Chemical Engineering Thermodynamics
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Lecture 1
Introduction

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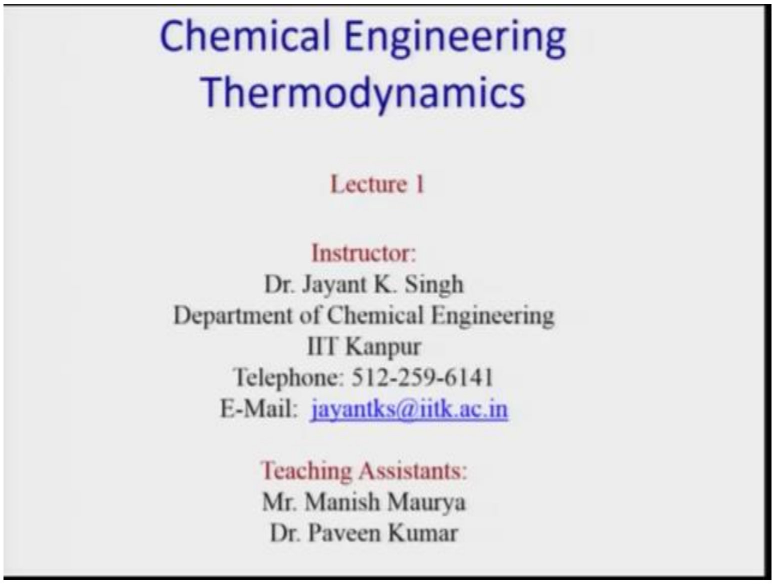

Chemical Engineering Thermodynamics

Lecture 1

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So, warm greetings to all of you. This is the first lecture of Chemical Engineering Thermodynamics. This meant for the second year Chemical Engineering students who have undergone first introductory course of engineering thermodynamics. This particular course will be assisted by my teaching assistants Mr. Manish Maurya and Dr. Praveen Kumar. I can be reached over phone by given this number and I can be also reached by email at this iitk email address. Okay. So, I am in the department of Chemical Engineering IIT. Kanpur.

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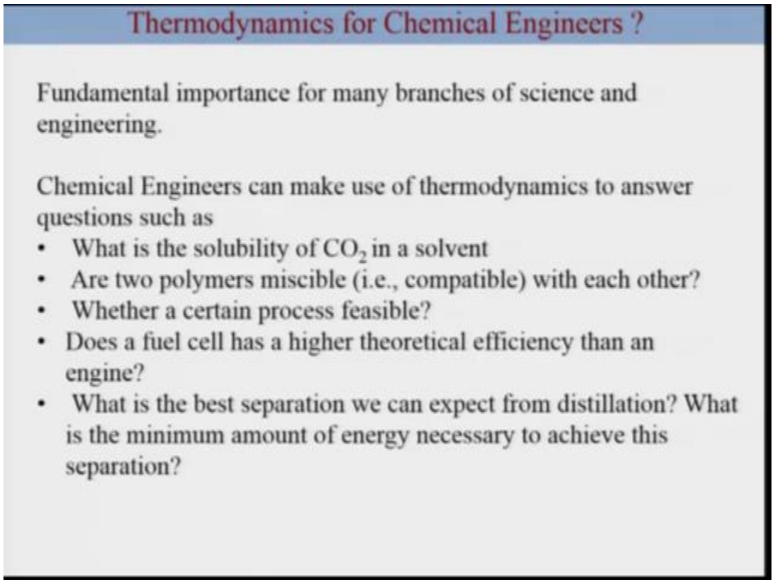

Thermodynamics for Chemical Engineers ?

Fundamental importance for many branches of science and engineering.

Chemical Engineers can make use of thermodynamics to answer questions such as

- What is the solubility of CO_2 in a solvent
- Are two polymers miscible (i.e., compatible) with each other?
- Whether a certain process feasible?
- Does a fuel cell has a higher theoretical efficiency than an engine?
- What is the best separation we can expect from distillation? What is the minimum amount of energy necessary to achieve this separation?

Okay, so let me start with a very philosophical question why thermodynamics for chemical engineers? You know whether it is a good or bad or whether you like it or not like it, all physical processes observed in the universe follows the laws of thermodynamics. So, this is something which we have to deal with it and chemical engineers cannot avoid that. In general thermodynamics plays an important roles in various branches of science and engineering but for chemical engineers.

It is relevant particularly to the industry dealing with chemical processes and particularly a materials where the phase diagrams are the properties becomes an important expects in the design of such processes. While we will talk about the modeling of the various different physical process such as for example, the separation of the fluids into vapor liquid or liquid liquid phase diagrams and where the thermodynamic aspects plays an important role, but we can start with a very simple questions and the questions such as what is the solubility of CO2 in the solvent?

These are some questions which are relevant for chemical engineers because it plays an important role in industrial applications. But fundamentally also it plays an important role to understand, for example are two polymers miscible or compatible with each other where certain process feasible at all or does the fuel cell has a higher theoretical efficiency than an engine.

What is the best separation we can expect from distillation? What is the minimum amount of energy necessary to achieve such separation?

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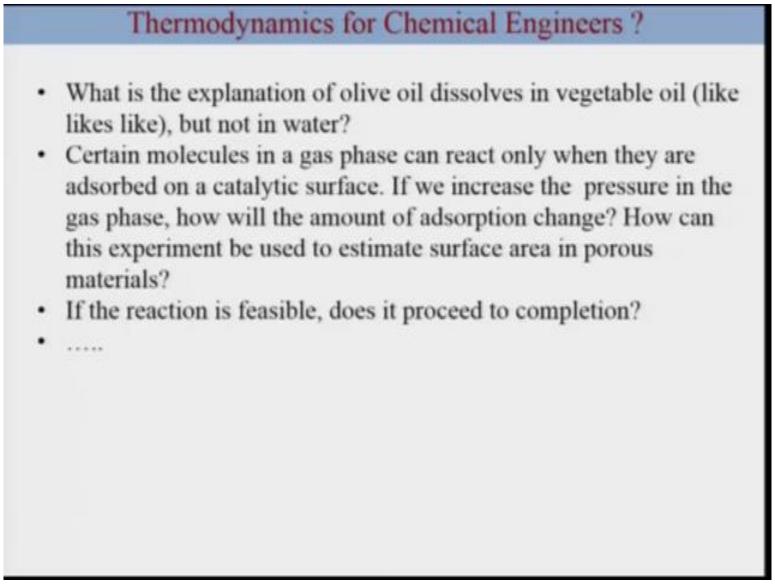

Thermodynamics for Chemical Engineers ?

- What is the explanation of olive oil dissolves in vegetable oil (like likes like), but not in water?
- Certain molecules in a gas phase can react only when they are adsorbed on a catalytic surface. If we increase the pressure in the gas phase, how will the amount of adsorption change? How can this experiment be used to estimate surface area in porous materials?
- If the reaction is feasible, does it proceed to completion?
- …..

Okay, and we can keep going on because the questions are unending but I will just thought to start with the basic set of questions to illustrate where the chemical engineering thermodynamics plays an important role in terms of addressing some relevant question particularly for chemical engineers. For example, what is the explanation of olive oil dissolves in the vegetable oil likes like but not in water. This you can think from the thermodynamics point of view as well as or from the physics chemistry point of view.

Now, I take a question. For example, certain molecules in the gas phase can react only when they are adsorbed on the catalytic surface. However, if we increase the pressure in the gas phase how will the amount of adsorption change? How can this experiment be used to estimate surface area in porous materials? Can the thermodynamics address such a question? Okay, or we can look at the aspect of the reaction if the reaction is feasible does it proceeded to completion?

Okay. So some similar kind of questions you can list down and the idea behind learning this particular subject is to equipped ourselves with tools and abilities to address such fundamental questions using theoretical means. Okay. And this is something which we are going to learn in deep in particular this course.

Will divide this course in two aspects, one the first part will be trying to build up the fundamental aspect of the chemical engineering thermodynamics where we will be focusing more on the philosophy of the development of potential functions in general all the thermodynamic rules and trying to build up the knowledge and later on apply to various different applications related to chemical engineering thermodynamics.

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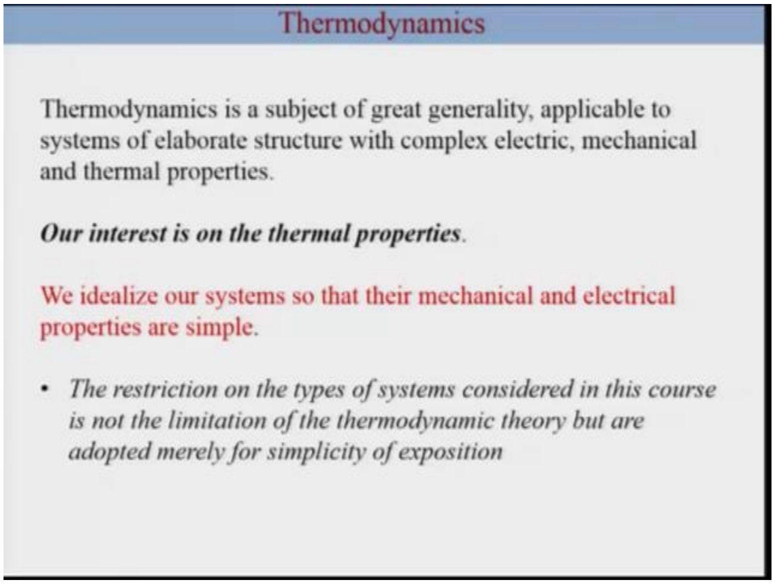

Thermodynamics

Thermodynamics is a subject of great generality, applicable to systems of elaborate structure with complex electric, mechanical and thermal properties.

Our interest is on the thermal properties.

We idealize our systems so that their mechanical and electrical properties are simple.

- *The restriction on the types of systems considered in this course is not the limitation of the thermodynamic theory but are adopted merely for simplicity of exposition*

As we already know introductory engineering thermodynamics that this is a subject of great generality applicable to systems of elaborate structure with complex electrical, mechanical and thermal properties. Essentially it means that this is widely applicable. However in chemical engineering will be to start with the dealing with only the thermal properties. Okay where the properties change as we change the temperature and basically also as we change the pressures.

Later on we will be looking into some changes in the compositions and how does that change the properties of the system. To start with we will be focusing only for very simple systems where the mechanical and electrical properties are simple that means the restriction on the types of the systems considered in this particular course is not limitations of the thermodynamic theory but are adopted merely for simplicity exposition.

So, basically tells you that what we are going to develop though is over for the very simple systems where we are not going to take a complex, electrical another kind of external field just for the sake of our expressions to be very simplified so that we can understand the theory. However, that is not the limitation of the thermodynamic theory.

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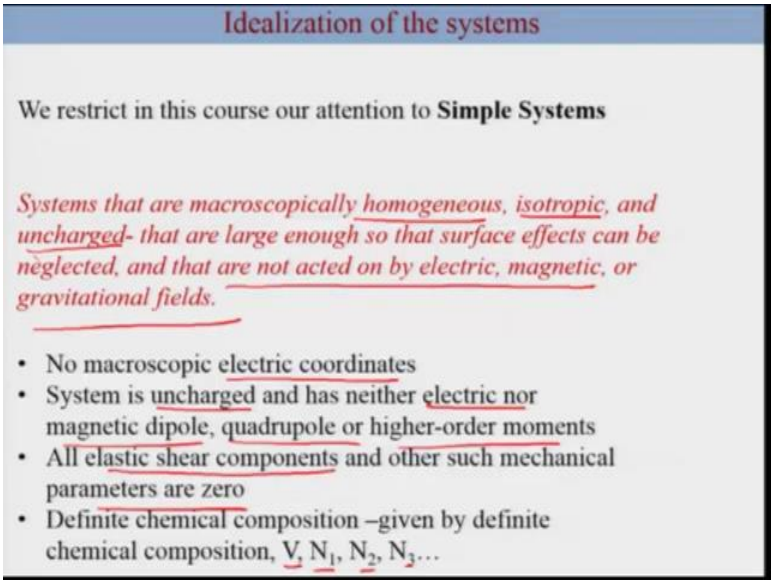

Idealization of the systems

We restrict in this course our attention to **Simple Systems**

Systems that are macroscopically homogeneous, isotropic, and uncharged- that are large enough so that surface effects can be neglected, and that are not acted on by electric, magnetic, or gravitational fields.

- No macroscopic electric coordinates
- System is uncharged and has neither electric nor magnetic dipole, quadrupole or higher-order moments
- All elastic shear components and other such mechanical parameters are zero
- Definite chemical composition –given by definite chemical composition, V, N_1, N_2, N_3…

So in other word, we will restrict our attention to simple system which are nothing but macroscopically homogeneous, isotropic and uncharged that are large enough so that the surface effects can be neglected and that are not acted on by electrical and magnetic and gravitational fields. Okay? So our systems are going to be very straightforward homogeneous, isotropic and uncharged.

Okay, so you can elaborate this that they have they will be no electrical coordinates in our system, system is uncharged neither electric nor magnetic dipole, quadrupole or higher order moments we will be considering in the system. All elastic shear component and other mechanical parameters are zero and there will be a definite chemical composition given by the volume and number of moles of different species. So the composition will be fixed. Okay. So this is the idealization of the system in our consideration.

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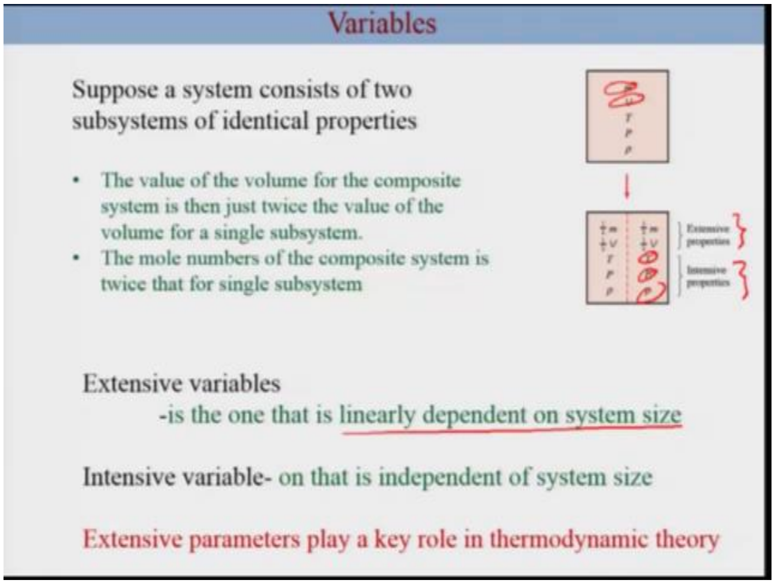

Variables

Suppose a system consists of two subsystems of identical properties

- The value of the volume for the composite system is then just twice the value of the volume for a single subsystem.
- The mole numbers of the composite system is twice that for single subsystem

Extensive variables

-is the one that is linearly dependent on system size

Intensive variable- on that is independent of system size

Extensive parameters play a key role in thermodynamic theory

Now in order to elaborate more on this I will just briefly describe a few things that will be dealing with variables the variables such as mass, volume temperature, pressure, density. Now, before I go for the further will just describe two aspects of such variables or the properties which are can be divided into extensive and intensive properties successive properties of variables is the one that is linearly dependent on system size. Okay, which you can clearly see the case of mass and volume in this case where as intensive variables are the one which are independent of the system size which in this case is temperature, pressure and density.

So, what we did here that we took a system can having this such a variables or so properties and we divided into two halves. So,, the volume gets divided by the rest of the variables remain the same and those kind of variables are called intensive variables and those which gets affected by this changes in the system size are the one which are extensive variables. Now extensive variables or parameters play a key role in thermodynamic theory, okay.

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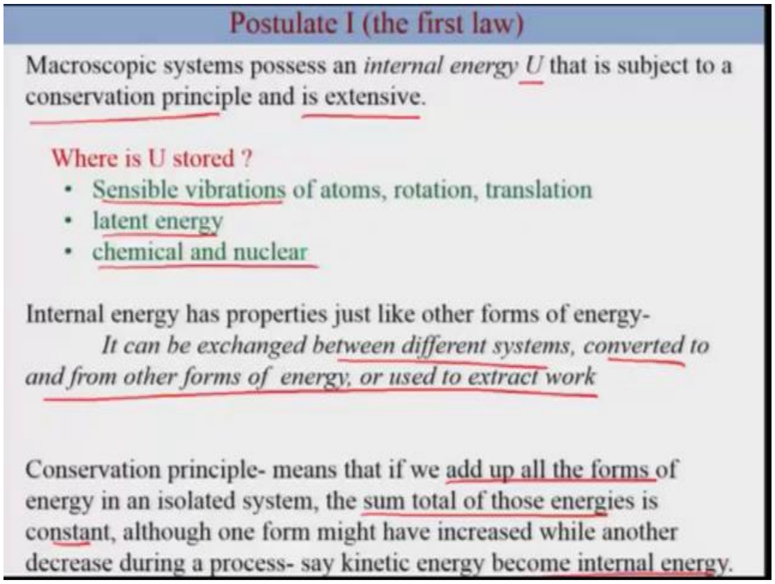

Postulate I (the first law)

Macroscopic systems possess an *internal energy U* that is subject to a conservation principle and is extensive.

Where is U stored ?

- Sensible vibrations of atoms, rotation, translation
- latent energy
- chemical and nuclear

Internal energy has properties just like other forms of energy-

It can be exchanged between different systems, converted to and from other forms of energy, or used to extract work

Conservation principle- means that if we add up all the forms of energy in an isolated system, the sum total of those energies is constant, although one form might have increased while another decrease during a process- say kinetic energy become internal energy.

So with this definition of variables, I will now describe the postulates or the foundation of the thermodynamics which are based on various different postulates to start with. Okay. So we will start with the first postulate of the thermodynamics and it says that "The macroscopic system possesses an internal energy, which is U that is subject to a conservation principle, and is also extensive."

So this is the first postulate so the idea is to understand the foundation how it was developed over the years and now which is considered to be a sound and this is what the theory we of thermodynamics we consider. Now, one of the questions is where this particular internal energy of the system stored. Now this we know from our introductory engineering thermodynamics course that U is stored in sensible vibrations of atoms rotation translation. Okay. So this is nothing but sensible energy and then you have this latent energy and chemical and nuclear energies.

Okay, so internal energy has property just like other forms of energy which essentially means this can change from one form to another form. Okay, so it can be exchanged between different systems converted to and from other forms of energy and used can be used to extract work. For the case of this conservation principle, which basically it means that if we add up all the forms of energy in an isolated system, then the sum total of those energy is constant.

Although one form might have increased while another form might have decreased during a process say for example, kinetic energy becomes internal energy. So, it means that for an isolated system all forms of energy, if you add it up basically should be constant whereas one form of energy can change during this process to another form.

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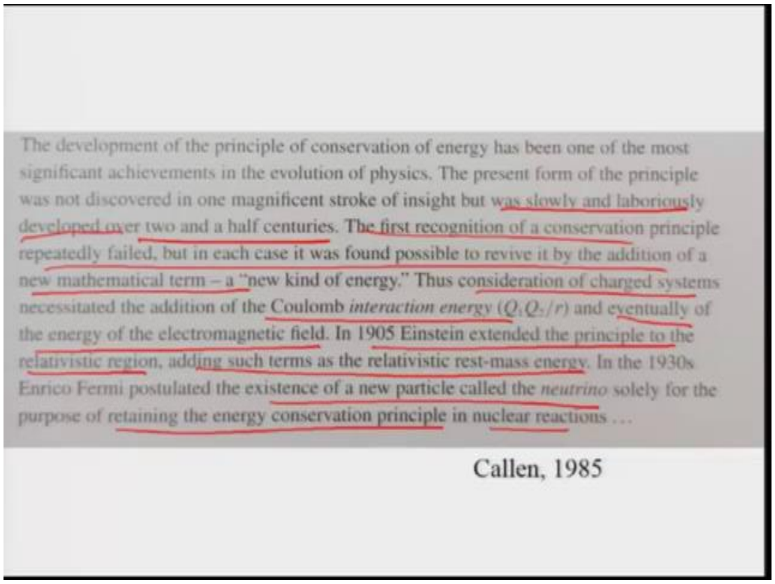

The development of the principle of conservation of energy has been one of the most significant achievements in the evolution of physics. The present form of the principle was not discovered in one magnificent stroke of insight but was slowly and laboriously developed over two and a half centuries. The first recognition of a conservation principle repeatedly failed, but in each case it was found possible to revive it by the addition of a new mathematical term – a "new kind of energy." Thus consideration of charged systems necessitated the addition of the Coulomb *interaction energy* (Q_1Q_2/r) and eventually of the energy of the electromagnetic field. In 1905 Einstein extended the principle to the relativistic region, adding such terms as the relativistic rest-mass energy. In the 1930s Enrico Fermi postulated the existence of a new particle called the *neutrino* solely for the purpose of retaining the energy conservation principle in nuclear reactions …

Callen, 1985

Now, at this point it is important to emphasize that this knowledge of conservation principle is not though it may look like very obvious now and a half centuries to develop. So, it has been a very slow and laborious process. The first recognition of conservation principle repeatedly failed, but in each case, it was found possible to revive it by the addition of the new mathematical term.

And during this this two and a half centuries people have come with a new terms in order to have this conservation principle to hold and this is something which suggests that this has become an extremely valuable process in which new kind of terms have been evaluated, for example, consideration of the charge system necessitate the addition of the coulombic interaction and eventually of the energy of the electromagnetic field.

In addition to that in 1905 Einstein extended the principle to the relativistic regions, which relativistic rest mass energy. In the 1930s Enrico Fermi postulated the existence of a new particle called a neutrino solely for the purpose of retaining the energy conservation principle in nuclear reaction. So, during this two and a half centuries this conservation of energy has become the significant achievement in the evolution of the physics and that is what tells you that this this knowledge, which we are which we have now is basically due to a lot of work done by scientist in doing last few centuries.

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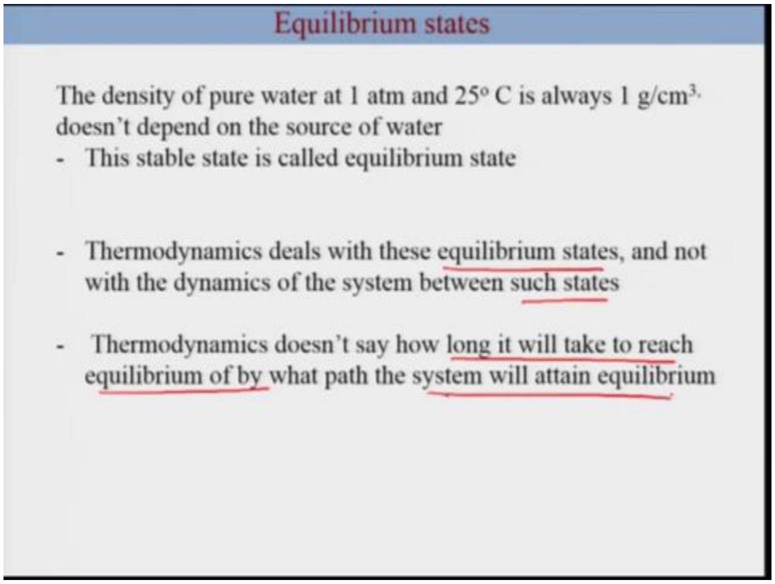

Equilibrium states

The density of pure water at 1 atm and 25° C is always 1 g/cm^3. doesn't depend on the source of water

- This stable state is called equilibrium state
- Thermodynamics deals with these equilibrium states, and not with the dynamics of the system between such states
- Thermodynamics doesn't say how long it will take to reach equilibrium of by what path the system will attain equilibrium

So the coming from this philosophically, we are going to more practical aspects, here we will start with the very fundamental question here that why the density of pure water at 1 atmosphere and 25 degrees Celsius is always 1 gram per centimeter irrespective of wherever you take it from. Whether it is from the Laddakh whether it is from Kanyakumari, you bring it to the room temperature and pressure you are going to get the same density that is one gram per centimeter Cube. So, it tells you that that this is a stable state of water at this particular temperature and pressure which is called equilibrium state.

So thermodynamics particularly deals with this equilibrium state and we are not going to talk about the dynamics of the states between such state. So, in general thermodynamics, which we are going to talk is basically equilibrium thermodynamics. We are the only the equilibrium states are going to be considered. So thermodynamics does not say how long it will take to reach equilibrium of by what path the system will attain the equilibrium. So this is something which is extremely important.

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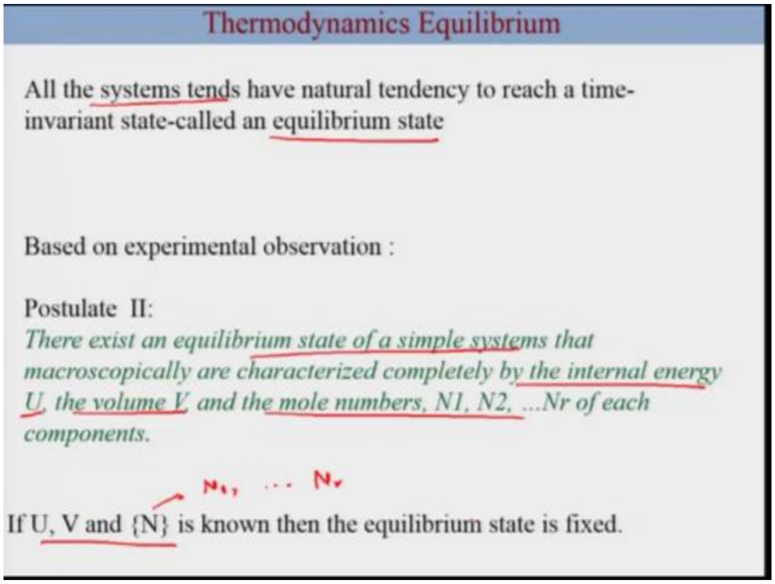

Thermodynamics Equilibrium

All the systems tends have natural tendency to reach a time-invariant state-called an equilibrium state

Based on experimental observation :

Postulate II:

There exist an equilibrium state of a simple systems that macroscopically are characterized completely by the internal energy U, the volume V and the mole numbers, N1, N2, ...Nr of each components.

$N_1, \ldots N_r$

If U, V and {N} is known then the equilibrium state is fixed.

So we do not talk about the transient path which will be taken by the process in order to attain the equilibrium state. Now, this is another important thing is it has picked over systems of different nature. It may take enormous time or slow time or some processes may be very fast, but all the systems tends to have a natural tendency to reach a Time invariant State call equilibrium state. So, all that systems tend to towards a equilibrium state.

Now, this is the observation we have. Now, so this leads to the second postulate that there exists an equilibrium state of a simple system that macroscopically are characterized completely by the internal energy, which is U the volume V and the moles number N1, N2 to Nr of each component. So in other word this postulate states that if you define U, V and mole numbers you are basically dividing the state of the simple system. So if U, V and this means your N1 till Nr if defined it means the equilibrium state is fixed for that particular system.

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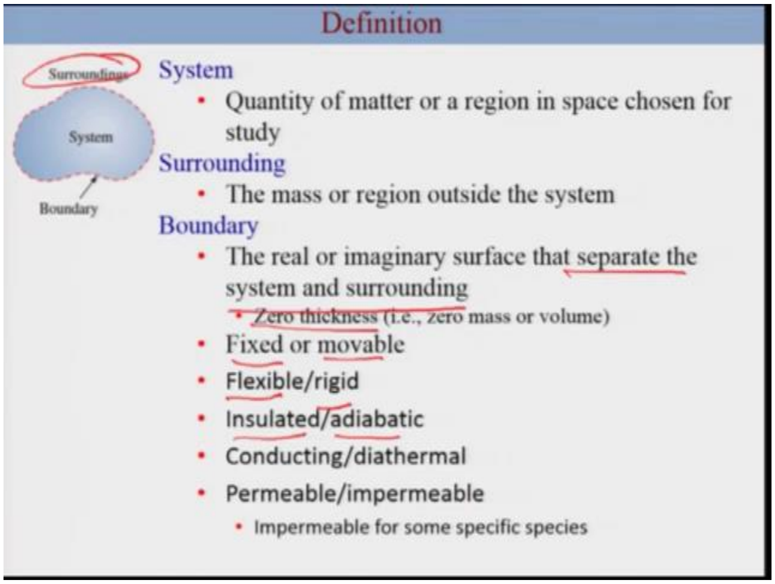

Definition

System

- Quantity of matter or a region in space chosen for study

Surrounding

- The mass or region outside the system

Boundary

- The real or imaginary surface that separate the system and surrounding
  - Zero thickness (i.e., zero mass or volume)
- Fixed or movable
- Flexible/rigid
- Insulated/adiabatic
- Conducting/diathermal
- Permeable/impermeable
  - Impermeable for some specific species

So, having said that now let me just quickly go through the basic definitions which we typically use in the thermodynamics and some of you or many of you have already seen this definitions, but for the sake of completion I will just go through quickly. So, when we talk about thermodynamics, we are typically interested in the system, of course, system is separated from the surrounding through a fixed or some kind of fictitious boundary.

But the system is basically nothing but a quantity of matter or a region in space chosen for the study, okay? And the surrounding is basically the mass or region outside the system. And the boundary is a real or imaginary surface that separate system and surroundings. So this is how we define it but the boundary could be of many types, the more important thing is the boundary has a zero thickness.

It has zero mass or volume, but it can be fixed or movable, flexible or rigid, insulated or a adiabatic, which means insulated means it does not allow any heat to transfer to let it or adiabatic is basically synonymous. So insulated is does not allow any heat to transfer and adiabatic of course that no heat is being transferred and the other possibility is conducting or basically diathermal. You can also have permeable an impermeable which essentially means that it may allow some species to transfer from surrounding or back and forth and impermeable which means basically the mass cannot flow in and out from the system.

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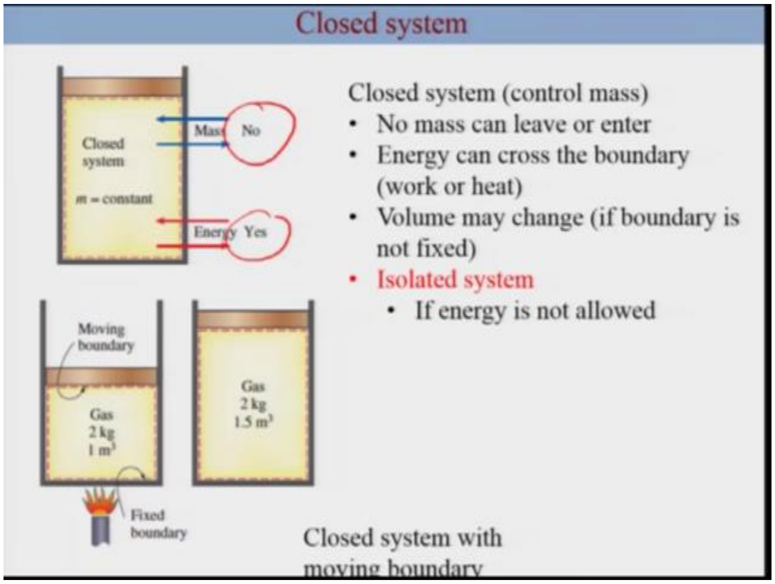

Closed system

Closed system (control mass)

- No mass can leave or enter
- Energy can cross the boundary (work or heat)
- Volume may change (if boundary is not fixed)
- Isolated system
  - If energy is not allowed

Closed system with moving boundary

So this is a type of the boundary which controls the nature of the particular system surrounding interaction. Now in addition to that we can specify kind of system by or the surrounding in terms of closed, open or isolated system. So for closed system, which could be in this form, the mass interactions are not allowed that we mean no mass can enter or exit from the system energy, however can cross the boundary. Volume volume on the other hand can be fixed or it can actually move also you have a piston movable piston that still would be a closed system. In case of isolated system no energy is allowed and as well as no mass is allowed.

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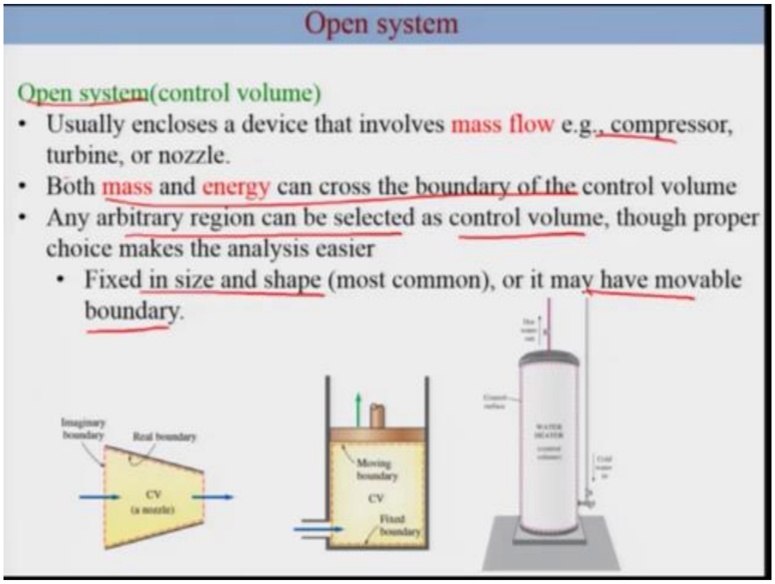

Open system

Open system(control volume)

- Usually encloses a device that involves mass flow e.g., compressor, turbine, or nozzle.
- Both mass and energy can cross the boundary of the control volume
- Any arbitrary region can be selected as control volume, though proper choice makes the analysis easier
    - Fixed in size and shape (most common), or it may have movable boundary.

So in case of open system such as for example the compressor, turbine or nozzle, in such case both mass and energy can cross the boundary of the control volume. So typically we define this kind of dotted line as a control volume, which is used for to define open system and it can be the same imaginary boundary or it can have this real boundary, this is the case for the nozzle where both mass and energy can cross the boundary, okay.

So here are the control column is an arbitrary region over which you can do this in a thermodynamic analysis. It can be fixed in size and shape or it can have a movable boundary. So, these are the examples of open system. Just for example heater, water heater here is basically continuous flow of cold water and heated hot water essentially leading to an open system kind of example.

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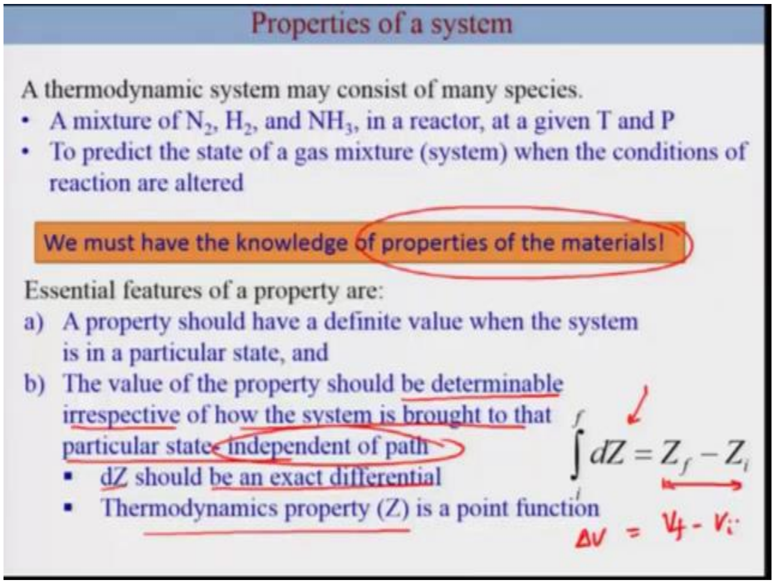

Properties of a system

A thermodynamic system may consist of many species.

- A mixture of N_2, H_2, and NH_3, in a reactor, at a given T and P
- To predict the state of a gas mixture (system) when the conditions of reaction are altered

We must have the knowledge of properties of the materials!

Essential features of a property are:

a) A property should have a definite value when the system is in a particular state, and

b) The value of the property should be determinable irrespective of how the system is brought to that particular state: independent of path

- dZ should be an exact differential
- Thermodynamics property (Z) is a point function

$$\int_i^f dZ = Z_f - Z_i$$

$$\Delta V = V_f - V_i$$

Now; the system has properties as we discussed the variables like pressure, temperature. These are basically the essential elements of the system, which is basically nothing but the properties. So system may have consists of many species like a mixture of a nitrogen hydrogen in a reactor leading to ammonia at a given temperature and pressure. Now, if you want to understand the state of the gas mixture which could be a mixture of all these three gases or in general if the conditions are changed the reaction may change and leading to a different state in order to predict such state, you need to know the properties of the material.

So which essentially will be elaborating more later part of the course, but one of the important thing we wanted to emphasize here is that a property should have a definite value when the system is in a particular state. For example, if you fix your temperature, pressure for of pure system it will have a specific state. Okay, and leading to a specific internal energy. So we will be elaborating this so I am taking this base that you have already undergone the first introductory course of engineering thermodynamics.

So a property should have a definite value when the system is in a particular state and the value of the property should be determinable irrespective of how the system is brought to the particular state that is it should be independent of the path. So if Z is a property then the from the initial to the final state along a path will be simply it can be given by the difference in the Z value.

So in such case dZ should be an exact differential that means thermodynamic properties that is a point function. So, for example, a change in the process, where the volume changes by V_f minus V_i will be given by ΔV. So in such case V is basically property because it just depends on the final conditions of the state and hence is a point property or Point function.

$$\int_i^f dZ = Z_f - Z_i$$

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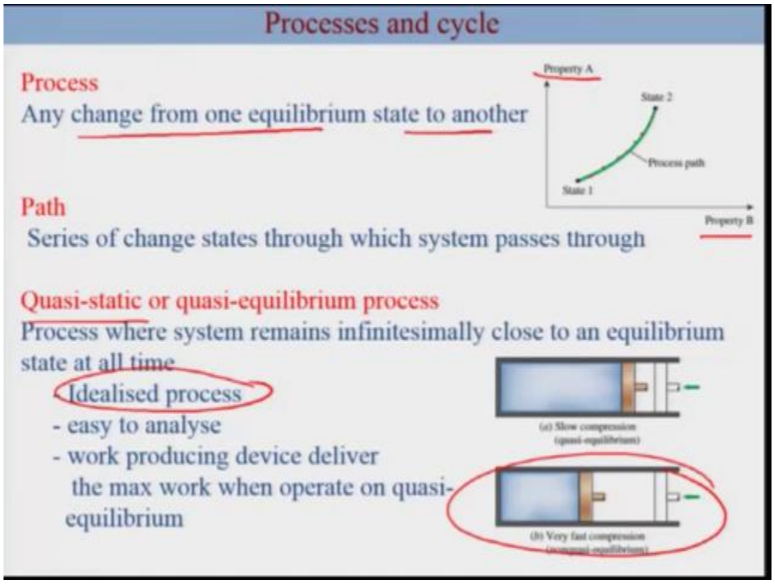

Processes and cycle

Process

Any change from one equilibrium state to another

Path

Series of change states through which system passes through

Quasi-static or quasi-equilibrium process

Process where system remains infinitesimally close to an equilibrium state at all time

- Idealised process
- easy to analyse
- work producing device deliver the max work when operate on quasi-equilibrium

Now, let me just quickly go through the process also a process basically is nothing but any change from one equilibrium state to another state. For example, this state one and state two along this grid line is nothing but a process, okay. This is drawn on a property A versus property B graph. This is called process diagram. The path here is basically a series of this dots which are equilibrium point that means these are so slope changes that we can draw a line or draw a curve along this dotted line and the assumption is that the process is extremely slow and each point is very close to an equilibrium state.

So, these are called quasi static or quasi equilibrium process which will be for the case of the slow compression or slow expansion but anything we have such as very fast compression, we cannot draw such process path for very fast compression, okay. So, these assumptions we consider, this is something we consider in our description of the thermodynamics part because it is easy to analyze and later on we will be discussing about that this is the case where the work producing delivers maximum work and the work receiving devices receive minimum work in order to operate.

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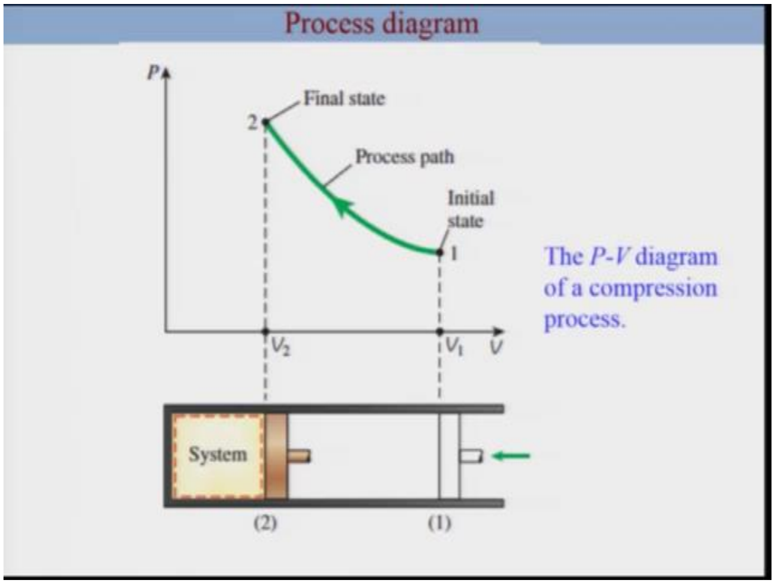

Process diagram

The P-V diagram of a compression process.

This is the process diagram. I have already gone through that.

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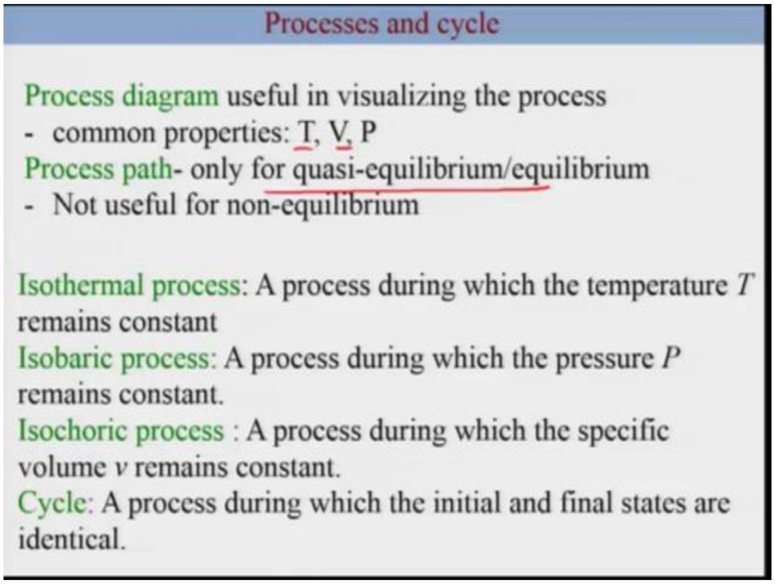

Processes and cycle

Process diagram useful in visualizing the process
- common properties: T, V, P

Process path- only for quasi-equilibrium/equilibrium
- Not useful for non-equilibrium

Isothermal process: A process during which the temperature *T* remains constant

Isobaric process: A process during which the pressure *P* remains constant.

Isochoric process : A process during which the specific volume *v* remains constant.

Cycle: A process during which the initial and final states are identical.

Now, process diagram is very useful in visualizing the process such the common properties are T, V, P. So you can have plots such as T versus V, T versus P, V versus P and so forth process path is used only for quasi equilibrium processes and is not useful for non equilibrium or very fast process. Now, in addition to that you can have many different processes whether you tempt you can fix the temperature, pressure, volume. This is isothermal, isobaric and isochoric. And as well as you can have a process during which the initial and final State are identical such as cyclic process.

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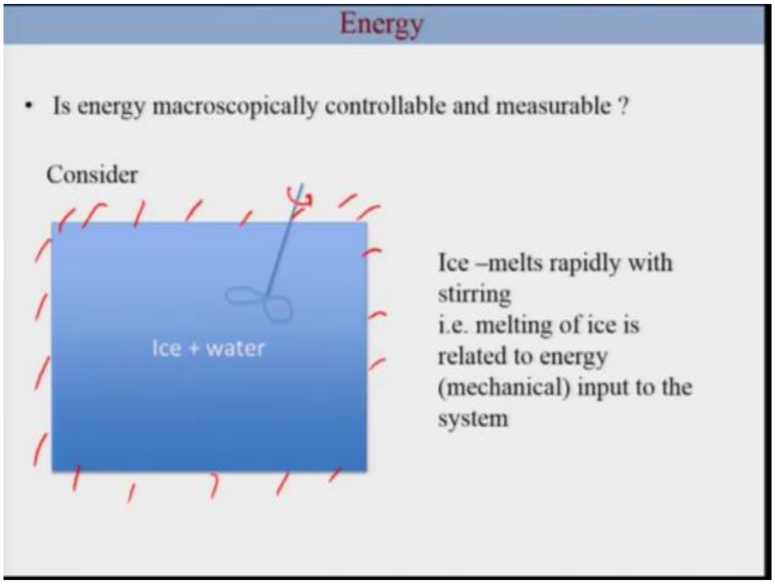

Energy

- Is energy macroscopically controllable and measurable ?

Consider

Ice –melts rapidly with stirring
i.e. melting of ice is related to energy (mechanical) input to the system

So this is was a very quick recap of the definitions which we already know, but just for the sake of going through that so that the terms becomes more easy for you to understand now having done that let us now ask very fundamental question. And that is about this energy, is this energy microscopically controllable or measurable? So can we measure the energy? That is a question which we would like to address.

Now consider a box having ice and water and you are looking at, you observing the ice or your interest is to melt the ice by providing this stir, so you are doing a mechanical work on the system, which is basically the ice and water. So, ice melts rapidly with stirring that we of course can visualize and understand so we can also can correlate that the melting of the ice is related to the energy or mechanical energy, which is transferred to the system.

Now, if this particular system is isolated or in this word insulated then whatever the melting or the energy transferred in order to melt would be given by the mechanical energy. Now in summer let us assume that this is not insulated this in this case the ice melts spontaneously without any work. So in other word, there is no stirrer in this particular case and in spite of that your ice will melt particular in summer. Now, this is something which you can imagine that the energy may have transferred in the form of some heat from system surrounding to system, right?

So, now you can consider also that can you control this heat transfer by changing the wall of the surface of the container. So, the rate of the melting of ice can be reduced if you change, let us say if you consider very thin metal sheet, then it will be it will allow heat transfer that, so it will be like dithermal. However, if you increase or if you replace by metal sheet by a thick glass then it will reduce the rate of the transfer from the surrounding to the system and if you replace that by the dewar wall, it will become more and more insulated, so you can control this rate of melting of ice.

So this is something essentially what it means that by changing the constraints of through wall, we can control the energy of the system, in another word you can find out precisely also the energy transfer. This is something which we should become clear in a later slide. So, in summary the walls can control and therefore energy is microscope microscopically be controllable. So this was the first question that can we control the energy.

The second question is can we measure the energy? So controlling the energy requires you to manage the boundary or the walls of the system but what about the measurement of this energy? So what we can do is basically will stop here and will take up this measurement of the energy in the next subsequent lecture. Okay, so have a good day.