R\,T\,ln\,\gamma_u m_u$$

Equation 6.72; where these mu triangles, the standard values, are functions of temperature and pressure, the same way as mu hash was. Of course,

$\gamma_i \to 1 \;\; as \;\; m_i \to 0$

in all these cases … to be in line with the definition that we have given earlier.

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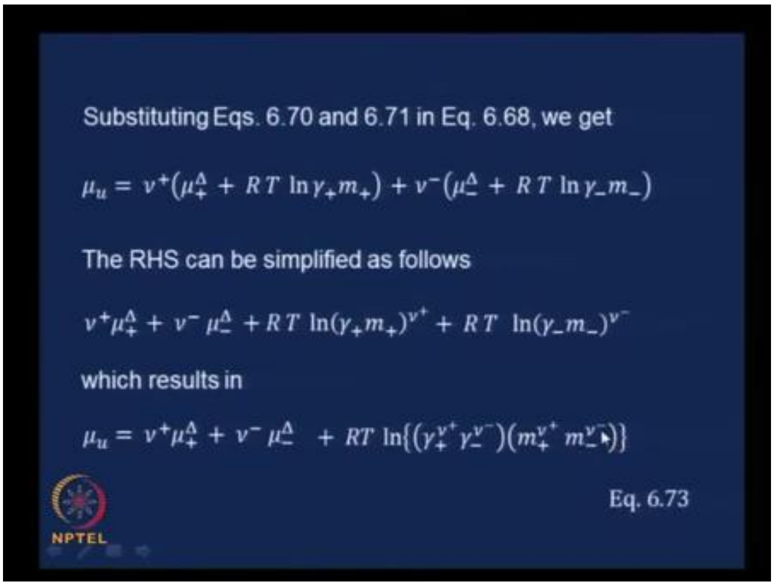

Substituting Eqs. 6.70 and 6.71 in Eq. 6.68, we get

$$\mu_u = \nu^+(\mu_+^\Delta + RT\ \ln \gamma_+ m_+) + \nu^-(\mu_-^\Delta + RT\ \ln \gamma_- m_-)$$

The RHS can be simplified as follows

$$\nu^+\mu_+^\Delta + \nu^-\ \mu_-^\Delta + RT\ \ln(\gamma_+ m_+)^{\nu^+} + RT\ \ln(\gamma_- m_-)^{\nu^-}$$

which results in

$$\mu_u = \nu^+\mu_+^\Delta + \nu^-\ \mu_-^\Delta \ + RT\ \ln\{(\gamma_+^{\nu^+}\gamma_-^{\nu^-})(m_+^{\nu^+} m_-^{\nu^-})\}$$

Eq. 6.73

Now, if we substitute equations 6.70 and 6.71 and 6.68 … what do I mean by that … 6.70 and 6.71, and 6.68 was this. This is the condition for ionic equilibrium,

$$\mu_u = \nu^+(\mu_+^\Delta + R\,T\ ln\,\gamma_+ m_+) + \nu^-(\mu_-^\Delta + R\,T\ ln\,\gamma_- m_-)$$

I have replaced the mu plus with mu plus triangle plus R T ln gamma plus m plus, and nu minus, mu minus by mu minus triangle plus R T ln gamma minus m minus.

Now, let us look at the right hand side alone, and just combine the terms … appropriately to make a point. nu plus mu plus, plus nu minus mu minus plus R T ln gamma plus m plus to the power of nu plus … you know, there is a ln here, there is a nu plus here. Therefore, this if it is taken inside the ln, it becomes a power. Therefore, ln of gamma plus m plus nu plus plus R T ln gamma minus m minus raised to the power of nu minus.

$$\nu^{+}\mu_{+}^{\Delta} + \ \nu^{-}\ \mu_{-}^{\Delta}\ \ R\,T\ \ ln(\gamma_{+}m_{+})^{\nu^{+}} + \ \ R\,T\ \ ln(\gamma_{-}m_{-})^{\nu^{-}}$$

Just a rearrangement, which would result in nu plus mu plus triangle plus nu minus mu minus triangle plus … you know, there are two logarithmic terms here, added together. If you put them together, the addition of logs is log of the products. Therefore, plus R T gamma plus raised to the power of nu plus, gamma minus raised to the power nu minus, m plus raised to the power nu plus, m minus raised to the power nu minus,

$$\mu_{u} = \ \nu^{+}\mu_{+}^{\Delta}\ + \ \nu^{-}\ \mu_{-}^{\Delta}\ \ + \ \ RT\ \ ln\{(\gamma_{+}^{\nu^{+}}\gamma_{-}^{\nu^{-}})(m_{+}^{\nu^{+}}\ m_{-}^{\nu^{-}})\}$$

equation 6.73.

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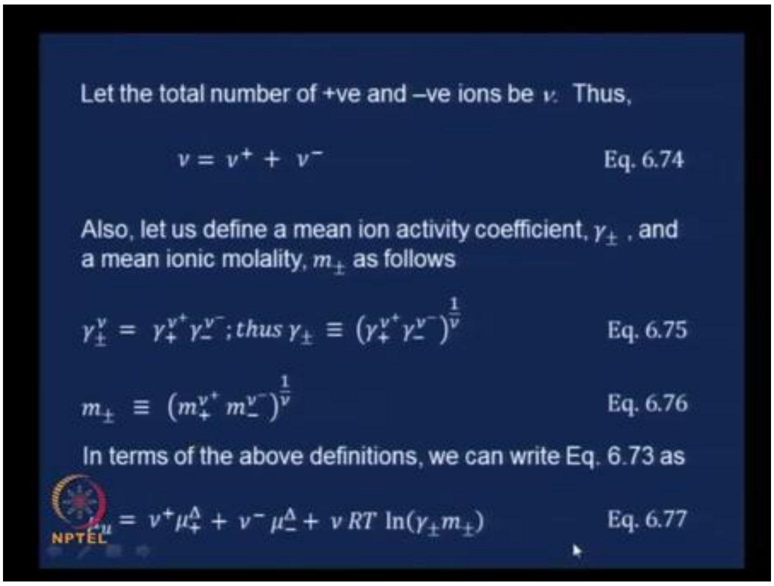

Let the total number of +ve and –ve ions be ν. Thus,

$$\nu = \nu^{+} + \nu^{-} \qquad \text{Eq. 6.74}$$

Also, let us define a mean ion activity coefficient, $\gamma_{\pm}$, and a mean ionic molality, $m_{\pm}$ as follows

$$\gamma_{\pm}^{\nu} = \gamma_{+}^{\nu^{+}}\gamma_{-}^{\nu^{-}};\ thus\ \gamma_{\pm} \equiv (\gamma_{+}^{\nu^{+}}\gamma_{-}^{\nu^{-}})^{\frac{1}{\nu}} \qquad \text{Eq. 6.75}$$

$$m_{\pm} \equiv (m_{+}^{\nu^{+}}\ m_{-}^{\nu^{-}})^{\frac{1}{\nu}} \qquad \text{Eq. 6.76}$$

In terms of the above definitions, we can write Eq. 6.73 as

$$\mu_{u} = \nu^{+}\mu_{+}^{\Delta} + \nu^{-}\mu_{-}^{\Delta} + \nu RT\ \ln(\gamma_{\pm}m_{\pm}) \qquad \text{Eq. 6.77}$$

If the total number of positive and negative ions is nu – that’s what it means –

$$\nu = \ \nu^{+}\ + \ \ \nu^{-}$$

If we define a mean ion activity coefficient as gamma plus minus, and a mean ionic molality as m plus minus … what do I mean by that? You know, there are these terms here. I am just trying to simplify these terms. There are two terms, gamma plus to the power of nu plus, gamma minus to the power of nu minus. And similarly, m plus to the power of nu plus, m minus to the power nu minus. …I am going to replace this with some mean value, I am going to replace this with some other mean value; that is what I am doing here.

So,

$$\gamma_{\pm}^{\nu} = \gamma_{+}^{\nu^{+}} \gamma_{-}^{\nu^{-}}$$

Therefore,

$$\gamma_{\pm} \equiv \left(\gamma_{+}^{\nu^{+}} \gamma_{-}^{\nu^{-}}\right)^{\frac{1}{\nu}}$$

let us call that Eq. 6.75. And, on the same lines

$$m_{\pm} \equiv \left(m_{+}^{\nu^{+}}\, m_{-}^{\nu^{-}}\right)^{\frac{1}{\nu}}$$

Eq. 6.76.

Therefore, using the mean values, in term of the above definition … that is what it is, we can write the previous equation as

$$\mu_u = \nu^{+} \mu_{+}^{\Delta} + \nu^{-} \mu_{-}^{\Delta} + \nu\, RT\ ln(\gamma_{\pm} m_{\pm})$$

– these are the mean values, that we have defined here. Let us call this equation 6.77.

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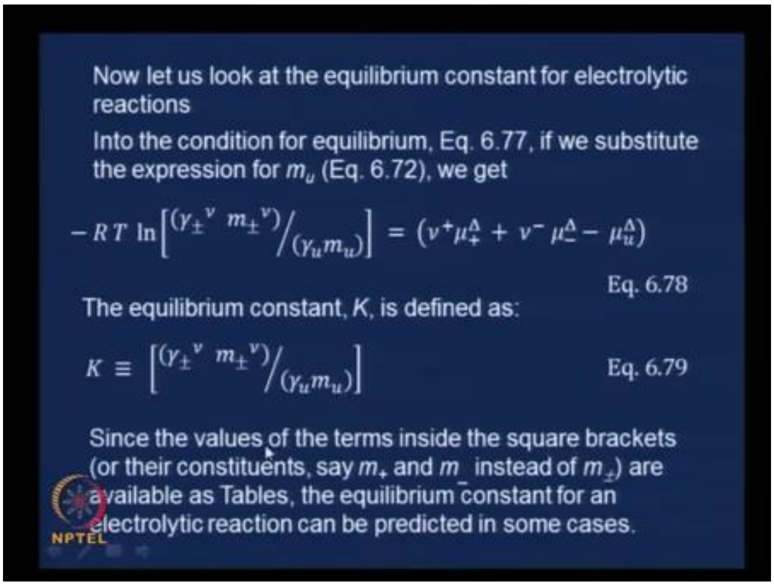

Now let us look at the equilibrium constant for electrolytic reactions

Into the condition for equilibrium, Eq. 6.77, if we substitute the expression for m_u (Eq. 6.72), we get

$$-RT\ \ln\left[{(\gamma_\pm{}^\nu\ m_\pm{}^\nu)}\Big/{(\gamma_u m_u)}\right] = (\nu^+\mu_+^\Delta + \nu^-\ \mu_-^\Delta - \mu_u^\Delta)$$

Eq. 6.78

The equilibrium constant, K, is defined as:

$$K \equiv \left[{(\gamma_\pm{}^\nu\ m_\pm{}^\nu)}\Big/{(\gamma_u m_u)}\right]$$

Eq. 6.79

Since the values of the terms inside the square brackets (or their constituents, say m_+ and m_- instead of $m_\pm$) are available as Tables, the equilibrium constant for an electrolytic reaction can be predicted in some cases.

Now, let us look at the equilibrium constant for the electrolytic reactions. It is nice to know of an equilibrium constant for the dissociation process, and relate it to the chemical potential. To do that, into the condition of equilibrium 6.77, which is the mu u equals nu plus mu plus, plus nu minus mu minus, if you substitute the expression for m u … you know, whatever we had written in terms of the other variables, we get minus R T ln of gamma plus minus raised to the power nu, m plus minus raised to the power nu, divided by gamma u m u, equals nu plus mu plus triangle plus nu minus mu minus triangle minus mu u triangle.

Just do this exercise on your own, and see whether you get it. It is a one step process, you must be able to get this;

$$-\,R\,T\ \ln\left[{(\gamma_\pm{}^\nu\ \ m_\pm{}^\nu)}\Big/{(\gamma_u m_u)}\right] = \ (\nu^+\mu_+^\Delta\ +\ \nu^-\ \mu_-^\Delta -\ \mu_u^\Delta)$$

equation 6.78. Now, it must be clear to you. Following the same strategy as for non-ionic reactions, we can see what equilibrium constant is going be defined as. Now, we are trying to get a minus R T ln K term here. Therefore, K is defined as

$$K \equiv \left[{(\gamma_{\pm}{}^{\nu}\ \ m_{\pm}{}^{\nu})}\big/{(\gamma_u m_u)} \right]$$

Let us call this equation 6.79.

Since the values of the terms inside the square brackets, which is this, or their constituents, m plus and m minus instead of m plus minus, are sometimes available in tables. So, there is a way by which you can a priori say, what the equilibrium constant of an electrolytic reaction would be. That is what makes this powerful. So, prediction of the equilibrium constant is possible, if these values are available.

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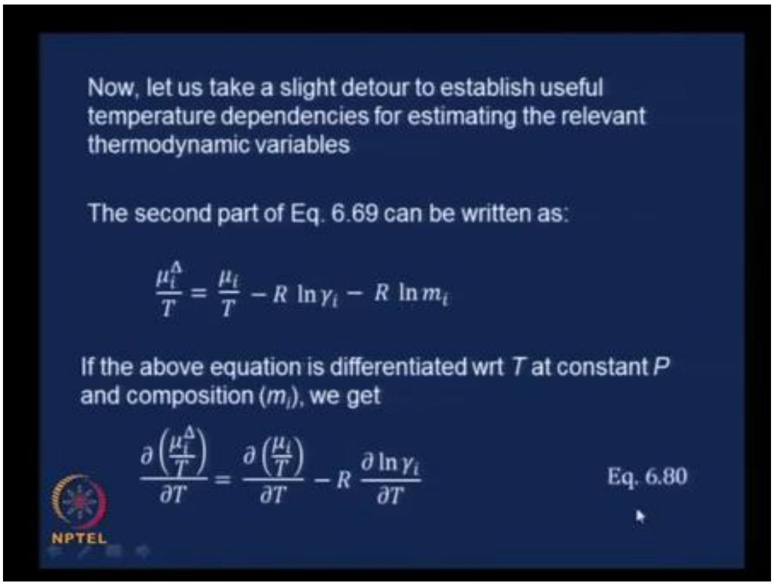

Now, let us take a slight detour to establish useful temperature dependencies for estimating the relevant thermodynamic variables

The second part of Eq. 6.69 can be written as:

$$\frac{\mu_i^{\Delta}}{T} = \frac{\mu_i}{T} - R\ln\gamma_i - R\ln m_i$$

If the above equation is differentiated wrt T at constant P and composition (m_i), we get

$$\frac{\partial\left(\frac{\mu_i^{\Delta}}{T}\right)}{\partial T} = \frac{\partial\left(\frac{\mu_i}{T}\right)}{\partial T} - R\,\frac{\partial \ln\gamma_i}{\partial T} \qquad \text{Eq. 6.80}$$

Now, we are going take a slight detour to establish useful temperature dependencies, for estimating the relevant thermodynamic variables here, the equilibrium constant and so on, and so forth. For that, we are going to write the second part of equation 6.69. What is 6.69? Let us go back and show that to you. … This was the formulation for the chemical potential of the solvent and solute, in terms of the special way for electrolytes. Solvent remains the same whereas, solute was mu i equals mu i triangle plus R T ln gamma i m i, where m i is a molal units. We are going to look at this particular equation now.

We can write the second part of the equation of 6.69 that we just saw, as

$$\frac{\mu_i^{\Delta}}{T} = \frac{\mu_i}{T} - R\ ln\gamma_i - R\ ln m_i$$

I just split it up as this and divided by the temperature. Therefore, these two T terms have gone. Now, if this equation is differentiated with respect to temperature at constant pressure, and composition, which means m i is constant, and therefore, the derivative with respect to temperature is going to be 0.

So, … if we differentiate this with respect to temperature, then we have

$$\frac{\partial\left(\frac{\mu_i^{\Delta}}{T}\right)}{\partial T} = \frac{\partial\left(\frac{\mu_i}{T}\right)}{\partial T} - R\,\frac{\partial\, ln\gamma_i}{\partial T}$$

Let us call this equation 6.80.

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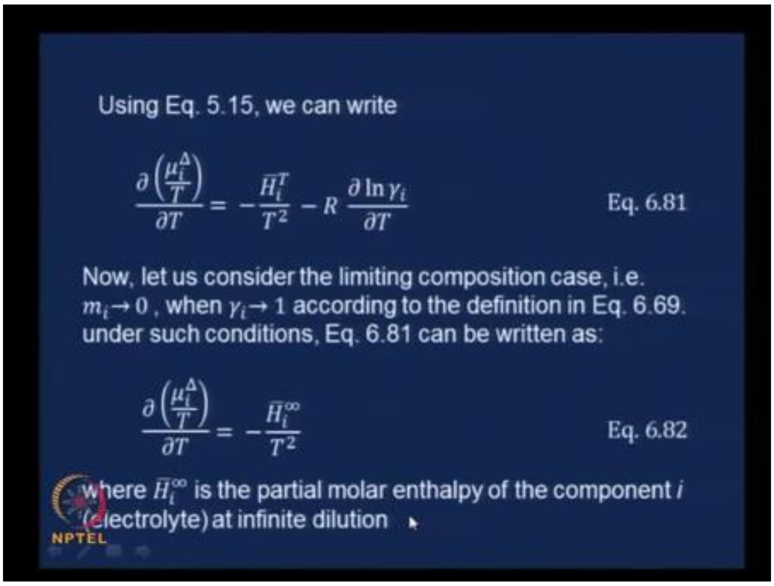

Using Eq. 5.15, we can write

$$\frac{\partial\left(\frac{\mu_i^{\Delta}}{T}\right)}{\partial T} = -\frac{\bar{H}_i^T}{T^2} - R\,\frac{\partial \ln\gamma_i}{\partial T} \qquad \text{Eq. 6.81}$$

Now, let us consider the limiting composition case, i.e. $m_i \to 0$, when $\gamma_i \to 1$ according to the definition in Eq. 6.69. under such conditions, Eq. 6.81 can be written as:

$$\frac{\partial\left(\frac{\mu_i^{\Delta}}{T}\right)}{\partial T} = -\frac{\bar{H}_i^{\infty}}{T^2} \qquad \text{Eq. 6.82}$$

where $\bar{H}_i^{\infty}$ is the partial molar enthalpy of the component i (electrolyte) at infinite dilution

And using 5.15, which will become … now we have seen this so many times, it will come back to you ..

$$\frac{\partial\left(\frac{\mu_i^{\Delta}}{T}\right)}{\partial T} = -\frac{\bar{H}_i^{T}}{T^2} - R\,\frac{\partial \ln\gamma_i}{\partial T}$$

This we had shown by an elaborate procedure, and by equation 5.15 … minus of course, the remaining terms are dou ln gamma i dou T; equation 6.81.

Now, let us consider the limiting composition case, that is m i tending to 0 when gamma i tends to 0. According to the definition given in 6.69, under such conditions, equation 6.81 can be written as

$$\frac{\partial\left(\frac{\mu_i^{\Delta}}{T}\right)}{\partial T} = -\frac{\bar{H}_i^{\infty}}{T^2}$$

m i tending to 0 – infinite dilution, $\bar{H}_i^{\infty}$ in the partial molar value at infinite dilution divided by T squared, equation 6.82, where this is actually called, the partial molar enthalpy of component i, which is the electrolyte, at infinite dilution.

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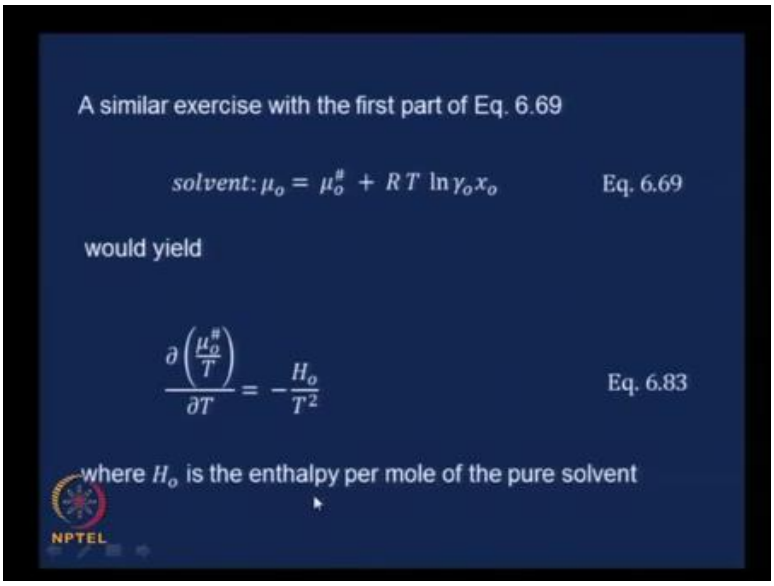

A similar exercise with the first part of Eq. 6.69

$solvent: \mu_o = \mu_o^{\#} + RT\ln\gamma_o x_o$ Eq. 6.69

would yield

$$\frac{\partial\left(\frac{\mu_o^{\#}}{T}\right)}{\partial T} = -\frac{H_o}{T^2}$$ Eq. 6.83

where H_o is the enthalpy per mole of the pure solvent

Now, if we do a similar exercise with the first part of that equation, divided by T and take the derivative with respect to temperature again and so on, this is the first part of the equation 6.69,

$$solvent: \qquad \mu_o = \mu_o^{\#} + RT\ ln\gamma_o x_o$$

that would give us

$$\frac{\partial\left(\frac{\mu_o^{\#}}{T}\right)}{\partial T} = -\frac{H_o}{T^2}$$

Eq. 6.83. Where H naught is the enthalpy per mole of the pure solvent. Now, if you substitute 6.83, into this 6.81, we are trying to substitute one of these values here.

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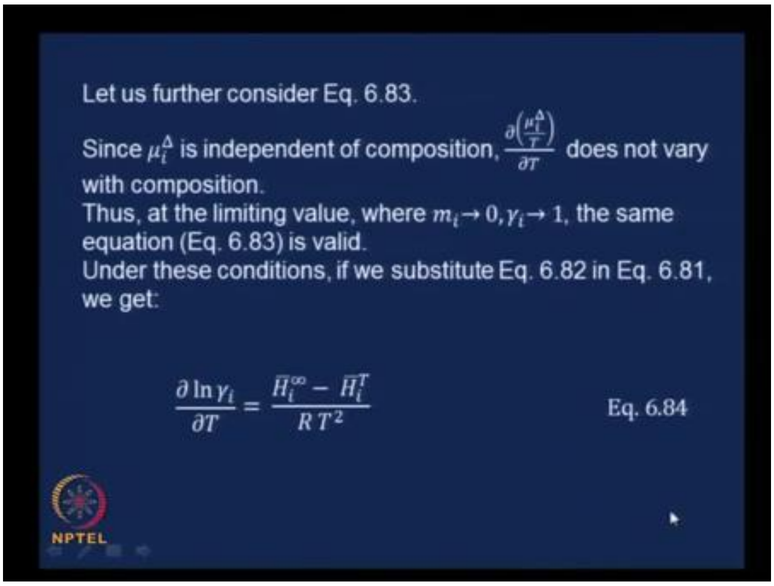

Let us further consider Eq. 6.83.

Since μ_i^{Δ} is independent of composition, $\frac{\partial\left(\frac{\mu_i^{\Delta}}{T}\right)}{\partial T}$ does not vary with composition.

Thus, at the limiting value, where $m_i \to 0, \gamma_i \to 1$, the same equation (Eq. 6.83) is valid.

Under these conditions, if we substitute Eq. 6.82 in Eq. 6.81, we get:

$$\frac{\partial \ln \gamma_i}{\partial T} = \frac{\overline{H}_i^{\infty} - \overline{H}_i^{T}}{RT^2} \qquad \text{Eq. 6.84}$$

Let us further consider 6.83 before we even substitute that. Note that mu i triangle is not dependent on composition. Therefore,

$$\frac{\partial\left(\frac{\mu_i^{\Delta}}{T}\right)}{\partial T}$$

does not vary with composition. Therefore, follow this argument a little carefully, we have done this argument earlier too, at the limiting value where the molality has gone to 0 and gamma is gone to 1, the same equation 6.83 is valid. So, it does not depend on composition. Therefore, this equation must be valid, even under these limiting conditions of infinite dilution.

And therefore, under these conditions, if we substitute 6.82 in 6.81 we get

$$\frac{\partial \ln \gamma_i}{\partial T} = \frac{\bar{H}_i^{\infty} - \bar{H}_i^{T}}{R\,T^2}$$

we are just substituting this into this, minus H i infinity hash by T squared onto this, and getting dou ln gamma i dou T, an expression for that. Dou gamma i dou T equals H i infinity hash minus H i T hash by R T squared. We will call this equation 6.84, and what this gives us is the temperature dependence of the activity coefficient.

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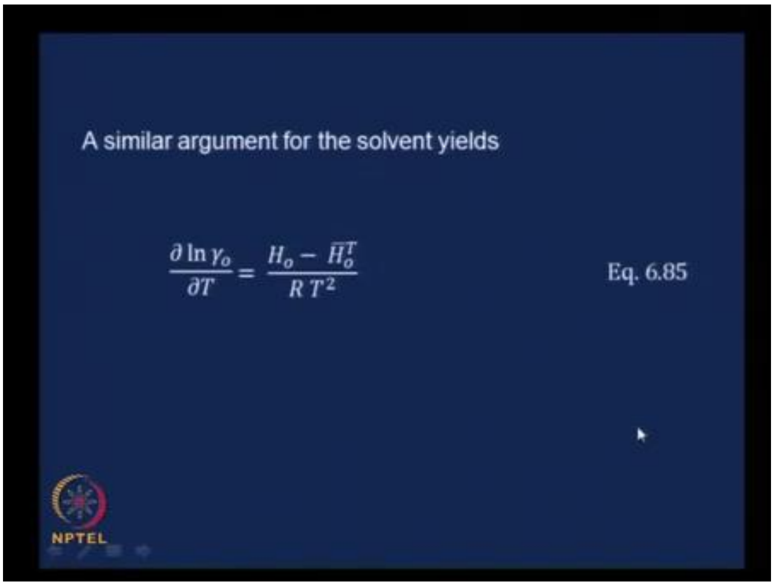

A similar argument for the solvent yields

$$\frac{\partial \ln \gamma_o}{\partial T} = \frac{H_o - \bar{H}_o^{T}}{R\,T^2} \qquad \text{Eq. 6.85}$$

If we do a similar exercise … substitute for the solvent, … the 0 case in the same equation, then we will get

$$\frac{\partial \ln \gamma_o}{\partial T} = \frac{H_o - \bar{H}_o^{T}}{R\,T^2}$$

Therefore, by knowing the right hand side, we can get the dependence of the activity coefficient on temperature for an electrolytic system, equation 6.85. This is all I have for the electrolytes, and when we meet in the next class, we will do a review of whatever we have done in this course. See you then.