Chemical and Biological Thermodynamics: Principles to Applications
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Lecture - 21
Partial molar volume

Today, we are going to further discuss about the partial molar properties. In fact, we have already introduced one partial molar property and that was chemical potential. Chemical potential was defined as the change in Gibbs energy when one mole of a substance is added at constant pressure, temperature and composition of everything else held constant. In the same way, we can write an expression for any partial molar thermodynamic quantity. For example, we can define partial molar enthalpy; we can define partial molar entropy and similarly other partial molar quantities.

But today we will discuss about partial molar volume, this is a very important thermodynamic quantity which can be used to discuss intermolecular interactions in solution with an in depth analysis. You know that the volume depends upon the mass and density; and the volume also depends upon the extent of intermolecular interaction. So, all these facts can be discussed in detail based upon the partial molar volume. Let us discuss, what is partial molar volume. In fact, we can define partial molar volume in the same way as we defined partial molar Gibbs energy that was chemical potential.

So, here we will define partial molar volume as the change in volume of the solution when one mole of a substance is added at constant pressure, temperature provided the composition of everything else is held constant. In other words, the change in volume when one mole of a substance is added to a large volume of the mixture at constant pressure and temperature. Let us take an example, let us mix one mole of water with large amount of water. The volume of one mole of water is about 18 centimeter cube, so that means, when we mix one mole of water with a large quantity of water, the change in volume is going to be 18 centimeter cube, because we have added 18 centimeter cube of water to large amount of water.

On the other hand, if we add one mole of water to large amount of ethanol then the change in volume is no more 18 centimeter cube. The change in volume is observed to be approximately 14 centimeter cube that means, the packing of water molecules when water is added to water is different than the packing of water molecule when water is added to ethanol. This packing of a solute into solvent will depend upon several factors, one of the factors is how it interacts with the neighboring molecules, or in other words it depends upon the intermolecular interactions and that is why I said that partial molar volume can provide information about intermolecular interactions in detail. Let us discuss further about the partial molar volume.

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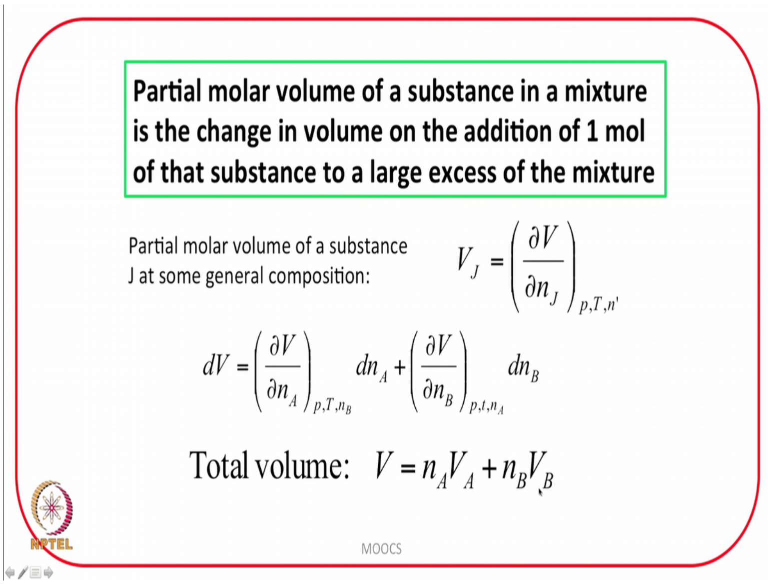

This is how we define the partial molar volume the partial molar volume of a substance in a mixture is the change in volume on the addition of one mole of that substance to large excess of the mixture. Mathematically, we can write an expression for partial molar volume of a substance J, VJ, we will read as partial molar volume of the substance J which is given by the change in volume when one mole of that substance J is added at constant pressure temperature and composition of everything, else held fixed.

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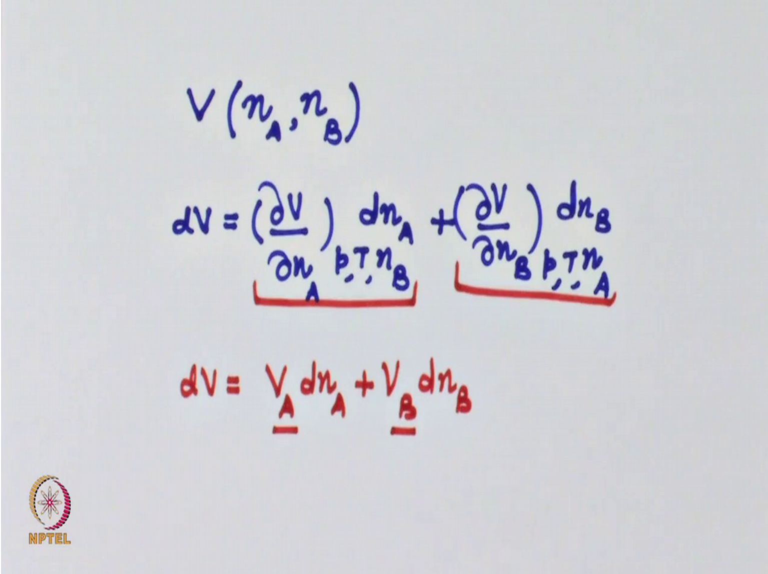

Now, the total volume of a solution will depend upon the number of moles of A, number of moles of B, if it is a binary mixture and let us assume that the pressure and temperature is constant. Then I can write dV is equal to partial derivative of volume with respect to n A at constant pressure temperature n B because we are holding pressure and temperature constant, it is d n A plus partial derivative of volume with respect to n B at constant pressure temperature n A d n B. Let us recognize these quantities as partial molar volumes that means, what I have is dV is equal to V A d n A plus V B d n B, where V A and V B are the partial molar volumes of the components A and component B.

Let us go back to the slide that is what I just discussed that dV is equal to partial molar volume of A into d n A plus partial molar volume of B into d n B. And now if I calculate the total volume I integrate this, partial molar volume being a constant quantity the total volume will be V is equal to partial molar volume of A into number of moles of A plus partial molar volume of B into number of moles of B. This is how we can express the total volume in terms of partial molar volume of its constituents that is the total volume is equal to number of moles of component A into partial molar volume of A plus number of moles of component B into partial molar volume of B.

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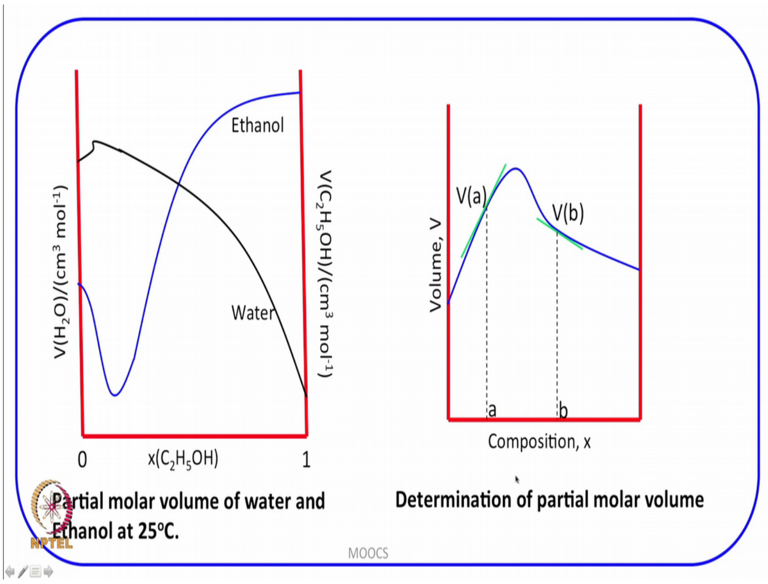

Let us take a look at this figure. This figure represents the variation of partial molar volume of ethanol and water when the mole fraction of ethanol changes from 0 to 1. For pure water, the value will be around 18. And as you see when the mole fraction of ethanol increases in solution, the partial molar volume of water is decreasing. And partial molar volume of ethanol is having an unusual kind of trend, this type of variation in partial molar volume, against the composition of one of the components provides good information on the nature of intermolecular interaction.

And as we just discussed that the partial molar volume is derivative of total volume with respect to the number of moles of a particular component. So, that means, let us take a look at the second figure, if the variation of volume with composition of a component is like this, the partial molar volume changes with composition. And at any given composition the partial molar volume is the slope of the tangent drawn at that composition. For example, at point A, the partial molar volume will be the slope of this dou V by dou n composition mole fraction can be expressed in terms of n, and this is how the partial molar volume of a substance in a mixture can be determined. That is if I know the variation of volume with composition, I can take the derivative the first derivative and that should give me the value of partial molar volume.

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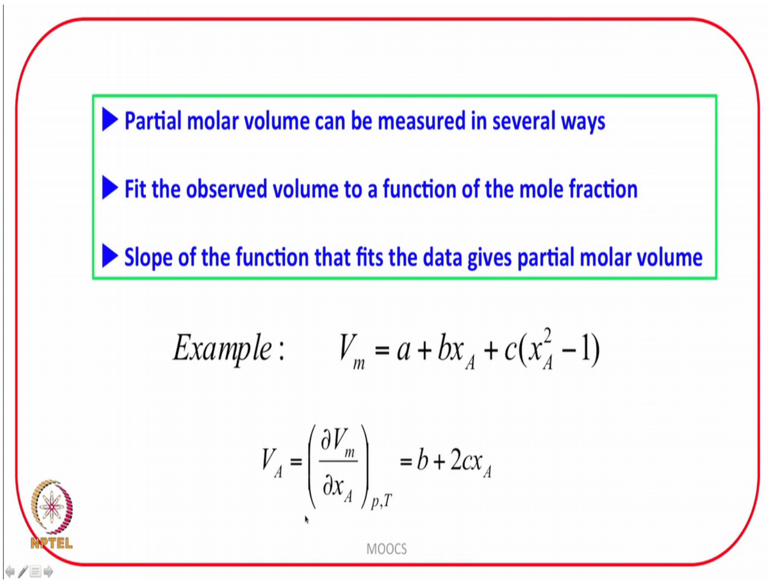

So, that is what is commented over here. Partial molar volume can be measured in several ways. What are the different ways of determining partial molar volume. We are talking about the volume; and the volume can be determined if we know the density. So, therefore, first of all in order to experimentally determine the value of partial molar volume, we need to experimentally determine the values of the densities of the solution. There are various techniques which are available for measuring the densities of the solution. An approximate method can be a pycnometer, specific gravity bottle and the sophisticated methods techniques which are available are vibrating tube, digital dense emitters, there are several varieties available in the market. And today it is possible to experimentally determine the densities of an aqua solution at least very accurately up to fifth decimal place.

So, if we are able to measure the densities, we will be able to determine the volume, and then what we do is we find out a mathematical expression that how the volume depends upon the composition, how the volume depends upon the mole fraction of one of the a component in the mixture. So, that is what is mentioned over here, fit the observed volume to a function of the mole fraction, slope of the function that fits the data gives partial molar volume. As an example, suppose if it is observed that the molar volume of a solution depends upon the mole fraction of the component A, and the mathematical function that fits the variation of volume is V m is equal to a plus b times x A plus c into x A square minus 1, where a, b c are constants. Then the way to determine the partial molar volume will be to take its derivative, why with respect to x A, because x A depends on n A, x A is equal to n A over the total volume or total a number of moles. So, when you take the derivative of this, the partial molar volume will be b plus 2 times c times x A. So, this is the way to determine the partial molar volume.

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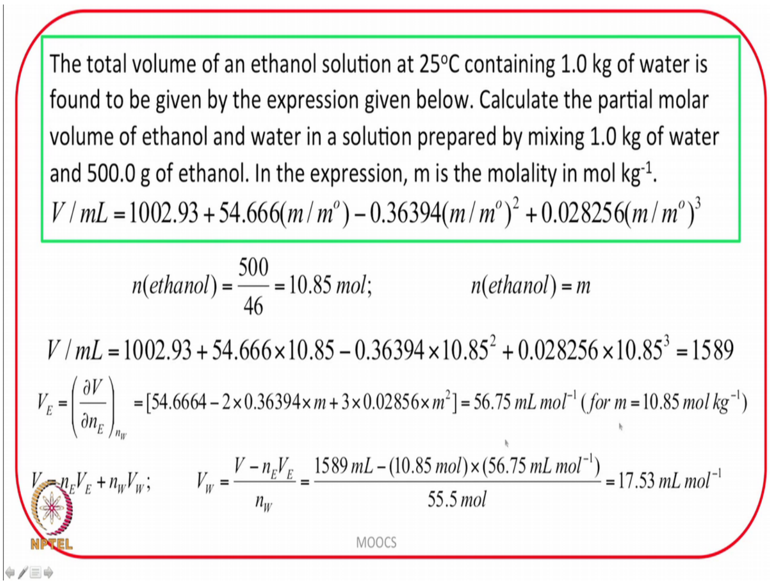

Now, let us discuss a numerical problem. The total volume of an ethanol solution at 25 degree Celsius containing 1 kilogram of water is found to be given by the expression given below. Calculate the partial molar volume of ethanol and water in a solution prepared by mixing 1 kg of water and 500 gram of ethanol. In the expression, m is the molality in mol per kg. And the expression that fits the molality is this, V is the total volume of the solution and its dependence on molality is given by this expression. So, let us see what information is given to us. The information given to us is that that the volume of ethanol solution contains 1 kilogram of water. And what you are doing is you are mixing 1 kilogram of water and 500 gram of ethanol.

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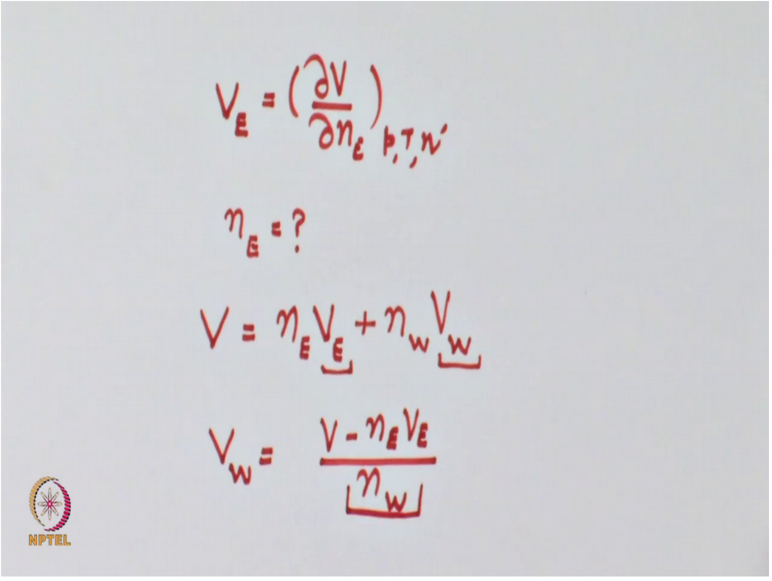

The definition of partial molar volume if I write partial molar volume of ethanol if I represent ethanol by E, this will be dou V by dou n E at constant pressure, temperature everything else constant. V is the total volume for which the information the expression is already given. And we want to know what is n E. Now, let us try to appreciate that the solution has been prepared by mixing 500 gram of ethanol in 1 kilogram of water. How do we define molality, molality is the number of moles of solute in 1 kilogram of solvent. And here the solute is ethanol and the solvent is water. And since the amount or the weight of solvent used here is 1 kg, therefore the number of moles of solute will be directly equal to the molality of the solution, because we are dissolving in 1 kilogram of the solvent.

We will make use of this fact and calculate the number of moles of ethanol. 500 gram of ethanol have been used molecular weight of ethanol is 46, therefore number of moles is 10.85. As we just discussed that we are dissolving 500 gram of ethanol in 1 kilogram of water, therefore the number of moles is equal to the molality of the solution that is what is written over here n is equal to m. So, since n is equal to m, in order to calculate the partial molar volume, we can just differentiate with respect to m instead of n, because n is equal to m. This is the point to be noted over here that since n is equal to m, the partial molar volume can be determined by differentiating this equation with respect to m.

When you differentiate, you will get the partial molar volume. But first of all we will need the total volume, the total volume of the solution when 500 gram of ethanol is added which is equivalent to 10.85 mol, you put instead of m 10.85 substitute, the answer that you will get is 1589 milliliter. This is the total volume of solution. In order to calculate partial molar volume, I need to differentiate this. Let us differentiate this and see what we get.

By differentiation of the total volume expression, we will get the partial molar volume of ethanol, which is equal to derivative of this is 0, and for this is 54.666 then minus 2 times 0.36394 into m plus 3 times 0.02856 into m square. And you substitute m, you will get an answer of 56.75 milliliter per mole for a value of m equal to 10.85. So, now we have the partial molar volume of ethanol. The total volume of the solution will be number of moles of ethanol into partial molar volume of ethanol plus number of moles of water into partial molar volume of water. We have already calculated partial molar volume of ethanol. What we need to now calculate is partial molar volume of water.

We know the total volume. Therefore, partial molar volume of water from this expression is going to be V minus n E V E over n W. And this we have discussed many times that 1 kilogram of water the number of moles of water in 1 kilogram of water is going to be 1000 divided by 18 which is 55.5. And let us use that information. Let us take a look at the slide. Now, we substitute for V, V we just calculated 1589 minus 10.85 that we have calculated number of moles of ethanol and volume of ethanol partial molar volume of ethanol we calculated as 56.75 milliliter per mole. So, on solving this, what we have is the partial molar volume of water to be 17.53.

The points to be noted in this problem is look at the values of partial molar volume of ethanol partial molar volume of ethanol is 56.75 milliliter per mole corresponding to a molality of 10.85. Whereas, the partial molar volume of water it is 17.53 milliliter per mole, the partial molar volume or the change in volume, when you add one mole of water to pure water is 18 centimeter cube. And what we find here is when you add 10.85 mole of ethanol in water when you mix 10.85 mole of ethanol with 1 kilogram of water, the partial molar volume of water is not 18, it is 17.53 milliliter per mole. So, these changes in partial molar volume are indicator of the difference in the packing of molecules in the solvent. We will discuss it further.

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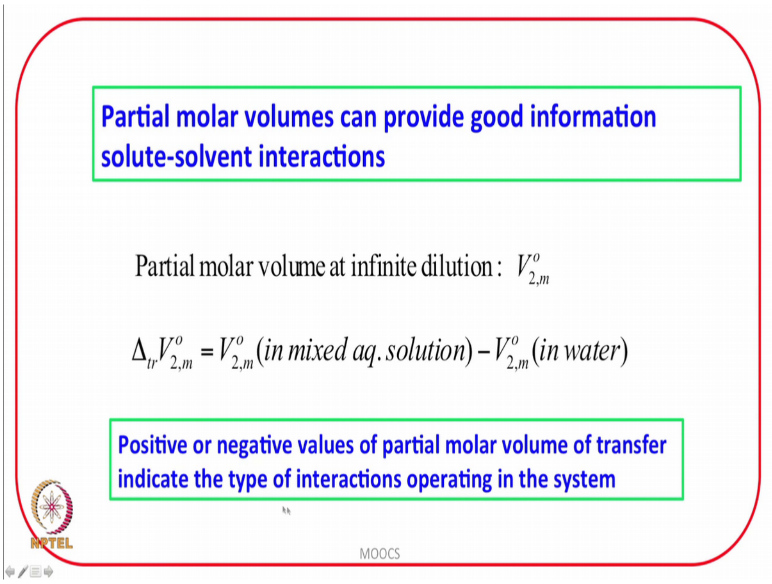

As I just pointed out partial molar volumes can provide good information about solute solvent interactions. The literature and many books write partial molar volume at infinite dilution as V 2 m naught. Now, here what is this concept of infinite dilution properties.

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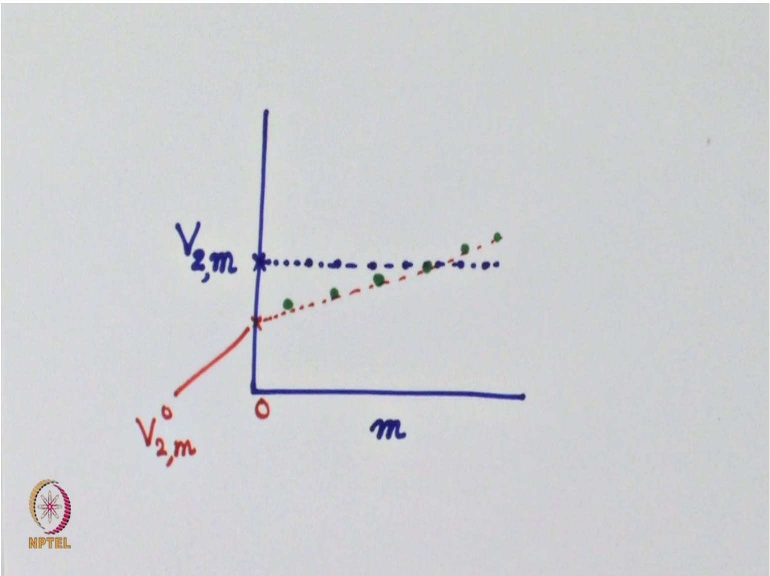

Suppose, if I measure the partial molar volume as I said in literature , you will see partial molar volume being written as V 2 m, where 2 is generally written for the solute and m denotes the molar quantity. If you plot against molality, there is a possibility that the variation can be like this. If the variation is like this, then the extra pollution to m equal to 0, which is infinite dilution is going to be the average of all these values. And if the variation is for example like this it depends upon the concentration then if you fit it to an appropriate equation or line, then this is infinite dilution value. Infinite dilution means the solute solvent interactions are predominant, and you are eliminating almost eliminating solute-solute interactions because at infinite dilution solute-solute molecules are far apart. Therefore, the infinite dilution properties are good indicators of the solute solvent interactions.

And as mentioned in this slide, the partial molar volume at infinite dilution, let us write as V 2 m naught. And the transfer means if I measure the partial molar volume in a mixed aqua solution and partial molar volume of that substance in water then the difference in these values which we call as the transferred partial molar volume is a good indicator of the nature of solute solvent interaction. Here we have a solution means there is a solute and the solvent is water and this is the solvent. When you take the values difference then transfer parameters are good indicators of the solute-solvent interaction. And as I said if we measure these properties determine these properties at infinite dilution then we are getting rid of solute-solute interaction and we are mostly talking about solute-solvent interactions.

So, this is commented over here positive or negative values of partial molar volume of transfer indicate type of interactions operating in the system, because this transfer value can be positive, this transfer volume can be negative. Volume is always a positive quantity, like entropy is always a positive quantity, but the partial molar properties need not be always positive, partial molar property can be negative. So, what I am trying to say is the volume is always a positive quantity, but partial molar volume can be negative quantity, whether it is positive or a negative quantity, it carries a lot of meaning.

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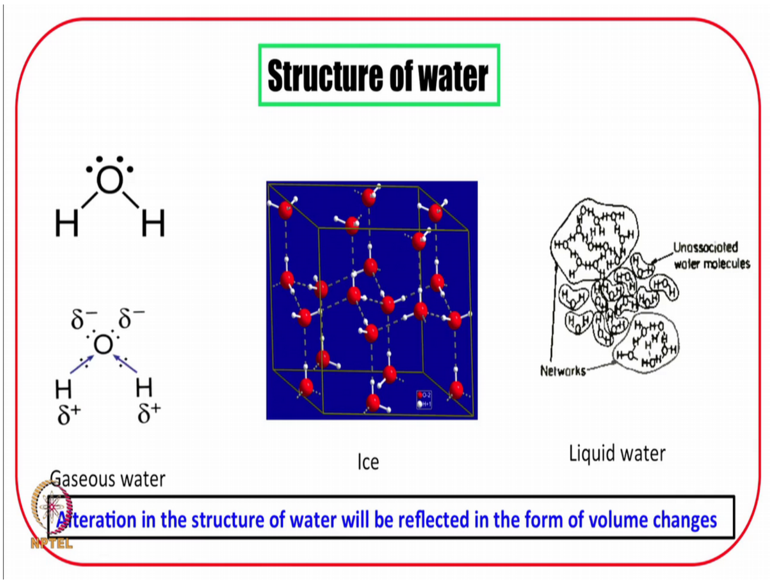

For example, let us talk about the structure of water. This is the structure in the figure structure of gaseous water molecule. In ice, there is a regular tetrahedral network of water molecules, and the water molecules are bonded to each other through hydrogen bonding. You can see each oxygen is tetrahedral is surrounded by 4 other oxygens; and in between 2 oxygens, there is hydrogen which is bound either through covalent bond or through hydrogen bond. But I want you to appreciate is the open structure of ice, which is a regular tetrahedral network structure. The liquid water is a partially broken down structure of ice. What happens is some of these water molecules are broken, they come out of the hydrogen bonded network and occupy the interstitial spaces, which are seen over here. And this is the cartoon diagram which represents the structure of liquid water which is the mixture of unassociated monomeric water molecules and the regular tetrahedral network like in ice. This is a very fast equilibrium at any given instant this monomeric water molecule will be a part of the regular tetrahedral network and vice versa.

Obviously the volume here is different than the unassociated water molecule that means, the volume of ice is different than the volume of liquid water. And that we have been taught even in school that the density of ice is different than the density of liquid water density of ice is less that is because the water molecules are far apart through hydrogen bonding. This alteration in structure of water will be reflected in the form of volume changes. What I mean is when you add a solute, if it strengthens the hydrogen bonding in water then the volume will change or if it disrupts the hydrogen bonding in water then the one they will change.

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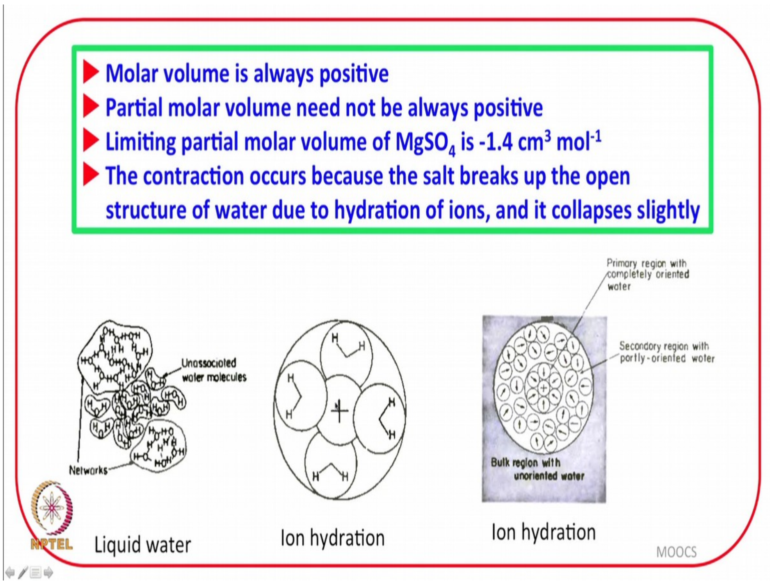

As an example I was discussing molar volume is always positive, partial molar volume need not be always positive. And if we take the example of magnesium sulfate then the limiting partial molar volume means partial molar volume at infinite dilution is minus 1.4 centimeter cube per mole. This is negative; that means, when you add 1 mole of magnesium sulfate into water then instead of increase in volume the overall volume decreases and that can only happen if there is a partial disruption of the structure of water.

So, as commented over here, the contraction occurs because the salt breaks up the open structure of water due to hydration of ions and it collapses slightly. This is seen in this figure; this is the structure of liquid water. When an ion is added, the ion under the influence of its electric field will orient some of the water around it. So, these water molecules which are surrounding the ion are not associated with rest of the water molecules. And here you see the ion hydration which leads two primary hydration and secondary region the details you will study in another course; but due to ion hydration, the water molecules are structured or oriented around the central ion. And it leads to partial breakdown of the structure of water because these water molecules come out of the regular tetrahedral network. And it is as a result of this breakdown of structure of water the volume decreases and the partial molar volume is negative.

So, I hope that we appreciate that the partial molar properties carry a lot of meaning. Today, we discussed about the partial molar volume. The partial molar volume is a good indicator of the nature of solute-solvent interaction. In fact, it also gives information about the solute-solute interaction, if it shows a molality dependence. So, therefore, not only the magnitude, but the sign of the partial molar volume is extremely important when it comes to identification of the nature of intermolecular interactions operating in the mixture. We will discuss further by taking some suitable numerical problems later on.

Thank you very much.