Advanced Thermodynamics and Combustion

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Module - 01
Review of Basic Thermodynamics
Lecture - 01
Temperature and Zeroth Law of Thermodynamics

Dear learners, welcome to this course Advanced Thermodynamics and Combustion. We are in the first module that is Review of Basic Thermodynamics.

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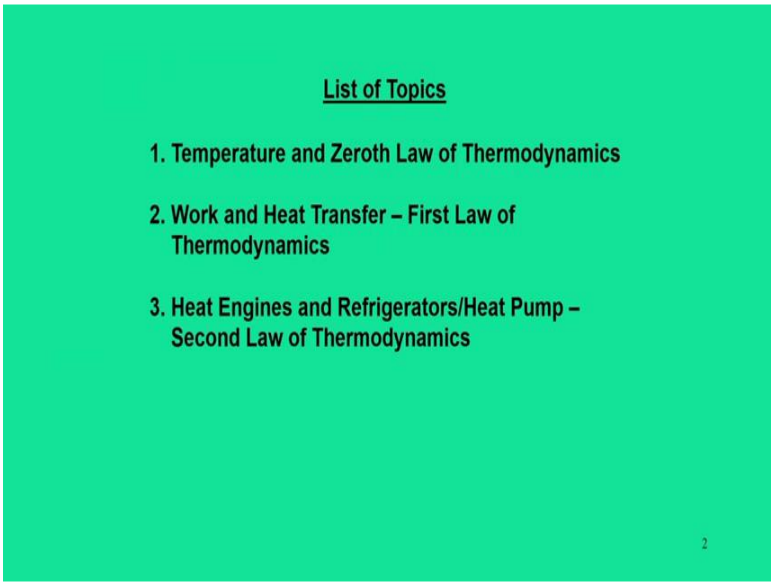

List of Topics

1. Temperature and Zeroth Law of Thermodynamics
2. Work and Heat Transfer – First Law of Thermodynamics
3. Heat Engines and Refrigerators/Heat Pump – Second Law of Thermodynamics

So, on this module we have following topics which we are going to discuss in the subsequent lectures, first lecture will be discussing about temperature and zeroth law of thermodynamics. It will be followed by the first law of thermodynamics which involves the introduction of work and heat transfer concepts. Moving further, we have the third lecture on this module that is second law of thermodynamics involving heat engines and refrigerator or heat pumps.

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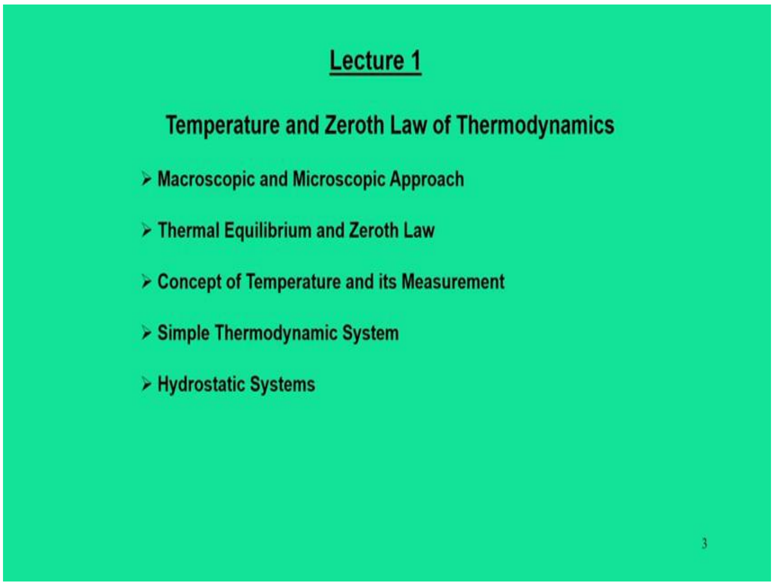

Lecture 1

Temperature and Zeroth Law of Thermodynamics

- Macroscopic and Microscopic Approach
- Thermal Equilibrium and Zeroth Law
- Concept of Temperature and its Measurement
- Simple Thermodynamic System
- Hydrostatic Systems

Now, we are in the first lecture and the title of this lecture is Temperature and Zeroth Law of Thermodynamics. On this lecture, we are going to discuss the following topics. One is macroscopic and microscopic approach; then we have thermal equilibrium and concepts of zeroth law. Then, we have concept of temperature and its measurements; then we are going to introduce simple thermodynamic systems and in particular hydrostatic systems.

Another point that I would like to emphasize here is that in the basic thermodynamic course we have covered all of them in some sense, but however, here our approach will be little bit different in a sense that because it is a advanced thermodynamics course and we are going to treat the same concept with different philosophy. And, everywhere we will try to to involve more towards the mathematical concepts apart from the physical background.

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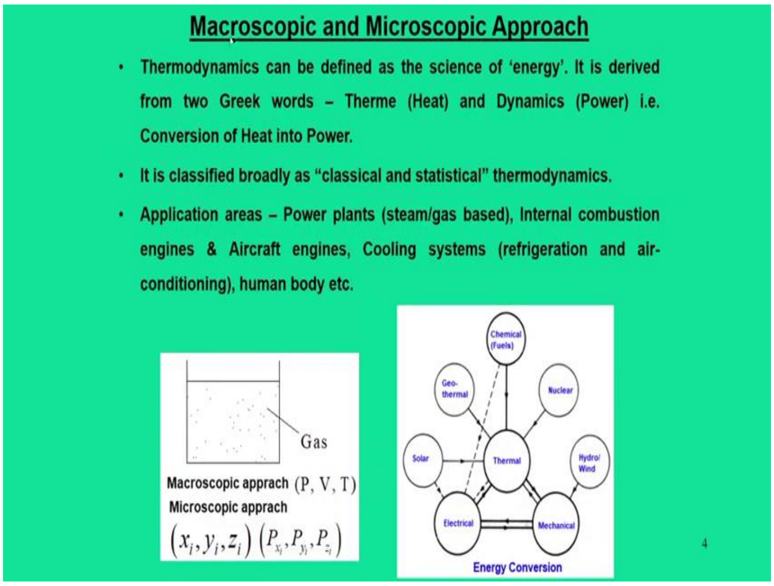

Macroscopic and Microscopic Approach

- Thermodynamics can be defined as the science of 'energy'. It is derived from two Greek words – Therme (Heat) and Dynamics (Power) i.e. Conversion of Heat into Power.
- It is classified broadly as "classical and statistical" thermodynamics.
- Application areas – Power plants (steam/gas based), Internal combustion engines & Aircraft engines, Cooling systems (refrigeration and air-conditioning), human body etc.

Energy Conversion

So, let us start the first segment that is macroscopic and microscopic approach. As the word indicates macroscopic is a global phenomena, microscopic is a kind of a molecular phenomena. So, in a same sense we deal this thermodynamics course either in a global phenomena or in a large scale situations and other way we are looking at this microscopic approach in the molecular level where we take the information at micron size or molecular size and try to grasp the information about the global properties.

However, both the approach have their own advantage and disadvantage, but at the end of the analysis we are going to conclude that both lead to the same inferences. So, this is the overall picture of this particular segment, but before you go deep into them let us see that what does this word thermodynamics means. It is nothing but the science of energy.

As you see that energy is available in many forms like we have thermal energy, we have electrical energy, we have mechanical energy, we have hydro or wind energy, nuclear energy, energy is also available in the form of chemicals that is in the fuels, energy is also available underground of earth and we call this as a geothermal energy, we also have solar energy. So, there are multiple source of energy and they can be linked together.

Now, this energy transfers either in the form of work or heat which is the essence of this course and these work or heat interactions they can be linked together and that is nothing but the science of energy. How we are going to link it that is the theme of this particular topic.

Now, when you say the energy conversion, it can be applied to many applications like power plants where we have steam or we can have gas based power plants we can have IC engines, internal combustion engines, aircraft engines we have also many cooling systems such as refrigeration, air conditioning and human body itself is also a kind of the source of energy.

Now, moving further to our basic topic that is macro and microscopic, so, this particular picture shows that there is a container that contains this gas. Now, when you deal this microscopic, in a gross sense we can say that the specifications of this gas in a thermodynamic viewpoint can be represented as its pressure and it occupies certain volume and it has some temperatures.

So, this is what we call as a macroscopic approach in defining the state of this gas. Now in same sense if you want to go to microscopic approach then we can view this entire gas to infinite number of molecules and each of them each placed at a particular locations, they are specified by their coordinates x_i, y_i and z_i in space.

And correspondingly each molecule has its own pressures in x, y, z directions and also similar information can be represented for volume and temperatures. Now, when you deal with these individual molecules and try to grossly integrate to the entire systems, then it becomes a macroscopic view point. So, this is the gross meaning of a microscopic and macroscopic approach.

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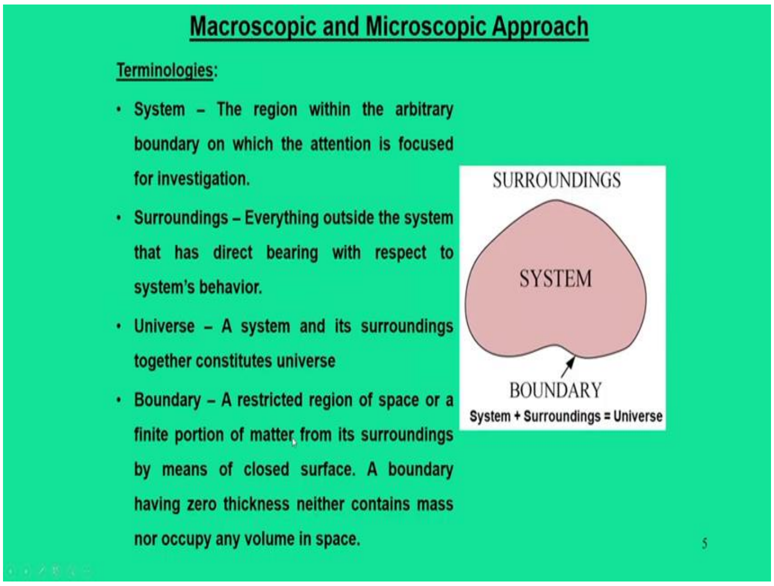

Macroscopic and Microscopic Approach

Terminologies:

- System – The region within the arbitrary boundary on which the attention is focused for investigation.
- Surroundings – Everything outside the system that has direct bearing with respect to system's behavior.
- Universe – A system and its surroundings together constitutes universe
- Boundary – A restricted region of space or a finite portion of matter from its surroundings by means of closed surface. A boundary having zero thickness neither contains mass nor occupy any volume in space.

And, before you go further let us understand some basic terminology which in fact, we all know from the basic thermodynamics course. First thing is system. System is nothing but the region within the arbitrary boundary in which our attention is a focused for investigations.

So, as you can see in this figure, we can draw a system where we want to study what is going within the system, but this system is limited with respect to surrounding by a boundary and there are possibilities that we can think of this boundary as a fixed boundary or we can say it is a stretchable boundary or moving boundary.

So, depending on the requirement we can say that system and surrounding are separated by a boundary and both when integrated together then we call them as a universe.

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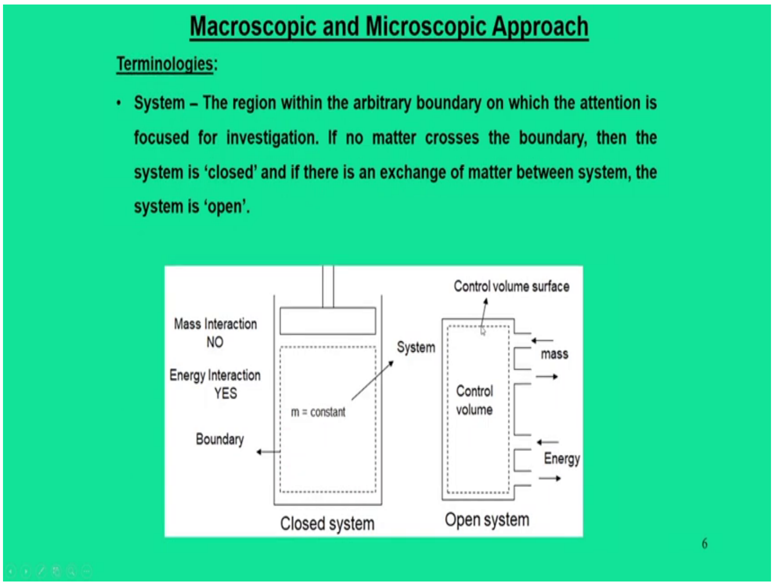

Macroscopic and Microscopic Approach

Terminologies:

- **System – The region within the arbitrary boundary on which the attention is focused for investigation. If no matter crosses the boundary, then the system is 'closed' and if there is an exchange of matter between system, the system is 'open'.**

Now, again another topic of discussions in the basic thermodynamics course was that system can be closed systems or are open systems or third category it can be isolated systems. When you say closed systems, then we say that there is no mass interactions, but there is a possibility of energy interaction. So, it is a fixed mass system.

So, this can be viewed as a piston cylinder arrangements where you have a constant mass. The piston can compress this gas or expand this gas. So, depending on the motion of the pistons we can say the gas inside the cylinder is either compressed or expanded, which means that there is some energy interactions that happens between the systems and surroundings across this boundary.

But, when you say an open systems there we relax this restriction of mass. So, there we say both mass and energy interactions are possible. So, as you can see that some flow can enter into the systems and the flow can come out, similarly energy can enter and energy can go out.

So, there is no way of specifying this volume, but rather we can say that there is a fixed volume or control volume where our attention is focused. And, the third category when you say it is an isolated systems, between the system and surroundings there is no mass and energy interactions.

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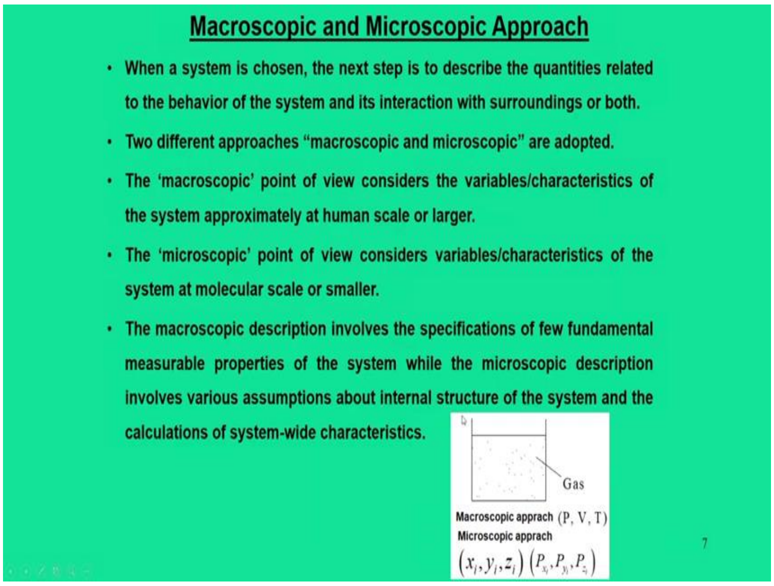

Macroscopic and Microscopic Approach

- When a system is chosen, the next step is to describe the quantities related to the behavior of the system and its interaction with surroundings or both.
- Two different approaches "macroscopic and microscopic" are adopted.
- The 'macroscopic' point of view considers the variables/characteristics of the system approximately at human scale or larger.
- The 'microscopic' point of view considers variables/characteristics of the system at molecular scale or smaller.
- The macroscopic description involves the specifications of few fundamental measurable properties of the system while the microscopic description involves various assumptions about internal structure of the system and the calculations of system-wide characteristics.

Macroscopic apprach (P, V, T)

Microscopic apprach

$(x_i, y_i, z_i)\ (P_{x_i}, P_{y_i}, P_{z_i})$

Then we move to more details on macroscopic and microscopic approach. So, when we start our thermodynamics view point that means when we are putting our attention or focus to a particular systems, then we have to think that what way we should proceed whether it is a microscopic view point or macroscopic viewpoint.

So, based on that, we say that when a system is chosen, the next step is to describe the quantities related to behavior of the systems and its interactions with surroundings or both. So, that way we can say that there are fundamental descriptions in which we can say we have a macroscopic description means that we need to specify some measurable properties of the systems and with an assumption that internal structure of the system and the calculations of system characteristics.

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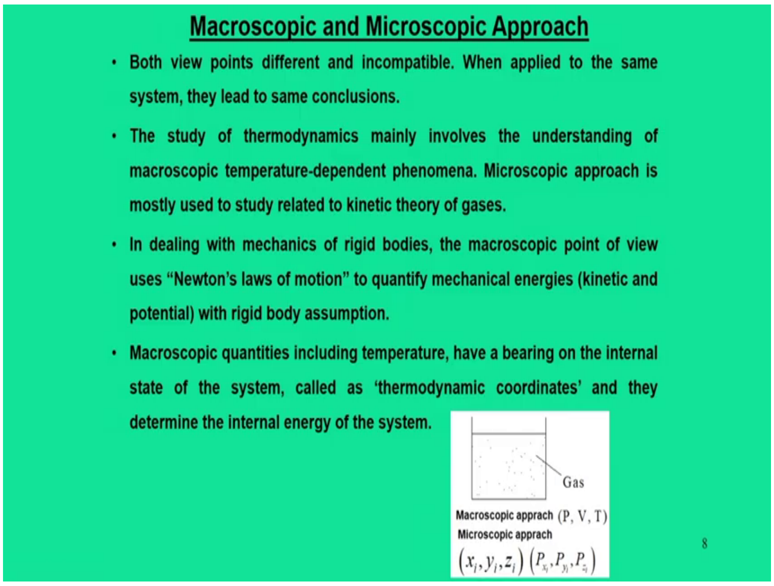

Macroscopic and Microscopic Approach

- Both view points different and incompatible. When applied to the same system, they lead to same conclusions.
- The study of thermodynamics mainly involves the understanding of macroscopic temperature-dependent phenomena. Microscopic approach is mostly used to study related to kinetic theory of gases.
- In dealing with mechanics of rigid bodies, the macroscopic point of view uses "Newton's laws of motion" to quantify mechanical energies (kinetic and potential) with rigid body assumption.
- Macroscopic quantities including temperature, have a bearing on the internal state of the system, called as 'thermodynamic coordinates' and they determine the internal energy of the system.

Macroscopic apprach (P, V, T)

Microscopic apprach

$\left(x_i, y_i, z_i\right) \left(P_{x_i}, P_{y_i}, P_{z_i}\right)$

Then, another significance of this macroscopic approach that it assumes the Newton's law of motion that is the fundamental laws of motion. So, Newton law of motions talks about force and acceleration that is mostly and passively it also says that is the what is the mechanical energy available for a system and that is in the form of kinetic and potential energy.

So, with this we have some energies that is taken care when we have the macroscopic approach. In addition to this, we also have another independent property that is the macroscopic quantities that gives the property what we called as a temperature and this temperature is nothing but the concept of another bearing to the energy of the systems and what we call as internal energy. So, ultimately in a macroscopic view point the thermodynamic coordinates mostly relies on Newton's law of motions and the concept of internal energy.

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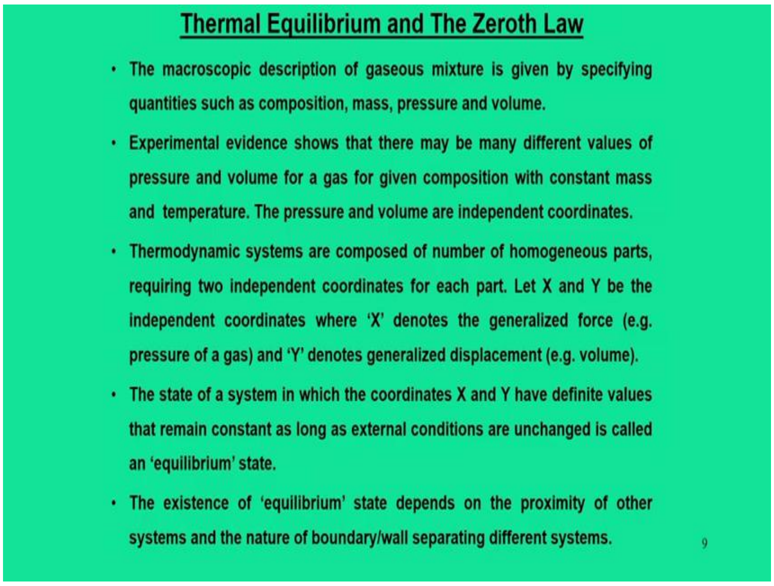

Thermal Equilibrium and The Zeroth Law

- The macroscopic description of gaseous mixture is given by specifying quantities such as composition, mass, pressure and volume.
- Experimental evidence shows that there may be many different values of pressure and volume for a gas for given composition with constant mass and temperature. The pressure and volume are independent coordinates.
- Thermodynamic systems are composed of number of homogeneous parts, requiring two independent coordinates for each part. Let X and Y be the independent coordinates where 'X' denotes the generalized force (e.g. pressure of a gas) and 'Y' denotes generalized displacement (e.g. volume).
- The state of a system in which the coordinates X and Y have definite values that remain constant as long as external conditions are unchanged is called an 'equilibrium' state.
- The existence of 'equilibrium' state depends on the proximity of other systems and the nature of boundary/wall separating different systems.

Now, having said this, again if you try to emphasize the Newton’s laws of motions it has two essential components one is force other is kind of acceleration or motion. So, when we try to correlate those Newton’s law with respect to macroscopic situations then we must relate to the thermodynamic systems.

So, let us say that we have two coordinates X and Y which are independent in nature and X represents the generalized force that comes from the Newton’s law, but we view this gas as a pressure of the gas in a thermodynamic viewpoint. Another category of our parameters that force is related to accelerations or in other words initially this body is in motion.

So, force is related to displacement and this displacement with view point of thermodynamics we call this as a volume. So, in a sense that with same concept of Newton’s law, the macroscopic view of thermodynamic coordinates of a system can be specified as a function of pressure and volume and they are related to each other that is one category.

Another category, I have already mentioned that which is independent to both that is the temperatures. So, both X and Y coordinates and side by side with temperatures they define the conditions of a systems and when the conditions of the system does not change we call this as a equilibrium state.

And, this particular equilibrium state gives the concept of zeroth law and in the subsequent slides we will talk about mostly on thermodynamic equilibriums and where we can say that how zeroth law is related to the thermal equilibrium. So, the existence of equilibrium state depends on the proximity of other systems and nature of the boundary wall which separates between these two systems.

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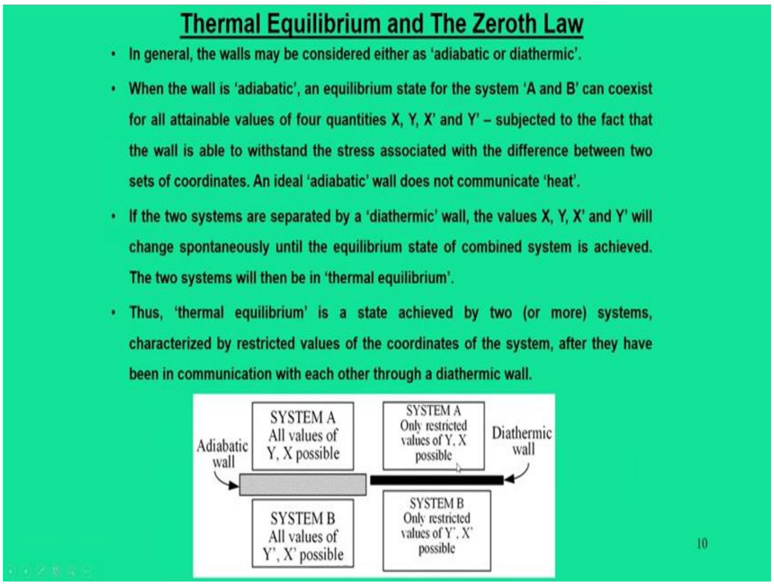

Thermal Equilibrium and The Zeroth Law

- In general, the walls may be considered either as 'adiabatic or diathermic'.
- When the wall is 'adiabatic', an equilibrium state for the system 'A and B' can coexist for all attainable values of four quantities X, Y, X' and Y' – subjected to the fact that the wall is able to withstand the stress associated with the difference between two sets of coordinates. An ideal 'adiabatic' wall does not communicate 'heat'.
- If the two systems are separated by a 'diathermic' wall, the values X, Y, X' and Y' will change spontaneously until the equilibrium state of combined system is achieved. The two systems will then be in 'thermal equilibrium'.
- Thus, 'thermal equilibrium' is a state achieved by two (or more) systems, characterized by restricted values of the coordinates of the system, after they have been in communication with each other through a diathermic wall.

So, to analyze further regarding thermal equilibrium and zeroth law let us consider this particular figure, what has been shown here is that there are two figures. One is the system A and system B which is separated by a adiabatic wall, other is same systems A and B is separated by diathermic wall.

The word adiabatic refers to the fact that communication of heat is not possible, but in a diathermic wall, communication between the systems with A and B is possible through heat transfer. So, it refers to our understanding is that if you say the first figure where system A and system B are separated by an adiabatic wall, what I can say is that if you have some state of the systems that is say values of X and Y. That means it can be generalized force or displacement or in terms of thermodynamic coordinates, it can be pressure and volume.

And, for system B those parameters are like Y` and X`. So, when there is an adiabatic wall which means there is no communication of the system A and system B is possible. So, it means the system can retain all possible values of X and Y, and system B can retain all possible values of Y` and X`.

As long as this adiabatic wall is there and it is sufficient to withstand the stress that is developed by system A and B and, of course, there is no communication of heat in between A and B. But looking for the other figure where the system A and system B are separated by a diathermic wall, we can say that only restricted values of X and Y are possible for system A and only restricted value of Y` and X` are possible for system B.

Because there is always a communication between system A and B through heat transfer and this particular mechanism, we call it as a thermal equilibrium. Since we have put this word adiabatic and diathermic and the change in the system that happens is through the heat transfer, then the word thermal equilibrium fits to this philosophy.

So, we can define this thermal equilibrium is a state that is achieved by two or more systems and it is characterized by the restricted values of coordinates of the systems after they have been in communication with each other through a diathermic wall.

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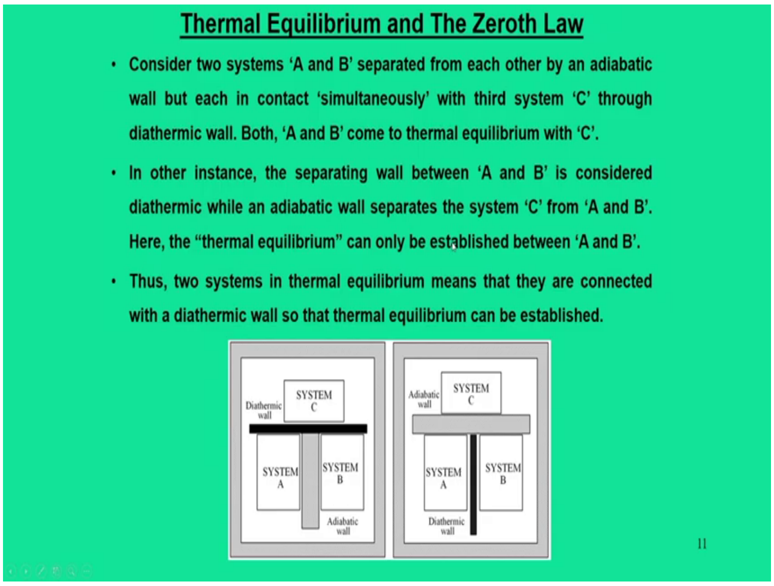

Thermal Equilibrium and The Zeroth Law

- Consider two systems 'A and B' separated from each other by an adiabatic wall but each in contact 'simultaneously' with third system 'C' through diathermic wall. Both, 'A and B' come to thermal equilibrium with 'C'.
- In other instance, the separating wall between 'A and B' is considered diathermic while an adiabatic wall separates the system 'C' from 'A and B'. Here, the "thermal equilibrium" can only be established between 'A and B'.
- Thus, two systems in thermal equilibrium means that they are connected with a diathermic wall so that thermal equilibrium can be established.

Now, moving further let us complicate a bit that in addition to the system A and B we will bring another system into picture that is system C. So, we put both diathermic wall and adiabatic wall into picture and they are arranged in a particular fashion.

So, in first figure here what we say that system A and system B are separated by an adiabatic wall and both integrated together, they are separated with respect to system C by a diathermic wall in a sense is that since system A and B are separated by a adiabatic wall so, there is no communication between A and B, but this communication between A and B can be possible through the system C; that means, system A can interact with system C system B can interact with the system C. In other scenario if the locations of the adiabatic wall and diathermic wall is changed.

So, it means that system A and system B are separated by a diathermic wall and both integrated together are separated with respect to system C by an adiabatic wall, which means that it is always possible system A and system B can come into the equilibrium and there is no communications between this A and B of integrated system with respect to C. So, in this case equilibrium can be achieved between A and B. But, in the first case the equilibrium can be achieved for A and B through the system C.

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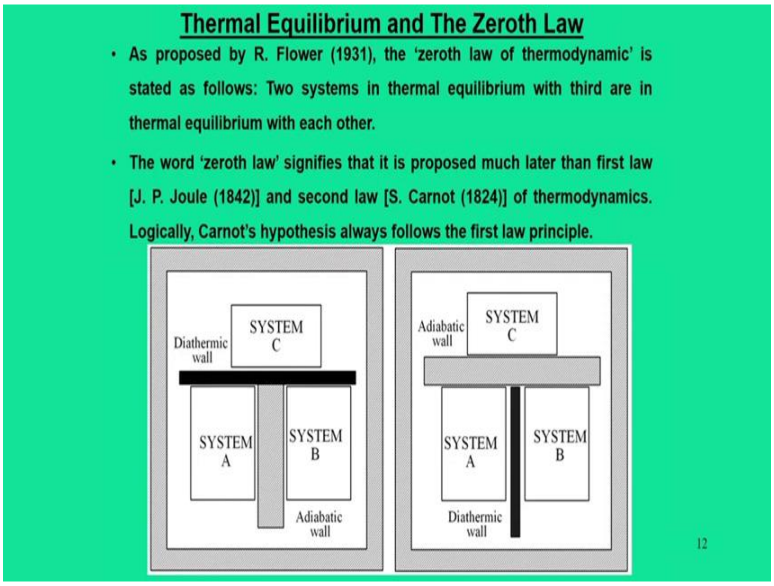

Thermal Equilibrium and The Zeroth Law

- As proposed by R. Flower (1931), the 'zeroth law of thermodynamic' is stated as follows: Two systems in thermal equilibrium with third are in thermal equilibrium with each other.
- The word 'zeroth law' signifies that it is proposed much later than first law [J. P. Joule (1842)] and second law [S. Carnot (1824)] of thermodynamics. Logically, Carnot's hypothesis always follows the first law principle.

So, this is the most essential concept of thermal equilibrium and zeroth law which says that the two systems are in thermal equilibrium with third then they are also in thermal equilibrium with each other and it was initially proposed by a scientist R. Flower which is in the year 1931.

And, in fact, why this word zeroth comes into picture here because since it was proposed in the year 1931, prior to this already first law and second law was developed. And the first law was proposed in the year 1842 by Joule and second law was proposed by Carnot which is 1824 and they have their own understanding and viewpoints. Since you know we need to follow a logical sequence, then based on this, the fundamental understanding will put this concept of thermal equilibrium as zeroth law of thermodynamics gives the concept of temperature. And, subsequently that concept of temperature was utilized in for first law and second law in the subsequent years. So, that is the reason the word zeroth law comes at its own significance.

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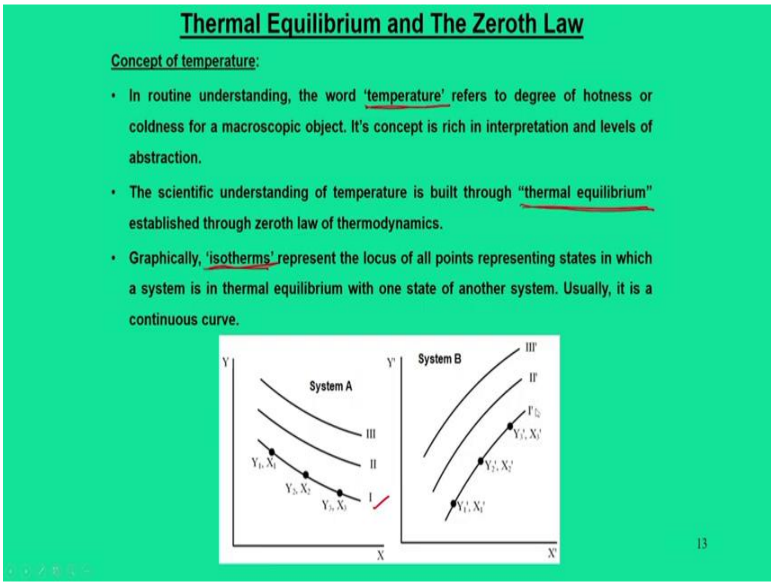

Thermal Equilibrium and The Zeroth Law

Concept of temperature:

- In routine understanding, the word 'temperature' refers to degree of hotness or coldness for a macroscopic object. It's concept is rich in interpretation and levels of abstraction.
- The scientific understanding of temperature is built through "thermal equilibrium" established through zeroth law of thermodynamics.
- Graphically, 'isotherms' represent the locus of all points representing states in which a system is in thermal equilibrium with one state of another system. Usually, it is a continuous curve.

Then let us move to further inferences that we get out of this zeroth law that is thermal equilibrium. Anyway first concept of zeroth law is the thermal equilibrium then while understanding this concept of thermal equilibrium if you want to quantify, then the word temperature drops in. And in a Layman sense it refers to the degree of hotness or coldness of a microscopic object.

But, the scientific understanding for this temperature can be interpreted through this thermal equilibrium which means that we need to plot them graphically. And, to understand this thermal equilibrium we must say that all the states are in same temperatures. So, in other words, graphically the same concepts can be interpreted and we call this as a isotherms.

So, isotherm represents locus of all points representing the state in which a system is in equilibrium with one state of another system and in fact, it is a continuous curve. So, bringing the same concept here if you understand this is a system A and this is the system B, and for a given set of conditions that is first condition I, we can say the system was initially at state point Y_1 and X_1, then it moves to Y_2 and X_2 it go then moves to Y_3 and X_3.

And, when moving these coordinates from one point to other, it is in thermal equilibrium with respect to it is surroundings. So, that means, we can represent this as a continuous curve and as if there is no change happens that means system undergoes a change of state without disturbing to the surroundings. Now, this happens at one particular set of conditions that is I, similar things it can be represented for condition II and III. In similar way we can put same logic for the system B for a set of conditions I`, II` and III`.

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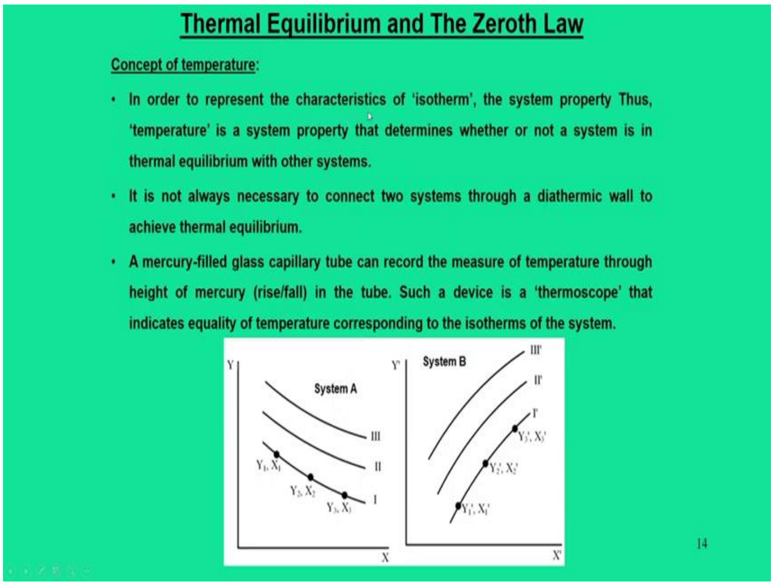

Thermal Equilibrium and The Zeroth Law

Concept of temperature:

- In order to represent the characteristics of 'isotherm', the system property Thus, 'temperature' is a system property that determines whether or not a system is in thermal equilibrium with other systems.
- It is not always necessary to connect two systems through a diathermic wall to achieve thermal equilibrium.
- A mercury-filled glass capillary tube can record the measure of temperature through height of mercury (rise/fall) in the tube. Such a device is a 'thermoscope' that indicates equality of temperature corresponding to the isotherms of the system.

So, to understand the characteristics of isotherm, we must say that the system property which is a temperature and it determines whether a system is in thermal equilibrium or not; that means, we can quantify this temperature with some number that will tell us whether the system is in thermal equilibrium with other systems or not. Now, we gave the concept of temperatures or thermal equilibrium through this diathermic wall, but always it is not necessary that you should use the diathermic wall.

So, for that things, we use some kind of mercury or some kind of liquid which can bear the properties of this diathermic wall and which can measure or record the temperature change while it is in equilibrium with its own surroundings. And, such a device we call this as a thermoscope and many times you interpret them as a thermometers. Ultimately what it indicates the equality of temperatures corresponding to one particular isotherms of the systems.

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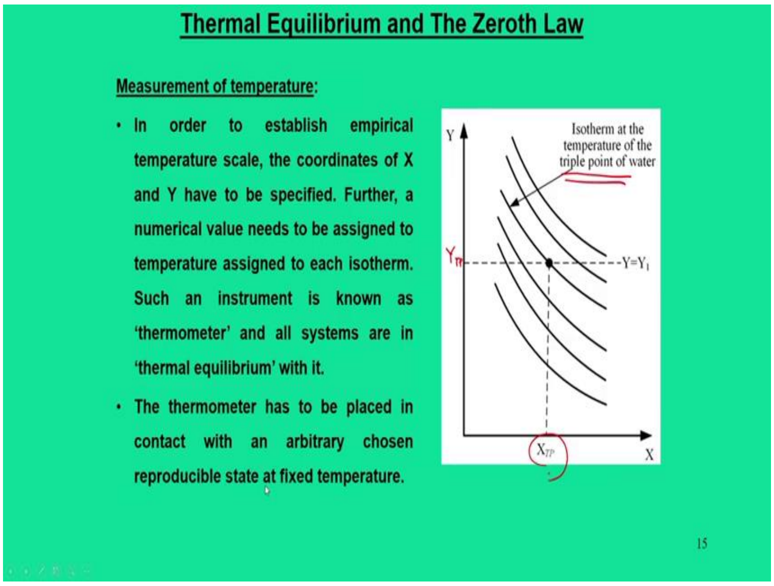

Thermal Equilibrium and The Zeroth Law

Measurement of temperature:

- In order to establish empirical temperature scale, the coordinates of X and Y have to be specified. Further, a numerical value needs to be assigned to temperature assigned to each isotherm. Such an instrument is known as 'thermometer' and all systems are in 'thermal equilibrium' with it.
- The thermometer has to be placed in contact with an arbitrary chosen reproducible state at fixed temperature.

Now, the first point we mentioned that in a Layman sense it gives the hotness or coldness of the systems. So, ideally people refer this hotness because it is hot and that is hot because it is with respect to some temperatures and that point of time the concept was the ice point and steam point. So, they were treated as a very basic reference temperatures and, with that respect people try to quantify this.

Now, similar concept if you introduce here that when we say we have plotted various isotherms for a system undergoing in different change of states, we can locate one particular point which will actually define the reference point and that reference point was chosen as the triple point of water.

Now, in the same X-Y plot, where Y and X are the two independent properties involving Newton's law or it can be pressure and volume. So, based on that we can locate one particular temperature on this entire set of isotherms which we can say is nothing but the triple point of water and for this triple point of water, we can define the set coordinates as X_{TP} and Y_{TP}. And, that is chosen as the reproducible state at a fixed temperature.

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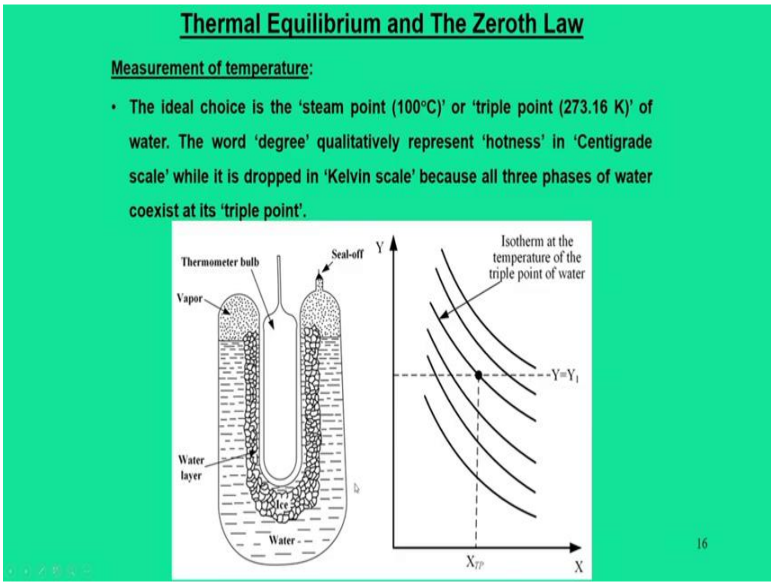

Thermal Equilibrium and The Zeroth Law

Measurement of temperature:

- The ideal choice is the 'steam point (100°C)' or 'triple point (273.16 K)' of water. The word 'degree' qualitatively represent 'hotness' in 'Centigrade scale' while it is dropped in 'Kelvin scale' because all three phases of water coexist at its 'triple point'.

So, what does this triple point of water means? Here we have a thermometer bulb and it is put in some medium or in a conditions which actually measures the triple point that is 273.16K which means that this thermometer bulb is in equilibrium with this complete systems involving water, ice and vapor.

And, at this particular conditions that is 273.16 Kelvin, we can say all the three states are in complete equilibrium or all the three states can coexist together. So, that was the basic point or one broad sense of viewing this reference temperatures and in many situations people also interpret this steam point as 100°C as reference and based on this we have different scales were proposed. And, this scales was now commonly called as centigrade scale or Kelvin scale.

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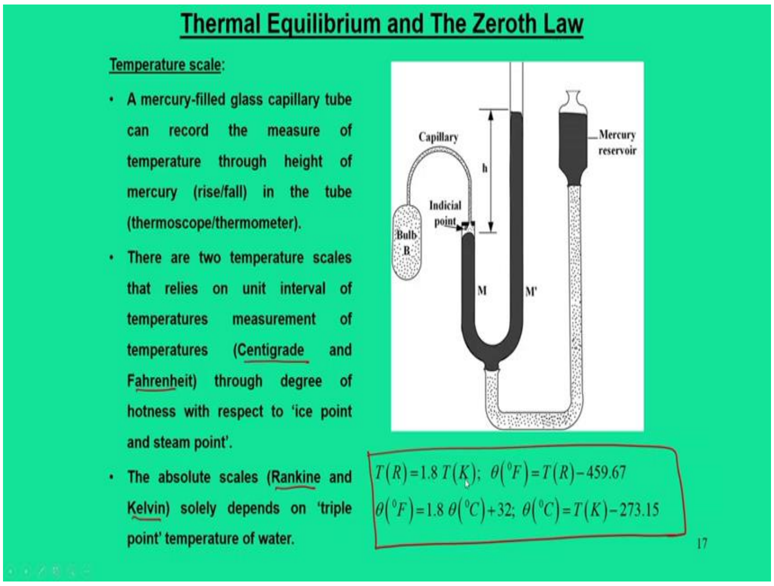

Thermal Equilibrium and The Zeroth Law

Temperature scale:

- A mercury-filled glass capillary tube can record the measure of temperature through height of mercury (rise/fall) in the tube (thermoscope/thermometer).
- There are two temperature scales that relies on unit interval of temperatures measurement of temperatures (Centigrade and Fahrenheit) through degree of hotness with respect to 'ice point and steam point'.
- The absolute scales (Rankine and Kelvin) solely depends on 'triple point' temperature of water.

$$T(R)=1.8\,T(K);\;\; \theta(^{0}F)=T(R)-459.67$$
$$\theta(^{0}F)=1.8\,\theta(^{0}C)+32;\; \theta(^{0}C)=T(K)-273.15$$

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So, what does this two scales means? That when you say centigrade scale or Kelvin scale, Kelvin scale refers to the absolute temperatures where the view was that it is referred to the absolute 0 temperature that is at that temperature the all the reference coordinates of temperatures were calculated.

And, when you say centigrade scale, it assumes that we have ice point, we have steam point, based on these things we can see there is a rise or fall of mercury in a particular device and we call this as a thermometer. Based on this rise and fall of mercury we quantify the temperature of the system.

Now, apart from this different countries use the philosophy of centigrade or Fahrenheit. In fact, the analogous to centigrade, there is another scale we call this is Fahrenheit scale. Here the only the magnitude of number changes means that in a Fahrenheit scale, the ice point and the steam points, they are different and based on that we can have this coordinate.

So, ultimately there are two scales which relies on ice point and steam point that is centigrade and Fahrenheit scale and there are two scales that relies on the triple point of water that is Rankine and Kelvin scale. So, the corresponding relations between the Rankine and Kelvin scale it can be written as this. This is the standard relations that can be used in our day to day life.

$$T(R) = 1.8\, T(K);\;\; \theta(^0F) = T(R) - 459.67$$
$$\theta(^0F) = 1.8\, \theta(^0C) + 32;\;\; \theta(^0C) = T(K) - 273.15$$

For example, if you want to specify a temperature which we know as a in Kelvin scale and when you multiply into 1.8 we will get the temperature in the Rankine scales. So, this is the relation between Rankine scale and Kelvin scale. Correspondingly there is a relations between Fahrenheit scale and Rankine scale. We can have relations between Fahrenheit scale and centigrade scale also we can have relations between centigrade scale and Kelvin scale.

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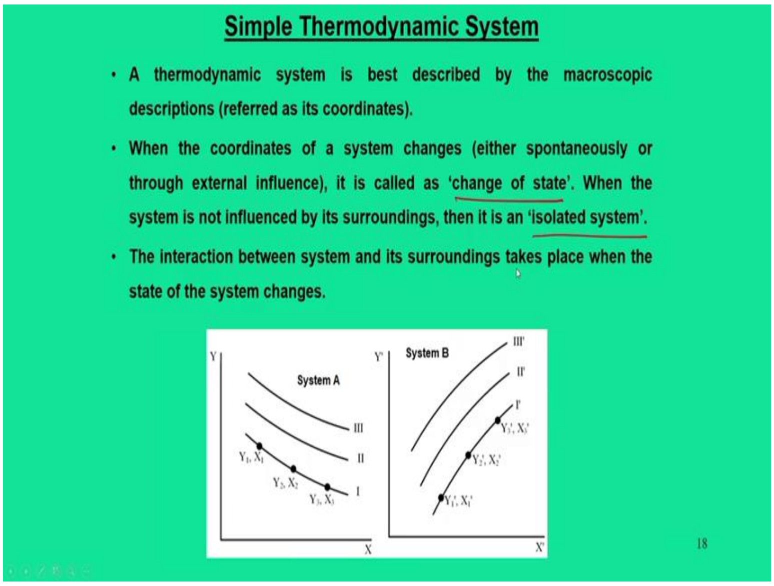

Simple Thermodynamic System

- A thermodynamic system is best described by the macroscopic descriptions (referred as its coordinates).
- When the coordinates of a system changes (either spontaneously or through external influence), it is called as 'change of state'. When the system is not influenced by its surroundings, then it is an 'isolated system'.
- The interaction between system and its surroundings takes place when the state of the system changes.

Then we will move to the next segment of our lecture that is simple thermodynamic system. So, from our previous understandings we say that any state of the systems can be represented by its coordinates and we call these as a thermodynamic coordinates with respect to macroscopic approach.

And, when this coordinates changes we call this as a change of state and when the system is not influenced by the surroundings we call this as a isolated systems. So, that means, the interaction between system and its surrounding takes place when there is a change in the system.

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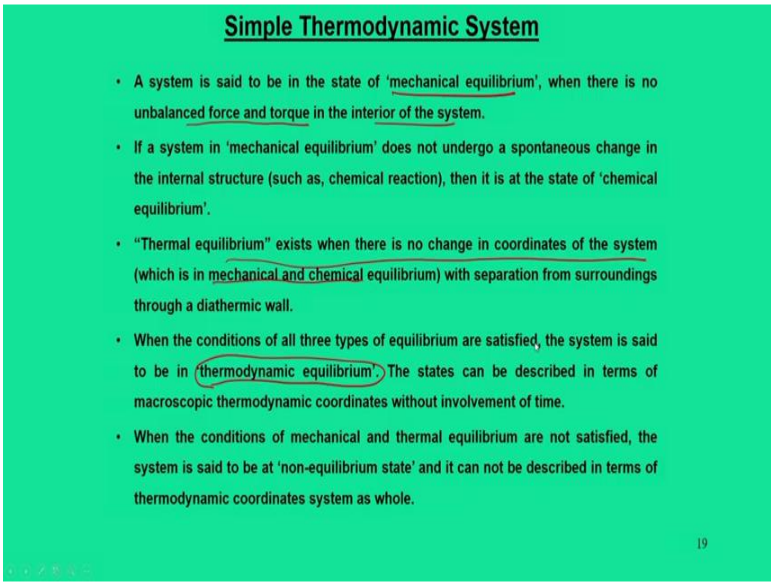

Simple Thermodynamic System

- A system is said to be in the state of 'mechanical equilibrium', when there is no unbalanced force and torque in the interior of the system.
- If a system in 'mechanical equilibrium' does not undergo a spontaneous change in the internal structure (such as, chemical reaction), then it is at the state of 'chemical equilibrium'.
- "Thermal equilibrium" exists when there is no change in coordinates of the system (which is in mechanical and chemical equilibrium) with separation from surroundings through a diathermic wall.
- When the conditions of all three types of equilibrium are satisfied, the system is said to be in 'thermodynamic equilibrium'. The states can be described in terms of macroscopic thermodynamic coordinates without involvement of time.
- When the conditions of mechanical and thermal equilibrium are not satisfied, the system is said to be at 'non-equilibrium state' and it can not be described in terms of thermodynamic coordinates system as whole.

So, we also know that that for a simple system to exist in equilibrium, there are three types of equilibrium. First is mechanical equilibrium and there we say that there is no unbalanced force and torque in the system. But, this mechanical equilibrium does not include the change or reactions that is happening within the internal structure of the systems. So, if that happens thermal equilibrium is not possible.

So, thermal equilibrium can also be possible only when there is no change in the coordinates in the systems; that means, system is in the mechanical as well as the chemical equilibrium. So, ultimately by clubbing all these three equilibrium conditions together that is mechanical equilibrium, chemical equilibrium and thermal equilibrium we represent the state of the system as a thermodynamic equilibrium in which we say that conditions of all the three types of equilibriums are satisfied.

That means, in the mechanical equilibrium there is no unbalanced force, in a chemical equilibrium there is no reactions and in a thermal equilibrium there is no change in the temperature. A thermodynamic equilibrium exists when all the three equilibrium conditions are satisfied otherwise we say it is a non-equilibrium state.

Then the philosophy of the equation state was introduced which means that entire systems can exist either in the solid phase, liquid phase or gas phase or when you say liquid and gas we say it is a fluid state. So, based on that, the thermodynamic coordinates bears certain relations.

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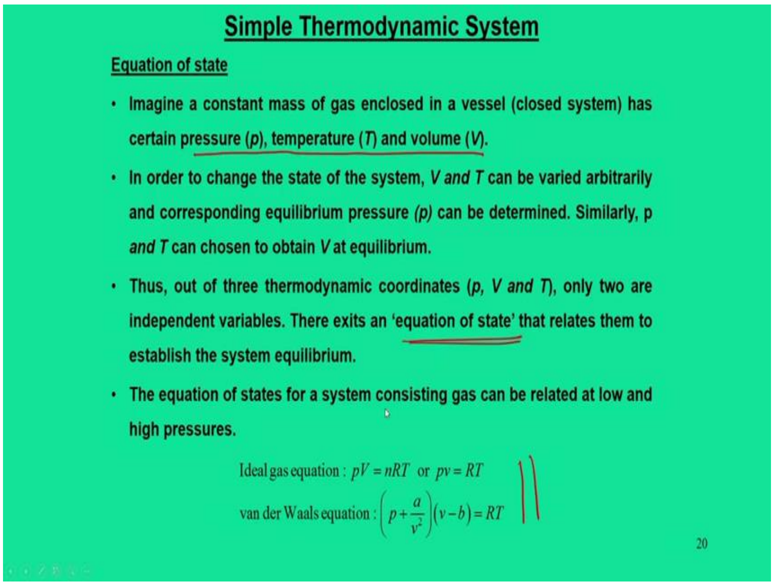

Simple Thermodynamic System

Equation of state

- Imagine a constant mass of gas enclosed in a vessel (closed system) has certain pressure (*p*), temperature (*T*) and volume (*V*).
- In order to change the state of the system, *V and T* can be varied arbitrarily and corresponding equilibrium pressure *(p)* can be determined. Similarly, p *and T* can chosen to obtain *V* at equilibrium.
- Thus, out of three thermodynamic coordinates (*p, V and T*), only two are independent variables. There exits an 'equation of state' that relates them to establish the system equilibrium.
- The equation of states for a system consisting gas can be related at low and high pressures.

$$\text{Ideal gas equation}: pV = nRT \text{ or } pv = RT$$

$$\text{van der Waals equation}: \left(p + \frac{a}{v^2}\right)(v - b) = RT$$

Those relations are in between pressure, temperature and volume. So, in order to change the state of the systems, V and T can be varied independently and corresponding equilibrium pressure can be determined. Similarly, p and T can be chosen to obtain V at the equilibrium.

What it means? Pressure and volume they can be integrated together; that means, when there is a change in the pressure, there is change in the volume and vice versa and temperature can be treated as an independent properties. And, when we define this particular states involving pressure, volume and temperatures we call this as a equation of state.

And, in particular we have this equation of state for gas when we call this as either ideal gas equations or it can be interpreted with respect to Van der Waal equations when you deal into the molecular approach. But, when you deal with the liquids, only pressure volume relations are possible because we require the coordinates of pressures and volume and all these things happens at for wide range of temperatures.

$$\text{Ideal gas equation}: pV = nRT \quad \text{or} \quad pv = RT$$

$$\text{van der Waals equation}: \left(p + \frac{a}{v^2}\right)(v - b) = RT$$

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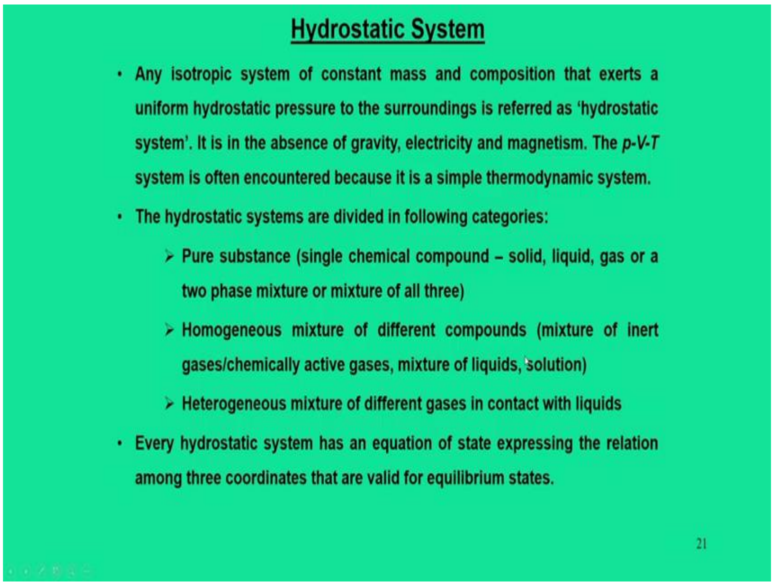

Hydrostatic System

- Any isotropic system of constant mass and composition that exerts a uniform hydrostatic pressure to the surroundings is referred as 'hydrostatic system'. It is in the absence of gravity, electricity and magnetism. The *p-V-T* system is often encountered because it is a simple thermodynamic system.
- The hydrostatic systems are divided in following categories:
  - Pure substance (single chemical compound – solid, liquid, gas or a two phase mixture or mixture of all three)
  - Homogeneous mixture of different compounds (mixture of inert gases/chemically active gases, mixture of liquids, solution)
  - Heterogeneous mixture of different gases in contact with liquids
- Every hydrostatic system has an equation of state expressing the relation among three coordinates that are valid for equilibrium states.

Then after this thermodynamic systems, then we will move to the hydrostatic systems. So, prior to this why the word hydrostatic comes into picture? Earlier we used to say it is a thermodynamic systems, now we say it is a hydrostatic systems because we deal with the behavior of a complete state of structures; that means, a system can exist in the liquid phase, gas phase or it can be mixed of both or if there may be concentration of the change in the mixture or it can exist in different phase.

So, depending on this for complete set of understandings, we call them as a hydrostatic systems. Now, within the domain of hydrostatic systems if you specify the particular characteristics for example, when you say pure substance which means it is a single chemical compound that is solid, liquid or gas or it can be a two phase mixture of mixture of all three. Then we can have a homogeneous mixture of different compounds that is mixture of inert gases, chemically active gases, mixture of liquids, solutions.

Then we can have the heterogeneous mixture of different gases which are in contact with liquids. So, all these three situations follow under the common domain we call this as a hydrostatic systems and. In fact, in our entire courses we will be dealing with how to address all these conditions of the systems and in terms of pressure, volume and temperature.

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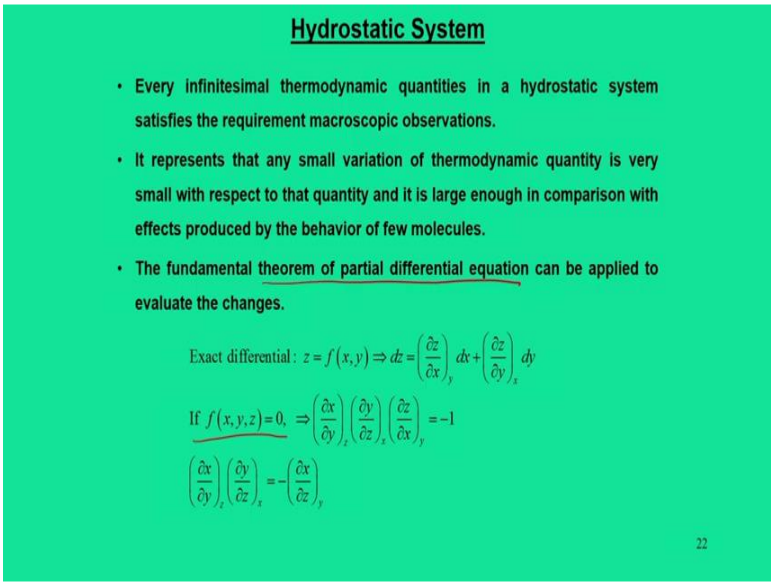

Hydrostatic System

- Every infinitesimal thermodynamic quantities in a hydrostatic system satisfies the requirement macroscopic observations.
- It represents that any small variation of thermodynamic quantity is very small with respect to that quantity and it is large enough in comparison with effects produced by the behavior of few molecules.
- The fundamental theorem of partial differential equation can be applied to evaluate the changes.

$$\text{Exact differential}: z = f(x,y) \Rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\text{If } f(x,y,z) = 0, \Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$$

So, another important segment of hydrostatic systems is that we say that pressure, volume, temperatures are three independent quantities and then need to be correlated. Now, to specify those systems we must have an understanding that how to quantify that. To quantify them we have to rely on certain mathematical concepts and that is nothing but the fundamental theorem of partial differential equations. And, in general

$$\text{Exactdifferential:} z = f(x,y) \Rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\text{If} f(x,y,z) = 0, \Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$$

And, in fact, why I gave these relations because we are going to rewrite our pressure, volume and temperatures for this situations. So, here we have said that the we have three parameters pressure volume and temperatures, and pressure volumes can be coupled together and temperature can be independent in nature.

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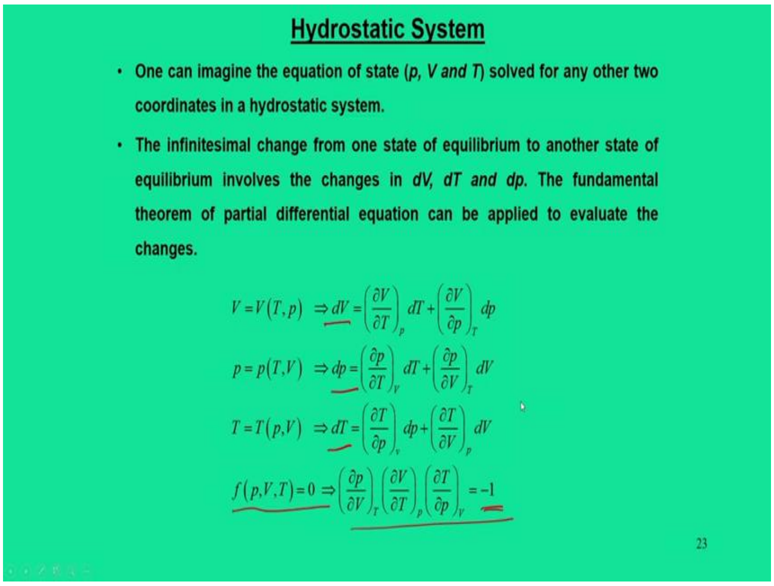

Hydrostatic System

- One can imagine the equation of state (*p, V and T*) solved for any other two coordinates in a hydrostatic system.
- The infinitesimal change from one state of equilibrium to another state of equilibrium involves the changes in *dV, dT and dp*. The fundamental theorem of partial differential equation can be applied to evaluate the changes.

$$V=V(T,p)\ \Rightarrow dV=\left(\frac{\partial V}{\partial T}\right)_p dT+\left(\frac{\partial V}{\partial p}\right)_T dp$$

$$p=p(T,V)\ \Rightarrow dp=\left(\frac{\partial p}{\partial T}\right)_V dT+\left(\frac{\partial p}{\partial V}\right)_T dV$$

$$T=T(p,V)\ \Rightarrow dT=\left(\frac{\partial T}{\partial p}\right)_V dp+\left(\frac{\partial T}{\partial V}\right)_p dV$$

$$f(p,V,T)=0 \Rightarrow \left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_V=-1$$

So, for that we can define these hydrostatic systems mathematically. So, there are in fact, three possibilities which we can write; that means, volume can be represented as as a function of temperature and pressure; pressure can be represented as temperature and volume; temperature can be represented as function of pressure and volume. So, accordingly the exact differential dV, dp and dT can be determined.

$$V = V(T,p) \Rightarrow dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$$

$$p = p(T,V) \Rightarrow dp = \left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV$$

$$T = T(p,V) \Rightarrow dT = \left(\frac{\partial T}{\partial p}\right)_v dp + \left(\frac{\partial T}{\partial V}\right)_p dV$$

$$f(p,V,T) = 0 \Rightarrow \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = -1$$

So, we are going to use these four relations exhaustively in our all the subsequent derivations or information.

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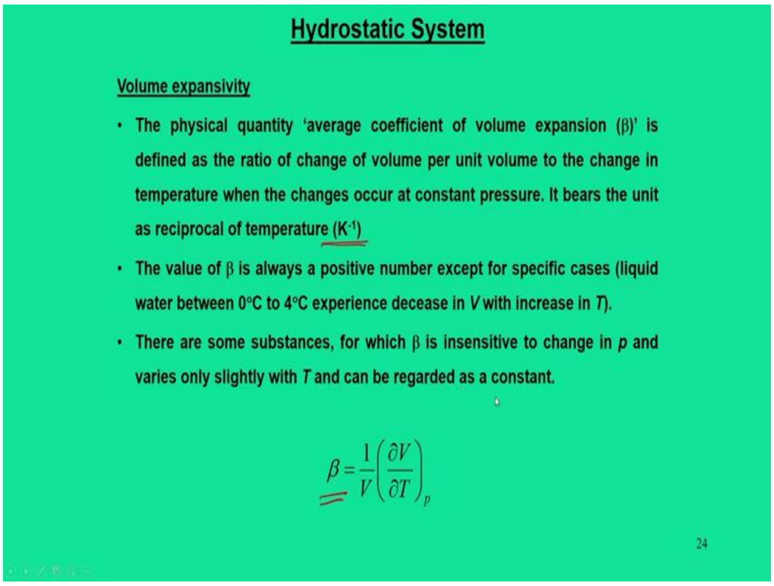

Hydrostatic System

Volume expansivity

- The physical quantity 'average coefficient of volume expansion (β)' is defined as the ratio of change of volume per unit volume to the change in temperature when the changes occur at constant pressure. It bears the unit as reciprocal of temperature (K^{-1})
- The value of β is always a positive number except for specific cases (liquid water between 0°C to 4°C experience decease in V with increase in T).
- There are some substances, for which β is insensitive to change in p and varies only slightly with T and can be regarded as a constant.

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

Now, based on this for an hydrostatic system, the first property that we are going to discuss is the volume expansivity. So, it talks about how volume changes with temperature by maintaining pressure constant. So, this parameter is represented as β which says that it is the ratio of change in of volume per unit volume to the change of temperature when the change occurs at constant pressures. $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

And, based on this unit we can say it has a unit of which we call as a reciprocal of temperatures. And, in fact, the β is always a positive number except some specific cases and in fact, it is seen that this value of β is insensitive to the change in the pressure and it varies only slightly with temperatures. So, it can be regarded as a constant for a particular gas or liquid or substance.

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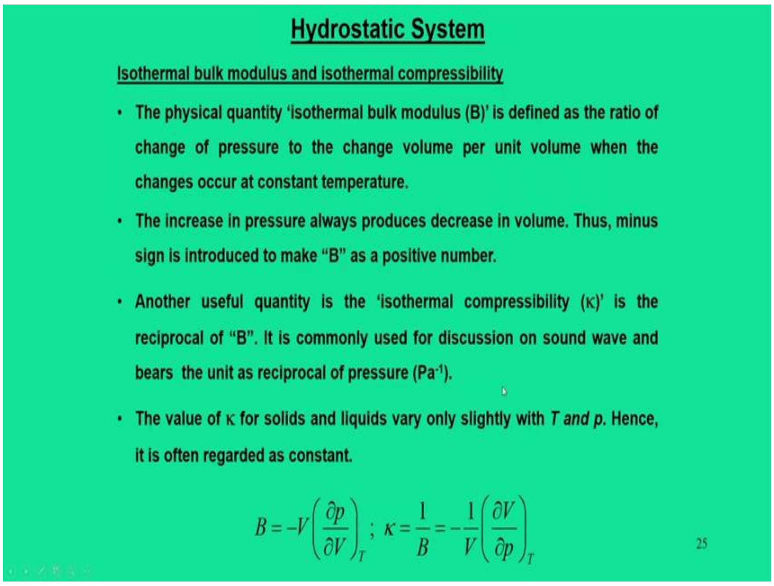

Hydrostatic System

Isothermal bulk modulus and isothermal compressibility

- The physical quantity 'isothermal bulk modulus (B)' is defined as the ratio of change of pressure to the change volume per unit volume when the changes occur at constant temperature.
- The increase in pressure always produces decrease in volume. Thus, minus sign is introduced to make "B" as a positive number.
- Another useful quantity is the 'isothermal compressibility (κ)' is the reciprocal of "B". It is commonly used for discussion on sound wave and bears the unit as reciprocal of pressure (Pa^{-1}).
- The value of κ for solids and liquids vary only slightly with T *and* p. Hence, it is often regarded as constant.

$$B = -V\left(\frac{\partial p}{\partial V}\right)_T \; ; \; \kappa = \frac{1}{B} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

The other property that we are going to discuss is isothermal bulk modulus and isothermal compressibility.

The first quantity that is isothermal bulk modulus B is defined as the ratio of change in the pressure to the change in the volume per unit volume when the changes occurs at constant temperatures. So, this you can write this expression mathematically as $B = -V\left(\frac{\partial p}{\partial V}\right)_T$.

So, here we can see that pressure and volume they are reverse relations; that means, increase in the pressure will lead to decrease in the volume and vice versa. So, in order to make this B as a positive number so, a negative sign is introduced here. Similarly, we have found out another correlations that can be derived as the reciprocal of B and that we call this as a isothermal compressibility.

This particular parameter was mostly used when you deal with the speed of sound and in fact, it when we say we use this in the compressible fluid mechanics or compressible flow. And, it is nothing but reciprocal of this isothermal bulk modulus and it is represented by $\kappa = \frac{1}{B} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$.

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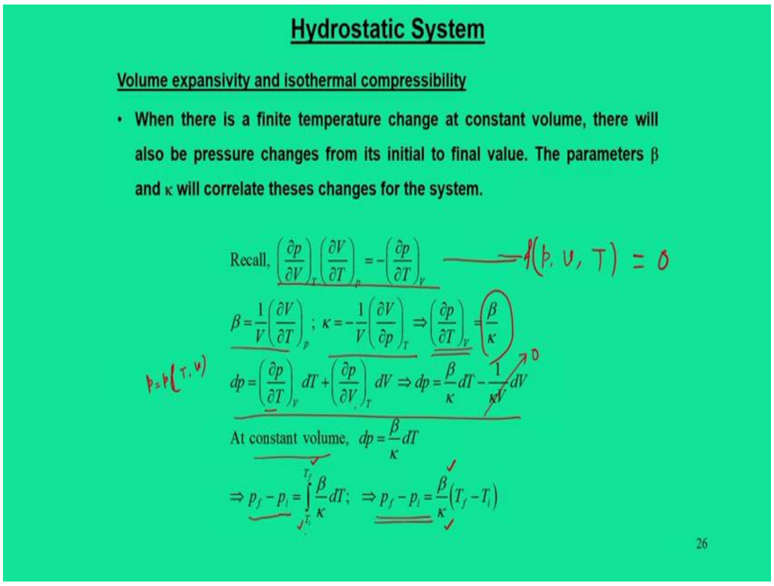

Hydrostatic System

Volume expansivity and isothermal compressibility

- When there is a finite temperature change at constant volume, there will also be pressure changes from its initial to final value. The parameters β and κ will correlate theses changes for the system.

Recall, $\underline{\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_V} \longrightarrow f(p, V, T) = 0$

$\underline{\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p}$; $\underline{\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T} \Rightarrow \underline{\underline{\left(\frac{\partial p}{\partial T}\right)_V}} = \boxed{\frac{\beta}{\kappa}}$

$p = p(T, V)$

$\underline{dp = \left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV \Rightarrow dp = \frac{\beta}{\kappa}dT - \cancelto{0}{\frac{1}{\kappa V}dV}}$

$\underline{\text{At constant volume,}}\checkmark \quad dp = \frac{\beta}{\kappa}dT$

$\Rightarrow \underline{p_f - p_i} = \int_{T_i}^{T_f}\frac{\beta}{\kappa}dT; \Rightarrow \underline{\underline{p_f - p_i}} = \frac{\beta}{\kappa}(T_f - T_i)$ ✓

Now, let us recall our understanding that how both volume expansivity and isothermal compressibilities are related. So, here we are going to apply the first relations that first relations is between pressure, volume and temperatures and that is nothing but the reciprocal relations we say $f(p, V, T) = 0$ and this equation was formed where $\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_V$

And, we have to recall the parameters that is β, κ. And, from these two parameters one can find out the ratio of beta by kappa and that is nothing but $\left(\frac{\partial p}{\partial T}\right)_V = \frac{\beta}{\kappa}$. Then when we are going to use it here, we can find $dp = \left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV \Rightarrow dp = \frac{\beta}{\kappa}dT - \frac{1}{\kappa V}dV$. What does mean means that we again start with another relations where p is function of temperature and volume.

And, from this we can say at constant volume so, $\frac{1}{\kappa V}dV$ term goes to 0. As a result we write $dp = \frac{\beta}{\kappa}dT$. And, from this we can have relations between the pressure change; that means, from final pressure and initial pressure and for a given substance for which we know β and κ. And, if a system changes from the initial temperature T_i to final temperature, T_f then we can find out what is the change in the pressures.

$$p_f - p_i = \int_{T_i}^{T_f}\frac{\beta}{\kappa}dT\,; \Rightarrow p_f - p_i = \frac{\beta}{\kappa}(T_f - T_i)$$

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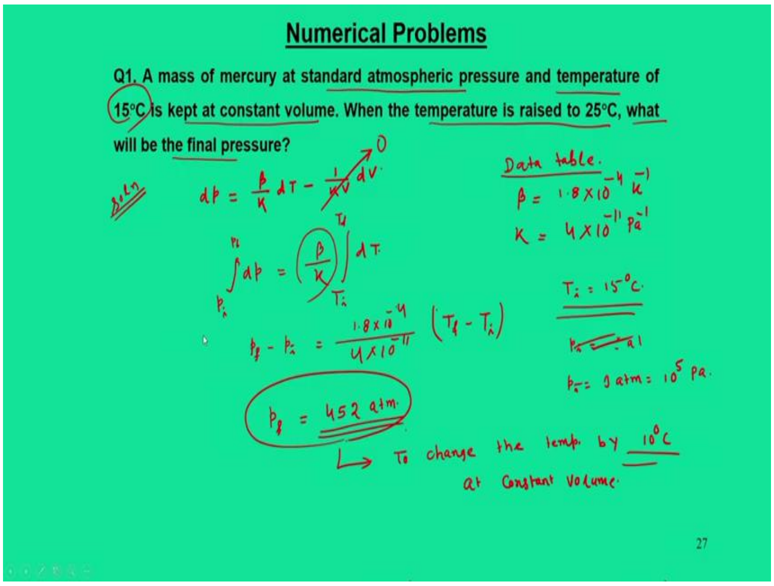

Numerical Problems

Q1. A mass of mercury at standard atmospheric pressure and temperature of 15°C is kept at constant volume. When the temperature is raised to 25°C, what will be the final pressure?

Soln

$$dp = \frac{\beta}{\kappa}\, dT - \cancel{\frac{1}{\kappa V}\, dV} \xrightarrow{} 0$$

$$\int_{p_i}^{p_f} dp = \left(\frac{\beta}{\kappa}\right) \int_{T_i}^{T_f} dT$$

$$p_f - p_i = \frac{1.8\times10^{-4}}{4\times10^{-11}} (T_f - T_i)$$

$$\boxed{p_f = 452\ \text{atm}}$$

→ To change the temp. by 10°C at Constant Volume.

Data table.

$\beta = 1.8\times10^{-4}\ K^{-1}$

$\kappa = 4\times10^{-11}\ Pa^{-1}$

$T_i = 15°C$

~~$p_i = 1$~~

$p_i = 1\ \text{atm} = 10^5\ Pa$

So, based on this concept let us see one important problem which states that a mass of mercury at standard atmosphere pressure and temperature that is 15°C, is kept at constant volume; that means, initially the condition was 15°C and atmospheric pressure. Now, what happens that at constant volume the temperature was raised to 25°C. So, we are going to find out what is the final pressures.

So, we have to recall our very basic understanding from the last slide, we derived this expression $dp=\beta/\kappa\ dT-1/\kappa V\ dV$. So, here what happens the system is at constant volume. So, dV goes to 0, then we can integrate these equations. So, we can write it as $p_f - p_i = \int_{T_i}^{T_f} \frac{\beta}{\kappa} dT$.

And, we do not know the value of $\frac{\beta}{\kappa}$. So, from this we have to use the data table; that means any thermodynamic book will give you this value of β and κ. And, for mercury this value I can note down as $\beta = 1.8 \times 10^{-4} K^{-1}$ and $\kappa = 4 \times 10^{-11} Pa^{-1}$.

So, $p_f - 10^5 = \frac{\beta}{\kappa}\left(T_f - T_i\right) = \frac{1.8\times10^{-4}}{4\times10^{-11}}(298-288),\ p_f = 452\ atm$

So, which means that we require 452 atmosphere to change the temperature by 10°C at constant volume. So, approximately 452 atmosphere pressure is required to raise the temperature of mercury by 10°C by maintaining constant volume that is most important.

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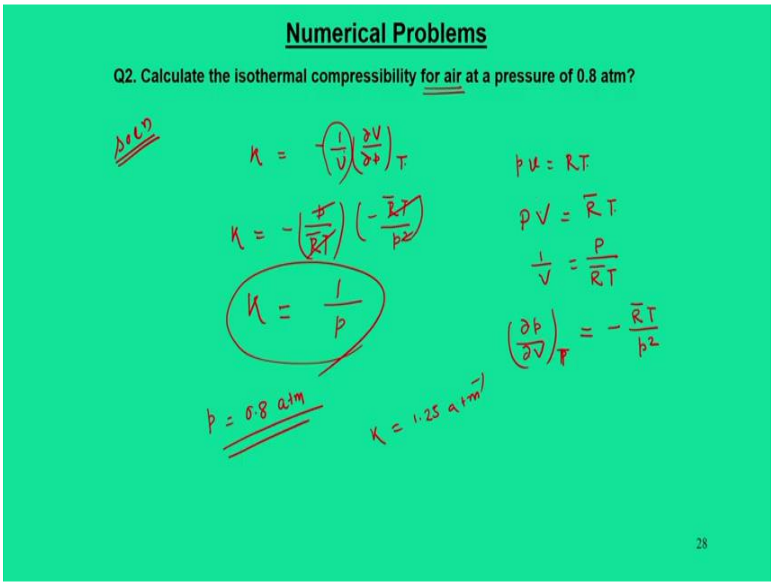

Numerical Problems

Q2. Calculate the isothermal compressibility for air at a pressure of 0.8 atm?

The next problem is about this isothermal compressibility for air at 0.8 atmospheres. So, this is also a simple problem. We have to start from the basic definitions what is the isothermal compressibility that is kappa and that is nothing but $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$. So, here we have used this working fluid as air. So, we say $pv = RT, pV = \bar{R}T, \frac{1}{V} = \frac{P}{RT}$.

From these things, we can write $\left(\frac{\partial p}{\partial V}\right)_T = -\bar{R}T/p^2$ And, when you put this equation here $\kappa = \left(-\frac{p}{RT}\right)\left(-\frac{RT}{p^2}\right),\ \ \kappa = \frac{1}{p}$.

So, kappa which is isothermal compressibility is equal to 1/p that is reciprocal of pressure. And, here pressure is given as 0.8 atmosphere, which means that $\kappa = 1.25\ atm^{-1}$. So, this is all about the calculation of thermodynamic properties of a substance. With this I will conclude the lecture for this class.

Thank you for your attention.