Chemical Engineering Thermodynamics
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Lecture 03: Postulates of Thermodynamics-I

Welcome back, in the last lecture we discuss that describe that a typical microscopic system contains internal energy, okay? In the second postulate we mentioned that a microscopic system can be completely describe by internal energy, volume and number of moles of the species. Okay? In other word the second postulate also states that a system they is in a equilibrium state for given microscopic system which can be described by internal energy, volume and number of moles. Now that brings the question that how do you find the equilibrium state of a given system?

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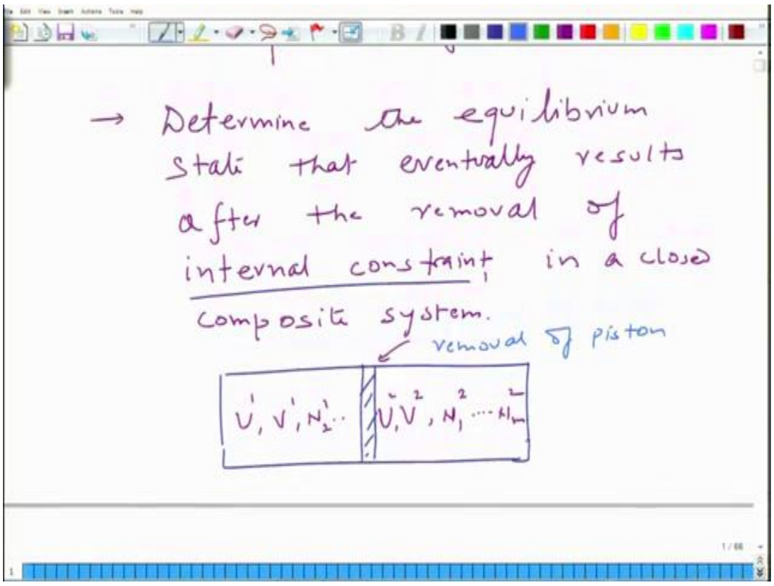
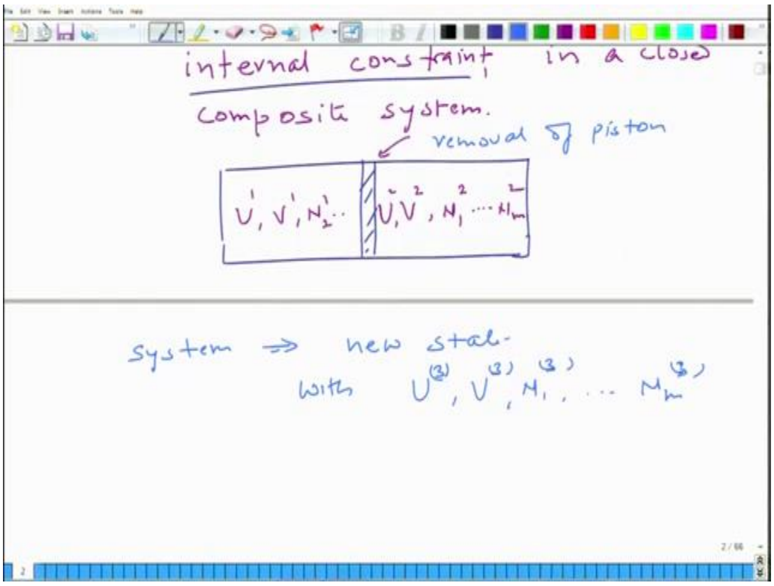


→ Determine the equilibrium state that eventually results after the removal of internal constraint in a closed composite system.



internal constraint in a closed composite system.

removal of piston

$U^1, V^1, N_2^1 \cdots$ | $U^2, V^2, N_1^2 \cdots N_m^2$

system ⇒ new state

with $U^{(3)}, V^{(3)}, N_1^{(3)}, \ldots N_m^{(3)}$

Now that becomes the central problem of thermodynamics. Okay? So having internal energy or having equilibrium state that is what we discuss in the last lecture, but the question is how do we obtain this equilibrium state? So the central problem of thermodynamics is to basically determine the equilibrium state that eventually results after the removal of internal constraint in a closed and composite system.

So internal constraints basically means that any constraints which prevents the flow of energy volume within the system in general in a given system, so when you remove such a internal constraint of course the system will tends to obtain a new particular state. So, let me just describe this by using an example, so let us consider this two compartment separated by this piston which is fixed.

So the compartment 1 will have let us say energy internal energy describe by u1, similarly volume1 and the most okay and the species and similarly volume2, internal energy2 1 so 2 volume 2 and the most of m species. Okay? Now, if you remove this piston essentially it means that removal of piston which is initially fixed which means that the system tend to a new state with let say energy u3v3 and the number of moles corresponding to this, okay?

And 3 stands basically for nothing but state. Now the basic problem of the thermodynamics or the centralized will be set to determine the final state which is the equilibrium state. Okay?

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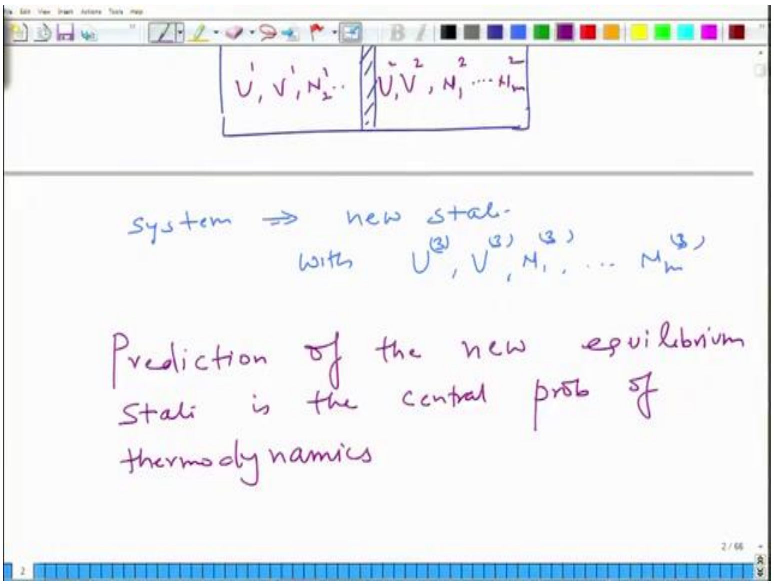

$U^{1}, V^{1}, N_2^{1} \cdots$ | $U^{2}, V^{2}, N_1^{2} \cdots N_m^{2}$

System ⇒ new state with $U^{(3)}, V^{(3)}, N_1^{(3)}, \dots N_m^{(3)}$

Prediction of the new equilibrium state is the central prob of thermodynamics

So, the prediction of the new equilibrium state is the basically the central problem of thermodynamics. Okay? So the question is what is the simplest mechanism in which we can obtain the thermodynamic state at equilibrium? Or find out the equilibrium state of thermodynamics? Okay?

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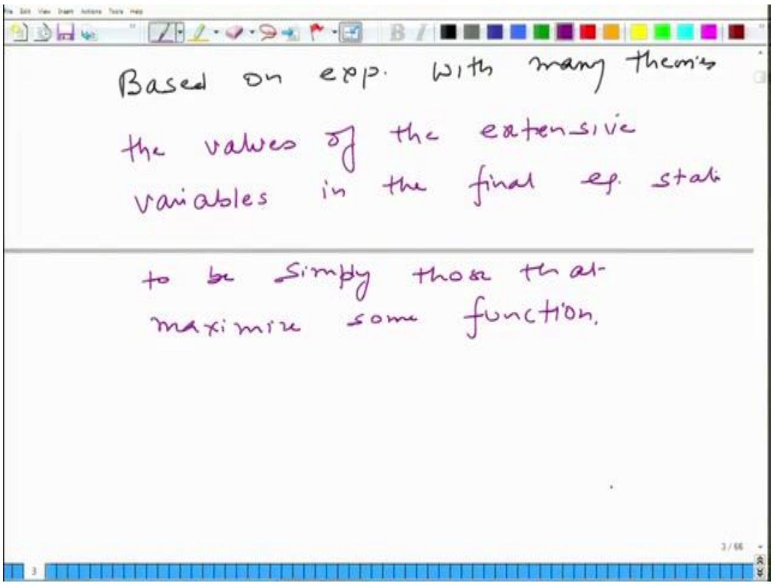

Based on exp. with many theories the values of the extensive variables in the final eq. state

to be simply those that maximize some function.

Now, the question is that how do we obtain such equilibrium state so we may take use of the existing theories and based on our experience with many theories the most economical form for the equilibrium criteria would be based on some extremum principle. Okay? In other words what we are going to obtain defines the thermodynamic variable in some function and we will look for the extremum value of that function leading to the equilibrium state, Okay.

We do not know the function yet okay? So what we are emphasizing here the values of the extensive variables in the final equilibrium state is simply those maximizes some function. Okay? So this is what we are trying to emphasize that based on our experience that the extensive variables corresponds to basically a thermodynamic variable, it attends a value at the equilibrium which corresponds to the extremum value of a some function which is the function of those extensive variables.

So apparently nature has also already chosen such a function okay? And what we are going to emphasize a criteria for such a function in a next few postulates.

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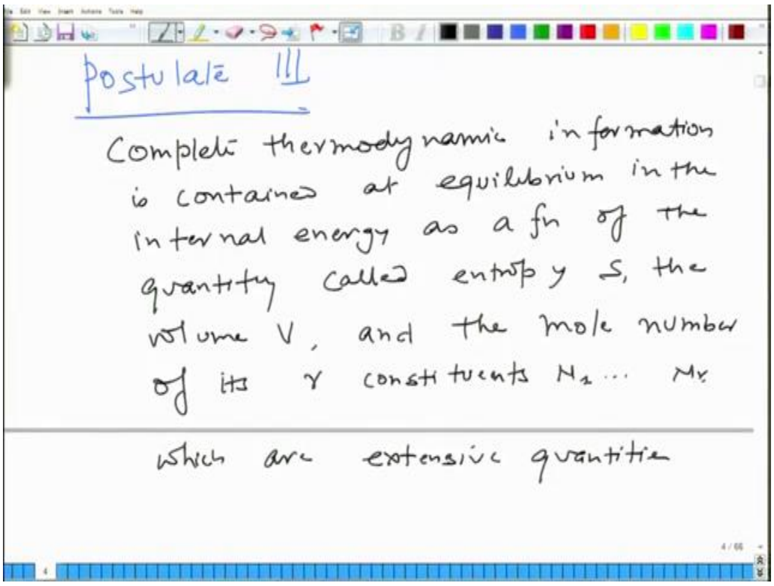

Postulate III

Complete thermodynamic information is contained at equilibrium in the internal energy as a fn of the quantity called entropy S, the volume V, and the mole number of its r constituents $N_1 \cdots N_r$

which are extensive quantities

So that brings us to our postulate number 3. So, what we are trying to emphasize is some function which satisfy several criteria which will be through this postulates, so here we state that complete thermodynamics information is contained at equilibrium in the internal energy as the function of the quantity called entropy. So, we are now introducing entropy, so the complete thermodynamic information is contained at equilibrium in internal energy as a function of quantity called entropy, the volume v and the mole number of its r constituents so basically species here, which can be given as N1 till Nr. Now, these are extensive quantity okay?

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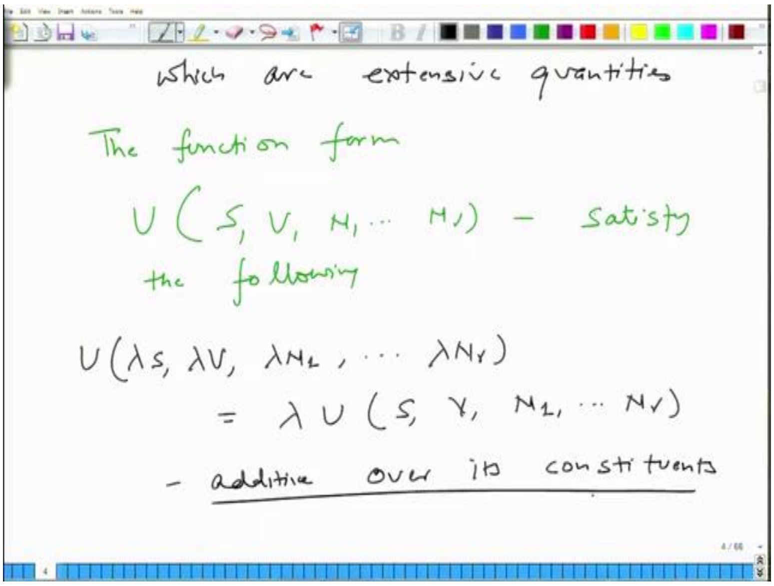

which are extensive quantities

The function form

$U(S, V, N_1, \cdots N_r)$ - satisfy the following

$$U(\lambda S, \lambda V, \lambda N_1, \cdots \lambda N_r) = \lambda U(S, V, N_1, \cdots N_r)$$

- additive over its constituents

So, having said that, it says very simply in mathematical form that the functional form is nothing but u as a function of s, v, N1 and Nr which has the following properties, that means it satisfies the following. The first we are saying that the function here is nothing but homogeneous of the first order which essentially means that u lambda s, lambda v, lambda N1 till lambda Nr is equivalent to lambda u, s, v, N1, till Nr okay?

It also means from this statement that these are additives over its constituents, okay? So, if you have many compartments in your system you can simply add internal energy, similarly you can add entropy and so forth. Okay? So, that is the definition of this extensive variable.

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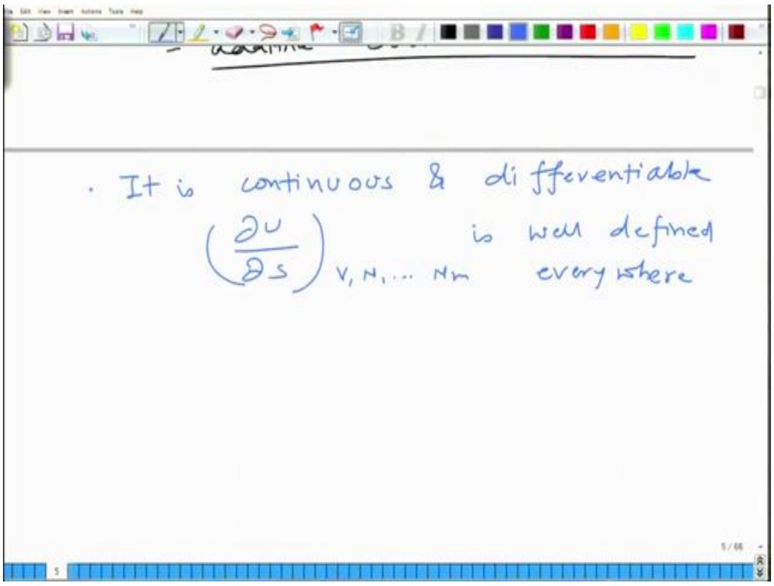

· It is continuous & differentiable

$\left(\frac{\partial U}{\partial S}\right)_{V, N_1, \ldots N_m}$ is well defined everywhere

The other property should meet or it should satisfy is that it is continuous and differentiable, okay? Which means that the derivative of first order derivative at a constant value and N ones are fixed is well defined everywhere, okay?

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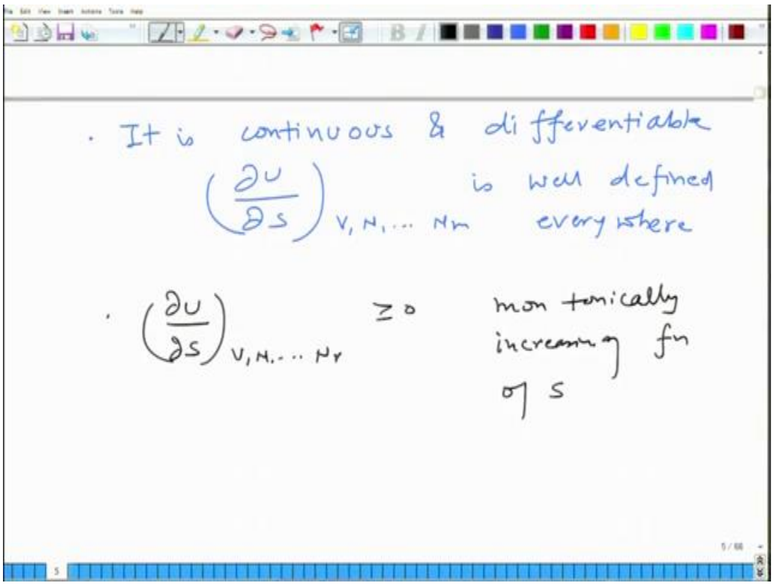

· It is continuous & differentiable

$\left(\frac{\partial U}{\partial S}\right)_{V, N_1, \ldots N_m}$ is well defined everywhere

· $\left(\frac{\partial U}{\partial S}\right)_{V, N_1, \ldots N_r} \geq 0$ monotonically increasing fn of S

The other this is that the next property which we are saying that is satisfies as a following of says that this derivative is greater than equal to zero that is monotonically increasing function of s. Now this particular postulate is meant for our system that is a thermodynamic limit okay?

$$\left(\frac{\partial U}{\partial S}\right)_{V, N_1, \ldots, N_r} \geq 0$$

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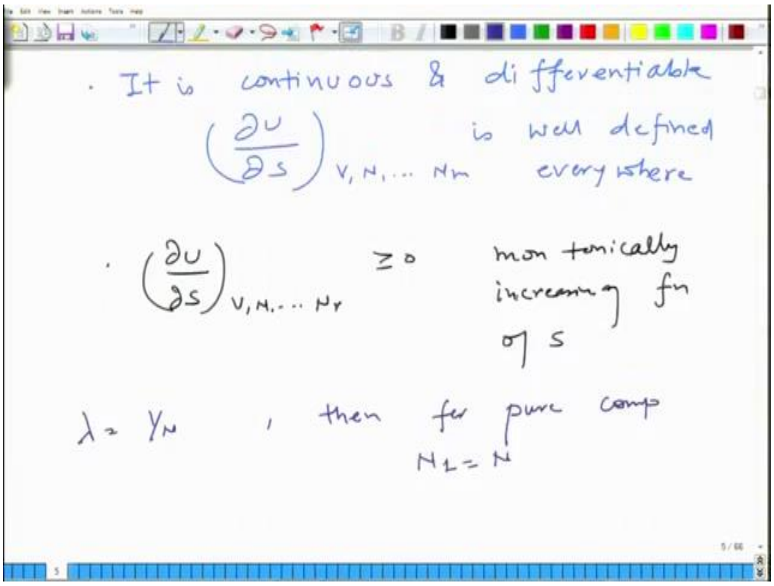

· It is continuous & differentiable

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· $\left(\frac{\partial U}{\partial S}\right)_{V,N_1,\ldots N_r} \geq 0$ monotonically increasing fn of S

$\lambda = 1/N$, then for pure comp $N_1 = N$

Now, based on this postulate and this particular function form with the property the following you can consider as a key observations, so consider

$$\lambda = \frac{1}{N}$$

And we are also assuming for the pure system, then for pure component N1 is the basically n okay?

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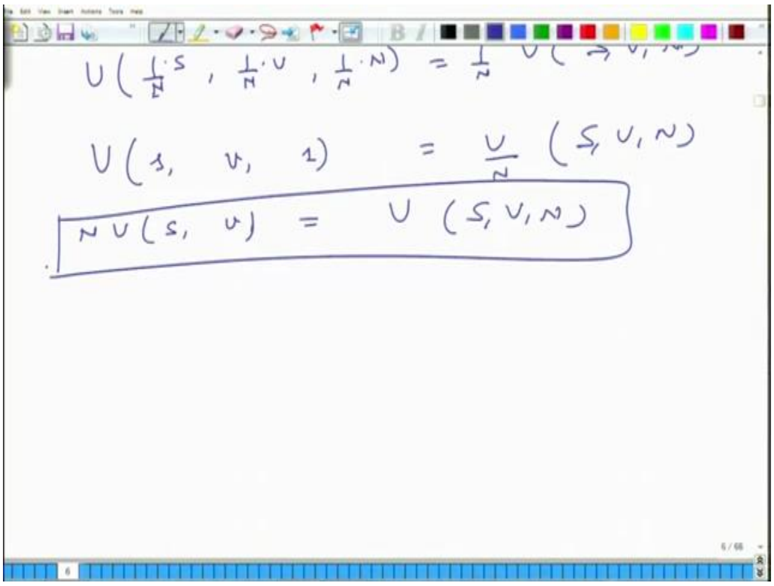

$U\left(\frac{1}{N}\cdot S, \frac{1}{N}\cdot V, \frac{1}{N}\cdot N\right) = \frac{1}{N} U(S, V, N)$

$U(s, v, 1) = \frac{U}{N}(S, V, N)$

$\boxed{N u(s, v) = U(S, V, N)}$

Now with this you can plug in here and obtain the following that u 1 by N and S 1 by N times v, 1 by N times by N this is 1 by N u, S, V N. okay? So, this is basically specific entropy, specific number of moles so hence say it's a molar entropy, molar volume, so essentially I can write this as U s, v, 1 equal to U by N S, V, N okay? Or this I can write as because it depends on molar properties hence this can written as now U S, V, N. okay?

$$U(s, v, 1) = \frac{V}{N}(S, V, N)$$

$$NV(s, v) = U(S, V, N)$$

So essentially this statement means that for the pure thermodynamic essentially this statement or this particular expression means it is for pure component.

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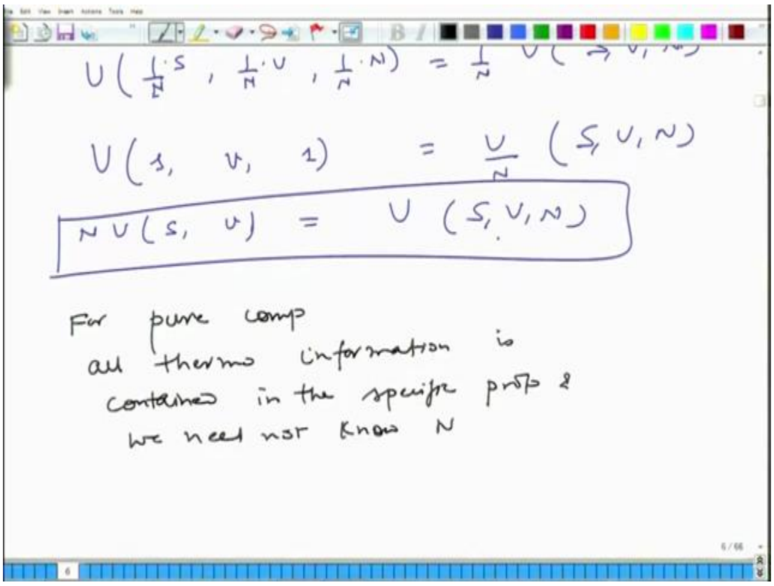

$$U\left(\frac{1}{N}\cdot S, \frac{1}{N}\cdot V, \frac{1}{N}\cdot N\right) = \frac{1}{N} U(S, V, N)$$

$$U(s, v, 1) = \frac{U}{N}(S, V, N)$$

$$\boxed{N\,U(s, v) = U(S, V, N)}$$

For pure comp
all thermo information is
contained in the specific prop &
we need not know N

All information thermodynamic information is contain in a specific property okay? And we need not know N okay?

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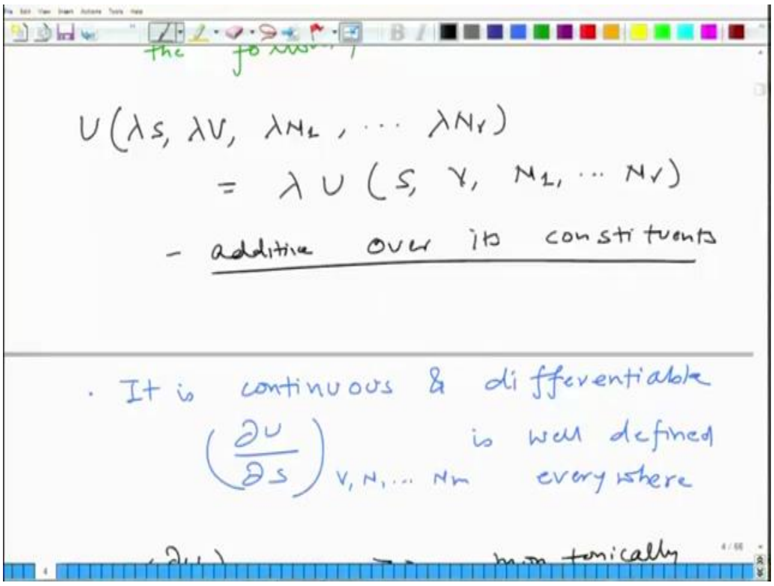


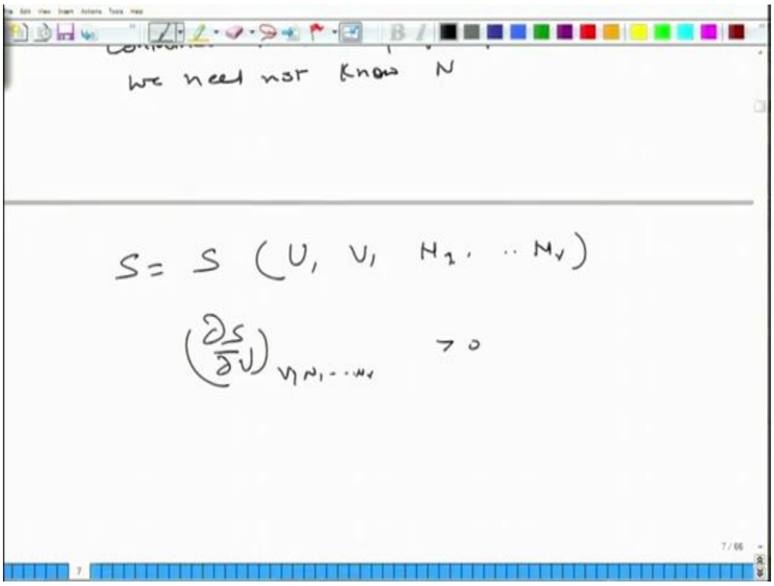
$$U(\lambda S, \lambda V, \lambda N_1, \cdots \lambda N_r) = \lambda U(S, V, N_1, \cdots N_r)$$

- additive over its constituents

· It is continuous & differentiable

$\left(\frac{\partial U}{\partial S}\right)_{V, N_1, \cdots N_m}$ is well defined everywhere

monotonically



we need not know N

$$S = S(U, V, N_1, \cdots N_r)$$

$$\left(\frac{\partial S}{\partial U}\right)_{V, N_1, \cdots N_r} > 0$$

So, that statement we can make based on this expression, now based on this expression here we can use this and this 2 statement here or 2 expression here we can invert it and obtain a expression for entropy we can write S as a function of U, V, N1, Nr okay? So it enjoys the similar properties as in the case of internal energy that means i can write dell S by dell U oaky.

So later on we will be looking at that the maximum value or maximum value of the entropy corresponds to the minimum value of internal energy that something we are look into that in the later part of the course. So this is also the well-defined property okay? So it also homogeneous of the order of first order or depending on your convenience you can choose the expression of a system in terms of entropy or in terms of internal energy oaky?

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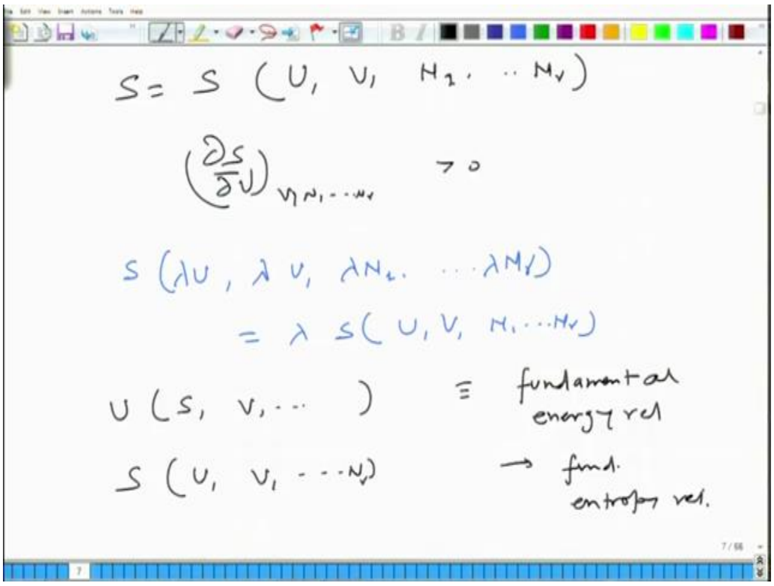

$S = S(U, V, N_1, \cdots N_r)$

$\left(\frac{\partial S}{\partial U}\right)_{V, N_1, \cdots N_r} > 0$

$S(\lambda U, \lambda V, \lambda N_1 \cdots \lambda N_r)$
$= \lambda S(U, V, N_1 \cdots N_r)$

$U(S, V, \cdots) \equiv$ fundamental energy rel

$S(U, V, \cdots N_r) \rightarrow$ fund. entropy rel.

So as i said the S is homogeneous which essentially of the order of 1 so we can write like this, okay? So let me summarize so the choice of expression thermodynamic function for a close system in term of internal energy or in terms of entropy as per your convenience, so but when you write it this S, V and this corresponds to the fundamental or this represents the fundamental energy relation whereas S, U, V N represents fundamental entropy relation.

$$S(\lambda U, \lambda V, \lambda N_1, \ldots, \lambda N_r) = \lambda S(U, V, N_1, \ldots, N_r)$$

Now, this means that if you know either information of a complete information of entropy volume is and you represent the system completely or you know the information of thermodynamics properties of the system or ultimately you know the internal energy volume and so forth you have the complete information thermodynamics.

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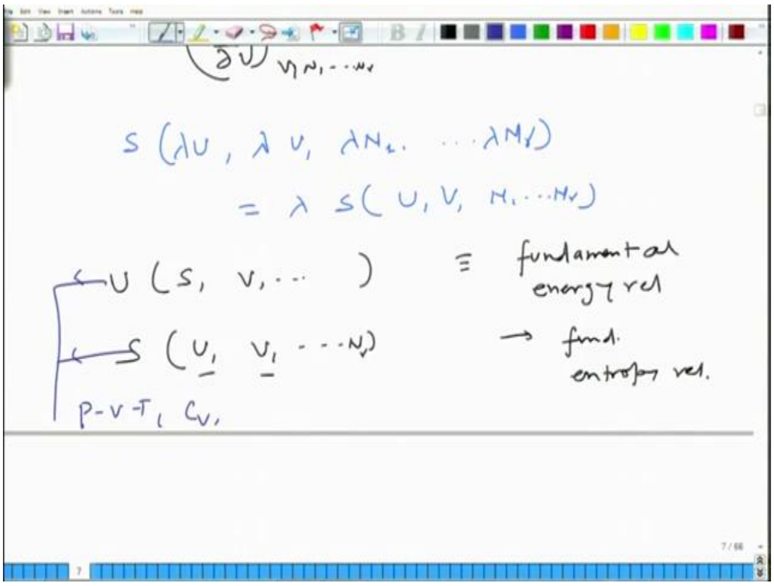

$S(\lambda U, \lambda V, \lambda N_1 \cdots \lambda N_r)$
$= \lambda S(U, V, N_1 \cdots N_r)$

$U(S, V, \cdots) \equiv$ fundamental energy rel

$S(U, V, \cdots N_r) \rightarrow$ fund. entropy rel.

P-V-T, C_V,

So, from either this equation or this expression either of them there we can find out the P, V, T relations we can find heat capacity, constant heat capacity and phase behavior and etc. and etc. Okay?

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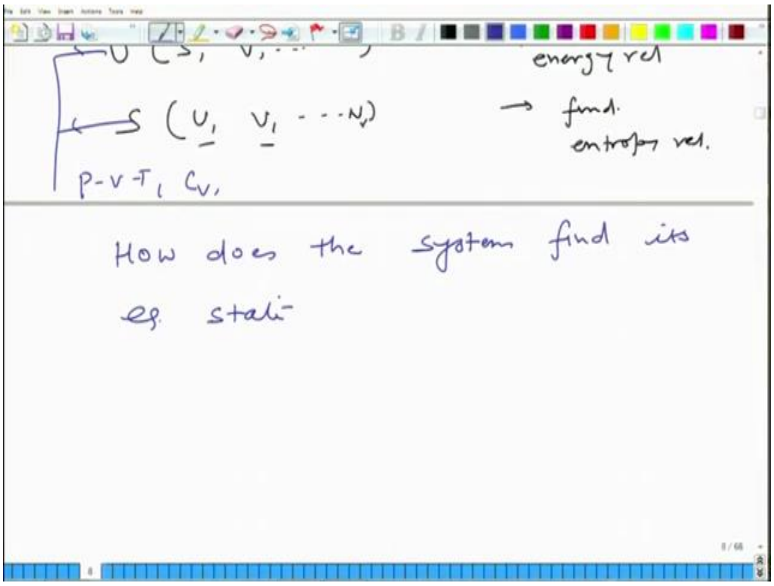

energy rel

$S(U, V, \cdots N)$ → find entropy rel.

P-V-T, C_v,

How does the system find its eq. state

So, let me come back to the question again of the idea of the equilibrium state, so the question is how does the system find its equilibrium state? Okay. And this is essential property of all the system. So if the system has let us say many non-equilibrium state with a different phase and different properties, different conditions it all teds towards the particular equilibrium state. Okay?

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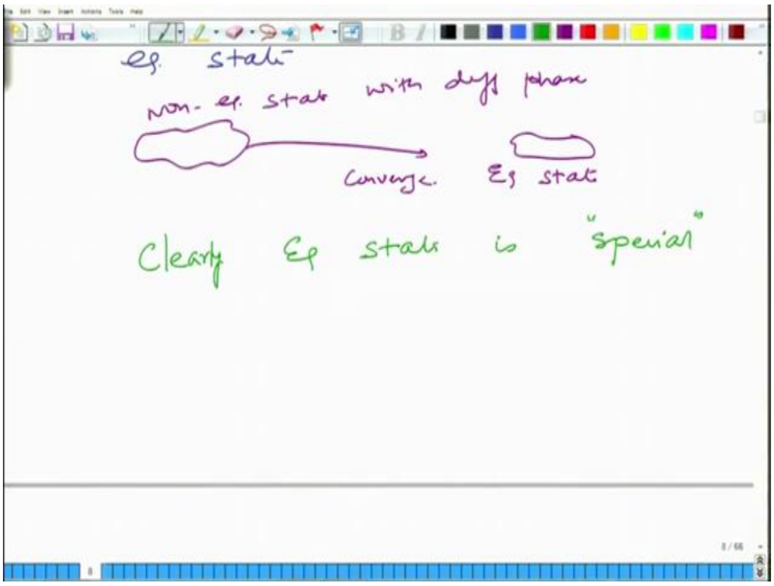

eq. state

Non-eq. state with diff phase

converge.

Eq stat

Clearly Eq state is "special"

So, essentially we are saying that if you have many possible non equilibrium state with different phase and condition it all tends towards an equilibrium state or point. Okay? So, it all converges basically to the equilibrium state which emphasizes that clearly equilibrium is something special. Okay? So that brings to the next postulates first that how this is happened that eventually everything converges to next level state.

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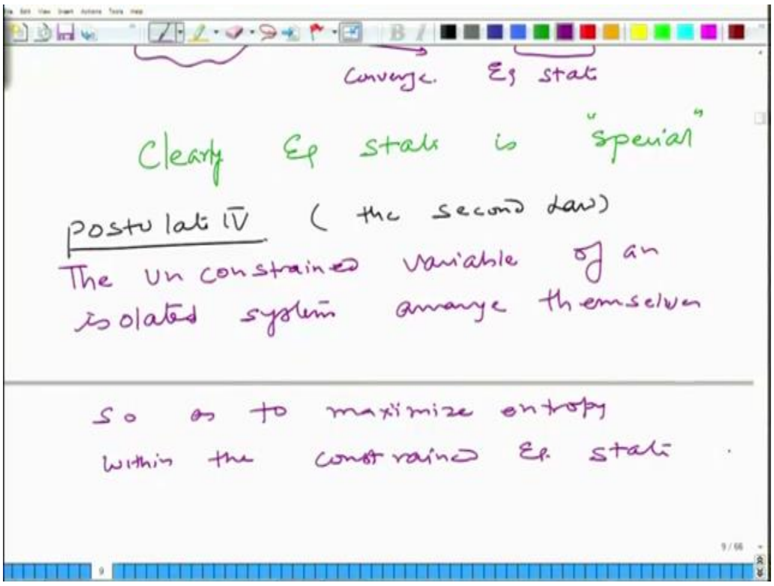

Converge. Eq state

Clearly Eq state is "special"

postulate IV (the second law)

The unconstrained variable of an isolated system arrange themselves

so as to maximize entropy within the constrained Eq. state .

And this what we refer as postulate 4 also can be state as second law of thermodynamics, so it says that the unconstrained variables of an isolated system avenge themselves in such a way so that a entropy of the system tends towards maximum. So, that is the postulate 4. It states that if you consider a system and then you isolate it okay?

Then the rest of the unconstrained variable tends to change themselves in a way so that the system overall system entropy is maximum and that is basically which corresponds to the equilibrium. So that is a postulate 4 which we called as the second law so in other words we can use some example to represent this concept.

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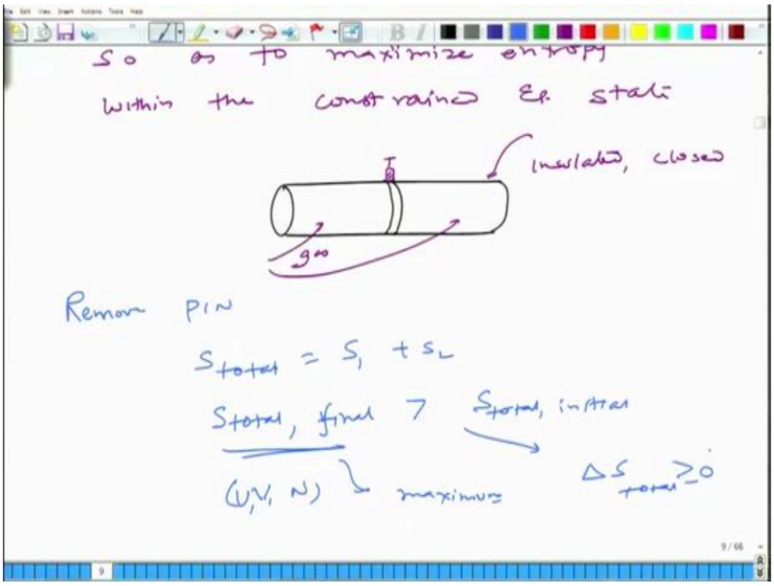

So as to maximize entropy

within the constraind Eq. state

Remove PIN

$S_{total} = S_1 + S_2$

$S_{total, final} > S_{total, initial}$

(U, V, N) maximum

$\Delta S_{total} \geq 0$

So, let us say you have a cylinder having a piston here that say it is initially pin, okay? And assuming this is insulated okay? And basically isolated oaky? And this is the close system, considering this is the gas both the side, if you remove this pin, you allow this piston to move okay? Then the piston will be positioned in the way which will maximize the total entropy of this 2 compartment, let us say

$$S_{total} = S_1 + S_2$$

So basically as total will final is more than as total initial okay? Or S total final for given total volume V, total internal energy U and N will be maximum, so remember that means what we are saying is

$$\Delta S_{total} \geq 0$$

If it is already in equilibrium state it will be 0 that means there will be no change in entropy otherwise it will always increase from this particular postulate. Now, for the sake of completeness in our postulate concept which is lying the foundation of thermodynamics.

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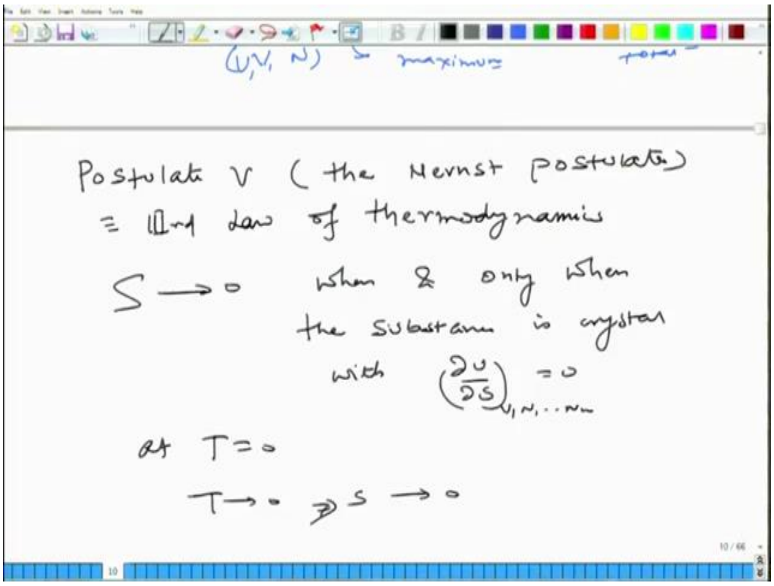

(U, V, N) → maximum total

Postulate V (the Nernst postulate)

≡ IIIrd law of thermodynamics

$S \rightarrow 0$ when & only when the substance is crystal with $\left(\frac{\partial U}{\partial S}\right)_{V, N, \ldots N_m} = 0$

at $T = 0$

$T \rightarrow 0 \Rightarrow S \rightarrow 0$

I am also going to emphasize the postulate 5 or the last one, which is sometimes also called the Nernst postulate, okay? So this is sometimes also called the third law of thermodynamics. Okay? So it says,

$$S \rightarrow 0, \qquad \textit{only when substance is crystal with,} \left(\frac{\partial U}{\partial S}\right)_{V,N_1,\ldots,r} = 0$$

In other word we will going to show this that this is nothing but saying that at T equal to 0 we shall see this that this is connected to this is nothing but T.

S is 0 or when T approaches 0, S approaches 0. Okay? So that is the end of the list of postulates which I planned to cover and we will start in next lecture with an example to express all this postulates in the form of some equational state, so we will see how can we can use his postulate in the subsequent language. So with that have a good, we will see you in the next lecture.