Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 29
Partial Molar Properties

Welcome!

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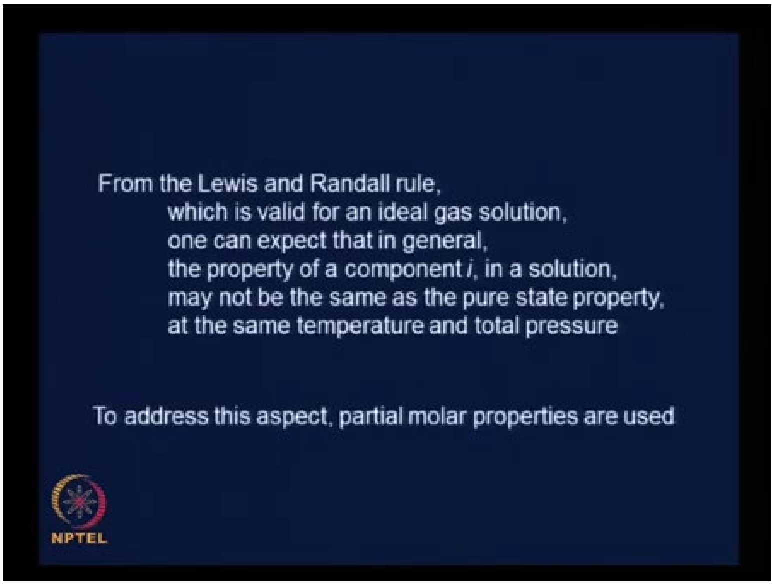

From the Lewis and Randall rule,
which is valid for an ideal gas solution,
one can expect that in general,
the property of a component *i*, in a solution,
may not be the same as the pure state property,
at the same temperature and total pressure

To address this aspect, partial molar properties are used

Now, we will look at something called partial molar properties, which are essential whenever you consider any mixtures or solutions. Let us start with the Lewis and Randall rule itself. From the Lewis and Randall rule, which is valid for an ideal gas equation, we can expect that in general, the property of a component i in a solution may not be the same as the pure state property at the same temperature and the same total pressure. Therefore, we cannot use a weighted average. What we did in the case of the ideal gas solution is that we use the weighted average: $\hat{f}_i = y_i f_i$; y_i was the waiting factor there. Here, if it is a non-ideal solution we cannot do that. We can do that only for an ideal gas solution.

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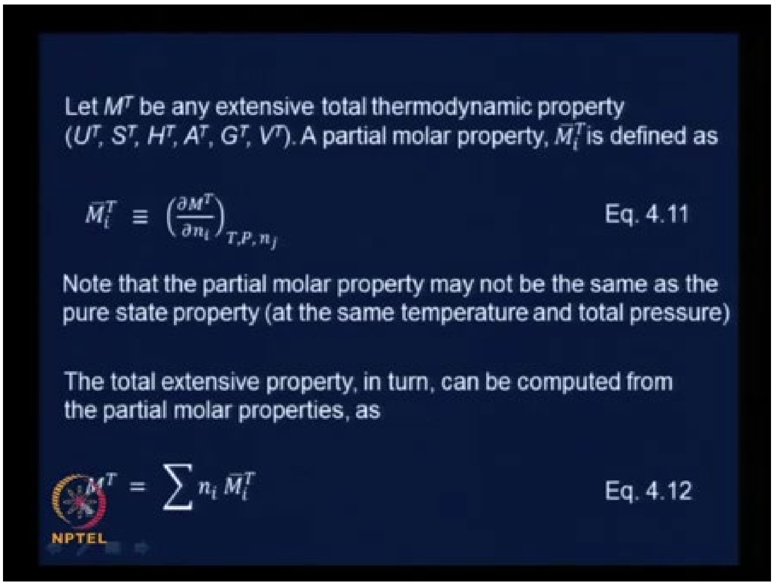

Let M^T be any extensive total thermodynamic property (U^T, S^T, H^T, A^T, G^T, V^T). A partial molar property, $\bar{M}_i^T$ is defined as

$$\bar{M}_i^T \equiv \left(\frac{\partial M^T}{\partial n_i}\right)_{T,P,n_j} \qquad \text{Eq. 4.11}$$

Note that the partial molar property may not be the same as the pure state property (at the same temperature and total pressure)

The total extensive property, in turn, can be computed from the partial molar properties, as

$$M^T = \sum n_i \bar{M}_i^T \qquad \text{Eq. 4.12}$$

Therefore, we use something called partial molar properties to know what partial molar properties are, let us take M superscript T, M^T, to be any extensive total thermodynamic property – we have seen this already. For example, it could be U^T, which stands for the total internal energy, S^T, total entropy, H^T, total enthalpy, A^T, total Helmholtz free energy, G^T, total Gibbs free energy or V^T, total volume. If this is the case, then the partial molar property which I am going to represent as M i T with the hash over it, M i T is the total property – I mean, is the property of the component i in the total solution. With the hat it becomes a partial molar property.

It is defined as

$$\bar{M}_i^T \equiv \left(\frac{\partial M^T}{\partial n_i}\right)_{T,\ P,\ n_j}$$

We will call this equation 4.11. This will become clearer as we go along. As we have said earlier, the partial molar property may not be the same as the pure state property at the same temperature and total pressure. That is a reason for defining something different as the partial molar property.

It is the property that it seems to exhibit when it is present in solution. In other words, it is some sort of hypothetical measure. Why are we using this measure? It gives us an easy means of calculating the total property or estimating the total property. The total extensive property, in turn, can be computed from the partial molar properties as

$$M^T = \sum n_i \overline{M}_i^T$$

So, this is a simplistic formulation. To be able to do this, we go in for some sort of a conceptual partial molar property.

What I would like you to do is take a few minutes and write down this expression for each one of these partial molar properties that you have seen so far. There are about six here. Please write them down for each of those properties, this expression. Go ahead, and I will present them in the next 5 minutes or so … after 5 minutes. Go ahead please.

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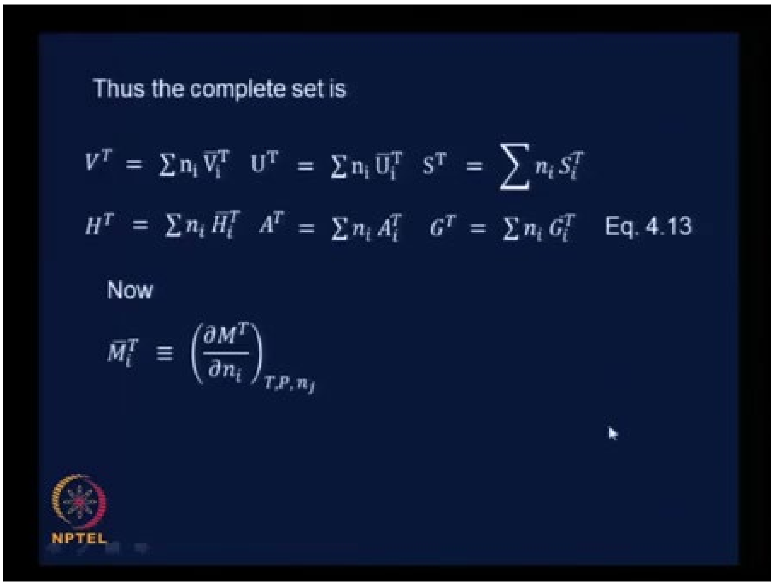

Thus the complete set is

$$V^T = \sum n_i \overline{V}_i^T \quad U^T = \sum n_i \overline{U}_i^T \quad S^T = \sum n_i \overline{S}_i^T$$

$$H^T = \sum n_i \overline{H}_i^T \quad A^T = \sum n_i \overline{A}_i^T \quad G^T = \sum n_i \overline{G}_i^T \quad \text{Eq. 4.13}$$

Now

$$\overline{M}_i^T \equiv \left(\frac{\partial M^T}{\partial n_i}\right)_{T,P,n_j}$$

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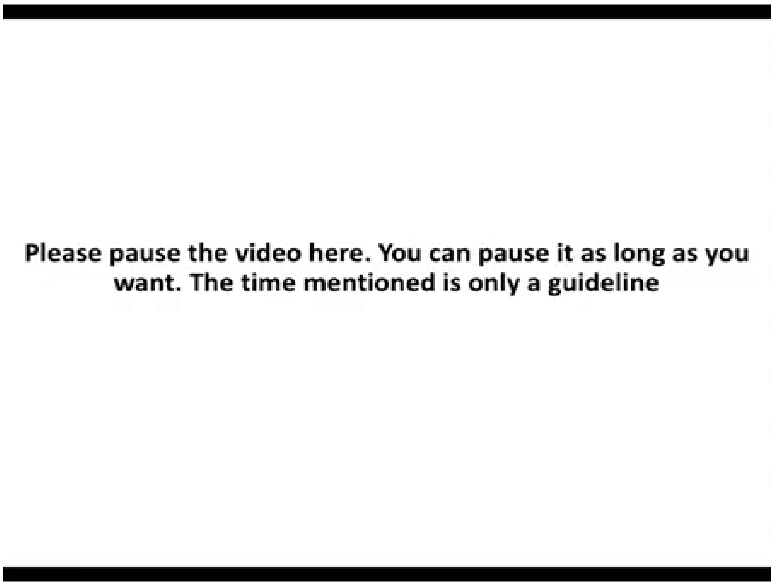

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You would have found it reasonably simple to write this down.

$$V^T = \sum n_i \bar{V}_i^T$$

$$\mathrm{U}^{\mathrm{T}} = \sum n_i \bar{U}_i^T$$

$$\mathrm{S}^{\mathrm{T}} = \sum n_i \bar{S}_i^T$$

$$H^T = \sum n_i \bar{H}_i^T$$

$$A^T = \sum n_i \bar{A}_i^T$$

$$G^T = \sum n_i \bar{G}_i^T$$

It is nice to have this here. You can refer to this from time to time equation 4.13.

The dashes are somehow not visible in some cases. Please make sure that these dashes are present in all your quantities. Now, you have already seen this that the partial molar property is defined as

$$\bar{M}_i^T \equiv \left(\frac{\partial M^T}{\partial n_i}\right)_{T,\ P,\ n_j}$$

Does this remind you of something that we have seen earlier in the earlier module? Think about it.

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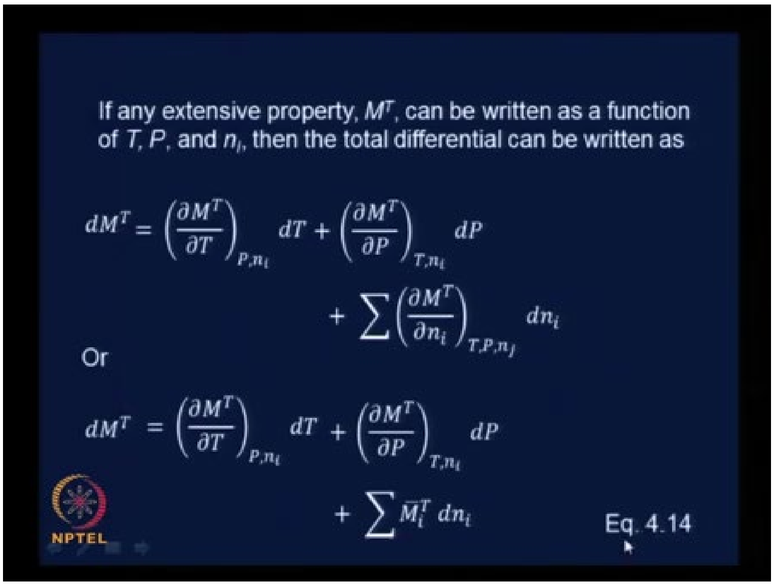

If any extensive property, M^T, can be written as a function of T, P, and n_i, then the total differential can be written as

$$dM^T = \left(\frac{\partial M^T}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial M^T}{\partial P}\right)_{T,n_i} dP + \sum \left(\frac{\partial M^T}{\partial n_i}\right)_{T,P,n_j} dn_i$$

Or

$$dM^T = \left(\frac{\partial M^T}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial M^T}{\partial P}\right)_{T,n_i} dP + \sum \bar{M}_i^T \, dn_i$$

Eq. 4.14

If any extensive property can be written as a function of T, P, and n i then the total differential can be written as … you know this is again an exact differential; therefore, you could write the total differential dM^T. Or, this is a state function. Therefore, you could write the total differential as

$$dM^T = \left(\frac{\partial M^T}{\partial T}\right)_{P,\ n_i} dT + \left(\frac{\partial M^T}{\partial P}\right)_{T,n_i} dP + \sum \left(\frac{\partial M^T}{\partial n_i}\right)_{T,\ P,\ n_j} dn_i$$

Here we have taken M^T as a function of T, P and n i. Or what is this? This is nothing but the partial molar property. Or,

$$dM^T = \left(\frac{\partial M^T}{\partial T}\right)_{P,\ n_i} dT + \left(\frac{\partial M^T}{\partial P}\right)_{T,n_i} dP + \sum \bar{M}_i^T \, dn_i$$

We will call this equation 4.14.

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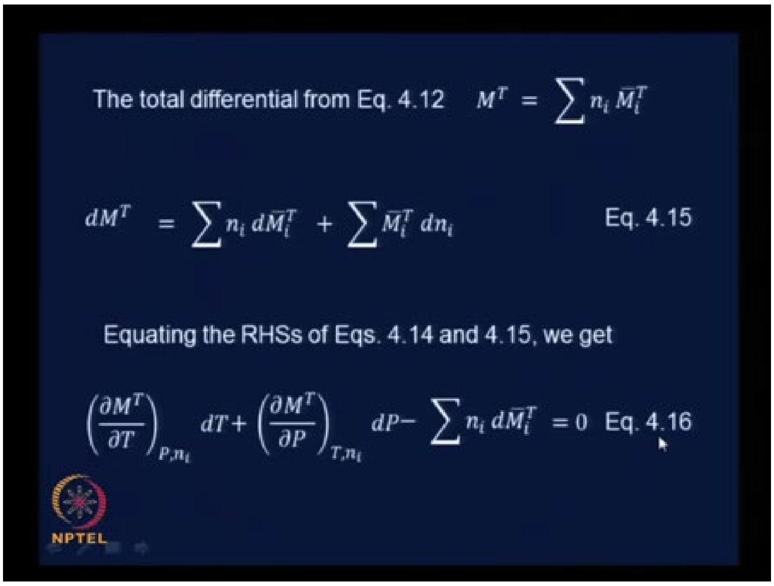

The total differential from Eq. 4.12 $M^T = \sum n_i \bar{M}_i^T$

$$dM^T = \sum n_i \, d\bar{M}_i^T + \sum \bar{M}_i^T \, dn_i \qquad \text{Eq. 4.15}$$

Equating the RHSs of Eqs. 4.14 and 4.15, we get

$$\left(\frac{\partial M^T}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial M^T}{\partial P}\right)_{T,n_i} dP - \sum n_i \, d\bar{M}_i^T = 0 \qquad \text{Eq. 4.16}$$

The total differential from equation 4.12, which is this,

$$M^T = \sum n_i \bar{M}_i^T$$

Take the product of each and sum them over. That will be equal to the total value, the total extensive property value. This is equation 4.12. If we differentiate this we get

$$dM^T = \sum n_i \, d\bar{M}_i^T + \sum \bar{M}_i^T \, dn_i$$

This essentially comes from using the chain rule here. Sum over each one of these terms you could do the chain rule for each of these terms. Then, separate the terms, group them appropriately to sum them over – essentially chain rule application.

So, we have the total differential from this expression 4.14 as this on the right hand side and the total differential here. What I would like you to do is equate the right hand sides of 4.14 and this particular expression which is equation 4.15 and tell me what you get. See whether you get something interesting. Take the next 10 minutes to do that. Go ahead please.

If we do that you can see that one of these terms is going to cancel out. Then … you should have gotten d M T d t at constant P n i d T. This is the same term as earlier plus d M T d P constant T n i d P. Again same term as earlier. What does not cancel and gets transpose to give you minus summation of n i d M i T is this term.

So, this term essentially gets cancelled with the same term as on the other on the right hand side of equation 4.14. Therefore,

$$\left(\frac{\partial M^T}{\partial T}\right)_{P,\, n_i} dT \;+\; \left(\frac{\partial M^T}{\partial P}\right)_{T,n_i} dP \;-\; \sum n_i\, d\bar{M}_i^T = 0$$

Are you able to see some nice thing here? We will call this equation 4.16. So, this is if you write it in terms of G, you will see that G is a function of T, P, and mu. Therefore, you can probably make the connection with something that you have already done earlier.

Now, at constant temperature and pressure this equation 4.16 that we saw. This we are writing it writing for all partial molar properties.

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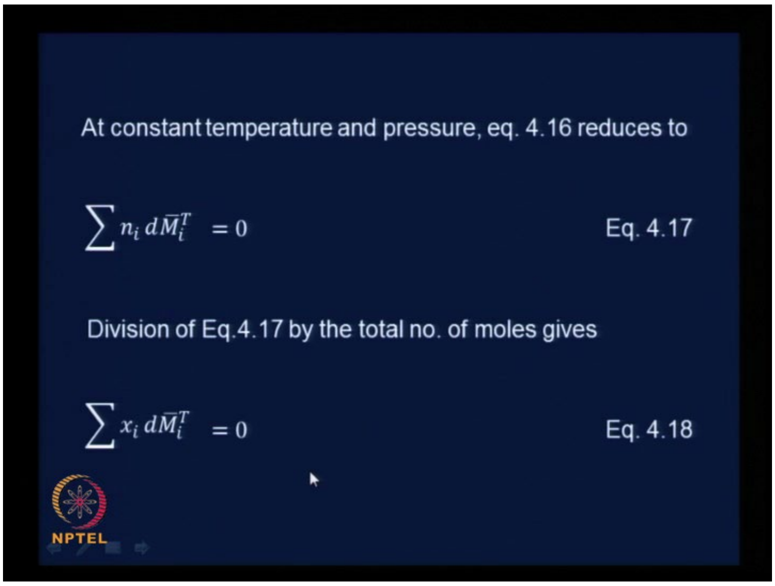

At constant temperature and pressure, eq. 4.16 reduces to

$$\sum n_i\, d\bar{M}_i^T = 0 \qquad \text{Eq. 4.17}$$

Division of Eq.4.17 by the total no. of moles gives

$$\sum x_i\, d\bar{M}_i^T = 0 \qquad \text{Eq. 4.18}$$

Instead of concentrating on G alone which we had done somewhat earlier in the earlier module, we will do it for any total property. If we do that at constant temperature and pressure these two terms are going to get to 0, because d T is 0, d P is 0. Therefore, what remains is

$$\sum n_i\, d\bar{M}_i^T = 0$$

We will call this equation 4.17. If we divide by the total number of moles – each term in the sum get divided by n. Therefore, each of these ni s can be replaced by the mole fraction.

That is the definition of mole fraction. n i by n is the mole fraction. Therefore, when you divide it by total number of moles you get

$$\sum x_i \, d\overline{M}_i^T = 0$$

This is equation 4.18. This is quite a powerful equation as we will see later. I think we are almost out of time for this particular lecture. Let us stop here and continue from here in the next class.