Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 22
Activities (Accounting for deviations from Ideal behaviour)

Today we will discuss a very important concept when it comes to solutions and that is called Activities. Whenever we prepare a solution we usually express it is concentration which is mole per decimeter cube or it is molality which is mole per k g or we express in terms of the mole fractions. However, when we experimentally determine a property and we plot that property against it is calculated value of molality or molarity or mole fraction, that dependence may be different then when you plot the same property against it is effective concentration.

Now, what is this effective concentration? It is something similar to the one that we discussed while discussing the gases we introduced the term fugacity, fugacity was effective pressure or escaping tendency and why the fugacity had to be introduced that was due to the deviations from ideal behaviour. Similarly in solutions we have to account for the deviations from ideal behaviour and that is why the concept of activities becomes very important.

The activities for ionic solutions we will not be discussing in this lecture because there is entirely a different treatment for that. However we will discuss in general that what are activities and under what circumstances we can treat activity to be same as concentration. First of all let us discuss about the solvent activity.

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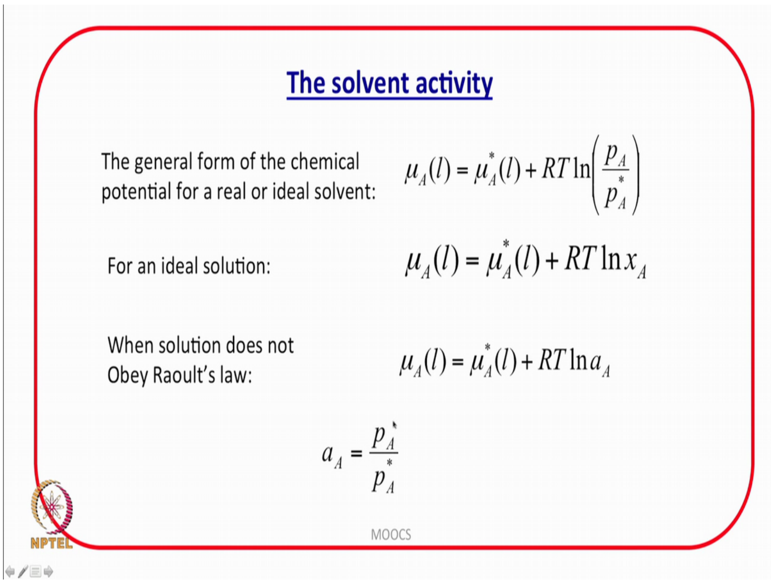

The solvent activity

The general form of the chemical potential for a real or ideal solvent: $\mu_A(l) = \mu_A^*(l) + RT\ln\left(\frac{p_A}{p_A^*}\right)$

For an ideal solution: $\mu_A(l) = \mu_A^*(l) + RT\ln x_A$

When solution does not Obey Raoult's law: $\mu_A(l) = \mu_A^*(l) + RT\ln a_A$

$$a_A = \frac{p_A}{p_A^*}$$

This we have discussed that the general form of chemical potential for a real or ideal solvent is defined as mu A l is equal to mu A star l plus R T log p A by p A star this we have derived earlier. But the chemical potential of a liquid is equal to chemical potential of the liquid in it is pure form plus R T log it is vapour pressure in the mixture divided by it is partial vapour pressure or it is vapour pressure in the pure form. And I am sure you remember that we further went on to discuss that rounds observed that this ratio is equal to the mole fraction and we came up with this equation that mu A is equal to mu A star for the liquid plus R T log x a. We discussed there that is solution in which both the solute and solvent Obey Raoult's law this equation is called an ideal solution.

Now, we want to allow deviations from ideality we know that the things are not usually ideal, and the non ideality which we call the real solution or non ideal solution it arises from the difference in the intermolecular interactions; and we also remember that we discussed that usually we retain these type of equations which we derive for the ideal system and change one of the parameters so that now it reflects the equation for a non ideal solution and that is what we will do here. When the solution does not Obey Raoult's law when the solution does not Obey Raoult's law means both the solute and solvent do not Obey this equation mu A is equal to mu A star plus R T log x A.

Then we can retain this type of equation, but in place of mole fraction we will write activity. So, for a non ideal solution A usually in books A is written for solvent and b is written for solute. So, for solvent the chemical potential is mu A is equal to mu A star for the liquid plus R T log activity of A. This activity we can call it as effective mole fraction and if you compare this equation which is in terms of the ratio of the vapour pressures, the activity of solvent is equal to the ratio of it is vapour pressure in the mixture divided by the vapour pressure in the pure form that is what is written over here that the activity of solvent A experimentally can be determined if we know the vapour pressure of A in mixture and if we know the vapour pressure of A when it is pure.

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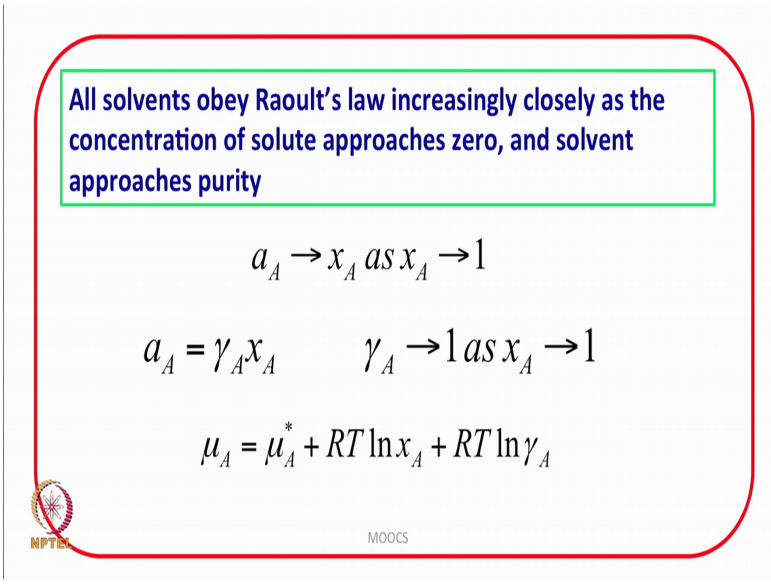

All solvents obey Raoult's law increasingly closely as the concentration of solute approaches zero, and solvent approaches purity

$$a_A \rightarrow x_A \; as \; x_A \rightarrow 1$$

$$a_A = \gamma_A x_A \qquad \gamma_A \rightarrow 1 \; as \; x_A \rightarrow 1$$

$$\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$$

We also discussed this previously that all solvents Obey Raoult's law increasingly closely as the concentration of solute approaches 0 and solvent approaches purity, this I showed cogent component diagram in the previous lecture that means, the activity will approach mole fraction when the mole fraction approaches a value of unity for the solvent how to interpret this? That when the solvent approaches purity when x ray approaches one means when the solvent approaches purity then you can replace activity by mole fraction.

And activity how is activity connected to mole fraction? Activity is equal to activity coefficient into mole fraction and obviously, when the mole fraction approaches a value of one the deviations from ideality will disappear and the activity coefficient will also approach a value of 1 and then we can instead of activity we can just write the mole fraction.

In fact, when we strictly talk about the solvent here and the mole fraction of solvent approaches purity, then we can simply replace activity by the mole fraction, and this is what is mentioned in this that all the solvents Obey Raoult's law increasingly closely as the concentration of solute approaches 0 and solvent approaches purity.

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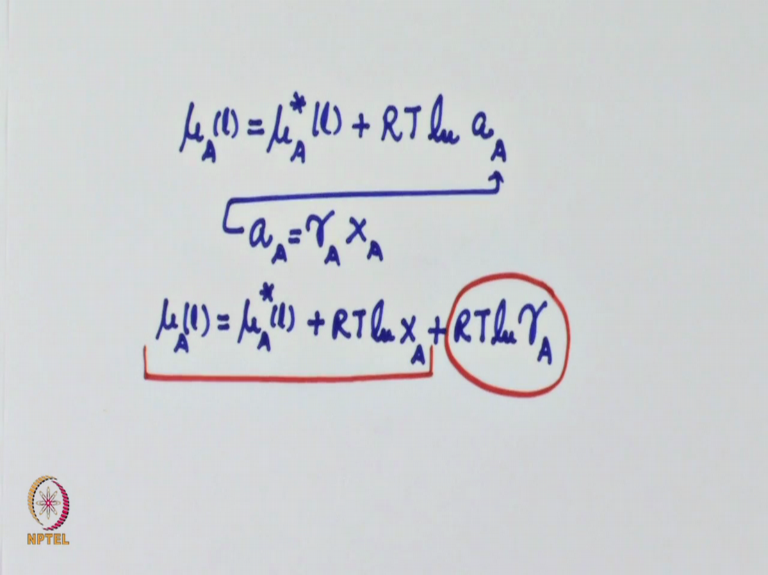

$$\mu_A(l) = \mu_A^*(l) + RT\ln a_A$$

$$a_A = \gamma_A x_A$$

$$\underbrace{\mu_A(l) = \mu_A^*(l) + RT\ln x_A} + \boxed{RT\ln\gamma_A}$$

And since we had earlier discussed that chemical potential of a liquid is equal to mu A star plus R T log activity of A and as we just discussed that activity of a is equal to activity coefficient into mole fraction, now if you substitute over here what I get is mu l is equal to of a mu A l star plus R T log x a plus R T log gamma, a term when I substitute this over here it is worth noticing here that this part is same as that for ideal solution.

So, the deviations from ideality are captured in this R T log gamma A term; that means, gamma has information on the deviations from ideality. So, this is how you write then the chemical potential for a solvent is equal to chemical potential of the pure solvent plus R T log x A plus R T log gamma A and then.

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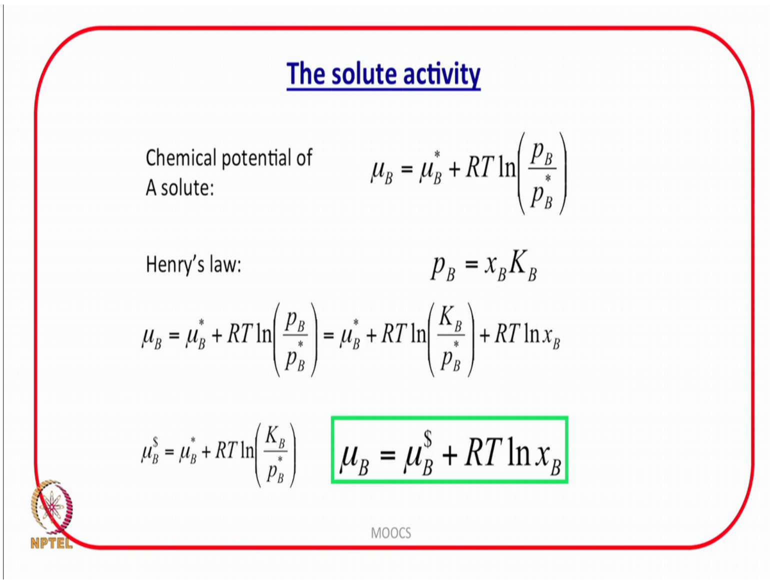

The solute activity

Chemical potential of
A solute: $\mu_B = \mu_B^* + RT\ln\left(\frac{p_B}{p_B^*}\right)$

Henry's law: $p_B = x_B K_B$

$$\mu_B = \mu_B^* + RT\ln\left(\frac{p_B}{p_B^*}\right) = \mu_B^* + RT\ln\left(\frac{K_B}{p_B^*}\right) + RT\ln x_B$$

$$\mu_B^\$ = \mu_B^* + RT\ln\left(\frac{K_B}{p_B^*}\right) \qquad \boxed{\mu_B = \mu_B^\$ + RT\ln x_B}$$

MOOCS

Now, let us discuss about the solute activity having discussed the solvent activity, and as I said that several books rise b for solute and a for solvent and we will also stick to the same notation we will write b for the solute. Chemical potential again we will write the same form mu B is equal to mu B star plus R T log P B by P B star this is the general form that we also wrote for the solvent.

However we know that in a dilute solution, the solvent Obeys Raoult's law and the solute Obeys Henrys law. So, for an ideal dilute solution we will assume that condition and write Henry's law. Henry's law was that the vapour pressure of P is equal to mole fractions into Henry's law constant and this is what we will substitute over here in the vapour equation; and once you substitute for P B over here the resulting equation is mu B is equal to mu B star plus R T log P B by P B star and ins place if you substitute P B over here then what you get is mu B star plus R T log K B over P B star plus R T log x B and I can combine because K B is a constant P B star is a constant I can combine these terms.

If I combine these term the resulting equation. So, when I combine mu B star plus R T log K B by P B star and let me write this as mu B dollar, that as resulting equation will be mu B is equal to mu B dollar plus R T log x B. Here I have defined the chemical potential of solute in terms of it is mole fraction. Earlier we discussed and define the chemical potential for the solvent and we introduced the activity of solvent here we will introduce the activity of solute, but what is the difference.

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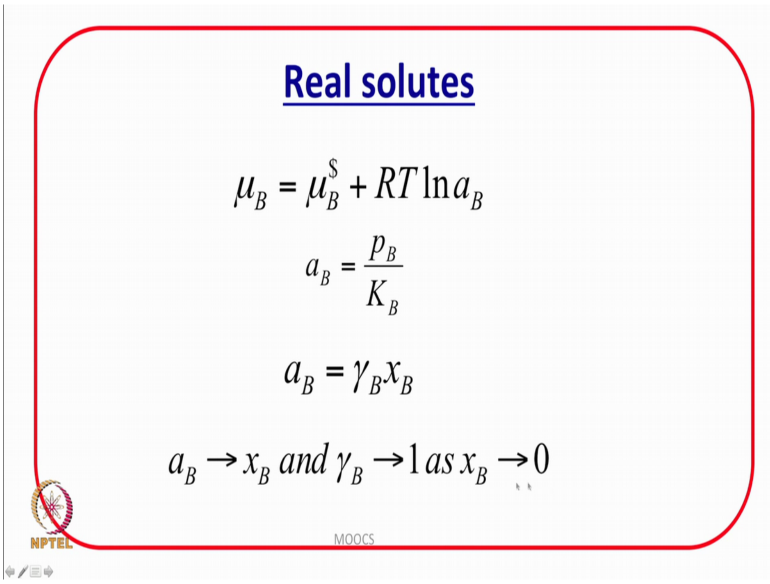

Real solutes

$$\mu_B = \mu_B^{\$} + RT\ln a_B$$

$$a_B = \frac{p_B}{K_B}$$

$$a_B = \gamma_B x_B$$

$$a_B \to x_B \; and \; \gamma_B \to 1 \; as \; x_B \to 0$$

MOOCS

For real solutes what we will do is because earlier we discussed for ideal dilute solutions.

Now, the solutions in which the solute does not Obey Henry’s law, we will call those as real solute and in place of mole fraction we will write activity. This is how one can determine the value of the activity; then instead of activity if we connect this activity with the activity coefficient activity is equal to activity coefficient into mole fraction in the same way; however, please note down the difference over here the solution for the solute or solute will start behaving in an ideal manner or the solute will start following Henry’s law when it is mole fraction in the solution approach is 0. When mole fraction of the solute approaches 0 it is activity coefficient will approach a value of 1 then instead of activity we can write mole fraction.

When you compare this with the solvent for solvent the activity coefficient was approaching a value of 1 when the mole fraction was approaching 1; that means, when the solvent was approaching purity, but for solute the ideal dilute solution is the one in which the solute Obeys Henry’s law. So, Henry’s law will be Obeyed when the solute concentration approaches the value of 0, it is there when the activity coefficient will approach one and in place of activity we can use mole fraction.

Now, activities can the activities be written in terms of moralities; definitely how do we do that.

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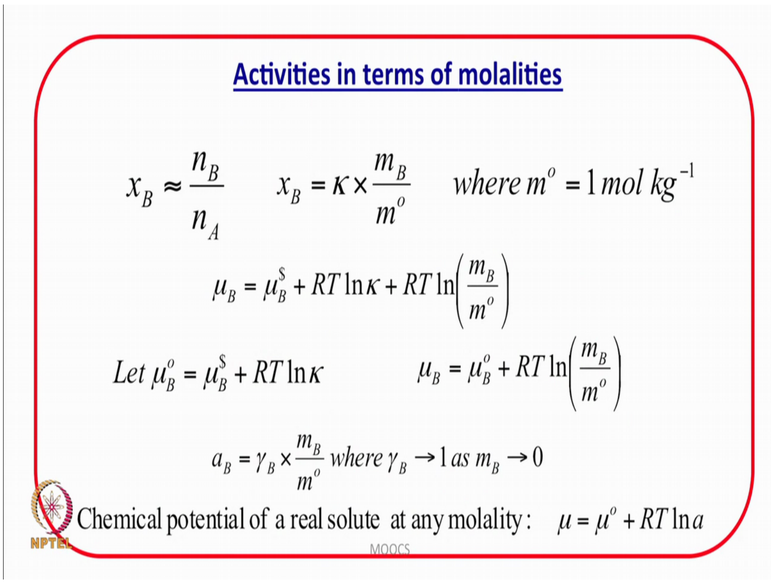

Activities in terms of molalities

$x_B \approx \frac{n_B}{n_A}$ $\quad x_B = \kappa \times \frac{m_B}{m^o}$ $\quad$ where $m^o = 1\,mol\,kg^{-1}$

$$\mu_B = \mu_B^{\$} + RT\ln\kappa + RT\ln\left(\frac{m_B}{m^o}\right)$$

Let $\mu_B^o = \mu_B^{\$} + RT\ln\kappa$ $\qquad \mu_B = \mu_B^o + RT\ln\left(\frac{m_B}{m^o}\right)$

$a_B = \gamma_B \times \frac{m_B}{m^o}$ where $\gamma_B \to 1$ as $m_B \to 0$

Chemical potential of a real solute at any molality: $\mu = \mu^o + RT\ln a$

Mole fraction of the component B is equal to number of moles of B over number of moles of A plus number of moles of B in a binary mixture.

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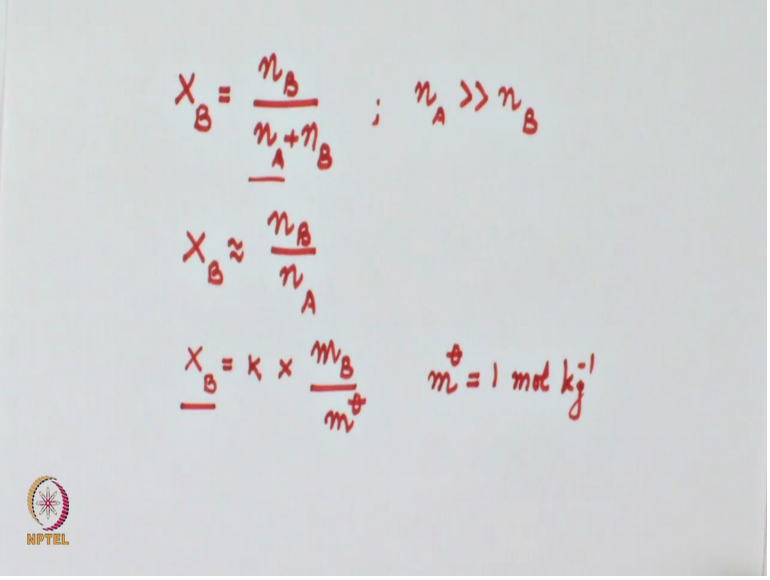

$X_B = \frac{n_B}{n_A + n_B}$; $n_A >> n_B$

$X_B \approx \frac{n_B}{n_A}$

$X_B = \kappa \times \frac{m_B}{m^{\ominus}}$ $\qquad m^{\ominus} = 1\ mol\ kg^{-1}$

Usually in a dilute solution number of moles of A which is solvent is much much larger than number of moles of B. If this is very large and this is small I can ignore this small quantity; that means, mole fraction of B I can write approximately same as number of moles of B divided by number of moles of A. Then is not this number of moles of solute in a given quantity of solvent will give us information on molality that means, the x B mole fraction of B is equal to some constant into molality of B divided by m naught.

Why I am introducing m naught over here? M naught which is equal to 1 mole per k g this is introduced to make this overall a dimensionless quantity, because mole fraction is a dimensionless quantity therefore, the right hand side has also to be a dimensionless quantity.

Let us go back to the slide now; mole fraction is the ratio of n B by n A approximately we just discussed. So, therefore, I can express mole fraction in terms of molality by this expression where m naught is 1 mole per k g; and now what will be the expression for mu B? We remember that mu B was written as mu B dollar plus R T log x B.

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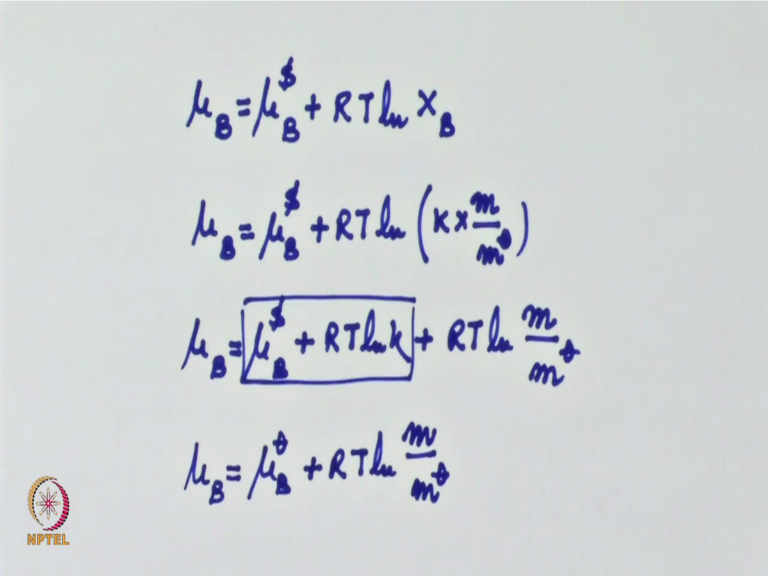

$$\mu_B = \mu_B^{\$} + RT\ln x_B$$

$$\mu_B = \mu_B^{\$} + RT\ln\left(k \times \frac{m}{m^{\ominus}}\right)$$

$$\mu_B = \boxed{\mu_B^{\$} + RT\ln k} + RT\ln\frac{m}{m^{\ominus}}$$

$$\mu_B = \mu_B^{\ominus} + RT\ln\frac{m}{m^{\ominus}}$$

And what I will write now is mu B is equal to mu B naught or mu B dollars plus R T log instead of x B I will write k into m by m naught. The resulting expression is mu B is equal to mu B dollar, plus R T log k plus R T log m by m naught.

And I can further combine these two terms and write mu B is equal to mu B naught I am combining all these and writing as mu B naught plus R T log m by m naught. We can if you want we can instead of m we can write m B when we write m we generally write the molality number of moles of solute. So, we are talking about solute.

So, whether we write m or m b it is the same thing and that is what we see in this slide that the chemical potential for a solute in terms of the molalities is also of the similar form, that is mu B is equal to mu B naught plus R T log m by m naught m b or m whatever way you want to write. The activity is connected to molality by the usual connector which is activity coefficient that is activity of a solute is equal to activity coefficient into m B by m naught.

One thing to be recognized here or to be remembered here when we were talking about the fugacity, fugacity was equal to fugacity coefficient times pressure.

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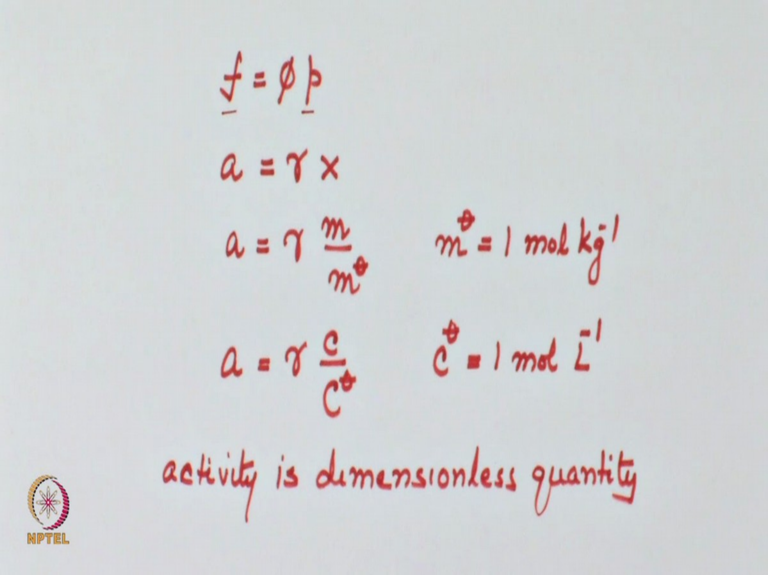

$$\underline{f} = \phi\, \underline{p}$$

$$a = \gamma\, x$$

$$a = \gamma \frac{m}{m^{\ominus}} \qquad m^{\ominus} = 1 \text{ mol kg}^{-1}$$

$$a = \gamma \frac{c}{c^{\ominus}} \qquad c^{\ominus} = 1 \text{ mol L}^{-1}$$

activity is dimensionless quantity

And we discussed that the dimensions of fugacity are same as that of pressure fugacity coefficient is the dimensionless quantity the units of f and p are same. When we express activity in terms of mole fraction we write like this activity is equal to activity coefficient times mole fraction mole fraction is a dimensionless quantity therefore, activity is a dimensionless quantity; and now we are writing activity is equal to activity coefficient times m by m naught where m naught is equal to 1 mole per k g. Why this m naught is introduced to make this as a dimensionless quantity, and if we want to express activity in terms of C this will be defined as C by C 0 where C 0 is equal to 1 mole per litter or per decimeter cube.

Here also c naught is introduced to make activity as a dimensionless quantity. So, please remember this that activity is dimensionless quantity; even though molality has unit m naught is introduced to make it dimensionless, similarly even though c has unit c naught is introduced to make it dimensionless. So, in general for a real solute the chemical potential of a real solute can be written as mu is equal to mu naught plus R T log A; where A is the activity of the solute. Now how we convert this A activity to molality or concentration it is a different matter.

So, what we have discussed today in this lecture is a very important concept of activities; activities are effective concentrations and you know this word effective, effective word comes because of the onset of intermolecular interactions. If the molecules are sticking to each other then they may not be acting they will not be acting to they are fully capacity the effective concentration will be different, and these deviations from ideality are captured into the activity coefficient.

We have discussed in the form of suitable equations that how to express chemical potential of a solvent in terms of it is activity or it is mole fraction, and the chemical potential of a solute in terms of it is mole fraction or activity, and since usually we talk about the solution in term of molality. Molality is number of moles of solute per k g of solvent we also developed an equation for chemical potential in terms of molality. For solvent one can replace activity by mole fraction when the solvent approaches purity. For solute one can replace the activity by mole fraction of solute or we can replace activity by concentration or molality when the solution is very very dilute, that is when the concentration of solute approaches a value of 0.

So, I hope the concept of activities is very clear and we will solve a few numerical problems, which will further make the meaning of activity coefficient more clearer.

Thank you very much.