Chemical Engineering Thermodynamics

Professor Jayant K. Singh

Department of Chemical Engineering

Indian Institute of Technology, Kanpur

Lec 5

Definition of Intensive Variables and Driving forces for temperature and Pressure flow

Welcome back, in the last lecture we defined a variables, temperature, pressure and chemical potential.

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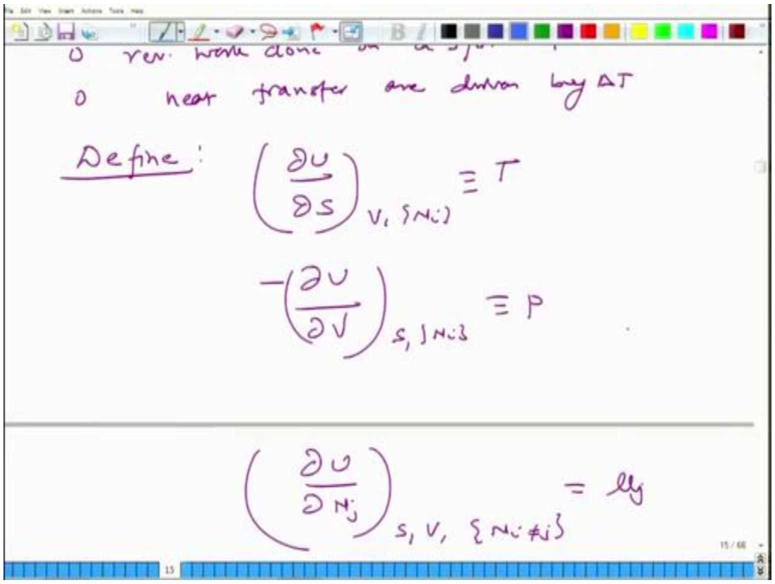

o rev. work done on a

o heat transfer are driven by ΔT

Define:

$$\left(\frac{\partial U}{\partial S}\right)_{V,\{N_i\}} \equiv T$$

$$-\left(\frac{\partial U}{\partial V}\right)_{S,\{N_i\}} \equiv P$$

$$\left(\frac{\partial U}{\partial N_j}\right)_{S,V,\{N_{i\neq j}\}} = \mu_j$$

A temperature was introduced as a derivative of internal energy, with respect to entropy. Now it is rather odd abstract quantity such as entropy to temperature and thus it is important that the definition and the postulate which we have shown here indeed, fulfills the experience which we have with respect to the temperature. So, I am going to write down a list of a typical experience we have with temperature or the observations we have.

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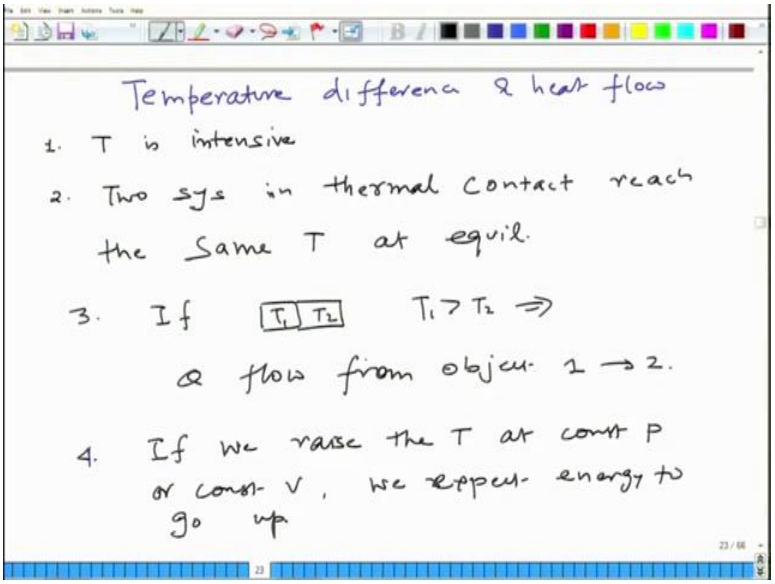
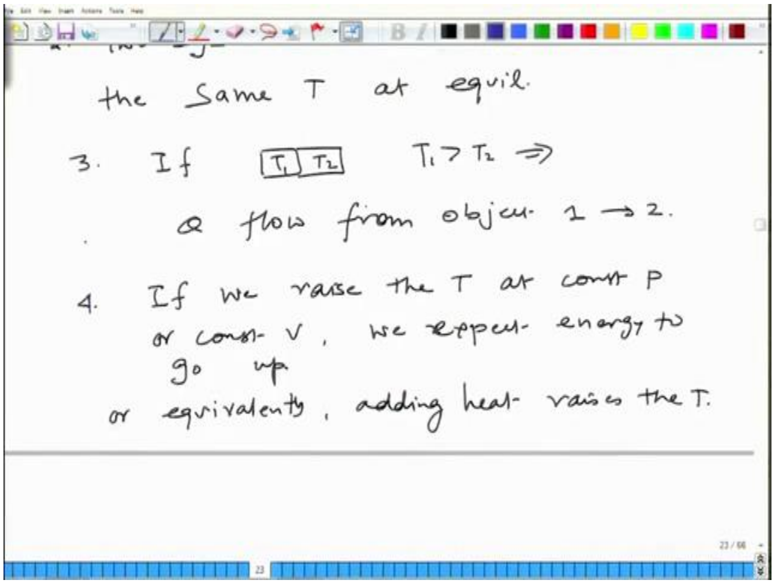


Temperature difference & heat flow

1. T is intensive
2. Two sys in thermal contact reach the same T at equil.
3. If $\boxed{T_1}\boxed{T_2}$ $T_1 > T_2 \Rightarrow$
   Q flow from object $1 \rightarrow 2$.
4. If we raise the T at const P or const V, we expect energy to go up



the Same T at equil.

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   Q flow from object $1 \rightarrow 2$.
4. If we raise the T at const P or const V, we expect energy to go up

or equivalently, adding heat raises the T.

The temperature is basically intensive. Second is, if two system in thermal contact and they will, they will reach equilibrium and attain the same temperature and third is, if let us say there are two particular blocks of object at thermal contact having temperature T1 and T2 with T1 go to then T2. This basically would imply than the heat, Q flow from object 1 to 2. So, this is something which we have feeling or intuitions, or observations. .

So what we are basically discussing is temperature difference and heat flow and the how our observations is basically can be related to the definition, which we have or the definition of the temperature in terms of the Internal energy and entropy or the definition is basically satisfying the observation which we are writing down here. And the fourth if we raise the temperature at constant p or constant v, we expect the energy should go up, so we expect energy to go up.

So this particular observation for its basically saying that energy will be raised upon application or supply of heat. So, this can be equivalently stated as follows, adding heat raises the temperature. Now, the first observation that temperature is (intent) intensive is part of the definition of the first law. , or engine is a definition indicates that he is intensive. So the first and second we can now look at, and the fourth view we discussing which will later. So, in order to prove that first and second observation holds with the specific definition of the temperature.

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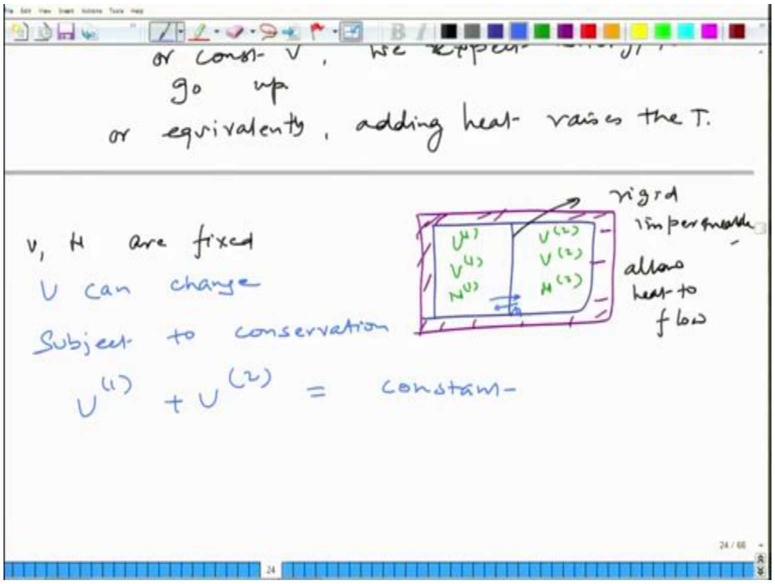

or const V , we expect

go up

or equivalently , adding heat raises the T.

V, N are fixed

U can change

Subject to conservation

$U^{(1)} + U^{(2)} =$ constant

So let us consider these two objects. It is contact by this rigid, impermeable separator. So this is a basically a rigid impermeable but it allows heat to flow. And now that is keep this, particular two blocks will isolated, so this is completely insulation here, and compartment one, it has its own internal energy, volume and number of modes and similarly for the second compartment. So initially we are assuming this compartment one and compartment two already are they equilibrated a state. So, they have this individual energies volume and they improved to the thermal contact.

Now, what happens subsequently? So if you look at it, the process, the total n here is fixed and total volume is fixed. VN1 are basically fixed, however because of the exchange of energy from the heat point of view, the internal energy is going to U can change. So internal can change here basically.. .

$U^{(1)} + U^{(2)} = constant$

$dU^{(1)} + dU^{(2)} = 0$

$dU^{(1)} = -dU^{(2)}$

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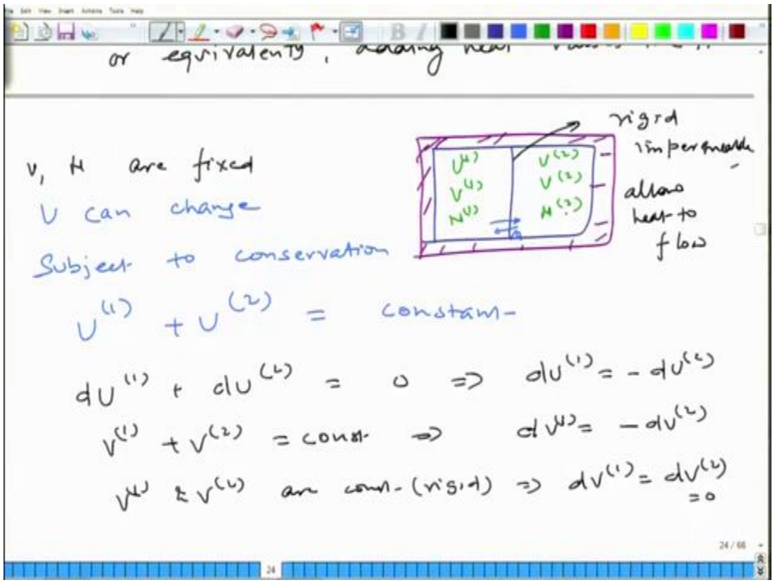


or equivalenty, adding

V, N are fixed

U can change

Subject to conservation

$U^{(1)} + U^{(2)} = \text{constant}$

$dU^{(1)} + dU^{(2)} = 0 \Rightarrow dU^{(1)} = -dU^{(2)}$

$V^{(1)} + V^{(2)} = \text{const} \Rightarrow dV^{(1)} = -dV^{(2)}$

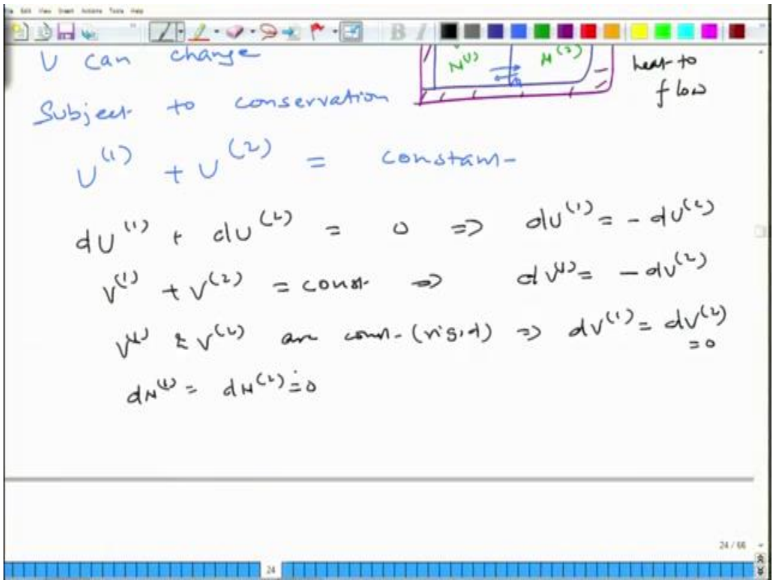
$V^{(1)}$ & $V^{(2)}$ are const (rigid) $\Rightarrow dV^{(1)} = \underset{=0}{dV^{(2)}}$

$$V^{(1)} + V^{(2)} = constant$$

$$dV^{(1)} + dV^{(2)} = 0$$

$$V^{(1)} \approx V^{(2)}$$

$$dV^{(1)} = dV^{(2)} = 0$$



U can change

Subject to conservation

$U^{(1)} + U^{(2)} =$ constant

$dU^{(1)} + dU^{(2)} = 0 \Rightarrow dU^{(1)} = -dU^{(2)}$

$V^{(1)} + V^{(2)} =$ const $\Rightarrow dV^{(1)} = -dV^{(2)}$

$V^{(1)}$ & $V^{(2)}$ are const (rigid) $\Rightarrow dV^{(1)} = \underset{=0}{dV^{(2)}}$

$dN^{(1)} = dN^{(2)} = 0$

Now since the separator itself is impermeable, that is a does not allow any particle to go from one compartment to another compartment. This means

$$dN^{(1)} = dN^{(2)} = 0$$

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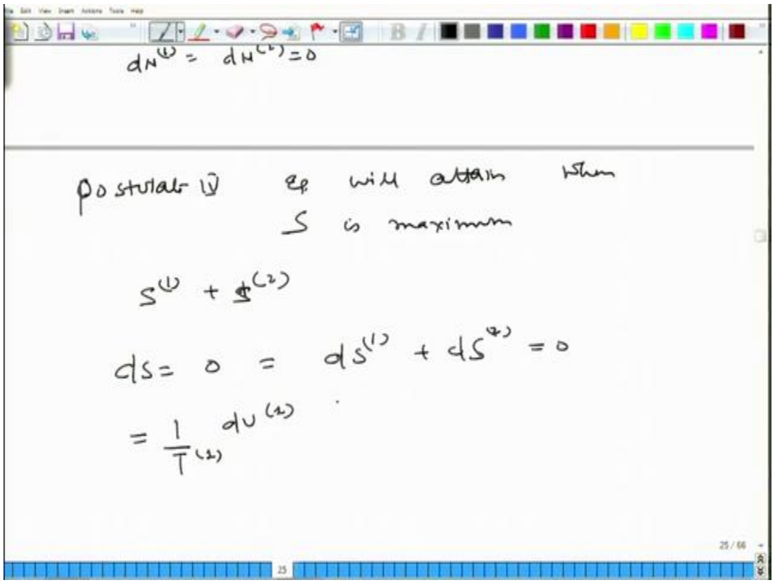


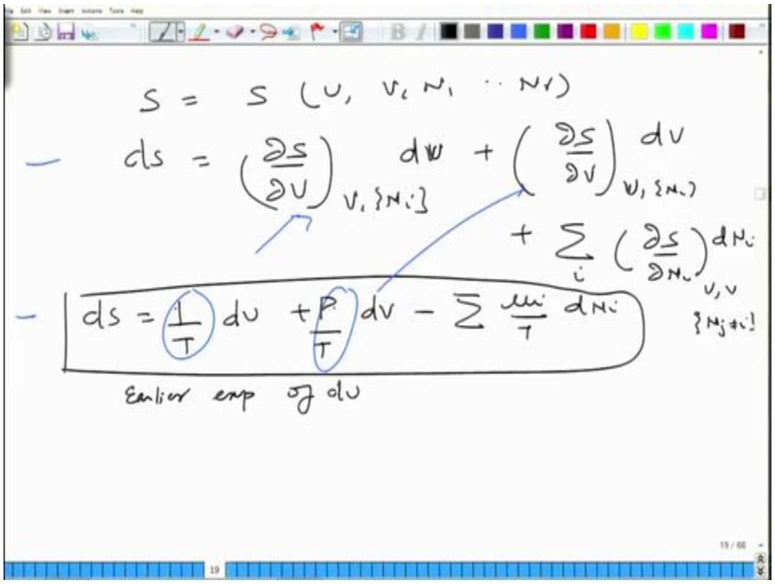
$dN^{(1)} = dN^{(2)} = 0$

postulate (V) eq will attain when S is maximum

$S^{(1)} + S^{(2)}$

$dS = 0 = dS^{(1)} + dS^{(2)} = 0$

$= \frac{1}{T^{(2)}} dU^{(2)}$

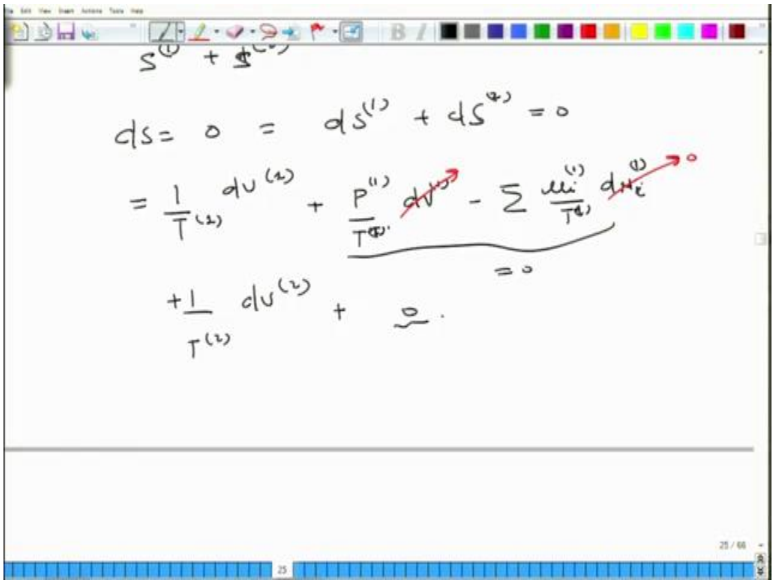


$$S = S(U, V, N_1 \cdots N_r)$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,\{N_i\}} dU + \left(\frac{\partial S}{\partial V}\right)_{U,\{N_i\}} dV + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{U,V,\{N_{j\neq i}\}} dN_i$$

$$\boxed{dS = \frac{1}{T} dU + \frac{P}{T} dV - \sum \frac{\mu_i}{T} dN_i}$$

Earlier exp of dU

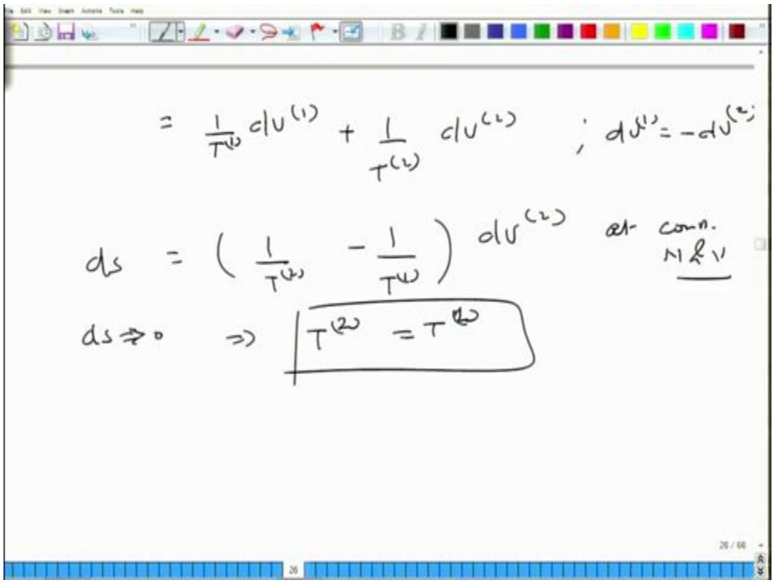


$$S^{(1)} + S^{(2)}$$

$$dS = 0 = dS^{(1)} + dS^{(2)} = 0$$

$$= \frac{1}{T^{(1)}} dU^{(1)} + \underbrace{\frac{P^{(1)}}{T^{(1)}} \cancelto{0}{dV^{(1)}} - \sum \frac{\mu_i^{(1)}}{T^{(1)}} \cancelto{0}{dN_i^{(1)}}}_{=0}$$

$$+ \frac{1}{T^{(2)}} dU^{(2)} + 0.$$



$= \frac{1}{T^{(1)}} dU^{(1)} + \frac{1}{T^{(2)}} dU^{(2)}$; $dU^{(1)} = -dU^{(2)}$

$ds = \left(\frac{1}{T^{(2)}} - \frac{1}{T^{(1)}} \right) dU^{(2)}$ at const. N & V

$ds = 0 \Rightarrow \boxed{T^{(2)} = T^{(1)}}$

Now, let us try to understand how to write down our fundamental equation here. We can consider or take the q from postulate for where we say that the equilibrium state is attained when S is a maximum, for this particular isolated state at isolated system. So equilibrium will attain when S is maximum. Now S of the system is basically

$$S = S^{(1)} + S^{(2)}$$

$$dS = 0$$

$$dS^{(1)} + dS^{(2)} = 0$$

Now we can write down their differential expression of s in terms of the other variables u,v and n.

$$dS = \frac{1}{T^{(1)}} dU^{(1)} + \frac{P^{(1)}}{T^{(1)}} dV^{(1)} - \sum_i \frac{\mu_i^{(1)}}{T^{(1)}} dN_i^{(1)} + \frac{1}{T^{(2)}} dU^{(2)}$$

Now since dv is equal to 0 and dn equal to 0. So the only term with respect to du will remain here. So this I can write down as the follows. This is equal to

$$dS = \frac{1}{T^{(1)}} dU^{(1)} + \frac{1}{T^{(2)}} dU^{(2)}$$

$dU^{(1)} = -dU^{(2)}$

$$dS = (\frac{1}{T^{(2)}} - \frac{1}{T^{1}})dU^{(2)}$$

$$dS = 0,\ T^{(1)} = T^{(2)}$$

So this is basically the conditions of thermal equilibrium which is attained when the equilibrium is raised when S a maximum value.

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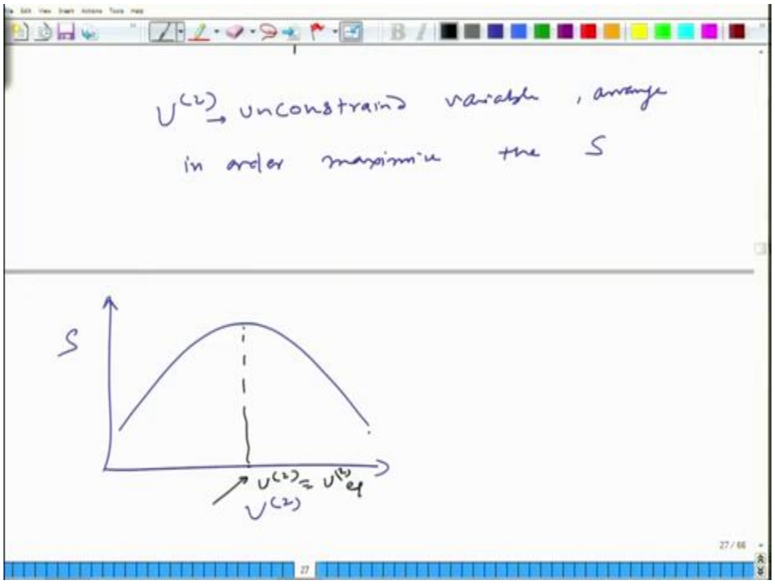
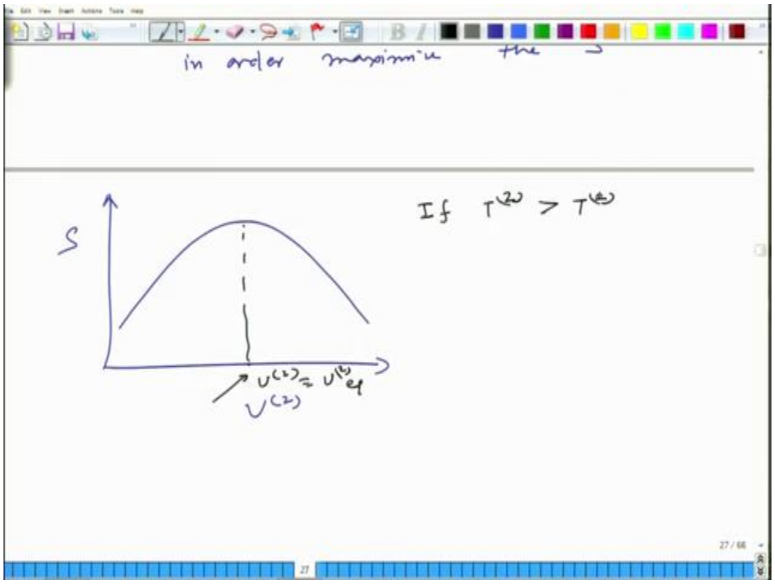


$U^{(2)} \rightarrow$ unconstraind variable, arrange in order maximize the S



Now we can connect to this expression to heat flow as well, if you relook at the postulate, the postulate came at unconstrained variable in case of a U2 so U2 considered as unconstrained variable, so U2 is unconstrained variable so it will arrange itself in order to maximize range in order to maximize the entropy. So let us little bit, look at it. What it does mean? It means basically that you are going to have this kind of plot for S as a function of U, and this is going to be U2 where this is the case where the U2 is equal to U2 at equilibrium. Now it does not tell you which part is going to follow either this one or this side. So let us assume that that if, initially T2 is greater than T1.

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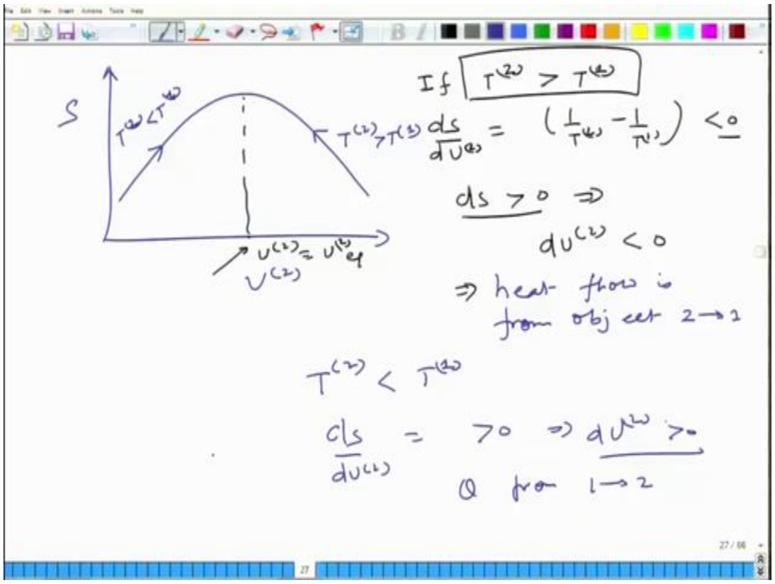


If $\boxed{T^{(2)} > T^{(1)}}$

$\frac{dS}{dU^{(2)}} = \left(\frac{1}{T^{(2)}} - \frac{1}{T^{(1)}}\right) \underline{< 0}$

$\underline{dS > 0} \Rightarrow$

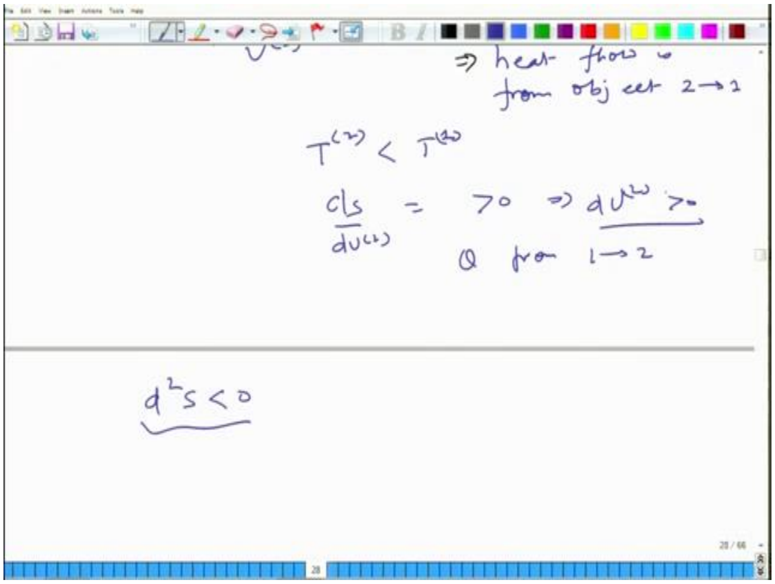
$dU^{(2)} < 0$

⇒ heat flow is from object 2 → 1

$T^{(2)} < T^{(1)}$

$\frac{dS}{dU^{(2)}} = > 0 \Rightarrow \underline{dU^{(2)} > 0}$

Q from 1 → 2



⇒ heat flow is from object 2 → 1

$T^{(2)} < T^{(1)}$

$\frac{dS}{dU^{(2)}} = > 0 \Rightarrow \underline{dU^{(2)} > 0}$

Q from 1 → 2

$\underline{d^2S < 0}$

Now we look at this expression again, this so tells you the falling that ds by du is 1 by T2 minus 1 by T1. Now if T2 is greater than T2 that means this expression is going to be less than 0. Now since ds is greater than 0, for this system before it reaches the equilibrium, at equilibrium ds is equal to 0, but until it reaches the equilibrium, the ds is greater than 0, which indicates that du of 2 should be less than 1. So, this means that the internal energy of U in this case decreases. So, if internal energy to compartment to decrease it, it essentially means that heat is flowing from 2 to 1 this implies that heat flow is from object to 2 to 1.

And in such case, this is the process here. That would be U is decreasing, for this particular case. Now, similarly if T2 is less than T1 or T1 is greater than T2, which essentially means ds by du2 is basically greater than 0, which essentially means U2 is greater than 0. That means U is basically U of 2 is increasing essentially means that it flows from 1 to 2. So this would be the case for the system where you have T2 is less than T1, .

This particular expression 2 clearly explains you that heat flows from hot object to cold object. That is what we could use and this means that our observation is in line with the definition of the temperature where we are related to an abstract quantity such as entropy. So, though we have used the concept of external we have not fully exploited the condition of entropy maximum and where of course for maximum ds should be less than 0, the second derivative of S.

So we are not discovering at this point, this will be discussed when we will be considering the stability and equilibrium, which will be taken much later. So, our focus at this point is to, to make use of the definition of the temperature pressure and then, relate to the observation which we have. So having explained the temperature difference and the heat flow, how these are related, we can now move to the pressure difference and volume change.

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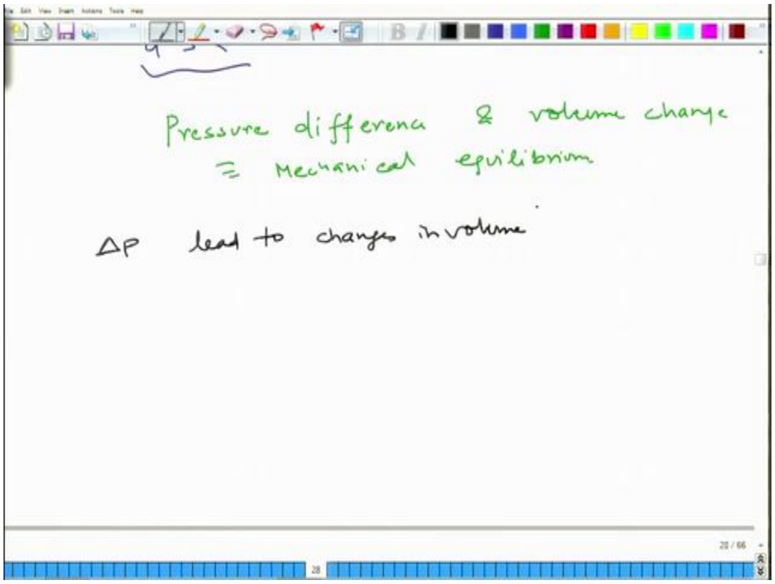
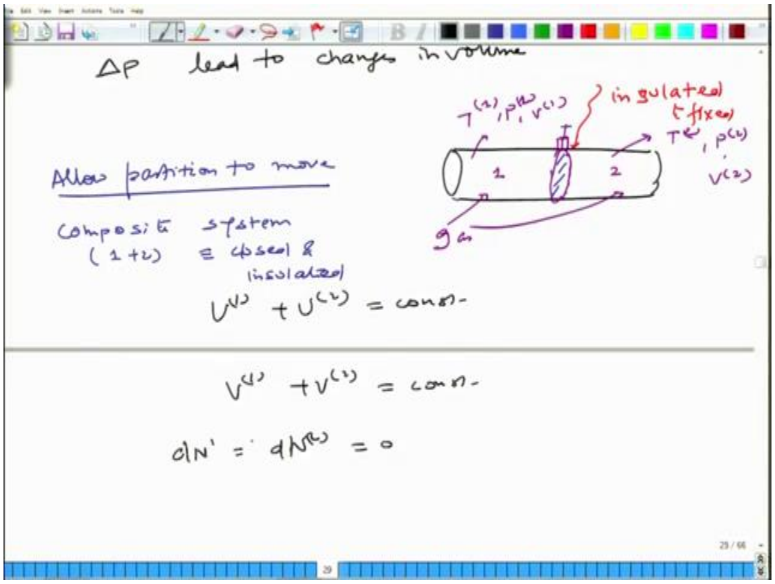


Pressure differenca & volume change

≡ Mechanical equilibrium

ΔP lead to changes in volume



Δp lead to changes in volume

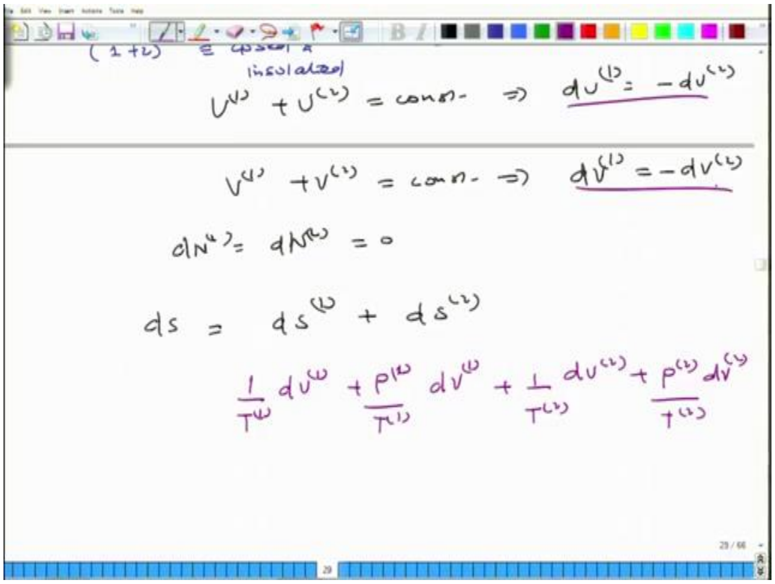
Allow partition to move

Composite system (1+2) ≡ closed & insulated

$U^{(1)} + U^{(2)} = \text{const.}$

$V^{(1)} + V^{(2)} = \text{const.}$

$dN^{(1)} = dN^{(2)} = 0$



(1+2) ≡ closed & insulated

$U^{(1)} + U^{(2)} = \text{const.} \Rightarrow \underline{dU^{(1)} = -dU^{(2)}}$

$V^{(1)} + V^{(2)} = \text{const.} \Rightarrow \underline{dV^{(1)} = -dV^{(2)}}$

$dN^{(1)} = dN^{(2)} = 0$

$dS = dS^{(1)} + dS^{(2)}$

$\frac{1}{T^{(1)}} dU^{(1)} + \frac{P^{(1)}}{T^{(1)}} dV^{(1)} + \frac{1}{T^{(2)}} dU^{(2)} + \frac{P^{(2)}}{T^{(2)}} dV^{(2)}$

So, how pressure difference and volume change and can be connected from the equilibrium point of view? So, this would be leading to some definition of finally in terms of pressure for mechanical equilibrium. So essentially what we intend to do is we want to show that Δp basically lead to change changes in volume. So for that, what we are going to do is we are going to consider a container where fixed volume insulated, where we have some kind of a mobile, separator which should be diathermal.

So, let us try to pictorially explain this. So you have this, let us say a container. This is insulated and fixed, this divided into two compartments, which is fixed by some inch, and this is let us compartment one, compartment two. So this has gas, both of them. They are at a different temperature and pressure. So this will be let us say, T1, P1 this is P2. And similarly, the volume is going to be different, all right.

So, now you allow this a partition to move by taking off this particular inch or you remove this inch and so that it can move. So, if we allow partition to move, now this partition will allow heat transfer and of course it will be mobile so that means the volume of each compartment can change, but it will not allow the particles or the molecules or suspicious to penetrate from one compartment to another compartment.

So, the number of moles, i going to be fixed. So, now let us consider this composite system because (inso) insulated. So, we consider this composite system based on a compartment one and two. , so this is compartment 1 plus 2, which is closed and insulated, which essentially means that your u1 plus u2 is to constant v1 plus v2 is also constant, in addition to that your dN1 is dN2 is it going to be 0, before I write down the fundamental equation here, we can differentiate this and write down the this expression in the form of differential form.

Now this partition can move until this will keep moving until it reaches that equilibrium position. what do you want to find out is the condition of equilibrium in such a case. So will start with the concept of again the entropy, the essential closed and insulated essentially means that entropy will reach a maximum or which can be now written terms of this expression here. Since, N is going to be 0 so we are not going to write the third term of a differential expression of S. So on only the volume and U term is going to be there. So, in other word, I can now write this as, so this is for compartment one and then for compartment two.

$$dS = \frac{1}{T^{(1)}}dU^{(1)} + \frac{P^{(1)}}{T^{(1)}}dV^{(1)} + \frac{1}{T^{(2)}}dU^{(2)} + \frac{P^{(2)}}{T^{(2)}}dV^{(2)}$$

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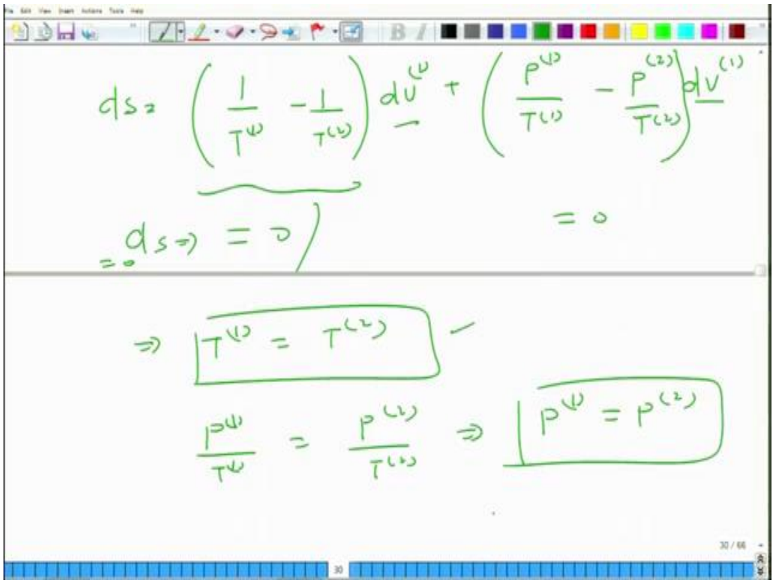

$$ds = \underbrace{\left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)}_{ds \Rightarrow \; = 0} dU^{(1)} + \left(\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}}\right) dV^{(1)}$$

$$= 0$$

$$\Rightarrow \boxed{T^{(1)} = T^{(2)}}$$

$$\frac{P^{(1)}}{T^{(1)}} = \frac{P^{(2)}}{T^{(2)}} \Rightarrow \boxed{P^{(1)} = P^{(2)}}$$

$$dS = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) dU^{(1)} + \left(\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}}\right) dV^{(1)}$$

$$dS = 0$$

$$T^{(1)} = T^{(2)}$$

$$\frac{P^{(1)}}{T^{(1)}} = \frac{P^{(2)}}{T^{(2)}}$$

$$P^{(1)} = P^{(2)}$$

So this expression, the first one will yield the following, the temperature should be equal of the two compartments at equilibrium and the second one will yield P1 by T1 is P2 by T2 and given that this is the case, this would lead to the equality of the pressure in the two compartment at equilibrium. This is at equilibrium, we can talk about, that this is the final conditions of the equilibrium.

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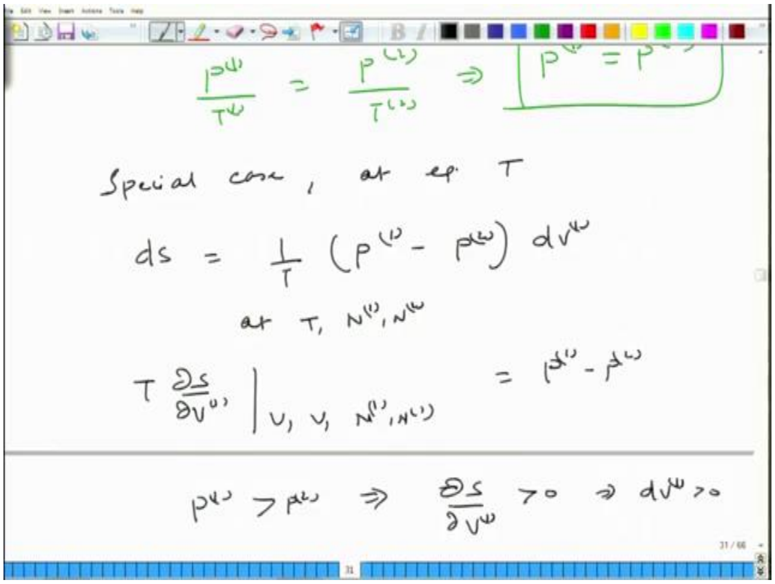


$$\frac{P^{(1)}}{T^{(1)}} = \frac{P^{(2)}}{T^{(2)}} \Rightarrow \boxed{P^{(1)} = P^{(2)}}$$

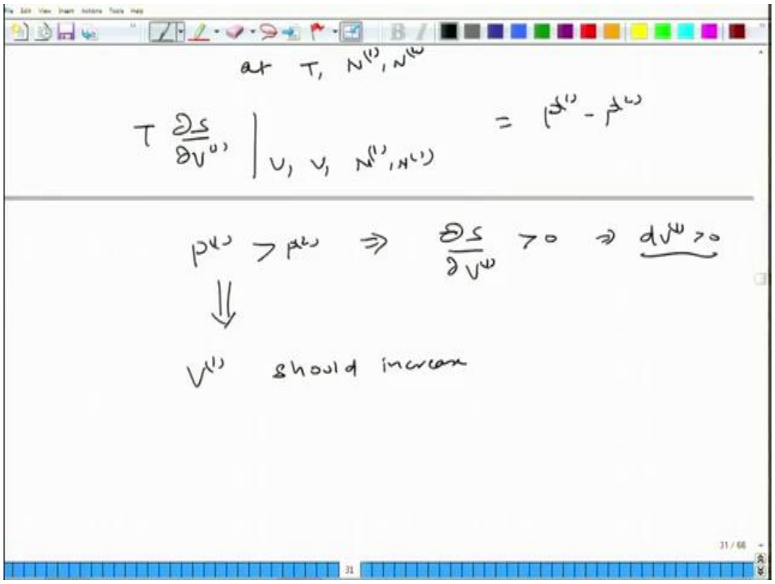
Special case, at eq. T

$$ds = \frac{1}{T}\left(P^{(1)} - P^{(2)}\right) dV^{(1)}$$

at $T, N^{(1)}, N^{(2)}$

$$T \frac{\partial S}{\partial V^{(1)}}\bigg|_{U, V, N^{(1)}, N^{(2)}} = P^{(1)} - P^{(2)}$$

$$P^{(1)} > P^{(2)} \Rightarrow \frac{\partial S}{\partial V^{(1)}} > 0 \Rightarrow dV^{(1)} > 0$$



at $T, N^{(1)}, N^{(2)}$

$$T \frac{\partial S}{\partial V^{(1)}}\bigg|_{U, V, N^{(1)}, N^{(2)}} = P^{(1)} - P^{(2)}$$

$$P^{(1)} > P^{(2)} \Rightarrow \frac{\partial S}{\partial V^{(1)}} > 0 \Rightarrow \underbrace{dV^{(1)} > 0}$$

$\Downarrow$

$V^{(1)}$ should increase

Now we are going to talk about if what happens with the flow of the volume if a considering that one of the compartment has a higher pressure. So just to conclude this discussion, we will be taking the case of that say we will write it down for a special case here, where we are going to just look at the compartment where the temperature is fixed at equilibrium temperature the same expression, now in case of temperatures equal ds can be written as the second term.

So with T1 is equal to T2, so ds is 1 by T, P1 minus P2 dv1. So this is at constant T1, N1, N2, now which means I can write this expression, as T del s by del v, total v is constant, total U is constant, total volume is constant N1 and N2. Now with this, if P1 is greater than P2 which essentially means this, this essentially implies that del s by del v1 is greater than 0. Which essentially means del v1 should be greater than 0, which means that volume should increase volume off compartment one should increase.

So this means that volume of one should increase. So, what does this indicate, this expression that means the pressure of compartment one is more, it is going to expand against the compartment two. So that means the volume of compartment one should increase. And similarly for the case of compartment to the volume is going to get suppressed. In other words, it will get compressed where the compartment one is going to compress compartment two until the pressure reaches an equilibrium.

So, this particular observation or this particular results agree with our observation indicating that our definition indeed fulfills the basic intuitions of our observation from my experiments. So we will continue with this particular exercise with an example, and then we will talk a talk about the chemical equilibrium, and that will conclude this particular subject and then we will take it up some other subject in the next lecture.

So, I will see you again in the next, the lecture with the continuation of this exercise. Have a good day.