Thermodynamics (Classical) for Biological Systems

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Module No. #02
Additional Thermodynamic Functions
Lecture No. #02
Need for Analysis
Additional Thermodynamics Functions
State and Path Variables

Let us begin today by looking at the need for analysis of a biological system. As we all know, engineers are typically introduced to the information or the knowledge; they understand the knowledge toward analysis and design of the relevant system. Taking that view for biological engineering, we can look at getting the information first, understanding that, and using that to analyse and design systems of biological importance. To understand this a little better, let us first consider bio-process industry; you know in the bio process industry, products of biological relevance or using biological systems are made for the use of mankind.

In a biological process, it is easy to imagine or let us imagine that a liquid needs to be moved from one place, A, to another place, B; typically this movement occurs through pipes of different sizes. And deciding on what pump to use to move the fluid from say point A to point B is a very important design aspect in a bioprocess. As you will learn later, or … you may have already done fluid flow courses; if you have done fluid flow courses, you would already know this. One of the important aspects in deciding what pump size to use is to know the type of flow that happens in the pipe. There are two major types of flows; one is the laminar flow, in which it is an ordered flow in layers, and the other is a turbulent flow, where pockets of fluid tumble over each other and flow through a pipe.

The power requirement depends on what kind of flow we have in the pipe, to move the fluid from one place to another. Let us say that we do not have any information about whether the flow is laminar or turbulent; and let us say that we do not really know how to decide whether the flow is laminar and turbulent. The way to go about, or the approach would be to visualize a flow in some fashion with itself it is quite difficult; you need transparent pipes and so on and so forth, which may not be suitable for all fluids that are applicable. We need to look at, what all aspects would change the type of flow involved. Do experiments one after another to figure out, what kind of flow exists in a particular piping system. We don't even know what decides the kind of flow that happens in a piping system.

Luckily for us, a lot of work has been done earlier starting from the 1900s, ~~1908~~/1883 Reynolds did the flow visualization experiment, where he, as a result of which, we know that there are four parameters that decide whether the flow is going to be laminar or turbulent. The four parameters are the density of the fluid, the velocity of the fluid, the diameter of the pipe through which the fluid is flowing, and the viscosity of the fluid. These four parameters decide on the nature of flow. Suppose we did not know this at all, we did not have to do experiments one after another may be thousands of experiments to arrive at the same information.

Somebody has done this, somebody has used the intuition to come up with, what you may already know as a Reynolds number, which is nothing but the (density x velocity x diameter)/ (viscosity), or (rho v D)/mu. In a pipe flow situation, you may know that if the Reynolds number is less than about 2000 or 2100, the flow is going to be laminar, otherwise the flow is ... or above 4000 let us say, in a pipe, the flow is going to be turbulent. What information we could get out of thousands and thousands of experiments, is all compressed into this one single beautiful relationship; it is called the Reynolds number. And that is the advantage in analysing something, and coming up with a useful parameter.

We are in the process of understanding biological systems better, and we are nowhere near that level of completeness in the case of a biological system.

Let me present something else to you to understand the need for analysis, so that the design can be much better. And, also analysis has its own benefits in terms of better and better understanding of the system. To do that, I am going to read out parts of a paper, this paper is titled, `Can a biologist fix a radio or what I learnt studying apoptosis'. This paper is authored by a person called Yuri Lazebnik. He is from the Cold Spring Harbour lab, which is a very prestigious lab. This was published in Cancer cell in 2002. I am going to read out parts of a paper.

Yuri Lazebnik considers the transistor radio, something that existed a long time ago, but I guess, he relates to that a lot better. He considers a transistor radio to be equivalent to the cell. The particular aspect that he is going to consider is an old broken transistor radio. And the objective here is to fix the radio or to repair the radio, so that it functions properly. Therefore, we can consider this radio to be equivalent to a human being or a cell to begin with; something is wrong, and we need to fix it, so that it functions properly.

Reading from this paper, some parts of it: conceptually, a radio functions similarly to a signal transaction path way in a cell, in that both convert a signal from one form to into another. A radio converts electromagnetic waves into sound waves. The radio has about a 100 various components such as resistors, capacitors and transistors, which is comparable to the number of molecules in a reasonably complex signal transduction pathway in a cell. If we take a biological way of looking at things right now, the way a biologist would look at it; he gives the … some of the ways, in which a biologist would approach this problem.

Biologist as – I am talking of a classical experimental biologist. I am sure a lot of people work in interdisciplinary areas now, but a classical biologist will approach it a certain way.

And eventually all the components will be catalogued; connections between them will be described, and the consequences of removing each component or their combinations will be documented. Can the information that we accumulated help us to repair the radio? The information itself is wonderful; it helps, it gives a lot more inside into what is happening, but is it good enough to repair the radio, is the question. The answer is, most likely no; unless there is a certain piece of luck that helps you in setting right the radio or the cell.

Coming back to this paper, yet we know with near certainty that an engineer could fix the radio; what makes the difference? I think it is the languages that these two groups use. It is common knowledge that the human brain can keep track of only so many variables. It is also common experience that once the number of components in a system reaches a certain threshold understanding the system without formal analytical tools requires geniuses, who are so rare even outside biology. In engineering, this scarcity of geniuses is compensated, at least in part, by a formal language that successfully unites the efforts of many individuals, thus achieving the desired effect.

Very nicely put here; let me read it again. In engineering, the scarcity of geniuses is compensated, at least in part by a formal language that successfully unites the efforts of many individuals, thus achieving a desired effect. The language that is relevant is mathematics; and the tools that are relevant for understanding the systems, as we are going to look at are thermodynamics, may be transport aspects, fluxes and forces and so on, and other relevant things. In this course, we will, of course, look at one aspect of thermodynamics, which can be used to analyse biological systems.

When we finished up in the last class, we had reviewed some of the principles that we already knew some of the concepts that we already knew in thermodynamics, from your earlier classes may be in your school or in the first year of engineering.

And we are going to take things further here. And one of the important things that we considered was classical thermodynamics versus statistical thermodynamics. We said that classical thermodynamics is very good to apply in the continuum regime, where individual molecules are not really important; whereas statistical thermodynamics is a lot more complete, and it gains better relevance, when it is applied to non continuum systems. With that, let us move forward here. Let us begin module 2; module 2, we will look at additional useful thermodynamic functions.

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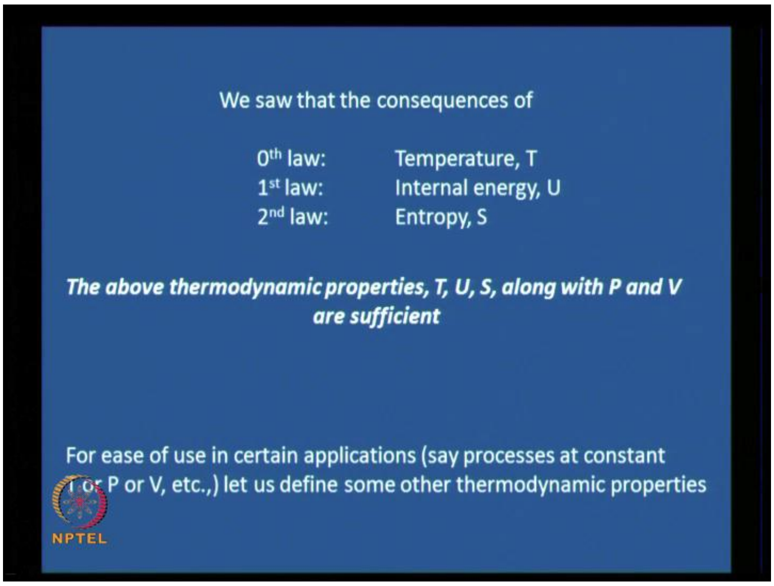

We saw that the consequences of

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

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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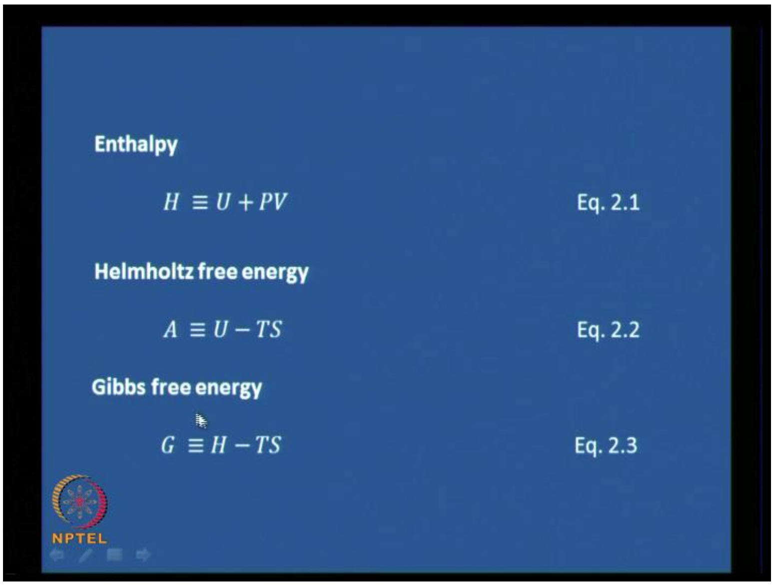

Enthalpy

$H \equiv U + PV$ Eq. 2.1

Helmholtz free energy

$A \equiv U - TS$ Eq. 2.2

Gibbs free energy

$G \equiv H - TS$ Eq. 2.3

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); 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.

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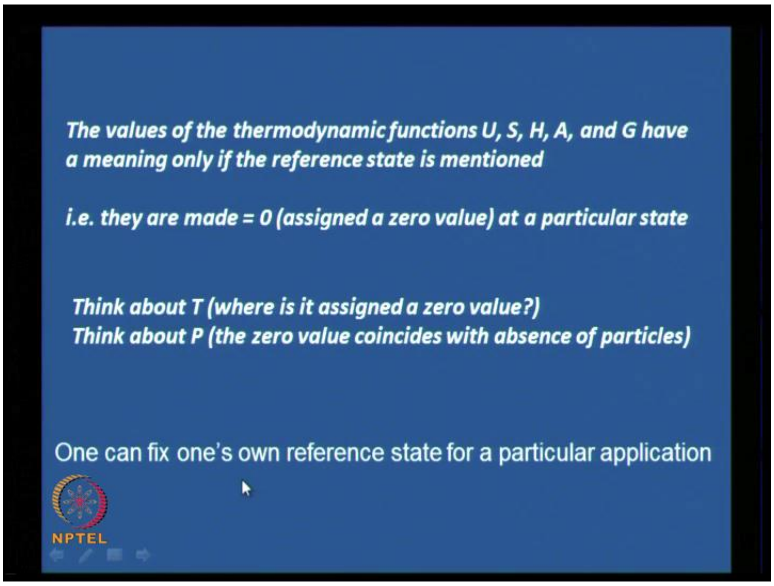

The values of the thermodynamic functions U, S, H, A, and G have a meaning only if the reference state is mentioned

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

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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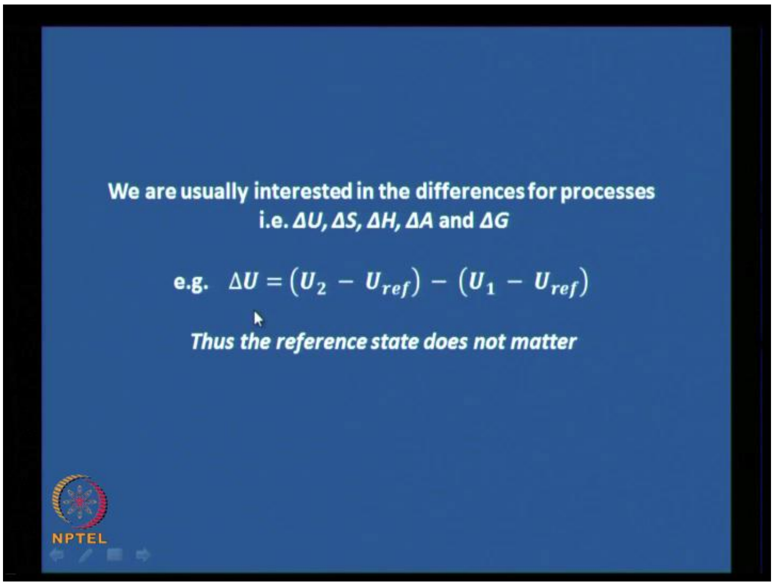

We are usually interested in the differences for processes
i.e. $\Delta U, \Delta S, \Delta H, \Delta A$ and ΔG

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

Thus the reference state does not matter

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 is nothing but U 2 minus U reference minus U 1 minus U reference. 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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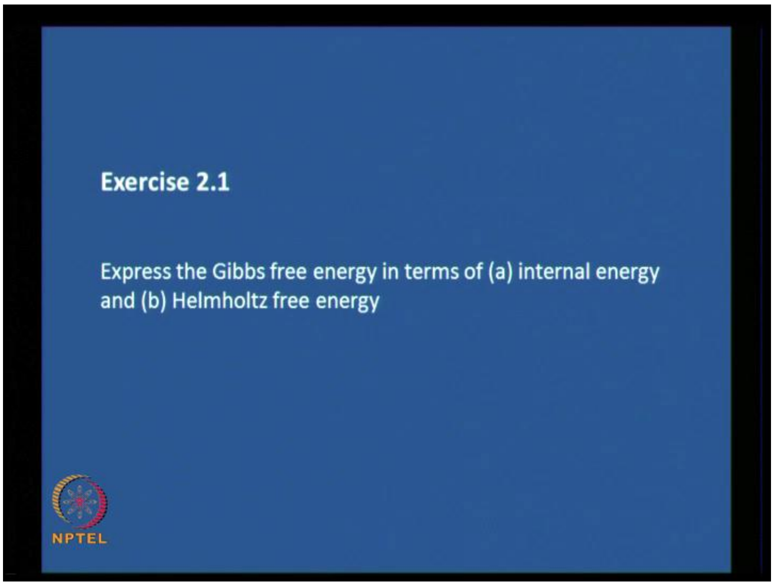

Exercise 2.1

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

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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You would have had time to work things out about 10 minutes. Now, let us look at the solution.

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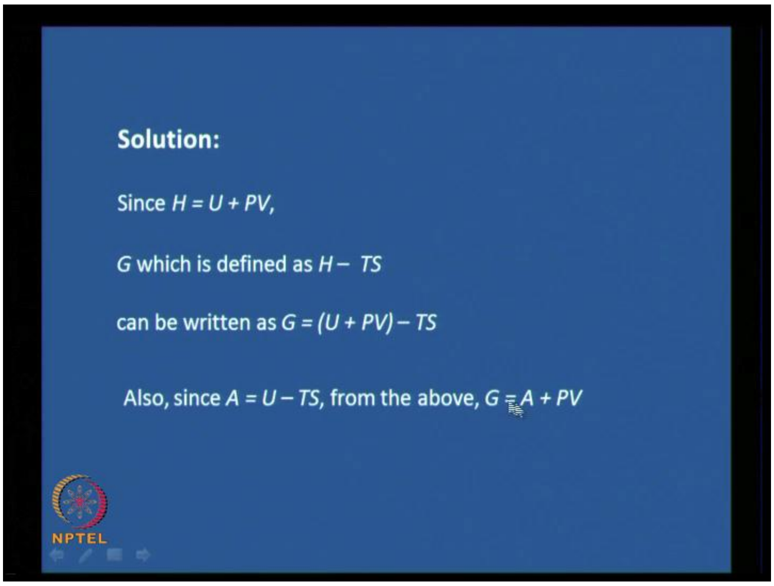

Solution:

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. And therefore, if G, which is defined as H minus (T S); 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); and 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 U … sorry A; A equals U minus (T S). 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). These are the two relationships that we were looking for, in that particular exercise.

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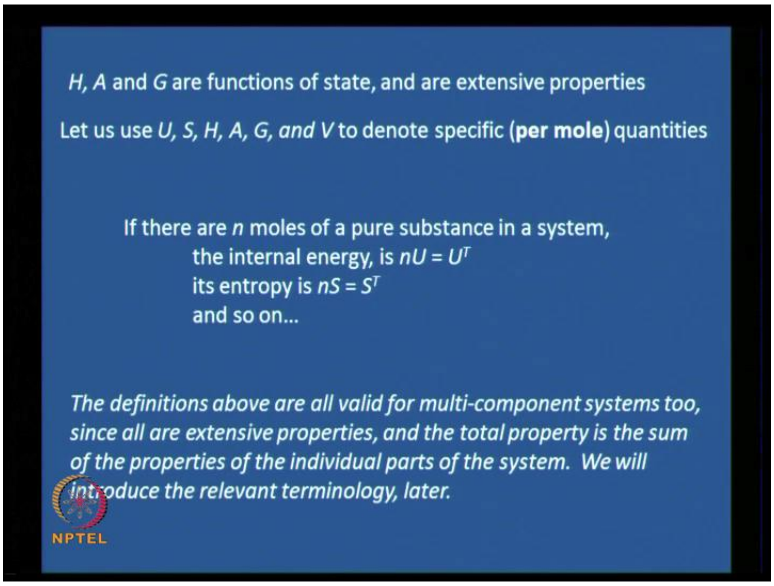

H, A and *G* are functions of state, and are extensive properties

Let us use *U, S, H, A, G, and V* to denote specific (**per mole**) quantities

If there are *n* moles of a pure substance in a system,
the internal energy, is $nU = U^T$
its entropy is $nS = S^T$
and so on...

The definitions above are all valid for multi-component systems too, since all are extensive properties, and the total property is the sum of the properties of the individual parts of the system. We will introduce the relevant terminology, later.

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, 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 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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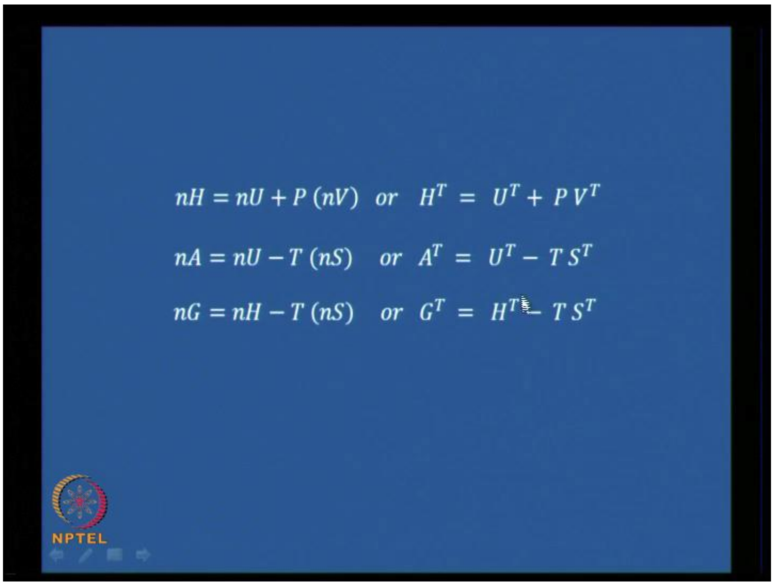

$nH = nU + P\,(nV)$ or $H^T = U^T + P\,V^T$

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

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

Therefore, we can write (n H), total enthalpy equals (n U) plus (P nV); 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.

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.

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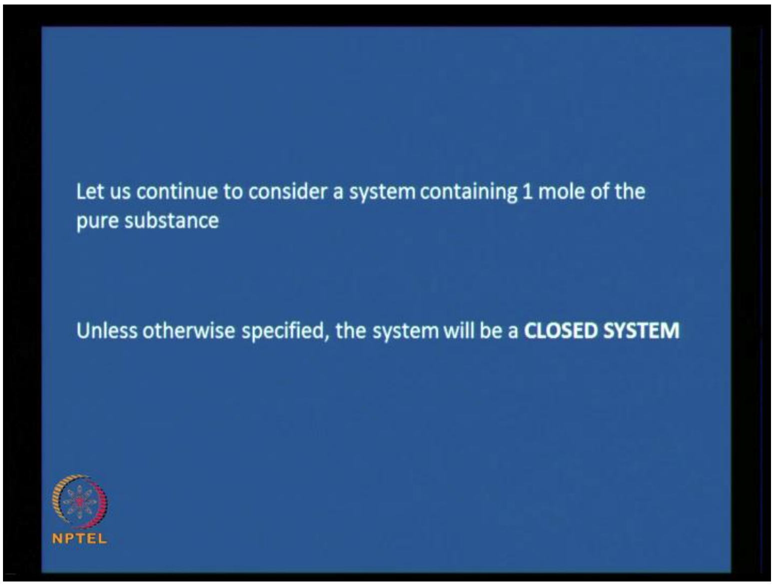

Let us continue to consider a system containing 1 mole of the pure substance

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

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.

Let us first consider a single component system, which is also in a single phase. For simplicity. Let us … go step by step. Single component for example, H_2O, and let us say that it is completely in the liquid phase; the temperature pressure combinations are such that it is completely in the liquid phase. And that is an example of a single component, single phase system.

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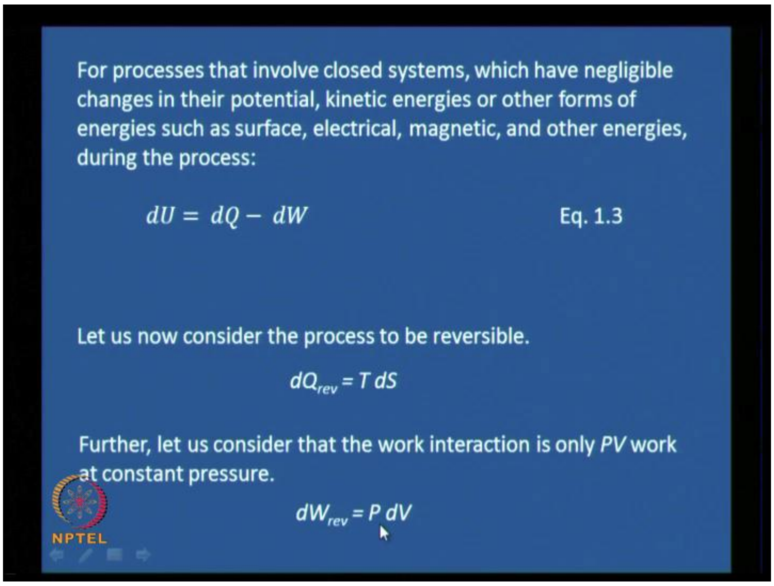

For processes that involve closed systems, which have negligible changes in their potential, kinetic energies or other forms of energies such as surface, electrical, magnetic, and other energies, during the process:

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

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.

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

For processes that involve closed systems, which have negligible changes in the other types of energies such as potential energy, kinetic energy, surface energy, electrical energy, magnetic energy and many other types of energies. Or in other words, there is only … some types of energies that are relevant here; the other things are not relevant. During such a process, dU equals dQ minus dW from first law. Recall the first law for a closed system. And this is nothing but the differential form of the first law: the total differential of U equals the total differential of Q minus the total differential of W. Recall that dQ …Q is nothing but the heat interaction across the system boundary, W is the work interaction across a system boundary.

Now let us consider the process to be reversible. We all know what the concept of reversible process is. If the process is reversible, from the second law, we know that dQ reversible equals T dS; recall that dS equals $dQ_{\text{reversible}}$ by T; from that we get dQ equals T dS … $dQ_{\text{reversible}}$ equals T dS. Now, let us further consider that the work interaction is only PV work at constant temperature … sorry, at constant pressure. Earlier we said that there are no other kinds of energies that are relevant, and then we considered the process reversible, and then now we are looking at only PV work. If it is only PV work we know from earlier classes that dW, the work term $dW_{\text{reversible}}$ in this case is P times dV.

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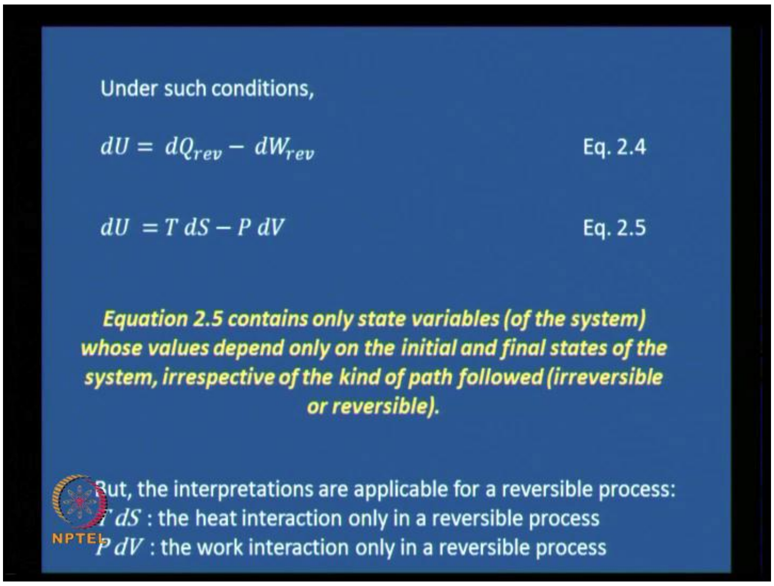

Under such conditions,

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

$dU = T\,dS - P\,dV$ 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

Now let us put this all together, we can write under such conditions dU equals $dQ_{reversible}$ minus $dW_{reversible}$; just substituting the terms into the first law. Looking at whatever we did earlier $dQ_{reversible}$ was nothing but T dS, and $dW_{reversible}$ in our particular case right now is nothing but P dV. Therefore, dU equals T dS minus P dV. And, please play a little bit of attention to this; this is the very important and a useful idea/concept … whatever you want to call it. If you look at equation 2.5, which is dU equals T dS minus P dV, it contains all state variables. What does it contain? It contains internal energy, which is a state variable temperature is of course, a state variable; entropy is a state variable; pressure is a state variable; and specific volume is a state variable.

We know that the values of the state variable depend only on the initial and final states of the system in a process. The value of a state variable depends only on the state; and when the system undergoes the process the value of the … of such thermodynamic variables are dependent only on the initial state and final state of the system, irrespective of the path that was followed to traverse the path between points 1 and 2 or states 1 and 2. Therefore, whether it was a reversible process or not, does not matter as long as the applicability of this equation 2.5 goes. Or, irrespective of the kind of path that is followed, whether it is an irreversible path or a reversible path, this equation 2.5 is valid.

I will strengthen this thought a little bit further, because this is a concept that we use again and again; and this is the very powerful kind of a concept to come up with useful relationships.

Nevertheless the interpretations of the various terms, you know that T dS as a heat interaction, and P dV as the work interaction, these are all applicable only for the kind of process, because these are path functions. T dS, … excuse me … T dS is the heat interaction only in a reversible process … excuse me…; and P dV is the work interaction only in a reversible process. Whereas, this equation 2.5, dU equals T dS minus P dV is applicable irrespective of the type of process that the system undergoes.

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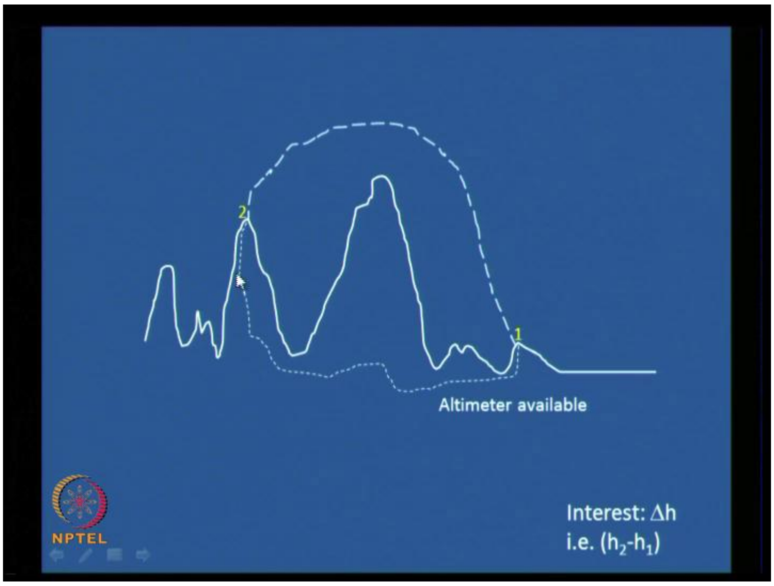

Interest: Δh
i.e. (h_2-h_1)

To understand this a little further, let us consider a mountainous region; for example, let us consider the north eastern part of India, which is huge, which is a huge place, and highly mountainous. Let us say that … I have represented the mountainous region by this. Let us say that we are interested in a place given … denoted by point 1 here, and another place denoted by point 2 here. The way to get from point 1 to point 2 or place 1 to place 2 could be very many different ways. I can take the road that leads nicely, may be a well paved road between point 1 and point 2. I can take a hilly path somewhere here, which is not indicated to go from point 1 to point 2. I can even take a helicopter and fly or a plane and fly from point 1 to point 2; and there could be many other ways.

But let us say only in this particular way, shown by this dotted line here, we have an altimeter that is available to us. Let us say that there is an altimeter shop right at the beginning of that path, and that is not available; let us assume … not very realistic, but let us assume that the altimeter is not available in any of the other paths. If our interest is in finding out the difference in heights between point 1 and point 2, which is indicated by delta h, h_2 minus h_1. We know that an altimeter gives us heights. So, all we need to do is measure the heights here with the altimeter. Go through the path, and measure the height here.

Irrespective of the path in which an altimeter is available, whether that is taken or not or whether the other parts are taken or not, the difference in heights is going to remain the same. It is just that this particular path gives us an easy measure of the difference in heights. This is what one needs to understand, to understand the concept of getting things in terms of state variables. Once we get things in terms of the difference in heights, it does not really matter, which path we follow – that would always remain the same. So, going back irrespective of the path that is followed as long as the relationship is in terms of the state variables, it does not really matter what path is experimentally taken to measure the various variables. As long as they are state variables, they would be valid.

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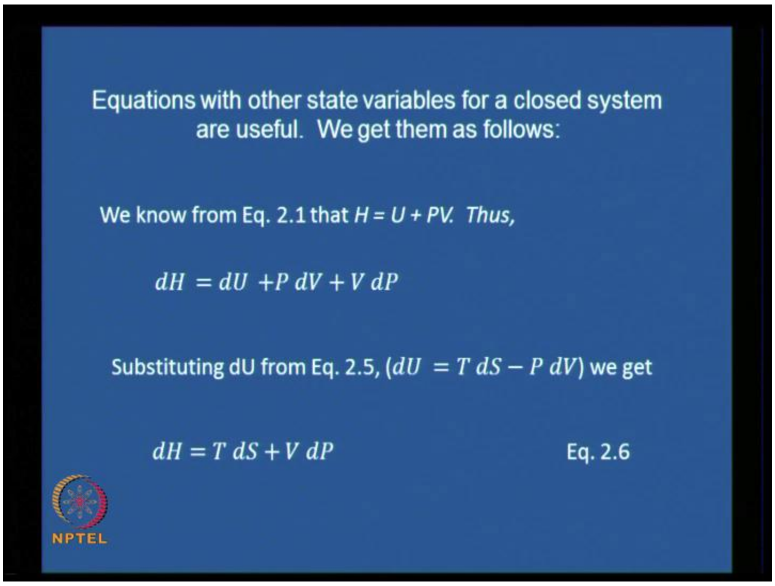

Equations with other state variables for a closed system are useful. We get them as follows:

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

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

Equations with other state variables for a closed system are also useful. And let me start showing you in the next minute or so before which we … after which we need to close this particular lecture down; let me show you how to get them. We know from equation 2.1, you can go back to your notes, if you are taking a notes, go back to the point in the video, we know that H equals U plus PV; this is the definition of enthalpy. Therefore dH, the differential of H is dU plus d of PV, d of P into V. By chain rule, we know that d of P into V is first function into the derivative of second function plus the second function into derivative of the first function. Therefore, P into dV plus V into dP; therefore, dH equals dU plus P dV plus V dP.

If we substitute dU as we know from equation 2.5 as T dS minus P dV, we get dH equals T dS plus V dP. Let us stay with this, for the time being, this is useful relationship for a closed system dH equals T dS plus V dP as represented by equation 2.6. And in the next class, I will show you how to get the other relationships, and move forward. Wish you a nice day.