# Material and Energy Balance Computations
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## Lecture –33
## Introduction to Energy Balance - III

Welcome back. Today we will continue our discussion on the basic concepts of materials and energy balance computations. We just started to talk about the introductory concepts. And we are getting used to the pedagogy or what are the critical terminologies. So, yes in the previous lecture we have talked about the ‘state’. So, we now understand what the state of a material is. So, we talked about the ‘steady state’ and the ‘unsteady state’. ‘state’ is essentially something that defines the condition of the material. Let us keep it very simple because this lower elementary level course. And, we also started to talk about equilibrium.

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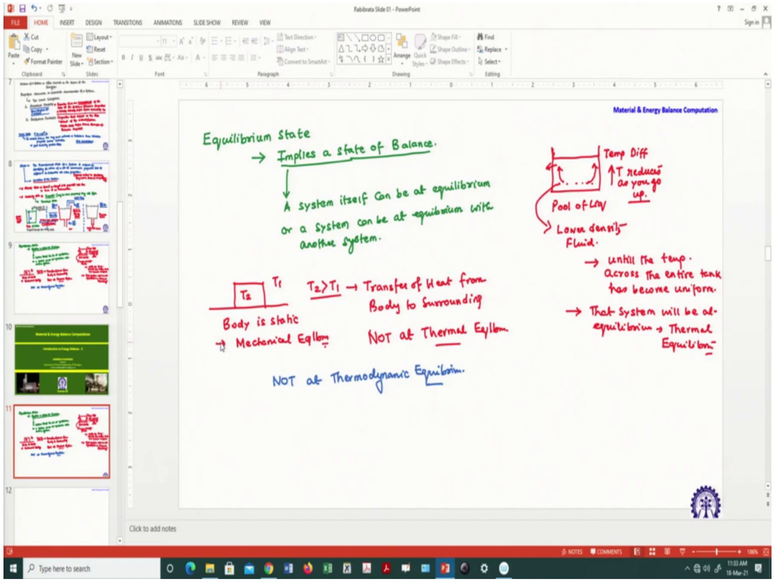

Material & Energy Balance Computation

Equilibrium State
→ Implies a state of Balance.
A system itself can be at equilibrium
or a system can be at equilibrium with another system.

Body is static
→ Mechanical Eqlbm
$T_2 > T_1$ → Transfer of Heat from Body to Surrounding
NOT at Thermal Eqlbm
NOT at Thermodynamic Equilbrim.

Temp Diff
↑T reduces as you go up.
Pool of Liq
Lower density Fluid.
→ until the temp. across the entire tank has become uniform.
→ That system will be at equilibrium → Thermal Equilibm

So, as we saw that equilibrium is essentially a state of balance. So, to simply put if you have a stationary object on a surface, it is in mechanical equilibrium. If you have an object which is at the same temperature with its surrounding you actually have a thermal equilibrium; if two reactants are in contact with each other and let us say two liquids are in contact with each other and there is no reaction or some reaction has happened and it has gone, no subsequent reaction is happening with time. Then it is in chemical equilibrium.

Similarly, between two systems when there is radiation happening, you can also have radiative equilibrium. So, essentially thermodynamic equilibrium is a concept or an axiom that expresses the internal state of a single thermodynamic system.

Thermodynamic equilibrium is a relation between several thermodynamic systems connected by impermeable or permeable wall under equilibrium, when there is no macroscopic flow of mass, energy either within the system for a single system or between the systems. So, you can just check out in any standard textbook what exactly is equilibrium. You will learn much better in thermodynamics and reaction kinetics and subsequent subjects. So, here we just have a quick idea about what is equilibrium.

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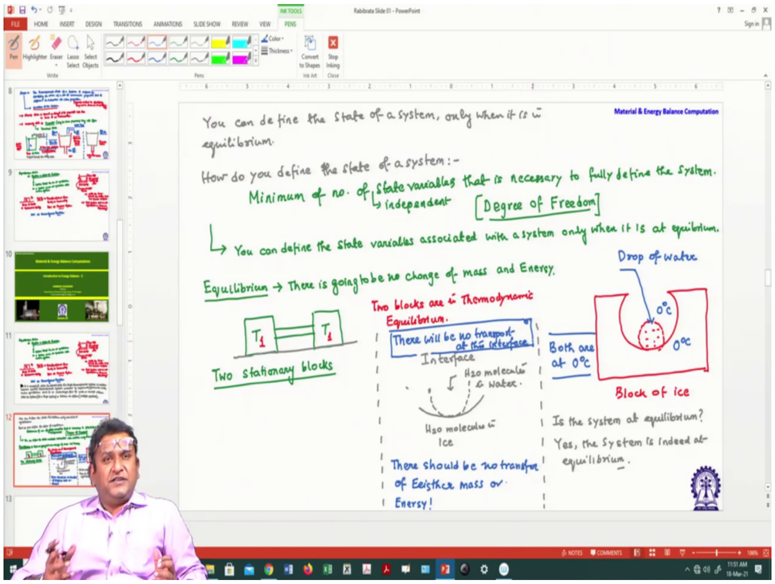

You can define the State of a system, only when it is in equilibrium.

How do you define the State of a system:-

Minimum of no. of State variables that is necessary to fully define the System.
↳ independent [Degree of Freedom]

↳ You can define the State variables associated with a system only when it is at equilibrium.

Equilibrium → There is going to be no change of mass and Energy.

Two blocks are in Thermodynamic Equilibrium.

There will be no transport at the interface.

There should be no transfer of Eeisther mass or Energy!

Both are at 0°C

Is the system at equilibrium?

Yes, the System is indeed at equilibrium.

More importantly, you can define the ‘state variable’ or you can define the ‘state of a system’ only when it is in equilibrium. And, how do you define the ‘state of a system’? It is the minimum number of state variables or I would say independent state variables that is necessary to fully define the system fully define the system.

So, for example if I say that water is at 50°C what immediately comes to your mind that it is liquid water which is slightly heated above the room temperature. But if I say that you can have water which is at 50°C and maybe its boiling. would you believe? Probably, you will have difficulty in accepting what I am saying. But the reality is that when you always conceive that water is a slightly warm liquid at 50°C, you are essentially assuming that pressure is equal to 1atm.

So, in order to define the state of liquid water for example which is a single component single phase system I am coming to the definition of ‘Phase’. You essentially need to define two independent state variables. So, by the way there is also I guess you might have studied in your physical chemistry already the difference between state variable or state function and path function. So, the properties of matter which are associated with the state they are called the state variable like temperature, pressure, internal energy, enthalpy, density these are all state variables.

They are associated with the physical state of any matter. In contrast, there are certain entities which are manifested only when the system undergoes a transition from one equilibrium state to another equilibrium state. And two such entities are ‘work’ and ‘heat transfer’ or ‘heat’. So, these are essentially path functions. So, a system which is at equilibrium has no ‘heat transfer’ associated with it or no ‘heat’ is transferred out of it. Or a system which is at rest no ‘work’ is associated with it. It has some energy which is a ‘state function’ which is mgh. When the system undergoes a change for example its volume is increasing, or it is moving from one level to other level or pushing something then only ‘work’ is manifested. Therefore, the difference between the ‘state variable’ and the ‘path variable’ is state variables can be represented in the form of exact differentials. For example, you can write dE i.e. the change in the internal energy and if you integrate it between those two states the initial state and the final state you can write delta E is equal to E 2 – E 1. However, you cannot write dq because it is a path function. And therefore it is an inexact differential and the convention that we typically write it $\Delta q$ and if you integrate between state 1 and state 2 you only get the q the amount of heat that is transferred it is not a difference between q 2 that is the heat associated at the final stage and the heat associated with the initial stage because there is no heat associated. The heat or work is manifested only when a system undergoes a transition from one state to the other one equilibrium state to another equilibrium state.

So, this is the importance of understanding equilibrium state in details and we will also understand certain more concepts more appropriately before we move on to the calculations. So, how do you define a system? And do you know what this particular entity is called? this is nothing but what is known as ‘degree of freedom’. So, ‘degree of freedom’ is essentially the minimum number of independent state variables that you need to define to fully define a state.

And also, another important thing to note is that you can define the state variables associated with the system only when the system is at equilibrium. So, if a system is undergoing a transition or is in between two equilibrium states you cannot define the state variable.

And therefore, you do not have any clear idea what is the exact state of a system that is undergoing transition except under certain approximations which we will talk about. So, when you are learning in your second year you, definitely like to follow whatever is the conventional understanding. But it is also good to have an idea about the unexplored or untold stories of science. Let us say if a system or two systems are at equilibrium, there is going to be no change of mass and energy. So, let us say that we have two stationary blocks which are connected with the metallic rod and initially let us say the temperatures.

As they are stationary, anyway they are under mechanical equilibrium. And as their compositions do not change. So, they are under chemical equilibrium. And, initially they were at different temperatures and so, you know heat is going to transfer from the high temperature block to the low temperature block and eventually they attain the same temperature T 1. Therefore, it can now be said that the two blocks are in thermodynamic equilibrium. Here is no transfer of mass there is no transfer of heat. So, therefore they are in thermodynamic equilibrium. now I pick up a very well-known example that all of you might have done in your school days or in your early engineering courses may be chemistry.

Suppose you have a block of ice and you have a drop of water and both are at 0°C. What will happen? This is an interesting question and probably many of you know the answer to this. Nothing will happen. So, the neither the ice will melt, nor the liquid will freeze. So, the liquid will retain its shape as a drop, and it will remain a liquid and ice will remain as ice.

If you do the same experiment at a temperature lower than 0°C, then slowly the liquid drop will freeze. If you perform the experiment at a temperature slightly higher than 0°C, then slowly the ice will melt. But if you perform the experiment at 0°C temperature then water will remain water and ice will remain ice. So, is the system at equilibrium? And the answer to it that is ‘yes’. the system is at equilibrium.

So, if we explore the interface what we have. We have the same $H_2O$ molecules in ice and $H_2O$ molecules in water. So, ideally according to the concept of equilibrium if we agree that the liquid drop and the block of ice are in equilibrium, there should be no transfer of either mass or energy. So, ideally as per the classical definition, at this interface there will be no transfer.

So, we did talk about equilibrium. So, equilibrium we essentially understand that it is a state of balance. So, you can either have equilibrium one system itself in equilibrium that means that there is no transfer of energy the temperature is uniform everywhere nothing is evaporating out nothing is condensing back. So, the system itself is in equilibrium within itself. So, that is important. or the system can be in equilibrium with another system and in many cases what may happen that another system is actually the surrounding.

So, you might actually have a system which is in equilibrium with the surrounding. A classic example of a ‘system in equilibrium with the surrounding’ is ‘a drop of water in contact with saturated air or saturated atmosphere’. Since the outside temperature outside air is saturated it cannot hold any additional amount of liquid. So, there is no evaporation there is no condensation and this is an example of a block of drop of water resting on a solid surface.

And if the atmospheric condition is not saturated you have relative humidity. What is relative humidity? also you will learn in greater detail towards the end of this course. then that can be a situation where you have a system is in equilibrium with the surrounding (at saturated atmosphere).

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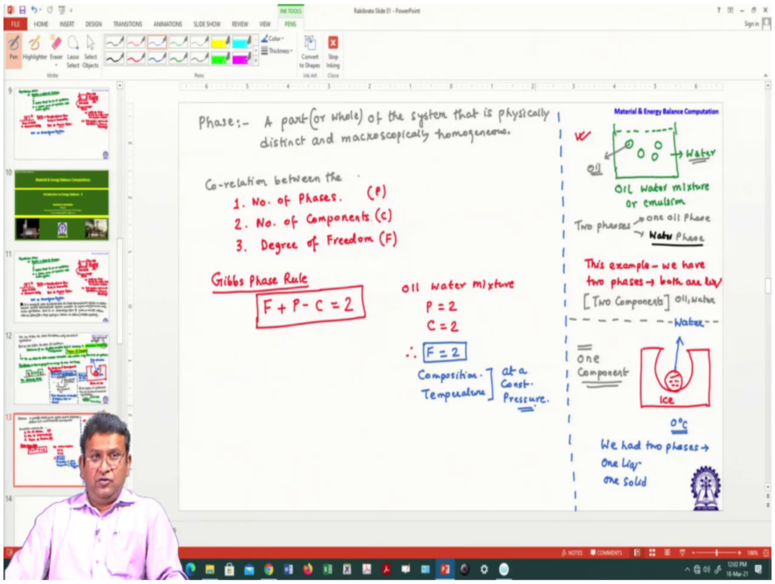

Phase:- A part (or whole) of the system that is physically distinct and macroscopically homogeneous.

Co-relation between the
1. No. of Phases. (P)
2. No. of Components (C)
3. Degree of Freedom (F)

Gibbs Phase Rule

$$\boxed{F + P - C = 2}$$

Oil water mixture
$P = 2$
$C = 2$
$\therefore \boxed{F = 2}$

Composition. Temperature ] at a Const. Pressure.

Oil water mixture or emulsion

Two phases → one oil Phase → Water Phase

This example - we have two phases → both are liq/ [Two Components] oil, water

One Component

We had two phases → One Liq- One Solid

So, if we understand equilibrium, then we need to define and what is most important in our context about equilibrium that you can define a state of a system or the state variables the values of state variables can be defined or assigned or known only when the system is at equilibrium that is a very, very important understanding.

We also learnt about another important concept that is what is known as the ‘degree of freedom’ and that is the minimum number of independent state variables that is necessary to fully define a system. So, whenever we say to fully define a system now you are all knowledgeable. So, it should immediately come to your mind that this system is actually an equilibrium system because if the system is not at equilibrium you cannot define the states.

So, with this much knowledge let us move on and lets also define another very important aspect which is known as the phase. So, what is a phase. it is a part or whole of the system that is physically distinct, macroscopically homogeneous, the properties or the compositions can actually vary. So, please do not write that the composition is uniform all over it may not be. So, essentially it is a part or the whole of a system that is physically distinct and macroscopically homogeneous.

So, for example if you have let us say if you again go back to this example how many phases are here. So, here you have two phases, one is a liquid phase one is a solid phase. you can have multiple other examples also. For example, you can have an oil-water mixture. Let us say these are oil and this is water. So, here again you have two phases one is an oil phase one is a liquid phase. So, here both the phases are liquid. sorry oil phase and water phase. I am sorry just have to give me a bit of time.

So, here what you have is you again have two phases. So, you it can also be like you if you pour some oil this coconut oil for example we all use in winter on water you can see that the oil is just making one large domain on the liquid surface so one is an oil phase and what is a water phase. So, what is the difference between this example and the previous example. So, this particular example, we have two phases both are liquid in the previous example we talked about we had two phases again but one liquid one solid.

So, I hope the concept of phase is clear to all of you. Of course, you need to whatever I am teaching you need to kindly look into one standard textbook I have suggested (Himmelblau's textbook). So, any other difference between the two systems? There is another major difference between the two systems here. Here we have two components. Two chemically distinct components the oil and the water.

Here though we have two phases its very interesting you have two components but both the components are in the liquid phase in contrast here though you have one phase in the solid state and one phase is in the liquid state you actually have only one component. So, there is an interesting correlation between this all of you know probably between the following… between number of phases, number of components and degree of freedom.

So, number of phases is represented as P; number of components is represented at C and degree of freedom is represented as F. And I guess most of you know what this correlation is. this is what is known as the Gibb's phase rule or simply people write it as the phase rule. and it turns out that it is equal to $F + P - C$ equal to 2. So, this is what is phase rule. So, this actually gives you if you now look into a system.

For example, we look into this particular system where we have this oil water mixture, you have number of phases equal to two number of components equal to two. So, what emerges from the Gibb’s phase rule is F is equal to 2 that is degree of freedom is equal to two and for example you can define this system fully based on the composition and let us say the temperature. So, the two variables that state variables you need to define the system fully is composition and temperature. of course it turned out to be little complicated example at a constant pressure.

And we will continue with our discussion on the phase rule and degrees of freedom and a little bit of discussion on phase diagram in the subsequent class, thank you.