Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 19
Mixtures – Part 1

So, in the last lecture, we discussed about phase transitions for one component system meaning we only discussed about pure substances.

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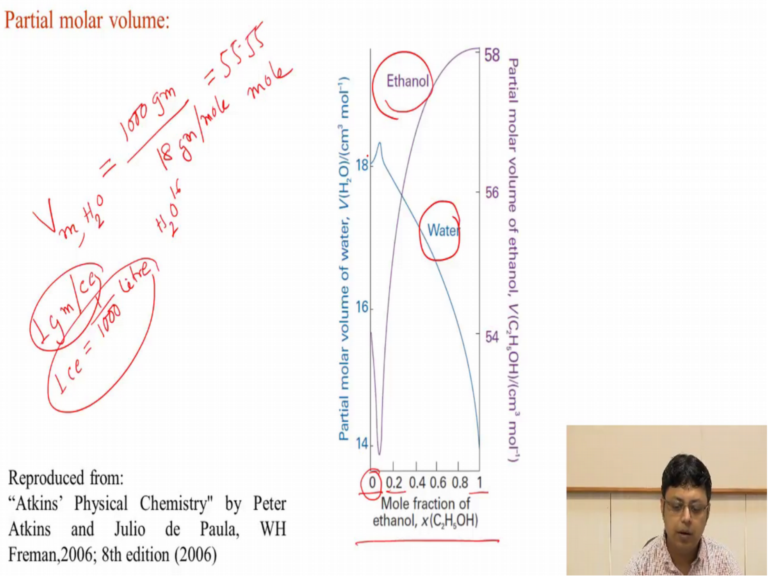

Partial molar volume:

$V_{m,H_2O} = \frac{1000 \text{ gm}}{18 \text{ gm/mole}} = 55.55$ mole

H_2O^{16}

1 gm/cc

1 cc = $\frac{1}{1000}$ litre

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So, in this lecture, we will discuss about mixtures which means what happens or how the thermodynamic properties change if we add 2 substances or more substances together. Now, we will first give you a very simple example. Suppose, we have 2 liquids which are immiscible; now, if we have say; for example, water and oil and if you add water and oil together, the change in volume, if you add say, 10 ml of water in 10 ml of oil or the other way since water and oil are immiscible.

So, the total volume will be nearly 20 mm. So, you can approximate that the volume total volume is V 1 plus V 2 or V water plus V oil; however, if the 2 liquids are miscible meaning they formed at the molecular level molecule of one liquid form a bonding or some interaction with the other liquid then the total volume actually is not just simply additive of the 2 volumes.

Now, we can give an quick example suppose you take ethanol and water and ethanol and water if you mix now ethanol molecules actually form hydrogen bonding with water and so, there is a strong interaction and you will not see the volume changing as an addition of the 2 liquid or the addition of volumes of the 2 liquids. Now, we will first show you some experimental data.

So, here what we show is how basically if we add ethanol and water together, how the volume changes now remember that the volume, we are talking about is a quantity which is known as a partial molar volume which means how the molar volume changes, if we keep on adding one particular component in this curve, we started from 0 mole fraction of eternal meaning we started from pure water and we kept on adding ethanol. So, 0.2 means this mixture will be 0.8 mole fraction of water and 0.2 mole fraction of ethanol.

In this way, we show up to 1.0 mole fraction of ethanol which means it is pure ethanol when water content is 0. Now, think about it when you start from pure water or the mole fraction of ethanol is 0, at that point the molar volume will be nothing, but the volume molar volume of water itself the molar volume of water, you can easily calculate. Remember, we are denoting the molar volume as V suffix m and that you can easily calculate water at normal pressure and temperature has density of one gram per cc.

So, one cc is nothing, but 1000 liter or one liter is 1000 cc. So, we can just write one by 1000 liter. So, in that way, you can ask one gram or how much weight one liter water has. So, one liter water it means actually 1000 cc water or the weight will be 1000 grams because the density is 1000 gram per cc. So, it will be nothing, but 1000 gram divided by the molar mass of water which is 55 if you take H2O 18 or sorry O 16.

So, I have to divide by 18 and then the molar mass will be 18 gram per mole. So, the molar volume is nothing, but you can easily calculate it, it will be 55.55 mole. So, if we take these to be all 16 isotope. So, you see here that the molar volume which we got here will be 18 gram per mole and that is why, it start; this is basically the density of the liquid. So, in this plot we show how the mole fraction of ethanol if we keep on changing that how the partial molar volume of water or ethanol changes now by partial molar volume, we mean that the change in molar volume per addition per unique addition of one fact one component in this case we are varying only ethanol.

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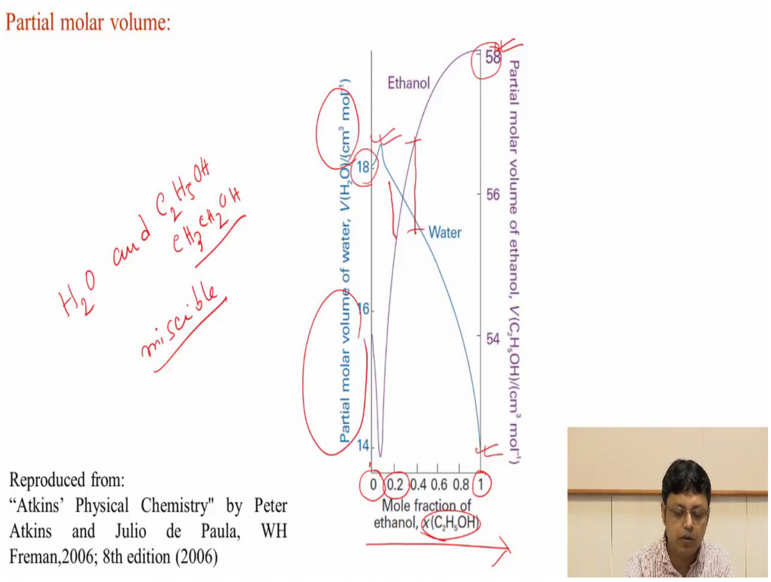

Partial molar volume:

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Now, think about it; here we start from 0 ethanol which means initially it was pure water, then we slowly keep on adding more and more ethanol which means at this point; 0.2 means it is 0.2 mole fraction of ethanol which automatically means it will be 0.8 mole fraction of water and then ultimately, we go to pure ethanol where the mole fraction of ethanol is one which means that the mole fraction of water at this point will be 0.

Now, you see here that the molar volume of water. So, in units of centimeter cube per mole it is nothing, but the 18; it should be 18 because the molar mass of water is 18 and then ethanol it is 58. So, you start from 18 here when it is pure water and then it drops directly to 0, when it is pure ethanol and ethanol similarly starts from nearly 0 and then. So, the 0 point is not shown here because it will be sharp rise and then deep and then you get the pure for pure ethanol it is 58.

Now the interesting point here is that if you add these 2 points, the addition of molar volumes it never follows the total volume so; that means, it is possible because H2O water and ethanol which is a CH3, CH2OH H; they are actually miscible. So, the volume is not simply addition of the 2 volumes.

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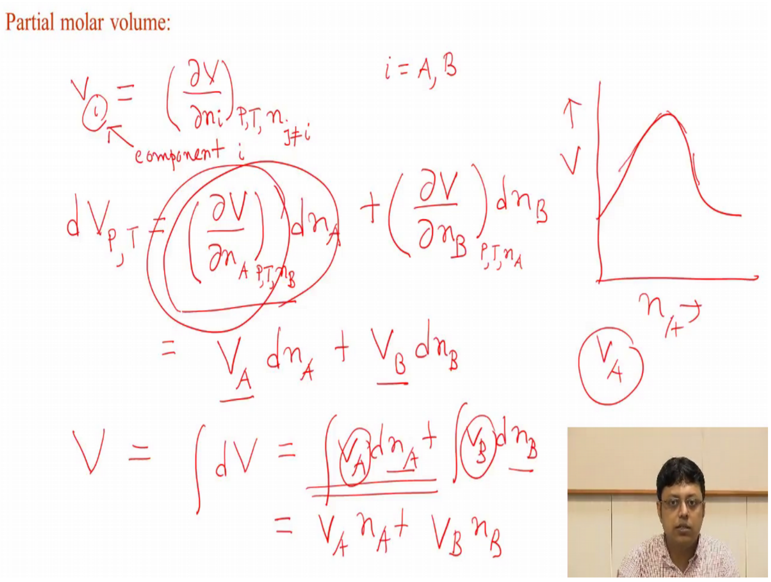

Partial molar volume:

$$\underset{\text{component } i}{V_{\boxed{i}}} = \left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_{j\neq i}} \qquad i = A, B$$

$$dV_{P,T} = \left(\frac{\partial V}{\partial n_A}\right)_{P,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{P,T,n_A} dn_B$$

$$= \underline{V_A}\, dn_A + \underline{V_B}\, dn_B$$

$$V = \int dV = \int \boxed{V_A}\, dn_A + \int \boxed{V_B}\, dn_B$$

$$= V_A n_A + V_B n_B$$

Now in order to quantify that this quantity partial molar volume, we define it as the partial molar volume of any component which we denote as i so, i is a component. So, in that previous example the components are ethanol and water. So, it is a 2 component system any arbitrary component i, we asked how the volume is changing if we keep change or if we keep adding the component i or if we change the number of moles of the component i at constant pressure temperature and of course, all other components which i denote as say in j where j is not equal to i which means we have to keep all the other components constant that meaning is if we are adding ethanol.

So, we cannot add water. Simultaneously, we are only seeing how the how addition of the ethanol is changing the mole how the volume is changing by addition of ethanol when the volume or the addition of water is not done. So, you can either could have changed we could have either added water, then the curve will look like this the car for water from 0 for water concentration per mole fraction to maximum one or you could also do it by adding ethanol.

Now, interestingly remember that the; if we if you just asked me that what will be the total differential of changing the volume. So, that differential at constant pressure and temperature should be the partial differential when we change the component a; suppose i is i can be here A and B. So, it is a 2 component system the example, I give a was water B was ethanol something like that and then we take the change in A plus the partial derivative; when we change should be free the change in volume the partial derivative with respect to n B and then multiplied by T and B, but when we change in A; which is the number of moles of A; if we keep on adding we have to keep in mind that we are keeping pressure constant temperature constant as well as in B constant. Similarly here we are keeping pressure constant temperature constant and n A to be constant.

So, we can integrate it and ask this question before integration we can just write it in a shorthand notation, we could write it as VA DNA plus P B d n B. So, where VA V B at the partial molar volume with respect to A and B respectively so, partial molar volume is defined as partial molar volume of a particular component is defined as how the total volume is changing, but if we add the particular constituent or component. So, we can ask this question what will be the total volume. So, that or the total change in volume due to this addition that will be simply integration of this change and we can easily find out the quantity.

So, it is nothing, but the VA DNA plus integral of V B d n B and if we assume that this quantity V and V B is not changing over the entire range of change which is an approximation of course, because we showed that the curves are not very linear the curves are very much non-linear in nature so, but still we are assuming that V and V; V are constant when we add when you change the n A and n B. So, then with some approximation we can write actually it is V n A plus vv VA n A plus PB n B.

Now, the question is how the curve will look like if we add some change some volume something like that. So, you see that a general nature of the curve is very non-linear in the sense that if we plot the V versus a mole fraction of A; the slope of the curve is nothing, but the partial molar volume because remember, they by definition this is the slope. So, dVA DNA or del VA del; del V del n A that slope is actually changing. So, this approximation which we made during this change VA is constant is not a correct approximation.

So, all we are saying that we did a small range maybe you can assume that this slope does not change. Now the next question we asked since we are doing all these experiments at constant pressure and temperature. Now the question we are asking is that what happens to the Gibbs free energy because Gibbs free energy is a natural choice to look at and from there we can actually calculate what are the conditions that these 2 liquids. So, will spontaneously mix or not;

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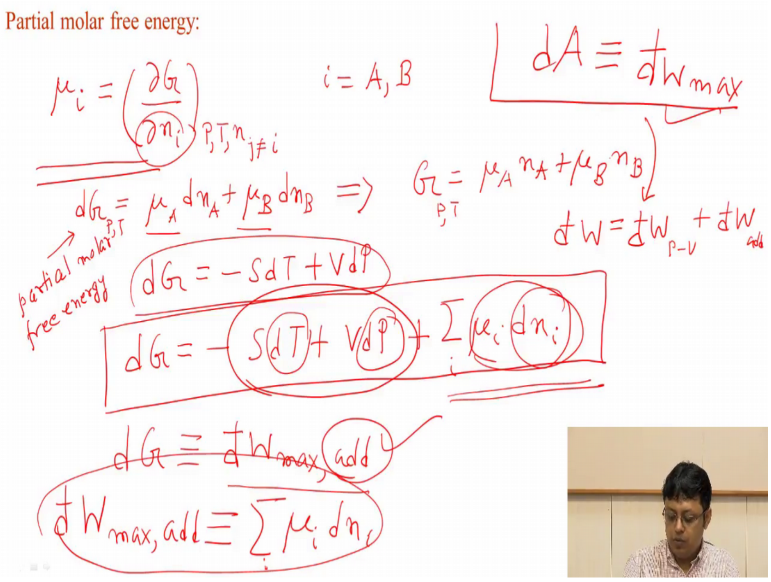

Partial molar free energy:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} \qquad i = A, B$$

$$dA \equiv \text{đ}W_{max}$$

$$dG_{P,T} = \underline{\mu_A} dn_A + \underline{\mu_B} dn_B \Rightarrow G_{P,T} = \mu_A n_A + \mu_B n_B$$

$$\text{đ}W = \text{đ}W_{P-V} + \text{đ}W_{add}$$

partial molar free energy

$$dG = -SdT + VdP$$

$$\boxed{dG = -SdT + VdP + \sum_i \mu_i dn_i}$$

$$dG \equiv \text{đ}W_{max, add}$$

$$\text{đ}W_{max, add} \equiv \sum_i \mu_i dn_i$$

Now, for that in a similar way instead of Gibbs free energy, we use the definition of chemical potential which we already discussed, but this quantity, we call as a partial molar Gibbs free energy the reason partial is coming because we are now talking about mixtures. So, we cannot say it is just molar Gibbs free energy or something like chemical potential. So, it is a chemical potential of a particular component in the mixture because there are multiple components at least there are 2 components that is why it is a mixture.

So, in a similar way just like we define the partial molar volume we can say that this quantity will be nothing, but change in the Gibbs free energy per unit mole of addition of the component i, when all other components are kept fixed. So, j not equal to i. So, we know that we already know this equation G is mu A or we can actually start from this equation first the dG will be nothing, but mu suppose we have 2 components and then if you ask this question what will be the finite change in the dG.

So, you can easily in the same way just like we did the partial molar volume if you remember that we showed it as VA DNA plus VB dnB in the same way, we can write it as mu A DNA plus mu B dnB square mu A and mu B are partial molar free energy in the sense it is partial that it we are lighting it for 2 component system where the components are again A and B and that is why it is a partial and it is molar because it is the part mole.

So, Gibbs free energy per mole is nothing, but the chemical potential that is very directly writing mu A here. So, this is nothing, but the finite change or the differential change in this context and we call it as a partial molar free energy and in the similar way we can write that if we integrate it will get Gibbs free energy which we wrote a can write as say mu A nA plus mu B n B.

Now, interesting thing to note here is that we already know expression for d G and the expression was if you remember. So, remember that this dG at cost is at constant pressure temperature that we should always keep in mind. So, just like here also we should always write that it is at constant pressure temperature now the general equation for dG if you remember that we wrote tG as minus S dT plus V dP. Now, if we make the condition at constant temperature and pressure this was for one component system now for multiple component system we see that there is a contribution of dG when the pressure and temperature is constant.

So, when the pressure and temperature is constant from this equation dG should be 0, but now we are saying that there is an additional component of Gibbs free energy which is coming from the Gibbs free energy due to mixing. So, we call it as a Gibbs free energy of mixing and. So, the total change in the Gibbs free energy if we vary temperature pressure as well as all these quantities can be written as minus S dT plus V dp plus all this quantities mu A DNA plus mu B T and B which we can write as a general equation that it will be a sum over all these terms which involve mu i dni.

So, this is a much more general equation where it not only contains the information how the Gibbs free energy is changing with respect to temperature or pressure it also contains information if we keep on changing the fraction or mole fraction of one particular component how the total Gibbs free energy is changing.

Now, remember that we also discussed that dG can be equated to the maximum additional work by additional work we meant that it is a norm TP work for example, some electrical work in when electrons flow in a circuit. So, it also does some electricity to flow and it does some work because the electron running through a potential difference will; I mean there will be a kinetic energy involved and there will be some work done.

So, that work is a non P V work non pressure volume work. So, those kind of work we talked about and we said that it is a additional work and we asked you to show it because for if you remember that we derived the other equation which is basically the Helmholtz free energy is equivalent to the maximum we should write the across here P V work or maximum work from the system similarly for the Gibbs free energy we found that we did not derive it in the lecture we asked you to derive that the Gibbs free energy change is equivalent to the maximum non P V work or the additional work.

Now; that means, that we can actually have a physical meaning of what is the change in Gibbs free energy or a what is the change in Helmholtz free energy it can be directly equated to the work done for Helmholtz free energy it was the pressure volume work done for Gibbs free energy is the non pressure volume work done now if we write it in this way.

So, we can easily see the meaning of this maximum additional work and this additional work is nothing, but d you can write it as d crossed a blue maximum additional work this is nothing, but the mu i DNA because remember that this part will involve the if you if you work it out you will realize that this part will be equivalent to the work done which is relevant to the P V work. So, when we solved it, we said that you take the d cross W as d cross W P V work which is P opposing plus dV and plus write it some additional work and then you can show the additional work will be equivalent to some non P V work which is this term and then we can easily show that d cross W maximum additional will be the change associated by changing the components of the mixture.

So, what you see here is that when we make a change or make a transformation. So, then there will be some at P V work or there can be some non P V work also in this case if you simply mix 2 liquids of say 2 fixed volumes what we are seeing is that the volume change is not just simply additive of the volume there is a change in volume and we define the partial molar volume for that and you saw that the curves are not just addition because there is a miscibility between the liquids and additionally you can also define some change in free energy associated due to the mixing will also quantify it we are right now just writing it as a phenomenologically just saying that we are assuming that there is a change in free energy and that would be equivalent to mu i dni, but that change now since there is no change in the pressure volume kind of work.

So, we are saying that this is a non pressure volume work it is just happening due to the mixing of the 2 liquids and that is nothing, but the summation of chemical potential of each term multiplied by the change in moles of that particular component and if we take the sum that will be equivalent to the maximum additional work which is the non P V work.

Now, let us move on and this partial molar free energy which we defined as say the G del n i. So, the mu i as we told it is known as a chemical potential of that particular component because it is not just mu in the when we are discussing the phased diagram or the phase transition for one component system which is a pure substance say for example, water or carbon dioxide there also we talked about mu versus d curve and. So, on that mu was just a chemical potential of a pure substance and mu suffix i is the chemical potential of that particular substance.

So, let us now try to understand this chemical potential can it be written a not only in terms of the Gibbs free energy, but also in terms of some other thermodynamic parameters for example, say internal energy or enthalpy or Helmholtz free energy now you can easily figure that out because we defined already chemical potential in terms of Gibbs free energy.

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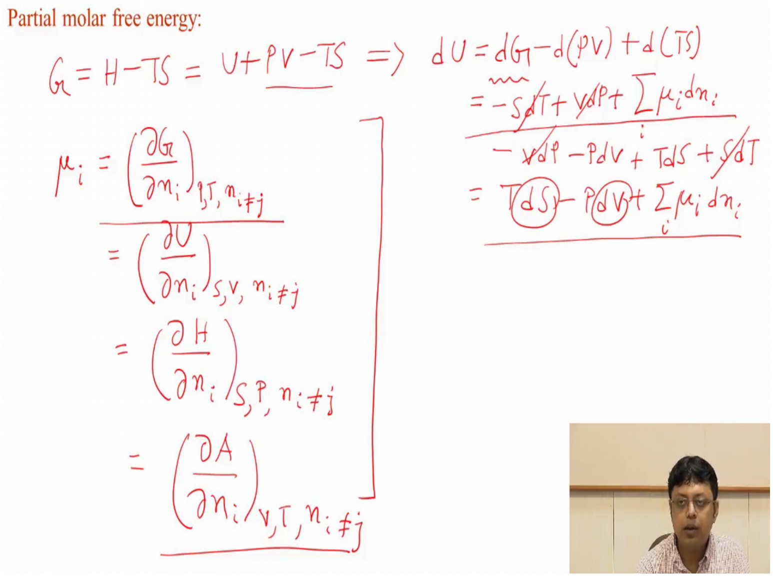

Partial molar free energy:

$$G = H - TS = U + \underline{PV} - TS \Rightarrow dU = dG - d(PV) + d(TS)$$

$$= -S\cancel{dT} + \cancel{V}dP + \sum_i \mu_i dn_i$$

$$- \cancel{V}dP - PdV + TdS + \cancel{S}dT$$

$$= TdS - PdV + \sum_i \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{i\neq j}}$$

$$= \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{i\neq j}}$$

$$= \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{i\neq j}}$$

$$= \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{i\neq j}}$$

Now Gibbs free energy is nothing but H minus TS and H is nothing but U plus P V minus TS. So, we can right away see that du will be nothing, but if I just take this P V minus TA term on the other side.

So, it will be minus d of PV. So, which will be we can just keep it like that for the timing plus d of TS and then you can show that this will be again nothing, but if we if we just keep the H constant. So, now, for dG you can write minus S dT plus V dP plus all these some of our mu i dni terms because we are considering mixing right now and then you can figure out all the other terms will cancel out because a it will be nothing, but minus if we take the pressure derivative first minus V dP, then it will be minus P dV plus we have T dS plus s dt.

So, this S dT cancels out and pdp cancels out. So, du will be nothing, but if we write it in this way the way we were writing T dS minusP dV plus now we have a term which is mu i dni. So, you can see here that just like we wrote dG as the S dT minus S dT plus V dP plus sum over mu i dni.

Similarly, the du equation is also modified as T dS minusP dV plus sum over mu i dn A. So, this mu I can be expressed not only in terms of dg, but also in terms of other quantities now remember that we started with this that mu i is nothing, but taking the partial derivative of Gibbs free energy as we change the component i keeping pressure temperature constant and all other component constant. Similarly, if you look at this equation we can take the partial derivative with respect to in I keeping this time, I have to keep entropy and volume constant I can keep entropy and volume constant plus all the component which are not I accept that particular component. So, we are changing only that component similarly we could also write it following the same logic a partial derivative with respect to enthalpy and remember the enthalpy equation it was T dS minus PdV.

So, we have to keep entropy and pressure constant for H and similarly we could also write it in terms of the Helmholtz free energy del a del ni and for Helmholtz free energy remember that it was P dV minus and T dS and P dv. So, S dT and P dV. So, basically the natural choice for Helmholtz free energy was to keep the volume and temperature constant and n i not equal to nj.

So, mu can be expressed in any of this thermodynamic quantities either G or U or H or a whichever you wish usually we use this definition because the transformations are happening at constant pressure and temperature in most of the cases, but you might have a situation where you have to use the Helmholtz free energy, but the volume and the temperature are kept constant, but in other cases you could also use a U or H, but those are rare because usually we are not considering or we are not giving example of a process or entropy and volume are kept constant or entropy and pressure are kept constant.

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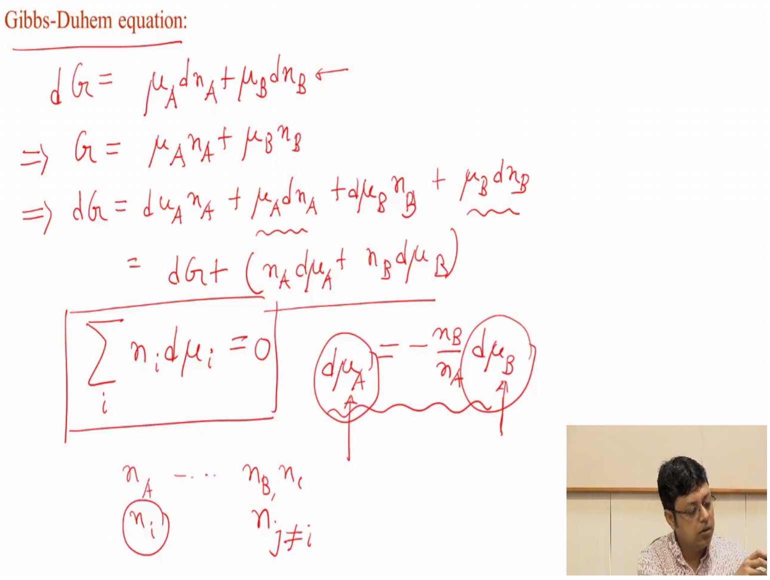

Gibbs-Duhem equation:

$$dG = \mu_A dn_A + \mu_B dn_B \leftarrow$$

$$\Rightarrow G = \mu_A n_A + \mu_B n_B$$

$$\Rightarrow dG = d\mu_A n_A + \underset{\sim}{\mu_A dn_A} + d\mu_B n_B + \underset{\sim}{\mu_B dn_B}$$

$$= dG + (n_A d\mu_A + n_B d\mu_B)$$

$$\boxed{\sum_i n_i d\mu_i = 0}$$

$$d\mu_A = -\frac{n_B}{n_A} d\mu_B$$

$$n_A \; \ldots \; n_B, n_C$$

$$n_i \qquad n_{j \neq i}$$

So, what we discussed so far is that we showed that for 2 component system we can write an integrated form which is a very compact form which is basically we can write mu A first mu A or we can actually start from the differential in one second mu i dn A plus mu B d n B and then we integrated it to get it as mu A n A plus mu B n B and remember that then you can actually start from this equation and again take a differential.

So, if I take the differential, I will have; if I apply the chain rule it will be T mu A n A plus I have to take a differential with respect to nA mu A DNA plus mu d mu B n A plus mu B d and B, but then you can easily see that these 2 terms appear here. So, these 2 terms are nothing, but d G itself. So, it is nothing, but d G plus we can just rewrite it as nA d mu A; A plus n B it should B d mu B.

So, what we see that this term must be 0 or in general if we write it as a summation for any arbitrary number of components we see that that sum over ni d mu i should be 0. Now, this equation is known as Gibbs Duhem equation. Now, what is the importance of this equation suppose we again, we are dealing with 2 components. So, we can write this d mu A. So, this is 0 which means suppose if we write it the d mu A in terms of d mu B will have it is nothing, but nB by n A into d mu B.

Now this is an interesting situation what it tells is that if I want to change the partial this is the chemical potential if I want to change the chemical potential of one component I cannot change it independently of the chemical potential of the other component because they are related; however, you could change the mole fraction remember we change the mole fraction of a keeping all other mole fractions constant n B n C whatever.

So, we said that we can change ni keeping all the n j's constant where j is not equal to i and then we can actually study how the Gibbs free energy or any thermodynamic quantity is changing; however, if we want to vary the chemical potential we cannot because the chemical potentials are coupled. So, which means that the chemical potential for one component cannot change all by its own so, it has to change all chemical predictions has to change keeping a relationship between them.

So, they cannot change independently. So, that is the essence of Gibbs Duhem equation now suppose we want to measure or we want to quantify the changes in Gibbs free energy for the mixing for say some system and to begin with of course, we will start with say ideal gas now since it is a mixing we have to talk about 2 or more ideal gases and suppose and remember that if we take the Gibbs free energy of mixing we have to keep the pressure and temperature also to be constant.

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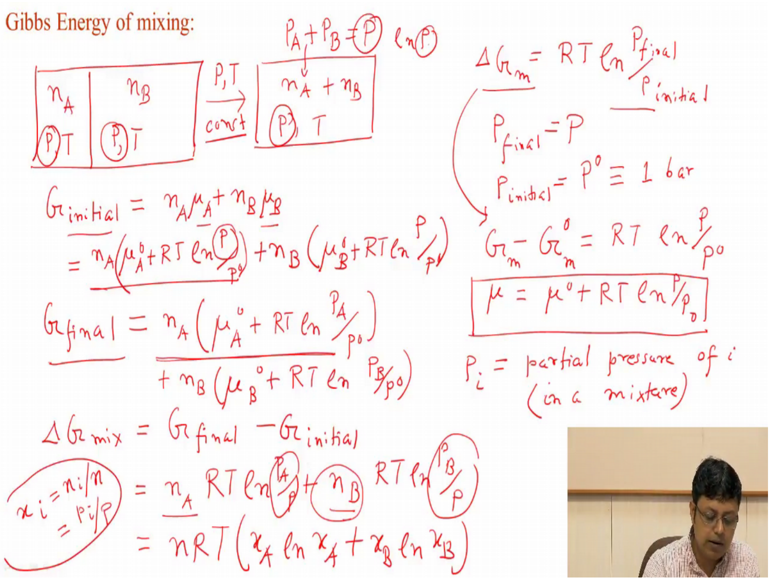
Gibbs Energy of mixing:

$P_A + P_B = \boxed{P}$ $\ln \boxed{P}$

$$G_{initial} = n_A \mu_A + n_B \mu_B$$
$$= n_A\left(\mu_A^0 + RT \ln \frac{P}{p^0}\right) + n_B\left(\mu_B^0 + RT \ln \frac{P}{p^0}\right)$$
$$G_{final} = n_A\left(\mu_A^0 + RT \ln \frac{P_A}{p^0}\right) + n_B\left(\mu_B^0 + RT \ln \frac{P_B}{p^0}\right)$$
$$\Delta G_{mix} = G_{final} - G_{initial}$$
$$= n_A RT \ln \frac{P_A}{P} + n_B RT \ln \frac{P_B}{P}$$
$$= nRT\left(x_A \ln x_A + x_B \ln x_B\right)$$

$x_i = n_i/n = P_i/P$

$$\Delta G_m = RT \ln \frac{P_{final}}{P_{initial}}$$

$P_{final} = P$

$P_{initial} = P^0 \equiv 1$ bar

$$G_m - G_m^0 = RT \ln \frac{P}{P^0}$$
$$\boxed{\mu = \mu^0 + RT \ln P/P_0}$$

P_i = partial pressure of i (in a mixture)

So, let us imagine that we have container something like say this and initially I had any moles of gas a or vapor a and any amounts of gas B and they were at same pressure and temperature because one once we mix it if we assume that the pressure and temperature is changing then you cannot apply it. So, you have to use the full equation which is dG is minus S dT plusP dV plus some of our mu i dni, but we are now focusing only that part which is some of our mu i dni. So, in order to do that the minus S dT term should preserve and the minus plus V dP term also has to be 0 which means pressure and temperature has to be kept constant.

So, the pressure and temperature does not change during mixing and after mixing what happens we have n A here and also we have n B here the total pressure does should not change and the temperature of course, should not change; however, as you can see the partial pressure of each component should change here and that is the trick to figure out what is the change in the Gibbs free energy.

Now, let us just use this notation that fine initially, we had I could have written a gi, but I am just not writing it because already we have chosen for to describe a component. So, the initial link the Gibbs free energy was nothing, but n A mu A plus n B mu b. So, this is the Gibbs free energy of the joint system now when you mix it, but before we discuss that let us also discuss we already had this discussion what is the Gibbs free energy, but the change of Gibbs free energy per mole when we change that pressure.

So, when you discuss the changes of Gibbs free energy as a function of pressure and temperature remember that we got this kind of equation where we used an ideal gas as an example and you can easily show that it will be RT PF by P i because it is nothing, but just the VTB term and this V. Now you are writing in terms of RT by P and if you just divide both side by n it will be RT by V and this G will be nothing, but gm the molar Gibbs free energy and then if you integrate it you easily get this equation.

So, this is a P final minus divided by P initial now. So, delta G is nothing, but G final minus P initial. Now we are writing suppose this final pressure as just P and the initial pressure as P 0. Now what is P 0 P 0 is nothing, but the standard pressure which by Si unit we are writing it as say one, but we are keeping the one bar as a standard. So, then this delta G n is nothing, but G final minus a initial that we write as G minus the G initial corresponds to a standard condition where the pressure was kept to be 1 bar that we write as z 0, let us write this 0 as a superscript. So, we get G minus z 0 and this is remember, this is a molar quantity. So, gm minus gm 0 is nothing, but RT ln P by P 0. So, in this case actually the initial condition was actually one bar of the standard condition or instead of G we could write it as in terms of mu because molar Gibbs free energy is nothing, but the chemical potential.

So, you can write that mu is mu 0 plus RT ln P by P 0. So, that equation we are now going to use. So, every mu here, we could write it in terms of mu 0 plus RT ln P by P 0. So, let us just write it. So, I will have n A mu A 0 plus RT ln P a by P 0 there is no point in writing PA 0 it is P 0 is same for everybody is just the standard condition which is one bar some textbook actually dropped this P 0 and which means actually there is a inherent P 0 and just they just write it as ln p, but remember that this P is unit less it has to be because the logarithm of a number.

So, the idea is that it is expressed in units of bar and then which means actually we are dividing it by one bar and similarly 4 mb component B, we can write mu B 0 plus RT ln PB by P 0 and now let us look at what happened to the final Gibbs free energy the final Gibbs free energy in our same notation we could write it as say n A and then suppose what is the change in the pressure now this pressure will be nothing, but now the partial pressure because now in the mixture the pressure contributed by a or the component a is nothing, but the partial pressure.

So, instead of VA we have to use some other quantity which we call as a partial pressure now remember it is this PA what is this PA, it was basically before mixing, but before mixing we took it to be pressure P. So, instead of PA and PB we could write it as P itself and will denote the partial pressure as P and P V because the initial pressure which is the pressure of a or pressure of B when the gases were not mixed that was nothing, but the P it was because the pressure was kept same for A and B, but in the final case we have the pressure of A is nothing, but the partial pressure and the pressure of B is the partial pressure of B of course, that should add up to P because we did not change the total pressure from going from here to here.

So, the pressure and temperature were kept constant which means the total pressure did not change; however, the partial pressure must have changed because now it is a pressure of a in a mixture. So, in that sense we are writing it as mu A 0 plus RT ln. Now we are writing P A by P 0. Now this PA means now partial pressure and the earlier P was the pressure for the total gas before mixing. So, that was the initial condition and similarly for m B, we can write nB into mu B 0 plus RT ln P B by P 0. So, P i is nothing, but the partial pressure of component i and of course, it has to be in a mixture. So, it is the pressure or pressure after mixing. So, we can easily calculate what is the delta G of mixing which is nothing, but we have to take the difference between the final and initial and then you can easily calculate this quantity you can see that we have a interesting relation here.

So, if you subtract G initial from G final you can see that all these terms mu A 0 mu B 0 they cancel and finally, we can get something like n A if we just collect the terms of nA together. So, look at it we are subtracting this term from this term. So, nA mu 0 nA mu 0 cancels. So, all we are left with is nA times RT ln. Now I will have RT lnp by P 0 minus ln PA by P 0, but that we can directly write as. So, this quantity instead of writing it as a lna minus ln B or written x minus ln y we can directly as ln x by y and this P 0 term will cancel.

So, we can write it as RT ln P a by P and similarly for in B, we can also write it as RT ln P B by P. Now what is PB by P or P a by P it is nothing, but the mole fraction because it is partial pressure by the total pressure and that is equal to the mole fraction of xA. Similarly this is nothing, but the mole fraction of B which you write as xA and xB now this n A and nB are nothing, but the moles of a and B that also you could write as a mole fraction into the total mole which is nothing, but if we write it as xA into nRT and here we can write it as a x B into n into RT. So, that n RT, you can take common and we can write xA ln xA plus xB ln x B.

So, this xA came from the definition that x i is nothing, but ni divided by n. So, we wrote instead of n i which is nA and nB as n into x i and then we took nRT common and for this this part we took the definition that the mole fraction is also defined as partial pressure divided by the total pressure. So, either way you can write it and you use the 2 definitions of mole fraction to arrive at this expression.

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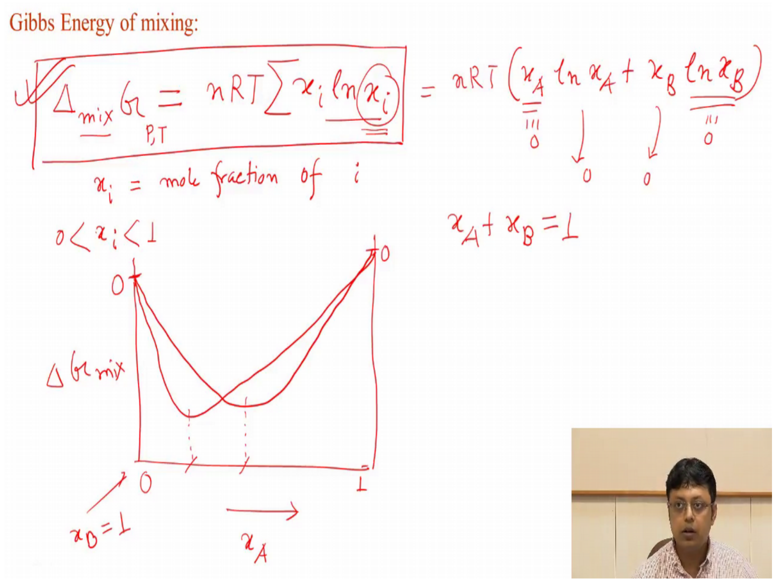

Gibbs Energy of mixing:

$$\boxed{\Delta_{mix} G \underset{P,T}{=} nRT\sum x_i \ln x_i} = nRT\left(x_A \ln x_A + x_B \ln x_B\right)$$

x_i = mole fraction of i

$0 < x_i < 1$

$x_A + x_B = 1$

So, what we get in general the delta G mixing. Now, instead of delta G mixing we could write it as delta mix of G because that was our rotation remember when we were talking about the transformation we always wrote like for example, for a fusion process how the enthalpy is changing we are writing is delta fusion of H in the similar way we are also saying that we will write it as a change in that delta or the basically the process we will write as a subscript for the delta and that quantity is nothing, but nRT some of our x i ln x i.

Where x i is the mole fraction of component i x i is nothing, but mole fraction of component i. Now the mole fraction, remember what is x i x i can be minimum 0 and maximum one. So, x i is a fraction which means ln x i; this quantity will be a negative quantity which means delta G mixing is always negative for each component. So, if we add up it will be always negative together. So, once we mix the things keeping the again do not forget that we have to always write at this is done at a constant pressure and temperature. So, when we mix 2 components together the free energy or the total free energy actually changes and it is negative which means actually it is a spontaneous process.

So, if we want to plot how the delta G mixing looks like if we vary say for 2 component system where I have xA and xB suppose we have varying xA a minimum value of xA can be one and 0 and the maximum value can be 1 and then the delta G for this minimum value should start from 0 because when x is 0 it means at this point xB is 1. So, it is a pure component which is basically pure b, but then if i put here that xA is 0 and xB is 1.

So, for 2 component it will be nothing, but nRT xA ln xA plus xB ln xb. So, when x is 0. So, this term is 0 and naturally xB at this term is one sorry when x is 0 this is 0 and at that point ln xB is 0. So, the total thing is also 0. So, delta G will start from 0 here, similarly when xA is one this part is 0 and at that point xB is 0. So, this term will be 0. So, again a delta G will be 0.

So, delta G will vary from 0 to 0 and in between it will have a minima. So, the curve will look like qualitatively something like this. So, it will have a minimum for a particular composition of xA. Now the way I have drawn it, it looks very symmetrical, it may not be very symmetrical meaning that we might heat and minima somewhere say here a particular mole fraction of xA which automatically tells the mole fraction of xB because always we are keeping it is xA plus xB to be equal to 1.

So, so far, what we have discussed is that we started our discussion with on mixers what happens if we have multiple components together and then ensure that initially how the volume can be interpreted or the how the volume changes as we keep on adding one component keeping all other components unchanged and then we showed that it is not just simply additive with keep on changes and then we try to define our quantity we are try to see how the chemical potential or Gibbs free energy per unit mole that changes if we keep on changing the amount of one particular substance and we showed that if we do it then we get a definition of chemical potential not only in terms of the amount of not only in terms of the Gibbs free energy, but also in terms of any thermodynamic quantity like internal energy or enthalpy or Helmholtz free energy which means actually the chemical potential is a very very useful and very general concept.

Now, when we are talking about chemical potential of a one component system we wrote it a mu versus T, but in this case it is a partial chemical potential or chemical potential of a substance and then for that we used the relation of our ideal gas starting our discussion that how free energy or Gibbs free energy changes with respect to pressure and then we can get a very interesting relation that mu is nothing, but mu 0 plus RT ln P by P 0 only for ideal gas and then you can use this to figure out. If we had 2 different gases and if we just mix it starting with the initial condition that pressure total pressure is nothing, but the initial pressure of each gas.

So, then if we mix the total pressure will not change; however, the partial pressure should change and that fact we used and we cleverly just wrote the mole fraction or depression pressures in terms of mole fraction as well as the moles of A and B in terms of mole fraction and then we saw that the general in equation for delta G mixing can be written as this and we have r good also that this delta G will go through a minimum it should be negative because it is a mole fraction.

So, this all, this excise are fraction and the reason for that is ln of a fraction is negative quantity. So, delta G will go through a minimum, but how it will go through a minimum it will depend on 1, I mean it will vary from one system to the other system that we will see.