**Lecture 10**

**Axiomatic Approach and Thermodynamic Equilibrium in Simple Systems**

I have talked about the first law and second law and their applications and cautious utility and all. So today's lecture I concentrate first on combining first and second law. So what we would like to do is we want to combine so second law gives you the definition of entropy and also it tells you that del Q reversible equals to d ds. Now if I want to combine it my first law is d which is the change in internal energy is equal to delta Q reversible plus delta Q and delta W we only consider mechanical work reversible mechanical work is minus pdV so then you have minus pdV delta W and delta Q equal to Q ds from the second law. So and remember that delta Q reversible is equal to Q ds and ds is greater than equal to delta Q by T which is cautious and equal to. Now once you combine this what you get is basically if you combine this you get pU equals to T ds right pdS is the definite minus pdV right so you get pU equal to T ds minus pdV.



Now since U is a state function it is an exact differential right so we can write dU as del U del s at constant volume ds plus del U del V at constant entropy T. Now you have del U del s at constant volume is partial derivative of U is equal to entropy s and this is partial derivative of this one is partial derivative of U with respect to volume partial derivative of U with respect to volume and this is also taken at a constant entropy. Now if I want to compare with this dU equals to T ds minus pdV what I get is del U del s del U del s constant volume is nothing but differential. This change in entropy change in entropy is basically giving you a definition of temperature right T equals to if you look at this if you compare this del U del s V is equal to T del U del s V is equal to T and del U del V s is equal to T so at constant entropy you can write that pressure is nothing but the change in temperature change in volume right at

constant entropy that is the pressure and there is a negative sign here and you can again understand it from this very simple idea that as you increase the as you reduce the volume as you apply external pressure to a system the volume is reduced right so you will get a change the change in volume will be negative so you have to put a minus pdV so that delta W that is what done on the system is possible. So you have T which is equal to del U del s T and minus p which is equal to del U del V right also previously we have noted that there is one new thermodynamic variable we defined it is called enthalpy, so heat content which combined U as well as p. So now if I do T H we get T U plus pdV plus V dp right because pdV plus V dp now at constant pressure T p will be 0 right at constant pressure T p will be 0. So T H is also basically so del H del T p right if you remember the definition of C p, C p is del H change in enthalpy respect which is temperature at constant pressure. So T H is basically C pdT which is T U plus pdV and T U is C vdT right so now using the combined law we will try to find out a relation between C p and C v we have already given that relation between C p and C v in terms of C p minus C v was a function of p V alpha p right we will try to prove that we will try to derive that using the combined statement of first and second law right this becomes a very important exercise and by the way you can do it for various other relations and this you get very useful many useful thermodynamic relations by the way I will introduce later.



Maxwell's relations which talks about the second derivatives and we will use some of it here however we will show more systematic way of deriving this Maxwell's relations and applying them to find relations between different thermodynamic properties right but here we will tell that the combination of first law and second law gives you a way to derive the generalized relation between C p and C v for any material whether it is a gas before we have defined C p minus C v equal to R only for ideal gas right now C p minus C v here we will try to or C p minus C v equal to n R where n is the number of moles and if I don't think of molar capacity so but C p minus C v is a function of temperature for volume alpha and beta and we have also shown that the expression falls down to C p minus C v equal to R for ideal gas for ideal gases if you think of C p as the molar heat capacity constant pressure and C v as the molar heat capacity constant wall now if you want to use so this is the statement the problem statement let us write the problem statement that use the combined use the combined first law and second law of thermodynamic right use the combined first and second law of thermodynamics basically use this expression B u equals to B dS minus B dv to prove C p minus C v is A v alpha square by beta okay so this is the relation that we want to prove now one thing is that whenever you have an whenever

whatever is a state function that state function will basically give rise to an exact differential so basically I can write this way I can write different relations say for example I can write volume as a function of temperature and pressure I want to express volume as a function of temperature and pressure now if we use exact differential right because volume is an exact differential volume is state function so it's an so we can write as an exact differential so if we express the differential in volume as an exact differential we get and with T and p as the independent variables like v is a function of T and p T and p are the independent variables v is a function of that and so what we get is del v del T p dT plus del v del v T dp now alpha which is the volumetric coefficient of thermal expansion is one by v del v del T p right that is something that we have defined previously and p is isothermal so this is volumetric coefficient of thermal expansion so I will just write it bigger here so alpha volumetric coefficient of thermal expansion is one by v del v del T p is a partial derivative of v this is temperature at concentration and beta is isothermal right because as you can see del v del p at constant temperature so isothermal compressibility and note the minus sign here right you should not forget the minus sign normalized with volume so derivative T p basically basically means v times alpha so it becomes v alpha dT dv equals to v alpha dT minus v so here we have got the derivative T p del v del p T is nothing but minus v beta so minus v beta dp d alpha dT minus v beta dp okay where del v del T p as you can see is v alpha and del v del T p is minus v beta so you can see that v as a function of temperature in a pressure gives this relation v alpha dT minus v beta dp where dv is expressed as an exact differential and in that exact differential the independent variables we have taken as temperature and pressure so we can take any state function to be any state function to be a function of some other variables that are again state functions themselves and we can express such relations right we can find this definitions and we can apply them right so that is something that we will do.



So for example here C p is written in terms of change in n curve with respect to change in temperature at constant pressure right del H del T p C v is change in internal energy with respect to change in temperature at constant volume and we as we know that the enthalpy is H equals to v plus v v so now if I take a differentiation so if I divide by dT so it's like I am dividing this dH which is du plus v dv plus v dp I am defining this relation so first what I have done from here write dH which is equal to du plus p dv plus v dp and now I divide both sides with dT right I define both sides by dT right so we get dH dT

equals to du dp by dt plus p dv by dt plus v dp by dt and now I consider isobaric condition that is dp equal to zero so what you get is del H del T p equal to del u del T p right del u del T change in internal energy with respect to temperature at constant pressure this is something that is unknown right we don't really know this right we know del u del T v but we do not know del u del T p plus because it's a constant pressure process so dp dT the term will go right dp is equal to zero so p del v del T at a constant pressure now del v del T p is something you already know right in terms of alpha right one by v del v del T p equal to alpha so we will now express we will take now another expression another again I will relate one state function to another combination of other state function variables so we will relate u to volume and temperature in the next step so in the next step so you have this equation del H del T p which is Cp equals to del u del T p which you do not know and p times you have del v del T p del v del T p you have seen previously is related to alpha v alpha this is basically v alpha right so this is basically it becomes p times v times alpha this is Cp but this guy don't know right this one this term don't know right you are now taking this expression u equal to function of v and T now if you take u as a function of v and T so you are taking here is following from u equals to u as a function of v which gives du which is del u del v T dv plus del u del T v dt right del u del v T right at constant temperature so this is the partial derivative of u with respect to volume change in volume at constant temperature by the way for ideal gases this term goes to zero right for ideal gases where there is no interaction between the molecules this term goes to zero but you have del u del T.



So but in general it is del u del v T and this is del u del v T and p now if I again use constant pressure and divide 2 that is this equation 2 by dT and take p constant right so divide 2 by dT and take p constant what I get is del u del T p see I want to find out del u del T so del u del T at constant pressure equals to del u del v at constant temperature times del v del T right dv by dT at constant pressure will be del v by del T at constant pressure right from here I get it because I am dividing dv by dT and take p constant so this becomes a partial derivative of del v del T plus del u del T so you have del u del T v and dT by dT is basically you can just cancel them out right so you have only del u del T v left now you have 3 here so this is equation number 3 this is equation number 3 now substitute this result into the result 1 right so you have del u del T p this is where we substitute this relation del u del T p del v del v p and del u del T v and then we see so 1 is exactly so I have written 1 this is again I have rewritten the expression that is why for your convenience now this del u del T p I have written this expression so now take the right

hand side right hand side and put it here so this term is substituted by this entire term right this entire term substitutes this term if you do that what you get is del H del T p because del u del v T times del v del T p plus del u del T v right plus del u del T v plus this term p del v del T so now you get another expression where del H del T p is Cp del u del v T is Cv and there is del u del v T which is not Cv sorry for this so del u del T v there is one term del u del T v here which is Cv so let us write this one so this one I substitute as Cv del u del v T we have to find out what is del u del v T so del u del v T and if you remember del u del v we have done it previously when we equated the first combine first law and second law and we equated the exact differential form of d u we found del u del v S right equal to minus p so later we have to now find out what is del u del v T so del u del v T which is pi T right we call it pi T which is like a internal pressure coefficient right so this is something we want to find out right so we are trying to find out so here we have represented this as Cv now you have this p del v del T p right del v del T p is again a function of its v times alpha so v alpha here comes so here it is so now if you see there is a v alpha term here right this is v alpha this is also v alpha so I take v alpha common then I get p right I get p and I get del u del v T right del u del v T we know del u del v S but we do not know del u del v T right and v alpha is common and v alpha if I take common then we get p plus del u del v T and del u del v is the changing term with temperature at constant volume which is Cv.



So p goes to Cv plus this right this is 4th term now once you have done this and once you have done this you have got du which is T dS minus p dv right T dS minus p dv you have got this relation and now you see and du is also this del u del dv and del u del v T dv right so now you have one very interesting way of writing this first second law combined so this is the combined expression for first and combined first and second laws you should do it by independently and you will see that once you do it there is a sequence here you will be able to follow the sequence so here what we have because you remember that we know about del u del v S del u del v S give me minus p right but I do not know del u del v T right we know that is pi T but pi T is something that does not appear in the expression that we were trying to find out right there is still no beta in our expression right so that is something that we have to think of now what I am doing is I rearrange this statement I rearrange this statement this combined first law second law so dS is something that I take out so then this becomes dS is so I can divide all sides by T so this becomes du by T because dS minus p by T dv and then if I rearrange so I get dS equals to du by T plus v

by T dv right 1 by T du plus v by T dv now again let us look at it so you have 1 by T du and du is del u del v dT right del u del v dT plus 1 by T del u del v dv by T plus 1 by T del v T dv right and plus p by T dv right you have three terms now because du I am using this definition of du here this du I am substituting right this expression right so instead of du I am writing del u del v dT right so this is the expression that I am substituting right so it becomes 1 by T del u del v dT plus 1 by T del u del v T dv plus v by T there is a plus p by T dv right p by T dv comes from here right when I arrange dS in terms of du and du right that is what I am writing so what I get is 1 by T del u del v dT that remains and here I take again 1 by T common and I see p plus del u del v T dv that is equation number 5 del u del v change in internal energy change in volume at a fixed energy now see this is something again comes back right now let us look at now again I will take another so again I can express now S because S as a function of T and v remember the objective is to basically not to find del u del v S but del u del v T so that is why we are making so many so many different invoicing so many different expressions so many different dependencies and we are trying to basically make sense.

$$S = S(T, V)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad - \textcircled{6}$$

Compare ⑤ and ⑥

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]$$

$$z = z(x,y) \rightarrow dz = M\,dx + N\,dy$$

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \Rightarrow \frac{\partial^2 z}{\partial y\,\partial x} = \frac{\partial^2 z}{\partial x\,\partial y}$$

$$\therefore \frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 S}{\partial V \partial T} \qquad M = \left(\frac{\partial z}{\partial x}\right)_y$$

$$\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T \qquad N = \left(\frac{\partial z}{\partial y}\right)_x$$

$$iv)\quad \frac{\partial}{\partial V}\left\{\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right\} = \frac{\partial}{\partial T}\left\{\frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T + \frac{p}{T}\right\}$$

$$or)\quad \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = \frac{1}{T}\left[\frac{\partial^2 U}{\partial V \partial T} + \left(\frac{\partial p}{\partial T}\right)_V\right] - \frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]$$

So these all these will make sense once you start looking at the relation between the second derivatives also or the Maxwell's relations also but so I just want to tell you say for example the way we started is like we started with the definition of u as a function of v and T right and we had the we started with the expression of dh dT right because del H del Tp is the Cp so and then we invoked u as a function of v and T and then we invoke after that we have invoked S as a function of T and v right so S as a function of T and v so u as a function of v and T gave me equation 4 and then again I readjust that means rewrote the combined first and second law statement in terms of dS right dS on the left hand side and the rest of terms of the so it is in terms of S as a function right dS as a function of du and dv is what we have written and now we want to find the relation between S and temperature and volume temperature and volume are independent variables here and S is the S is dependent on T and v again S being a state function we can now write it again as an exact differential now you can see why I am doing this then immediately see we equate the coefficients right we have shown that from the combined first and second law you got du equals to p dS minus p dv and then from the exact differential definition you got del u del Tv and del u del Tp del u del v S and del u del S v and del u del S v for example we equate it to temperature right del u del S v was temperature and del u del v at a constant entropy is basically minus p

right so this is something that we could easily find out so here now we can see what are the derivatives del S del Tv and del S del v T but we have already got dS as a function of dT and dv right if you look at equation 5 dS is a function of dT and Tv and what are the coefficients 1 by T del u del Tv and another case 1 by T p plus del u del v right now if I compare 5 and 6 right we get del S del Tv is nothing but 1 by T del u del v right and del S del v T is 1 by T del u del v T plus p right so these are the two expressions that you are getting by comparing 5 and 6 right now this is something that I want to tell you now comes this relation the basis of Maxwell relations and that is if you have an exact differential Tz right Tz is a function of z so it comes from z being a function of x and y and so we are writing here dz equals to m dx plus m dy and m is nothing but m is del z so m is what m is del z by del x at constant y and so we are writing here dz equals to m and n is del z by del y at constant x what we see here and that is the property of an exact differential that del m del y equal to del m del x that means del 2z del y del x equal to del 2z del x del y right so this is the property of an exact differential right del 2z del y del x so if the order of differentiation in the case of second derivative is not matter del 2z del y del x is equal to del 2z del x del y we will just use this identity here and therefore if we use this identity for S as a function of p and v we can write del 2z del t del v is equal to del 2z del v del t so del del v of del s del t v is del del t of del s del v right now del s del t v we have already found out right del s del t v is basically 1 by T del u del v right so we are writing del del v of 1 by T del u del v because del del T of del s del v T also we have found out is p plus del u del v T and there is a 1 by T in the front of the black right 1 by T del u del v plus p by T right we have taken T inside and then this is del v so what we get is 1 by T if I take it out from here take out from here so it becomes del 2 u del v del t is equal to take 1 by T here out so it becomes so here basically I am basically using the chain right del del T so if I take in the first case I am writing 1 by T I am taking it out and I am writing del 2 u del v del t plus del p del t v and with a common 1 by T and the other one is this term del v del v plus p remains as it is and you have minus 1 by T right differentiation of 1 by T with respect to T will give you minus 1 by T square right so what I get here is this expression right so 1 by T del 2 u del v del t and there is 1 by T del v u del v del t again right you have these two terms right so if you expand you get 1 by T del 2 u del v del v here 1 by T del v u del v del v here which you can basically cancel so what are the terms that are remaining you have 1 by T del p del t v that term remains equal to 1 by T square del v del u del v remember this is del u del u del v T plus 1 by T square del u del v T plus p is 1 by T del p del T that is what we are writing right 1 by T del p del v because you see the secondary term this term this term and this term cancels right now you get 1 by T del p del v equals 1 by T square del u del v T del u del v T note that this is T right del u del v T plus p so T del p del p v so equal to del u del v T plus p now you see some familiarity immediately because del u del v T is something you know which is minus v beta right we already know that right del u del v T not del u del v T sorry sorry so this will be del v yeah the beta is again minus 1 by T del v del v I still want this relation so it is still a little bit far away so right 1 by T change in volume with respect to change in pressure at this isothermal so at constant temperature right so this is not what is so we still have to wait a little bit so we now know T del p del T v but the good thing is now we know del u del v T del u del v T is T del p del p v right change in pressure with respect to change in temperature at constant volume minus T right this is equation number 7 this is your equation number 7 now again I invoke and we have to so we have p and T and v as a function of T and p so if I write that then dv equals to del v del

p e dp plus del v del p dT which we have already written right so now if v is fixed now it is the thing so it is basically this is the isocode say for example like an isochoric process so where dv dv is equal to 0 right if v is fixed volume is fixed volume cannot change so in that case dv becomes equal to 0 and del v del p T dp because del v del p dT and now what you get which is basically del v del p T and if I divide by dT for example and at constant volume so it becomes del p del T so this term this term becomes del p del p v and this is del v del p T so del p del T v so this is where this del p del p v term that we have this del p del p term is what is used and this is nothing but minus del v del p T by del v del p T now this del v del p T term basically gives you minus v beta right so this gives you minus v beta and above there is a v alpha and there is a minus sign minus minus minus plus and so this del p del p del p del T v becomes alpha by beta now you have got the expression that you want to use because you now have Cp plus Cv what we Cp equals to what we have got previously let us look at this Cp equals to Cv plus v alpha p plus del u del v right that was the expression and then we also found del u del v T so that is equation 7 equals to T del p del T v minus T now del p del T v is what we have used as alpha by beta no.



We can now put all of this together so it becomes Cp equal to Cv plus v alpha e plus del u del v T and del u del v T is again coming from T del p del p at constant volume minus p right so now p and p as you can see cancels out so you have T del p del p here and you have v alpha here and T remains but del T del p del T v we have found out to be alpha by beta so if we put all of this together we basically get Cp equals to Cv plus Tv alpha square by beta and this is the relation between Cp and Cv for any material and this is something that you will be using but however you have used from there if you take what is alpha for the ideal gas and beta for ideal gas if you remember you got Cp minus Cv if it is a one mole of ideal gas it is equal to right if you take alpha and beta by the way in alpha for ideal gas try to find out what is the relation in alpha and temperature and what is the relation between beta and pressure for the ideal gas then it is something that I have proved already so you can check that I don't want to repeat it here but you can see that you invoke multiple relations however one of the central relations that you started with was the combined first and second law so combined state of first and second law is important to understand the relation between different thermodynamic properties and remember this is something that is very very useful when you also want to express or want to find indirectly measurable

thermodynamic quantities for example the S or U in terms of measurable quantities such as Cp Cv alpha beta temperature volume pressure so that is one thing that immediately follows from the combined statement of first and second laws so there are several such relations that we will explore later and this is something that you have to remember that whenever you use this combined statement you get this you can arrive at this relations however it takes some sort of thinking about the relations and obviously it requires some algebraic manipulation it is not always easy to remember this and you require to do a little bit of trial and error that is also true but once we use Maxwell relations again it may become slightly easier for you to find this relations however as you can see it does require a little bit of algebraic manipulation and little bit of patience because we have to basically find out what are the relations particularly what are the partial derivatives that we want to really find so for that what type of dependency we should consider right we know the properties of exact differential but how to use that to get into this relations it is always possible for example to use a simpler way to arrive at the same relations right the relation that I have arrived at you can arrive at it in a simpler way that is always always possible right by using a different combination of variables now as you know that for any given phase or any given system right for example liquid water or whether it is solid silver or silver in the molten state or whatever it is you can write this type of relations right this type of equations and these equations are generally found from experimental technique right CPT so please note that for a given this is always for a given phase for example if it is liquid water I have a dependency of heat capacity at constant heat capacity as a function of temperature right heat capacity as a function of temperature this relation involves this coefficients like a, b, c, d so it can be also much more complicated in terms of c, p and temperature dependence the point is that once you have this relation these relations are derived from experimental data and these are derived for a given phase right the experimental data the data that you obtain from calorimetry and from there you can express a you can find out the values of a, b, c and d and this is something that we often use to find out right we have to find out the change in entropy for example right change in entrop.





How do you find change in entropy is very simple you see delta Q equals to T dS that is we have written right delta QP reversible so it is delta QP is the heat transfer at constant pressure at constant pressure means it is equal to dH right equal to dH which is Cp dP right dH becomes equal to Cp dP by plus dH equals to Tu plus dv right at constant pressure and if it is so which is equal to delta QP and which is

nothing but Cp dP and here we are using because it is constant pressure isoparic therefore we are using Cp that is heat capacity constant pressure now dH equals to Cp dT basically now gives you an idea because delta QP is also equal to PdS this is also equal to PdS now therefore it immediately gives an idea to measure entropy or to find entropy or change in entropy as a function of Cp and T right Cp and T are measurable quantities these are directly measurable quantities T you can use tau meter Cp you can use a calorimeter so calorimeter gives you Cp it gives you even the temperature dependence of Cp and now if you know this relation Cp dT equals to TdS that means dS equals to Cp dT by T right dS equal to that is what I have written dS equal to Cp by T into Tu so if I do this integration if I do this integration from some temperature initial temperature to some temperature I can basically find out the change in entropy because change in entropy cannot be directly measured but change in Cp can be measured right change in Cp can be measured Cp can be measured itself so because see for example this is an empirical relation right between temperature and heat capacity and this empirical relation is derived from experimental data of experimental data from calorimeter right and you also know how to measure temperature so if I know the initial temperature and final temperature I can find the change in entropy so this is how we can measure the indirectly measurable quantities like delta S or delta U correct say for example this is again please note that when you use this relation when you use this parameters A B C and D make sure that you are doing it in the applicable range for example for silver solid A is 21 B has an unit of 1 by Kelvin which is 8.5 into 10 to the power minus 3 and C has an unit of Kelvin square right C by T square so it has an unit of Kelvin square and it is 1.
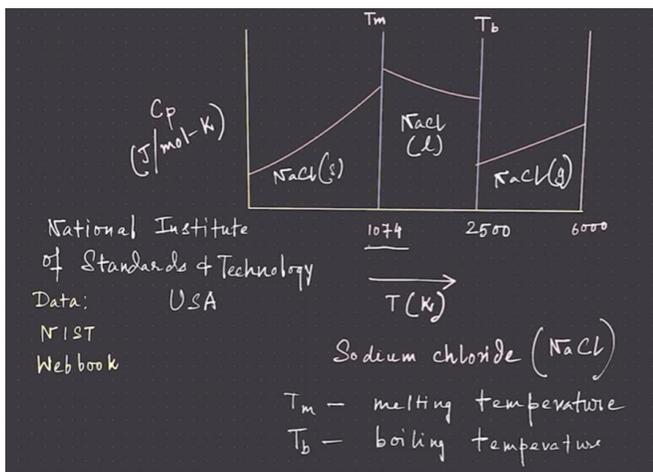




5 into 10 to the power 5 and D T square D is not reported so A B C are sufficient for silver solid but note that the temperature range in which it is applicable is 298 to 1234 Kelvin so therefore if you want to see a change in entropy in these temperature range where the process involves solid silver in some way then basically you can use this relation but always note the applicability in the temperature range in these temperature range only this A B C values are done right for example nickel liquid has only A right which is constant but the constant is between 1728 and 1900 Kelvin so between 1728 and 1900 Kelvin 1728 Kelvin to 1900 Kelvin and 1900 Kelvin this liquid nickel or molten nickel has a constant heat capacity at constant pressure right so the heat capacity is constant by the way this is something that you can prove and you can show that the C p and C v in case of solids and liquids this is something I have

already given an example even in assignment I have given a problem like that so you will see that the difference in C p and C v becomes much much less and often negligible when it comes to phases like when it comes to condensed phases such as solids and liquids but you have to also understand that it depends on the problem for which you want to neglect the difference between C p and C v so please read the problem statement carefully and see in that problem statement is it okay to neglect the difference between C p and C v because sometimes the C p and C v difference if it is purely condensed phases sometimes it is possible that there is some difference and that difference cannot be neglected for a particular type of problem where the range is such that if you neglect this difference you may actually get a large error in the outcome right so if the see if the difference is like 1% or 2% or 5% in some cases it is okay to neglect but in some cases it becomes very difficult to neglect such differences okay so this is it depends on the problem where you want to say okay C p is nearly equal to C v for solids and liquids okay so this is something that you should always take into account now think of a process where there is phase change for example if you have a phase change say you are constantly say giving heat to the system and the system starts with a solid now the solid is basically so you can think of some origin you can think of origin to be 0 kelvin origin to be 298 kelvin right so there is a special property of entropy that is what I am going to express soon and before that I that is what I want to tell you that what is your origin depends on the choice relevant to the problem right if you think of entropy you start from 298 kelvin and you start heating and we are heating the solid and the solid then transforms to liquid now one interesting thing and this is something all of us know that there will be a temperature at which solid and liquid are in liquid right that is the that is called the melting temperature at which solid and liquid are in liquid right and when it solid is transformed to liquid then instead of looking at the sensible heat which is given by C p dt you look at something called latent heat right or enthalpy of transformation that is something that we have already talked about so enthalpy of transformation is something that you have to invoke here now when you talk of enthalpy of transformation you want to you have this in the solid equilibrium case you have this heat input you continue to have this heat input but there is no change in temperature right there is no change in temperature at the in this equilibrium process right when you have solid liquid once it changes completely liquid again you can see the you can estimate the sensible heat otherwise it is called that is why it is called latent heat right so in solid liquid we know the temperature remains fixed right this is at the melting point so this point basically is the melting point in fact if you go the other way then it is also called the melting temperature or solidification temperature or fusion temperature fusion at temperature at which the solid melts or temperature at which liquid solidifies and that is the temperature where solid and liquid are at equilibrium right again you start with the liquid go up so as it is going up it should go up so as it goes up then liquid converts to vapor so again there is a another equilibrium and that is the equilibrium which is given by the boiling point that is the liquid change so this is called the boiling point or you can think of like condensation point like vapor condensation point again at that point you have only the heat of transformation right or latent heat evolution right so for example if I want to convert solid to liquid then the solid has to absorb some amount of heat right so it is an if solid solves it so it is an endothermic process and but on the other hand when liquid solidifies to solid then liquid releases it so it is an exothermic process so similarly you can do it for liquid to vapor transformation right so at liquid vapor transformation again the temperature

remains fixed now that all these are fine this is something that we already know right and then again for the purpose then it will go on increasing then you get super steam and stuff like you think of what so this is basically the phase change process is something that we already know and we have been reading it for quite some time now in this process how does your heat capacity change does the heat capacity change or show any change in this process if I look at that you can see if you look at different data say for example for heat capacity at so this is basically for sodium chloride right sodium chloride again we are looking at solid sodium chloride that solid sodium chloride melts and then at certain temperature at so Tm here melting temperature or equilibrium temperature between liquid sodium chloride and solid sodium chloride so this is the melting temperature and Tb is the boiling temperature what you know is that you remember that at the solid liquid equilibrium there is no change in temperature right you do not see any change in temperature thermometer does not install any change in temperature again for liquid or liquid.
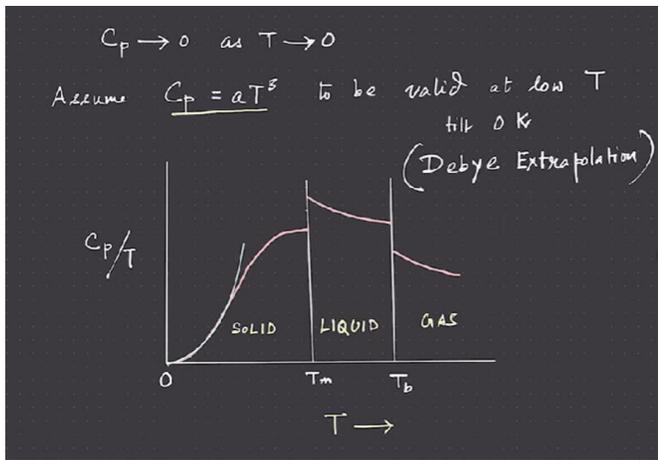


So there as a result as you can see here so at so it is like 1074 Kelvin is for sodium chloride and this is for and the boiling point is the 3000 Kelvin here you get the sodium chloride vapor right so this 3005 and now you have basically so this is the sodium chloride solid right MSCR solid it is like MSCR liquid state molten state and here it is like in the vapor is gas MSCR there about the one as you can see the variation Cp is increasing as a function of temperature and then there is a discontinuity the idea here is discontinuity happens at the melting temperature right there is a discontinuous change in Cp there is a here for example the Cp has jumped right the Cp of solid has changed to Cp of liquid as soon as this transformation has completed once the transformation completes then the Cp of solid has changed to Cp of liquid which is different so you can see a distance here similarly you go further down so here you can see one interesting thing that is the heat capacity of sodium chloride liquid is slightly reducing temperature and once again this is from the data and once you have got this data now go to the boiling point and immediately you see a change in Cp the Cp has gone down right when sodium chloride from liquid has changed to sodium chloride gas right so this is coming from so by the way if you want to get all this data for different compounds and different elements you can visit NIST this is NIST by book where NIST stands for National Institute of Standards and Technology so this is called NIST yeah so National Institute of Standards and Technology so USA which has this wave book very nice so it is in it

is located in Washington DC which is called the thing they maintain this wave book where they have all this thermochemical data of different compounds and you can look at the values of A B C D and all for different compounds in their solid state in their liquid state in the in the in the vapour state and you can plot this and you will find that one interesting the important thing that I want to tell that you will always see and this is something that is very very logical and understandable that there will be a discontinuous change in Cp right at the melting temperature at the condition temperature like this the melting condition and this is the boiling condition so you will see a change right that is one thing now in general you will see that so this is something that you will see in general you will have gases will possess lower heat capacity than solids only this now why do why does it happen so you think about it these gases you may have a lower heat capacity than solids or liquids and remember this is one thing when you have gas when you have a gas phase even if for a real gas the interactions are much much weaker than in a solid or liquid, liquid and solid they are much much denser than gas and so as a result the amount of interactions will be the interactions between the molecules will be much stronger when you look at liquids and solids so as a result to break these bonds you made you will require a much higher amount of heat so the heat capacity in general because of the interactions being stronger heat capacity in general for gases will be smaller than because in solids and liquids the interactions are much stronger right.





So they have much stronger interactions as a result it requires much more much the larger amount of heat to break these interactions right so for these different transitions to take place so they will have solids and liquids will have higher heat capacity than gases now there is one interesting thing that in some cases it is often means you will see that liquids have slightly higher heat capacity than solids it is also true the reverse is also true so liquids often poses slightly higher heat capacity than solids for example sodium vapor at 1200 Kelvin so at 1200 Kelvin it will be the thing is not 1200 Kelvin it is 1200 Kelvin C I will have to check that so it is basically vapor we have to check the temperature it is not definitely not 1200 Kelvin so sodium vapor so which is above 2500 Kelvin it has to be above 2100 Kelvin and you see that sodium vapor has a Cp and has a Cp of 12.47 joules per minute Kelvin you can check the data from this to find out at what temperature sodium has this 12.47 joules per minute Kelvin and liquid has 31.51 joules per minute Kelvin right solid has 28.20 so as you can see the Cp of liquid Cp

liquid Cp Na liquid is slightly greater than Cp Na solid and is much much greater than Cp sodium this is sodium right so it is not sodium chloride so yeah so above 1200 Kelvin it is correct at 1200 Kelvin is the vapor phase and you get 12. 47 joules per mole Kelvin so Cp of Na right so gases it is very easily understandable because gases have much weaker interactions you don't require much energy to break these bonds on the other hand for solids and liquids if they have much higher energy or heat input and as a result they will generally possess much higher heat capacity right so this is something that is fine now one thing how to fix the origin there are two problems one is how to fix what is the origin that will fix that is one problem right we have talked about if you remember Debye's theory of heat capacity of solids and you will see that at very very low temperatures Debye has this theory where the heat capacity of solids go to tend to be zero as the temperature approaches zero right so that is one interesting observation that or interesting outcome of Debye's theory of heat capacity of solids right and as a result for solids at very low temperatures we use something called Debye's preparation where we assume Cp to be equal to A p cubed right at very low temperature till 0 Kelvin right it goes to till 0 Kelvin right again at room temperature at high enough temperature again for solids we can use to longitude to longitude its law right and then from now it converts to liquid then we again have to look at how the Cp will change now this is Cp by T right this is what we are plotting here is not Cp but Cp by T right so Cp by T as a function of temperature gives you a characteristic term like this so this is a point building point and this is a flowing point but this is something that I want to tell that Cp tends to 0.



$$\Delta H^{tr} \ (gray \to white) = +2.1 \ kJ/mol$$

Find $\Delta S^{tr}$

$$\Delta S^{tv} = \frac{\Delta H^{tv}}{T^{tv}}$$



Thermodynamic Temperature

$$\epsilon = 1 - \frac{T_C}{T_H}$$

$$\frac{T_C}{T_H} = 1 - \epsilon$$

$$T_c = \left(1 - \epsilon\right) T_H$$

Put $\epsilon = 1$, then $T_C = 0 \ K$

So this is observed even from Debye's theory of heat capacity of solids that Cp tends to 0 and p tends to 0 right and delta S as you know is equal to T by T dT just now I am sure so it is Cp by T dT this S so and the integral is between Ti that is the starting temperature the initial temperature is the final temperature right so S Tf minus S Ti is the so let us give an example right find its molar heat capacity so what is this Debye's extrapolation and how do we apply right we give an example here so you have here the problem involves constant pressure molar heat capacity okay or heat capacity so I am removing this M but what we are looking at is the Cp denotes molar heat capacity in this problem okay because see it is the molar heat capacity of a certain solid at 10 Kelvin is 0.51 joules per mole Kelvin find its molar entropy at 10 Kelvin now at low temperatures Cp of T equals to 80 Kelvin is valid till 0 Kelvin right so

Tf equals to 10 Kelvin and Ti I will be taking as 0 Kelvin so S M that is molar entropy that is T minus molar entropy at 10 to the power 0 is integral 0 to T Cp by T dT right Cp by T and Cp I am using Debye's extrapolation so AT cube AT cube by T dT which is basically AT square dT which is 1 by 3 AT cube right so T square by integral T square dT is T cube by 3 so 1 by 3 AT cube so 1 by 3 AT cube and Cp is AT cube so this is nothing but one-third of Cp AT cube right because what is the approximation we use Cp equals to AT cube now the integral gives me one-third AT cube and instead of AT cube I substitute Cp so this is one-third Cp so SM at 10 Kelvin is SM at 0 Kelvin plus one-third into 0.51 which is SM at 0 plus 0.17 joules per mole Kelvin right so we want to know so what we require we have an unknown here what is SM of that pure solid of the solid at 0 Kelvin right at 0 Kelvin so this is something if we know then we can tell that SM at 10 Kelvin is equal to SM at 0 Kelvin plus 0.17 joules per mole Kelvin right now if you look at that the change in entropy now I know Cp by T and we know dS equals to Cp by T dT so I can also plot the change in entropy now as you can see here now I have used an origin of 0 and I am telling Cp tends to 0 right as T tends to 0 I am telling S so again at T tends to 0 remember that so and we are using a Debye extrapolation AT cube right so that means at 0 Kelvin Cp is basically going to be 0 so now if you look at S the change in S right so you again see there is a jump in S right that delta S melting and delta S boiling there has to be right because there is a jump in Cp right or jump in Cp by T as well so as a result delta S melt and delta S boiling then there is this this is like this is correspond what does it correspond to? It corresponds to delta H boil by T right and this corresponds to right delta H is basically equal to T delta S right.



So that is what we are addressing so this is delta H boil so that is basically delta H transformation right from liquid to gas and this is delta H this again corresponds to delta H transformation from solid to liquid right so this is the change in S with temperature what we have done here is we have basically extrapolated in such a way that S tends to S becomes 0 at 0 Kelvin this now if I have this curve then how do I find S? Again S at T can be estimated at any temperature T can be estimated at this point S at T equal to S at 0 plus 0 to Tm Cp S by TdT Cp S can be a function of temperature then there is a delta H by Tm right solid to liquid and then Tm to Tb there is again CpL by TbV and then delta H liquid to gas by Tb right for the boiling point again you have the heat at the heat of transformation delta H by T is delta S and then you have Cp gas by TbV right so that way we can go to that temperature what we want to find but we require to know what is S right so that is something that we want to know right so say for

example so you have Ts which is equal to Th by T right TqP equal to Th TqP equal to Tds from second law so Ts equal to TdT of transformation now think of this transformation this is a very interesting transformation that actually like T gray to Tm this is the two allotropes of T one is gray T one is white T gives you this phenomenon called T gray so below 13 degree Celsius alpha is stable and above 13 degree Celsius beta which is white and metallic and ductile is stable and so one is metallic and ductile and this is brittle right gray is brittle by the way there is a legend that Napoleon's Russia campaign failed because of this important transformation that took place they the soldiers used to have pin buttons on their uniforms and these pin buttons and it's a very cold in Russia so it's below 13 Celsius so the pin buttons became powdery and crumbled so and they got affected by very severe cold and as a result it did not fight and they will and therefore Napoleon's Russian campaign failed so that is one legend that is there so this is such an important transformation see one very interesting in this transformation delta H transmission is plus 2. 1 kilo square right is basically gray to white transformation is an endothermic transformation now if you want to find delta X transformation what you will do you just take delta X transformation delta H transformation by T transformation but T transformation is basically 13 degree Celsius and you can see that it is also positive delta H is positive delta S is positive you will later see that this gives you a very interesting problem that delta H is positive right so you generally will tend to think that this may not means it may not because the heat is not evolving but it is getting absorbed so that means it requires some sort of a heat to be input and as a result it may be a non-spontaneous process but that is something that we will soon show that this is a possible process and what is written in deed is correct and alpha to beta transformation takes place at 13 degree Celsius and this is a possible transformation at 13 degree Celsius and you get this alpha to beta transformation above so it becomes beta above 13 and becomes alpha below 13 however at 13 tin gray and tin white are in equilibrium this is something that you should write in this case therefore the heat of transformation if you want you do not involve the heat capacity right we do not involve the heat capacity when we calculate heat of transformation because the temperature does not change right now we know about so one thing I assumed in this curve before that at S0 if you look at that I have put a 0 here right 0 Kelvin but for the y-axis I haven't put any value so I need to find some value right so this value will come soon but before that we just very quickly tell about thermodynamic temperature thermodynamic temperature is 1 minus Tc by Th right we know this is not thermodynamic this is called Carnot efficiency this is called Carnot efficiency or efficiency of a reverse efficiency of a heat engine right efficiency of the Carnot cycle right efficiency of the Carnot cycle which is basically so which is undergoing this reversible cyclic process right so now you see 1 minus Tc by Th as I told you that we can we can change either Tc or the Th and we can vary the efficiency right so if I want to make the efficiency equal to 1 I have to put Tc to be equal to 0 whatever be the Th if I put Tc equal to 0 because Tc by Th is 1 minus epsilon or Tc equals to 1 minus epsilon to Th so put epsilon equal to 1 then Tc becomes equal to 0 Kelvin right here also you can immediately see that Tc is equal to 0 Kelvin so at 0 Kelvin if Tc is at 0 Kelvin and if you can have the temperature of the cold sink at which the heat is ejected at 0 Kelvin I get a Carnot efficiency of 1 right that's the maximum Carnot efficiency now comes so basically there is a 0 Kelvin at which this dissipation basically is not really there right so because efficiency becomes exactly equal to 1 right in some sense so that is where comes third law again it's a law that basically gives you the scale of absolute

scale of temperature right there exists this absolute scale of temperature where the entropy change is with any physical or chemical transformation as the temperature approaches 0 so goes to 0 right the entropy change associated with any physical chemical transformation goes to 0 right as temperature approaches 0 this is a definition of this is called Nernst heat theorem and this is the statement of third law this is the statement of third law so Nernst heat theorem comes from this Carnot cycle right from this Carnot cycle and we can find out that there is a Tc of 0 Kelvin at which the Carnot efficiency goes to 1 and we non-strictly state that entropy changes between physical or chemical transformation as the temperature approaches 0 it tends to 0 right it tends to 0 entropy change tends to 0 so at absolute 0 Kelvin this is the statement of third law that at absolute 0 Kelvin all perfect crystalline substances so please note this all perfect crystalline substances because in material science you have also this other different forms of matter for example glass right which is not really an equilibrium form of matter but a non-equilibrium form of matter so remember at absolute 0 Kelvin please note all perfect crystalline substances have the same entropy and it is 0 so S at 0 Kelvin is 0 for all substances in perfectly crystalline form this important part is perfectly crystalline form and so at absolute 0 so the absolute 0 is a temperature where all perfectly crystalline substances tend to have 0 entropy right they tend to have the same entropy and the same value the value is basically 0 so it basically tells us now you remember that it is an SM 0 now if you are looking at SM 0 then you can take SM 0 to be 0 right third law lets us calculate absolute entropy that's the important part so I will start from there from the next in the next lecture I will start from here and I will also give you the necessary tools to understand equilibrium in thermodynamic systems.



Statement of third law

At absolute zero $(T=0\ K)$ all perfect crystalline substances have the same entropy, and it is zero.

$$S(0k) = 0 \quad \text{for all substances in perfectly crystalline form}$$



Third law lets us calculate absolute entropies.

$$\Delta S_{0 \to T} = \int_0^T \frac{C_p(T)\,dT}{T}$$

$$S(0) = 0 \quad \to \quad S^{\ddagger}(T) \text{ or } S^{\circ}(T)$$

Standard entropy at temperature T

$$S_m^{\ddagger} \left( J/mol\text{-}k \right)$$

| | |
|---|---|
| Graphite, C(s) | 5.7 |
| Diamond, C(s) | 2.4 |
| Water, $H_2O(\ell)$ | 69.9 |
| Hydrogen, $H_2(g)$ | 130.7 |