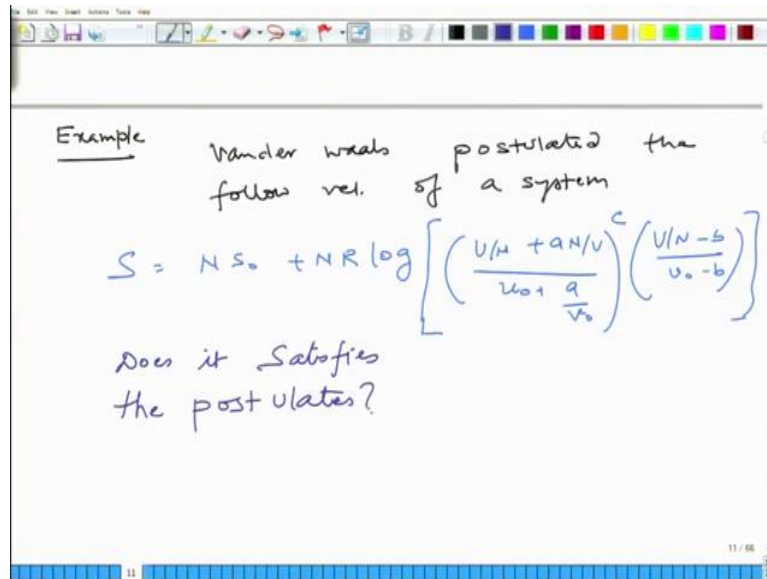


**Chemical Engineering Thermodynamics**  
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**Lecture 04: Postulates of Thermodynamics-II**

Welcome back, in the last few lectures we have discuss the postulates which have led down the foundation of thermodynamics, in today's lecture we will start with an example.

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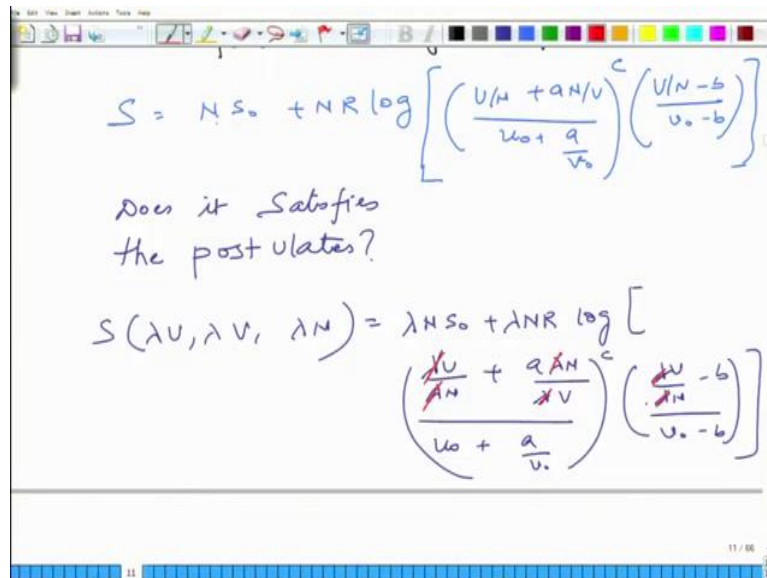
Let, us consider that a particular fundamental entropy relation of a system which was postulated by Vander Waals, let us say Vander Waals postulated the following relation of a system, so

$$S = NS_0 + NR \log \left[ \left( \frac{\frac{U}{N} + aN/V}{u_0 + a/v_0} \right)^c \left( \frac{\frac{V}{N} - b}{v_0 - b} \right) \right]$$

So this is basically the relation. So the question is does is satisfies the postulates? Okay?

So the first one is basically that contains U, okay? so we have to asset that if U is conserved basically the system has its internal energy, given U, V, N this postulate to be satisfied that it describes the system or it describes the systematic equilibrium condition so the major question in this thing we can address very well is the postulate 3, that means the extensity of the entropy function S, so let us first start with that.

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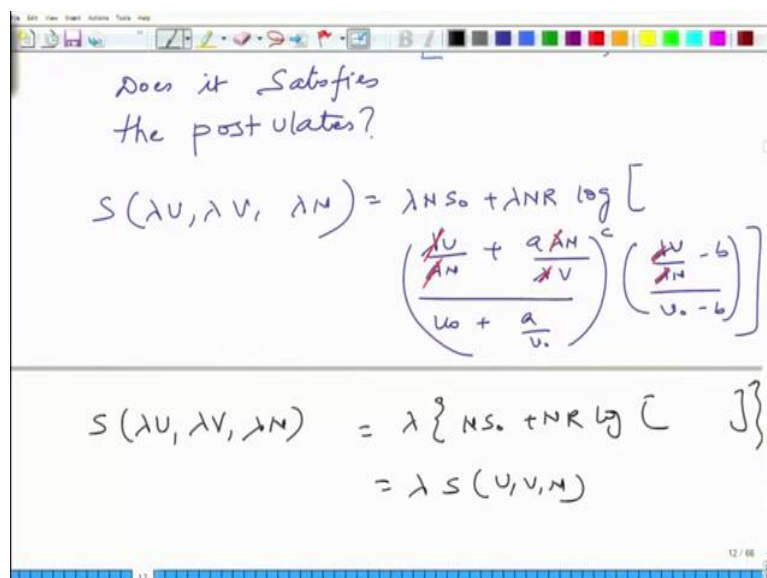


$$S(\lambda U, \lambda V, \lambda N_1, \dots, \lambda N_r) = \lambda S(U, V, N_1, \dots, N_r)$$

$$= \lambda N S_0 + \lambda N R \log \left[ \left( \frac{\lambda U + a\lambda N/\lambda V}{u_0 + a/v_0} \right)^c \left( \frac{\lambda U - b}{v_0 - b} \right) \right] \lambda$$

So naturally this gets cancelled all of this, okay?

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So that prove the first part of postulate 3, the extensity of the function S is the homogeneous of the first order. The second is this that the function is continuous and it should be greater than 0.

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$$S(\lambda U, \lambda V, \lambda N) = \lambda \{ NS_0 + NR \} [ ]$$
$$= \lambda S(U, V, N)$$
$$\left( \frac{\partial S}{\partial U} \right)_{V,N} = \frac{cR}{\frac{U}{N} + \frac{aN}{V}} \quad cR > 0, a > 0$$

$$\left( \frac{\partial S}{\partial U} \right)_{V,N} = \frac{cR}{\frac{U}{N} + \frac{aN}{V}}$$

Now what is being given first that this variable as  $U$ ,  $a$ ,  $V$ ,  $N$  these are all positive values and constant so this  $c$  of  $R$  is greater than 0 and  $a$  is greater than 0 and thus this is essentially going to be continuous function, okay?

It tells you that it exists at each point, it has definite value at each point and it satisfies the second postulate, okay? Now we cannot make use of that we can find out whether this is maximum, so we cannot talk about whether the  $S$  is maximum for the given condition here, okay.

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Handwritten notes on a whiteboard:

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{cR}{\frac{U}{N} + \frac{aN}{V}} \quad CR > 0, a > 0$$

$$\lim_{S \rightarrow 0} \left(\frac{\partial U}{\partial S}\right)_{V,N} \rightarrow 0 \implies \frac{\frac{U}{N} + \frac{aN}{V}}{S} \rightarrow 0$$

$S \rightarrow -\infty$

But what we can find out is the postulate 5 where it says that  $\text{dell } U \text{ by } \text{dell } S, V \text{ by } N$  is 0 this is the condition where when your  $S$  would be also 0, so this your postulate 5. Okay? So let us look at postulate 5 here, okay?

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} \rightarrow 0; S \rightarrow 0$$

$$\frac{U}{N} + \frac{aN}{V} \rightarrow 0; S \rightarrow -\infty$$

So which means that this particular relation violates postulate 5 and that means that this particular relation is not valid for extremely low temperature in some sense or it has very limited range or validity, okay?

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Example van der Waals postulated the  
follows rel. of a system

$$S = N S_0 + NR \log \left[ \left( \frac{U/N + aN/V}{u_0 + \frac{a}{v_0}} \right)^c \left( \frac{V/N - b}{v_0 - b} \right) \right]$$

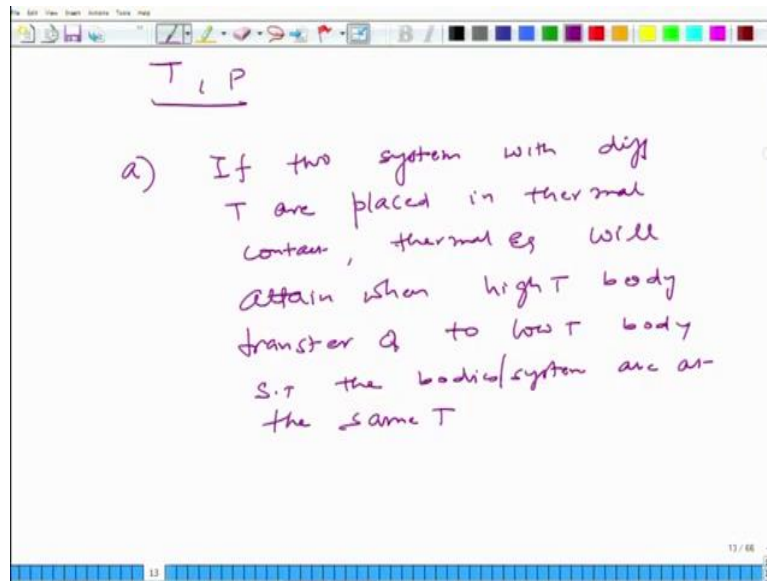
Does it Satisfies  
the postulates?

$$S(\lambda U, \lambda V, \lambda N) = \lambda N S_0 + \lambda NR \log \left[ \left( \frac{\lambda U}{\lambda N} + \frac{a \lambda N}{\lambda V} \right)^c \left( \frac{\lambda V - b}{\lambda N - b} \right) \right]$$

So this is something very you know philosophically way of solving problems where we are being given the relation in terms of Should, you can also consider in terms of relation U and so show the same set of you can undergo the same set of exercise where you try to prove that whether this holds other all the postulates valid for given relation. Okay?

Now this was just to give you glimpse of what can be done when we are using a generic kind of expressions, we will come back to this again, we will make use of this particular equation later but let us first ask ourselves, because we have talked about temperature and the pressure but this postulate does not define this important thermodynamic quantities temperature and pressure.

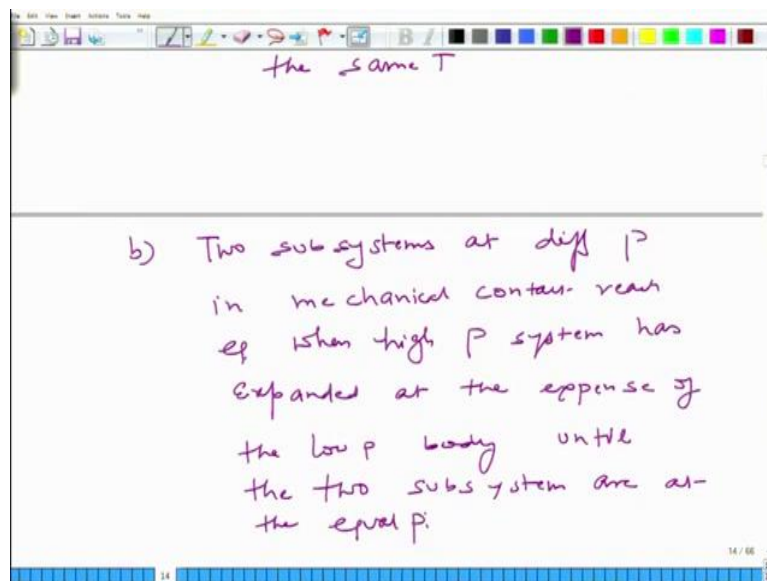
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So, let us now talk about temperature and pressure, okay? Now based on our observation about temperature and pressure we can show that two important intuitive predictions that if two system with different  $T$  are placed in thermal contact then thermal equilibrium will attain when there is heat transfer from high temperature body transfer heat to low temperature body, okay.

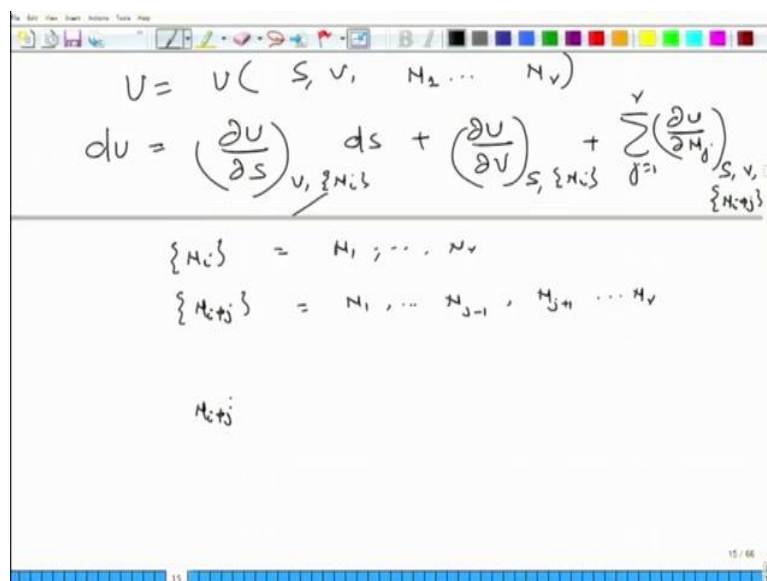
Such that the bodies final what is the system are finally at the same temperature, so we are trying to emphasize this base on the definition actually in the principle with postulates, but this are very two important intuitive predictions and later we are going to show that this what we are talking about something can be proven, a proven from the base of the postulates. Okay? So this is for the case of the temperature and we can also use the similar intuitions for the pressure.

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So for the pressure we say that the two sub system at different pressure in mechanical contact reach equilibrium when high-pressure system expands at the expense of the low-pressure body, okay. So, the high pressure basically will be compressing the low-pressure body and this will happen until the two system are at the same pressure, okay? So this is based on the pressure which we have intuitions of that. Now let us tie and look at again how to make use of our fundamental relations which we have evaluated from the postulates, so we will start with the internal energy.

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So, let us assume all I start with the fundamental energy relation, U S, V, N1 till Nr where I is the number of species in the system, S is entropy, V is total volume, now we make use of the

differential expression here. So we can write this as dU and this will be your dell U by dell S at constant V and all the moles at constant or i kept at constant value, so this is going to be dS similarly we can do that for dV and then for all the different components S, V, and this Ni and j not equal to Ni where j is over 1 to r okay?

So, this essentially means Ni stands for N1 till Nr and here stands for this is N1 and j minus 1, Nj plus 1 and Nr, okay? So let me correct this, this has to be, so this should be Nj because we are using j in this so j is equal to 1 to r and this should have been Ni not equal to j. So we have now a differential expression okay? Now based on our experience we know that if there is a change in a temperature there will be heat transfer, okay? If there is a change in the pressure or there is a pressure great then there is going to be a volume change, if the boundaries can move. So this is something, which we know from experience. Okay.

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

$$du = \left( \frac{\partial U}{\partial S} \right)_{V, \{N_i\}} dS + \left( \frac{\partial U}{\partial V} \right)_{S, \{N_i\}} dV + \sum_{i=1}^r \left( \frac{\partial U}{\partial N_i} \right)_{S, V, \{N_j\}} dN_i$$

$$\{N_i\} = N_1, \dots, N_r$$

$$\{N_{i+j}\} = N_1, \dots, N_{i-1}, N_{i+j}, \dots, N_r$$

0 rev. work done on a syst -pdv  
 0 heat transfer are driven by  $\Delta T$

So the first term here corresponds to the temperature that is something that we are going to emphasize, okay. And the second term here is something, which can be related to the work because we know the following that reversible work done on a system for the boundary work is pdv okay? that is something which we know, we have intuitions that heat transfer are driven by delta T and third thing is something which suggest that this part is suggest that there is a property that should drive the mole transfer to the system, okay?

The mole transfer of the number of species or species mole transfer to the system okay? So the first term is something which we can relate to the temperature, second term can be related



to the pressure, third term is something which we are going to relate to something we are going to say as chemical potential. Okay?

(Refer Slide Time: 15:40)

The image shows two screenshots of a digital whiteboard. The top screenshot (slide 14) contains the following text and equations:

0 heat transfer one direction only

Define:

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

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


---


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

The bottom screenshot (slide 15) contains the following text and equations:

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


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

$\mu_j \equiv$  electrochemical or chemical potential of species  $j$

So, based on basic observation we are going to define the following,

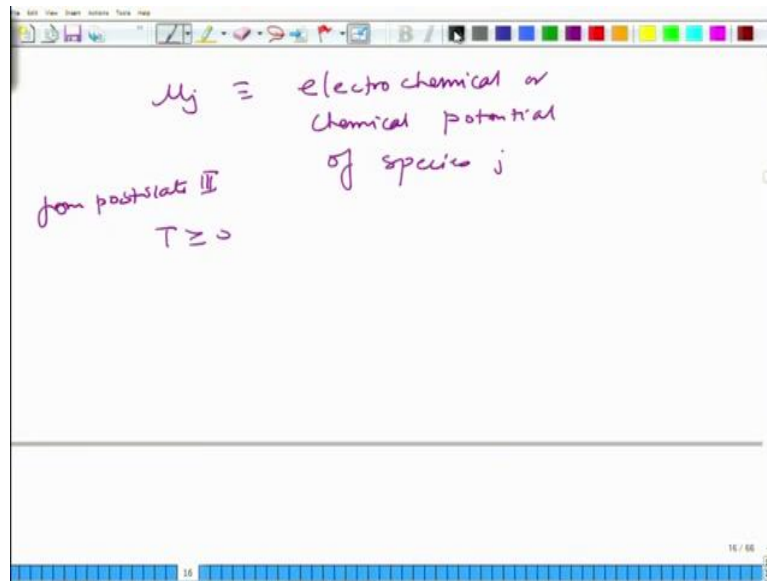
$$\frac{\partial U}{\partial S_{V, N_i}} = T$$

$$-\frac{\partial U}{\partial V_{S, N_i}} = P$$

$$\frac{\partial U}{\partial N_j_{V, S, N_i \neq j}} = \mu_j$$

we will define this point,  $dU$  by  $dS$ ,  $V$   $N$  is nothing but temperature,  $dU$  by  $dV$  with negative sign,  $S$   $N_i$  as pressure okay? and  $dU$  by  $dN_j$  keeping  $S$ ,  $V$  and all of the  $N_i$  not equal to  $j$  as chemical potential, so the  $\mu$  here is going to be electrochemical or chemical potential or species  $j$  okay?

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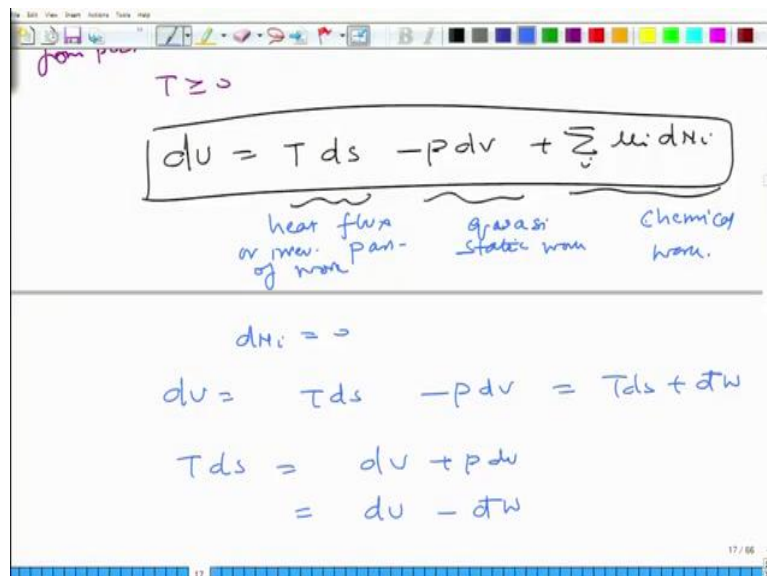
Handwritten text on a whiteboard:

$\mu_j \equiv$  electrochemical or  
chemical potential  
of species  $j$

from postulate III  
 $T \geq 0$

So with postulate 3, this is  $T$  so essentially says that  $T$  should be greater than or equal to 0, okay? So we will try to show that this definition, which we are trying to mention here, is fixed to our intuitive understanding of temperature, pressure and basically the mole transfer, okay? So something which we are going to show later.

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Handwritten text on a whiteboard:

from postulate III  
 $T \geq 0$

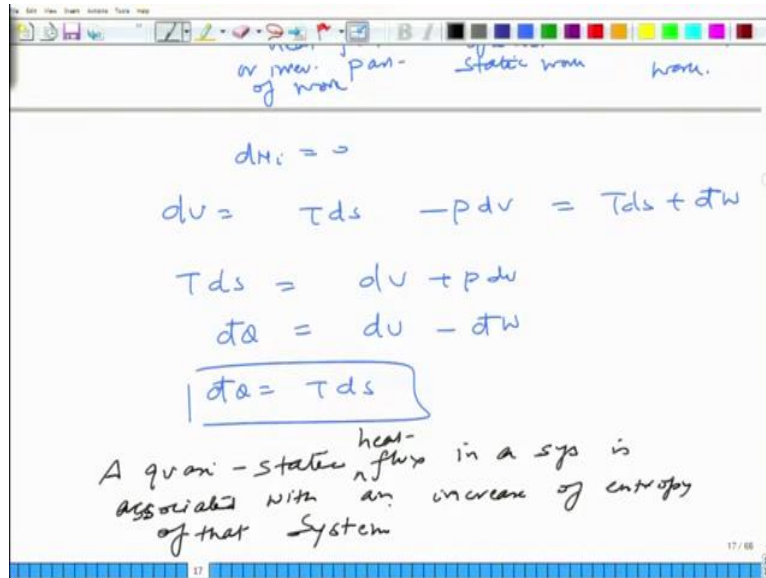
$$dU = T ds - p dv + \sum_i \mu_i dn_i$$

heat flux or mech. part of work      quasi-static work      chemical work.

$dn_i = 0$

$$dU = T ds - p dv = T ds + \delta W$$

$$T ds = dU + p dv = dU - \delta W$$



So let me now write the expression of internal energy in differential form based on this definition of temperature, pressure and chemical potential, so this can be now written as:

$$dU = Tds - PdV + \sum_i \mu_i dN_i$$

Now this is something which you can remember is a straight forward expression and something which should automatically come to your mind that if somebody wants to write down the expression of the first law in the open system then this is something which comes to that.

So we will talk about the open system and close system later on little bit more, but this is the expression of internal energy where the first term talks about heat flux or basically the irreversible part of the work and second part is basically the quasi-static work and third part is nothing but a chemical work, okay? Now if you consider a constant N then essentially your  $dN_1$  or  $dN_i$  is going to be 0 and I can write,

$$dU = Tds - PdV$$

which is essentially for pure system.

$$dQ = dU - dW$$

$$dQ = TdS$$

This tells you very simple statement here that if you increase the heat or if your heat fluxes supplied to the system it is as the entropy of the system. So that is what you can conclude

from the exercise that a quasi-static flux of quasi-static heat flux in a system is associated with an increase of entropy of that system.

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from postulate II of species  $j$

$T \geq 0$

$$dU = T ds - p dv + \sum_i \mu_i dN_i$$

heat flux or mech. pan. of work      quasi-static work      chemical work.

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$dN_i = 0$

$$dU = T ds - p dv = T ds + dW$$
$$T ds = dU + p dv$$
$$T ds = dU - dW$$

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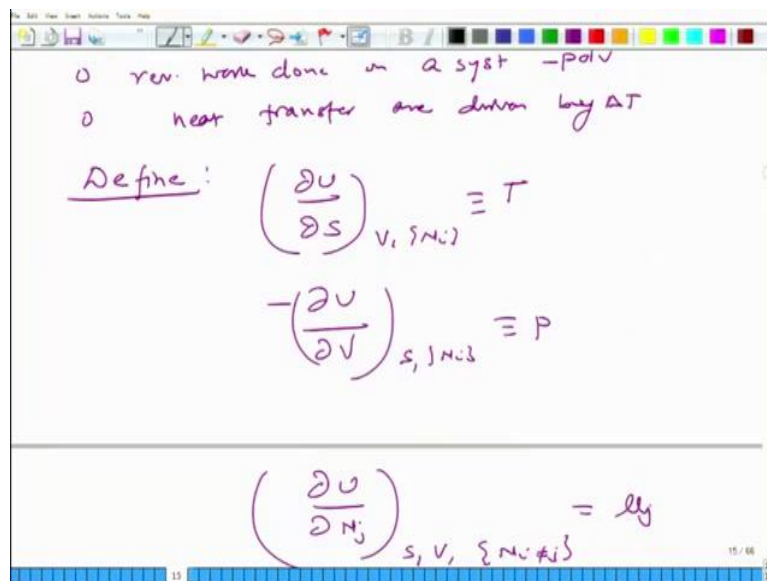
A quasi-static process in a system is associated with an increase of entropy of that system

$$\sum_i \mu_i dN_i \equiv \text{quasi-static chemical work}$$

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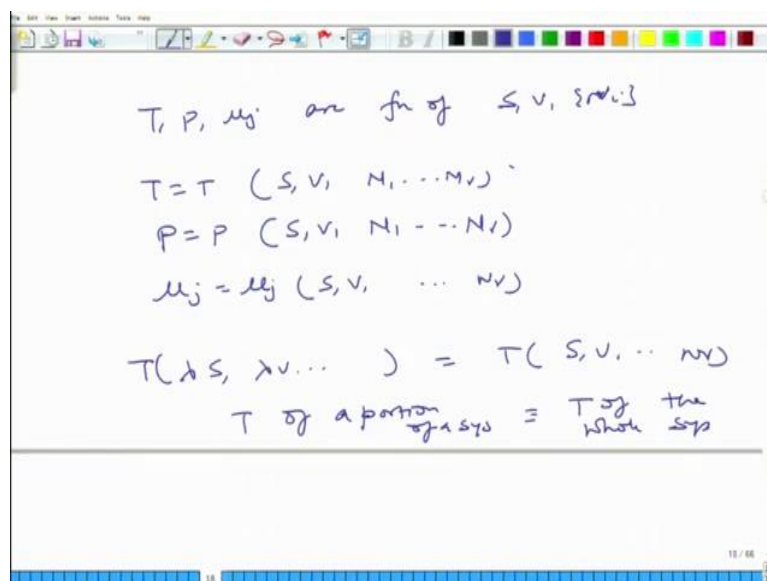
now having say that lets focus on the last term here, the last term tells you that internal energy can be increased by changing the moles of the system or matter of the system. So, that is why sometime we say that  $\sum_i \mu_i dN_i$  is nothing but quasi static chemical work.

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Now coming back to the again the definition T, the T,  $\mu$  these are the partial derivatives of U and U is the function of S, V, N and hence since, T is the partial derivative of this variables so essentially the T, P,  $\mu$  will be the function of S,V,N.

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So, in other words the T,P,  $\mu$  are function of S,V,N so we have functional relation, T as function of S,V,N, P is P, similarly I can write for  $\mu_j$ . so, note that this T are basically the TP are partial derivatives so essentially this are intensive variables. In other word

$$T(\lambda S, \lambda U, \dots) = T(S, V, \dots, N_r)$$

so it tells you that the T of a portion of a system is same is equal to the T of the whole system.

So, that means the T is basically not additive and for such system where the intensive variables are a function of the extensive variables we called it equation of states, so basically this what we have written here T is this is nothing but your thermal equation of state, this is a mechanical equation of state and this is a chemical equation of state. So this is basically a equation of state. Now we have derived this expression based on the energy fundamental relation, you can also make use of the entropy fundamental relation.

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$T$  of a portion of a sys  $\equiv$   $T$  of the whole sys  
 $S = S(U, V, N_1, \dots, N_i, \dots, N_j, \dots, N_k)$   
 $ds = \left(\frac{\partial S}{\partial U}\right)_{V, \{N_i\}} dU + \left(\frac{\partial S}{\partial V}\right)_{U, \{N_i\}} dV + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{U, V} dN_i$   
 $ds = \frac{1}{T} dU + \frac{P}{T} dV - \sum \frac{\mu_i}{T} dN_i$   
 Earlier exp of  $dU$

So, we can do the same exercise but with a starting point S and in that case you can write,

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

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



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$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V, \{N_i\}}$$

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

$$\frac{\mu_i}{T} = - \left( \frac{\partial S}{\partial N_i} \right)_{U, V, \{N_j \neq i\}}$$

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

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

Earlier exp of dU

Now if you compare this expression and this expression,

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V, \{N_i\}}$$

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

$$\frac{\mu_i}{T} = - \left( \frac{\partial S}{\partial N_i} \right)_{U, V, \{N_j \neq i\}}$$

So, now you have two relations, basically the one which we have defined and then we made use of the internal energy came up with the differential equation of U in terms of other

variables and the second is we can use the entropy relation and making use of the earlier definition you can come up with this expression where this are related to the derivative of S with respect to other extensive variables.

Now, I can end this particular lecture with a simple example and the example would be to derive the equation of state as we already stated that this definition of intensive variable as a function of extensive variable is nothing but equation of state and something which we can now exercise.

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Example  
 To derive Thermal & mechal EOS for the vdW entropy rel

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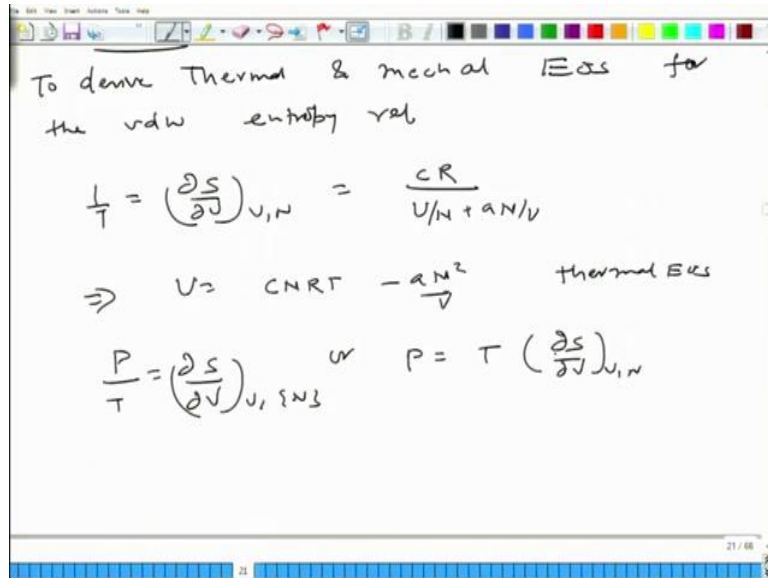
Example Vander waals postulated the follow rel. of a system

$$S = N S_0 + N R \log \left[ \left( \frac{U/N + aN/V}{u_0 + \frac{a}{V_0}} \right)^c \left( \frac{V/N - b}{v_0 - b} \right) \right]$$

Does it Satisfies the postulates?

$$S(\lambda U, \lambda V, \lambda N) = \lambda N S_0 + \lambda N R \log \left[ \left( \frac{\lambda U}{\lambda N} + \frac{a \lambda N}{\lambda V} \right)^c \left( \frac{\lambda V}{\lambda N} - b \right) \right]$$

10



So, let us consider the same expression of Vander Waal where S is related to the other variables and there making use of that entropy relation we need to find out thermal and mechanical equation of the state. So, to derive mechanical equation state for the Vander Waal entropy relation, so essentially if you go back notes and if you go back and check your notes you will see, so, this is our relation here.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{U,\{N_i\}} = \frac{cR}{\frac{U}{N} + aN/V}$$

If you solve then you can come up with this expression and this is nothing but thermal equational state.

$$U = CNRT - \frac{aN^2}{V}$$

Similarly, you can do you can make the use of the expression

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

$$P = \frac{RT}{\frac{V}{N} - b} - \frac{aN^2}{V^2}$$

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Handwritten derivation on a whiteboard:

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

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


---


$$\Rightarrow P = \frac{RT}{V/N - b} - \frac{a(N^2/R)}{V^2} \quad \frac{T}{V/N + aN/V}$$

$$\boxed{P = \frac{RT}{V/N - b} - \frac{aN^2}{V^2}} \quad \text{VdW Eqn}$$

$$\boxed{\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U, V}}$$

Handwritten derivation on a whiteboard:

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V, \{N_i\}}$$

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

$$\cdot \frac{\mu_i}{T} = - \left( \frac{\partial S}{\partial N_i} \right)_{U, V, \{N_j \neq i\}}$$

This is nothing but the Vander Waal equational state which is well known, so this is nothing but Vander Waal equational state. So, similarly you can also come up with the expression of the chemical potential, okay? So, I am not going to derive that but you have entropy relation and you can take the derivative and you can find it out.

So, this expression directly comes from our definition based on entropy relation which we come. So, I hope that you got the idea behind how to come up with this relation and then we will now use this information, this understanding in the next lecture to derive thermal equilibrium conditions, mechanical equilibrium conditions, conditions for chemical equilibrium. So, with that I will stop and hope to see you in the next lecture.

