Heat Transfer and Combustion in Multiphase Systems
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Lecture 02
Thermodynamics of Multiphase systems

Welcome to lecture 2 okay. So, this we are going to do a recap of the thermodynamics first and after we do the recap we will try to see that what is relevant in the multiphase systems.

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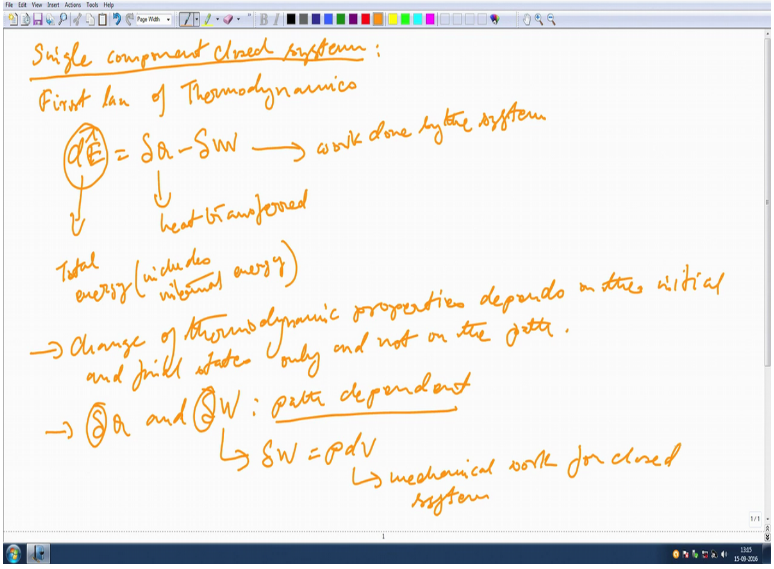

Single component closed system :

First law of Thermodynamics

$dE = \delta Q - \delta W \longrightarrow$ work done by the system

δQ ↓ heat transferred

dE ↓ Total energy (includes internal energy)

→ change of thermodynamic properties depends on the initial and final state only and not on the path.

→ δQ and δW : path dependent

↳ $\delta W = pdV$

↳ mechanical work for closed system

Say, so, let us start with the problem that let us look at a single component single component closed system okay. Now in the signal component closed systems okay what can we say about the first law of thermodynamics. So, the first law of thermodynamics basically is okay, so in this particular this term is basically the heat transferred.

This term is basically the work done by the system and this is basically the total energy total energy. This includes the internal energy. So this is the first law that you know for any single component closed systems all right. So, as we can see from this particular expression over here the change of thermodynamic properties depends on the initial and the final states only and not on the path.

So, this we already know that the change of thermodynamic properties dynamic property depends on the initial and final states only and not on the path this is already know. But however quantities like dQ and dW okay are path dependent. So, that is why we have written them by that tilde kind of a symbol right okay. And in most cases the work will be basically the mechanical work.

Which is basically Pdv this is the mechanical work for closed system okay, so, this is the first law of thermodynamics for any closed single component closed system okay. This we already know and we already know about these features that this is path dependent the internal energy is basically part independent and all those things okay.

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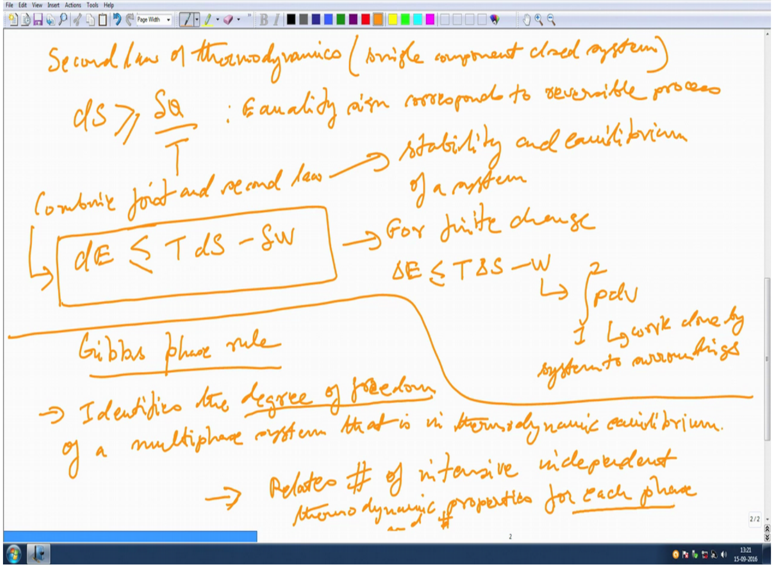

Second law of thermodynamics (single component closed system)

$dS \geq \frac{\delta Q}{T}$: Equality sign corresponds to reversible process

Combine first and second law → stability and equilibrium of a system

↳ $\boxed{dE \leq T\,dS - \delta W}$ → For finite change

$\Delta E \leq T\Delta S - W$

↳ $\int_1^2 p\,dV$

↳ work done by system to surroundings

Gibbs phase rule

→ Identifies the degree of freedom of a multiphase system that is in thermodynamic equilibrium.

→ Relates # of intensive independent thermodynamic properties and # for each phase

So, going to the next page the second law of thermodynamics look at. So, we have looked at the first law the second law of thermodynamics okay. Again for a single component closed system okay. Let us look at that, in that particular case if you recall the second law the Clausius inequality okay. So, the equality sign is greater than equal to right.

So, the equality sign as we know equality sign corresponds to the reversible process. This is what we all know right okay. So, if we combine the first and second law okay. So, if you combine the first and the second law to determine basically the purpose of this is to determine the stability and equilibrium of a system okay.

Now in that particular case okay, if you combine these two and neglecting the non internal energy parts. You can write it like this ds - dw okay. So, this particular thing combines the first and the second law of thermodynamics essentially. Now for a finite change, so this is for infinitesimal change for finite change okay, we have where w is basically nothing but the integral from 1 to 2 whatever is the process okay Pdv that is the mechanical work.

That is the work done by the system to surroundings, okay. So, this is the second law and the first law combined we get this right and we have also seen that if we; this is an equal in quality statement because the second law as we know that is also an inequality statement in itself okay. So, now these are all for single component systems okay.

Now let us look at one more important parameter over here which is basically called the Gibbs phase rule. Now what is Gibbs phase rule? Gibbs phase rule basically identifies the degree of freedom and we will come in a second what degree of freedom means degree of freedom of our multiphase system okay that is in thermodynamic equilibrium okay.

So, the Gibbs phase rule is basically identifies the degree of freedom of a multiphase system that is in thermodynamic equilibrium okay. And it basically what it tries to also do okay is that it tries to relate the number this is number of intensive independent thermodynamic properties the dynamic properties okay for each phase okay.

The number of intensive independent thermodynamic properties for each phase and the number of phases of a system this is not coming. So, we move on to the next page.

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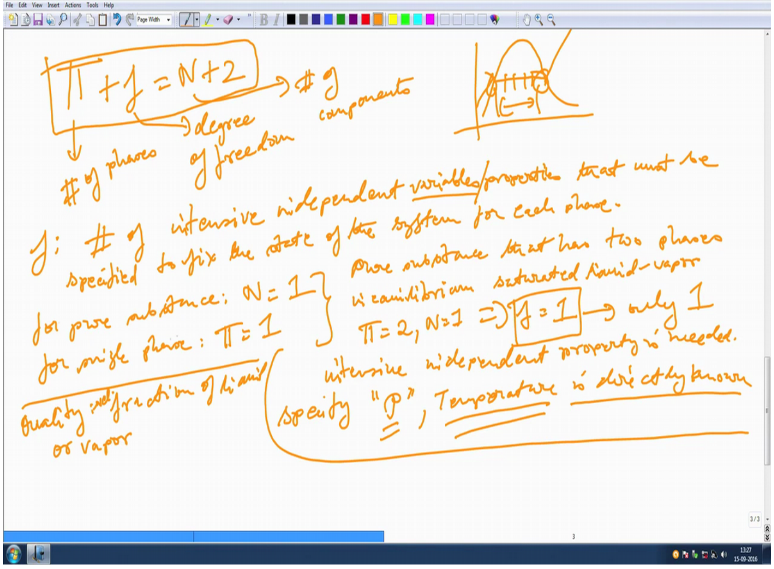

$$\boxed{\Pi + f = N + 2}$$

→ # of components

→ degree of freedom

→ # of phases

f: # of intensive independent variables/properties that must be specified to fix the state of the system for each phase.

for pure substance: N = 1

for single phase: $\Pi = 1$

pure substance that has two phases in equilibrium saturated liquid-vapor

$\Pi = 2$, $N = 1 \Rightarrow \boxed{f = 1}$ → only 1 intensive independent property is needed.

specify "P", Temperature is directly known

Quality and fraction of liquid or vapor

So, it basically relates the number of intensive independent thermodynamic properties for each phase and the number of phases for our system. So, in an equation form we have to write this will be something like this N + 2. Now what are each of these things this is the number of phases, this is the degree of freedom is the most important thing degree of freedom okay.

These are the number of components as I said multiphase system can also be multi component okay number of components of the system. So, f is basically by degree of freedom what we mean is that, f is the number of intensive mark the words, number of intensive independent variables okay or independent properties.

Properties that must be specified must be specified to fix the state of the system for each phase. So, that is a very clear cut indication that what we mean by the degree of freedom. The degree of freedom essentially means the number of intensive independent properties that must be specified to fix the state of the system for each phase okay.

So, let us say for pure substance let us take some examples for pure substance that means single component, it can be of course of two phases also. For single pure substance N is basically equal to 1 because the number of component is equal to 1. For single phase this is equal to 1 because the number of phases is equal okay.

Now let us take an example of a pure substance that has two phases in equilibrium. Let us take this is an example a pure substance which have got two phases in equilibrium okay like for example are saturated liquid vapour this can be water and water vapour for example that is the easiest example that you can think of.

In those cases this is equal to 2, N = 1 leads to the degree of freedom is equal to 1. So, that implies that only one intensive independent property needs to be specified to determine the state of the system correct. So, pure substance which has got two phases here it implies that if f = 1 only one intensive independent property is needed this would imply that for such a system if you specify P which is basically the pressure right.

Temperature is directly known right, is not that what happens actually in a thermodynamic system as well. If you recall the vapour pressure dome right you would find that in the saturation region where liquid and the vapour are existing in equilibrium you will find that you just need only one property to specify the temperature and the pressure are not two independent properties in that particular case right.

And that is why you have a saturation pressure, saturation temperature kind of a table you can look it up right. So, there is a unique these are like unique combinations correct so the temperature is directly known because the Gibbs phase rule actually states that only one is actually needed. However we do not know the relative abundance of each of the phases.

That means if you have heard the word quality, quality means what is the fraction of liquid or vapour right. What is the quality? Quality means what is a relative fraction essentially. So, this is a relative fraction of vapour and liquid now the relative fraction of vapour and liquid if you see if that is not known in many cases it may not be known right.

So in that particular case you do not know the relative abundance but you can definitely know that if you specify temperature the pressure is known. So, you just need one thermodynamic parameter to specify this. So, if we look at it basically in a chart like this right. So, this is the portion that you all know is basically the two-phase region right.

Now in this two phase region as you can see the pressure and the temperature they are interrelated to each other but however as we move from this side to that side the quality actually changes. There is less amount of water vapour to more amount of water vapour, this is like any saturation chart will actually show you that okay.

So, I think this part is quite understood that the Gibb's phase rule gives an important tool to basically calculate that. What is the number of variables that you need that this would be vitally important as we move; as we will see in a later part of this particular course, now where did the mouse go okay.

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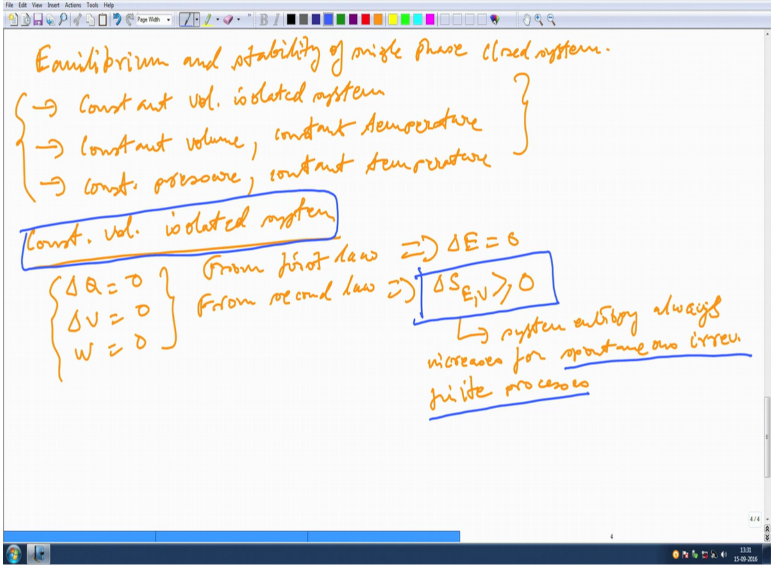

Equilibrium and stability of single phase closed system.

- → Constant vol. isolated system
- → Constant volume, constant temperature
- → Const. pressure, constant temperature

Const. vol. isolated system

$$\left\{\begin{array}{l}\Delta Q = 0\\ \Delta V = 0\\ W = 0\end{array}\right\}$$

From first law ⟹ $\Delta E = 0$

From second law ⟹ $\boxed{\Delta S_{E,V} \geq 0}$

↳ system entropy always increases for spontaneous irreversible processes

So, now in the remaining time that we have let us look at the equilibrium and stability of single phase closed system. So, equilibrium and stability of single phase closed system okay. So, there are several possible ways one is basically if you assume that the system is of constant volume and isolate it from your previous knowledge of thermodynamics you already know what a constant volume isolated system can be.

If you consider the system as constant volume, constant temperature, temperature system, the system can be also of constant pressure, constant temperature okay. So, there are like we will see three possible systems over here okay. So, the first one which is basically a constant volume isolated system let us look at that.

In that particular system as you know because it is isolated that net heat that is transferred is basically zero okay and it is a constant volume. So, the net volume change is also equal to zero. The work that has been done by the system is also equal to zero. So, these are the three things that we know that it is true.

From first law what else do we know from the first law we know that the change of internal energy of the system is also equal to zero correct that is because it is an isolated system right. So, from second law we can tell that a change of entropy of the system for constant energy internal energy and constant volume should be always greater than equal to 0 correct okay.

So, the system entropy is proof that the system entropy for this isolated constant volume system, the system entropy always increases for spontaneous okay irreversible finite processes got it. So, that is very obvious that the entropy always increases, so, if I look at this the entropy always increases for our system which is constant volume and isolated.

And then, if the process is spontaneous and irreversible that is the important word and finite then the system entropy will always increase. So, that is the stability criteria for a constant volume isolated system right okay. So, let us look at the stability criteria for a constant temperature and volume system.

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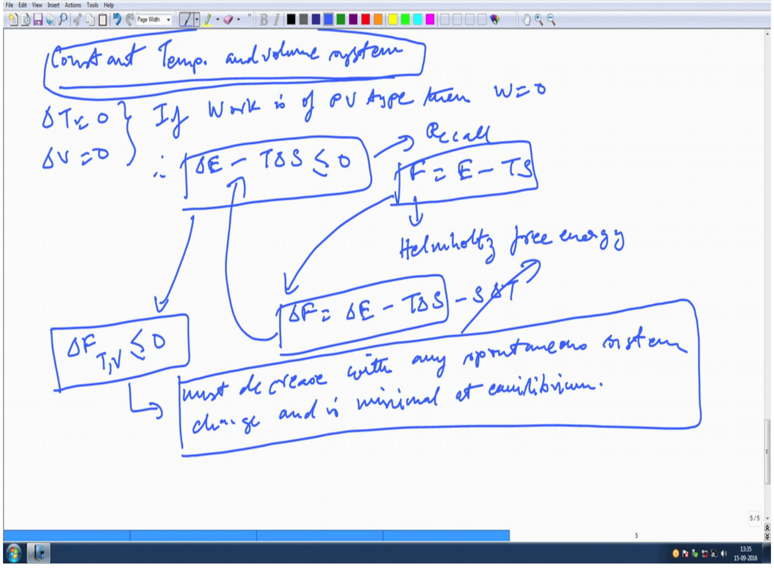

Constant Temp. and volume system

$\Delta T = 0$, $\Delta V = 0$ } If Work is of PV type then $W = 0$

$\therefore \Delta E - T\Delta S \leq 0$

Recall $F = E - TS$ → Helmholtz free energy

$\Delta F = \Delta E - T\Delta S - S\cancel{\Delta T}$

$\Delta F_{T,V} \leq 0$ → must decrease with any spontaneous system change and is minimal at equilibrium.

So, a constant temperature and volume system if we have okay, now in that particular kind of a system what we have is that delta T = 0 because it is a constant temperature. The volume is also equal to 0 that is a constant volume. If the work is Pdv type work is of PV type that is mechanical work then w is also equal to 0 correct because there is no change in volume okay.

So, therefore your change of internal energy and the change of entropy must be less than equal to 0 okay that is a relationship that we can say. Also recall that F will come to the; see what F is. F is basically nothing but the Helmholtz free energy right. This you know from your undergraduate thermo; Helmholtz free energy is given by this particular expression right okay.

So, if I apply, so if I just basically see the change in Helmholtz free energy that is basically given by delta E - T delta S - S delta T. Now for this particular process this is of course equal to 0 because it is a constant temperature system. So, this is the relationship that is valid. So, substituting this over here right, what we get as a result of that is delta F.

That means the change in Helmholtz energy for constant temperature and constant volume must be less than equal to 0 okay. So, the Helmholtz free energy must decrease the entropy was must increase for an isolated system. Must decrease with any spontaneous system change and is minimal at equilibrium okay.

So, that shows basically the Helmholtz free energy must actually decrease okay for a constant temperature and a constant volume kind of a system and this we have just used the first and the second law of thermodynamics for this right okay.

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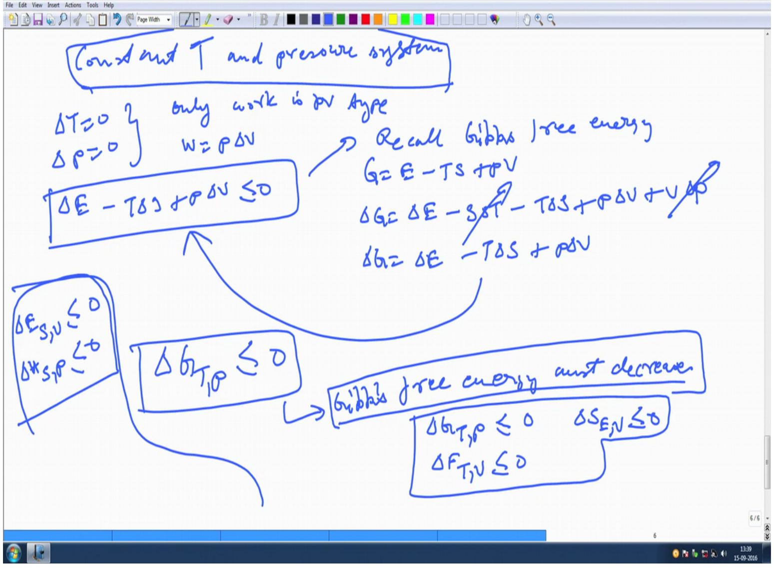

Constant T and pressure system

$\Delta T = 0$, $\Delta p = 0$ } only work is pV type

$W = p\Delta V$

$\Delta E - T\Delta S + p\Delta V \leq 0$

Recall Gibbs free energy

$G = E - TS + pV$

$\Delta G = \Delta E - \cancel{S\Delta T} - T\Delta S + p\Delta V + \cancel{V\Delta p}$

$\Delta G = \Delta E - T\Delta S + p\Delta V$

$\Delta E_{S,V} \leq 0$

$\Delta H_{S,P} \leq 0$

$\Delta G_{T,P} \leq 0$

Gibbs free energy must decrease

$\Delta G_{T,P} \leq 0$ $\Delta S_{E,V} \leq 0$

$\Delta F_{T,V} \leq 0$

So, similarly and this would be the last thing that we will do for constant temperature sorry and pressure system okay. What we have that was a third system that I said delta T = 0 delta P is also equal to 0. So, the only work is done of Pv type once again right. So, the work done is basically P into delta v remember here the volume constant is not there okay.

So it is a constant temperature and constant pressure system right. So, just by using these two expressions we can see Tds + P delta v is less than equal to 0. So, that is the first and the second law combined correct okay. Now we call once again now like you we call Helmholtz free energy at that particular point recall Gibbs free energy now okay.

So, what is Gibb's free energy G = E - TS + PV so the change in Gibbs free energy will be given by delta sorry will be given by delta E - S delta T - T delta S okay + P delta V + V delta P okay. Now of course this is equal to zero, this is also equal to zero. So, the Gibbs free energy is basically therefore given as delta E - T delta S + P delta V which is basically the same as this so I substitute it over here right.

So, and we get the expression that the change in Gibbs free energy for constant temperature and pressure must be less than equal to 0. So, the same statement holds that the Gibb's free energy must decrease like the Helmholtz free energy for a constant temperature and pressure system okay. So, this is; these are one of the three main equilibrium statements that we will make for three types of systems okay.

So, we will end lecture to kind of here and we will take up we will move forward to the two phase part of the same thing in the next lecture but however remember that the equilibrium constraints therefore are given as delta GTP less than equal to 0, delta F TV is also less than equal to 0, delta SEV is less than equal to 0 okay.

Similarly you can show it for other types of systems as well okay and we are not going to do that but we can show the other equivalent statements that means sorry. We can show that delta E that is the change in internal energy comma V is less than equal to 0, delta S okay rather sorry delta H S comma P should be less than equal to 0.

So, these are also equivalently other systems that you can prove that they also follow a similar type of framework. So, all the systems the stability part can be represented in this kind of forms okay. So, you will see in the next class what happens afterwards okay. So, this is the end of lecture 2 and we will meet you next in lecture 3.