Thermodynamics And Kinetics Of Materials

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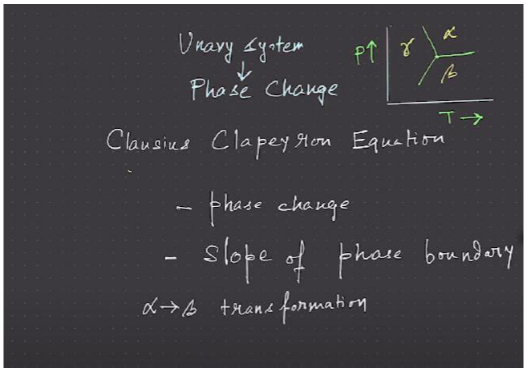
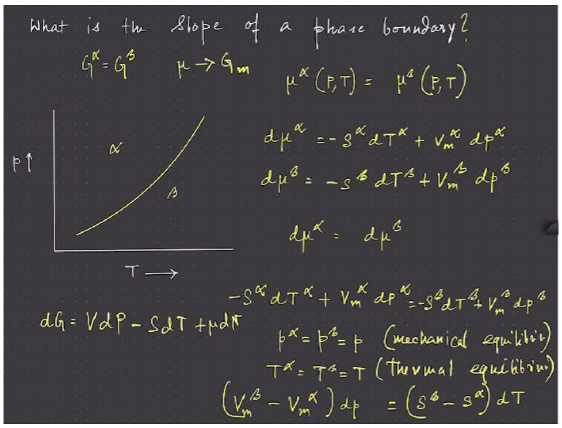
Lecture 20

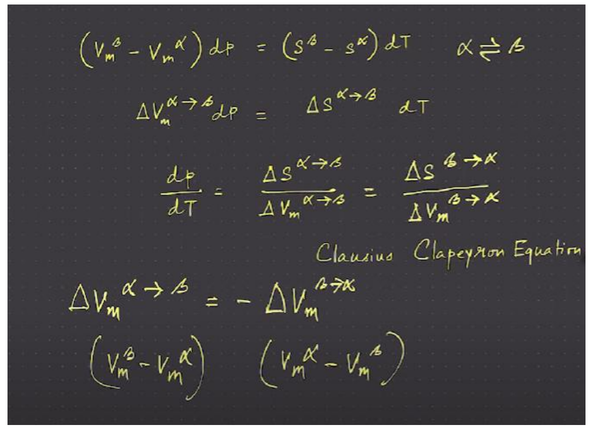
Applications of Clausius-Clapeyron Equation

Welcome to this first lecture in week 7. So I will start, I will just reprise some stuff that we have learnt during phase change in unary. So we discussed unary systems, right, and in an unary system we discussed something called phase change. So phase change and phase equilibria in unary systems. So we looked at these. So for phase change, as you know, and we also looked at the phase diagrams in unary systems, and we remembered that the phase diagrams we drew, usually you can draw different types of phase diagrams, mu t, v t.



But in general, the phase diagrams that are drawn are having pressure. pressure as the y-axis and temperature as the x-axis and we also saw some sort of like a triple points and all this stuff and we looked at means how the phases will coexist and all and we if you remember we told that we introduced Garcia's weapon equation and we told that the DP DT that is a slope of the phase boundary slope of the phase boundary here for any transformation say for example you have three phases you have say gamma phase here beta alpha phase here beta so gamma is here beta is here so you are telling that in such a case gamma alpha phase boundary or gamma beta phase boundary or alpha beta phase boundary the slopes will be given by Clausius Clapeyron equation okay so this is something that we discussed but i just want to reprise because we want to see for different types of systems for example a system that contains only condensed phases like for example solid liquid transformation Or let us look at liquid vapor transformation or solid vapor transformation such as sublimation. How does the phase boundary slope, how does the slope of the phase boundary change? okay so we have to look at what is the slope of the phase boundary this is basically a reprise of the last lecture so slope of the phase boundary how do you calculate you first you first know that if two phases are in coexistence right or they are in equilibrium alpha and beta are in equilibrium then g alpha has to be equal to g beta g alpha the free energy of alpha phase has to be equal to the free energy of the beta phase at any given pressure temperature combination, which is along the phase boundary, right. So, basically, here, so let us look at these points.





For example, if I am looking at a point here, alpha and beta are in coexistence at this temperature, at this temperature and at this pressure, right. This is the pressure, this is the temperature at which at this point alpha and beta are in equilibrium. Again, let us look at this point. If you look at this point, then this is the pressure and this is the temperature right at which alpha and beta will be in equilibrium right so for example so so or say for example at this point again you have this pressure and this is your temperature right that at this point so along the phase boundary all points represent the equilibrium between alpha and beta at right along the phase boundary all points each point along the phase boundary points represent equilibrium between alpha and beta and the equilibrium between alpha and beta corresponds to a certain pressure and a certain temperature so in such a case as you know g alpha equals to g beta now you have only it's a unary system so it's a unary system that means you are basically looking if you are looking at partial means if you are looking at the chemical potential chemical potential is nothing but the so in this case the chemical potential of all say chemical potential of some component there is no other component there is only one component so the chemical potential is nothing but mu is nothing but gm that is the molar free energy right mu is basically molar free energy so mu alpha that means is the molar free energy of alpha phase equals to molar free energy of beta phase now as you know that d mu alpha this is something that we know right that means this is from that dg equals to vdp minus s dt right we know dg we know we have done this uh DG equals to VDP minus SDT. see there is a plus mu dn but here n equal to means that basically there is only one component so if i if i divide by n then what we get if i divide by n n is the number of moles of that component then dg by n which is basically g by n here is nothing but mu equal to vm vm basically is the molar volume vm dp minus is d t or you can also write S m d t, S basically the small s, lowercase s basically represents, lowercase s basically represents the entropy per mole, right, so the entropy per mole.

So, this is coming from d g equals to V d p minus S d t, okay. So, if I have and then you have also mu d n here, but as you know that you have only n moles of component 1. So, if you divide by n on all sides, then basically n by n is nothing but 1 and d of 1 is 0, right. So, basically d mu equals to V alpha, V, Vmdp minus lowercase s dt and lowercase s represents the molar entropy. So, so basically, Mu alpha represents molar Gibbs free energy of alpha phase.

This is molar entropy of alpha phase. This is molar volume of alpha phase. Similarly for beta, this is molar Gibbs free energy of beta phase, molar entropy of beta phase and molar volume of beta phase. And you have d mu alpha equals to d mu beta. d mu alpha equals to d mu beta.

So, you get minus s alpha dt alpha. So, if this is so, then these equal to this, right, these and these are equal. So, this equals to this. So, if that is so, minus s alpha dt alpha plus vm alpha dp alpha equals to minus s beta dt beta plus vm beta dp beta. Now, as you know, at equilibrium, the pressures have to be equal, right? For all phases, all the phases that are existing, the pressures have to be equal, right? There should be no difference in pressure, right? If you remove all the internal constraints, right? This we have proved for different subsystems or different phases.

that are basically separated by phase boundaries and these phase boundaries are basically like constraints and if you remove all internal constraints basically you make the boundary flexible that is responsive to volume change and the boundary is diathermal and the boundary is permeable to diffusion or mass transfer. Again, here there is no mass transfer because there is only one component or one species available but this comes from mechanical equilibrium right this is basically nothing but the mechanical equilibrium that pressures so since alpha and beta are in equilibrium therefore the pressures inside alpha and inside beta have to be equal when the alpha when alpha and beta are in equilibrium similarly there is thermal equilibrium right so this is coming from mechanical equilibrium mechanical equilibrium and this is coming from thermally now See, there is no additional species, this is a unary system. So, you have only mechanical and thermal equilibrium to consider, right, because the chemical equilibrium, which is for each species, is not required, right, here it is not required, it is a unary system. Now, if you see, then P alpha and P beta are basically same as P, right, some common value P, and T alpha and T beta are equal, and they are equal to some common value T. So, then, If you rearrange, you get this.

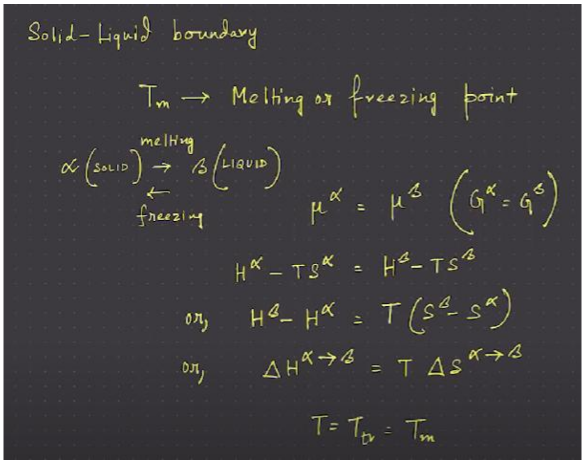
If you rearrange, you get this. Vm beta minus Vm alpha dp equals to S beta minus S alpha dt. So, now Vm beta minus Vm alpha is delta Vm alpha to beta, right. Vm beta minus Vm alpha is basically, according to our convention, that is the delta Vm that is change in molar volume when there is a transformation from alpha to beta right delta Vm alpha to beta note that this is very important to note delta Vm alpha to beta is just the negative of delta Vm according to our convention beta to alpha because alpha to beta means the way we calculate alpha to beta basically Sorry, so the.

.. Yeah, so delta Vm alpha to beta equals to minus delta Vm beta to alpha, and delta Vm alpha to beta is nothing but Vm beta minus Vm alpha, while this is equal to, so this is this, this is basically Vm alpha minus Vm beta. See look at the arrow sign. If you look at the arrow sign then you will see so beta to alpha. So it is like so basically beta to alpha transformation how much is the volume change. So then what we are doing Vm alpha minus Vm beta.

If it is alpha to beta transformation it is Vm beta minus Vm alpha. I think now you are very clear with this. So, if you are clear, then you see, if you arrange this, right, so, here we are looking at Vm beta minus Vm alpha, which is basically delta Vm alpha to beta, right, because final, final is final minus initial, or you can think of like final state minus initial state. Obviously, remember, this is a, at the transmission temperature, at a given pressure, at different pressures and temperatures, basically alpha and beta are in equilibrium. right it's a reversible equilibrium along the phase boundary right both are in coexistence but depending on the convention so you can use vm delta vm beta to alpha then this will be also delta s beta to alpha right delta is that entropy of transformation molar entropy of transformation from beta to alpha to beta or it you can write it as beta to alpha so it does not really matter so this is basically what i am trying to say is that if you write this way delta s beta to alpha and delta v m beta to alpha it does not really matter because the negative sign that is there on both side on on the numerator there is a negative sign on the denominator there is a negative sign so they are basically getting cancelled out and this is called the famous clausius clapidon equation and that is the equation of the phase boundary right it gives the slope of the phase boundary as you can see again that this is pressure temperature and the slope of the phase boundary the slope of the phase boundary is this one right i go to any point and if i have to draw a slope i'll draw tangent right and that tangent line will make a slope and that is the slope right this is the slope and that slope is nothing but dp by dt right because you have pressure y and x are so if you have y and x so this is y axis this is x axis dy dx is the slope right of the xy curve so dy dx at any point is the slope of the xy curve same so exactly that's what we have written dp dt is the slope of the pressure temperature the the pressure temperature curve that delineates the phase boundary right so the phase boundary that delineates the equilibrium coexistence between alpha and beta basically has a slope of dp by dt, which is given by the ratio of molar entropy of transmission from alpha to beta or beta to alpha by the change in molar volume during transmission from beta to alpha or from alpha to beta.

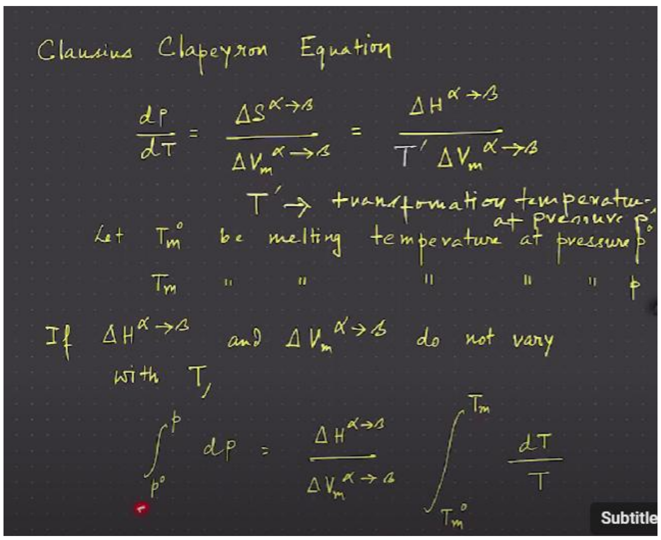
So, this is the ratio. So, the slope depends on this ratio. Now, let us think of the solid-liquid boundary. First, let us look at the solid-liquid boundary. So, you can, at the solid-liquid boundary, at different pressures, you will have different melting or freezing point, right? You can call it either melting point or freezing point, again, because it's a reversible thing.

So, as alpha, say, for example, alpha is solid and beta is liquid, so if solid transforms to liquid, it's called melting, and while liquid transforms to solid, it's called freezing. right. So, now, again mu alpha equals to mu beta. Now, mu alpha is nothing but H alpha minus Ts alpha. Again, H alpha is the enthalpy per mole of alpha.

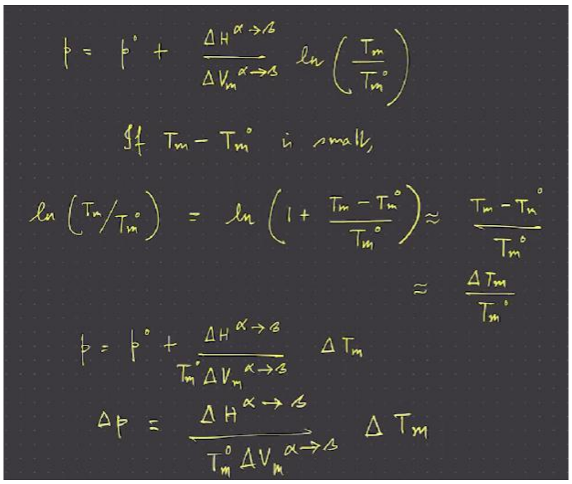


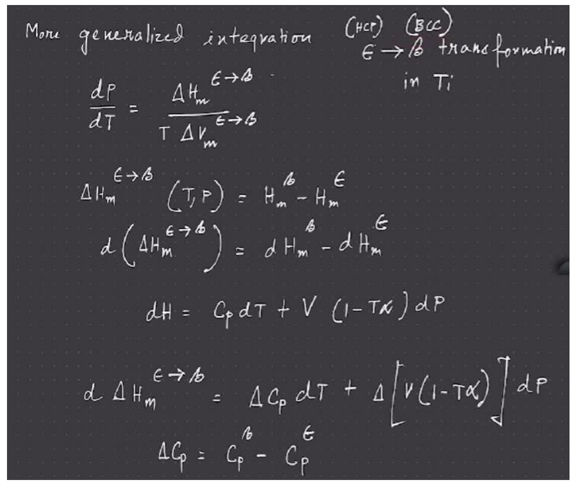
H beta is enthalpy per mole of beta and S is entropy per mole of alpha and S beta is entropy per mole of beta so as you can see h beta minus h alpha equals to t s beta minus s alpha now what is this t the t this t is the temperature at which alpha and beta are in equilibrium and in solid liquid bound in the solid liquid coexistence the temperature at which they are in equilibrium at different pressures are called the melting point or the freezing point right so basically this t is going to be this t you can call it tm or you can call it also t transformation right t transformation ttr or tm right this is the t but what you are seeing is h beta minus h alpha see there is a nice relation that you get h beta minus h alpha that is the enthalpy of transformation from alpha to beta right enthalpy of transmission from alpha to beta equals to t times entropy of transmission from alpha to beta again each quantity is calculated per mole okay so basically now you can rewrite this as dp by dt equals delta s alpha to beta to delta vm alpha to beta now delta s you are replacing by delta h alpha to beta by t delta vm alpha to beta what is t t is basically ttr or tm now basically Remember, Tm0, let us call Tm0. So, let us think of this as Tm0 is the melting temperature at pressure P0. That means Tm0 is the equilibrium or coexistence temperature between alpha and beta, solid phase and liquid phase and that is nothing but the melting temperature or freezing temperature. Similarly, let us consider Tm as the melting temperature or freezing temperature or the coexistence temperature or the transformation temperature at some pressure P. Now, if we assume that delta H alpha beta and delta Vm alpha beta does not, means do not vary with T, then we can just integrate Clausius-Clapeyron equation.

So, remember, so that's why I avoided writing TTR because you have this DT. and dT by T and then I will put this limits, right, dT by T, so instead of writing here directly dT tr, we know that this is the transformation temperature, this T is the transformation temperature at different pressures, right, T is transformation temperature at pressure p, at some pressure p prime, say, let us say, at some pressure P prime. Maybe we can call it T prime and put a T prime. So, T prime is transformation temperature at pressure P prime. Now, if you see, you have this dT by T or dT prime by T prime.



So, basically this is like ln T and here you have P and you have P minus P0 and as I told you delta is alpha beta and delta Vm alpha beta, if we assume that they do not vary with pressure or temperature and this is reasonable because both are condensed phases so there is not much change with pressure. So there is PV work is negligible. So as a result you can just write it as So, this integral can be written from this equation, from this equation you can write this integral, write this integral and you can put the limits Tm0, Tm as you can see when it is Tm0 pressure is P0 and when it is Tm pressure is P. So, if you now plug it in you get P equals to P0 plus delta h alpha to beta by delta Vm alpha to beta ln Tm by Tm0. So, if tm by tm0, if tm minus tm0 is small, then ln tm by tm0 can be approximated as ln 1 plus tm minus tm0 by tm0 and basically I take only the linear term because tm minus tm0 is small, I take only the linear term, it is like ln 1 plus x.

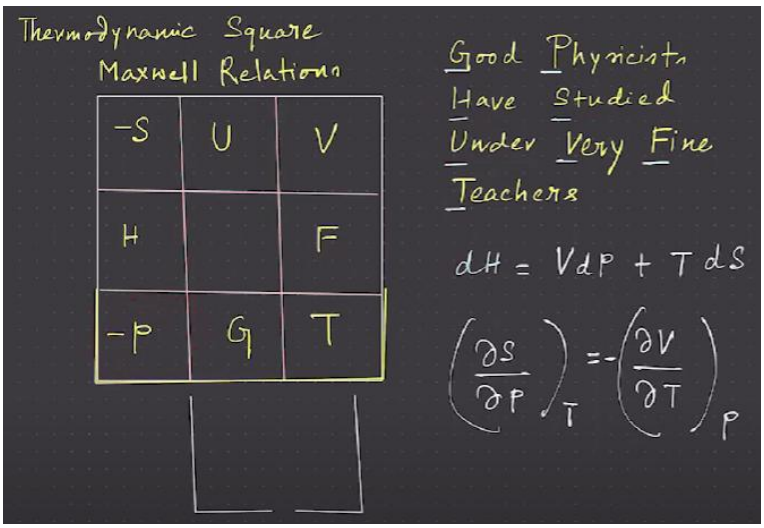




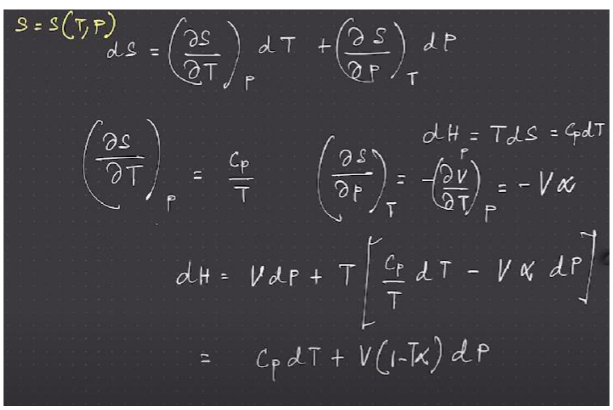
So, if I do ln 1 plus x where x is small, we can write this as x plus x square by 2 factorial and stuff. but x is small so x square will be even smaller so basically i can just take the first term there is a linear term in the expansion which is tm minus tm0 by tm0 and that is basically tm minus tm0 is nothing but the change in melting temperature due to change in pressure so change in melting temperature due to change in pressure now you can see a very nice relation you get p minus p0 so basically which is like delta p so i can write this as delta p equals to delta h alpha to beta and then I can put a temperature Tm not okay so that is my reference temperature and this is Delta Vm alpha to beta into delta t. So you can basically if I know the change in melting temperature I can estimate the change in pressure or if it is change in pressure I can estimate the change in melting temperature. Basically I can directly write dp dt as delta h by t delta v and if delta h and t delta v are basically the if delta h and delta v are independent of temperature so they do they come out of the integration right they come out of the integration but if you want to do more generalized integration for example you think of this epsilon to beta transmission in titanium epsilon to beta so epsilon is hcp phase okay at lower temperature you have epsilon phase and at higher temperatures okay and for different pressures you can have BCC phase. So, you have HC phase, you have BCC phase and there is a transmission temperature Ti.

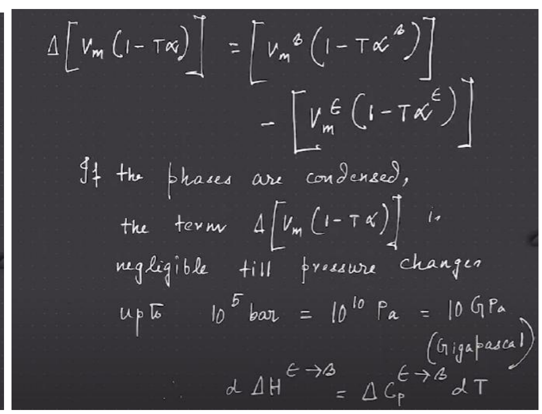
Now, if you think of this, now let us write this way. So, what is the, in the pressure temperature diagram, what is the slope? Delta Hm, that is the molar enthalpy of transmission from epsilon to beta divided by T, T is the transition temperature times delta Vm, that is the change in molar volume from epsilon to beta. right. So, now, delta H m epsilon to beta is again as I do not want to confuse you and it is a function of temperature and pressure. Note that this can be, so we told in the last approximation that let us assume that delta H alpha to beta is not a function of temperature and pressure.

Delta V m is not a function of pressure and temperature. So, then it becomes a very, very simple relation, right, this relation, right. Many a times we use this relation. However, if we tell, no, delta H m is a function of temperature and pressure that is it will also change with temperature and pressure so basically what does it mean hm beta is also a function of temperature and pressure and hm epsilon is also a function of temperature and pressure now if that is so now you have delta hm epsilon to beta is nothing but hm beta minus hm epsilon right this is how we have looked at right beta is the final state this is the initial state so this will be final minus initial now if i do differential that is d of delta hm is dhm minus dhm dhm beta minus dhm epsilon Now dh, again, this comes from applying Maxwell's relation and doing further simplification, okay, so I'll take, so if you do this approximation, so I'll just skip once, I just want to tell you what is the genesis of this, so if you want to see that, you can think of, by the way, this is something I haven't told, so it is something that is used i haven't told this previously when i taught maxwell's relation that you have to basically ultimately maxwell's relation is basically equating the second derivatives right so if you look at maxwell so it's called maxwell relations so max born basically when you looked at this maxwell relations and i think you are also having some difficulty in remembering right because you have to equate stuff so basically this So, Max Born created this mnemonics. There are 100 versions of this, there are different versions of this.



So, he created this mnemonics where he starts from G and he goes, this is a thermodynamic square. So, you go, good physicists have studied under very fine teachers. So, you can see G, P, H, S. good physicists have studied under very fine teachers right so if you look at that now if you see then if you I want to go for for say I want to write a differential say I take this H okay I take this H I directly get VA so when I use H I will take the two signs here so DH equals to VDP plus so you have TDS right you have VDP plus TDS right and and also you can look at so remember in the differential so when it comes to the only only differential thing that comes in is here so the sign of the differential so minus s is there so there is a d of minus s and there is a vdp here and tds here as you can see here h has s and p here and v and t here so v will come here and t will come here see both are positive but when it comes to differentials you ignore the sign okay you ignore the sign so you get vdp plus tds again When you have differentials, you ignore the sign. So, del s del p t is equal to, so if you see this, del s del p t equals to minus del v del t p.





Why minus? Because p is now not part of the differential, right. p is not a part of the differential, but if you can see this, when I am looking at del s del p, And then I am fixing, when I am looking at these, then I am fixing this. So, del s del p t equals to, now I have this. If I have this, then I will take this. So, this becomes del v del t, but there is a minus p, because if I take the opposite one, then I have a negative sign here.

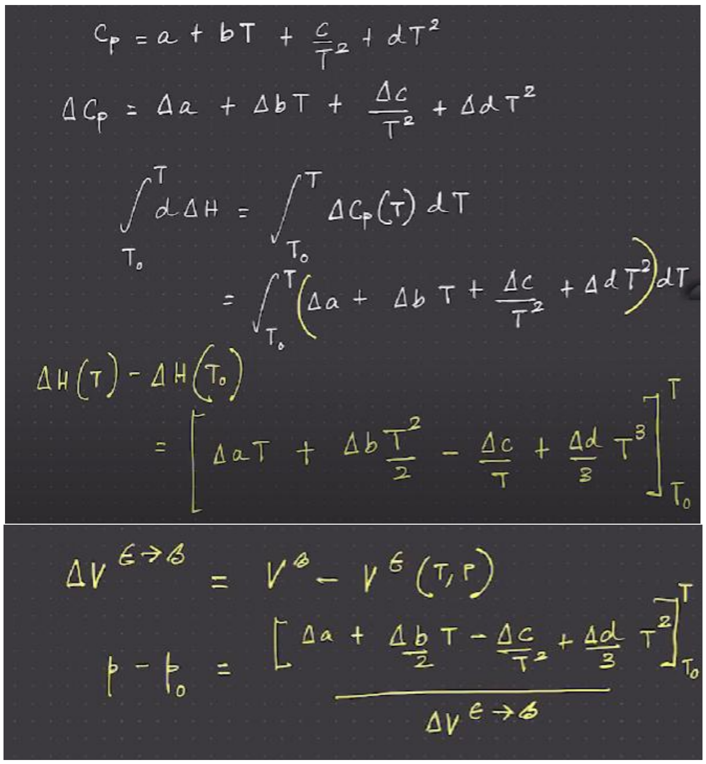
So, this becomes minus del v del t of p. right now you know ds is del s del t so i have taken basically this thing so i have taken s is a function of temperature and pressure then i am basically using the exact differential so i am writing ds equals del s del t dt plus del s del p dp again del s del t is evaluated at constant pressure and del s del t p we have already shown and it's very easy so it comes from here dh equals to tds right which is equal to cp dt so basically if dh is tds then then basically del S by del T, so because T dS is Cp dT, so dS by dT is Cp by T or del S by del T equal to Cp by T at constant pressure, at constant pressure. So, now this is equals to minus del V del Tp which comes from the Maxwell relation minus del V del Tp and that is nothing but, because alpha is nothing but alpha equal to 1 by V del V del Tp. right, and this comes out to be, so then this becomes minus del v del t p, again remember, when you apply thermodynamic square, only in the constant terms that you are having here, you are applying the signs, right, the negative signs, otherwise it is just, you ignore the signs and del s del p is nothing but del v del t, you can do it for various cases and you can equate the second, the second derivatives and you can see that you can derive all the Maxwell's relations, but you go for the simplification because what I have done, I have expressed this now, del S del P I have expressed in terms of measurable quantity, del S del T I have expressed in terms of measurable quantities, right, this is all measurable, this is all measurable. So, then I write dH, right, which is T dS, right, dS I am now expressing this, right, this is basically nothing but dS.

So, T ds plus V dp. So, basically this is, so you have Cp dT, see Cp dT, T into T, T times 1 by T, this is cancelled. So, basically this becomes Cp dT and this is minus V alpha and this is, there is a V here, there is a V, minus V alpha multiplied by T. So, I can take V common and it becomes 1 minus T alpha T. As you can see here, as you can see here, dh is cp dt plus v1 minus d alpha dp. Now, if that is so, you apply this, you apply this relation and you get back, you get back, so basically I am going back to the slide here, so this is nothing but this is the relation that I have used, right, and remember what I have done, I have differentiated the delta H m, right, so delta H m is nothing but differentiate d H m beta, d H m epsilon, so d delta H m to beta is nothing but delta Cp dT, this has a delta Cp because dH equals to Cp dT, but this is epsilon to beta.

So, delta Cp is Cp beta minus Cp epsilon. See, Cp, the heat capacity of at constant pressure of the beta phase and heat capacity of constant pressure at the, of the epsilon phase and you have delta Cp dT plus delta V into 1 minus T alpha dP. Now, as you can see for condensed phases, Delta, this change in molar volume, this quantity, change in this quantity is Vm beta 1 minus T alpha beta and this is Vm epsilon 1 minus T alpha epsilon. U for condense phases, this term is very, very negligible, right, because the pressure changes up to 10 to the power 5 bar, which is like 10 gPa. So, up to 10 gPa pressure, you can neglect this term.

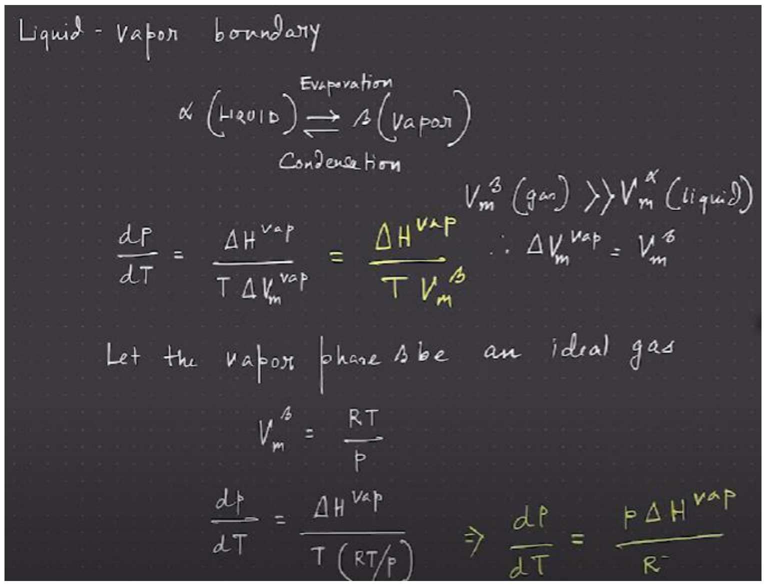
Up to 10 gPa pressure, you can neglect this term. Basically, the So, the term associated with dp can be neglected because the change in pressure if unless you go to like 10 gpa, you do not have a very big influence of that. So, then basically practically for condensed phases dh is nothing but cp dt, but here as you can see dh is a function of Cp and T, and

Cp itself, by the way, can be a function of temperature, right, Cp itself, so basically d delta H epsilon to beta, that is, this is, this is the enthalpy of transmission, the molar enthalpy, so if I can put, like, here m, then this becomes molar heat capacity, so that, that d delta H, and that is the differential of the entropy of transformation from epsilon to beta is nothing but delta Cp molar, this is the change, the change in molar heat capacity when phase transforms from epsilon to beta times dt, right. So, basically now Cp we can write,



so for each phase we can write Cp is nothing but a plus bt plus c by t square plus dt square, this comes from, this comes from experimental data. see I am giving you recipes to calculate even when things become slightly more complex in terms of dependencies but the calculations are quite straightforward so only thing you have to calculate when you calculate you have to be patient and you have to calculate terms correctly right so basically if you look at Delta CP according to this expression then Delta CP is the difference in CP between the epsilon phase and the beta phase or between the two co-existing phases which is basically nothing but the difference in the coefficient a difference in the coefficient b times t difference in the coefficient c by t square and difference in the coefficient d times t square right this is times t square remember this is by t square okay so now If I do from T0, which is a some reference temperature to T, d delta H, then this is basically delta CPT dt, which comes out to be this, right.

So, if you do this delta A plus delta B T plus delta C, so then delta H at some temperature T minus delta H at some temperature T0, which is the reference state, I can write this as delta A times T, delta B times T square by 2, delta and this will be delta c by t square. So, this is minus delta c by t and delta d by t cube delta d into t cube by 3 right and again this has to be put as t and t naught. So, if I do that so basically I get the I get the change in the change in enthalpy during the transformation as a function of the coefficients that we have determined experimentally of the of the heat capacities of the

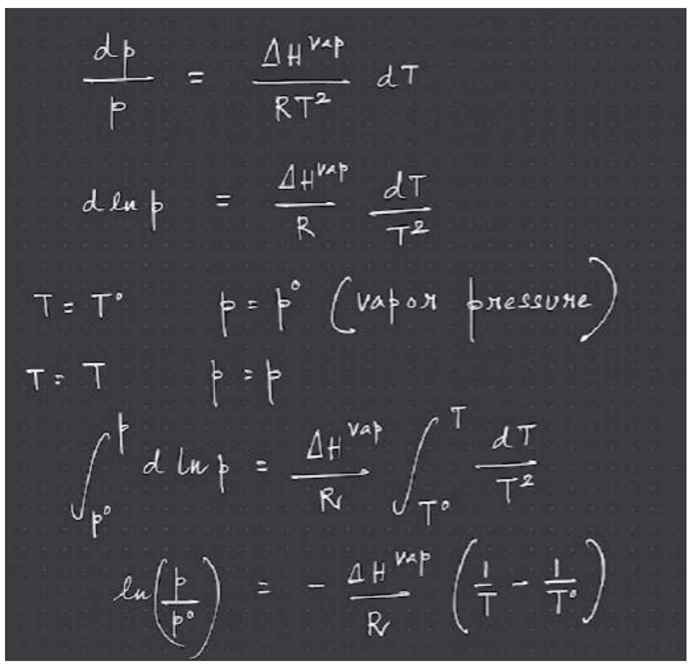


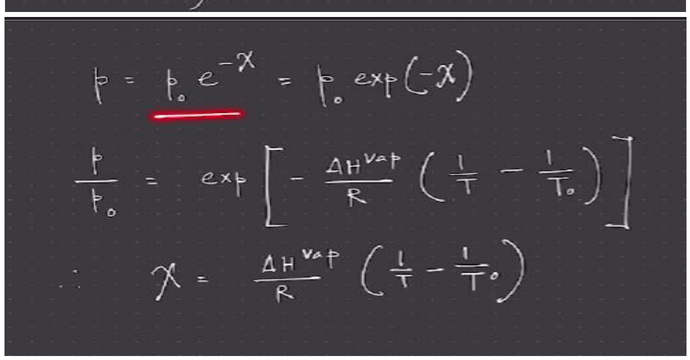
coexisting phases that is here in this case it is epsilon and beta. So, if I do that then the relation just becomes and delta V epsilon to beta is nothing but V beta minus V epsilon which can be a function of temperature pressure, but we are if we neglect that So, this just becomes a constant, right, because I told that V into 1 minus T alpha, you can delta V in 1 minus T alpha can be neglected for a solid liquid, solid liquid coexistence. So, then this becomes P minus P naught, there is a change in pressure from a reference, pressure is equals to this by basically so this is the delta H by and there is a temperature if you remember so if you can see here delta T was there that T and there is T and T naught and this becomes just delta V epsilon to beta so basically this is coming from this relation what is the relation this relation right you can simplify this relation you can finally write this relation as after integrate obviously after integration so we have to do the integration so basically previously my integration was this right this was my integration where delta h as well as delta v m delta h as well as delta v m were independent of temperature and pressure however if delta h itself is a function of temperature then only thing that changes is the numerator, right, then the numerator is changing and you have p minus p.

okay so please check the expression derived by yourself and make sure that you are doing it correctly so that if i can also make see if you do this little bit of algebra sometimes there is always possibility that you can make some mistake here and there you please check it and confirm that what i am getting here when delta h is a function of temperature and pressure and cp is also a function of temperature temperature right by the way what we told delta h can be a function of temperature and pressure but that pressure term we have neglected so delta h here is a function of temperature but delta h is related to the the heat capacities or the differences in the heat capacities of the two coexisting phases and that that his capacities also can be functions of temperature so you look at the differences and then you basically plug it in and you get this relation you please check this relation okay this is for a more generalized approach in general you will often see the problems are such that the temperature ranges are such that the Delta H mostly may be independent of temperature and pressure however if the temperatures range is slightly larger and you have RCP variation then you have to take into account of that and basically if you have even the molar volume variation that also has to be taken into account But see, these are calculations, and thermodynamics gives you a way to calculate all these changes in the phase boundary, how the phase boundary, instead of becoming linear, becomes curved, you can basically know by just looking at this relation, right, that relation that you have derived for different systems, for example, the epsilon to beta transformation in that area, right, so that's the idea. So, again, thermodynamic square, I just went there and I told you that it is a very, very useful tool. You can use it, but again, use it cautiously. Remember that in the differentials, these negative signs that are given here are neglected. But in other cases, you have to use these negative signs, right? Say, for example, V, is it negative? No, it is positive.

So, I have used positive. Temperature, positive. But ds and dp, whether they are negative or positive, these signs in the differential is neglected. So, this is something that is a take home message and you can quickly use this and then use your own strategy. See, remember there are many books with different strategies. They will tell that you do this and then do this and see ultimately all the strategies, one important thing is you have to focus on the relation that you want and that you want to use based on what are the parameters that are known to you, what are the measurable parameters that are known to you. based on that you construct the relation and based on that you come up with an useful relation, right.

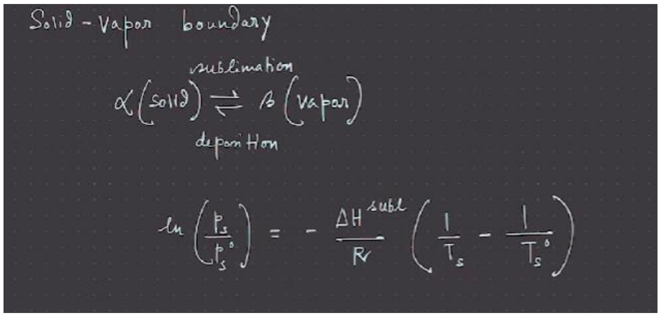
So, basically there will be different strategies, you can follow some strategy, some strategies may work in some cases and some strategies may not work in some other cases. As a result, your strategy should be to look at the final relation, look at what are the measurable quantities, what are the measurable quantities available, based on that how do you approximate all that indirectly measurable quantities. that is change in enthalpy that is important or it's change in entropy or change in free energy this is something you have to basically looking at the problem uh in focus you can basically find out which are important quantities now think of liquid vapor boundary so you have alpha is liquid and beta is vapor and you are the process that we are talking about is like evaporation liquid to vapor is like evaporation of boiling and vapor to liquid is like condensation right and again you have this equation now if in general as you know that gas has a much larger molar volume compared to the any condensed phase whether it is liquid or whether it's solid so basically delta vm vaporization is nothing but vm beta where beta is the gaseous phase or the right so so basically you can write this as so so delta vm can be just represented as so basically if i do this then i get delta h paperization by P VM right, Vm alpha can be neglected. Now, we can think of, and many a times it is indeed a very good approximation that beta phase, that is the gaseous phase or the vapor phase, okay, above the liquid is an ideal gas, okay, is approximated as an ideal gas or a perfect gas, then basically it becomes, life becomes simpler, you get Vm beta equal to, the molar volume of beta can be expressed in terms of the universal gas constant, the temperature, right, the temperature by by pressure. So, you have, as you can see here, Vm beta is nothing but RT by P, right, Vm beta is nothing but RT by P, right, because P Vm equals to RT.



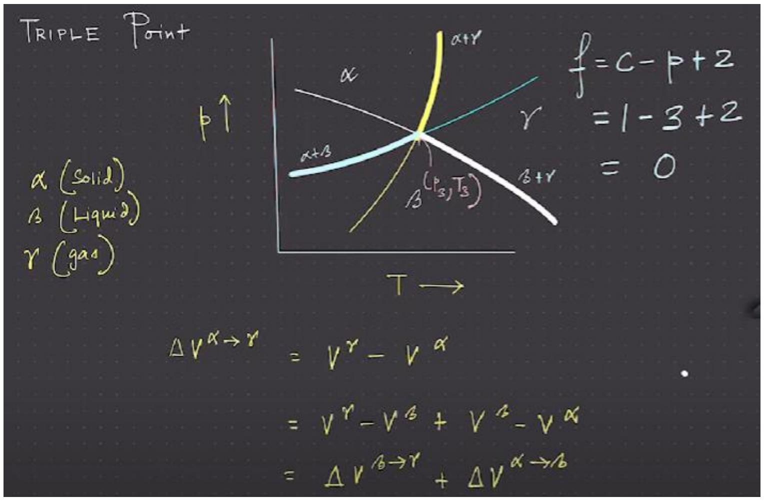


So, then dP by dt equals to delta H vaporization and T times RT by P. So, basically, if you calculate a little bit, so this becomes dP by P, right, because you see, You have RT by P here, so P goes up, right? P goes up. So now this P, when I take this P, so I'll just write here. So DP, this implies DP by DT equals to P delta H by RT square. right so Okay, now you integrate, so it becomes d ln p, this becomes d ln p, and this becomes delta h vaporization by r, dt by t square, and at t equal to t0, let us assume p equals to p0, that is the reference vapor pressure, and at t equal to t is p equal to p, and then you do the integral, and if you do the integral, you have dt by t square, so dt by t square is minus 1 by t, is the, the, the, the, the, the integral, whether the integral is minus 1 by T after you do this integral and then you put the limits T0 to T, then you get minus delta H vaporization by R, this term and again remember we are assuming that delta H vaporization is independent of temperature, it does not change with temperature.

So, basically if I do that, again if you want to put put in all the dependence of temperature if the problem demands that you have to do that and again the same recipe, the more generalized recipe that I have shown earlier will follow. So, right now it becomes very easy, it becomes a very easy integration. So, ln P by P naught where P naught is the reference vapor pressure is given by minus delta H by R 1 by T minus 1 by P naught. now look at this consequence there is a negative sign here and this is a delta h of vaporization so vaporization is a process in which a liquid will absorb it which is basically an endothermic process but you have a negative here so how does the pressure change with temperature you can basically find out very easily from this expression right basically you can further simplify this as p equals to so you are writing p equals to say for example p naught e to the power minus chi or p naught exponential minus chi, this e to the power minus chi is basically you can also write it as exponential, e is nothing but exp. So, then if you write that way, then as you can see p by p naught equals to exponential of this entire term, exponential of this term.



So, where chi is nothing but this, delta h, so it is e to the power minus chi, p0 e to the power minus chi, so chi is nothing but this factor, delta h. by R, delta H vaporization by R, 1 by T minus 1 by T. For solid vapor boundary, you can go the exactly the same way, here it is solid to vapor sublimation or deposition and then you get ln P3 by P30 is equals to this term, right, minus delta H sublimation, that is a change in transformation. Again, this is, we are assuming that delta H sublimation does not depend on temperature. but again the vapor phase has a much much bigger molar volume than the solid phase and so you end up with the same equation only thing Ts is that the temperature of interest for this is the transmission temperature of interest right transmission or sublimation temperature of interest and Ts naught is the temperature at the at the reference state at a reference state and Ps naught correspondingly is the pressure at the reference state right so now think of triple point right you often see triple points right so basically you have this diagram like this one and then you have this one and this one these are the branches right so these are the branches so if I if I make these guys slightly thicker so you have one branch like this and you have one branch like this and you have one branch like this I will not use the blue color I will use the white color right so only thing here I have drawn a straight line instead of straight line it should be so You can approximate this as a straight line also.



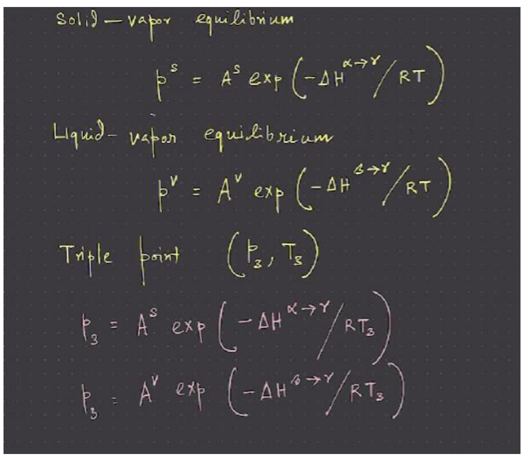
So, if you approximate it as a straight line, but if you do not want to approximate, that is also fine. So, you can write this way and think of, so this is your, right, this is your, these are your phase boundaries, right. These are your, the thick lines are your phase boundaries. So, alpha, beta I have drawn linear, but if you want, you can make it also, so. you have a non-linearity here so i can replace that so i'll put the alpha beta line here is this line and i can basically So these thicker lines are your These thicker lines represent your phase boundaries and these external lines are basically the extension.

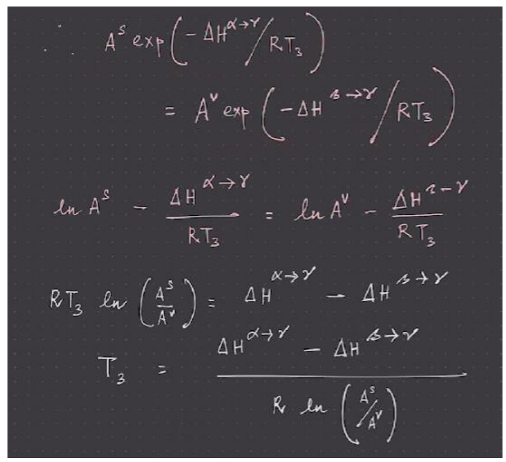
These are like some sort of a, you can think of like, these are like continuations of this line. So, these thick lines are the phase boundaries. So, the yellow thick line, as you can see here, the yellow thick line represents the phase boundary between alpha and gamma and this is the alpha plus gamma coexistence. This phase boundary has alpha plus gamma coexistence. Please note, you can actually derive the change in the degrees of freedom when you move from the single phase alpha to single phase gamma through this phase boundary.

So how the degrees of freedom changes? Again, it is for the alpha plus beta or beta plus gamma. This is the beta plus gamma phase boundary. So this is beta, gamma. But see, the interesting part here is the triple point.

So if you look at that, there is this triple point. Where this is like a pressure and temperature at which solid, liquid and gas coexist. So at that point you have degree of freedom as you remember equal to you remember degree of freedom f equals to c minus p plus two c is the number of components in the unitary system it is one minus number of phases is three and plus two so this equals to zero so the triple point as you as you remember was fixed right but how do you determine it now you see a very interesting idea so you have alpha phase which is your solid phase beta phase which is your liquid phase and gamma phase which is your gaseous phase as you can see solid phase has the lowest the lowest molar volume or lowest entropy and your gamma that is the has the highest entropy right so gamma appears here right and beta so gamma appears so if you see you have alpha phase here gamma phase here gamma phase is your so this is your beta phase and this is your gamma phase so gamma phase as you can see at higher temperatures gamma phase will be favored because gamma phase the gaseous phase which has a much higher entropy in this case right so you have now delta v let us assume now a sublimation that is basically from alpha solid phase it is going to gamma phase, but we can, so that is basically nothing but Vm gamma, so you can put an m here, I am not putting but it is implied, this all part mole is implied. So, basically if I am doing that delta V alpha to gamma which is Vm gamma minus Vm alpha or V gamma minus V alpha, we can write this as as you can see here v gamma we can write this as v gamma minus v beta plus v beta minus v alpha so what i have done i have just written this as v gamma minus so i have just added one term minus v beta and then i have to take it out right minus v beta then i do plus v beta So, it is like I am telling it is a stepwise process. I am imagining this as a stepwise process. One step is gamma to, so basically beta to gamma transformation, beta to gamma transformation, another is alpha to beta transformation.

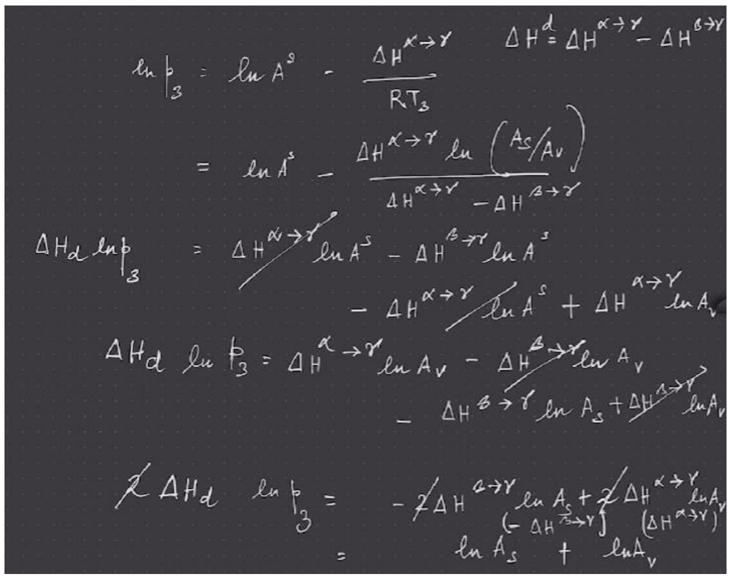
So, basically I am telling delta V alpha to gamma, so what I am telling is delta V alpha to gamma is going through one process like this which is beta to gamma transformation and this is alpha to beta transformation. So, basically I am writing this, this is basically solid to gas is equal to sol, so beta to gamma is like liquid to gas and this is like solid to liquid. So, you have solid to liquid, liquid to gas which gives you solid to gas transformation. Now, as you know, that using this minus e to the power minus chi type of idea, that you can write, say this is for the solid vapor equilibrium, so P s, s indicates sublimation process, so you can write P s equals to some coefficient a s exponential minus delta h alpha to gamma by RT, and liquid vapor equilibrium again, it is like P vapor equals to a v exponential minus delta h beta to gamma RT, right, this is alpha to gamma, alpha to gamma is, alpha is solid, gamma is gas, right, alpha is solid, gamma is gas, so you have this expression, here it is liquid to vapor, so it is PV and this is AV, so I am just using some, some, some coefficient here and I am using some superscript here to distinguish between this equation and this equation and you have obviously the main distinction is here, right, this is delta H alpha to gamma and here it is delta H beta to gamma.

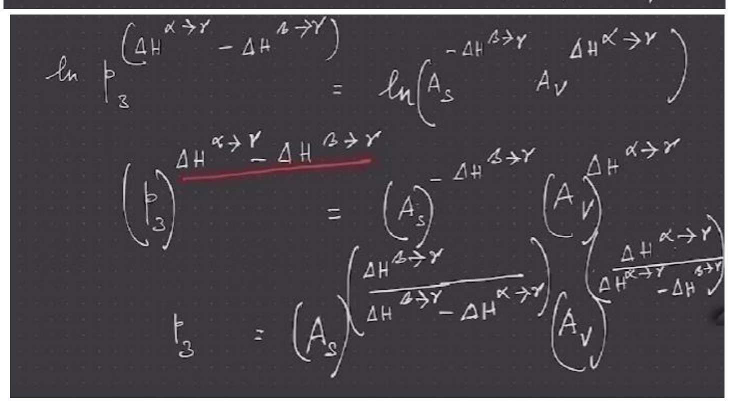




Now, at triple point, P3 and T3, both these equations are satisfied. Triple point P3, T3 basically satisfies both these equations. So, P3 equals to AS times exponential minus delta H alpha to gamma RT3. Similarly, P3 equals to AV. exponential minus delta H beta to gamma right this is the beta to gamma transformation enthalpy by RT3 so I have substituted T by T3 here and P by P3 here similarly here also I can substitute P by P3 and T by T3 because at the triple point all of these are satisfied right solid vapor is equilibrium is satisfied liquid vapor equilibrium is satisfied solid liquid equilibrium is satisfied right so now if you have this you have a s so as you can see here a s exponential minus this equals to and you see i am not considering all of these i don't have to consider that and as you can see here a s exponential so I am doing what I am taking this term and this term to be equal right because this is p3 this is also p3 so these terms are equal so if I do that I get a little bit of manipulation I get so basically I do ln a s and then this is exponential so ln of exponential is only this term right and there is ln a v and this equation so you get r t3 ln a s by a v because delta h alpha to gamma minus delta h beta to gamma or basically delta H alpha to gamma minus delta H beta to gamma, which is basically T3. And as you can see here, delta H alpha to gamma, delta H beta to gamma, if you look at that, you can also basically plug in delta H alpha to beta, because the same idea, for the molar volume, the same idea will hold, right, delta H alpha to gamma, because delta H beta to gamma plus delta H alpha to beta, right.

So, if you have that, So now if you see you have delta H. So if you if you just write say D is the transfer. So delta H D is delta H alpha to gamma minus delta H beta to gamma right. Delta H alpha to gamma minus delta H beta to gamma.



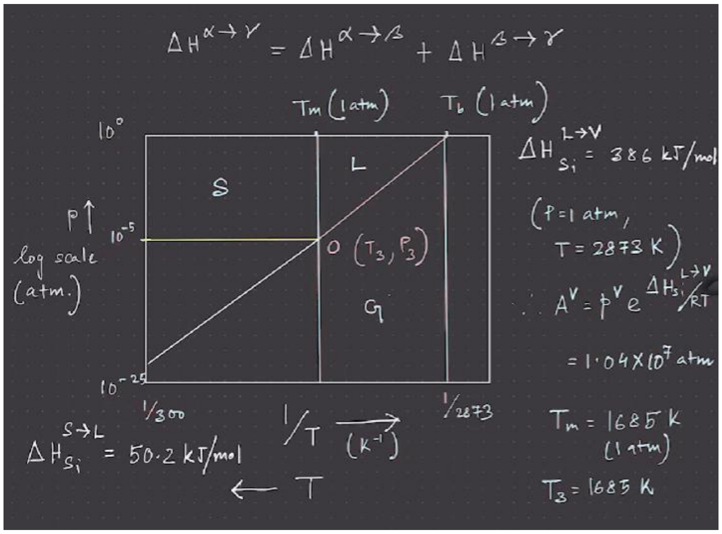


So delta H D ln P3. we just do a little bit of algebraic manipulation. So, basically you get delta H d ln p 3 is nothing but ln As plus ln As to the power minus delta H beta to gamma and ln Av to the power minus plus delta H alpha to gamma. you just follow this derivation then you will see that ln p3 to the power this equation equals to ln as to the power this equation so as to the power minus delta h beta to gamma this is plus delta h alpha to gamma so basically this becomes delta h beta to gamma so if I rearrange so I have this term here right, I have this entire term here in the, as the power and here we have this term and you have this term, so basically if you separate this out, you get P3, okay, so you have got T3, basically you have got T3 already, right, so this is the T3. Right, and you just do a little bit of algebraic manipulation and you will get P3 as a function of s to the power delta h beta to gamma. So basically you are taking the coefficients, assume the coefficients are known and the AV coefficients are known and assume the heats of transformation from beta to gamma or alpha to gamma. Beta to gamma is like liquid to gas and alpha to gamma is like solid to gas.

If we know all these heats of transformation, you can also get P3. Right, you can get P3. okay so that's the idea okay so how do you get it so let us tell so this is exactly so this is one example so remember this is one equation that i have drawn so this is this is an equation that i have derived okay this is one equation that i have derived so you have as you can see you have two equations you have two unknowns So basically if you can basically get T3, you should be able to get P3, right? You have two equations, right? So basically P3s are equal, you have made and you got T3 and once you got T3, you plug it back, right? Once you got this T3 expression, you plug it back. and do a systematics and basically you do some manipulation, algebraic manipulation, you will get into a P3, right. So, where AS has to be known, so the idea is here. So, if I give such formula, what you are seeing here, what is the take home here? AS has to be known, AV has to be known and these transformations have to be known.

Now, I will tell you a very easy way to estimate the triple point. You may not have to, so exponentials actually help you here, Because if you can, if you have these exponentials, you know that if I can plot log in the p, in the log scale, things become easier. Now think of this, one important thing I have to tell you. Say for example, if the liquid is, solid is melting to liquid and a liquid is boiling and it is converting to vapor, obviously the boiling point is always going to be higher than the melting point as long as the pressure, So, here I am talking about an axis. If you please note this axis, this is like 1 atmosphere pressure or 1 bar pressure and this is like 10 to the power minus 25 bar pressure.

Obviously, you can see that this is log scale. So, you have 10 to the power minus 25 bar pressure, very low pressure, then you have moderately low pressure and this is like the atmospheric pressure. I am not going beyond atmospheric pressure, you see that. Now, if you look at this atmospheric pressure, at atmospheric pressure, you know melting point, you know boiling point. In general, at atmospheric pressure, the boiling point has to be greater than the melting point. Now, one thing, delta H alpha to gamma, that is delta H, this is alpha is basically the solid phase to gaseous phase.



Again, I can write the same way, like in steps of two. So, this is delta H alpha to beta, which is basically solid to liquid and this is liquid to gas. beta to gamma. Now, you have, say for example, for silicon, this is done for silicon, for silicon, delta H silicon is this, okay, 386 kilojoules per mole, okay, so this is from liquid to vapor. So, silicon from liquid to vapor transformation is 386 kilojoules plus, liquid to vapor, remember, this has to be plus 386 kilojoules per mole, right, so it has to, it's an endothermic process because liquid has to absorb the heat and convert to vapor, right, liquid has to absorb the heat. Now, this is basically, the pressure is 1 atmosphere and T is 2873 Kelvin, okay, then in that case, this is the transmission temperature and then you have Av equals to Pv, right, because see, what I told is If you look at that, pv equals to av exponential this.

So, basically, av equals to pv exponential, but this minus will become plus. That's all, right. So, that's what I have done here.