

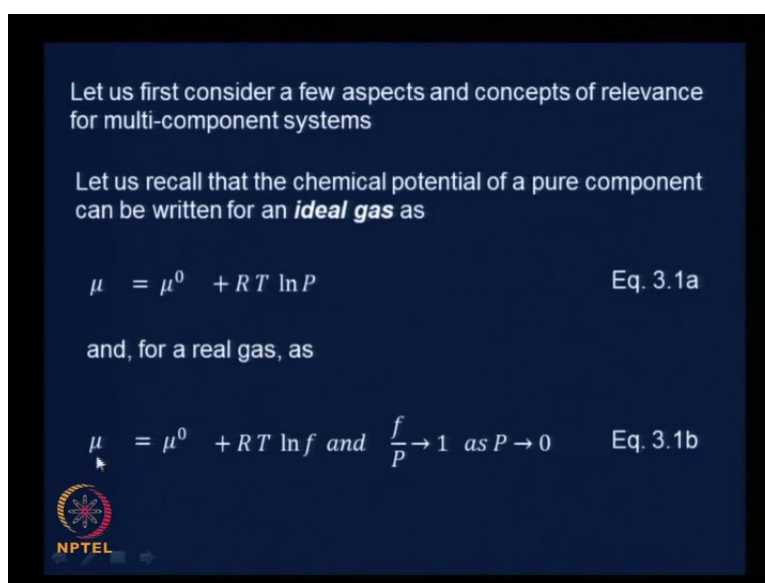
**Thermodynamics for Biological Systems:
Classical and Statistical Aspects
Prof. G.K. Suraishkumar
Department of Biotechnology
Indian Institute of Technology - Madras**

**Lecture – 28
Lewis and Randall Rule**

Welcome!

In the last class we started looking at multi-component systems. We initially started out with the ideal gas, and since we are doing everything in terms of the chemical potential, we had written down the chemical potential expressions for an ideal gas, which we had already seen in the earlier module, the third module.

(Refer Slide Time: 00:36)




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

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



And then we said that the real gas ... in the expression for the real gas, you replace the pressure here,

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

where μ^0 is a function of temperature alone. This was for an ideal gas, and when you write it for the real gas, it becomes

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

Then we looked at something called perfect gas mixtures and imperfect gas mixtures. Then we looked at something called ideal gas mixtures and non-ideal gas mixtures. And with that formulation we saw that we could expand them or extend that to ideal mixtures of liquids and solids as well as non-ideal mixtures of liquids and solids.

So, essentially, ideal gas, real gas that was initial formulation where we went from P to f and then we used the perfect and imperfect gas mixtures. That is only a concept, which we will kind of borrow on from time to time. So, let us keep it aside for the time being. We will go through it and see how we defined it in a little bit. Then we went into ... ideal gas mixtures and real gas mixtures. Then we saw that we could extend that formulation to ideal mixtures of liquids and solids as well as non-ideal mixtures of liquids and solids.

(Refer Slide Time: 02:27)

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

NPTEL

So, we have already seen this. The ideal gas is

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

For the real gas it was

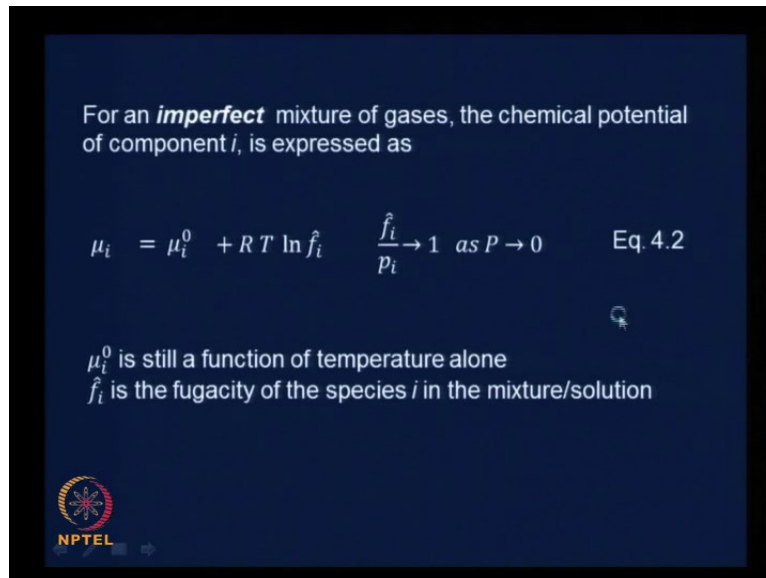
$$\mu = \mu^0 + R T \ln f \quad \text{and} \quad \frac{f}{P} \rightarrow 1 \quad \text{as} \quad P \rightarrow 0$$

Concept-wise, the perfect mixture of gases is something for which the following can be used ... as the chemical potential. For every component i

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

This is the partial pressure of the component i in the gas mixture.


(Refer Slide Time: 02:49).



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



And then for the imperfect gas mixture ... we said we should replace this partial pressure with \hat{f}_i , the fugacity of the species i in the mixture.

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

(Refer Slide Time: 03:13)


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

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

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



The fugacity coefficient for the species i in the mixture becomes

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

The earlier one the pure gas fugacity coefficient we had defined as f by total pressure P has been equal to ϕ_i .

Therefore, we could write

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


for an imperfect gas mixture.

(Refer Slide Time: 04:00)

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



Then, this one is what we need to focus on, the ideal gas solution. The formulation that we had used is

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


The important thing being that $\mu_i^\#$ is a function of both temperature and pressure. And here we have a convenient formulation in terms of the mole fraction. This is for an ideal gas solution.

(Refer Slide Time: 04:27)

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



For the ideal solutions of liquids and solids, we use x_i as the mole fraction of the component i in the liquid or the solid solution.

(Refer Slide Time: 04:43)


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

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

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

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

x_i is the mole fraction of the component i
 γ_i is called the **activity coefficient** of species, i , $f(T, P, comp)$



Then, for the non-ideal gas solution ... I had earlier said real gas solution, make it non-ideal gas solution. We write

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

This ϕ_i brings in the non-ideality of the component in the gas solution. And for the non-ideal liquid or solid solution we could write

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


This is what we had essentially seen yesterday and reinforced and again reinforced this morning in this class.

(Refer Slide Time: 05:43)

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)



Then we found that that definition especially for the non-ideal liquid and solid solutions work well in most liquid solution cases. Whereas, when the when the component happens to be either a gas or a solid at the temperature and pressure of the solution in question, then we may run into some difficulties, because as we change the mole fraction of the component in the solution, the phase could change. Therefore, we have to come up with a different formulation. We had used two equation formulation for that. For the solvent we had used a subscript o and the solute we had used the subscript i.

(Refer Slide Time: 06:19)


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



And therefore, we could write for the solvent

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

This is for the solvent and for the solute

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

This was equation 4.9 and this is where we had finished up in the last class.

(Refer Slide Time: 06:49)

Now, let us return to ideal solutions for a while

Let us consider Eq. 4.2 $\mu_i = \mu_i^0 + R T \ln \hat{f}_i$

Since ideality is a special case of `real`, we can use the `real` eq. 4.5 to represent the same: $\mu_i = \mu_i^\# + R T \ln y_i$

From Eqs. 4.2 and 4.5, we can get

$$\mu_i - \mu_i^0 = R T \ln \hat{f}_i$$
$$\mu_i - \mu_i^\# = R T \ln y_i$$

Subtracting the second equation from the first, we get

$$\mu_i^\# - \mu_i^0 = R T \ln \frac{\hat{f}_i}{y_i}$$

NPTEL

Now, let us return or look back at ideal solutions for a little bit. We are going to develop something important here. So, let us concentrate on ideal solutions. You know that equation 4.2, you can go back to your notes; it is already given here,

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

This works for the ideal solution case where $\mu_i^\#$ is the function of temperature alone. Now, we know that ideality is nothing but the special case of reality. Therefore, the expression for the real case must also be valid here.

If we write it for the real case it should be valid for the ideal case also. The `super` thing should should always include the special case also. Therefore, this 4.5 equation,

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

This equation should also be valid. Now, from equation 4.2, you know, just by transposing this equation, μ_i or in other words, subtracting $\mu_i^\#$ from both sides, we get

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

And doing the same thing to equation 4.5 we could write

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

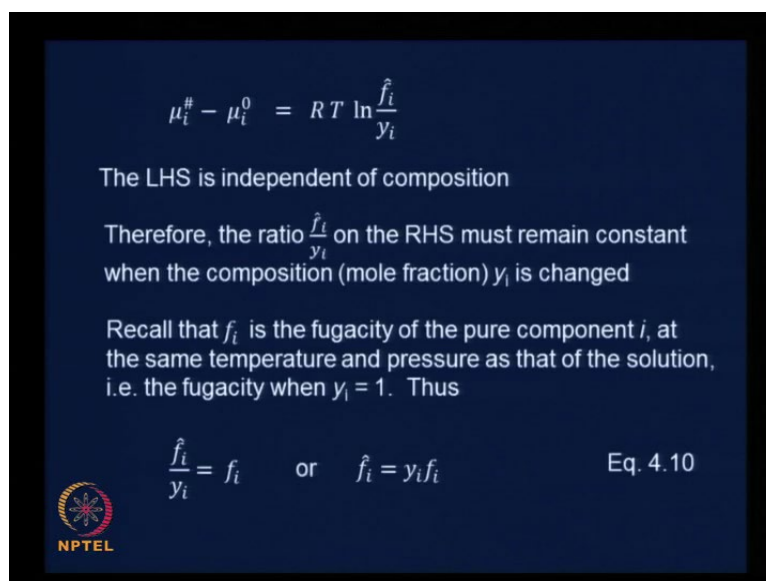
Now, what I would like you to do is just subtract the second equation from the first equation and tell me what you get. Take about five minutes – good to juggle, little bit, your brain and your hands and so on so forth. So, just work this out subtract equation two from equation one and tell me what you get. 5 minutes please.

If you subtract equation two from equation one, you would get

$$\mu_i^\# - \mu_i^\# = R T \ln \frac{\hat{f}_i}{y_i}$$

$\ln a$ minus $\ln b$ equals \ln of a by b . Therefore, this becomes $R T \ln \hat{f}_i / y_i$. Same equation here.

(Refer Slide Time: 15:20)




$$\mu_i^\# - \mu_i^\# = R T \ln \frac{\hat{f}_i}{y_i}$$

The LHS is independent of composition

Therefore, the ratio $\frac{\hat{f}_i}{y_i}$ on the RHS must remain constant when the composition (mole fraction) y_i is changed

Recall that f_i is the fugacity of the pure component i , at the same temperature and pressure as that of the solution, i.e. the fugacity when $y_i = 1$. Thus

$$\frac{\hat{f}_i}{y_i} = f_i \quad \text{or} \quad \hat{f}_i = y_i f_i \quad \text{Eq. 4.10}$$


Now, note this argument a little carefully. We will be using this argument a few more times in this particular course. $\mu_i^\# - \mu_i^0$: this is the left hand side of the equation. You know that in any equation whatever applies to the left hand side must apply to the right hand side. So, we will look at dependencies here. $\mu_i^\#$ is a function of temperature and pressure. μ_i^0 is a function of temperature alone, and ... the left hand side, therefore, is definitely independent of composition.

So, that is clear here. Therefore, the right hand side must also be independent of composition. Let us let us look at that point alone. It has to be independent of composition. Therefore, see this is R what is on the right hand side R and T here. There is no problem here. If at all we need to worry about composition it has to be in this term. This ratio $\frac{\hat{f}_i}{y_i}$ on the right hand side must remain constant when the composition is changed, because you have a left hand side, which is independent of composition. Therefore, when you change y_i here the only way that this remains independent of composition is that this ratio becomes independent of composition.

Therefore, $\frac{\hat{f}_i}{y_i}$ must remain constant when the composition is changed, or when y_i , which represents the mole fraction, is changed. I hope this is clear. f_i is the fugacity of the pure component i at the same temperature and pressure as that of the solution – that we know. Or, in other words, f_i is \hat{f}_i when y_i equals 1. f_i is pure component \hat{f}_i is the fugacity of that component in solution. Now, f_i can be considered as \hat{f}_i when y_i becomes 1. Now, you know where I am getting it. Therefore,

$$\frac{\hat{f}_i}{y_i} = f_i$$

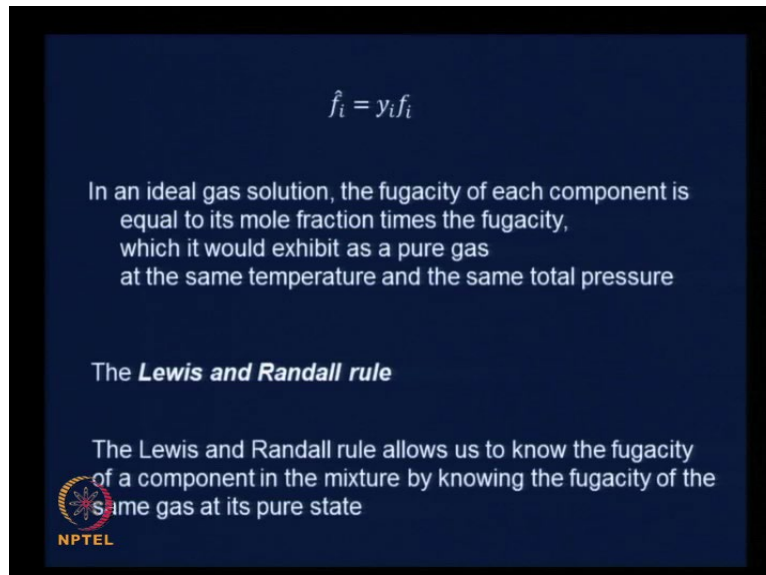
Or, by transposing the equation:

$$\hat{f}_i = y_i f_i$$

We will call this equation 4.10. This is something powerful. Before I go forward, let me go through this argument once again, because we will be using this argument a few times. We have a quantity here on the left hand side, which is independent of composition. Therefore, the right hand side must also be independent of composition. The only term that changes with composition is this. Therefore, this has to remain constant when y_i is changed between the ranges that it can take. If we look at one particular value there, which is when y_i equals 1, \hat{f}_i by y_i must equal

f_i by 1, ... because when y_i becomes 1 \hat{f}_i becomes f_i , and therefore, \hat{f}_i equals y_i into f_i .

(Refer Slide Time: 19:24)




$$\hat{f}_i = y_i f_i$$

In an ideal gas solution, the fugacity of each component is equal to its mole fraction times the fugacity, which it would exhibit as a pure gas at the same temperature and the same total pressure

The **Lewis and Randall rule**

The Lewis and Randall rule allows us to know the fugacity of a component in the mixture by knowing the fugacity of the same gas at its pure state



This says something powerful. It says in an ideal gas solution – we are looking only at ideal gas solution; remember, that is what we decided to focus on earlier – the fugacity of each component

$$\hat{f}_i = y_i f_i$$

To repeat, in an ideal gas solution, the fugacity of each component, \hat{f}_i , is equal to its mole fraction times of fugacity which it would exhibit as a pure gas at the same temperature and the same total pressure.

This is something powerful. What has it given us? It has given us a way of estimating \hat{f}_i if f_i is known. This is called the Lewis and Randall rule. This name you may have heard. The Lewis and Randall rule, which essentially says that \hat{f}_i equals y_i times f_i . And as mentioned, the Lewis and Randall rule allows us to know the fugacity of a component in the mixture by knowing the fugacity of the same gas at its pure state, which is quite powerful.

See you in the next class.