Thermodynamics And Kinetics Of Materials

Prof. Saswata Bhattacharya
Dept of Materials Science and Metallurgical Engineering,
IIT Hyderabad

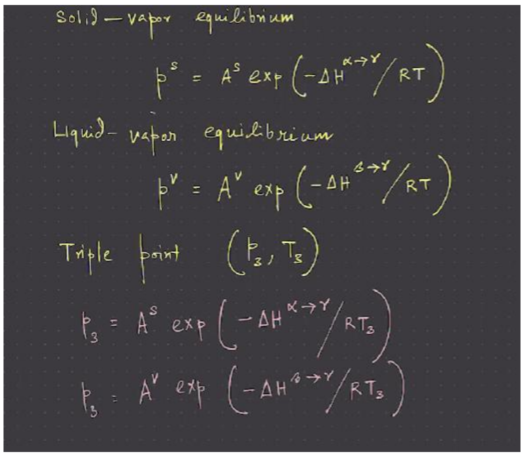
Lecture 21

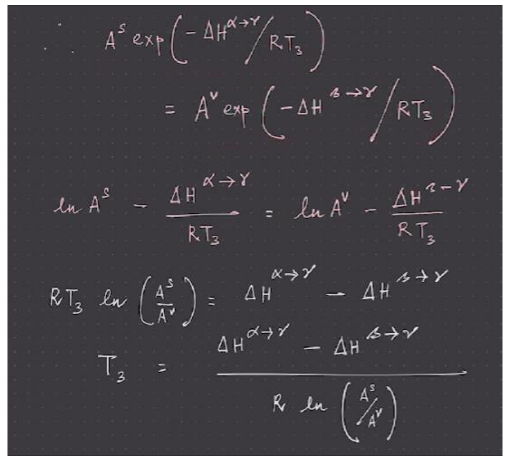
Thermodynamics of solutions 1

So, as you have seen for the triple point, solid vapor, liquid vapor, basically solid liquid vapor coexistence, right? We have derived that, we have derived, right, that T3, which is the triple point temperature, is related to the difference in the heats of transformation of alpha to gamma, alpha to gamma is solid to gas and liquid to gas transformation, right, beta to gamma is liquid to gas and it has also this relation to this As and Av, right, this is the coefficients, right, As and Av. Now this is T3, again some algebraic manipulation later, we have shown that P3, that is the triple point pressure, again is related to these coefficients. As and Av and remember the coefficients this is something that you have to remember how did we look at the coefficients we did this thing right p equal to p0 e to the power minus chi so p0 basically for example e to the power minus chi so here p0 is the coefficient right here p0 is the coefficient so we can basically the coefficients are related to the p vapor or p sublimation means the temperature at which sublimation occurs or the pressure at which sublimation occurs the temperature at which sublimation occurs So, these are basically the pressures are going to be the coefficients. So, if you look at that, Av, if you see the relation, this is pressure, right, this is pressure. So, this is in Pascal. So, then the exponent has no unit, right, the exponent has no unit, right, it is joule by joule.

So, it has no unit. So, obviously, As. So, basically, As. these are basically going to be units of pressure.

So these are units of pressure and if you compare these are nothing but, AS and AV are nothing but some standard pressures of transformation from either from solid to gas, here it is solid to gas transformation or say liquid to gas transformation and As for example is basically a standard pressure of, so it can be like standard pressure of sublimation, right, this or this can be standard, so in this case this is beta to gamma, so this is like standard pressure of vaporization and then there is some, so we can think of some standard or reference state and this is again at that reference state P is not S. So, basically P naught as or so basically as and av are related to we can tell are related to P naught s or P0V right P0S basically or P0 sublimation and this is P0 vaporization right. So these are related AS and AV are related right. AS is related to P0 sublimation and AV is related to P0 vaporization. Now see you have this then think of this you have this relation again you see here this is as and this is av both have the units of pressure so again within ln there is no unit so you have here joules per mole kelvin and you have here also you have so r is joules per mole this is joules per mole and this is joules per mole kelvin so you can see this gives you kelvin right it gives you So, temperature the unit is in Kelvin and you see these are related to the difference in heats of transformation of alpha to gamma, alpha to gamma remember this is like solid, this is solid to vapor, this is liquid to vapor, solid to vapor and this is liquid to vapor.





Now, as you know solid to vapor is like solid to liquid, liquid to vapor, you can think of that. Now, if you do a little bit of algebra, again taking ln on both sides basically, you are taking ln on both sides, you have taken this expression of T3, you put that here, you have taken this expression of T3, you put T3 expression here. Right. Right. So or say in the in the previous expression here.

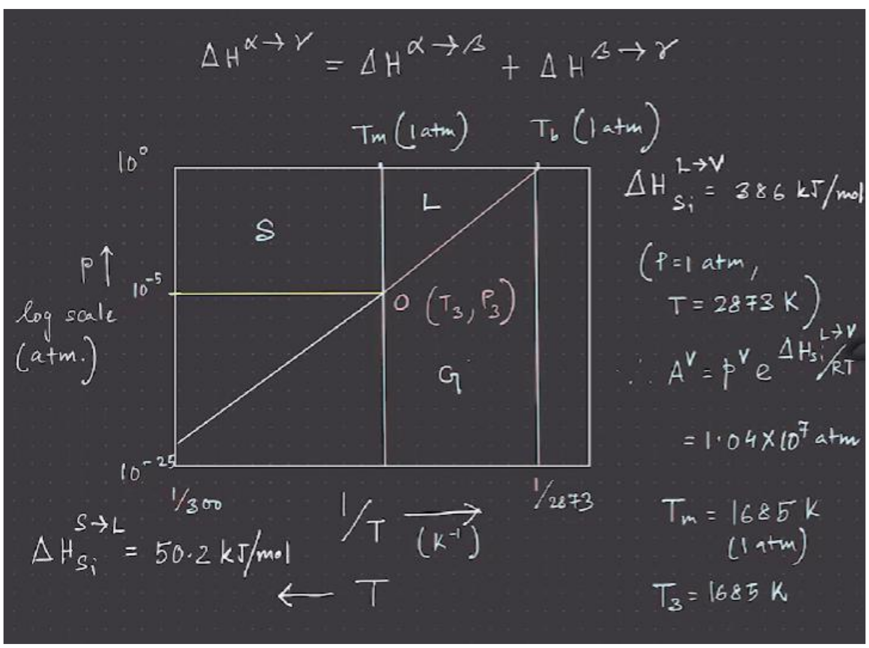
OK. So here you are taking the expression for T3. Right. At R T3. So if you do that and then you take log on both sides logarithm on both sides and you can basically come up with. So delta H D for example here I have told is basically the difference between this.

Right. Alpha to gamma transformation enthalpy minus beta to gamma transformation enthalpy. So, now you can basically with a little bit of rearrangement and algebraic manipulation, you can come up with this expression. By the way, in the exam, if I give a question related to this, I will basically give these expressions. You don't have to remember anything, but you have to understand. What you have to understand is that P3 is related to this again, the pressure.

There is a pressure and there is an exponent. And this exponent is, again, you see AS is related to beta to gamma by beta to gamma minus alpha to gamma. Basically, the exponent is the ratio of enthalpy of beta to gamma by the beta to gamma minus alpha to gamma that enthalpy difference. This is the transformation, the enthalpy of transformation, difference in the enthalpy of transformation and this is the enthalpy of transformation from liquid to vapour. In this case, this is from solid to vapour and again this is the difference between the enthalpies of transformation of solid to vapour, difference between solid to vapour and liquid to vapour, right.

And again Av is one pressure term. Now, if you have this, you please try to understand that this is an exponent here, this is a power here. So, as you know that this logarithm and exponents becomes gives you a very nice way to deal the triple point calculation. So, basically what it tells you is that if you do ln P3, then this guy comes down or this guy comes down, right. So, if you do ln P3, you can write it as a very simple expression in terms of some, this coefficient times ln As plus this coefficient times ln P.

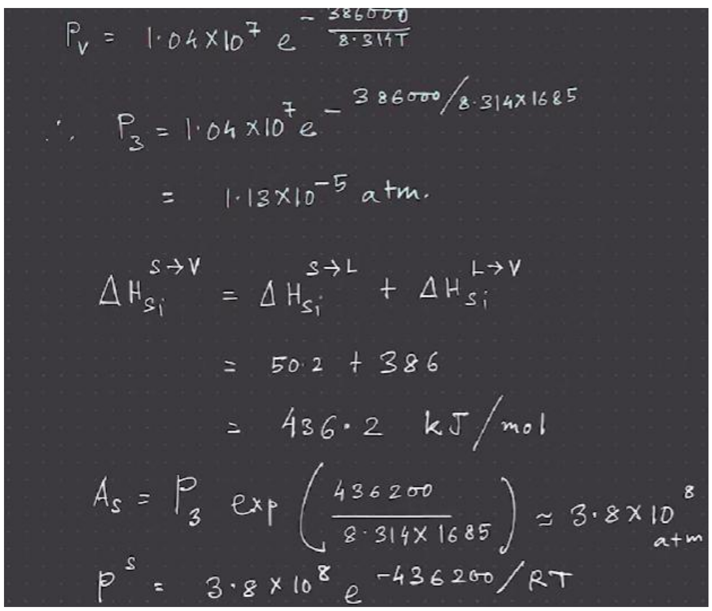
So, basically logarith, so P, if I can use a logarithmic scale, calculations become easier. further you can make some approximation that the triple point in general at one atmosphere pressure or at not one atmosphere pressure at at pressures below one atmosphere the triple points are very close to the melting point. So, how do you do that is coming this example right I was start I started with this example. So, I will go further down. So, we have this is basically phase diagram of silicon.



It is a very important material now, it is a semiconductor, so it is a phase diagram of silicon, you have to process silicon, you have to make silicon as pure as possible. Now, again look at silicon and if you look at silicon, silicon can sublimate, say basically the sublimation that enthalpy, the enthalpy of sublimation from alpha to gamma for silicon, again can be written as sum of enthalpy of melting of silicon plus right alpha to beta is melting right liquid to solid and enthalpy of beta to gamma right delta is alpha to gamma. So, alpha to gamma process is divided subdivided into two processes alpha to beta and beta to gamma. Now see, another thing, as I told in the previous lecture, that boiling point has to be greater than the melting point, right. The boiling point usually is greater than the melting point at one atmosphere pressure.

See, 10 to the power zero. So the, excuse me. So as you can see, this is pressure in the log scale, okay. We have plotted pressure in the log scale. the pressures unit is in atmosphere.

So, this is 10 to the power 0. So, 10 to the power 0 means 1 atmosphere. So, this is basically 1 atmosphere pressure and these pressures are much below, right. You can see here it is 10 to the power minus 25, right. It is 10 to the power minus 25 which is like a very very low pressure and then this is like 10 to the power minus 5.



How did I get into this point? So, basically if you now look at it, you have pressure plotted in the log scale and you have temperature on the above axis I am plotting temperature and it means at one atmosphere so you can see I have plotted here two points I know the melting point and say I know the boiling point at one atmosphere for pure silicon right this is pure silicon right I know the I know the pure silicon this is room temperature so this is one atmosphere and this point corresponds to room temperature these points corresponds to melting point and this is the boiling point so I have plotted these three points only okay now you see at one atmosphere and 300 Kelvin this part is definitely going to be this part is definitely going to be solid right and then beyond melting point this is liquid right and then beyond so this part is liquid right this is solid this is liquid and this part is basically the vapor the silicon vapor right so because it is above boiling point now this is all at one atmosphere right we know at one atmosphere now you see i have the three points I also need to know the enthalpy say for example this is the delta H of pure silicon from liquid to vapor and we know say that it has 386 kilojoules per mole right 386 kilojoules per mole at measured at 1 atmosphere and at the boiling point which is 2873 Kelvin right. So we need to know the boiling point right at 1 atmosphere so we know that. Now if I know that if I know that then basically I can calculate av, which is basically equal to pv times e to the power, now this becomes, so pv was av times e to the power minus delta hsi by RT. So, av will be pv times e to the power plus delta hsi by RT, this minus sign is not there, so minus sign has become plus, because I have taken P v on this side, so I have taken the exponent on the P v side, on the pressure side, P v side and this is the P v naught and so basically P v if I put in as 1 atmosphere then I get 1.04 into 10 to the power 7 atmosphere as A v, right.

So, basically I get A v coefficient as 1.04 into 10 to the power 7 atmosphere if I plug in this value of 386 kilojoules per mole for liquid to vapor and I plug in R and I plug in T equals to 2873 then I get this. Now I also know Tm. Now I make an assumption. I tell that in such a setting the T3 is not very much different than Tm, because Tm, T3 has to lie between melting and boiling point, right.

So, if T3 has to lie between melting and boiling point, we are assuming that, let us assume that Tm at 1 atmosphere, that 1685, that T3 at whatever be the pressure, I do not know the pressure yet, I do not know the pressure yet, but I am assuming T3 to be 1685. Now, I also know the enthalpy of transformation of silicon from solid to liquid which is 50.2. Again it is plus because solid has to absorb it and then it will transform to liquid. Now if you have all this information, what information do you have? You have this information, you have this information and you also know the coefficient Av, right.

But you are also assuming T3. Now if you are assuming T3, you can calculate P3. How? You have Pv which is basically 1.04 into number 7, right, PV is equal to 1.04 into number 7 into e to the power minus 38600.

by 8.314 T. Now, P at P3, T has to be equal to T3, right, T has to be equal to T3. So, as you can see here, first of all, I calculated Av. How did I calculate Av? I substituted PV equals to 1 atmosphere and then I looked, right, because we are looking at 1 atmosphere boiling point and then I plugged in the boiling point here and I got Av. Now, I take the same expression here, so PV equals to AV exponential minus delta HSI, so PV equal to AV times, now if I take it this way, exponential minus delta HSI L2V by RT, but we are telling T3 is the same as Tm, this is an approximation, T3 is the same as Tm and Basically, I plug in T3 here, right, if I plug in T3 here, so I get P3.

So, P3 is 1.13 in the minus 5 atmosphere. At this point, I mark this point, so I join them, I join them, right, I join them and then I have also Tb, so I join this and I go further down. Now, what is this pressure? Can anyone tell me? So, this is the pressure, this is, see, this pressure corresponds to something like slightly above 10 to the minus 25, but that's 300 Kelvin. So what does it tell you? So you think about it, but I'll tell you.

Now if you see, so I got P3. So basically I know, if I know T3 that it does not shift too much, then T3 does not shift too much from melting point if I tell, right? Why can I tell that? because T3 has to lie between Tm and Tb and in all, for all practical purposes as I go towards the, as I go towards low pressure, so it will shift more towards Tm, right, the T3, the triple point has to shift more towards Tm, so basically this point O signifies your, so this point O signifies your T3, so T3 and Tm are same and we got P3 from this expression, right, from this expression. and we have calculated Av assuming P equal to 1 atmosphere and Tb equals to 2873 Kelvin. But as you know that this equation holds true for P3 means for the temperature when T equal to T3 or the triple point temperature. So, we know the pressure. Now, you see as I told you that the enthalpy of transformation of pure silicon from solid to vapor is the sum of enthalpy of silicon from solid to liquid and enthalpy of pure silicon from liquid to vapor.

That's the sum, right? Solid to vapor is solid to liquid, liquid to vapor. So you can see here 50.2 plus 386, which is 436.2 kilojoules per mole. and basically now AS, so basically you can get now AS value, you have 1685 and what will be, this is P3, so basically from there you can get the heat of, the pressure, the pressure of sublimation, the pressure of sublimation at different temperatures.

Now tell me at temperature T equal to, at temperature T equal to say if i take temperature t equals to say 300 kelvin then find out what will be ps okay so that is one task that you have you find out the pressure okay now remember bs is the pressure of vaporization so So, here, when we are looking at here, what is the phase we are looking at? Is it the solid phase? Now, solid phase here is going to gaseous phase. Are you seeing that? So, basically the solid phase at this point, if you see, this is a critical point which basically or this is like a phase boundary point between solid phase and vapour phase. At 300 Kelvin, this is the pressure that will basically, this is the pressure of transformation or at this, at 300 Kelvin and at this pressure, solid and gas will coexist, right? Solid silicon will coexist with gaseous silicon, right? Or vapor silicon. right so find out this pressure you see whether you get a pressure which is corresponding to this this value so you have t equal to 300 and you find out the pressure okay so this is how you can check that you are more or less more or less um correct with the assumption that tm In the log, because see the variation in pressure is very, very minuscule, right, that is why I am using, so the variation, means basically like 1 atmosphere, this is 10 to the power minus 5 atmosphere where you are getting this thing, right, and you see the, for solid to vapor, the pressure has to be very, very small, right, pressure has to be very, very small for solid to vapor coexistence in silicon, right. So, and the pressure has to be reasonably high for solid to liquid coexistence.

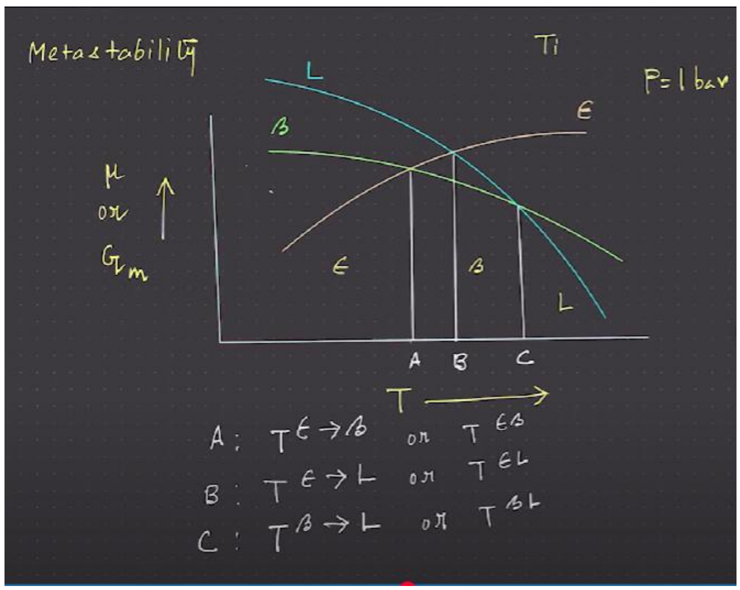
happen right and this is where solid liquid and gas right solid liquid and gas can coexist okay so that is the idea that I am trying to tell okay So this is coming from, by the way, this is a book, this is a book example. This is an example from Robert Professor DeHoff's book. So this is Robert DeHoff's book. If you look at Robert DeHoff's book on thermodynamics in material science, you will basically get this example in chapter 7.

You will get this example. It's a very nice example and a demonstration that Tm and T3 does not really... change too much. And as you can see what we have done we have taken a baseline of one atmosphere and we are looking at pressures that are lower and as we know that the triple point always will shift to the triple point where solid liquid and gas will coexist will always shift to lower pressures.

It will always shift to lower pressures. You can think of any other example you can repeat the same idea and you will basically see that the triple point is where the solid liquid gas coexistence in most of the pure substances basically shifts towards lower pressures near the melting point. So, now there is one very important example that I will give. Again, it comes from a problem that is given in an exercise in Professor Dehoff's book. So, this problem is basically, so as I told you, so this is again, the way I have drawn this, these are all, assume that these are all, basically this is not like I am taking it from a CALFAT database or something, this is an approximate analysis, but although it's an approximate analysis, it gives you a very good approximation of the actual values, okay. I am not taking the CALFED, I am not taking the database that is basically coming from the experimental data and fitting it to some curves.

I'll come to how this CALFED procedure is done. I'll give a brief about how this is done, but please try to understand these are basically approximate free energy curves and So these are basically the molar free energy curves as a function of temperature for three phases, okay, so in pure titanium. So this is the epsilon phase or the HCP phase. As you can see, as you go towards, as you are in the, lower temperature regime, so basically less than T A or T epsilon beta, A is nothing but T epsilon beta, as you are less than T epsilon beta, you see epsilon to be the lowest energy phase, epsilon, so basically below A, epsilon is the lowest energy phase, this is mu versus T, remember this is not a phase diagram, this is basically giving you three free energies, one is for liquid, one corresponds to beta, one corresponds to epsilon, this is the epsilon free energy, function of temperature. Let us assume the pressure is kept constant at 1 atmosphere or 1 bar.

Pressure is kept constant 1 bar. We are looking at the variation in free energy as a function of temperature and this is pure titanium and as you can see below TA, below TA, epsilon, right, epsilon has the lowest energy, below TA. Then between A and B, that is below TB, which is epsilon, so B is basically a very special point, so I will come to that. But as you can see, between A and C, between A and C, look at the green curve here. Look at this. This is the, the green curve corresponds to the energy of the BCC phase beta, okay.



BCC allotrop of titanium or BCC structure of titanium, okay, or this BCC phase of pure titanium which is beta, right. Now, as you can see here, in this regime between A and C, this has the lowest energy right this has the lowest energy from the diagram so basically here so here if epsilon is stable here beta is stable and here as you can see this blue corresponds to the liquid phase the blue curve corresponds to liquid phase which has higher energy up to C but beyond C titanium has so titanium has become liquid right it has become liquid so Now I will talk about metastability. Metastability is, when does it happen? Metastability is, means basically a phase that has higher energy somehow appears because the lowest energy phase somehow does not form. For example, diamond has formed instead of graphite, although graphite is the lowest energy phase of carbon, somehow due to certain conditions, you see that graphite is absent and you have formed diamond and diamond to graphite transformation does not take place at all. So it remains as it is unless you give a very large energy or there is a very large energy input, diamond will remain as diamond.

It does not convert to graphite. Okay, so you will soon see that in steels, for example, there is something called, some phase called cementite, okay, which is an integral part of pearlite, right, of pearlitic steels in cementite. The cement, the lowest form of the lowest form, the lowest energy phase, okay, at room temperature is not cementite, but it's graphite. But once cementite is formed, it does not transform to graphite. or diamond, okay, so that is the point. So see, think of this, you have now, if you, if you look at this, if you do not think of metastability, you do not think of metastability, everywhere you have epsilon, epsilon is the lowest energy phase below Ta, beta is the lowest energy phase between Ta and Tc and beyond Tc, beyond Tc or T beta liquid, This is the, liquid is the lowest energy phase, right, the blue phase is the lowest, the blue free energy curve is lowest.

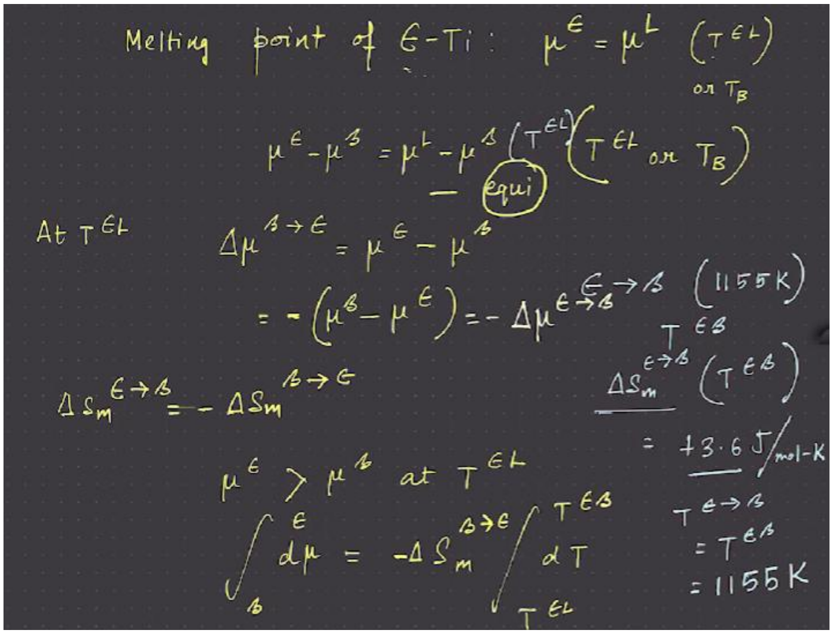
Then green free energy curve is the lowest in the A to C regime and here this orange one is the, so orange one is here, the, so if you look at that, orange one is here and the green one is here and this is where it is the liquid, right, the blue one. right so basically you can see that these coexistence happens these coexistence happens if you have no metastability now think of this so I'll just try to select this and I'll paste it Now as you can see here, I will erase this curve. Now if I erase this curve, there is no beta. There is no beta. And you have now only one, one, only one Temperature here because now beta phase does not exist.

Beta phase which was a stable phase at the intermediate temperature between A and C does not exist. If that does not exist, then these lines are also not there. Now you have epsilon L coexistence. You have epsilon L coexistence, right? So epsilon is the low temperature phase, okay? And liquid is the high temperature phase.

So epsilon converts to liquid. So we are telling now find T epsilon L. So, what we told, I know 2T epsilon beta, which is the equilibrium transformation. So, I know T epsilon beta, right, which is basically A point. I know T beta L, which is again an equilibrium point. I want to find T epsilon L, which is basically, see, the T epsilon L should not have appeared.

If there would have been beta, then T epsilon L does not exist because this is that much higher the energy is much higher than the green phase right the green green curve the green curve corresponds to beta phase so beta phase will obviously appear below this right so basically beta phase is more uh more favorable here however because of some reason beta is not formed so what is this temperature and that's what i am telling here okay so this is basically where the beta phase which is the more stable phase at the temperatures between A and C right at the at temperatures between A and C beta phase is the more stable phase but it is somehow absent it did not form so now you have a metastability between epsilon and L right a metastable equilibrium between epsilon and L right now you want to find out this Okay, now see, think of this. We know, now you want to find out this, right? Relating point of epsilon ti. You want to find out relating point of epsilon ti. Again, when you do Any such problem, any such problem, as you have seen before, whenever I have given examples, whenever I have given examples, what I have done, I have gone to the final expression, then I have put values.

Then I have put values. I don't put values from the beginning, okay, because then sometimes you may make mistake in getting the correct expression. First of all, if you think of melting point of epsilon ti, you have to think of this equilibrium, right, the free energy of epsilon, this is the metastable equilibrium, that the free energy of epsilon equal to free energy of liquid, that's a metastable equilibrium. Now, think of this, if mu epsilon equal to mu liquid, I can take mu beta out on both sides, so now you have mu epsilon minus mu beta equal to mu L minus mu beta, now if you think of this, the way we have written that means this is delta mu beta to epsilon and this is delta mu beta, this is delta mu beta to epsilon which is basically minus of delta mu epsilon to beta, which is minus of delta mu epsilon to beta. And this is happening at what temperature? This is happening at T epsilon L.



So that means this equation is also valid at T epsilon L. And we want to know what is T epsilon L. So now think of this. You also know, for example, the delta SM, that is the entropy change, obviously the entropy, so the more stable phase, that higher temperatures, the more stable phase will have more entropy. So if you think of that, then delta SM epsilon to beta, which is SM beta minus SM epsilon, which is equal to plus 3.6, right? SM beta minus epsilon epsilon at 1155 Kelvin. So TA equals to, so basically T epsilon to beta is equal to or T epsilon beta in short is equal to 1155 k and for epsilon to beta transformation at T epsilon beta temperature that the entropy change is plus 3.6 joules per mole Kelvin remember it's plus 3.6 moles per joules per mole Kelvin and as you know that at T epsilon L Okay, as you know from this curve that at T epsilon L, the free energy at T epsilon L, nu epsilon is greater than mu beta, right, the free energy of epsilon is greater than free energy of beta at T epsilon L. So now think of this, you are doing an integration, okay, you are doing an integration. okay and also remember we are doing it at constant pressure and you know mu equals to minus s small s okay this is entropy per mole dt plus v dp and its constant pressure so it is minus s dt because dp goes to zero so you have minus sm dt okay so similarly you can write d mu beta to epsilon is minus delta sm beta to epsilon remember it is minus delta sm phi it is minus s dt And you see, you are going from beta to epsilon, right, minus delta S m beta to epsilon, okay.

$$\mu^{\epsilon} - \mu^{\beta} = \Delta S_m^{\epsilon \to \beta} \left(T^{\epsilon\beta} - T^{\epsilon L} \right) \quad \text{— (1)}$$

$$\int_{\beta}^{L} d\mu = -\Delta S_m^{\beta \to L} \left(T^{\beta L} - T^{\epsilon L} \right)$$

$$\mu^{L} - \mu^{\beta} = -\Delta S_m^{\beta \to L} \left(T^{\beta L} - T^{\epsilon L} \right) \quad \text{— (2)}$$

From (equi), (1) = (2)

$$\Delta S_m^{\epsilon \to \beta} \left(T^{\epsilon\beta} - T^{\epsilon L} \right) = -\Delta S_m^{\beta \to L} \left(T^{\beta L} - T^{\epsilon L} \right)$$

$$\therefore \Delta S_m^{\epsilon \to \beta} T^{\epsilon\beta} + \Delta S_m^{\beta \to L} T^{\beta L} = \left(\Delta S_m^{\epsilon \to \beta} + \Delta S_m^{\beta \to L} \right) T^{\epsilon L} \quad \text{— (3)}$$

And what is the temperature? You started with T L, right, you were here, you were in the T epsilon liquid, right, that was your temperature, right. This is the equation we have written at T epsilon liquid, right, this is T epsilon liquid or T b. So, this equation is valid at T b, right. So, if you see, we are starting with T epsilon L and we are going to T epsilon beta.

Now, you please note that this is beta to epsilon. So, basically you are looking at beta to epsilon transformation. Now, beta to epsilon transformation, so this is basically epsilon to beta transformation which is plus. So, beta to epsilon will be negative. So, basically, so delta, minus delta sm beta to epsilon is nothing but delta sm epsilon to beta. and this is nothing but t epsilon beta right this is t epsilon t epsilon beta minus t epsilon liquid so this is your first equation so this is your first equation mu epsilon minus mu beta is basically delta s epsilon to beta t epsilon beta minus t epsilon liquid now remember t epsilon beta is lower right according to our our curve d epsilon beta is at a lower temperature than this is higher temperature right and this is delta sm epsilon to beta okay now you see mu epsilon is greater than mu beta is what we have, we know, right? But now this mu epsilon is greater than mu beta at T epsilon liquid.

Now but at T epsilon beta, just below T epsilon beta for example, mu epsilon is less than mu beta. right so these are the things that you have to understand and from and if you see i just use this equation mu equals to minus stt to get this equation right and i have taken t epsilon l as a reference right this is the temperature that i want to find out right but t epsilon beta the equilibrium temperature is known and we know delta sm beta to epsilon Okay, beta to epsilon at, so I know say for example delta SM beta to epsilon. Now I have made an approximation here. I am telling that I know the delta SM beta to epsilon or epsilon to beta at the transmission temperature T epsilon beta but I do not know at T epsilon liquid but I am assuming it to be the same, that's why I have taken it out of the integration, otherwise I should have known this variation and I should have, so this is an approximation that we are using, right, that is an, this is an approximation, because delta SM can be a function of temperature and it will change from one equilibrium temperature to another, so this is the metastable equilibrium temperature, that is the epsilon, this is the epsilon beta equilibrium temperature, at this temperature only I know this, but we are assuming that we, this is the same here also.

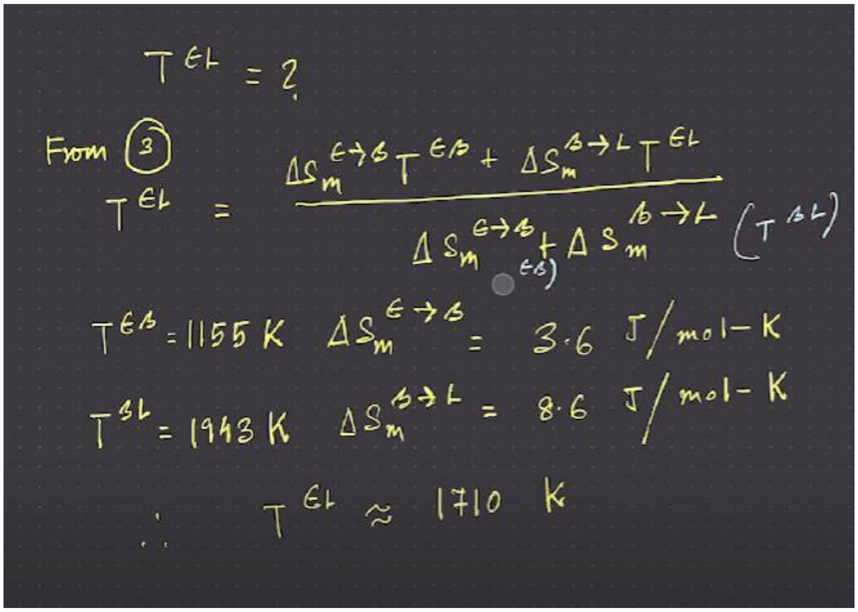
Okay, so now we are telling this equation. So that's how we arrive at this equation. Similarly, from beta to liquid, you have minus delta SM beta to liquid. Now beta to liquid is all are equilibrium. Only thing that you have to remember that you have T epsilon L as the reference temperature.

That is the starting temperature. So minus delta SM beta to liquid, again minus delta SM beta to liquid, T beta liquid minus T epsilon liquid. Here remember T beta liquid is greater than T epsilon liquid. This is less than T epsilon liquid. Now, you see mu L minus mu beta is this.

Now, this is your equation number 2. So, equation number 2. Now, if you see, this I have labeled as equi. So, equi tells you this equal to this, mu epsilon minus mu beta equal to mu L minus mu beta at T epsilon, liquid. So, we are telling that from equate 1 and 2 are equal, right, 1 and 2 are equal because all of these we are looking at the changes, but we are looking at the changes from the same reference state which is the T epsilon liquid which we do not know. Now, if I do that, if I equate that, then I basically get this relation delta S m epsilon to beta T epsilon beta minus T epsilon liquid equal to minus delta S m beta to liquid T epsilon beta liquid minus T epsilon liquid.

Now if I arrange a little bit, I get this. See delta is same as 7 to beta. So basically this one, this guy and this guy and this guy and this guy I am taking to the same side. So this times this and this times this and see there is a minus sign. So if I take it here, then it becomes plus. And this is this. So basically now you want to find out Tf sine liquid and as you can see Tf sine liquid terms I am taking to the, so this term I am taking to this side.

So if I do that the minus sign minus sign so it is plus sign. And this also has a minus sign, so this becomes plus. So, this becomes just a summation of this times T epsilon liquid, delta S m epsilon to beta, beta to liquid. See, if you see, there is a very interesting connotation here. See, epsilon to beta, beta to liquid, the sum is there.

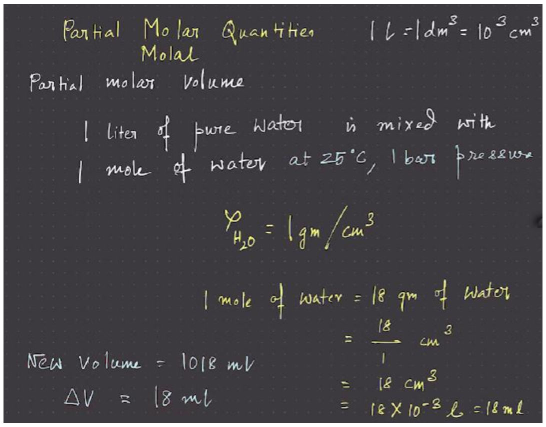


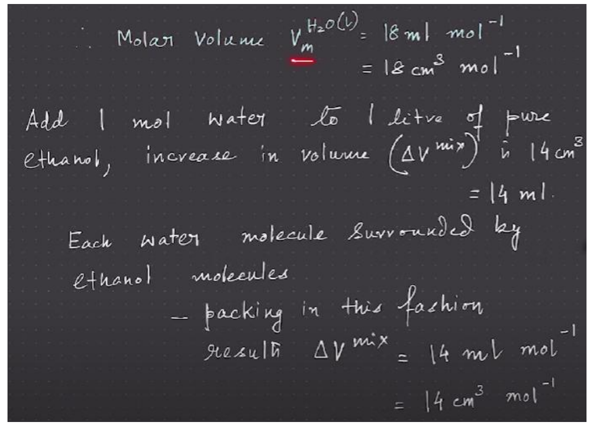
So, this is basically delta S m epsilon to liquid at T epsilon liquid. So, basically I want to find out, but I still do not know T-acid and liquid again. These we know at the transformation temperatures. Remember, we know this as T beta L, this we know at T epsilon beta right these these but we are assuming that the values do not change the values do not change at t epsilon liquid okay if we use this approximation since i know these values now see i am plugging in the values if i plug in the values then basically i get and this is delta some epsilon to beta is 3 plus 3.6 beta to liquid plus 8.6 so what we get is t epsilon liquid equal to 7 17 10 kelvin Right? We get 1710 Kelvin.

Think of this now. It's very, very interesting. This is 1155 Kelvin, which is epsilon beta coexistence. And what is the beta liquid coexistence temperature? Beta liquid coexistence temperature is 1943 Kelvin. So, if you see this, if you see the curve, this is 1155 Kelvin. How much is 1155? Yeah, 1155 Kelvin.
and this is 1943 and this we found out to be 1710. Basically, if you do with any CALFER, later I will show you that even with CALFER databases, you will get very close to this temperature when you are looking at this metastable epsilon to liquid transmission. Okay, remember metastable epsilon to liquid transformation only can happen if beta phase somehow does not form in the system. Beta phase is not formed, although beta phase has lower energy, right? So metastability is always greater than, means in terms of energy, metastability is having a, metastable equilibrium has a higher energy corresponding to the stable equilibrium. Stable equilibrium is the lowest energy state. So if I say the stable equilibrium does not happen, then what you, now look at is, is there any metastable equilibrium in the system.

So, this is how we do the analysis. So, this is one example I gave you. I think that this makes sense to you and if it is not, you please let me know where you are not understanding in the comment section, then I will definitely try to answer as quickly as possible. So, this you do not have to care about. So, I have already done this. So, you do not require to look at this. Means this is one more approach by which you can get it, but I do not think that is required.

Again and again what I am trying to say, only thing that see I have come up with an expression I have come up with an expression where I haven't used any values. At the end only from, in this expression, in this expression that I have derived, I plug in the values and I get the metastable transmission temperature. So this is something that you should follow. Now I come to a very interesting topic called Thaunian sub-solutions or mixtures.





You can call it Thaunian sub-mixtures. Mixture means you are now looking at a multi-component system. However, I will in this case, in this particular case, I will think of a multi-component So there can be solution, say for example, salt dissolving in water. So you have two components, salt and water, and it forms a solution or a mixture, right? Or sugar-water mixture, or say for example, copper-nickel mixture, like copper-nickel alloy, it's a mixture of copper and nickel, okay, which forms a solution, okay? A solid solution, you can have a liquid solution where two liquids are mixing, for example, water and alcohol, or water and oil, okay at some high temperatures they mix so or if so two liquids mixing is one case a solid dissolving in a liquid is another case or uh two solids mixing is also another case okay these are all like one is a solid solution one is a liquid solution one is um some sort of a see ultimately sodium chloride is mixing with sodium a solid mixing in a so in a dissolving in a liquid site forming a solution so we are looking at all of this however we are looking at non-reactive So, we are not, currently we will not consider reaction, but soon I will consider it, but this is a non-reacting system. Currently we are considering multi-component non-reacting system. The first thing that comes in is i will define now formally that see i have already defined something called a partial molar quantity but i will tell you what does it so for example i have introduced chemical potential right for a multi-component system i have already done it so these quantities like chemical potential are called partial molar quantities or partial molar some books like de hoff's book calls it molal okay so partial molar or partial molal quantities.

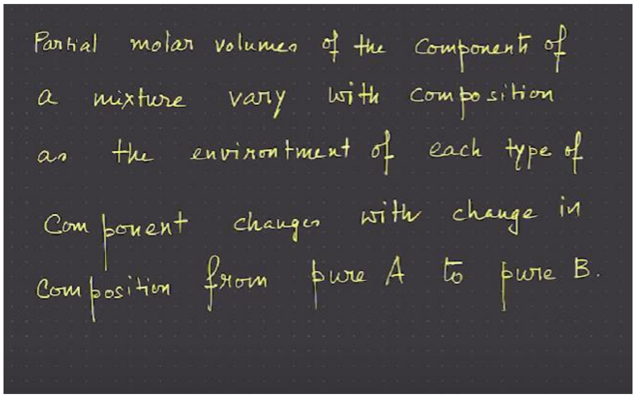
Okay, so partial molar, in DeHoff's book it is called, instead of molar, DeHoff writes it as molal quantity, partial molal Okay, now, so think of this, you have a liter of pure water and is mixed with one mole of water. One mole of water at 25 degree Celsius, one bar pressure. Now, raw water is one gram per centimeter cube that we know and one mole of water contains 18 grams of water. So, 18 grams and divided by density gives me 18 centimeter cubed, which is like 18 to the power minus 3 liter or 18 milliliters.

18 milliliters is the same as 18 cc. So, basically the delta, so new volume is, the new total volume is 1018 ml because it was 1000 ml, 1000 ml to begin with. Now, you have mixed

water with water. So, it has gone to 1018 and you get delta V, which is 18 ml. Now, see the, now you will see an interesting problem.

Now if you have, so you have this molar volume of water which is 18 cm3 per mole. We have mixed 1 mole of water and you are basically when you mix 1 mole of water you raise the volume by 18 milliliters or 18 centimeter cube. So that means the molar volume of water has to be 18 centimeter cube per mole. Now think of this, you have 1 mole of water but you have 1 liter of pure ethanol and there is an increase in volume but this delta V mix now is 14 centimeter cube. or 14 ml. Why? See, it has to be, see you have the same one mole of water, so it should have raised by 18 millilitre or 18 centimetre cube, but it has raised only by 14 ml.

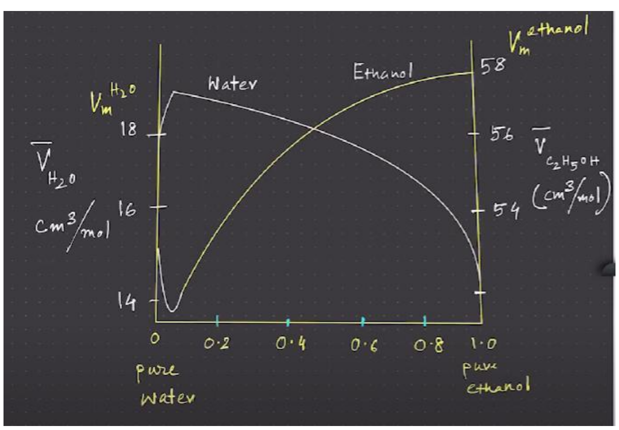
This is because of the association of water molecules with the ethanol molecules. What will you see if you look at the microstructure, if you look at the, if you look under a microscope, you will see, means a powerful microscope, you will see that each water molecule is surrounded by ethanol molecules. Again, each Ethanol molecule is surrounded by water molecule. So there is some pack means, so the packing happens in this say fashion like you have water molecule, you have say a water molecule and then there is this ethanol molecules and then again you have one water molecule each water molecule is surrounded by several ethanol molecules and each ethanol molecule is separate. So, basically if you go to a water molecule you will see in surrounded by ethanol and if you go to a ethanol molecule you will see it surrounded by water.



So, in some way this association has taken place and that results in a delta V mix which is less. The association that has happened, the association that has happened has reduced the increase in volume. It is no longer 18 milliliter is now 14 milliliter okay because of this association something has happened some packing some interaction something has happened in such a way that the delta v mix has come out to be 14 milliliter per mole so now now think of this now think of partial molar volume what is the definition of components of a mixture vary with composition as the environment of each type of component changes with the changing composition from pure A to pure B. So pure A for example is a pure ethanol and pure B is like pure water. Now as you change from pure A to pure B, pure ethanol to pure water that means I am adding some little bit of water to pure ethanol Every time my association is changing, association between A and B is changing, right? Because A is surrounded by B is surrounded by A like that. So as a result, the volume, the, the, the, the, the, the, the amount of volume that will, that the volume, that overall volume change the solution.

can basically be less than that where with pure water or with pure ethanol. Like we have pure ethanol, you add some little bit of one mole of ethanol, you will get a molar volume of ethanol. Now, if you add water to one liter of water, you will get some, the one mole of water, you get molar volume of water, right? You get molar volume of water, the exact molar volume of water, when you add one mole of water to one liter of water and find the change in volume. That change in volume is the molar volume of water. Similarly, for pure ethanol, if you add one mole of ethanol and you find the change in volume of the mixture, then you can tell that is the molar volume of ethanol. however when it changes from a to b that is from pure ethanol to pure water right you are adding more and more water so that you know you go to such an extreme dilution that ultimately it's all pure water there is no ethanol left but you think of this as you change from pure a to pure b what is happening is because of the association between a and b and because of the interactions between a and b What you will see is the volume change, the delta V does not correspond to the molar volume of ethanol or molar volume of water.

It is something different because of the way association has happened. We will look at how this association happens, what are the different interactions that can happen like AA interactions can happen, BB interactions can happen, AB interactions can happen. Which interactions are stronger, which interactions are more favorable. All these things basically lead to this change. Okay. And that change, that change, that the amount of the contribution of water to the volume change of the mixture of ethanol and water is what is called as partial molar volume.



So if you think of this, see this is the partial molar volume of water. So this is again from Atkins book. I have erupted this drawing. So if you look at that, this is partial molar volume of water. This is partial molar volume of ethanol, pure ethanol in centimeter cube per mole. as you can see this is basically if you think this this is basically changing now this is 0 to 1.0 so here you are looking at like say for example you think about it okay so you think about it which is so if you are looking at this you are having a 14 so if you drop here so you as you can see the partial molar volume of ethanol so partial molar volume of ethanol here is low on this side is low on this side it is very very high right on this side it has increased so is it so and again for water it is here quite high which is 18, are you seeing that 18 centimeter cube per mole.

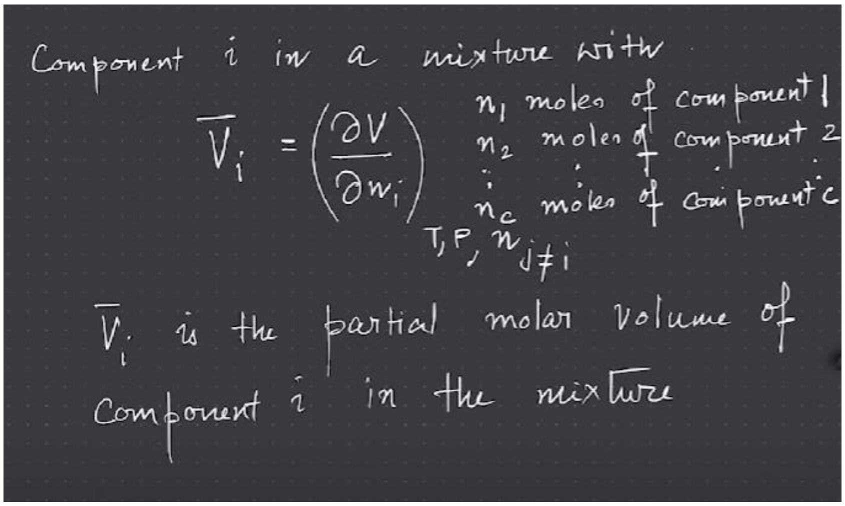
So, that means this is the pure water. So, it was 18 like pure water which is basically zero ethanol and this is pure ethanol. which has 58. So, this 58 number and 18 number are basically the molar volume of water itself, VH2O, VM, basically you can call it like VMH2O, when you have pure water and this is VM ethanol. but as you can see it is changing right it is changing from it has it when you go towards pure water it has not roughly gone to you know zero or anything right but it has some value here actually this is an approximation here In general, if you look at it, you will say that it has gone to a very, very low. So basically, if you see it's a pure alcohol, it's like pure alcohol, then it's not, so zero to one is not, is some sort of an exaggeration, but you can see that at pure ethanol end, at pure ethanol end, the molar volume of water has changed to 14.

It has changed to 14. See like this. Pretty near pure ethanol, it has changed to 14. So, you remember, please note that the partial model volume does not exist. Basically, it is like an, if you see that it is going towards 1 and it is going towards 0. So, it is not like, it is like 99.99%. It means it is like a, it is not full, one pure ethanol, if you think that way also is fine, but it is like pure, now pure ethanol has a molar volume as you can see as 58.

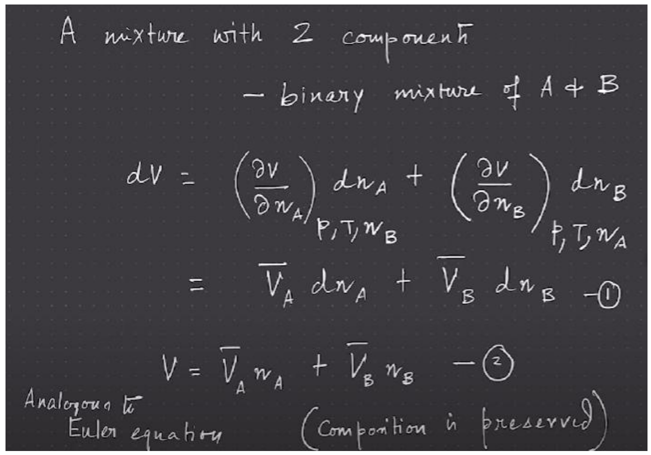
So, now I am telling in that approximation means the concentration of the solvent tends to pure ethanol at that concentration where you add some water, 1 mole of water, which is very little amount of water in a very large volume of ethanol, then the volume, the molar volume contribution is coming out to be 40. right and then it rapidly increases as it increases as you can see this is the molar volume of ethanol right molar volume ethanol increases increases increases and as it the partial molar volume it goes to It goes to, so this is for the ethanol. This is corresponding, this is the V bar that I am plotting in this curve. This is the V bar that I am plotting in this curve, okay, of ethanol, right? So this is the molar volume of ethanol.

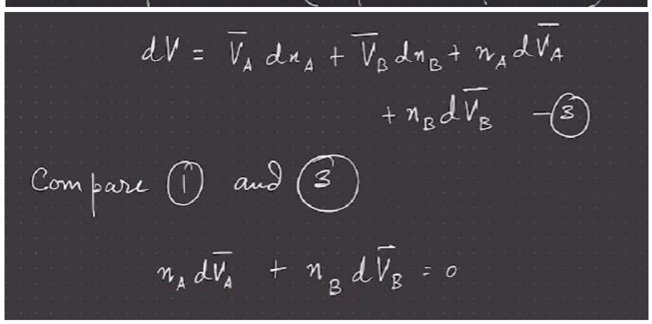
How does it change? How does it change? It changes, it drops. You see, molar volume of ethanol drops as you increase the amount of water. molar volume of ethanol drops as you increase the amount of water. And it goes to somewhere like between 14 and 16, something like 15. But if you look at molar volume of water, as you increase the ethanol content, it goes from pure water and then it decreases, it decreases and it decreases up to 14.

It goes to like 14. As you have like nearly 100% ethanol. Obviously, it is not fully 100 percent ethanol, then water is not there, but water is there, it is a very high volume of ethanol and water is very very small, it is like dilute solution. So, I will talk about dilute solution, I will talk about Raoult's law and all. So, but you have to understand the concept, the concept is this, partial molar volume is the molar volume concentration or molar volume, the change, the contribution of water to the change in the overall volume of the mixture of ethanol and water.



So you have a mixture of ethanol. So please try to understand the concept here. You have a mixture of ethanol and water. plus water solution you can call it water solution now in this solution what is the contribution of water okay if water is the solute and and say ethanol is a solvent that means ethanol is in much larger proportion now what is the partial contribution of water to the overall volume of the mixture overall volume of the mixture this is what is basically defined as the partial molar quantity or partial molar volume. So, that means if you have a mixture where you have N1 moles of component 1, say N1 moles of ethanol, N2 moles of water and you have some Nc moles of some ink and so on. So, you have all of these and you are mixing it. Now, if you want to find say the molar, the partial molar volume of component i. okay, partial molar volume, note the very important term here, distinction here, you are looking at partial molar volume of component I, you want to see the overall volume of this mixture, how the overall volume changes as a function of change in the mole number of I, keeping temperature, pressure and mole number of all other components fixed, if you see the partial molar volume is This Vi bar then is termed as the partial molar volume of component I or contribution of component I to the total volume in the mixture.



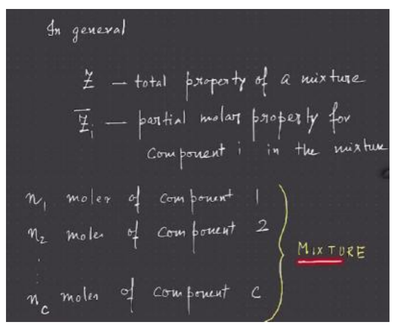


Okay, so the partial molar volume is the contribution of one of the components to the total volume of the mixture. Okay, so if you have a mixture of two components, for example, you can write and say you are taking fixed temperature and pressure, then you can write an exact because volume is an exact differential, right? Volume is an exact differential. It's a function of temperature, pressure, mole number of A and B. So it's a binary mixture of A and B. So, mole number of A is N A and mole number of B is N B, then dV equals to del V del N A, where P and T are fixed, again P and T I have kept as fixed, ok. So, that is why I did not care about writing that term with dP and term with dT, because dT and dP are equal to 0, right, at fixed pressure and temperature.

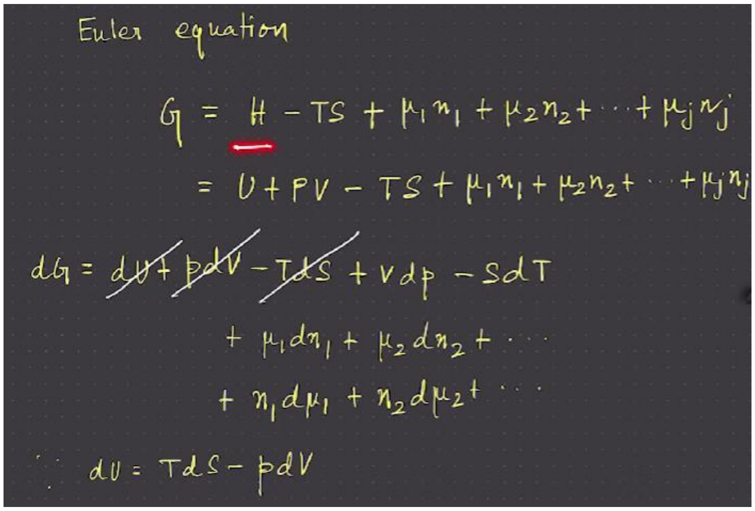
Now, you have del v del n a p t n b into d n a right plus del v del n b and differential of n b and you have here p t and n a constant. Note that here n a is constant, n a does not change, here n b does not change. here i am looking at the change in volume overall volume due to change in mole number of a due to change in mole number of a keeping pressure temperature and n b constant in the other way it is like change in volume due to change in mole number of b keeping pressure temperature and n a constant now this you can express as v bar d n a plus v bar b d n b now think of Euler equation. Euler equation tells you V is nothing but V bar NA because you have done this Euler equation.

So, it is analogous to Euler equation. See, ultimately, if you integrate this, for example, the amount of NA and NB are fixed, say. If the amount of NA and NP are fixed, so you are going from, say, if you want to integrate and if you want to integrate and if you want to integrate, it goes from 0 to NA and this goes from 0 to NB. But overall NA and MB are fixed. So amount of NA, if I add more NA, I have to take out some MB.

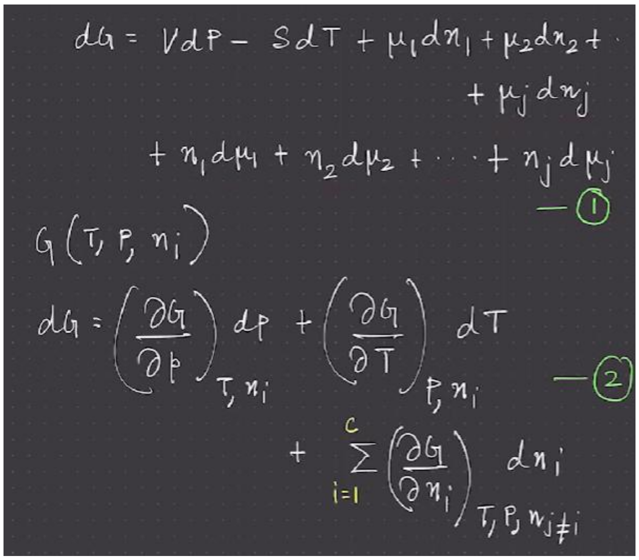
So basically, if that is so, then basically you can write that V equals to nothing but V bar ANA plus V bar MB. This is exactly analogous to Euler equation which we wrote as u equals to pv minus Ts plus mui ni. So, if you do that then dv equals to v bar a dna plus v bar b dnb plus na dva bar. See, there is a na and the differential of the molar volume of A and there is a differential of the molar volume of B.



Now, compare three. and 1, compare this equation, compare this equation to 1. Now, if you do that, you see Va bar and Vb, see Na dVa bar change in the differential of the molar volume of component A and differential of the molar volume of component B. So, differential of molar volume of component A is weighted with the mole number of A and this is weighted with the mole number of B, what you are getting Na dVa bar plus Nb dVa bar equal to 0. So, that is the idea. So, in general, if Z or Z represents total property of a mixture, Zi bar or Zi bar is a partial molar property of component I in the mixture.



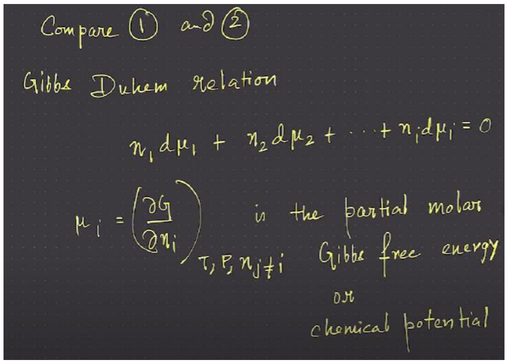
Partial molar component, property of component I in the mixture is given by Zi bar. You have N1 moles of component 1, N2 moles of component 2, Nc moles of component C in the mixture. okay so and as you know this z you can identify z with g also say for example euler equation for g argues for energies h minus ts plus mu 1 n 1 see this i have all defined i have defined and derived right so it becomes this right which is h minus ts is nothing plus u plus bv minus ts mu 1 n 1 mu 2 n 2 up to mu j n j right you have say n j j components Now, as you know, if I do dg, dg is du plus pdv minus tds plus vdp, right, pdv plus vdp and this is minus sdt, then mu1 dn1, mu2 dn2, n1 dmu1, n2 dmu2, right. Now, if you think of that, You have du, since du is TdS minus PdV according to first law.

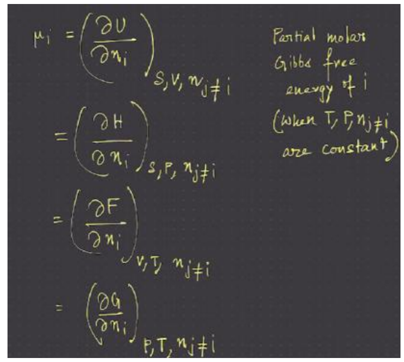


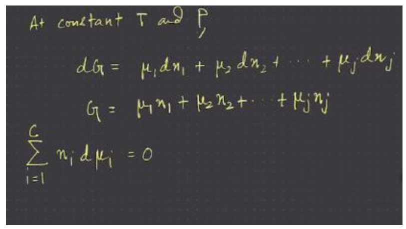
So, du, PdV and TdS cancel. So, you have VtP minus SdT and all these terms, right.

Now, what I am telling is this is VgV minus SdT plus all these terms, right. So, this is your equation 1. But we also know g is a function of temperature, pressure and mole number and we can write an exact differential. which is del g del p t n i which is basically v del g del t is minus s d t p n i constant and there is this summation right we are writing this this entire thing as summation del g del n i d n i right del g del n i d n i remember del g del n i d n i this is a alternate way this is the exact differential right that is the exact differential and it's a function of temperature pressure and mole number of different components i right i varies from one to c say so it's an exact differential way and this is coming from the euler equation if you now compare one and two you get what is called a gives to m relation remember for all partial molar property whether it is partial molar volume whether it is partial molar enthalpy partial molar entropy partial molar gives free energy Or partial molar gives free energy is basically nothing but chemical potential, right? So you have already seen this that gives Duhain relation basically gives you n a n 1 d mu 1 plus n 2 d mu 2 plus n i d mu i equal to 0 and mu i is del g del n i t p n j not equal to i right j not equal to i because we are changing mole number of i we are not changing mole number of any other component which is the partial molar gives free energy and or more commonly known as chemical protection.

of component i in the mixture or the solution. So in the next, in the subsequent lecture, the last lecture, I will continue with this and I will show how differently, say for example, mu i can be written as del u del n i as you remember that all of these are related by Legendre transform and you basically replace one by the other. So for example, del u del n i, you are taking s, v and n j constant. in del h del n i you are taking s and instead of v you are taking the conjugate right which is p right s p and n j constant del f del n i which is basically the helmholtz free energy you are taking v instead of instead of instead of s you are replacing it with t and p you are replacing with v right so physically if you think of this s and v and n so here you have taken v is there but t right instead of s you are taking So, basically s and as you remember t, s are conjugate, have conjugate relation, p, v have conjugate relation, mu, n have conjugate relation, right. So, basically if I am looking at mu, so I do not care about this conjugate relation, but see ultimately if I instead of s and v, I replace it by p and t, right, s and v I replace by p and t.







I basically get the chemical potential in terms of Gibbs free energy. So, this is a change in Gibbs free energy, total Gibbs free energy. Remember, G here is an extensive quantity, it is not Gm. G is an extensive quantity, the change in total Gibbs free energy as a function of, due to change in mole number of component I keeping all other components mole number constant and pressure and temperature constant. okay so this is how we will continue in the next lecture we will continue and see that what are the consequence of this and how to model this and how to create this different models of solution right quasi chemical models i will come to that okay so in the following lectures in some of the following lectures again if you have any problem in understanding the concepts, please drop a line in the forum and also I am going to, I am trying to arrange to give you all the solutions up to week 8. Once week 8 is completed, I will give you all the solutions, the consolidated solutions from week 0 to week 8 assignments. So, in fact I am planning to conduct a live session after week 8. I will let you know once everything is finalized. Thank you.