Advanced Chemical Thermodynamics & Kinetics
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Lecture – 04
Review of Classical Thermodynamics 04

So, in the last part we talked about the phase diagram of pure substances. So, we will now discuss briefly I will give you an overview of the properties of mixtures, basically the thermodynamics of mixtures.

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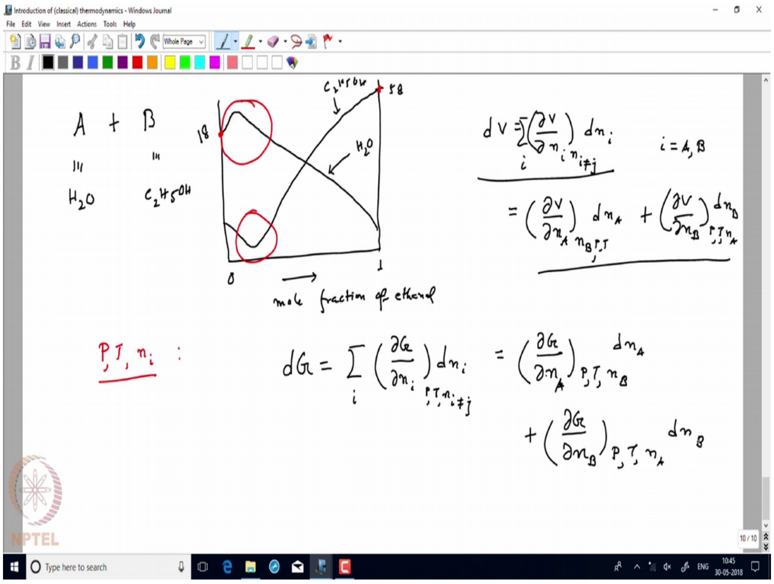

$$dV = \sum_i \left(\frac{\partial V}{\partial n_i}\right)_{n_{i \neq j}} dn_i \qquad i = A, B$$

$$= \left(\frac{\partial V}{\partial n_A}\right)_{n_B, P, T} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{P, T, n_A} dn_B$$

P, T, n_i :

$$dG = \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_{i \neq j}} dn_i = \left(\frac{\partial G}{\partial n_A}\right)_{P, T, n_B} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{P, T, n_A} dn_B$$

Now, when you talk about mixture if you remember you are old literature that if I have say a mixture of two components like A and B which are non reactive. So, and then suppose we are mixing these two together so, the first thing we ask this question suppose A and B are both liquid let us take an example let us say A is water and B say ethanol and then if we want to actually plot how much the volume will change, if I add a little bit amount of B into A or the in the reverse way. So, what I am plotting right now is basically the mole fraction of ethanol and I am adding ethanol into water.

Now, interestingly what will be the partial molar volume of A water. So, we know that the molar volume of water if the mole fraction it is a fraction. So, it can go to 0 to 1 only. Now, when it is 0 so, it is pure water. So, the molar volume will be nothing, but 18 so because we know that so, the water if I take the density as 1 gram per cc and if we take the fact that a molecular weight of water is 18 gram per mole. So, that will give you the molar volume.

And, then we see that for ethanol it will be like 58 you can easily calculate it from the, but the densities required and then the variation of the partial molar volume will be something like this. So, this curve is for a partial molar volume of water and this curve is partial molar volume for ethanol. Now, the partial molar volume is defined as the change in the total volume if we just add some amount of the ith component and this is the definition of the partial molar volume that change in the total volume.

Now, since water and methanol are mixable and we see that the volumes just do not get added up. So, it is a very the nature of the curve is very complicated as you can see there is a initial increase in the partial molar volume and then there is a decrease and similarly there is a decrease in the partial molar volume of ethanol and then it increases.

So, in the pure case like when mole fraction of ethanol is 0, it will be of course, 18 because it is means actually pure water and similarly the if the mole fraction is 1 it will be pure ethanol. So, it will be 58, but in between we see that if the volume is not actually being added up as the I mean one constituent is constantly being added into the system.

Now, similarly just like partial molar volume we can also define something relevant to the chemists actual or the chemical problems and the as you said that the most of the chemical reactions are done under constant pressure and temperature the question we are asking is that a constant and pressure and temperature if you also change the number of moles of the constituents which quantity you should look at and that is by the choice is; obviously, the Gibbs free energy.

So, in a similar way we can actually define partial molar Gibbs free energy. So, which is defined as this in the same way like we define the partial molar volume. So, this is the change in the Gibbs free energy if we keep on adding one constituent and keeping all other parameter cells. So, in this case actually I have to keep pressure and temperature fixed and also the other constituents I have to keep fix. So, and then I have to take the sum over i. So, here actually I have to always keep in mind that when I am changing one component I am keeping the all other constituent same.

For example if I have i equal to A and B. So, I have only two component system. So, the partial molar volume will be defined as the change in the volume if I change the amount of A times the change in amount of A, but when I did this change I kept the amount of B constant and also other thermodynamic parameters which are pressure and temperature constant plus I had del v del n B at constant pressure temperature n A into d n B. So, this is the overall expression.

So, similarly if we want to write an overall expression for a d G or the partial change in the Gibbs free energy so, then for a two component system it will be something like del G del n i if I have the components as A and B we will have constant pressure temperature an n B into d n A plus I will have the corresponding change with respect to B if I keep the pressure temperature and amount of A constant.

So, in this way you can actually define the partial molar volume and one of the interesting thing is that since we are talking about the change in Gibbs free energy part change in the mole, so, I will know that Gibbs free energy per unit mole is nothing, but the chemical potential.

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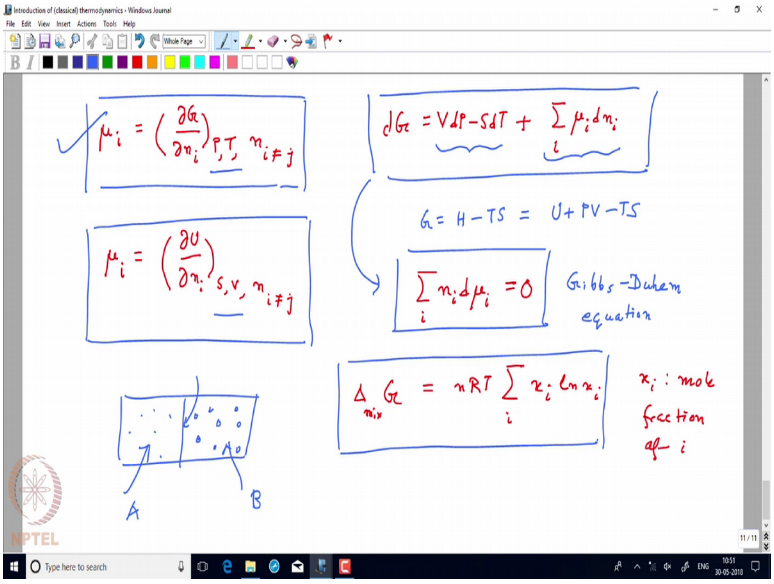

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{\underline{P,T},\, n_{i\neq j}}$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{\underline{S,V},\, n_{i\neq j}}$$

$$dG = \underbrace{VdP - SdT}{} + \underbrace{\sum_i \mu_i dn_i}{}$$

$$G = H - TS = U + PV - TS$$

$$\sum_i n_i d\mu_i = 0$$

Gibbs-Duhem equation

$$\Delta_{mix} G = nRT \sum_i x_i \ln x_i$$

x_i : mole fraction of i

So, by definition we see that the chemical potential of the ith component is actually defined as del G del n i at constant pressure, temperature and all other components. So, we can actually rewrite this equation the d G equation as it will be actually sum over mu i d n i sum over i. So, the mu i is defined as this quantity. So, we know that actually the total differential of d G is nothing, but V d P minus S d T, this is for one component system this part or actually I have only a pure substance, but for a mixture I will have an addition because for mixture I can also change the number of moles keeping the pressure and temperature constant and that gives rise to an additional term.

So, this is basically the change in Gibbs free energy a differential change in Gibbs free energy for a mixture. Now, we can actually just like we define the mu i as derivative in G you can also express it in terms of derivative of the other thermodynamic parameters let us say for example, at the internal energy. Now how do you do it, because you can always get back your expression for U, because you know that G is nothing, but H minus T S

Now, what is H? H is nothing, but U plus P V minus T S and then you can actually take the derivative. What is the relationship between d G and d U and from that you can easily figure out that if we use that. So, then you will see that this mu i is also equal to the partial derivative of the internal energy with respect to the change in constituents when the entropy and the volume and the all other constituents are kept constant. Now, these are actually equivalent definition, I can define the mu i in terms of the change in Gibbs free energy I can define the mu i in terms of change in internal energy.

But, for Gibbs free energy change the other than the constituents the constant parameters are pressure and temperature whereas, for internal energy the constant parameters are entropy and volume. Now, since in most of the chemical process I stated it again and again we have the natural choice that the pressure and the temperature are kept constant this is a more useful definition to use than this definition. So, all these are all equivalent definitions.

Now, let us move ahead and then after this discussion we usually in the basic thermodynamic course we take the total derivative of G because and then you can always integrate this equation and then again you can differentiate it and then what you will figure out is that you will get a very interesting relation that sum over n i d mu i is basically 0 or if I and this is very easy to show because I have mu i d n i when you integrate it will be mu i n i. Then you need to take the derivate once again you will have derivative with respect to mu and derivative with respect to n and then you arrive at this equation this is the sum is over i and this equation as you know is known as Gibbs-Duhem equation.

And, then what usually we talk about is basically the thermodynamics of mixing and the first thing which we talk about there if we have say two ideal gases and if we are just mixing them what will be the change in the Gibbs free energy again this is basically an the driving force here is entropic, in the sense that we have actually one particular species one finding one particular region let us say something like that. So, I have say A molecules are here and suppose these are all gaseous species and then I have actually B molecules here confined here into two chambers and then all of a sudden I remove this boundary between them.

So, there will be a spontaneous diffusion of the molecules and the a will occupy the entire space and B will also occupy the entire space that Gibbs free energy will of course, decrease due to basically mixing and this mixing we can formulate very easily and what we will see is that the change in Gibbs free energy the total change and this change is due to mixing. So, we are using a suffix as delta mix G is nothing, but n R t sum over this is the general expression if we have actually lot many components there will be summation over x i ln x i where x i is the mole fraction of constituent i mole fraction of i. So, thus we see that this is basically a general equation for the Gibbs free energy for mixing.

Now, moving on we see that we talked about mixing and then the next thing which we always emphasize is basically what is the thermodynamics of solution.

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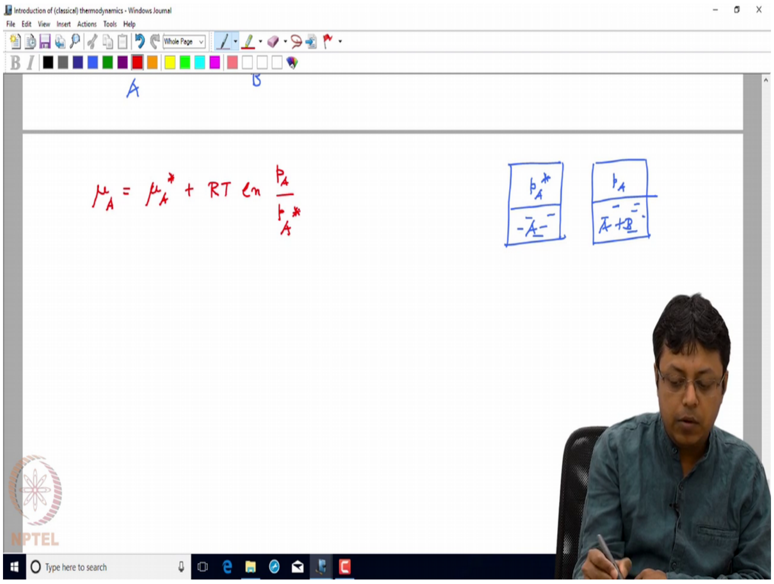

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$$

Now, when you talk about solution we have basically two constituents. So, one a solute and one is solvent. So, the question here is that suppose I have a solvent to begin with and I am slowly adding a solute into it. Now, if can actually express everything in terms of the partial pressure let us say p A is the or the pressure or basically the vapor pressure also you can think about it like what I am saying here it is suppose I take do this experiment in a closed vessel and I have a pure solid and then I will have a vapor pressure which I am denoting as p A star.

So, star actually denotes the pure components and then I have something like say A plus B together, where B is the solute in this case and the solute does not evaporate I am saying that only the solvent evaporates which is A and now the A actually will be dominating because it is solvent by definition. So, what we see here is that the you can actually do the thermodynamics and then you will find that these chemical potential of a will be nothing, but chemical potential of A in the solution where actually in presence of B there will be nothing, but the chemical potential of A the pure A plus R T ln p A by A star.

Now, again in this equation or in the previous equation for delta G mixing you see that we have used n R t and this n R t comes from p V equal to n R t or the ideal gas equation. So, here also we are assuming that these vapors are actually behaving ideally. Now, if we proceed with this we can easily figure out that we have to establish a relationship of this p A by p A star.

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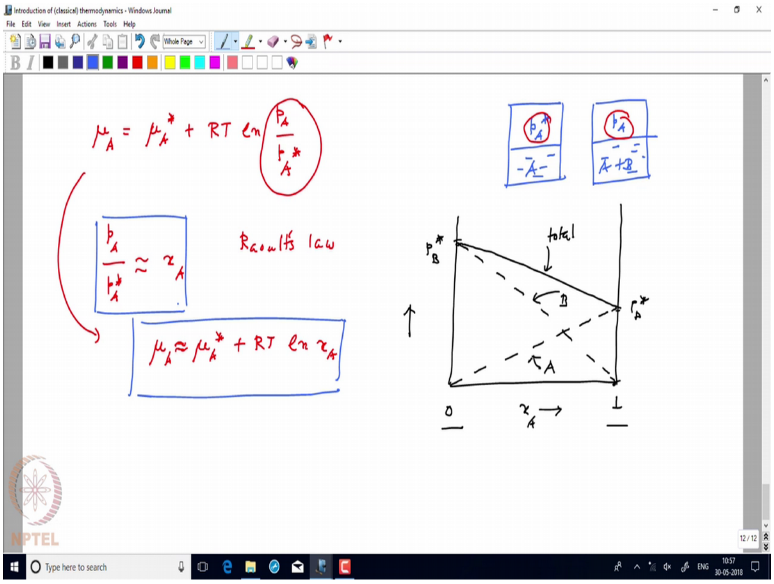

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$$

$$\boxed{\frac{p_A}{p_A^*} \simeq x_A}$$

Raoult's law

$$\boxed{\mu_A \approx \mu_A^* + RT \ln x_A}$$

Now, p A by p A star are again p A is basically the pressure or at the vapor pressure a of the solution and p A is the paper pressure of the pure solvent. Now, what we can assume this p A p A star are the relationship between then is that p A and p A star is nothing, but related to the mole fraction of A which is not very correct because as you can see if the mole fraction is 1 then p A will be equal to p A star which is fine and which has to be, but in other cases it is it is an approximation and this is basically known as Raoult's law; which is valid for ideal solution and this Raoult's law was developed from the perspective of the solvent. Now, again and the solvent and solute are all arbitrary in the sense that we call solvent that part of the solution which is present in large excess and solute is the smaller part.

Now, if we actually plug in into this original equation then you basically see that mu A is basically mu A star plus R T ln x A. Now, this is again this is an approximate equation and these actually is followed from Raoult's law. Now, if you want to actually plot how it will look like the if I just plot the mole fraction and how the partial pressures are changing for A and B we can actually have a similar plot like we did for our partial molar volume.

Now, if think about it like suppose let us plot the mole fraction of A so, which can go from 0 to 1 because it is a fraction. So, when it is 0 the pressure will be totally equal to the pressure of B and this is pure B. So, it will be p B star and when it is purely 1 the pressure will be like p A star because it is all everything is in A. So, it is a pure A, pure solvent. So, the way I have drawn it here that p B star is higher than p A star, but it is not necessary and then in between you will see that the total pressure that should actually the total partial pressure that should change from p A star to p B star that is for sure. So, the partial pressure like how the B will change B actually when the mole fraction of A is 0, it will be p B star, but when it is 1, it has to be actually 0 because this axis is basically the pressure partial pressure.

So, the B curve should be like this similarly the A curve should be like this and this should be the total partial pressure. So, this curve is for B this curve is for A and this curve is for the total vapor pressure. Now, what is interesting here that in reality actually you will not see it we will plot the real situation and the Raoult's law as we can see is basically tells you as if it is a linear relationship of the vapor pressure with respect to the mole fraction which we which is obtained here which is shown here.

So, if I have actually mole fraction I mean if it reaches to the pure thing of course, it will be the vapor pressure of the pure state which is the pure solvent which we denoted as star, but in between we are assuming that it is it obeys a linear relationship.

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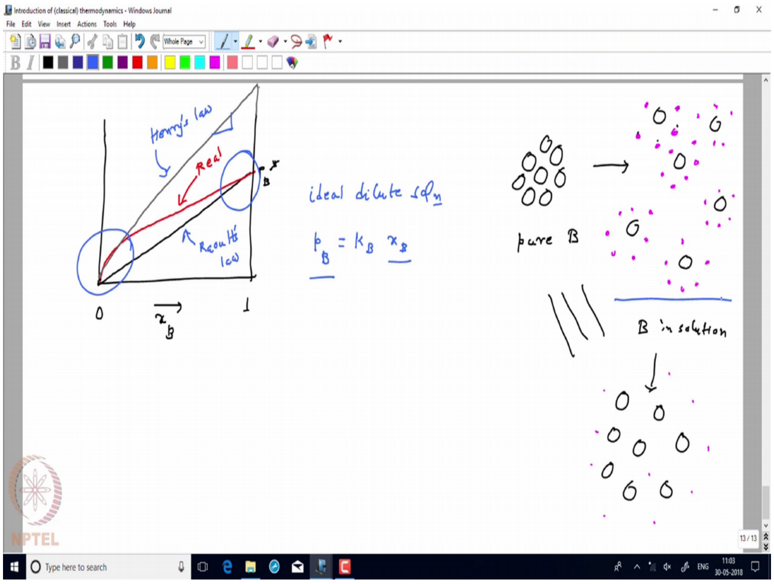

However, we can actually think what about the perspective with respect to the solute. Now, suppose if I add a little bit of the solute and the solution is very much dilute now think about it suppose we take sodium chloride into water. Now, when sodium chloride is very much impure so, the salt the sodium chloride actually sees or any solid let us not talk about sodium chloride because it is an ionic solid let us talk about suppose I have sugar and then all these sugar molecules in the pure phase; pure phase means actually it is a solute sugar molecule.

So, in that pure phase suppose the solutes are like this in that solid. So, this is nothing, but pure solute and the solute we are denoting as B, but moment I dissolve it into a solution in an ideal solution then what will happen due to salvation these solid molecules will be far away and then all the solvent molecules let me actually denote it with a different color, they will actually surround the solid molecules. So, this will be the situation in a solution. So, what we see here the solutes actually experience very different environment in a solution. So, what will happen is that their mole fraction or their partial pressure will be very different so, this is a B in solution.

So, if we plot the similar quantities, but this time I am plotting the mole fraction of B and remember that B is our solute. Now, when it is 0 now there is no basically solute present then what we will see here is that it should actually if the Raoult's law is valid and suppose this is going to p B star for if 1 means actually the B is impure thing. B is pure means actually now B is acting as a solvent and then the total vapor pressure will be nothing but equivalent to p B star because it is in the pure state, but what is what happens in reality is that the real curve looks like something like this, let me draw it once again.

So, at a very early concentration we will see something like this. Now, look at it carefully that at a higher mole fraction of 1 I have mole fraction when actually x B is approaching 1 which means now B is in excess. Now, if the B is in excess we can actually try to draw a figure. So, it will be something like this and then there are less solvent molecules around it because the solvents are A and then these actually now resembles something like pure B, it is close to that.

So, actually now B starts behaving as if it is a solvent and then for the solvent we said that the Raoult's law is valid. So, actually there is a nice agreement; however, when there is a question of dilute solution when B is present in very small amount then there is a significant departure and to account for that Raoult basically said that we can actually take the initial slope. So, the drawing is not very correct here so, you can actually try to redraw once again because the slope was very higher. So, let me just redraw it once again.

So, for solute we are saying that the initial slope will be very different and then we can actually take a slope which is basically fits to this initial amount and this again at a later part actually it matches because actually it is just like Raoult's law. This is basically the real life situation or the real solutions pressure changes.

But, to match the initial part Henry proposed that for a dilute solution or usually we call it as a this these are all basically ideal behavior we will call it as a ideal dilute solution the mole fraction I mean like or the partial pressure of B in that solution will be nothing, but equal to some constant times the x B which means actually it is proportional to the mole fraction of b, but that constant is an empirically derived constant and which will be obtained from the slope of this curve.

So, this is the Henry's law and then we see the when actually it Henry's law is valid and when the Raoult's law is valid. So, it is again Henry's law is from the solutes perspective. When actually you have a very dilute solution the solute is in less amount, but the departure is more from the ideal solute which is in solid I mean like pure solute if you think and then if you think and solute in a very dilute solution because then the environment is very different there are a lot of solid molecules around so, which we depicted in this figure. So, it is a very different environment.

So, actually the deviations will be huge, but when we are adding the mole the x B or the increasing the mole fraction which is x B we see that B is actually reaching a pure state then actually it will behave as if actually it is a it is just like a solvent and then our Raoult's law will be valid. So, this is the major difference between henrys and Raoult's law and then you can also get some expression for K B again this K B is a proportionality constant it is just an empirically derived quantity.

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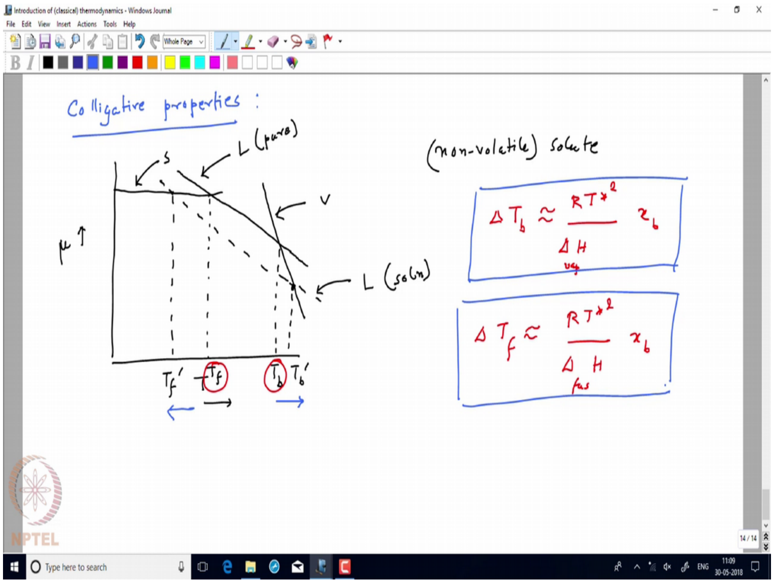

Colligative properties :

(non-volatile) solute

$$\boxed{\Delta T_b \approx \frac{RT^{*2}}{\Delta H_{vap}} x_b}$$

$$\boxed{\Delta T_f \approx \frac{RT^{*2}}{\Delta H_{fus}} x_b}$$

And, then the next thing what we discussed in the previous course is basically known as colligative properties. Now, colligative means actually it is a collective property and again so, there are several observations like freezing point depression, melting point, boiling point elevation and then also osmosis and solubility all these things you can actually explain based on the change in the chemical potential of the solute in the solution.

Now, what do you mean by that let us just draw our phase diagram for any general system and suppose we are plotting the chemical potential and versus temperature or the Gibbs free energy versus temperature and we know that initially I mean the solid actually dominates and this will be the mu versus T curve for the solid and then there is phase were actually the liquid dominant. So, and this is the cross point for solid and liquid.

So, that cross point we talk we basically call it as a freezing point and then finally, the vapor actually dominates and this is the vapor temperature curve and this is the volume point. Now, what happens here is that if we suppose this is suppose for a pure liquid let us say water; now, suppose if we add salt into water what will happen? So, this is for solid this is for liquid and this is for vapor, now this is for pure water again.

Now, if I add some amount of salt into the liquid water what will happen the chemical potential due to actually new constituent will actually decrease in solution. So, the new curve will actually lie somewhere here new curve for the liquid. So, this is for liquid pure and this is liquid in solution.

Now, as a result as we can see the cross points of the liquid curve with the solid and the vapor has now changed. Now, why we are not changing the solid and the vapor curve the assumption here is that when you are adding a salt have the vapor phase at a very high temperature in the vapor phase only water goes not the salt. Similarly, when we freeze it the water actually the assumption here is that the water is actually freezing out from the solid. So, in the solid phase or in the vapor phase it is always the pure water, there is nothing called a solution is getting vaporized or a solution is getting solidified. So, only the solvent gets frozen or the solvent goes into the vapor phase, but not the solid.

So, this will be true for a non volatile solute something like salt and this salt will actually change the chemical potential of the solution only in the liquid phase. So, as a result what we can see here the new freezing point will be actually lower than the earlier freezing point and the new boiling point will be actually higher than the earlier boiling point and so, this is known as a basically freezing point depression, because we are having a lowering on the depression in the freezing point and then we are having elevation in the boiling point.

So, this can be successfully explained from again by working out the changes in Gibbs free energy and if you calculate it you can actually get an estimate for the boiling point the elevation and that you can again connect it to some constant times the mole fraction of B and that constant if I assume the ideal behavior. So, we can show it that it will be nothing, but RT square divided by delta H. Now, this process is basically a vaporization we are talking about because it is a boiling point elevation and delta H vaporization into x B.

Similarly, you can also get a similar expression for the freezing point depression and you can show it will be something like RT star square. Now, T star is basically corresponds to the pure freezing point or pure boiling point according to this equation and this delta H will be nothing, but delta H fusion times x B. So, these are again empirical relations that actually connects the boiling point elevation and the freezing point depression and this up to this actually we talked about the thermodynamics of mixing and then in some courses we actually discuss the phase diagram of multiple components and which we actually did not discuss in the earlier course.

There are also like one more part is remaining which is the thermodynamics of electrochemical cells and also chemical equilibrium. So, we first covered these two topics which is the thermodynamics of chemical equilibrium and what are the conditions that actually modify the equilibrium constant and then we will move on to discussing about the thermodynamics of electrochemical cells and from that point onward we will be talking about electrochemistry and in much more detail.

And, there will be a thermodynamics part of the electrochemical phenomena where we will talk about the stability of colloids and many other interesting properties and there will be also a kinetic phenomena, where we will be talking about movement of ions and this movement of ions is connected to the electrical conductivity. So, those things we will cover, but first we will give you an overview of the thermodynamics of electrochemical cells.

Thank you.