Advanced Chemical Thermodynamics & Kinetics

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Lecture – 36
Non-ideal solutions, Activity of ions (Debye-Huckle theory) – I

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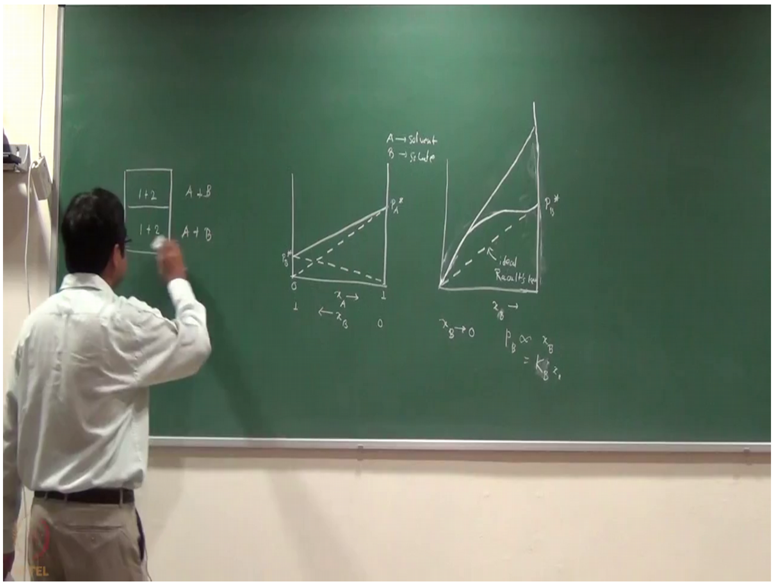

We have suppose two solvent, so we write it 1 and 2 at this is writing in the components as A plus B that is just the same.

And remember that suppose we have two solvents right and suppose for example, we have mole fraction ok. If I just plot the mole fraction of the component A ok, which means the mole fraction of the component is plotted like this for me right, when this is 0 x B is 1 ok. I am define x A is 1, x B is 0 something like that ok. So, when x A is 0 it will be basically p B vapour pressure of the 0 solvent of and when x A is equal to 1 and the p A star ok.

Similarly, when so, this will be basically the total variation for the two solvents, but individually so you can understand that this will be something like this ok. It one component was present and the other one will be something like this, and this is the ideal get it ok. Now, when you talk about solute solvent ok we only talked about solvents activity in the sense like A is suppose present in the large excess, when it is pure ok. So, it will approach this line right that is Raoult's law.

But then the question was fine, if I plot it for A real system as I told you that point x A goes to 1 right for the pure system then actually the curves actually coincide right, but there is a huge deviation at the (Refer Time: 02:14) stage right I think next sense because actual these two point should match ok, but here the deviation is more because x A is less right clear. Now suppose different situation, in the sense like let me actually call this as x B in the sense that I am calling a as the solvent index and B as the say solute. So, I just reverse the curve ok. So, this is basically P B star ok.

Let us think in terms of B ok. This is basically the like variation of the vapor pressure with mole fraction for B. Now when B is present in less amount then actually we call it as solute right. There were some solutes which are in volatile by definition is solute, but suppose I am actually mixing two solvents. Let us say acetone and chloroform that is the standard example. When acetone is less chloroform is in large excess then you call chloroform as the solvent acetone as the solute, but if the situation is reverse that is that the solute and solvent concept is reversed.

Now, x B usually we call it as a solute when x B is closed to 0. Now you think in the other way for that situation ok. If this is the ideal curve as you see that when x B is close to 0 ok. So, things do not actually like match right and then empirically there is a law is called Henry's law right. So, it will be basically a slope like this, I draw it in better way where is a duster ok. So, what Henry's law says is that if I actually take the limit when x B is tends to 0.

Then I have a situation which is known as dilute solution ok. What I am saying here? This is actually ideal behavior which is the Raoult's law right. Raoult's law strictly speaking is valid when the solvent is in the pure form right. Now when call it as a solvent? When it is in the large excess like when it is approaching one right, but on the other limit when actually that is in a very less amount right. So, then there is a huge departure, meaning if x B actually excess a solute. There is a huge departure and to describe that basically Henry empirical said that ok. Fine let us consider the similar thing ok. Similar thing in the sense that here when x B tends to 0 the vapour pressure P B will be proportional to of course, mole fraction ok, but this proportionality constant is not P B star because as I see that it cannot be say P B star into x B why because when x B is equal to 1 this is P B star.

But actually this slope actually I showing this is something else right. So, he empirically say that which is some other constant which we write as K B which is known as the like Henry's law of constant which is different as the from the basically P A star clear ok, but again these are all empirical thing because I am assuming that if it behaves ideally for all concentration range meaning the P B is varying with x B ok. The vapour pressure of the solute, solute means when we are started from lower concentration is valid as a mole fraction and the proportionality constant is K B then are not this line. So, this line is actually an ideal behavior, but this is for ideal dilutes option because usually is valid for x B tends to 0 and this line will called as a ideal behavior Raoult's law, that is why Henry's law people write it as a ideal dilutes solution.

All the straight lines are ideal behavior. Why straight lines? Because actually it is linearly valid with mole fraction, but when it is approaching pure solvent then actually it is merging the real, this is the real curve basically between ok. The real curve will merge the Raoult's law while thus basically the mole fraction is going to 1 that is why people said the Raoult's law is valid for solvent. And Henry's law he is actually valid for the other limit, but the initial thing of the real curve merges with that other straight line. When? When x B needs goes to 0 which means actually x B is a behaving as a solute. So, basically Raoult's law and Henry's law are both empirical and both are proportional to the mole fraction constants are different ok.

And the second thing is that it is your perspective how will you look at? In the sense like I could not like drawn are like real curve for these two together, then in one limit one becomes solvent in other limit other becomes solvent and the solute solvent notations are different. Now the reason I wanted to introduce this thing, already know all this thing is that this simple thing does not hold if I use electrolytes.

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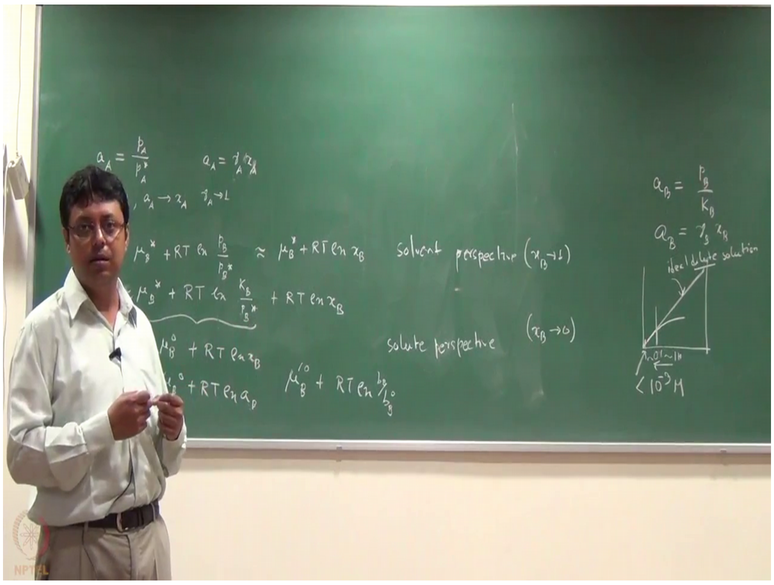

So, because electrolytes are generally solutes and so, what I am saying here, already you know this thing, the activity we define as basically p by P star. Earlier case we have using 1 notation I am just using A notation right now instead of 1 and I am use B notation instead of 2 all right, but A and B again are just your choice like what is solute in you know definition can be solvent in the other limit all right. And already we know that if the mole fraction tends to 1 right, then actually this thing will tends to this and A by definition we actually like say and it is proportional to the mole fractions through a proportionality constant that will called as a gamma which is activity coefficient right.

Now, the similar thing we can also write for the solute, which means similar thing we can also write it for B, when B is in less amount mostly because in that sense the remember this things like when x A tends to 1, these things are valid mostly right. The activity is basically approaching x A as well as this gamma activity coefficient is also approaching 1 right and have basically the opposite situation if I write it for B, again do not get confused the same thing can be valid for A if A is in the other limit ok. A and B are just arbitrary all right.

So, if I just use the similar notation for the B. Now look at it for B also. So, I can write it the chemical potential as mu B star plus RT ln p B by P B star and this is exact. For solvents we actually wrote this as x A ok. Solvents we are using A. If actually B is solvent I am write it as x B, but right now I am constant B solute meaning B is the component which is less as simple as. Now the problem here is that I this is not actually if I write it as a x B that will be actually Raoult's law ok, but I have to use actually Henry's law which says the P B is basically K B into x B, but KB is an empirical constant clear the other straight line ok.

So, basically there are two straight lines ok. The real curve actually merges with this straight line when the mole fraction is less. It merges with the other straight line when the mole fraction is more which means that is more solvent line and this is more solute line. I am now a looking at or casting the problem entirely from the solutes perspective ok. Now this is correct up to this point. Now I can actually write it look at PB mu B star ok. Now what I am write here instead of PB ok? I can write K B into x B right and then I will just write it like this KB into x B this K B by P B star that I am write it separately and the x B I will write it separately clear ok.

Now, think about it this thing look at the Raoult's law thing if I have written it as a Raoult's law for A ok. How do I write it? I write mu B is mu B star plus RT ln x right. I want to write a similar thing. So, I will just write it as something like this is mu B 0 kind of a standard error potential this entire thing plus RT ln x B clear and this is if this value is valid for all the concentration then this is called Henry's law then this is basically the Henry's law version for the solute ok, but again it does not vary for all it will not be true for all concentration. So, what that should write is that if B excess A solvent right then actually I am written as a mu B star plus RT ln x B this is actually Raoult's law.

Right, but condition is that this is valid for all concentration then only Raoult's law is valid which is this line ok, but actually it does not, it only is valid when x B tends to 1 we will discuss it right. Now I am saying another limit ok. I am saying if this is valid for all concentration or all mole faction x B then it is Henry's law ok, but actually in reality it is valid only when x B tends to 0 on the other limit ok, but the common thing point to point out here is that the standard state definition is slightly different. It is not exactly the mu B star clear. It makes sense why because how do you define the standard check?

Let us say when x B is equal to 1 ok. What I will have? I am basically have this term will vanish ok. Now x B is equal to 1 means P B or K B are equal right which means actually this is 1. So, this term will vanish. So, mu B is equal to mu B star make sense ok. So, if I am acts started with the pure solute 100 percent pure solute, then mu B will be equal to mu B star. So, this is an effective standard check which actually takes into account of not only mu B star, but also the other constants clear ok.

Now, in practice whenever people write for solutes people do not use this equation, why? Because people usually do not I am try to avoid everything to write in terms of mole fraction, but rather they use molality. Now again you might you can write any equation in the sense that you can actually define the activity also from this thing later we will do first define the activity (Refer Time: 14:55).

So, this is from a solvent perspective and this is for a solute perspective right. Again this is an approximation right because written here, because I am replacing this thing P B by P B star ok. Basically P B as K B into x B that is an approximation because that is valid only for x B tends to 0 and from a solute perspective we always write it in this way ok. Strictly speaking this is valid in the limit when x B tends to 1 and this is valid strictly in the limit when x B tends to 0. Usually textbooks actually write whenever they write this equation they write in terms of A and whenever they write this equation they write in terms of B, but what is A actually can become B I mean just solute ok. So, that always keep that in mind ok.

Now, the similar way we defined activity ok. We said that find for real solution. It will not be mole fraction it will be just activity and then we made a connection, but we (Refer Time: 16:17) said that there is no surprise of the activity of like the solvent right because it is directly defined as P B by P B star because up to this point remember the equation is exact ok. Similarly I can also define the activity for the solute.

So, how do we define it activity for the solute? See it will not be now P B by P B star ok. So, it will be basically P B by K B. Now why it is P B by K B like one? Why I am agree, not P A by P A star or P B by P B star for this thing? See when I am saying here is that I can write this equation as mu B 0 plus RT ln x B that is an exact equation ok. This is an approximate equation. Why approximate? Because I have written here Henry’s law. Even if I plot it versus x B I know that is a straight line, but that straight line matches when x B tends to 0 the other straight line and this straight line is small Raoult’s law which is the lower straight line the way I draw it and that is one point the x B tends to 1 actually everything is like a real solution ok.

Now, I said that for real solution I will request these equation as mu B star plus RT ln a right and then I compare this thing with this thing and I got actually a definition is P B by P B star clear. Now similar way I can also define that ok. So, this is not actually a exactly ok, but I could have actually got an exactly something like mu B star plus RT ln activity of B. Now we just compare this with this. We can easily figure out the activity has to be P B by K B just check it like if I write it as P B by K B then what it will be it will be P B by K B that I can combine these two things. It will be P B by P B star which is exact clear, but it is not coming as P B by P B star why because I define this as the standard step that is why the K B actually 1 extra term is coming out clear ok. It is just like notation, how you do define the standard step. Because I am looking at now everything from the solute perspective ok now this is exact ok. This is an approximate thing ok.

Exact with the approximate can I actually write this exact term and connect it to the approximate? Again it is a same thing like I can write a B as if it is proportional to x B or effective mole fraction and then I will I can write the activity in terms of the activity coefficient times the mole fraction same one ok. So, mean I can actually just write, I wrote this equation assuming, that this is always for the approximate thing, but a real thing which is the activity ok, which describes the real solution for all condition ok. Can (Refer Time: 19:48) thought of a something like its proportional to the mole fraction and the proportionality constant is gamma, but then gamma actually is not an simply just a number because it is accounting for all the real thing, you know that the curve is very much non-linear ok.

So, gamma is a function of x actually always, because if it is just a number then again it is same problem, it is just straight line that cannot be true ok. So, the real challenge so, really charm is now everything is sitting inside the gamma ok. Gamma is the non-linear form. Similarly here also I can write x B a B is proportional to x B or something like a B is gamma B into x B where gamma B is basically activity coefficient for the solute clear ok. Notations are just parallel, but only thing be careful is that this is P B by K B and that was P B by P B star all right.

Now, this is one way of defining the activity ok, but you are free to actually right this equation any way in the sense that suppose I do not want to write this activity in. I do not want to write it in terms of activity. I can write in terms of mole fraction ok. When in the same question I can actually write it ok. I will not use these equation and rather like write something like which is mu B 0 plus RT ln B by B 0 where B is basically the mole fraction of type del B sorry molarity of capital B ok.

Now, when you write it when you read; that means, this is a very confusing thing then these two mu 0 are different. This is just an equation I am writing so, that this just is valid and assuming that fine everything will have a variation will instead of a mole fraction is switching will have variation molarity right. I can write the concentration in terms of mole fraction. I can write it molarity I can write molarity whatever useful thing is usually molarity for solutes ok. So, I things has written this equation, but these mu basically this mu basically are different because there is no proper reason you can see right.

So, this mu is 0 must be very different this is a empirical thing. So, let us not like discuss anything about it, but the point here is that you can write everything in terms of just a amount like in any case like activity or mole fraction molarity or whatever you write ok. You just add the amount and then you talk about it and you can approximate everything in terms of say like the a proportionality constant which is basically activity coefficient for the solute ok. Problem is now if you look at the curves. I show that when the solute actually close to 0 meaning when it is a dilute solution right then it behaves ideal. So, there are two ideal curves remember and there is a ideal dilute solution that concept is there.

Now, how dilute is the dilute? That is a good question. Now say when you look at the player blocks you will see like when the mole fraction it is a let say 0.21 or less than 0.1. Now less than 0.1 means what one-tenth like 10 percent of the solvent is present ok, the 90 percent is the solute. Now just take a number like say for example, I take a solute in water pure water if you take. What is the molarity of molarity of pure water? 55 mole per liter pure water you just take the way divided by the (Refer Time: 23:44) you will get this number ok.

Like on the order of say few ten like moles per liter of a solvent right. Now which means if I have a one mole of solute added to it roughly ok. So, that is 0.1 mole fraction will create for the solute ok. One mole means actually it is a one molar solution is actually two considered solution. If you add one molar solute of sodium chloride now to water and if you we think that things will be similar because its already ideal dilute solution it will never be a ideal.

The reason is for electrolytes which have actually charge species they show ideal behavior much much lower concentration not actually one molar it shows at least a milli molar or even less ok. Why? Because now everything is charged and all this Henry’s law is not well. So, long (Refer Time: 24:42) what I am saying here is that I add Henry’s law this is ideal thing and that was basically there was a range where a real curve matches with the ideal thing in the meaning when the mole fraction is very small, that is why call we at this curve is called ideal dilute solution slash from the perspective of the solute ok.

And when I say that the mole fraction of the something like let us say less than 0.1 ok, but if you had done it not with acetone benzyl or all this thing ok. Acetone chloroform itself something like that if this was actually sodium chloride and water. This thing will be very very different the real curve and actually it will show like real kind of behavior in a very very small range which is something like less than 10 to the power minus 3 mole (Refer Time: 25:46) 0.1 mole fraction means actually it is roughly like one molar solution that is not calculate it right because the solvent is usually 10 moles per liter.

Now, see there is a huge change in order of magnitude which is arising because of the specific nature of ions that ions are strongly like interacting with the solvent and that interaction you cannot ignore, even for a ideal solution if it for a dilute solution sorry ok. Now the question is how to tackle that problem ok. So, we have to do the similar way we have to define an activity ok. We have to define an activity coefficient and we can empirically get an equation ok, but can you actually do and like this empirical constant like say K B is an empirical constant for example, can you actually solve this in a analytical way ok?

And then basically two scientist which are very very well known Richard Jeevan and Adic Huckle basically took challenge to solve this problem and they basically came up with the theory which is known as the Debye Huckle theory ok. But before I go to the Debye Huckle theory letter me first just tell you ok how will you write first formal is activity coefficient for ions or in ionic solution. Again from now one of we are thinking in terms of say solute meaning the ions which are present and very very small quantities ok.

And again ionic solutions show that ideal behavior in a very very dilute limit like 10 to the power minus 3 molar or so and the challenge is why a little bit concentrated solution show so much departure. So, there must be something which means that Henry's law of the empirical constant which is K B is strictly valid for non ionic solution and all the duty is now left with for ionic solution, but it is very important to know because that interaction controls like many things in biology, in chemistry everything and activity right.

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Now, before I start that just like I wrote an empirical way like I said that I can write, I have a chemical potential and that is varying and there will be something like RT ln something here. Now I defined this as activity I said that I could have written it as ratio of the mole molarity that is the basically standard molarity, which means what is the unit 1 kilogram per 1 mole per 100000 kilogram or something. So, that is basically to make it unit less ok. For a solution which has say protons ok. Many people actually use the concentration of or activity was the H plus meaning you can actually write in terms of the pH, but then every time you write it the mu 0 will be different different mu 0 ok. All the mu 0 are not same, because that is defined as when pH will be 7 then it will be the standard state ok. Your gas phase mu 0 was defined when actually it is 1 bar atmospheric pressure right.

So, those standards checks are different ok. So, all these mu 0 are will be different, but it is your choice, you are adding something like suppose I am adding ph and looking at the activity of something of an iron reaction is where proton is present something like that. So, you can actually write this chemical potential in many language ok. The variable is your choice whether you are using mole fraction or molarity or pH it is your choice ok, but the corresponding standard checks will also change, clear all right. Actually activities as a discussion on the like biological activity, but he has written these in terms of activity or the concentration of H plus.

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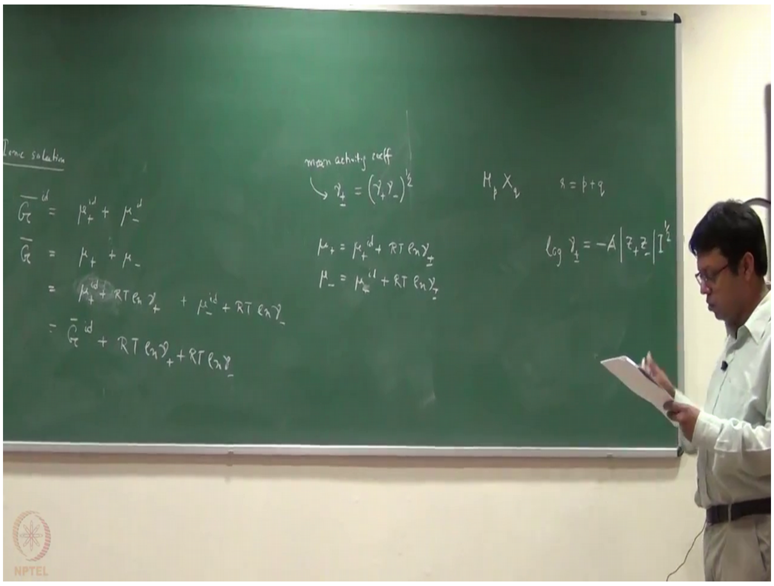

Now so what am I saying? Take is that I have suppose a Gibbs free energy for the ion solution. Now when I am saying ion solution? The ions are basically solute. They are present in less amount. So, by definition they are solutes ok. Now the molar Gibbs free energy that will of course, will have something like I can actually write it as basically the free energy for the cations at the free energy for the anions because energy is ionic as simple as that ok. Mu plus I will just write for cations mu minus is for anions so, the Gibbs free energy is basically adding.

Now the idea is that if the b m ideally I can use the cations as ideally anions as ideally and if I am just adding and get a addition of the total Gibbs free energy which is basically behaving ideal ok. Again this is basically what we wrote as mu B, the solute. But the solute now dissociates into cations and anions as simple as ok. Every step if you are do not understand anything please let me know all right.

Now what I am writing is that fine? Exactly the similar approach I can write for the real solution, I am not writing real here. If I write G bar it makes the sense like it is just the real ok. For ideal thing I am just write I here ok. So, that is the again the sum of the cation and the anion and that I can always define something like the ideal thing and then some activity coefficient because we know that what was the difference between the real and the ideal thing? Mu minus mu ideal was basically adding in terms of activity coefficient. So, that I am just writing it as something like say G bar ideal plus or let me just write one more step.

So, what I am write it as mu plus is nothing, but mu plus ideal plus RT ln some gamma for the cation ok. Similarly for mu minus I will just write mu minus ideal plus RT ln some gamma for that anion because cations and anions will have different activities make sense because the sodium ion interacting with water and that interaction will be very different like chloride ions interacting with water for the solute being sodium chloride and the solvent being water clear all right. So, these mu ideals are nothing, but my original like G bar ideal and so I see that there is basically two terms. RT ln gamma plus and RT ln gamma minus ok. Now the question is.

So, for every electrolyte then I have to define two activity coefficient which is very difficult to handle ok. So (Refer Time: 33:04) look I mean this is just a empirical thing which I am assuming to be real, but of course, I have to find that within coefficient. So, that it behaves really as a real solution ok, but instead of writing two constant I could have write an a single constant ok. Meaning I am talking about not a activity of a cation and activity of a anion some mean activity of cation and anion and that I am writing as something like gamma plus minus ok. You will have seen this thing right and that I am defining it as gamma plus gamma minus to the power half ok.

Now, this half is coming because actually I took like its a 1 to 1 charge like sodium chloride, but you can actually derive the general expression. General expression in the sense, suppose the cation is, sorry the solute is something like say has the formula of this ok. Meaning I have m is the cation and p cations and x is the anion q is the charge then actually you can actually derive all these thing. Now before going that too I am sorry single gamma plus minus I want to replace it by gamma plus minus.

So, what will be the relation ok. So, if I just want to go switch from here to here. So, you can think that there is basically gamma plus to gamma minus right and then it will be square of that right gamma plus 1 that is square. Basically you can think 2 RT ln gamma plus minus that two factor I am saying as if one goes to cation, one goes to anion in the sense what I am trying to say here is that this mu plus thing ok. Now I should have written as mu plus ideal plus one combination of this thing RT ln gamma plus minus as similarly the anion I am just writing mu plus sorry mu minus ideal plus RT ln gamma plus minus. If you add these two things you will get back your original definition ok.

Now, what did you do? Actually we said that there is a deviation from ideal wave length, but the deviation for the cation and for the anion is basically same, meaning the cation and the anion is behaving similarly which is a big approximation. However, we will see of course, I mean that is the approximation in the theory because you can think that the cations and the anions might have very different like sizes and they can have a very different polarizabilities right so, but that is a molecular feature very much at this point we are saying that the cations polarizability for the solvent and anions polarizability are same only the thing is that there is a stoichiometreic difference ok.

But the activity was there are just same and that I can always define as a mean activity coefficient; I can always define that, but then my task is that what is the expression for this mean anionic activity coefficient where as everything is now adding here ok. The ideal part by the way when I am writing the ideal means actually its just a whatever is shown so far like the Henry's law which means actually when charges are absent like cations are there, but as if they are just particles, but there is no charge ok. So, everything in that gamma plus minus if you want to think very conceptually we have to think like what is the effect of charge ok.

If I add charges on the solute what will come out clear ok. So, that is all we will basically approach ok. Now again we could have actually written it as M p X q that way ok, but its again the same thing and then what we will just make a notation is that that total s, s is what s is basically the total number of cations and anions because see that will be reflected after all because the cations and the anions are the similar activity coefficient ok. It is a mean activity coefficient mean activity coefficient and so then the total number of charges will be basically s which is p plus q ok.

Total number of ions present per mole actually if I add up to multiplied by anion and cation as simple that. Now (Refer Time: 37:54) theory where they actually give an expression for this gamma plus minus, because that is what we need ok, because if I know the gamma plus minus the activity coefficient I know how this derivating from ideal. Ideal behaviour, because the ideal thing we already know clear now they said ok. So, that we are going to see; however, if basically you say that let me first write it ok. I am just writing the simple notation we have seen it earlier ok.

So, what is this? They said that if I take the logarithm of the mean ionic activity right and then it is some constant a times z plus is the charge of the cation ok. Z minus is the charge of the anion and this is the modulus of it why because suppose if I have sodium chloride it will be just 1 is to 1 because the charges when they multiply there is already a minus sign that I have already taken out and then there is something called ionic strength already you know right. And ionic strength is defined as half sum over usually we used to write mu i n i square, but here actually the actives notation.

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He is writing as Z i square b i by b 0 ok, where b i is basically the molality, but ionic strength is a unit less thing right. So, that is why I am dividing it by basically the units of molality as Z i is I want to take basically summation over Z i square that i here is basically two species one is cation one is anion clear ok. So, there will be two sums like for example, if I take magnesium sulphur for example, MgSO 4. So, you can easily calculate it right or say Na2SO4 something like that.

So, then actually Z will be accordingly right. So, you have to take the basically two factor here because, so you will know all these things right sodium sulphate right, because some molality will be twice when if I take one molality thing right it will dissociate into like basically every (Refer Time: 40:20) of sodium two mole of sodium and one sulphate right. So, I have two here, but it will have one square, but for the sulphate it will be 2 square and one two of this and that is how we will calculate and in this formula very well known do ok.

Question is what is a, that is a constant, but this is not an empherical constant. This is an analytically derivable constant that divide and local gate. Now before this thing Peter divide it lot of on electrostatics you know right and like he had like monumental work on dipole movements of molecules right basically what gives rise to inter molecular sources which will stand at some point in this course electro statics of molecules and (Refer Time: 41:15) Huckel.

He is the same Huckel, who gave basically the Huckel molecular orbital and it was as per as I notice pre I mean like the Huckle molecular orbital theorem. It is around 1930s or so and 1935 the Huckle molecular orbital, but that may be wrong anyway. So, in the derivable description what they said is that ok? Fine let us just think about very pictorially as if I have some ions ok.

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And these ions are basically randomly moving as in the solution whatever. Now this is kind of a snapshot ok. Now they said think about a one situation like if I start from a cation and if I just go outside and then if I just take fixed length and just take a sphere ok.

I will encounter many cations and many anions of course, ok. This is the snapshot in the sense that in the next minute everything will be changed because they are moving around ok. But they saying that on a average the number of cations entering the sphere number of anions leaving the sphere will be same and not only that if I actually take a sphere of some fixed length on average I should encounter 1 excess anion around a cation because the solution has to be vertically neutral something like that or if it has something like M q and like that kind of formula ok.

So, at similar number of like say if I have let us say Na2SO4 ok. So, like if I consider 1 sodium ion how many sulphates are there in that particular sphere ok? Then it is half of the sulphate ion on statistical basis. If you actually look at 1 sulphate ion at the centre take as sphere of larger sphere of course, there will be many, but statistically there will be 1 2 excess sodium anion because it is Na2SO4 something like that ok. Now that thing is basically they say I can actually think about it as a kind of continuum although I am just calculate the number of ions in it because these are discrete species ok.

And there is a this sense I will call it as some kind of local atmosphere and then write it as this is called as ionic atmosphere ok. Now this is a very like pictorial thing ok. So, I have the ionic atmosphere and now where the activity is coming from the activity is coming from this ionic atmosphere is creating a potential ok. All I have to do is basically calculate ok. Before we go to that what is the physical interpretation of Gibbs free energy; Gibbs free energy actually is a kind of you can say non p v work right. Now the non p v work means here also we are talking about non p v work because it is a solution right, it is not a expanding there is no pressure volume work.

All the work is basically electrical work ok. While we will wrote as remember at a very beginning the in the thermo dynamics that the first law we said that every time we are writing that d cross all the term as minus p opposite in p v only for p v work then can be non p v works also ok. Now you can say that there are change in Gibbs free energy is basically related to the non framing work. So, all we have to calculate is basically what is the electrostatic work done ok, because you can think that there is a electrostatic potential and then if I mark it by the electrical charge and then basically the energy stored in the system, which is the roughly the work done due to the presence of the ions.

Secondly, this work does not this will basically increase the activity or the chemical potential. I mean reduce the chemical potential basically why, because the as you can say there is a attractive force of this ok, because it is a cation anion and they are getting stabilized. So, there is something extra we are having one drop of Gibbs free energy or mixing and other things, but the mixing and everything I already told. These are the mu plus ideal mu minus ideal that we are not going to write all we are going to write is the non ideal part, because the non ideal part is directly connected to the gamma, but I defined a new gamma which is gamma plus minus clear ok.

Which is the mean ionic activity all right? Now the question is this is known as Debye Huckel limiting turn in the sense like it is also having for the lower part of the concentration ok; although it correctly match like few I mean above few milli moles, but not up to say one mole, one mole is a too strong ionic strength clear. So, there actually we see departure because there are lot of like assumptions here ok. Now let us just try to understand like how Debye Huckel across this problem. Now all I said is that I have to somehow calculate the work done ok. Now what is work done again? Work done again is irrelative to the Gibbs free energy right. This is actually non p v work in the sense I am writing it as a electrical work done ok.

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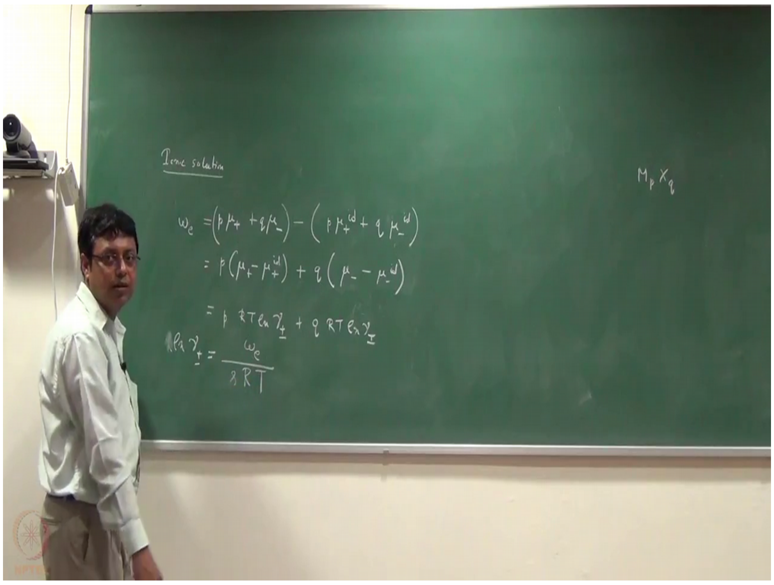

Now electrical work done will be basically the chemical potential like ok. So, think about it like I have cat ions and anions ok. Now how many cations I have? I noted a formula here this M p X q then so I have p cations and q anions ok. I have discussed p moles of cations and q moles of anions something like that ok. All these expressions which I am writing is for a 1 mole clear. Now how do you think like there will be the electrical work done. The electrical work done will be the total work done minus I can think the ideal work done because that is the non ideality and that is the origin of the electrical work right.

So, what I am trying to say here is that there will be total thing which means there will be something like mu plus which is the work done, but mu plus is for something like NaCl plus and plus mu minus ok, but t value suppose I have p cations and n anions ok. So, the total work will be p times mu q times mu minus right that is the work done because everything is energy right. Gibbs free energy is related to the work done that is the total thing, but again in the total thing there is an ideal and non ideal contribution. So, I have to basically subtract the ideal contribution.

Then only I will get the electrical work because there is also a mixing part that is a purely like statistical mean some ok. The Gibbs free energy is also changing due to that, but that will happen even for electrically neutral species that I do not want to calculate. So, I have to just subtract from a this thing clear and then I can always rewrite it something like this is nothing, but mu plus minus mu plus ideal plus I will just write the cations together anions together mu minus minus mu minus ideal and then this thing as you can see that we have already written it.

Remember what we wrote for mu plus? We wrote that it is mu plus ideal plus RT ln gamma plus minus remember ok. So, what I have here is T for that q also it is all same because I said that it is mean the ionic activity ok. So, I will just write it as mu and RT ln gamma plus minus and p and q it is together I am writing as s ok this s RT ln gamma plus minus ok. So, whatever is this RT or ln gamma plus minus that will be something like work done we right divided by p plus q into RT p plus q I am just writing as s RT when I was written it ok.

Sachin Raj Tendulkar S R T is coming [laughter] anyway. So, now, this is still like I have common for ln gamma plus minus, but what is total work done ok. I just said that work done is the difference of the chemical potentials right. I have to calculate it from that model which model I actually shown you ok, but here is the challenge like how will I do basically the work done ok? Now let us do pretty step by step. Now theta for it all of you know basics of electro statics right, like how the go on potential varies for an anion.

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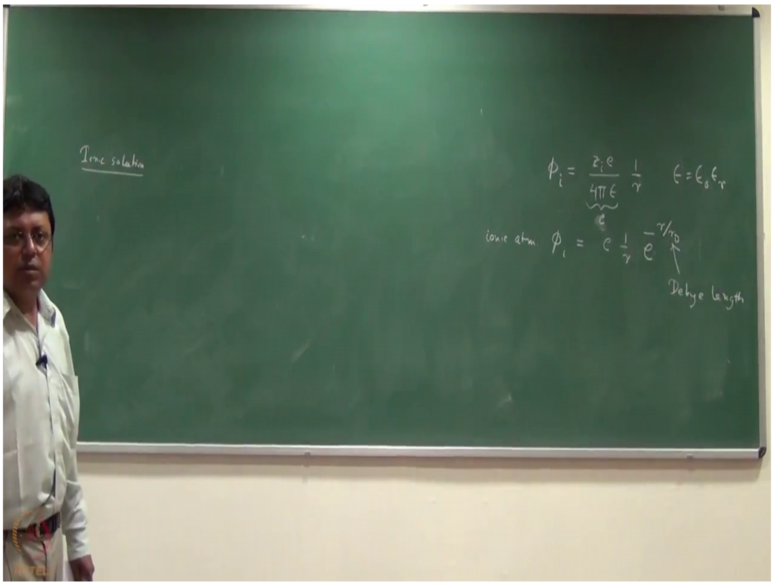

I am just using the same notation here suppose a potential. Due to charge I it can be cation, it can be the anion only two species are there ok. So, that already I know that it is something like charge of the species right times e, e is basically the electrical charge 4 pi epsilon and then it is r I am just writing like this. So, this is a constant times r; that means, as written is a z I may use it as say some constant c. Now this epsilon is the permittivity which means actually this is nothing, but epsilon 0 the atom magnitivity times the relative permittivity clear. Now this is for perculum potential ok. Now Debye Huckel said for a charge as (Refer Time: 51:39) you can show it; that means, you will show it later ok. This variation would be more rapid in the sense like suppose I have a charge cloud right remember what is the picture right?

Like there is a cation and suppose cation is also moving suppose that is your central cation and suppose you are sitting on that cation ok. So, you see there is no relative motion for that cation. Now you are seeing everything else around it, it is also moving ok, so you will see a defused charge cloud the ionic atmosphere. If I actually now where move along this defused ionic atmosphere you will see for a charge cloud interacting with a point charge. The potential will not vary like this because this is between two point charges ok. Let me slightly modify it and which may it will actually decay more rapidly ok. So, for a diffused cloud this is called a point charge.

Unit point charge this will be something like the same expression like some constant 1 by r, but there will be something like it will also vary as e to the power minus i ok, but of course, there should be some characteristic these terms because this should be dimensionless and that characteristic constant is of course, a dimension of length which we called as Debye length, but after this one this is the basically the interaction potential for an ionic atmosphere which ionic atmosphere which is just I have shown ok.

So, this is how the potential is change clear. Now all I have to do first is to calculate see the how will I am going to approach this thing? There is a charge right, there is a potential perfect. So, basically I will do just charge potential combination would give me (Refer Time: 53:29) algorithm. If I get the electrical algorithm I will just write it divided by s RT s is known r is a current year constant ok. I will get gamma plus minus as simple as that ok, but this is not so simple anyway. We will see, now what the first thing first I have to that figure out what is the RT? RT is a constant for a species. Now how to calculate RT ok?

Now, again how is the ionic atmosphere? Remember it is actually spherically symmetric. Now, near to statics there is a constant term charge density where do we use charge density if we have a continuous distribution of charges. Now this is these interesting thing which Debye and Hukle said, think about it there is a central charge I am saying which is discrete, but with respect to that all other and since they are moving around this ion is saying as if its a continuous distribution of a charge cloud where in the charge cloud if for it is sodium chloride I have an basically the charge curve charge is minus 1.

Just like if you talk about a very beginning when you talk about like hydrogen atom ok. There is one nucleus sitting and there is a diffused electron cloud, but with respect to other some other charge this ion which I am I just say it as a discrete that is also moving ok. So, there is a continuous charge distribution as if around these particular charge ok. So, we can actually write in terms of the charge densities and usually you wrote the charge density as rho ok.

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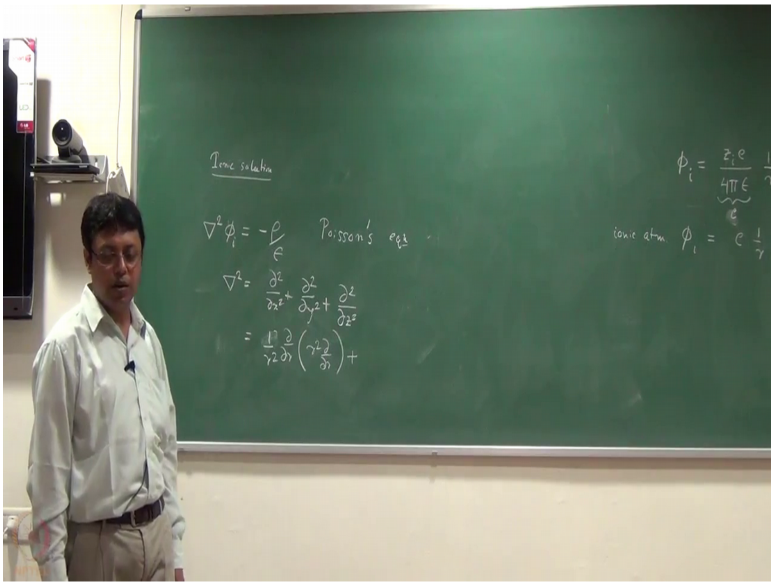

Now so then basically there is a relationship between that potential and the charge density ok. Now if I can find the relation and this is a standard relation and then that is known as anyone Poisson's relation ok. Poisson relation and there are many Poisson relations. So, like there are also a Poisson equation for probably for diffusion I do not remember yeah. It is basically vector calculus and it basically says that if I take the del square of this phi. I should get negative of charge density divided by the permeability. This we are just taking as it is. I am not going to derive this thing of course, because since it has lot of discussions ok. Now what is this form of the del square? Del square already I know dell square is what hydrogen atom bound ok.

Del 2 divided x 2 plus del 2 2 divided by del y 2 del 2 del z 2 right, but looking at the symmetry of the problem it is a charge surround by this thing actually better actually is the spherical bound version ok. What is the spherical polar version? R square del del r this is r.

Student: One plus (Refer Time: 56:43).

Yeah x square by 1 by r right.

Students: 1 by x square.

1 by x square first term and then I will have 1 by r square sin theta del n theta and then like (Refer Time: 56:54) r r, it was r square sin square theta and that thing right, but again why I am writing because it is spherically symmetric. So, theta phi I am assuming that they are not changing. So, now, I am in a better position in the sense that we prefined this is only the constant of this thing and instead of partial derivative I can write here g d r, because r is the only variation variable ok. Now I have basically the form of del square. I have to write it at the top phi which phi basically that see 1 by r e to the power minus i by r 0 ok.

R by sorry r d if I do it and connect it to rho then I will get a relationship between rho and RT the Debye length clear all right. So, let us do that, basically try to work these out. So, I am going to basically take the del square of phi i ok, but before doing that so del square of phi i is nothing, but we just saw that is 1 by r square divide it by d dr, because I do not need to write del this. There is no theta and phi dependence and I have here r square d d r right, r square d d r yeah.

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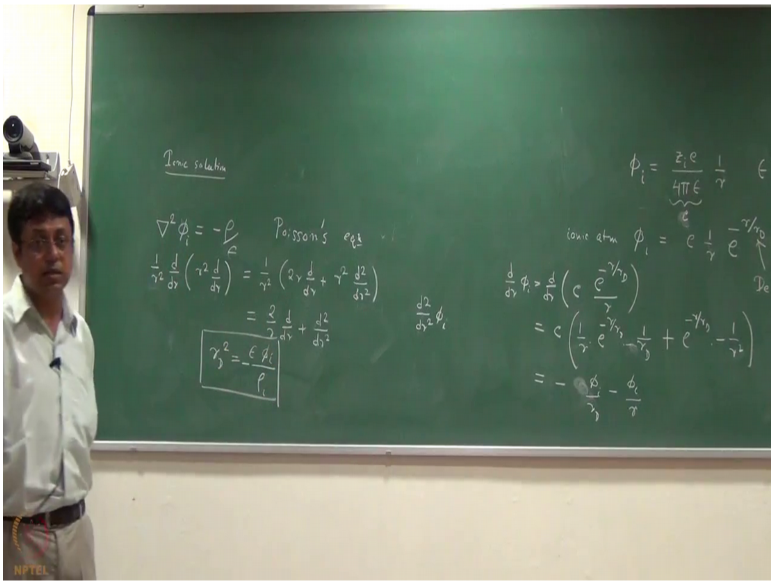

I can right now write phi here, but let us not do it let us concentrate in simplified these thing itself ok, we can do it in right any (Refer Time: 58:25) So, I have basically 1 by r square d dr of this ok. So, I will have basically 2 r d dr and then basically the first function second function differentiation chain rule right. So, I will have basically r square d 2 dr 2 right. So, basically I have two terms, one be 2 by r right d dr and the second term will be d 2 dr 2 ok. One side just written, now phi has the form which has basically two other parts, one is 1 over r, 1 is basically e to the power minus r by r 0 ok. So, let us do it ok.

So, let us first calculate this thing d dr and phi i which is basically d dr of some constant e to the power minus r by r D divided by r clear. Again chain rule just take out the c first e to the power minus r by r D (Refer Time: 59:39) and there is also one by r first function is say e to the power minus r by r D ok. So, what I will have e to the power minus r by r D e to the power mx derivative is 1 over m e to the power mx right. So, that 1 over n is basically times I will have minus 1 over 1 by r D. So, it will be minus r D clear now differentiate the second function, second function was like 1 by r basically. So, the first function was e to the power r by r D, second function if I differentiate it will be minus 1 by r square there is a yeah minus yeah minus sign clear just simple chain rule of differentiation ok.

Now**,** I can leave it and then take the second derivative, but I will I will actually play a think I will actually write in an phi there because phi is acting here right how basically c times this divided by r is phi ok. So, this just look at it c times this divided by r is the phi. So, the first term is nothing, but minus r D into phi i right, second term is c times this then this second term is basically minus phi i by r clear. I think I am right yeah correct.

Student: (Refer Time: 61:14).

I think it is correct (Refer Time: 61:17) I am just taking 1.

Student: Sir.

Yeah.

Student: (Refer Time: 61:21) like that will be 1 by r D.

(Refer Time: 61:25).

Student: Differentiation of e to the power of minus r by r D will be minus 1 by r D, differentiation of e to the power minus r by r D.

It will be minus 1 over r D.

Student: (Refer Time: 61:35).

This one right.

Student: That mean minus 1 over.

This is correct right.

Student:Yes sir.

E to the power minus r by r D; now, the second thing basically what I will do is that chain rule basically. If you we will just use d 2 d r 2 ok. I have phi i which is basically d d r of phi i, but d d r of phi i I have already computed and then you proceed with this thing ok. I am not just leaving this thing that will that will move it ok. So, I am have d d r and I am have d 2 d r 2. Now I will put back in this equation ok. So, with d d r you have to multiply 2 by r D 2 d r 2 you have to just the term and then you add it you could actually do it just simply like the full thing, but that will be just reduce the number of steps ok.

So, if you do it you will see that it will just reduce the very compact relationship. What do you get like r D square ok? How I will get r D square? We will get another r D whole in the term.

Here so you get basically 1 r D square. So, you get r D square and is equal to epsilon phi i by r. I am just using rho (Refer Time: 63:02) just check this because most of the terms will cancel.

Student: (Refer Time: 63:09).

I mean there will be fourth terms and then two of them will cancel which is that not four actually there will be more terms ok. Now, so this is basically relationship of the r D square with the charge density and that is also this potential, but that potential I like wrote it like that ok. So, I what I did is basically using Poisson's equation for a spherically averaged charge density ok. I established the relationship or definition what you mean by the (Refer Time: 63:41) clear ok, but still I have to do lot of more things because I am still I do not know what are the rho 1 this thing right. So, that I have to work out yet all right.

So, this will be useful I mean like in the in the next step actually I will be going to use this. So, basically I can actually keep it somewhere here all the relations actually you could write here. So, I will got r D square with minus epsilon phi i divided by rho i we will be using that thing shortly.

(Refer Slide Time: 64:09)