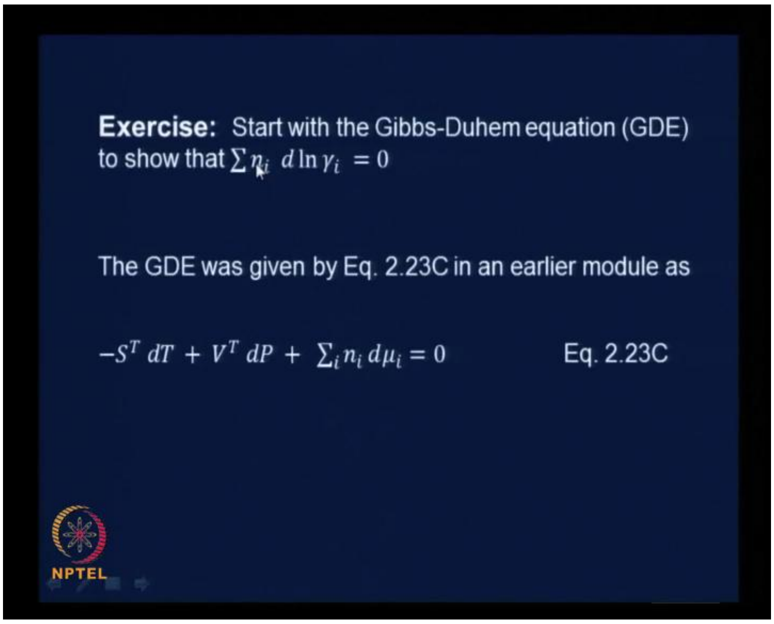
Thermodynamics (Classical) for Biological Systems

Prof. G.K. Suraishkumar
Department of Biotechnology
Indian Institute of Technology Madras

Module No. # 04
Thermodynamics of Solutions
Lecture No. # 24
Activity Coefficient from Excess Property (continued)

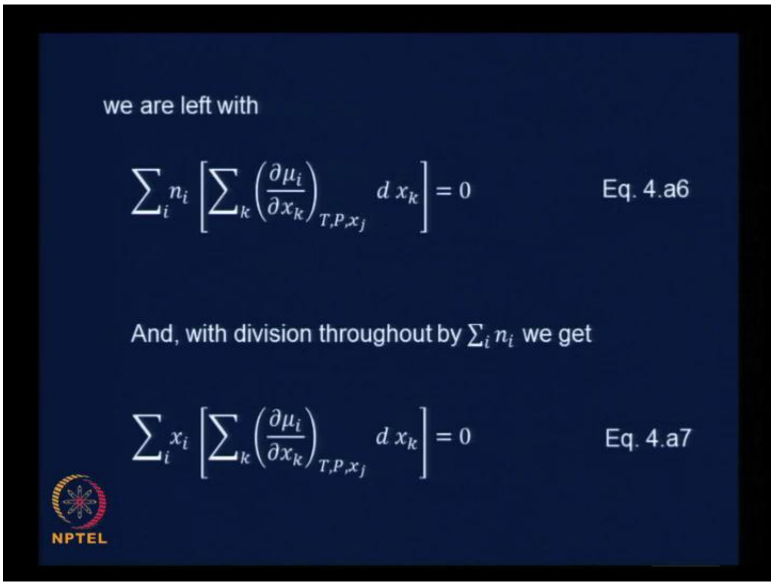
(Refer Slide Time: 00:20)



Welcome!

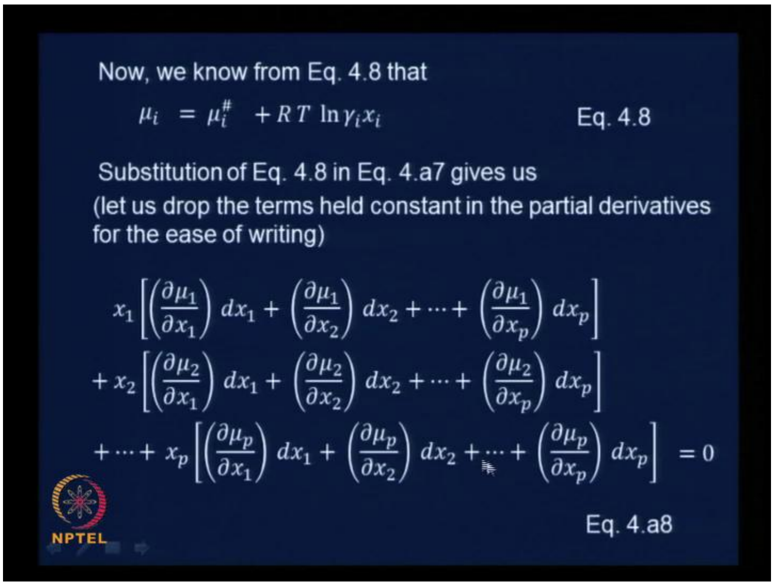
We are in the middle of this exercise now, which we said, would take some time to derive, and to make it effective, we are deriving it together. The exercise that we … began in the last class was: starting with the Gibbs-Duhem equation, show that summation over n i d ln gamma i equals 0.

(Refer Slide Time: 00:50)



And we arrived at a point (No audio from 00:44 to 00:52) where all other terms vanished, and we were left with summation over x i, the inside sum, you know … when this is varied the whole range of this k is taken into account, and then this is varied, and so on. So, summation over k dou mu i by dou x k at constant T, P, x j, d x k equals 0. We have arrived at this stage equation, 4 a 7, at the end of the last class. This class, we will move forward; again we will do it together, because this one helps clarify many different aspects in their ways of representation, and so on and so forth. So, you would develop much better ease, if you do this yourself, or if you are able to do some parts of it. So, let us work together on this.

(Refer Slide Time: 01:51)



Now we know from equation 4.8, that mu i equals mu i hash plus R T ln gamma i x i. This is the definition of mu i for a non ideal solution. And, this is what we are going to take forward. We will derive it for the most general case, the non ideal solution case. If we substitute 4.8, equation 4.8, in the previous equation, 4.a 7 – 4. a7, we had brought it down to a simple form of this. We are going to substitute mu i with the expression in terms of mu i hash and the gamma i x i, and so on.

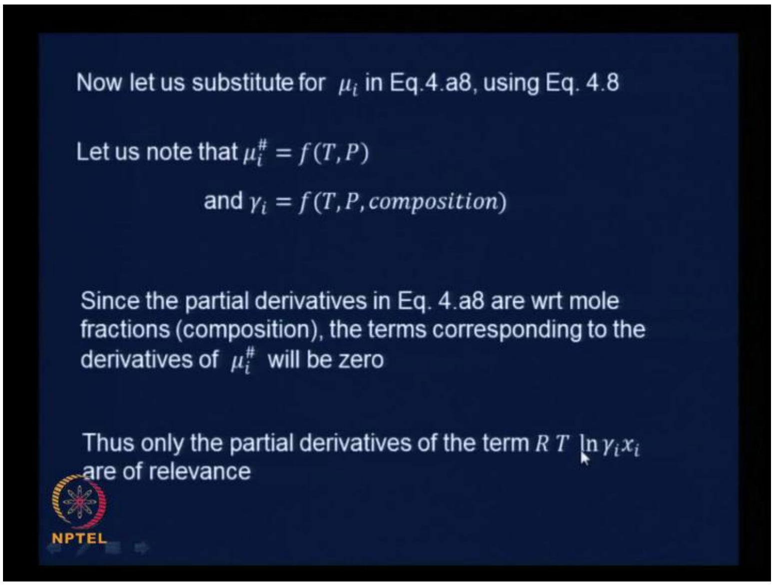
Let us do that. I will show you one step and leave you to work through a few more and while doing that I am going to drop the terms that are held constant in the partial derivatives. We are very clear that the temperature, pressure, and all other mole fractions except the one that is taken for the differentiation, are held constant. So, that we will take for granted now, in the remaining part of this derivation alone just for the ease of writing, because, otherwise, we will have to write so many different terms being held constant in each partial derivative there.

So, if we do that, this becomes x 1 this is the first term – you know x 1; dou mu i dou x k it was so dou mu 1 dou x 1 d x 1 d x k plus dou mu 1 – this is i, this corresponds to i. Therefore, that remains at 1 dou mu 1 dou x 2 d x 2 plus, so on, until dou mu 1 dou x p d x p. This is just a first term, and then when we change this you know, we are summing over i s; so, that is what brings in the second term. Summing over k s is what results in the term in the square brackets.

So, let us look at the second term x 2 dou mu 2 dou x 1 d x 1 plus dou mu 2 dou x 2 d x 2, and so on till dou mu 2 dou x p d x p. What I meant by dropping the terms is we need to write here constant T, P, x j and so on. That is what I am not going to do here just for ease of writing, but it is well understood here so there is no difficulty. And so on ... you go on by changing the i term to cover all i s, and so on, till x p dou mu p dou x 1 d x 1 dou mu p dou x 2 d x 2, and so on, … until dou mu p dou x p d x p. So, this is what happens if mu I … I have still not substituted mu i in terms of mu i hash plus R T ln gamma i x i into equation 4.a 7. What I have just done in this step is to expand 4.a 7 to show you all the terms – the complexity of that particular term, the last term on the left hand side. If you expand it will contain all these terms; of course equal to 0.

Now, let me show you few more steps. Let us call this equation 4 a 8, and let me show you a few more steps before I leave you to work some of the things out.

(Refer Slide Time: 05:37)



Now, we will substitute for mu i in equation 4.a 8 using equation 4.8. Note … this is important … note that mu i hash is a function of temperature and pressure alone. See what that means in terms of the partial derivatives in equation 4.a 8 – that is a big hint.

But, gamma i is a function of temperature, pressure, … excuse me … and composition. Composition, as represented by x 1 and x 2 and so on and so forth, in terms of mole fractions, at this stage. Earlier, we had represented composition in terms of mole numbers n 1 n 2 and so on.

Here we have brought it down to mole fractions which makes it a little easier to work with.

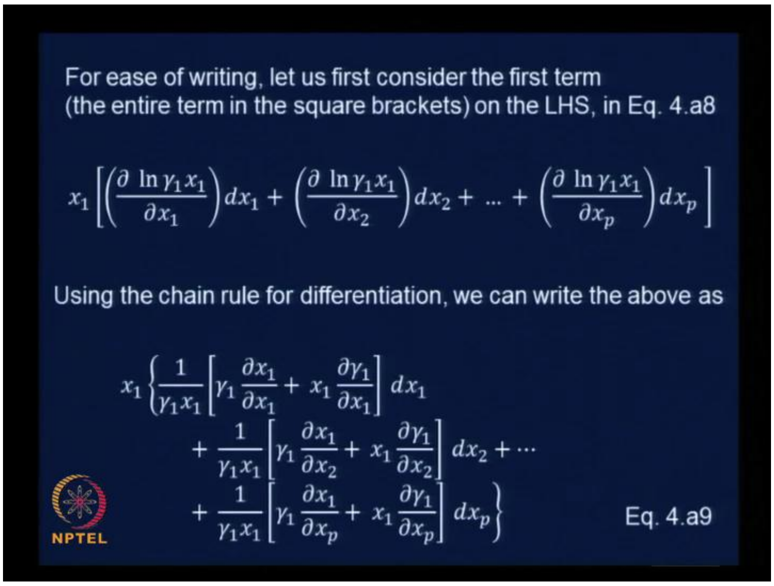
I will leave you with this for about 15 minutes. I would like you to substitute the expression from mu i from equation 4.8 into equation 4.a 8, and realize that mu i hash is a function of temperature and pressure alone, whereas gamma i is a function of temperature pressure and composition. Let us see where you get. Substitute, then see what terms go to 0, see what terms can be cancelled out if at all, and see how it can be reduced to its minimum representable form. Go ahead. Please take 15 minutes to do it

(No audio: 07:12 to 22:20).

Let us continue. You would have reached a certain stage. If we had gone enough, enough ahead, you would have gotten down to a very compact kind of a representation. I do not know, whether you have gone that far. Let us see at least some of the steps before I leave you again to do things yourself. The partial derivatives in equation 4.a 8 are with respect to mole fractions. Therefore, the terms corresponding to the derivatives of mu i hash are going to be 0 because mu i hash is only a function of temperature and pressure and not of composition.

Therefore, if you take the partial derivative with respect to the mole fraction that is going to be automatically 0 because, it is a constant value with respect to mole fraction. Therefore, you can just drop all the mu i hash terms completely, and only the partial derivatives of the term R T ln gamma i x i are of relevance here.

(Refer Slide Time: 23:29)



Let us see what happens, if you put that in. … Again, for ease of writing or not taking up too much space and not getting confused with the various terms I am just going to take the first term. We are going to write the first term, develop the first term completely with the clear understanding that, whatever goes with the first term is going to go with the other terms. They are all very similar. So we whatever we write and bring it down should be applicable for the other terms also.

Let us, do that at least to a certain stage. What I mean by the first term is the entire term in the square brackets on the left hand side of equation 4 a 8, which is this 4 a 8 is this. So, this is the term including x 1 that is, x 1 times whatever is there in the square bracket. This is what I am going to take up first as we can see all the other terms here are all similar to the first term.

So, the same form should be applicable for the other terms also. That is the reason I am just going to consider the first term. If I do that now … just a mere substitution … it is R T ln gamma 1 x 1. So R T is a constant that can be taken out. We will assume that the R T has been taken out here; anyways the right hand side is 0. So, that is going to go to 0; that will come later.

So, x 1 dou ln gamma 1 x 1 by dou x 1 d x 1; this is whatever remains of that mu 1 mu 1 was mu 1 hash plus R T ln gamma 1 x 1. mu 1 hash went because, mu 1 hash is not a function of x 1 and R T has been taken out as a common term in all these expressions and it is kind of cancelled with 0. Therefore, what remains is ln of gama 1 x 1 dou the partial of ln of gamma 1 x 1 dou x 1 d x 1 plus dou ln of gamma 1 x 1 dou x 2 d x 2 and so on, till dou ln gamma 1 x 1 dou x p d x p. Can you do the math here? This is, as you can see, this is a composite function; it is derivative with respect to x 1. What would you get if you do this derivative, … or probably I will show you another step before I leave you alone.

What I essentially meant was using the chain rule there, chain rule for differentiation, first function into derivative the second function plus the second function into derivative the first function, and so on. You know that this is function of a function therefore, x 1 into the derivative of ln would be 1 by that argument. So, 1 by gamma 1 x 1 times dou dou x 1 of gamma 1 x 1 which becomes gamma 1 dou x 1 by dou x 1. We will just keep this term now for completeness. I know it is 1, but we will keep this term, so that there is some form that arises as a part of keeping that there. We will keep that there.

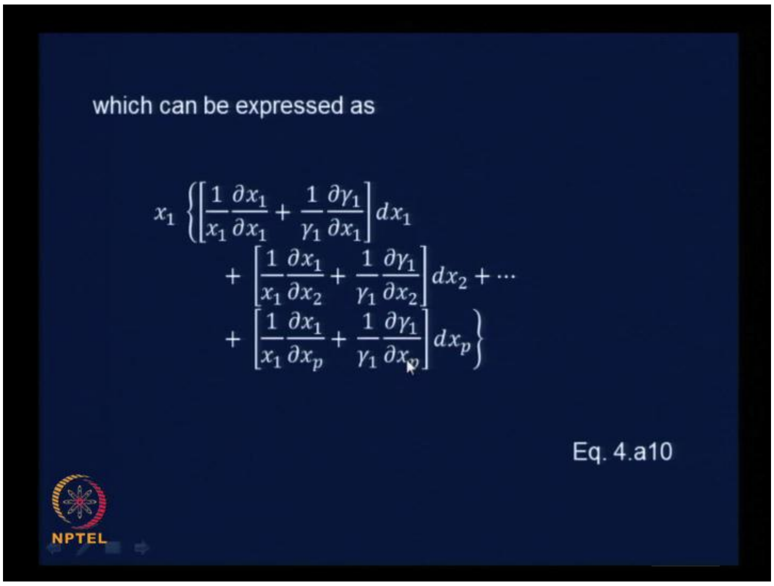
Plus the second one, x 1 dou gamma 1 by dou x 1 d x 1. Similarly, this one would be the ln part of it would be taken care of 1 by gamma 1 x 1 and then you have gamma 1 x 1 remaining. So, gamma 1 dou x 1 by dou x 2 plus x 1 dou gamma 1 by dou x 2 d x 2. Now, you get the hang of it … there … and so on.

What I would like you to do is take a next 10 minutes and reduce this to a nice compact form. It is essentially algebra that I would like you to do – cancelling the terms that are common, and combining them into a form … that would take care of combining many terms together, and so on. Take the next 10 minutes and do that please. It is a straight forward exercise – this one; it will take time of course. Go ahead, please.

(No audio: 27:33 to 35:35).

Again if you had gone all the way, you would just gotten a very small or a compact term, left. Let us, see how we get to that this of course, was equation 4.a 9 our numbering scheme.

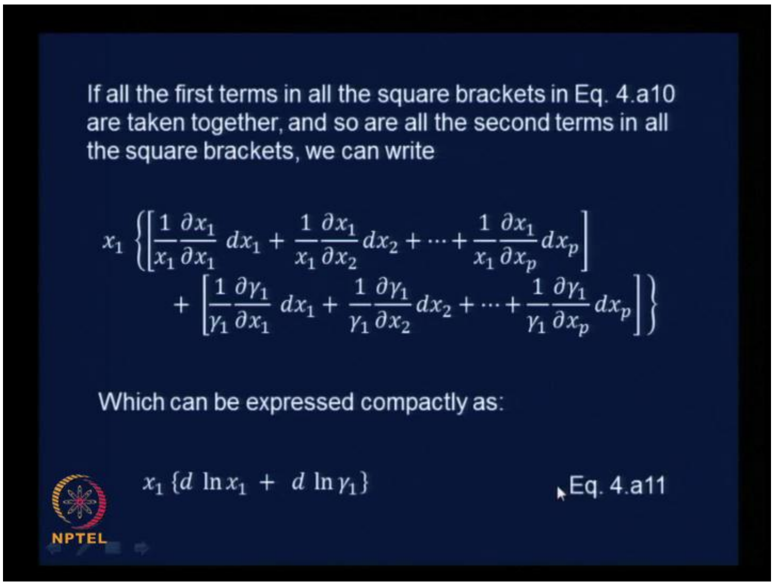
(Refer Slide Time: 35:52)



Which can of course, be expressed as … you know, you take that gamma 1 x 1 inside. You will get x 1 into 1 by x 1 dou x 1, dou x 1 dou x 1, plus 1 by gamma 1 dou gamma 1 dou x 1 d x 1, this is the first term inside the brackets … plus, you know, again there is a gamma 1 x 1 in the denominator there earlier. If you take that inside you will have 1 by x 1 dou x 1 dou x 2 plus 1 by gamma 1 dou gamma 1 dou x 2 d x 2, and so on till you reach 1 by … excuse me … 1 by x 1 d x 1 d x p plus 1 by gamma 1 … dou gamma 1 dou x p d x p; this also is partial. We will call this equation 4 a 10. …

If all the first terms in the square brackets of equation 4 a 10 are taken together,r and all the second terms in the square brackets are taken together … what I mean by that is this. This is 4 a 10. So, we will … combine 1 by x 1 dou x 1 dou x 1 d x 1 plus 1 by x 1 dou x 1 dou x 2 d x 2 and so on, plus 1 by x 1 dou x 1 dou x p d x p this is still inside the flower bracket that would be one combined term. The other combined term is going to be 1 by gamma 1 dou gamma 1 dou x 1 d x 1 plus 1 by gamma 1 dou gamma 1 dou x 2 d x 2, and so on, till 1 by gamma 1 dou gamma 1 dou x p d x p.

(Refer Slide Time: 37:46)



If we combine, this is what arises, and what I would like you to do is spend the next 5 minutes looking at this, and, whether you can write this in a compact form. I am sure quite of you are few are seeing this already. What can this be written as – just one term – that is what I am looking at; this just one term.

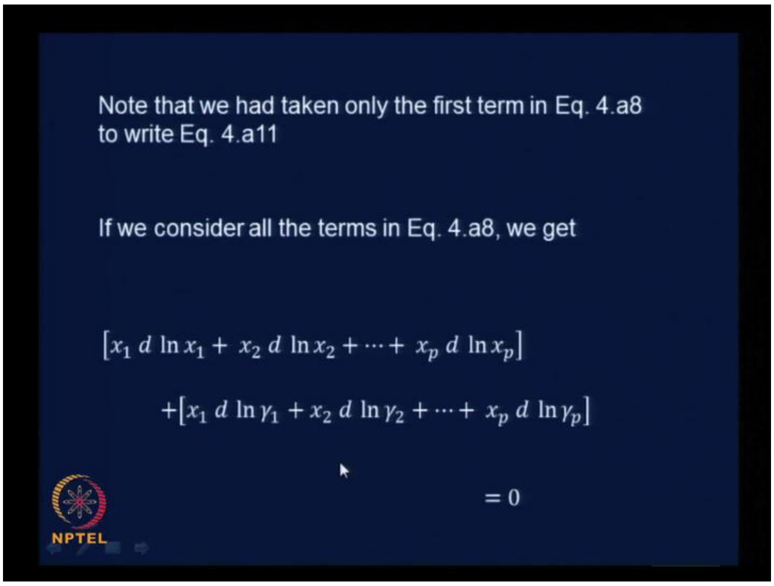
Take the next 5 minutes, even if you need to juggle your memory and come to some form. What does this look like, you know, if you use this 1 by x 1 dou x 1 dou x 1. Or, let us look at this. This might be easier to look at: 1 by x 1 dou x 1 dou x 2 d x 2, and so on so forth. Or, just this alone, how can this be combined, and then what does this remind you in terms of an expansion of a function in terms of its partial derivatives, the total derivative in terms of its partial derivatives. These are the hints that I am going to … leave you with for the next 5 minutes. Go ahead please.

(No audio: 38:54 to 43:54).

I am sure all of you would have gotten it by now. You know, that 1 by x 1 dou x 1 dou x 1 is nothing but dou ln x 1 dou x 1. So, you have dou ln x 1 dou x 1 d x 1 dou ln x 1 dou x 2 d x 2, and so on … till dou ln x 1 d x p dou x p d x p. And what is this? This is nothing but an expansion of the total differential d of ln x 1 when x 1 is a function of x 1 x 2 x 3 and so on, till x p. That is it.

So, this becomes d ln x 1. This becomes, in the same fashion, d ln gamma 1. And, of course, you have an x 1 here; therefore, this becomes x 1 into d ln x 1 plus d ln gamma 1. This is just the first term, remember that. We will call this equation 4 a 11.

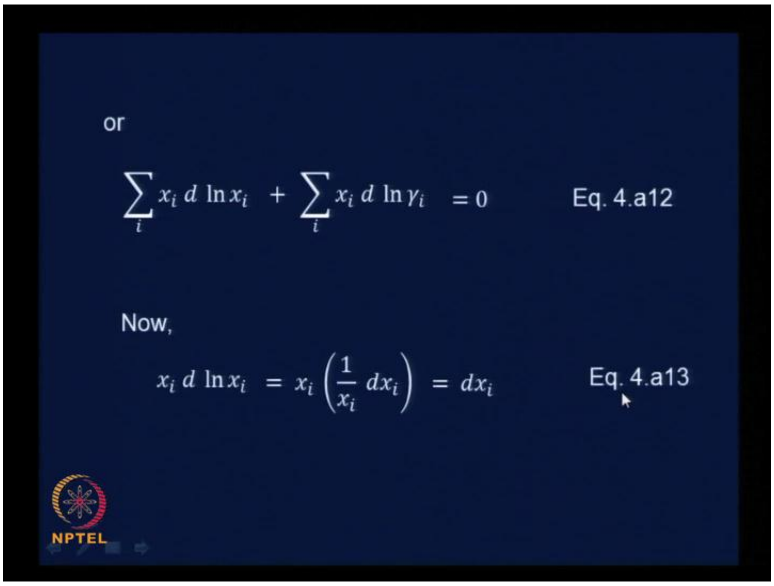
(Refer Slide Time: 45:01)



And as mentioned, that is just the first term. All other terms are going to are going to reduce to that compact form. In other words, … the first term is going to be x 1 d ln x 1 plus x 2 d ln x 2 and so on, plus x p d ln x p. This can all be combined together, plus x 1 d ln gamma 1 plus x 2 d ln gamma 2 plus … x p d ln gamma p .You … would be able to see this quite easily by expanding this … you know, x 1 d ln x 1, the second term will be x 2 d ln x 2 plus d ln gamma 2, and so on so forth. So, if we combine all these terms together and all these terms together, we are going to get this as the expanded form.

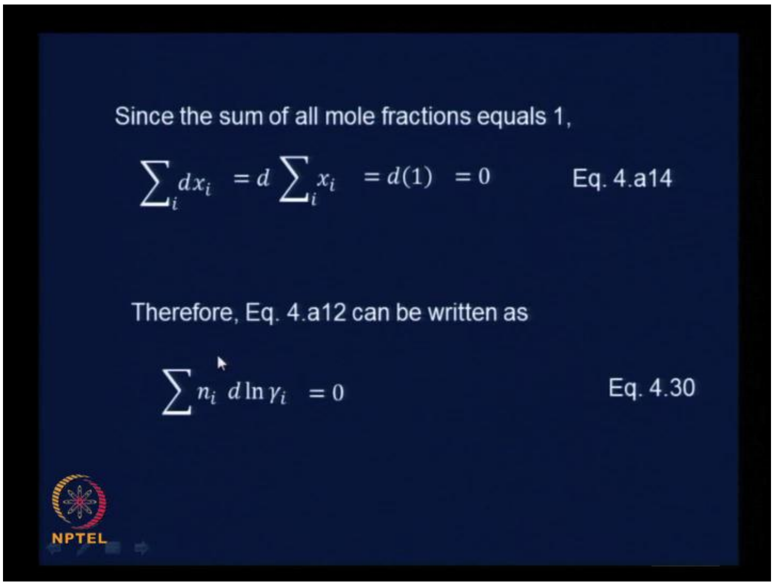
Now, take a look at this, it is very nice here … equals 0, of course, on the right hand side, We will call this … we are not going to give a number to that. But also note this x 1 d ln x 1 x 2 d ln x 2, and so on and so forth. And, hopefully you would be seeing the light at the end of the tunnel. Whatever we needed to prove, we are almost there.

(Refer Slide Time: 46:25)



This can, of course, be written in a compact form as sum over i x i d ln x i plus sum over i x i d ln gamma i equals 0. Let us call this equation 4 a 12. So, this is what we need to prove is 0. Therefore, now explicitly, we need to prove that this is 0. This looks complicated, but it is not. Now, let us expand this d ln gamma x i again, in terms of this. x i d ln x i is nothing but x i into 1 by x i d x i. d ln x i, is nothing but xi into 1 by x i d x i from the definition. Therefore, this is nothing but d x i because x i and x i are going to cancel out. And now if we take the sum over all terms …before that let us call this equation 4 a 13.

(Refer Slide Time: 47:26)



Now, if we take the sum over all i s, with the note that sum of all mole fractions is 1, which is a constant … here is how it goes is 0 … this is sum over all d x i over I – remember, this is what was left over here d x i; … and we need to sum over all i of d x i. And therefore, this is by the commutative property … in other words, you know, d is a differential, the difference amounts; and therefore the sum of the differences is nothing but the difference of the sum. The commutative property holds here. Therefore d for sum over x i, and what is sum over x i? It is nothing but 1, because the sum of mole fractions equals 1. And derivative of a constant, we know 0; and therefore, this goes to 0; equation 4 a 14. Well, we are almost done.

Therefore, equation 4 a 12 can be written as sum over n i d ln gamma i or x i d ln gamma i, which can be written as n i d ln gamma i equals 0. Equation 4 30. Now I think we should stop here. We are out of time any way; need to adjust in the working times a little bit. When we start up the next class, we will see how to use this, you know this is what we had proved as an exercise … how to use this to relate it to find or estimate activity coefficients. We will meet then.