Thermodynamics (Classical) for Biological Systems

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Module No. # 02
Additional Thermodynamic Functions
Lecture No. # 08
Maximum Work, Lost Work; Review of Closed Systems

In this class, let us begin by considering maximum work as well as lost work. When we are considering a process, we would like to know, what is the maximum amount of work that can be expected from that process, for various reasons. It could be for designing the process or it could be for … may be evaluating the claims made by others toward the maximum work that is possible from a particular process. In the same vein, we would also like to know the amount of work that is lost. In other words, in comparison to the maximum work or the ideal work, what is the actual work that you are getting out of the system and in the process how much work is being lost compared to the maximum of work.

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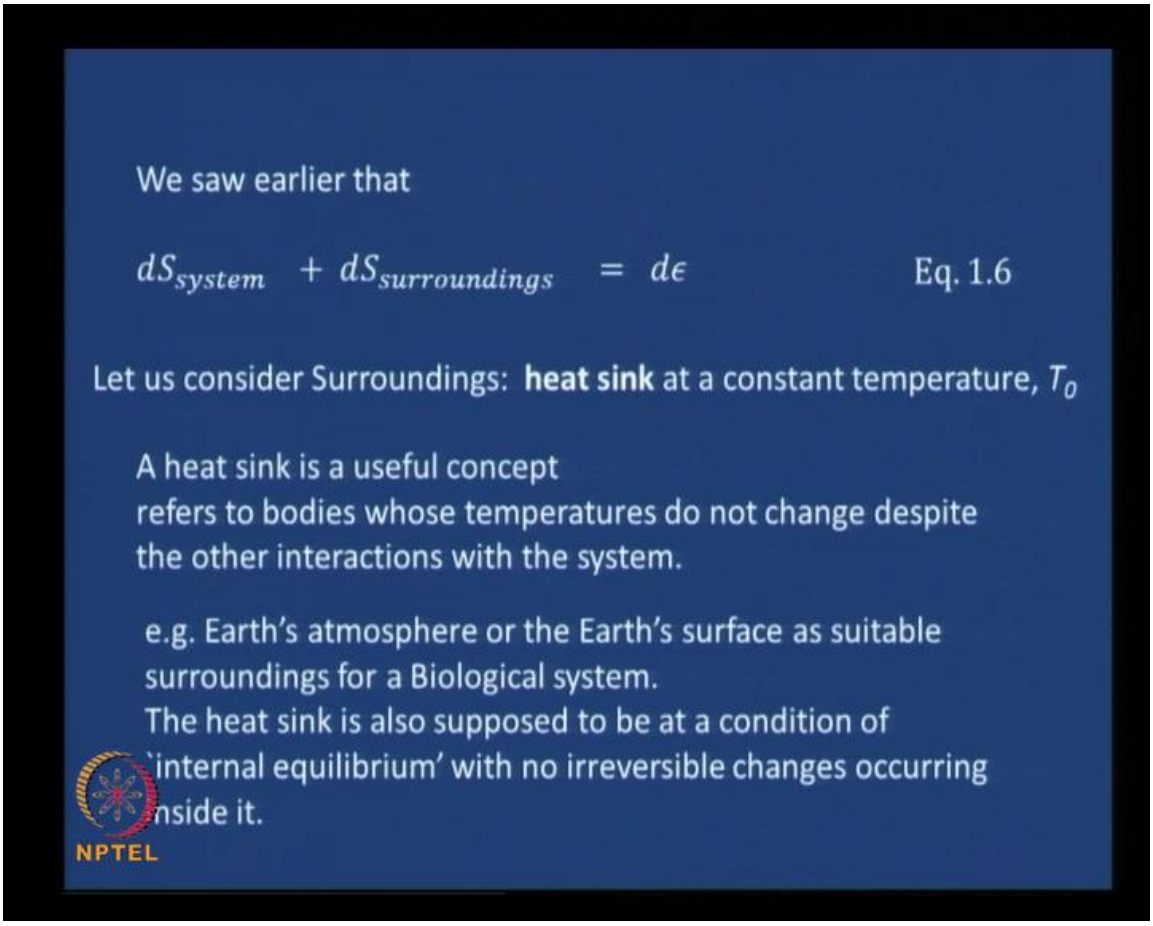

We saw earlier that

$$dS_{system} + dS_{surroundings} = d\epsilon \qquad \text{Eq. 1.6}$$

Let us consider Surroundings: **heat sink** at a constant temperature, T_0

A heat sink is a useful concept
refers to bodies whose temperatures do not change despite
the other interactions with the system.

e.g. Earth's atmosphere or the Earth's surface as suitable
surroundings for a Biological system.
The heat sink is also supposed to be at a condition of
'internal equilibrium' with no irreversible changes occurring
inside it.

To do that, let us start here. We have already seen that the change in entropy of the system plus the change in entropy of the surroundings is a positive quantity – let us call that d epsilon – way back into equation 1.6. We also said that the entropy of the universe can only increase – that was one of the statements of the second law. Now let us consider these surroundings as a heat sink, as it is called, at a constant temperature T 0. This heat sink is a very useful concept; it actually refers to the bodies whose temperatures do not change despite the interactions with the systems that they are in contact with. For example, there are many things that can be considered as sinks or approximated as sinks; some of them are given here. We can consider the earth's atmosphere as a sink … it remains at a constant temperature for a certain period of time. Or, the earth's surface could also be considered as a suitable sink especially for biological systems of relevance.

Let me also state this; it may not be completely clear right now, but it will become clear may be after the fifth module or so. The heat sink is also supposed to be in a condition of internal equilibrium with no irreversible changes occurring inside it. This needs to be stated as one of the conditions of the heat sink. Let me state it again and leave it at that, and let us wait till the fifth chapter or fifth module to make a little better sense of it: The heat sink is supposed to be at a condition of internal equilibrium with no irreversible changes occurring inside it.

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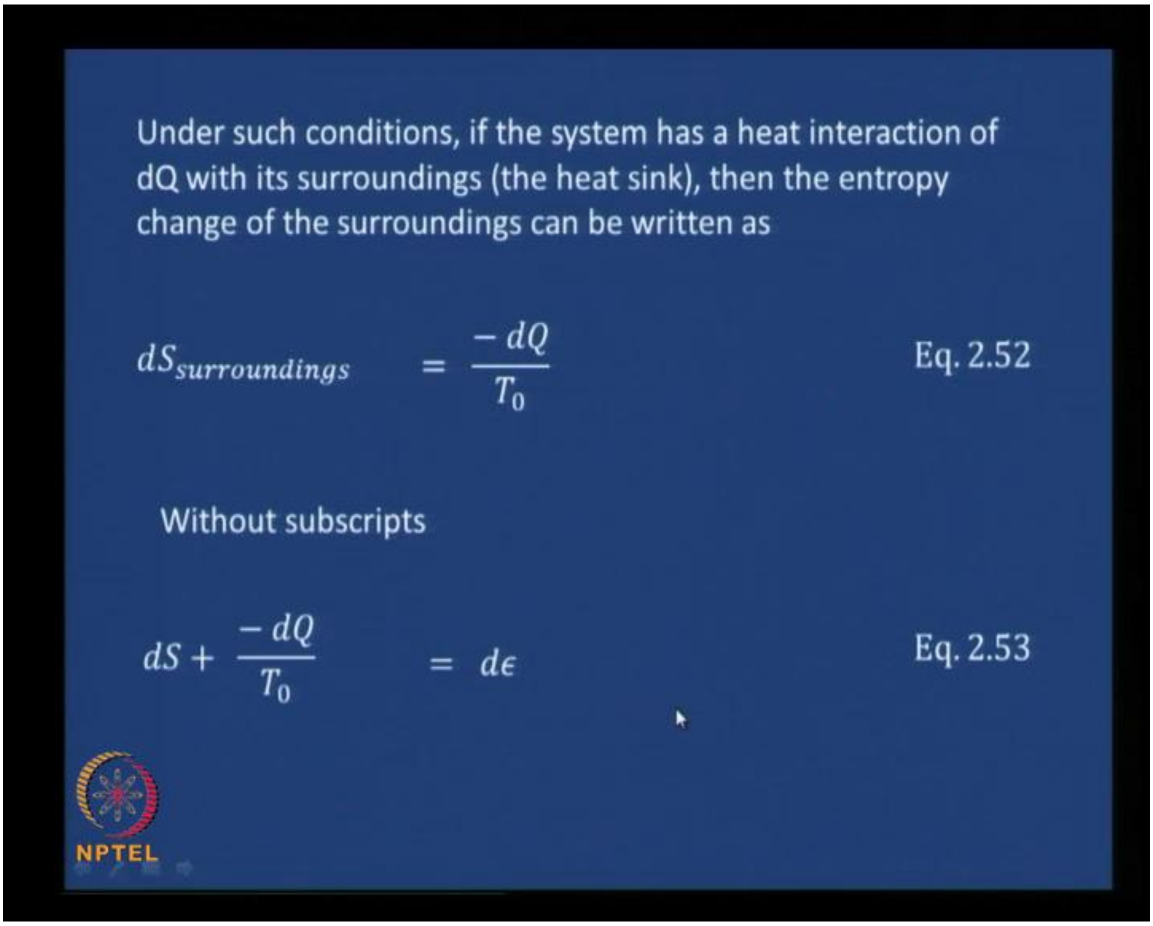

Under such conditions, if the system has a heat interaction of dQ with its surroundings (the heat sink), then the entropy change of the surroundings can be written as

$$dS_{surroundings} = \frac{-dQ}{T_0} \qquad \text{Eq. 2.52}$$

Without subscripts

$$dS + \frac{-dQ}{T_0} = d\epsilon \qquad \text{Eq. 2.53}$$

Under such conditions, if the system … has a heat interaction of dQ, a differential Q, with its surroundings, which is the heat sink in this case. The entropy change or the surroundings can be written as – remember the second law that we looked at earlier, dS of the surroundings is nothing but minus dQ by T 0; minus because of the convention, the direction with which this negative is associated. Remember we are writing this for the surroundings; so, minus dQ by T 0. Let us call this equation 2.52. Since we have already identified dS surroundings as minus d q by T 0, we will drop the subscripts now just for convenience and d S will, as usual, correspond to the system. d S system plus d S surroundings, which is being replaced by minus d q by T 0 … is the same d epsilon; d S minus d q by T 0 equals d epsilon. Let us call this equation 2.53.

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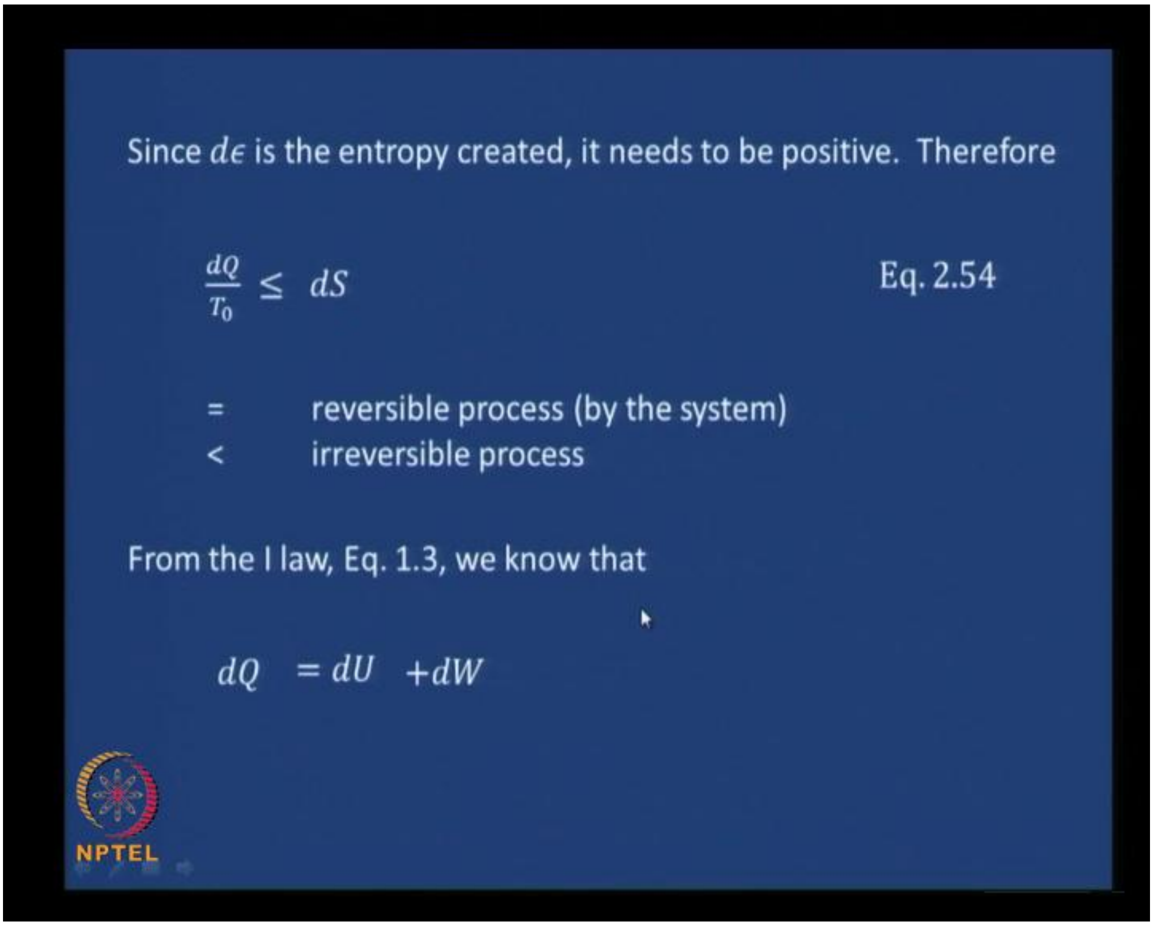

Since $d\epsilon$ is the entropy created, it needs to be positive. Therefore

$$\frac{dQ}{T_0} \leq dS \qquad \text{Eq. 2.54}$$

= reversible process (by the system)

< irreversible process

From the I law, Eq. 1.3, we know that

$$dQ = dU + dW$$

.

Remember, the d epsilon is the entropy that is created and according to the second law, expanding universe and so on, it definitely needs to be positive. Therefore, the d q by T 0 needs to be either less than or equal to d S. This directly follows from this equation … we are comparing this and this, this needs to be less than or equal to d S for this to be positive. We will call this equation 2.54. These are all very generic coming right from the second law. And this equals dS for a reversible process that is undergone by the system; and is less than dS for an irreversible process.

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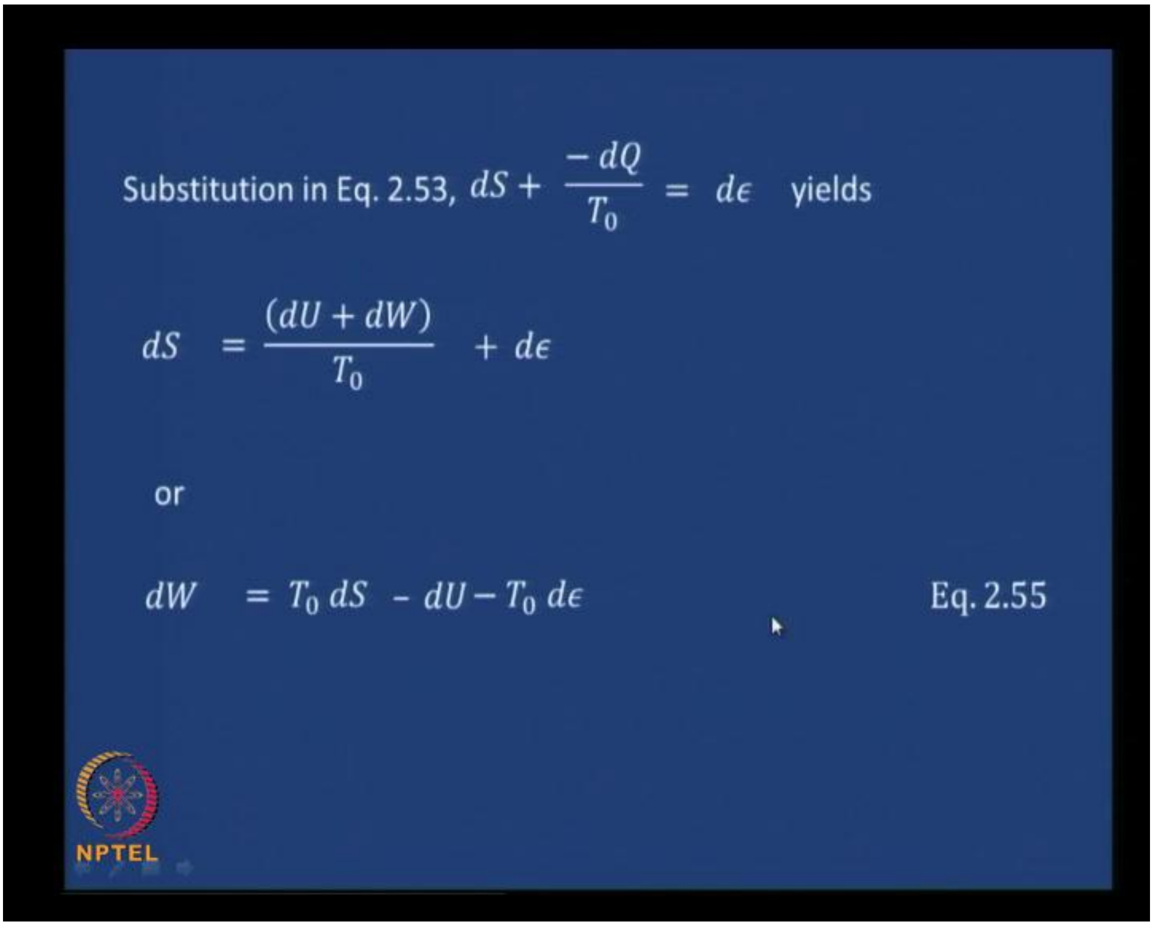

Substitution in Eq. 2.53, $dS + \frac{-dQ}{T_0} = d\epsilon$ yields

$$dS = \frac{(dU + dW)}{T_0} + d\epsilon$$

or

$$dW = T_0\,dS - dU - T_0\,d\epsilon \qquad \text{Eq. 2.55}$$

Now, let us look at the first law – some very basics again. Equation 1.3: we know that dQ – this is for a closed system – dQ equals dU plus dW. If we substitute the first law … excuse me … first law of thermodynamics in this equation 2.53, dS plus minus of dQ by T 0 equals d epsilon, we are in fact going to substitute for dQ we will get d S plus dQ being replaced by dU plus dW by T 0 plus d epsilon. We have transposed the equation; therefore, the negative sign goes away there; or if we multiply throughout by T 0 and then transpose the equation, we will get T 0 d S equals d U plus d w plus T 0 d epsilon and then grouping the terms appropriately, we can write d W equals T 0 d S minus d U minus T 0 d epsilon. We will call this equation 2.55.

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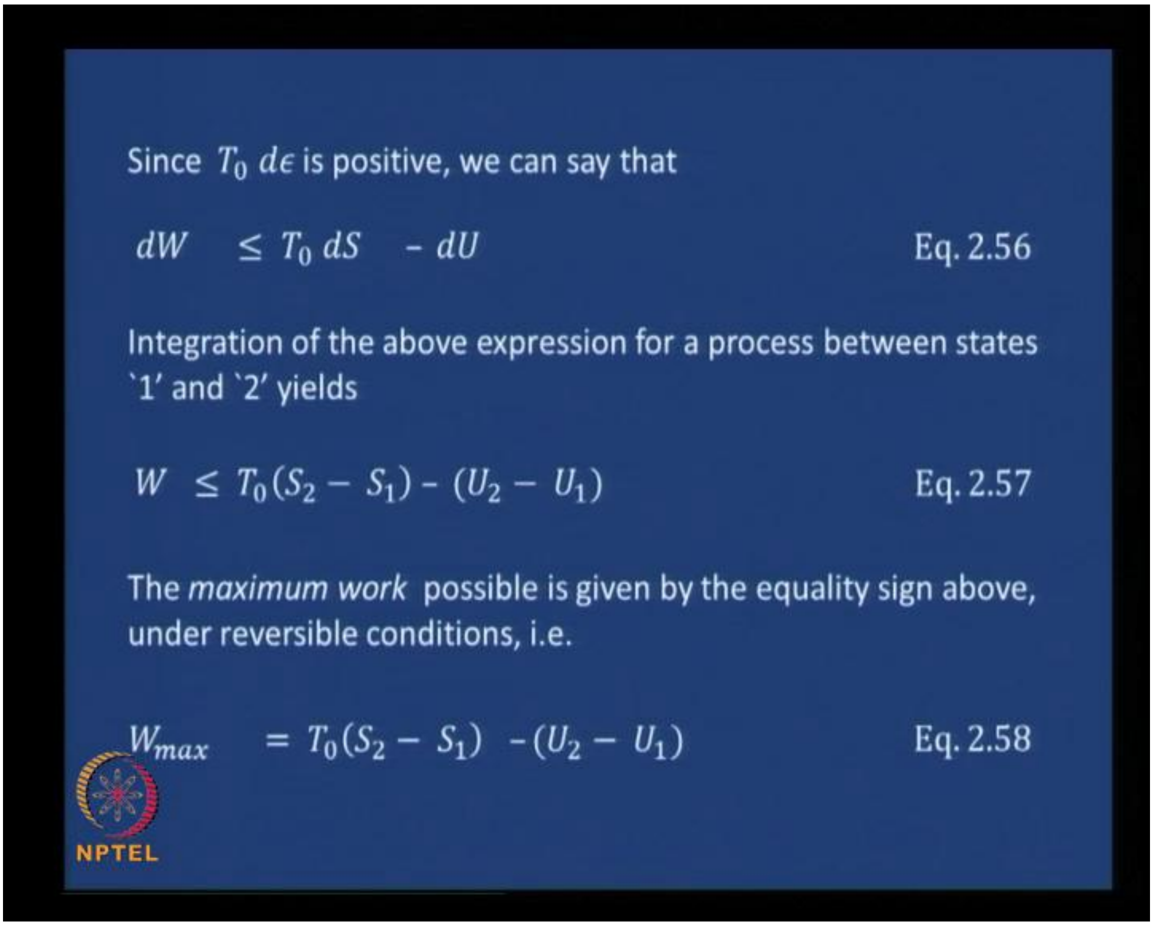

Since $T_0\, d\epsilon$ is positive, we can say that

$$dW \quad \leq T_0\, dS \quad - dU \qquad \text{Eq. 2.56}$$

Integration of the above expression for a process between states `1′ and `2′ yields

$$W \leq T_0(S_2 - S_1) - (U_2 - U_1) \qquad \text{Eq. 2.57}$$

The *maximum work* possible is given by the equality sign above, under reversible conditions, i.e.

$$W_{max} \quad = T_0(S_2 - S_1) \ -(U_2 - U_1) \qquad \text{Eq. 2.58}$$

Now note that d epsilon is positive, T 0 is of course, the temperature that needs to be positive in Kelvin. Therefore, the product of those two terms T 0 d epsilon is positive, and thus d W needs to be less than T 0 d S. Now from here; this needs to be positive and d W needs to be less than or equal to T 0 d S minus d U; d U we do not really know what is happening here. We will call that equation 2.56. Now, if we integrate this expression, let us say between the states of 1 and 2. It’s a straightforward integration: integral d W is W. This remains … this inequality remains less than or equal to T 0 d S between … integrated between 1 and 2 gives you S 2 minus S 1 minus d U integrated between 1 and 2 gives you U 2 minus U 1, we will call that equation 2.57.

Now, note this equation. This is some quantity, and this is some quantity. And the maximum work possible since W is less than this, the right hand side … less than or equal to the right hand side, the maximum work that is possible is when W equals the right hand side. And therefore, the maximum work possible which happens to be under reversible conditions, if indicated by W max can be written as T 0 S 2 minus S 1 minus U 2 minus U 1. Therefore, we have a measure of the maximum work that is available from a process in terms of it is the state variables of the system T 0 … T 0 is of course, the temperature of the surroundings S 2, S 1, U 2, U 1 – all correspond to the state variables of the system. Let us call that equation 2.58.

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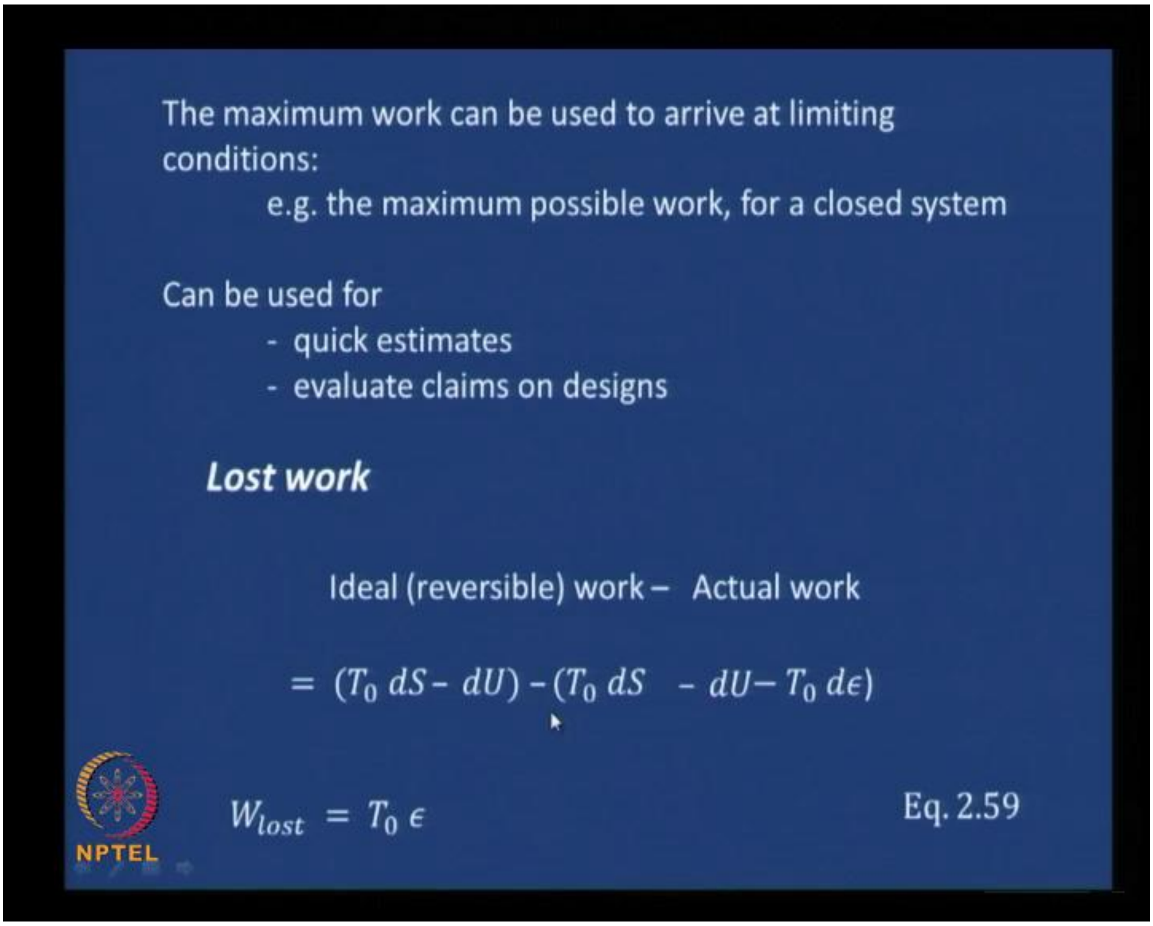

The maximum work can be used to arrive at limiting conditions:

e.g. the maximum possible work, for a closed system

Can be used for

- quick estimates
- evaluate claims on designs

Lost work

Ideal (reversible) work – Actual work

$$= (T_0\, dS - dU) - (T_0\, dS - dU - T_0\, d\epsilon)$$

$$W_{lost} = T_0\, \epsilon$$

Eq. 2.59

We started out by saying this; let me complete this part by reemphasizing this: the maximum work can be used to arrive at limiting conditions. For example, the maximum possible work for a closed system, which can in turn be used for quick estimates, to evaluate claims on design as well as to begin with the design itself. The lost work, as we said, is a difference between the maximum work and the actual work therefore, the ideal or the reversible work minus the actual work; the reversible work, we have an expression here T 0 d S minus d U that we got from earlier. The actual work happens to be T 0 d S minus d U minus T 0 d epsilon. Therefore, these two terms cancel, these two terms cancel we have an expression for the lost work as T 0 times epsilon. This is integrated; after integration we get work lost equals T 0 times epsilon in terms of the sink temperature the surroundings temperature assumed to be constant times the entropy that is created. We will call this equation 2.59.

At this juncture, … we have looked at many different things so far in this module and therefore, it will be good to review whatever we have seen so far especially, thermodynamics lots of relationships, lots of seeming confusions. Actually, there is not much if you look at it another time, things would be a lot clearer. We will do that, before we get on to open systems.

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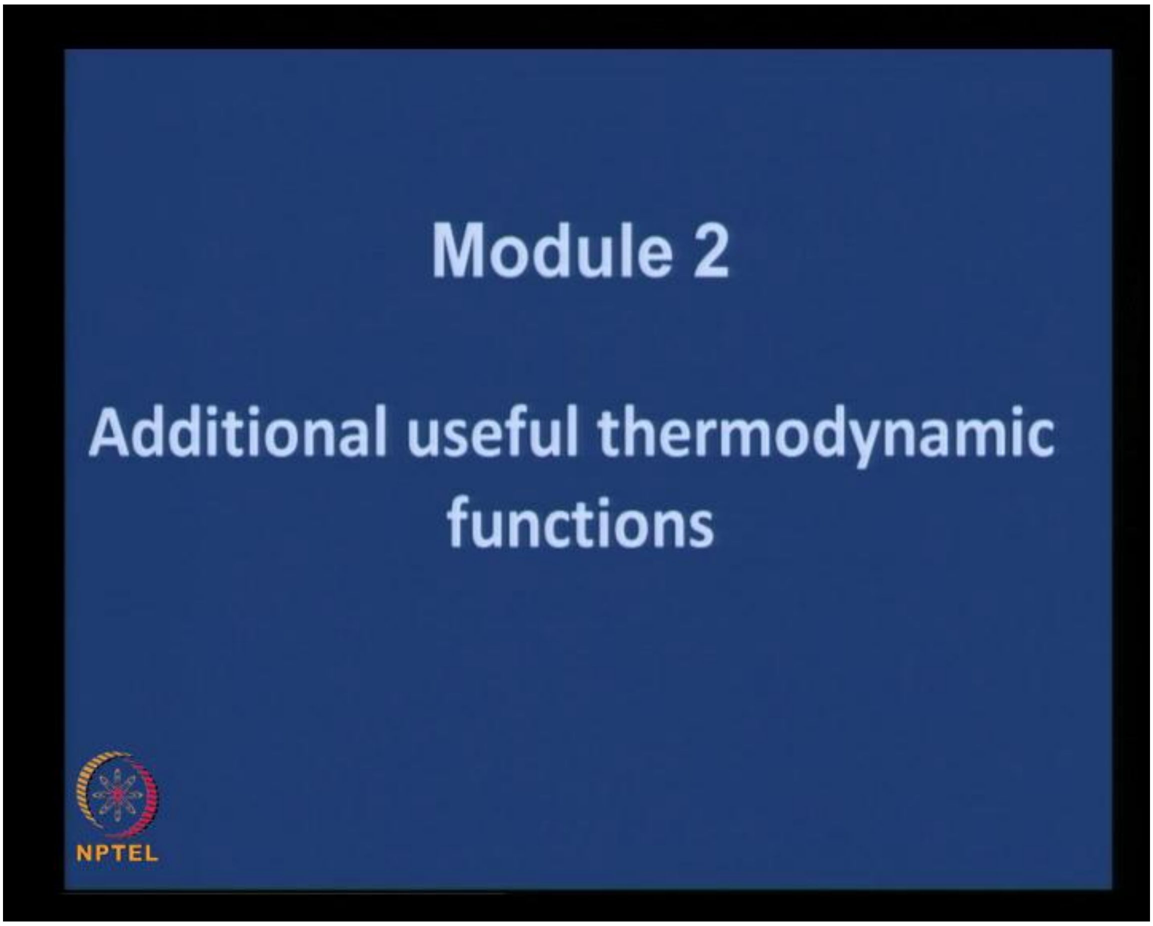

Module 2

Additional useful thermodynamic functions

So, let us start some sort of a review before we go on to the open systems. We began this module to look at additional useful thermodynamic functions. We said that the internal energy U, the entropy S are … along with P, V, T are typically good enough thermodynamic functions. And in certain cases, we said that certain functions would turn out to be more useful.

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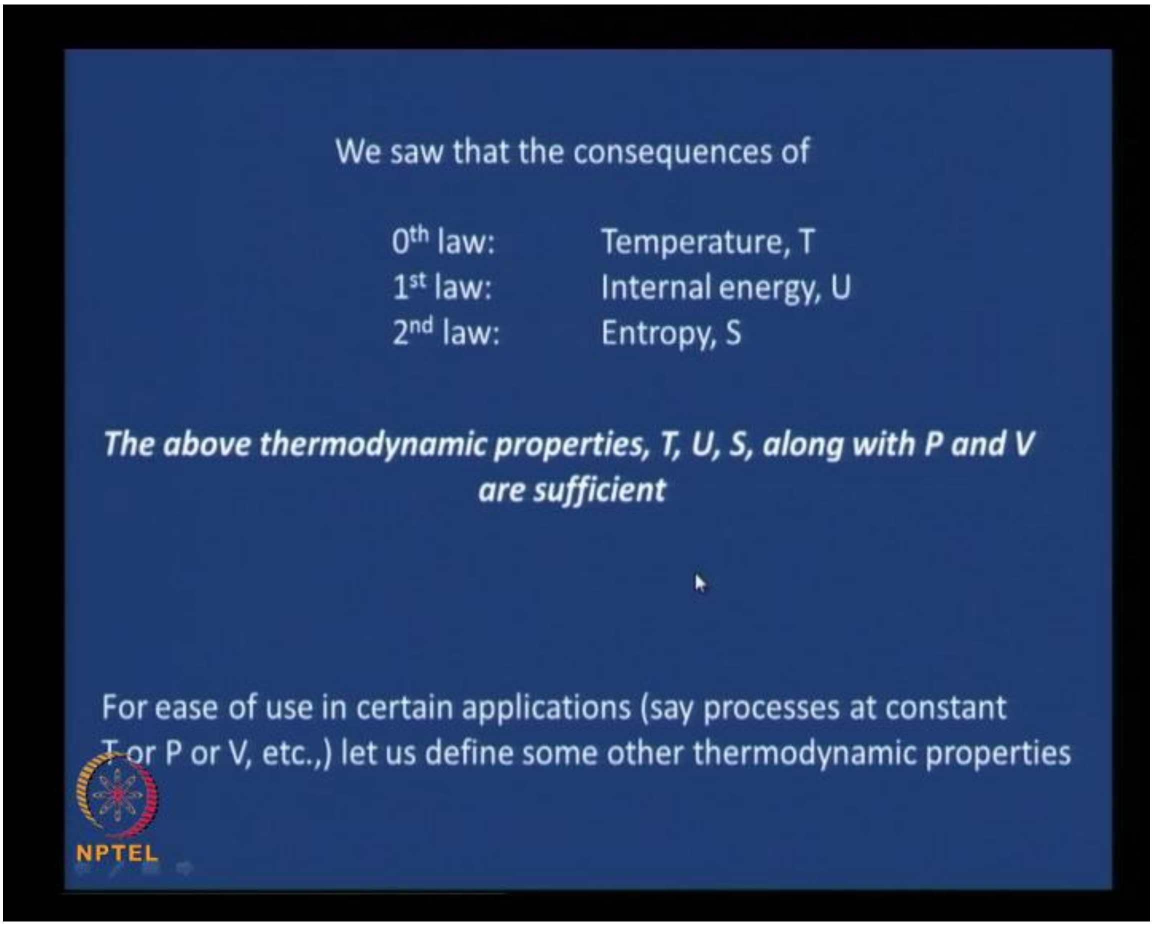

We saw that the consequences of

0th law: Temperature, T
1st law: Internal energy, U
2nd law: Entropy, S

The above thermodynamic properties, T, U, S, along with P and V are sufficient

For ease of use in certain applications (say processes at constant T or P or V, etc.,) let us define some other thermodynamic properties

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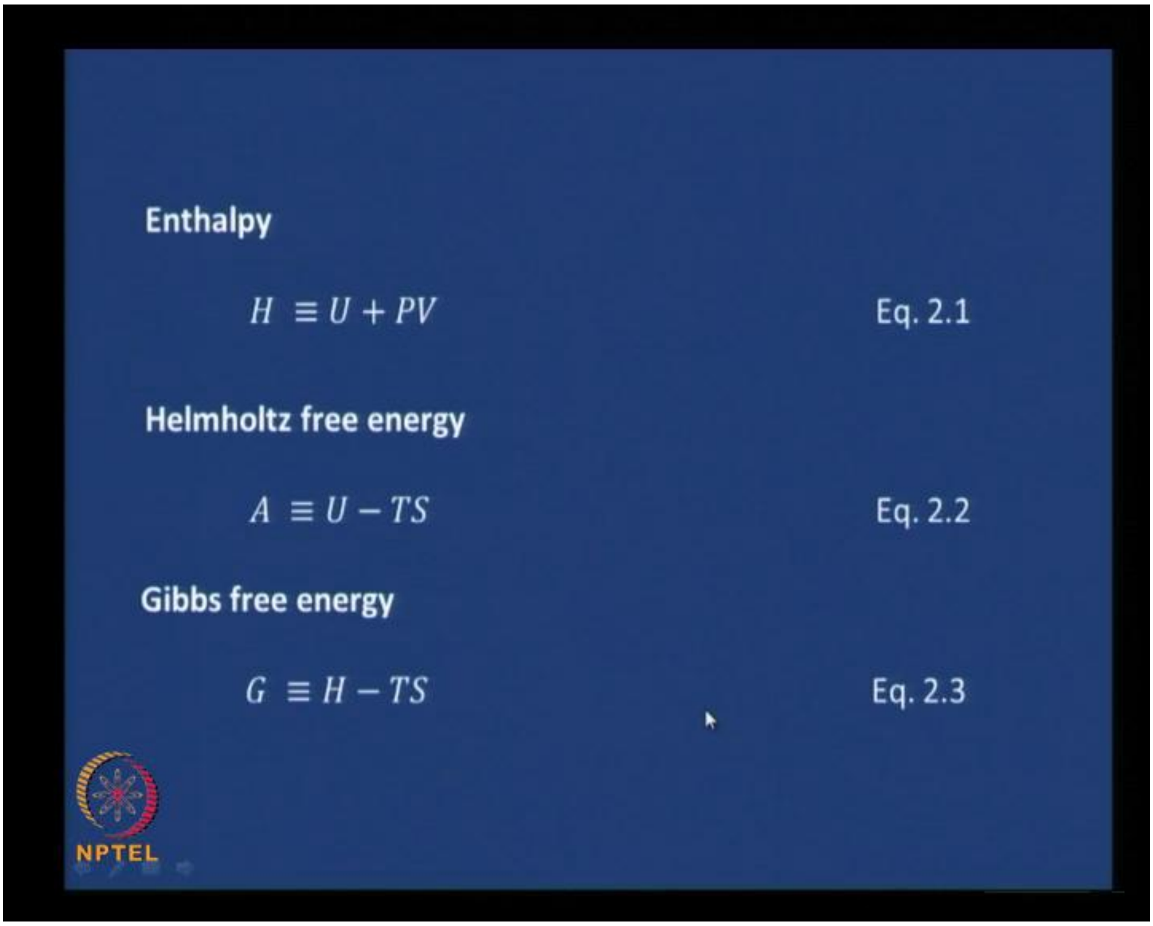

Enthalpy

$$H \equiv U + PV \qquad \text{Eq. 2.1}$$

Helmholtz free energy

$$A \equiv U - TS \qquad \text{Eq. 2.2}$$

Gibbs free energy

$$G \equiv H - TS \qquad \text{Eq. 2.3}$$

And we went ahead and defined them the first one was enthalpy which was defined as internal energy plus the product of P and V. The next was the Helmholtz free energy which we will use to a certain extent in this course but in general it is useful. Helmholtz free energy indicated as A is the difference between internal energy and the product of temperature and entropy. And Gibbs free energy, which is G, which is the difference between enthalpy given here and the product of temperature and entropy. These were the three additional functions that we defined.

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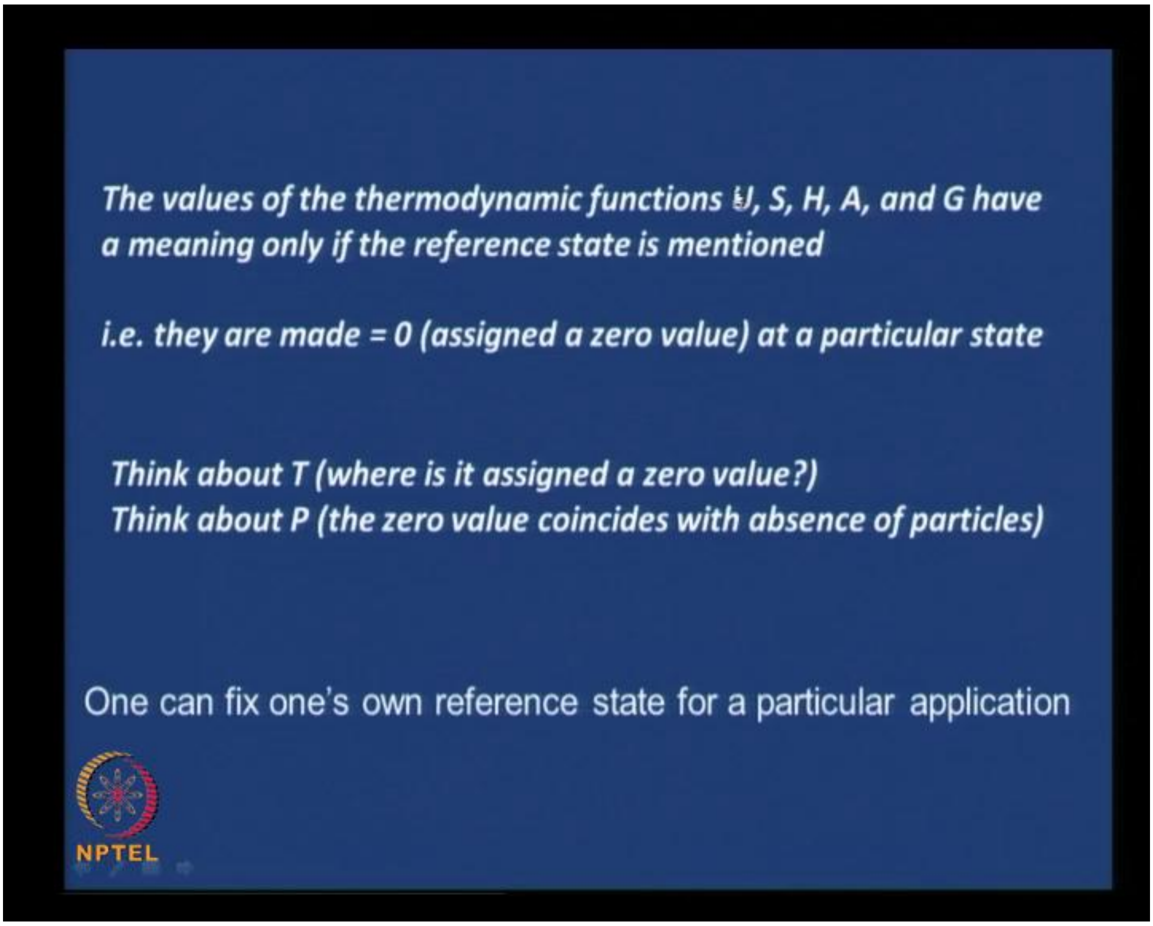

The values of the thermodynamic functions U, S, H, A, and G have a meaning only if the reference state is mentioned

i.e. they are made = 0 (assigned a zero value) at a particular state

Think about T (where is it assigned a zero value?)
Think about P (the zero value coincides with absence of particles)

One can fix one's own reference state for a particular application

And then we said that any thermodynamic function needs to be given a reference state, the value of the … thermodynamic function either U, S, H, A, G or the others make sense only with a reference state being mentioned. At the reference state we assigned a value of 0 to it. And we went through the exercise of thinking about, where the temperature is actually assigned a 0 value; if you think about it is just an assignment of a 0 value at a certain condition, where there is no movement of molecules and so on. And we also looked at where the 0 value of pressure is assigned, where we said it as equal to 0, when there is no even there are no particles with complete absence of particles. And the nice thing about thermodynamic manipulations is that one can fix ones own reference state for a particular application. But only with at a certain point at a certain reference state the value being 0, only if that is done, will any of the thermodynamic functions make sense.

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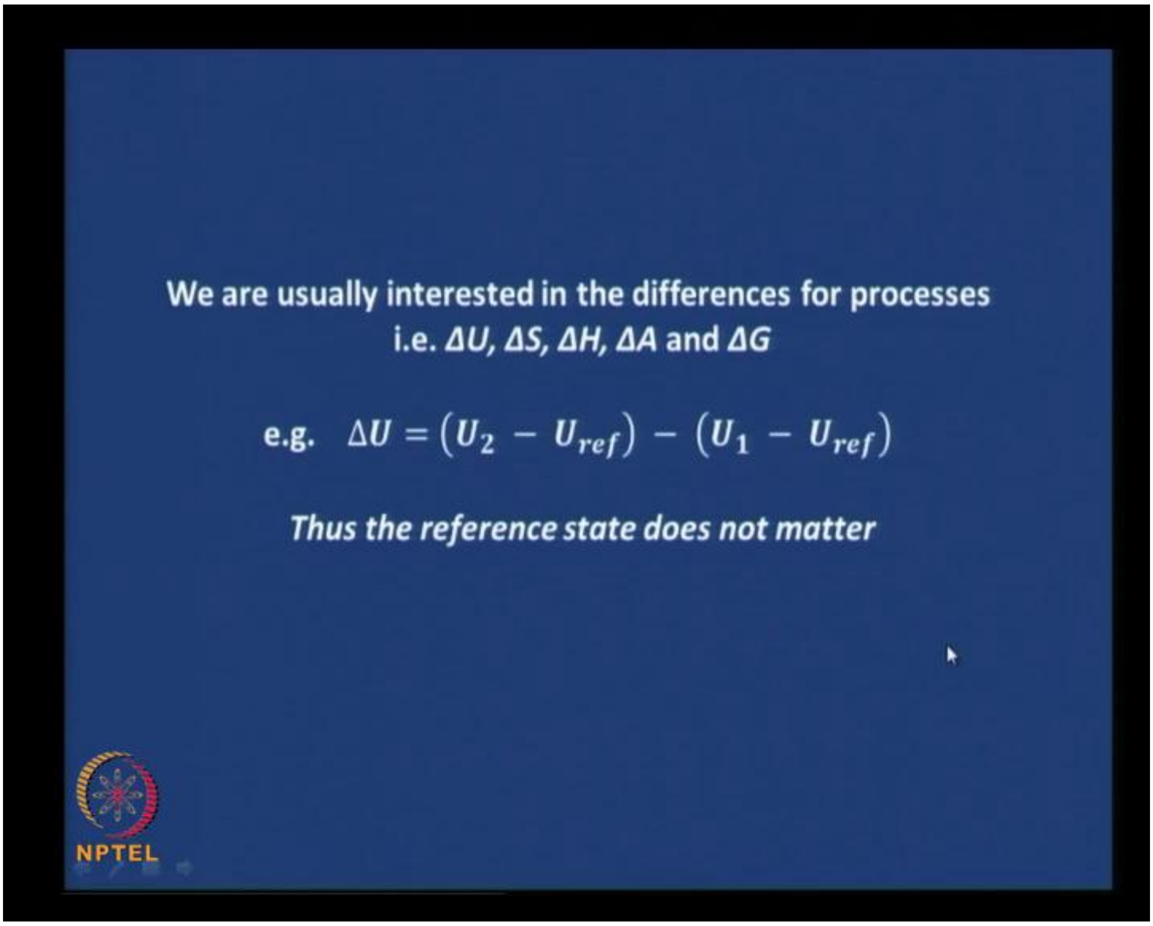

We are usually interested in the differences for processes
i.e. $\Delta U, \Delta S, \Delta H, \Delta A$ and ΔG

e.g. $\Delta U = (U_2 - U_{ref}) - (U_1 - U_{ref})$

Thus the reference state does not matter

And then we said that reference state does not really matter, we demonstrated that by considering the difference in say U – it could have been difference in anything – for a particular process, we said that if U 2 is some value and U 2 minus U reference is the value that make sense at a state 2; and U 1 minus U reference is the value that make sense at state 1; U 2 minus U reference minus of U 1 minus U reference; U reference, U reference get cancelled out it leading to U 2 minus U 1. Therefore, whatever is chosen as a reference state does not really matter, because we take differences all the time.

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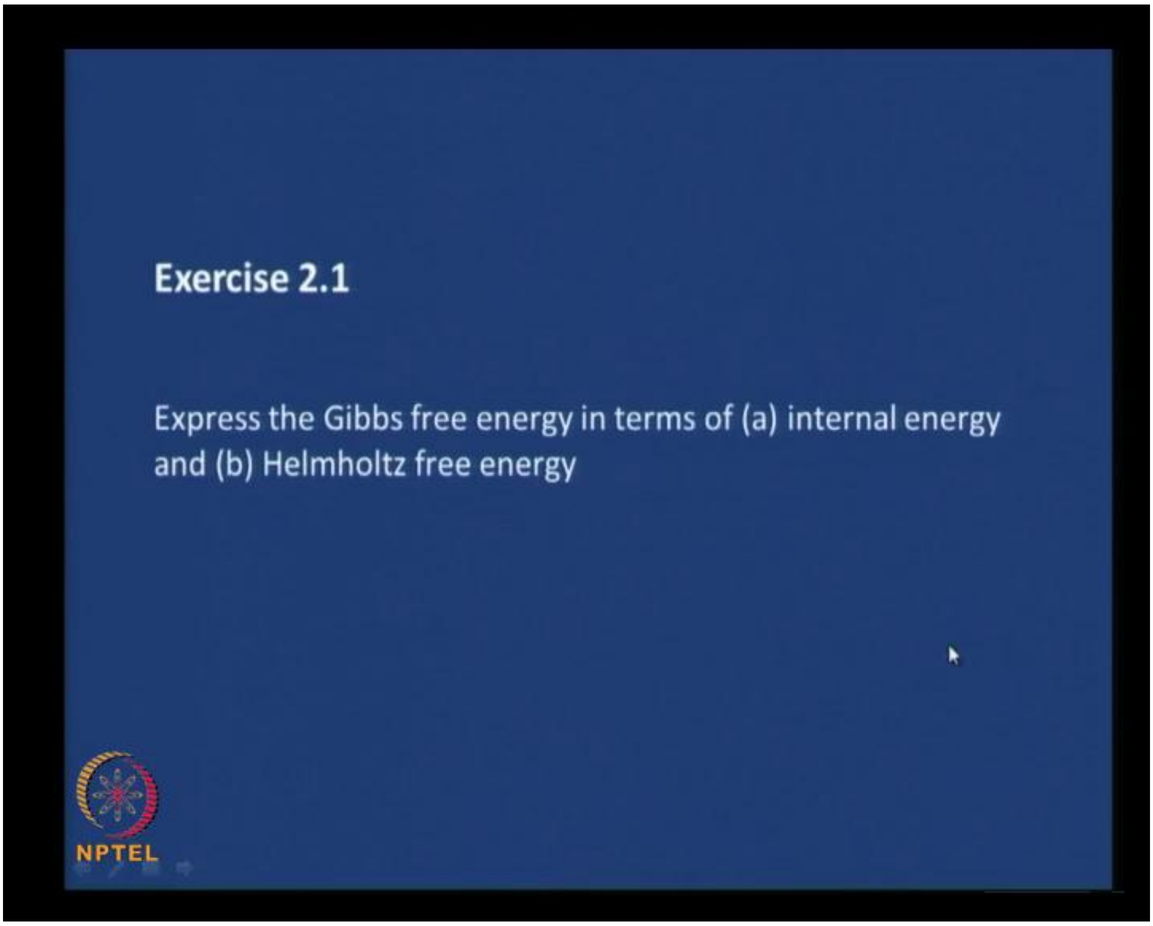

Exercise 2.1

Express the Gibbs free energy in terms of (a) internal energy and (b) Helmholtz free energy

And then we went and did some exercises.

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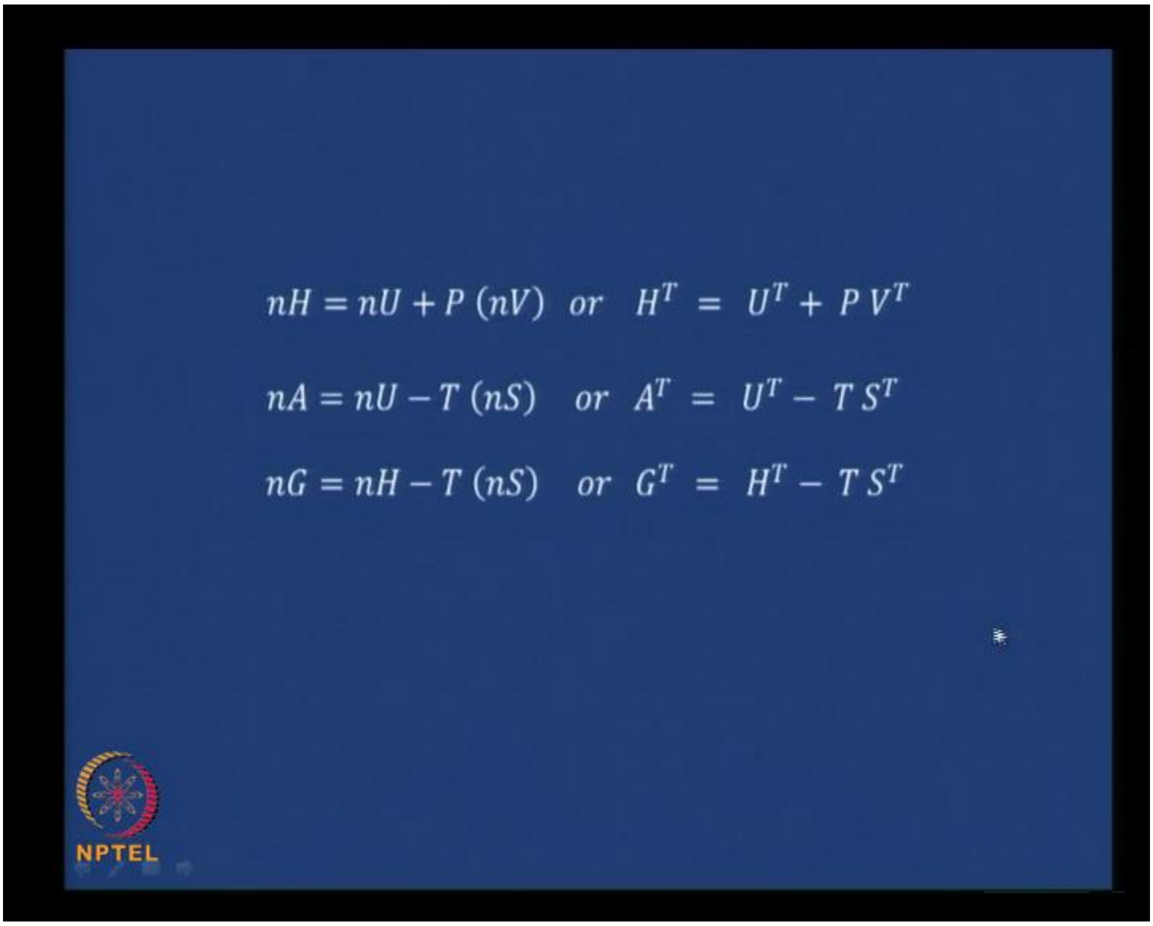

$$nH = nU + P\,(nV) \quad or \quad H^T = U^T + P\,V^T$$

$$nA = nU - T\,(nS) \quad or \quad A^T = U^T - T\,S^T$$

$$nG = nH - T\,(nS) \quad or \quad G^T = H^T - T\,S^T$$

And we also said that the H, A, and G were defined for 1 mole and if there are n moles of a pure substance, then we can either call that as n H, the value of enthalpy as n H, which will be defined as n U plus P times n V. P is an intrinsic variable, it does not depend on the number of moles that are available. But we said that a better terminology would be to consider a superscript T for total values, when there is more than 1 mole that is present. Therefore H T equals U T plus P V T. A T equals U T minus T S T these are all definitions, and Gibbs free energy total G T was equal to H T minus T S T.

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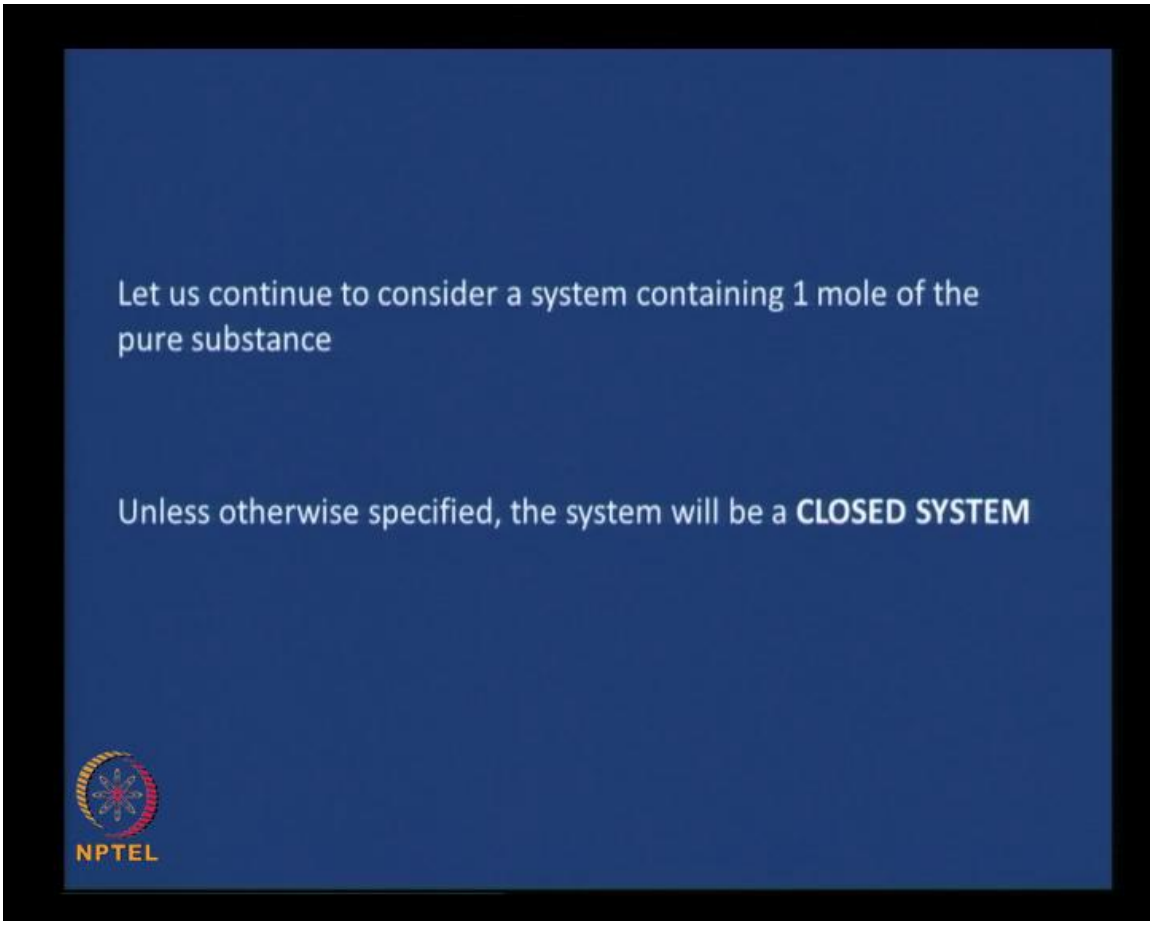

Let us continue to consider a system containing 1 mole of the pure substance

Unless otherwise specified, the system will be a **CLOSED SYSTEM**

And then we went on to consider 1 mole of a pure substance, and we also said at this point that whatever we are going to develop in this module, unless otherwise stated, will be for a closed system. And that is where we have stopped right now; we have developed all the necessary fundamentals for a closed system. And therefore, before we went on to open systems we thought we could do a review.

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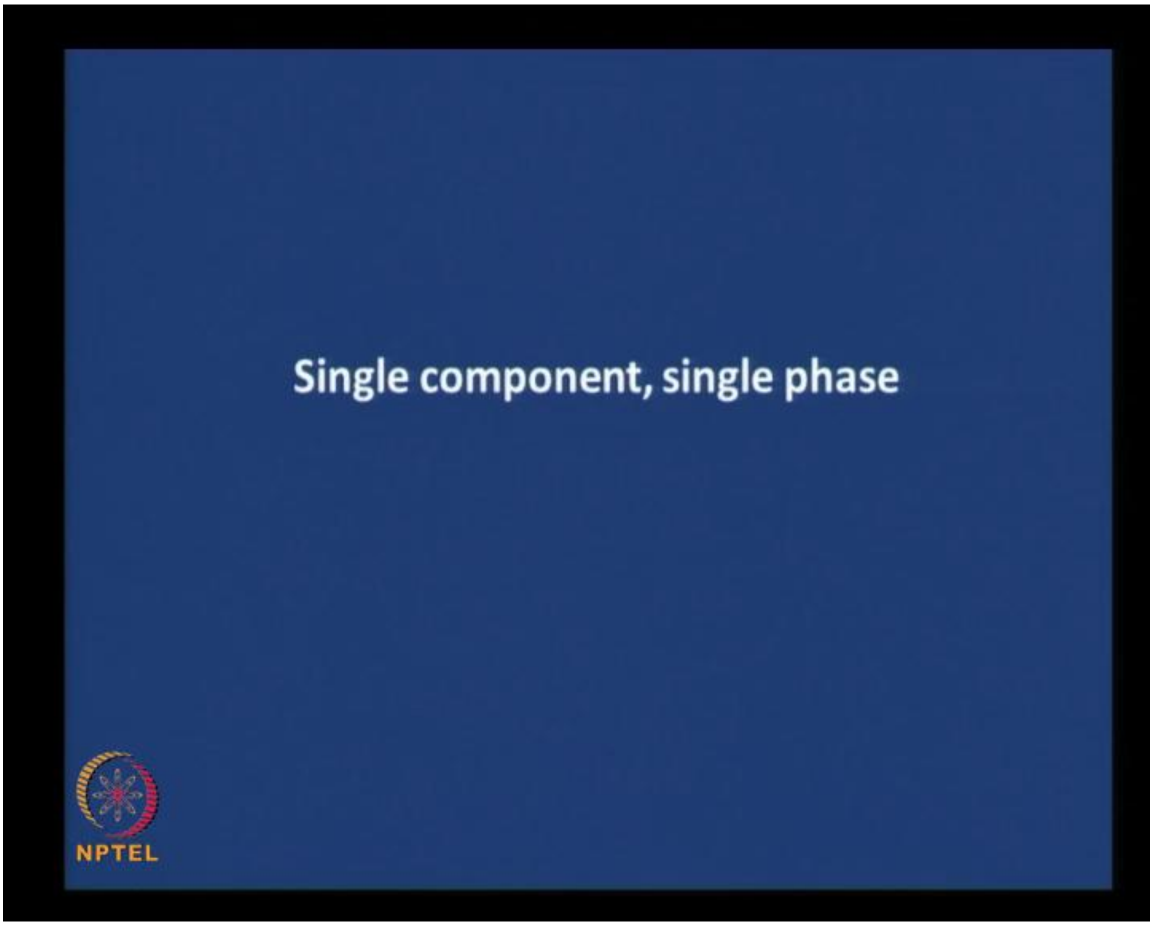

Single component, single phase

We started by considering a single component system, which exists in a single phase. As we all know, phases that are being considered in this course are only three; either a gas or a liquid or a solid. Gas … is also called vapor.

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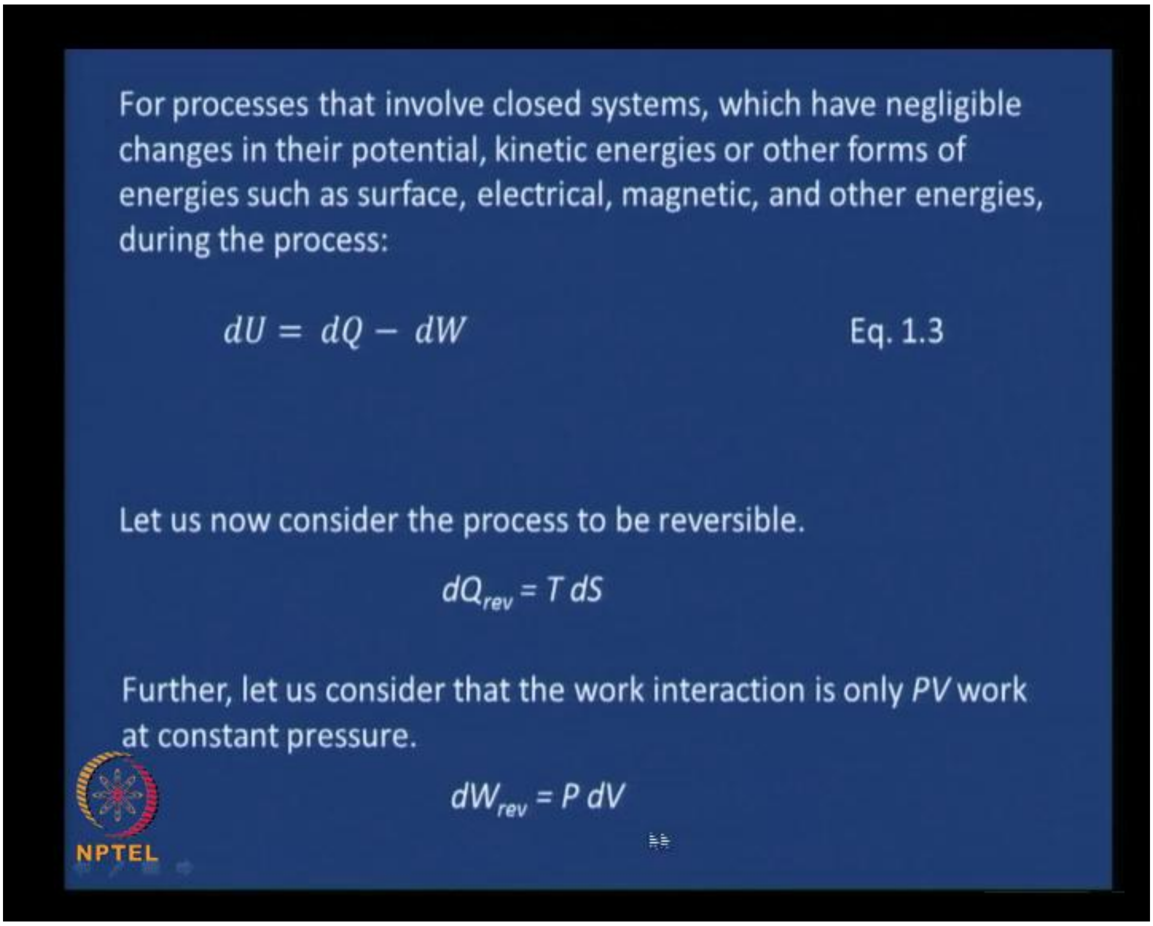

For processes that involve closed systems, which have negligible changes in their potential, kinetic energies or other forms of energies such as surface, electrical, magnetic, and other energies, during the process:

$$dU = dQ - dW \qquad \text{Eq. 1.3}$$

Let us now consider the process to be reversible.

$$dQ_{rev} = T\,dS$$

Further, let us consider that the work interaction is only *PV* work at constant pressure.

$$dW_{rev} = P\,dV$$

And we said that for processes that … involve closed systems, which have negligible changes in their potential, kinetic or other forms of energies such as a surface energy, electrical energy, magnetic energy, we could write d U equals dQ minus dW. This is the first law. And if we consider the process to be reversible, we could write the second law as dQ reversible equals T dS. And … if P V work is the only work interaction that is considered at constant pressure, then dW reversible was P dV.

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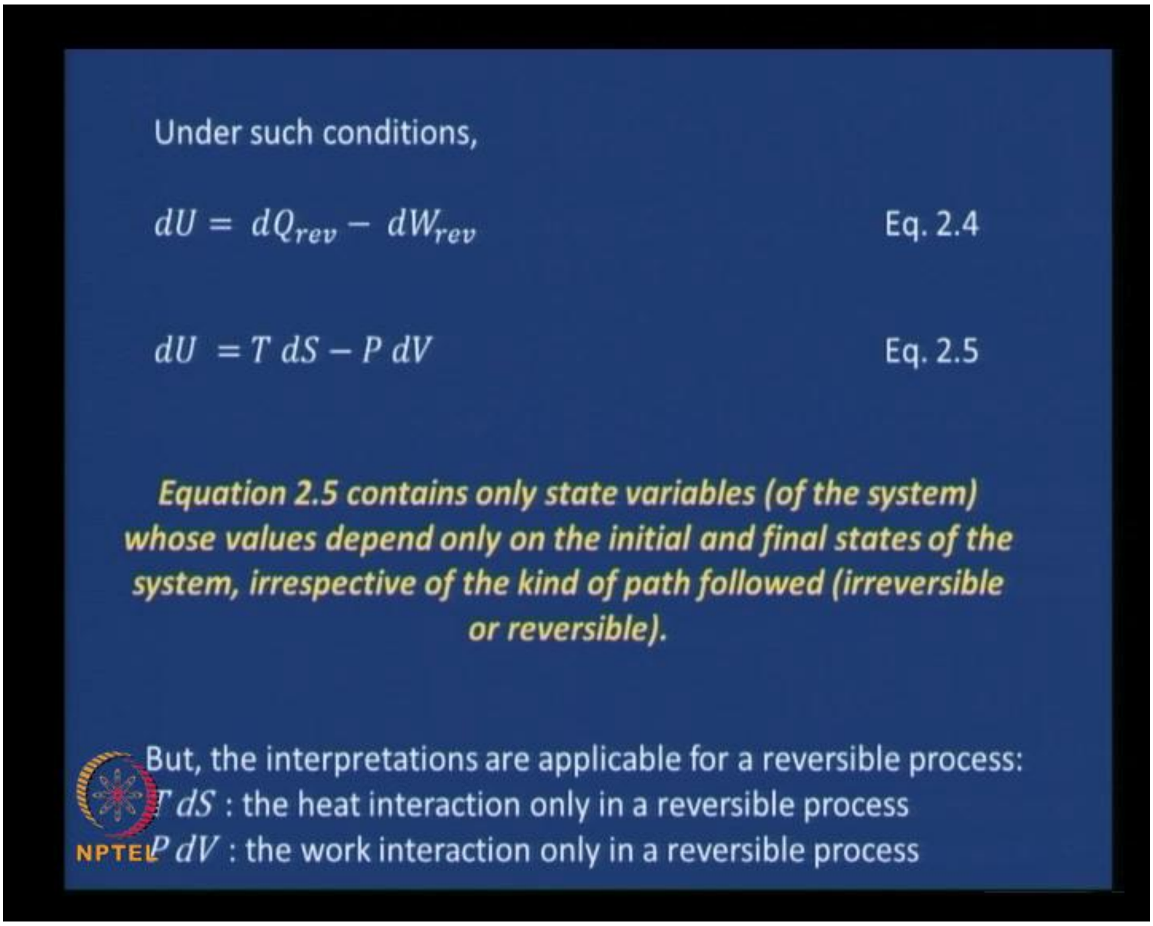

Under such conditions,

$$dU = dQ_{rev} - dW_{rev} \qquad \text{Eq. 2.4}$$

$$dU = T\,dS - P\,dV \qquad \text{Eq. 2.5}$$

Equation 2.5 contains only state variables (of the system) whose values depend only on the initial and final states of the system, irrespective of the kind of path followed (irreversible or reversible).

But, the interpretations are applicable for a reversible process:

$T\,dS$: the heat interaction only in a reversible process

$P\,dV$: the work interaction only in a reversible process

Under such conditions we could modify the first law as … dU equals dQ reversible minus dW reversible. And therefore we could write d U equals T d S minus P d V. You could recall that this became one of the most basic equations for a closed system. And we also said that although we considered various things to arrive at this particular point that is dU equals T d S minus P d V, we said that since this equation contains only state variables, which depend only on the state of the system and not on the path taken to reach say state 2 from state 1; this is valid for anything, as long as it is that of a closed system.

And to understand that a little better … before I get into that … nevertheless, the equation as a … rather the equation as a whole is applicable for anything; nevertheless, the interpretation of the individual terms is applicable only for that particular path. For example, in this case; T d S represents heat interaction only for a reversible process and P d V represents work interaction only for a reversible process. That does not change. Nevertheless the difference between the two, which is d U – that is applicable in general.

Whether the path is it reversible/irreversible, whether it has kinks in … it or a smooth path – nothing of that sort matters.

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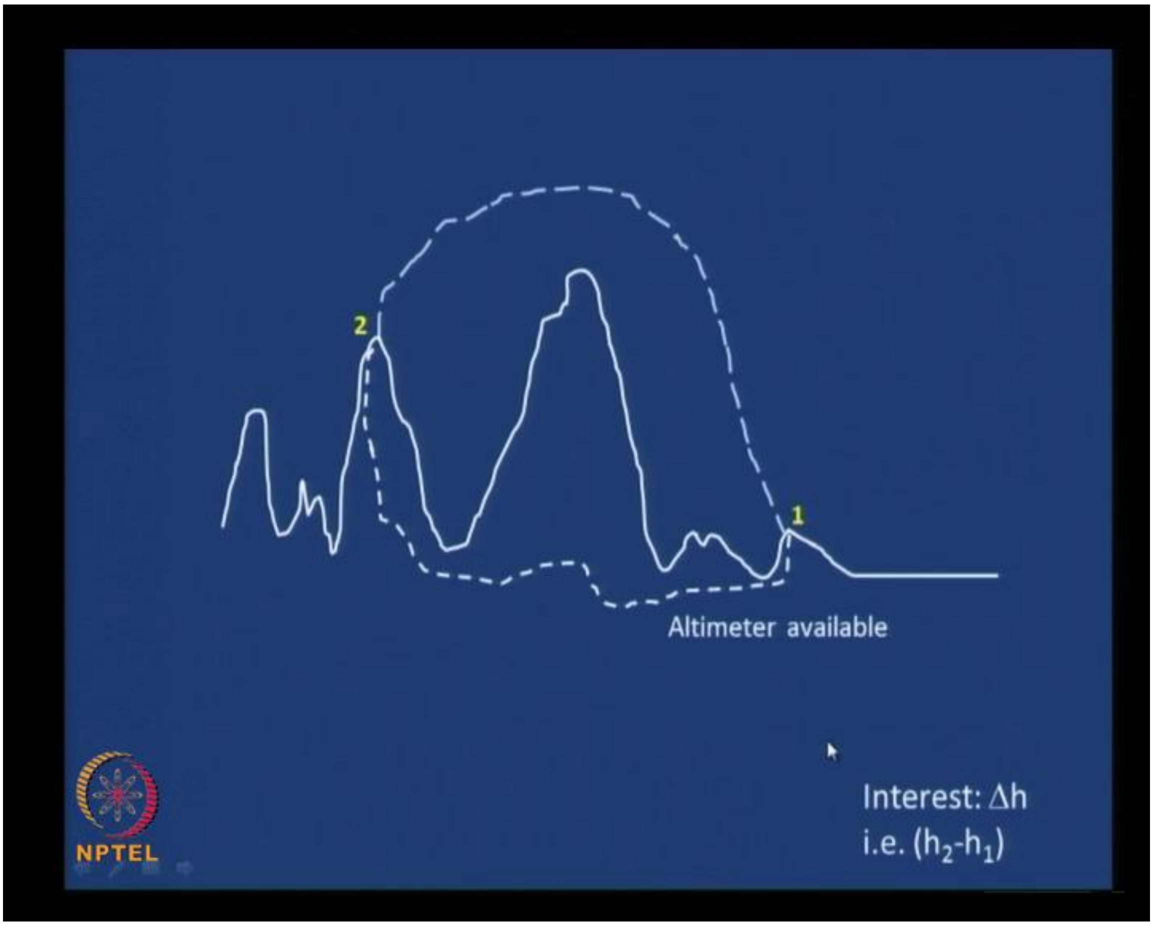

And to understand that a little better because this was one of the central concepts that we are going to use repeatedly later, we sought to understand that better by considering a mountainous region in which our interest was the difference between the heights between two points, let us say 1 and 2 or states, if you want to call it state 1 and state 2; our interest was h 2 height 2 minus height 1, difference in heights. We said that they could be different paths that can be taken; you could take a path on the road, nice road, or you take a hilly road, which is not well charted out; you take a helicopter and land here. Whatever path you take the difference in heights between these two remains same and does not really depend on the path. That is a same thing that happens whenever we have the final equation in terms of state variables, irrespective of the path that is considered.

Also we said that some paths could make it easier for us to compute the difference in values, difference in thermodynamic functions between the two states. For example, it could be considered that in one of these paths say along the road, nice road, an altimeter is available. Therefore, you could actually measure the heights at various points and the difference between 2 and 1 would give you the delta h that is required. That would always happen therefore, we choose a path, an experimental path if you will, where the altimeter or the means of measuring the variable of interest is available to us. And once we do the measurement, and we bring it down to an equation, which consists only of state variables, then we can use that equation in general.

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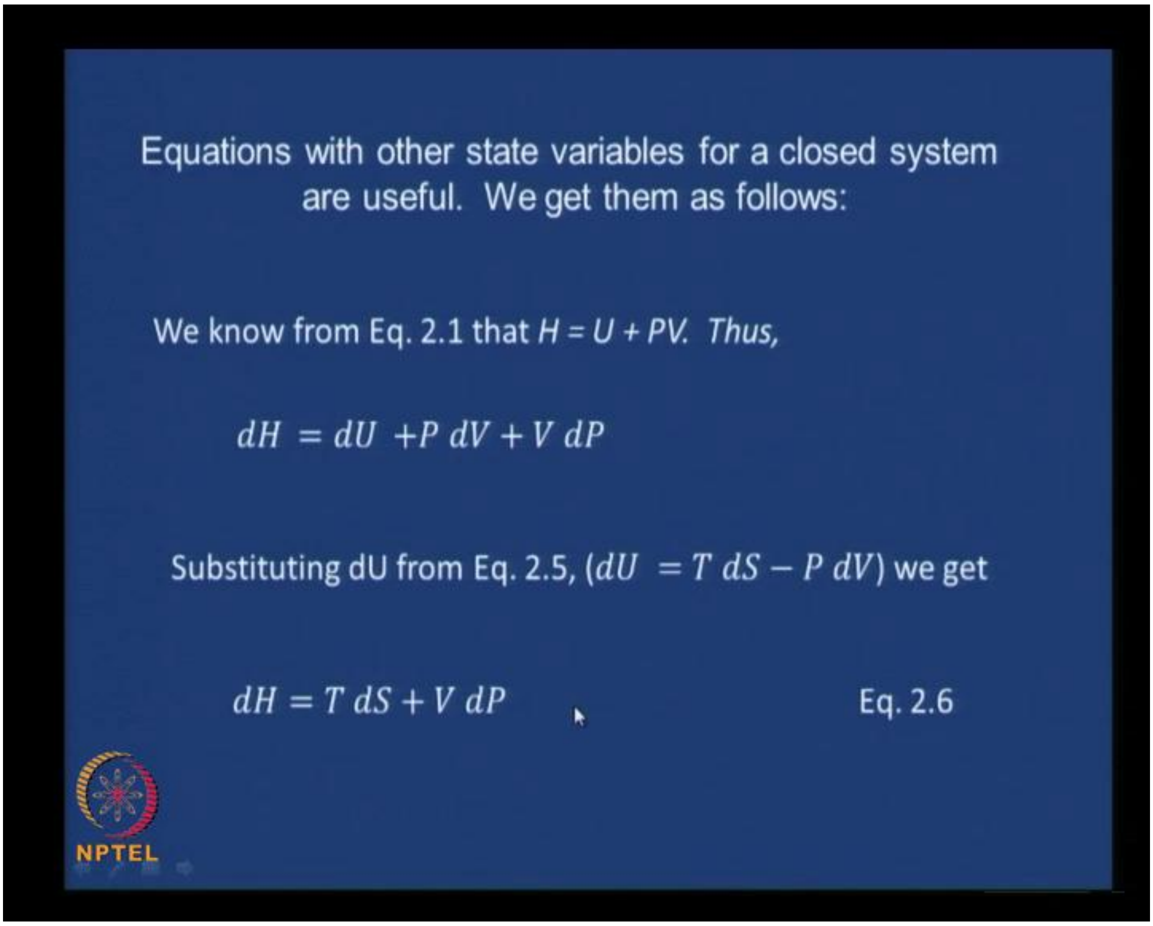

Equations with other state variables for a closed system are useful. We get them as follows:

We know from Eq. 2.1 that $H = U + PV$. *Thus,*

$$dH = dU + P\,dV + V\,dP$$

Substituting dU from Eq. 2.5, ($dU = T\,dS - P\,dV$) we get

$$dH = T\,dS + V\,dP \qquad \text{Eq. 2.6}$$

We also said that there could be other equations for a closed system, which would come in useful; and we derived them also. d H equals … we will not go through the derivation, but tell you just the final expressions. You go back to the slides and look at how we derived them. we said that d H equals T d S plus … V d P.

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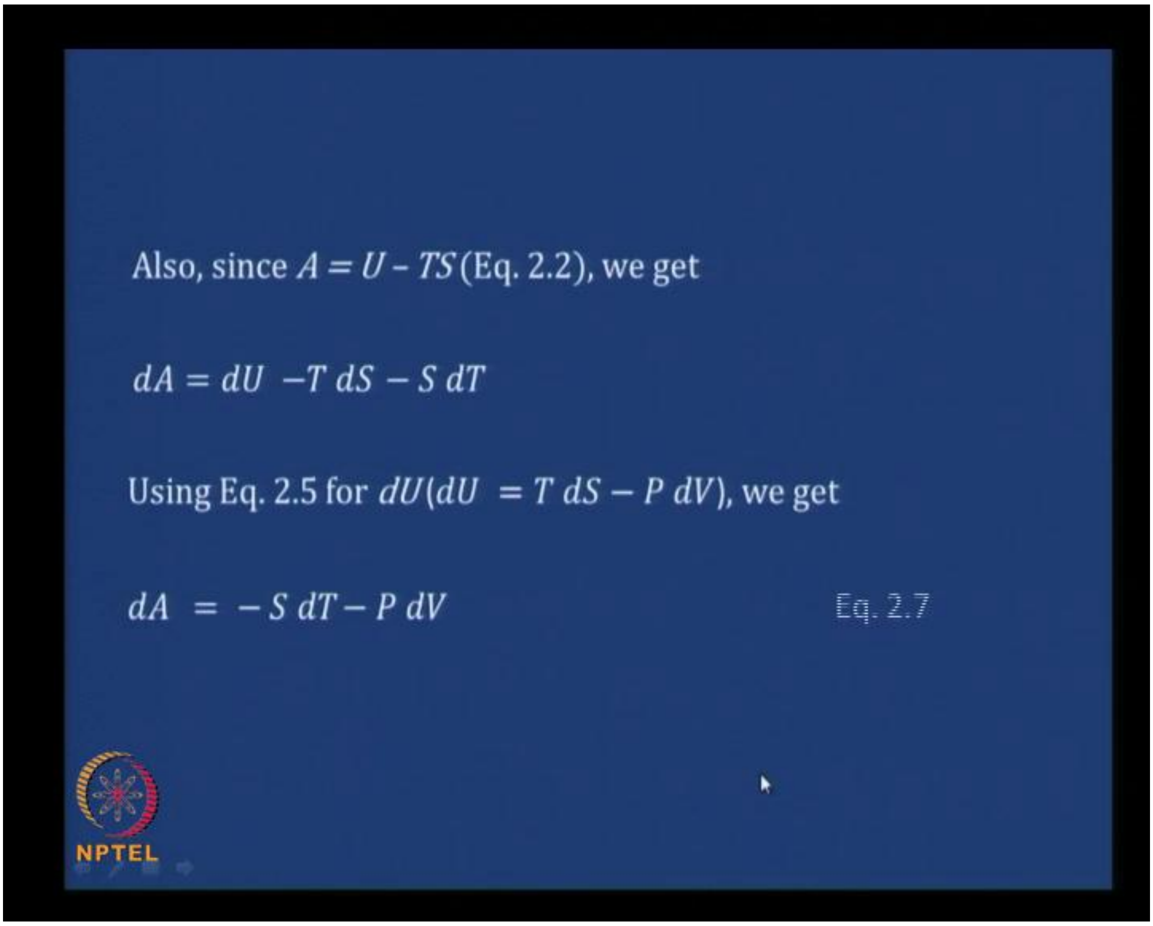


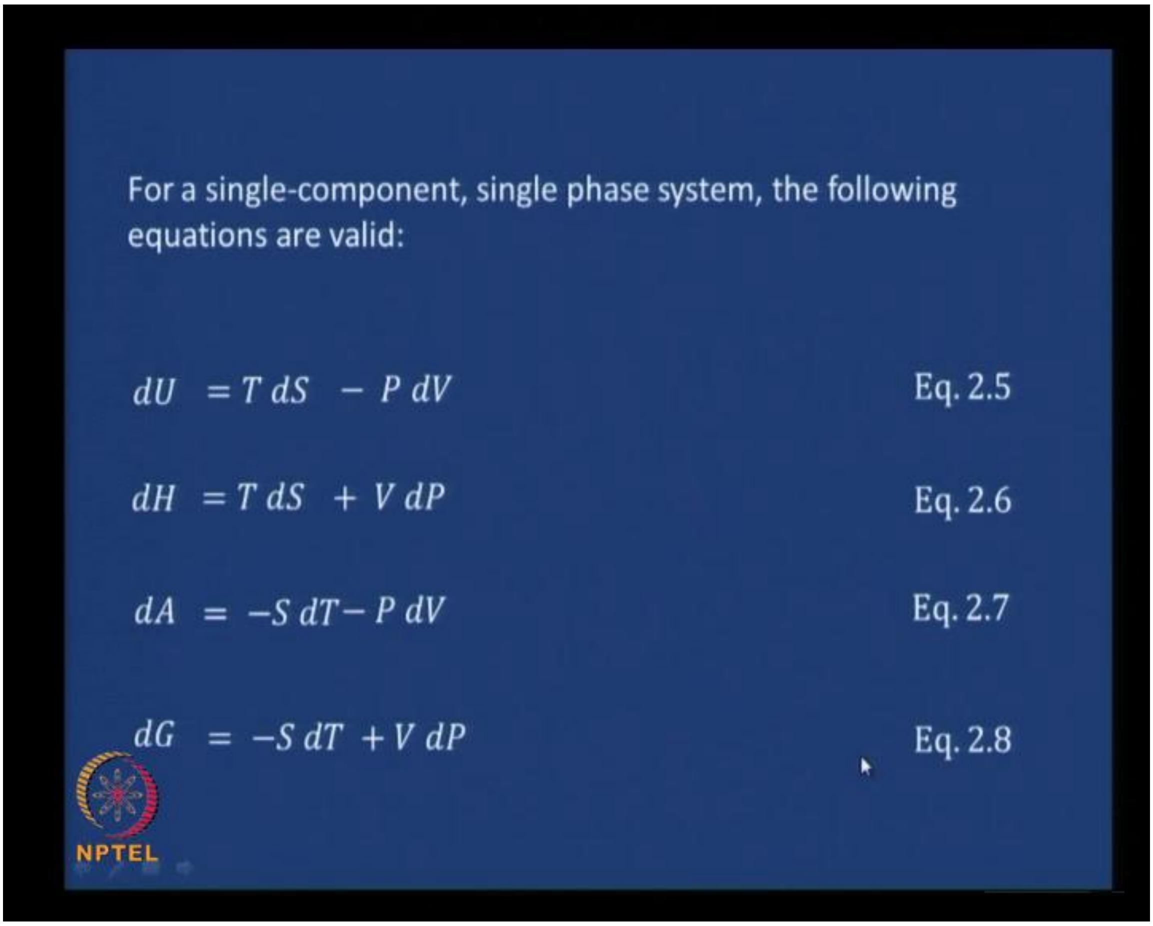
Also, since $A = U - TS$ (Eq. 2.2), we get

$$dA = dU - T\,dS - S\,dT$$

Using Eq. 2.5 for dU ($dU = T\,dS - P\,dV$), we get

$$dA = -S\,dT - P\,dV \qquad \text{Eq. 2.7}$$

And d A was minus S d T minus P d V and d G was minus S … d T plus V d P. (Refer Slide Time: 21:29)



For a single-component, single phase system, the following equations are valid:

$$dU = T\,dS - P\,dV \qquad \text{Eq. 2.5}$$

$$dH = T\,dS + V\,dP \qquad \text{Eq. 2.6}$$

$$dA = -S\,dT - P\,dV \qquad \text{Eq. 2.7}$$

$$dG = -S\,dT + V\,dP \qquad \text{Eq. 2.8}$$

So think we also put it all together somewhere yes … d U equals T d S minus P d V, d H equals T d S plus V d P, d A equals minus S d T minus P d V, d G equals minus S d T plus V d P. These are nice equations to remember: 2.5 to 2.8, especially if you have close book exams as … it typically happens in the university exams if not you know how to derive them. And therefore, you can derive them reasonably quickly and you do not have to remember these.

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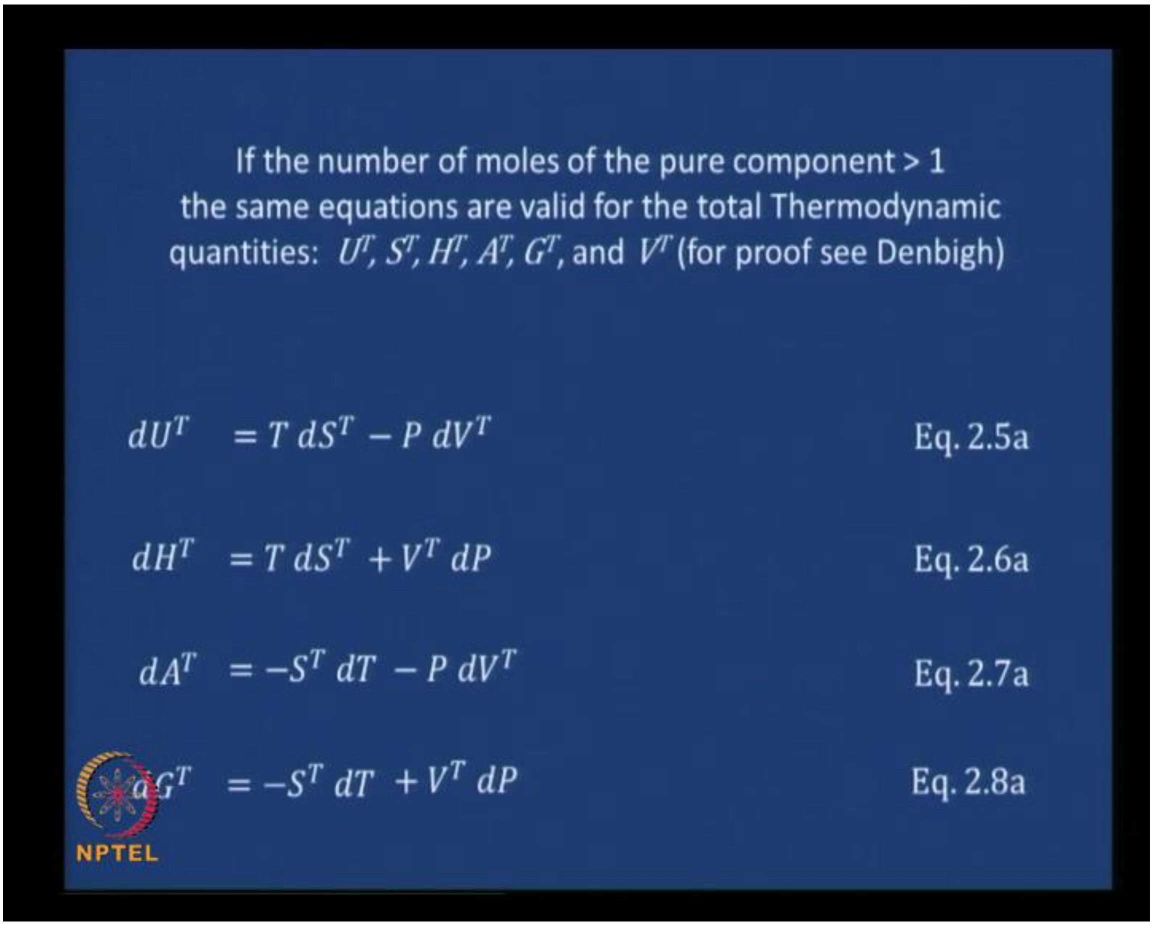

If the number of moles of the pure component > 1
the same equations are valid for the total Thermodynamic
quantities: U^T, S^T, H^T, A^T, G^T, and V^T (for proof see Denbigh)

$$dU^T = T\,dS^T - P\,dV^T \qquad \text{Eq. 2.5a}$$

$$dH^T = T\,dS^T + V^T\,dP \qquad \text{Eq. 2.6a}$$

$$dA^T = -S^T\,dT - P\,dV^T \qquad \text{Eq. 2.7a}$$

$$dG^T = -S^T\,dT + V^T\,dP \qquad \text{Eq. 2.8a}$$

We also said that if the number of moles is more than 1 (the earlier equations were all for 1 mole of a closed system, pure component) – if this is the case, then the same equations are valid. This is not very obvious and therefore, you were asked to look at your one of your reference books by Kenneth Denbigh. You could look at … you could do that, and there the proof would be given as to why the same forms are applicable, even for total … even for variables, the thermodynamic variables, taken for systems with more than 1 mole of the pure substance.

Therefore, d U T equals T d S T – T is a intrinsic variable therefore, it does not have it does not need to have any superscript – T d S T minus P d V T. Similarly, P is an intrinsic variable; d H T equals T d S T plus V T d P, d A T equals minus S T d T minus P d V T, and d G T equals minus S T d T plus V T d P. So, we looked at equations for a closed system consisting of a single mole, equations for a closed system consisting of more than 1 mole but, of only one pure substance.

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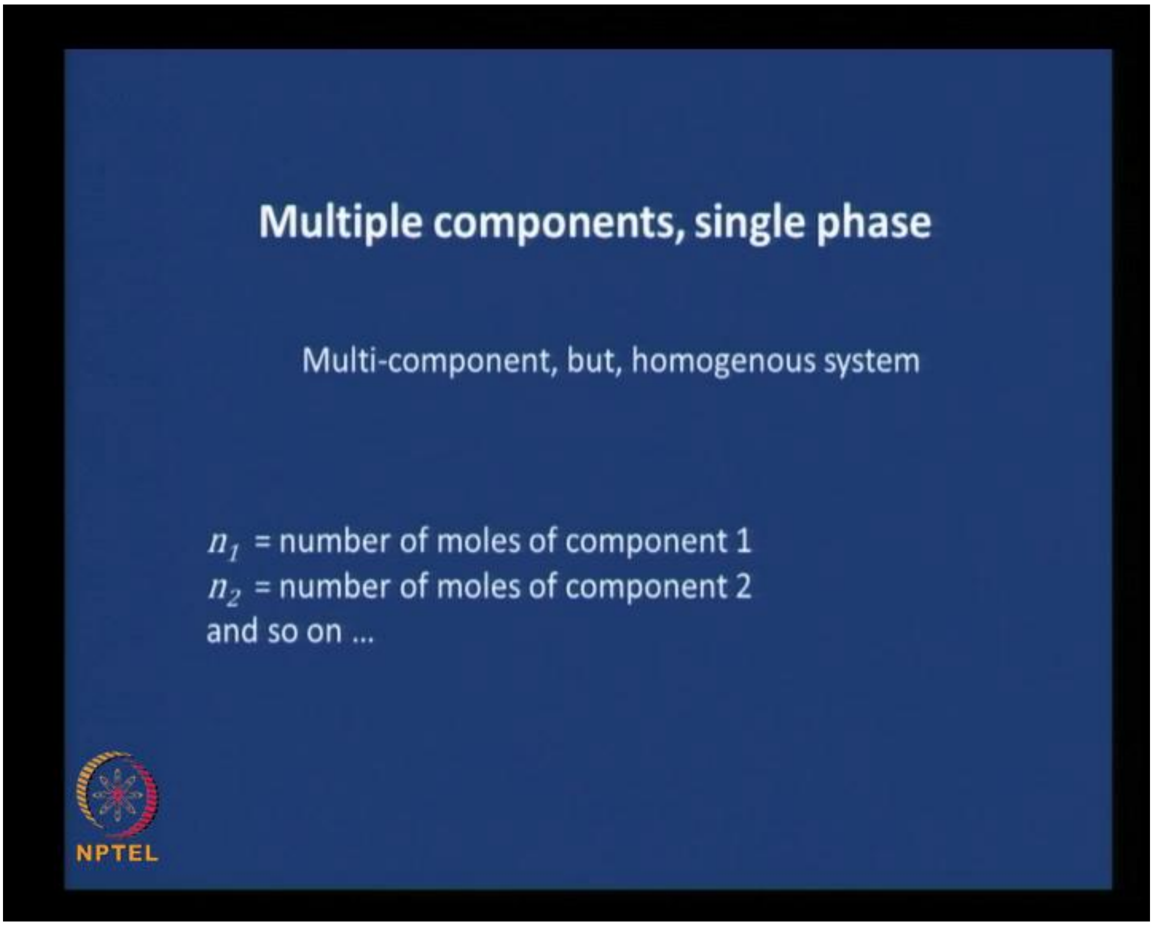

Multiple components, single phase

Multi-component, but, homogenous system

n_1 = number of moles of component 1
n_2 = number of moles of component 2
and so on ...

Then we complicated it a little bit by considering a multicomponent system, but we retained the single phase in the nature of the substance. For example, this was some terminology and 1 was a number of moles of component 1 and 2 number of moles of component 2 and so on. Let me give you the example if it consists … this could be multicomponent single phase system – could consist of let us say air – the example could be air, which contains water vapor; air by itself has many different components in the gaseous phase such as oxygen, nitrogen, carbon dioxide and so on. If you add water vapor to it, it also has H 2 O. So, that is a very good example of a multicomponent system, but which exists in a single phase.

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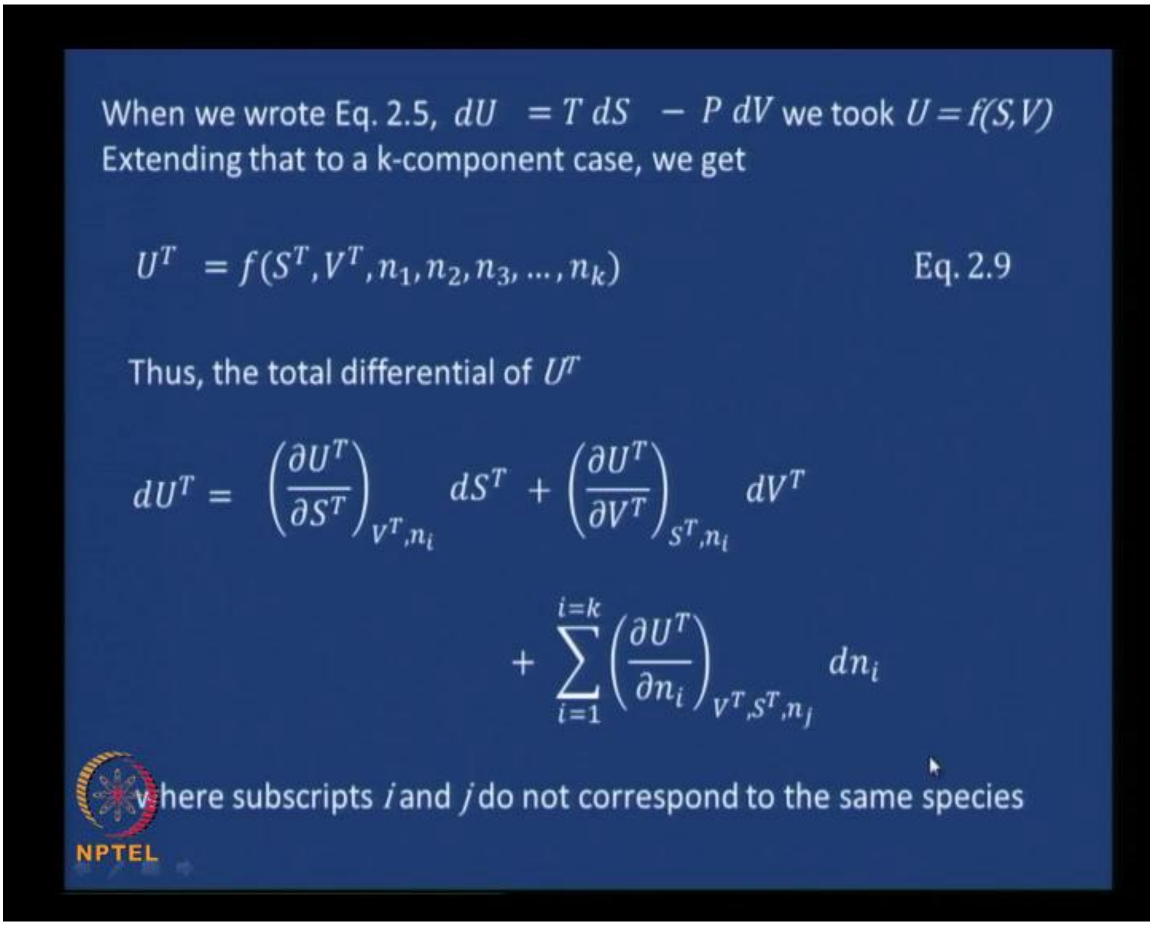

When we wrote Eq. 2.5, $dU = T\,dS - P\,dV$ we took $U = f(S,V)$
Extending that to a k-component case, we get

$$U^T = f(S^T, V^T, n_1, n_2, n_3, \ldots, n_k) \qquad \text{Eq. 2.9}$$

Thus, the total differential of U^T

$$dU^T = \left(\frac{\partial U^T}{\partial S^T}\right)_{V^T, n_i} dS^T + \left(\frac{\partial U^T}{\partial V^T}\right)_{S^T, n_i} dV^T + \sum_{i=1}^{i=k} \left(\frac{\partial U^T}{\partial n_i}\right)_{V^T, S^T, n_j} dn_i$$

where subscripts i and j do not correspond to the same species

For that, we looked at what equations would be useful to use. To derive that we started out with the generic mathematical representation of a function … of a variable in terms of its dependent values. We took U T as a function of S T V T and so on and so forth. And, we wrote the total differential, going by one of the theorems in calculus: total differential is partial differential … rather d U T total differentialis dou U T dou S T. S T is the first variable that is taken here with all other variables remaining constant V T n 1, n 2, n 3 the constancy of which is represented as n i here; dou U T dou S T d S T plus the second variable dou U T dou V T with all other variables remaining constant times d V T; and dou U T dou n 1 with all other variables remaining constant d n 1 plus dou U T dou n 2 d n 2 and so on. We have combined all the n terms into this summation sign for compact notation … as some of dou U T dou n i at constant V T S T n j, which represents the constancy of all n s, except the n that is considered for the differentiation here d n i

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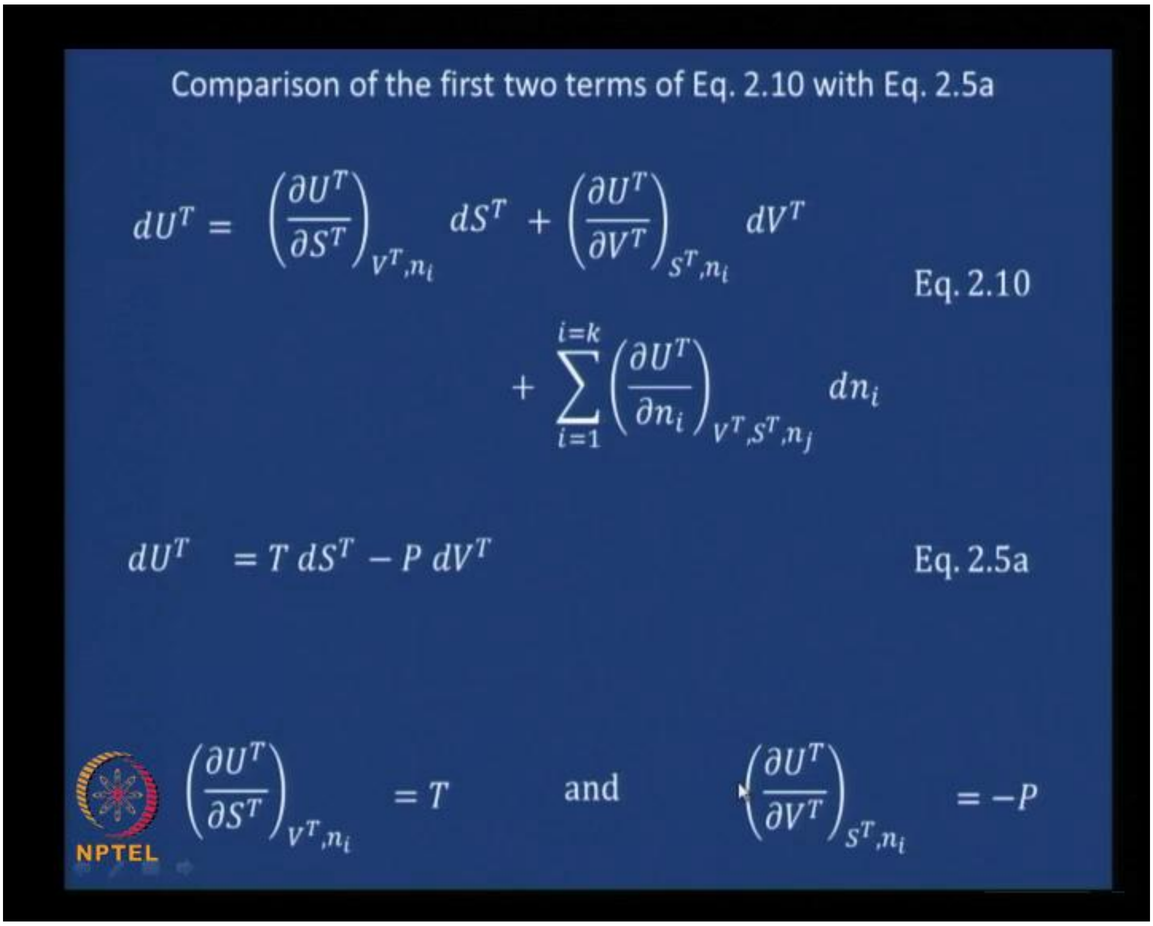

Comparison of the first two terms of Eq. 2.10 with Eq. 2.5a

$$dU^T = \left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,n_i} dS^T + \left(\frac{\partial U^T}{\partial V^T}\right)_{S^T,n_i} dV^T + \sum_{i=1}^{i=k}\left(\frac{\partial U^T}{\partial n_i}\right)_{V^T,S^T,n_j} dn_i \qquad \text{Eq. 2.10}$$

$$dU^T = T\,dS^T - P\,dV^T \qquad \text{Eq. 2.5a}$$

$$\left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,n_i} = T \quad \text{and} \quad \left(\frac{\partial U^T}{\partial V^T}\right)_{S^T,n_i} = -P$$

And then we got down to dou U T dou S T at constant V T dou n i equals T and dou U T dou V T constant S T n i equals minus P.

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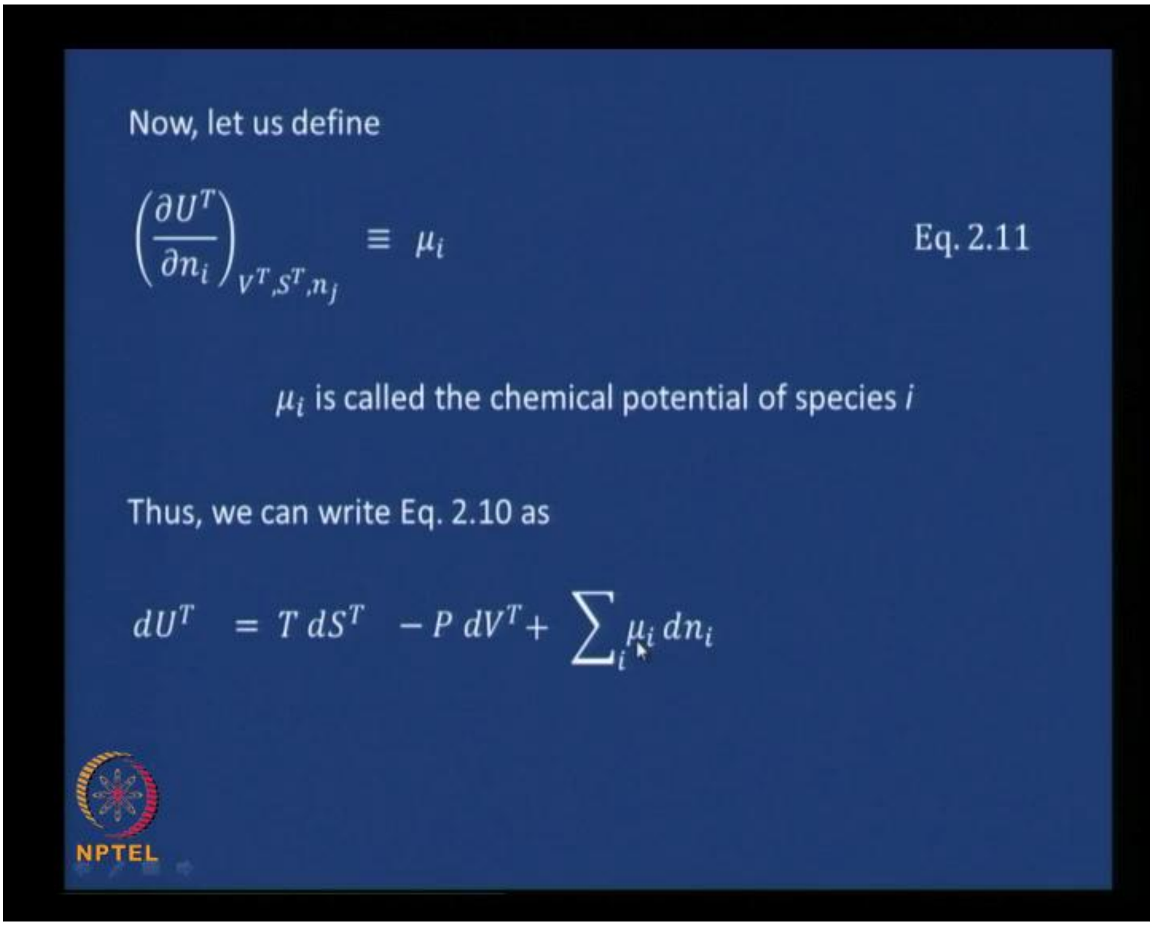

Now, let us define

$$\left(\frac{\partial U^T}{\partial n_i}\right)_{V^T, S^T, n_j} \equiv \mu_i \qquad \text{Eq. 2.11}$$

μ_i is called the chemical potential of species *i*

Thus, we can write Eq. 2.10 as

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i$$

And we said that … then we went ahead and defined one of the fundamental intrinsic properties, which will pretty much form the backbone of this course as you will find out in the later modules. We said that dou U T dou n i at constant V T S T and n j equals the chemical potential. And therefore, you could write the equation as d U T equals T d S T minus P d V T plus sum over mu i d n i’s.

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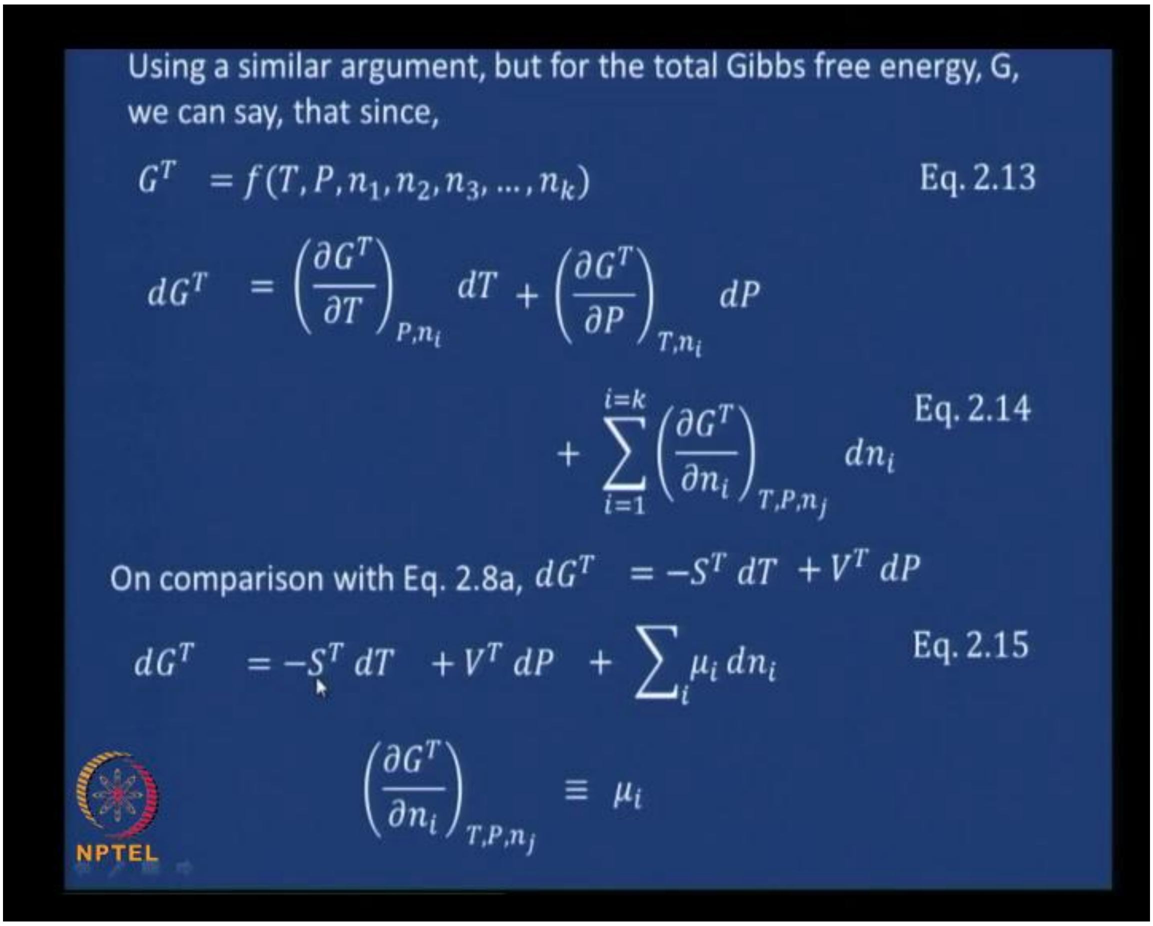

Using a similar argument, but for the total Gibbs free energy, G, we can say, that since,

$$G^T = f(T, P, n_1, n_2, n_3, \ldots, n_k) \qquad \text{Eq. 2.13}$$

$$dG^T = \left(\frac{\partial G^T}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G^T}{\partial P}\right)_{T,n_i} dP + \sum_{i=1}^{i=k} \left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j} dn_i \qquad \text{Eq. 2.14}$$

On comparison with Eq. 2.8a, $dG^T = -S^T\, dT + V^T\, dP$

$$dG^T = -S^T\, dT + V^T\, dP + \sum_i \mu_i\, dn_i \qquad \text{Eq. 2.15}$$

$$\left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j} \equiv \mu_i$$

And we could derive the other equations also. d G T equals minus S T d T plus V T d P plus sum over all i mu i d n i. And since we had used the same term here mu i whether we started from G T or U T, we had to prove that they were the same. And before that one of the important points to note is that dou G T dou n i at constant T P n j equals mu i this definition is predominantly used essentially, because look at the terms that are held constant here T P n j these all are easy to manipulate from an experimental point of view. And therefore, this is pretty much a preferred definition of mu i although you can define it by the other three means also.

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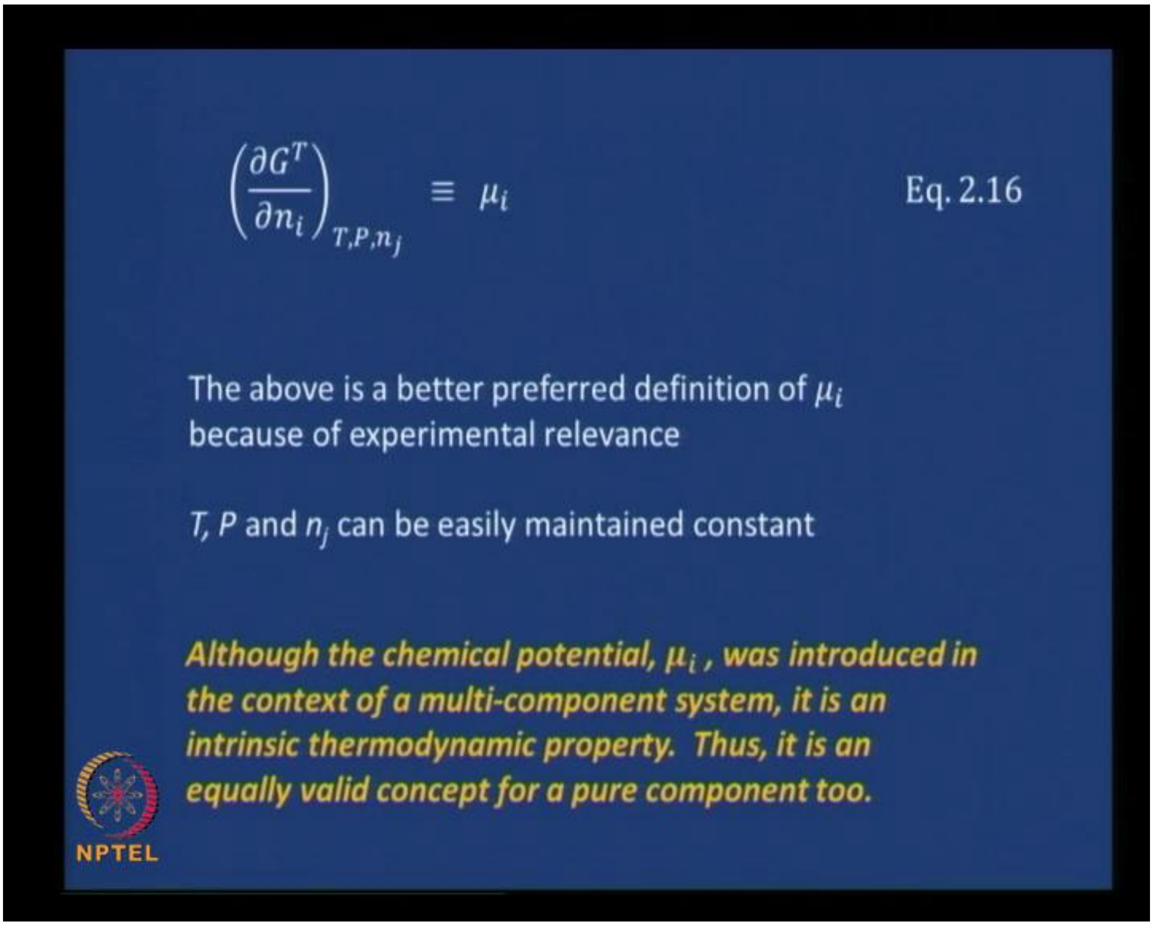

$$\left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j} \equiv \mu_i \qquad \text{Eq. 2.16}$$

The above is a better preferred definition of μ_i because of experimental relevance

T, P and n_j can be easily maintained constant

Although the chemical potential, μ_i, was introduced in the context of a multi-component system, it is an intrinsic thermodynamic property. Thus, it is an equally valid concept for a pure component too.

And this is how we went about proving that the mu i is the same whether you whether we started from U T or whether we started from G T. I will not go through the proof you could go back to your notes and see how we proved it.

And this is important; although the chemical potential mu i was introduced in the context of a multicomponent systems; it is an intrinsic thermodynamic property. Thus it is an equally valid concept for a pure component also.

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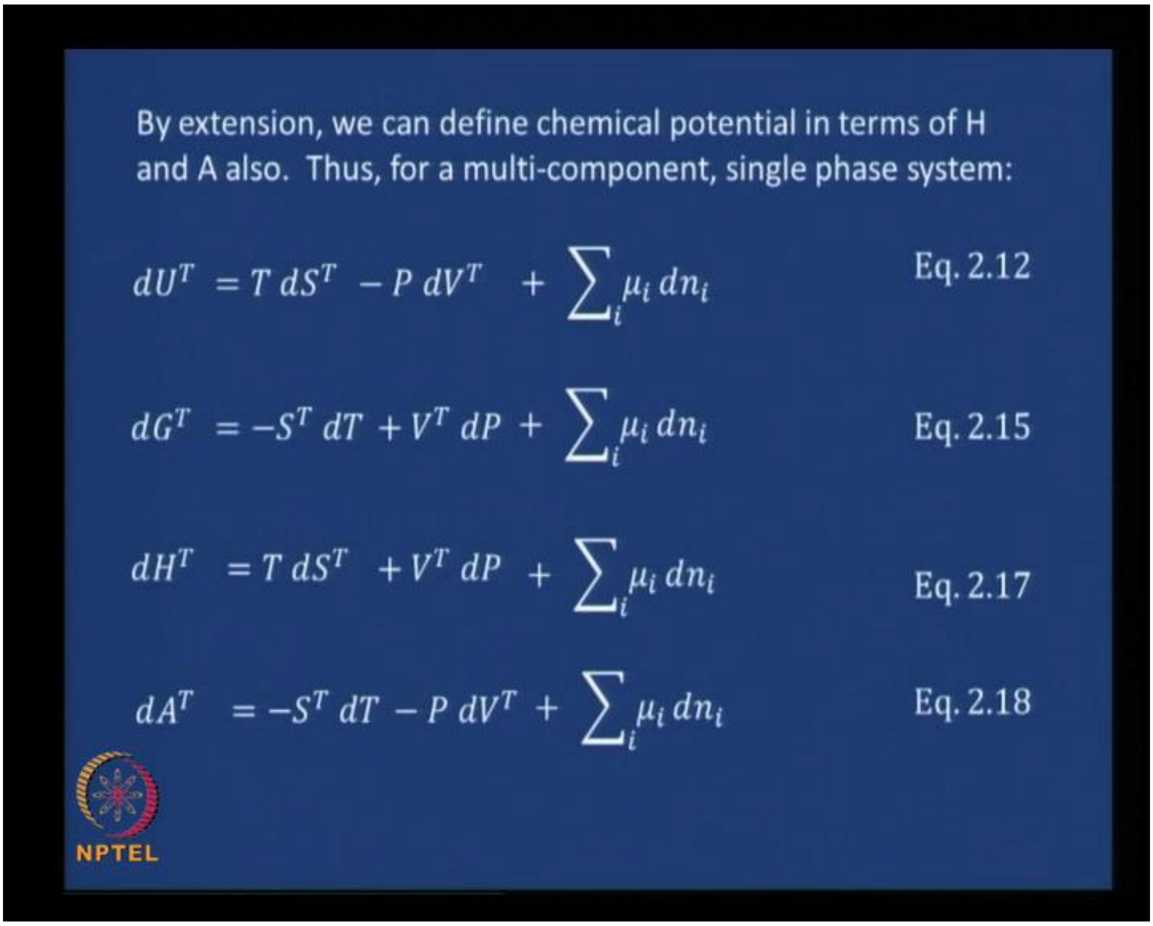

By extension, we can define chemical potential in terms of H and A also. Thus, for a multi-component, single phase system:

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.12}$$

$$dG^T = -S^T\,dT + V^T\,dP + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.15}$$

$$dH^T = T\,dS^T + V^T\,dP + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.17}$$

$$dA^T = -S^T\,dT - P\,dV^T + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.18}$$

And we extended the derivation to other thermodynamic variables of interest such as A T and H T; you could do that. And we have a comprehensive set of equations that are valid for a closed system consisting of multiple components, but in one phase. d U T equals T d S T minus P d V T plus summation of mu i d n i; d G T equals minus S T d T plus V T d P plus summation of mu i d n i; d H T equals T d S T plus V T d P plus summation of mu i d n i; d A T equals minus S T d T minus P d V T plus sum of mu i d n i. So irrespective of how the mu i is defined, they are all the same.

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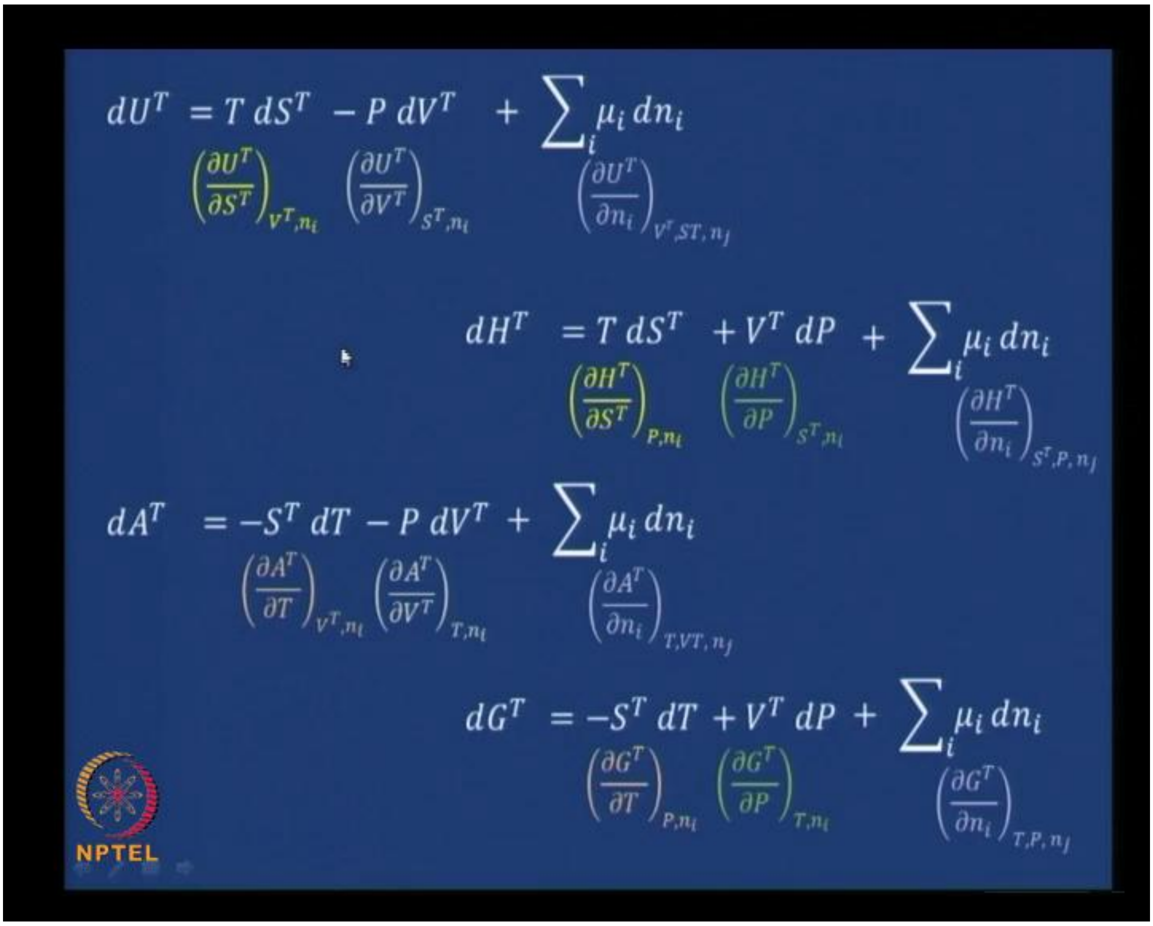

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i$$

$$\left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,n_i} \quad \left(\frac{\partial U^T}{\partial V^T}\right)_{S^T,n_i} \quad \left(\frac{\partial U^T}{\partial n_i}\right)_{V^T,ST,n_j}$$

$$dH^T = T\,dS^T + V^T\,dP + \sum_i \mu_i\,dn_i$$

$$\left(\frac{\partial H^T}{\partial S^T}\right)_{P,n_i} \quad \left(\frac{\partial H^T}{\partial P}\right)_{S^T,n_i} \quad \left(\frac{\partial H^T}{\partial n_i}\right)_{S^T,P,n_j}$$

$$dA^T = -S^T\,dT - P\,dV^T + \sum_i \mu_i\,dn_i$$

$$\left(\frac{\partial A^T}{\partial T}\right)_{V^T,n_i} \quad \left(\frac{\partial A^T}{\partial V^T}\right)_{T,n_i} \quad \left(\frac{\partial A^T}{\partial n_i}\right)_{T,VT,n_j}$$

$$dG^T = -S^T\,dT + V^T\,dP + \sum_i \mu_i\,dn_i$$

$$\left(\frac{\partial G^T}{\partial T}\right)_{P,n_i} \quad \left(\frac{\partial G^T}{\partial P}\right)_{T,n_i} \quad \left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j}$$

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Now, we did a nice exercise, by which we could compare the equations with the standard expansions written in terms of partial derivatives. And therefore, we could assign some partial derivatives to the thermodynamic functions. Example we said that this is nothing but dou U T dou S T at constant V T n i going by a standard expansion for the total differential which is nothing but T. And therefore, this T is also dou H T dou S T at constant P, n i. And similarly, dou U T dou V T at constant S T n i was P and this P is dou A T dou V T at constant T n i; minus S T, here in terms of an expansion dou AT dou T at constant V T n I; here, it is dou G T dou T at constant P n I; V T was dou H T dou P at constant S T n i; and V T was dou G T dou P at constant T n i.

And this is quite straightforward, we have already seen this: mu i here was dou U T dou n i at constant V T S T n j; here it was a dou H T dou n i at constant S T P n j, here it was dou A T dou n i at constant T V T n j has to be a superscript here; and … here it was dou G T dou n i at constant T P and all other n j's. So, this is a nice relationship between thermodynamic properties and derivatives, which will come out to be … will turn out to be useful in many manipulations. This is just listing it out. I do not think I will go through it again you have already seen it.

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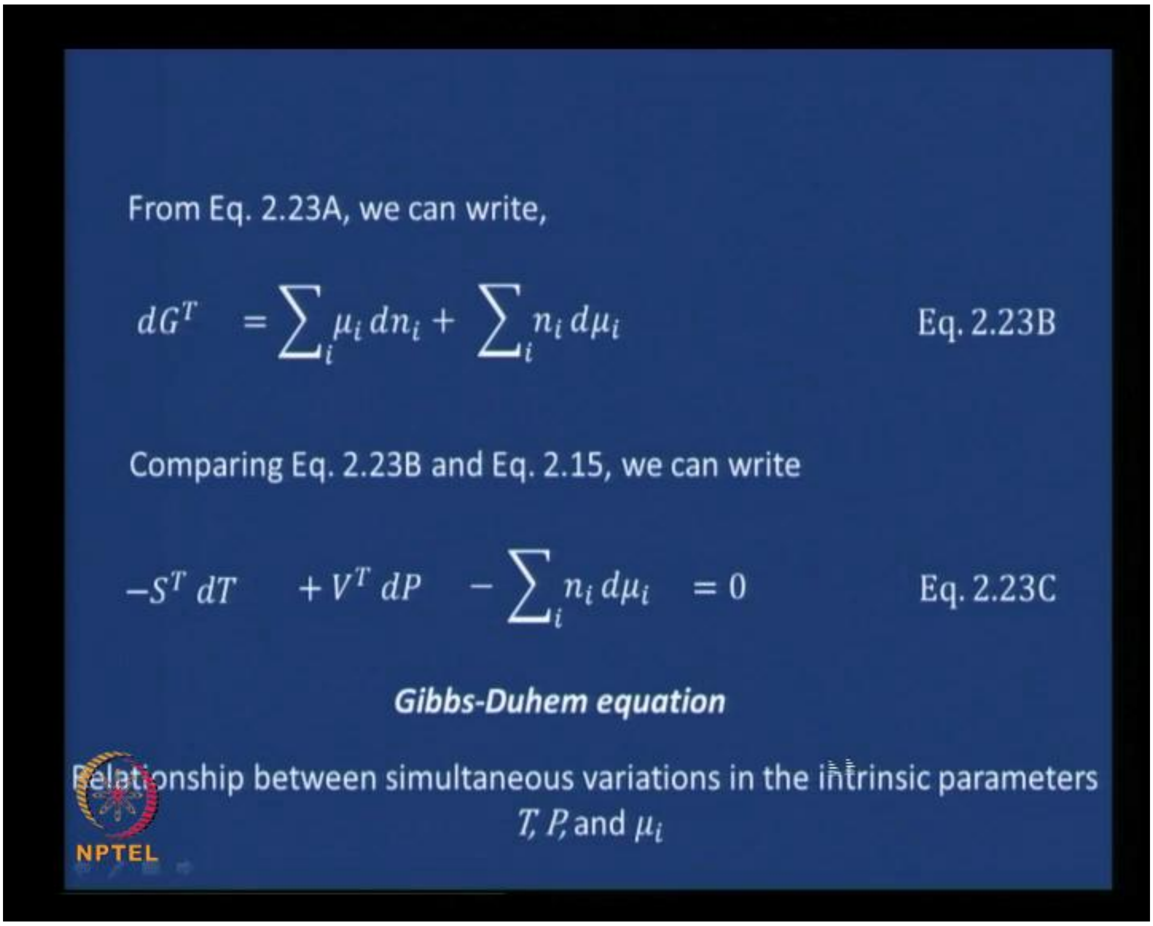

From Eq. 2.23A, we can write,

$$dG^T = \sum_i \mu_i \, dn_i + \sum_i n_i \, d\mu_i \qquad \text{Eq. 2.23B}$$

Comparing Eq. 2.23B and Eq. 2.15, we can write

$$-S^T \, dT + V^T \, dP - \sum_i n_i \, d\mu_i = 0 \qquad \text{Eq. 2.23C}$$

Gibbs-Duhem equation

Relationship between simultaneous variations in the intrinsic parameters T, P, and μ_i

Then we looked at one of the central equations in thermodynamics, in classical thermodynamics, call the Gibbs-Duhem equation. We went ahead and derived it by starting with the expression for d G and integrating it to arrive at … for the integration, we consider a system being made larger and so on so forth. And we arrived at this equation 2.23C: minus S T d T plus V T d P minus sum of n i d mu i equal 0. Here note that this gives you the variation with temperature, pressure and chemical potential, the three major intrinsic quantities of a system. And this is called the Gibbs-Duhem equation.

You also said this as this will have a relevance later, because the temperature gradient would form the driving force for energy transport as heat, the pressure differential would form one of the driving forces for bulk flow; and chemical potential gradient would form would be the driving force for mass flow. And so this has some special relevance, the Gibbs-Duhem equation. This relationship between simultaneous variations in the intrinsic parameters T P and mu I – it is worth reemphasizing this.

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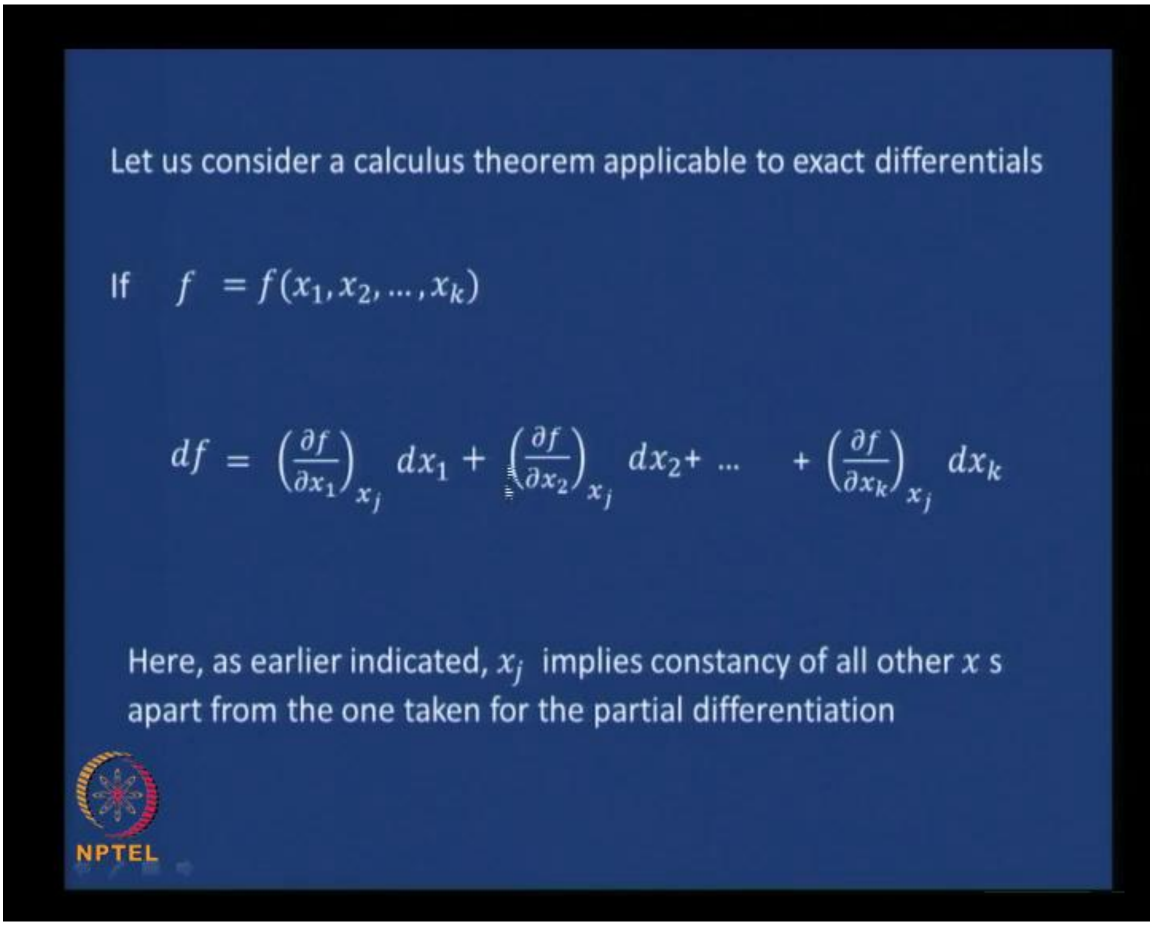

Let us consider a calculus theorem applicable to exact differentials

If $f = f(x_1, x_2, \ldots, x_k)$

$$df = \left(\frac{\partial f}{\partial x_1}\right)_{x_j} dx_1 + \left(\frac{\partial f}{\partial x_2}\right)_{x_j} dx_2 + \ldots + \left(\frac{\partial f}{\partial x_k}\right)_{x_j} dx_k$$

Here, as earlier indicated, x_j implies constancy of all other x s apart from the one taken for the partial differentiation

Then, we looked at Maxwell’s relations by applying a very simple theorem … or I should say, a basic theorem in mathematics called the reciprocity relationship, which is nothing but … if we are considering exact differentials – all thermodynamic variables can be written as exact differentials – and if it is a function of let us say x 1, x 2 and so on, till x k then d f can be written as, by a standard means dou f by dou x 1 x j d x 1 plus dou f dou x 2 at constant x j d x 2 and so on, till dou f dou x k at constant x j d x k. And if we … let say if each one of these are replaced by y’s say this one becomes y 1, this one becomes y 2 and so on.

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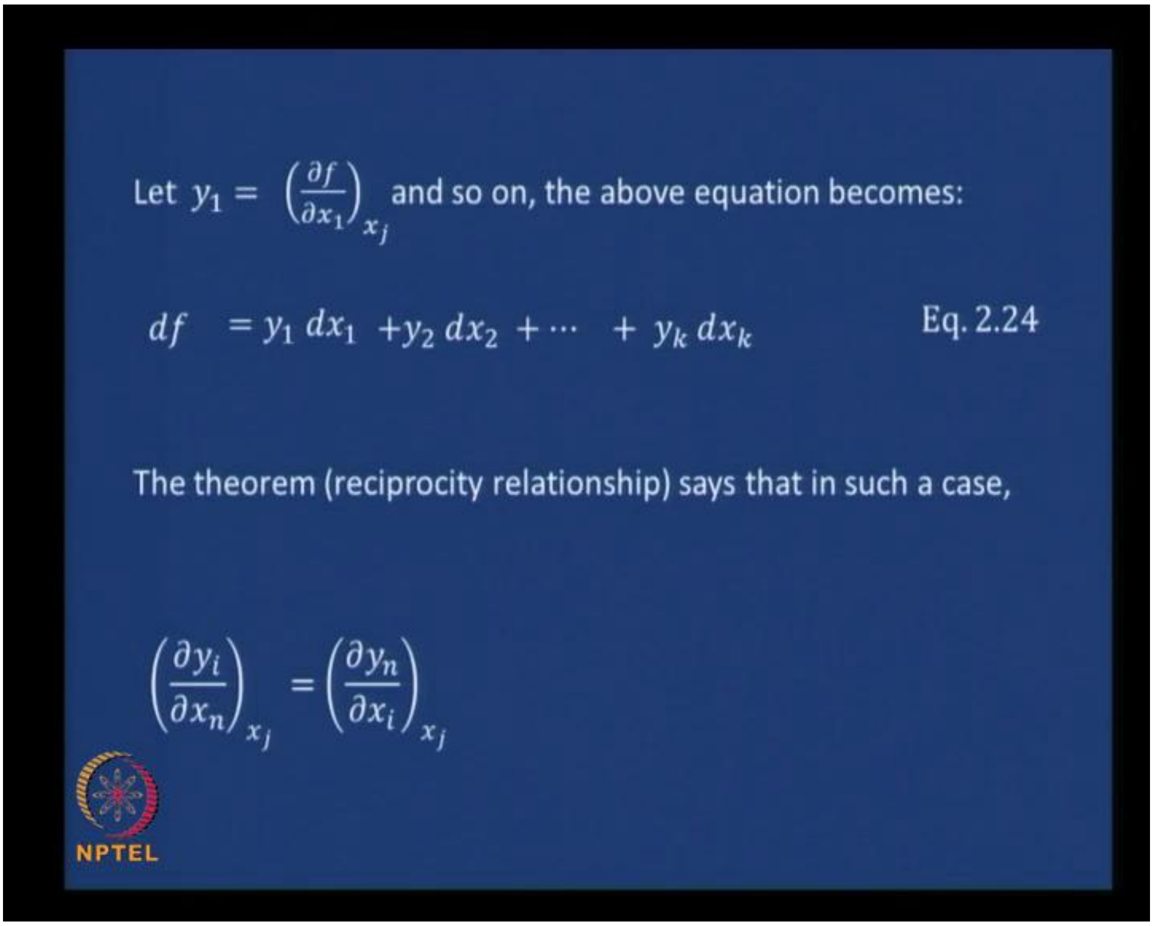

Let $y_1 = \left(\frac{\partial f}{\partial x_1}\right)_{x_j}$ and so on, the above equation becomes:

$$df = y_1\, dx_1 + y_2\, dx_2 + \cdots + y_k\, dx_k \qquad \text{Eq. 2.24}$$

The theorem (reciprocity relationship) says that in such a case,

$$\left(\frac{\partial y_i}{\partial x_n}\right)_{x_j} = \left(\frac{\partial y_n}{\partial x_i}\right)_{x_j}$$

Then the reciprocity relationship says that dou y i by dou x n, y could be anything here, x could be anything here, and x j with all other x is remaining constant equals dou y n dou x i at all other x j's … all other x j's remaining constant. If we apply this theorem to our expansions of differentials of thermodynamic functions U H A and G

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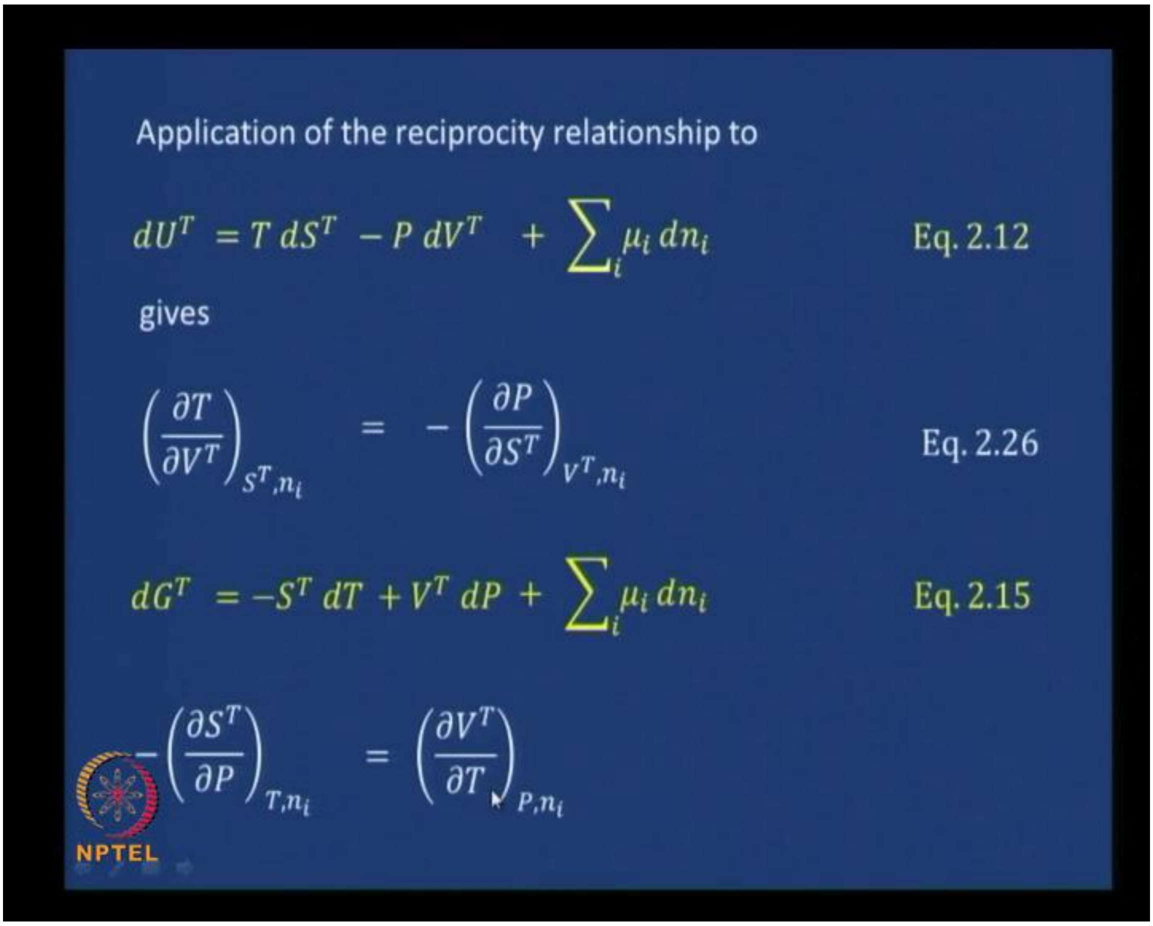

Application of the reciprocity relationship to

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.12}$$

gives

$$\left(\frac{\partial T}{\partial V^T}\right)_{S^T,n_i} = -\left(\frac{\partial P}{\partial S^T}\right)_{V^T,n_i} \qquad \text{Eq. 2.26}$$

$$dG^T = -S^T\,dT + V^T\,dP + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.15}$$

$$-\left(\frac{\partial S^T}{\partial P}\right)_{T,n_i} = \left(\frac{\partial V^T}{\partial T}\right)_{P,n_i}$$

Then we get dou T dou V T at constant S T n i equals minus dou P dou S T at constant V T n i dou S T dou P at constant T n i equals dou V T dou T at constant P n i.

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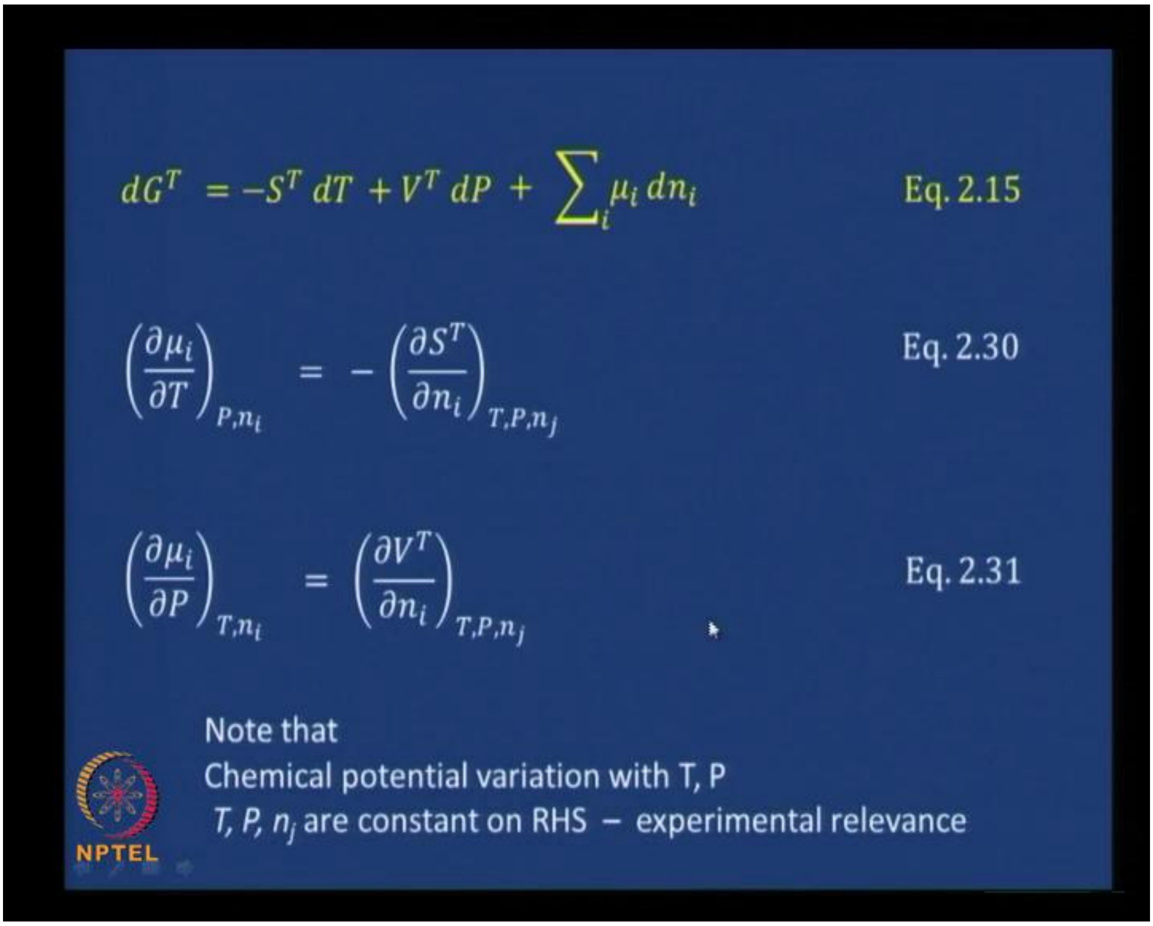

$$dG^T = -S^T\, dT + V^T\, dP + \sum_i \mu_i\, dn_i \qquad \text{Eq. 2.15}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} = -\left(\frac{\partial S^T}{\partial n_i}\right)_{T,P,n_j} \qquad \text{Eq. 2.30}$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} = \left(\frac{\partial V^T}{\partial n_i}\right)_{T,P,n_j} \qquad \text{Eq. 2.31}$$

Note that

Chemical potential variation with T, P

T, P, n_j are constant on RHS – experimental relevance

dou T dou P at constant S n i equals dou V T dou S T at constant P n i. And dou S T dou V T at constant T n i equals dou P dou T at constant V T n i. And there were already couple of others yes … yeah these two were interesting dou mu i dou T at constant P n i equals minus dou S T dou n i at constant T P n j. Similarly, this was by comparison of this and this; and by comparing this and this dou mu i dou P T n i equals dou V T dou n i at constant T P n j. So, this gives you variation of chemical potential with temperature, variation of chemical potential with pressure, which could turn out to be very useful. So these were the Maxwell’s relations that we considered and we had written these for a generic case, a general case consisting of … for a pure component consisting of … I am sorry, for a multicomponent system in a single phase.

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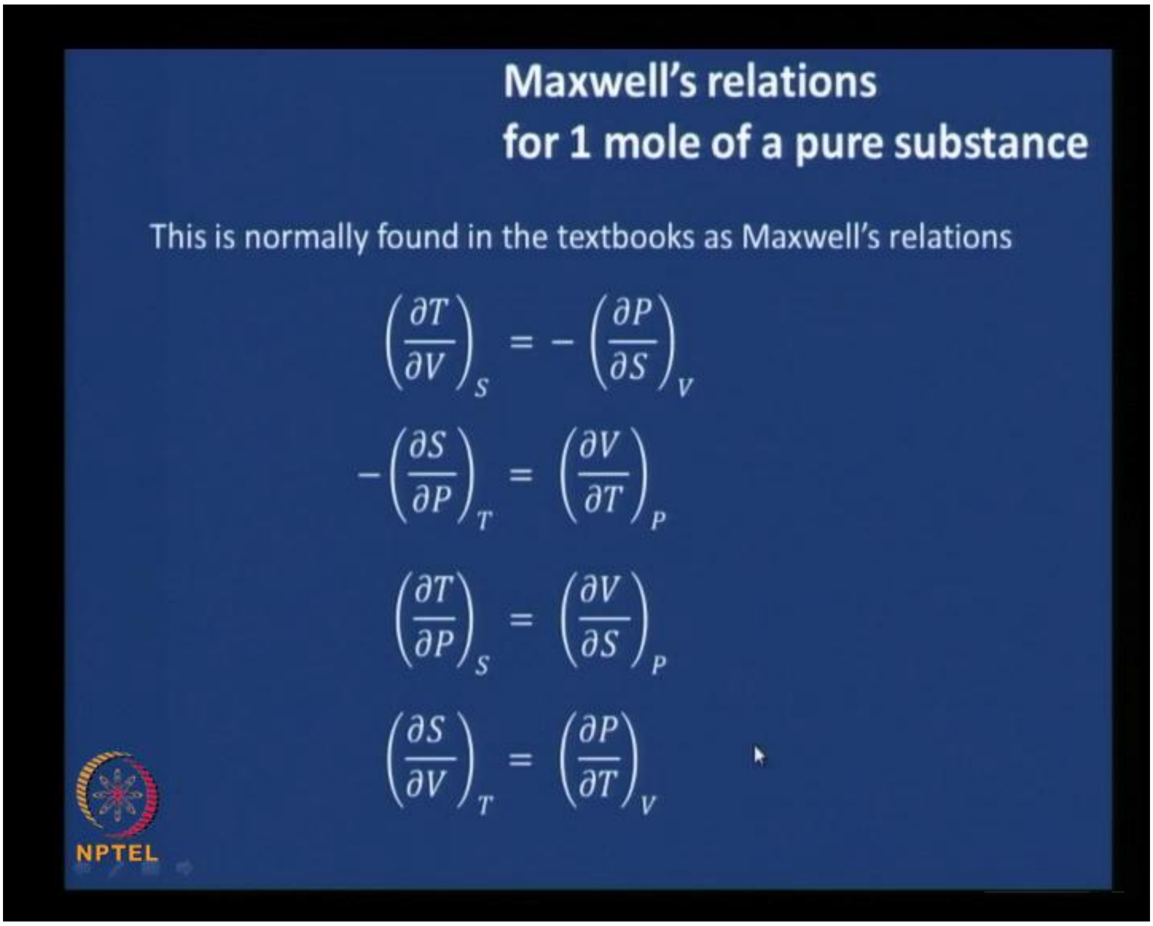

Maxwell's relations for 1 mole of a pure substance

This is normally found in the textbooks as Maxwell's relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Whereas, what is found typically in text books initially at least is for a single mole of the pure substance. And for that we could write the first four equations directly anything relevant to n will drop out therefore, dou T dou V at constant S equals minus dou P dou S at constant V, minus dou S dou P at constant T equals dou V dou T at constant P, dou T dou P at constant S equals dou V dou S at constant P, and dou S dou V at constant T equals dou P dou T at constant V.

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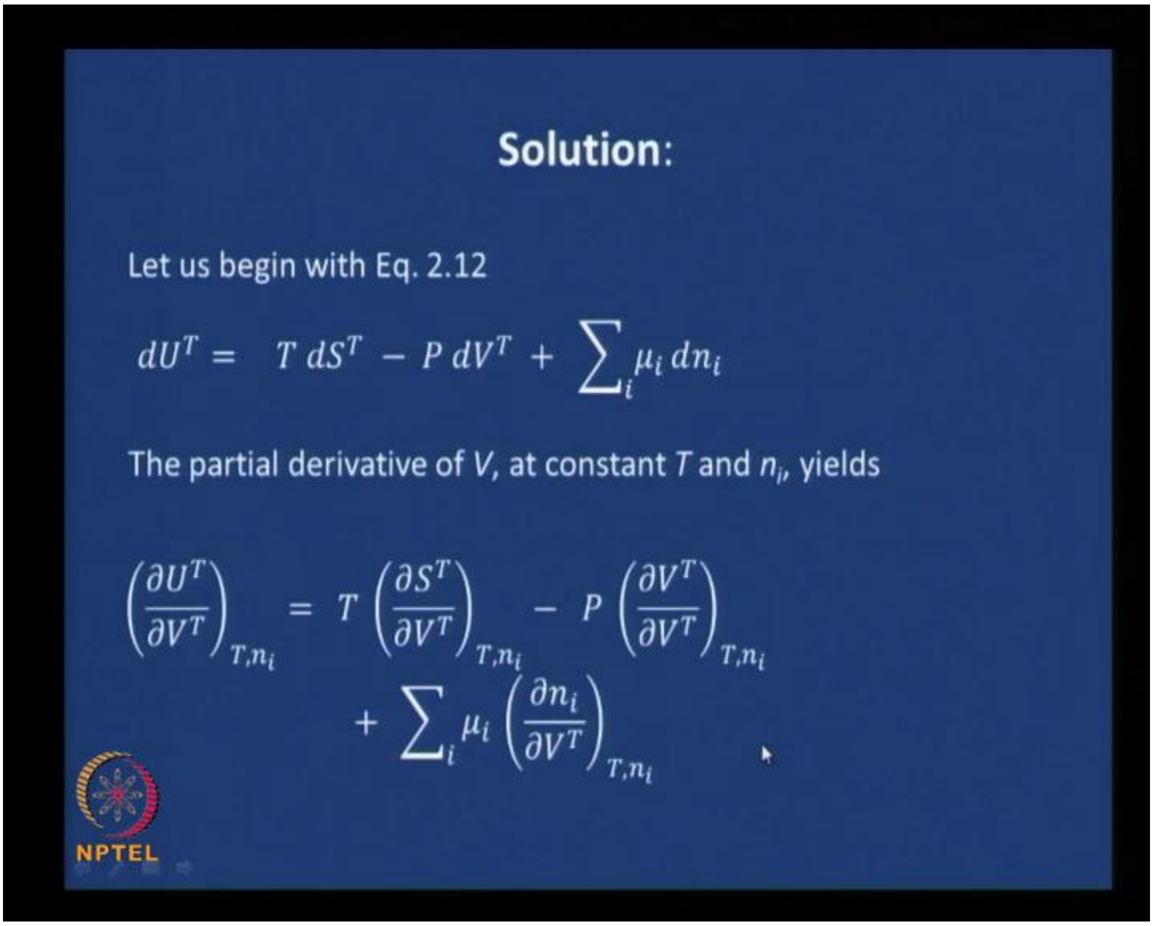

Solution:

Let us begin with Eq. 2.12

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i$$

The partial derivative of V, at constant T and n_i, yields

$$\left(\frac{\partial U^T}{\partial V^T}\right)_{T,n_i} = T\left(\frac{\partial S^T}{\partial V^T}\right)_{T,n_i} - P\left(\frac{\partial V^T}{\partial V^T}\right)_{T,n_i} + \sum_i \mu_i\left(\frac{\partial n_i}{\partial V^T}\right)_{T,n_i}$$

And then I think we went through some exercises, where we saw the use of these equations to solve some useful aspects. Please go through them again. And then we said that we brought in this idea of expressing difficult to measure thermodynamic variables in terms of easy to measure thermodynamic variables; easy to measure thermodynamic variables where temperature, pressure, volume either specific volume or the total volume.

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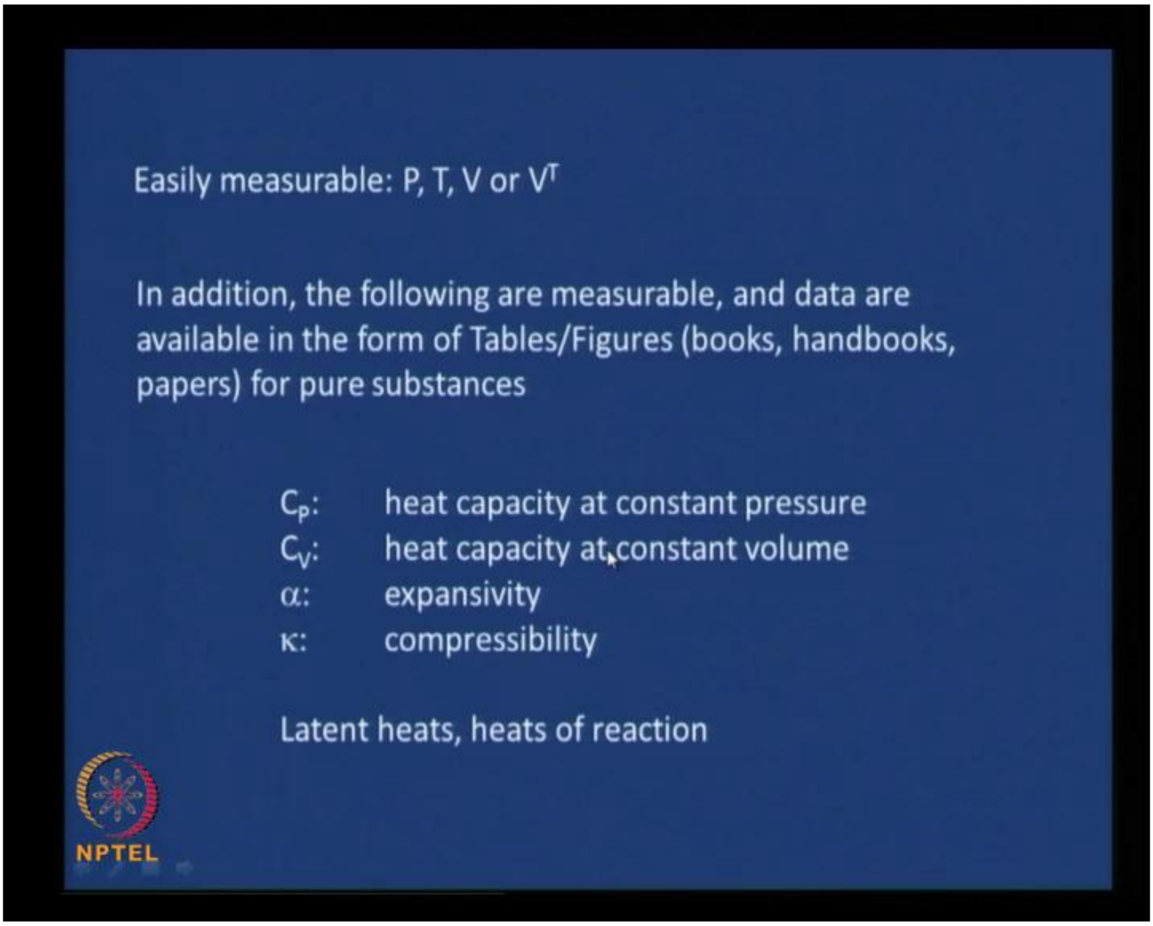

Easily measurable: P, T, V or V^T

In addition, the following are measurable, and data are available in the form of Tables/Figures (books, handbooks, papers) for pure substances

C_P: heat capacity at constant pressure
C_V: heat capacity at constant volume
α: expansivity
κ: compressibility

Latent heats, heats of reaction

Along with that we had added the heat capacity at constant pressure, heat capacity at constant volume expansivity, compressibility. And we are also said latent heats and heats of reaction, although we did not consider these in great detail, in this particular module. Since, the values of these are available if we have, if we can express the other thermodynamic variables in terms of these variables, it will be that much easier to evaluate the not so easy to measure thermodynamic variables.

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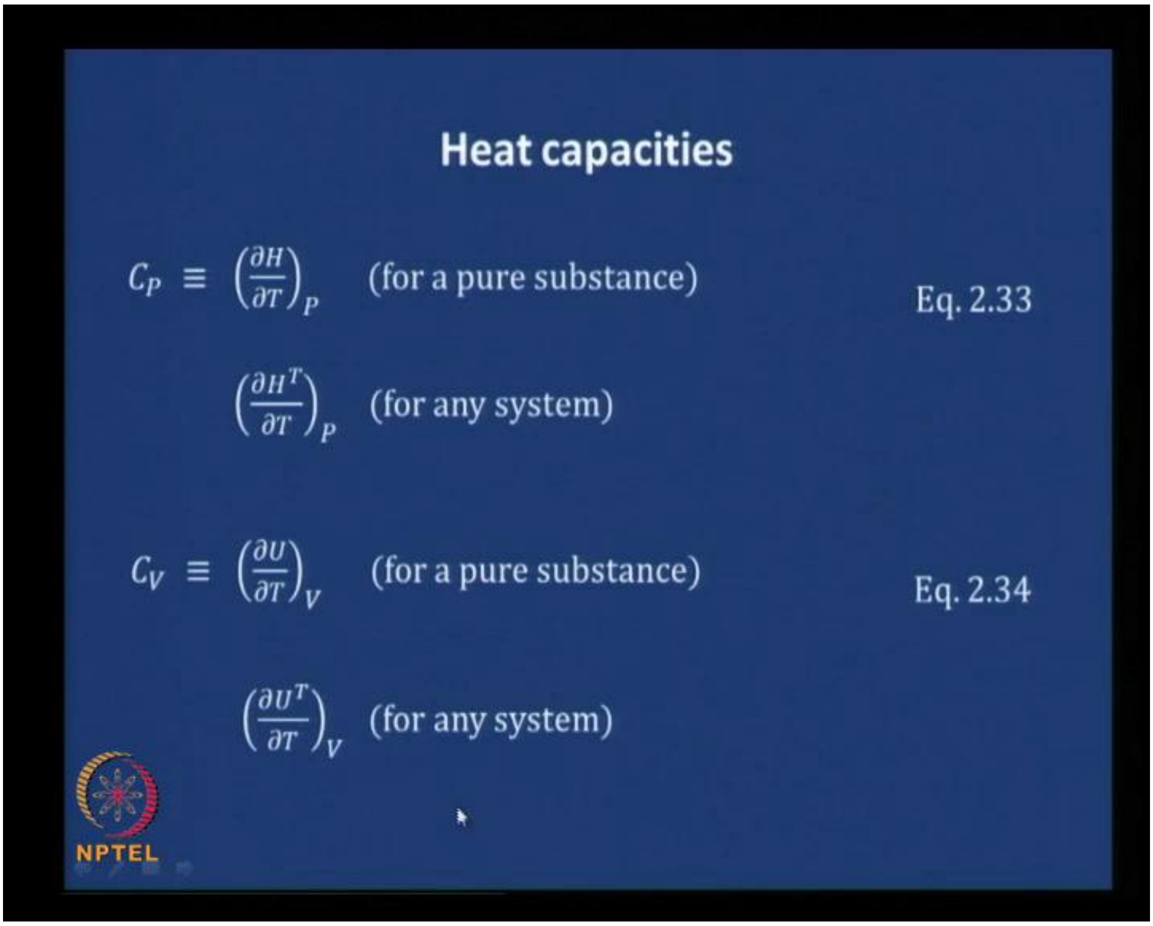

Heat capacities

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P \quad \text{(for a pure substance)} \qquad \text{Eq. 2.33}$$

$$\left(\frac{\partial H^T}{\partial T}\right)_P \quad \text{(for any system)}$$

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V \quad \text{(for a pure substance)} \qquad \text{Eq. 2.34}$$

$$\left(\frac{\partial U^T}{\partial T}\right)_V \quad \text{(for any system)}$$

And that is demonstrated here we had defined a heat capacity at constant pressure dou H dou T at P and either for a pure substance or for any system in terms of T. Similarly, this was specific heat at constant volume dou U dou T at constant V for a pure substance or the relevant other for any system.

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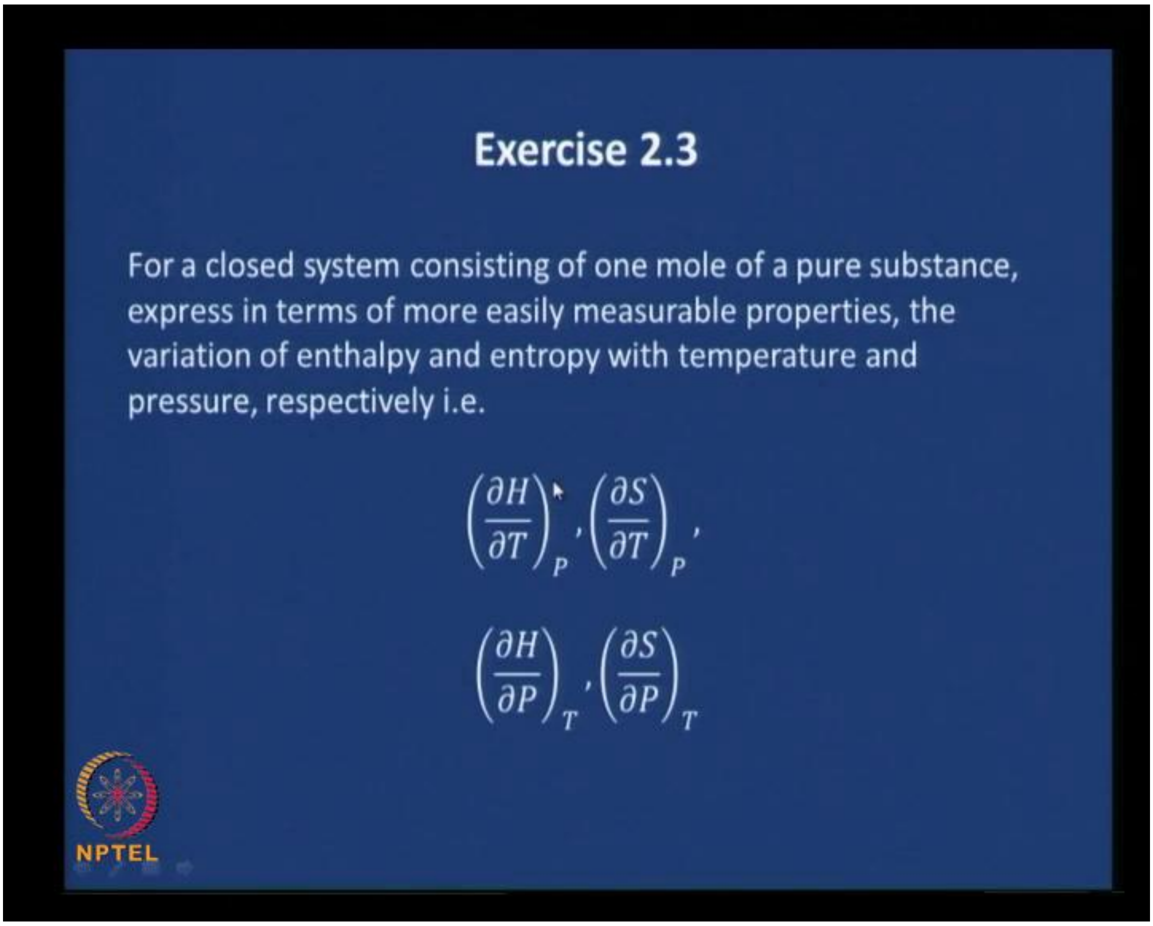

Exercise 2.3

For a closed system consisting of one mole of a pure substance, express in terms of more easily measurable properties, the variation of enthalpy and entropy with temperature and pressure, respectively i.e.

$$\left(\frac{\partial H}{\partial T}\right)_P, \left(\frac{\partial S}{\partial T}\right)_P,$$

$$\left(\frac{\partial H}{\partial P}\right)_T, \left(\frac{\partial S}{\partial P}\right)_T$$

And we saw … worked out an exercise by which we could actually express in terms of easy to measure variables, quantities such as these, dou H dou T at constant P, dou S dou T at constant P and so on.

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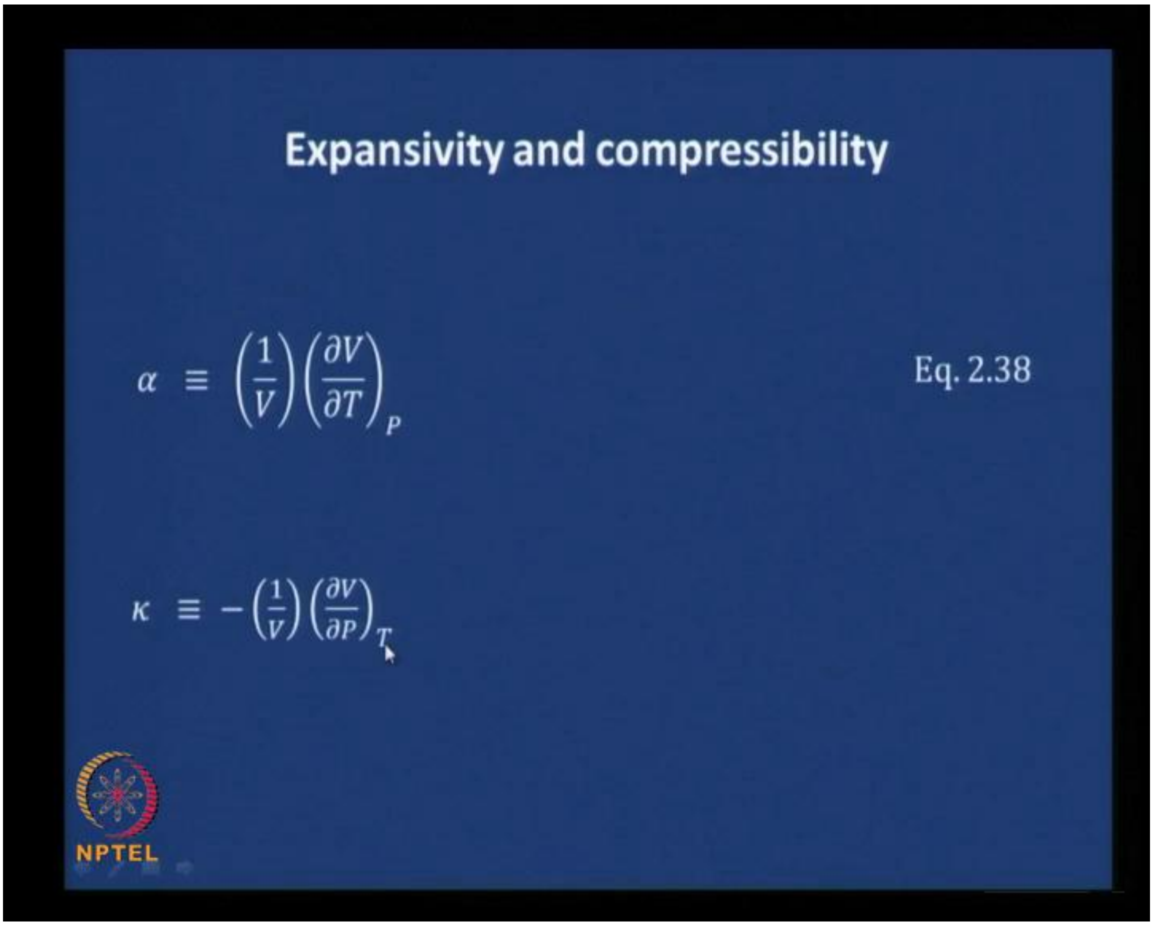

Expansivity and compressibility

$$\alpha \equiv \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{Eq. 2.38}$$

$$\kappa \equiv -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T$$

The other two variables, somewhat easy to measure for which values are available as stables and figures, as tables is the end of your text book even; alpha - expansivity defined as 1 by V dou V dou T at constant P, kappa - the compressibility defined as minus 1 by V dou V dou P at constant T, V in terms of T, V in terms of P are variation of volume … in the molar volume in terms of temperature at constant pressure, this is variation of molar volume in terms of pressure at constant temperature.

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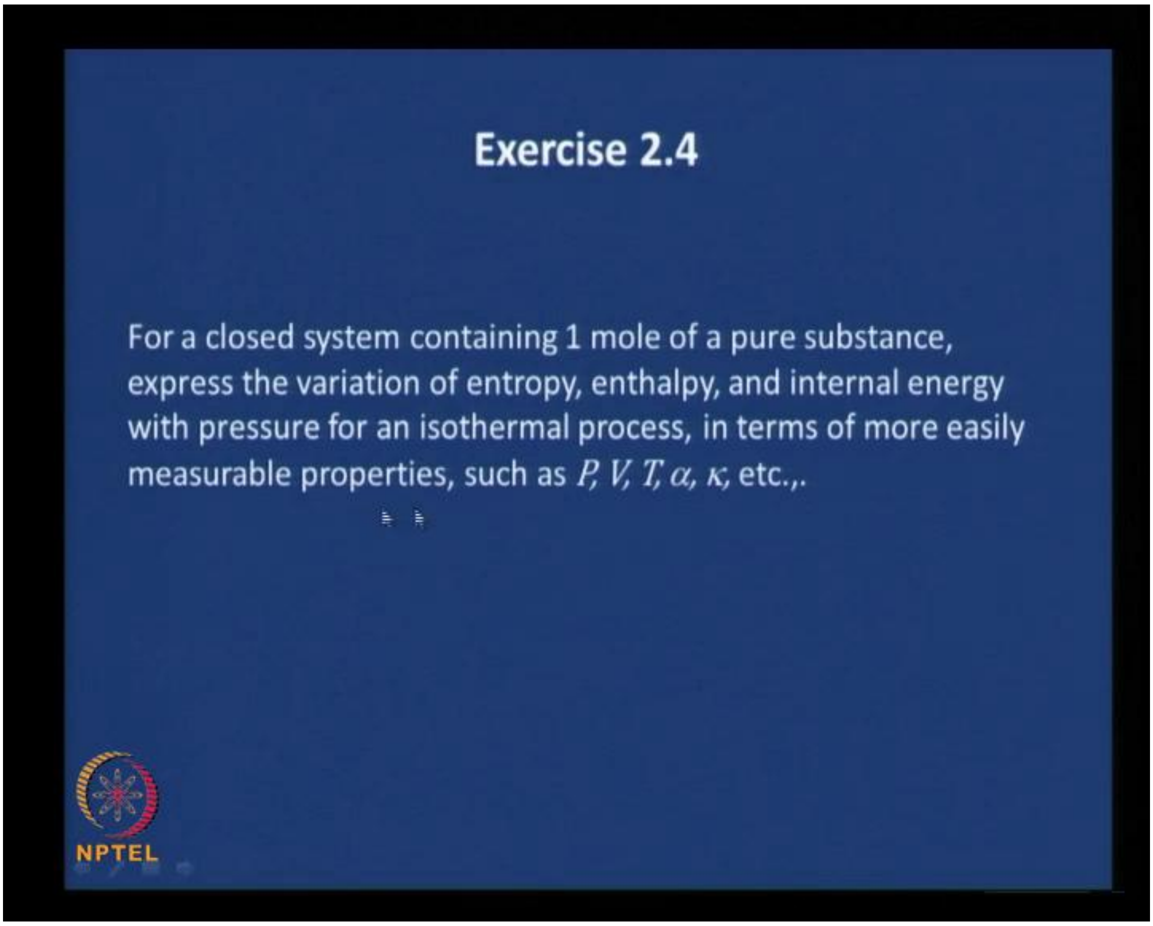

Exercise 2.4

For a closed system containing 1 mole of a pure substance, express the variation of entropy, enthalpy, and internal energy with pressure for an isothermal process, in terms of more easily measurable properties, such as P, V, T, α, κ, etc.,.

And we saw an exercise, which demonstrated the use of these variables; and finding out the not so easy to measure quantities in terms of these variables. We had utilized mathematics and manipulations quite a bit to do this.

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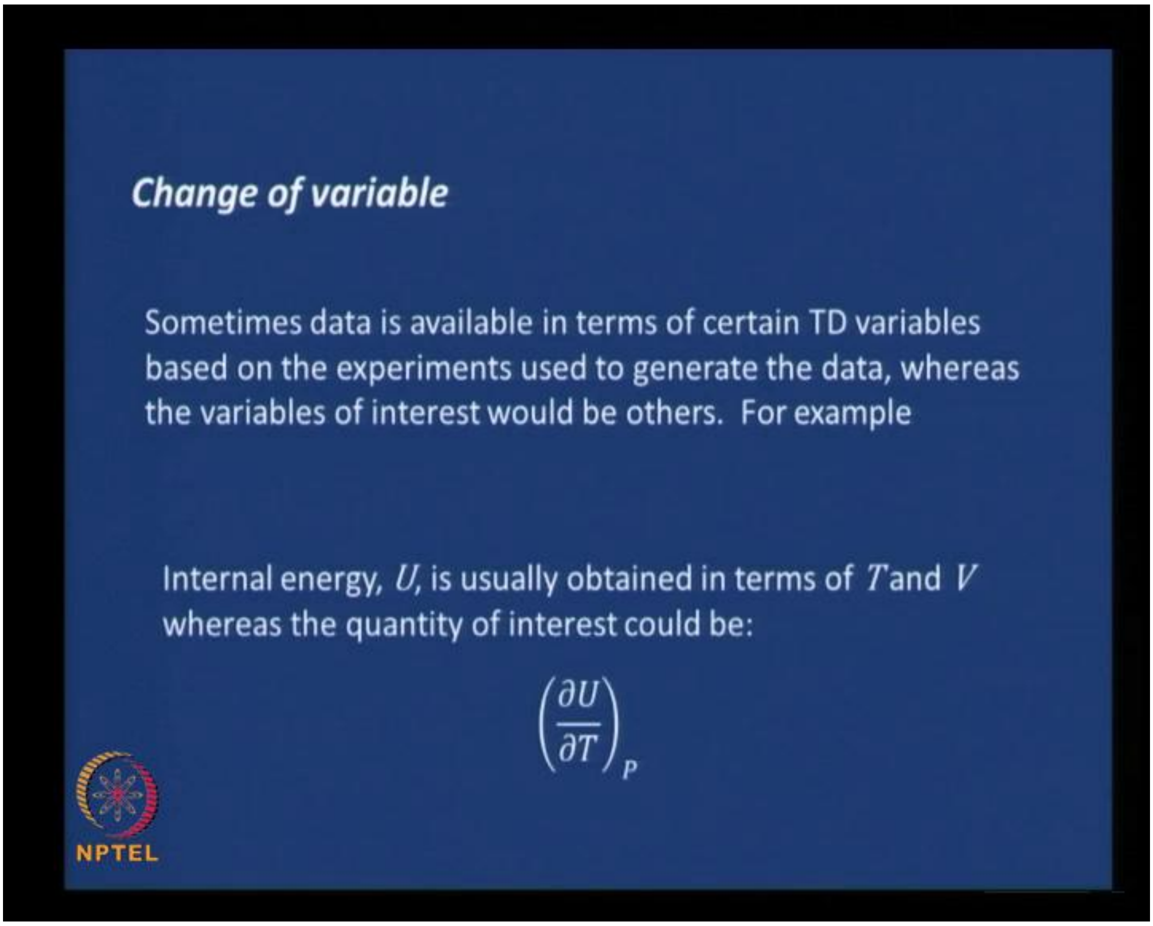

Change of variable

Sometimes data is available in terms of certain TD variables based on the experiments used to generate the data, whereas the variables of interest would be others. For example

Internal energy, U, is usually obtained in terms of T and V whereas the quantity of interest could be:

$$\left(\frac{\partial U}{\partial T}\right)_P$$

And then we introduced two useful mathematical manipulations; one was change of variable where you could express … where data could be available in terms of one set of variables; you would you would want the same information in terms of another set of variables. Therefore, you could use a mathematical technique called change of variable to do that.

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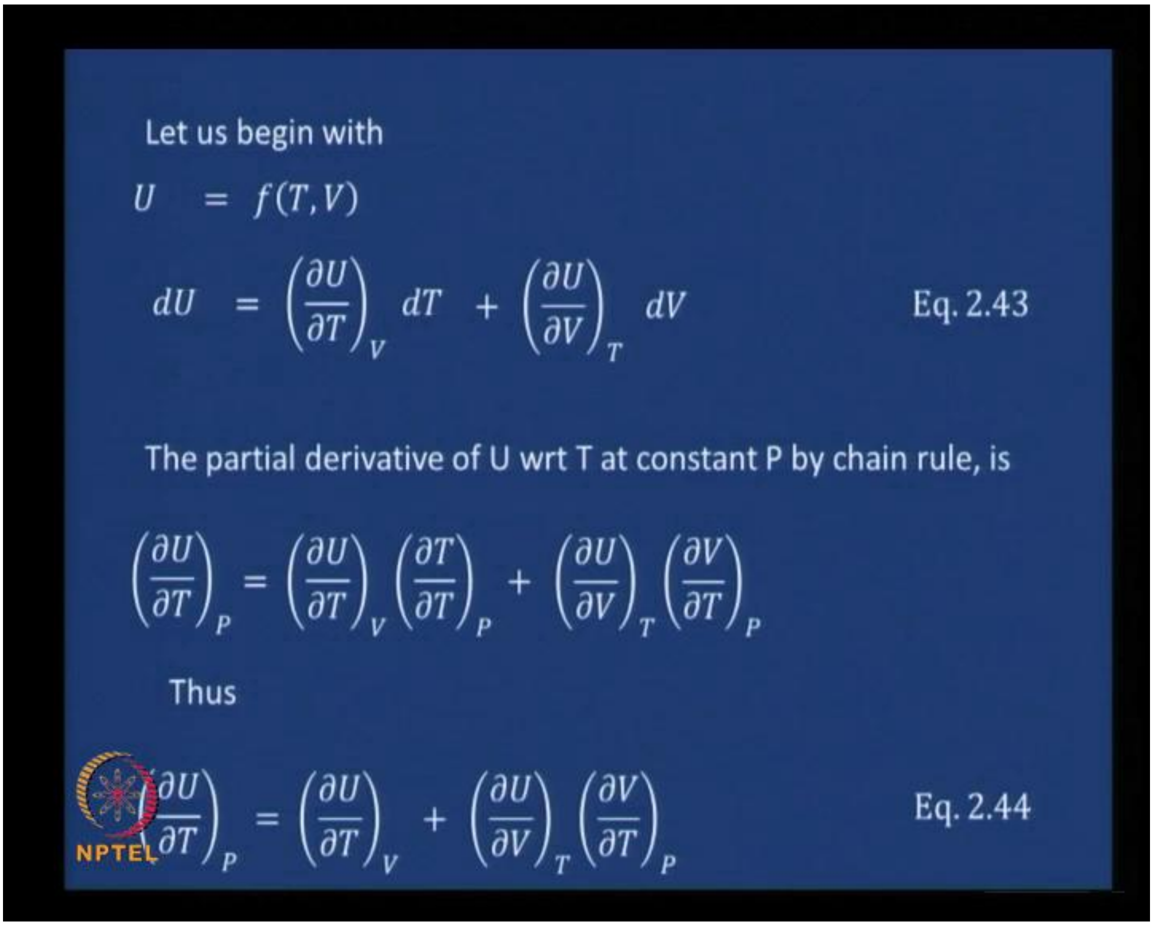

Let us begin with

$$U = f(T,V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \text{Eq. 2.43}$$

The partial derivative of U wrt T at constant P by chain rule, is

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Thus

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \qquad \text{Eq. 2.44}$$

We had given an example in terms of internal energy as a function of temperature and volume, which is typically known, and you wanted the terms of temperature and pressure, then you can do this manipulation and estimate the values.

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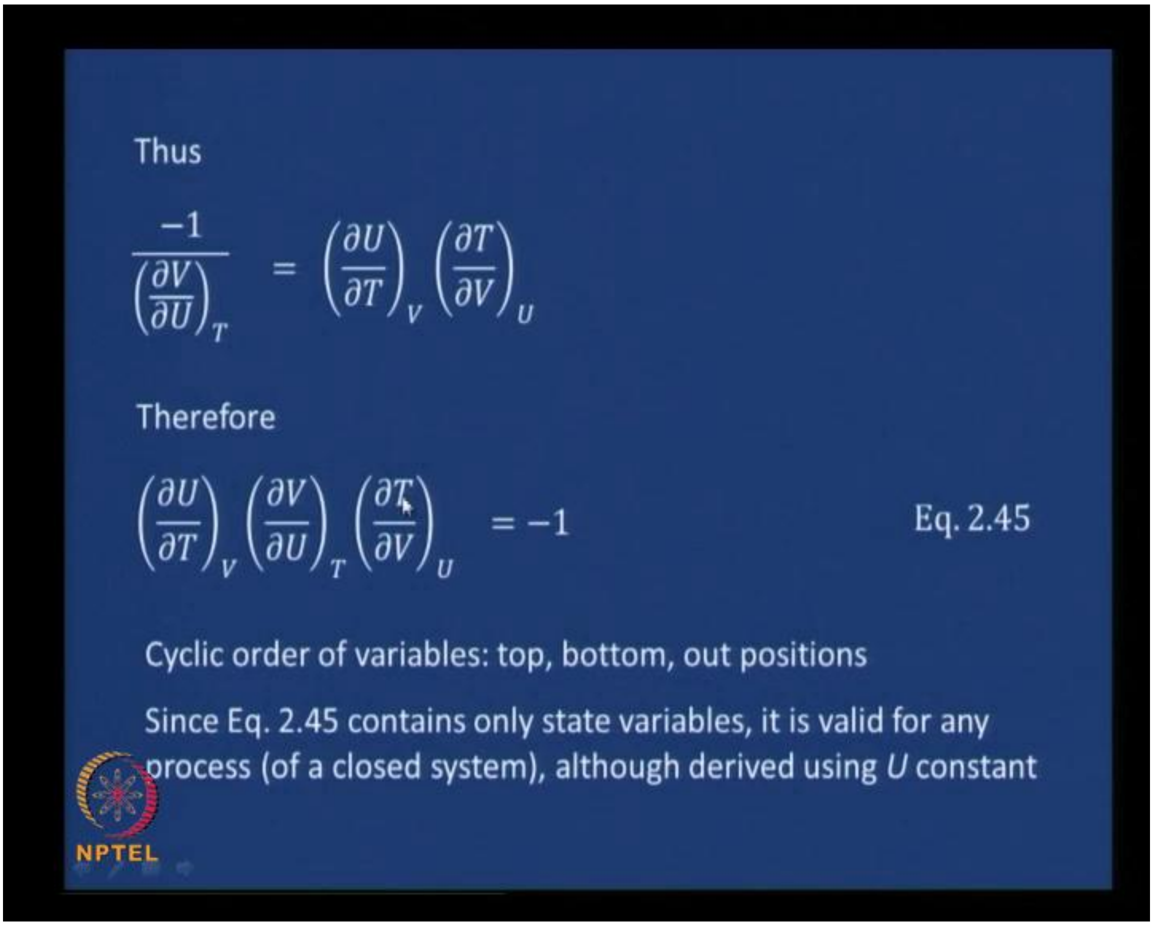

Thus

$$\frac{-1}{\left(\frac{\partial V}{\partial U}\right)_T} = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U$$

Therefore

$$\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial V}{\partial U}\right)_T \left(\frac{\partial T}{\partial V}\right)_U = -1 \qquad \text{Eq. 2.45}$$

Cyclic order of variables: top, bottom, out positions

Since Eq. 2.45 contains only state variables, it is valid for any process (of a closed system), although derived using *U* constant

Then we considered cyclic transformation, which is a very useful, as we saw. Let us go to the final expression we … derived it, which is a strength of this particular course – we derive everything. This was one cyclic transformation, and we had … let me write this down, and then point this out. We had this dou U dou T at constant V, dou V dou U at constant T, dou T dou V at constant U equals minus 1. We said that this follows a cyclic pattern, whatever isat the top goes to the bottom, whatever is at the bottom goes out, and whatever is whatever is outside goes to the top. And this can be written for many different thermodynamic variables, the cyclic transformation, equals minus 1. And we also applied that to some sort of a real life situation.

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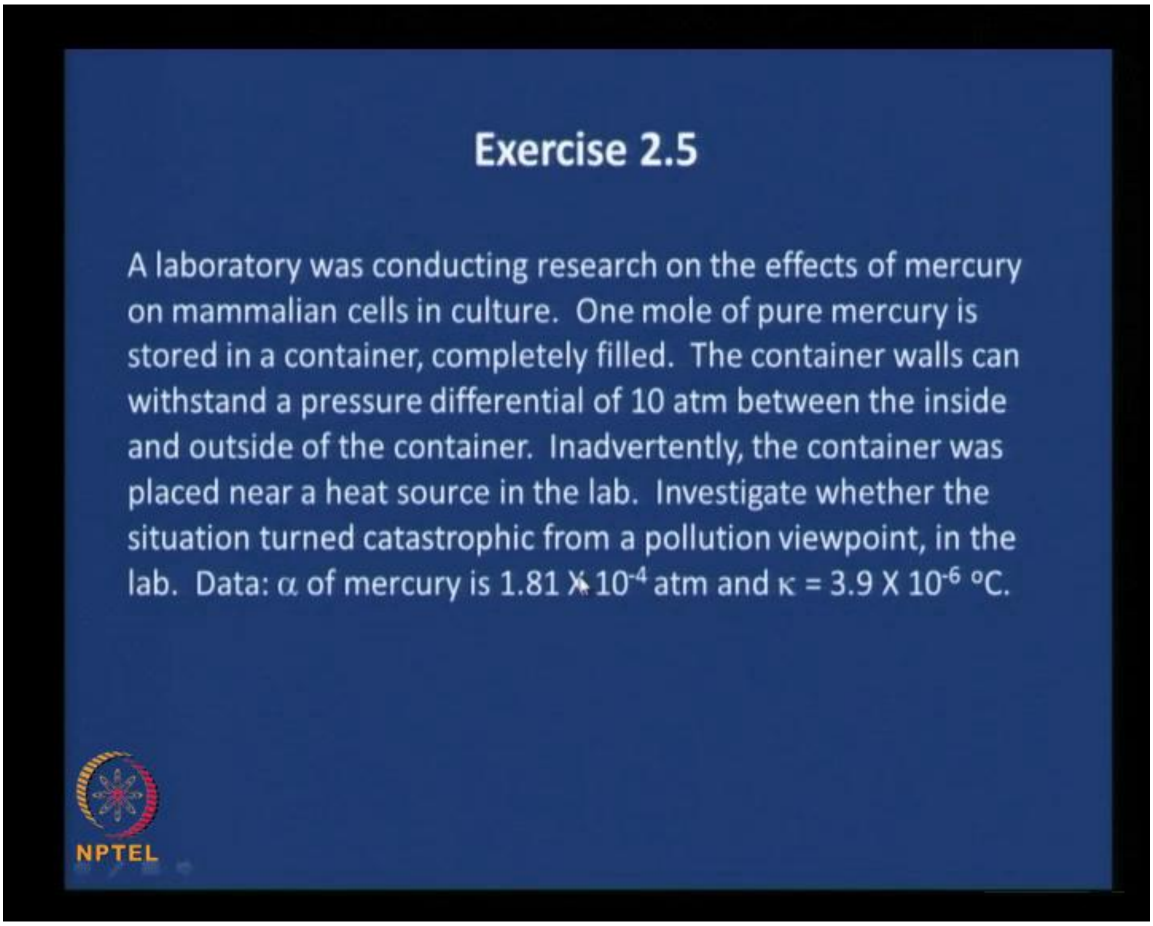

Exercise 2.5

A laboratory was conducting research on the effects of mercury on mammalian cells in culture. One mole of pure mercury is stored in a container, completely filled. The container walls can withstand a pressure differential of 10 atm between the inside and outside of the container. Inadvertently, the container was placed near a heat source in the lab. Investigate whether the situation turned catastrophic from a pollution viewpoint, in the lab. Data: α of mercury is 1.81 X 10^{-4} atm and κ = 3.9 X 10^{-6} °C.

Then for ease of use, I had gone ahead and shown you changes in enthalpy and entropy for 1 mole of a closed system in terms of changes in temperature and pressure; this is more of convenience not really very fundamental but useful nevertheless.

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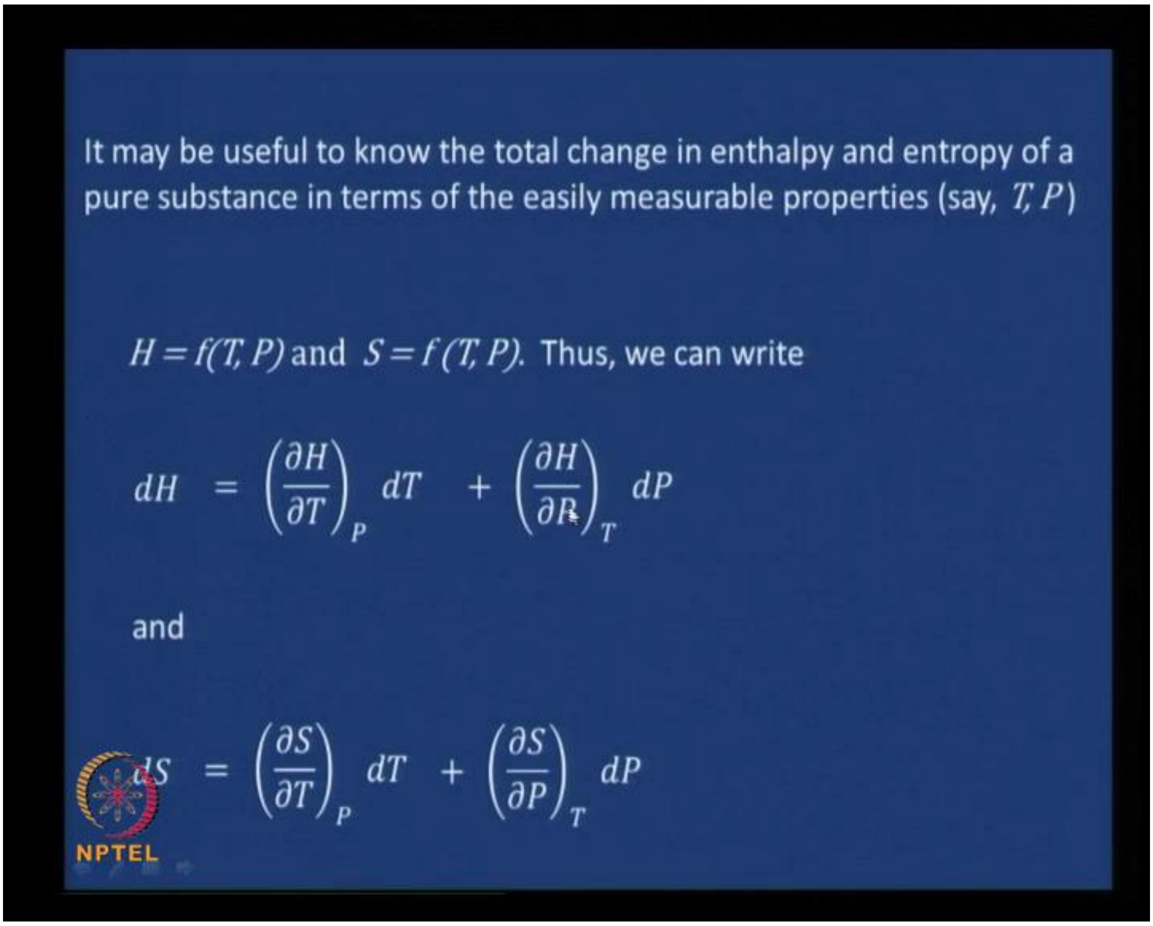

It may be useful to know the total change in enthalpy and entropy of a pure substance in terms of the easily measurable properties (say, T, P)

$H = f(T, P)$ and $S = f(T, P)$. Thus, we can write

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

and

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

d H was dou H dou T d T plus dou H dou P at constant T d P, and S was also written in terms of temperature and pressure. Then we got these in terms of easy to measure thermodynamic variables.

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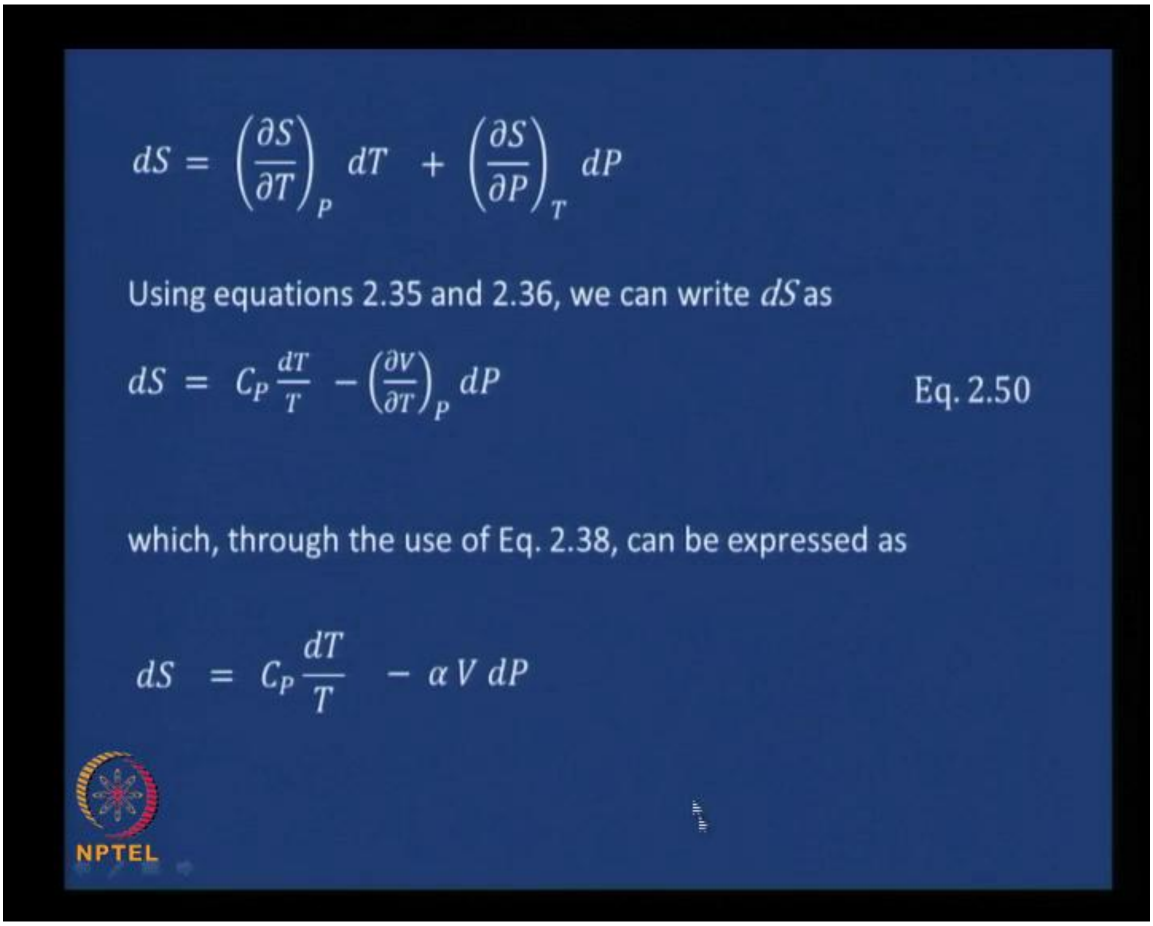

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Using equations 2.35 and 2.36, we can write dS as

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{Eq. 2.50}$$

which, through the use of Eq. 2.38, can be expressed as

$$dS = C_P \frac{dT}{T} - \alpha V \, dP$$

d H equals C P d T plus V into 1 minus alpha times T, d P; and d S we got in terms of C P by T D T minus alpha V times d P; we work out a problem.

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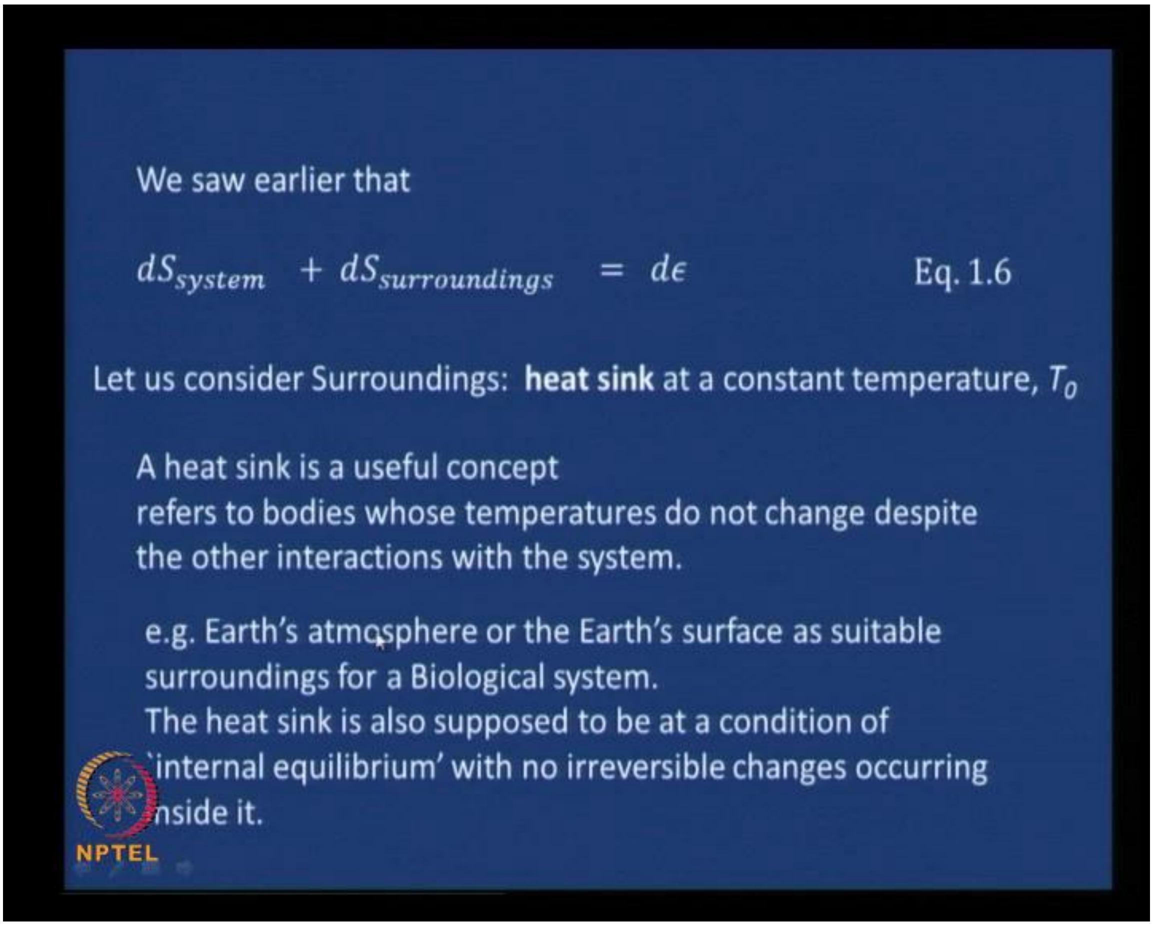

We saw earlier that

$dS_{system} + dS_{surroundings} = d\epsilon$ Eq. 1.6

Let us consider Surroundings: **heat sink** at a constant temperature, T_0

A heat sink is a useful concept
refers to bodies whose temperatures do not change despite
the other interactions with the system.

e.g. Earth’s atmosphere or the Earth’s surface as suitable
surroundings for a Biological system.
The heat sink is also supposed to be at a condition of
‘internal equilibrium’ with no irreversible changes occurring
inside it.

And today, we saw what maximum work was, and what lost work is. We started out from the very fundamentals first law and second law second law and first law – in that order. And we derived the expression for maximum work, and we had introduced the concept of something called a heat sink, which is useful concept which refers to bodies, whose temperatures do not change, despite the other interactions with the system. And we said that earth’s atmosphere or the earth’s surface is a suitable surrounding for … suitable surroundings for a biological system. Rather, which can be considered as a heat sink. And we also said that heat sink … there is internal equilibrium, and so on.

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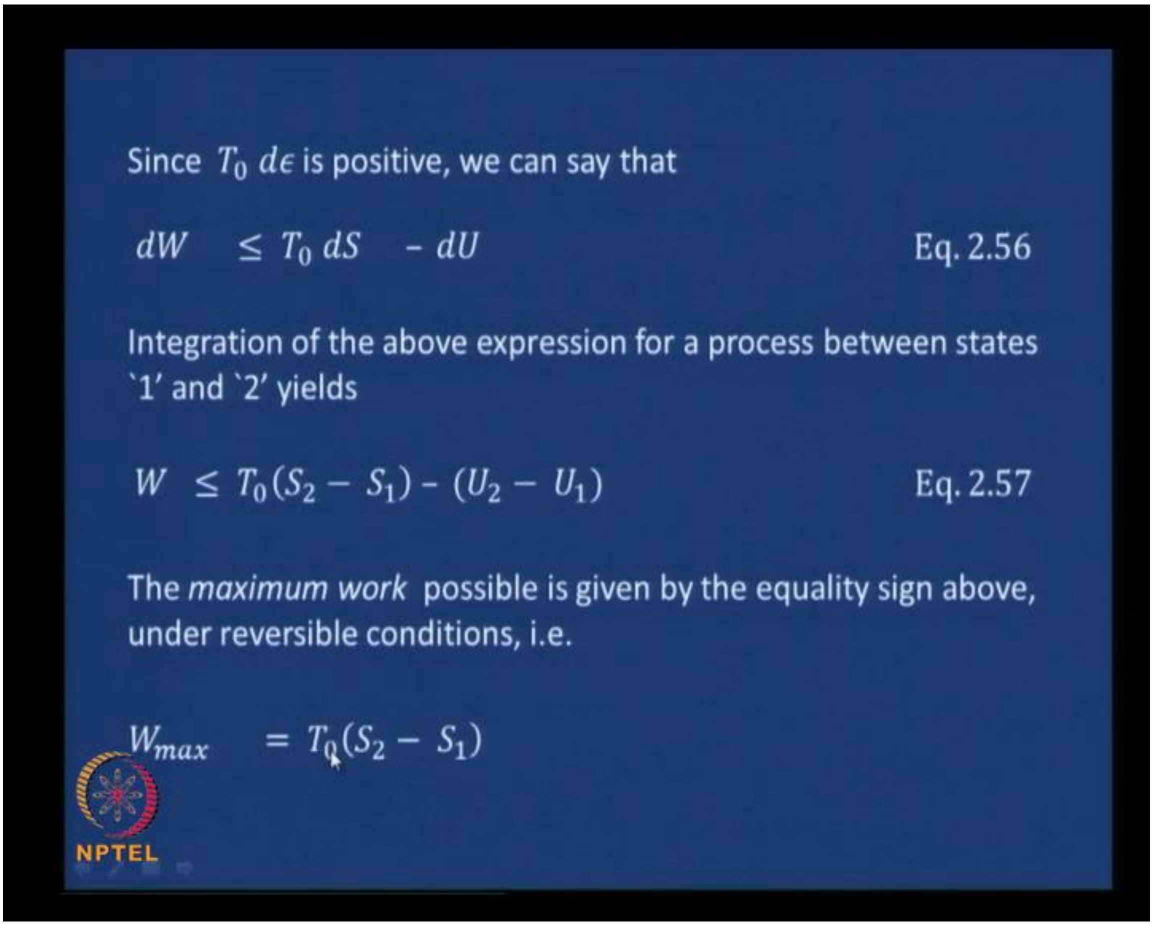

Since $T_0 \, d\epsilon$ is positive, we can say that

$$dW \le T_0 \, dS - dU$$

Eq. 2.56

Integration of the above expression for a process between states `1' and `2' yields

$$W \le T_0(S_2 - S_1) - (U_2 - U_1)$$

Eq. 2.57

The *maximum work* possible is given by the equality sign above, under reversible conditions, i.e.

$$W_{max} = T_0(S_2 - S_1)$$

And we arrived at an expression for maximum work which was W max equals T 0, the sink or the surroundings temperature times S 2 minus S 1 minus U 2 minus U 1.

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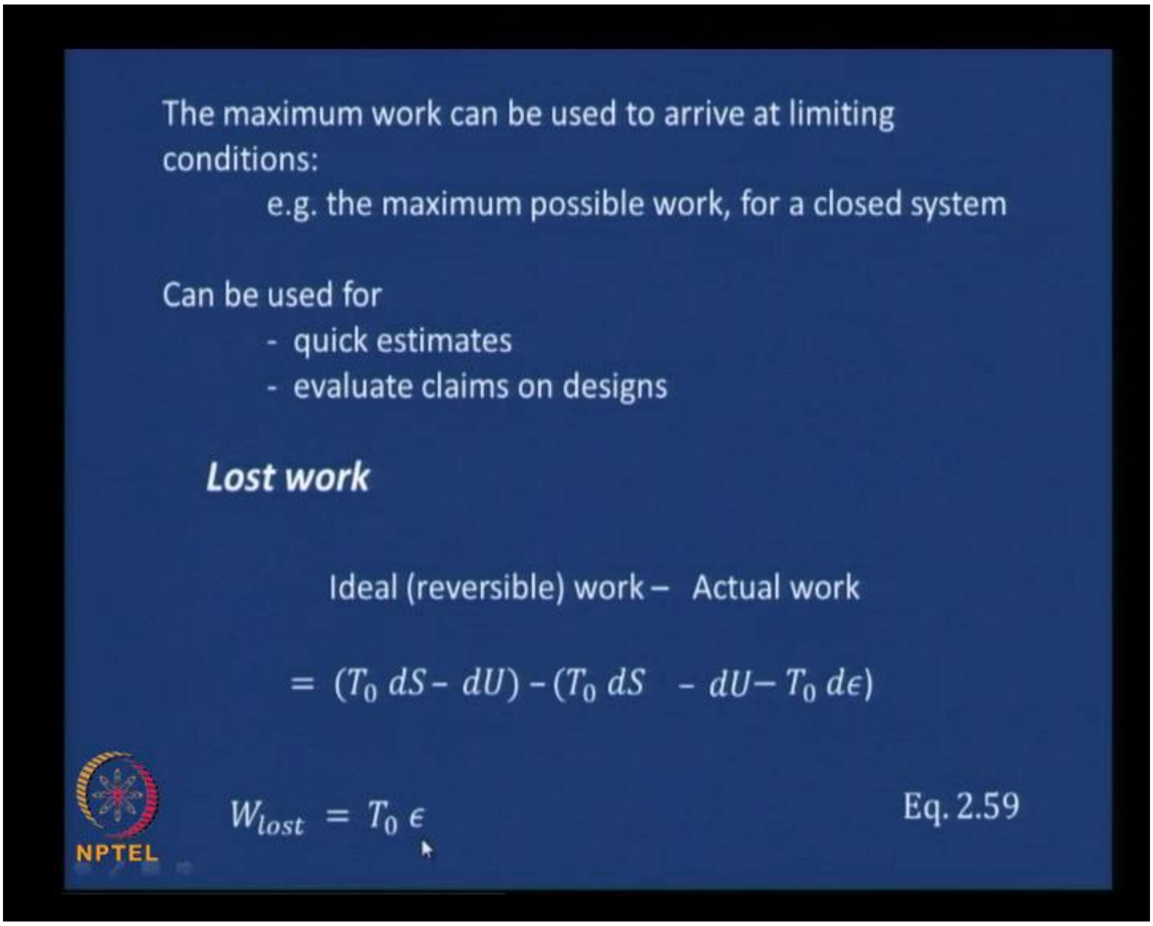

The maximum work can be used to arrive at limiting conditions:

e.g. the maximum possible work, for a closed system

Can be used for

- quick estimates
- evaluate claims on designs

Lost work

Ideal (reversible) work – Actual work

$$= (T_0\, dS - dU) - (T_0\, dS \;\; - dU - T_0\, d\epsilon)$$

$$W_{lost} = T_0\, \epsilon \qquad \text{Eq. 2.59}$$

And we said the maximum work can be used to arrive at limiting conditions, the maximum possible work for a closed system for example, or can also be used for quick estimates or to evaluate claims on designs or to start design itself. And then we arrived at an expression for lost work as equal to T 0 times the entropy created epsilon. That was a review of whatever we have done in this module. … So far we have considered closed systems, and in the next class we will look at open systems.