

Material and Energy Balance Computations
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Lecture –32
Introduction to Energy Balance - II

Welcome back to the second lecture on the energy balance basic concept or introduction to the energy balance concepts. In the first lecture we essentially have learnt about the preliminary ideas and concepts.

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The screenshot shows a presentation slide with the following handwritten text:

- Nature of a System → often depends on the Nature of the Boundary.
- Property → Observable or Calculable characteristic of a System.
 - ↳ Two broad Categories:
 1. INTENSIVE PROPERTY → Property that are INDEPENDANT of the Size of the System → Intensive Properties: → Density, Viscosity, Surface Tension, Conductivity etc.
 2. EXTENSIVE PROPERTY: Properties that depend on the Size of the material/system. → Examples of Extensive Properties: Weight, Mass, Surface Area.
- Nano Scale $1 \text{ nm} = 10^{-9} \text{ m}$
 - ↳ In certain cases → For very small materials or particles → Some intensive properties become extensive. → Gold nanoparticles.
 - ↳ Semi conducting quantum dots.

And we understood that the nature of a system that is whether it is open closed or isolated often depends on the nature of the boundary. This is sort of a new understanding for some of you because we typically do not examine it from this standpoint. So, once we have understood about the nature of a system. Now we sort of look into another interesting word or terminology or definition you can say and that is property.

So, what is property? it is very difficult to actually define what is property? because whatever you define or the way you distinguish anything is actually based on its 'property'. For example that steel is a solid and oxygen is a gas you are distinguishing it based on its property that one is at in the solid state one is in the gaseous state that plastic is not that hard and steel is very tough

or very strong. Again, you are distinguishing based on some property or the other some materials like hydrogen sulphide.

For example, some gases have pungent smell while other gases do not have any smell, or any foul smell is again based on some property water is colorless it is itself a property as compared to some other liquid for example which have some color. So, it is actually very difficult to define what is property? but we do understand that 'property' is observable or calculatable characteristic of a system.

So, let us not get into this or get overburdened with these definitions. Let us understand the characteristic of a system. That is what a property is but more importantly property can be broadly divided into two categories. So, there are essentially two broad categories and they are intensive property and extensive property. I guess many of you know this also. So, what is extensive property? extensive property is 'properties that depend on the size, Or essentially extent of the material or system or whatever'. For example, weight, mass, surface area etc. They are all examples of extensive property. However, there are many other properties which do not depend on the size of the material; for example, density, thermal conductivity etc.

There are many other properties like resistivity, elasticity, ductility, hardness, magnetic strength, C_p and C_v (specific heat capacities) none of them depend on the size. So, for example if you take 1 kg or of steel versus 100 kg of steel its density is going to be same in both the samples.

Properties that are independent of the size of the system are known as 'intensive properties' and examples for these include density, viscosity, surface tension, conductivity and so on. So, I guess this all of you understand what the difference between intensive property and extensive property is. In fact, here I would like to touch upon a very interesting aspect which is associated with the so-called nanoscale or the nanoscience.

Many of you know about the nanotechnology; the wonders that nanotechnology is creating etcetera. This is not exactly related to our course, but this is a good point to understand what is so special about nanoscience or nanotechnology and we all know that what is the first thing that

everybody will tell you; everybody will tell you one nanometer is 10^{-9} meter which is all fine.

What exactly is so special? So, you take something very, very small fine you can reduce size and you can make things very small. So, what exactly happens? What is so unique about the nanoscale? And it turns out that in certain cases what happens is, for very small materials or let us say particles some intensive property become extensive. This is most commonly observed in semi conducting quantum dots you can check out in the internet.

So, if you take cadmium selenite, cadmium sulphide time quantum dots semiconducting quantum dots of semiconducting materials because of what is known as the quantum confinement effect which is nothing but 'you make sizes very small and certain internal properties certain intensive properties become extensive'. And one such intensive property is the band structure of the materials which actually is related to the conductivity.

Whether a material whether a material is conducting, insulating or semi conducting; I guess most of you know it depends on the band structure what the gap is or whether there is an overlap between their valence band and the conduction band. Kindly check out in the net.

In certain very specific cases, extensive properties at the nanoscale become intensive another beautiful example is. So, semiconducting quantum dots here there was some problem. So, if you have these quantum dots of different sizes and then if you excite them with the same energy light of wave of same energy it may emit different colors this is a very common and well-known example.

So, you can just check it out another interesting thing is that if you look into gold nanoparticles for example they do not look as bright as normal or bulk gold looks like I mean in fact that is what makes it so expensive, the luster and it is attributed to some property which is called the surface plasmon resonance. And what happens is that if you make gold very small the nature of the surface plasmon resonance is completely gone. In fact, gold nanoparticle looks dirty brown dirty brown in colour.

And it is very, very almost impossible to distinguish that this is gold anyway. So, for our understanding this is good enough. So, we have understood what is intensive property? and what is extensive property? And we also sort of as an addendum we do understand that how essentially what is. So, special about the nanoscale where intensive properties because of the confinement effect can become extensive. The next thing that we will talk about is what is known as state.

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The slide content is as follows:

- State** → The thermodynamic state of a system is defined by specifying the values of a set of measurable properties that is sufficient to determine all other properties. (Typically defined by specifying Temperature, Pressure, Composition etc)
- Condition of the System.**
- **Steady State** → There is no change in the properties with time → There is no accumulation.
- **Unsteady state** → Properties (may be some properties) vary with time.
- ↳ **Transient State**
- ↳ **Static Steady State**: Tank of Water, Perfect Example of a Steady state. Evaporation is Neglectable. $\frac{\partial H}{\partial t} = 0$, $Q_1 = Q_2$. Is there any difference or outflow lanes.
- ↳ **Dynamic**: Tank of Water. Inlet Pipe: Q_1 m³/hr. Outlet Pipe: Q_2 m³/hr. $\frac{\partial H}{\partial t} \neq 0$. Water will drain.

So, next and we will have a complete recapitulation. So, do not worry about it. So, state is it is sort of the thermodynamic state I am just writing the definition slowly. So, that everybody can follow but slowly we will pick up speed of a system is defined by specifying the values of a set of measurable properties that is sufficient to determine all other properties this is tricky but what it means is the state of a system is defined by specifying a bare minimum set of values which is enough to fully define the system.

So, or in other words the number of independent variables that needs to fully define a particular system and all other properties are essentially functions of those independent properties. So, the nature of properties you can also distinguish as dependent and independent properties I mean it is not a very conventional way of looking into it. But that is how it goes and again the issue is why it is not very conventional is depending on the situation the definition of a property can be independent, or it can also become dependent.

I will try to pick up some examples of these. So, in essentially the state means that what is the condition of the system. So, typically it is defined by specifying temperature, pressure, composition etcetera. Primarily, what it means is what is the condition of the system? So, we all know I mean this much all of us know we all know about what is known as the steady state and the unsteady state.

So, a steady state is defined as a system where there is no accumulation with time. So, state you can straight away divide into two categories: steady state and unsteady state. So, in a steady state there is no change in the properties with time and what is also important is there is no accumulation and a consequence of that there is no accumulation. in contrast in an unsteady state there is the or in one can write that properties most important to notice even may be some properties vary or with time.

So, this is how it goes the steady state and unsteady state. unsteady state is also called the transient state, for example let us try to understand very interesting aspect of this steady state. So, it is often related to the equilibrium but we i am coming to the definition of an equilibrium. So, if I have a glass of water for example and it has water up to this level and for the time being you say evaporation is neglected.

So, that level and it is let us say isothermal it is in equilibrium with the outside temperature. So, temperature of the water in the liquid is equal to atmospheric temperature. So, this is a perfect example of a steady state. On the other hand, if you have the same glass we will pick up examples which are very, very simple rather than talking about chemical reactions and all that right now which might be difficult for you to understand and slowly as you will become a more mature chemical engineer you can correlate all these concepts to whatever we are learning or discussing.

So, again let us say you have a tank of water or glass of water. So, this can be a tank of water also to maintain parity for example. right. So, let this be a tank of water. this is also a tank of water, but this tank has a pipe at the bottom let us say it comes with a valve and once you open

the valve you all know what will happen water will drain. So, this everybody understands this is an example of an unsteady state and why I wrote some properties will change with time because the height will change with time but let say density of water will not change with time but it is it is a classic example of an unsteady state.

So, we understand what is the difference between a steady state and unsteady state? Now I give you a third example it is the same tank of water with this outlet connection, the same tank of water with an outlet connection. But in addition, what we have here we have an inlet pipe and let us say water is flowing at a rate of q_1 meter cube per hour and moving out or draining at a rate of q_2 meter cube per hour and let us say q_1 is equal to q_2 .

Now is it a steady state or an unsteady state? It turns out that since the inlet flow rate is equal to the outlet flow rate. Since the inlet flow rate is equal to the outlet flow rate this is actually a steady state; because dH/dT if you calculate there is a variation of height of water with time is going to be zero. So, one can define if this is H.

So, if this is H the height of the tank is h in the first case, we all understood that dH/dT is equal to zero in the last case where there is unsteady state we all understand that dH/dT is not equal to zero. So, this is H and here dH/dT is not equal to zero. In fact, one can instead of having a drain one can also have a tank no drain but with an inlet pipeline that there also dH/dT will be zero the only difference is in the example that we have taken dH/dT is negative.

On the other hand, if you or even for this central picture if you close the outlet and just keep the inlet open, we understand dH/dT is equal to positive. Now coming to the picture, we have drawn in the middle or the case we are considering at the middle what would you say. So, is it steady state? or is it unsteady state? well it turns out it is actually at steady state because dH/dT is not equal to zero. But is there any fundamental difference between these two steady states or they are same? Well, it turns out you can all imagine all of you are intelligent students.

So, you can all imagine that there is of course a difference. This particular system is at a steady state because of the fact that the inlet flow rate equals the outlet flow rate and the moment you

either turn off one of the flow rates or you vary or q_1 does not that is a precise reason I did not say that it is q entering and q leaving. the moment you set q_1 is not equal to q_2 the height in the tank is going to change.

So, therefore this is a very simple with this very, very simple example we can qualitatively understand what is the difference between it is not a term that is very often or regularly used but for your understanding it is perfectly ok if you understand it like that this is sort of you can say statist static steady state and this is sort of a dynamic steady state. So, this is in a in a nutshell how we can talk about the state and the different states of a system.

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The image shows a presentation slide titled "Equilibrium State" with handwritten notes and diagrams. The slide is displayed in a software window titled "Material & Energy Balance Computation". The handwritten text on the slide includes:

- Equilibrium State**
 - Implies a state of Balance.
 - ↓
 - A system itself can be at equilibrium or a system can be at equilibrium with another system.
- Diagram: A box labeled T_s and T_r with the text "Body is static → Mechanical Eqly".
- Text: $T_2 > T_1$ → Transfer of Heat from Body to Surrounding. NOT at Thermal Eqlym.
- Text: NOT at Thermodynamic Equilibrium.
- Diagram: A vertical tank with a "Pool of LIQ" at the bottom. A red arrow points upwards from the pool, labeled "Temp Diff". A red arrow points downwards from the top, labeled "AT reduces as you go up".
- Text: → until the temp. across the entire tank has become uniform.
- Text: → That system will be at equilibrium → Thermal Equilibrium.

Now agreeing to the fact that we now understand what is a state? I think it is the appropriate time for us to pick up some more exciting examples and define what is known as the equilibrium state? In fact, if you refer to Edgar Himmelblau's book which is the prescribed textbook for this particular course. It says that it is sort of in a implies that a state of balance. Equilibrium is a very critical concept and I will not go into full details of what exactly is equilibrium because you do understand about equilibrium in your thermodynamics.

And then subsequently in your mass transfer text etcetera but we will have a working understanding of what exactly is equilibrium? it essentially means. So, another very important thing you must note down. So, equilibrium means that there is no change I mean properties do

not change with time. right. So, things are in a state of balance as it is very loosely mentioned. But there is a very interesting aspect you should pick up or you should understand that equilibrium a system itself can be at equilibrium.

Or a system can be at equilibrium with another system this I feel is a very, very important understanding what I mean by a system itself can be at equilibrium. Let us say we have a pool of liquid where there is a temperature difference. So, let us say the top temperature is low; temperature reduces. So, in this case what will happen? we all know that lower temperature is associated with higher density and higher temperature is associated with lower density.

So, you will have lower density fluid out here right and higher density fluid out here. So, this low-density fluid will try to go up and the high-density fluid will come down right and this process will continue until. So, this is a system where the system itself is not at thermal equilibrium also when i use the word 'thermal equilibrium' just bear with me for a couple of minutes there can be different types of equilibrium.

So, this will continue, or this motion will continue until the temperature across the entire tank has become uniform and then that system if you neglect evaporation, will be at equilibrium but what type of equilibrium? it will be at 'thermal equilibrium'. So, question to ask is when we talk about this the particular term 'equilibrium' what exactly are we meaning? it means that its thermal properties, mechanical properties and chemical properties they are at balance.

So, there is no gradient of temperature; there is no movement and there is no chemical potential. So, independently a system can be at different equilibriums for example if an object or a body is static, right it does not move. So, that means it is at 'mechanical equilibrium' however this body can be at a higher temperature as compared to surrounding. So, therefore there will be transfer of heat from body to surrounding.

Therefore, it is not at thermal equilibrium; though it is at mechanical equilibrium and therefore this body is not at 'thermodynamic equilibrium' or in other words now we can say that if a body or if two bodies are at 'thermodynamic equilibrium' it guarantees that they are at mechanical

equilibrium they are at 'chemical equilibrium' and they are at 'thermal equilibrium'. So, we are running out of time.

And in the next class we will start our discussion from here we will talk a little bit more about some interesting case studies about equilibrium and then move on thank you very much.