**Thermodynamics And Kinetics of Materials**

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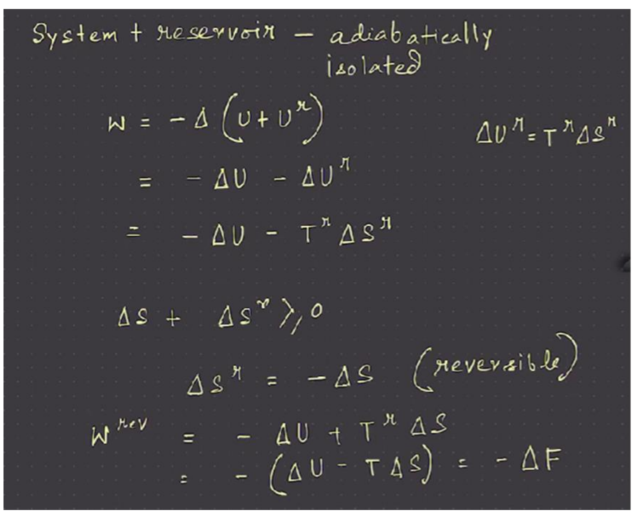
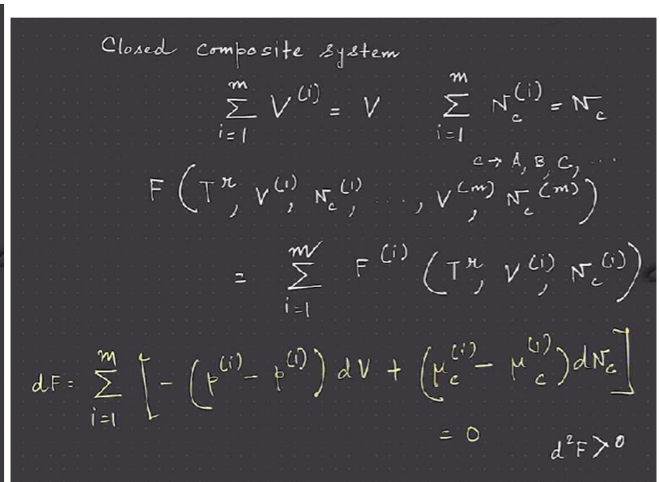
**Lecture 13**

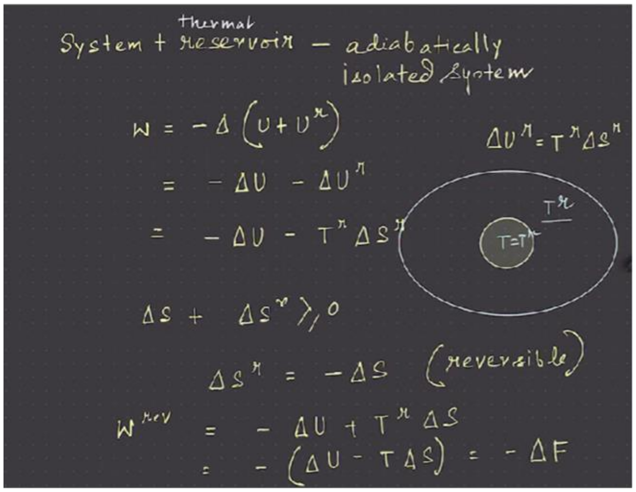
**Maxwell relations and their application**

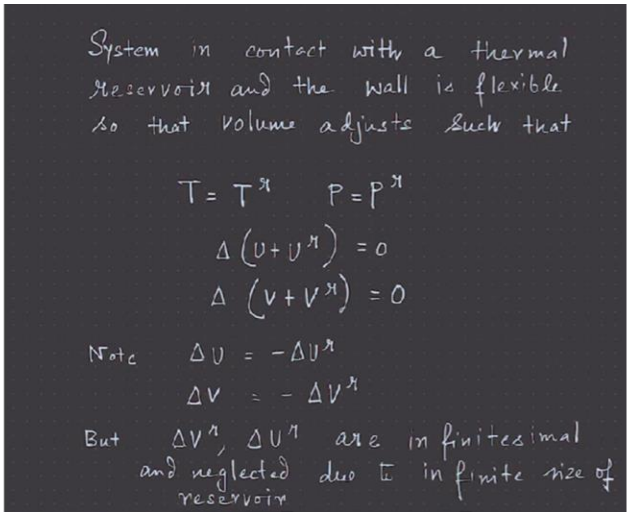
We have introduced the constant of preserver, we have introduced the composite orthogonal potentials and how are they arrived at and we have already defined previously in week 3 also we have defined like G and F but how are they coming and how are they related and what is this conjugate relationship that we are talking about we have explained them. Now you have system and preserver right we have talked about system and preserver if you remember the previous lecture we talked about that if I have Helmholtz free energy minimum principle that basically means that F which is a function of now T right F is a function of T and V and N and DF has to be equal to 0 and D2F has to be greater than 0 so it is the Helmholtz free energy minimum principle so instead of using a energy minimum principle or in our entropy maximization principle where we require the equations of state.



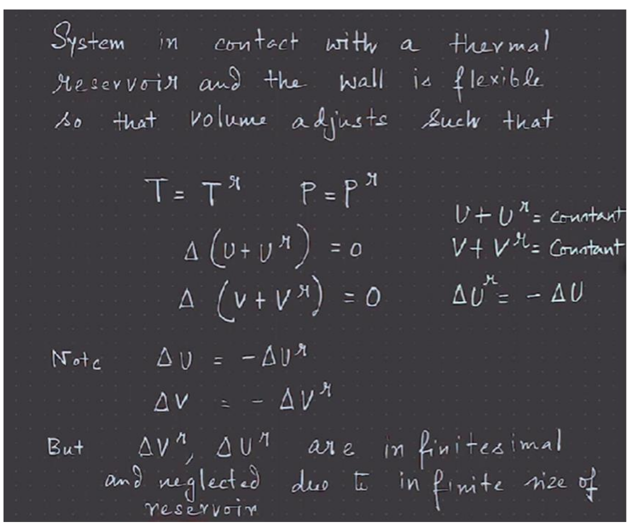



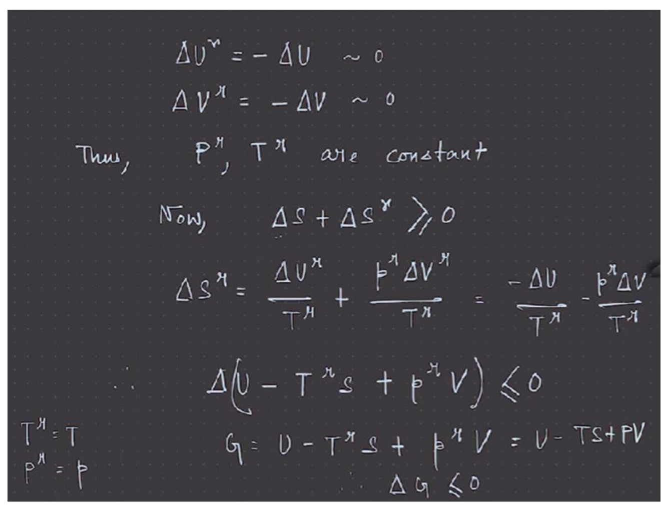

Now if I talk about a system in contact with the reservoir is very large then basically we can and it is a thermal reservoir then we use Helmholtz free energy and in case of Helmholtz free energy we have seen that DF has to be equal to 0 right that is an extremum condition and D2F is greater than 0 right we basically have seen that the delta F has to be less than or equal to 0 delta F equal to 0 when the process reversible but if you now look at DF in terms of D means the exact differential of F then DF has to be equal to 0 for extremum and D2F has to be greater than 0 for this extremum to be a minimum right D2F has to be greater than 0 now think of this this is another very interesting thing that comes in which follows is that system plus reserver that system plus reserver and this is a thermal reserve right we are anyway talking about a reserver in case of Helmholtz free energy because where we have replaced S with its conjugate variable T then system plus thermal reserver if you take together then basically they together form an adiabatically isolated system right which does not permit that does not permit exchange of energy with the surroundings right so system plus reserver so reserver is your thermal reserver so system plus thermal reserver together is an adiabatically isolated system right which does not permit any exchange of heat with the surround right so you can think of this as an adiabatically isolated system so basically we are trying to say you have system and then you have a reserver so this is your system and this is your reserver and say the reserver has a temperature TR and your system has a temperature T so what we are basically telling the constraint here is that if the system is in contact with the reserver then T equal to TR right so T takes the temperature of the reserver right so T has become equal to TR I should write T equal to TR right and TR is the temperature of the reserver now if you look at this entire system so this basically this entire system is an adiabatically isolated right system right which is adiabatically isolated from the rest of the universe right it is basically adiabatically isolated from the rest of the universe so if it is so it does not permit any exchange of heat here so it is not Q this is not converted right so there is no exchange of heat in that case if you think of system plus reserver as your adiabatically isolated system then if you look at the definition of W here is minus of delta U plus ER now this follows from so if you think of the W is a work done by the system then this is nothing but equal to minus of delta U plus ER right which is basically U is the change in internal energy of the system and ER is a change in internal energy of the reservoir now you have like minus delta U minus delta ER so minus delta so basically delta U plus delta ER plus W.



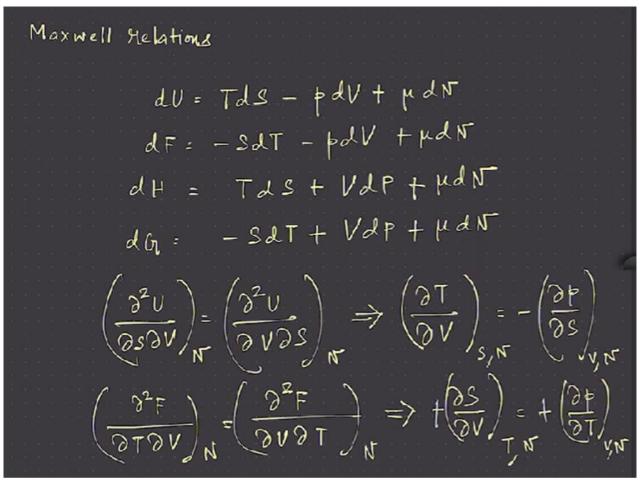



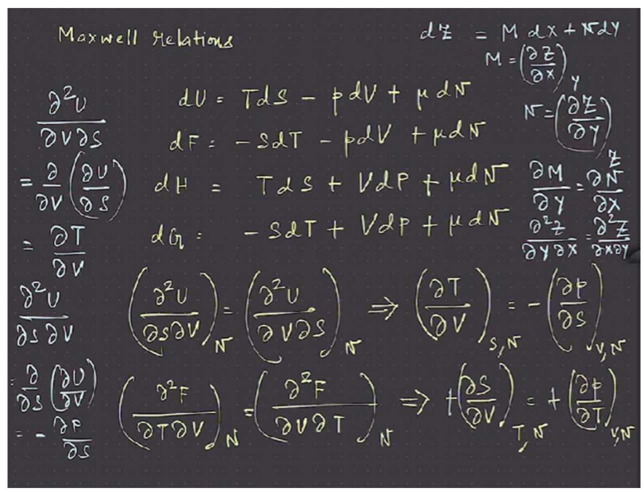

Basically will give you either equal to means will be equal to 0 so now that is one very interesting thing that comes in here is that you have delta UR right delta UR is a change in internal energy of the reservoir and assume a reversible process so delta UR is nothing but TR delta SR right so it is TR delta SR right delta SR is the change in entropy of the reservoir so we can write minus delta U minus TR delta SR now we have from second law that delta S plus delta SR has to be greater than equal to 0 right for a reversible process if only reversible process is taking place delta S plus delta SR equal to 0 right this plus this equal to 0 equality condition happens so that means delta SR is nothing but minus delta S so now think of this work as reversible then you can write W reversible is minus delta U right minus delta U plus TR delta S but delta S is the change in entropy within the system right not within the reservoir but within the system so minus delta U plus TR delta S but TR and T are same so we can write minus of delta U minus T delta S now delta U minus T delta S is nothing but minus of delta F so that drop W reversible that is a maximum work that is done that W reversible is equal to negative of the change in almost free energy right and as we know that W irreversible the work done by if the processes are irreversible then the work done the network done by an irreversible process is always less than the work that you can get or obtain from a reversible process and that for a reversible process you have the maximum work and that maximum work is basically equal to negative of the change in almost free energies right almost free energy this is also basically called maximum work principle right so maximum work that is derived is the negative of the almost free energy so almost free energy in some way defines the maximum work that can be obtained right and the maximum work that can be obtained is always through a reversible process right irreversible process the amount of work that can be obtained is always less than that of the reversal process right that we have already discussed in the purview of second law right okay now let us look at another means we have in general in materials science we deal with the change in Gibbs free energy right we will look at and as you see later that when we look at solution thermodynamics and we look at the phase equilibria and phase diagrams and their relation to phase equilibria.



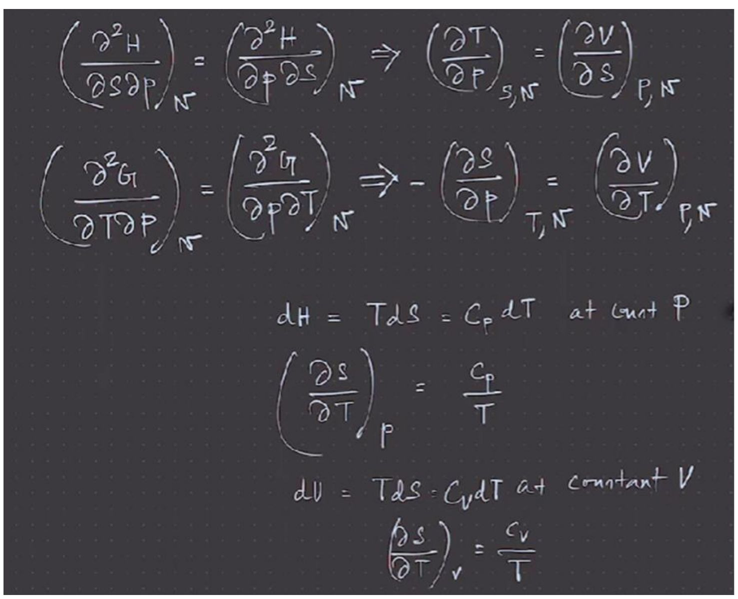



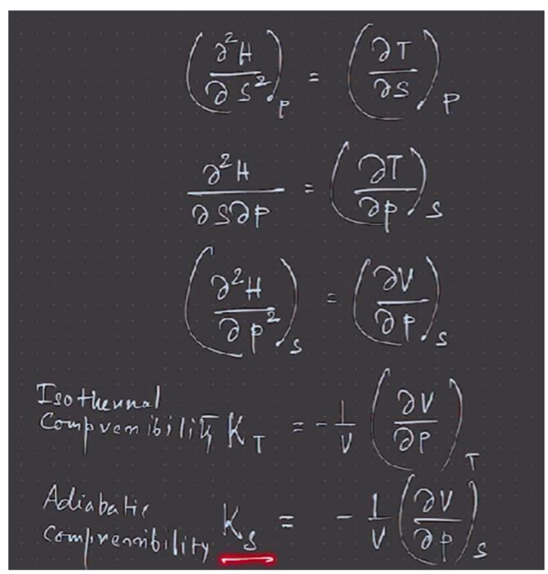

We will always consider Gibbs free energy right why Gibbs free energy because we are assuming so in why Gibbs free energy is because when we have this multi component multi phase systems and we are looking at the equality of chemical potential we often want to use a thermal reservoir as well as a mechanical reservoir so that means if I think of thermal mechanical reservoir we have T equals to TR and P equals to PR that means pressure of the system so T is T system right P system is equal to the temperature of the reservoir and P system equals to temperature pressure of the reservoir so basically a system that is in contact with the thermal reservoir and the wall is flexible so that the volume as just such that P also is equal to P right so basically you have a system that is in contact with the thermal reservoir but now the wall of the system with the reservoir is flexible so that the volume adjust in such a way that the pressures are also the pressure inside the system is equal to the pressure of the reservoir right now again let us look at this idea that you have system plus reservoir and the total so system plus reservoir itself is like an isolated system and in that case the change in U plus UR is the total that in the there is the total change in energy right the energy is concept written as is constant so the total energy tell you that U plus UR for that system equal to constant so this system basically is nothing but this isolated system is nothing but system plus reservoir and the reservoir is a thermal as well as a pressure reservoir right thermal as well as a mechanical reservoir you can think of right now if that is so then if this is so then immediately this implies this right delta U plus UR is equal to 0 similarly the total volume if I think of the total volume V plus VR right V plus VR that is also going to be constant so as a result delta V plus VR equal to 0 right.



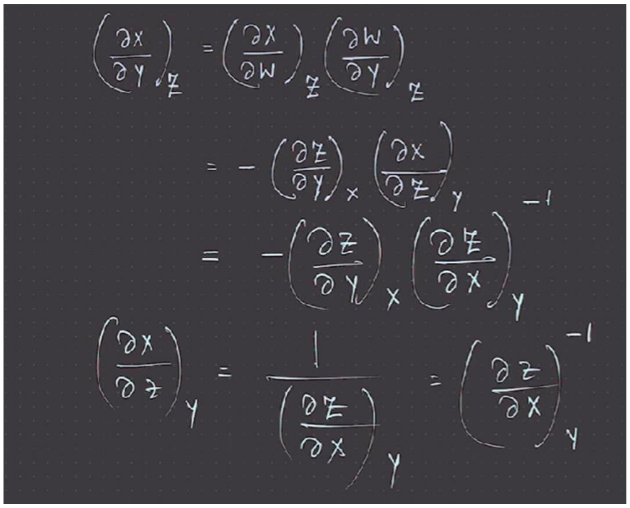



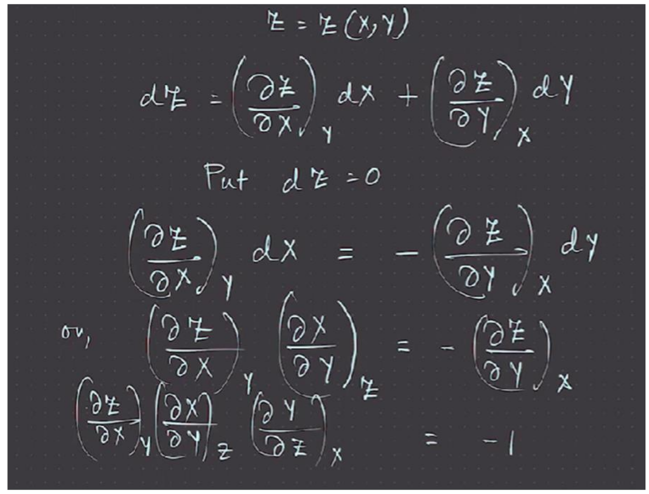

So delta V plus VR equal to 0 delta U plus UR equal to 0 that means delta U is equal to minus delta UR again delta V is minus delta VR however delta VR and delta UR because the reservoir is assumed to be infinite compared to the size of the system so reserve so always we assume that the reserves size or the size of the reserves is much much larger that means it is almost infinite compared to the size of the system reservoir is so huge that it is infinite compared to the size of the system so in such a case delta VR and delta UR are going to be even though there is see if there is a change in the energy of the system there is definitely a change in this see this relation we have already shown that the delta U is going to be minus of delta UR or basically you can tell delta UR is going to be equal to minus delta U that means if my if there is a change in the energy of the system then there is also a change in the energy of the reservoir however the system is the reservoir is so huge that the temperature of the reservoir remains TR even though there is a very infinitesimal change in the internal energy of the reservoir so del UR equals to minus delta U but delta UR and delta VR right delta VR and delta UR are infinitesimal and neglected due to the infinite size of the reservoir this is a very important point that delta VR and delta UR although they are there but they are infinitesimal and they are neglected because of the infinite size of the reservoir right although that this relation is indeed true that delta U equals to minus delta UR or delta V equals to minus delta UR so these are true but delta UR and delta VR are really small right so delta UR which is minus delta U is negligible right it is negligible and you can call it like 0 delta VR also is negligible thus PR and TR that is the pressure of the reservoir as well as the temperature reservoir are constant but from second law you tell that delta S of the system and delta S of the reservoir have to be greater than equal to 0 now delta S reservoir is nothing but delta UR by TR and also you have now you have also change in volume of the reservoir right so you have PR, TR is the pressure of the reservoir into delta VR because there is a change in volume because the wall is flexible between the system of the reservoir so you have PR delta VR and delta UR by TR so you have delta SR which is delta U plus P delta V right so delta SR which is delta UR by TR plus P delta PR delta VR by TR which is basically delta UR is nothing but minus delta U right minus delta U by TR and this will be PR delta V because delta VR is minus of delta so you have a minus sign so therefore delta so from this relation you can see you are replacing delta SR with this term okay so then it becomes I take delta common it becomes U minus TR S plus PRV is less than equal to 0 now G because TR equal to T since TR equals to T right and PR equals to P thermal and mechanical equilibrium then G is U minus TR S plus PRV which is U minus TS plus PV and U minus TS plus PRV is nothing but G right so which is U minus TS plus PV and instead of T I am writing TR and instead of P I am writing TR because indeed the system is taking the temperature of the reservoir and system is taking the pressure inside the reservoir right so basically at mechanical equilibrium means indicates that the pressure of the reservoir and the pressure of the system is the same right and the pressure of the reservoir is held constant because reservoir is infinite compared to the system right.



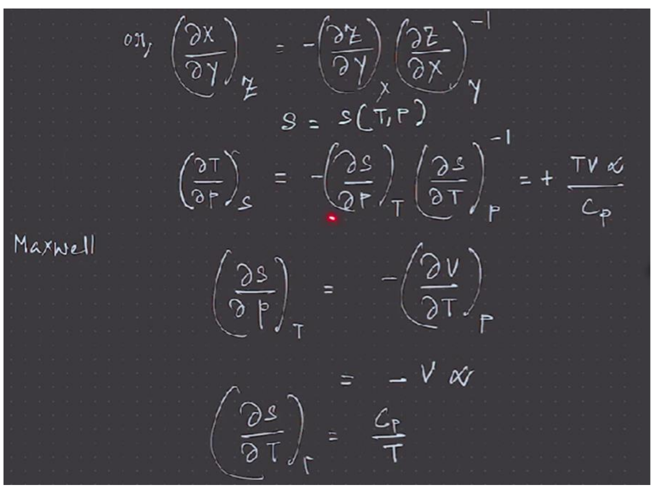



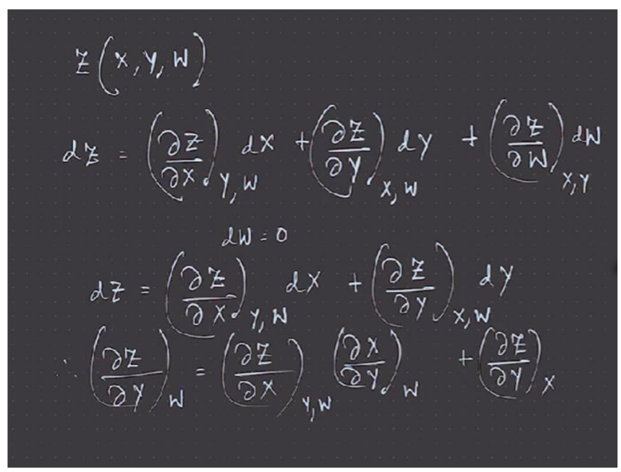

I am repeating several times to emphasize this very important points and therefore we can try directly from this relation which comes from the second law remember this is coming all of these are coming to the second law right second law tells this and delta SR I have written in terms of minus change in internal energy of the system and change in volume of the system right there are two quantities delta SR is expressed in terms of change in internal energy as well as in volume and also we have made sure that we see that we have PR here and we have TR here because the PR and TR are not only the temperature of the reservoir and pressure of the reservoir there are also temperature and pressure of the system at thermal and mechanical equilibrium is given so as a result we can directly write delta G less than equal to 0 again it gives you the Gibbs free energy minimum principle right it gives you the values of the internal unconstrained internal parameters that they will assume is basically the those which will minimize the free energy and the free energy change is less than means so the extremization conditions if I if I write in terms of differential form is dG equal to 0 and d2G is positive and here what we are telling is delta G that is the that is not an infinitesimal but a macroscopic change the delta G has to be either equal to 0 or less than C now we want to discuss so basically we have now discussed these different thermodynamic potentials like Helmholtz free energy even enthalpy can be is one thermodynamic potential enthalpy is one thermodynamic potential again related to the led to U and S and V so via the Legendre transform where we are basically replacing V by P so enthalpy, Helmholtz free energy, Gibbs free energy okay so we have defined at least these three thermodynamic potentials using the conjugate relations and or using the conjugate variables now comes one very important consequence of exact differential so these are called max-free relations now if you remember we discussed already that dz if it is an exact differential MDX plus NDY and where M is basically del z del x and again if I am using partial derivative it implies that del z del x with constant y and n equals to del z del y at constants by the way Maxwell relations you will see that are basically very useful to derive many important thermodynamic relations between directly measurable quantities in thermodynamics like temperature, pressure, volume, thermal expansion coefficient, heat capacities and the indirectly measurable quantities such as energies right different energies or different thermodynamic potentials so you have this and we have also told that the property of exact differential is that del M del y should be equals to del M del x that means the second derivative is where we are looking at so we are telling del 2z del y del x is the same as del 2z del x del y that means the change in order of differentiation does not really matter if you are dealing with an exact differential that means del 2z del y del x see the order is different right first we are doing del z if I am finding del z del x and then we are differentiating with respect to y in this case here it is first with respect to y and then with respect to x but that does not matter the order does not matter as long as dz is an exact differential and we know that all state functions in thermodynamics are exact differentials no so then we can basically replace them so we can write like du as tds minus pdb plus mu dn remember t is del u del s p is minus p is del u del v and mu is del u del m similarly I can write df now in the case of f we have to use t right we are instead of using s we are using t so it is minus s dt minus pdb plus mu dp for h it is tds plus vdp right here what we are basically replacing we are replacing v by its conjugate that is p right so basically we have tds plus vdp and mu dm and dg where we are replacing s with t and v with p then basically becomes minus s dt plus vdp plus mu dm so these are four exact differential relations right in in this these are the common common in potentials that are used in all thermodynamic analysis of simple systems and you have du df dh and dg right now you see a very interesting consequence that your du as a function of s and v now we are just keeping n constant for for time being we are not for n is already n is assumed to be constant see all of them have mu dm mu dn and mu dn.



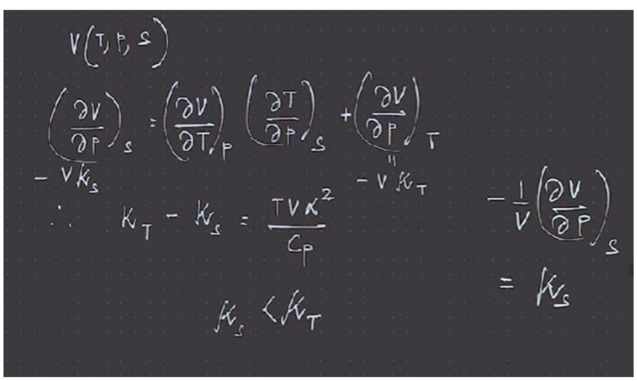



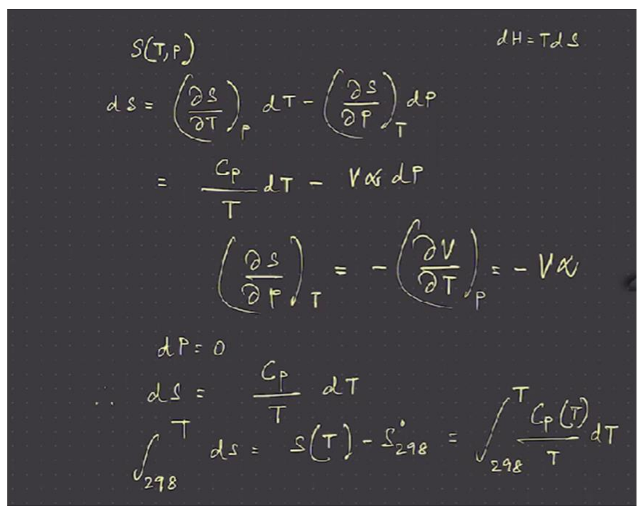

So now it becomes del 2 u del s del v n now as you can see is because again this is coming from this definition of exact differential so del 2 u del s del v n is same as del 2 u del v del s n the order does not matter so as a result now you see in one case it is del u del s and then del u del v another case is so what this implies is basically if i tell that del v is there so del t del v so here we are using t t is what t is nothing but del u del s t is nothing but del u del s so what we are basically telling is del 2 u del v del s is basically del del v of del u del s and del u del s is nothing but t which is equal to del t del v on the other hand del 2 u del s del v is nothing but del del s del u del v so so this is what we have written del t del v s n is equals to minus del p del s v n right now if you look at the helmholtz free energy we have t as one of the variables t and v right so del 2 f del t del v is equal to del 2 f del v del t again that gives you del s del v is equals to del p del t how because del f by if you think of this del f by del t equals to minus s del f by del t equal to minus s and del f by del v equals minus p so you have if you again look at the sequence so you have del f del v del f del v is basically equal to minus p so this becomes minus del p del t and this becomes minus del s del v and so minus minus cancels out with both become plus so basically you have this relation del s del v t equal to del p del t v right del p del t v n also r is fixed right as i as i am telling that i have written n but you can neglect this n right n is fixed because we are not using doing anything with n and in both sides so you have del s del v and del p del t equality again coming from this equality of the second derivatives right the equality of the second derivatives is giving you equality some useful relation between so this useful relation is coming because del s means you are replacing the so the order does not matter but del f del t we are replacing by minus s and then you are basically replacing del f del v by so you get another useful relation so all these relations are coming by equating the second derivatives and telling that the order does not matter as a result if the order does not matter i can basically tell that if i do del del v of del u del s or del del s of del u del v they are the same and del u del v we are replacing by minus p and del u del s we are replacing by t so we are getting this very useful relations right so again for example if it is h you have s and p so you can write del 2 h del s del p equals to del 2 h del p del s which gives you del t del p you see it gives you del t del p as a because you have del h del s is equal to t right so del 2 so del h del s is equal to t so del t by del p equals to del h by del p so del h by del p here is equal to v so we are using which is basically del v by del s right del v by del s right del h del p is v and del del s of del h del p is basically del v del s so del v del s equals to del t del p okay so there are many ways to remember this relations there is something called thermodynamic square i'll not get into that but what i want to tell is that it gives you maxwell relations although it initially looks bit tedious you will see that these maxwell relations can be used okay this can be used to derive many useful relations between the indirectly measurable quantities and directly measurable quantities again we have del 2 g del t del p equals to del 2 g del p del t which tells you minus del s del p equals to del v del t again another useful relation why are these useful relations we can immediately see here for example del v del t has a relation with alpha right del s del t has a relation with c p right so so because dh equals to t ds say at constant pressure for example we know at constant pressure dh equals to t ds equals to c p dt so del s del t p is c p by t we have already seen that then similarly del s del t v equals to c v by t because du equals to t ds right at constant volume which is equal to c v dt and so therefore del s del t v equals to c v by t right so and you can see here that we have used we have got these other relations here so now if we look at this del 2 h del s square for example now del 2 h del s square okay at constant pressure is basically the double differentiating enthalpy with respect to entropy.



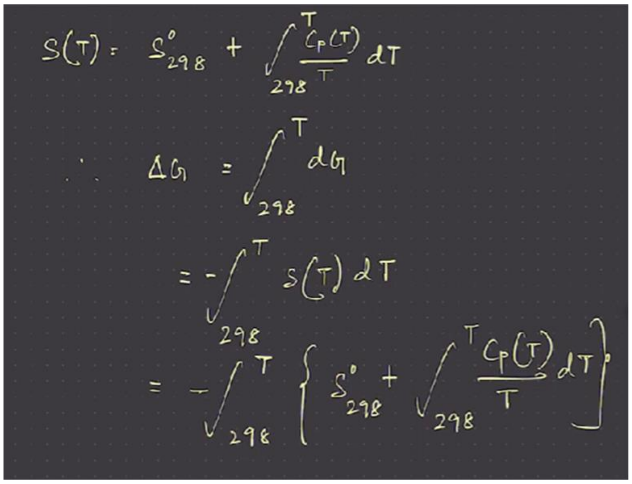



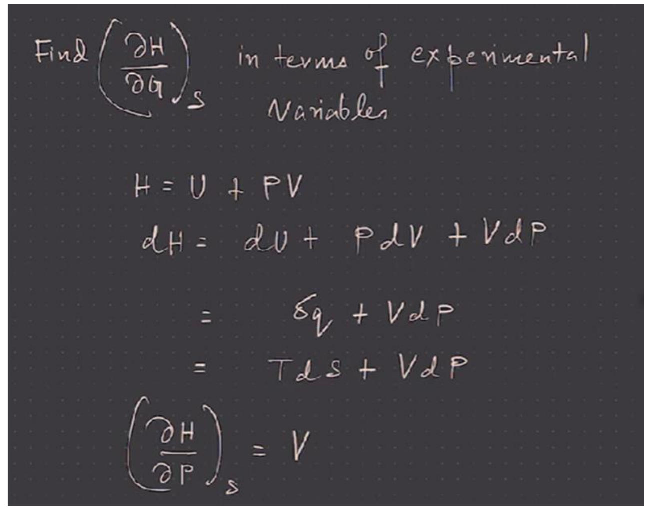
What we get is del t del s because del h del s is equal to t right del h del s because dh equal to t ds right so del t ds plus vdp plus mu dm so t ds so del h del s del h del s with at constant pressure del h del s at constant pressure right is equals to del h del s at constant pressure is equal to t right so now you are using t so del t del s p now del t del s p is nothing but inverse of del s del t so you get immediately a measurable quantity del s del t is nothing but c p by t at constant pressure right also this becomes yeah so now you have del 2 h del s del p which is del t del ps right again we are using del h del p del h del p if you write so you have pdp so del h del p is v right so you have del 2 h del s del p and we are doing del h del s so basically we are writing this way del h del s and so in fact i should have written del 2 h del p del s but it does not matter right the order does not matter so del 2 h del s del p is del 2 h del s del p del s which is basically del t del p at constant right again del 2 h del p squared if i do which is nothing but del h del p which is v and so this becomes del v del p at constant pressure right now if you look at this now if these three relations give you an example see i want to give you an example that how these relations of second derivatives and the relations between the second derivative and first derivatives which gives you from the second derivatives we get a very useful relation between the first derivatives which relates temperature and pressure change at constant entropy or volume change with pressure at constant entropy or volume or temperature change with entropy at constant pressure and all of these are related to some useful quantities like c p c v or alpha or beta or beta or here we call it kappa t and kappa s kappa t basically is isothermal compressibility that is at constant temperature which we have defined previously as minus 1 by v del v del p at constant temperature we can also think of adiabatic compressibility where entropy is constant so k s or kappa s which is minus 1 by v del v del p s so you have del v del p t here you have del v del p s here now if i tell you find the relation between k t and kappa t and kappa s that is isothermal compressibility and adiabatic compressibility you can use these relations how you see first of all if i want to use these relations if i want to use these relations we have to use some properties of derivatives so one property that we immediately can see is that del x del y z can be written as del x del w z and del w del y z right it is basically we have some variable called w so del x del y is replaced by del x del w.



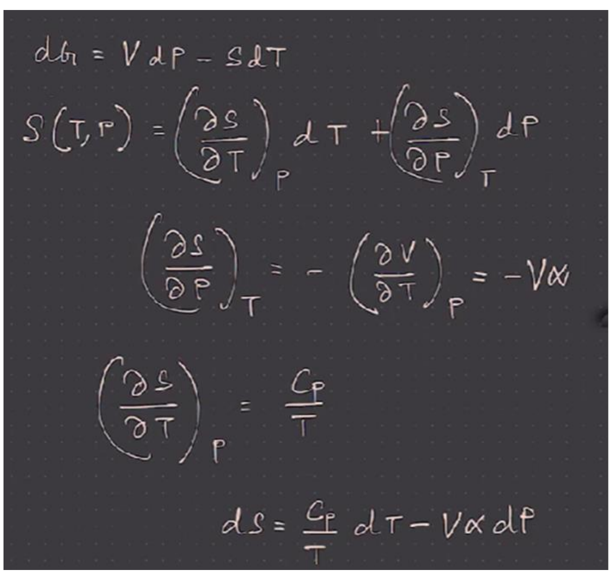



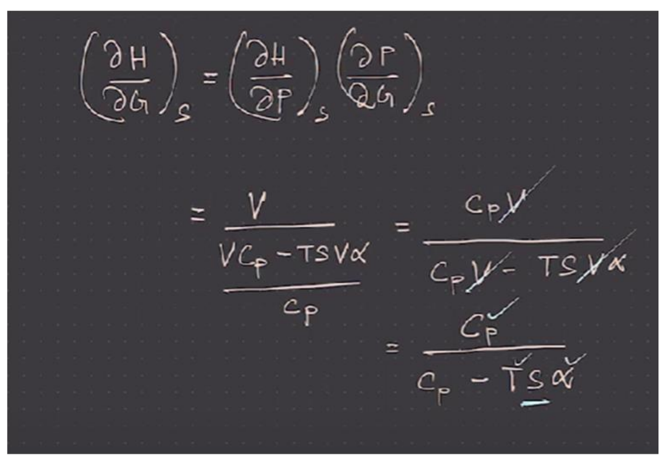

So there is one another variable w which is again a function of say y so we are telling del x del w and and it is also a function of so x is a function of w and x is also a function of y so i am telling that del del x del y is nothing but del x del w del w del y right this is very classic chain rule now this also means that del x del y we can also write as minus del z del y x or del x del z y or we can also write it as minus del z del y x and this is del z del x y the power minus one right so it is inverse so so basically what we are telling is del x del z y is nothing but one by del z del x y or equal to del z del x del z del x y to the power minus one now this relation is quite interesting right it is it is a cyclic relation a chain rule how does it come so let us look at this we have already discussed that but again just to recollect just to recollect dz if z is a function of x and y one can quickly write that dz equals to del z del x again just writing del z del x means that y is constant right del z del x means y is constant dx plus so dz again is a exact differential so this will be del z del y is fixed and this is now put dz equal to zero so what you get is del z del x y dx equal to minus del z del y x dy or you can write del z del x y del x del y right sorry del x del y so del z del x y del x del y so what I am doing here here dx here we have dy I am doing differentiating x with respect to y keeping z constant differentiating x with respect to y keeping z constant and because I am just taking dy here so del x del y z and this is minus del z del y x right or if I take this also here so it will be inverse of del z del y x if I take it to the if I take this guy to the left hand side then del z del y x will be coming to the denominator right one by del z del y x which is basically nothing but del y del z x right so this becomes equal to so this is minus one and this becomes see del z del x y del x del y z fixed and del y del z x fixed which is equal to minus one see del z del x del x del y del y del z right this is like del z del x del x del y del y del z and it's like a cyclic chain rule and we have del z del x when we are writing we are writing y fixed del x del y z fixed del y del z x fixed equal to minus one see this is something that we have used in the previous lecture also so I am just and we have proved it in the first week itself in the first week or second week and this is something that we will continue to use so many of this remember one of the means when you want to find useful relations there is a little bit of algebraic manipulation involved right it's a little bit of mathematical jugglery involved and that basically centers around the only logic or that you have to use or only math that you have to use is the properties of partial differentials right and the properties of exact differentials or inexact differentials so basically a little bit of understanding of partial derivatives and the relations between them will be very useful for deriving very useful important relations in thermodynamics however note that when you are deriving any relation remember that whatever relation you derive it is always important to derive relations in a way so that you can relate or the relations should be such that we you can involve several measurable quantities then only you have the directly measurable quantities for example temperature is a directly measurable quantity using a thermometer or pressure is a directly measurable quantity using a parameter measuring tape can measure volume right volume is a directly measurable quantity now think of C when the Cp and Cv like heat capacity at constant pressure or constant volume these are these can measure we have already discussed by calorimetry and then you have alpha which can measure using that is a volume expansion coefficient means thermal expansion coefficient means change in volume with respect to temperature again we can be related to the linear expansion the thermal expansion coefficient and this can measure using something like dilatometry and then you have beta which is our beta or kappa t kappa s these are like isothermal compressibility and adiabatic compressibility which can also be measured right so now if you have this type of relations what we have is now we have basically the relation between we want to find a relation between kappa t kappa s and all these derivatives so if I use these relations now you see since so again following this relation that we have del z del x del y del y del z equal to minus one we can write del x del y z is minus del z del y fixed x times del z del x inverse fixed y so basically what we are now trying to replace is t so basically my x is t so z is basically s so s is a function of t comma p is what we are considering now that is so you have del t del p which is we had fixed s which is nothing but minus of del s del p times del s del t inverse right we are just using the the cyclic chain rule so we have this relation now as you can see del s del p what is del s del p if you remember or if you do not also I just remind you so let us look at del s del p so we have found this so del s del p is nothing but del v del t which is nothing but see alpha is one by v del v del t p now therefore del v del t p is nothing but v alpha so v alpha so del s del p minus of del s del p t is equal to v alpha so now using that relation minus of del s del p t is nothing but v alpha del s del t p is del s del t p is c p by t but this is del s del t p inverse.




So this is t by c p so this becomes t v alpha by c p now you have del s del p t which is minus del v del t p which is minus v alpha del s del t p is c p by t now you can see that you have c p by t and another relation if z is a function of x y and w we can also write dz equals to del z del x y comma w and del z del y x comma w and del z w x comma y and now we are telling dw equal to zero so if dw equal to zero then we can write this as dz equals to del z del x y comma w dx del z del y x comma w dy or if i can if i can differentiate again with respect to y basically i am taking dividing both sides by dy i get del z del y w equals to del z del x y w del x del y w plus del z del y x right this is some relation that also we are very familiar with and we can easily derive now if you use all this relation and then i write the volume so this is the point that i am trying to say whenever we measure we first want to find out what is the most useful relation that we should use so here for example to find the relation between isothermal compressibility and adiabatic compressibility we are using the relation between v and v is related to temperature pressure and entropy right we are writing v as a function of temperature pressure and entropy right and we are now telling isentropic that means entropy is fixed so that means i am going to directly use this relation here w is fixed right here w is fixed so we are going to use this relation and so instead of w here we are talking about s fixed right s fixed so if i use this now you have del v del ps equals to del v del t p del t del ps plus del v del p del v del v t right so now del v del ps basically is one by v del v del ps is minus one by v del v del ps is basically your so if i have if you remember minus one by v del v del ps was defined as right so so therefore this is nothing but minus so this is nothing but minus v k s so now del v del t p already we know is v alpha then you have del t del ps now what is del t del ps again what is del t del ps you can have del t del ps equal to we have done this del t del ps is equals to t v alpha by c right we have been just now we derived it so we will use t v alpha by c p so you have t v alpha by c p here so here p v alpha by c p and this is v alpha so so and you have here v k s now if you see and here del v del p t is nothing but minus v kappa t which is now if you do this and if you rearrange so what do you get minus v k s kappa s equals to v alpha times del t del ps which we have got as t v alpha by c p v alpha t v alpha by c p minus the which is isothermal so this is isothermal concrete compressibility increases at a very compressibility you can take out one of the v's right you can take out one of the v's now so what happens is kappa t minus kappa s kappa t minus kappa s is basically going to be t v you have two alphas right t v alpha squared t v alpha squared by c p now you see these two relations which again can be measured maybe with some difficulty are related to some very easily measurable quantities right what are the easily measurable quantities t by thermometer v by measuring tape or right we can be easily measured by just measuring the dimensions right of of the of the of the container and alpha basically is the or dimensions of the system right it is the dimension of the system so v is the dimension of the system when i talk about container the container is the wall basically so the system is contained inside the container right so v is the volume of the system t is the temperature of the system which is made by a thermometer c p can be measured by calorimeter and alpha can be measured by a telemetry meter so you have now a relation between isothermal and adiabatic compressibility and with thermal expansion coefficient volumetric thermal expansion coefficient heat capacity volume and temperature right so this is something that we can immediately appreciate that t is t is positive v is positive c p is positive and alpha is for positive so in that case kappa s it means kappa s is basically the adiabatic compressibility will always be less than isothermal now let us look at how do you use this how do you use this type of relations you just find out which relation to apply for example if i tell you find the delta g there is a change in free energy for magnesium oxide.

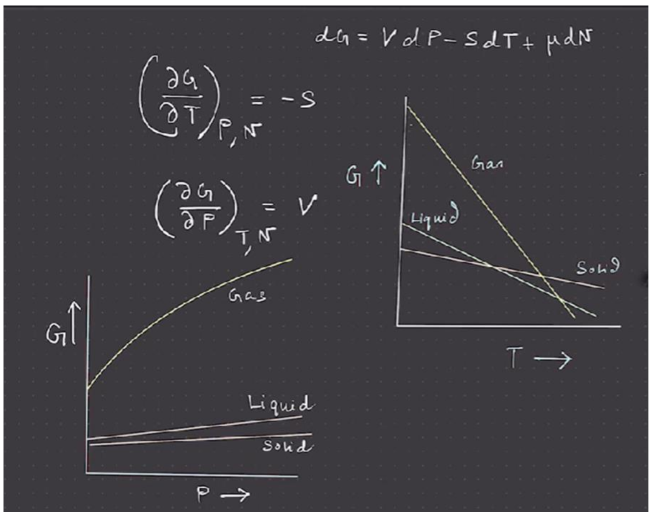


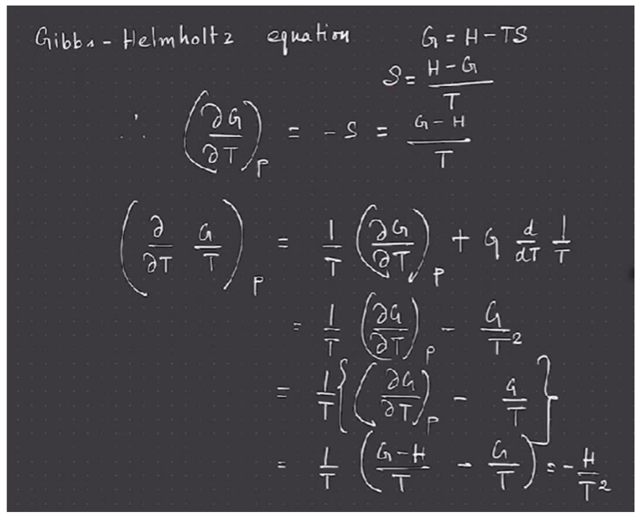




When one mole of magnesium oxide is heated from 25 degrees celsius to 1027 degrees celsius at one atmosphere pressure and what we have given is the property of magnesium oxide in terms of c p which is 48 point so this is a point 0.99 plus 3.43 10 minus 3 t minus 11.34 10 to the power minus

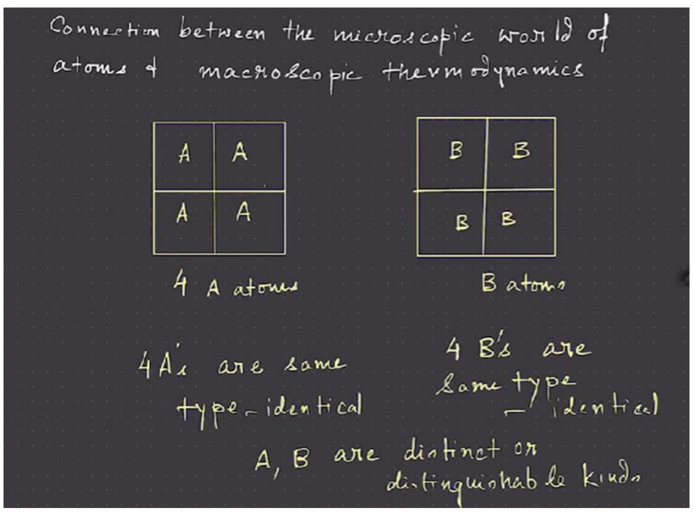
5 by t square joule per mole kelvin right c p here is the molar heat capacity s 0 to 90 it is also given which is basically the reference entropy right standard entropy at 298 kelvin or room temperature which is given as 26.9 right and t is equals t plus t at degree celsius so t this is absolute scale is equals t degree celsius plus 273 as we know now the identify the variables what are the variables we want to find g and we have pressure we have temperature right so g as a function of t p we already know dg equals minus s t plus vdp dp equal to zero why because we are telling one atmosphere pressure we are not seeing the pressure so basically one the pressure is fixed at one atmosphere so dg becomes equals to minus s dt now s now if i have that now s again can be determined as a function of temperature and pressure so ds equals to del s del t p dt del s del p t dt dp and you can immediately see del s del p t dp is nothing but v minus v alpha t and then del s del t p is nothing but c p by t dt so del s del p t is nothing but again minus del v del t p which is minus v alpha so now if v p equal to zero if v p equal to zero ds equals to c p by t dt right because we have constant pressure right atmospheric non atmospheric pressure now you are basically finding out the change in entropy from 298 kelvin to the temperature of interest what is the temperature of interest 25 degree celsius is 298 kelvin right the lower temperature is 298 kelvin and this is one zero two seven degree celsius you can multiply that add 273 so one zero two seven plus two seven three which is zero thirteen hundred kelvin right so it is 1300 pressure is one atmosphere and it's constant constant pressure so that's why dp equal to zero now you can see you can find ds which is c p by t dt you can now integrate why you can integrate because you know the s zero 298 right you know s zero 298 from addition so basically that gives you c p t by t c p by t dt right 298 and c p t also you already know now once you know that you get s t which is s zero 298 plus this and delta g is nothing but integral of dg from 298 to t and dg is nothing but s dt and s of t is what you have obtained you directly use that and do apart there is a remember that there is a minus sign here now phi minus sign because dg equals to minus s dt right so minus s dt so you now integrate and you basically you have an integral c p by t here and then s zero 298 and this has to be integrated from 298 to t to get the delta g there is another problem so it is again coming from one exercise problem given by dr so and you see again you see what we are telling is del h del g but h and g enthalpy and gis free energy these are basically not directly measurable quantities but because they cannot be obtained directly from experiments right but you can basically measure them in terms of experimental variables in this case there is one variable that i will tell is may not be that it is isentropic so basically if i know the standard entropy i can estimate the entropy right i can estimate the entropy and i can also find del h del g in terms of some experimentally measurable quantities i start with so if i want to look at del h del g i want to look at dh i want to look at dg now dh equals du plus pd mu plus vdu p which is nothing but delta q plus vdp now delta q is nothing but tds for reversal process so tds plus so dh equals tds plus vdp that means del h del ps right del h del ps is going to be equal to v right del h del ps equal to v now you see del g dg equals vdp minus this we have shown and s of s tp is equals to minus v alpha dp equals c p by t dt right so we know ds right now c p by t dt uh c p by t dt and v alpha dt ds equals to this right c p by dt equals ds plus v alpha dp right from this relation from this relation you can write ds plus v alpha dp equals to c p by t dt right c p by t dt now dt equals to t ds by c p plus t b alpha by c p into dp right so you can get this right because dt so t ds and v alpha t uh by c p and uh you can see

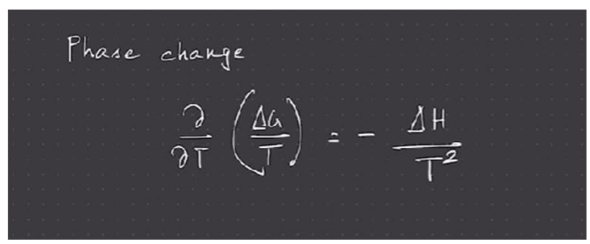
this is equal to dt now dg equals to vdp minus s dt which is basically vdp minus s and this dt i instead of dt so this is dt i am substituting this dt here now if i do that i get v minus t s v alpha by c p dp and so i'm just doing this calculation and t s by c p ds so del g del ps i get s v minus t s v alpha by c p you can do this uh little algebraic manipulation you can basically easily arrive at this relation so you got del g del ps and you have also del h del ps now as you can see del h del g s is nothing but del h del ps and del p del g s right this is basically chain rule so del h del p and del p del g there now you are using del h del p which is basically v by del g del ps inverse right this del p del gs right so this is v by v c p by t s minus t s v alpha by c p which is c p v by c p v minus t s v alpha so i can take v out right v is not since v is not equal to 0.




I can take the v is uh because v is common in all so basically i get c p which is equal to c p by c p minus t s alpha if i know the isentropic condition that means if i know entropy value c p and t and alpha are all experimentally measurable quantities right another thing i just very quickly want to tell that if we look at phase change problems for example the definition of g becomes very useful um keeping the number of moles fixed for currently if i look at just dg equals to vdp minus s d plus mu dn this expression you know del g del t with as fixed pressure and mole number of components is equal to minus s and del g del p t is equals to v now as you can see if i write g so these are these are schematics okay so g if i write or express as a function of t the slope has to be minus s but s is positive right s is positive is the entropy and for gases gases have will have a very large entropy right because the the molecules are far apart they can be arranged more randomly so the randomness is more in gases liquid has little more order but still the molecules can move around liquid has more order than gas gas has almost no order and then you have solid solid where all the this solid the the atoms are very closely packed right in solids so as a result it's like you can assume like some springs are connected between these spheres right if you think of and this all this this has a bit much regular patterns solid has a much regular pattern than liquid so in general solid has the lowest entropy and liquid has uh liquid has slightly higher entropy than that of solid but in gas case it is very very large and as you can see as you increase temperature the randomness basically increases so temperature again as i wanted to tell you temperature and entropy are conjugate variables so if you increase temperature the entropy goes higher so minus s that means tells me that gases will have free energies which will have a very steep slope of minus s for liquids it will not be as as steep with temperature for solids there will be very little change in slope right means minus s because s itself is small for solids compared to that of gases however now if i look at volume del g del p which is at a fixed temperature you get v right now volume obviously gases will have a very large volume change right as a function of pressure so for gases you can see how dramatically the free energy changes on the other hand on the other hand for liquids and solids the change is very very small now this is something that we would like to emphasize right these are very schematic diagrams but see for phase 6 problems the trends basically become very evident just by looking at the slopes like del g del t or del g del t right so one very useful relation that i can think of is the gibbs's homogeneous relation which is g again we know g equals to h minus t s from there we can write s which is h minus g by t and del g del t p equal to minus s which is basically g minus h by t now if i do the differentiation del t of d by t i get one by t del g del t p and g del del t of one by t which is minus g by t square i take one by t common and i get del g del t p minus g by t which is g minus h by t by g minus g by t which is basically coming out to be minus h by t square.




You will see that this becomes a very very useful relation particularly when we have phase change problems so this is the phase change problems we will deal with in the next week of lecture and you will see that for phase change this type of relation becomes very useful del by t of delta g by t which is equal to minus delta h by t square right if i know the details and we will also look at in the next week the connection between macroscopic world of the microscopic world of atoms right the microscopic thermodynamics are we are looking at macroscopic variables like volume temperature pressure and all but there is this microscopic world and i have talked about say some molecular interpretation for example is what we will be talking about molecular interpretation of energy is already something that we have given molecular interpretation of temperature is also something that we have given or heat capacity now we will try to find out the connection between entropy in the defined in macroscopic thermodynamics and the entropy that you can realize in the microscopic world so we will try to do that or discuss that in the next class right next class in the next week that week five okay then thank you very much and another thing before i end this lecture i would like to tell you let's see when i am recording for nptel lectures in general uh means it might be possible that i am going a little bit faster right because you know the there is not a we do not have a live interaction with the students here so as a result we might be going a bit faster and sometimes it concepts if i go fast you may not be able to understand very clearly so as a result if you have any doubt if you can somehow post comments and let me know i would take up these problems in my subsequent lectures thank you very much for your attention