Mechanical Engineering

Thermodynamics

▶ Short Notes

IMPORTANT FORMULAS TO REMEMBER

CHAPTER-1 BASICS OF THERMODYNAMICS

INTRODUCTION

Thermodynamics is the branch of science which deals with energy interaction between one body to another body and the effect of the energy transfer on them.

BASIC TERMS

1. SYSTEM

A system is defined as a quantity of matter (control mass) or a region (control volume) in space chosen for study.

2. SURROUNDINGS

Everything external to the system is called the surroundings or the environment.

3. BOUNDARY

- A real or imaginary surface that separates the system from its surroundings
- Mathematically, the boundary has zero thickness, and thus it can neither contain any mass nor occupy any volume in space.
- The boundary may be either fixed or moving.

4. Universe

- A system and its surroundings together comprise a universe.
- Universe consist of everything, so everything happening whether energy transfer or transformation or losses remain inside universe.

TYPES OF SYSTEM

**A. Depending upon the mass and energy interaction.**

a. Open System

- when there is mass as well as energy can transfer across the boundary.
- Example - air compressor, boiler, pump, IC engine with valve open etc.

b. Closed system

- if its mass remains fixed but there may be energy transfer into or out of the system
- Example – a certain quantity of fluid in a completely enclosed cylinder, Tea in kettle etc.

c. Isolated system

- when there is no mass and energy interaction between the system and the surroundings.
- Example – thermo-flask, Universe (since all energy interaction taking place between systems and surrounding which is the part of universe)
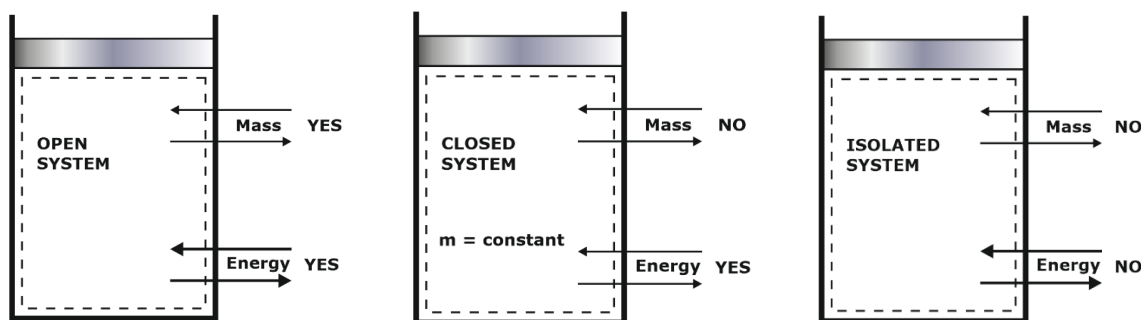
B. Depending upon the Chemical Composition

a. Homogeneous System

- A quantity of matter homogeneously distributed throughout system with respect to its chemical composition and physical structure is called homogenous system.
- A system consisting of a single phase is called a homogeneous system.

b. Heterogeneous System

- A system consisting of more than one phase is known as a heterogeneous system.
- Heterogenous system is the combination of two or more homogeneous system.

Macroscopic Approach

- In the macroscopic approach, a certain quantity of matter is considered, without molecular level being taken into account.
- It is also known as **classical approach**. All the properties will be the average of the properties of each molecule passing through that space.

Microscopic Approach

- From the microscopic point of view, matter is composed of numbers of molecules and study is made on molecular level.
- It is also known as **statistical approach**. In this approach, we sit on a particular molecules and whatever changes occurs is recorded and average of this will be our required properties.

CONCEPT OF CONTINUUM

- The concept of continuum is an idealization of the continuous description of matter where the properties of the matter are considered as continuous functions of space i.e. the space between the molecules (mean free path) is almost zero or very small as compare to the size of the system.
- At very low pressure (i.e. space outside earth atmosphere) gas is studied by **Gas rarefied theory** in which microscopic approach is used.
- Example: Density is calculated assuming continuum concept, so we assumed same uniform density all over the material.

Extensive Properties

- The properties which dependent on mass is known as extensive properties.
- It is also known as Extrinsic properties.
- Example – Volume, Enthalpy, Weight, All forms of energy etc.

Intensive Properties

- extensive properties per unit mass, are intensive properties.

- These properties do not dependent on mass of the system.
- It is system property independent of quantity.
- It is also known as intrinsic properties.
- Example– Temperature, Pressure, Density, Viscosity, Ratio of two extensive properties, specific energy, specific enthalpy etc.

THERMODYNAMIC EQUILIBRIUM

- A system is said to exist in a state of thermodynamic equilibrium when no change in any macroscopic property is registered.
- Above condition satisfy, if the following three types of equilibrium are satisfied:
  - **a. Mechanical Equilibrium**
  - **b. Chemical equilibrium**
  - **c. Thermal equilibrium**
- When the conditions for any one of the three types of equilibrium are not satisfied, a system is said to be in a **non-equilibrium** state.
- Thermodynamic properties defined only for thermodynamic equilibrium states.

State

- When all the properties of a system have definite values, then it is said to exist at a definite state.
- The number of properties required to fix the state of a system is given by the state postulate.

Change of state

Any operation in which one or more of the properties of a system changes is called a change of state.

Process

Any change that a system undergoes from one equilibrium state to another equilibrium state.

Path

The succession of states passed through during a change of state is called the path of the change of state. Or curve by joining the two equilibrium states of the system is known as Path.

Quasi-Static Process

- 'Quasi' meaning 'almost' and 'Static' means 'at rest'.
- Infinite slowness is the characteristic feature of a quasi-static process. Such a process, which is a locus of all the equilibrium states is known as a quasi-static process.

Cycle

A thermodynamic cycle is defined as a series of state changes such that the final state is identical with the initial state.

Reversible and Irreversible Process

- Reversible process is subset of Quasi static process which is also frictionless.
- A reversible process is defined as a process that can be reversed without leaving any trace on the surroundings. Processes that are not reversible are called irreversible processes.
- While plotting the curve, reversible processes are shown by continuous line or curve whereas irreversible processes are shown by dotted line or curve.
- Reversible processes actually do not occur in nature. They are merely idealizations of actual processes.

Point function and Path function

- If $\int\limits_{1}^{2} d\varphi = \varphi_2 - \varphi_1$, hence φ depend only on Initial and final states. φ is called Point Function

- All thermodynamic Properties are point function.

- If $\int\limits_{1}^{2} d\varphi \neq \varphi_2 - \varphi_1$, hence it depends on Path followed by the process irrespective of their end point,

  is known as path function.

- Path function are inexact differential, so we use $\delta\varphi$ instead of $d\varphi$

IDEAL GAS EQUATION

- Ideal (perfect) gas equation is a special equation of state, which is applicable to ideal gases.

- The molecular forces of attraction between gas molecules are zero, a gas is called a **perfect gas**.

- In addition, the volume of the molecules should be negligible compared to total volume for a perfect gas.

- The perfect or ideal gas equation of state is given by: $PV = n\bar{R}T$ or $PV = mRT$

  Where   P = Absolute Pressure = atmospheric pressure + Gauge pressure (in pascal)

             V = Volume in m^3

             $\bar{R}$ = Universal Gas constant = 8.314KJ/Kmol-K

             T = Absolute temperature in kelvin

             n = number of moles (in k-mol)

             R = characteristic gas constant $R = \dfrac{\bar{R}}{\text{Molecular weight}} = \dfrac{\bar{R}}{M}$

             m = weight (in kg)

- Deviations from ideal behaviour are observed particularly at high pressures or low temperatures.

- A gas which does not obey the ideal gas equation, PV = nRT strictly at all temperatures and pressures is said to be a real gas.

Boyle's Law

Boyle's law states that when the temperature is kept constant, the volume of a given mass of gas

varies inversely with the pressure, $P \propto \dfrac{1}{V}$

Charles Law

Charles's law, if the pressure remains constant then volume occupied by a fixed amount of gas is

directly proportional to its absolute temperature, $V \propto T$

Some important values for air

Specific heat at constant pressure = C_P = 1.005KJ/ kg – K

Specific heat at constant Volume = C_V = 0.718KJ/ kg – K

Specific heat ratio = $\gamma = \dfrac{C_P}{C_V} = 1.4$

Characteristic gas constant, $R = \dfrac{8.314}{29} = 0.287 \dfrac{kJ}{kg - K}$

Mayer's equation = $C_P - C_V = R$

by using Mayer's equation and specific heat ratio, $C_P = \dfrac{R\gamma}{\gamma - 1}$, $C_V = \dfrac{R}{\gamma - 1}$

PURE SUBSTANCE

- one that is homogeneous and invariable in chemical composition throughout its mass.
- The relative proportions of the chemical elements constituting the substance are also constant.
- Examples: Atmospheric air, steam-water mixture and combustion products of a fuel etc.
- But the mixture of air and liquid air is not a pure substance, since the relative proportions of oxygen and nitrogen differ in gas and liquid phases in equilibrium.

GIBBS PHASE RULE

It is an empirical formula to calculate the degree of freedom when number of component and number of phases are known in a given substance. $P + F = C + 2$

Where, P = number of phases, F = degree of freedom, C = number of components

DEGREE OF FREEDOM

- It is defined as the minimum number of independent intensive variables required to fix the position of any system.
- NOTE – degree of freedom of triple point is ZERO
- NOTE – degree of freedom of Critical point is ZERO

ZEROTH LAW OF THERMODYNAMICS

- It is the basic law of thermodynamics which define the temperature.
- Zeroth law states that: "When a body A is in thermal equilibrium with a body B, and also separately with a body C, then B and C will be in thermal equilibrium with each other".
- It is the basis of temperature measurement. Zeroth law comes after 1st law of thermodynamic.

THERMOMETRIC PROPERTIES

- The selected physical characteristic of the body which changes with temperature, is called the thermometric property.
- the reference body which is used in the determination of temperature is called the thermometer.
- For linearly varying thermometer property **T =a*N** where **a** is random constant & **N** is the thermometric property

$$\frac{T_1}{T_2} = \frac{N_1}{N_2}$$

- Five different kinds of thermometer, each with its own thermometric property

Thermometer	Thermometric property	Symbol
1 Constant volume gas thermometer	Pressure	p
2. Constant pressure gas thermometer	Volume	V
3. Electrical resistance thermometer	Resistance	R
4. Thermocouple	Voltage/ EMF.	e
5. Mercury-in-glass thermometer	Length/ Volume	L

TEMPERATURE SCALE

a. Method Used Before 1954

- Two fixed points were chosen and intermediate point are interpolated as straight line.
- Two points are, ice point and steam point selected at one atmosphere pressure, and

b. Method in Use After 1954

- only one fixed point has been in use, viz. the triple point of water, the state at which ice, liquid water and water vapour co-exist in equilibrium.
- The temperature at which this state exists is arbitrarily assigned the value of 273.16 degrees Kelvin, or 273.16 K

ENERGY

A closed System and its Surroundings can interact by work transfer and Heat transfer, whereas open system can interact by work, Heat and mass transfer (because mass also carries energy).

REPRESENT OF ALL PROCESSES IN SINGLE P-V GRAPH

Any process can be represented as $PV^K = C$
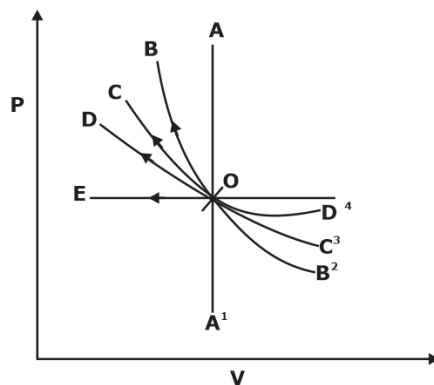
OA → Constant Volume → $k = \infty$

OB → Reversible adiabatic → $k = \gamma$

OC → Reversible Polytropic → $k = n$

OD → Isothermal → $k = 1$

OE → Constant Process → $k = 0$

WORK TRANSFER

- Work can be defined as force multiplied by distance moved by object in the direction of applied load; we call it as mechanical work.
- "Work is said to be done by a system if the sole effect on things external to the system can be used to raising of a weight".
- **Sign Convention**- Work done by system is taken as Positive and work done on system is negative.

NON-FLOW OR CLOSED SYSTEM WORK FOR VARIOUS PROCESS

- $W = \int P\,dV \Rightarrow$ area under the P -V graph projected on volume axis.

- Work is a Path function. It is written as δW not dW. $\int_{1}^{2} \delta W \neq W_2 - W_1$

- For closed system $dV = \frac{1}{P}\delta W$, Here $\frac{1}{P}$ is integrating factor. Integrating factor is defined as the factor which when multiplied by inexact differential gives exact differential.

  ➢ **Reversible Constant Volume or Isochoric Process** (V = Constant)

  $$W = \int_{1}^{2} P \, dV = 0 \text{, since } dV = 0$$

  ➢ **Reversible Constant Pressure or Isobaric Process or Isopistic Process** (P = Constant)

  $$W = \int_{1}^{2} P \, dV = P \, (V_2 - V_1)$$

  ➢ **Reversible Isothermal Process** (T = Constant)

  Using Ideal Gas Equation PV = mRT = Constant ⇒ This is equation of Rectangular Hyperbola.

  $$W = P_1 V_1 \ln\left(\frac{V_2}{V_1}\right) = P_1 V_1 \ln\left(\frac{P_1}{P_1}\right) = mRT_1 \ln\left(\frac{V_2}{V_1}\right) = mRT_1 \ln\left(\frac{P_1}{P_1}\right)$$

  $$\frac{dP}{dV} = \frac{-P}{V} \Rightarrow \text{Slope of reversible Isothermal process.}$$

  ➢ **Reversible Adiabatic Process** (Q = 0, No Heat transfer, PV^{γ} = Constant)

  Using Ideal Gas Equation $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$, where γ =adiabatic Index and greater than 1

  $$W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} = \frac{mR(T_1 - T_2)}{\gamma - 1}$$

  $$\frac{dP}{dV} = -\gamma . \frac{P}{V} \Rightarrow \text{Slope of reversible adiabatic process.}$$

  Hence slope of Reversible adiabatic process γ times more than slope of Reversible Isothermal process. Hence slope will be steeper.

  ➢ **Reversible Polytrophic Process** (PV^{n} = Constant)

  Using Ideal Gas Equation $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} = \left(\frac{V_1}{V_2}\right)^{n-1}$, Generally $1 < n < \gamma$

  $$W = \frac{P_1 V_1 - P_2 V_2}{n - 1} = \frac{mR(T_1 - T_2)}{n - 1}$$

FLOW OR OPEN SYSTEM WORK FOR VARIOUS PROCESS

- $W = -\int V \, dP \Rightarrow$ area under the P -V graph projected on pressure axis.

  ➢ **Reversible Constant Volume or Isochoric Process** (V = Constant)

  $$W = -\int_{1}^{2} V \, dP = -V(P_2 - P_1) = V(P_1 - P_2)$$

  ➢ **Reversible Constant Pressure or Isobaric Process or Isopistic Process** (P = Constant)

$W = \int_1^2 -VdP = 0$. since dP = 0

➤ **Reversible Isothermal Process** (T = Constant)

Using Ideal Gas Equation PV = mRT = Constant ⇒ This is equation of Rectangular Hyperbola.

$$W = P_1V_1 \ln\left(\frac{V_2}{V_1}\right) = P_1V_1 \ln\left(\frac{P_1}{P_1}\right) == mRT_1 \ln\left(\frac{V_2}{V_1}\right) = mRT_1 \ln\left(\frac{P_1}{P_1}\right)$$

Thus, work flow process and non-flow process is same for isothermal process.

➤ **Reversible Adiabatic Process** (Q = 0, No Heat transfer, Pv^γ = Constant)

Using Ideal Gas Equation $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$, where γ = adiabatic Index and greater than 1

$$W = \gamma\left(\frac{P_1V_1 - P_2V_2}{\gamma - 1}\right)$$

$W_{open} = \gamma \times W_{close}$

➤ **Reversible Polytrophic Process** (Pv^n = Constant)

Using Ideal Gas Equation $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} = \left(\frac{v_1}{v_2}\right)^{n-1}$, Generally 1 < n < γ

$$W = n\left(\frac{P_1V_1 - P_2V_2}{n - 1}\right)$$

$W_{open} = n \times W_{close}$

OTHER TYPES OF WORK TRANSFER

➤ **ELECTRICAL WORK**

Work $W = \int_1^2 VI\, dt$, where V is Voltage, I is Current and t is time

Power P = VI Watt

This is the rate at which work is transferred.

➤ **SHAFT WORK**

Work $W = \int_1^2 Td\theta$, Where T is the torque on shaft and dθ is the angular displacement of shaft

Power P $= \int_1^2 T\frac{d\theta}{d\tau} = T\omega$, where ω is the angular velocity

➤ **PADDLE-WHEEL WORK OR STIRRING WORK**

As the weight is lowered, and the paddle wheel turns, and there is work transfer into the fluid system which gets stirred.

➤ **WORK DONE IN STRETCHING A WIRE**

$W = - \int_1^2 FdL$, where F is force, dL means an expansion of the wire, Minus sign is used for negative work

➤ **WORK DONE IN CHANGING THE AREA OF A SURFACE FILM**

The work done on a homogeneous liquid film in changing its surface area by an infinitesimal amount dA is $W = -\int_1^2 \sigma \, dA$ where σ is the surface tension (N/m).

HEAT TRANSFER

- "The energy transfer because of the temperature difference is known as Heat"

- If mass of the body B is m and specific heat of the body is C, then heat gain by the body B or heat transfer between both the body A & B will be given by $Q = mC(T_A - T_B)$

- **"Specific heat** is the amount of heat required to raise the temperature of unit mass by unit degree centigrade (or Kelvin)"

$$C = \frac{Q}{m(T_A - T_B)} = \frac{Q}{m.\Delta T}, \quad \text{Unit -} \quad C = \frac{Q}{m.\Delta T} = \frac{kJ}{kg - K} \text{ or } \frac{kJ}{kg - ^\circ C}$$

- **NOTE –** value of specific heat varies with the process for gases whereas in case of solid and liquid it remains constant irrespective of process because solid and liquid both can be assumed to be incompressible.

- Values of specific heat for air $C_p = 1.005 \, \frac{kJ}{kg - K}$, $C_v = 0.718 \, \frac{kJ}{kg - K}$ and water $C_{water} = 4.18 \, \frac{kJ}{kg - K}$

- The specific Heat at Constant Pressure greater than specific Heat at constant volume because in constant pressure Process, the Heat is utilized to raise the temperature and to do PdV work.

$$C_P > C_v, \quad \gamma = \frac{C_p}{C_v}$$

- **Sensible Heat-** Heat transfer because of the temperature difference between two bodies is known as sensible heat. $Q = mC\Delta T$

- **Latent Heat-** Energy released or absorbed by a substance when it is subjected to change in phase.
  latent heat of fusion - Amount of energy absorbed during melting of a substance is called the latent heat of fusion and is equivalent to the amount of energy released during freezing.
  latent heat of vaporization - Amount of energy absorbed during vaporization is called the latent heat of vaporization and is equivalent to the energy released during condensation.

- **Sign Convention for Heat Transfer**
  Heat supplied to the system is taken as positive. Heat rejected from the system is taken as negative.

  1. **Enthalpy, H**: It represents the total heat content of the system.

  2. **Specific Enthalpy, h**: Summation of specific internal energy and flow work. $\Rightarrow h = u + P\upsilon$

  3. **Flow work:** It is amount of work which is required to displace a infinitely small fluid element to enter or exit from the control volume known as flow work.

Process	Work (Non0flow)	Heat

Reversible Constant Volume or Isochoric Process	$\delta W = 0$	$Q = dU = mC_v\Delta T$
Reversible Constant Pressure or Isobaric Process or Isopistic Process	$\delta W = \int\limits_{1}^{2} P \, dV = P\left(V_2 - V_1\right)$	$Q = dH = mC_p\Delta T$
Reversible Isothermal Process	$\delta W = P_1V_1 \ln\left(\dfrac{V_2}{V_1}\right) = mRT_1 \ln\left(\dfrac{V_2}{V_1}\right)$	$Q = W$
Reversible Adiabatic Process	$W = \dfrac{P_1V_1 - P_2V_2}{\gamma - 1} = \dfrac{mR\left(T_1 - T_2\right)}{\gamma - 1}$	$Q = 0$
Reversible Polytrophic Process	$W = \dfrac{P_1V_1 - P_2V_2}{n - 1} = \dfrac{mR\left(T_1 - T_2\right)}{n - 1}$	$Q = \left(\dfrac{\gamma - n}{\gamma - 1}\right) \times W_{polytropic}$

CHAPTER-2 : FIRST LAW OF THERMODYNAMICS

FIRST LAW OF THERMODYNAMICS

- First law of thermodynamics is to relate the various form of energy and energy interaction.

- Its states that "Energy can be neither created nor destroyed during a process; it can only change forms". It is also known as "conservation of energy principle"

- It represents by E,

  E = Mechanical Energy + Thermal Energy + Internal Energy + potential Energy + Kinetic Energy + Chemical Energy ETC.

FIRST LAW FOR A CLOSED SYSTEM UNDERGOING A CYCLE

- Net heat interaction in a cycle is equal to the net Work interaction. $(\Sigma\ W)_{cycle} = J(\Sigma\ Q)_{cycle}$ where J is the Joule's equivalent.

- This is also expressed in the form $\oint \delta W = \oint \delta Q$, where the symbol $\oint$ denotes the cyclic integral for the closed path.

FIRST LAW FOR A CLOSED SYSTEM UNDERGOING A CHANGE OF STATE (for a process)

- If Q is the amount of heat transferred to the system and W is the amount of work transferred from the system during the process, then, net energy transfer (Q – W) will be stored in the system.

- Energy in storage is neither heat nor work, and is given the name internal energy or simply, the energy of the system. Therefore, $\delta Q = dE + \delta W$, where dE is the increase in the energy of the system

CONSEQUENCES OF 1ST LAW OF THERMODYNAMICS

- Heat is a path function; hence, heat transfer does not depend only end point but also depends upon the followed by the process.

- Energy has a definite value for every state of the system. Hence, it is a point function and a properly of the system. The energy E is an extensive property. So $\oint dE = 0$

- As we know that, for an isolated system, Heat and work interaction from the surrounding is zero. Energy of isolated system is Constant. So, Q =0, W = 0 $\rightarrow$ $\Delta E = 0 \Rightarrow E_2 - E_1 = 0 \rightarrow E_2 = E_1$

- Perpetual motion machine of first kind-PMM1 is not possible. Thus, $\oint \delta W \neq \oint \delta Q$

PERPETUAL MOTION MACHINE

- Any device which violate any of the thermodynamic laws is called a perpetual motion machine.

- A device which violate the first low of thermodynamic is called perpetual motion machine of first kind. (PMM-1)

STEADY FLOW ENERGY EQUATION (SFEE)

If the rates of flow of mass and energy through the control surface does change with time, then it is said to be steady flow.
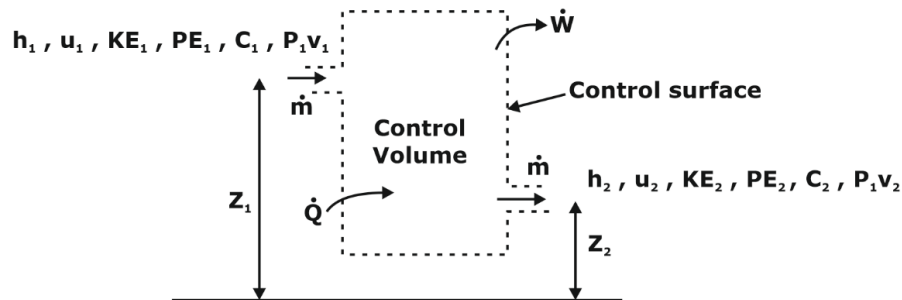
Here   i and e subscripts used for inlet and exit condition respectively.

A_i, A_e – cross-section of stream, m^2

$\dot{m}_i, \dot{m}_e$ – mass flow rate, kg/s

P_i, P_e – pressure, absolute, N/m^2

V_i, V_e – volume, m^3

υ_i, υ_e – Specific volume, m^3/kg

u_i, u_e – Specific internal energy, J/kg

C_i, C_e – Velocity, m/s

z_i, z_e - Elevation above an arbitrary datum, m

$\dfrac{dQ}{dt} = \dot{Q}$ = Net rate of heat transfer through the control surface, J/s

$\dfrac{dW}{dt} = \dot{W}$ = Net rate of work transfer through the control surface, J/s

- **Continuity Equation** or **Conservation of mass**, $\dot{m}_i = \dot{m}_e \Rightarrow (\rho AC)_i = (\rho AC)_e \Rightarrow \left(\dfrac{AC}{\upsilon}\right)_i = \left(\dfrac{AC}{\upsilon}\right)_e$

- **Energy balance** $E_{in} = E_{out} \Rightarrow E_i = E_e$

$$U_i + (KE)_i + (PE)_i + (PV)_i + \dot{Q} = U_e + (KE)_e + (PE)_e + (PV)_e + \dot{Q}$$

$$\dot{m}_i \left(u + P\upsilon + \frac{1}{2}C^2 + gz\right)_i + \dot{Q} = \dot{m}_e \left(u + P\upsilon + \frac{1}{2}C^2 + gz\right)_e + \dot{W}$$

$$\dot{m}_i \left(h + \frac{1}{2}C^2 + gz\right)_i + \dot{Q} = \dot{m}_e \left(h + \frac{1}{2}C^2 + gz\right)_e + \dot{W}$$

UNSTEADY FLOW ENERGY EQUATION

In this type of flow, the flow rate is changing with respect to time, so these are also known as variable flow process.

Here   1 and 2 subscripts used for initial and final condition inside control volume respectively.

m_1, m_2 = initial and final mass inside the control volume

Others notation are same as previously explained

- **Continuity Equation** or **Conservation of mass -** $\frac{d}{dt}(m_{cv}) = \frac{d}{dt}(m_2 - m_1) = \dot{m}_i - \dot{m}_e$

- **Energy balance –** $\frac{d}{dt}(E_{cv}) = \frac{d}{dt}(E_2 - E_1) = \dot{E}_i - \dot{E}_e$

$$\frac{d}{dt}(E_{cv}) = \frac{d}{dt}\left[m_i \left(h + \frac{1}{2}C^2 + gz \right)_i + Q \right] - \frac{d}{dt}\left[m_e \left(h + \frac{1}{2}C^2 + gz \right)_e + W \right]$$

Assumptions- Neglecting KE and PE changes $\Rightarrow E = U + KE + PE \Rightarrow E = U$

$$\frac{d}{dt}(U_{cv}) = \frac{d}{dt}(m_i h_i + Q) - \frac{d}{dt}(m_e h_e + W)$$

Neglecting the variation of enthalpy at inlet and outlet with respect to time $\frac{dh_i}{dt} = \frac{dh_e}{dt} = 0$

$$\frac{d(U_{cv})}{dt} = \dot{m}_i h_i + \dot{Q} - \dot{m}_e h_e - \dot{W}$$

APPLICATIONS OF STEADY FLOW PROCESSES

➢ **Nozzle and Diffuser**

- A nozzle is a device of variable cross section which increases the velocity or Kinetic Energy of a fluid at the expense of its pressure.

- A Diffuser is a device of variable cross section which increases the Pressure Energy of a fluid at the expense of its kinetic energy.

- Both devices are work **transforming device** in which one form of energy is transformed into another form so no work interaction will be there.
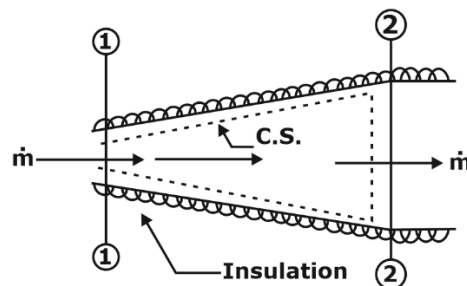
If the inlet is 1-1 then it will work as diffuser

If the inlet is 2-2 then it will work as nozzle

Assumption –

1. It is completely insulated so, Q=0

2. No work interaction, so W = 0

3. It is assumed to be horizontal so, $\Delta PE \sim 0$

- Thus, from SFEE $h_1 + \frac{1}{2}C_1^2 = h_2 + \frac{1}{2}C_2^2$

- In case of nozzle, generally, $C_1 \lll C_2$, Then $C_1 \approx 0 \Rightarrow C_2 = \sqrt{2(h_1 - h_2)}$

- In case of diffuser, generally, $C_2 \lll C_1$, Then $C_2 \approx 0 \Rightarrow C_1 = \sqrt{2(h_2 - h_1)}$

> ➢ **Turbine and Compressor**
>   - Turbines are power producing device in which the fluid imparts its energy to the rotor and due to which mechanical energy generates
>   - Compressor or pump are power consuming device in which the mechanical energy of the rotor is given to the fluid which results in increase in temperature and pressure of the fluid.
>   - Both devices are work **transferring device** in which work input is required from the outside in case of compressor whereas work is produced in case of turbine.
>   - **Assumption –**
>   1. It is completely insulated so no heat transfer, Q = 0
>   2. It is assumed to be horizontal thus PE can be neglected
>   3. Kinetic energy is very low as compare to enthalpy so KE of the fluid is neglected.
>   - From SFEE, For turbine $\dot{W} = \dot{m}(h_1 - h_2)$, For compressor, $\dot{W} = \dot{m}(h_2 - h_1)$

> ➢ **Boiler and Condenser**
>   - Both are a type of heat exachanger in which energy from high energy fluid is imparted to low energy fluid.
>   - In boiler, heat is being absorbed by working fluid at constant pressure,
>   - In condenser heat is being rejected by working fluid at constant pressure.
>   - **Assumption** –
>   1. No work interaction, so W = 0
>   2. It is assumed to be horizontal thus PE can be neglected.
>   3. There is no change in kinetic energy.
>   - From SFEE, For Boiler $\dot{Q} = \dot{m}(h_2 - h_1)$, For Condenser $\dot{Q} = \dot{m}(h_1 - h_2)$

> ➢ **Throttling Device -**
>   - When a fluid flows through a restricted passage, like a partially opened valve, an orifice, or a porous plug, there is an appreciable drop in pressure, and the flow is said to be throttled.
>   - **Assumption –**
>   1. It is completely insulated so no heat transfer, Q = 0
>   2. No work interaction, so W = 0
>   3. It is assumed to be horizontal thus potential energy can be neglected
>   4. There is no change in kinetic energy,
>   - From SFEE $\dot{m}h_1 = \dot{m}h_2$ $\Rightarrow h_1 = h_2$
>   - During the throttling process enthalpy of fluid remains constant whereas pressure of fluid decrease.
>   - It is an irreversible process.

APPLICATIONS OF UNSTEADY FLOW PROCESSES

> ➢ **Bottle filling process or Charging of tank**
>   - Assumption –
>   1. In this case, mass is not leaving the system boundary, so $m_e = 0$
>   2. Bottle is initially vacuum and work against Vacuum is zero, W = 0

3. System is insulated, Q = 0

4. Initially mass in the bottle is zero, so m_1= 0, thus m_i =m_2

- With above assumption, if the working fluid is ideal gas then $u_2 = h_i$ i.e. Enthalpy is converted to internal energy and $T_2 = \gamma T_i$ i.e. the final temperature inside the tank is γ times the temperature of supply line.

- Note: notation has usual meaning

➢ **Discharging of tank**

- Assumption –

1. Mass is not entering the system boundary, so m_i = 0

2. Pipeline is initially vacuum and work against Vacuum is zero, W =0

3. System is insulated, Q = 0

4. Neglecting the variation of enthalpy at inlet $\dfrac{dh_i}{dt} = 0$

5. The pressure in the supply line remains constant

- With above assumption, discharging from a tank is adiabatic process.

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$$

- Note: notation has usual meaning

FREE EXPANSION

- It is also known as unrestrained expansion or Expansion against vacuum

- It is a case of irreversible process.

- Since the system is insulated and gas is expanding against the vacuum thus, dQ=0, dW=0

- From the 1st law of thermodynamics $dQ = dE + dW \Rightarrow dE = 0$

CHAPTER-3 SECOND LAW OF THERMODYNAMICS

INTRODUCTION

- Satisfying the first law alone does not ensure that process will actually take place.

- Thus, second law of thermodynamic asserts that.

  1. A process can occur in certain direction.

  2. Energy has quality as well quantity.

- A process if to occur must satisfy both 1st law and 2nd law.

THERMAL ENERGY RESERVOIR (TER)

- A TER is a Hypothetical body which have relatively very large thermal heat capacity, that can supply or absorb finite amount of heat without undergoing any change in temperature. ΔT = 0

- We know $\Delta T = \dfrac{Q}{mC}$, So mC has to be large. It is possible under 2 cases-

  o Any physical body whose specific capacity is large relative to amount of energy can be TER.

  o Large water bodies such as oceans, lakes, rivers, atmospheric air can be modeled as TER.

- A two-phase system can also be modeled as reservoir since it can absorb and release large quantities while remaining of constant temperature.

- **Source** ⇒ A thermal energy reservoir that supplies energy in form of heat is called source.

- **Sink** ⇒ A thermal energy reservoir that absorbs energy in the form of heat is called sink.

HEAT ENGINE

- Heat engine is a device which converts the part of heat energy into work and rejects remaining to sink or surrounding.
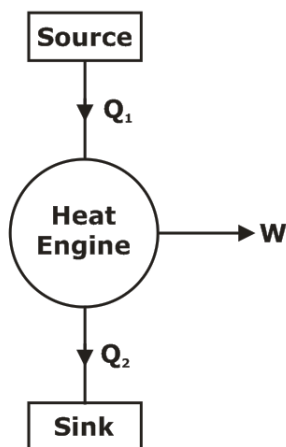
- Heat engines are characterized by following

  1. They receive heat from high temperature source = Q_1

  2. They convert part of this heat into work = W

  3. They reject the remaining heat to low temperature sink = Q_2

  4. They operate on cycle.

- Heat engines and other cyclic devices usually involve a fluid to and from which heat is transferred while undergoing a cycle this fluid is called **working fluid.**

- **Thermal Efficiency -** The fraction of the heat input that is converted to net-work output is known as thermal efficiency and is the measure of the performance of heat engine.

$$\eta = \frac{\text{Net work output}}{\text{Total Heat input}} = \frac{W_{net}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

REFRIGERATOR

- A refrigerator is a device which maintains lower temperature as compared to surrounding. As lower temperature is to be maintained continuously, refrigerator must operate on cycle.

- The efficiency of a refrigerator is expressed as coefficient of performance. For refrigerator, Desired effect is extracting Q_2.

$$(COP)_{Ref.} = \frac{\text{Desire effect}}{\text{Work Input}} = \frac{Q_2}{W_{net\ in}} = \frac{Q_2}{Q_1 - Q_2}$$

- This equation is valid for reversible as well as irreversible cycle.

- The COP may or may not be greater than 1, that's why a new term coefficient of performance is used.
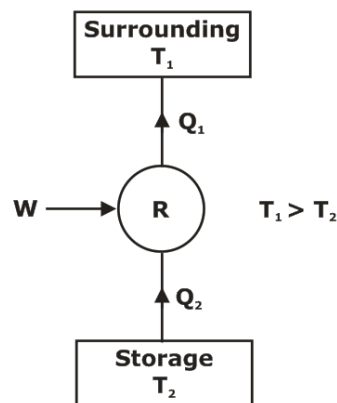
HEAT PUMP

- Heat pump is a device which maintains higher temperature compared to surroundings.

- The thermodynamic cycle of refrigerator and heat pump are same, but they differ in their objective and the temperature limits under which they operate.

$$(COP)_{HP} = \frac{\text{Desire effect}}{\text{Work Input}} = \frac{Q_1}{W_{net\ in}} = \frac{Q_1}{Q_1 - Q_2}$$

- This equation is valid for reversible as well as irreversible heat pump.

- Since $Q_1 > W_{net\ in}$, the COP of heat pump is always greater than 1.

- Relationship between cop of a heat pump and refrigerator operating between same temperature limits $(COP)_{HP} = 1 + (COP)_{Ref.}$
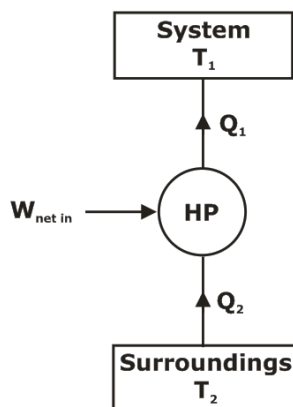
TWO STATEMENT OF SECOND LAW OF THERMODYNAMIC

- **KELVIN PLANCK STATEMENT-**
  - It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.
  - Hence a heat engine can not 100% efficiency this limit to the efficiency is not due friction or other dissipative effect but applies to both idealized and actual heat engines.

- **CLAUSIUS STATEMENT-**
  - It is impossible to construct a device that operates in a cycle and produces no effect other than the heat transfer of heat from a lower temperature body to a higher temperature body.

- **Note:** Both the Kelvin-Planck and Clausius statements of second law are negative statements and a negative statement cannot be proved.

- The Kelvin-Planck and the Clausius statements are equivalent in their consequences and either statements can be used as expression of second law of thermodynamic.

PERPETUAL MOTION MACHINE

- Any device which violate any of the thermodynamic laws is called a perpetual motion machine.

- A device which violates the second law of the thermodynamic is called perpetual motion machine of 2nd kind (PMM-2)

IRREVERSIBILITIES

- The factor that causes a process to be irreversible are called irreversibilities.

- The irreversibilities of a process may be due to either one or both of the following.
  1. Lack of equilibrium (e.g. mechanical, thermal, chemical equilibrium)
  2. Involvement of dissipative effect (e.g. Friction)

CARNOT CYCLE (REVERSIBLE CYCLE)

- Carnot cycle is the best-known reversible cycle which is both internally and externally reversible.

- The theoretical heat engine that operates on Carnot cycle is called Carnot heat engine.

- The four reversible process that make up the Carnot cycle are as follows

    1-2 ⇒ Reversible Isothermal expansion process ⇒ slow

    2-3 ⇒ Reversible adiabatic expansion process ⇒ fast

    3-4 ⇒ Reversible isothermal compression process ⇒ slow

    4-1 ⇒ Reversible adiabatic compression process ⇒ fast.
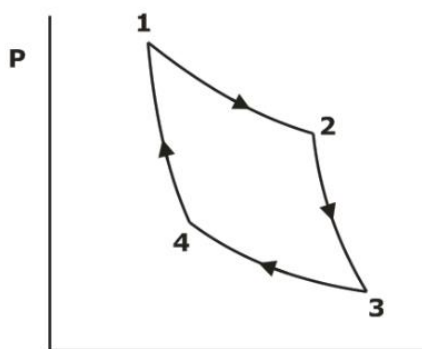
CARNOT THEOREM OR PRINCIPLES

1. The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between same two reservoirs. $\eta_{rev} > \eta_{irrev}$

2. The efficiency of all reversible heat engine operating between same two reservoir are same.

3. Efficiency of a reversible cycle depends only on temperature limit.

- A temperature scale that is independent of the properties of the substance that are used to measure temperature is called **thermodynamic temperature scale.**

- As per Kelvin Experiment taking simplest function $\dfrac{Q_1}{Q_2} = \dfrac{T_1}{T_2} \Rightarrow$ valid for reversible cycle.

- We know for heat engine $\eta = 1 - \dfrac{Q_2}{Q_1}$, **Efficiency of reversible heat engine** $\eta_{rev} = 1 - \dfrac{T_2}{T_1}$

- for refrigerator $(COP)_R = \dfrac{Q_2}{Q_1 - Q_2}$, **Efficiency of reversible refrigerator** $(COP)_R = \dfrac{T_2}{T_1 - T_2}$

- for heat pump $(COP)_{HP} = \dfrac{Q_1}{Q_1 - Q_2}$, **Efficiency of reversible heat pump** $(COP)_{HP} = \dfrac{T_1}{T_1 - T_2}$

DRAWBACKS OF CARNOT CYCLE

- It consists of mainly isothermal & adiabatic process to achieve isothermal condition the process has to be extremely slow whereas to achieve adiabatic condition the process has to be extremely fast, so both the process is not possible in a single cycle.

- The area under P-V curve is having very narrow region therefore the net workout of Carnot cycle is having low value, moreover to obtain the same workout the swept volume is very large.

Note:

- The max possible efficiency of reversible engine is given by Carnot

- the expression of Carnot efficient is $\eta_{Carnot} = 1 - \dfrac{T_L}{T_H}$, T_L and T_H are low and high temperature limit.

- Carnot efficient is function of temperature limits only.

- If there are n number of reversible engines operative between same temperature limits with different working fluid then the value of Carnot efficiency or ideal efficiency or maximum possible efficiency is having same value. Carnot efficiency is independent of working fluid.

COMBINATION OF HEAT ENGINE

- If two reversible heat engines operating in series and heat rejected by engine A directly supplied to engine B.

- **Combined efficiency of the engine**

We know that $\eta = \dfrac{W_{max}}{Q_{supplied}}$, So $\eta_1 = \dfrac{W_1}{Q_1}$ & $\eta_2 = \dfrac{W_2}{Q_2}$

$\eta_{Overall} = \dfrac{W_1 + W_2}{Q_1} = \eta_1 + \eta_2\left(1 - \eta_1\right) = \eta_1 + \eta_2 - \eta_1\eta_2$ (As per Kelvin Experiment $Q \propto T$)

- **Expression of intermediate temperature if both engines are equally efficient**

We know $\eta_1 = 1 - \dfrac{T_2}{T_1}$ and $\eta_2 = 1 - \dfrac{T_3}{T_2}$, Since, $\eta_1 = \eta_2 \Rightarrow T_2 = \sqrt{T_1 T_3}$

Thus, when efficiency of both engines is same then intermediate temperature is geometric mean of higher and lower temperature.

- **Expression of intermediate temperature if both engines produces same amount of work**

Since $W_1 = W_2 \Rightarrow Q_2 = \dfrac{Q_1 + Q_3}{2} \Rightarrow T_2 = \dfrac{T_1 + T_3}{2}$

Thus, when work produced by both engines are same then intermediate temperature is arithmetic mean of higher and lower temperature.
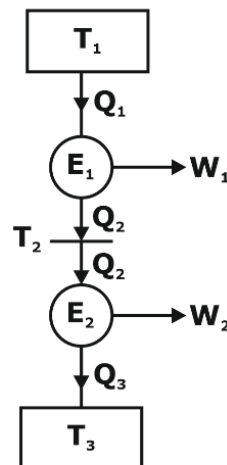
CLAUSIUS INEQUALITY

- The cyclic integral of $\dfrac{\delta Q}{T}$ is less than or equal to zero. $\oint \dfrac{\delta Q}{T} \leq 0$

$\oint \dfrac{\delta Q}{T} = 0 \Rightarrow$ Reversible cycle

$\oint \dfrac{\delta Q}{T} < 0 \Rightarrow$ Cycle is Irreversible

CHAPTER-4 ENTROPY

INTRODUCTION

- From Clausius inequality, cyclic integral of $\dfrac{\delta Q}{T}$ is zero for a reversible process & if cyclic integral of any variable is zero then it must be property of system, Thus $\dfrac{\delta Q}{T}$ is a property of the system.

- So, a new property Entropy is defined.

- "S" is an extensive property named as entropy, sometimes is referred to as total entropy. Entropy per unit mass, designated "s", is an intensive property.

- **Units –** unit of entropy is $\Delta S = \int\limits_1^2 \dfrac{\delta Q}{T} = \dfrac{kJ}{K}$,   unit of Specific entropy is $\Delta s = \dfrac{\Delta S}{mass} == \dfrac{kJ}{kg-K}$

- the integral of $\dfrac{\delta Q}{T}$ gives the value of entropy change only if the integration is carried out along an internally reversible path between the two states.

- The integral of $\dfrac{\delta Q}{T}$ along an irreversible path is not a property, and in general, different values will be obtained when the integration is carried out along different irreversible paths.

- For a reversible process, $\dfrac{\delta Q}{T} = dS_{rev.process}$,   For an irreversible process, $\dfrac{\delta Q}{T} + S_{gen} = dS_{rev.process}$

- For a reversible process, $S_2 - S_1 = \int\limits_1^2 \dfrac{dQ}{T}$,   For an irreversible process, $S_2 - S_1 = \int\limits_1^2 \dfrac{dQ}{T} + S_{gen}$

Note:

- The word 'entropy' was first used by Clausius, taken from the Greek word `tropee' meaning `transformation'.

- Entropy is a thermodynamic property that measures the degree of randomization or disorder at the microscopic level.

- A macroscopic feature which is associated with entropy production is a loss of ability to do useful work. Energy is degraded to a less useful form, and it is sometimes said that there is a decrease in the availability of energy.

- The notion that entropy can be produced, but never destroyed, is the second law of thermodynamics.

- **Area under the T -S plot** on S axis will give the heat transfer in a reversible process.

$$Q_{rev} = \int_i^f TdS$$

- **Slope of Constant Volume Process in T-S diagram** $\left(\dfrac{dT}{ds}\right)_{v=c} = \dfrac{T}{C_v}$

- **Slope of Constant Pressure Process on T-S diagram** $\left(\dfrac{dT}{ds}\right)_{P=c} = \dfrac{T}{C_P}$

- As we know that, $C_P > C_v$, thus, $\dfrac{T}{C_P} < \dfrac{T}{C_v}$

- So, slope of constant volume line on T-S Curve is always greater than the slope of constant pressure line.
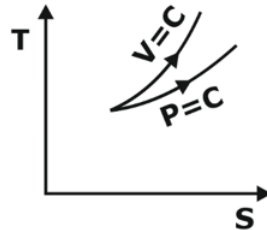
ENTROPY GENERATION

- Entropy charge of the system is summation entropy change due to internal irreversibility S_{gen} and entropy change due to external interaction $\dfrac{\delta Q}{T}$.

- Entropy generation S_{gen} is always a positive quantity or zero $S_{gen} \geq 0$. Its value depends on the process, and thus it is not a property of the system. $S_{gen} < 0$ (impossible Process)

- Some entropy is generated or created during an irreversible process, and this generation is due entirely to the presence of **irreversibilities**.

- For an isolated system dQ = 0, Therefore, for an isolated system $dS_{iso} \geq 0$

- Entropy of an isolated system can never decrease. It always increases and remains constant only when the process is reversible. This is known as **entropy principle.**

- If the system is reversible then entropy change of the system is given by $S_{gen} = 0$

- If the system is irreversible then entropy change of the system is given by $S_{gen} \neq 0$

- If the system is reversible and adiabatic it must be isentropic.

- Entropy change on the system may be positive, Negative or zero but entropy change of the universe can never have negative value.

CONCLUSIONS

1. Processes can occur in a certain direction only, not in any direction. A process must proceed in the direction that complies with the increase of entropy principle, that is, $S_{gen} \geq 0$.

2. A process that violates this principle is impossible.

3. Entropy is a non-conserved property, and there is no such thing as the conservation of entropy principle. Entropy is only conserved during the idealized reversible processes only.

4. Performance of engineering systems is degraded by the presence of irreversibilities, and entropy generation is a measure of the magnitudes of the irreversibilities present during that process.

5. The greater the extent of irreversibilities, the greater the entropy generation. Therefore, entropy generation can be used as a quantitative measure of irreversibilities associated with a process.

EXPRESSION OF ENTROPY FOR VARIOUS PROCESSES (of Ideal gas)

➢ **For Reversible process** (Using 1st Law equations, T-dS equations and Ideal gas equations)

$$s_2 - s_1 = C_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right) = C_P \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{p_1}\right) = C_P \ln\left(\frac{V_2}{V_1}\right) + C_V \ln\left(\frac{P_2}{p_1}\right)$$

Notations have usual meanings.

➢ **Adiabatic Process**

- For an adiabatic process, dQ_{rev}, $= 0$, → $dS = 0$, → $S =$ constant
- A reversible adiabatic process is, therefore, an isentropic (constant entropy) process.

➢ **Isothermal process**

- The system is taken from i to f reversibly.
- For reversible isothermal heat transfer $\therefore Q_{rev} = T\int_i^f dS = T(S_f - S_i)$

$$s_2 - s_1 = R \ln\left(\frac{V_2}{V_1}\right) = -R \ln\left(\frac{P_2}{p_1}\right) = C_P \ln\left(\frac{V_2}{V_1}\right) + C_V \ln\left(\frac{P_2}{p_1}\right)$$

➢ **Constant Volume Process –**

$$s_2 - s_1 = C_v \ln\left(\frac{T_2}{T_1}\right) = C_P \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{p_1}\right) = C_V \ln\left(\frac{P_2}{p_1}\right)$$

➢ **Constant Volume & constant Pressure Process –**

$$s_2 - s_1 = C_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right) = C_P \ln\left(\frac{T_2}{T_1}\right) = C_P \ln\left(\frac{V_2}{V_1}\right)$$

APPLICATIONS OF ENTROPY PRINCIPLE (ΔS_univ ≥ 0)

➢ **Transfer of Heat through a Finite Temperature Difference Reservoir**

- Q be the rate of heat transfer from reservoir A at T_1 to reservoir B at T_2
- For reservoir A, $\Delta S_A = - Q/T_1$. It is negative because heat Q flows out of the reservoir.
- For reservoir B, $\Delta S_A = +Q/T_2$. It is positive because heat Q flows into the reservoir.
- The rod connecting the reservoirs suffers no entropy change, as it is in the steady state.

$$\Delta S_{univ} = \Delta S_A + \Delta S_B = -\frac{Q}{T_1} + \frac{Q}{T_2} = Q\cdot\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
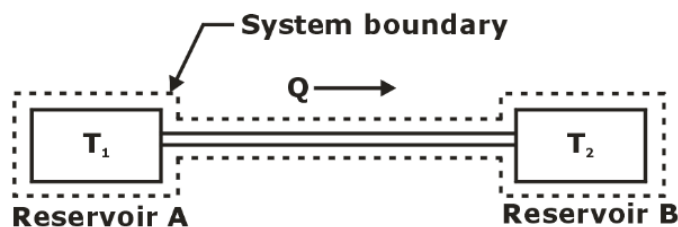

1. If $T_1 > T_2$, ΔS_{univ} is positive.

2. If $T_1 = T_2$, ΔS_{univ} is zero, and the process is reversible.

3. If $T_1 < T_2$, ΔS_{univ} is negative and the process is impossible.

➢ **Mixing of two fluids (excluding gas) or Transfer of Heat through a Finite body at Temperatures T₁ and T₂ brought together into thermal contact**

- Subsystem-1 (mass m_1, specific heat C_1, temperature T_1) and Subsystem-2 (mass m_2, specific heat C_2, temperature T_2) comprise a composite system in an adiabatic enclosure.

- After partition is removed, the two fluids mix and T_F be the final equilibrium temperature.

- If the two bodies are merely brought together into thermal contact, delivering no work, the final temperature T_F reached would be the maximum.

- From Energy conservation $T_F = \dfrac{m_1 C_1 T_1 + m_2 C_2 T_2}{m_1 C_1 + m_2 C_2}$

- Entropy change for subsystem 1 and 2, $\Delta S_1 = m_1 C_1 \ln \dfrac{T_f}{T_1}$, $\Delta S_2 = m_2 C_2 \ln \dfrac{T_F}{T_2}$

$$\Delta S_{uni} = \Delta S_1 + \Delta S_2 = m_1 C_1 \ln \frac{T_F}{T_1} + m_2 C_2 \ln \frac{T_F}{T_2}$$

- ΔS_{univ} will be positive definite, and the mixing process is irreversible.
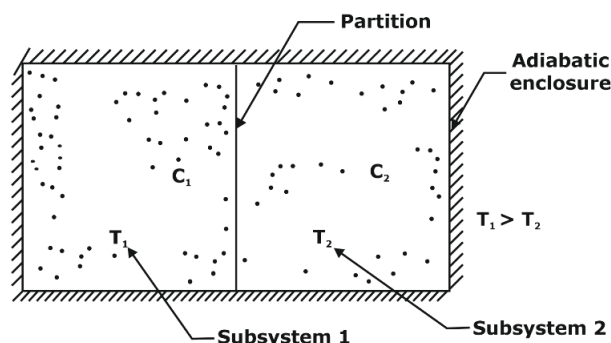
- **SPECIAL CASE** – If $m_1 = m_2 = m$ & $C_1 = C_2 = C$. Then, $T_F = \dfrac{T_1 + T_2}{2}$

$$\Delta S_{univ} = 2mC \ln \frac{T_F}{\sqrt{T_1 . T_2}} = 2mC \ln \left(\frac{AM}{GM} \right),$$ Where AM & GM are the Arithmetic mean &

Geometric mean of temperatures. This is always positive, since the AM of any two numbers is always greater than their GM.
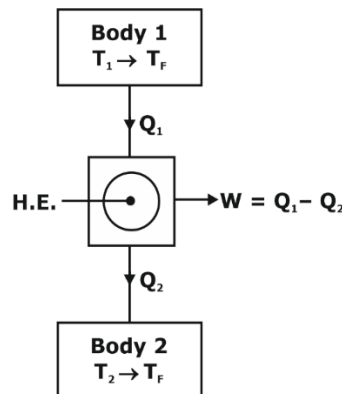
➢ **Transfer of Heat through a Finite body at Temperatures T_1 and T_2 interacting through reversible Heat Engine**

- Consider two finite bodies of constant heat capacity at temperatures T_1 and T_2, ($T_1 > T_2$).

- Via Heat Engine, part of the heat from body 1 converted to work W, and the remainder is rejected to body 2. HE will stop operating when bodies attain the final temperature T_F.

- Total heat withdrawn and rejected from body 1 to 2, $Q_1 = m_1 C_1 (T_1 - T_F)$, $Q_2 = m_2 C_2 (T_F - T_2)$

- Amount of total work delivered by the heat engine, $W = Q_1 - Q_1 = m_1 C_1 (T_1 - T_F) - m_2 C_2 (T_F - T_2)$

- Entropy change for body 1 and 2, $\Delta S_1 = m_1 C_1 \ln \dfrac{T_f}{T_1}$, $\Delta S_2 = m_2 C_2 \ln \dfrac{T_F}{T_2}$

$$\Delta S_{uni} = \Delta S_1 + \Delta S_2 = m_1 C_1 \ln \frac{T_F}{T_1} + m_2 C_2 \ln \frac{T_F}{T_2}$$

- For given values of mC, T_1 and T_2, the magnitude of work W depends on T_F. Work obtainable will be maximum when **T_F is minimum**.

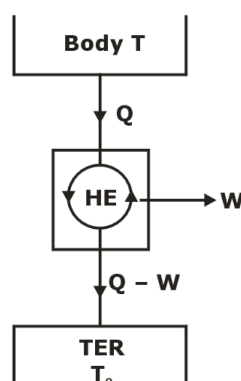- For **maximum work** in the heat engine cycle, entropy change should be **ΔS$_{univ}$ ≥ 0**

- **SPECIAL CASE** – If $m_1 = m_2 = m$ & $C_1 = C_2 = C$. Then, $T_F = \sqrt{T_1 . T_2}$ → The lowest attainable final temperature T_F corresponds to ΔS$_{univ}$ = 0. T_F will be GM of the initial temperatures.

  The largest possible amount of work $W_{max} = mC(T_1 + T_2 - 2\sqrt{T_1 T_2}) = mC\left(\sqrt{T_1} - \sqrt{T_2}\right)^2$

> **Transfer of Heat from a Finite body at Temperatures T and TER at T$_o$ interacting through reversible Heat Engine**

- Let finite body of constant heat capacity at temperatures T_1 and TER is at temperature T_o
- Via Heat Engine, part of the heat from body 1 converted to work W, and the remainder is rejected to TER. The engine stop working, when the temperature of the body reaches T_o.
- Total heat withdrawn and rejected from body 1 to TER, $Q_1 = Q = mC(T - T_o)$, $Q_2 = Q - W$

- Entropy change for body 1 and 2, $\Delta S_{Body} = mC \ln \dfrac{T_0}{T}$, $\Delta S_{TER} = \dfrac{Q - W}{T_0}$

$$\Delta S_{univ} = \Delta S_{Body} + \Delta S_{TER} = mC \ln \dfrac{T_0}{T} + \dfrac{Q - W}{T_0}$$

- For **maximum work** in the heat engine cycle, entropy change should be **ΔS$_{univ}$ ≥ 0**

$$\Rightarrow W_{max} = Q + T_0 mC \ln \dfrac{T_0}{T} = mC\left[(T - T_0) - T_0 \ln \dfrac{T}{T_0}\right]$$

- For **max efficiency** $\eta = \dfrac{W_{max}}{Q_{supplied}} = 1 - T_o\left[\dfrac{\ln(T/T_o)}{T - T_o}\right]$

# CHAPTER-5 AVAILABILITY & IRREVERSIBILITY

INTRODUCTION

- Available energy or Exergy is the energy which is used for doing useful work. It is the amount of low-grade energy that can be completely converted into useful work.

- In exergy analysis the initial state of system is specified, the work output would be maximum when the process is ideal or reversible. Finally, the system must be at dead state to obtain maximum useful work. → Exergy = f (Initial state, Reversible process, dead state)

- **Dead state** is the state of the system in equilibrium with the environment. At the dead state, a system is at environment temperature and pressure, it has no KE & PE relative to environment.
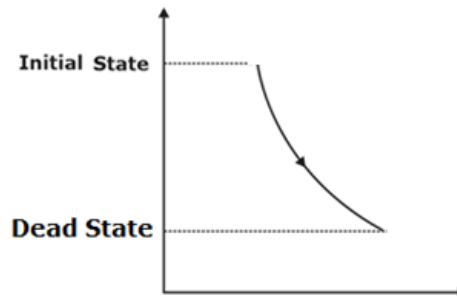
- A system delivers the maximum useful work as it undergoes a reversible process from specified initial state to dead state. This maximum useful work is called **exergy** or **availability**.

EXERGY OR AVAILABLE ENERGY OF HEAT

- Heat is a low-grade energy. For abstracting the max. useful work out of particular amount of heat available at high temperature T_1, we fix a reversible heat engine between T_1 and surrounding T_0.

- Available energy = W = $Q_1 - Q_2$

- $\left(W\right)_{max} = \eta_{reversible} \times Q_1 = \left(1 - \dfrac{T_0}{T_1}\right)Q_1$

- The energy which cannot be utilised for doing useful work is called **unavailable energy**.
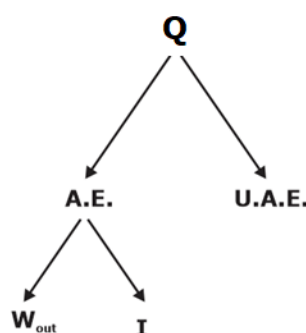
- **Irreversibility I** is equivalent to energy destroyed, hence also known as energy destruction.

    Work Producing device $\left(W_{Rev}\right)_{out} > \left(W_{act}\right)_{out}$ $\Rightarrow I = \left(W_{Rev}\right)_{out} - \left(W_{act}\right)_{out}$

    Work Consuming device $\left(W_{Rev}\right)_{in} < \left(W_{act}\right)_{in}$ $\Rightarrow I = \left(W_{act}\right)_{in} - \left(W_{Rev}\right)_{in}$

EXERGY ASSOCIATED WITH KINETIC AND POTENTIAL ENERGY

- Kinetic energy is a form of mechanical energy (high grade energy) and thus it can be converted to work completely. Hence the exergy of KE of a system is equal to KE itself.

- Potential energy is also a form of mechanical energy (high grade energy) and thus it can be converted to work completely. Hence exergy of PE of a system is equal to PE itself.

SURROUNDING WORK

- When a gas in Piston cylinder device expands, part of work done is used to overcome atmospheric pressure. This work which cannot be recovered and utilized for any useful purpose is called surrounding work. $(W)_{surr} = P_0(V_2 - V_1)$
- Surrounding work is equal to irreversibility associated with above process.

DECREASE IN AVAILABILITY or INCREAE IN IRREVERIBILITY WHEN HEAT TRANSFER THROUGH FINITE TEMPERATURE DIFFERENCE

- Consider a reversible heat engine operating between T_1 and T_0 and Heat transfer is Q_1
- Another reversible heat engine operating between T_1' and T_0 and Heat transfer is Q_1
- Available energy and entropy for 1st case $W = AE = Q_1\left(1 - \dfrac{T_0}{T_1}\right)$ and $\Delta s = \dfrac{Q_1}{T_1}$
- Available energy and entropy for 2nd case $W' = AE' = Q_1\left(1 - \dfrac{T_0}{T_1'}\right)$ and $\Delta s' = \dfrac{Q_1}{T_1'}$
- We know $\Rightarrow T_1 > T_1'$, So $\Rightarrow \Delta s' > \Delta s$ and $\Rightarrow W > W'$
- Decrease in AE or Increase in UAE = $W - W' = T_0\left(\dfrac{Q_1}{T_1'} - \dfrac{Q_1}{T_1}\right) = T_o\left(\Delta s' - \Delta s\right)$
- Hence increase in UAE and the shaded portion represent increase in UAE.
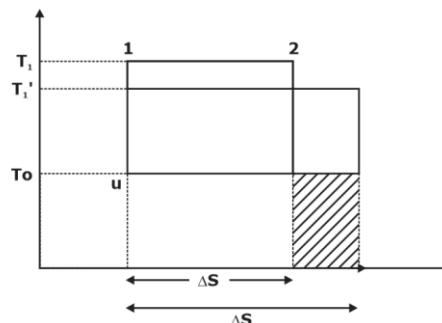
SECOND LAW EFFICIENCY

- Second law efficiency is the ratio of the exergy recovered to the exergy spent.
- It is the ratio of actual work produced to the max work produced under reversible condition.

$$\eta_{II} = \frac{\text{Exergy Re cov ered}}{\text{Exergy spent}} = \frac{W_{act}}{W_{max}}$$

- The second law efficiency is measure of the performance of a device relative to its performance under reversible conditions.

EXERGY OF A CLOSED SYSTEM

- Consider a piston cylinder device that contains a fluid of mass m at temperature T and pressure P. The system is then allowed to undergo a differential change of state.
- For change of exergy from state 1 to state 2
  Exergy at state 1 $\Phi_1 = (E_1 - E_0) + P_0(V_1 - V_0) - T_0(S_1 - S_0)$

Exergy at state 2 $\Phi_2 = (E_2 - E_0) + P_0(V_2 - V_0) - T_0(S_2 - S_0)$

Change in Exergy $\Phi_1 - \Phi_2 = (E_1 - E_2) + P_0(V_1 - V_2) - T_0(S_1 - S_2)$

EXERGY OF OPEN SYSTEM

- A flowing fluid has an additional form of energy, called flow energy, which is the energy needed to maintain flow in Pipe. $W_{flow} = PV$

- The flow work essentially is the boundary work done by a fluid on fluid downstream and thus energy associated with flow work is equivalent to energy associated with boundary work.

- For change of exergy from state 1 to state 2 $\Phi_{flowing\ fluid} = \varphi_{non\ flow\ fluid} + \varphi_{flow}$

    Exergy at state 1 $\Phi_{flowing\ fluid} = (E_1 - E_0) + P_0(V_1 - V_0) - T_0(S_1 - S_0) + P_1V_1 - P_0V_0$

    $= U_1 - U_0 + (KE)_1 - (KE)_0 + (PE)_1 - (PE)_0 + P_1V_1 - P_0V_0 - T_0(S_1 - S_0)$

    $= (U_1 + P_1V_1) - (U_0 + P_0V_0) - T_0(S_1 - S_0) + (KE)_1 - (KE)_0 + (PE)_1 - (PE)_0$

    $= (H_1 - H_0) - T_0(S_1 - S_0) + (KE)_1 - (KE)_0 + (PE)_1 - (PE)_2$

EXERGY BALANCE

- The exergy transfer can be by heat, work and mass.

- Consider an **Open System**, the exergy balance is as follows

    (Total Exergy Entering – Total Exergy leaving)= (Change in total exergy of system + Irreversibility)

    $$m_{in}\phi_{in} + Q_{in}\left(1 - \frac{T_0}{T}\right) + W_{in} - m_{out}\phi_{out} - Q_{out}\left(1 - \frac{T_0}{T}\right) - W_{out} = m_2\phi_2 - m_1\phi_1 + I$$

- For **Closed system** $m_{in} = 0$, $m_{out} = 0$, and $m_1 = m_2 = m$

    The exergy balance gives $m(\phi_2 - \phi_1) + I = Q_{in}\left(1 - \frac{T_0}{T}\right) + W_{in} - Q_{out}\left(1 - \frac{T_0}{T}\right) - W_{out}$

CHAPTER-6 PROPERTIES OF PURE SUBSTANCES

INTRODUCTION

- A pure substance is a substance of constant chemical composition throughout its mass.
- It is one component system and may exist in one or more phases.

SOME IMPORTANT DEFINITIONS

➢ **Sensible heating & cooling:**
- It refers to the heating of substance in single phase. It causes rise in temperature of substance.
- In case of cooling in above conditions it shall be called sensible cooling.

➢ **Latent heating & cooling:**
- It is the heating of substance for causing its phase change without any change in temperature.
- If heat is extracted for causing phase change without any change in its temperature it will be called latent cooling.

➢ **Normal boiling point:**
- It is the temperature at which vapour pressure equals to atmospheric pressure and at this temperature, phase change from liquid to gas begins.
- Examples: Boiling point of water 100 °C, Boiling point of nitrogen −195.8 °C

➢ **Melting point:**
- It is the temperature at which phase change from solid to liquid takes place upon supplying latent heat.

➢ **Saturation states:**
- Saturation state of a substance refers to the state at which its phase transformation takes place without any change in pressure and temperature.
- These can be saturated solid state, saturated liquid state and saturated vapour state.

➢ **Saturation pressure:**
- It is the pressure at which substance changes its phase for any given temperature.
- Example: For water at 100°C the saturation pressure is 1 atm pressure.

➢ **Saturation temperature:**
- It refers to the temperature at which substance changes its phase for any given pressure.
- Example: For water at 1 atm pressure the saturation temperature is 100°C.

➢ **Triple point:**
- Triple point of a substance refers to the slate at which substance can coexist in all three phases (in solid, liquid and gaseous phase) in equilibrium.
- For water it is P_{tp} = 0.611 KPa, T_{tp} = 0.01 °C i.e. at this temperature ice, water and steam can coexist in equilibrium.

- **Critical states:**
  - "Critical state refers to that state of substance at which liquid and vapour coexist in equilibrium."
  - In case of water at 22.12 MPa (221.2 bar), and 374.15°C the water and vapour coexist in equilibrium. Thus, it is the highest pressure and temperature at which distinguishable water and vapour exist together. Specific volume at critical point for water is 0.00317 m^3/kg.

- **Dryness fraction:**
  - It is the mass fraction of vapour in a mixture of liquid and vapour at any point in liquid-vapour mixture region. It is generally denoted by 'x'. It is also **called quality of steam.**
  - $x = \dfrac{m_v}{m_L + m_v}$, where m_v = mass of water vapour and m_L = mass of the liquid

- **Compressed liquid or subcooled liquid:**
  - Liquid at temperature less than saturation temperature corresponding to a given pressure is called compressed liquid or subcooled liquid.
  - Degree of subcooling is given by the temperature difference between liquid temperature and saturation temperature of liquid at given pressure.

- **Superheated steam:**
  - Steam having temperature more than the saturation temperature corresponding to given pressure is called superheated steam.
  - Degree of superheating is given by difference between temperature of steam and saturation temperature at given pressure.

- **Vapor pressure:**
  - When a liquid or solid is in equilibrium with its vapour at a given temperature, the vapour exerts a pressure that depends only on the temperature which is known as **Vapor pressure.**
  - In general, the greater the temperature, the higher is the vapour pressure.
  - The temperature at which the vapour pressure is equal to 760 mm Hg is called the **normal boiling point**.
  - If v_f is the specific volume of the saturated liquid at a given pressure, and v_g the specific volume of the saturated vapour, then $(v_g - v_f)$ or v_{fg} is the change in specific volume during phase transition (boiling or condensation) at given pressure.
  - As pressure increases, v_{fg} decreases, and at the critical point v_{fg} becomes zero.

P-V DIAGRAM FOR A PURE SUBSTANCE

- The saturated liquid line with respect to vaporization and the saturated vapour line with respect to vaporization incline towards each other and form what is known as the saturation or vapour dome. The two lines meet at the critical state.
- The liquid-vapour mixture region (L + V) exists within the vapour dome between the saturated liquid and saturated vapour lines known as Wet region.
- To the right of the saturated vapour line is the vapour region.
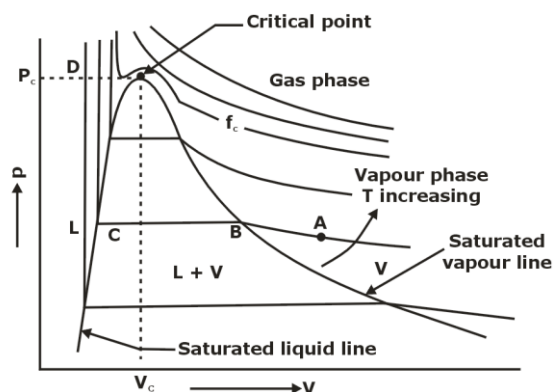
- ABCD is a typical isotherm of a pure substance.

- If the vapour at state A is compressed slowly and iso-thermally, the pressure will rise until there is saturated vapour at point B. If the compression is continued, condensation takes place, the pressure remaining constant so long as the temperature remains constant. At any point between B and C, the liquid and vapour are in equilibrium. Since a very large increase in pressure is needed to compress the liquid, line CD is almost vertical.

- As the temperature increases, the liquid- vapour transition, as represented by BC, decreases, and becomes zero at the critical point. Below the critical point only, there is a liquid-vapour transition zone, where a saturated liquid, on heating, absorbs the latent heat of vaporization, and becomes saturated Vapour at a constant pressure and temperature.

- Above, the critical point, a liquid upon heating suddenly flashes into vapour, or a vapour upon cooling suddenly condenses into liquid. There is no distinct transition zone from liquid to vapour and vice versa.

- The isotherm passing through the critical point is called the **critical isotherm**, and the corresponding temperature is known as the **critical temperature (t_c)**. The pressure and volume at the critical point are known as the **critical pressure** (p_c) and critical **volume** (v_c) respectively.

- Above the critical point, the isotherms are continuous curves that at large volumes and low pressures approach equilateral hyperbolas.

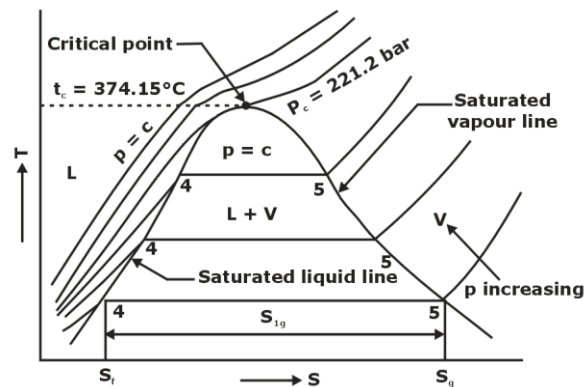## P–T DIAGRAM FOR A PURE SUBSTANCE

- The state changes of a pure substance, upon slow heating at different constant pressures, are plotted on P–T coordinates.

- There are 3 curves on P-T diagram, **fusion curve, vaporization curve, sublimation curve** which divide entire region in 3 phases- **solid, liquid, gas.**

- The fusion curve, the vaporization curve, and the sublimation curve meet at the triple point.

- The slopes of the sublimation and vaporization curves for all substances **are positive.** The slope of the fusion curve for most substances is positive, but **for water, it is negative.**
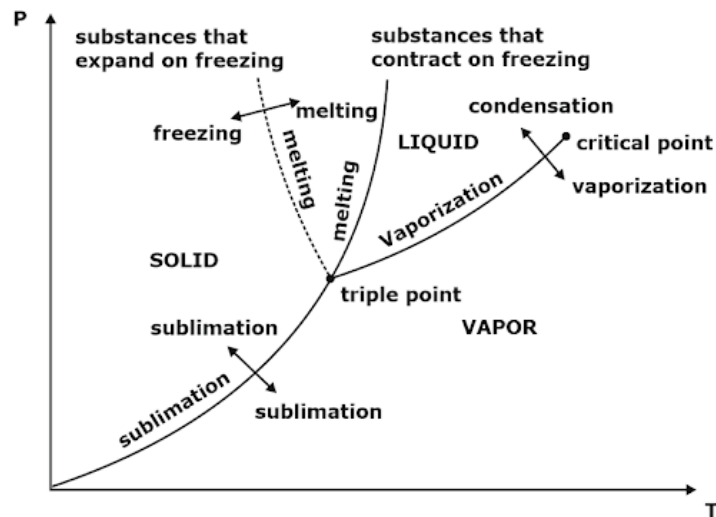
Note:

- The triple point line when projected to the p–T plane becomes a point.
- The critical isotherm has a point of inflection at the critical point.
- It has been found that on a 'P-T' diagram the triple point is represented by **a point.**
- On a 'P-V' diagram and "T-S' diagram triple point is **a line**.
- On a 'u-v' diagram triple point is **a triangle**.

T–S DIAGRAM FOR A PURE SUBSTANCE

- At particular pressure if s_f is the specific entropy of saturated water, and s_g is that of saturated vapour. The entropy change of the system during the phase change from liquid to vapour at that pressure is s_{fg} (s_g – s_f).
- The value of s_{fg} decreases as the pressure increases and becomes zero at the critical point

h—s DIAGRAM OR MOLLIER DIAGRAM FOR A PURE SUBSTANCE

- From the first and second laws of thermodynamics, the following property relation was obtained. This equation forms the basis of the h–s diagram of a pure substance, also called Mollier diagram.

$$\left(\frac{\partial h}{\partial s}\right)_P = T$$

- The slope of an isobar on the h–s coordinates is equal to the absolute saturation temperature, T (t_{sat} + 273) at that pressure. If the temperature remains constant the slope will remain constant. If the temperature increases, the slope of the isobar will increase.

- Below figure is the h –s or Mollier diagram indicating only the liquid and vapour phases.
- Constant pressure lines diverge from one another, and the critical isobar is a tangent at the critical point. In the vapour region, the states of equal slopes at various pressures are joined by lines, as shown, which are the constant temperature lines.
- Although the slope of an isobar remains, continuous beyond the saturated vapour line, **the isotherm bends towards the right and its slope decreases asymptotically to zero**, because in the ideal gas region it, becomes horizontal and the constant enthalpy implies constant temperature.
- At particular pressure, h_f is the specific enthalpy of saturated water, h_g is that of saturated vapour, and h_{fg} (h_g — h_f) is the latent heat of vaporization at that pressure, As the pressure increases. h_{fg} decreases, and at the critical pressure, h_{fg} becomes zero.
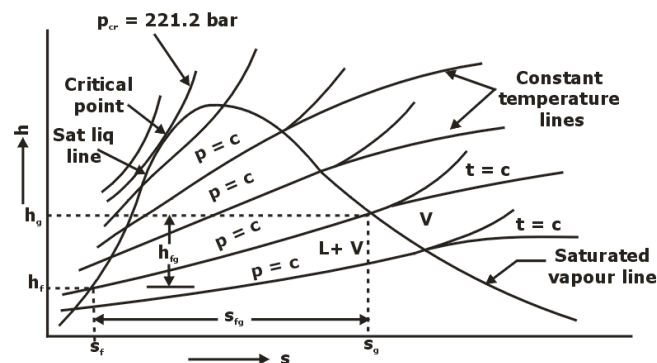
QUALITY OR DRYNESS FRACTION

- If in 1 kg of liquid-vapour mixture, x kg is the mass of vapour and (1 – x) kg is the mass of liquid. Then x is known as the quality or dryness fraction of the liquid-vapour mixture. Therefore, quality indicates the mass fraction of vapour in a liquid vapour mixture,

$$x = \frac{m_v}{m_v + m_L}$$, where m_v and m_L are the masses of vapour and liquid respectively in the mixture.

- The value of x varies between 0 and 1.
- For saturated water (when water just starts boiling): x = 0.
- For saturated vapour (when vaporization is complete): x = 1
- Also   s = (1 – x) s_f + xs_g

    h = (1 – x) h_f + xh_g

    v= (1 – x) v_f + xv_g

    u = (1 – x) u_f + xu_g , where s, h, v and u refer to specific entropy, specific enthalpy and specific internal energy of the mixture of quality x, the suffix f and suffix g indicate the conditions of saturated liquid and saturated vapour, respectively.

MEASUREMENT OF STEAM QUALITY

- The state of a pure substance gets fixed if two independent properties are given. A pure substance is thus said to have **two degrees of freedom**.
- Of all thermodynamic properties, it is easiest go measure the pressure and temperature of a substance. Therefore, whenever pressure and temperature are independent properties, it is the practice to measure them to determine that state of the substance.

- This is done in the compressed liquid region or the superheated vapour region, where the measured values of pressure and temperature would fix up the state.

- But when the substance is in the two-phase region, the measured values of pressure and temperature could apply equally well to saturated liquid point f, saturated vapour point g, or to mixtures of any quality, points x_1, x_2 or x_3.

- Now, of the two properties, P and T, only one is independent; the other is a dependent property. If pressure is given, the saturation temperature gets automatically fixed for the substance. In order to fix up the state of the mixture, apart from either pressure or temperature, one more property, such as specific volume, enthalpy or composition of the mixture (quality) is required to be known.
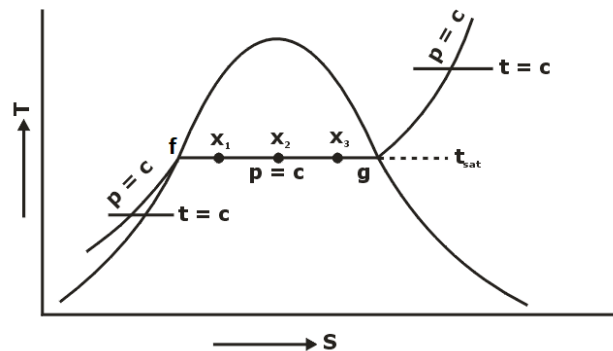
- Since it is relatively difficult to measure the specific volume of a mixture, devices such as calorimeters are used for determining the quality or the enthalpy of the mixture.

- In the measurement of quality, the object is always to bring the state of the substance from the two-phase region to the single-phase or superheated region, where both pressure and temperature are independent, and measured to fix the state, either by **Adiabatic Throttling** or **Electric heating**.

CHAPTER-7 THERMODYNAMIC RELATIONS

INTRODUCTION

- Properties such as temperature, pressure, volume and mass can be calculated directly. Other properties such as density and specific volume can be determined from these properties using some simple relations.

- However, energy, enthalpy and entropy are not so easy to determine because they cannot be measure or related to easily measurable properties through some simple relations.

- Therefore, thermodynamic relations are fundamental relations between commonly encountered thermodynamics properties and express the properties that cannot be measured properties.

PARTIAL DIFFERENTIAL RELATION

Theorem: 1	**Theorem: 2**	**Theorem: 3**
$z = f(x,y)$ $dz = \left(\dfrac{\partial z}{\partial x}\right)_y dx + \left(\dfrac{\partial z}{\partial y}\right)_x dy$ $\qquad$ M $\qquad$ N dz = Mdx + Ndy A function is said to exact, if $\left(\dfrac{\partial M}{\partial y}\right)_x = \left(\dfrac{\partial N}{\partial x}\right)_y \Rightarrow$ exact	$z = f(x,y)$ $\left(\dfrac{\partial z}{\partial x}\right)_y \left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial z}\right)_x = -1$ This relation is known as cyclic relation.	$f = \varphi(x, y, z)$ $\left(\dfrac{\partial x}{\partial y}\right)_f \left(\dfrac{\partial y}{\partial x}\right)_f \left(\dfrac{\partial z}{\partial x}\right)_f = 1$

MAXWELL'S 4 EQUATIONS

- The equations that relate the partial derivative of properties P, V, T and S of a simple compressible system to each other are called Maxwell relations. They are obtained from the **four Gibbs equations** by exploring the exactness of the differentials of thermodynamic properties.

- Two of them are taken from TdS relations.

$$dU = TdS - PdV$$
$$dH = TdS + VdP$$

- The other two are based on Helmholtz and Gibbs function.

    Helmholtz function   F = U – TS (availability of closed system)

    Gibb's function   G = H – TS (availability of open system)

- For all real processes the value of Helmholtz function & Gibbs function decreases & attains a min value at equilibrium. These four relations will be used to derive Maxwell relations by two important theorems of partial derivative.

MAXWELL 4 RELATIONS

$$\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial P}{\partial S}\right)_v \qquad \left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial S}\right)_P \qquad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

COEFFICIENT OF VOLUME EXPANSION (β)

$\beta = \dfrac{1}{v}\left(\dfrac{\partial V}{\partial T}\right)_P$, It is rate of change of volume with respect to temperature at constant pressure.

ISOTHERMAL COMPRESSIBILITY (K_T)

$K_T = -\dfrac{1}{v}\left(\dfrac{\partial V}{\partial P}\right)_T$, It shows the rate of change of volume with respect to pressure at constant

temperature or at isothermal conditions.

T-dS EQUATIONS

Using S = f(T, V) & Maxwell relations $\Rightarrow TdS = C_v dT + T\left(\dfrac{\partial P}{\partial T}\right)_v dV$ → **first Tds equation**

Using S = f(T, P) & Maxwell relations $\Rightarrow TdS = C_p dT - T\left(\dfrac{\partial v}{\partial T}\right)_T dP$ → **second TdS equation**

MAYER'S FORMULA

Using both TdS equation and using $T = \phi(P, V)$, we have $\qquad \Rightarrow C_p - C_v = \dfrac{-Tv\beta^2}{k_T}$

ENERGY EQUATIONS

Using TdS relation & U= f (T, P, V) & Ideal gas equations $\qquad \Rightarrow \left(\dfrac{\partial U}{\partial V}\right)_T = 0 \ \ \& \ \ \left(\dfrac{\partial U}{\partial P}\right)_T = 0$

→ This shows that the internal energy of an ideal gas does not vary with respect to pressure under isothermal conditions. Therefore, **Internal energy of an ideal gas is a function of temperature only.**

JOULE THOMSON COEFFICIENT (μ)

- When a fluid passes through porous plug, capillary tube or valve, its pressure decreases.
- Throttling process is isenthalpic in nature. The temperature behaviour of the fluid during throttling is described by joule Thompson coefficient (μ).

$$\Rightarrow \mu = \left(\dfrac{\partial T}{\partial P}\right)_h = \dfrac{1}{C_P}\left\{T\left(\dfrac{\partial v}{\partial T}\right)_P - v\right\}$$

- Hence, for an ideal gas, μ = 0, if enthalpy is constant then on changing or reducing pressure, temperature will not change. Therefore, when we use air as refrigerant in aircraft refrigerant throttling is not used instead, we use an isentropic expander or turbine.
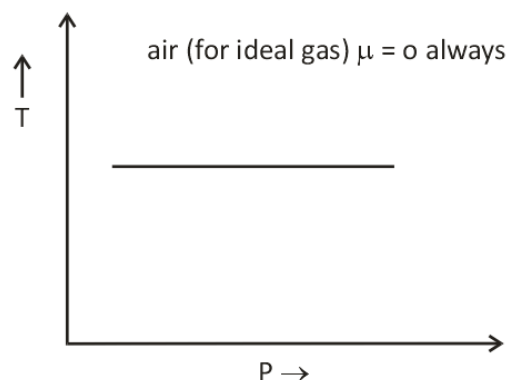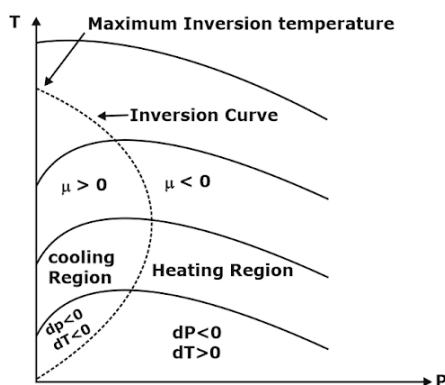
- μ is +ve in cooling region i.e. slope of isenthalpic curve on T – P diagram is +ve in cooling region
- μ is −ve in heating region i.e. slope of isenthalpic curve on T – P diagram is −ve in heating region
- There is nothing as heating or cooling region for an ideal gas & value of μ is zero everywhere.

CLAUSIUS CLAPEYRON EQUATION

- Clausius Clapeyron equations is a relationship between saturation pressure, temperature and enthalpy of vaporisation and the specific volume of two phases involved.
- This equation helps in calculations of properties in two phase regions.
- The Clausius Clapeyron equation can be derived using the Maxwell equation during phase change

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = \frac{ds}{dv} = \frac{s_{fg}}{v_{fg}} = \frac{h_{fg}}{T_{sat}v_{fg}} = \frac{h_{fg}}{T_{sat}(v_g - v_f)} \rightarrow \text{Clapeyron Equation}$$

- If $v_g >>> v_f$ and behaviour of vapour is like ideal gas $v_g = \frac{RT_{sat}}{P_{sat}}$

$$\frac{dP}{dT} = \frac{P_{sat} \times h_{fg}}{RT_{sat}^2} \rightarrow \text{Clausius Clapeyron equation}$$

- Integrating above equation $\quad \ln\left(\frac{P_1}{P_2}\right) = \frac{h_{fg}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \rightarrow$ It helps to determine enthalpy change

associated with phase change by measuring pressure, temperature and volume.

CHAPTER-8 BEHAVIOUR OF IDEAL AND REAL GAS

IDEAL GAS EQUATION

- Deviations from ideal behaviour are observed particularly at high pressures or low temperatures.
- A gas which does not obey the ideal gas equation, PV = nRT strictly at all temperatures and pressures is said to be a real gas.

COMPRESSIBILITY FACTOR (Z)

- The deviation from ideal behaviour is expressed by introducing a factor Z known as compressibility factor in the ideal gas equation.
- Z may be expressed as, Z = PV / nRT
    - In case of ideal gas, PV = nRT ∴ Z = 1,   In case of real gas, PV ≠ nRT ∴ Z ≠ 1
    - Also, $z = \dfrac{v}{v_i} = \dfrac{\text{volume at an instant}}{\text{volume predicted by ideal gas}}$
- Compressibility factor (z) can be viewed as the ratio of actual volume of a real gas to the volume predicted by ideal gas equation.
- In case of real gases, Z can be less than 1 or greater than 1. Farther the value of z from unity, the more will the behaviour of gas deviates from ideal gas.
- When Z < 1, it is a negative deviation. It shows that the gas is more compressible than expected from ideal behaviour.
- When Z > 1, it is a positive deviation. It shows that the gas is less compressible than expected from ideal behaviour.

CAUSES OF DEVIATION FROM IDEAL BEHAVIOUR

- The causes of deviations from ideal behaviour may be due to the following two assumptions of kinetic theory of gases.
    1. Volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas. The first assumption is valid only at low pressures and high temperature.
    2. The forces of attraction between gas molecules are negligible. The second assumption is also valid at low pressures and high temperature. Otherwise, forces of attraction become appreciable and cannot be ignored.

CRITICAL PROPERTIES

- **Critical Temperature (T_c)-** It is the maximum temperature at which a gas can be liquefied i.e. the temperature above which a gas can't exist as liquid.
- **Critical Pressure (P_c)-** It is the minimum pressure required to cause liquefaction at T_c .
- **Critical Volume (V_c)-** It is the volume occupied by one mol of a gas at T_c and P_c

REDUCED PROPERTIES

- The gases follow the ideal-gas equation closely at low pressure and high temperature. But what exactly constitutes low pressure or high temperature?
- pressure or temperature of a substance is high or low relative to its critical temperature or pressure

- Gases behave differently at a given temperature and pressure, but they behave very much the same at temperature and pressure normalized with respect to their critical temperature and pressure. The normalization is done as

Reduced pressure $P_R = \dfrac{P}{P_{cr}}$

Reduced temperature $T_R = \dfrac{T}{T_{cr}}$

Reduced volume $V_R = \dfrac{V}{V_{cr}}$

- The ratios of pressure, temperature and specific volume of a real gas to the corresponding critical values are called the reduced properties.

COMPRESSIBILITY CHART

- The compressibility chart is drawn between compressibility factor & reduced pressure.
- Behaviour of different real gases can be predicted approximately by use of compressibility chart.
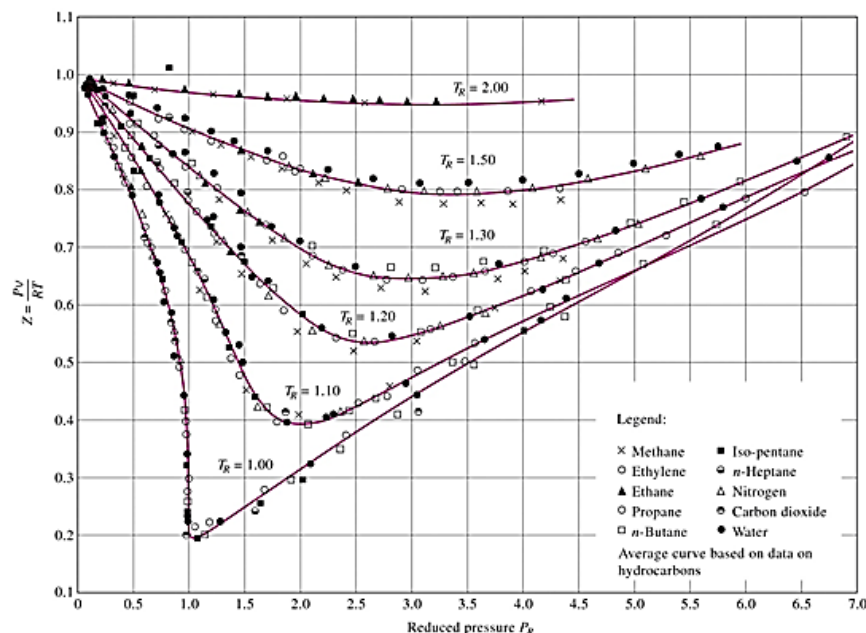
- The following observations can be made from the generalized compressibility chart
    1. At very low pressure, gases behave as an ideal gas regardless of temperature.
    2. At high temperature, ideal gas behavior can be assumed with good accuracy regardless of pressure.
    3. The deviation of a gas from ideal gas behavior is greatest in the vicinity of the critical point.

VAN DER WAALS EQUATION OF REAL GASES

- Van der Waals equation explains quantitatively observed behaviour of real gases, so it is an improvement over the ideal gas equation.

- Vander wall equation is given as, $\left(P + \dfrac{a}{v^2}\right)(v - b) = \bar{R}T$ per mole

    a → correction factor to account for intermolecular attractions

b → correction factor to account for the finite size of the molecules

* The determination of the two constants appearing in this equation is based on the observation that the critical isotherm on a P-V diagram has a horizontal **inflection point** at the critical point. Thus, the first and the second derivative of P with respect to V at the critical point must be zero.

i.e. $\left(\dfrac{\partial P}{\partial v}\right)_{T=T_c} = 0$ and $\left(\dfrac{\partial^2 P}{\partial v^2}\right)_{T=T_c} = 0$
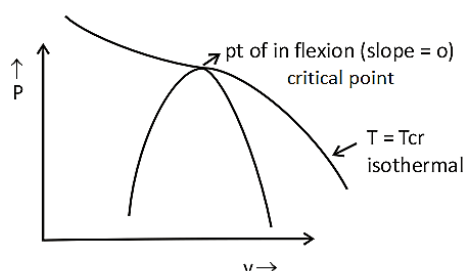
Using Van der Waals equation and above derivatives, we get

$T_c = \dfrac{8a}{27\bar{R}b}, \quad P_c = \dfrac{a}{27b^2}, \quad V_c = 3b$

$a = \dfrac{27\bar{R}^2 T_c^2}{64 P_c}, \quad b = \dfrac{\bar{R}T_c}{8 P_c}$

Compressibility factor at critical point $Z_c = \dfrac{P_c V_c}{\bar{R}T_c} = \dfrac{3}{8}$

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