

Thermodynamics And Kinetics of Materials

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Lecture 12

Fundamental relations and alternative formulations of equilibrium criterion

I will start with this Euler equation again. So, as you can see here that here u which is the internal energy or energy is a function of S, V, N_1, N_2 . So, this N_1 and N_2 are the species or components 1, component 2 and this is the mole numbers right. N_1 is the mole number of component 1, N_1 is mole number of component 1 and N_2 again mole number. So, these are N_1, N_2 and all. So, you can tell that is like if I have this. So, you can tell S is the, so u is a function of S, S is entropy of the system, V is volume and N_i mole number of component i right. Now, as we know from this because u is a function of S, V, N and u is also homogeneous we have just discussed in the previous lecture. It is a homogeneous first order function and λ is an arbitrary multiplier that is greater than 0. Okay, so now if you have this, so $u = \lambda S, \lambda V, \lambda N_1, \lambda N_2$ that means each of these extensive parameters on which u depends on are multiplied with this multiplier λ . This becomes equal to λ times u because λ to the power 1 times λ to the power 1 is basically nothing but λ , λ times u so on. Now, here I do something very interesting here. Instead of differentiating with respect to say in general what we have seen we have differentiated with respect to S , we have differentiated with respect to V or N_1 or N_2 .

Euler equation $U(\lambda S, \lambda V, \lambda N_1, \lambda N_2, \dots) = \lambda U(S, V, N_1, N_2, \dots)$

Differentiate w.r.t. λ

$$\frac{\partial U(\lambda S, \dots)}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U(\lambda S, \dots)}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} = U(S, V, N_1, \dots)$$

*S - Entropy
V - Volume
N_i - mole number of component i*

True for any λ . Put $\lambda=1$.

$$\frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \sum_{j=1}^r \frac{\partial U}{\partial N_j} N_j = U$$

λ - arbitrary multiplier > 0

$$U = TS - PV + \mu_1 N_1 + \dots + \mu_r N_r$$

$$U(\lambda S, \lambda V, \lambda N_i) = \lambda U(S, V, N_i)$$

$$\frac{\partial \lambda U}{\partial \lambda} = U \quad \frac{\partial U}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda N_i)} \frac{\partial(\lambda N_i)}{\partial \lambda} = U(S, V, N_i)$$

Gibbs-Duhem relation

$$dU = T dS - P dV + \mu_i dN_i \quad (\text{from } U = U(S, V, N)) \quad (1)$$

$$U = TS - PV + \mu_i N_i \quad (\text{from Euler relation}) \quad (2)$$

$$dU = T dS + S dT - P dV - V dP + \mu_i dN_i + N_i d\mu_i \quad (\text{from (2)}) \quad (3)$$

Compare equations (1) and (3):

$$S dT - V dP + N_i d\mu_i = 0 \quad (\text{Gibbs - Duhem})$$

$$H = U + PV \quad F = U - TS$$

$$G = H - TS$$

Here what we are doing is we are differentiating with respect to λ , differentiate with respect to λ . Now, if you do that so using chain rule what you can write ∂u then you have this all this $\lambda S, \lambda V$ so on ∂u and now we are basically say differentiating with respect to

λS but we are actually we are differentiating with respect to λ . So, how do I do that? So, I can write this way as I have written here it is $\frac{\partial u}{\partial \lambda S}$, $\frac{\partial u}{\partial \lambda S}$, $\frac{\partial u}{\partial \lambda N_1}$. Again $\frac{\partial u}{\partial \lambda V}$, $\frac{\partial u}{\partial \lambda V}$, $\frac{\partial u}{\partial \lambda N_1}$ and so on which is going to be if I differentiate here on the right hand side it is $\frac{\partial \lambda u}{\partial \lambda}$, $\frac{\partial \lambda u}{\partial \lambda}$ basically it is 1. So, this if I do differentiating λ with respect to λ will give me 1 unity. So, as a result here we do not have λ here it is 1. So, now you have $u = \lambda S + \lambda V + \lambda N_1$ so if you look at the right hand side and the left hand side we are differentiating with respect to λ and we are using a chain rule. So, $\frac{\partial u}{\partial \lambda S}$, $\frac{\partial u}{\partial \lambda S}$, $\frac{\partial u}{\partial \lambda}$, $\frac{\partial u}{\partial \lambda S}$, $\frac{\partial u}{\partial \lambda V}$, $\frac{\partial u}{\partial \lambda V}$, $\frac{\partial u}{\partial \lambda}$, $\frac{\partial u}{\partial \lambda N_1}$, $\frac{\partial u}{\partial \lambda N_1}$, $\frac{\partial u}{\partial \lambda}$ so on and so forth right. So, that is what we are doing. So, basically if I have say only one component if I have only one component I can show you. So, this is nothing but what we are writing is $u = \lambda S + \lambda V + \lambda N_1$ equals to $\lambda (S + V + N_1)$. Now differentiate so you write with respect to λ . So, $\frac{\partial u}{\partial \lambda S}$, $\frac{\partial u}{\partial \lambda S}$, $\frac{\partial u}{\partial \lambda}$ plus $\frac{\partial u}{\partial \lambda V}$, $\frac{\partial u}{\partial \lambda V}$, $\frac{\partial u}{\partial \lambda}$ plus $\frac{\partial u}{\partial \lambda N_1}$, $\frac{\partial u}{\partial \lambda N_1}$, $\frac{\partial u}{\partial \lambda}$ equals to $S + V + N_1$ right because since $\frac{\partial \lambda u}{\partial \lambda}$ and whatever with this λ equal to nothing but u right. $\frac{\partial \lambda u}{\partial \lambda}$ is nothing but u itself. So, you write so that is why you have $u = \lambda (S + V + N_1)$ here. Now once you have done that these equation because it is an arbitrary multiplier we can take it is true for any λ . So, this differentiation that we are doing is true for any λ . So, put λ equal to 1 so what do you get $\frac{\partial u}{\partial S}$ into S right because $\frac{\partial \lambda S}{\partial \lambda}$ so this is the point so if you write $\frac{\partial \lambda S}{\partial \lambda}$ this is nothing but S right. Similarly $\frac{\partial \lambda u}{\partial \lambda}$ is u . So, you have if you have that let's erase this so it's clear you see from the first term this first term if you look at this term then from here you get this $\frac{\partial u}{\partial S}$, $\frac{\partial u}{\partial V}$ and then $\frac{\partial u}{\partial N_j}$ right or $\frac{\partial u}{\partial N_1}$ so this as I told you that it is like for each N which is J starts from 1 to R right so you have R components and so it becomes $\frac{\partial u}{\partial N_j}$ equals to u . So, what you can write now is $u = T S + P V + \sum_{j=1}^R \mu_j N_j$ right $\frac{\partial u}{\partial S}$ is T right $\frac{\partial u}{\partial S}$ when I am talking about $\frac{\partial u}{\partial S}$ remember what we are telling is V is constant in N all the $N_1 N_2$ all for all components all components small numbers are constant the volume is constant then $\frac{\partial u}{\partial S}$ so $\frac{\partial u}{\partial S}$ is nothing but T right so $\frac{\partial u}{\partial S}$ is nothing but T and $\frac{\partial u}{\partial V}$ is minus P right and $\frac{\partial u}{\partial N_j}$ is μ_j right so you have $\mu_1 N_1 + \mu_2 N_2 + \dots + \mu_R N_R$ so up to R components. Now with this relation if you have that you also know from this exact differential because du is an exact differential $du = T dS - V dV + \sum_{j=1}^R \mu_j dN_j$ but from the Euler relation what you get is $u = T S - P V + \sum_{j=1}^R \mu_j N_j$ now if I use Euler relation that is if I use 2 if I use 2 right if I use this relation then I can write $du = T dS + S dT - P dV - V dP + \sum_{j=1}^R \mu_j dN_j + \sum_{j=1}^R N_j d\mu_j$ see this is coming from 2 right because say for example if I write $u = T S$ then $du = T dS + S dT$ right similarly minus $P V$ if I have I have 2 variables right P and V so this becomes minus $P dV - V dP$ then again I have plus $\mu_j N_j$ so and again $\mu_j N_j$, μ_j is repeating and we are summing over j , j goes from 1 to R so this becomes $\sum_{j=1}^R \mu_j N_j$, μ_j equal to 1 to R this is so then we can write this as plus summation j equal to 1 to R $N_j d\mu_j + \sum_{j=1}^R \mu_j dN_j$ now compare if you compare you have μ_j

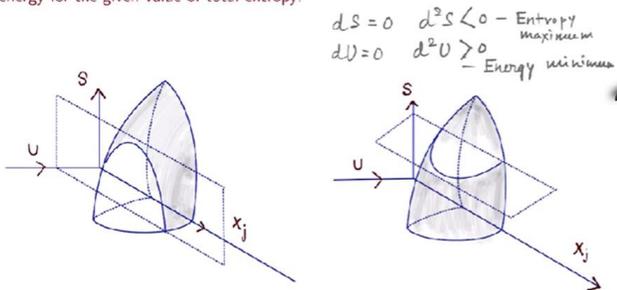
d N I already right in equation 1 you have mu I d N I but there is no N I d mu I right so if I look at 3 and look at 1 so 1 and 3 if I compare this one with this one compare this one and this one then immediately you can see that S dT right this term S dT minus V dP and N I d mu I these are coming extra and so S dT minus V dP plus N I d mu I have to be equal to 0 and this is called GIBBS-DUEM relation this GIBBS-DUEM relation I am writing for U I can write similarly for G or H or Helmholtz free energy some of these which we have defined earlier so now we will try to understand how are these related how are these different thermodynamic potentials related so you have U you can write U as a function of S V and N U as a function of S U as a function of S V and N similarly you can write S as a function of U V and N and then there are also other thermodynamic potentials that can come in how are they coming right you can define other thermodynamic potentials for example what are the different thermodynamic potentials we have defined we have defined for example H equals to U plus V then we have different G equals to H minus righ.

Entropy maximum principle

The equilibrium value of any unconstrained internal parameter is such as to maximize the entropy for the given value of the total internal energy.

Energy minimum principle

The equilibrium value of any unconstrained internal parameter is such as to minimize the energy for the given value of total entropy.



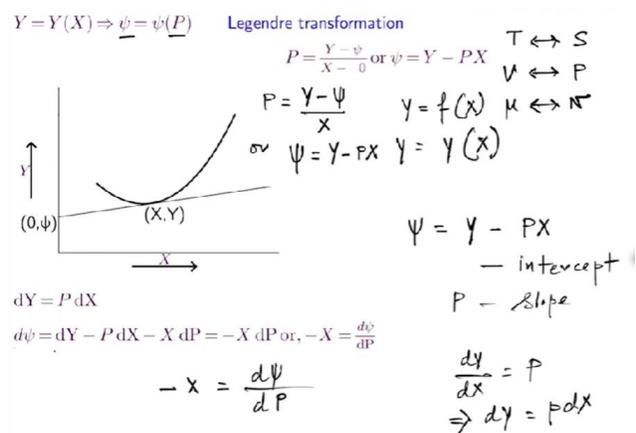
$$\begin{aligned}
 S &= S(U, V, N) \equiv S(U, \gamma) & \gamma &= V, N_1, N_2 \\
 S &= S(U, V) & & \\
 \text{Assume } \left(\frac{\partial S}{\partial V}\right)_U &= 0 & \left(\frac{\partial^2 S}{\partial V^2}\right)_U &< 0 & \text{ - Entropy maximum principle} \\
 U &= U(S, V) & & \\
 \left(\frac{\partial U}{\partial V}\right)_S &= -P = -\left(\frac{\partial S}{\partial V}\right)_U = -T \left(\frac{\partial S}{\partial V}\right)_U & & \\
 Z &= Z(x, y) & & \\
 \left(\frac{\partial Z}{\partial y}\right) \left(\frac{\partial x}{\partial Z}\right) \left(\frac{\partial y}{\partial x}\right) &= -1 & & \\
 \frac{\partial Z}{\partial y} = -\frac{\left(\frac{\partial x}{\partial y}\right)_Z}{\left(\frac{\partial x}{\partial Z}\right)_y} & \left(\frac{\partial^2 U}{\partial V^2}\right)_S = -\left(\frac{\partial P}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial V}\right)_U & & \text{ (from our assumption)}
 \end{aligned}$$

So you have defined H you have defined G and then if you have defined F right Helmholtz free energy how do you define all of this thermodynamic Helmholtz free energy Gibbs free energy enthalpy how are you defining this means what's the basis of defining this so you will see soon how we define such different functions right how are they related right so H H equals to H minus TS F equals to let's say F equals to U minus TS so different different formulations or different thermodynamic potentials can be used to describe basically the energy of the system so in one case we call it internal energy in one case we call it Helmholtz free energy in one case we call it Gibbs free energy right all of these how are they related right so we want to see them right so obviously we know how are they related but how are these relations coming and means what is there a fundamental connection between all of these right is there a commonality between all of these or we can we define any type of thermodynamic potential that we want to so we will look at that but before that one very important point that we have talked about see we have talked about that you can do either of ds equal to 0 and d2 s less than 0 for maximization of entropy or dU equal to 0 and d2 U greater than 0 for minimization of energy so this tells entropy maximum principle and this is energy minimum principle however we have also discussed that when we do the second one we are

keeping the total entropy of the composite system constant in the other case we are telling the total energy of the composites of the simple composite system constant so here we had so basically if you look at the principle the equilibrium value of any unconstrained internal parameter so unconstrained internal parameter can be U it can be S so in this case this the it can be V and all this so basically the equilibrium value of any unconstrained internal parameter this unconstrained parameter example is like $V_\alpha V_\beta$ then say for example $n_1^\alpha n_1^\beta U^\alpha U^\beta$ if you take say two subsystems α and β is such as to maximize the entropy for the given value of total internal energy that means total internal energy is given or fixed right given value means it's fixed total internal energy is fixed and we are telling that equilibrium value of any unconstrained internal parameter unconstrained again constant is put by 1 right unconstrained internal parameter means where we are allowing the subsistence to exchange energy exchange matter and we also perform mechanical work that is redistribute volume all of these if we are telling that means we are completely relaxing all the internal the relaxing all the constraints that are imposed by the wall right so we are making the wall diathermal we are making the wall flexible we are making the wall permeable to exchange of species right between subsystems so in such case the equilibrium value demands the equilibrium value demands the entropy to be maximized but energy minimum is telling you exactly the same statement in this way that equilibrium value of any unconstrained parameter again the same set of in constrain parameters or maybe slightly different so for example the internal parameters are same $V_\alpha V_\beta$ and then you have n_1^α and n_1^β but now you have S^α and S^β right so if you look at that the equilibrium of any unconstrained internal parameter again unconstrained means the constraints that we impose by using a wall we are lifting this constraint so that means we are making the wall flexible we are making the wall diathermal we are making the wall permeable to exchange of species or assume matter is such as to minimize so in this case for example let us look at the contrasting words that is maximizing the entropy for given value of total internal energy and this is minimize the energy or the given value of total enthalpy now from Galen's book this is we haven't reproduced I have drawn it I have redrawn the diagram but the idea is this is your surface this is your energy surface for example this is the S as a function of so what you have drawn here essentially is S as a function of U and all other parameters like V, n so instead of that I am writing it as $S(U)$ and all the other parameters X, J right so this surface now if you see this plane the plane that I have drawn here see U this is the U axis this is the S axis and this is the X, J axis okay so this is a this axis is X, J basically you see it's like a multi-dimensional surface but we are telling that this axis contains all the X, J so if in that case what we are telling is when you may try drawing this plane when you were drawing this plane as you can see here what we are telling is that we are fixing the U axis we are fixing a plane right that means we are fixing the value of U and drawing this plane this plane intersects the $S(U, V, N)$ surface and the way it intersects is this means if you see the diagram you will understand easily that for this value the equilibrium will be obtained by maximization of entropy now look at the same surface now instead of look at the same surface that you take a plane of fixed entropy fixed entropy you can immediately see is basically indicating there is an energy minimum here right you are seeing the section here so I am talking about fixed entropy plane in the other case I am talking about a fixed

energy plane fixed energy plane there is entropy maximization right entropy is in the this axis right so entropy is maximized right if you look at this curve that is made by the plane you can immediately see the shape that is a maximum now more formally you can prove this how do you prove this you want to say say for example how do I prove one from the other if I assume that entropy maximum principle is indeed true then I should see that entropy from entropy maximum principle we can follow that we can get the energy minimum principle or vice versa now that is what we are going to do now so as you can see I started with the entropy maximum principle so in when we talk about when I talk about entropy maximum principle we are basically telling S is a function of U that is the energy of the system volume of the system and mole number of components that constitute the system right so basically this U V N so V and N I am substituting by Y so Y represents the N1 N2 and all other such variables like if you have multi components.

$$\begin{aligned}
 \left(\frac{\partial P}{\partial V}\right)_S &= \left(\frac{\partial P}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_S + \left(\frac{\partial P}{\partial V}\right)_U \left(\frac{\partial V}{\partial V}\right)_S \\
 \left(\frac{\partial U}{\partial V}\right)_S &= -P = \left(\frac{\partial P}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_S + \left(\frac{\partial P}{\partial V}\right)_U \\
 &= -P \left(\frac{\partial P}{\partial U}\right)_V + \left(\frac{\partial P}{\partial V}\right)_U \\
 &= \left(\frac{\partial P}{\partial V}\right)_U \quad \text{at } P=0 \\
 dP &= \left(\frac{\partial P}{\partial U}\right)_V dU + \left(\frac{\partial P}{\partial V}\right)_U dV \\
 \left(\frac{\partial P}{\partial V}\right)_S &= \left(\frac{\partial P}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_S + \left(\frac{\partial P}{\partial V}\right)_U
 \end{aligned}$$



So we have N1 mole number of component 1 N2 moles of component 2 N3 moles of component 3 and so on right now what we are telling is S is a function of U right S is a function of energy and other variables like V N1 N2 which we are lumping into this variable Y right so the Y basically Y basically contains all these variables V N1 N2 so on now let us assume say S is a function of so for example let us assume instead of lumping all variables if I tell that okay it is a one component system and S in that component system is a function of U comma V okay so we are thinking of S is a function of U comma V okay and maybe you have one component and that component mole number is always fixed so I am not taking U comma N and here again U comma N so I am neglecting this N completely just for the ease of notation right so you have now in this case what we are assuming is the extremum condition for entropy or maximization of entropy if I considering maximization of entropy first thing first derivative of entropy with respect to volume right is a function of U and V keeping energy fixed right for a given internal energy right keeping energy fixed as you can see has to be equal to 0 and another now this is the extremization condition now this extremum has to be a maximum so we have to look at the second derivative the second derivative tells you del 2 S del V square del 2 S del V square for of the same fixed internal energy has to be less than 0 that means it has been negative if it is negative indeed it is the maximum value

so we are maximizing right so as you can see here that we know that $\left(\frac{\partial U}{\partial V}\right)_S$ right $\left(\frac{\partial U}{\partial V}\right)_S$ is equal to minus P right now we are trying to look at so we know $\left(\frac{\partial S}{\partial V}\right)_U$ we want now assuming this assuming that assuming the entropy maximum principle for a given internal energy I want to prove the energy minimum principle that indeed it leads to this energy minimum principle so in the energy minimum principle again what we are writing first U as a function of S and V and now I will try to find out $\left(\frac{\partial U}{\partial V}\right)_S$ right $\left(\frac{\partial U}{\partial V}\right)_S$ as a function of S now $\left(\frac{\partial U}{\partial V}\right)_S$ as a function of S should be equal to so this means for a fixed entropy right this is this means this means fixed entropy right for a given entropy we are trying to find the derivative of U with respect to change in volume right $\left(\frac{\partial U}{\partial V}\right)_S$ as a function of with fixed S or for a given value of S right and we will try to find out that whether it is 0 right so now as you can see $\left(\frac{\partial U}{\partial V}\right)_S$ is equal to minus P right because $\left(\frac{\partial U}{\partial V}\right)_S$ is into dV so which is minus P degree so $\left(\frac{\partial U}{\partial V}\right)_S$ is definitely equal to minus P now we can write this as this $\left(\frac{\partial U}{\partial V}\right)_S$ look at this term we can write this as $\left(\frac{\partial S}{\partial V}\right)_U$ so we have discussed different types of the partial differentiation formula and you can see that one of the ways to write this is basically you take $\left(\frac{\partial S}{\partial V}\right)_U$ so S is your fixed quantity but here we are writing in terms of U and V as fixed quantities so we can write this derivative this one in terms of a ratio of $\left(\frac{\partial S}{\partial V}\right)_U$ and $\left(\frac{\partial S}{\partial U}\right)_V$ right and there is a negative sign here so this is something you can basically prove and I can show you that it is indeed it is possible to prove this is basically you have Z as a function of X and Y if you have that what you are telling is basically $\left(\frac{\partial Z}{\partial Y}\right)_X$ times $\left(\frac{\partial Z}{\partial X}\right)_Y$ times $\left(\frac{\partial X}{\partial Z}\right)_Y$ so you will have X here so $\left(\frac{\partial X}{\partial Z}\right)_Y$ see it's nothing but a chain rule $\left(\frac{\partial X}{\partial Z}\right)_Y$ and this will be so $\left(\frac{\partial Z}{\partial Y}\right)_X$ $\left(\frac{\partial Z}{\partial X}\right)_Y$ and this will be $\left(\frac{\partial X}{\partial Y}\right)_Z$ right so this indeed will be equal to so $\left(\frac{\partial Z}{\partial Y}\right)_X$ $\left(\frac{\partial Z}{\partial X}\right)_Y$ is goes to minus 1 this is something that we have shown previously right we have shown this either we have shown this relation right so $\left(\frac{\partial Z}{\partial Y}\right)_X$ times $\left(\frac{\partial Z}{\partial X}\right)_Y$ times $\left(\frac{\partial X}{\partial Z}\right)_Y$ will be equal to minus 1 right you can try to derive this so if you derive this then we can basically see that $\left(\frac{\partial Y}{\partial X}\right)_Z$ which is nothing but an inverse of $\left(\frac{\partial X}{\partial Y}\right)_Z$ right if we use that then $\left(\frac{\partial Z}{\partial Y}\right)_X$ is nothing but minus of you see now both terms go up so you have here it is $\left(\frac{\partial X}{\partial Z}\right)_Y$ by $\left(\frac{\partial Z}{\partial X}\right)_Y$ and this is $\left(\frac{\partial Y}{\partial X}\right)_Z$ below so this becomes $\left(\frac{\partial X}{\partial Y}\right)_Z$ now when I do $\left(\frac{\partial X}{\partial Y}\right)_Z$ what is fixed Z is fixed when I do $\left(\frac{\partial X}{\partial Y}\right)_Z$ Y is fixed so exactly this is the one that we are using here so if we use this relation then what we basically get is minus $\left(\frac{\partial S}{\partial V}\right)_U$ for a fixed U and minus $\left(\frac{\partial S}{\partial U}\right)_V$ now note that $\left(\frac{\partial S}{\partial V}\right)_U$ is something for entropy maximum principle is equal to 0 $\left(\frac{\partial S}{\partial V}\right)_U$ is 0 and $\left(\frac{\partial S}{\partial U}\right)_V$ is nothing but 1 by T right $\left(\frac{\partial S}{\partial U}\right)_V$ is nothing but 1 by T so 1 by 1 by T is basically T and there is a minus sign so minus T $\left(\frac{\partial S}{\partial V}\right)_U$ and $\left(\frac{\partial S}{\partial V}\right)_U$ according to the entropy maximum principle which we have taken to be true right we have assumed entropy maximum principle to be true and what we want to prove is entropy maximum principle implies energy minimum principle right so immediately so this is equal to 0 so this becomes this is equal to 0 because we have assumed the entropy maximum principle so $\left(\frac{\partial S}{\partial V}\right)_U$ equal to 0 is given right so from our assumption right from our earlier assumption of entropy maximum so we can now see that $\left(\frac{\partial U}{\partial V}\right)_S$ is indeed 0 if $\left(\frac{\partial S}{\partial V}\right)_U$ is 0 that means change in entropy with respect to change in volume for a given internal energy equal to 0 implies that change in internal energy with respect to volume or a fixed entropy to be also equal

to 0 right which is an extremum condition now which is an extremum condition for U right del U del V S equal to 0 is an extremum condition now whether this extremum condition basically leads to an energy minimum principle what we have to prove that del 2 U del V square for a given S is greater than 0 right so this is what we want to do now del 2 U del V square is nothing but minus of if you see this del U del V S is minus P so del 2 U del V square is nothing but minus del P del V S right so which is equals to minus del P del V S now this is going to be written as minus del P del V U how does this term right so think about it and try to derive it so now see I will derive this but see first I start with del P del V S so I am starting with del P del V S now del P del V S is nothing but del P del U V del U del V S again I am using a chain rule so I am using the chain rule del P del U V del U del V S and plus right so P is a function of U and V so think of this P is a function of U and V we are assuming because see this is the this is the this is the this is one equation of state right P is a function of U and V right.

Legendre Transformation

$$Y = Y(X)$$

$$P = \frac{dY}{dX}$$

$$\psi = -PX + Y$$

Elimination of X and Y $\psi = \psi(P)$

$$\psi = \psi(P)$$

$$-X = \frac{d\psi}{dP}$$

$$Y = XP + \psi$$

Elimination of ψ and P $Y = Y(X)$

Helmholtz potential or Helmholtz free energy

$$U = U(S, V, N_1, \dots)$$

$$T = \partial U / \partial S$$

$$F = U - TS$$

Eliminate U and S to get

$$F = F(T, V, N_1, \dots)$$

$$F = F(T, V, N_1, \dots)$$

$$S = -\partial F / \partial T$$

$$U = F + TS$$

Eliminate F and T to get

$$U = U(S, V, N_1, \dots)$$

$$dF = -S dT - P dV + \mu_1 dN_1 + \mu_2 dN_2 + \dots$$

So what I am writing here is dP so basically C equals to del P del U V dU plus del P del V U dV right now what we are doing is we are differentiating this the left hand side the left hand side and right hand side with respect to V right so we are so this becomes del P del V so now this implies del P del V when I do del P del V what I am fixing is S equals to del P del U V is remaining and this becomes del U del V S so del P del U V and del U del V plus del P del V U and this is del V del V which is basically del V del V S right this is because del V del V S which is basically equals to 1 right so now what you have del P del U V so what you have here is del P del U V del U del V S plus del P del V right now you see del U del V S right del U del V S we know del U del V S is minus P right del U del V S we know is minus P right so I am writing minus P del P del U del P del U again here we have V here and this is del P del V U right now which is nothing but del P del C now minus P is equal to 0 right del U del V S is equal to 0 so basically P equal to 0 if P equal to 0 right from the extremization condition for U right del U del V S which is minus P which we found that for energy minimum principle first thing is the energy extremum which is indeed equal to 0 right and if this is equal to if we assume the entropy maximum principle then del U del V S is equal to 0 or minus P equal to 0 so if minus P equal to 0 this term goes up so you have del P del V U so we can we have proved them that del P del V S equals to del P del V U right del P del V U fixed energy right so at P equal to 0 P equal to 0 means del U del V S equal to 0 now this means del P del V U can be written as del del V of so you can just look at this so this becomes del P del V U right at P equal to 0 now I am writing del del V and P is del U del V S right so del U del V S I can write as del S del V U again you can prove this but there is a again a minus sign here right there is a minus

sign here note the so note here that there is a minus sign right and you can again prove that minus sign again using the relation like this right so if you have that if you have that you have $\frac{\partial S}{\partial V}$ U you have $\frac{\partial S}{\partial U}$ V and there is a minus sign here which is minus now because if you see here $\frac{\partial S}{\partial U}$ and there is $\frac{\partial S}{\partial V}$ right so if you look at this it is nothing but $\frac{\partial U}{\partial V}$ right in some sense it is you can immediately see here that this is $\frac{\partial U}{\partial V}$ which I am writing in terms of this $\frac{\partial S}{\partial V}$ and $\frac{\partial S}{\partial U}$ again using the relation the chain rule that we have proved with a minus 1 remember that has minus 1 if I multiply then we basically get minus 1 so then $\frac{\partial}{\partial V}$ of this entire stuff so basically if that is so we can now again use the product rule if we use the product rule for partial differentiation then $\frac{\partial}{\partial V}$ of $\frac{\partial S}{\partial V}$ U keeping $\frac{\partial S}{\partial U}$ V as constant so we put we have the minus sign and this becomes $\frac{\partial}{\partial V}$ of $\frac{\partial S}{\partial V}$ is nothing but $\frac{\partial^2 S}{\partial V^2}$ and here this becomes $\frac{\partial S}{\partial V}$ U I am now fixing and so this is $\frac{\partial}{\partial V}$ of minus 1 by $\frac{\partial S}{\partial U}$ so this is going to be $\frac{\partial S}{\partial V}$ U and minus 1 by so minus 1 by X if I have so the differentiation so basically it's like minus of 1 by X so it will be minus of so you if you do $\frac{\partial}{\partial X}$ of minus of 1 by X basically you get minus of so if you just do $\frac{\partial}{\partial X}$ of 1 by X this is equal to minus 1 by X square right because it is X to the power minus 1 so minus 1 S to the power minus 2 which is minus 1 by X square if I put a minus sign here then there is a minus sign already from the derivative so minus and minus becomes plus so it is $\frac{\partial S}{\partial U}$ square and above it is $\frac{\partial^2 S}{\partial U \partial U}$ right $\frac{\partial^2 S}{\partial U \partial U}$ now if you see this you have $\frac{\partial S}{\partial U}$ $\frac{\partial S}{\partial U}$ is 1 by T so this becomes minus T $\frac{\partial^2 S}{\partial V^2}$ square but here $\frac{\partial S}{\partial V}$ U right this is something that from the entropy maximum principle we have already told $\frac{\partial S}{\partial V}$ U is equal to 0 right $\frac{\partial S}{\partial V}$ equal to 0 means this entire term goes to 0 and so you have minus T $\frac{\partial^2 S}{\partial V^2}$ square right minus T $\frac{\partial^2 S}{\partial V^2}$ square and $\frac{\partial^2 S}{\partial V^2}$ square is less than we also know since $\frac{\partial^2 S}{\partial V^2}$ square from entropy maximum principle is less than 0 therefore so basically $\frac{\partial^2 S}{\partial V^2}$ square is negative minus T so this there is a minus sign negative sign here and T is positive right so this term what is this term the term that we are talking about here is $\frac{\partial^2 U}{\partial V^2}$ square S right so this is basically what we are trying to do is $\frac{\partial^2 U}{\partial V^2}$ square S equal to this term which comes out to be right which is equals to coming out to be minus $\frac{\partial P}{\partial V}$ U first of all this minus $\frac{\partial P}{\partial V}$ S but we have proved that this minus $\frac{\partial P}{\partial V}$ U and minus $\frac{\partial P}{\partial V}$ U again we are writing in this way and then we basically get from entropy maximum that this term $\frac{\partial S}{\partial V}$ U equal to 0 so you have minus T $\frac{\partial^2 S}{\partial V^2}$ square and as you can see $\frac{\partial^2 S}{\partial V^2}$ square is less than 0 from entropy maximum principle this makes this negative this is also negative T is positive so this has to be greater than 0 therefore U has to be a minimum right the extremis condition is so basically we have proved two conditions here we have proved that given $\frac{\partial S}{\partial V}$ U equal to 0 and $\frac{\partial^2 S}{\partial V^2}$ square less than 0 for a fixed energy implies that $\frac{\partial U}{\partial V}$ S that is for a given entropy the partial derivative of U with respect to V is equal to 0 and $\frac{\partial^2 U}{\partial V^2}$ square is basically greater than 0 $\frac{\partial^2 U}{\partial V^2}$ square for a fixed entropy is greater than 0 that means entropy maximum principle implies energy minimum principle we can show it graphically we can show it otherwise right we can also prove the other means we can assume energy minimum principle and prove the entropy maximum principle so that means these are equivalent and interchangeable in the case of entropy maximization we keep the energy fixed

energy of the system fixed in case of energy minimum principle we are keeping the entropy fixed right total entropy of the system fixed now comes one very interesting thing means I won't go into the detail if you want to go into the detail you can look at Callen or some other book like Callen right or some modern books that use the treatment of Callen so where we come to this interesting transformation in math which is called Legendre transformation.

Helmholtz potential or Helmholtz free energy

$$\begin{aligned}
 U &= U(S, V, N_1, \dots) & F &= F(T, V, N_1, \dots) \\
 T &= \partial U / \partial S & S &= -\partial F / \partial T \\
 F &= U - TS & U &= F + TS \\
 \text{Eliminate } U \text{ and } S \text{ to get} & & \text{Eliminate } F \text{ and } T \text{ to get} & \\
 F &= F(T, V, N_1, \dots) & U &= U(S, V, N_1, \dots)
 \end{aligned}$$

Enthalpy $H \equiv U + PV$

$$\begin{aligned}
 U &= U(S, V, N_1, \dots) & H &= H(S, P, N_1, \dots) \\
 -P &= \partial U / \partial V & P &= P(S, V, N_1, \dots) & V &= \partial H / \partial P \\
 H &= U + PV & U &= H - PV \\
 \text{Eliminate } U \text{ and } V \text{ to get} & & \text{Eliminate } H \text{ and } P \text{ to get} & \\
 H &= H(S, P, N_1, \dots) & U &= U(S, V, N_1, \dots)
 \end{aligned}$$

$$\begin{aligned}
 dF &= -SdT - PdV + \mu_1 dN_1 + \mu_2 dN_2 + \dots & U &= U(S, V, N_1, \dots, N_k) \\
 & & F &= F(T, V, N_1, \dots, N_k) \\
 U &= U(S, V, N_1, \dots, N_k) & & \\
 T &= T(S, V, N_1, \dots, N_k) & & \\
 & & & \int F = F(T, V, N_1, \dots)
 \end{aligned}$$

The idea of Legendre transformation is this if you have a function in general how do you write a function say y equals to f of x or y equals to y of x so y is a function of x this means y is a function of x now how do you plot it so you have some graph say for example you have y in the y axis so y is varying and here x is varying so you have x varying this way and this way and this is your curve right and you basically this curve represents y as a function of x right this can be written the same curve same curve can be written as a function of a tangent to this curve a tangent to this curve which has a slope right which has a slope and intercept the intercept is basically psi right psi is the intercept and right 0 comma psi means this is equal to psi and P is the slope now as you can see here you look at this line you have drawn a tangent at some arbitrary point x comma y and you have the intercept which is basically 0 comma psi then immediately you can see P the slope is basically y2 minus y1 by x2 minus x1 so right the slope dy dx is nothing but y2 minus y1 this is simple coordinate geometry y2 minus x1 which is y minus psi by x minus 0 or psi equals to so if that is so so what what does this mean P equals to y minus psi by x or psi equal to psi equal to so I have taken Px so this becomes y minus Px right because I am taking x to the left hand side so it becomes Px and you have psi here you take psi now here so Px comes to the right hand side so y minus Px so psi equal to y minus Px right so basically if you have this so what we have done is basically we have used down one relation which is psi equal to y minus Px which is the intercept right so let's write this way psi equal to y minus Px is the intercept right on the y axis so it is the intercept and P is nothing but the slope now if you see that so you have dy by dx is equal to P right so dy equals to Pdx right that's why dy equals to Pdx so T psi is equals to dy minus Pdx right from this equation you can write d psi equals dy minus Pdx minus x dP right so this is so now dy minus Pdx minus x dP right which is equal to minus x dP why is that so this is because dy so dy dx equal to P dy by dx equal to P implies that dy equals to Pdx but if I write d psi which is dy minus Pdx minus x dP so we have this extra term so this term this guy is equal to 0 we have minus x dP so you have d psi equals to minus x dP or minus x equals to d psi by dP right so you have minus x so let us write this way

$-\mu dx = d\psi$ and you have also $\psi = y - Px$ now if you see that it is possible to write this entire curve the idea is this it is possible to write or express this curve as a function of ψ and P that means it is a function of intercept and slope this is indeed true because if you do this series of intercepts and slopes if you write a series of intercepts of slopes so you see if I draw a series of intercepts and slopes then basically this curve comes as an envelope right so this this this different so this different so I am basically varying the intercepts I have intercept here here here so for each and then I have different types of tangents so I can go on drawing a series of tangents I can go on drawing a series of tangents what I am describing from the envelope is the curve itself so basically what we are telling the usual form that we write y is a function of x can be written in terms of the slope and the series of slopes and intercepts of the curve right basically the slopes and intercepts made by the tangent point right made by the tangent to the curve at different points right you have a series of tangents that can you can draw on the curve and sweeping that series of tangents I have this tangents are described by their slopes and intercepts right the tangents are described by slopes and intercepts and you have the series of tangents so basically the series of tangents the envelope represented by the series of tangents and the series of tangents are characterized by their slope and their intercepts because tangents are straight lines right so using this series of tangents and the inner envelope described by it we can basically define an alternate form the curve in terms of ψ and P this is something that becomes very very useful when you define different thermodynamic potentials like Gibbs free energy Helmholtz free energy and so on basically what I want to show you is this that T and S are conjugate V and P are conjugate then μ and N have conjugate relation so all of these we can basically show if we apply a transformation like Legendre transformation however here we are talking about a single variable Legendre transformation just for the purpose of demonstration but ultimately you can do it for multiple variables and you can do this basically you have a curve which is given in this form Z as a function of X and Y now you write the same curve in terms of tangent planes in the case of or means yeah tangent planes so if you write that then basically you are representing it in terms of slopes and intercepts made by the tangent right so that's the idea so more formally you have Y as a function of X and from there you have Y as a function of X from there you can define a slope which is $\frac{dY}{dX}$ and intercept which is $Y - PX$ now you see using these two I can eliminate X and Y and get $\psi = \psi(P)$ now inverse Legendre transformation is $\psi = \psi(P)$ again I can write $-\mu dx = \psi dP$ and $Y = X P + \psi$ right $Y = X P + \psi$ and now I have these two equations and I eliminate ψ and P and I get Y is a function of X right now if I think of that now very intuitively you can immediately realize this see you have U as a function of S V N and so on now you are replace you want to replace S by its conjugate which is T and T is nothing but $\frac{\partial U}{\partial S}$ as a function $\frac{\partial U}{\partial S}$ keeping V and all other components mole number constant right and F which is an intercept of what $U - TS$ T is the right $U - TS$ see $F = U - TS$ immediately comes in now if you do this you eliminate U so you have these two relations you eliminate U and S from these two relations to get F as a function of T V right it is a function of P V N right so if V N are not changing anything right so only thing that we have done is $T = \frac{\partial U}{\partial S}$ and $F = U - TS$ which is the intercept and I am writing now in

terms of intercept and slope right intercept and slope so F is a function of T V N 1 and here we are writing if I write F as a function of T V N 1 now S as you can see is minus del F del T right S is nothing but minus del F del T how does it come you have F here if you do del F del T if you do del F del T then basically what you get is minus S right you get is minus S so S equals to minus of del F del T and U is equals to F plus TS right now elimination of F and T gives you U as a function of S V N 1 right so the way to understand this is very simple so you have U as a function of S V N 1 NR what you are writing is a new definition which is U minus TS which basically is replace replacing U by F right which is basically an intercept U minus TS right we have seen F equals to U minus TS and S is replaced now by T its conjugate and V N 1 to N right so this is a so basically F is a logistic transform of U where the slope del U del S right del U del S is replacing the original function S right the slope del U del S which is nothing but temperature is replacing the original function S right and F is defined as the intercept U minus TS right so now if that is so we can write DF you can write so why we do this so why I have done this is because is to make you understand that basically since this conjugate relationship exists and we can use this agenda transform where when we are we are replacing the curve U equals to function U as a function of S we are replacing in terms of F as a function of T.

Gibbs Free Energy $G=U[T,P]$

$$U = U(S, V, N_1, \dots)$$

$$T = \partial U / \partial S \quad S \rightarrow T$$

$$-P = \partial U / \partial V \quad V \rightarrow P$$

$$G = U - TS + PV$$

Eliminate U, S, and V to get

$$G = G(T, P, N_1, \dots)$$

$$H = H(S, P, N_1, \dots)$$

$$-S = \partial G / \partial T$$

$$V = \partial G / \partial P$$

$$U = G + TS - PV$$

Eliminate G, T, and P to get

$$U = U(S, V, N_1, \dots)$$

Helmoltz potential minimum principle: The equilibrium value of any unconstrained internal parameter in a system in diathermal contact with a heat reservoir minimizes the Helmholtz potential over the manifold of states for which $T = T^{\text{reservoir}}$

Gibbs free energy minimum principle: The equilibrium value of any unconstrained internal parameter in a system in contact with a thermal and a pressure reservoir minimizes the Gibbs free energy at constant temperature and pressure $T = T^r, P = P^r$

$$d(U + U^r) = dU - T^r dS + P^r dV = 0$$

$$\therefore T = T^r, P = P^r \quad dG = d(U - TS + PV) = 0$$

$$d^2G = d^2(U - T^r S + P^r V) = d^2U > 0$$

$$d(U + U^r) = 0$$

$$d^2(U + U^r) = d^2U > 0$$

subject to $d(S + S^r) = 0$

$$dG = -S dT + V dP + \mu_1 dN_1 + \mu_2 dN_2 + \dots$$

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, N_1, \dots} dT + \left(\frac{\partial G}{\partial P} \right)_{T, N_1, \dots} dP + \left(\frac{\partial G}{\partial N_1} \right)_{T, P, N_2, \dots} dN_1 + \dots$$

So basically F as a function of T the advantage here there is a big advantage here see in case of U as a function of S you have to also define equations of state right which where T is a function of see when we write this energy minimum principle you have U as a function of S V N 1 N R but you also require a relation this T which is a function of S so it's a homogeneous 0th order function of all these extensive parameters right you require all of this now this two can be replaced now by a new thermodynamic potential F which is directly a function of T V N 1 so you don't require this additional relation or this additional equation of state right you do not require this equation of state in this case if you consider that you have a system you have a system with fixed volume and mole number and this system is in contact with a thermal reservoir right or a temperature reservoir if you have that then basically you are telling that the system will assume the temperature of the reservoir right it will become based on thermal equilibrium because reservoir is like an infinite reservoir temperature right so if there is a small change in U in the reservoir it does not change T of the

reservoir means the temperature of the reservoir so according to thermal equilibrium the system will assume always the temperature of the thermal reservoir that it is in contact with right so as a result we are now making this equation means basically we are basically telling that this equation of state is no longer required we can directly use in such a case the minimization of F instead of minimization of U when I do minimization of U I require this equation of state to be supplied but if I do minimization of F only thing that we are talking about is that the system is in contact with the thermal reservoir so as you can see now the equivalence between U and F so U as a function of S is replaced by F as a function of T right V N_1 remains V N similarly we can define H H is a function of so U as a function of S V N now what we are doing is S remains we do not touch S but we are touching the another slope which is $\frac{\partial U}{\partial V}$ which is minus P so H is written as a function of S but V is replaced by its conjugate right and then we have $N_1 N_2$ so on so minus P equals to $\frac{\partial U}{\partial V}$ and H is nothing but U plus P right H is the intercept which is U plus P V so as you can see H is the intercept P is pressure which is the slope of $\frac{\partial U}{\partial V}$ and U is your original function right U as a function this is this is your Y as a function of X which is now replaced by ψ as a function of P right P is the slope here right so H becomes a function of S V N_1 and so on now if you see the inverse regenerative transform is you are given H but you know V which is nothing but $\frac{\partial H}{\partial P}$ right V is nothing but $\frac{\partial H}{\partial P}$ and U which is nothing but H minus P V right so V is $\frac{\partial H}{\partial P}$ U is H minus P V because H plus U plus P V and then you eliminate H and P and you get that U as a function of S now again if you do U as a function of S V and you want to basically minimize again you require P you require here the relation of P as a function of if you would have done directly with U or minimization of energy then P as a function of S V N_1 was required however now if we think that we have a pressure reservoir basically a pressure reservoir is such that there is a there is a wall between the system and the reservoir and the wall is flexible but the change in whatever be the change in volume there is no change in pressure right the pressure in the reservoir is kept constant right the pressure there is no the because the change in volume is so infinitesimal in terms of when you consider this infinite reservoir then basically what we are telling is the pressure inside the reservoir remains unchanged so obviously the system will assume the pressure of the reservoir as because of mechanical equilibrium right now in that case I can directly use dH or extremization of dH which does not which does not require another equation of state right when you do minimization of energy you require an any an equation of state which lets P to the extensive variables S V N however if I do directly if I use directly H then I am only considering a pressure reservoir right we are considering a pressure reservoir and as a result we eliminate or the need for this equation of state right now comes one very important function we have already defined it we can see that see all of this means all this exercise is done to make you understand that all this thermodynamic potentials are related by a very simple transformation right by a transmission called Legendre transformation and as a result all of these are connected right so it's not like means there is a the connection is very mathematical and we can basically look at these different types of principles like entropy maximization principle or energy minimization principle which requires the equations of state but using these transformations was useful because instead of using S and V right S and V if I can replace S and V by their conjugate like S conjugate is T and V 's

conjugate is P then I can think of a thermal reservoir I can think of a pressure reservoir right a mechanical reservoir so if I am thinking of that then basically see for example if I am doing that so basically there are two slopes T which is ΔU by ΔS in this case T is ΔU by ΔS is the first one and then there is minus P which is ΔU by ΔV and we are writing G as U minus TS plus PV which is nothing but H U plus PV is H so this is H minus TS so now if you see you have three equations and you have U S and V if you eliminate them then you get G as a function of P P and M right and again if you have that you can write dG equals to minus S dT plus V dP plus $\mu_1 dN_1$ plus $\mu_2 dN_2$ now you can see here so this is something that I just want to tell you dG equals to ΔG ΔT and this because $dN_1 dT$ and $\Delta G \Delta T$ is nothing but minus S right $\Delta G \Delta T$ is nothing but minus S and then you have $\Delta G \Delta P$ and in this case this T is constant fixed and N M 1 N R and you have P and then you have $\Delta G \Delta M_1$ and T and P are fixed and N 2 dot dot dot so basically and D so and so on.

System at constant T
 System + reservoir \rightarrow Isolated System
 $\Delta(U + U^r) = 0$
 U - Internal energy of System
 U^r - Internal energy of Reservoir
 $\Delta S + \Delta S^r \geq 0$ (Second law)
 Assumption - Size of the reservoir is infinite compared to the size of the system

$\Delta U^r = -\Delta U$
 Temperature of reservoir T^r is kept constant
 Reservoir - ΔU^r is infinitesimal change in energy
 $\Delta S^r = \frac{\Delta U^r}{T^r} = \frac{-\Delta U}{T^r}$
 $\Delta S + \Delta S^r \geq 0 \Rightarrow \Delta S - \frac{\Delta U}{T^r} \geq 0$

So this becomes $\Delta G \Delta T$ is nothing but minus S $\Delta G \Delta P$ is nothing but $\Delta G \Delta P$ is nothing but V and $\Delta G \Delta N_1$ is nothing but μ_1 right so μ_1 so this is one relation second like we define that Gibbs-Duhem relation Gibbs-Duhem relation when we talked about the Euler relation and the Gibbs-Duhem relation we have given in terms of U right but for G also I can write another Gibbs-Duhem relation so G is U minus TS plus PV so dG can then be written as dU minus T dS minus S dT plus V dV plus V dP now one term is missing so plus it will be μ_N missing because we have neglected that right we are not concerned with that but here definitely there is a G U minus TS plus dV plus μ_N right because we are not replacing μ with N means we are not using any conjugate relation between μ and N here right so anyway define G so μ_N remains as μ_N so this becomes plus $\mu_N dN$ μ_N I so you can write $\mu_i N_i$ so $\mu_i dN_i$ plus $N_i d\mu_i$ but again if you look at this relation one and this one two immediately it follows from that dU minus T dS plus dV plus right dU so minus S dT plus V dP remains dU minus T dS plus P dV plus $\mu_i dN_i$ plus $N_i d\mu_i$. Now dU plus P dV from first law you can see dU plus dV means combined first and second laws is nothing but T dS right dU plus P dV minus T dS basically cancels out so you have $N_i d\mu_i$ equal to C right that is a Gibbs free energy relation right so we have done this Gibbs free energy relation here again you can see that we get back the Gibbs free energy relation $N_i d\mu_i$

equal to C from the definition of G so this Gibbs free energy minimum principle or potential Helmholtz potential minimum principle you can see that the equilibrium free value now of any unconstrained internal parameter in a system in diathermal contact with a heat reservoir minimizes the Helmholtz potential over the manifolds of states for which T of the system equal to T of the reservoir in the case of Gibbs free energy minimum we are telling the equilibrium value of any unconstrained internal parameter in a system right any unconstrained parameter in a system it can be like different μ 's right in contact with a thermal and pressure reservoir minimizes the Gibbs free energy at constant temperature and pressure basically T assumes the T assumes the temperature of the reservoir which is $T = T_R$ and $P = P_R$ so basically if you see this $dU + U_R$ equals to $dU - T_R dS + P_R dV$ which is equal to C right you can if it follows this way let's see d of what we are telling here is the system plus reservoir is your universe and so you are telling $dU + U_R$ as to be 0 and $dU + dU_R + U_R$ where U_R is basically the energy of the reservoir which you can tell that it is fixed because it is an infinite reservoir so basically dU_R is greater than 0 subject to that $S + S_R$ is basically fixed right this is what we are basically doing now if you do that it follows you can easily see that it follows that dG has to be equal to 0 and $d^2 G$ has to be equal to $d^2 \mu$ which has to be greater than 0 right so let us assume means let us understand why it is so say for example let us start with system at constant temperature in contact with a reservoir now system plus reservoir is one isolated system where $\Delta U + U_R$ equals to 0 where U is the internal energy of the system and U_R is the internal energy of the reservoir right you have U_R which is the internal energy of the reservoir and you have U is internal energy of the system and we are also telling that there is a change in entropy $\Delta S + \Delta S_R$ which can be equal to 0 for reversible processes $\Delta S + \Delta S_R$ can be equal to 0 or it can be it has to be either equal to 0 or greater than 0 right now one of the assumptions when I am talking about a reservoir when I define a reservoir size of the reservoir is infinite compared to the size of the system right that's what we are telling right there is a very infinite change so nothing basically changes the temperature even if there is a some change in terms of say for example the internal energy say U_R is changing so slightly that the temperature of the reservoir remains fixed so how does so basically if you see if $\Delta U + U_R$ equal to 0 this means ΔU_R right change in the internal energy of the reservoir equals to minus of the change in the internal energy of the system but temperature of the reservoir is kept constant that means mine so ΔU_R that change the ΔU_R is an infinitesimal change in energy which basically does not change the temperature of the reservoir it remains constant because reservoir is infinite compared to the system so T_R remains fixed right T_R remains fixed always so if that is so ΔS_R is ΔU_R by T_R which is minus ΔU by T_R so from the second law $\Delta S + \Delta S_R$ is greater than equal to 0 implies then that ΔS minus right because ΔS_R is nothing but minus ΔU by T_R which is minus ΔU by T_R is greater than equal to 0 now ΔU by T_R minus ΔS is less than that means equal is less than equal to 0 which means $\Delta U - T_R \Delta S$ is less than equal to 0 now if $T = T_R$ right we are telling that the system assumes the temperature of the reservoir right at thermal equilibrium so $T = T_R$ so if $T = T_R$ instead of T_R I can write T right so then because $\Delta U - T \Delta S$ is less than equal to 0 or $U - T S$ as we know F equals to $U - T S$

S now you can see this basically so basically as you can see here if you start with this delta U plus U R equal to 0 or delta S plus delta S R greater than equal to 0 basically gives you this condition that delta F has to be less than equal to 0 and delta F is equal to 0 only when the process is universal right okay so if you look at that so if you look at a closed composite system now you have this knowledge now you have the sum of so you have the subsystems M there are M subsystems so for each subsystem you have some volume so and the summation of this subsystem volumes is equal to the total volume it does not change then summation of if I do summation of components so basically here this will be N C right so it will be N C right where C is basically it can be like this C is this is small c which is basically represent instead of C yeah C is fine so this is small C now small c can be capital A means capital A is this component A component capital B component capital C and so now if you have F as a function of the temperature of reservoir right it's a function of temperature of reservoir and volume of all these subsystems right because temperature is now fixed right temperature of each subsystem is that of the reservoir right so basically that's what we are doing and then you have VI so V1 V2 V3 so on like V1 up to VN then you have got all components you have N C1 up to N Cm right and then basically this is the sum of I equal to 1 to M FI right F is a function of sum of FI that is almost free energy of the subsystems where each subsystem assumes the temperature of the reservoir right it gets the temperature of the reservoir because it is always at thermal equilibrium with the reservoir so T F now the extremization that where we have proved this this implies that T F has to be equal to 0 and T 2 F will be greater than 0 right this is the almost free energy minimum principle okay so in the next lecture we will continue this and we will come to another very important relation called Maxwell's equation.

$$\begin{aligned}
 & \frac{\Delta U}{T^R} - \Delta S \leq 0 \\
 \text{or, } & \Delta(U - T^R \Delta S) \leq 0 \\
 & T = T^R \\
 & \Delta(U - TS) \leq 0 \\
 \text{or } & \Delta F \leq 0 \\
 & \Delta F = 0 \text{ - reversible process}
 \end{aligned}$$

Closed Composite System

$$\begin{aligned}
 \sum_{i=1}^m V^{(i)} &= V & \sum_{i=1}^m N_c^{(i)} &= N \\
 & & c \rightarrow A, B, C, \dots & \\
 F(T^R, V^{(1)}, N_c^{(1)}, \dots, V^{(m)}, N_c^{(m)}) & \\
 &= \sum_{i=1}^m F^{(i)}(T^R, V^{(i)}, N_c^{(i)}) & \\
 dF &= \sum_{i=1}^m \left[- (P^{(i)} - P^{(i)}) dV + (\mu_c^{(i)} - \mu_c^{(i)}) dN_c \right] \\
 &= 0
 \end{aligned}$$