Thermodynamics (Classical) for Biological Systems

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Module No. # 04

Thermodynamics of Solutions

Lecture No. # 19

Learning Aspects Chemical Potential Formulations

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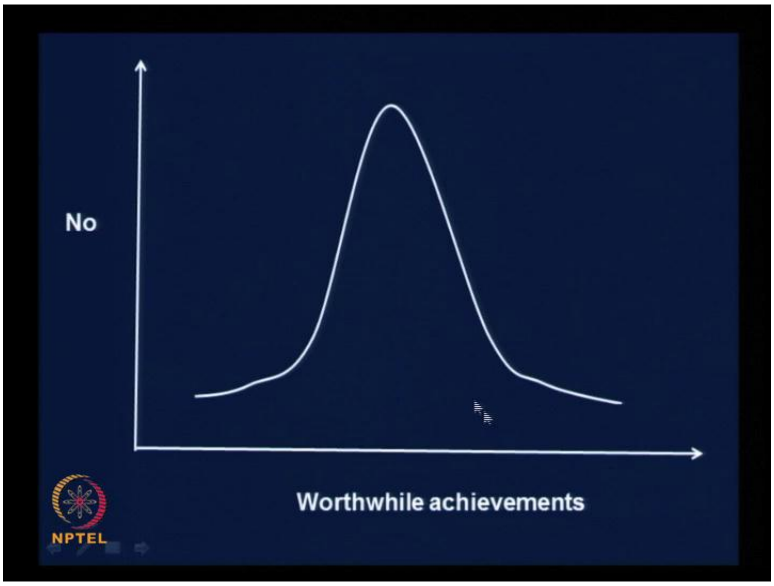

Welcome.

Today, let us began module 4, which is on thermodynamics of solutions. Before we begin the details of this particular module, I think it is high time that we talked about the class itself. I have been presenting the material at a particular level to the class, and I am sure some of you have gotten bored with the extent of detail that is been presented – a small number, that is. And some may have found it difficult to follow what has been happening.

If you look at the number of students – this is, in terms of worthwhile achievements. I have been kind of careful and picking out this word …, these set of words, `worthwhile achievements', because … the performance in examination, whether it is worthwhile or not, is debatable. What I mean by worthwhile achievement is the level of understanding that you have, the comfort level that you have with the information, the confidence with which you could apply this information to real world situations, and so on and so forth.

If you look at worthwhile achievements such as those, on the x axis … this definitely includes the performance in the examinations, but not necessarily so. For example, certainly people who are good would perform well in examination also; … good, in the appropriate skills would perform well in the examinations also. But the lack of examination performance does not preclude people having some of these skills.

If you look at the worthwhile achievements here on the x axis – this being high and this being on the lower side – in a class of a reasonable number, may be about 30 or above, we distinctly find this normal distribution. Please assume that this is a normal distribution – this is some sort of a, you know, freehand sketch. Sometimes it is slightly skewed to one side, and so on and so forth. But, by and large, this is valid.

What this says is, most people in a class are somewhere in the middle, and there are some people who are very high achievers in terms of worthwhile achievements. And some, here, who would need a lot of help to achieve … to get to a certain level of achievement. What I normally do is teach my courses at this level. It is very easy to teach courses at this level, because we already know the material, but that is not being fair. So, I try to teach at this level. And, in this course particularly, I felt that the majority of the students have a shown much better inclination to the class, much better interest in the class, if they know the basis of the information, the equations that we come up with and so on. That is a reason, why we spend quite a lot of time on those … the details of those derivations.

In any case I tend to teach to people, here. So, if you have been comfortable in the course you know where you are. For people, here, in regular class i.e. in a classroom, I have different means of handling them, which broadly fall under the ambit of cooperative learning. I pair them up with other students who probably are on this end, and thereby these people pick up and perform to a certain level.

Here, for people here, these people are the ones who are expected to contribute significantly to the improvement of aspects of the field, and improvement of aspects of certain relevant things which relate to this course, and so on and so forth. Or, any course for that matter. So, some attention is paid to these people also. But, as a class each one is important.

If you look at the western literature, Bloom's taxonomy and so on and so forth. According to Bloom's taxonomy, there are supposed to be six levels of learning. I think it is knowledge, it is comprehension, it is application, analysis, synthesis and evaluation. If I remember those six things correctly; sometimes … of late there have been some changes in the hierarchy of the last two things, and so on and so forth. This is the way Bloom has seen it in his taxonomy. … Many people see it even now, in terms of a student getting to various levels of learning across these six levels, upward.

If you read some of our literature … I have read some by Sri Aurobindo. … His views do not conflict with whatever is … whatever I have said just now in terms of Bloom's taxonomy, but, it goes beyond that. He says that the role of a teacher is essentially to point out, not even to bring forth. The `bring forth' has probably been the meaning of the term education – to educe, and so on and so forth. Sri Aurobindo says it is not even to bring forth, it is juts to point out to the student the latent aspects in a student and allow it to rise to the surface. Which I feel is a very complete way of looking at things.

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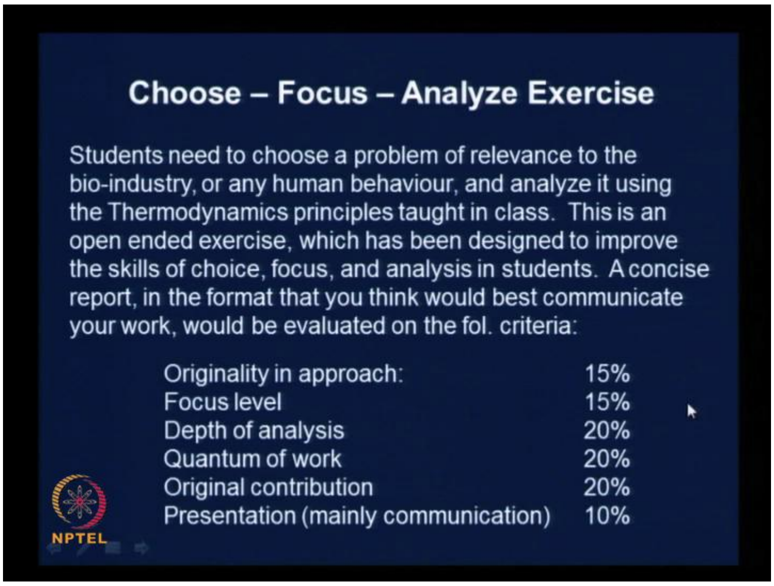

Choose – Focus – Analyze Exercise

Students need to choose a problem of relevance to the bio-industry, or any human behaviour, and analyze it using the Thermodynamics principles taught in class. This is an open ended exercise, which has been designed to improve the skills of choice, focus, and analysis in students. A concise report, in the format that you think would best communicate your work, would be evaluated on the fol. criteria:

Originality in approach:	15%
Focus level	15%
Depth of analysis	20%
Quantum of work	20%
Original contribution	20%
Presentation (mainly communication)	10%

To cater to these people or this part of the population, in this particular course, let me give you an exercise, the choose, focus, and analyze exercise. This exercise is typically assigned, so that you could spend a few months on that exercise, I typically assign it in the beginning of the class. In this case, since this is a different kind of a course, I am assigning it here. Let me first tell you what this exercise is all about. Let me read it out from here: … students need to choose a problem of relevance to the bio-industry; need not be necessarily limited by that – it could be relevant to any human behavior or endeavor – and analyze it using the thermodynamic principles taught in class. This is endeavor, human endeavor, and analyze it using the thermodynamics principles taught in class. This is an open ended exercise, which has been designed to improve the skills of choice – it is a very difficult to develop – focus, and analysis in students. And a concise report in the format that you think would best communicate your work would be evaluated on the following criteria.

Originality in approach 15 percent, focus level is 15 percent, depth of analysis 20 percent, quantum of work 20 percent, original contribution 20 percent, presentation which is mainly communication about 8 percent and 2 percent for the professional appearance of the report will carry 10 percent. … This criteria, I usually strictly follow. Let me assign this to you. Let me see if you feel bored with some aspects the course, whether you can fulfill you potential and do an exercise of this sort. Once you do the exercise you can always get back to me and let us discuss that.

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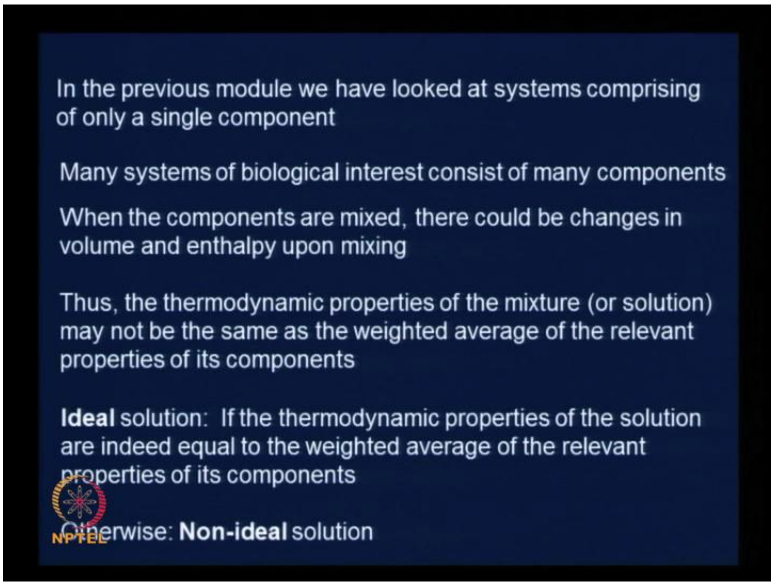

In the previous module we have looked at systems comprising of only a single component

Many systems of biological interest consist of many components

When the components are mixed, there could be changes in volume and enthalpy upon mixing

Thus, the thermodynamic properties of the mixture (or solution) may not be the same as the weighted average of the relevant properties of its components

Ideal solution: If the thermodynamic properties of the solution are indeed equal to the weighted average of the relevant properties of its components

Otherwise: **Non-ideal** solution

Now, let us get back to the module 4, thermodynamics of solutions. In module 3, previous module, we had looked at systems comprising of a single component or a pure substance. We had developed the various useful aspects from a thermodynamics view point for a pure substance, such as the P V T relationships or the equations of state in different degrees of general applicability. Then we looked at how to get the other thermodynamic variables U, S, H, A, G and so on, in terms of P V T, using the reduced properties and things like that. And, evaluation of fugacity coefficient also we saw. All those were for a single component.

Nevertheless, … the focus of this course is biological systems, and many systems of biological interest consist of many components. It is rare to find a system with a pure component all the time. It is quite easy to see that when you mix pure components we get a mixture or a solution; we'll look at that a little more closely. So, with the components are mixed to make this mixture or the solution, there could be changes in volume, enthalpy, and so on, upon mixing. You know what I mean by that is, you could take volume one and volume two, V 1 and V 2. When you mix them together the total volume may not be V 1 plus V 2, it could be something different from V 1 plus V 2.

Similarly, enthalpy H 1, enthalpy H 2, and may be H 3, H 4, depending on the number of components we are mixing together. Put them all together the total enthalpy may not be equal to the algebraic sum of the enthalpies of individual components. Therefore, the thermodynamic properties of the mixture or the solution may not be the same as the weighted average of the relevant properties of its components. I should have said the weighted average for example, you have the enthalpy H 1 and enthalpy H 2 and when you mix then together total enthalpy would be what fraction of component 1 you have times the enthalpy of that component plus what fraction of the component 2 you have times the enthalpy of that component. That is not going to be equal to the total enthalpy, all the time.

If that is so, then it becomes an ideal solution. The ideal solution in other words happens, if the thermodynamic properties of the solution are indeed equal to the weighted average of the relevant properties of its components. If not, we have a non-ideal solution. You notice the terms here; we have seen probably seen these may times, but, notice them from a fresh angle now. There is something called an Ideal solution and there is something called a Non-ideal solution. We will come back to this again and again.

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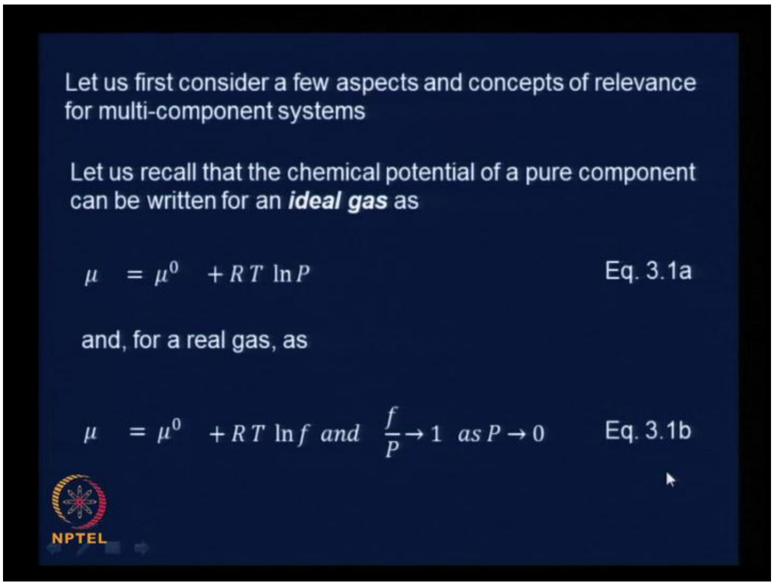

Let us first consider a few aspects and concepts of relevance for multi-component systems

Let us recall that the chemical potential of a pure component can be written for an ***ideal gas*** as

$$\mu = \mu^0 + RT \ln P \qquad \text{Eq. 3.1a}$$

and, for a real gas, as

$$\mu = \mu^0 + RT \ln f \;\; and \;\; \frac{f}{P} \rightarrow 1 \;\; as\, P \rightarrow 0 \qquad \text{Eq. 3.1b}$$

Now, let us first consider a few aspects and concepts of relevance for multi-component systems. Please pay a little bit of attention to this. This forms the bedrock of the further development for multi-component systems or solutions. Let us recall that the chemical potential of the pure component, especially if it is an ideal gas. We will start with simple things. If it is an ideal gas, we can write the chemical potential of a pure component as mu equals mu naught plus R T ln P; this we have already seen, way back in equation 3.1a. And for a real gas, you could write mu equals mu naught plus R T ln f, the P gets replace by f for a real gas, and for completeness of the definition f by P pressure, total pressure tends to one as P tends to 0; this was equation 3.1b.

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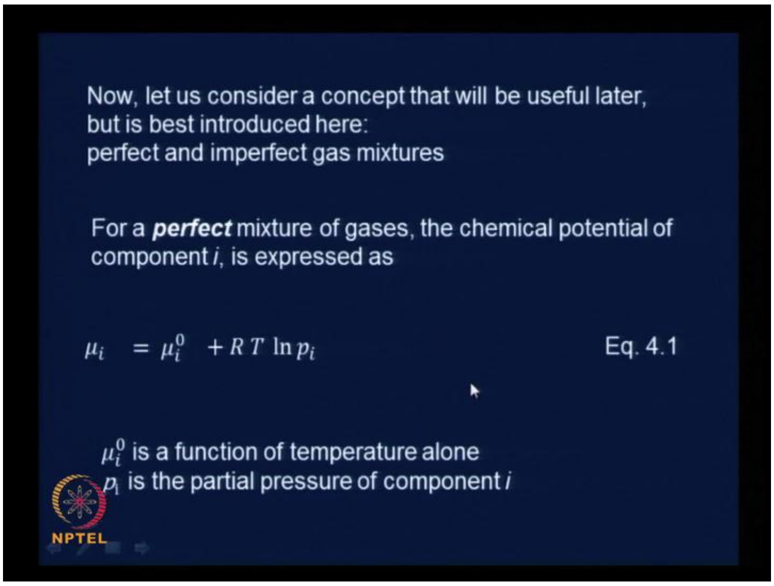

Now, let us consider a concept that will be useful later, but is best introduced here:
perfect and imperfect gas mixtures

For a ***perfect*** mixture of gases, the chemical potential of component *i*, is expressed as

$$\mu_i = \mu_i^0 + R\,T\,\ln p_i \qquad \text{Eq. 4.1}$$

μ_i^0 is a function of temperature alone
p_i is the partial pressure of component *i*

Now, let us consider a concept – this is purely a concept, it is not reality. We are extracting out something for convenience in terms of the interaction between molecules and so on and so forth. We are not getting to the details here, but let us introduce a concept here and the concept is that of perfect and imperfect gas mixtures. To repeat, perfect and imperfect gas mixtures.

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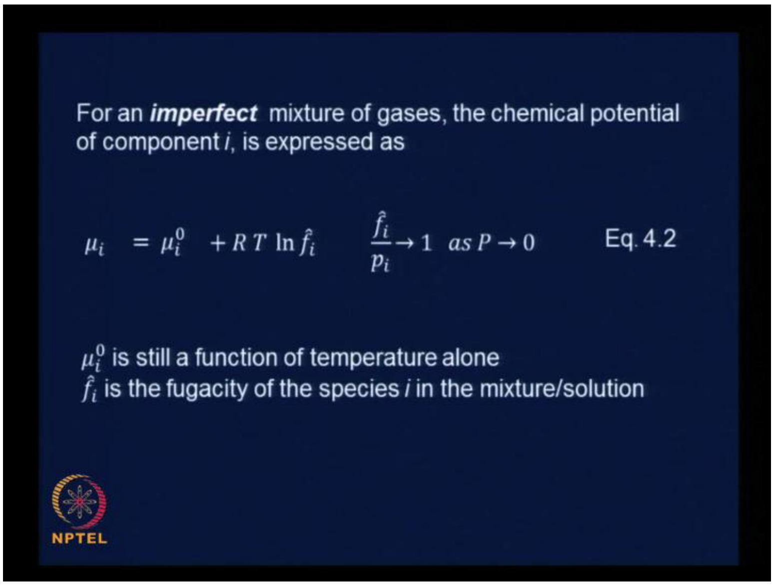

For an ***imperfect*** mixture of gases, the chemical potential of component *i*, is expressed as

$$\mu_i = \mu_i^0 + R\,T\,\ln \hat{f}_i \qquad \frac{\hat{f}_i}{p_i} \rightarrow 1 \;\; as\; P \rightarrow 0 \qquad \text{Eq. 4.2}$$

μ_i^0 is still a function of temperature alone
$\hat{f}_i$ is the fugacity of the species *i* in the mixture/solution

For a perfect mixture of a gas, the chemical potential of a component i, in that mixture … it is made up of many different components; let us take one component I … it is expressed as chemical potential of I, mu i equals some mu i naught plus R T ln p i. p i is the partial pressure of the component i as given here. p i is the partial pressure of the component i and mu i naught is a function of the temperature alone as we had seen earlier. This is for a perfect mixture of gases.

For an imperfect mixture of gases, the chemical potential of a component i, in the mixture, is expressed as mu i equals mu i naught plus R T ln of a certain f i hat, fugacity of the component i in solution. That hat implies solution, the component in solution, because the pure component fugacity may not be equal to the fugacity of that component in solution. To differentiate between that the pure component fugacity was f i that we had already seen earlier, the fugacity of the component i in solution is given as f i hat. And, again, we should state for completeness, that f i hat by the partial pressure of i p I – as you know partial pressure is the pressure exerted by that part of the gas mixture alone which corresponds to the component I – f i hat by p i tends to 1 as the total pressure tends to 0. Let us call this equation 4.2.

Here mu i naught is still a function of temperature alone and let me repeat this, it will become a little clearer. f i hat is the fugacity of the species i in the mixture or the solution, which may not be the same as the fugacity of the pure component when it exists separately.

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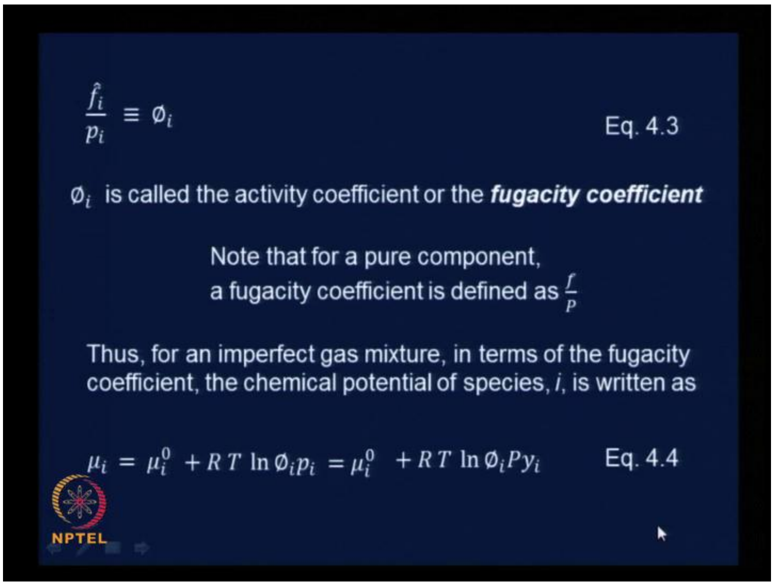

$$\frac{\hat{f}_i}{p_i} \equiv \emptyset_i \qquad \text{Eq. 4.3}$$

$\emptyset_i$ is called the activity coefficient or the ***fugacity coefficient***

Note that for a pure component,
a fugacity coefficient is defined as $\frac{f}{P}$

Thus, for an imperfect gas mixture, in terms of the fugacity coefficient, the chemical potential of species, *i*, is written as

$$\mu_i = \mu_i^0 + RT\ \ln \emptyset_i p_i = \mu_i^0 + RT\ \ln \emptyset_i P y_i \qquad \text{Eq. 4.4}$$

f i hat by the partial pressure is defined as the fugacity coefficient phi i of that component. We will call that equation 4.3 and phi i is sometimes called the activity coefficient also. We will call it the fugacity coefficient in this course; sometimes called the activity coefficient. In this course, we will use this term activity coefficient for something else, which we will talk about later. So, we will limit our terminology to fugacity coefficient. But, in some books, you know may be in some of your reference books given earlier, you will find this term activity coefficient. You should not get confused, when you find phi i being referred to as the activity coefficient.

And this is again to re-emphasize: Note that for a pure component a fugacity coefficient is defined as f by total pressure whereas, for a mixture the fugacity coefficient of the component i is defined as f i hat by partial pressure. Thus, for an imperfect gas mixture, in terms of the fugacity coefficient the chemical potential of a species i, is written as mu i equals mu i naught plus R T ln phi i p i. We have replaced our f i hat as phi i p i, which can further be written as mu i naught plus R T ln phi i partial pressure is nothing, but, the total pressure times the mole fraction of that component in the gas mixture. And therefore, R T ln phi i which comes from here and p i has been expanded to P y i. We will call this equation 4.4.

We will do this again and again because this is quite a concentrated part of the course, and it will help to repeat things to get things smoothly and clearly. Initially, we saw ideal gas and non-ideal gas in terms of the chemical potential. Then we brought in the concept of perfect and imperfect gas mixtures; you put various gases together, various pure gases together. Then you get a gas mixture and we had looked at perfect and imperfect gas mixtures definition that was again a concept.

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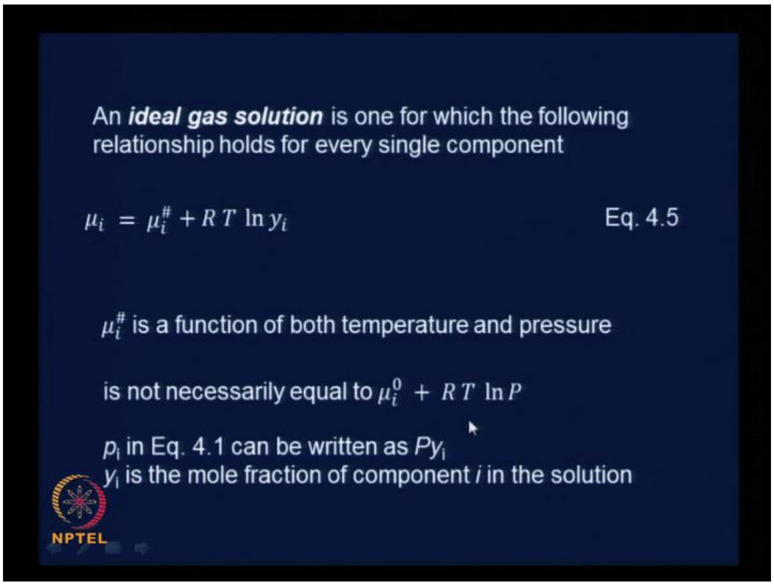

An ***ideal gas solution*** is one for which the following relationship holds for every single component

$$\mu_i = \mu_i^{\#} + RT \ln y_i \qquad \text{Eq. 4.5}$$

$\mu_i^{\#}$ is a function of both temperature and pressure

is not necessarily equal to $\mu_i^0 + RT \ln P$

p_i in Eq. 4.1 can be written as Py_i
y_i is the mole fraction of component *i* in the solution

Here, let us look at an ideal gas solution. An ideal gas solution is one for which the following relationship holds for every single component in the solution. mu i equals a certain mu i hash – this mu i hash is different from mu i naught – mu i hash plus R T ln of the mole fraction of the gas in the mixture y i. Let us call this equation 4.5. It is a nice, simple definition; it is good to remember this: mu equals mu i hash plus R T ln y i.

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Here mu i hash, is a function of both temperature and pressure. You will have to note this. Earlier … mu i naught was a function only of temperature. Here mu i hash is a function of both the temperature and pressure. And note, this could be a little tricky now, … you will get comfortable with this later. It is not necessarily equal to mu i naught plus R T ln P. Because, if you expand this, you could write mu i naught plus R T ln P y i and so on. But note that mu i hat need not necessarily equal mu i naught plus R T ln P. Just take it on face value for now; this is a definition.

p i in equation 4.1 can be written as P y i where y i is the mole fraction of component i in the solution; we have seen this earlier itself. That is, you know, you could write this definition, mu i naught plus R T ln P, and the p i in 4.1, could have been written like this for expanding, that is just making a point again.

Now, note this form: mu i equals mu i naught plus R T ln y I, equation 4.5. This is in terms of a certain function, which is a function of both temperature and pressure and the mole fraction. This is a very convenient form to write our chemical potentials.

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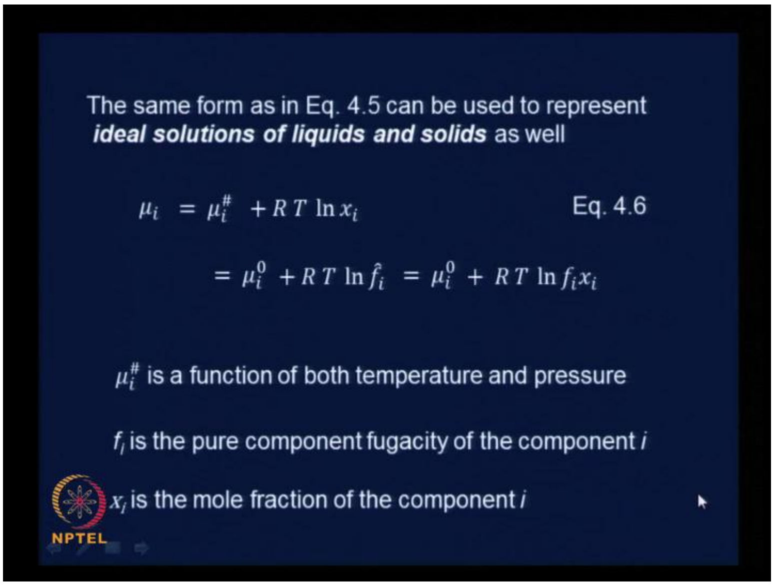

The same form as in Eq. 4.5 can be used to represent ***ideal solutions of liquids and solids*** as well

$$\mu_i = \mu_i^{\#} + RT\ln x_i \qquad \text{Eq. 4.6}$$

$$= \mu_i^0 + RT\ln \hat{f}_i = \mu_i^0 + RT\ln f_i x_i$$

$\mu_i^{\#}$ is a function of both temperature and pressure

f_i is the pure component fugacity of the component i

x_i is the mole fraction of the component i

The same form can be used to represent ideal solution of liquids and solids as well. Mixtures of liquids and solids, homogenous mixtures of liquids and solids … well, mixtures of liquids and solids. Earlier it was for the mixtures of gases alone. So, for an ideal solution of liquids and solids, for every component i mu i equals a certain mu i hash plus R T ln x i. This is equation 4.6 which can be written as mu i naught plus R T ln f i hat going by a previous way of writing things. This is a more convenient thing to remember; please go by this. This is … only in certain ways of representing it, if there is an interest to represent it in other ways … Equals mu i naught plus r ln f i x i. f i hat has been written as f i x i.

mu i hash, we know, is a function of both the temperature and the pressure, and f i is the pure component fugacity of the component i. … x i is the mole fraction of the component i. Note this form mu i equals mu i hash plus R T ln x i. And … with this you know – earlier we had mu i equals mu i hash plus R T ln y I, and here we have mu i equals mu i hash plus R T ln x i – and therefore, we have essentially covered gases, liquids and solids. So, pretty much we have a comprehensive way of representing things for all the systems that we would be interested in.

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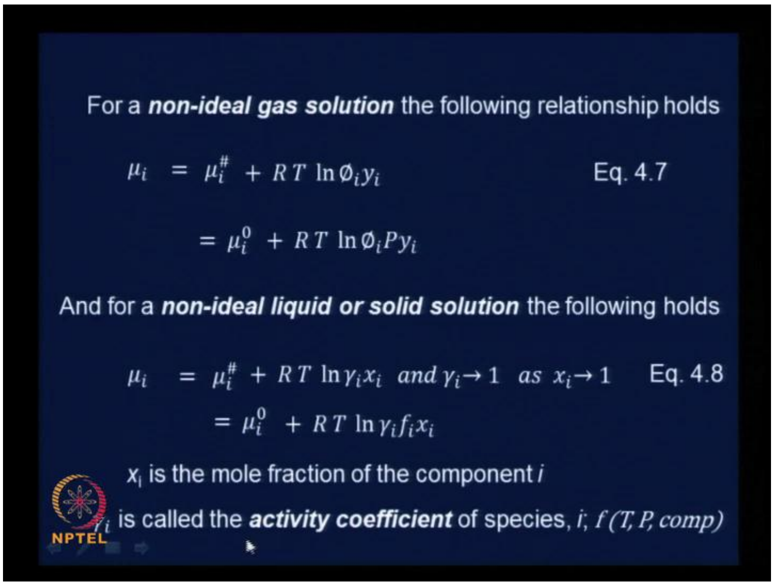

For a ***non-ideal gas solution*** the following relationship holds

$$\mu_i = \mu_i^{\#} + RT \ln \emptyset_i y_i \qquad \text{Eq. 4.7}$$

$$= \mu_i^0 + RT \ln \emptyset_i P y_i$$

And for a ***non-ideal liquid or solid solution*** the following holds

$$\mu_i = \mu_i^{\#} + RT \ln \gamma_i x_i \;\; and\; \gamma_i \rightarrow 1 \;\; as\;\; x_i \rightarrow 1 \qquad \text{Eq. 4.8}$$

$$= \mu_i^0 + RT \ln \gamma_i f_i x_i$$

x_i is the mole fraction of the component *i*

γ_i is called the ***activity coefficient*** of species, *i*; *f (T, P, comp)*

Now, let us bring in the non-ideal gas solution. For a non-ideal gas solution the following relationship holds for every component i in that non-ideal gas solution. This is again gas solution. mu i equals mu i hash plus R T ln phi i y i. This is equation 4.7, which can be written as mu i naught plus R T ln phi i P y i. … What I would like you to note is that for an ideal gas solution, our formulation was mu i equals mu i hash plus R T ln y i. Here, for a non-ideal gas solution it is mu i equals mu i hash plus R T ln phi i y i. This phi i is what brings in the non-ideality aspect.

And for a non-ideal liquid or a gas solution, you could have this mu i in the same form equals mu i hash plus R T ln (a certain gamma i), which brings in the non-ideality of the solution, times x i. … What did we mean by non-ideality? If you go back, we said that if you put in various components then … the weighted average of their properties may not equal the actual property of the solution itself. So, that is the non-ideality that we are talking about. So, here mu i equals mu i hash plus R T ln gamma i x i, which can also be written in terms of … Well, before I say that, this needs a certain completion, or a certain part of the definition needs to be given for completion, gamma i tends to one as x i tends to 1.

Note … in the earlier case it was f by P tending to 1 as P tending to 0. In the same way vein here, but, different details. Here, mu i equals mu i hash plus R T ln gamma i x i, gamma i tends to 1 as x i tends to 1; the mole fraction tends to 1. We will call this equation 4.8, which can be written in terms of mu i naught as mu i naught plus R T ln gamma i f i x i. Gamma i is called the activity coefficient of the species i. This is a new concept that we are introducing in this particular module. It is called gamma i, it is called the activity coefficient of the species i. And most importantly note, that … it is a function of temperature, pressure as well as composition. We have all three things coming in here; we need to be a little careful when we handle gamma i.

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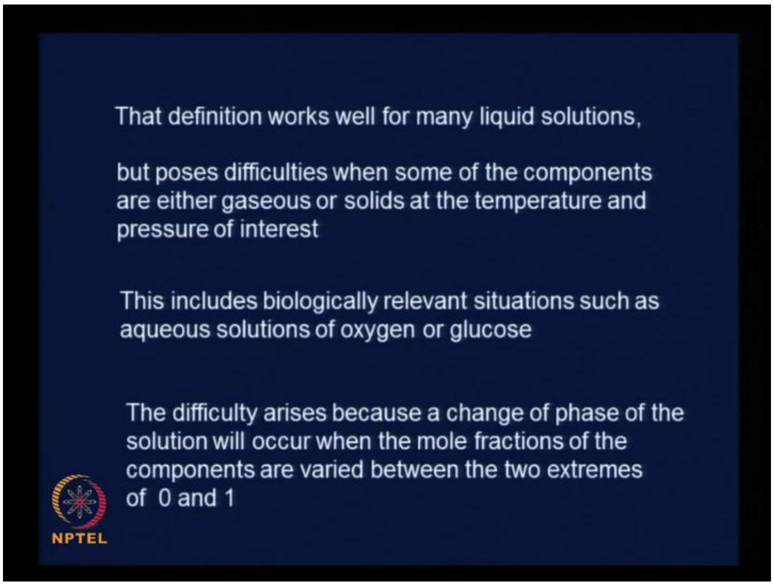

That definition works well for many liquid solutions,

but poses difficulties when some of the components are either gaseous or solids at the temperature and pressure of interest

This includes biologically relevant situations such as aqueous solutions of oxygen or glucose

The difficulty arises because a change of phase of the solution will occur when the mole fractions of the components are varied between the two extremes of 0 and 1

Now, that definition that we gave, works well for many liquid solutions. You know the definition was mu i equals mu i hash plus R T ln gamma i x i and gamma i tends to 1 as x i tends to 1. Now that works well for many liquid solutions, but not all. It poses difficulties when some of the components of the solution are either gaseous or solids at temperature and pressure of interest by themselves. You know in the solution there in solution, whether liquid solution or a solid solution and so on and so forth. But they exist in a different phase when you consider them as a pure component.

Why does this become a problem? It will become very clear now. Before I say why it becomes a problem, it is very relevant here because it includes biologically relevant situations such as aqueous solutions of oxygen or glucose. You know when we have a bioreactor for producing various biologicals, and if the organisms aerobic in the bioreactor we need to provide it with oxygen. The oxygen under normal conditions, you know, standard temperature, pressure, or room temperature, pressure, is a gas, which is in the gas phase and it needs to be dissolved in the liquid for the organisms in the broth, in the bioreactor broth to take it up.

Therefore, there we have a solution of oxygen in the water predominantly or the broth in which the organisms are grown. In the broth, the oxygen is in the liquid phase; whereas, under normal conditions at the same temperature and pressure as the broth, it is a gas phase. In other words, if the mole fraction of oxygen in the broth is hypothetically varied from 0 to 1, the phase changes, the phase of the component changes. And that is a problem. We will come to that formally in a little while.

Similarly, it is with glucose. You know, glucose is a solid at normal temperature pressure – the powder that we eat, and so on and so forth – glucose. When we use it for growing microorganisms, we need to dissolve it in a liquid, and we have a liquid solution that contains glucose. And therefore, when we change the concentration of glucose hypothetically in the solution from 0 to 1 mole fraction of glucose, let us say, then it goes from being a complete liquid at mole fraction slightly more than 0 to a solid at a mole fraction of 1. So, there we have some difficulty; we will see how to handle that.

Again that is what is said here, the difficulty arises because a change in phase of the solution will occur when the mole fractions of the components are varied between the two extremes of 0 and 1.

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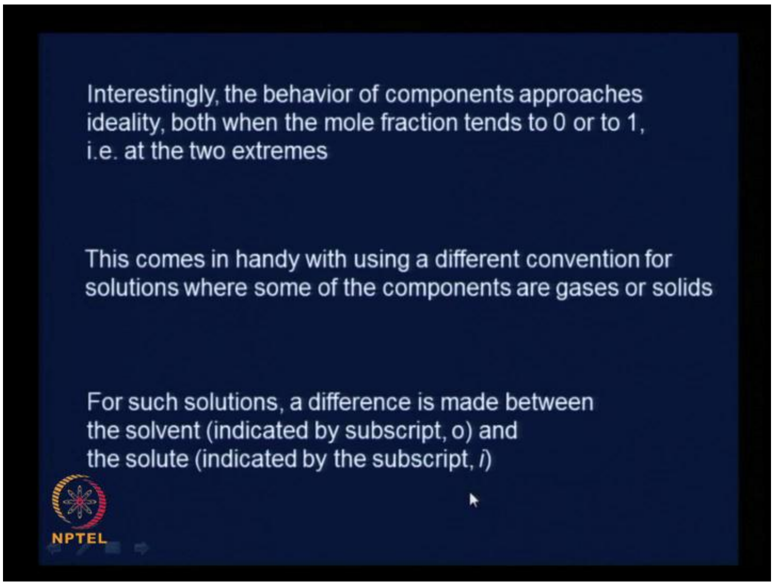

Interestingly, the behavior of components approaches ideality, both when the mole fraction tends to 0 or to 1, i.e. at the two extremes

This comes in handy with using a different convention for solutions where some of the components are gases or solids

For such solutions, a difference is made between the solvent (indicated by subscript, o) and the solute (indicated by the subscript, *i*)

But we are saved by this note or by noting this aspect. The behavior of the components approaches ideality both when the mole fraction tends to 0 or 1. The mole fraction is 0, it is a complete solution with no component in it. When it tends to one it is all pure component. Therefore, at the two extremes, we approach ideal behavior; we are not in the solution regime. And therefore, when we come with the convention … we can use a suitable convention that involves this. This comes in handy with using a different convention for solutions when some of the components are gases or solids.

For such solutions a difference is made between the solvent. We write an equation for the solvent and another equation for the solute. For the solvent we indicated by the subscript 0 or o, and for the solute we use the subscript i.

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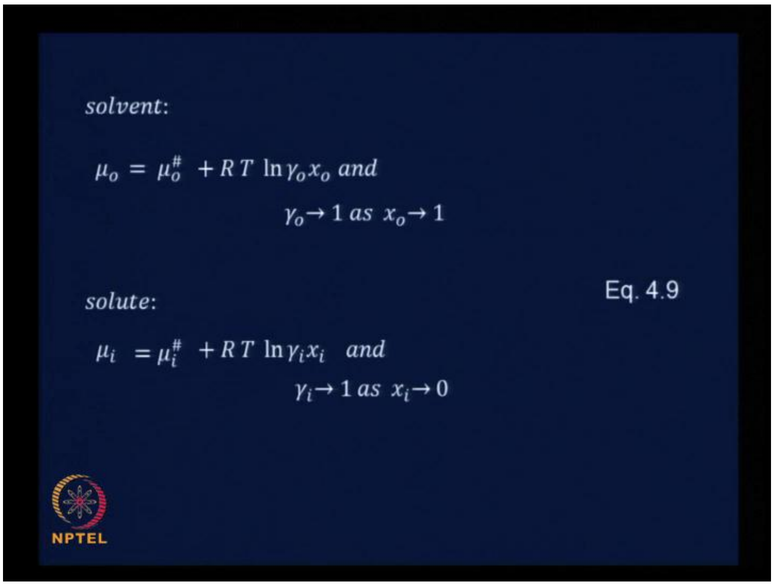

solvent:

$$\mu_o = \mu_o^\# + RT \ln \gamma_o x_o \text{ and}$$

$$\gamma_o \to 1 \text{ as } x_o \to 1$$

Eq. 4.9

solute:

$$\mu_i = \mu_i^\# + RT \ln \gamma_i x_i \text{ and}$$

$$\gamma_i \to 1 \text{ as } x_i \to 0$$

For example, the solvent chemical potential is expressed as mu 0 equals mu 0 hash plus R T ln gamma 0 x 0. You can use o also mu o equals mu o hash plus R T ln gamma o x o. And of course, this needs completion. Therefore, gamma o tends to 1 as x o tends to 1. Whereas, with the solute we write this as mu i equals mu i hash plus R T ln gamma i x i and gamma i tends to 1 as x i tends to 0. Now, the difference is here. x o tends to 1 gamma o tends to 1. Here, as x i tends to 0 for the solute gamma i tends to 1. Therefore, this makes it consistent, and this is the set of definitions that I used while dealing with tricky solutions. … As usual biological systems are full of tricky solutions. So, we need to use this. We will call this equation 4.9.

Where are we? OK. Since we have covered quite a bit of intense, intense material today, let us go through it again for completeness. You know, this is going to become a part of you only if you look at it a few times. I am going to help you, as a part of the class itself to look at it one more time. We said that we have an ideal solution … Just reviewing in a systematic fashion what we did so far today. I think it is worthwhile doing that now.

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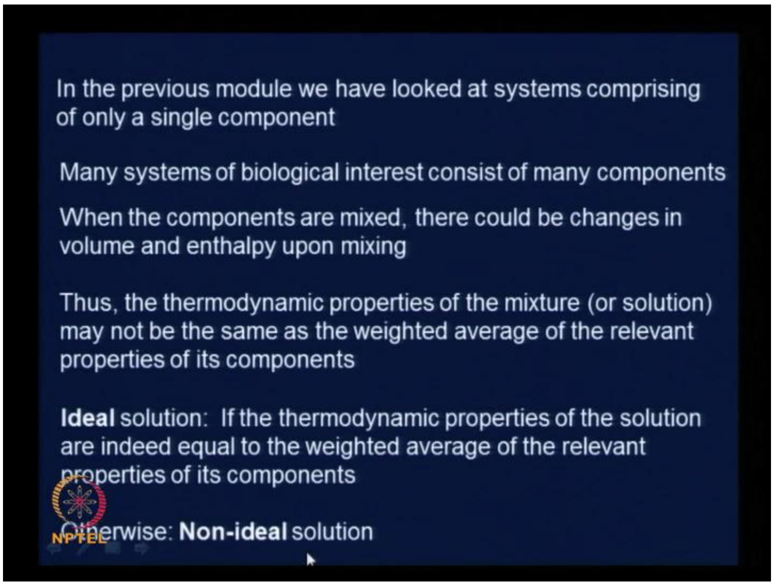

In the previous module we have looked at systems comprising of only a single component

Many systems of biological interest consist of many components

When the components are mixed, there could be changes in volume and enthalpy upon mixing

Thus, the thermodynamic properties of the mixture (or solution) may not be the same as the weighted average of the relevant properties of its components

Ideal solution: If the thermodynamic properties of the solution are indeed equal to the weighted average of the relevant properties of its components

Otherwise: **Non-ideal** solution

Ideal solution is the one if it happens if thermodynamics properties of the solution are equal to the weighted average of the relevant properties of the components, which may not always be the case. When it is not equal to the weighted average it becomes a non-ideal solution, which is the usual case. And then we said we will look at a few aspects and concepts of relevance for multi-component systems. We recalled initially, the expression for chemical potential for a pure component that we wrote for an ideal gas. We said that for an ideal gas the chemical potential mu can be expressed as mu naught plus R T ln P. And, when it became a real gas, when, you know, there is interaction between molecules that need to be considered and so on and so forth, then, we said, we could write mu equals mu naught plus R T ln f, fugacity, and f by P, total pressure, tends to 1 as P tends to 0. So, what was mu equals mu naught plus R T ln P for an ideal gas became mu equals mu naught plus R T ln f for a real gas. And we said that we will introduce a concept that we will use later which is that of perfect and imperfect gas mixtures. Please take this on face value as if now. For a perfect gas mixture, the chemical potential of component i in the solution is expressed as (No audio from 36:32 to 36:42) mu i equals mu i naught plus R T ln p i.

Here you have the partial pressure, and mu i naught is a function of temperature alone. And for an imperfect mixture of gases, we had the chemical potential of component i as mu i equals mu i naught plus R T ln f i hat. f i hat is the fugacity of the component i in solution, which could be different from the fugacity of the pure component itself, which is given without the hat. And for completeness we will have to say f i hat by the partial pressure p i tends to 1 as P tends to 0.

I will be with you in a minute, the animation is not working. Now we are fine.

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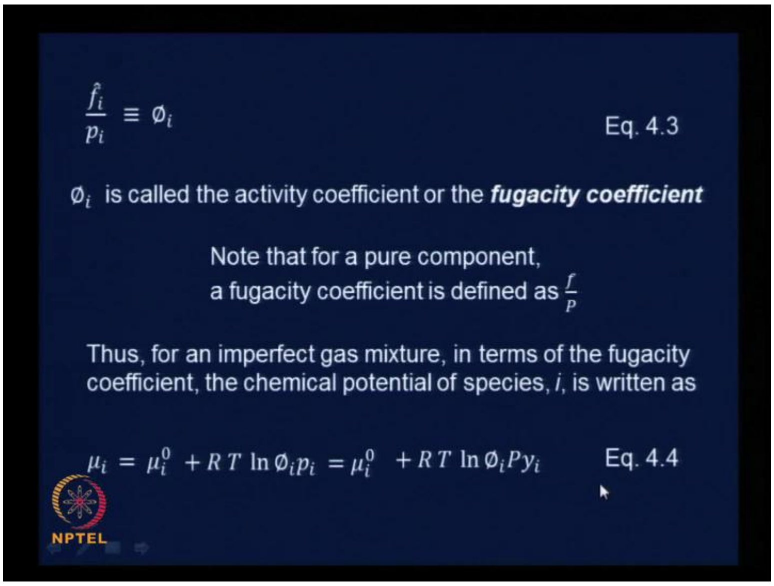

$$\frac{\hat{f}_i}{p_i} \equiv \emptyset_i \qquad \text{Eq. 4.3}$$

$\emptyset_i$ is called the activity coefficient or the ***fugacity coefficient***

Note that for a pure component,
a fugacity coefficient is defined as $\frac{f}{P}$

Thus, for an imperfect gas mixture, in terms of the fugacity coefficient, the chemical potential of species, *i*, is written as

$$\mu_i = \mu_i^0 + R\,T \ln \emptyset_i p_i = \mu_i^0 + R\,T \ln \emptyset_i P y_i \qquad \text{Eq. 4.4}$$

So, we then we said that the same way that we defined the fugacity coefficient phi for a pure component, there it was just f by P … and here we have for a component and solution of an imperfect gas mixture. f I hat by p i was defined as phi i, fugacity coefficient. Sometimes called the activity coefficient also, but, do not confuse this with the activity coefficient that we use later. So, in this course I said that we will use fugacity coefficient for phi i and activity coefficient for gamma i. For an imperfect gas mixture in terms of fugacity coefficient, we could write, mu i equals mu i naught plus R T ln phi i p i, which was mu i naught plus R T ln phi i P into y i.

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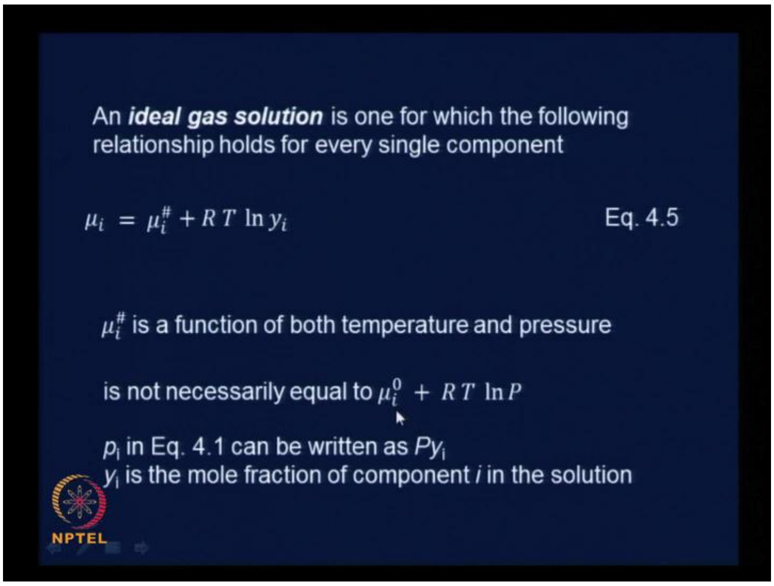

An ***ideal gas solution*** is one for which the following relationship holds for every single component

$$\mu_i = \mu_i^{\#} + R\,T\,\ln y_i \qquad \text{Eq. 4.5}$$

$\mu_i^{\#}$ is a function of both temperature and pressure

is not necessarily equal to $\mu_i^0 + R\,T\,\ln P$

p_i in Eq. 4.1 can be written as Py_i

y_i is the mole fraction of component *i* in the solution

Now, we looked at ideal gas solutions. The ideal gas solution is one for which the following relationship holds for each component, which was mu i equals mu i hash – mu i hash is a function of both temperature and pressure – plus R T ln (the mole fraction, y i) in the gas phase. And also note that mu i hash need not necessarily be equal to mu i naught plus R T ln P.

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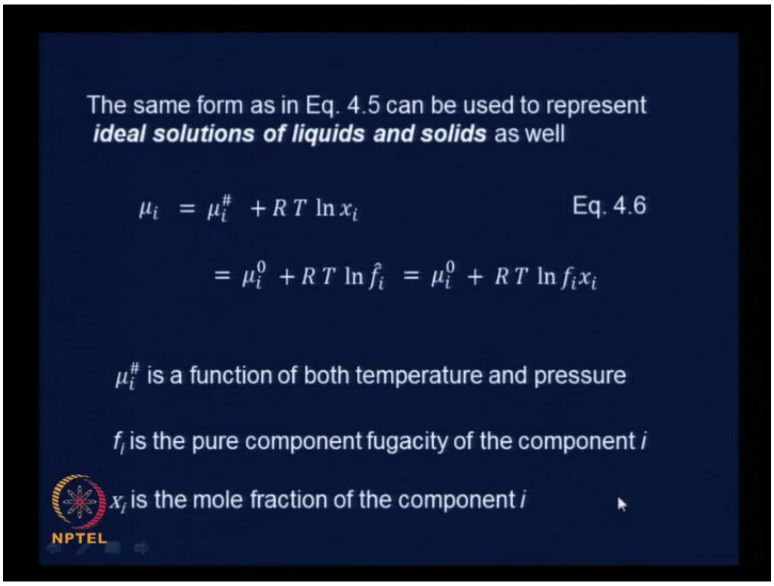

The same form as in Eq. 4.5 can be used to represent ***ideal solutions of liquids and solids*** as well

$$\mu_i = \mu_i^{\#} + R\,T\,\ln x_i \qquad \text{Eq. 4.6}$$

$$= \mu_i^0 + R\,T\,\ln \hat{f}_i = \mu_i^0 + R\,T\,\ln f_i x_i$$

$\mu_i^{\#}$ is a function of both temperature and pressure

f_i is the pure component fugacity of the component *i*

x_i is the mole fraction of the component *i*

And what is nice about this formulation is that you can directly extend it to the ideal solutions of liquids and solids as well. I hope you are able to visualize liquid solutions.

That is a little easier, but, solid solutions too, where all the components of this solution are solids. Here mu i was mu i hash plus R T ln x i. x i is the mole fraction of the component i in that particular liquid or solid solution; which can be written as mu i naught plus R T ln f i hash or f i hat, which is equal to mu i naught plus R T ln f i x I; this expresses f i hat as f i x i. And, of course, mu i hash was a function of both the temperature and the pressure and f i is the pure component fugacity of the component i.

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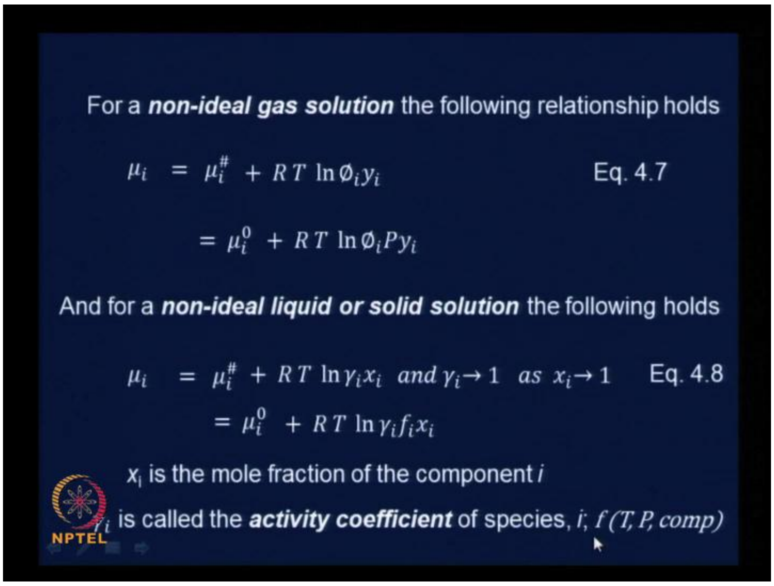

For a ***non-ideal gas solution*** the following relationship holds

$$\mu_i = \mu_i^{\#} + RT \ln \emptyset_i y_i \qquad \text{Eq. 4.7}$$

$$= \mu_i^0 + RT \ln \emptyset_i P y_i$$

And for a ***non-ideal liquid or solid solution*** the following holds

$$\mu_i = \mu_i^{\#} + RT \ln \gamma_i x_i \quad and\ \gamma_i \to 1 \quad as\ x_i \to 1 \qquad \text{Eq. 4.8}$$

$$= \mu_i^0 + RT \ln \gamma_i f_i x_i$$

x_i is the mole fraction of the component *i*

γ_i is called the ***activity coefficient*** of species, *i*; *f (T, P, comp)*

Then for a non-ideal gas solution, we said that the following relationship holds. Again, the same beautiful formulation, mu i equals mu i hash plus R T ln phi I – you know this phi i is one that brings in the non-ideality – phi i times y I; y i is the mole fraction and which could also be written as mu i naught plus R T ln phi i P into y i. For a non-ideal liquid or a gas solution, we could write mu i equals mu i hash plus R T ln gamma i x i. So, gamma comes in for a non-ideal liquid or a gas solution, and gamma i tends to 1 as x i, the mole fraction, tends to 1. Which could also be written as mu i naught plus R T ln gamma i f i x i. Also, I said note that … gamma i, is a function of temperature pressure and composition.

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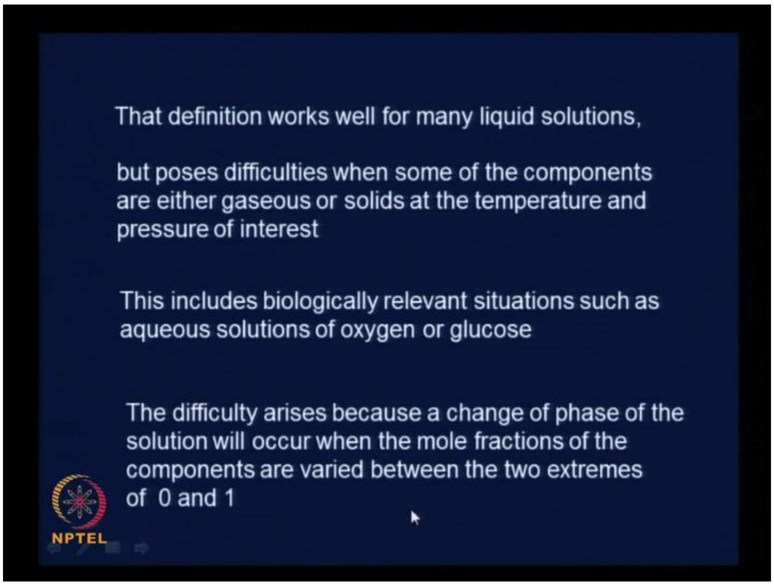

That definition works well for many liquid solutions,

but poses difficulties when some of the components are either gaseous or solids at the temperature and pressure of interest

This includes biologically relevant situations such as aqueous solutions of oxygen or glucose

The difficulty arises because a change of phase of the solution will occur when the mole fractions of the components are varied between the two extremes of 0 and 1

Then we said that this definition works well for many liquid solutions, but, falls apart when one of the components is either a gas or a solid as the case with some of the … biologically relevant solutions such as aqueous solutions of oxygen or glucose. We said that when the mole fraction is near 0 then of course, it is a liquid solution – mole fraction of oxygen in a solution is near 0, then it is a liquid solution. If the mole fraction of oxygen is increased to 1, it of course, becomes a total gas at the conditions of interest, you know the room temperature and so on and so forth.

Similarly, glucose in solution is a liquid solution as we slowly increase the mole fraction to 1, it becomes pure glucose which is a solid. For such cases, this definition will not work, essentially because there is a change of phase that occurs when the mole fraction of the components are varied between the two extremes of 0 and 1.

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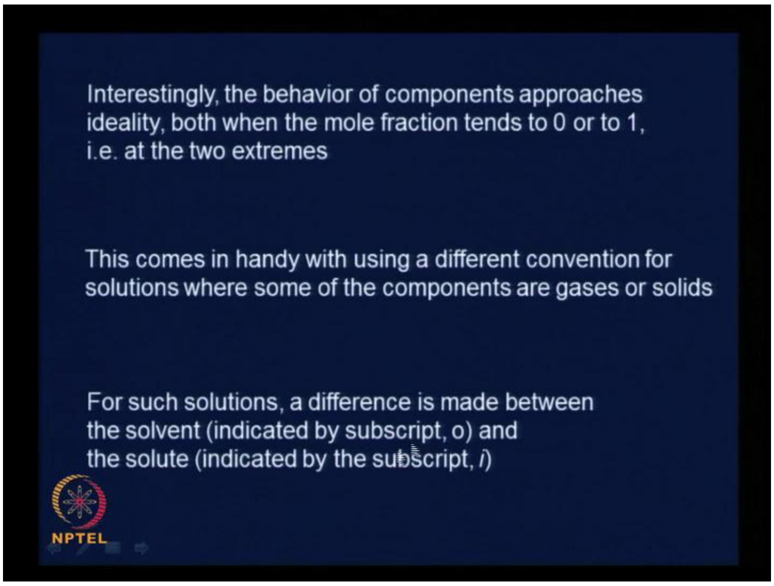

Interestingly, the behavior of components approaches ideality, both when the mole fraction tends to 0 or to 1, i.e. at the two extremes

This comes in handy with using a different convention for solutions where some of the components are gases or solids

For such solutions, a difference is made between the solvent (indicated by subscript, o) and the solute (indicated by the subscript, *i*)

For this, we need at a different formulation and we had used the fact that the behavior of the components approaches ideality then the mole fraction tends to either 0 or to 1. At both extremes the behavior becomes ideal as expected; 0 there is no component one that is the only component. So, that will be either none, or a pure component. So, that is an ideal situation.

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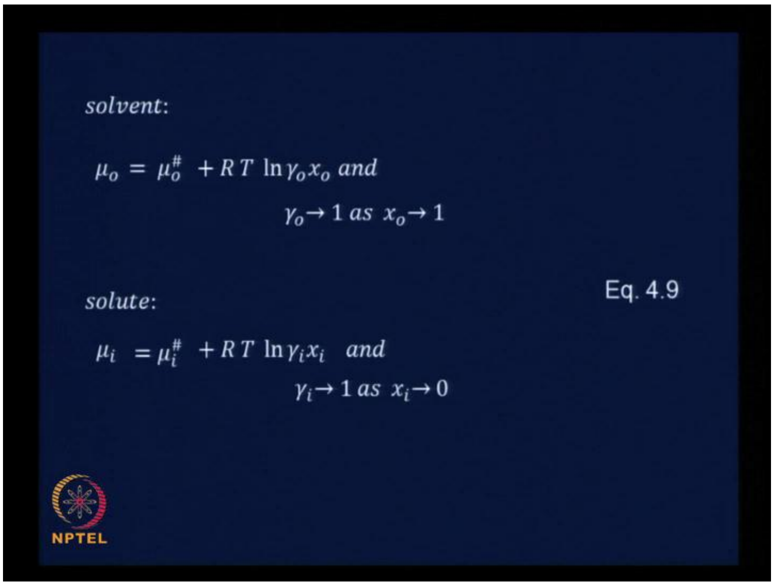

solvent:

$$\mu_o = \mu_o^{\#} + RT \ln \gamma_o x_o \ and$$

$$\gamma_o \rightarrow 1 \ as \ x_o \rightarrow 1$$

Eq. 4.9

solute:

$$\mu_i = \mu_i^{\#} + RT \ln \gamma_i x_i \ and$$

$$\gamma_i \rightarrow 1 \ as \ x_i \rightarrow 0$$

So, for that if we represent the solvent by subscript o and the solute by subscript i. Then for the solvent we wrote mu o equals mu o hash plus R T ln gamma o x o. And gamma o tends to 1 as x o tended to 1. And for the solute, we needed to write mu i equals mu i hash plus R T ln gamma i x i and gamma i tends to 1, as the solute mole fraction tends to 0. … Both these put together, needs to be used in such a situation – as we said in many biological systems – that we call as equation 4.9. Since, we have seen some intense material today, let us stop here. We are also all most out of time, and when we come back tomorrow, we will continue.