Chemical Engineering Thermodynamics
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Lecture - 01
Introduction to Thermodynamics

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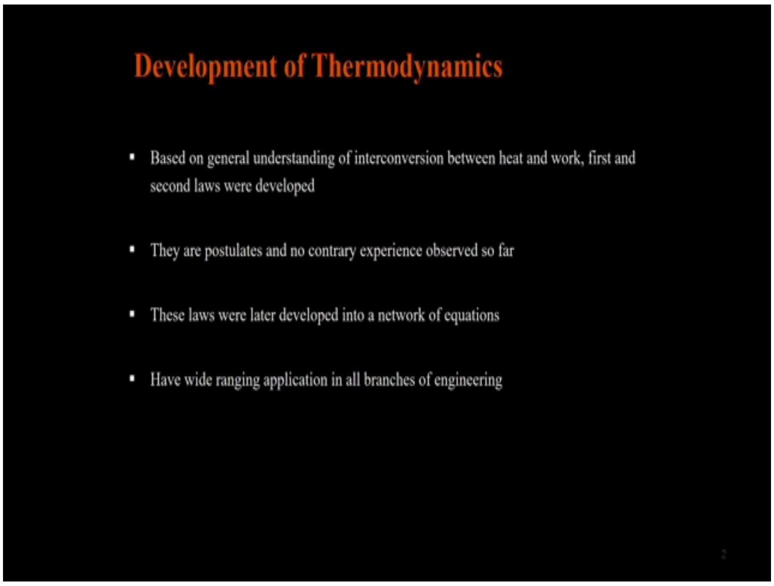

Development of Thermodynamics

- Based on general understanding of interconversion between heat and work, first and second laws were developed
- They are postulates and no contrary experience observed so far
- These laws were later developed into a network of equations
- Have wide ranging application in all branches of engineering

Hello and welcome back. Let us start our first lecture on Chemical Engineering Thermodynamics. As I talked over in the introductory lecture the development of thermodynamics is based on general understanding of inter conversion between heat and work, and based on those the first and second laws of thermodynamics were developed.

They are simply postulate and no experience contrary to these postulates has been observed so far, so we take them as such. And based on this first and second laws a wide network of equations were developed which have a range of applications in several branches of engineering. Let us define some basic quantities before we actually start working with these first and second laws of thermodynamics.

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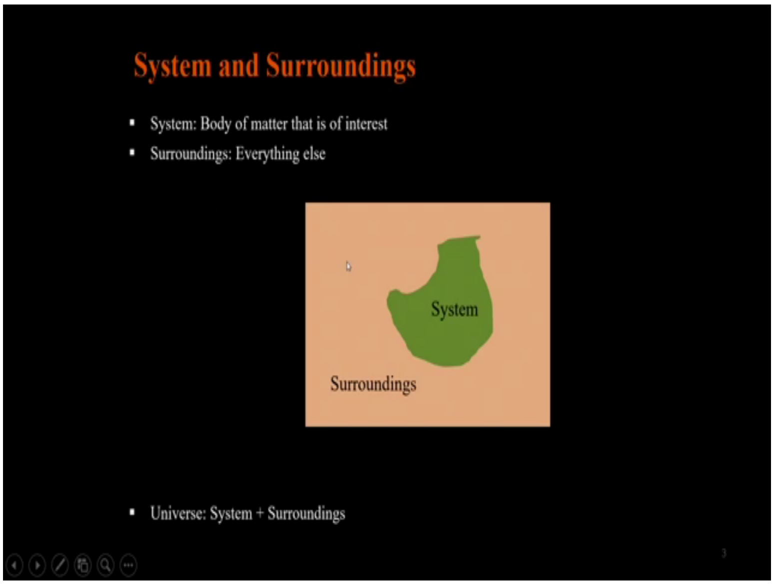

System and Surroundings

- System: Body of matter that is of interest
- Surroundings: Everything else

- Universe: System + Surroundings

First thing we are interested in thermodynamics is what is known as a system. It is the body of the matter that is of interest in our analysis and everything else that is not system is what we call as the surroundings. And the system and the surroundings together make what is known as the universe.

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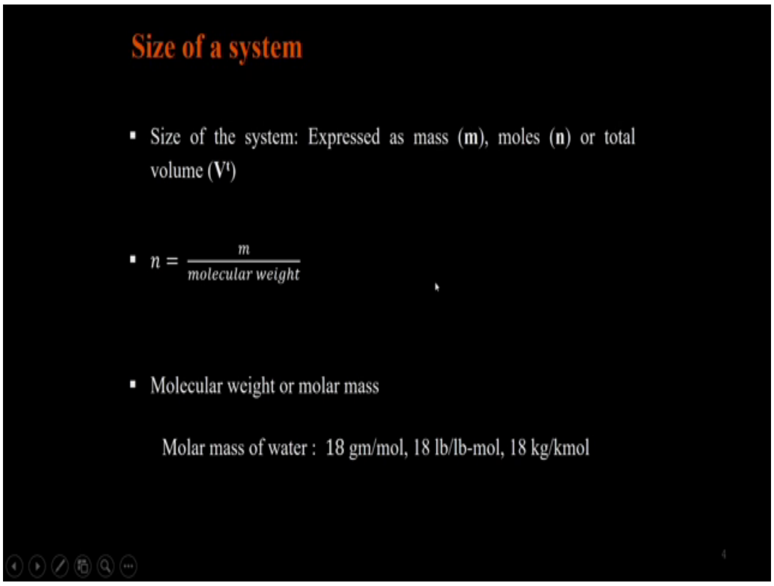

Size of a system

- Size of the system: Expressed as mass (**m**), moles (**n**) or total volume (**V^t**)
- $n = \frac{m}{molecular\ weight}$
- Molecular weight or molar mass

  Molar mass of water : 18 gm/mol, 18 lb/lb-mol, 18 kg/kmol

The size of a system is expressed either in as a mass m or moles n or the total volume V t that superscript t there stands for the total volume of the system. I will come back to the other type of volume we are it we usually encounter in thermodynamics in a minute.

Now, as all of you know it is pretty straightforward conversion between the moles and the mass of a system. The moles n is going to be mass m over the molecular weight. The units for molecular weight or molar mass are going to be grams per mole, pounds per pound mole, or kilograms per kilomole in all of these units for water of course, the number is 18.

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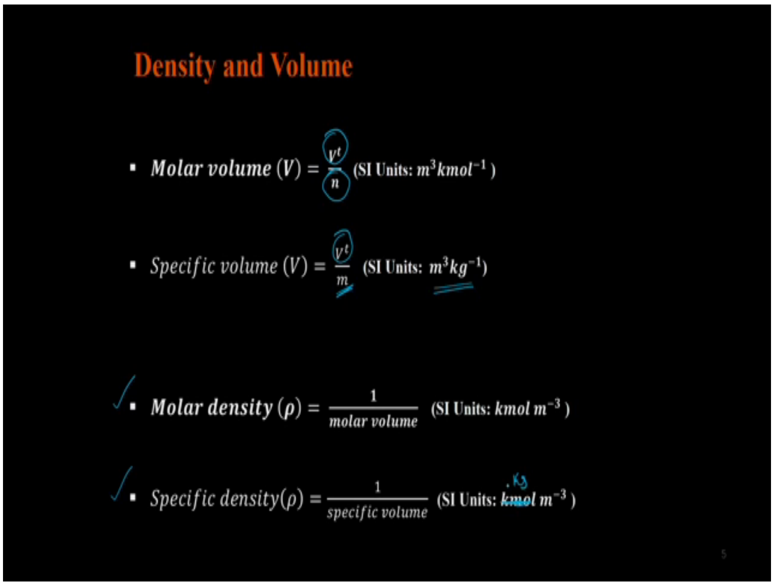

Density and Volume

- Molar volume $(V) = \frac{V^t}{n}$ (SI Units: $m^3 kmol^{-1}$)
- Specific volume $(V) = \frac{V^t}{m}$ (SI Units: $m^3 kg^{-1}$)
- ✓ Molar density $(\rho) = \frac{1}{\text{molar volume}}$ (SI Units: $kmol\, m^{-3}$)
- ✓ Specific density$(\rho) = \frac{1}{\text{specific volume}}$ (SI Units: $\overset{Kg}{\cancel{kmol}}\, m^{-3}$)

Then we have a quantity which is known as molar volume. As the name indicates molar volume is volume occupied by 1 mole of a substance or 1 kilo mole of a substance or a unit mole or the substance. And one can obtain this quantity V, if we divide the total volume v t right if we divide the total volume v t with the number of moles n. On the other hand, if I divide the total volume v t with the mass of the system m then we get what is known as the specific volume or volume occupied by unit mass of the substance.

Both these quantities molar volume and specific volume if we invert them, we get the two densities one is known as the molar density the units are going to be inverse of the molar volume. So, it is going to be kilo moles per meter cube. And if I invert the specific volume, we get what is known as the specific density it is going to be kilograms per meter cube right.

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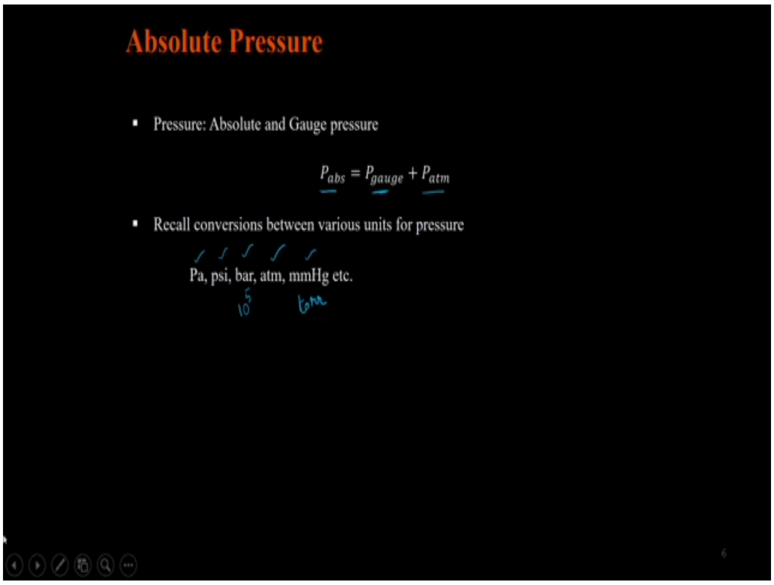

Absolute Pressure

- Pressure: Absolute and Gauge pressure

$$\underline{P_{abs}} = \underline{P_{gauge}} + \underline{P_{atm}}$$

- Recall conversions between various units for pressure

Pa, psi, bar, atm, mmHg etc.

10^5 torr

The other quantity we commonly encounter in thermodynamics is what is known as pressure. We simply call it as pressure, but then just to make sure there are two types of pressures: an absolute pressure and a gauge pressure. The absolute pressure is essentially the gauge pressure plus the atmospheric pressure right. And one we have several units for pressure the SI unit is Pascal's, then we have pounds per square inch, bar which is 10 power 5 Pascal's, then we have atmospheres. Then we have mm hg or what is also known as torr etcetera. So, we need to know the inter conversions between several units to be able to apply them as they are needed.

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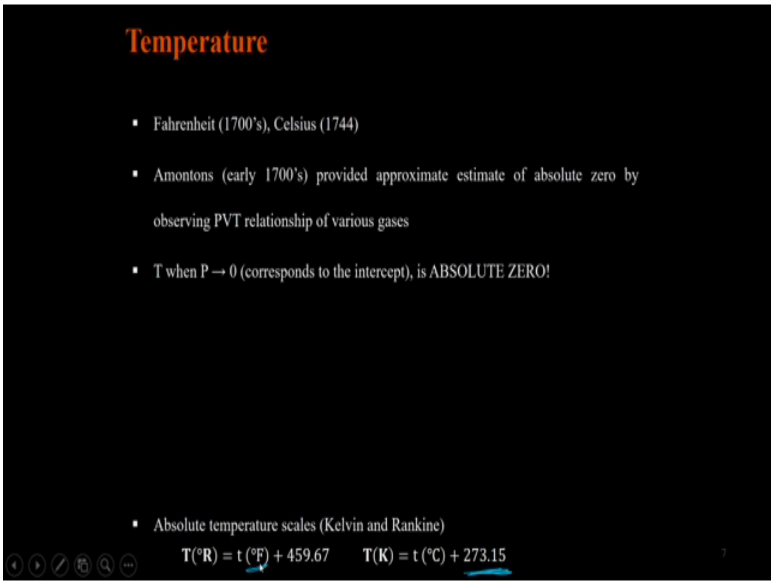

Temperature

- Fahrenheit (1700's), Celsius (1744)
- Amontons (early 1700's) provided approximate estimate of absolute zero by observing PVT relationship of various gases
- T when P → 0 (corresponds to the intercept), is ABSOLUTE ZERO!

- Absolute temperature scales (Kelvin and Rankine)

$T(°R) = t(\underline{°F}) + 459.67$ $\qquad$ $T(K) = t(°C) + \underline{273.15}$

The other quantity apart from pressure that is of interest in thermodynamics is temperature. The Fahrenheit scale started in early 17100s followed by Celsius scale in mid 1700s right. The absolute zero or the estimate for absolute zero was provided early on by observing the PV behavior of gases, it was observed that the product PV is fairly constant and or linear with temperature I should say. And if one interpolate, extrapolates that the behavior, we get an intercept which corresponds to the absolute zero. And based on those ideas and rough estimate for absolute zero was given on in early 1700s.

Based on the units for temperature, we use we have two absolute temperature scales. One is Rankine and the other one is Kelvin. So, in centigrade the absolute zero is going to be negative 273.15 right. And in Rankine or in Fahrenheit, the absolute zero is going to be negative 459.67.

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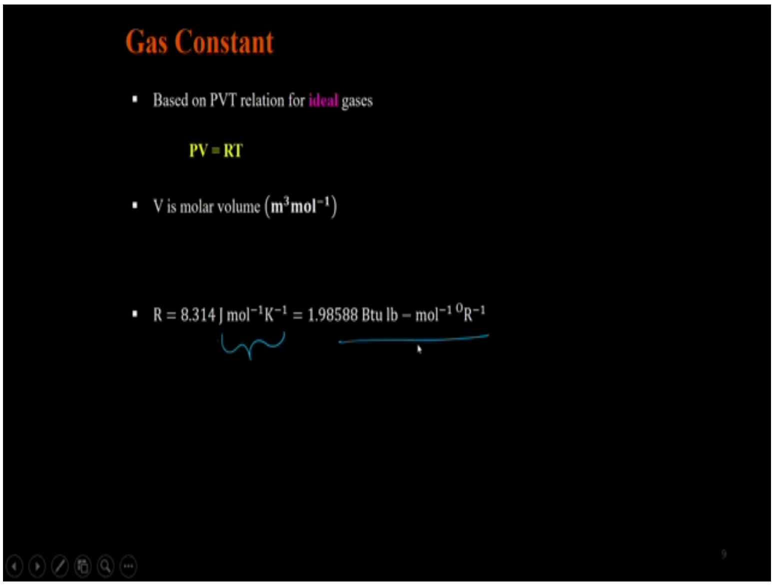

Gas Constant

- Based on PVT relation for ideal gases

$$PV = RT$$

- V is molar volume $(\mathbf{m^3mol^{-1}})$
- $R = 8.314\ \mathrm{J\ mol^{-1}K^{-1}} = 1.98588\ \mathrm{Btu\ lb-mol^{-1}\ {}^0R^{-1}}$

The other quantity of interest is the universal gas constant or simply the gas constant as it is called it is based on the PVT relationship for as I said ideal gases. So, it turns out that the product PV is going to be proportional to temperature and the constant of proportionality for an ideal gas is known as R or the gas constant. In this expression of course V is the molar volume, so based on that the units for our SI units for R are going to be joules per mole per Kelvin right. The product PV is a work term. So, it is going to be in joules, and since v is the molar volume it is going to be in joules per mole divided by the temperature is going to be Kelvin. So, the units for R are joule per mole per

Kelvin. And in SI, it is going to be 8.314 joule per mole per Kelvin, and similarly in other units.

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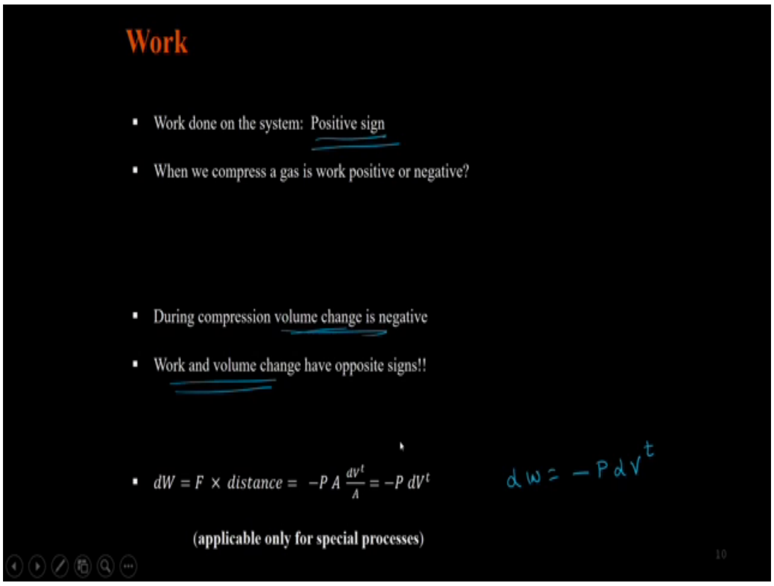

Work

- Work done on the system: Positive sign
- When we compress a gas is work positive or negative?
- During compression volume change is negative
- Work and volume change have opposite signs!!
- $dW = F \times distance = -P\,A\,\frac{dV^t}{A} = -P\,dV^t$

$dw = -P\,dV^t$

(applicable only for special processes)

The other quantity of interest since we are going to be talking a lot about work and heat requirements in a process is work. When we have a system, we can do work on the system or the system can do work on the surroundings. We need to have a convention for which work is positive and which work is negative. The usual sign convention that is adopted is if we have work that is being done on the system the system is going to gain energy. So, it is going to be a positive sign. If the work is done on the system, so when we compress a gas if one asked the question is the work positive or negative we are compressing the gas we are doing work on the system of the surroundings are going to do work on the system. So, it is always going to be positive.

On the other hand when we compress a gas the volume change is negative. So, the work and volume always have opposite signs right. So, the way we write it is dW is going to be minus P dV, and this is the total volume. So, we keep that superscript t. So, just to account for the difference in science, we put a negative sign there, so that both of them have this sign according to our sign convention. Now, this relation is applicable only for special processes. We will come back and talk about this special type of processes known as reversible processes.

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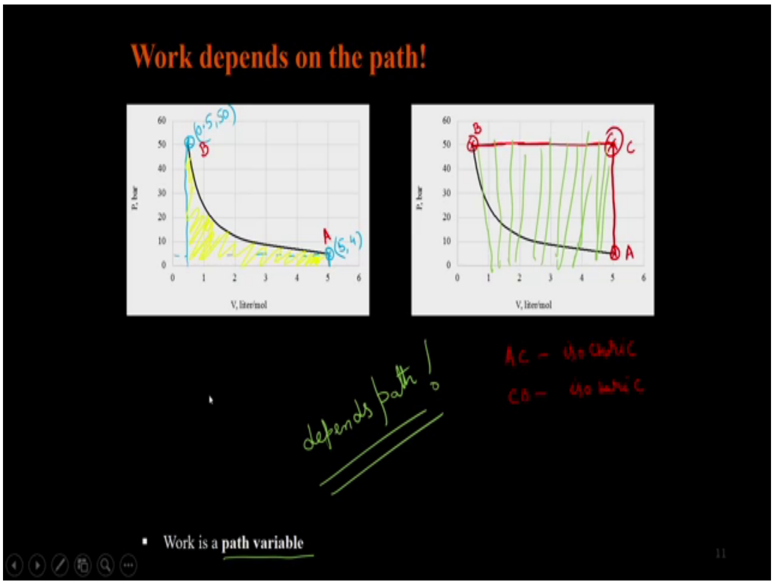

Work depends on the path!

- Work is a path variable

Now, let me give an example. If I have work that is being done let us say I start at about this volume of 5 liters per mole and a pressure. So, let us say it is 4 bar. So, 5 liters per mole and 4 bar we start with this pressure and compress the gas. As we compress the gas the volume is going to reduce and the pressure is going to increase and we compress the gas all the way to this point. And during the compression, we follow this path, then the black curve shows the path we are following during the compression process and we are compressing it from 5 liter per mole and 4 bar to let us say about half liter per mole and 50 bar.

Now, during this compression process if I follow the black curve, then turns out following what we said earlier for this special process this work done is going to be the area under the curve I am shading in yellow. This would be the work done for the process if it follows that curve. Now, instead of doing that instead of following the black curve, I can achieve the same state, but I will do what is known as an isochoric compression which means I will keep, so I am going to start from here instead of going to the final point following the black curve I will first go along this path to this point.

So, this was my point A; this was my point B. I am going to go from point A to point B, but not along the black curve, but now I decide to go along the vertical and horizontal red lines I am drawing right now. So, the first point A to C is a isochoric, isochoric meaning constant volume process, A to C is an isochoric process. And C to B is a isobaric process or a constant pressure process. So, instead of following the black curve, now I am going to follow the two red lines to achieve the same change in state from A to B. If I do that it turns out that for the first process. There is no work done.

And for the second process is going to be this area I have shaded in green. Now, as you see in both cases I am going from A to B, but then the work done is different, because I have chosen different paths. Remember work is P dV, so the area under this curve is going to give me the work done. In first case, it is going to be the yellow shaded region because I am going along the black curve. In the second case, it is going to be the shaded in green because I am following the two red lines and both these work dones are different. So, we say that work is a path variable or it depends on the path I take to achieve the change in states. We will contrast this with other thermodynamic variables we will encounter later.

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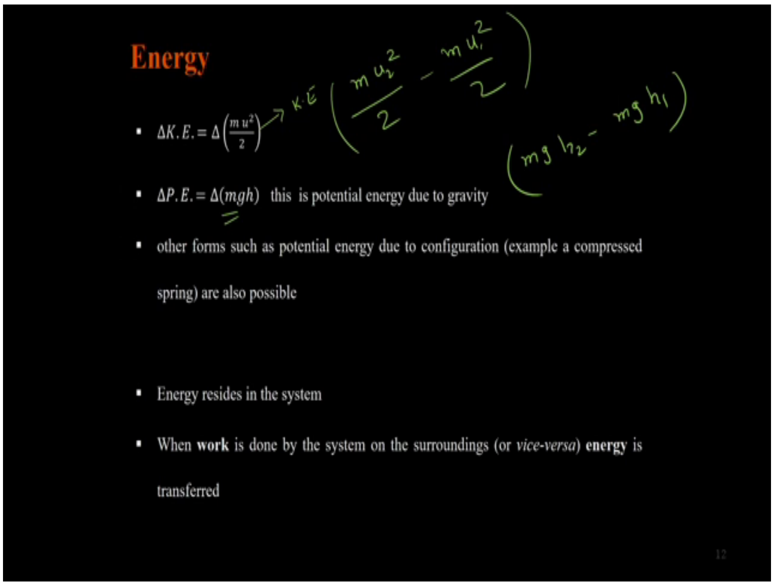

Energy

- $\Delta K.E. = \Delta\left(\frac{m u^2}{2}\right) \rightarrow K.E. \left(\frac{m u_2^2}{2} - \frac{m u_1^2}{2}\right)$
- $\Delta P.E. = \Delta(mgh)$ this is potential energy due to gravity $\left(mg h_2 - mg h_1\right)$
- other forms such as potential energy due to configuration (example a compressed spring) are also possible

- Energy resides in the system
- When **work** is done by the system on the surroundings (or *vice-versa*) **energy** is transferred

The other quantity that is of interest to us in thermodynamics is what is known as energy. The change in kinetic energy as you all know is the change in mu square over t this is the kinetic energy term. So, let us say the mass is not changing. So, the mass is always m the initial and final velocities are u 1 and u 2 respectively then the change in kinetic energy is going to be mass times u 2 squared over 2 minus mass times u 1 squared over 2. But as the change in potential energy if it is due to gravity is simply m g h 2 minus mg h 1 right. In addition to these two quantities kinetic and potential energies there are other forms of energies such as energy that is stored in a compressed spraying etcetera. Now, when we do work on the system or work is done by the system on the surroundings in either case, there is a transfer of energy from the system to the surroundings or vice versa right. So, we have to keep that in mind. So, energy is transferred whenever there is work done between the system and the surroundings. We talked about work being a path function; we talked about temperature pressure or volume etcetera.

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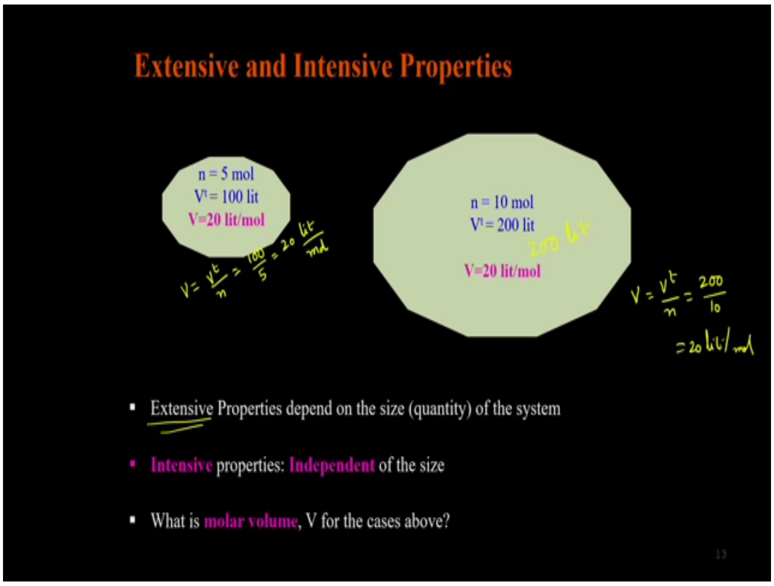

Extensive and Intensive Properties

$n = 5$ mol
$V^t = 100$ lit
$V = 20$ lit/mol

$V = \frac{V^t}{n} = \frac{100}{5} = 20\ \frac{lit}{mol}$

$n = 10$ mol
$V^t = 200$ lit
200 lit
$V = 20$ lit/mol

$V = \frac{V^t}{n} = \frac{200}{10}$
$= 20$ lit/mol

- Extensive Properties depend on the size (quantity) of the system
- Intensive properties: Independent of the size
- What is molar volume, V for the cases above?

Let us also introduce another type of properties what are known as extensive and intensive properties. For example, I have a system with 5 moles in it. And the total volume of these 5 moles is 100 liters right. Now, if I change the size of the system from 5 moles to 10 moles, and I pose a question everything else being the same what would be the total volume of the system? And it is pretty straightforward answer right. This value is going to be the number of moles of doubles. So, the size is going to double. So, it is going to be 200 liters right. So, these type of quantities the volume here the total volume here is called as an extensive property, this word extensive referring to a property which depends on the size of the system. So, the moment I change the size from 5 moles to 10 moles, the quantity has changed from 100 to 200 liters.

On the other hand, there are properties which are known as intensive properties which do not depend on the size of the system. Now, if we ask a question what is the molar volume for each of these two cases, let us calculate the molar volume. Remember that the molar volume is the total volume over the number of moles, so that is going to be 100 over 5 or 20 liters per mole. In the second case also it turns out that the molar volume is still going to be 20 liters for both cases the molar volume is same 20 liters per mole. This quantity is not depending on the size of the system and we call such a quantity as an intensive property.

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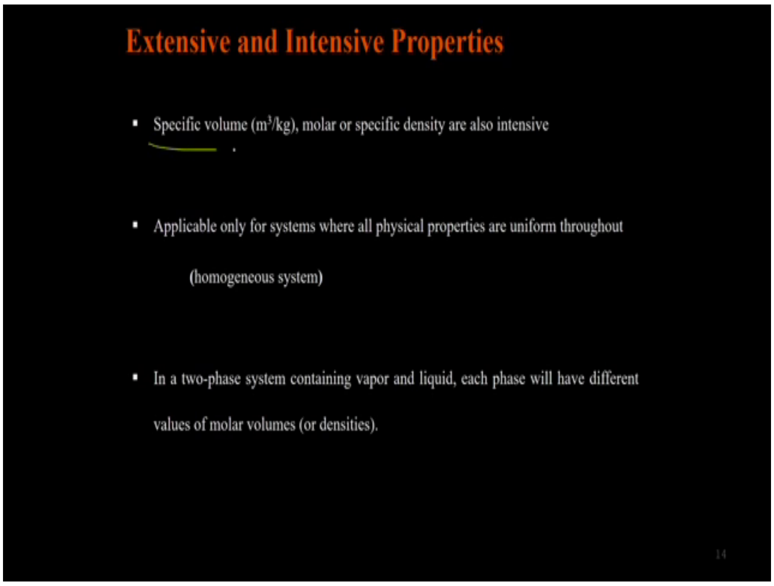

Extensive and Intensive Properties

- Specific volume (m^3/kg), molar or specific density are also intensive
- Applicable only for systems where all physical properties are uniform throughout (homogeneous system)
- In a two-phase system containing vapor and liquid, each phase will have different values of molar volumes (or densities).

So, things such as specific volume or molar volume, specific density all of these are intensive properties. This definition of course, is going to be strictly applicable when all the physical properties are uniform throughout the entire system. We are considering we call such systems as homogeneous systems. If we have two phase system containing vapor and a liquid, then of course it is no longer homogeneous the density of the vapor is going to be different from the density of the liquid, certain portions of the system have different density, certain other portions of the system have different density right.

So, each phase is going to have its own value of molar volume or molar density etcetera. Only that particular homogeneous part of the system can be taken into account or the subsystem can be taken into account when we define such properties.

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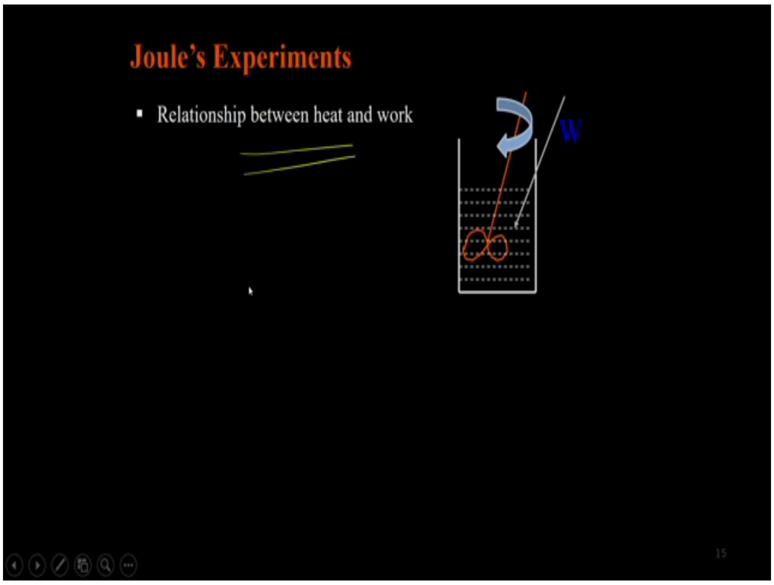

Joule's Experiments

- Relationship between heat and work

There is a very famous experiment that has been done by Joule to demonstrate the relationship between heat and work. What he has done is he has taken a vessel containing liquid water put a stirrer in it and stir right. When you do that, what we are essentially doing is we are doing work on the system, and when the work is being transferred by the stirrer to the water which is our system of interest in this case. And when we do that turns out that the temperature of the water is going to raise or whatever work we have transferred through the stirrer ended up heating the liquid water which is our system.

So, through this experiment he has demonstrated that there is a direct relationship between heat and work. And this direct relationship between heat and work is what we are interested when we start working with the first law of thermodynamics. So, when we come back in the next lecture we are going to look at how this heat and work are interrelated to one another, and how we do an energy balance on a process. Now finally, we have talked about several processes.

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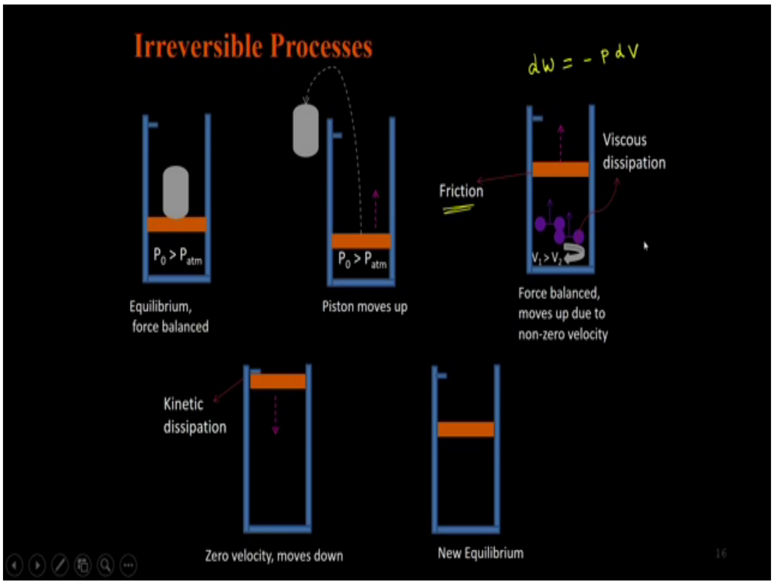

Irreversible Processes

And when we derived the or when we have written the equation for work done in a process is that only for special cases it is negative P dV dW is negative P dV right. What special cases are we talking about, let us take an example, let us look at an example to make a point. Let us say I have a piston and a cylinder assembly there is some gas inside this cylinder which is compressed at a higher pressure than the atmospheric pressure. I can put a counterweight on top of this piston, so that the it is at equilibrium and the forces are balanced.

What happens if I remove this way the piston is going to move up right. And as it moves up there are several gas molecules inside which are going to expand and as the piston moves up first thing that comes to mind is there is a friction between the piston and the cylinder right. In addition the molecules move maybe sitting next to one another, but they will start moving with different velocities. And when they move with different velocities not all of that momentum goes into expansion, they will end up using some of those momentum in terms of what is known as viscous dissipation imagine as if this molecule is going to rotate because they have different velocities when they are sitting next to each other.

There is going to be a viscosity of the gas and then when one of the molecule on the top moves up with a different velocity than the one at the bottom then it will end up imparting some rotation to the molecule below it, so that is in a sense a law a dissipation of energy. Then when this piston is going to go to the top all the way to the top and hit this latch which is preventing the piston from flying away. Then once it hits the latch, it comes down so at that point where it is hitting the latch there is a loss of kinetic energy does transfer some of the kinetic energy to the cylinder and then it starts moving down in the other direction, so that is what is known as a kinetic dissipation right.

Eventually the forces are going to balance out and we establish a new equilibrium. So, during this whole process, the moment right after I have taken the weight away until it reached the new equilibrium point that is frictional losses, there is losses due to viscous dissipation, there is losses due to kinetic dissipation etcetera. All of these losses are not useful forms of energy that I am interested in a process and such losses account for the irreversibility in a process.

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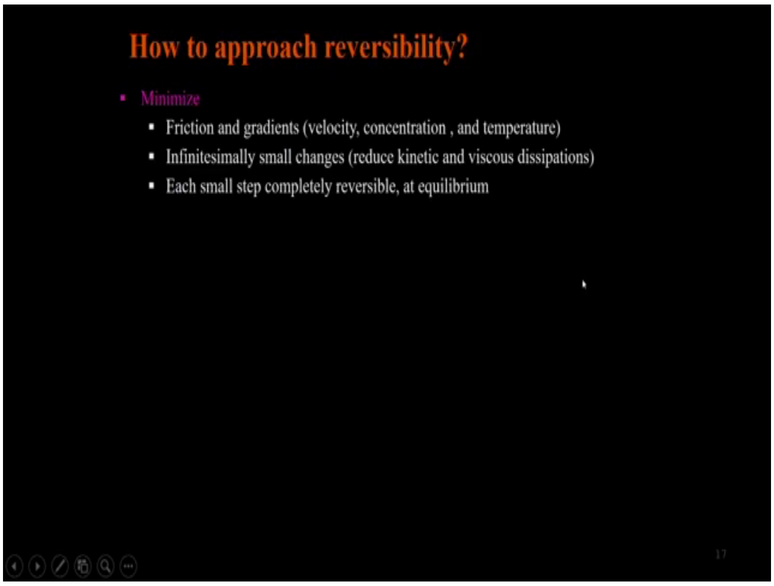

How to approach reversibility?

- Minimize
  - Friction and gradients (velocity, concentration , and temperature)
  - Infinitesimally small changes (reduce kinetic and viscous dissipations)
  - Each small step completely reversible, at equilibrium

Now, how can one minimize irreversibility and approach a more reversible process for one we have to reduce the gradients the velocity gradients, the concentration gradients, in case of mass transfer the temperature gradients for heat transfer etcetera. We should have only infinitesimally small changes, so that we can reduce the kinetic and viscous dissipations. Each step should be completely reversible the infinitesimally small change will reduce that each will ensure that each step is completely reversible.

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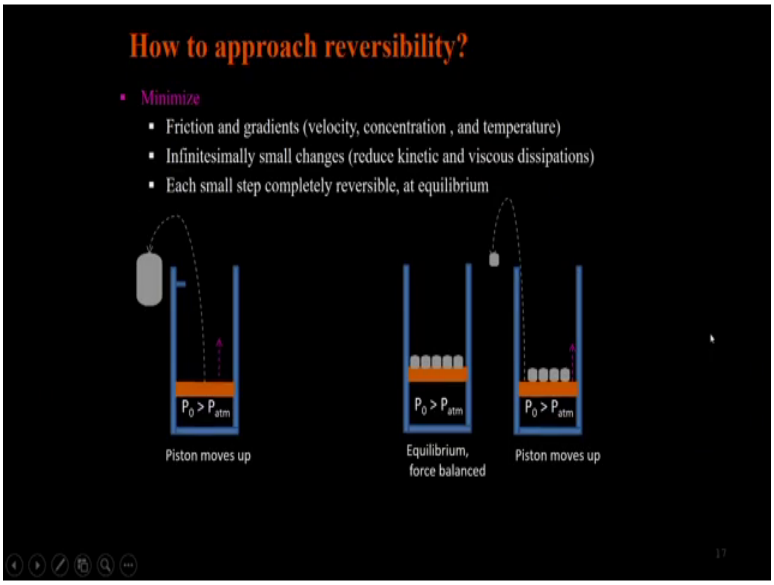

How to approach reversibility?

- Minimize
  - Friction and gradients (velocity, concentration , and temperature)
  - Infinitesimally small changes (reduce kinetic and viscous dissipations)
  - Each small step completely reversible, at equilibrium

And at equilibrium throughout the process physically we can think of it as such instead of putting a large counterweight imagine the same assembly we discussed in the previous slide, but this time the large counterweight is replaced with small grains of sand right. And I pick each grain out at a time, there is only an infinitesimally small shift in the position from the previous equilibrium state to the new equilibrium state. And the moment I do that I make these infinitesimally small changes, most of these gradients are going to be minimized most of the dissipations are going to be minimized and I move closer and closer to thee to a reversible process.

This is how we can achieve reversibility we are interested in reversibility because that minimizes the losses, we otherwise have which actually affect our economics of any process the heat and work requirements for any process. We will talk more about reversible and irreversible processes, and how we can calculate work and heat requirements for such processes as we move along after the first block. With that I would end today’s lecture.

See you in the next one.