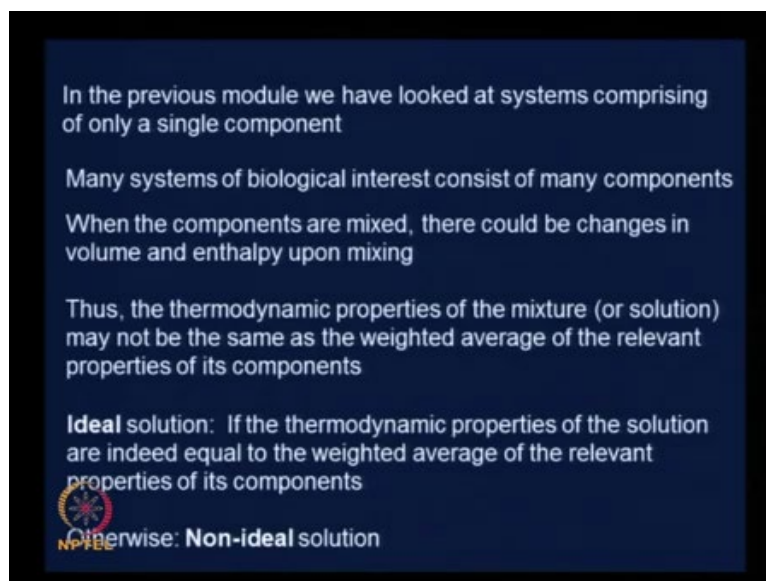


**Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Department of Biotechnology
Indian Institute of Technology - Madras**

**Lecture – 27
Chemical Potential Formulation**

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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**

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Welcome!

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.

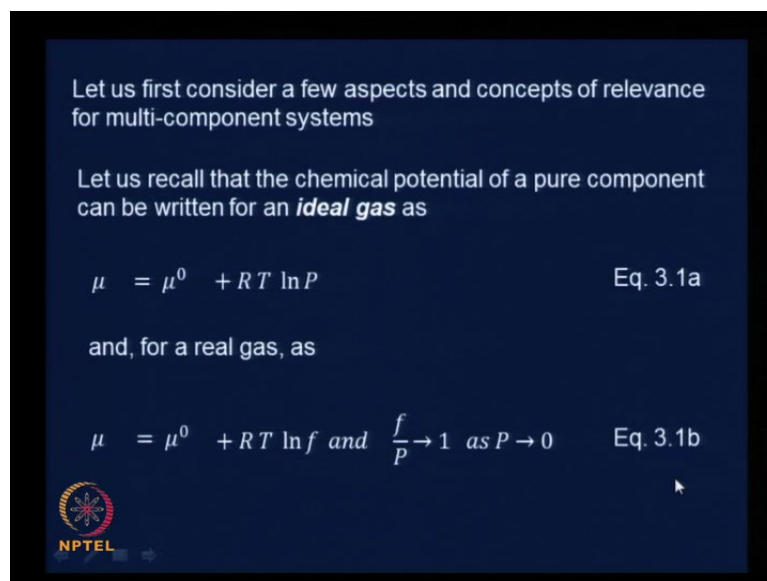
However, the focus of this course is biological systems, and many systems of biological interest consist of many components. It is rare to find a system with a pure component all the time. It is quite easy to see that when you mix pure components we get a mixture or a solution; we'll look at that a little 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 could take

volume one and volume two, V_1 and V_2 . When you mix them together the total volume may not be $V_1 + V_2$, it could be something different from $V_1 + V_2$.

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 happens, in other words, 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 many 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

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

and, for a real gas, as

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

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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 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

$$\mu = \mu^0 + R T \ln P$$

This we have already seen, way back in equation 3.1a. And for a real gas, you could write

$$\mu = \mu^0 + R T \ln f \quad \text{and} \quad \frac{f}{P} \rightarrow 1 \quad \text{as} \quad P \rightarrow 0$$

The P gets replaced 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

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

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

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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

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

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

$$\mu_i = \mu_i^0 + R T \ln p_i$$

p_i is the partial pressure of the component i as given here. p_i is the partial pressure of the component i and μ_i^0 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

$$\mu_i = \mu_i^0 + R T \ln \hat{f}_i \quad \frac{\hat{f}_i}{p_i} \rightarrow 1 \text{ as } P \rightarrow 0$$

\hat{f}_i is the 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 the pure component fugacity that we had already seen earlier, the fugacity of the component i in solution is given as \hat{f}_i . And, again, we should state for completeness, that \hat{f}_i 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 –

$\frac{\hat{f}_i}{p_i} \rightarrow 1 \text{ as } P \rightarrow 0$. Let us call the above equation 4.2.

Here μ_i^0 is still a function of temperature alone. Let me repeat this, ... it will become a little clearer. \hat{f}_i 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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$$\frac{\hat{f}_i}{p_i} \equiv \phi_i \quad \text{Eq. 4.3}$$

ϕ_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

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

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$$\frac{\hat{f}_i}{p_i} \equiv \phi_i$$

ϕ_i is the fugacity coefficient of that component. We will call that equation 4.3

ϕ_i is sometimes called the activity coefficient. We will call it the fugacity coefficient in this course. 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, 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 ϕ_i being referred to as the activity coefficient.

This is to re-emphasize: Note that for a pure component a fugacity coefficient is defined as f by total pressure, P , whereas, for a mixture the fugacity coefficient of the component i is defined as $\frac{\hat{f}_i}{p_i}$. Thus, for an imperfect gas mixture, in terms of the fugacity coefficient the chemical potential of a species i , is written as

$$\mu_i = \mu_i^0 + RT \ln \phi_i p_i = \mu_i^0 + RT \ln \phi_i P y_i$$

We have replaced our \hat{f}_i as $\phi_i p_i$. Note that partial pressure is nothing but, the total pressure times the mole fraction of that component in the gas mixture. And therefore, p_i can be 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 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

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

$\mu_i^{\#}$ 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 $P y_i$
 y_i is the mole fraction of component i in the solution

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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

$$\mu_i = \mu_i^{\#} + R T \ln y_i$$

This $\mu_i^{\#}$ is different from μ_i^0 . Let us call this equation 4.5. It is a nice, simple definition; it is good to remember this.

Here $\mu_i^{\#}$ is a function of both temperature and pressure. You will have to note this. Earlier μ_i^0 was a function only of temperature. And note, this could be a little tricky now, ... you will get comfortable with this later. It is not necessarily equal to $\mu_i = \mu_i^0 + R T \ln P$. Because, if you

expand this, you could write μ_i^0 plus $RT \ln P y_i$ and so on. But note that $\mu_i^\#$ need not necessarily equal $\mu_i^0 + RT \ln P$. Just take it on face value for now; this is a definition.

Now, note this form:

$$\mu_i = \mu_i^\# + RT \ln y_i$$

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

$$\mu_i = \mu_i^\# + RT \ln x_i \quad \text{Eq. 4.6}$$
$$= \mu_i^0 + RT \ln \hat{f}_i = \mu_i^0 + RT \ln f_i x_i$$

$\mu_i^\#$ 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

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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

$$\mu_i = \mu_i^\# + RT \ln x_i$$

This is equation 4.6, which can be written as

$$\mu_i = \mu_i^\# + RT \ln \hat{f}_i$$

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 ...

$$\mu_i = \mu_i^0 + R T \ln f_i x_i$$

f_i is the pure component fugacity of the component i x_i is the mole fraction of the component i . Note this form

$$\mu_i = \mu_i^\# + R T \ln x_i$$

Earlier we had

$$\mu_i = \mu_i^\# + R T \ln y_i$$

and here we have

$$\mu_i = \mu_i^\# + R T \ln x_i$$

Therefore, we have essentially covered gases, liquids and solids. So, 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


$$\begin{aligned} \mu_i &= \mu_i^\# + R T \ln \phi_i y_i && \text{Eq. 4.7} \\ &= \mu_i^0 + R T \ln \phi_i P y_i \end{aligned}$$

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

$$\begin{aligned} \mu_i &= \mu_i^\# + R T \ln \gamma_i x_i \text{ and } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1 && \text{Eq. 4.8} \\ &= \mu_i^0 + R T \ln \gamma_i f_i x_i \end{aligned}$$

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.

$$\mu_i = \mu_i^\# + R T \ln \phi_i y_i$$

This is equation 4.7, which can be written as

$$\mu_i = \mu_i^0 + R T \ln \phi_i P y_i$$

What I would like you to note is that for an ideal gas solution, our formulation was

$$\mu_i = \mu_i^\# + R T \ln y_i$$

Here, for a non-ideal gas solution it is

$$\mu_i = \mu_i^\# + R T \ln \phi_i y_i$$

This ϕ_i is what brings in the non-ideality aspect.

For a non-ideal liquid or a solid solution, you could have

$$\mu_i = \mu_i^\# + R T \ln \gamma_i x_i \text{ and } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1$$

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. This needs a certain completion, or a certain part of the definition needs to be given for completion, $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$.

Note ... in the earlier case it was $\frac{\hat{f}_i}{p_i} \rightarrow 1$ as $P \rightarrow 0$. In the same way vein here, but, different details. Here,

$$\mu_i = \mu_i^\# + R T \ln \gamma_i x_i \text{ and } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1$$

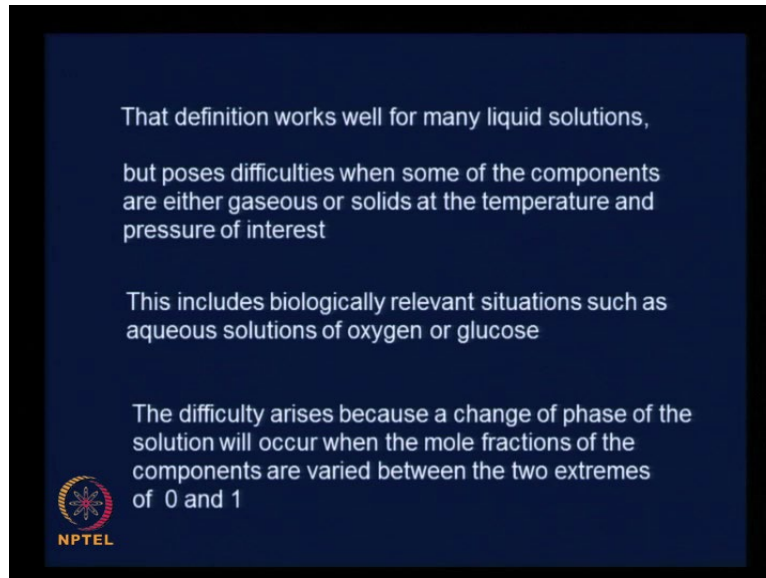
We will call this equation 4.8, which can be written in terms of

$$\mu_i = \mu_i^0 + R T \ln \gamma_i f_i x_i$$

γ_i is called the activity coefficient of the species i. This is a new concept that we are introducing in this particular module. γ_i is called the activity coefficient of the species i. 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 γ_i .

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Now, that definition that we gave, works well for many liquid solutions. The definition was

$$\mu_i = \mu_i^\# + RT \ln \gamma_i x_i \text{ and } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1$$

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. 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 are aerobic in the bioreactor we need to provide it with oxygen. The oxygen under normal conditions, standard temperature, pressure, or room temperature, pressure, is a gas, and it needs to be dissolved in the liquid for the organisms in the broth, in the bioreactor broth to take it up.

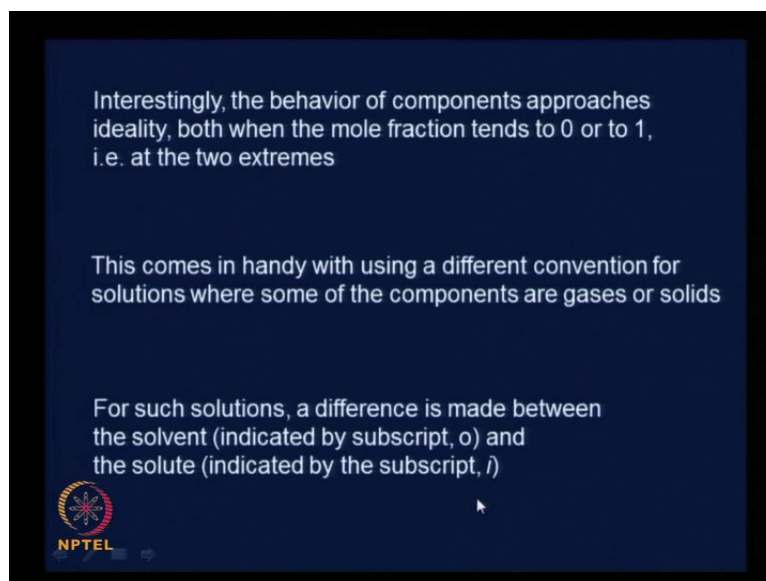
Therefore, there we have a solution of oxygen in the water predominantly or the broth in which the organisms are grown. In the broth, the oxygen is in the liquid phase; whereas, under normal conditions at the same temperature and pressure as the broth, it is a gas phase. In other words, if

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 – 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, 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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But we are saved by noting this aspect. The behavior of the components approaches ideality both when the mole fraction tends to 0 or 1. When the mole fraction is 0, it is a complete solvent 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. Therefore, we need a suitable convention that involves this. We need to use a different convention for solutions when some of the components are gases or solids.

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

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solvent:

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

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

solute:

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

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

Eq. 4.9

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For example, the solvent chemical potential is expressed

$$\mu_o = \mu_o^\# + RT \ln \gamma_o x_o \quad \text{and } \gamma_o \rightarrow 1 \text{ as } x_o \rightarrow 1$$

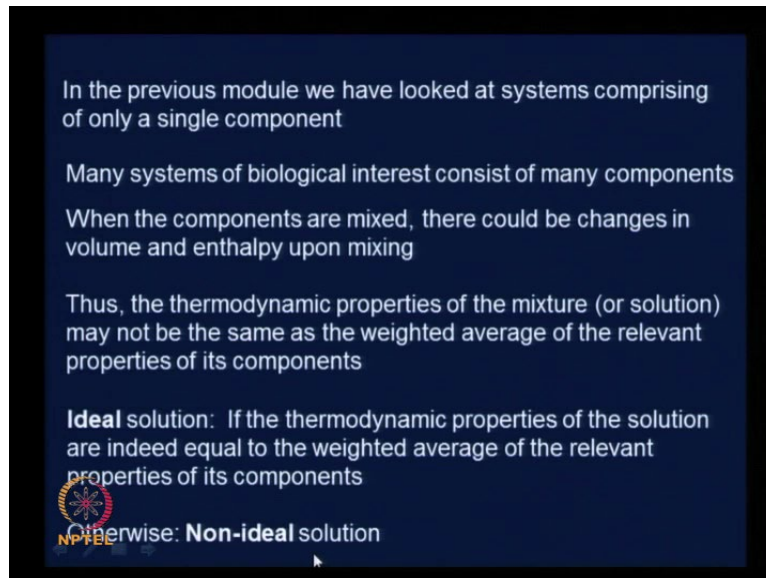
Whereas, with the solute we write this as

$$\mu_i = \mu_i^\# + RT \ln \gamma_i x_i \quad \text{and } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 0$$

Here, as x_i tends to 0 for the solute γ_i tends to 1. Therefore, this makes it consistent. This is the set of definitions that I use 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.

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**

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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. 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

$$\mu = \mu^0 + RT \ln P$$

When it became a real gas, when, there is interaction between molecules that need to be considered, then, we said, we could write

$$\mu = \mu^0 + RT \ln f \quad \text{and} \quad \frac{f}{P} \rightarrow 1 \quad \text{as} \quad P \rightarrow 0$$

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

$$\mu_i = \mu_i^0 + RT \ln p_i$$

Here you have the partial pressure, and μ_i^0 is a function of temperature alone. For an imperfect mixture of gases, we had the chemical potential of component i as

$$\mu_i = \mu_i^0 + RT \ln \hat{f}_i \quad \frac{\hat{f}_i}{p_i} \rightarrow 1 \text{ as } P \rightarrow 0$$

\hat{f}_i 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. For completeness we will have to say $\frac{\hat{f}_i}{p_i} \rightarrow 1 \text{ as } P \rightarrow 0$.

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$$\frac{\hat{f}_i}{p_i} \equiv \phi_i \quad \text{Eq. 4.3}$$
 ϕ_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

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

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We then we said that the same way that we defined the fugacity coefficient ϕ_i for a pure component,

$$\frac{\hat{f}_i}{p_i} \equiv \phi_i$$

there it was just f by P ... and here we have for a component and solution of an imperfect gas mixture. Sometimes called the activity coefficient also, but, do not confuse this with the activity coefficient that we use later. In this course I said that we will use fugacity coefficient for ϕ_i and activity coefficient for γ_i . For an imperfect gas mixture in terms of fugacity coefficient, we could write,


$$\mu_i = \mu_i^0 + RT \ln \phi_i p_i = \mu_i^0 + RT \ln \phi_i P y_i$$

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

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

$\mu_i^\#$ is a function of both temperature and pressure
is not necessarily equal to $\mu_i^0 + R T \ln P$
 ρ_i in Eq. 4.1 can be written as $P y_i$
 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,

$$\mu_i = \mu_i^\# + R T \ln y_i$$


$\mu_i^\#$ is a function of both temperature and pressure – in the gas phase. Also note that that $\mu_i^\#$ need not necessarily equal $\mu_i^0 + R T \ln P$.

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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

$$\begin{aligned} \mu_i &= \mu_i^\# + R T \ln x_i && \text{Eq. 4.6} \\ &= \mu_i^0 + R T \ln \hat{f}_i = \mu_i^0 + R T \ln f_i x_i \end{aligned}$$

$\mu_i^\#$ 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



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

$$\mu_i = \mu_i^\# + R T \ln x_i$$

x_i is the mole fraction of the component i in that particular liquid or solid solution. This can be written as

$$\mu_i = \mu_i^\# + R T \ln \hat{f}_i$$

which is equal to

$$\mu_i = \mu_i^0 + R T \ln f_i x_i$$

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

$$\begin{aligned} \mu_i &= \mu_i^\# + R T \ln \phi_i y_i && \text{Eq. 4.7} \\ &= \mu_i^0 + R T \ln \phi_i P y_i \end{aligned}$$

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

$$\begin{aligned} \mu_i &= \mu_i^\# + R T \ln \gamma_i x_i \text{ and } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1 && \text{Eq. 4.8} \\ &= \mu_i^0 + R T \ln \gamma_i f_i x_i \end{aligned}$$

x_i is the mole fraction of the component i
 f_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,

$$\mu_i = \mu_i^\# + R T \ln \phi_i y_i$$

y_i is the mole fraction. This equation could also be written as

$$\mu_i = \mu_i^0 + R T \ln \phi_i P y_i$$

For a non-ideal liquid or a gas solution, we could

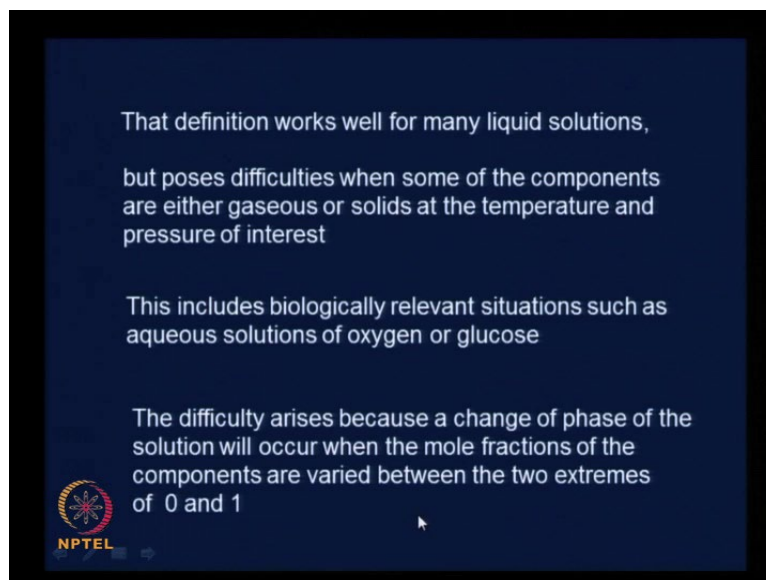
$$\mu_i = \mu_i^\# + R T \ln \gamma_i x_i \text{ and } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1$$

γ_i comes in for a non-ideal liquid or a gas solution. This could also be written as

$$\mu_i = \mu_i^0 + R T \ln \gamma_i f_i x_i$$

γ_i is a function of temperature pressure and composition.

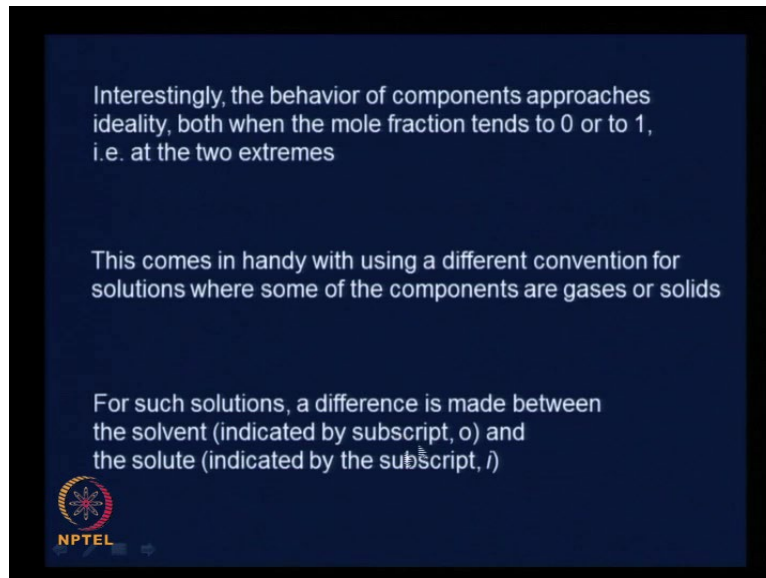
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Then we said that this definition works well for many liquid solutions, but, falls apart when one of the components is either a gas or a solid as the case with some of the biologically relevant solutions such as aqueous solutions of oxygen or glucose. 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, the room temperature and so on.

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

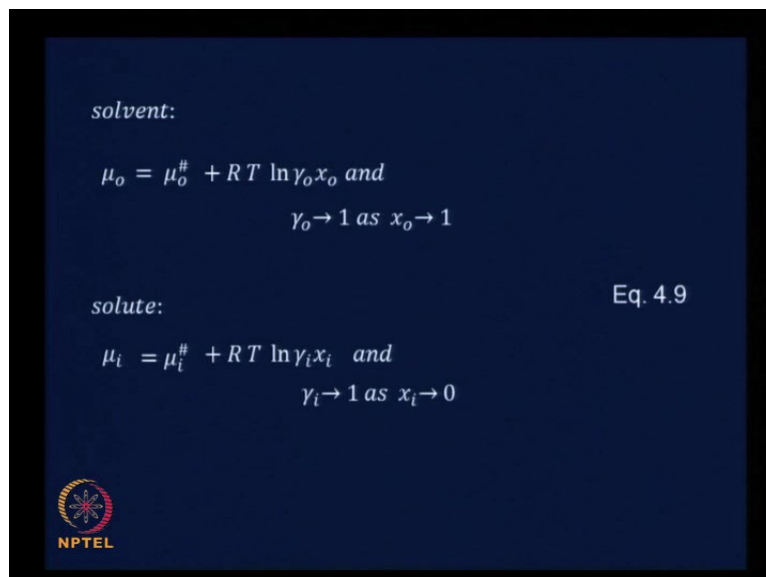
This comes in handy with using a different convention for solutions where some of the components are gases or solids

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; 1: 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:

$$\mu_o = \mu_o^\# + RT \ln \gamma_o x_o \text{ and}$$
$$\gamma_o \rightarrow 1 \text{ as } x_o \rightarrow 1$$

solute:

$$\mu_i = \mu_i^\# + RT \ln \gamma_i x_i \text{ and}$$
$$\gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 0$$

Eq. 4.9



For that if we represent the solvent by subscript o and the solute by subscript i. Then for the solvent we wrote

$$\mu_o = \mu_o^\# + RT \ln \gamma_o x_o \quad \text{and } \gamma_o \rightarrow 1 \text{ as } x_o \rightarrow 1$$

And, for the solute, we needed to write

$$\mu_i = \mu_i^\# + RT \ln \gamma_i x_i \quad \text{and } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 0$$

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.

See you in the next class.