Thermodynamics And Kinetics of Materials

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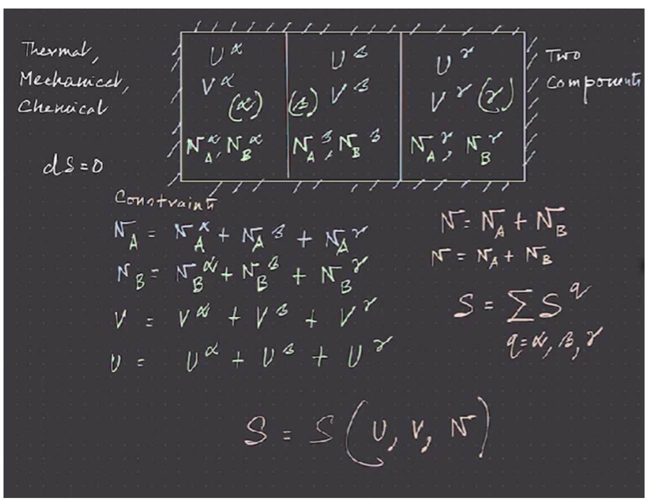
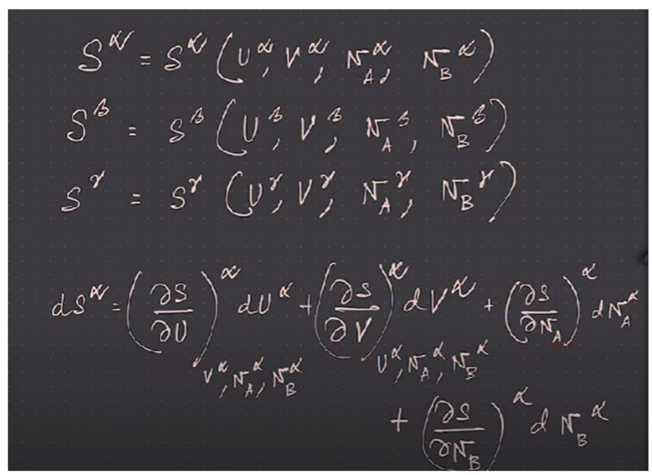
Lecture 11

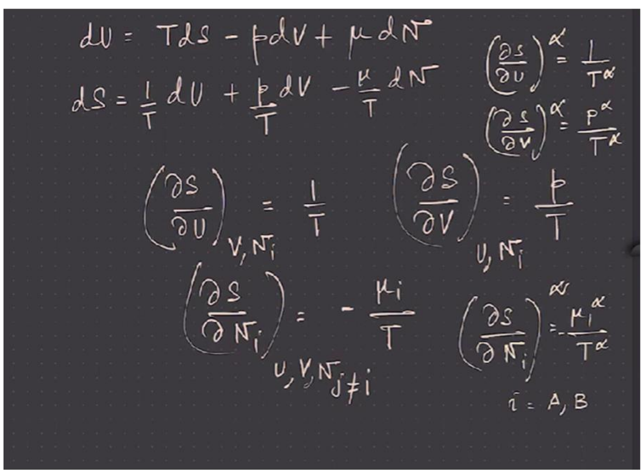
Formulations of Equilibrium in Thermodynamic Systems

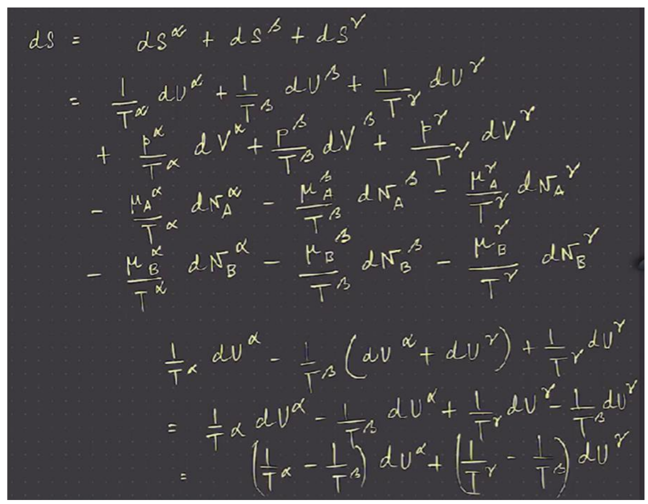
Ok, so in the previous lecture I talked about thermal equilibrium, how to achieve thermal equilibrium, how to achieve mechanical equilibrium and how do you remove the internal constraints that are basically through the wall and how do you basically arrive at different types of equilibrium. What types of equilibrium are there? You have thermal equilibrium for a simple system we are talking about. So you have thermal equilibrium, you have mechanical equilibrium and also chemical equilibrium. So these are the equilibria that we have considered. Now as you can see here you can extend it to, so for example we talked about two subsystems right two subsystems and their boundary this is the wall, here this is one wall and this is another wall. Now you have now three subsystems and for example you have two components.





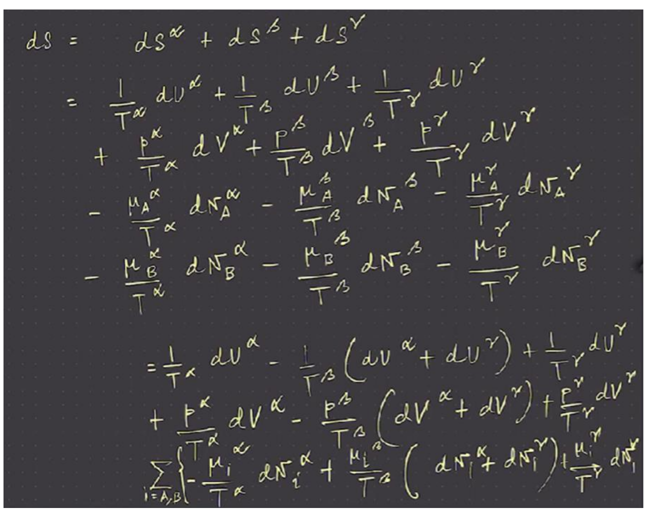
So let us assume a system. So I just want to show you that the approach that we used where we made dS equal to zero and we told the total energy of the system, the system is isolated so basically the system is the overall composite system is isolated. Overall, the composite system is isolated but that means it cannot exchange any matter or energy with the surroundings and it contains three subsystems here alpha, beta and gamma right alpha subsystem, beta subsystem and gamma subsystem and U alpha is the internal energy of the alpha subsystem, U beta is that of the beta subsystem and U gamma is that of the gamma subsystem and you also have the volumes. So this is the volume, this is capital V, V alpha, V beta and V gamma right these are the volumes of the three subsystems. Then U and V these are all extensive variables and this is now we have two components A and B. So I have NA alpha that is the mole number of component A in alpha subsystem and NB alpha it is number of, so NB alpha is basically mole number of B in alpha subsystem. Similarly NA beta represents the mole number of A in beta and NB beta is mole number of B in beta. Similarly you have NA gamma which is mole number of A in gamma and NB gamma which is mole number of B in gamma subsystem. Now what are the constraints? So this is something that we have to talk about. Now first thing the wall, so the equilibrium is achieved over which the total the entropy of the system has to be maximized right ds, so entropy has to be maximized and we also talked about the extremization of entropy of total entropy basically boils down to ds equal to 0 where as is the total entropy of the system right. Another thing we talked about and this maximization when we have removed all internal constraints that are imposed through the walls. So for example the initial internal constraints were like say the walls were rigid, the walls were rigid, these walls is a rigid wall and it is impermeable to A and B, exchange of A and B. So basically the subsystems cannot exchange A and B. So impermeable, rigid and adiabatic that means no energy exchange between alpha and beta or beta and gamma. Now I remove all these internal constraints, so basically the walls have become now diathermal permeable to the exchange of A and B that means A and B can basically diffuse through these walls right across alpha, beta and gamma and also the walls are flexible that means they are movable. So you are allowing the change in volume of alpha phase, change in volume of beta phase and change in volume of gamma phase. But what are the constraints? The constraints are the total mole number of A is constant right, that cannot change right, you cannot basically create A or destroy A but total mole number is constant. So this means Na which is equals to Na alpha that is the mole number of A in alpha, mole number of A in beta and mole number of A in gamma, now you sum it up you get Na and this Na is fixed. Similarly, Nb which is Nb alpha, Nb beta and Nb gamma the sum of these, this is also fixed. So Na is, so and also the total mole number, so basically total mole number N is Na plus Nb that is also basically fixed. So total mole number of A and B are fixed, Na the amount of Na is also fixed, Nb is also fixed and total volume which is V alpha plus V beta plus V gamma. See for example, the wall can displace, the wall can displace, wall can displace this way and the wall can displace this way, the volumes can readjust like V alpha can increase, V beta can decrease, V gamma can increase or V beta can increase, V gamma can decrease. However, the total volume of the isolated composite system remains constant like V equals to V alpha plus V beta plus V gamma which is constant. Similarly, the total energy, see the total energy which is U alpha, the internal energy of alpha subsystem, beta is, internal energy of beta subsystem and gamma, internal energy of gamma subsystem, the sum total of that like U alpha plus U beta plus U gamma equal to U which is constant. And as you know that S is a thermodynamic variable and it is an extensive function of these three extensive parameters U, V and N. So, S itself is an extensive function or additive function and it is a function of these three, so S itself is a function of three extensive parameters, that is what we are writing. So U, V and N and as you can see total U, total V and total N in this isolated systems conserved. Now, if we proceed the same way, so we can now write S alpha which is S alpha, so as you know in postulate 2 that S alpha is for each subsystem, the entropy of the subsystem is a function of the extensive variables in that subsystem, so S alpha is a function of U alpha, V alpha, NA alpha and NB alpha. Similarly, you can do it for S beta and S gamma. Now if that is so, now you can basically write the change that is the exact differential dS alpha is equals to del S del U alpha, dU alpha, then del S del V alpha, dV alpha, del S del NA alpha, dNA alpha and del S del NB alpha, dNB alpha. So this is for the alpha subsystem, this is for the alpha subsystem and you see you have del S del U alpha, del S del V alpha and del S del NA alpha, these are supposed to be the intensive parameters or a combination of intensive parameters, right. So and these are part, del S del U is basically 1 by T, so this will be del S del U alpha will be then, del S del U alpha is nothing but 1 by T alpha. Similarly, del S del V alpha is plus P by, so del S del V alpha equals to P alpha by T alpha and del S del N, so del S del NA or I, I can be A or B, if it is I is A then B is constant, right, del S del I alpha is nothing but minus nu I alpha by T alpha, there is a minus sign here and I can be, you can be, I can be A or B, right. You know this, we know this relation, we have talked about this in the previous class, but what I am telling is, we are trying to prove here that the same, we can derive the same laws if we consider multiples of systems with multiple components and this is exactly what I am going to do here. So if I now use total dS, there is a total change in entropy, total change in entropy which we are basically at equilibrium dS has to be equal to 0, right, the extremum value has to be 0. So dS equal to 0 means dS alpha plus dS beta plus dS gamma which basically gives you dS, right, that has to be 0. If I write this dS alpha, dS beta and dS gamma and we substitute the, we substitute the M and N values means basically the coefficients in the exact differential expression, in the exact differential expression what are the coefficients we have already seen for alpha sub system is 1 by T alpha, for beta it will be 1 by T beta. So like that and for gamma it will be 1 by T gamma, for when I am associating dU alpha, dU beta and dU gamma, so dU alpha 1 by T alpha, dU beta it is 1 by T beta, dU gamma it is 1 by T gamma. Similarly, you have this expression d alpha by T alpha dV alpha, V beta by T beta dV beta, P gamma by T gamma dV gamma. Now you have minus mu A, so for this for species A, so mu A alpha by T alpha dN A alpha minus mu A beta by T beta dN A beta minus mu A gamma by T gamma dN A gamma, right. Now you do it for B also. Now once you have done this, you now make use of this relation that, U alpha plus U beta plus U gamma which is U is constant. Now that means, that means what, that means that you can basically write dU beta equals to minus dU alpha because dU equal to, since dU equal to 0 because U is constant, total value is constant, since dU equal to 0, dU beta plus dU alpha plus dU gamma that is also 0 or then we can write any of these we can substitute, we can tell dU beta is minus dU alpha minus dU gamma, right. Because dU, total dU is what, dU is equal to dU alpha plus dU beta plus dU gamma. Now dU itself is 0, right. So therefore, dU beta is minus dU alpha minus dU gamma, right. So if it is clear, now we can see one very interesting thing here. Now we can write this as 1 by T alpha dU alpha, we keep it as it is but what we have done here is for plus 1 by T beta dU beta, you have written minus 1 by T beta dU alpha plus dU gamma, right. It is a minus common, right. This is basically, minus 1 is common or minus is common, then what I get? dU alpha plus dU gamma, right. That is exactly what we have written here, right. So I do not want to confuse you, so I am just erasing this here. So what we are, and this is all happening because dU equal to 0. So we are substituting dU beta by minus of dU alpha plus d gamma. And then you may have 1 by T gamma dU. So what is the value for, you do it for? So you are doing it for, so if I do it for, similarly, so I will just do one thing. I have written this. Similarly I can do it for V. So it will be plus d alpha by T alpha dV alpha and total V is constant, so dV equal to 0. So minus P beta by T beta dV alpha plus d, so we are substituting dV beta by minus of dV alpha plus dV gamma plus V gamma by T gamma dV. And then we have mu's, the mu's also we can do the same thing. So mu A and mu B separately, just writing this as minus mu I, I can be A or B, mu I alpha T alpha by T alpha dNA alpha. And this will come plus not dNA, this will be dNI alpha where I can be either A or B. So means basically with some I over A and B. So we have this sum as well as this sum. So you have mu I, so you are doing a sum here, I equal to 800 B and you are putting a bracket here. So this will be mu I alpha by T alpha, but see it is minus, there is a minus here. So let us put the minus inside them, this bracket minus mu I alpha by T alpha dNI alpha and this one will be, so you have minus of mu B beta by T beta. So this is minus of mu B, mu I or mu I beta by T beta minus of mu I beta by T beta. Here I am substituting dNI beta as minus of dNI alpha minus of dNI gamma and then we have also mu I gamma by T gamma dNI and this minus I can take as common and therefore this and this I can take as common, so this becomes plus, this minus and this minus becomes plus.

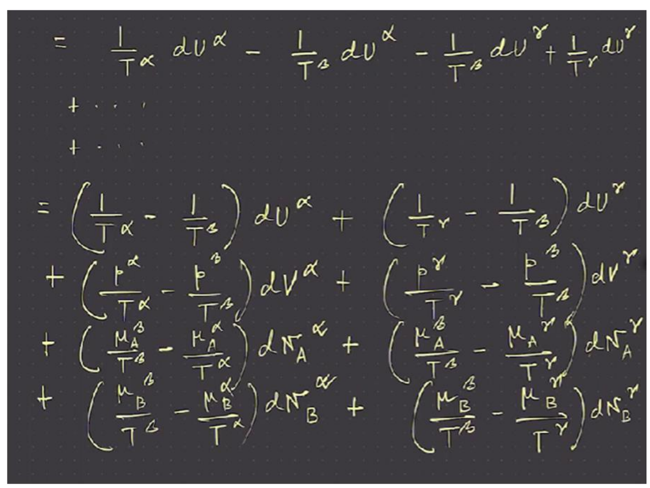




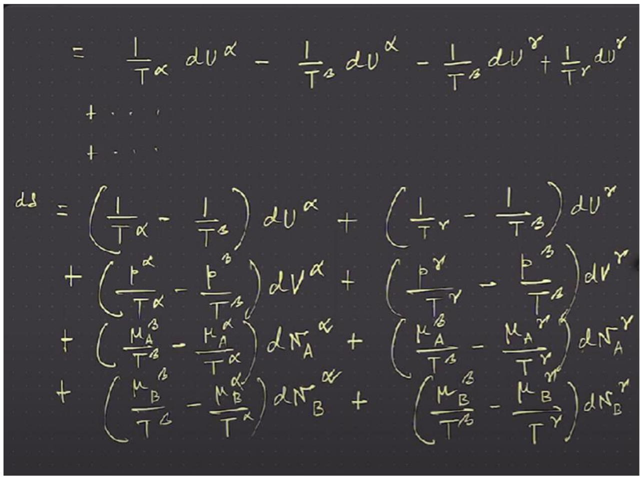
Now if you look at individually, if you separate them, you have 1 by T alpha du alpha minus 1 by T beta du alpha. So basically if I group them now, what I get is equal to, we get this 1 by T alpha du alpha minus 1 by T beta du beta, sorry not du beta, this is again 1 by T beta du alpha and you get minus 1 by T gamma, not gamma, just T beta, 1 by T beta du gamma plus 1 by T gamma du. We have eliminated or we have substituted du beta. So du alpha, so this and plus dot dot dot, we can write everything in dv alpha minus dv alpha, dv gamma minus dv gamma and dv gamma. And similarly for the mu. Now in that case, I can now group them like 1 by T alpha minus 1 by T beta du alpha plus 1 by T gamma minus 1 by T beta du. Similarly we can write p alpha by T alpha minus p beta, minus of p beta by T beta dv alpha and p gamma by T gamma minus p beta by T beta du, it's not du, this is dv gamma. Then we can write minus then here there is a summation sign. So first let us do the summation sign, there is a plus sign here, so you put a plus sign here and then there is summation over In. So basically if I do it separately that is also fine. So I do it for A as well as for

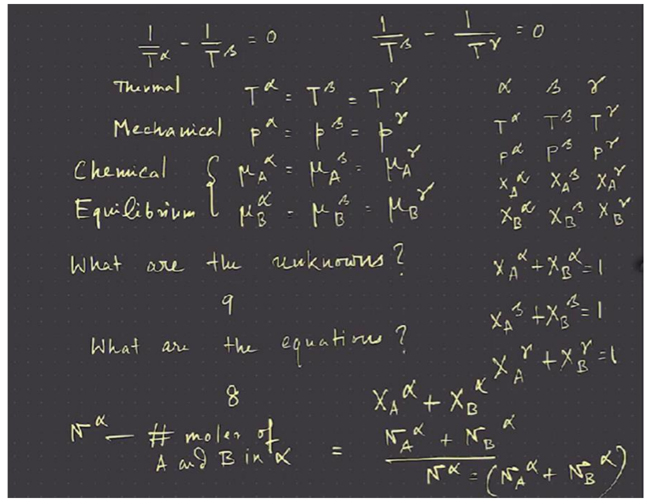
B, so I get minus, so this was minus, right, mu A alpha by T alpha dna alpha and then you have mu A beta by T beta and this will be dna beta is substituted by dna alpha and dna gamma and you have minus dna alpha. So now this is minus or plus of mu beta by T beta minus mu A alpha by T alpha and this will be dna alpha, right, and then this will be plus mu beta by T beta minus mu A gamma by T and this will be dna, right, you have dna gamma, right. So this is minus, plus and here please note that here there is a minus and then you can write it as mu A beta by T beta minus mu A gamma by T gamma dna. Similarly plus mu B beta by T beta minus mu B alpha by T alpha, see the dna, this will be dna alpha, so this is also dna alpha, dnB alpha, yeah, dnB alpha plus mu B beta by T beta minus mu B gamma by T gamma dmB. Now as we know that dU alpha, dU gamma, dV alpha, dV gamma, dna alpha, dna gamma, dnB beta and dnB alpha and dnB gamma they can be chosen arbitrarily, right, previously we have shown that, right, we have told that these are basically arbitrary. Now if these are arbitrary then if ds, now this is basically equal to what, this is equal to ds. Now ds, if I tell ds equal to 0, the individually each of these coefficients like 1 by T alpha minus 1 by T beta has to be equal to 0, 1 by T gamma minus 1 by T beta because dU alpha, dU gamma, dV alpha, dV gamma these are arbitrary, right, because why? Because U alpha, V alpha or U gamma, V gamma these are chosen as independent coefficients, right, so independent variables, right, so basically the changes are also, the ds of these are also going to be arbitrary. So as a result for ds to be 0, for ds to be 0 the coefficients, each of these coefficient pairs have to be 0. Now that implies 1 by T alpha minus 1 by T beta equal to 0. Similarly 1 by T beta minus 1 by T gamma equal to 0. As a consequence of this relation and this relation one can write T alpha equal to T beta equal to T gamma. Similarly one can write P alpha equal to P beta equal to P gamma.



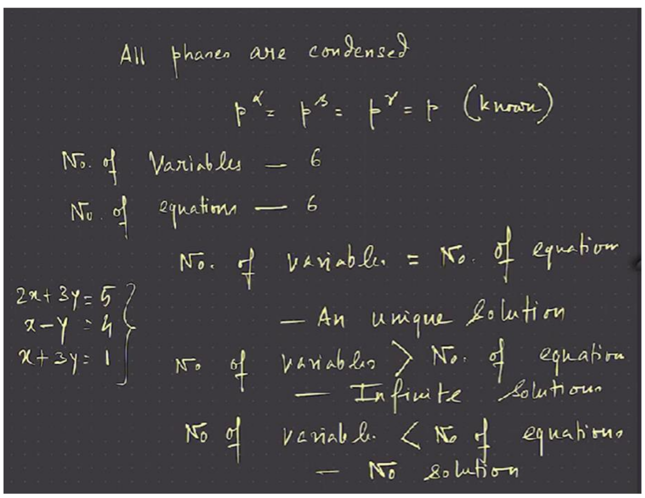


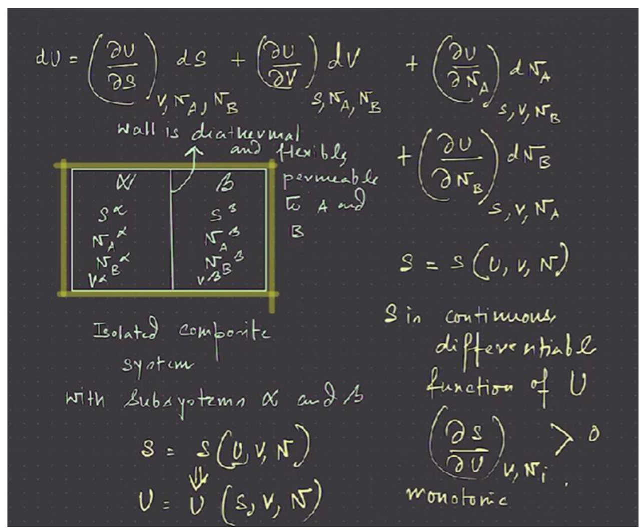
Now if you see this is the statement of thermal equilibrium. This is between three subsystems and this is P alpha equal to P beta equal to P gamma is something you can write that is basically mechanical and then you have this chemical equilibrium for each species, right, so this is called chemical. These are all equilibrium conditions. Now you will see here, so if I am looking at this please try to understand although I am solving this T alpha, T beta, T gamma, P alpha, P beta, P gamma or mu A alpha equal to mu A beta equal to mu A gamma, mu B alpha equal to mu B beta equal to mu B gamma, if you look at the chemical equilibrium what we are basically solving for, if this chemical potential is equal what are the, what is the consideration of A that is in alpha that is in equilibrium with A, with beta and that is in equilibrium with gamma. So basically if you see you have these unknowns. You want to find out XA alpha, XB alpha, XA gamma, XA alpha, XA beta and XA gamma at equilibrium. Similarly XB alpha at equilibrium means at equilibrium between these three subsystems, right, at equilibrium between these three subsystems. Similarly you want to find XB alpha, XB beta and XB gamma. See instead of mole number we are looking at X, right, X is mole fraction, right, but that is exactly, so basically we are trying to find out what is the concentration of A in alpha that is in equilibrium with A in beta that is in equilibrium with A in gamma. Similarly for B, right. However there is one interesting point. So if you see that XA alpha plus XB alpha equal to 1. Similarly XA beta plus XB beta equal to 1, right, because XA alpha plus XB alpha is nothing but you see that XA alpha plus XB alpha is nothing but equals to NA alpha plus NB alpha by N alpha. N alpha is the, N alpha is the total number of moles of A and B put together in alpha. Similarly you can have N beta and N gamma. Now NA alpha by N alpha is basically XA. NA beta by, sorry, NB alpha by N alpha is basically XB alpha. Now as you can see for alpha subsystem you have two components and XA plus XB have to be equal to 1, right. You can immediately see because N alpha is nothing but NA alpha plus NB alpha. So you have same denominator and numerator which is basically going to be equal to 1, right. So now if you see these relations, what these relations imply? These relations imply that one of them can be, so one of them can be taken as an independent variable, right. So XA and XB alpha, if I know XB alpha, XA alpha is nothing but 1 minus XB alpha. Similarly XB beta, similarly XB gamma, right. Now if you look at this originally you have how many unknowns? T alpha, T beta, T gamma, P alpha, P beta, P gamma and then you have say some XA alpha, XA beta, XA gamma or XB alpha, XB beta, XB gamma. Now I can take any one of these. So I have now 1, 2, 3, 4, 5, 6 and we can take any of these 7, 8, 9. So I have 9 variables and I have 8 equations. Now if I have more variables than equations then basically the number of solutions become infinite, right. So basically you cannot define the equilibrium state because one of the variables you have known. We can basically specify anything. So I can take one variable unknown, I can take any value of it and then I will always get a solution and I have like infinite number of solutions. So basically if my number of variables is more than the number of equations then one of the variables I can choose arbitrarily. As a result the number of solutions become infinite, right. But you do not want to determine such a system because you do not have a way to determine an exact equilibrium values of T alpha, T beta, T gamma or XB alpha, XB beta and XB gamma if you basically have more unknowns than equations, right. Now what do we do? We assume, first thing we can do is that if we assume all phases are condensed that means the pressure dependence or PV work is negligible, right. Pressure dependence is negligible and we can tell that P alpha, P beta, P gamma have to be the same and that is equal to say some P that is known. So P is already known or specified. So P is basically say 101325 pascals or 1 atmosphere pressure. Now you have, you can take one set, right. You can take either these things or these things, right. You can take XA alpha, XA beta and XA gamma to be independent variables then XB alpha, XB beta and XB gamma automatically determine. So now if you see if I remove P alpha, P beta, P gamma because I am talking about condensed phases that means P alpha, P beta, P gamma are no longer P means are all fixed to a value P, right. All fixed to some value P that P can be atmospheric pressure, it can be 3 times atmospheric pressure, it can be also like one third of atmospheric pressure or whatever it is.





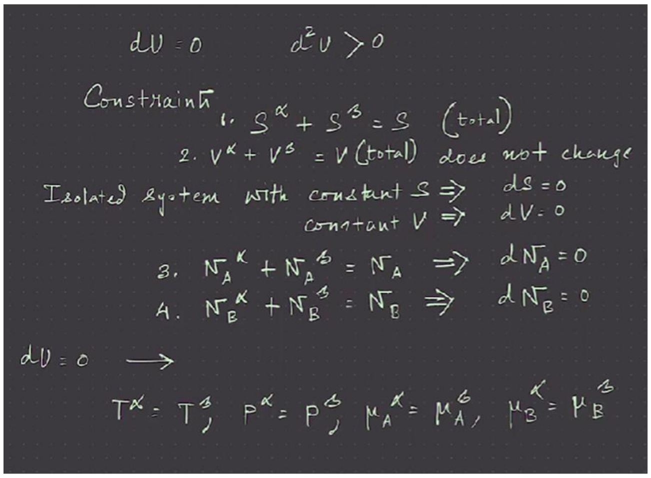
It can be some arbitrary pressure but all subsystems will have the same pressure, right and we are basically removing this equation, right. This equation is already implied when I am talking about solids or liquids. Now in that case you have 1, 2, 3 and either XA or XB can be your variables. So we have 1, 2, 3, 4, 5, 6. Now if you see if I remove this equation, if I remove this equation for time being I have 1, 2, 3, 4, 5, 6 equations. I have exactly 6 equations, I have exactly 6 unknowns. So my number of, if I have that, so variables equal to equations you will have unique, so we have, so number of variables equal to number of equations you have an unique solution, right. So this is something that we have to understand. So please try to understand in this case if I basically use another subsystem say delta and if I tell that you have now this two components A and B you will see that it becomes insufficient because in that case number of equations is more than the number of variables. So in such a case solution does not exist if number of variables is less than the number of equations then you have more equations than variables then definitely no solution exists because you can only choose a combination of equations, other equations become redundant but you cannot do that. So which equations to choose therefore the matrix that comes in becomes non-invertible and as a result you cannot means, yeah, so basically since that it is not possible to invert that matrix so therefore there is no solution at all, there is no solution if number of variables, see if number of variables is greater than number of equations you have an infinite solution to the problem but if number of variables is less than the number of equations there is no solution. Right, say for example I write 2x plus 3y equal to 5 then I write x minus y equal to 4 then I write x plus 3y equal to 1. Now immediately if you see this you will tell you have two unknowns x and y but you have three equations now which equation combination should I use right there is no means we cannot so as a result these matrix becomes non-invertible and no solution exists right so number of if the number of variables is less than number of equations then there is no solution but if number of variables is greater than number of equations then on any of this arbitrarily I can choose one of the variables and fix their value and as a result and I can since it is arbitrary and I am fixing one of the variables arbitrarily I can take infinite values for that so I have infinite solutions. Now when it comes to unique solution number of variables have to be equal to number of variables have to be equal to the number of equations so this is very very important and this is something that will again come back when here I am talking about subsystems please check in a system that contains two components in a system that contains two components if I am considering an equilibrium across four subsystems you will check that in such a case you have more equations than unknowns right so this is something that I will come back to when we discuss Gibbs phase rule right so we will come back to that. Now similarly one can so we know that we have written this type of function S equals to SUVN but we also told that S is continuous function it is a differentiable function of U and del S by del U with other things constant V comma Ni is greater than so if I have del S by del U then it has to be greater than 0 that means it is monotonically varying monotonically varying so or monotonically check this say for example del S by del U has to be so for constant V and Ni has to be greater than 0 right that is the thing so it is a monotonic function so you can write monotonic function of so it is a differential continuous and monotonically increasing function of U.

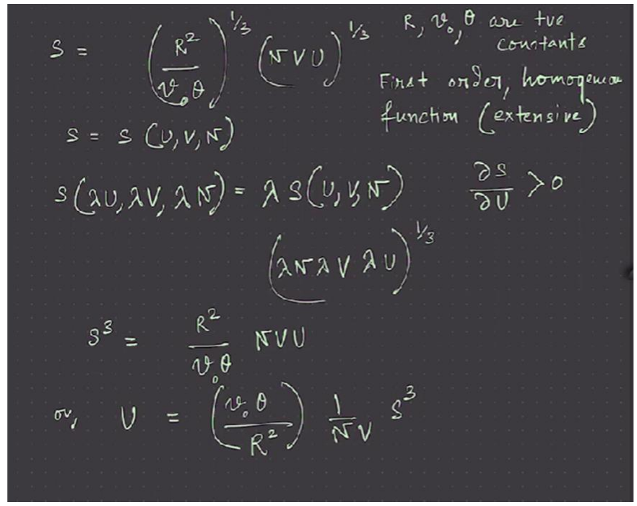




So as a result you can invert the relation right so basically if you have S is equal to SUVN that means entropy is a function of internal energy extensive parameter volume extensive parameter N extensive parameter number of moles then we can basically write this U because it is continuous and differentiable as well as monotonic function of U right S so you can now you can invert and you can write U as a function of S V and both are possible so if I do that if I do U then the exact differential will look like this dU equals del U del S del U del V del U del NA and del U del NB right and in this case also the extremization that we will do will come to dU equal to 0 right we will do dU equal to 0 you have again the subsystems but here what we are telling please note this here what we are telling is slightly means it is not really means how do you say it is not intuitively clear immediately write this approach because what we are demanding now in such a case if I start with dU see what we are demanding is you have S alpha and S beta for alpha and beta subsystems right and we are taking like diathermal flexible permeable to A and B and you have alpha and beta subsystems and you have S alpha you have S beta NA alpha NA beta NB alpha NB beta and V alpha and V beta now if I look at the constraints you have constraints which is like in A V alpha plus V but see we are not talking about constant energy what we are talking about because what we are trying to do is we are trying to do dU equal to 0 when we write this exact differential dU equals to del U del S dS plus del U del V dV plus del U del NA dNA plus del U del NB dNB what we are fixing here we are fixing for example in del U del V or in the case of del U del NA or del U del NB we are fixing some part S we are fixing S is total entropy cannot change of this isolated system so what is the total entropy S and which is equals to S alpha plus S beta and this cannot basically this total S is basically fixed so the total S cannot change right which is S alpha plus S beta but the equilibrium can definitely so basically we are telling total energy constant it is very very intuitive it is intuitive and we can easily understand it right total energy cannot change right it's an isolated system whatever with the systems of this different subsystems that total energy is constant or total energy cannot change right that is something that we can easily understand and realize however if I tell the other way when I do it dU I am talking about the other way where I am telling S equals to S alpha plus S beta has to be fixed so basically what we are telling that for dU equal to 0 the constraints are NA alpha plus NA beta equal to NA so these are called constraints and these are meaningful constraints right because when I tell that it's a isolated system now amount of NA that you have put now it has distributed into NA alpha for alpha subsystem and NA beta for beta subsystem but total NA cannot change total V cannot change similarly total B right that also cannot change but instead of writing U alpha plus U beta equals to U, U alpha plus U beta equal to U and telling that U is constant or U cannot change instead of that what I am talking about here when I write dU equal to 0 way then it becomes S alpha plus S beta equals to S that cannot is fixed for the isolated system right now if you have that so this does not basically it does not evoke come out naturally right we generally do not talk about like total entropy is fixed right for an isolated system also in general total energy is fixed not total entropy so that is why I am repeatedly emphasizing there that even with the dU equal to 0 approach the same equilibrium will come okay however the equilibrium will be achieved that constant entropy right as you can see here dU dV is taken at constant entropy dU dNA again entropy is constant dU and dNV entropies also right and then only this dU dS term is coming right so entropy here is fixed the total entropy of the system is fixed is what we are talking about right in that case also so as you can see S alpha plus S beta equal to S the total that is your constraint and then V alpha plus V beta equals V total that also cannot change right so if you have constant S you have dS equal to 0 dV equals to 0 for constant V and then total nA cannot change so dN A equal to 0 and dN V equal to 0 now so when I do dU equal to 0 I can directly I can show that this is like T alpha equal to T beta V alpha equals to V beta mu A alpha equals to mu beta and mu B alpha equals to mu B beta so you basically whether you are doing an extremization of entropy if the dS means extremization of entropy or extremization of energy both are equivalent right another very important thing I have mentioned this already let's see when I am looking at the coefficients we are seeing these coefficients are basically for example if I look at the coefficients here dU del U del S is nothing but del U del S is nothing but temperature right del U del

S is nothing but temperature del U del V is nothing but pressure minus P right and del U del nA is mu A and del U del nB is mu B right and what we are telling that the equilibrium is basically T alpha equal to T beta P alpha equal to P beta mu alpha equals to mu A beta and mu B alpha equals to mu B beta.





Now we have these equations of state right we have this equations of state where T itself so by the way these are if you recall these are homogeneous T P and mu are homogeneous zeroth order is I have explained to you functions so if they are all homogeneous zeroth order function that means T P and mu now if it is homogeneous zeroth order function what does it mean is that intensive variables these variables do not depend on the extent although S V n are all extensive variables right so this is how we can think of this say for example if I give this example say this is from Callens book that S which is equal to R square by V0 theta now R V0 and theta are positive constants okay these are all positive constants and then you have S equals to R square by V0 theta or one-third and N V u whole to the power one-third now we know entropy total entropy is an extensive property so if it is an extensive property what we know that if you have S equals to S U V n you put S if you use a multiplier lambda and then write S lambda u lambda v lambda n equals to nothing but lambda S U V but on the other hand if I write T S V n right so this basically remains as so even if S has been multiplied by lambda V has been multiplied by lambda N has multiplied by lambda lambda can be like a fraction lambda can also be like two three four right so lambda can have any value but this is lambda because zero so whatever amount or extent I change S V or N T remains as T right T lambda S lambda V lambda N is the same as T S V and this example what we are talking about is some sort of a relation between S N V and U right basically S as a function of U V N so this is one relation where R square by V 0 theta are basically positive these are positive constraints right now we will try to see that whether S remains a first order of monotonous function so or an extensive function so how do we check that we write S equals to S U V N now what I am doing is I am changing U to lambda U V to lambda V and N to lambda N and if I do that that this relation is already known right this is known now in this case S is a function of N V U S is a function of what is this S this S is a function of this where you have extensive parameter N extensive parameter V extensive parameter U same thing right here now what I am going to do is I am going to put N equal from N I go to lambda N from V I go to lambda from U lambda U okay now if you do that but there is a one-third are you seeing it yeah so now lambda N lambda V lambda U to the power one-third now if I am looking at that it becomes lambda cube to the power one-third which is nothing but lambda to the power one-third lambda cube to the power one-third means lambda and then this is basically going to be N V U right so basically lambda times N V U to the power so like this right so this is a valid function right this is a valid function which relates S to N V and E right so this is one example that I have taken from Callens book exercise okay now if you look at another example again from callens book that again you have R theta which are positive constants but now it is given as S equals to a nu by V to the power 2 power 2 I use the same same property that S lambda U lambda V lambda N so I use the same property S lambda U lambda V lambda N now if I do that I am changing here N by lambda N U by lambda U V by lambda V now if I do that you see the lambdas cancel here and it becomes lambda to the power two-third R by theta square to the power one-third N U by V to the power 2 right so this is really not first-order homogeneous function S no longer remains a first-order homogeneous function it is now a two-third order homogeneous function so right it's a fractional so that means in this example or in this equation S does not seem to be extensive right if it means extensive first-order homogeneous function right it has to be a homogeneous first-order function first-order function means lambda to the power 1 however what we are getting here is lambda to the power 2 so therefore definitely this is not a varied expression it is not a valid expression right so now I will proceed to Euler equation right we will do Euler equation next right so now means I am ending here and then I will start with Euler equation.