Lecture - 4
Additional Thermodynamic Functions

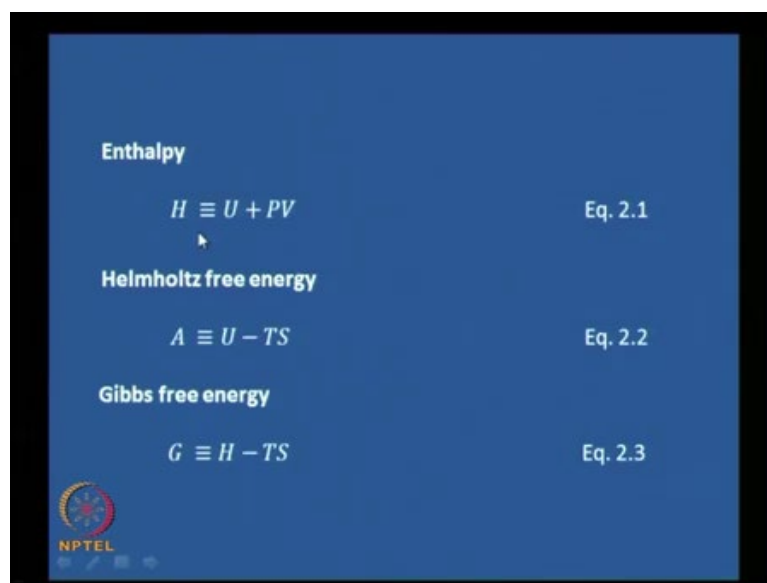**(Refer Slide Time: 00:28)**

Welcome!

Module 2 will look at additional useful thermodynamic functions. We also saw during the review that the consequences of the 0th law – if you … recall what 0th law was: if X is an thermal equilibrium with Z, Y, another body, in thermal equilibrium with Z, i.e. separately, they are in thermal equilibrium with Z, then they are in thermal equilibrium with each other. And what came out as a consequence of the 0th law, was temperature.

What came out of the first law, which essentially related the energy … energies that cross the system boundaries to the energy changes that happen inside the system; that give rise to the first law. And the consequence of the first law was the thermodynamic property called internal energy, which is represented by the symbol U.

The consequence of the second law, which essentially gave us a means for the directionality of the process is – what we saw in the review was the thermodynamic quantity entropy, which is represented by the letter S.

These three thermodynamics properties T, U and S along with pressure and volume … specific volume are actually sufficient to describe the thermodynamics or thermodynamic relationships of any system. Nevertheless, for ease of use in certain applications, say processes at constant temperature or at constant pressure or at constant specific volume and so on and so forth, we could derive certain other thermodynamic variables that will turn out be easier to use. And let us define some other … some such thermodynamic properties next.

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The first thermodynamic property that we are going to … additional thermodynamic property that we are going to introduce is called the enthalpy, which is represented by the letter H; and it is defined as the sum of U and (P x V);

$$H \equiv U + PV$$

U is internal energy, … pressure and the specific volume. The equation numbers are being given here; please keep noting them, and we may keep referring back to the equations from time to time.

The next additional thermodynamic relationship, which would be useful is called the Helmholtz free energy, represented by the letter A, and defined as U - internal energy minus the product of temperature and entropy.
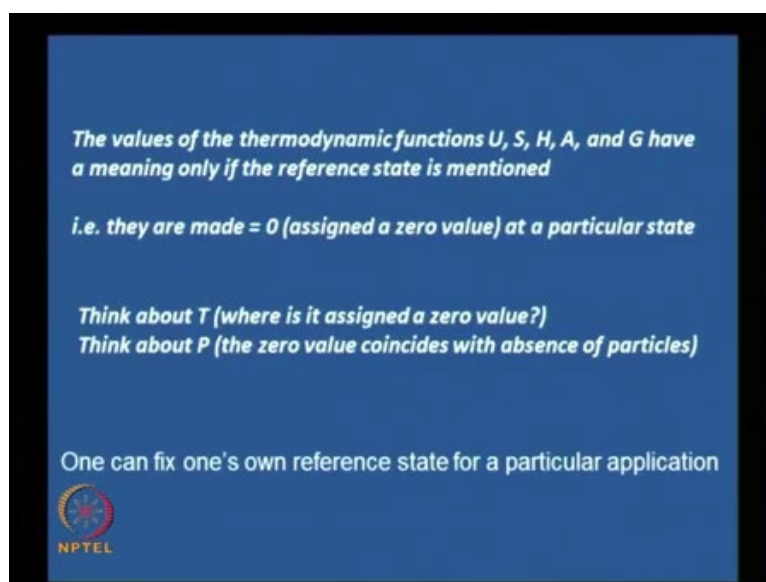
$$A \equiv U - TS$$

The third additional property is Gibbs free energy, represented by the letter G, and defined as enthalpy minus the product of temperature and entropy.

$$G \equiv H - TS$$

These are all definitions. Essentially the starting point; enthalpy is U plus P V, Helmholtz free energy is U minus T S, and Gibbs free energy is H minus T S.

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The values of the thermodynamic functions, we have given you a pneumonic here; U, S, H, A and G; internal energy, entropy, enthalpy, Helmholtz free energy and Gibbs free energy – they all have a meaning, only if the reference state is mentioned. Remember these are the variables that we are defining, and they all have a meaning only if a certain reference status mentioned. What I mean by that is you need to have a certain state, at which these variables are assigned a zero value. To understand this reference state a little better, let us think about, where T is assigned a zero value, a temperature in Kelvin is assigned a zero value? It will be very interesting.

I will give you a couple of minutes to think about it; at the same time, also think about, where P is assigned a zero value?

I will give you the answer here, the zero value actually coincides with the absence of particles;

complete vacuum is given a zero value for pressure, a variable that we already know.

I would like you to think about, where the temperature is assigned a zero value?

Also what is nice about thermodynamics is one can fix once own reference state for any particular application. The reference state could be different for different applications, but once we fix the reference state, we need to stick to it for that particular application.

When we look at processes, by processes we meant the locus of the thermodynamic variables as it moves from state 1 … as the system moves from state 1 to state 2. The locus of the states … right. What are the states? It is a set of thermodynamic properties that would describe a particular state.

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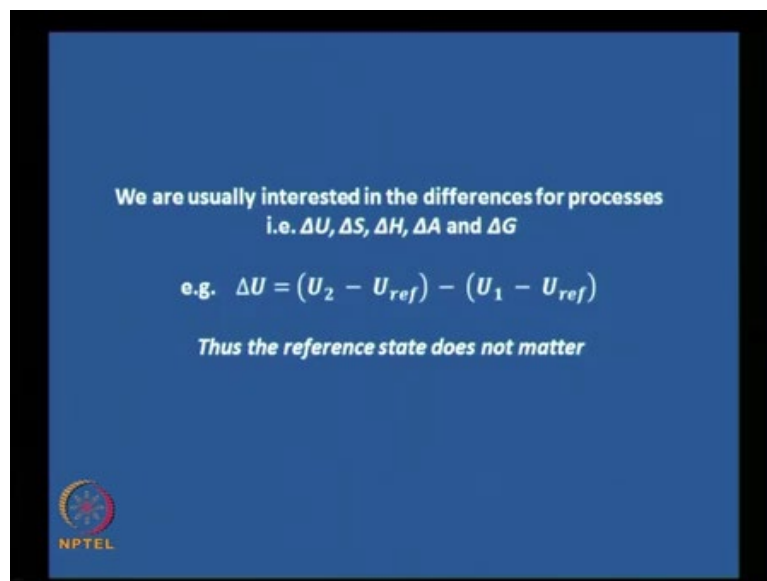
When we look at a process, we are usually interested in the differences in the thermodynamic variables such as delta U, delta U is the value of the internal energy at state two, the final state minus the value of the internal energy at initial state. Similarly delta S change in entropy, delta H change in enthalpy, delta A change in Helmholtz free energy, and delta G change in Gibbs free energy. Mathematically, for example,

$$\Delta U = \left(U_2 - U_{ref}\right) - \left(U_1 - U_{ref}\right)$$

Therefore, the U reference and U reference will cancel out, whenever we look … whenever we are looking for delta U. And, thus whatever we choose as a reference state, will not really matter in the calculations.

This aspect gives us the freedom to choose whatever reference state we want in terms of processes. Not just that even when we are looking at actual properties, even when we are looking at a process, that is, we need a reference state for a value to make sense … for a thermodynamic variable value to make sense, because we need to assign the value of 0 at some point.

What we will do in this particular course is, once we look at a … look at a concept, I will give you a small exercise. And, I will also give you some time to work it out during the lecture itself, which I find is very effective. And the first such exercise is here or probably, we did one in the module 1.

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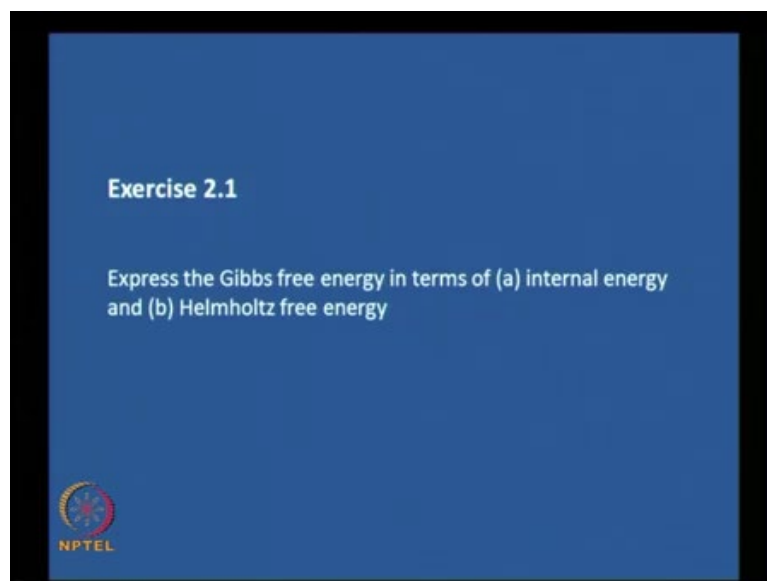
This is the first exercise in module 2. What I would like you to do is, express the Gibbs free energy G in terms of the internal energy U, and in terms of the Helmholtz free energy A. You have 10 minutes; this is reasonably straight forward exercise, but since you are looking at this for the first time, you may take some time. Therefore, take about 10 minutes and work out this. After 10 minutes, I will give you the solution, but do make an effort to work through this, because these are the exercises that will help you feel comfortable with the material, which will help you understand the material lot better. And at the end of the course, you would be a lot more prepared, and be ready to attack real problems, in addition to the exercises that would be discussed
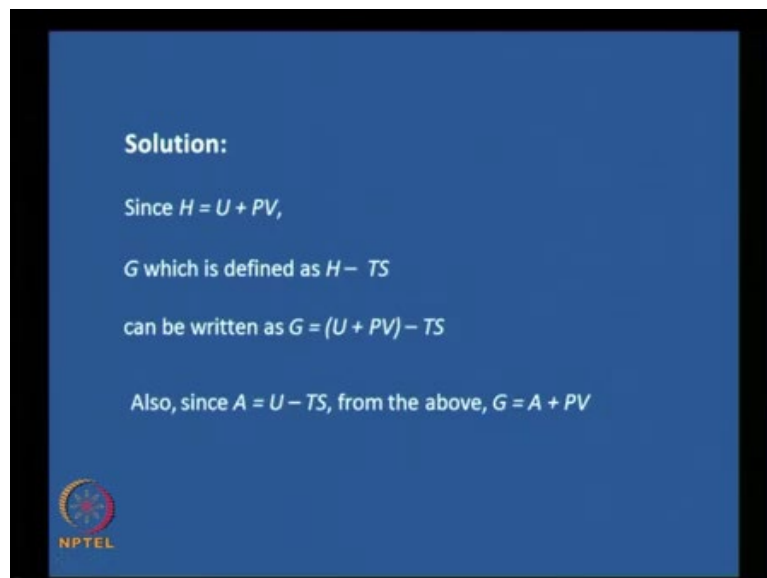
separately. Please go ahead.

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Please pause the video here. You can pause it as long as you want. The time mentioned is only a guideline

Now let us look at the solution.

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Solution:

Since $H = U + PV$,

G which is defined as $H - TS$

can be written as $G = (U + PV) - TS$

Also, since $A = U - TS$, from the above, $G = A + PV$

We know that H equals U plus (P V) by the definition.

$$H = U + PV$$

And therefore,

G which is defined as *H – TS*

you can go back to the equation; take a look at it. G, which is defined as H minus (T S) can be written as you replace this H with this definition U plus (P V), and therefore you have U plus (P V) minus (T S).

$$G = (U + PV) - TS$$

That is the relationship that we are looking for the first part. Also since A the Helmholtz free energy is defined as U minus T S, we also know that A equals U minus (T S).
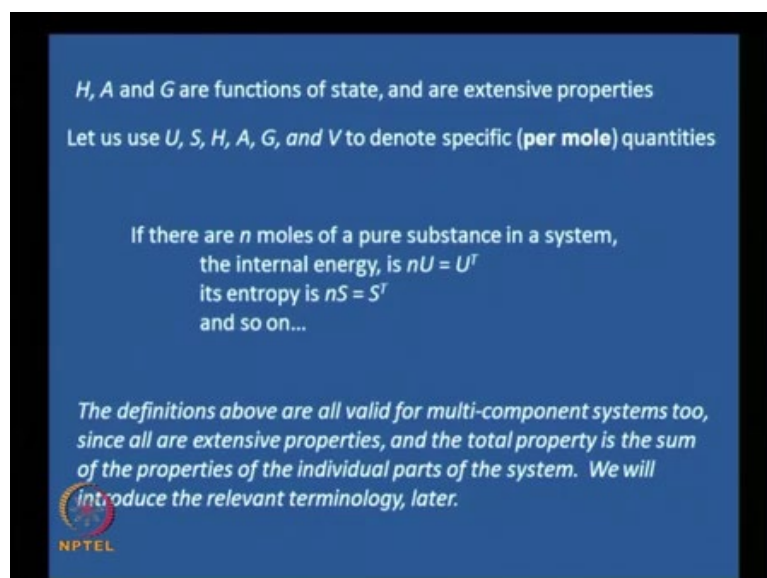
$$A = U - TS$$

And from here, we know that U plus (P V) minus (T S) is G, and we can combine this and this U minus (T S) as A, and write G as A plus (P V).

$$G = A + PV$$

These are the two relationships that we were looking for, in that particular exercise.

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H - Enthalpy, A - Helmholtz free energy and G - Gibbs free energy are functions of state, which means their value depends only on the state of a particular system. And these are extensive properties, by which we meant that the amount … the value of the property depends on the amount of material that is present; and these properties are also additive with the amount of material. If you putting more material, the value of H will go up, the value of A will go up, the value of G will go up, and so on. In this particular course, let us use these symbols, U, capital U, capital S, capital H, capital A, capital G, and capital V to denote specific or per mole quantities. You take a value, and we normalize it or we divide it by the number of moles or the mass of the system, then we get a specific quantity. In this particular case, we are going to use U, S, H, A, G and V to denote per mole quantities or mole specific quantities.

But not all systems will be composed of one mole; therefore, we need to have a terminology, which will address different number of moles if present in a system.

Let us first consider a pure substance, and let us say that there are n moles of the pure substance in this system. Then since we know that the internal energy is an extensive property, the total internal energy would be n times U, the number of moles times the internal energy per mole, which can also be represented as U superscript T, $nU = U^T$, which is what we are going to use in this course. The entropy would be n times S, which can be represented as S^T, $nS = S^T$, and so on and so forth.

Note that we started with per mole quantities; these symbols referring to per mole quantities, and we said that if there are n moles of a pure substance, we would use (n U), (n S) and so on to represent the total internal energy, the total entropy, and so on. These definitions that we have used here can also be used for multi component system, where you have different moles of different species present, because they are extensive properties; the total property is a sum of the properties of individual parts of a system. When it becomes relevant, we will introduce or we will take this terminology a little further.

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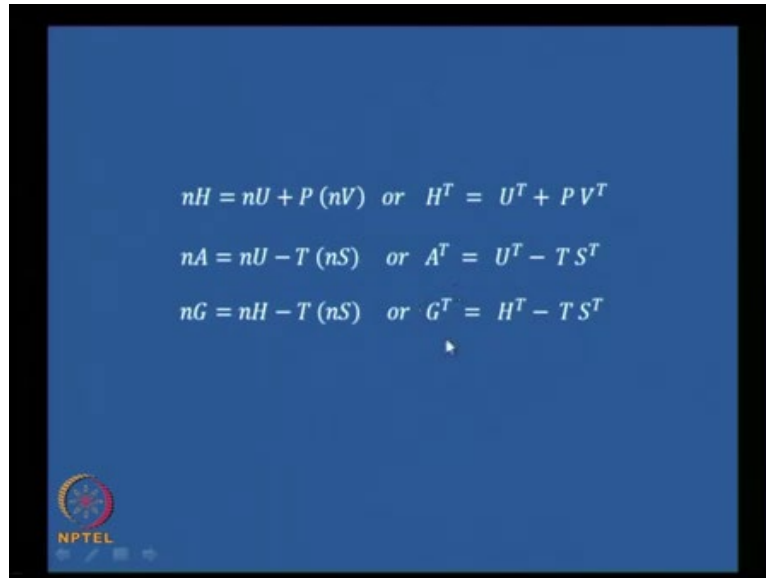
Therefore, we can write

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

Remember H equals U plus P V, and this is for n moles of a pure component. Since we are using H^T to represent (n H), U^T to represent (n U), and P times V^T. Note that P is an intrinsic quantity. Even if the number of the moles of a system are different, as long as it is internally at equilibrium, and so on … in most cases that is, we will have P to be the same throughout the system. Since it is an intrinsic quantity, it is not going to depend on the number of moles. So P times (n V), V is going to depend upon the number of moles. And therefore, (n H) equals (n U) plus P times of (n V) or H^T equals U^T plus P times V^T. Similarly, (n A) equals (n U) minus T times (n S). This directly comes from A equals U minus (T S), the definition of Helmholtz free energy.

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

Since, we have represented (n A) as A^T and so on; A^T equals U^T minus T times (S T); T stands here separately, because T is also an intrinsic variable, which is not dependent on the amount of substance that is present. And (n G) equals (n H) minus T times (n S) or G^T, the total Gibbs free energy of a system equals total enthalpy of the system, H^T, minus T times the total entropy of the system S^T.

$$nG = nH - T(nS) \quad or \quad G^T = H^T - TS^T$$
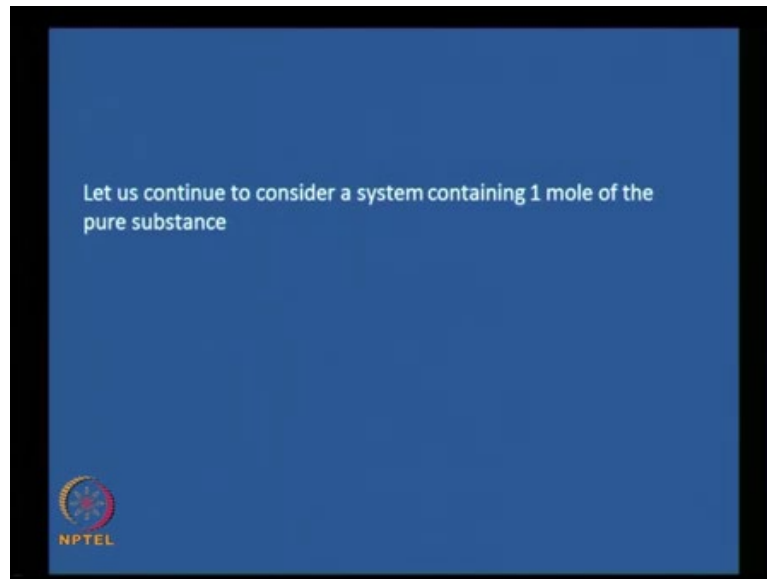
Now let us continue to consider a system containing 1 mole of the pure substance. This is for initial development; it is easier to understand things for one mole, and then we can generalize. Also, unless otherwise specified … or in other words, we will specify things when things become different, we are going to consider a closed system. To recall what a closed system is, we know that a closed system is something that can exchange energy with … its environment, whereas it cannot exchange mass with this environment.

See you in the next class.