

Thermodynamics of Fluid Phase Equilibria
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Lecture - 01
Review of basic concepts of thermodynamics

Welcome to the course of thermodynamics of fluid phase equilibria and in these few first lectures, we are going to review the engineering thermodynamics to build the base for dealing with the more complex thermodynamics for fluid mixtures ok.

So, I will start was first with the objectives of few lectures. So, we will be covering basic concept and definition system and surrounding property of a system state in equilibrium, I will define intensive and extensive property of a system.

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Learning objectives
1. Basic concepts and definition
2. The system and surrounding
3. Properties of a system
4. State and Equilibrium
5. Define intensive and extensive properties of system
6. Zeroth law of Thermodynamics (Temperature)
7. Pressure

So, let me start first with the dimensions of units.

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Importance of dimension and units

- Any physical quantity can be characterized by **dimensions**.
 - The magnitudes assigned to the dimensions are called **units**.
- Primary or fundamental dimensions**
 - Some basic dimensions such as mass m , length L , time t , and temperature T
- Secondary dimensions, or derived dimensions**
 - velocity V , energy E , and volume V are expressed in terms of the primary dimensions
- Metric SI system**: A simple and logical system based on a decimal relationship between the various units.

To be dimensionally homogeneous, all the terms in an equation must have the same unit.

$A \times B = C$

Dimension	Unit
Length	meter (m)
Mass	kilogram (kg)
Time	second (s)
Temperature	kelvin (K)
Electric current	ampere (A)
Amount of light	candela (cd)
Amount of matter	mole (mol)

Multiple	Prefix
10^{12}	tera, T
10^9	giga, G
10^6	mega, M
10^3	kilo, k
10^2	hecto, h
10^1	deka, da
10^{-1}	deci, d
10^{-2}	centi, c
10^{-3}	milli, m
10^{-6}	micro, μ
10^{-9}	nano, n
10^{-12}	pico, p

So, any physical quantity which we are interested in the thermodynamics will have to have a certain dimensions which are defined in terms of units, and these are associated with certain magnitude. Some are primary dimensions and some are which we call it fundamental dimensions and others are the derived dimensions.

The primary dimensions are mass, length, time and temperature and the secondary dimensions or derived dimensions are the one which depends on the private dimensions such as velocity energy and volume ok.

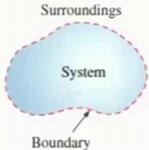
Now, there are many ways to represent these dimensions and that is what we call it systems one example is standard international or international standard systems, which we call it Si metric Si systems which is a simple and logical system based on decimal relationship between various units the examples of Si units for for example, length is meter. So, length is meter for mass its kilogram, for time its seconds temp for temperature its Kelvin and so forth. In addition to this fundamental seven fundamental dimensions which is listed here, we also make use of standard prefixes for example, 10 to power 12 Pascal, could be terapascal 10 to the power 3 Kelvin would be kilokelvin and I usually we know that it is a kilogram for example, that would be a 1000 gram and so forth ok.

So, of course, we make use of the perifix which we commonly see in our calculations. Now in addition to this for given equations which we often deal with thermodynamics,

we must make sure there is a dimensional homogeneity or what does it mean? It means for example, if you have an equation $A \times B = C$, it means that these terms will have the same dimensions and this has to be ensured.

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System and control volume



System

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

Surrounding

- The mass or region outside the system

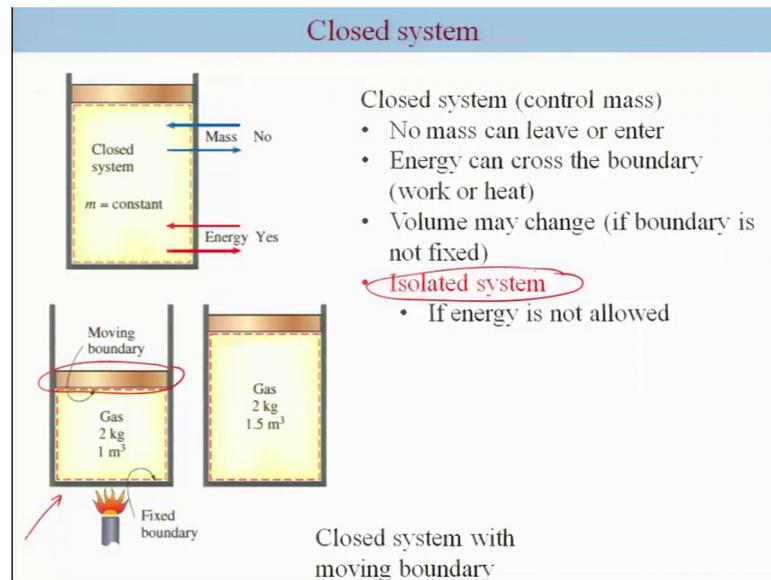
Boundary

- The real or imaginary surface that separate the system and surrounding
- Fixed or movable
- Zero thickness (i.e., zero mass or volume)
- Adiabatic/diathermal

Now, whenever we deal with thermodynamics we often are interested in certain systems certain particular devices, where we are interested to understand what is the typical changes in the energy of a system. So, we must go through formal definition of the system surrounding in the boundary, the system is a quantity of matter or region in space chosen for study; and surrounding is whatever is outside the system that is mass or region outside the system and this is separated by boundary, does not have any a specific volume there does not have any volume.

So, thus the boundary could be a real or imaginary surface, it usually is fixed, but it could be also movable depending on the system, which we are interested in ok. In addition to that it could be adiabatic or it could be diathermal.

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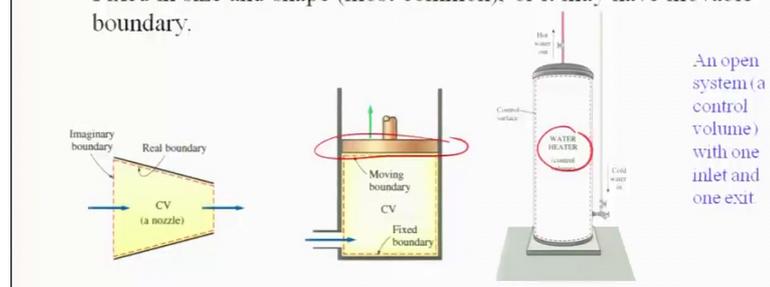
So, let me just go through now specific examples, the closed system and open system. So, what are the closed system? The closed system is where basically no mass can leave or enter, but energy can cross the boundary in the form of work or heat which we are going to define more specifically later. In addition to that the volume may change because the boundary need not be fixed. So, this is an example of a moving boundary cylinder piston system, where piston will move depending on if there is a specific if there is a heat supplied to the system, and thus the volume can change ok. Volume may change, but no mass can interleave that is basically the closed system. If you do not allow the energy to get in or get out it will become an isolated system ok.

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Open system

Open system (control volume)

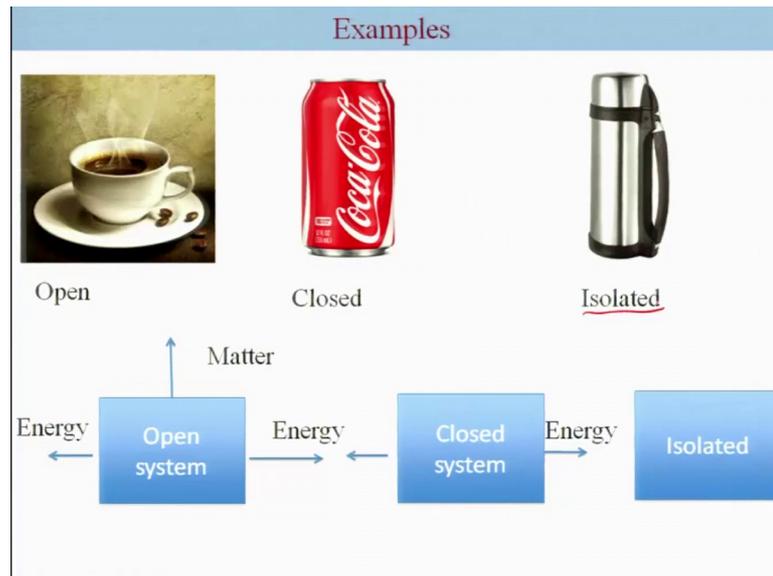
- Usually encloses a device that involves **mass flow** e.g., compressor, turbine, or nozzle.
- Both **mass** and **energy** can cross the boundary of the control volume
- Any arbitrary region can be selected as control volume, though proper choice makes the analysis easier
 - Fixed in size and shape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



Now, what are the open systems? The open systems are often seen in many devices the examples are widespread compressor and so forth, now in this case, what happens? The mass energy both can cross the boundary ok. So, both mass and energy can cross the boundary of the open system, which often we make use of the definition or the synonymous synonymously we also define it as control volume. So, when somebody says control volume, it essentially means also open system. So, when this is an example of a real boundary, where the boundary is a fix it is not moving. So, and this is a combination of her actually the real boundary and imaginary boundary, where the boundary is fixed and the mass can flow in out energy of course, can also flow in and out.

This is an example where one boundary is movable the others are fixed and this is an example where the boundary is completely fixed for the control volume, this example of a water heater ok. So, a control volume can be any arbitrary region which basically would help in analyzing the system need not be a specific way to define a control volume, it is basically entirely dependent of yourself in order to solve a certain problem you have to define the control volume more thoughtfully.

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Now, there are many examples in nature what we do in regular life. For example, this is a coffee this is an example of open system the next is of course, can closed system when it is closed it is not used it will be a closed system, and then you have this kind of thermos which is a usually used in order to maintain the temperature of the whatever the fluid we put there, and this essentially is an example of isolated system ok.

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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
- Predicting 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 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 that particular state- independent of path
 - dZ should be an exact differential
 - Thermodynamics property (Z) is a point function

$\int_i^f dZ = Z_f - Z_i$

All right, now what we are interested in when you deal with the system, we are essentially interested in the property of a system and the property may change depending on the condition of the system. So, conditions such as temperature and pressure. An example is a basically a container containing nitrogen and the hydrogen where the

reaction is occurring forming ammonia, and this will depend on the temperature and pressure or in other words the gas mixture depends on the temperature and pressure; and thus it is important that we must understand the property of material as we change the variables ok.

So, how do we define a property or in other words what are the essential features of a property. So, property should have a definite value ok, when a system is in this particular state. So, in other words it does not depend on how the system has arrived to a certain state ok. It will have a value once you arrive at a certain state it will have a specific property.

So, the value of the property should be determinable irrespective of how the system is brought to the particular state, in other words the property is independent of path ok. So, if Z is a property and usually we are interested in the difference in the property from initial state to the final state, then dZ should be an exact differential leading to this integral. In other words the property or thermodynamic property is a point function because it does not depend on any specific path ok.

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Properties of a system

- Examples:
 - Pressure, P
 - Temperature, T
 - Volume V ,
 - Mass, m

Properties are considered to be either intensive or extensive

- **Intensive**
 - Independent of mass : T, P, ρ
- **Extensive**
 - Depend on the size, or extent of the system, m, V , total momentum

Specific properties: extensive properties per unit mass

e.g. : specific volume

Now, what are the examples of the property? The properties such as pressure temperature volume these are the properties the properties can be extensive which depends on the mass, I know and all can be intensive. So, the intensive property which is independent of mass for example, this temperature pressure and density.

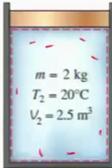
So, if you consider system having a mass v volume temperature pressure and density and you divide by 2 or you divide this into two half, then mass will get if divided by half volume will get divided by half, but this will not and this is the reason that it is basically an intensive property whereas, the extensive property are those which depends on the extent of the system such as mass volume total momentum. You can also extract a specific property out of extensive property by dividing it by mass such as specific volume.

(Refer Slide Time: 09:15)

State and equilibrium



(a) State 1



(b) State 2

State

- System is not undergoing change
- One can measure all the properties describing the condition

20°C	23°C
30°C	
35°C	40°C
42°C	

32°C	32°C
32°C	
32°C	32°C
32°C	

(a) Before (b) After
A closed system reaching thermal equilibrium.

Equilibrium

- State of balance. no driving force or no unbalanced potentials within the system
- An isolated system at equilibrium undergoes no change.

So, let me now define the state and equilibrium a state is nothing, but a when the system arrived at a condition where nothing undergoes any change. So, us and that is what we call it a state. So, a system is not undergoing any change, and at this condition one can measure all the properties describing the condition.

So, for example, this is one state and this is state 2 for the same gas, but in a different volume and what we are interested here is the property and usually the property in such a case will be uniform that is what we assumed when we define a state, and when we fix the parameter such as temperature volume a specific property comes out of it.

Now, in addition to state let me now define equilibrium. So, a equilibrium, but nothing, but is obvious is when there is a no state of driving force or there is no driving force and the state of balance; that means, there is no unbalanced potential within the system. So, for example, this is an example of a closed system before reclamation and this is an

example of closed system before the equilibration, and this equilibration we call it thermal equilibration because here all the points are fixed or rather are not changing. An isolated system at equilibrium; that means, it is not interacting with the surrounding eventually it means that it undergoes no change ok. Because its isolated there is no interaction with the surrounding and hence all the properties remain same as long as it is under isolation.

So, in this course in general thermodynamics particularly equilibrium thermodynamics; so, we are interested to understand a system at equilibrium.

(Refer Slide Time: 10:56)

State and equilibrium

A system at equilibrium should have

Thermal equilibrium

- No temperature gradient i.e., no driving force for heat flow

Mechanical equilibrium

- No change in pressure at any point in the system with time (pressure can change within the system with elevation)

Chemical equilibrium: If the chemical composition of a system does not change with time, that is, no chemical reactions occur.

Phase equilibrium: If a system involves two phases and when the mass of each phase reaches an equilibrium level and stays there.

$\alpha \quad \} \quad \beta$

So, when we talk about equilibrium or thermodynamic equilibrium there are three important criteria one is thermal equilibrium where there is no temperature gradient in other word no heat flow and second is a mechanical equilibrium; that means, there is no force grade in general there is no change in the pressure within the system, but of course, the pressure can change along here along the vertical direction, but the pressure will remain same along the horizontal and in other word, the forces are balanced in order to achieve a mechanical equilibrium. And chemical equilibrium is the; if the chemical composition of the system does not change with time, that is there is no chemical reaction.

So; that means, all the compositions here and here will be constant, and there is no mass transfer from this point to this point that will indicate a chemical equilibrium. And a

phase equilibria which we are going to deal with more intensely in the later part of this course is a system involving two phases alpha and beta and the mass of each phase reaches an equilibrium level and stays there so; that means, they effectively there is no mass change from this phase to this phase it remains as a constant effective rate of mass will be exchange will be 0 ok. But of course, phase equilibria there is more formal definition which we are going to deal with little later ok.

(Refer Slide Time: 12:32)

The state postulate

- The number of properties required to fix the state of a system is given by the **state postulate**:
 - *The state of a simple compressible system is completely specified by two independent, intensive properties* T, P
 - **Simple compressible system**: If a system involves no electrical, magnetic, gravitational, motion, and surface tension effects.
 - Need to specify one variable (T or P) for saturated vapor/liquid system

Nitrogen
 $\hat{T} = 25^\circ\text{C}$
 $\hat{v} = 0.9 \text{ m}^3/\text{kg}$

The state of nitrogen is fixed by two independent, intensive properties.

Gibbs Phase Rule }
 $F = C - P + 2$.)

13

Now, in order to define a system the property, then it say would be certain property which will be required, and now that will depend on whether this system is a single phase or two phase and or many phases. But let me just define a formal definition of something called state postulate which is nothing, but a state of a simple system compressible system, its completely specified by two independent intensive properties ok.

So, which could be a temperature of pressure and what is the simple compressible systems such as this example of nitrogen? If a system involves no electrical magnetic gravitational motion and the surface tension effect, then the system is called simple compressible system. So, in this case we used two variables intensive variables to define the state of the system ok. But as I said now it depends on whether the system is in the single phase in two phase and so forth. For example, in this case the single the system is in one phase and hence we needed to, but if it is a saturated vapor or liquid we just need

one variable or it could be temperature or pressure other variables are fixed for a single component system. In the formal way to define the number of variables needed to define a system is given by a Gibbs phase rule.

So, this is the number of degree of freedom which is required to define system, this is C is a component number of component of the system, P is the number of phases and plus 2. So, we will be discussing this part more in detail later in the course let me also define process.

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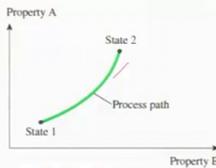
Processes and cycle

Process
Any change from one equilibrium state to another

Path
Series of change states through which system passes through

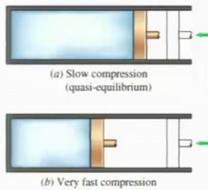
Quasi-static or quasi-equilibrium process
Process where system remains infinitesimally close to an equilibrium state at all time

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



(a) Slow compression (quasi-equilibrium)

(b) Very fast compression (nonquasi-equilibrium)

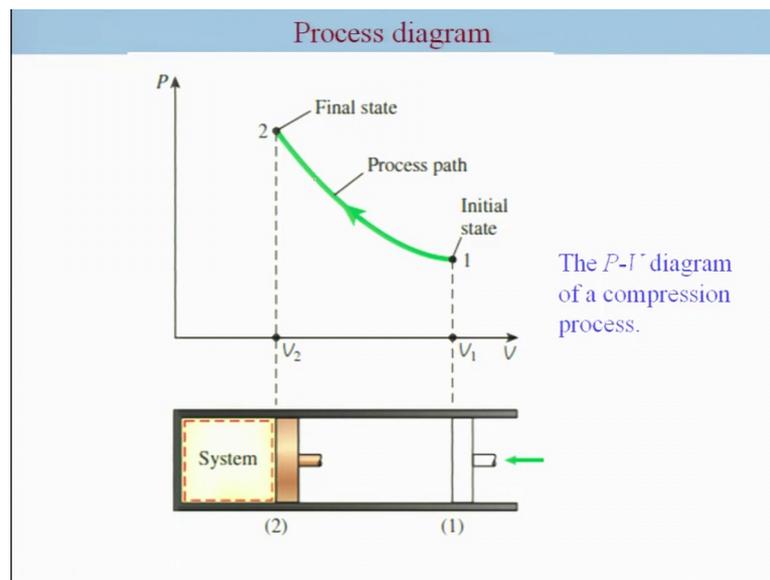


A process is any change from one equilibrium state to another says state. So, this is state 1 and this is state 2; and this property A versus property B plot is called process diagram and from state 1 to state 2 there is a change and this change is drawn by this or they shown by this green line this is a process path.

We could show this green line for an equilibrium or quasi static or quasi equilibrium that is very slow process for very fast process we cannot show it on the process diagram such a change ok. So, this is a path as I said quasi static and quasi electro equilibrium process are the process which are very slow says that the system remains in fact, is merely close to an equilibrium state at all time. So, very fast compressible compression would be a non quasi equilibrium process and we cannot draw such a process on the process diagram ok.

Now, there is a reason for making an assumption like this, because by considering quasi static equilibrium process we can idealize processes and analyze devices and find out maximum work to be done or the minimum work required for example, by a pump in order to operate or similarly well producing devices such as turbine how much maximum work can be extracted from there ok. So, this is all based on the quasi equilibrium concepts.

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So, as I said this is a process diagram example is a PV diagram property A and property B is p and v and in a compression it is shown that it is slow compression you can draw it in this form ok.

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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 in addition to process diagram process path there are ways different processes that depends on the conditions, which we are imposing isothermal process is the one where the temperature is fixed ok. Isobaric where the pressure is fixed isochoric where the volume has fixed particularly specific volume or where the volume is fixed and the cycle is the process during which the initial and final states are identical ok.

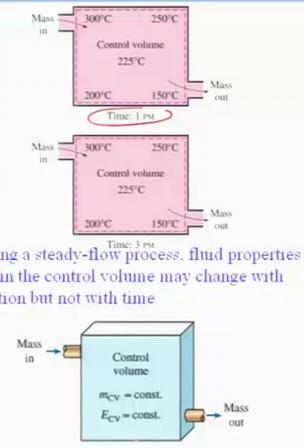
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Steady flow process

Steady- No change in time
Uniform- no change with location

Steady-flow process- process during which a fluid flows through a control volume steadily.

Closely approximated for continuous operated devices such as **turbines, pumps, boilers, condensers, and heat exchangers or power plants or refrigeration systems**



During a steady-flow process, fluid properties within the control volume may change with position but not with time

Under steady-flow conditions, the mass and energy contents of a control volume remain constant.

In addition to this processes we have a conditions where the flow is being considered where many example of such processes and these are turbine pump, boilers condenser and so forth. Now for the case of for such a system when the process itself has reached a

steady flow, which means there is no change in the time of the property this would be called like steady flow process so ok.

So, the steady flow process is a process, during which a fluid flows through a control volume steadily. Now in addition to that this is something called uniform. So, uniform is no change within location ok. So, a steady flow process need not mean a uniform process steady means for example, you have a time at one where the temperature distribution on this control volume is 300 is this given here, where the effectively there is a average temperature, but it can change within this control volume, but at 3 pm there is no change in the change in the temperature and thus it has reached a steady flow process.

In other word in the control volume, the mass or energies will remain constant and general property will remain constant, but it can value within the control volume ok, but it will not vary with time ok.

So, with this basic definition we will and this particular lecture and we will see again the next time we will continue this review process from the few lectures see you next time.