MODULE 1
FUNDAMENTAL CONCEPTS AND DEFINITIONS

OBJECTIVE:

Students will be familiar with

- **Thermodynamic concepts.**
- **Zeroth law of thermodynamics**

STRUCTURE:

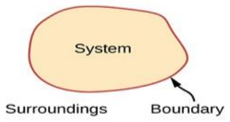
1.1.1 Introduction
1.1.2 Basic concepts and definitions
1.1.3 Zeroth law of thermodynamics
1.1.4 Measurement of Temperature.
1.1.5 Comparison of Temperature Scales:

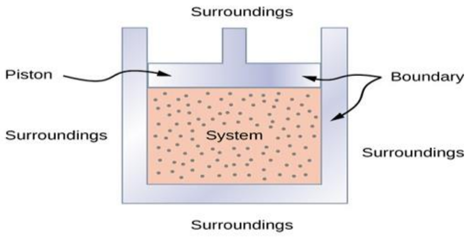
1.1.1 Introduction:

- Thermodynamics is derived from two greek words Therme which means HEAT & Dynamics with mean STRENGTH/POWER.
- Thermodynamics is the science of energy transfer and its effect on the physical properties of a substance.
- Its application is in
    - Steam & Nucelar power plant
    - IC Engines
    - Gas turbines
    - Air Conditioning
    - Refrigeration
    - Jet Propulsion Etc.

1.1.2 Basic concepts and definitions:

- **System:** It is defined as a quantity of matter or a Region in space chosen for study.
- **Surroundings/Environment:** The mass or region outside the system is called Surroundings.
- **System Boundary:** The real or imaginary surface that separates the system from its surroundings is called the system boundary or just boundary.
- **Universe:** Combines System & Surroundings forms Universe.





- **Types of Systems:**

a) **Closed system:** System of fixed content or matter (mass) in which only energy transfer takes place is called Closed system. Thus in a closed system, mass doesn't cross the system boundary even though energy may cross the system boundary. For Example of a closed system – a pressure cooker with closed Lid.

Fig 1.1: Closed system

b) **Open System:** System in which both mass and energy interaction takes place across the system boundary. **For example:** boiling water without a lid. Here Heat escape into the air. At the same time steam (which is matter) also escapes into the air.

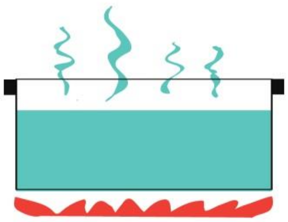
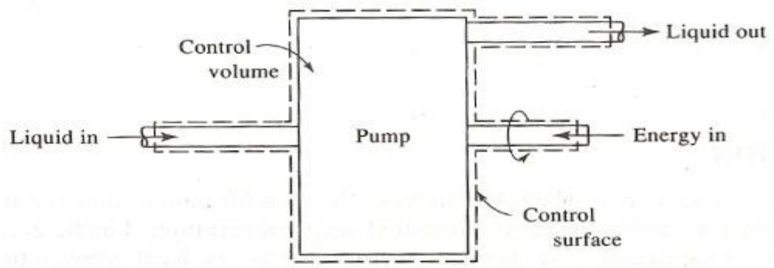


Fig 1.2: Open system

c) **Isolated System:** In an isolated system neither mass nor energy crosses the system boundary. **For example:** A thermoflask is an isolated system.

- **Control Volume:** It is defined as volume in space through which matter, momentum and energy may flow. The control volume may be stationary or may be moving at a constant velocity. If control volume changes both in size and in position, the control volume is equivalent to an open system. If no mass transfer occurs then it is equivalent to closed system.
- **Control Surface:** Control volume is bounded by a surface called control surface.



Example for Control Volume and Control Surface

- **Macroscopic and Microscopic Approach/Point of View:**

Table 1: Differentiation of Microscopic and Macroscopic Approach

SL.No	Microscopic Approach	Macroscopic approach
1	This approach considers that the system is made up of a very large number of discrete particles known as molecules. These molecules have different velocities and energies.	In this approach the behaviour of individual molecules is not considered but studies the properties of particular mass of the substance.
2	The behaviour of system is found by using statistical method as the number of molecules is very large	The analysis of macroscopic system requires simple mathematical formulae
3	The properties like velocity, momentum, impulse, Kinetic energy etc, which describes the molecules cannot be easily measured by instruments	The properties like temperature and pressure which are required to describe the system can be easily measured by instruments.
4	Large number of variables is needed to describe such a system. So approach is complicated	Only few properties are needed to describe such system

- **Phase:** A Quantity of mater which is homogeneous in chemical composition and in physical structure is called a Phase.

Example: Solid phase: Ice
Liquid Phase: Water
Gaseous Phase: Water vapour /Steam

- **Homogeneous System:** A system is called as Homogeneous system if it consists of a single phase. Example water inside a container.
- **Heterogeneous System:** A system consisting of more than one phase is called Heterogeneous System. Example: Ice in liquid water.
- **Property:** Any characteristic of a system is called Property. It is defined as any quantity that depends on the state of the system and is independent of the path by which the system has reached the given state. Example: Pressure, Volume, Temperature, Mass, Modulus of Elasticity, Electric Resistivity, Thermal Expansion Coefficient Etc.
  - Classification of Property:
    - a) **Intensive Property:** Properties that are independent of the mass of the system Example: Temperature, Pressure, Density **(Density of water is constant i.e 1000kg/m3 and the value does not depends on mass of water).**
    - b) **Extensive Property:** Properties that are dependent of the mass or extent of the system. Example: Mass, Volume, Entropy, Enthalpy, Energy Etc.
    - c) **Specific Property:** Extensive Property Per unit mass are called Specific Property. Example: Specific Volume (v), Specific Enthalpy (h), Specific Energy (e) Etc.

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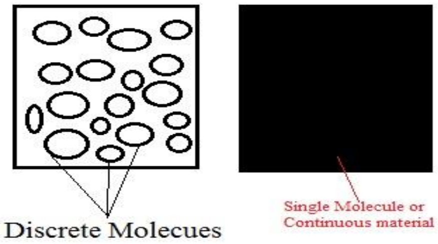
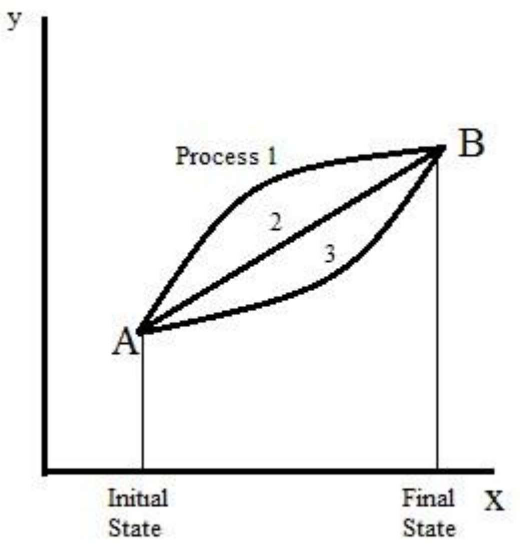
- **State of a system**: It is the condition of existence of a system at a particular instant. Example: Liquid can exist in Solid liquid & Gaseous phase at each phase the property values will be different which denotes the state of the system.

- **Concept of Continuum:** Since thermodynamics doesn't deal with the behaviour of individual molecule we treat the substance as continuous ignoring the action of individual molecule. This Concept is known as continuum.

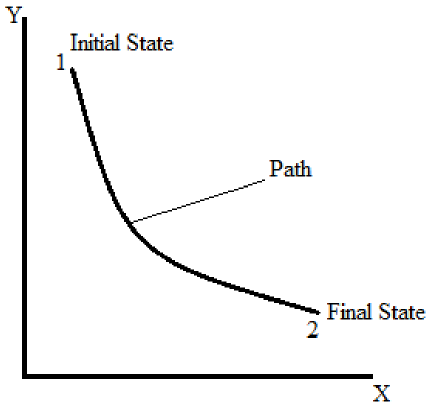
  "The continuum hypothesis states that large systems made up of many discrete molecules or atoms may be treated as though they are made up of continuous material"



- **Thermodynamic Process:** It is defined as the path of the thermodynamic states that a system passes through as it goes from an initial state to a final state.



- **Path of a process**: The series of states thrpugh which a system passes during a process is called the Path.

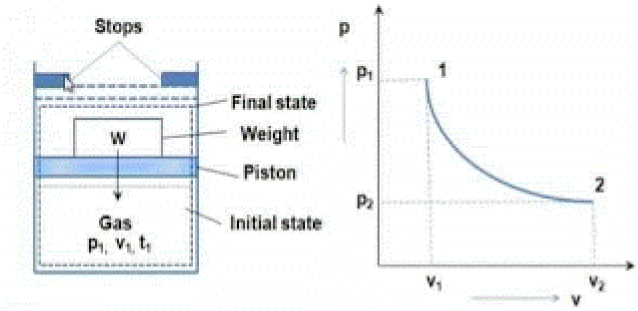


- **Equilibrium Process:** If the process goes on so slowly that the state of equilibrium exists at every moment, then such a process is referred to as an equilibrium process otherwise it is referred to as a Non-equilibrium process.

- **Quasi-Static or Quasi-Equilibrium Process:** "When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times is called a Quasi-static Process.

Quasi static process: Example

Let us consider the assembly of cylinder and piston as shown in figure. Cylinder is contained with gas and system is in equilibrium condition initially. Let us see the state of the system initially is at state 1 and indicated by its thermodynamic properties P1, V1 and T1. At this state pressure will be high and specific volume will be less at a temperature

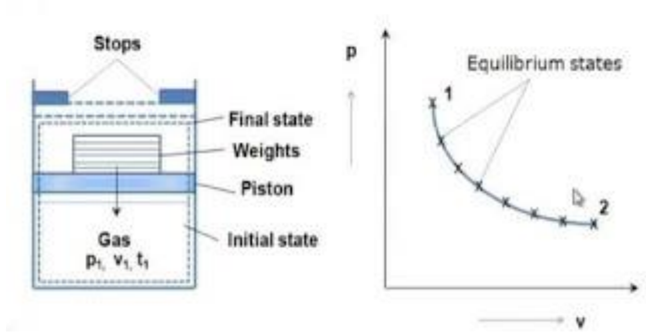


Weight placed over the piston is just balancing the force which is exerted in upward direction by gas. If we remove the weight from the piston, system will have unbalanced force and piston will move in upward direction due to force acting over the piston in upward direction by the gas.

Piston will move in upward direction and will be stopped once it will strike the stops. This condition of the system is expressed as final state and indicated by state 2 and will have its thermodynamic properties P2, V2 and T2. At this state pressure will be less and specific volume will be high.

Initial and final state of the system displayed here with the help of thermodynamic properties as state 1 and state 2 respectively, but intermediate states could not be displayed here by thermodynamic properties as intermediate states by which system has arrived at state 2 were not in equilibrium condition.

Quasi-static processes



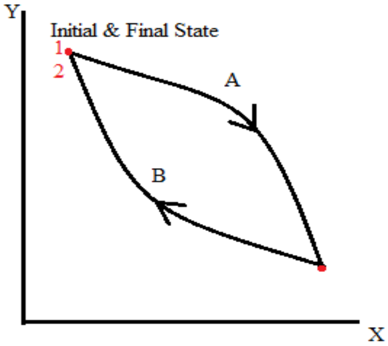
Let us consider the above single weight, placed over the piston, replaced by few infinitesimally small weights and these infinitesimally small weights are placed over each other and also resultant weight of all infinitesimally small weights is equivalent to the single weight placed earlier over the piston.

When we remove the first infinitesimally small weight from the piston, piston will move very slowly as well as with infinitesimally small amount and will secure its next equilibrium state. Due to removal of infinitesimally small weights, one by one and also quite slowly, system will process from one state to another state with succession of equilibrium states.

Hence we can say here that system will arrive to final state from initial state with various equilibrium intermediate states and these intermediate states are displayed in above figure.

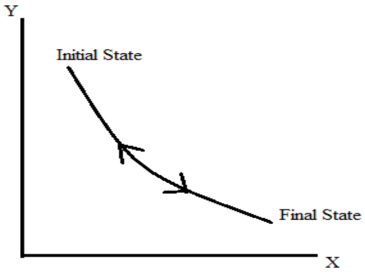
Such a process, where system process in such a manner as studied above, will be termed as quasi static process or quasi equilibrium process in the field of thermal engineering.

- **Thermodynamic Cycle:** It is the one in which a system in a given state goes through a number of different process & finally returns to its initial state .Example: Steam Power Plant constitutes Steam cycle.



From figure the system follows process A and Process B and comes back to initial state 1. If a system undergoes cyclic process then its initial and final state will be same (1 & 2).

- **Reversible Process:** It is defined as the process that occurs in a reverse direction such that the initial state & all energies transferred or transformed during the process can be completely restored in both system and surrounding. In this process there will be no net change in the system or in the surroundings. Example: Reversible adiabatic process.



- **Irreversible Process:** It is defined as the process that is not reversible. Thus during such process the system & the surroundings are no restored to their initial state, if it is restored also their respective initial states with a net change in the system & in the environment. Example: Flow through pipes involving friction.

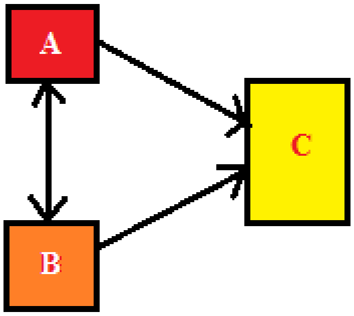
- **Thermodynamic Equilibrium:** When all the conditions of mechanical, chemical, thermal, electrical equilibrium are satisfied, the system is said to be in Thermodynamic Equilibrium.
  1. **Mechanical Equilibrium:** System is said to be in Mechanical equilibrium if there is no unbalanced force within the system or at its boundaries.
  2. **Chemical Equilibrium:** System is said to be in chemical equilibrium when there is no chemical reaction or a process such as diffusion within the system or at its boundaries.
  3. **Thermal Equilibrium:** System is said to be in thermal equilibrium when there is no temperature gradient within the system or between the system and its surroundings.
  4. **Electrical Equilibrium:** System is said to be in electrical equilibrium when there is no electrical potential gradient within a system or between the system and its surroundings.

- **Equality of Temperature:** When two systems at different temperatures are perfectly insulated from the surroundings and brought into contact their will be changes in their physical properties. After some period of time both physical properties and temperature remains constant. This concept is called **Equality of Temperature.**

1.1.3 Zeroth Law of Thermodynamics: "If two bodies are in thermal equilibrium with a third body separately, then they are also in thermal equilibrium with each other.

Or

"If body A is in thermal equilibrium with body B and also separately with body C, then B and C will be in thermal equilibrium with each other.



- **Temperature:** It is the measure of the average heat or thermal energy of the particles in a substance. It does not depend on the size or type of object **(OR)** it is a measure of degree of hotness and coldness of the body.

- **Thermometric property:** The characteristics or physical properties oa a reference body which changes with temperature is called thermometric property.

  The reference body which is used in the determination of temperature is called **Thermometer.**

Type of thermometer	Thermometric Property	Symbol

Constant Volume Gas Thermometer	Pressure	P
Constant Pressure Gas Thermometer	Volume	V
Electrical Resistance Thermometer	Resistance	R
Thermocouple	Thermal emf	ε
Liquid in Glass Thermometer	Length	L

1.1.4 Measurement of temperature:

1) **Two standard fixed points method:**

To establish a temperature scale an easily reproducible state of an arbitrarily chosen standard system is considered which is called fixed points i.e ICE POINT and STEAM POINT**.**

ICE POINT: The lower fixed point or ice point is the temperature at which pure ice melts at standard pressure.

STEAM POINT: The upper fixed point or steam point is the temperature at which pure water boils at standard pressure.

These points are considered as fixed points. In this method the thermometer is first placed in contact with the system whose temperature θ(X) is to be measured, then it is placed in contact with arbitrarily chosen standard system at ice point where temperature is say $\theta(X_1)$. The variation of temperature can be assumed to be a linear function of 'X' which is a thermometric property.

Hence for the first system

$$\frac{\theta(X_1)}{\theta(X)} = \frac{X_1}{X}$$

Then the thermometer at temperature θ(X) is placed in contact with another chosen standard system at steam point where temperature is $\theta(X_2)$.

Hence for the second system

$$\frac{\theta(X_2)}{\theta(X)} = \frac{X_2}{X}$$

By dividing the equations we get

$$\frac{\theta(X_1) - \theta(X_2)}{\theta(X)} = \frac{X_1 - X_2}{X}$$

$$\theta(X) = \left[\frac{\theta(X_1) - \theta(X_2)}{X_1 - X_2}\right].X$$

2) **Single standard fixed point method:**

Kelvin pointed out that a single fixed point such as triple point of water where ice, liquid water and water vapour co-exist in equilibrium. The temperature at which this state exists is arbitrarily assigned the value of 273.16K.

If θ_t = Triple point of water

X_t = Thermometric propert when the body is placed in contact with water at its triple point.

Then we can write,

$$\theta_t = a.X_t$$

$$a = \frac{\theta_t}{X_t} = \frac{273.16}{X_t}.X$$

and if $\theta = a.X = \frac{273.16}{X_t}.X$

$$\theta = \frac{273.16}{X_t}.X$$

Different Types of Thermometer:

1) **Liquid in glass thermometer:** A small quantity of liquid enclosed in a glass capillary is called liquid in glass thermometer. In this the thermometer, the expansion of the liquid which is the length of liquid column is used as the thermometric property Example: Mercury in glass thermometer.

$$\boldsymbol{\theta(L) \text{ or } T(L) = 273.16\left[\frac{L}{L_{tp}}\right]}$$

2) **Constant Volume Gas Thermometer:** It consists of a capillary tube, a gas bulb and a U-tube manometer with flexible tubing. The flexible bend is used to raise or lower the limb which is kept opened to the atmosphere. This helps in adjusting the meniscus of mercury upto the fixed point 'A' and hence maintains constant volume in the gas bulb. The capillary tube connects the bulb to one limb of the manometer whereas; the other limb is kept open to atmosphere. The pressure in the bulb is used as a thermometric property and is given by

   $P = P_o + \rho_M.g.h.$

   Where, P_o = Atmospheric pressure, ρ_M = Density of Mercury

   When the bulb is brought in contact with the system whose temperature is to be measured, Heat transfer from the system into the bulb takes place and the bulb in course time comes in thermal equilibrium with the system. Due to heat addition the gas in the bulb expands and pushes the mercury level downwards. The flexible limb of the manometer is then adjusted so that the mercury again touches the fixed mark 'A' (For keeping volume of gas constant). The difference in the mercury level 'h' is recorded and the pressure 'P' of the gas in the bulb is estimated by using the formulae. Thus temperature increase is proportional to the pressure increase when volume is kept constant in constant volume gas thermometer.

   In **constant pressure gas thermometer** the mercury levels have to be adjusted to keep 'h' constant and the volume of gas 'V', which would vary with the temperature of the system becomes the thermometric property. Thus temperature increase is proportional to the volume increase when pressure is kept constant.

International Temperature scale:

Fixed Points	**Standard system at 1atm Pressure**	**Temperature**	
		°C	**K**
Oxygen point	Normal boiling point of oxygen	-182.97	90.19
Ice point	Melting point of ice	0	273.16
Steam point	Normal boiling point of water	100	373.16
Sulphur point	Normal boiling point of sulphur	444.60	717.76
Silver point	Melting point of silver	960.80	1233.96
Gold point	Melting point of gold	1063	1336.16

Different types of scales:

Temperature Scale	**Ice point**	**Steam Point**	**Triple Point**
Kelvin Scale	273.15K	373.15K	273.16K
Rankine Scale	491.67R	671.67R	491.69R
Fahrenheit Scale	32°F	212°F	32.02°F
Centigrade Scale	0°C	100°C	0.01°C

1.1.5 Comparison of Temperature Scales:

Let the Temperature ‘T’ be linear function of thermometric property ‘L’ of the mercury column.

Considering the Celsius scale

T = a.L + b ……………(1)

Where a and b are constants

Applying the above equation for steam point and ice point respectively, we have

$100 = a.\, L_S + b$

$0 = a.\, L_I + b$

Solving the above equation for a and b we get

$a = 100 / (L_S - L_I)$

$b = -100 / (L_S - L_I)$

Substituting a and b in equation (1) we get

$$T(°\mathrm{C}) = \left[\frac{L - L_I}{L_S - L_I}\right] \times 100$$

Similarly for Fahrenheit , Rankine and Klevin scale we get

$$T(°F) = \left[\frac{L - L_I}{L_S - L_I}\right] \times 180 + 32$$

$$T(R) = \left[\frac{L - L_I}{L_S - L_I}\right] \times 180 + 491.67$$

$$T(K) = \left[\frac{L - L_I}{L_S - L_I}\right] \times 100 + 273.15$$

Relation between scales:

$$T(°C) = \frac{5}{9}[T(°F) - 32]$$

$$T(°C) = \frac{5}{9}[T(R) - 491.67]$$

$$T(°C) = \frac{5}{9}[T(K) - 273.15]$$

$T(R)$ = T (°F) + 459.67 = 1.8 × T(K)

IMPORTANT THEORY QUESTIONS:

1) Distinguish between i)Microscopic and Macroscopic approaches ii) Intensive and Extensive property iii) Point and Path function iv) Quasistatic and Actual process v) Open and close system vi) Adiabatic wall and diathermic wall.
2) Define thermodynamic equilibrium. Explain different conditions that a system should satisfy to attain thermodynamic equilibrium.
3) Explain zeroth law of thermodynamics. How this law forms the basis of temperature measurement.
4) Name a few measurements (or) quantities that can be conveniently used as thermometric properties in order to quantify the temperature.

PROBLEMS:

1) The reading t_A and t_B of two Celsius thermometers A & B agree at the ice point and steam point and are related by the equation $t_A = L + M.t_B + N.t_B^2$. Between these two points L,M,N are constants. When both are immersed in an oil bath, thermometer 'A' indicates 55℃ and thermometer 'B' indicates 50℃. Determine the values of L,M,N and also find the reading on 'A' if 'B' reads 25℃.

Solution: As the two thermometers A and B agree at the ice point and steam point we have

at Ice point : $t_A = 0℃$, $t_B = 0℃$

$t_A = L + M.t_B + N.t_B^2$

$0 = L + 0 + 0$

$\mathbf{L = 0}$

at Steam point: $t_A = 100℃$, $t_B = 100℃$

$t_A = L + M.t_B + N.t_B^2$

$100 = L + M.100 + N.100^2$

$\mathbf{M = 1 - 100.N}$

when ‘A’ indicates 55℃ , ‘B’ indicates 50℃ hence

$t_A = L + M.t_B + N.t_B^2$

$55 = 50.M + 2500.N$

$11 = 10.M + 500.N$

Substituting for ‘M’ in the above equation we get

$\mathbf{N = \frac{-1}{500}}$

From equation M = 1 – 100.N

M = 6/5

When thermometer ‘B’ reads 25℃ , thermometer ‘A’ reads

$t_A = L + M.t_B + N.t_B^2$

$t_A = 28.75℃$

Thus when ‘B’ reads ℃ , ‘A’ reads 28.75℃

2) The e.m.f in a thermocouple with the test junction at t℃ on gas thermometer scale and reference junction at ice point is given by $\varepsilon = 0.20.t - 5\times10^{-4}.t^2$ mV. The millivoltmeter is calibrated at ice and steam points. What will this thermometer read in a place where the gas thermometer reads **50℃.**

Solution: At ice point, when t = 0℃ , $\varepsilon_I = 0$ mV

At steam point , when t = 100℃ , $\varepsilon_s = [0.20\times100] - [5\times 10^{-4}\times(100)^2]$

$\varepsilon_s = 15$mV

At t = 50℃ , $\varepsilon = (0.20\times50) - [5\times 10^{-4}\times(100)^2] = 8.75$mV

For linear scale we have

$$t(°C) = \left[\frac{\varepsilon - \varepsilon_I}{\varepsilon_S - \varepsilon_I}\right] \times 100$$

When ε = 8.75 m.V t(℃) = 58.33℃

Thus when gas thermometer reads 50℃, thermocouple reads 58.33℃

3) In 1709, Sir Issac Newton proposed a new temperature scale. On this scale, the temperature was a linear function on Celsius scale. The reading on this at ice point (0˚C) and normal human body temperature (37˚C) were O˚N and l2˚N, respectively. Obtain the relation between the Newton scale and the Celsius scale.

List of Formulae:

1. $T(°C) = \frac{5}{9}[T(°F) - 32]$
2. $T(°C) = \frac{5}{9}[T(R) - 491.67]$

3. $T(°\mathrm{C}) = \frac{5}{9}[T(K) - 273.15]$

4. $T(R) = \mathrm{T}\ (°\mathrm{F}) + 459.67 = 1.8 \times \mathrm{T(K)}$

5. $T(°\mathrm{C}) = \left[\frac{L-L_I}{L_S-L_I}\right] \times 100$

6. $T(°F) = \left[\frac{L-L_I}{L_S-L_I}\right] \times 180 + 32$

7. $T(R) = \left[\frac{L-L_I}{L_S-L_I}\right] \times 180 + 491.67$

8. $T(K) = \left[\frac{L-L_I}{L_S-L_I}\right] \times 100 + 273.15$

OUTCOME: Explains thermodynamic systems, properties, Zeroth law of thermodynamics, temperature scales and energy interactions.

FURTHER READING:

- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
- http://www.nptel.ac.in/courses/112104113/4#

WORK & HEAT

OBJECTIVE: Understand various forms of energy including heat transfer and work

STRUCTURE:

1.2.1 Work
1.2.2 Other types of work transfer
1.2.3 Heat
1.2.4 Comparison between work and heat

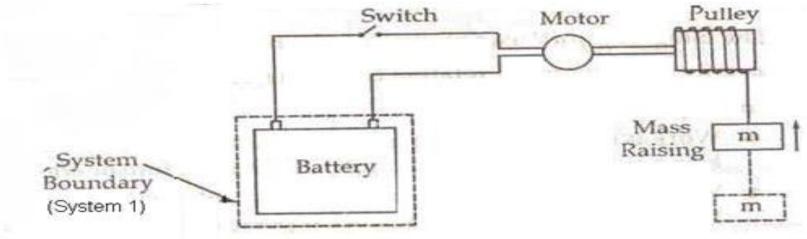
1.2.1 WORK

1. **Mechanics definition of work**: Work is done when the point of application of a force moves in the direction of the force. The amount of work is equal to the product of the force and the distance through which the point of application moves in the direction of the force. i.e., work is identified only when a force moves its point of application through an observable distance.

   Mathematically, $W = \int F.dx$

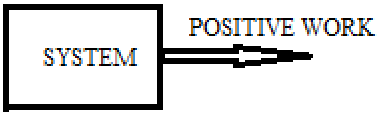
2. **Thermodynamic definition of work**: Work is the energy transfer across the system boundary in an organized manner such that its sole use could be reuced to lift a weight (mass) against gravitational effect.

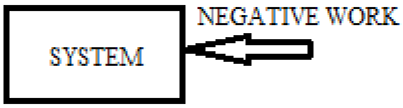
   Let us consider the battery and the motor as a system. The motor is in turn driving a fan. As the fan rotates, the system (Battery & motor) is doing work upon the surroundings. When fan is replaced by a pulley and a weight, the weight may be raised with the pulley which is driven by the motor. Thus the energy from the system gets transferred to the surrounding in an organized manner and it is utilised to lift the weight against gravitational effect. This energy is called Work.



3. Sign convention for Work:

- When work is done by the system, it is arbitrarily taken to be positive.
- When work is done on the system, it is arbitrarily taken to be negative.





Note: 1) Unit of work is N-m, Joules (J)

1) **The rate at which work is done by or upon the system is known as power and its unit is J/s or N-m/s or Watts (W)**

4. P.dV work or Displacement Work:

Consider a system which contains a cylinder filled with a gas and a piston moving in the frictionless cylinder as shown in the figure. Let the piston move outward through a small distance 'dx' in time interval 'dt'. Since the piston moves only a small distance, the pressure acting on the face of the piston can be assumed constant.

The infinitesimal (small amount) workdone by the system is

$$\begin{aligned} \delta W &= \text{Force} \times \text{Displacement} \\ &= (P \times \text{Area of the piston} \times \text{Distance moved by the piston}) \\ &= (P\times A\times dx) \\ &= (P\times dV) \quad \{ A\times dx = dV \} \end{aligned}$$

$$\boldsymbol{\delta W = P\times dV}$$

If the piston moves through a finite distance, the workdone by the piston is obtained by integrating the above equation between the initial and final state, thus we get

$$\int_1^2 \delta W = \int_1^2 P \times dV = W_{1\text{-}2}$$

If the process proceeds from state 2 to state 1 we can write

$$W_{2\text{-}1} = \int_2^1 \delta W = \int_2^1 P \times dV$$

This equation is applicape for i) Reversible or frictionless or quasistatic process ii)closed system iii) Effect due to viscous force, magnetic force, gravitational force and electric force are negligible.

5. Point function and Path function:

1) **Point function:** A quantity say 'x' that have a value at every point within its domain of definition or a quantity that depends on the states of the system but not on the path followed by the system is called point function. Its derivative is given by 'dx' and its integral is

$$\int_1^2 dx = x_2 - x_1$$

Example: All intensive and extensive property

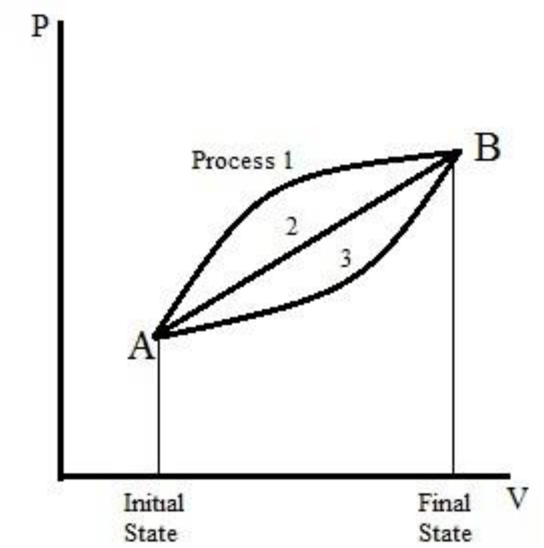
2) **Path Function:** A quantity say 'y' , whose value depends on the mathematical path followed by the system to reach from initial state to the final state is called path function. It is an exact differential hence its derivative it is denoted by 'δy'. Thus we can write between two states 1 & 2

$$\int_1^2 \delta y = y_{1-2}$$

6. Prove that work is a path function:

Consider the P-V diagram as shown in the figure. It is possible to reach final state(state 2) from initial state (state 1) or vice versa by following different paths A,B & C. As the area under the curve represents the work for each process, it is evident that the amount of work involved in each process is dependent only on the path followed but not the end points. We can observe that the area under each curve of process is different hence we can conclude that work is a path function. Thus

$$\int_1^2 \delta W = W_{1-2}$$



1.2.2 Other Modes of Work:

1) **Shaft Work:** Consider an engine shaft rotated by means of an external force. The shaft undergoes an angular displacement when a constant torque ‘T’ is applied to it
Shaft work is given by

$$\delta W = T.d\theta$$

for finite changes shaft work is given by

$$W_{1-2} = \int_1^2 T.d\theta$$

Shaft power = P = $\int_1^2 T.\frac{d\theta}{dT} = T.\omega$

Where ω = Angular Velocity

2) Electrical Work:

$$I = \frac{dC}{dt}$$

Where dC= Charge in coulombs that cross system boundary in time dt .
Electrical work done by the flow of current is given by

$$\delta W = V.dC$$

$$\delta W = V.I.dt$$

Between two states $W_{1-2} = \int_1^2 VI.$

Electrical Power = P = V.I

3) Stretching of a wire:

$\delta W = -F.dL$………(1)

Where , F = External force of tension , dL= Change in length

Stress = $\sigma = \frac{F}{A} = E.\varepsilon$……….(2)

Where, A = Cross sectional area of the wire, E = Modulus of elasticity, ε = Strain

$d\varepsilon = \frac{dL}{L}$…………(3)

Substituting 2,3 in 1 we get

$$\delta W = -A.E.L.\varepsilon.d\varepsilon$$

For finite changes in length

$$W = -A.E.L\int_1^2 \varepsilon.d\varepsilon = \frac{-A.E.L}{2}\left(\varepsilon^2 - \varepsilon^1\right)$$

4) Surface film work or stretching liquid film:

workdone by the wire frame is given by

$\delta W = -\sigma_s.dA$

σ_s = Surface tension of a film, dA = Change in area for finite changes, $W = -\int_1^2 \sigma_s . dA$

5) **Flow work:** work is needed to push the fluid into or out of the boundary of a control volumeif mass flow is involved. This work is called the flow work (flow energy). Flow work is necessary for maintaining a continuous flow through a control volume.

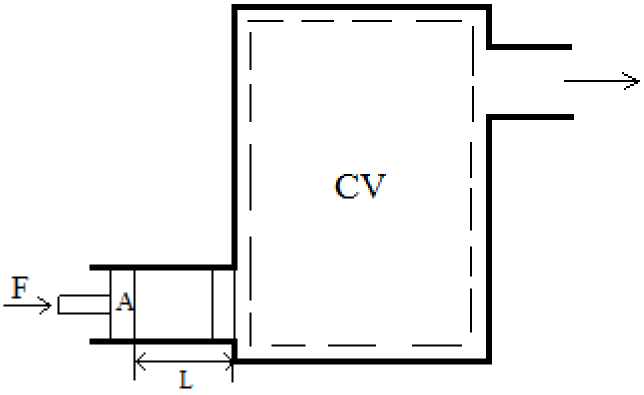
Consider a fluid element of volume V, pressure P, and cross sectional area A as shown in figure. The flow immediately upstream will force this fluid element to enter te control volume, and it can be regarded as an imaginary piston. The force applied on the fluid element by the imaginary piston is F = P. A.

The work done due to pushing the entire fluid element across the boundary into the control volume is

$W_{Flow} = F.L = P.A.L = P.V$

For unit mass = $w_{flow} = P.v$

$W_{Flow\ in} = W_{Flow\ out}$



6) **Stirring Work**:

$\delta W = T.d\theta$

If 'm' is the mass of the weight lowered through a distance 'dZ' , then

$\delta W = T.d\theta = m.g.dZ$

For finite variation we have,

$$W_{1-2} = \int_1^2 m.g.dZ$$

Special Cases:

1) **Restricted or Resisted expansion:**

Consider any piston cylinder machine. During expansion of the fluid, the fluid pressure remains uniform throughout the cylinder against a slow moving piston. Such process is called restricted expansion. The work delivered at the output shat can be determined by using the equation

$$W = a.S.\frac{V_S}{L} = P_m.V_S$$

Where, a = Area of the indicator diagram of Length 'L'

S = Spring number

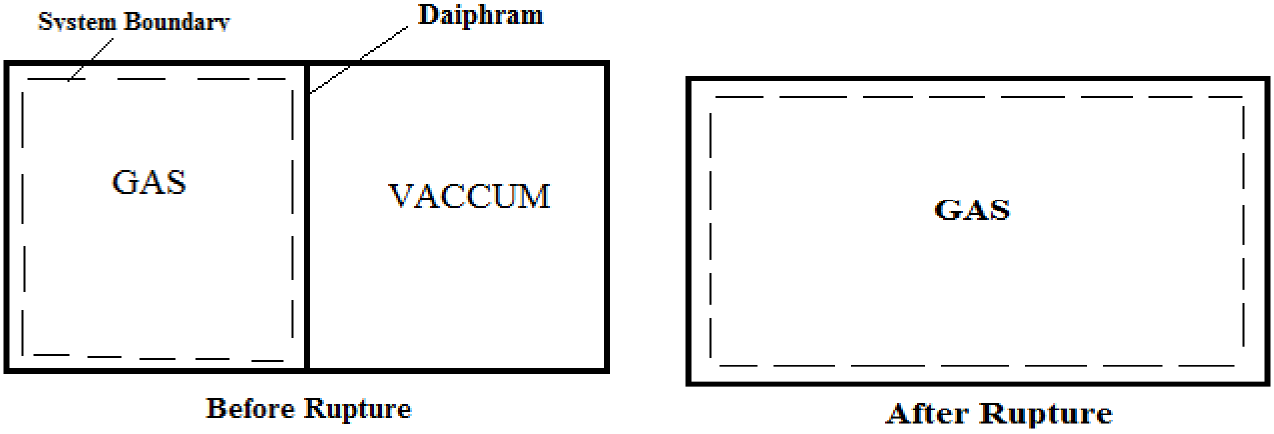
V_S= Swept volume

P_m= Mean effective pressure

If 'N' is the revolutions per second we have power developed = P = P_m.L.A.N

2) Unrestricted Expansion:

Consider a rigid vessel divided by a light diaphragm. One compartment formed by the diaphragm contains a gas whereas the other compartment is evacuated. When the diaphragm is ruptured, the gas moves towards the evacuated compartment. Due to this there will be a change in volume . The process is not reversible even though the initial and final states are in equilibrium. Since vaccum offers no resistance to expansion, the process doesn't pass through equilibrium states and hence there will no well-defined path inturn work transfer will be zero.



1.2.3 HEAT:

Heat is defined as the form of energy that is transferred between two systems or between system and its surroundings by virtue of a temperature difference.

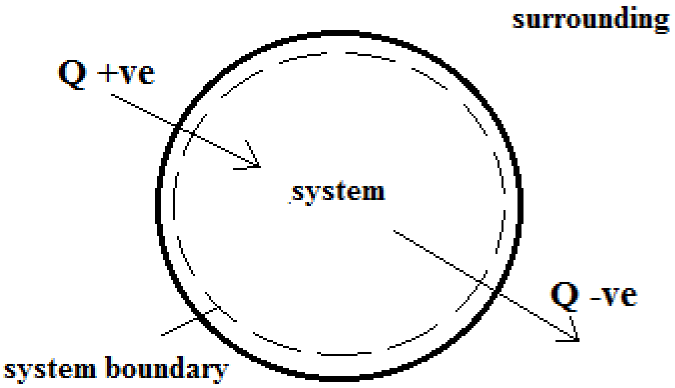
- **Adiabatic process:** A process during which there is no heat transfer is called an adiabatic process (Q =0)

Note: Although heat transfer is not there in adiabatic system, The Temperature of a system may change due to work transfer in adiabatic system.

- **Diathermic wall:** A wall which is permeable to heat flow is a diathermic wall.
- **Adiabatic wall:** A wall which is impermeable to heat flow is adiabatic wall.

Sign Convention for Heat:

- Heat transfer into the system is considered as **positive.**
- Heat transfer from the system is considered as **negative.**
- Unit of Heat transfer(Q) is **KJ**



Modes of Heat Transfer:

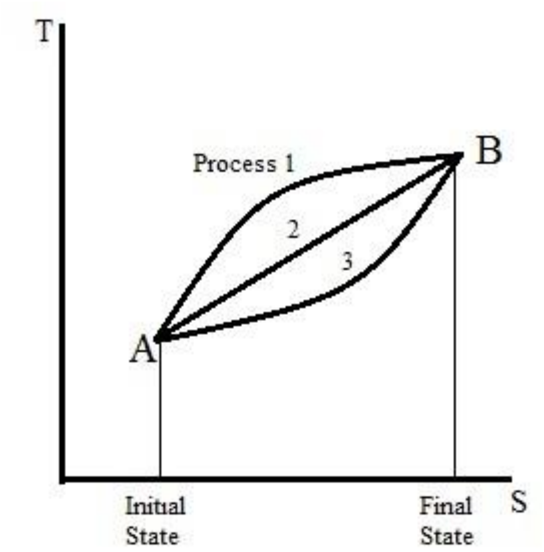
1) **Conduction:** Heat transfer due to direct contact between the elementary particles of a body that is molecules, atoms, free electrons.
2) **Convection:** Heat transfer from one body to another by the moving particles of liquid , gas or loose solids during their relative motion in space.
3) **Radiation:** Heat transfer by electromagnetic waves through a medium which is transparent to thermal radiation. Fraction of the internal energy of a hot body is converted into radiant energy changing in the form of heat.

Heat is a Path Function:

Similar to work the amount of heat transferred from state 1 to state 2 depends on the path of the system. The area under different process is different hence the amount of heat transfer also varies. Hence for a quasi-static process heat transferred is written as

$$\int_1^2 \delta Q = Q_{1-2} = \int_1^2 T.dS$$

Where, S = it is an extensive property called Entropy



1.2.4 Comparison between work and heat:

Similarities:

1. Both are path functions and inexact differentials.
2. Both are boundary phenomenon i.e., both are recognized at the boundaries of the system as they cross them.
3. Both represent transient phenomenon; these energy interactions occur only when a system undergoes change of state i.e., both are associated with a process, not a state. Unlike properties, work or heat has no meaning at a state.
4. A system possesses energy, but not works or heat.

Dissimilarities:

1. Heat is energy interaction due to temperature difference only; work is by reasons other than temperature difference.
2. In a stable system, there cannot be work transfer; however there is no restriction for the transfer of heat.
3. The sole effect external to the system could be reduced to rise of a weight but in the case of a heat transfer other effects are also observed.
4. Heat is a low grade energy whereas work is a high grade energy.

IMPORTANT THEORY QUESTIONS:

1. Define work from thermodynamic point of view and derive an expression for flow work.
2. What are the similarities and dissimilarities between work and heat.
3. Show that work and heat are path fuction
4. Derivean expression for displacement work or P.dV work for a quasistatic process.

5. Explain briefly a quasistatic process and displacement work.
6. Explain With an example how thermodynaim work is different from mechanics definition of work
7. Specify the most widely used sign convention for work & Heat inetraction.
8. Does heat transfer inevitable cause a temperature rise, what is the other cause for rise in temperature.

PROBLEMS:

1. The piston of an oil engine, of area $0.0045 m^2$ moves downwards 75mm, drawing $0.00028 m^3$ of fresh air from the atmosphere. The pressure in the cylinder is uniform during the process at 80kPa, while the atmospheric pressure is 101.375 kPa, the difference being due to the flow resistance in the induction pipe and the inlet valve. Estimate the displacement work bdone by the air.
2. A cylinder contains one Kg of fluid at an initial oressure of 20bar . The fluid is allowed to expand reversible behind a piston according to law $PV^2 = C$ until the volume is doubled. The fluid is then cooled reversibly with the piston firmly locked in this position until the pressure rises to the original value of 20bar. Calculate the net work done by the fluid for an initial volume of $0.05 m^3$.
3. A fluid contained in a horizontal cylinder fitted with a frictionless leak proof piston is continuously agitated by a stirrer passing through the cylinder cover. The diameter of the cylinder is 40cm and the piston is held against the fluid due to atmospheric pressure equal to 100kPa. The stirrer turns 700 revolutions with an average torque of 1Nm. If the piston slowly moves outwards by 50cm determine the net work transfer to the system.
4. A spherical balloon has a diameter of 20cm and contains air at 1.5bar. The diameter of the balloon increases to 30cm in a certain process during which pressure is proportional to the diameter. Calculate the work done by the air inside the balloon during the process.
5. A balloon of flexible material is to be filled with air from a storage bottle untill it has a volume $0.7 m^3$. The atmospheric pressure is 1.013bar. Determine the workdone by the system comprising the air initially in the bottle,given that the ballon is light and requires no strtching.

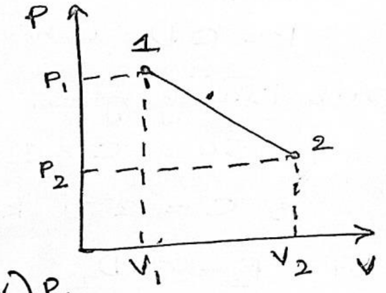
   Solution: $W_d = \int_{\mathrm{balloon}} \mathrm{P_b} . \mathrm{dV} + \int_{\mathrm{Bottle}} \mathrm{P_b} . \mathrm{dV}$

   = $P_{atm} \int dV + 0$ { No change in volume of the bottle hence Zero}

   = 1×(0.7-0)×100 = 70 KJ

Problems :-

1) An engine cylinder has a piston of area $0.12 m^2$ & contains gas at a pressure of 1.5 MPa. The gas expands according to a process which is represented by a straight line on p-V diagram. The final pressure is 0.15 Mpa. Determine the magnitude & direction of work transfer if the piston stroke is 0.30 m



→ Given A of piston $= 0.12 m^2$

$P_1 = 1.5$ Mpa

$P_2 = 0.15$ Mpa

$L = 0.30 m$

$$\text{Workdone} = {}_1W_2 = W_{1-2} = \text{Area under the curve 1-2}$$

$$= \frac{1}{2}(V_2 - V_1)(P_1 - P_2) + (V_2 - V_1)P_2$$

$$= (V_2 - V_1)\left[\frac{P_1}{2} - \frac{P_2}{2} + P_2\right]$$

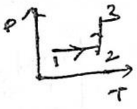
$$W_{1-2} = \frac{1}{2}(P_1 + P_2)(V_2 - V_1) = \frac{1}{2}[1.5 + 0.15] \times 1000 \times (0.12 + 0.$$

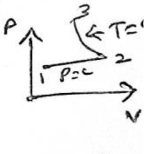
$$\boxed{W_{1-2} = \cancel{59.4}\ \text{KJ}}$$

$= 2$

+ve hence work is done by the system //

2) An ideal gas contained within a cylinder with a movable piston as shown in fig. Evaluate the work per unit mass by the gas for the path indicated in the system. Assume known conditions at state 1 & 3

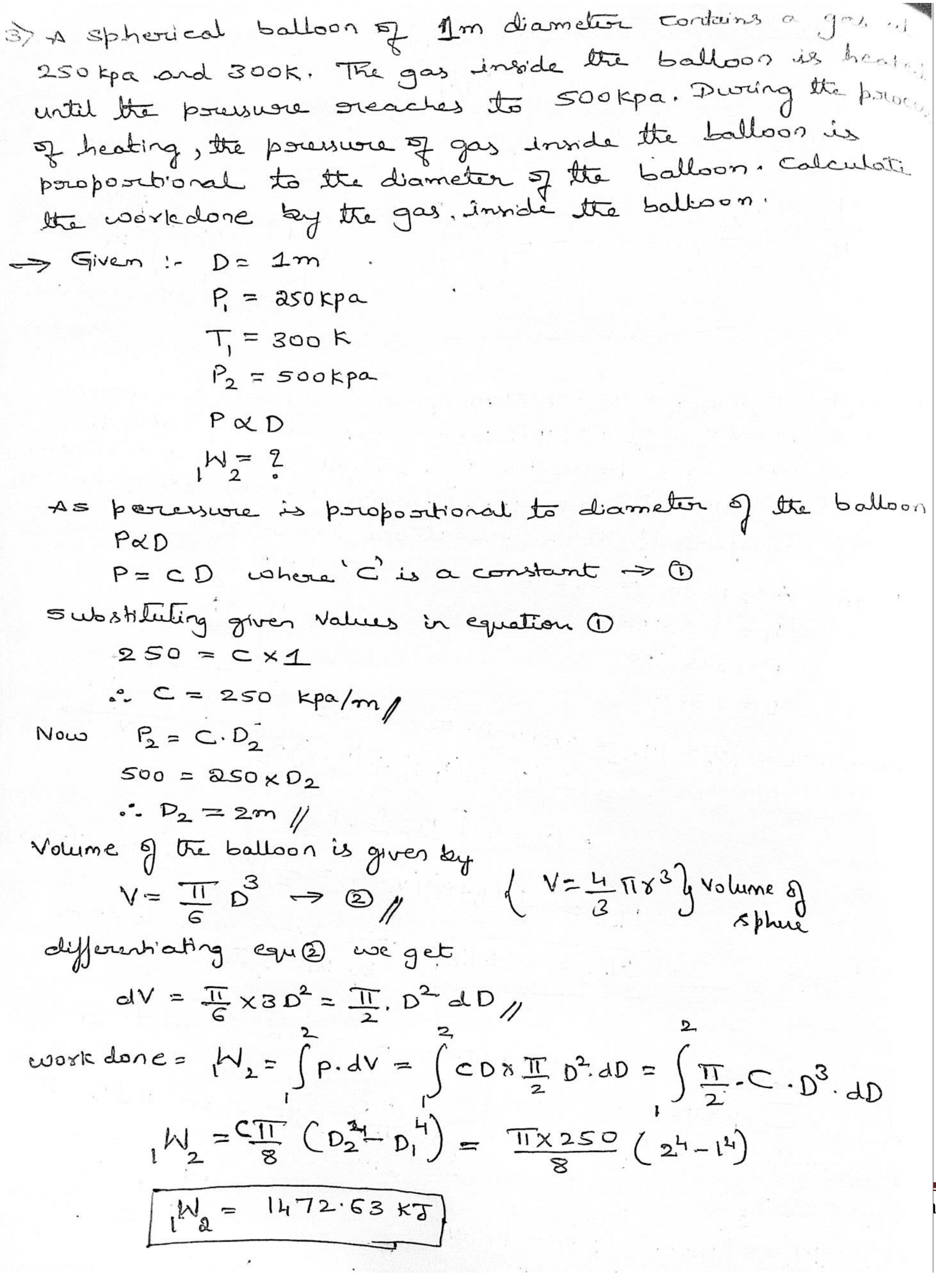




$${}_1W_3 = \int_1^3 p\,dV = \int_1^2 p\,dV + \int_2^3 p\,dV$$

$$= P_1(V_2 - V_1) + P_3V_3 \ln\left(\frac{V_3}{V_2}\right)$$

$$V_2 = \frac{RT_2}{P_2} = \frac{RT_3}{P_2} = \frac{RT_3}{P_1}$$



3) A spherical balloon of 1m diameter contains a gas at 250 kpa and 300K. The gas inside the balloon is heated until the pressure reaches to 500kpa. During the process of heating, the pressure of gas inside the balloon is proportional to the diameter of the balloon. Calculate the workdone by the gas inside the balloon.

→ Given :- $D = 1m$

$P_1 = 250 kpa$

$T_1 = 300 K$

$P_2 = 500 kpa$

$P \propto D$

$_1W_2 = ?$

As pressure is proportional to diameter of the balloon

$P \propto D$

$P = CD$ where 'C' is a constant → ①

substituting given values in equation ①

$250 = C \times 1$

$\therefore C = 250$ kpa/m //

Now $P_2 = C \cdot D_2$

$500 = 250 \times D_2$

$\therefore D_2 = 2m$ //

Volume of the balloon is given by

$$V = \frac{\pi}{6} D^3 \rightarrow ② //$$

$\{ V = \frac{4}{3} \pi r^3 \}$ volume of sphere

differentiating equ② we get

$$dV = \frac{\pi}{6} \times 3D^2 = \frac{\pi}{2} \cdot D^2 \, dD //$$

work done $= {}_1W_2 = \int_1^2 P \cdot dV = \int_1^2 CD \times \frac{\pi}{2} D^2 \cdot dD = \int_1^2 \frac{\pi}{2} \cdot C \cdot D^3 \cdot dD$

$$_1W_2 = \frac{C\pi}{8} \left(D_2^4 - D_1^4 \right) = \frac{\pi \times 250}{8} \left(2^4 - 1^4 \right)$$

$$\boxed{_1W_2 = 1472.63 \text{ kJ}}$$

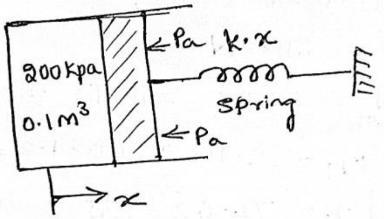
4) Consider the system shown in fig. Initial conditions of the gas are $V_1 = 0.1 m^3$ & $P_1 = 200 kpa$. The ambient atmosphere pressure is 100kpa. The spring exerts a force which is proportional to the displacement from its equilibrium position. The gas is heated until the volume is doubled at which point $P_2 = 600 kpa$. Determine the work done by the gas.

→ Force balance at any position

Total ~~pres~~ force acting on system = Force due to atmospheric air + Force due to the spring

$$\therefore p \cdot A = P_a \cdot A + k \cdot x \qquad \left\{ \because F \propto x \Rightarrow F = k \cdot x \right\}$$

$$\text{Displacement} = x = \frac{\text{Volume}(V)}{\text{Area}(A)}$$



$$\therefore p \cdot A = P_a \cdot A + k \cdot \frac{V}{A}$$

$$\boxed{P = P_a + k \cdot \frac{V}{A^2}} \ *** \rightarrow ①$$

Work done is given by $${}_1W_2 = \int_1^2 P \cdot dV = \int_1^2 \left\{ P_a + \frac{k \cdot V}{A^2} \right\} \cdot dV$$

Given
$P_1 = 200 kpa$
$V_1 = 0.1 m^3$
$P_2 = 600 kpa$
$V_2 = 2V_1 = 0.2 m^3$

$${}_1W_2 = \int_1^2 P_a \cdot dV + \int_1^2 k \cdot \frac{V}{A^2} \cdot dV$$

$${}_1W_2 = P_a (V_2 - V_1) + \frac{k}{A^2} \times \left[\frac{V_2^2 - V_1^2}{2} \right]$$

$${}_1W_2 = P_a (V_2 - V_1) + \frac{k}{2A^2} \left[(V_2 + V_1)(V_2 - V_1) \right]$$

$${}_1W_2 = (V_2 - V_1) \left[P_a + \frac{k}{2A^2} (V_2 + V_1) \right]$$

from equation (1) $$k \cdot \frac{V}{A^2} = (P - P_a)$$

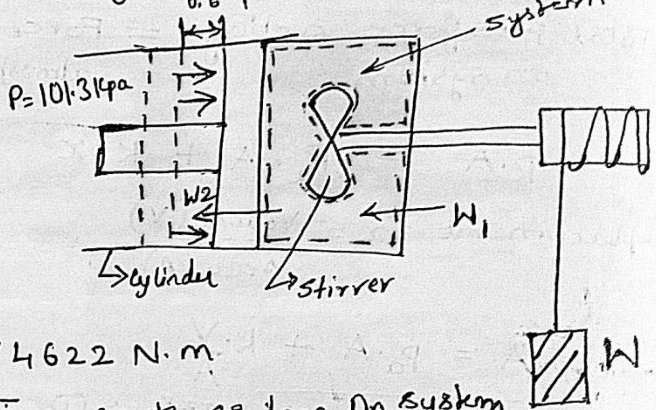
at state 1 we can write $$\frac{k \cdot V_1}{A^2} = P_1 - P_a$$

at state 2 we can write $$\frac{k \cdot V_2}{A^2} = P_2 - P_a$$

$$\therefore {}_1W_2 = (V_2 - V_1) \left[P_a + \frac{P_2 - P_a}{2} + \frac{P_1 - P_a}{2} \right]$$

$${}_1W_2 = (V_2 - V_1) \left[\frac{P_1 + P_2}{2} \right] = (0.2 - 0.1) \left[\frac{200 + 600}{2} \right] = 40 kJ$$

5) A piston & cylinder machine containing a flui
system has a stirring device as shown. The pis
is frictionless, & it is held down against the fluid du
to atmospheric pressure of 101.3 kpa. The stirrin
device is turned 9500 revolutions with an averag
torque against the fluid of 1.25 N·m. Meanwhile
the piston of 0.65m diameter moves out 0.6m.
Find the net work transfer of the system.



→ Work done by the stirring device upon the system = shaft work

$T = F \cdot r$

$S = 2\pi r \cdot N$

$W_{sh} = F \cdot S = 2\pi \cdot NT = W_1$

$W_1 = 2 \cdot \pi \cdot 9500 \cdot 1.25 = 74622 \text{ N.m}$

$\boxed{W_1 = 74.622 \text{ KJ}}$ negative work ∵ done On system

Work done by the system upon the surroundings

$W_2 = F \cdot L = p \cdot A \cdot L$

where, $p = 101.3$ kpa, $A = \frac{\pi}{4} \times (0.65)^2 = 0.3318 \text{ m}^2$, $L = 0.6$ m

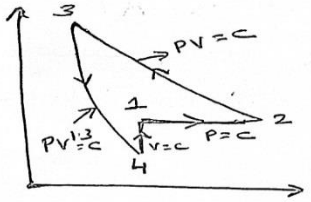
$W_2 = 101.3 \times 0.3318 \times 0.6 = 20.167 \text{ KJ}$ // +ve work

Hence Net work transfer for the system

$W_{net} = W_1 + W_2 = -74.622 + 20.167$

$\boxed{W_{net} = -54.455 \text{ KJ}}$

=> A fluid undergoes the following processes in sequence to complete a cycle. i) Heated reversibly at P=C of 1.05 bar untill it has a volume of 0.02 m³ ii) It is then compressed reversibly according to a law PV=C to a pressure of 4.2 bar iii) It is then allowed to expand reversibly according to a law $PV^{1.3}=C$. iv) Finally it is heated at constant volume back to initial conditions. If the work done during the constant pressure process is 515 N-m. calculate the net work done on or by by the cycle. sketch the cycle on P-V diagram.



Solution :- Given

$$ {}_1W_2 = 515\ \text{N-m} $$

$$ P_1 = P_2 = 1.05\ \text{bar} = 1.05\times10^5\ \text{pa} $$

$$ P_3 = 4.2\ \text{bar} = 4.2\times10^5\ \text{pa} $$

$$ V_2 = 0.02\ \text{m}^3 $$

work done during P=C (1-2) process

$$ {}_1W_2 = P_1(V_2-V_1) \Rightarrow 515 = 1.05\times10^5(0.02-V_1) $$

$$ V_1 = 0.0151\ \text{m}^3 = V_4 $$

To find $\; {}_2W_3 = P_2V_2 \ln\left(\frac{V_3}{V_2}\right).$

$\cdot\ V_3 = ?$

To find V_3, we know that for constant temp process

$$ V_3 = \frac{P_2V_2}{P_3} = \frac{1.05}{4.2}\times0.02 = 5\times10^{-3}\ \text{m}^3 // $$

$$ \therefore\ {}_2W_3 = 1.05\times10^5\times0.02\ \ln\left(\frac{5\times10^{-3}}{0.02}\right) = -2911.2\ \text{J} // $$

To find $\; {}_3W_4 = \frac{P_3V_3 - P_4V_4}{n-1}$

to find P_4 for an polytropic process

$$ \frac{P_3}{P_4} = \left(\frac{V_4}{V_3}\right)^{1.3} \Rightarrow P_4 = 0.998\ \text{bar} // $$

$$ \therefore\ {}_3W_4 = \frac{(4.2\times5\times10^{-3} - 0.998\times0.0151)\times10^5}{1.3-1} = 1975.7\ \text{J} // $$

Net work done = $W_{net} = {}_1W_2 + {}_2W_3 + {}_3W_4 + {}_4W_1 = -419.5\ \text{J} //$

List of Formulas:

1. Displacement work = $W_{1-2} = \int_1^2 P.dV$

2.Workdone and heat Transfer equation for different processes

- **Constant Volume Process or Isobaric Process (P/T = Const)**

  $\frac{P_1}{P_2} = \frac{T_1}{T_2}$

  $W_{1-2} = 0$

  $Q_{1-2} = m(u_2 - u_1) = mC_V (T_2 - T_1)$

  $du = C_V/dT$

- **Constant Pressure Process (V/T = Const)**

  $\frac{V_1}{V_2} = \frac{T_1}{T_2}$

  $W_{1-2} = P(V_2 - V_1)$

  $Q_{1-2} = m(h_2 - h_1) = mC_p (T_2 - T_1)$

  $dh = C_p/dT$

- **Constant Temperature Process (PV = Const)**

  $\frac{P_1}{P_2} = \frac{V_2}{V_1}$

  $W_{1-2} = P_1V_1 \ln\frac{V_2}{V_1} = P_2V_2 \ln\frac{V_2}{V_1}$

  $Q_{1-2} = W_{1-2}$

- **Adiabatc Process(PV^{Υ} = Const)**

  $P_1V_1^{\Upsilon} = P_2V_2^{\Upsilon}$

  $W_{1-2} = \frac{P_1V_1 - P_2V_2}{\gamma-1}$

  $Q_{1-2} = 0$

  For Adiabatic process only you can use following formulas

  $\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$

OUTCOME: Interelation between heat and work . concept of work and different types of work.

FURTHER STUDY :

- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008

- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
- http://www.nptel.ac.in/courses/112104113/4#

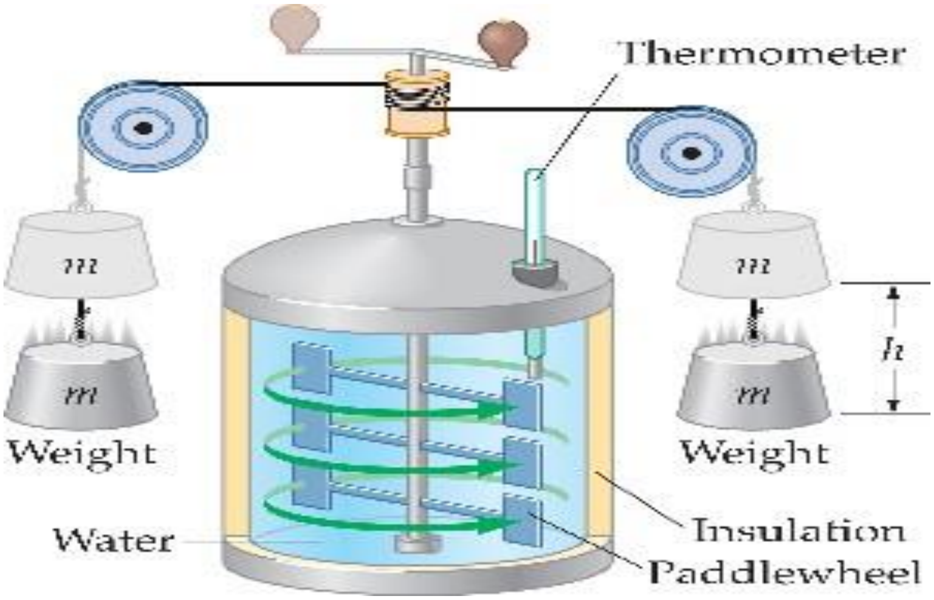
MODULE 2

OBJECTIVES: Study the basic laws of thermodynamics including, conservation of mass, conservation of energy or first law of Thermodynamics and second law of Thermodynamics.

STRUCTURE:

2.1 FIRST LAW OF THERMODYNAMICS

2.1.1 Joule's Experiment:



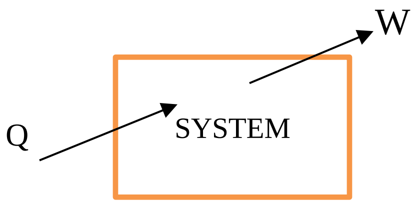
Joules Paddle wheel experiment setup

- Experimental apparatus consists of insulated cylindrical calorimeter, Spindle consisting of Paddles, Weights, Pulley, String, Thermometer and a Handle.
- A known mass of water M1 was taken inside the calorimeter

- By rotating the handle the weights where raised through a height ‘h’, again by rotating the handle in the reverse direction the weights where allowed to fall down through same height ‘h’.
- The falling weights rotated the spindle and thereby stirring the water contained in the calorimeter as a result mechanical energy was converted into heat & the temperature of the water increased.
- The process was repeated and noted the raise in temperature in each case and found that work transfer is directly proportional to Heat transfer. By conducting a series of experiments joule found that when the falling weights lost 4.186kJ of Mechanical Energy a temperature of 1kg of water raised by 1°C.
- Thus potential energy of the falling masses was converted into kintetic energy and finally into heat energy

$$\mathrm{W \,\alpha\, Q}$$
$$\mathrm{W = J.Q}$$
$$\mathrm{W = 4.186.Q}$$

2.1.2 First law applied to closed system undergoing non-cyclic process:



“If a system undergoes a change of state during which both heat transfer and work transfer are involved, the net energy transfer will be stored or accumulated within the system.”

If Q is the amount of heat transferred to the system and W is the work transferred from the system during the process, then,

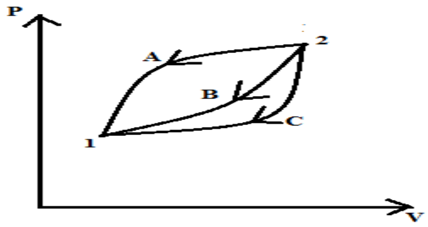
$Q - W = \Delta E$

The Energy in storage is neither heat nor work, but is given the name **internal energy.**

If more than one heat transaction and more than one work transaction are happening at the same time on a system then,

$(Q_1+Q_2+Q_3) = (W_1+W_2+W_3) + \Delta E$

2.1.3 Energy a Property of the System:



Existence of property

Consider a system undergoing a cycle, changing from state1 to state2 by process A and returning from state2 to state1 by process B.
Then, we have from First law of Thermodynamics,

$$\oint \partial Q = \oint \partial W$$

For the process 1-A-2-B-1

$$\oint_{1A}^{2B} \partial Q + \oint_{2B}^{1B} \partial Q = \oint_{1A}^{2B} \partial W + \oint_{2B}^{1B} \partial W \ldots\ldots\ldots\ldots (1)$$

Now, consider another cycle 1-A-2-C-1, for this process we can write,

$$\oint_{1A}^{2A} \partial Q + \oint_{2C}^{1C} \partial Q = \oint_{1A}^{2A} \partial W + \oint_{2C}^{1C} \partial W \ldots\ldots\ldots\ldots (2)$$

Now, eqn (1) – eqn (2) gives,

$$\oint_{2C}^{1C} \partial Q - \oint_{2B}^{1B} \partial Q = \oint_{2C}^{1C} \partial W - \oint_{2B}^{1B} \partial W$$

by rearranging, we get,

$$\oint_{2C}^{1C} (\partial Q - \partial W) = \oint_{2B}^{1B} (\partial Q - \partial W)$$

Hence, we can say that the quantity $(\boldsymbol{\partial Q - \partial W})$ is same for processes between state1 and state2. This value depends only on end states and not on the path it follows.
Therefore,
$(\boldsymbol{\partial Q - \partial W}) = \boldsymbol{\partial E}$ is a point function and hence, a **property of the system**.
If it is integrated between the state1 and state2, we get,

$$\mathbf{Q_{1\text{-}2} - W_{1\text{-}2} = E_2 - E_1}$$

2.1.4: Modes of Energy:

The property E (stored energy) in the first law of TD equation represents the sum of energy transfers across the boundary. This may present in any forms of energy namely, Kinetic energy, Potential energy, Chemical energy, Electrical energy etc.
However, in Thermodynamics it is a practice to consider Kinetic and Potential energies separately and group all other types under one category known as Internal energy (U). Thus,

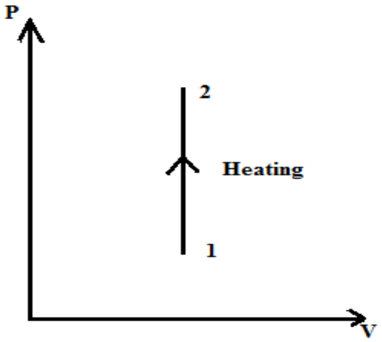
E= Internal energy + Kinetic energy + Potential energy

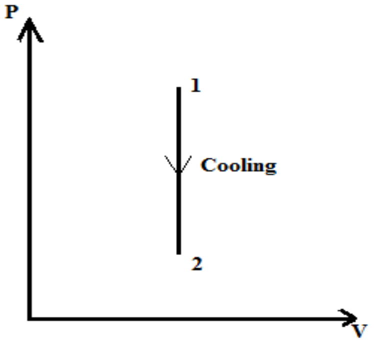
In the absence of motion and gravity effect further E reduces to Internal energy only in Thermodynamics.
Hence the First law for a Non-flow process can be written as

$$(\boldsymbol{\partial Q - \partial W}) = \boldsymbol{\partial U}$$

2.1.5: First law applied to various TD processes.

2.1.5a: Constant Volume Process:





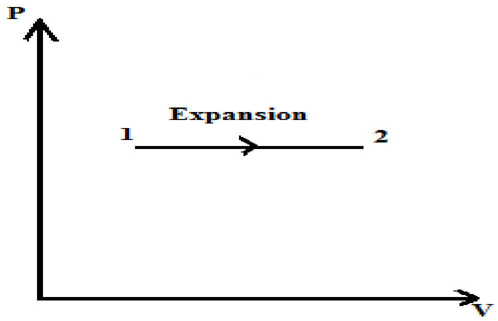
We Know that, Work done= Zero for a constant volume process from state1 to state2,
From First law, 2

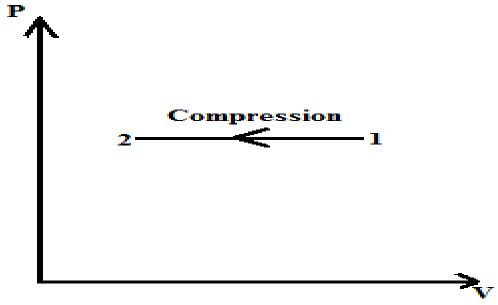
$$\int_1^2 \partial Q = \int_1^2 \partial W + \int_1^2 \partial U$$

$$\text{or, } Q_{1\text{-}2} = W_{1\text{-}2} + U_2 - U_1$$

$$\mathbf{Q_{1\text{-}2} = U_2 - U_1 \text{ ……… Change in Internal energy}}$$

2.1.5b: Constant Pressure Process:





We know that for a Constant pressure process, Work done is $W_{1\text{-}2} = P(V_2 - V_1)$
From First law,

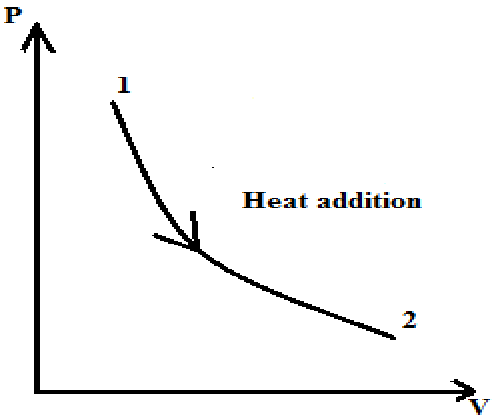
$$\int_1^2 \partial Q = \int_1^2 \partial W + \int_1^2 \partial U$$

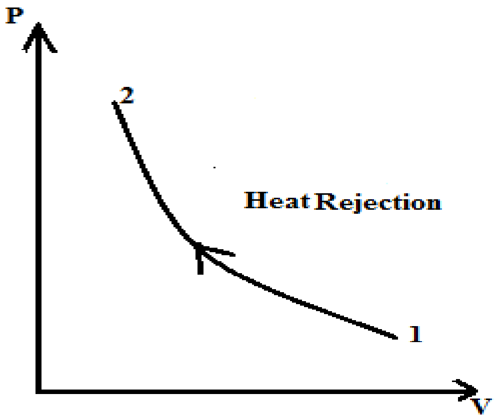
$$Q_{1\text{-}2} = P(V_2 - V_1) + U_2 - U_1$$

$$= (U_2 + P_2V_2) - (U_1 - P_1V_1)$$

$$\mathbf{Q_{1\text{-}2} = H_2 - H_1} \qquad \textbf{……Change in Enthalpy}$$

2.1.5c: Constant Temperature process (PV=Constant):





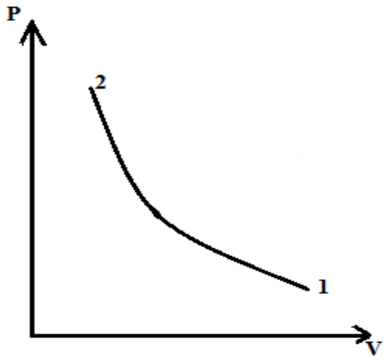
We know that work done $W_{1\text{-}2} = P_1V_1 \ln(V_2/V_1)$
From First law,

$$\int_1^2 \partial Q = \int_1^2 \partial W + \int_1^2 \partial U$$

$Q_{1\text{-}2} = P_1V_1 \ln(V_2/V_1) + mC_v(T_2 - T_1)$ but, $T_1 = T_2$

Therefore, $\mathbf{Q_{1\text{-}2} = P_1V_1 \ln(V_2/V_1)}$ **= Work done**

2.1.5d: Adiabatic Process. (PV^γ = Constant)



We know that, Work done = $\frac{P_1V_1 - P_2V_2}{\gamma - 1}$

From First law,

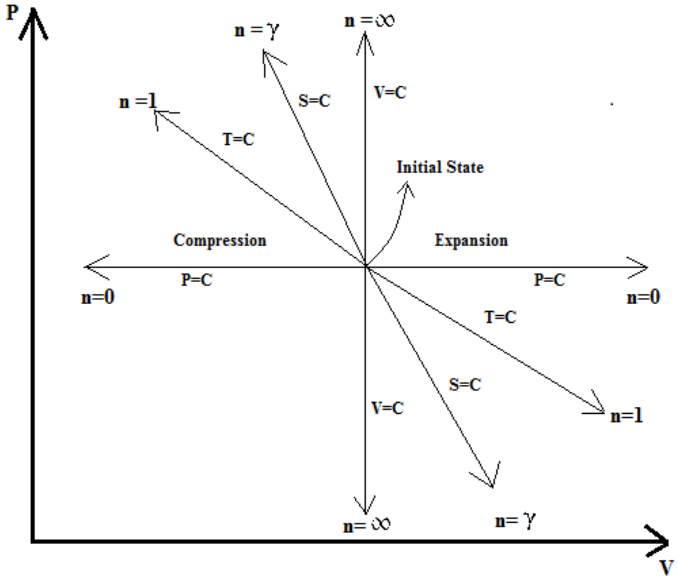
$$\int_1^2 \partial Q = \int_1^2 \partial W + \int_1^2 \partial U$$

But, $Q_{1-2} = 0$

Therefore, $0 = W_{1-2} + U_2 - U_1)$

or **Work done = Change in Internal energy**

2.1.5e: Polytropic process (PV^n = Constant):



Polytropic process

We Know that, Work done $= W_{1-2} = \frac{mR(T_1-T_2)}{n-1}$ and $\delta U = mC_v(T_2-T_1)$

From First law of TD,

$$\int_1^2 \partial Q = \int_1^2 \partial W + \int_1^2 \partial U$$

Substituting and simplifying we get,

$$Q_{1-2} = \frac{\gamma - n}{\gamma - 1} \times \frac{mR(T_1 - T_2}{n - 1}$$

or $$\boldsymbol{Q_{1-2} = \frac{\gamma-n}{\gamma-1}} \times \textbf{Polytropic Work done}$$

2.1.6: Extension of the First law to control volume:

<u>Control Volume:</u>

It is defined as any volume of fixed shape, position and orientation relative to the observer.

<u>Comparison and differences between Control Volume and Closed system</u>

Comparison:

Both Control Volume and Closed system are derived from the concept of boundary.

Differences:

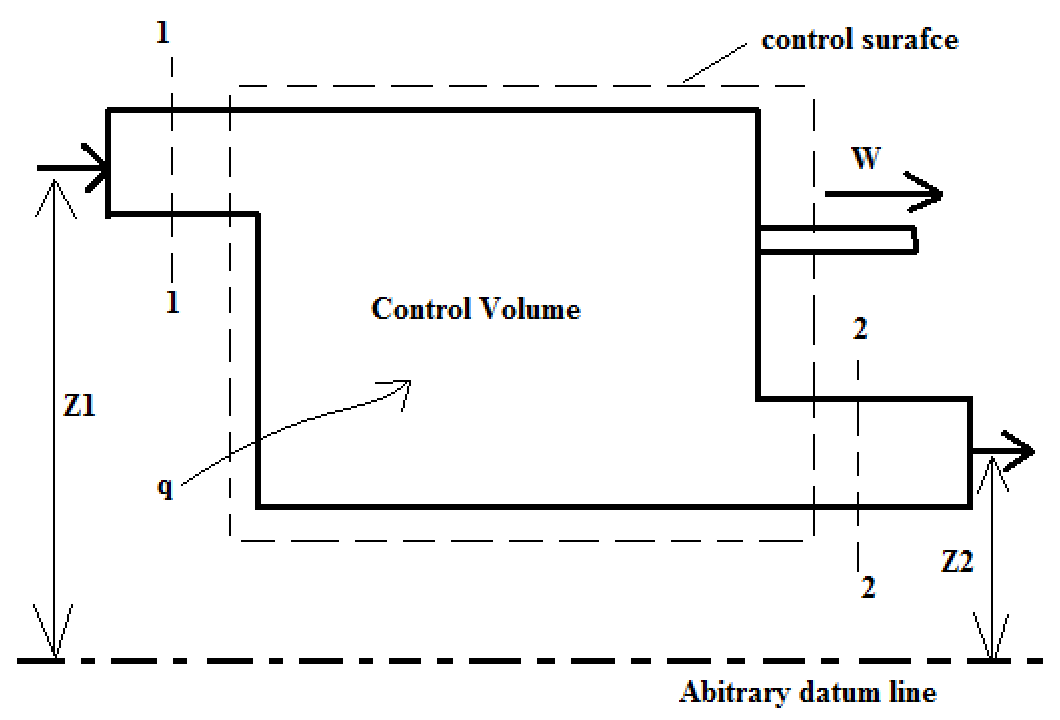
1) The Closed system boundary may(usually) change its shape relative to the observer, where as control volume does not change.
2) Mass usually crosses the control volume, where as it does not cross the boundary in a closed system.

Steady Flow process:

Steady Flow Process means that the rate of flow of **Mass** and **Energy** across the control volume are constant.

Mass/Energy entering the Control volume per unit time is equal to Mass/Energy leaving the system per unit time.

2.1.7: Steady Flow Energy Equation (SFEE) and its important applications:



Control volume for Steady flow process

Let,

P_1 = Pressure of the working substance entering the control volume in N/m^2.

v_1 = Specific volume of the working substance in m^3/kg.

V_1 = Velocity of the working substance entering the control volume in m/s.

u_1 = Specific internal energy of the working substance entering the control volume in kJ/kg.

Z_1 = Hight above the datum for inlet in m.

P_2, v_2, V_2, u_2, and Z_2 = corresponding values for the working substance leaving the control volume.

Q_{1-2} = heat supplied to the control volume in kJ/kg.

W_{1-2} = Work done by the system in kJ/kg.
Considering 1 kg of mass of the working substance. ie., m = 1 kg.

We know that total energy entering the control volume per kg of the working substance.
e_1 = Internal energy + Displacement work + Kinetic energy + Potential energy + Heat supplied.

$$e_1 = u_1 + P_1v_1 + \frac{V_1^2}{2} + gZ_1 + q_{1-2} \quad \text{in kJ/kg}$$

Similarly, total energy leaving control volume per kg of the working substance is,

$$e_2 = u_2 + P_2v_2 + \frac{V_2^2}{2} + gZ_2 + W_{1-2} \quad \text{in kJ/kg}$$

Assuming no loss of energy during flow (Steady Flow conditions), then according to First law of Thermodynamics,

$$e_1 = e_2$$

$$u_1 + P_1v_1 + \frac{V_1^2}{2} + gZ_1 + q_{1-2} = u_2 + P_2v_2 + \frac{V_2^2}{2} + gZ_2 + W_{1-2}$$

We know that,
$u_1 + P_1v_1$ = h_1 = Enthalpy of the working substance entering the control volume in kJ/kg.
$u_2 + P_2v_2$ = h_2 = Enthalpy of the working substance leaving the control volume in kJ/kg.

Therefore, $$\boldsymbol{h_1 + \frac{V_1^2}{2} + gZ_1 + q_{1-2} = h_2 + \frac{V_2^2}{2} + gZ_2 + W_{1-2}}$$

This is the Steady Flow Energy Equation for unit mass of the working substance.
When this equation is multiplied by mass ‘m’ , then we get total energy input and total energy output.

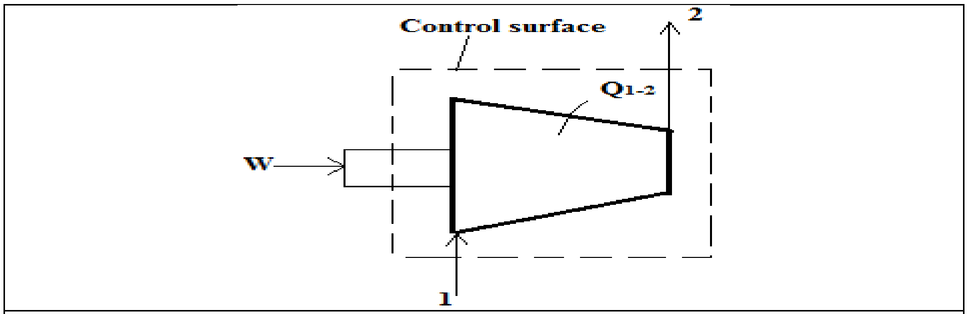
$$m_1\left(h_1 + \frac{V_1^2}{2} + gZ_1 + q_{1-2}\right) = m_2\left(h_2 + \frac{V_2^2}{2} + gZ_2 + W_{1-2}\right)$$

But in a steady flow process $m_1 = m_2$
Therefore,

$$\boldsymbol{m\left(h_1 + \frac{V_1^2}{2} + gZ_1 + q_{1-2}\right) = m\left(h_2 + \frac{V_2^2}{2} + gZ_2 + W_{1-2}\right)}$$

2.1.8 Important applications of SFEE:

1) Rotary Compressor:



Rotary Compressor

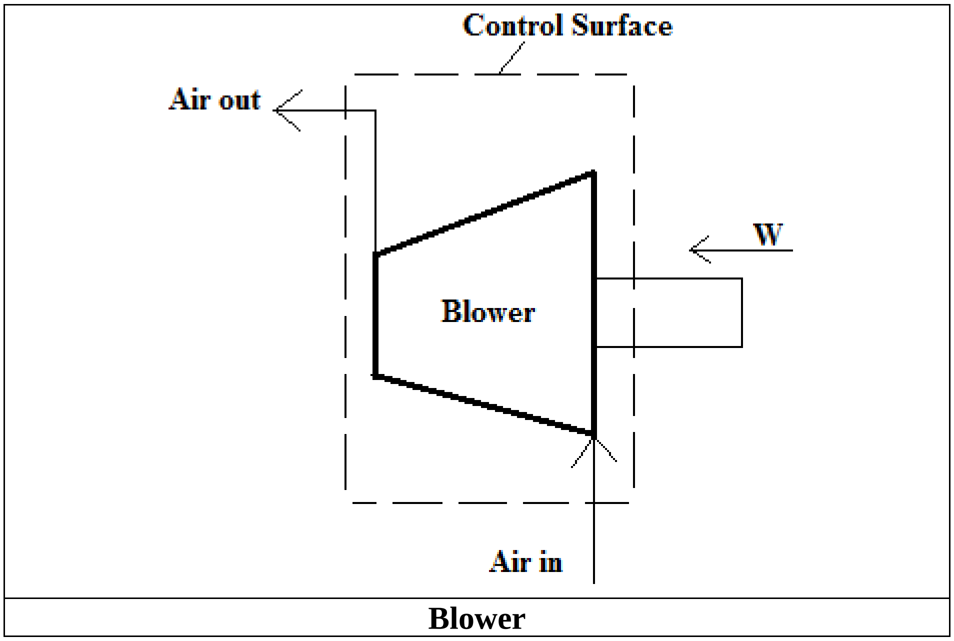
For a Rotary compressor,

a) Work is done on the system ie., W_{1-2} is Negative.
b) Heat rejected by the system, ie., Q_{1-2} is Negative and is negligible
c) Change in Potential Energy and Kinetic Energy is negligible.

Applying the above conditions to SFEE we get,

$$\mathbf{W_{1-2} = m\,(h_2 - h_1)}$$

2) Blower:



Blower

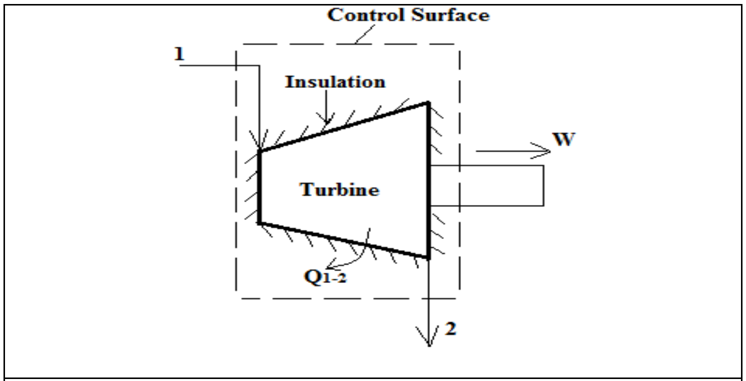
For a Blower,

a) Heat Transfer is Zero, ie., $Q_{1-2} = 0$,
b) Work done on the system is negative,
c) Change in Potential Energy and Internal Energy is negligible,
d) V_1 is very small when compared to V_2

Applying the above conditions to SFEE we get,

$$\boldsymbol{W_{1-2} = \frac{V_2^2}{2}}$$

3) Steam or Gas Turbine:



Turbine

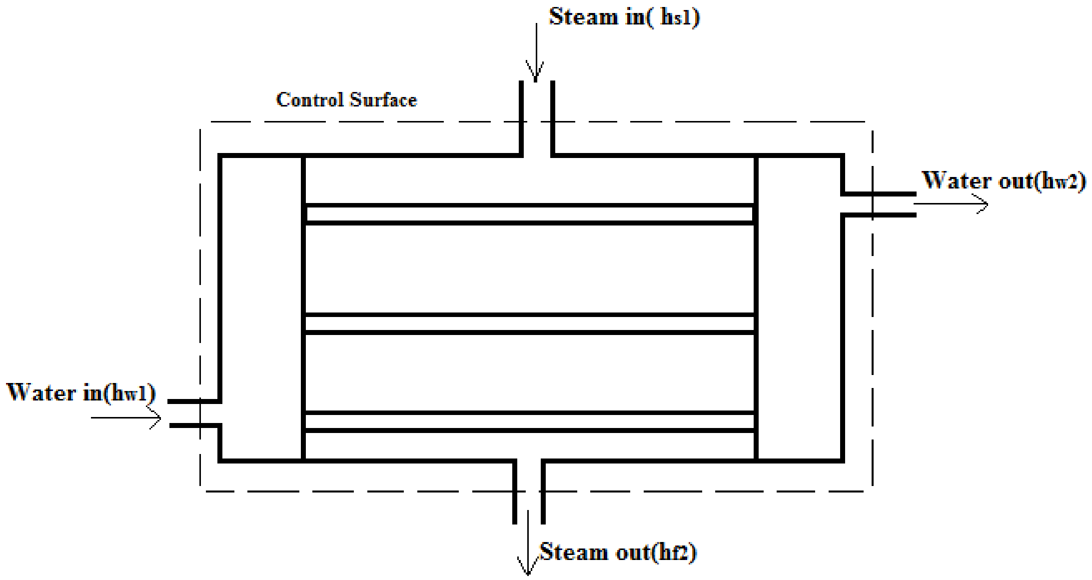
For a Turbine,

a) Work done is Positive,
b) Change in KE and PE is negligible.
c) Heat transfer is negligible

Applying the above conditions to SFEE we get,

$$W_{1-2} = m(h_1 - h_2)$$

4) Heat Exchanger(Condenser)



Heat Exchanger or Condenser

For a heat exchanger,

a) Change in KE and PE is negligible,
b) Work done is zero,
c) Heat transfer to the surroundings is also negligible,

Applying the above conditions to SFEE we get,

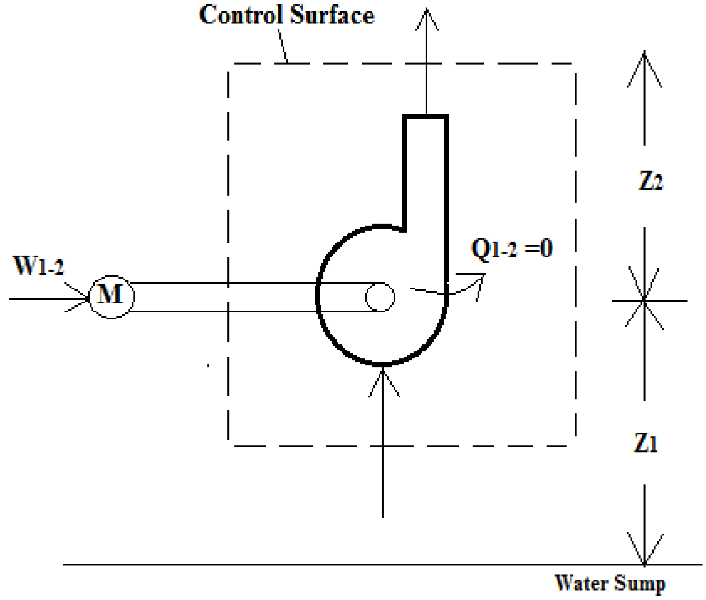
$$m_S h_{S1} - m_s h_{s2} = m_w h_{w2} - m_s h_{w1}$$

Heat lost by steam = Heat gained by water

or $$\boldsymbol{m_s\left(h_{s1} - h_{f2}\right) = m_W\left(h_{w2} - h_{w1}\right)}$$

Where m_W and m_s are mass flow rates of water and steam respectively,
and h_{W1}, h_{S1}, are the enthalpy of water and steam at inlet,
h_{W2}, h_{S2} are the enthalpy of water and steam at outlet.

5) Centrifugal Pump:



Centrifugal Pump

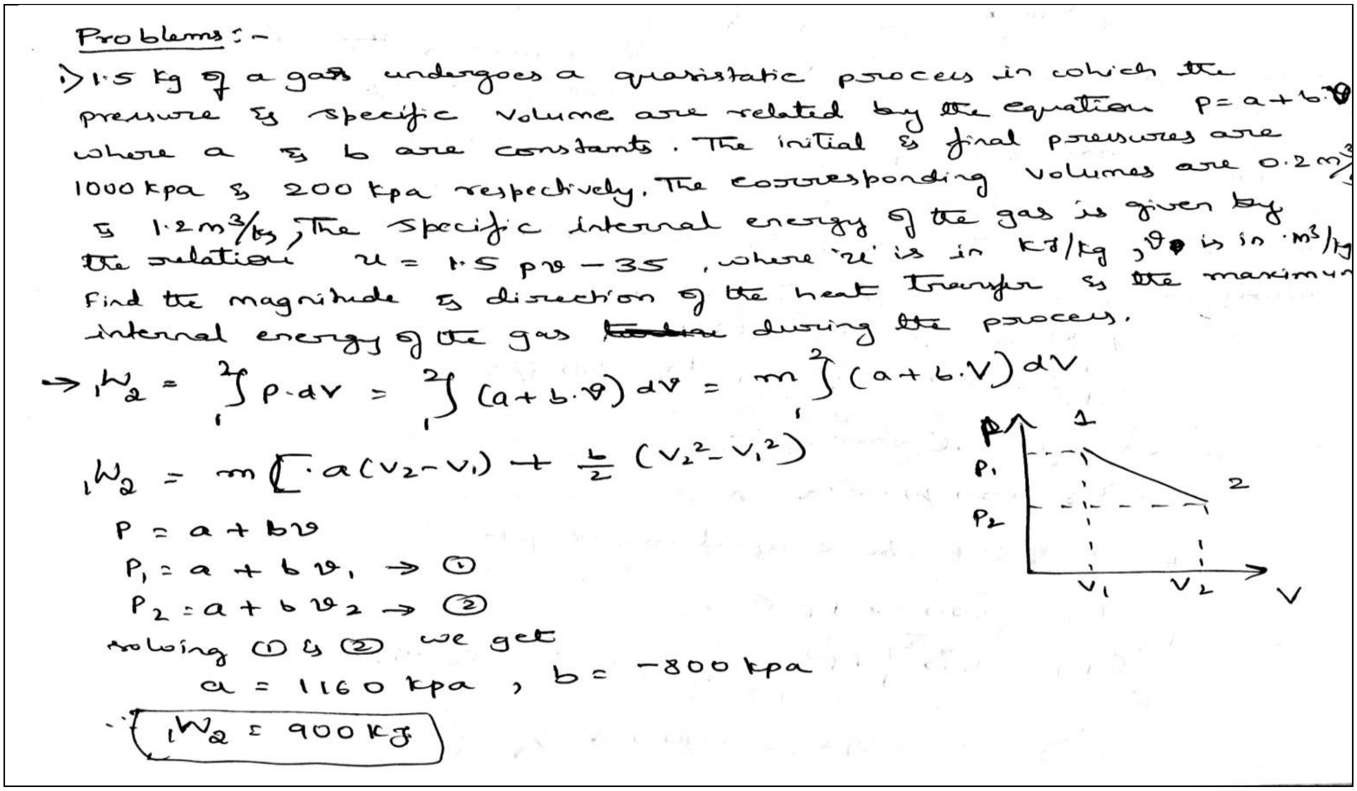
For centrifugal Pump
a) Work is done on the system which is considered as negative.
b) Heat transfer is Zero
c) Change in internal energy is Zero due to no change in temperature of water
Applying the above conditions to SFEE we get,

$$m\left(P_1 v_1 + \frac{V_1^2}{2} + gZ_1\right) = m\left(P_2 v_2 + \frac{V_2^2}{2} + gZ_2\right) - W_{1-2}$$

IMPORTANT THEORY QUESTIONS:

1. State second law of thermodynamics and Explain equivalence of Kelvin Planck and Clausius statements of second law of thermodynamics.
2. What is thermal energy reservoir? Explain source and sink
3. Represent schematically heat engine , heat pump, refrigerator. Give their performance.
4. Show that COP of the heat pump is greater than COP of a refrigerator by unity.
5. Explain Carnot cycle with P-V and T-s Diagram.
6. State and prove Carnot theorem.

PROBLEMS:



Problems :-

i) 1.5 kg of a gas undergoes a quasistatic process in which the pressure & specific volume are related by the equation $p = a + b\cdot v$ where a & b are constants. The initial & final pressures are 1000 kpa & 200 kpa respectively. The corresponding volumes are 0.2 m³/ & 1.2 m³/kg, The specific internal energy of the gas is given by the relation $u = 1.5\,pv - 35$, where 'u' is in kJ/kg, v is in m³/kg Find the magnitude & direction of the heat transfer & the maximu internal energy of the gas during the process.

$$\rightarrow {}_1W_2 = \int_1^2 p\cdot dV = \int_1^2 (a + b\cdot v)\,dv = m\int_1^2 (a + b\cdot V)\,dV$$

$${}_1W_2 = m\left[a(V_2 - V_1) + \frac{b}{2}(V_2^2 - V_1^2)\right]$$

$P = a + bv$

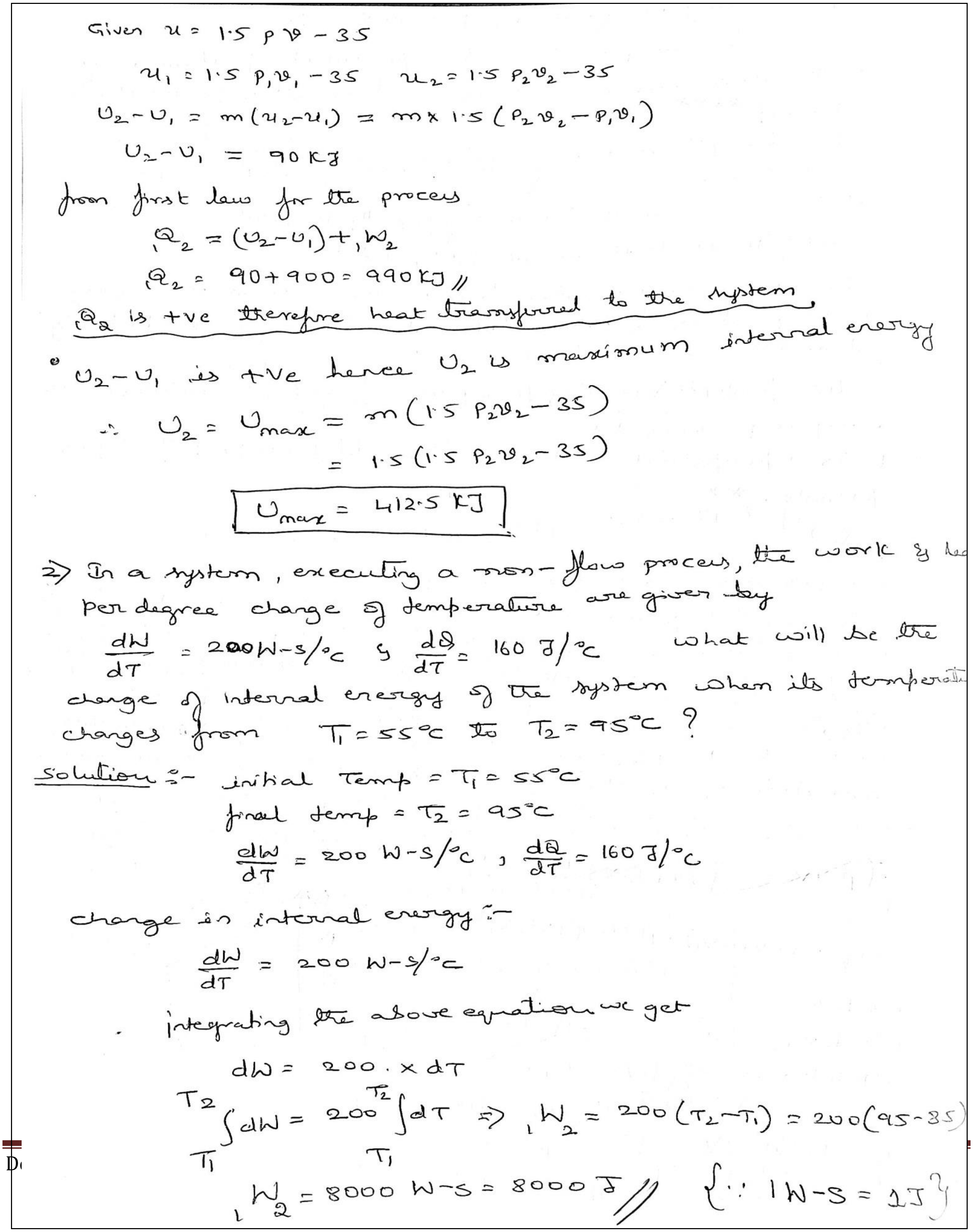
$P_1 = a + bv_1 \rightarrow$ ①

$P_2 = a + bv_2 \rightarrow$ ②

solving ① & ② we get

$a = 1160$ kpa , $b = -800$ kpa

$$\therefore \boxed{{}_1W_2 = 900\text{ kJ}}$$



Given $u = 1.5\,pv - 35$

$u_1 = 1.5\,p_1v_1 - 35 \quad u_2 = 1.5\,p_2v_2 - 35$

$U_2 - U_1 = m(u_2 - u_1) = m \times 1.5\,(p_2v_2 - p_1v_1)$

$U_2 - U_1 = 90\ \text{KJ}$

from first law for the process

$_1Q_2 = (U_2 - U_1) + {_1W_2}$

$_1Q_2 = 90 + 900 = 990\ \text{KJ}$ //

$_1Q_2$ is +ve therefore heat transferred to the system.

- $U_2 - U_1$ is +ve hence U_2 is maximum internal energy

$\therefore\ U_2 = U_{max} = m(1.5\,p_2v_2 - 35)$

$= 1.5\,(1.5\,p_2v_2 - 35)$

$\boxed{U_{max} = 412.5\ \text{KJ}}$

2) In a system, executing a non-flow process, the work & hea per degree change of temperature are given by $\frac{dW}{dT} = 200\ \text{W-s}/°\text{C}$ & $\frac{dQ}{dT} = 160\ \text{J}/°\text{C}$ what will be the change of internal energy of the system when its temperat changes from $T_1 = 55°\text{C}$ to $T_2 = 95°\text{C}$?

Solution :- initial Temp $= T_1 = 55°\text{C}$

final temp $= T_2 = 95°\text{C}$

$\frac{dW}{dT} = 200\ \text{W-s}/°\text{C}\ ,\ \frac{dQ}{dT} = 160\ \text{J}/°\text{C}$

change in internal energy :-

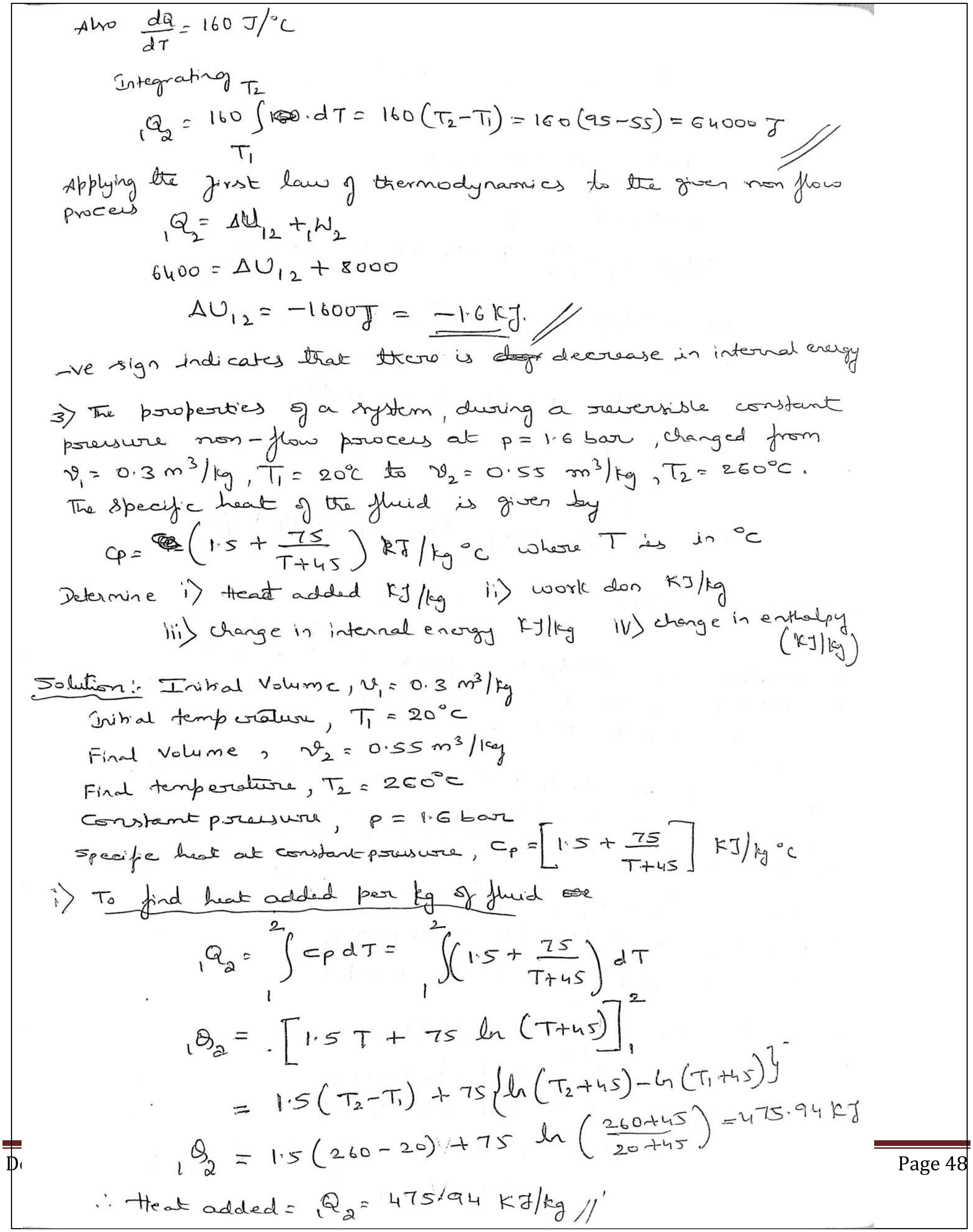
$\frac{dW}{dT} = 200\ \text{W-s}/°\text{C}$

integrating the above equation we get

$dW = 200 \cdot \times dT$

$\int_{T_1}^{T_2} dW = 200 \int_{T_1}^{T_2} dT \Rightarrow {_1W_2} = 200(T_2 - T_1) = 200(95 - 35)$

$_1W_2 = 8000\ \text{W-s} = 8000\ \text{J}$ // $\{\because 1\ \text{W-s} = 1\text{J}\}$



Also $\frac{dQ}{dT} = 160\ J/°C$

Integrating

$${}_1Q_2 = 160\int_{T_1}^{T_2} dT = 160(T_2 - T_1) = 160(95-55) = 64000\ J$$

Applying the first law of thermodynamics to the given non flow process

$${}_1Q_2 = \Delta U_{12} + {}_1W_2$$

$$6400 = \Delta U_{12} + 8000$$

$$\Delta U_{12} = -1600\,J = \underline{\underline{-1.6\ KJ.}}$$

-ve sign indicates that there is decrease in internal energy

3) The properties of a system, during a reversible constant pressure non-flow process at p = 1.6 bar, changed from $v_1 = 0.3\ m^3/kg$, $T_1 = 20°C$ to $v_2 = 0.55\ m^3/kg$, $T_2 = 260°C$. The specific heat of the fluid is given by

$$C_p = \left(1.5 + \frac{75}{T+45}\right) KJ/kg\,°C \quad \text{where } T \text{ is in } °C$$

Determine i) Heat added KJ/kg ii) work don KJ/kg
iii) Change in internal energy KJ/kg iv) change in enthalpy (KJ/kg)

Solution :- Initial Volume, $v_1 = 0.3\ m^3/kg$

Initial temperature, $T_1 = 20°C$

Final volume, $v_2 = 0.55\ m^3/kg$

Final temperature, $T_2 = 260°C$

Constant pressure, $p = 1.6$ bar

Specific heat at constant pressure, $C_p = \left[1.5 + \frac{75}{T+45}\right] KJ/kg\,°C$

i) To find heat added per kg of fluid

$${}_1Q_2 = \int_1^2 C_p\,dT = \int_1^2\left(1.5 + \frac{75}{T+45}\right) dT$$

$${}_1Q_2 = \Big[1.5\,T + 75\ln(T+45)\Big]_1^2$$

$$= 1.5(T_2 - T_1) + 75\left\{\ln(T_2+45) - \ln(T_1+45)\right\}$$

$${}_1Q_2 = 1.5(260-20) + 75\ln\left(\frac{260+45}{20+45}\right) = 475.94\ KJ$$

$\therefore$ Heat added $= {}_1Q_2 = 475.94\ KJ/kg$ //

ii) The work done per kg of fluid is given by

$$ {}_1W_2 = \int_1^2 p \cdot dv = p(v_2 - v_1) = 1.6 \times 10^2 (0.55 - 0.3) \text{ kN-m/kg} $$

$$ {}_1W_2 = 40 \text{ KJ/kg} = \text{work done} // $$

iii) change in internal energy

$$ \Delta u_{12} = {}_1Q_2 - {}_1W_2 = 475.94 - 40 = 435.94 \text{ KJ/Kg} // $$

iv) Change in enthalpy (for non flow process)

For a constant pressure process

$$ {}_1Q_2 = m(h_2 - h_1) = m \, \Delta h_{12} $$

for 1 kg = m

$$ {}_1Q_2 = \Delta h_{12} $$

∴ change in enthalpy $\Delta h_{12} = 475.94$ KJ/Kg //

4) In a gas turbine unit, the gases flow through the turbine is 15 Kg/s & the power developed by the turbine i 12000 KW. The enthalpies of gases at the inlet & outlet ar 1260 KJ/kg & 400 KJ/kg respectively. & the Velocity of gases at the inlet and outlet are 50 m/s & 110 m/s respecti calculate

i) The rate at which heat is rejected to the turbine &

ii) The area of the inlet pipe given that the specific Volume of the gases at the inlet is 0.45 m³/kg.

→ Rate of flow of gases, $\dot{m} = 15$ kg/s

Volume of gases at the inlet, $v = 0.45$ m³/kg

power developed by the inlet, $P = 12000$ KW

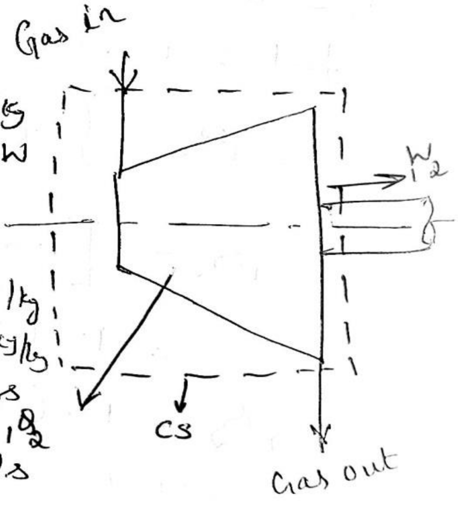
$$ \therefore \text{work done} = \frac{12000}{15} = 800 \text{ KJ/kg} $$

Enthalpy of gases at the inlet, $h_1 = 1260$ KJ/kg

Enthalpy of gases at the outlet, $h_2 = 400$ KJ/kg

Velocity of gases at the inlet $V_1 = 50$ m/s

Velocity of gases at the outlet $= V_2 = 110$ m/s



i) Heat rejected ${}_1Q_2$:-

using the flow equation;

$$h_1 + \frac{V_1^2}{2} + {}_1q_2 = h_2 + \frac{V_2^2}{2} + W$$

$\left\{ \text{Note } 1N = \frac{1\,kg\,m}{s^2} \right\}$

$$1260\ (kJ/kg) + \frac{50^2}{2000}\ \frac{kg\,m^2}{s^2\,kg} = \frac{Nm}{kg}\ (kJ/kg) + {}_1q_2 = 400 + \frac{110^2}{2000} + 800$$

$$\boxed{{}_1q_2 = -55.2\ kJ/kg}$$

$${}_1Q_2 = -55.2 \times 15\ kJ/s$$

$${}_1Q_2 = -828\ kW$$ -ve sign indicates heat rejected

$$\therefore \boxed{{}_1Q_2 = 828\ kW}$$

★★ Note:- Converting $\frac{V_0^2}{2}$ to kJ/kg

$$\left\{ \frac{m^2}{s^2} = \frac{kg\,m^2}{s^2\,kg} = \frac{Nm}{kg} = \frac{J}{kg} \right.$$

$$\left. \boxed{\frac{m^2}{s^2} = 10^{-3}\ kJ/kg} \right\}$$

ii) inlet area, A :

using the relation

$$\dot{m}_1 = \rho_1 A_1 V_1$$

$$\cancel{A = \dot{m} V_1} \quad \text{or} \quad A_1 = \frac{\dot{m}_1}{\rho_1 V_1} = \frac{\dot{m}_1 v_1}{V_1} = \frac{15 \times 0.45}{50}$$

$$\boxed{A_1 = 0.135\ m^2}$$

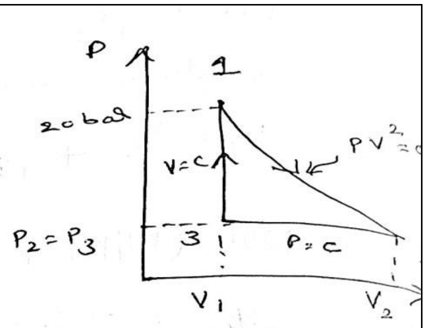
5) A cylinder contains 1 kg of a certain fluid at an initial pressure of 20 bar. The fluid is allowed to expand reversible behind a piston according to law pV^2 = constant untill the Volume is doubled. The fluid is then cooled reversibly at constant pressure until the piston regains its original piston, Heat is then supplied reversibly with the piston firmly locked in position until the pressure rise to the original value of 200 bar. calculate the net workdone by the fluid for an initial Volume of $0.5\,m^3$

→ Given, $m = 1\,kg$, $P_1 = 20\,bar = 20 \times 100\,kPa$, $V_2 = 2V_1$,

$P_2 = P_3$, $V_1 = V_3$, $V_1 = 0.5\,m^3$, $\oint \delta W = ?$

Solution:-

To find $\oint \delta W = W_{net} = {}_1W_2 + {}_2W_3 + {}_3W_1$



P-V diagram

To find ${}_1W_2$

Considering process 1-2 (polytropic ~~adiabatic~~ process)

$PV^2 = C$

$V_1 = 0.5\ m^3$, $P_1 = 2000$ kpa

$V_2 = 2 \times V_1 = 1\ m^3$, $P_2 = ?$, $n = 2$

w.k.T

$${}_1W_2 = \frac{P_1V_1 - P_2V_2}{n-1}$$ {polytropic work done}

To find ~~a~~ P_2 for process 1-2

$$P_1V_1^2 = P_2V_2^2$$

$$P_2 = P_1\left(\frac{V_1}{V_2}\right)^2 = 20000 \times 0.5^2$$

$$P_2 = 500\ \text{Kpa}$$

Hence ${}_1W_2 = 300$ KJ

~~For~~ To find ${}_2W_3$: $P(V_3 - V_2) = \underline{-250}$ KJ

$${}_3W_1 = 0 \quad (V=C)$$

$\therefore$ $W_{net} = 250$ KJ

OUTCOMES: Determine heat, work, internal energy, enthalpy for flow & non flow process using First Law of Thermodynamics.

FURTHER READING:

- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
- http://www.nptel.ac.in/courses/112104113/4#

SECOND LAW OF THERMODYNAMICS

OBJECTIVE: Determine heat, work, internal energy, enthalpy for flow & non flow process using Second Law of Thermodynamics.

STRUCTURE:

2.2.1 Limitations of First Law of Thermodynamics
2.2.2 Device Converting Heat to Work
2.2.3 Device Converting Work to Heat
2.2.4 Statements of Second Law Of Thermodynamics:
2.2.5 Equivalence of Kelvin Planck And Clausius Statements
2.2.6 PMM-II
2.2.7 Carnot Cycle & Carnot Theorem

2.2.1 Limitations of first law of thermodynamics:

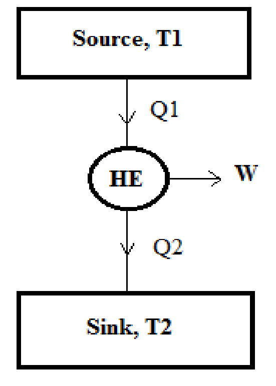
1. First law explains about the inter conversion of heat and work without placing any restriction on the direction.

2. All simultaneous processes proceed only in one particular direction and to reverse such processes, energy from external source is required.

3. First law provides all necessary conditions for a process to occur but in doesn't give sufficient conditions namely direction of the process.

2.2.2 Device converting Heat to Work:

A Heat Engine may be defined as a system operating in a cycle and producing useful work by abstracting heat from a suitable heat source.



Heat Engine

Consider a heat engine that receives Q_1 amount of heat from a high temperature source at T_1. Some of the Heat thus received is utilized to do mechanical work W. The engine rejects Q_2 amount of heat to a low temperature sink at T_2.

Applying the first law to the heat engine,

$$\oint \delta Q = \oint \delta W$$

Net Heat Transfer = Net Work Transfer

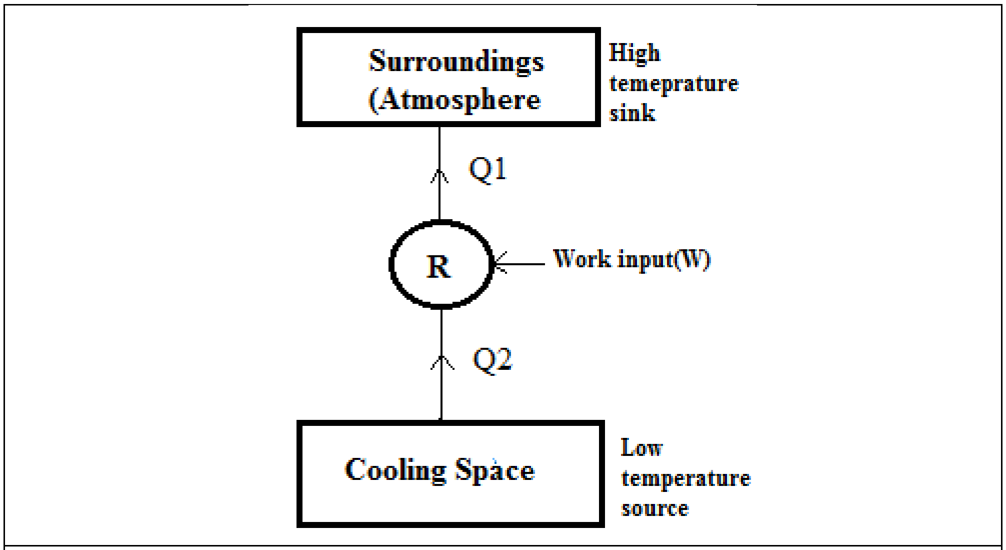
Generally performance of the heat engine is expressed in efficiency of the engine . Thus thermal efficiency of heat engine,

$$\eta_{th} = \frac{\text{Net work output}}{\text{Gross heat input}} = \frac{\mathbf{Q_1 - Q_2}}{\mathbf{Q_1}} = \mathbf{1} - \frac{\mathbf{Q_2}}{\mathbf{Q_1}}$$

2.2.3 Devices converting work to heat (Reversed Heat Engine):

1. Refrigerator: A refrigerator is a device which working in a cycle delivers heat from low temperature to a high temperature region.

The performance of a refrigerator is expressed in terms of COP or coefficient of performance.

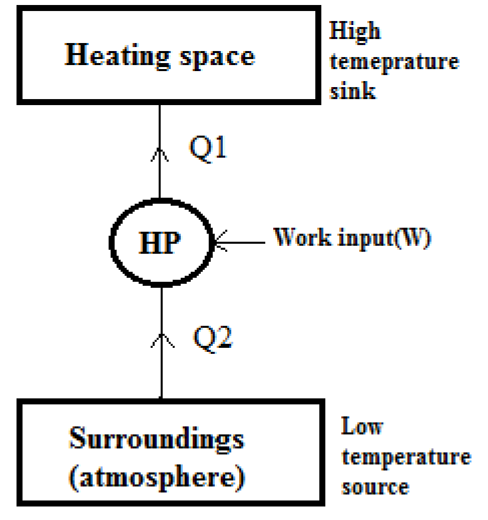


Refrigerator

$$\mathbf{COP_R} = \frac{\textbf{Desired effect}}{\textbf{Work input}} = \frac{\textbf{Heat extracted at low temperature}}{\textbf{Work input}} = \frac{\mathbf{Q_2}}{\mathbf{W}} = \frac{\mathbf{Q_2}}{\mathbf{Q_1 - Q_2}}$$

2. Heat Pump:

A heat pump is a device which working in a cycle delivers heat from low temperature region to high temperature region.The efficiency of heat pump is expressed in terms of COP.Thus,



Heat Pump

$$\mathrm{COP_{HP}} = \frac{\text{Desired effect}}{\text{Work input}} = \frac{\text{Heat to high temperature sink}}{\text{Work input}} = \frac{Q_1}{W}$$

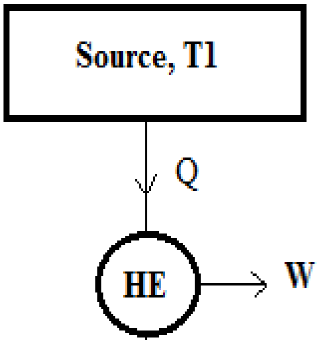
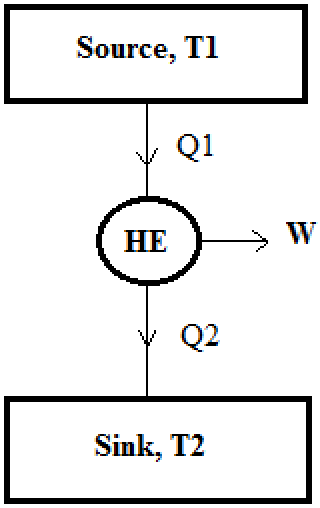
$$\mathbf{COP_{HP}} = \frac{\mathbf{Q_1}}{\mathbf{Q_1 - Q_2}} = \mathbf{1} + \frac{\mathbf{Q_2}}{\mathbf{Q_1 - Q_2}}$$

$\mathrm{COP_{HP}}$ = 1 + COP of refrigerator

2.2.4 Statements of Second Law of Thermodynamics:

Kelvin – Planck statement:

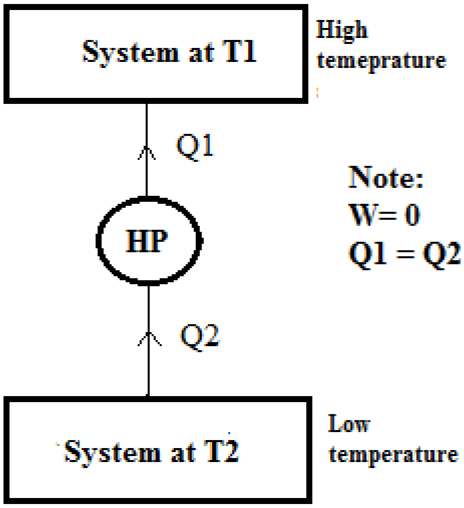
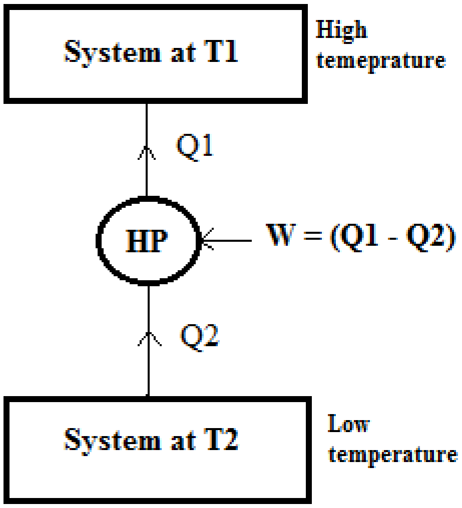
“It is impossible to construct an engine which operating in a cycle, will produce no other effect than the extraction of heat from a single heat reservoir and performs an equivalent amount of work”

	
impossible	**Possible**

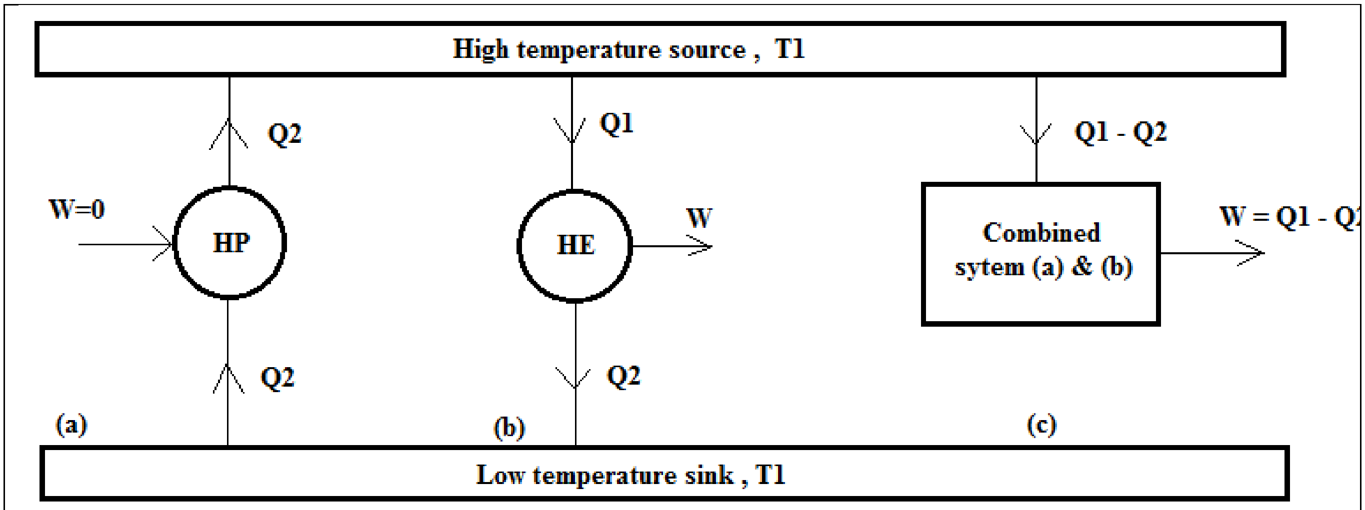
Heat engine can receive Q_1 amount of heat from a high temperature source, a part of it is utilized to do work W before Q_2 amount of heat is rejected to the low temperature sink as shown in the above figure.

Clausius statement:

"It is impossible to construct an engine which is operating in a cycle, transfers heat from a body at a lower temperature to a body at a higher temperature without the assistance of external work" or "It is impossible for heat energy to flow from a lower temperature body to a higher temperature body without the assistance of external work"

	
Impossible	**Possible**

2.2.5 Equivalence of Kelvin Planck and Clausius Statements:



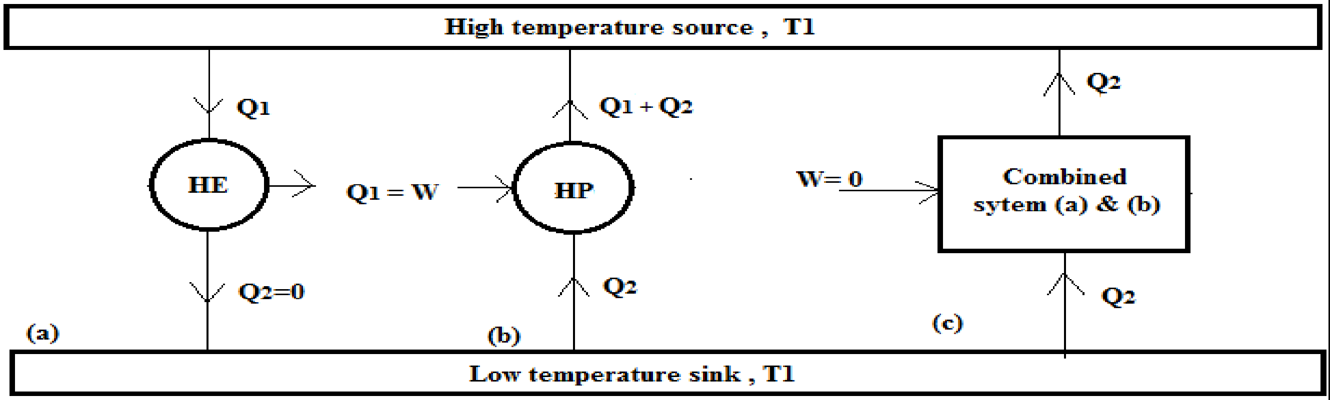
Violation of Clausius statement leads to violation of Kelvin Planck statement

Consider fig(a) in this case a heat pump HP operates in a cycle and transfers Q_2 amount of heat from a low temperature source without any work input. This system violates Clausius statement.

Consider fig(b) in this case , a heat engine HE operates in a cycle absorbing Q_1 amount of heat from a high temperature source. The engine does W amount of work and finally rejects Q_2 amount of heat to the low temperature sin. This system operates as per Kelvin Planck statement.

Consider fig(c) in this case both the heat pump and the heat engine are combined together to form a combined system. This system constitutes a device that receives $(Q_1 - Q_2)$ amount of heat from high temperature source and does an equivalent amount of work $W = (Q_1 - Q_2)$. Hence this system violates Kelvin Planck statement.

Thus, violation of Clausius statement leads to violation of Kelvin Planck statement.



Violation of Kelvin Planck statement leads to Violation of Clausius statement

Consider fig(a) in this case a heat engine extracts Q_1 amount of heat from a high temperature source and does an equivalent amount of work $W = Q_1$ without rejecting heat to the low temperature sink. This system violates Kelvin Planck statement

Consider fig(b) in this case , a heat pump working in a cycle extracts Q_2 amount of heat from a low temperature sink. The heat pump also receives $W = Q_1$ amount of work from an external source and supplies (Q_1+Q_2) amount of heat temperature source. This system works as per clausis statement.

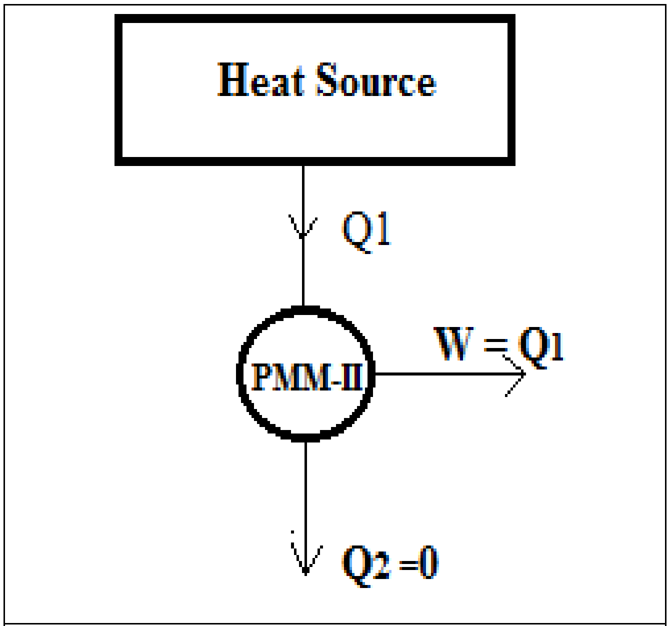
Consider fig(c) in this case, both the heat engine and the heat pump are clubbed together to form a combined system. Since the output of the engine W is used to drive the heat pump, input to the combined system is only from the Q_2 amount of heat extracted from the low temperature sink. The system rejects same amount of heat to the high temperature source without any external work input. This system violates Clausius statement.

Thus violation of Kelvin Planck statement leads to violation of Clausius statement.

Hence we can conclude that both Kelvin Planck and Calusius statements are equivalent in sense.

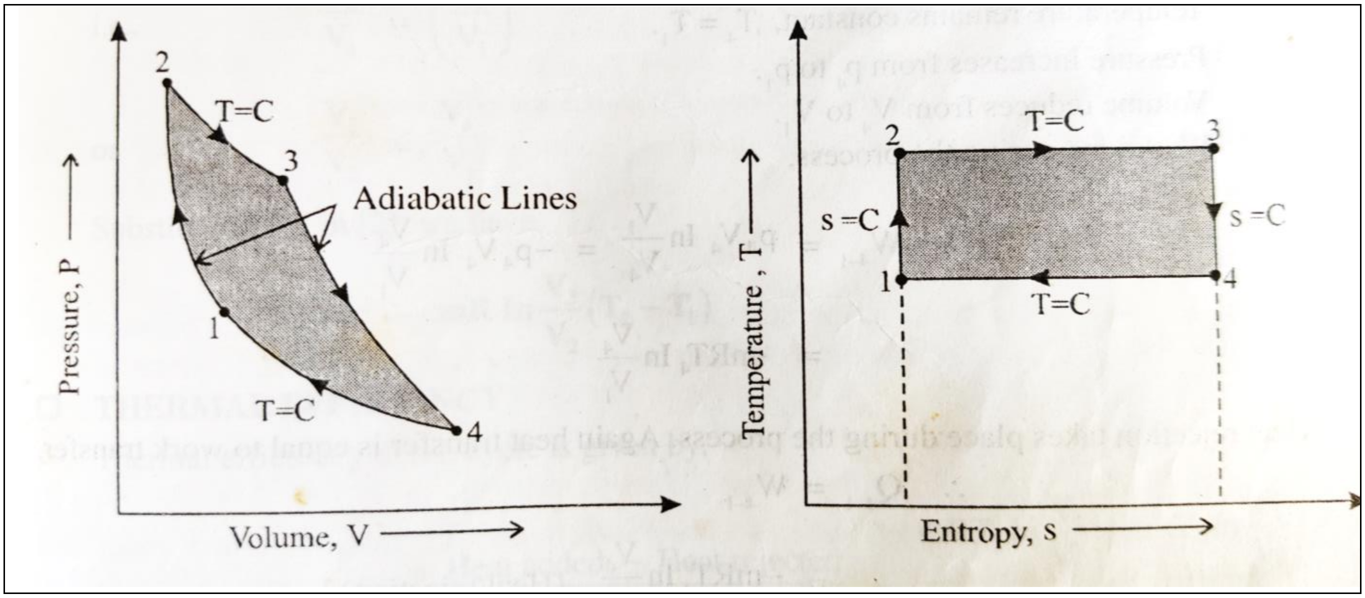
2.2.6 Perpetual Motion Machine of Second Kind (PMM-II):

It is an engine working in a cycle developing net work by exchanging heat from a single heat source. PMM-II Violates Kelvin Planck statement.



PMM-II

2.1.8 Carnot Cycle:



Carnot cycle consists of four reversible processes

1-2: Adiabatic compression

$$W_{1-2} = \frac{P_1V_1 - P_2V_2}{\gamma - 1} = \frac{-(P_2V_2 - P_1V_1)}{\gamma - 1} = -m.R.(T_1 - T_2)/(\gamma - 1)$$

$Q_{1-2} = 0$

2-3: Isothermal Expansion

$$W_{2-3} = P_2V_2 \ln\frac{V_3}{V_2} = m.R.T_2 \ln\frac{V_3}{V_2}$$

$$Q_{2-3} = W_{2-3} = m.R.T_2 \ln\frac{V_3}{V_2}$$

3-4: Adiabatic Expansion

$$W_{3-4} = \frac{P_3V_3 - P_4V_4}{\gamma - 1} = m.R.(T_3 - T_4)/(\gamma - 1)$$

$Q_{3-4} = 0$

4-1: Isothermal Compression

$$W_{4-.1} = P_4V_4 \ln\frac{V_1}{V_4} = -P_4V_4 \ln\frac{V_4}{V_1} = -m.R.T_4 \ln\frac{V_4}{V_1}$$

$$Q_{4-1} = W_{4-1} = -m.R.T_4 \ln\frac{V_4}{V_1}$$

Net Work done /cycle = $\oint \mathbf{W} = -m.R.\ln\frac{V_3}{V_2}(\mathbf{T_2} - \mathbf{T_1})$

Thermal Efficiency of the cycle:

$$\eta = 1 - \frac{T_1}{T_2}$$

Carnot Theorem: "No engine, operating between two heat reservoirs each having fixed temperatures, can be more efficient than a reversible heat engine operating between the same temperatures"

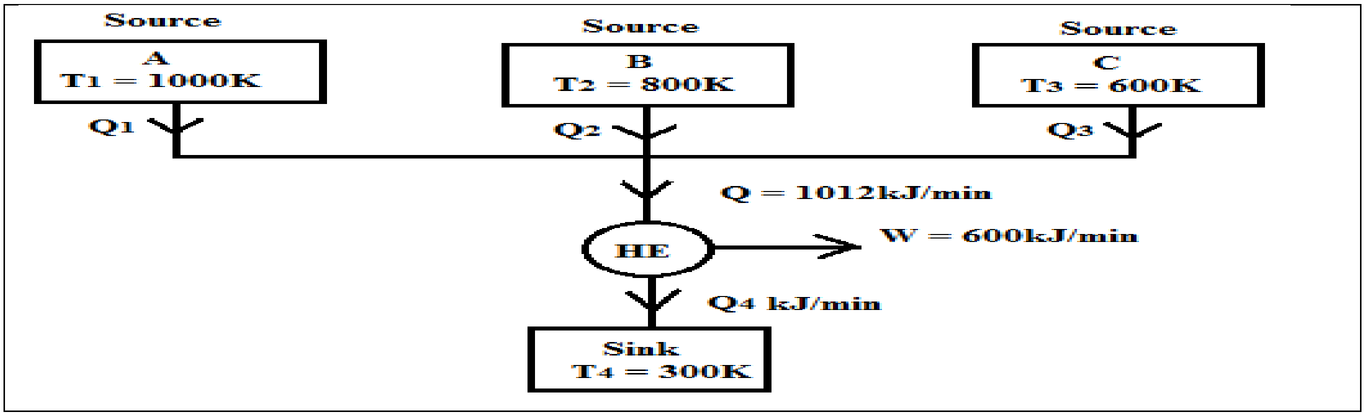
IMPORTANT THEORY QUESTIONS:

1. Write Kelvin Planck and Clausius statement of Second law of thermodynamics and prove that they are equivalent.
2. Define i) Heat Engine ii) Refrigerator and its COP iii) Heat Pump and its COP.
3. Sate Carnot theorem and derive an expression for work done by a system undergoing Carnot cycle.

Problems:

1. A reversible engine operates between 3 heat reservoirs 1000K , 800K and 600K and rejects heat to a reservoir at 300K, the engine develops 10kW and rejects 412kJ/min. If heat supplied by the reservoir at 1000K is 60% of heat supplied by the reservoir at 600K , find the quantity of heat supplied by each reservoir.

Solution:



Work output = 10kW = 10×60 = **600kJ/min**

From first law of thermodynamics

Total Heat supplied = W + Heat rejected

= 600 + 412

= 1012kJ/min

Let Q_1 be the heat absorbed by the engine from the source at 600K

Then , heat absorbed from the source at 1000K is **($0.6\times Q_1$)**

Therefore heat taken from the source at 800K is

$Q_2 = 1012 - Q_1 - (0.6\times Q_1)$

As engine is reversible, Clausius theorem becomes,

$$\oint \frac{dQ}{T} = 0 = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} - \frac{Q_4}{T_4}$$

Substituting the values in the above equation we get

$Q_1 = 405$ kJ/min

$Q_2 = 364$ kJ/min

$Q_3 = 218.4$ kJ/min

2. An inventor claims that his engine has the following specifications

Power developed = 76kW

Fuel burned per hour = 4kg

Heating value of fuel = 75000kJ/kg

Temperature limits = 727°C and 27°C

Solution:

For given Engine, Work done = 76kW = 76×3600 = 273600 kJ/hr

Heat supplied = Mass of fuel × Heating value of fuel

$= 4\times 75000 = 3\times 10^5$ kJ/hr

Thermal efficiency, $\eta_{th} = \frac{\text{Work done}}{\text{Heat supplied}} = \frac{273600}{3\times 10^5}$

= 91.2%

Thermal efficiency of a reversible engine working between the same temperature limits

$$\eta_{th} = \frac{T_1 - T_2}{T_1} = \frac{1000 - 300}{1000} = 70\%$$

Since the thermal efficiency is greater than the efficiency of reversible engine the claim is false and engine needs to be redesigned

OUTCOMES: Determine efficiency and COP of refrigerator and equivalence of statement's of Second law of thermodynamics, efficiency of carnot cycle

FURTHER READING:

- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
- http://www.nptel.ac.in/courses/112104113/4#

MODULE 3

Reversibility: Definitions of a reversible process, reversible heat engine, importance and superiority of a reversible heat engine and irreversible processes; factors that make a process irreversible, reversible heat engines. Unresisted expansion, remarks on Carnot's engine, internal and external reversibility, Definition of the thermodynamic temperature scale. Problems

Entropy: Clasius inequality, Statement- proof, Entropy- definition, a property, change of entropy, entropy as a quantitative test for irreversibility, principle of increase in entropy, entropy as a coordinate

REVERSIBILITY

OBJECTIVE:

- **Concept of reversible process and condition for a system to be reversible**

STRUCTURE:

3.1 Reversible process:
3.2 Factors that make process irreversible:
3.3 Free expansion process or Unresisted expansion:
3.4 Remarks on carnot Engine:
3.5 Externally Reversible Processes
3.6 Internally Reversible Processes
3.7 Carnot Theorem

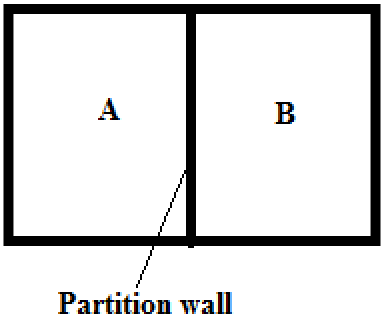
3.1 Reversible process:

A Reversible or ideal process is one in which both the systems and surroundings can be restored to their respective initial states by reversing the direction of process.

3.2 Factors that make process irreversible:

1. Friction
2. Electrical resistance
3. In elastic solid deformation.
4. Free expansion (Unrestrained expansion)
5. Transfer of energy in the form of heat through a finite temperature difference
6. Lack of equilibrium during the process.

3.3 Free expansion process or Unresisted expansion: Consider an adiabatic vessel separated by a partition wall as shown in the figure. If the partition wall is suddenly removed, the air will fill the entire volume of the vessel instantaneously, and this process is not quasi-static and the air is not interacting with surroundings.



To restore original state of the system, the air is to be compressed by an imaginary piston and heat transfer also occurs. These work and heat interactions cause a change in the surroundings and the surroundings are not restored to their initial states. This indicates that, freee expansion is an irreversible process.

3.4 Remarks on carnot Engine:

1. The efficiency of carnot engine depends only on source and sink temperatures and sink temperature and is independent of working fluid. The efficiency becomes maximum when sink temperature T2 = 0 , but this is impossible and it violates Kelvin Planck statement of second law.
2. As the temperature difference between source and sink increases, efficiency also increases and is directly proportional to T1 –T2.
3. The efficiency can be increased either by increasing source temperature or by decreasing sink temperature.

The Carnot Engine is a hypothetical device because:

1. All 4 processes are reversible. For this to happen there should not be any inernal friction between particles of working fluid and no friction exists between the piston and cylinder walls.
2. The heat absorption and rejection have to take place with infinitesimal temperature differences.
3. The piston has to move very slowly to achieve isothermal compression or expansion. In the meantime, piston movement must be very fast to achieve adiabatic compression or expansion . It is impossible to achieve different speeds of the piston during different processes.

3.5 Externally Reversible Processes

- No irreversibilities exist in the surroundings.
- Heat transfer can occur between the system and the surroundings, but only with an infinitesimal temperature difference.
- There may be irreversibilities within the system.

3.6 Internally Reversible Processes

- No irreversibilities exist within the system.
- The system moves slowly and without friction through a series of equilibrium states.

- Irreversibilities may exist in the surroundings, usually due to heat transfer through a finite temperature difference.

3.7 CARNOT THEOREM

Define Carnot Theorem and also give its proof.

Carnot theorem states that no heat engine working in a cycle between two constant temperature reservoirs can be more efficient than a reversible engine working between the same reservoirs. In other words it means that all the engines operating between a given constant temperature source and a given constant temperature sink, none, has a higher efficiency than a reversible engine.

Proof:

Suppose there are two engines E_A and E_B operating between the given source at temperature T_1 and the given sink at temperature T_2.

Let E_A be any irreversible heat engine and E_B be any reversible heat engine. We have to prove that efficiency of heat engine E_B is more than that of heat engine E_A.

Suppose both the heat engines receive same quantity of heat Q from the source at temperature T1. Let W_A and W_B be the work output from the engines and their corresponding heat rejections be $(Q – W_A)$ and $(Q – W_B)$ respectively.

Assume that the efficiency of the irreversible engine be more than the reversible engine i.e. $\eta_A > \eta_B$. Hence, $W_A /Q>W_B /Q$

I.e. $W_A > W_B$

Now let us couple both the engines and E_B is reversed which will act as a heat pump. It receives $(Q – W_B)$ from sink and W_A from irreversible engine E_A and pumps heat Q to the source at temperature T_1. The net result is that heat $(W_A – W_B)$ is taken from sink and equal amount of work is produce. This violates second law of thermodynamics. Hence the assumption we made that irreversible engine having higher efficiency than the reversible engine is wrong.

Hence it is concluded that reversible engine working between same temperature limits is more efficient than irreversible engine thereby proving Carnot’s theorem.

Thermodynamic Temperature scale:

A temperature scale which is independent of the property of thermometric substance is known as Thermodynamic temperature scale.

OUTCOMES: Explain the concept of reversible and irreversible process and factors affecting it.

IMPORTANT THEORY QUESTIONS:

1. List the factors that renders a system reversible.
2. What is thermodynamic temperature scale and deduce the relation between Q and T as proposed by Lord Kelvin.
3. Why it is impossible to carry out the Carnot cycle in real engines.

FURTHER READING:

- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
- http://www.nptel.ac.in/courses/112104113/4#

ENTROPY

OBJECTIVES:

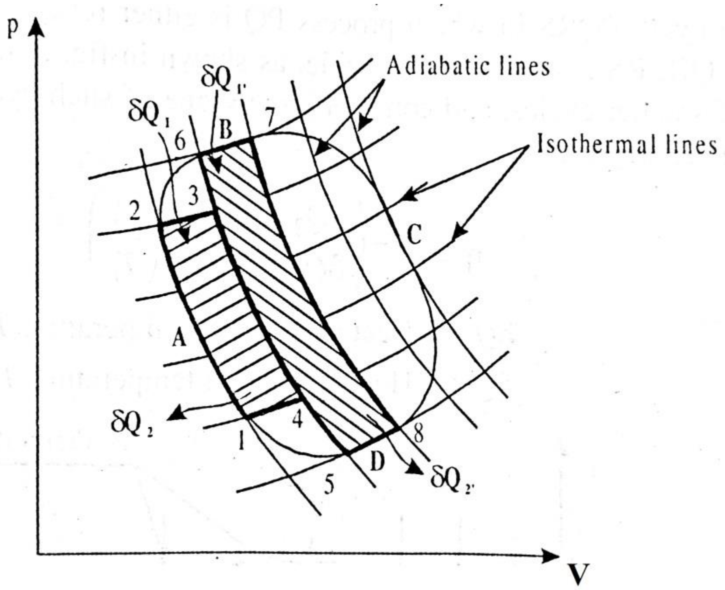
1. Clausius theorem and concept of entropy
2. Entropy as a state property
3. Entropy principle

STRUCTURE:

3.2.8 Entropy
3.2.9 Clausius theorem
3.2.10 Clausius Inequality
3.2.11 Entropy is a property

3.2.8 Entropy: The measure of a system's thermal energy per unit temperature that is unavailable for doing useful work.

3.2.9 Clausius theorem:



- Consider a system undergoing a cycle A-B-C-D as shown in the figure in the p-V diagram.
- This cycle is broken into a large number of sall carnot cycles by a family of reversible adiabatic and eversible isothermal lines on the p-V diagram.
- Thus the whole cycle is represented by a small numbe of carnot cycles 1-2-3-4 , 5-6-7-8 etc.
- Now consider carnot cycles 1-2-3-4 and 5-6-7-8. In these two cycles 3-4 and 5-6 represent adiabatic expansion and adiabatic compression respectively in which heat rejection and heat addition takes place.Thus process 3-4 is cancelled out as far as energy transfer with process 5-6 is concerned.
- Also the adiabatics have no contribution to the heat added. Furtherr, if the number of carnot cycles is very large and the adiabatic lines are close to one another, in the limiting case all these small carnot cycles coincide with the given reversible cycle A-B-C-D.
- Let Q_1 , $Q_{1'}$ …. be the amount of heat exchanged during heat absorption and let Q_2 ,$Q_{2'}$ …. be the amount of heat exchanged during rejection.
- Then for small Carnot cycle 1-2-3-4 we may write

  we know that for a reversible process $\oint \frac{\delta Q}{T} = 0$

  Then we can write $\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0$ ……. 1

Similarly for cycle 5-6-7-8

$$\frac{\delta Q_{1\prime}}{T_{1\prime}} + \frac{\delta Q_{2\prime}}{T_{2\prime}} = 0 \ldots\ldots.2$$

Adding the equation 1 and 2 we get

$$\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} + \frac{\delta Q_{1\prime}}{T_{1\prime}} + \frac{\delta Q_{2\prime}}{T_{2\prime}} = \sum \frac{\delta Q}{T} = 0$$

Replacing the summation by cyclic integral in the limit we can write

$$\oint \frac{\delta Q_{rev}}{T} = 0$$

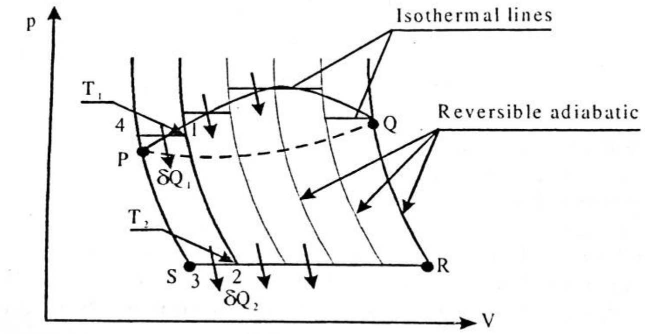
The above equation is known as **CLAUSIUS THEOREM**, Which states that the cyclic integral of $\frac{\delta Q}{T}$ for a **Reversible cycle** is equal to zero

3.2.10 Clausius Inequality:

Consider a cycle PQRS in which process PQ is either reversible or irreversible, whereas other processes QR,RS and SP are reversible as shown in the fig.

Dividing this cycle into large number of smaller cycles and considering any one of such cycles say 1-2-S-4-1, we can write thermal efficiency as

$$\eta = 1 - \left(\frac{\delta Q_2}{\delta Q_1}\right) = 1 - \frac{T_2}{T_1}$$



If the cyclic integration is applied to cyclic irreversibilities, then $\oint \frac{\delta Q}{T}$ never becomes Zero.

Thus for any small carnot cycles operating between temperature T_1 and T_2 with heat exchange δQ_1 and δQ_2 and with some irreversibility the efficiency is smaller than or equal to that of a reversible engine

Thus. $\eta_{irr} \leq \eta_{rev}$

i.e $1 - \left(\frac{\delta Q_2}{\delta Q_1}\right)_{irr} \leq 1 - \left(\frac{\delta Q_2}{\delta Q_1}\right)_{rev}$

or $$\frac{\delta Q_2}{\delta Q_1} \geq \left(\frac{\delta Q_2}{\delta Q_1}\right)_{rev}$$

$$\frac{\delta Q_1}{\delta Q_2} \leq \left(\frac{\delta Q_1}{\delta Q_2}\right)_{rev}$$

$$But \quad \left(\frac{\delta Q_1}{\delta Q_2}\right)_{rev} \leq \frac{T_1}{T_2}$$

Substituting 2 in 1 we get

$$\frac{\delta Q_1}{\delta Q_2} \leq \frac{T_1}{T_2}$$

In general, if δQ is the heat supplied at temperature 1, then we can modify equation 3 as

$$\frac{\delta Q}{\delta Q_2} \leq \frac{T}{T_2}$$

or

$\frac{\delta Q}{T} \leq \frac{\delta Q_2}{T_2}$ For any process PQ reversible or irreversible

For reversible process,

$$\frac{\delta Q_{rev}}{T} = \frac{\delta Q_2}{T_2}$$

For any process PQ, $\frac{\delta Q}{T} \leq ds$

Thus for any engine working in a cycle

$$\oint \frac{\delta Q}{T} \leq \oint ds$$

Since the cyclic integral of any property is zero

$$\oint \frac{\mathbf{\delta Q}}{\mathbf{T}} \leq \mathbf{0}$$

THIS IS CLAUSIUS INEQUALITY

<u>Note:</u> If,

$\oint \frac{\delta Q}{T} = 0$ **, The cycle is reversible**

$\oint \frac{\delta Q}{T} < 0$ **, The cycle is irreversible and possible**

$\oint \frac{\delta Q}{T} > 0$ **, The cycle is impossible since it violates second law.**

3.2.11 Entropy is a property:

Consider two reversible paths A and B joining the states 1 and 2.

If path B is reverse, that is transversed from 2 to 1 , then path A and B constitute a reversible cycle.

That is

$$\oint \frac{\delta Q}{T} = \int_1^2 \frac{\delta Q}{T}_{\text{path A}} + \int_2^1 \frac{\delta Q}{T}_{\text{path B}}$$

$$\int_2^1 \frac{\delta Q}{T}_{\text{path B}} = \int_1^2 \frac{\delta Q}{T}_{\text{path A}}$$

It applies to any reversible processes joining states 1 and 2

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_{rev} = S_2 - S_1$$

Thus entropy is independent of path and therefore entropy is a property

OUTCOME:

- Explains the concept entropy and its characteristics

IMPORTANT QUESTIONS:

1. State and prove clausius inequality? What is the significance of clausius inequality
2. An adiabatic vessel contains 85kg of oil at a temperature of 27˚C. A spherical ball made of steel of 10kg AT 727˚C is immersed in oil. Determine change in entropy for the universe. Tke specific heat of oil = 3.5 kJ/kg.K, Specific heat of steel ball = 0.5kJ/kg.K
3. 0.5 Kg of air initially at 27C is heated reversibly at constant pressure until the volume is doubled and is then heated reversibly at constant volume until the pressure is doubled . For the total path , find work transfer , heat transfer and change of entrpy.
4. Explain principle of increase of entropy.
5. Prove that for a cyclic process $\int \frac{\delta Q}{T} \leq 0$, Hence define entropy

FURTHER READING:

- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
- http://www.nptel.ac.in/courses/112104113/4#

MODULE 4

Availability, Irreversibility and General Thermodynamic relations: Introduction, Availability (Exergy), Unavailable energy, Relation between increase in unavailable energy and increase in entropy. Maximum work, maximum useful work for a system and control volume, irreversibility, second law efficiency.
Pure Substances: P-T and P-V diagrams, triple point and critical points. Sub-cooled liquid, saturated liquid, mixture of saturated liquid and vapor, saturated vapor and superheated vapor states of pure substance with water as example. Enthalpy of change of phase (Latent heat). Dryness fraction (quality), T-S and H-S diagrams, representation of various processes on these diagrams. Steam tables and its use. Throttling calorimeter, separating and throttling calorimeter.

AVAILABILITY, IRREVERSIBILITY AND GENERAL THERMODYNAMIC RELATIONS

OBJECTIVE: **To determine the amount energy available for work in a system and the thermodynamic relations applied to a system**

STRUCTURE:

4.7. The Maxwell relationships

4. Introduction:

There are many forms in which an energy can exist. But even under ideal conditions all these forms cannot be converted completely into work. This indicates that energy has two parts: Available part, Unavailable part

Available energy: is the maximum portion of energy which could be converted into useful work by ideal processes which reduce the system to a dead state (a state in equilibrium with the earth and its atmosphere). Because there can be only one value for maximum work which the system alone could do while descending to its dead state, it follows immediately that ‘Available energy’ is a property.

Unavailable energy: A system which has a pressure difference from that of surroundings, work can be obtained from an expansion process, and if the system has a different temperature, heat can be transferred to a cycle and work can be obtained. But when the temperature and pressure becomes equal to that of the earth, transfer of energy ceases, and although the system contains internal energy, this energy is

4.1. Available energy referred to a cycle:

The available energy (A.E.) or the available part of the energy supplied is the maximum work output obtainable from a certain heat input in a cyclic heat engine (Fig. 6.1). The minimumenergy that has to be rejected to the sink by the second law is called the unavailable energy (U.E.), or the unavailable part of the energy supplied.

$$Q1 = A.E. + U.E.$$

or Wmax = A.E. = Q1 – U.E.

For the given values of the source temperature T1 and sink temperature T2, the reversible efficiency,

$$\eta_{rev} = 1 - \frac{T_1}{T_2}$$

For a given T1, ηrev. will increase with the decrease of T2. The lowest practicable temperature of heat rejection is the temperature of the surroundings, T0.

$$\eta_{max} = 1 - \frac{T_0}{T_2}$$

$$W_{max} = \eta_{max}\left(1 - \frac{T_0}{T_2}\right)$$

And

$$W_{max} = \eta_{max}\left(1 - \frac{T_0}{T_2}\right) . Q_1$$

Consider a finite process l-m, in which heat is supplied reversibly to a heat engine (Fig. 6.2). Taking an elementary cycle, if dQ1 is the heat received by the engine reversibly at T1,

Then $dW_{max} = \eta_{max}\left(1 - \frac{T_0}{T_2}\right) . dQ_1$ = A.E

For the heat engine receiving heat for the whole process l-m, and rejecting heat at T_o

$$\int dW_{max} = \int_l^m dQ_1 - \int_l^m \frac{T_O}{T_1} dQ_1$$

W_{max} = A.E. = $Q_{l\text{-}m} - T_o (S_l - S_m)$

or unavailable energy, U.E. = $Q_l - m - W_{max}$

or U.E. = $T_o (S_l - S_m)$

Thus unavailable energy is the product of the lowest temperature of heat rejection, and the change of entropy of the system during the process of supplying heat

4.2. Decrease in available energy when heat is transferred through a finite temperature difference:

When transfer of heat takes place through a finite temperature difference, there is a decrease in the availability of energy so transferred. Consider a reversible heat engine operating between temperatures T_1 and T_0

$Q_1 = T . \Delta s$

$Q_2 = T_0 \Delta s$

and W = A.E. = $[T_1 - T_0] \Delta s$

Assume that heat Q1 is transferred through a finite temperature difference from the reservoir or source at T1 to the engine absorbing heat at T1′, lower than T1. The availability of Q1 as received by the engine at T1′ can be found by allowing the engine to operate reversibly in a cycle between T1′ and T0 receiving Q1 and rejecting Q2′.

Now, $Q1 = T1\Delta s = T1'\Delta s'$

_ $T1 > T1'$

$\therefore \Delta s' > \Delta s$

$Q2 = T0 \Delta s$

$Q2' = T0 \Delta s'$

_ $\Delta s' > \Delta s$

$\therefore Q2' > Q2$

$\therefore$ W′ = Q1 – Q2′ = T1′ Δs′ – T0 Δs′

and W = Q1 – Q2 = T1 Δs – T0 Δs

$\therefore$ W′ < W, because Q2′ > Q2

The loss of available energy due to irreversible heat transfer through finite temperature difference between the source and the working fluid during the heat addition process is given as :

W – W′ = Q2′ – Q2 = T0 (Δs′ – Δs)

i.e., Decrease in available energy, A.E.

= T0 (Δs′ – Δs)

Thus the decrease in A.E. is the product of the lowest feasible temperature of heat rejection and the additional entropy change in the system while receiving heat irreversibly, compared to the case of reversible heat transfer from the same source. The greater is the temperature difference (T1 – T1′), the greater is the heat rejection Q2′ and the greater will be the unavailable part of the energy supplied.

Energy is said to be degraded each time it flows through a finite temperature difference. That is, why the second law of thermodynamics is sometimes called the law of the degradation of energy, and energy is said to ‘run down hill’.

4.3 Availability in non-flow systems:

Let us consider a system consisting of a fluid in a cylinder behind a piston, the fluid expanding reversibly from initial condition of p_1 and T_1 to final atmospheric conditions of p_0 and T_0. Imagine also that the system works in conjunction with a reversible heat engine which receives heat reversibly from the fluid in the cylinder such that the working substance of the heat engine follows the cycle O1LO as shown ,where $s_1 = s_l$ and $T_0 = T_L$ (the only possible way in which this could occur would be if an infinite number of reversible heat engines were arranged in parallel, each operating on a Carnot cycle, each one receiving heat at a different constant temperature and each one rejecting heat at T_0). The work done by the engine is given by :

Wengine = Heat supplied – Heat rejected = $Q - T_0 (s_1 - s_0)$ ...(i)

The heat supplied to the engine is equal to the heat rejected by the fluid in the cylinder. Therefore, for the fluid in the cylinder undergoing the process 1 to 0, we have

$-Q = (u_0 - u_1) + W_{fluid}$

i.e., $W_{fluid} = (u_1 - u_0) - Q$ ...(ii)

Adding eqns. (i) and (ii), we get

Wfluid + Wengine = $[(u_1 - u_0) - Q] + [Q - T_0 (s_1 - s_0)]$

$= (u_1 - u_0) - T_0 (s_1 - s_0)$

The work done by the fluid on the piston is less than the total work done by the fluid, since there is no work done on the atmosphere which is at constant pressure p0

i.e., Work done on atmosphere = $p_0 (v_0 - v_1)$

Hence, maximum work available

$= (u_1 – u_0) – T_0 (s_1 – s_0) – p_0 (v_0 – v_1)$

Note. When a fluid undergoes a complete cycle then the net work done on the atmosphere is zero.

$W_{max} = (u_1 + p_0 v_1 – T_0 s_1) – (u_0 + p_0 v_0 – T_0 s_0)$ ...(6.3)

$\therefore W_{max} = a_1 – a_0$

The property, $a = u + p_0 v – T_0 s$ (per unit mass) is called the non-flow availability function.

4.4 Helmholtz and gibbs functions:

The work done in a non-flow reversible system (per unit mass) is given by :

$W = Q – (u_0 – u_1)$

$= T.ds – (u_0 – u_1)$

$= T (s_0 – s_1) – (u_0 – u_1)$

i.e., $W = (u_1 – Ts_1) – (u_0 – Ts_0)$

The term $(u – Ts)$ is known as Helmholtz function. This gives maximum possible output when the heat Q is transferred at constant temperature and is the case with a very large source. If work against atmosphere is equal to p0 (v0 – v1), then the maximum work available,

$W_{max} = W$ – work against atmosphere

$= W – p_0 (v_0 – v_1)$

$= (u_1 – Ts1) – (u_0 – Ts_0) – p0 (v_0 – v_1)$

$= (u_1 + p_0v_1 – Ts_1) – (u_0 + p_0v_0 – Ts_0)$

$= (h_1 – Ts_1) – (h_0 – Ts_0)$

i.e., $W_{max} = g_1 – g_0$

where $g = h – T.s$ is known as Gibb’s function or free energy function.

The maximum possible available work when system changes from 1 to 2 is given by

$W_{max} = (g_1 – g_0) – (g_2 – g_0) = g_1 – g_2$

Similarly, for steady flow system the maximum work available is given by

$W_{max} = (g_1 – g_2) + (KE_1 – KE_2) + (PE_1 – PE_2)$

where K.E. and P.E. represent the kinetic and potential energies.

It may be noted that Gibb’s function $g = (h – Ts)$ is a property of the system where availability function $a = (u + p_0v – T_0s)$ is a composite property of the system and surroundings.

Again, $a = u + p_0v – T_0s$

$b = u + pv – T_0s$

$g = u + pv – Ts$

When state 1 proceeds to dead state (zero state)

$a = b = g$.

4.5. IRREVERSIBILITY:

The actual work which a system does is always less than the idealized reversible work, and the difference between the two is called the irreversibility of the process.

Thus, Irreversibility, I = $W_{max} - W$ ...(6.8)
This is also sometimes referred to as ‘degradation’ or ‘dissipation’.
For a non-flow process between the equilibrium states, when the system exchanges heat only with environment, irreversibility (per unit mass),
$i = [(u_1 - u_2) - T_0(s_1 - s_2)] - [(u_1 - u_2) + Q]$
$= T0\ (s_2 - s_1) - Q$
= T0 (Δs)system + T0 (Δs)surr.
i.e., i = T_0 [(Δs)system + (Δs)surr.] ...(6.9)
∴ $i \geq 0$
Similarly, for steady flow-process
$i = W_{max} - W$ (per unit mass)
$= T_0\ (s_2 - s_1) - Q$
$= T_0\ (\Delta s)_{system} + T_0\ (\Delta s)_{surr}$.
i.e., i = T_0 (Δssystem + Δssurr.)
The same expression for irreversibility applies to both flow and non-flow processes.
The quantity $T_0\ (\Delta s_{system} + \Delta s_{surr}.)$ represents (per unit mass) an increase in unavailable energy (or energy).

4.6. EFFECTIVENESS

Effectiveness is defined as the ratio of actual useful work to the maximum useful work. The useful output of a system is given by the increase of availability of the surroundings. Effectiveness, ∈ = Increase of availability of surroundings Loss of availability of the system For a compression or heating process the effectiveness is given by ∈= Increase of availability of system Loss of availability of the surroundings
The effectiveness of an actual process is always less than unity. Thus effectiveness of a process is the measure of the extent to which advantage has been taken of an opportunity to obtain useful work.

4.7. The Maxwell relationships:

As we have seen, the fundamental thermodynamic relation $\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V$ implies that the natural variable in which to express E are S and V: $E = E(S, V)$.

That means that on purely mathematical grounds, we can write

$$\mathrm{d}E = \left(\frac{\partial E}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial E}{\partial V}\right)_S \mathrm{d}V$$

But comparison with the fundamental thermodynamic relation, which contains the physics, we can make the following identifications:

$$T = \left(\frac{\partial E}{\partial S}\right)_V \qquad \text{and} \qquad P = -\left(\frac{\partial E}{\partial V}\right)_S$$

These (especially the second) are interesting in their own right. But we can go further, by differentiating both sides of the first equation by V and of the second by S:

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial}{\partial V}\left(\frac{\partial E}{\partial S}\right)_V\right)_S \qquad \text{and} \qquad \left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial}{\partial S}\left(\frac{\partial E}{\partial V}\right)_S\right)_V$$

Using the fact that the order of differentiation in the second derivation doesn't matter, we see that the right hand sides are equal, and thus so are the left hand sides, giving

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

By starting with F, H and G, we can get three more relations.

$$\begin{array}{lllll}
dE = TdS - PdV & \Rightarrow & T = \left.\dfrac{\partial E}{\partial S}\right|_V \ \& \ P = -\left.\dfrac{\partial E}{\partial V}\right|_S & \Rightarrow & \left.\dfrac{\partial P}{\partial S}\right|_V = -\left.\dfrac{\partial T}{\partial V}\right|_S \\
dF = -SdT - PdV & \Rightarrow & S = -\left.\dfrac{\partial F}{\partial T}\right|_V \ \& \ P = -\left.\dfrac{\partial F}{\partial V}\right|_T & \Rightarrow & \left.\dfrac{\partial P}{\partial T}\right|_V = \left.\dfrac{\partial S}{\partial V}\right|_T \\
dH = TdS + VdP & \Rightarrow & T = \left.\dfrac{\partial H}{\partial S}\right|_P \ \& \ V = \left.\dfrac{\partial H}{\partial P}\right|_S & \Rightarrow & \left.\dfrac{\partial V}{\partial S}\right|_P = \left.\dfrac{\partial T}{\partial P}\right|_S \\
dG = -SdT + VdP & \Rightarrow & S = -\left.\dfrac{\partial G}{\partial T}\right|_P \ \& \ V = \left.\dfrac{\partial G}{\partial P}\right|_T & \Rightarrow & \left.\dfrac{\partial V}{\partial T}\right|_P = -\left.\dfrac{\partial S}{\partial P}\right|_T
\end{array}$$

The two equations involving derivatives of S are particularly useful, as they provide a handle on S which isn't easily experimentally accessible.

For non-hydrodynamic systems, we can obtain analogous relations involving, say, m and B instead of P and V; for instance by starting with $\mathrm{d}E = T\mathrm{d}S + m\mathrm{d}B$ we get. $(\partial T/\partial B)_S = (\partial m/\partial S)_B$

To fully exploit these relations, some properties of partial derivatives are useful. See here for a refresher course!

In maths, it's usually quite obvious what the independent variables are: either x, y, z or r, θ, ϕ, for instance, and if you differentiate with respect to one you know that you are keeping the others constant. In thermal physics it isn't obvious at all, so **always** specify what is being held constant. Expressions like

$$\frac{\partial P}{\partial T} \quad \text{and} \quad \frac{\mathrm{d}P}{\mathrm{d}T}$$

are simply meaningless. (OK, we met the latter in the Clausius-Clapeyron equation, but there it really was the slope of a line: the restriction to points of phase coexistence was understood.)

OUTCOMES:

- Apply the thermodynamic relation for determining the system properties

IMPORTANT QUESTIONS:

1. Derive an expression for work done in a steady flow polytropic process.
2. Explain maxwell’s relation and Clausius-Clapeyron equation
3. Write Maxwell’s relation and explain terms involed
4. 0.2 Kg of air with pressure 1.5 bar and temperature 27˚C is compressed to a pressure of 15 bar according to the law $PV^{1.25} = C$. Determine i) Work done ii) Heat floe to or from the air iii) Change of entropy.
5. Derive an expression for change in entropy for an ideal gas undergoing isobaric process

FURTHER READING:

- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
- http://www.nptel.ac.in/courses/112104113/4#

THE PURE SUBSTANCE

OBJECTIVE: **Introduce the concept of a pure substance and Illustrate the P-v , T-v and P-T property diagrams and P-v-T surfaces of pure substances. Demonstrate the procedures for determining thermodynamic properties of pure substances from tables of property data.**

STRUCTURE:

4. Introduction
4.1 Application of 1st law of thermodynamics for a closed system

4. Introduction: The system encountered in thermodynamics is often quite less complex and consists of fluids that do not change chemically, or exhibit significant electrical, magnetic or capillary effects. These relatively simple systems are given the generic name the Pure Substance.

"A system is set to be a pure substance if it is (i) homogeneous in chemical composition, (ii) homogeneous in chemical aggregation and (iii) invariable in chemical aggregation."

Pure Substances

Define Pure Substance:

A substance that has a fixed chemical composition throughout is called a pure substance such as water, air, and nitrogen.

A pure substance does not have to be of a single element or compound. A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same.

Phases of a Pure Substance

A pure substance may exist in different phases. There are three principal phases solid, liquid, and gas.

A phase: is defined as having a distinct molecular arrangement that is homogenous throughout and separated from others (if any) by easily identifiable boundary surfaces.

A substance may have several phases within a principal phase, each with a different molecular structure. For example, carbon may exist as graphite or diamond in the solid phase, and ice may exist in seven different phases at high pressure.

Molecular bonds are the strongest in solids and the weakest in gases.

Solid: the molecules are arranged in a three-dimensional pattern (lattice) throughout the solid. The molecules cannot move relative to each other; however, they continually oscillate about their equilibrium position.

Liquid: the molecular spacing in liquid phase is not much different from that of the solid phase (generally slightly higher), except the molecules are no longer at fixed positions relative to each other.

Gas: the molecules are far apart from each other, and a molecular order does not exist. Gas molecules move randomly, and continually collide with each other and the walls of the container they are in.

Molecules in the gas phase are at a considerably higher energy level than they are in liquids or solid phases.

Phase-Change Processes of Pure Substances:

Consider a process where a pure substance starts as a solid and is heated up at constant pressure until it all becomes gas. Depending on the prevailing pressure, the matter will pass through various phase transformations. At P_0:

1. Solid
2. Mixed phase of liquid and solid
3. Sub-cooled or compressed liquid (means it is not about to vaporize)4. Wet vapor or saturated liquid-vapor mixture, the temperature will stop rising until the liquid is completely vaporized.

5.Superheated vapor (a vapor that is not about to condense).

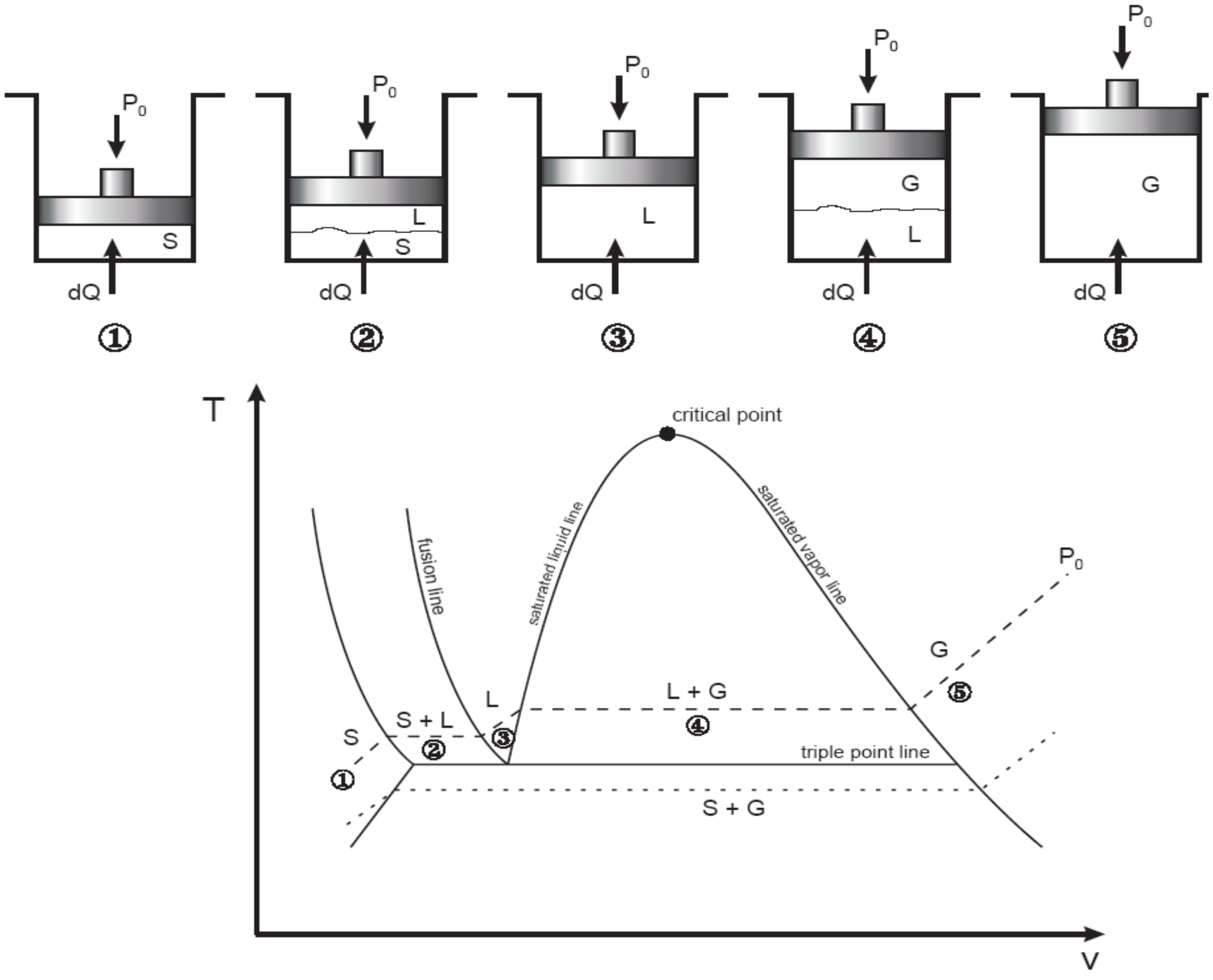


Fig. 1: T-v diagram for the heating process of a pure substance.

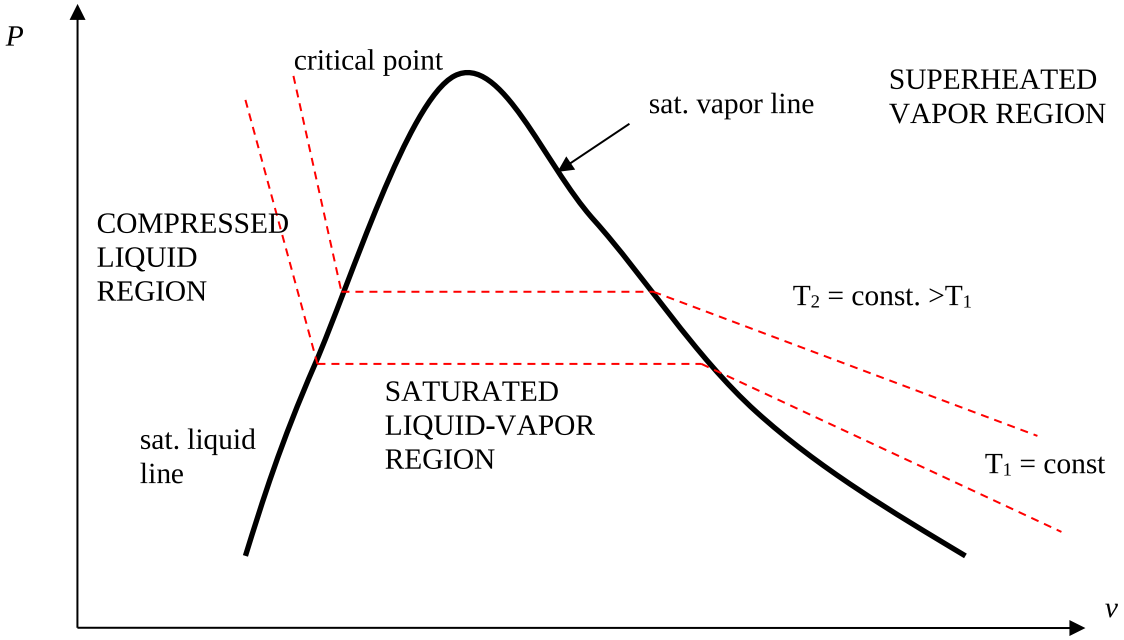
- At a given pressure, the temperature at which a pure substance starts boiling is called the saturation temperature, T_{sat}.
- Likewise, at a given temperature, the pressure at which a pure substance starts boiling is called the saturation pressure, P_{sat}.
- During a phase-change process, pressure and temperature are dependent properties, $T_{sat} = f\ (P_{sat})$.
- The critical point is the point at which the liquid and vapor phases are not distinguishable
- The “triple point” is the point at which the liquid, solid, and vapor phases can exist together. On P-v or T-v diagrams, these triple-phase states form a line called the triple line.

Table 1: Critical and triple point for water and oxygen.

	Critical Point		Triple Point	
	P (atm)	T (K /°C)	P (atm)	T (K /°C)
H_2O	218	647.30/(374.14)	0.006	273.17 (0.01)
O_2	50.136	154.80/(−118.36)	0.0015	54.16/(−219)

Vapor Dome

The general shape of a P-v diagram for a pure substance is very similar to that of a T-v diagram.

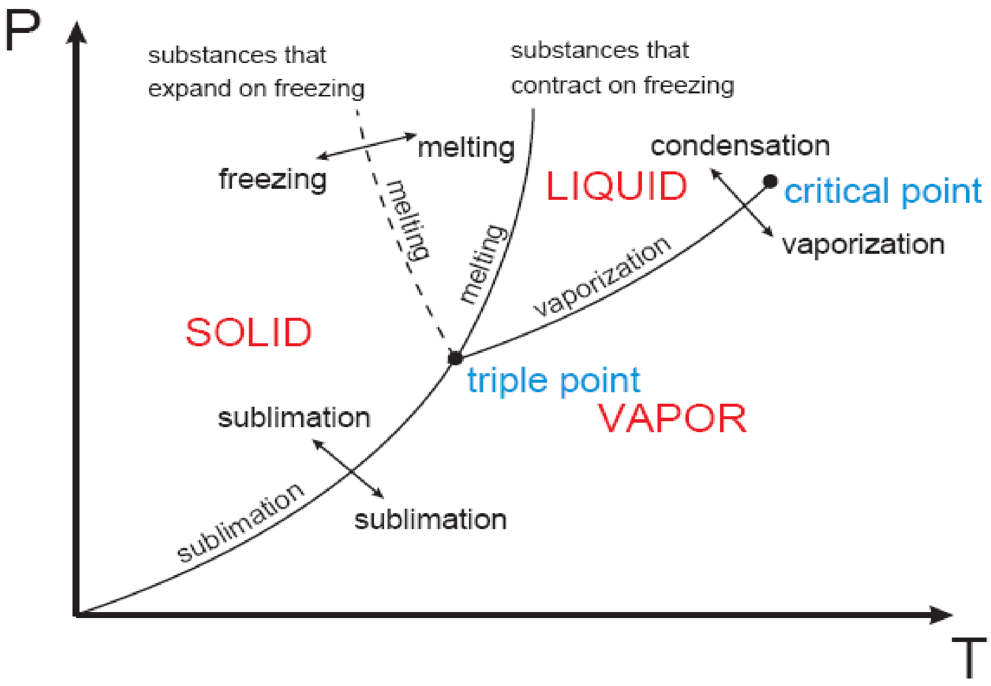


P-v diagram of a pure substance.

The P-T or Phase Change Diagram

This is called phase diagram since all three phases are separated from each other by three lines. Most pure substances exhibit the same behavior.

- One exception is water. Water expands upon freezing.



phase diagram of pure substances.

There are two ways that a substance can pass from solid phase to vapor phase i) it melts first into a liquid and subsequently evaporates, ii) it evaporates directly without melting (sublimation).

- the sublimation line separates the solid and the vapor.
- the vaporization line separates the liquid and vapor regions
- the melting or fusion line separates the solid and liquid.
- these three lines meet at the triple point.
  - if $P<P_{TP}$, the solid phase can change directly to a vapor phase
  - at $P<P_{TP}$ the pure substance cannot exist in the liquid phase. Normally ($P>P_{TP}$) the substance melts into a liquid and then evaporates.
  - matter (like CO_2) which has a triple point above 1 atm sublimate under atmospheric conditions (dry ice)
  - for water (as the most common working fluid) we are mainly interested in the liquid and vapor regions. Hence, we are mostly interested in boiling and condensation.

Property Tables

For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations. Thus, properties are frequently presented in the form of tables, see Table A-4.

The subscript "f" is used to denote properties of a saturated liquid and "g" for saturated vapor. Another subscript, "fg", denotes the difference between the saturated vapor and saturated liquid values of the same property.

For example:

v_f = specific volume of saturated liquid

v_g = specific volume of saturated vapor

v_{fg} = difference between v_g and v_f ($v_{fg} = v_g - v_f$)

Enthalpy: is a property defined as $H = U + PV$ (kJ) or $h = u + Pv$ (kJ/kg) (per mass unit).

Enthalpy of vaporization (or latent heat): represents the amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure. It decreases as the temperature or pressure increase, and becomes zero at the critical point.

1- Saturated Liquid-Vapor Mixture

During vaporization, a mixture of part liquid part vapor exists. To analyze this mixture, we need to know the proportions of the liquid and vapor in the mixture. The ratio of the mass of vapor to the mass of the total mixture is called quality, x:

$$x = \frac{\mathrm{m}_{\text{vapor}}}{\mathrm{m}_{\text{total}}} \qquad m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$$

Saturated liquid-vapor mixture is treated as a combination of two sub-systems (two phases). The properties of the "mixture" are the average properties of the saturated liquid-vapor mixture.

$$V = V_f + V_g$$

$$m_t v_{ave} = m_f v_f + m_g v_g$$

$$m_f = m_t - m_g \rightarrow m_t v_{ave} = (m_t - m_g) v_f + m_g v_g$$

dividing by m_t

$$v_{ave} = (1 - x) v_f + x v_g \qquad \text{and} \qquad x = m_g / m_t$$

$$v_{ave} = v_f + x v_{fg} \qquad (m^3 / kg)$$

or,

$$x = \frac{v_{ave} - v_f}{v_{fg}}$$

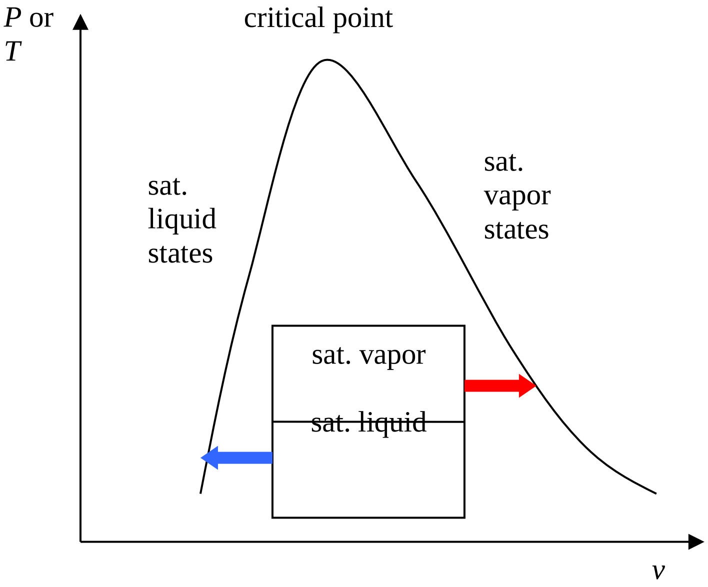


Fig. 4: The relative amounts of liquid and vapor phases (quality x) are used to calculate the mixture properties.

Similarly,

$$u_{ave} = u_f + xu_{fg}$$

$$h_{ave} = h_f + xh_{fg}$$

Or in general, it can be summarized as $y_{ave} = y_f + x.y_{fg}$. Note that:

$$0 \le x \le 1$$

$$y_f \le y_{ave} \le y_g$$

Note: pressure and temperature are dependent in the saturated mixture region.

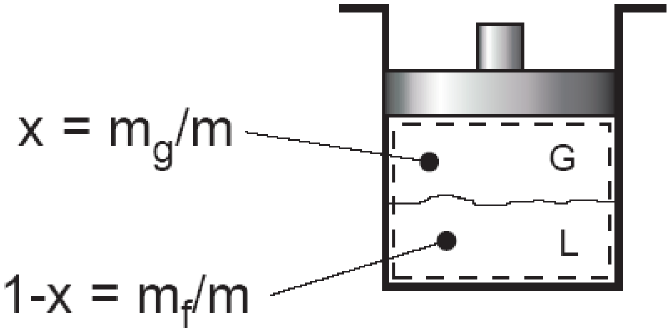


Fig. 5: Quality defined only for saturated liquid-vapor mixture.

Example 1: Saturated liquid-vapor mixture

A closed, rigid container of volume 0.5 m^3 is placed on a hot plate. Initially the container holds a two-phase mixture of saturated liquid water and saturated water vapor at P_1= 1 bar with a quality of 0.5. After heating, the pressure in the container is P_2=1.5 bar. Indicate the initial and final states on a T-v diagram, and determine:

a) the temperature, in °C, at each state.

b) the mass of vapor present at each state, in kg.

c) if heating continues, determine the pressure, in bar, when the container holds only saturated vapor.

Solution:

Assumptions:

1. Water in the container is a closed system.
2. States 1, 2, and 3 are equilibrium states.
3. The volume of container remains constant.

Two independent properties are required to fix state 1 and 2. At the initial state, the pressure and quality are known. Thus state 1 is known, as mentioned in the problem. The specific volume at state 1 is found using the given quality:

$$v_1 = v_{f1} + x_1(v_{g1} - v_{f1})$$

$$\text{From Table A-5 at P} = 1\,\text{bar} = 100\,\text{kPa}$$

$$v_1 = 0.001043 + 0.5\ (1.694 - 0.001043) = 0.8475 \quad m^3/kg$$

At state 2, the pressure is known. Volume and mass remain constant during the heating process within the container, so v_2=v_1. For P_2= 0.15 MPa, Table A-5 gives v_{f2}= 0.001053 and v_{g2}=1.1593 m^3/kg. Since

$v_{f2} < v_2 < v_{g2}$

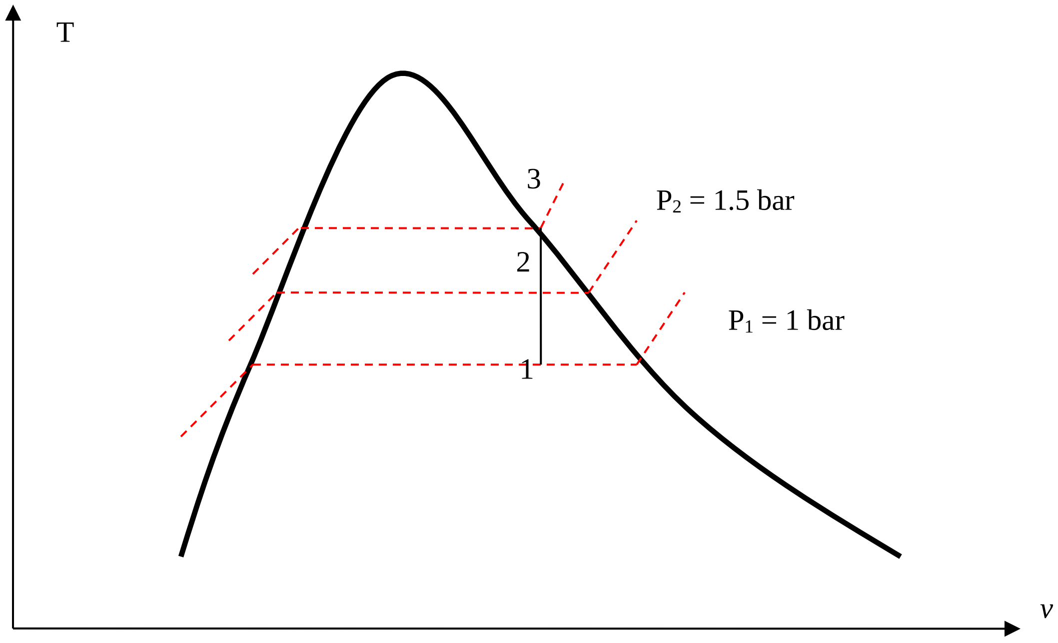
<u>State 2 must be in the two-phase region</u> as well. Since state 1 and 2 are in the two-phase liquid-vapor region, the temperatures correspond to the saturation temperatures for the given. Table A-5:

T_1 = 99.63 °C and T_2 = 111.4 °C

To find the mass of water vapor present, we first find the total mass, m.

$$m = \frac{V}{v} = \frac{0.5m^3}{0.8475m^3/kg} = 0.59kg$$

$$m_{g1} = x_1 m = 0.5(0.59kg) = 0.295kg$$



The mass of vapor at state 2 is found similarly using quality x_2. From Table A-5, for P_2 = 1.5 bar, we have:

$$x_2 = \frac{v - v_{f2}}{v_{g2} - v_{f2}}$$

$$x_2 = \frac{0.8475 - 0.001053}{1.159 - 0.001053} = 0.731$$

$$m_{g2} = 0.731(0.59kg) = 0.431 \quad kg$$

If heating continued, state 3 would be on the saturated vapor line, as shown in on the T-v diagram above. Thus, the pressure would be the corresponding saturation pressure. Interpolating in Table A-5 at $v_g = 0.8475$ m^3 /kg, we get P_3 = 2.11 bar.

2- Superheated Vapor

Superheated region is a single phase region (vapor only), temperature and pressure are no longer dependent. See Table A-6 for superheated vapor properties.

If $T >> T_{critical}$ or $P << P_{critical}$, then the vapor can be approximated as an “ideal gas”.

3- Compressed (or Sub-cooled) Liquid

The properties of a liquid are relatively independent of pressure (incompressible).

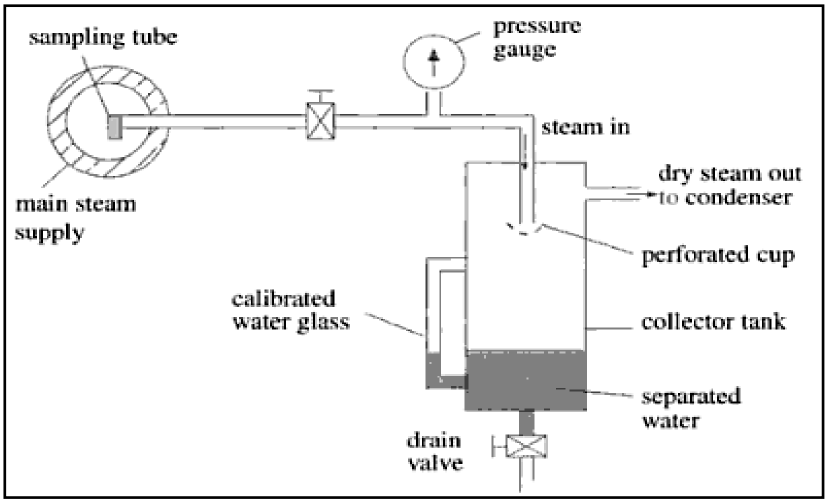
A general approximation is to treat compressed liquid as saturated liquid at the given saturation temperature.

Determination the dryness fraction:

- **Separating calorimeter:**

The quality of wet steam is usually defined by its dryness fraction. When the dryness fraction, pressure and temperature of the steam are known, then the state of wet steam is fully defined. In a steam plant it is at times necessary to know the state of the steam. For wet steam, this entails finding the dryness fraction. When the steam is very wet, we make use of a separating calorimeter.

Construction of separating calorimeter is as shown in figure:



The steam is collected out of the main steam supply and enters the separator from the top. The steam is forced to make a sharp turn when it hits the perforated cup (or any other mechanism that produces the same effect). This results in a vortex motion in the steam, and water separates out by the centrifugal action. The droplets then remain inside the separator and are collected at the bottom, where the level can be recorded from the water glass. The dry steam will pass out of the calorimeter into a small condenser for the collection of the condensate. However, not all the water droplets remain in the collector tank. Some water droplets pass through to the condenser, and hence this calorimeter only gives a close approximation of the dryness fraction of the steam.

From the results obtained from the two collectors, the dryness fraction may then be found from

$$\textbf{Dryness fraction} = \frac{\textbf{Mass of dry steam}}{\textbf{Mass of wet steam containing dry steam}}$$

This can be expressed as:

$x = \frac{M}{m+M}$

Where,

M is the mass of dry steam and

m is the mass of suspended water separated in the calorimeter in the same time.

- **Throttling calorimeter:**

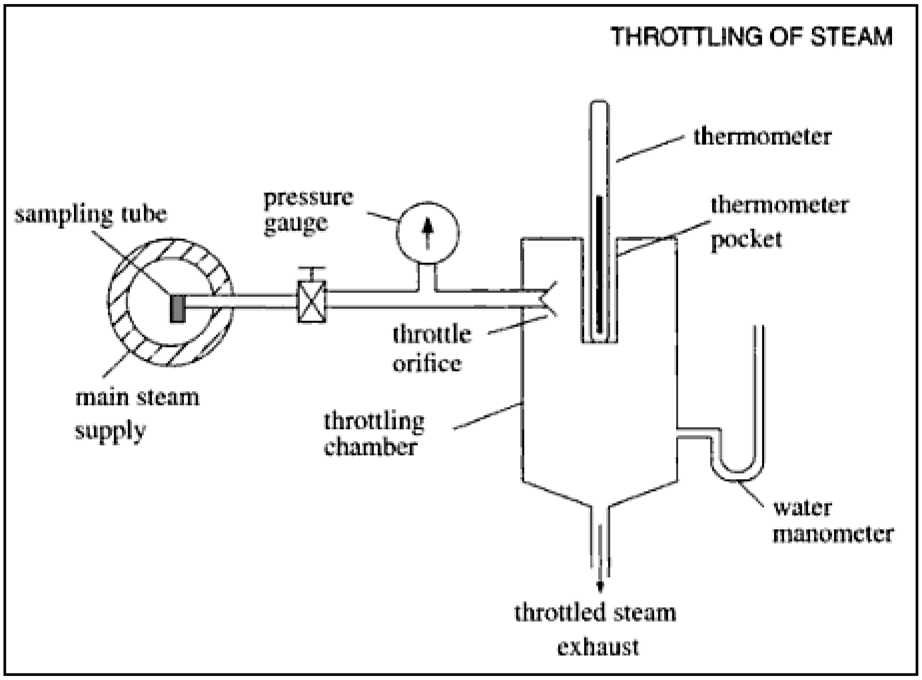
If we have steam that is nearly dry, we make use of a throttling calorimeter as shown in figure. This calorimeter is operated by first opening the stop valve fully so that the steam is not partially throttled as it passes through the apparatus for a while to allow the pressure and temperature to stabilize. If the pressure is very close to atmospheric pressure, the saturation should be around 100°C, it may be assumed that the steam is superheated.

When the conditions have become steady, the gauge pressure before throttling is read from the pressure gauge. After throttling, the temperature and gauge pressure are read from the thermometer and manometer respectively. The barometric pressure is also recorded.

From equation $h_1 = h_2$,

We have h_w at p_1 = h_{sup} at p_2

And thus $x = \frac{h_{g2} + Cp\ (T_{sup} - T_{sat}) - h_{f1}}{h_{fg1}}$



List of Formulas:

1. Dryness fraction of steam sample entering Separating Calorimeter = $x = \frac{M}{m+M}$

Where,M is the mass of dry steam and

m is the mass of suspended water separated in the calorimeter in the same time.

2. Dryness fraction of steam sample entering Throttling calorimeter

We have h_W at $p_1 = h_{sup}$ at p_2

And thus $x = \frac{h_{g2} + Cp\ (T_{sup} - T_{sat}) - h_{f1}}{h_{fg1}}$

3. Dryness Fraction = x = Mass of dry steam / Mass of wet steam

4. Specific Enthalpy of wet steam at Pressure P = $h = h_f + x\ h_{fg}$ KJ/Kg (Similarly specific entropy, specific volume can be calculated)

5. Enthaply(h) = Internal energy(u) + (P.v)

6. Specific heat at constant volume = $C_V = du/dt$

7. Specific heat at constant pressure = $C_P = dh/dt$

8. Specific heat at constant pressure for dry steam = C_{Ps} = 2.1KJ/Kg.K

OUTCOME: Demonstrate understanding of key concepts including phase and pure substance, state principle for simple compressible systems, p-v-T surface, saturation temperature and saturation pressure, two-phase liquid-vapor mixture, quality, enthalpy, and specific heats.Apply the closed system energy balance with property data.

IMPORTANT QUESTIONS:

1. With a neat sketch explain how Combined separating and throttling calorimeter can be used to measure the dryness fraction of wet vapour
2. With a neat sketch explain throttling calorimeter can be used to measure the dryness fraction of wet vapour
3. Draw phase equilibrium diagram of water on P-T Coordinates indicating triple and critical point
4. Steam initially at 1.5 MPa 300˚C expands reversibly and adiabatically in a steam turbine to 40˚C . Determine the ideal work output of the turbine per kg of steam

FURTHER READING:

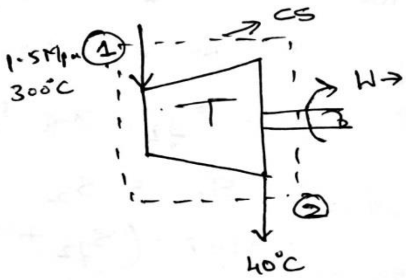
1. Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
2. Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
3. http://www.nptel.ac.in/courses/112104113/4#

Problems

Question paper problems

1) steam initially at 1·5 Mpa, 300°c expands reversibly & adiabatically in a steam turbine to 40°c. Determine the ideal work output of the turbine per kg of steam

→ SFEE for the control volume



for Turbine $d(K.E) = 0$

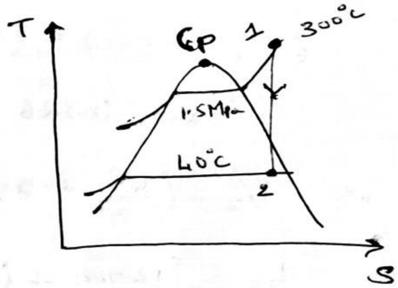
$d(P.E) = 0$

W is +ve

$Q = 0$ (adiabatic)

$$\therefore \quad W = (h_1 - h_2)$$

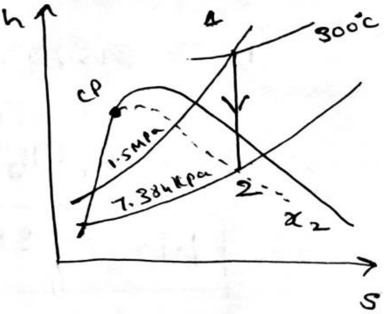
The process is reversible & adiabatic, so it is isentropic hence the line 1-2 will be vertical in T-s & h-s diagram



from steam table (15 bar)

since at $P_1 = 1{\cdot}5$ Mpa, $T_1 = 300°c$

$T_1 > T_S$ (saturation temperature) hence we have to check $P_1 = 15$ bar, $T_{sup} = 300°c$ in superheated steam table for properties at state 1 (superheated condition)



$h_1 = 3038{\cdot}9$ KJ/kg $= h_{sup}$

$S_1 = 6{\cdot}9207$ KJ/kg·K $= S_{sup}$

for state 2 :- (Liquid vapour mixture region).

$P_1 = P_{saturation} = 0{\cdot}073750$ bar $= 7{\cdot}375$ Kpa

$s_f = 0{\cdot}5721$ KJ/kg K $\qquad h_f = 167{\cdot}5$ KJ/kg

$s_{fg} = 7{\cdot}6845$ KJ/kg K $\qquad h_{fg} = 2406{\cdot}9$ KJ/kg

To find h_2

$$h_2 = h_{f2} + x_2 h_{fg2}$$

To find x_2 which is unknown

we have $s_1 = s_2$ (adiabatic expansion)

$$s_1 = 6.9207 \text{ kJ/kg K}$$

$$s_2 = s_{f2} + x_2 s_{fg2}$$

$$s_1 = s_2$$

$$6.9207 = (s_{f2} + x_2 s_{fg2})_{40°C}$$

$$6.9207 = 0.5721 + x_2 \times 7.6845$$

$$x_2 = 0.826 \text{ or } 82.6\%$$

$$\therefore h_2 = (h_{f2} + x_2 h_{fg2})_{40°C}$$

$$h_2 = (167.5 + (0.826 \times 2406.9))$$

$$h_2 = 2152.57 \text{ kJ/kg}$$

$$\therefore W = h_1 - h_2 = (3038.9 - 2152.57) = 885.03 \text{ kJ/kg}$$

$$\boxed{W = +885.03 \text{ kJ/kg}}$$

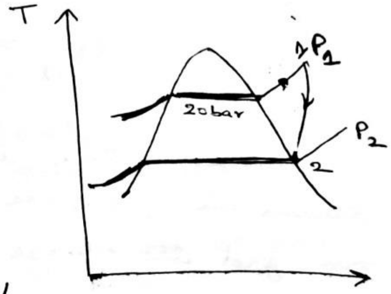
2) A rigid vessel of $2m^3$ volume is filled with super heated steam at 20bar & 300°C. The vessel is cooled untill the steam ~~at~~ is just dry saturated. Calculate the mass of steam in the vessel, the final pressure of steam & the amount of energy transferred as heat to the surroundings. Represent the process on T-s diagram

15

Solution:-

At state point 1,

$P_1 = 20\text{bar}$, $T_1 = 300°C$, $V_1 = 2m^3$

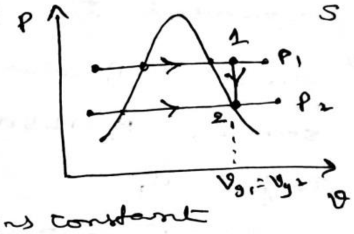


from steam table

superheated steam table

$P_1 = 20\text{bar}$, $T_1 = 300°C$,

specific volume $= v_{sup} = v_1 = 0.12550 m^3/kg$



Mass of steam in vessel

$$m = \frac{V_1}{v_1} = \frac{2}{0.12550} = 16 kg$$

Since the tank is rigid the volume remains constant

$$\therefore v_2 = v_1 = 0.12550 m^3/kg$$

The steam is just dry & saturated at point 2 & so

$$v_{g2} = v_2 = 0.12550 m^3/kg$$

from steam tables, the pressure of dry saturated steam corresponding to specific volume $0.125 m^3/kg$ is 16 bar

For constant volume process, workdone is zero & therefore from the principle of energy ~~[illegible]~~ conservation

heat transferred $= {}_1q_2 = du = u_2 - u_1$

$${}_1q_2 = (h_2 - P_2 v_2) - (h_1 - P_1 v_1)$$

$$= (h_2 - h_1) - v_1(P_2 - P_1) \quad \{\because v_2 = v_1\}$$

At 20bar & 300°c $h_1 = 3023.9 kJ/kg$

At 16bar & $x = 1$ $h_2 = h_g = 2791.7 kJ/kg$ (dry saturated)

$$\therefore {}_1q_2 = (2791.7 - 3023.9) - \left[0.12550(16-20)\times 100\right]$$

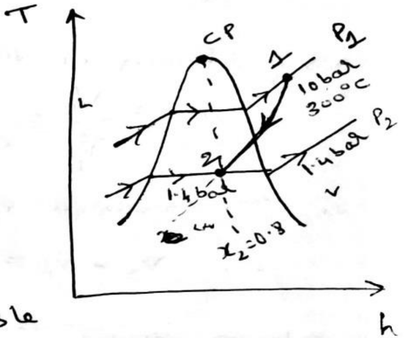
$${}_1q_2 = -182.4 kJ/kg$$

16

∴ Total energy transferred as heat to Surroundings

$$ {}_1Q_2 = m\,{}_1q_2 = 16\,(-\cancel{1}82.4) = \cancel{-4518.4\text{ kJ}} \quad -2924\text{ kJ} $$

3) calculate the internal energy per kg of superheated steam at pressure of 10 bar & a temperature of 300°C. Also find the change in internal energy if this steam is expanded to 1.4 bar & dryness fraction 0.8



Process 1-2 represents the expansion process

→ state 1 :- $P_1 = 10\text{ bar}$, $T_1 = T_{sup} = 300°C$

state 2 :- $P_2 = 1.4\text{ bar}$, $x_2 = 0.8$

To find u_1

$u_1 = h_1 - P_1 v_{1}$ {superheated steam}

from superheated steam table

$h_1 = 3052.1\text{ kJ/kg}$; v_g

v_1 at $P_1 = 10\text{ bar}$ from ~~saturated~~ superheated steam table

$v_1 = v_{sup} = 0.25798\ m^3/kg$

$\therefore u_1 = 3052.1 - (10\times10^2 \times 0.25798)$

$u_1 = 2794.12\text{ kJ/kg}$

To find u_2

$u_2 = h_2 - x_2 P_2 v_{g2}$

$u_2 = (h_{f2} + x_2 h_{fg2}) - x_2 P_2 v_{g2}$

- at $P_2 = 1.4\text{ bar}$ from Saturated steam table

$h_{f2} = 458.4\text{ kJ/kg}$, $x_2 = 0.8$ (Given)

$h_{fg2} = 2231.9\text{ kJ/kg}$, $P_2 = 1.4\times10^2\text{ kPa}$

$v_{g2} = 1.2363$

$\therefore u_2 = 2105.4544\text{ kJ/kg}$

change in internal energy $= u_2 - u_1 = 688.66\text{ kJ/kg}$

17

4) The following data were obtained with a separating & throttling calorimeter

pressure in pipeline = 1.5 Mpa

condition after throttling = 0.1 Mpa, 110°C

During 5 min, moisture collected in the seperator = 0.15 ltr at 70°C

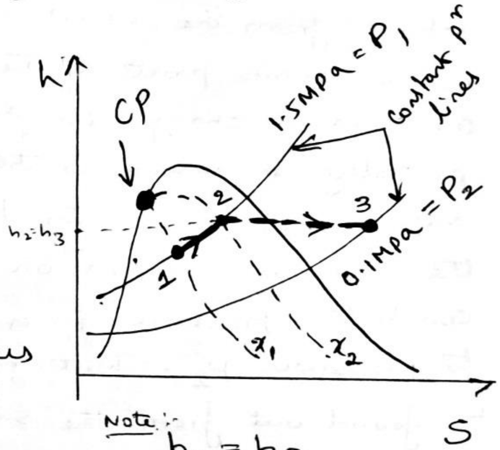
steam condensed after throttling during 5 min = 3.24 kg

Find the quality of steam in the pipe line

→ Let m_1 = mass of moisture collected in a separator in 5 min

& m_2 = mass of steam condensed after throttling in 5 min

then $x_1 = \frac{x_2 m_2}{m_1 + m_2}$



Note:- $h_2 = h_3$

from h-s diagram & steam table

To find x_2:-

at state 3, at 0.1Mpa & 110°C

$h_3 = 2696.2$ kJ/kg

we ~~that~~ know that for a throttling process enthalpy at inlet = enthalpy at outlet

$h_2 = h_3$

$(h_f + x_2 h_{fg})_{1.5Mpa} = h_3 = 2696.2$

$844.89 + x_2 \times 1947.3 = 2696.2$

$\boxed{x_2 = 0.955}$

To find m_1

at 70°C moisture collected in the separator $= V_1 = 0.150$ ltr $= 0.150 \times 10^{-3}$ m^3

to convert m^3 to kg

at 70°C, $v_f = 0.001023$ m^3/kg

$\therefore m_1 = \frac{0.150 \times 10^{-3} \text{ m}^3}{0.001023 \text{ m}^3/\text{kg}} = 0.1462$ kg

$m_2 = 3.24$ kg (Given)

$\therefore \boxed{x_1 = 0.915}$

⑱

5) Steam flows in a pipeline at 1.5 Mpa. After expanding to 0.1Mpa in a throttling calorimeter, the temperature is found to be 120°c. Find the quality of steam in the pipeline. What is the maximum moisture at 1.5 Mpa that can be determined with this set up if at least 5°c of superheat is required after throttling for accurate readings?

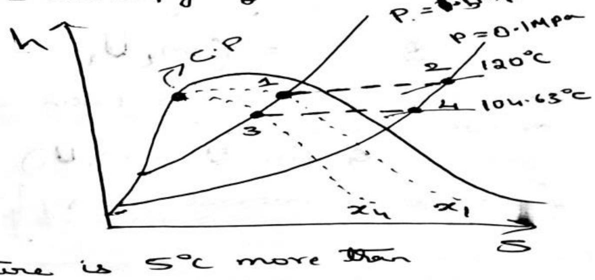
→ At state 2, when P = 0.1Mpa, t = 120°C by interpolation superheated table & by interpolation we get

$h_2 = 2716.2$ kJ/kg

At pressure 1.5 Mpa = 15 bar from saturated steam table

$h_f = 844.89$ & $h_{fg} = 1947.3$ kJ/kg

To find x_1, we know that across throttling valve during throttling process enthalpy at inlet = enthalpy of at outlet



$\therefore \quad h_1 = h_2$

$[h_{f_1} + x_1 h_{fg_1}]_{P=15bar} = 2716.2$

$844.89 + x_1 \times 1947.3 = 2716.2$

$\boxed{x_1 = 0.963}$

To find x_2 :-

Its given that the exit temperature is 5°C more than the saturation temperature at pressure P_2 = 0.1 Mpa = 1 bar

$\therefore$ Temperature at exit of the value for condition 2 is at P = 1 bar from saturated steam table $T_S = 99.63$

$\therefore$ Exit temperature = superheated temperature at exit = 99.63 + 5

T_{sup} for condition 2 = 104.63°C

$\therefore$ from superheated steam table at 1 bar & 104.63°C

$h_{sup} = h_4 = 2685.5$ kJ/kg

Since $h_4 = h_3$

$2685.5 = [h_{f3} + x_3 h_{fg3}]_{P=10bar}$

from saturated steam table

$2685.5 = 844.89 + x_4 \times 1947.3$

$x_3 = 0.948$

dryness fraction = 0.948 = 94.8%

moisture fraction = 1 − 0.948 = 0.052 = 5.2%

The maximum moisture that can be determined with the setup = 5.2%

6) A steam boiler initially contains 5 m^3 of steam & 5 m^3 of water at 1 Mpa. Steam is taken out at constant pressure untill 4 m^3 of water is left. What is the heat transferred during the process

$$\rightarrow \left\{\begin{matrix}\text{heat transfered}\\ \text{during the process}\end{matrix}\right\} = \left\{\begin{matrix}\text{Final energy}\\ \text{stored in saturated}\\ \text{water \& steam}\end{matrix}\right\} - \left\{\begin{matrix}\text{Initial}\\ \text{energy}\\ \text{stored}\end{matrix}\right\} + \left\{\begin{matrix}\text{Energy going}\\ \text{out with}\\ \text{steam removed}\\ \text{of } (m_s) \text{ mass}\end{matrix}\right\}$$

$$Q = (m_2 U_2 - m_1 U_1) + m_s h_g$$

Assuming that steam taken out is dry $(x = 1)$ $\therefore Q_s = m_s h_g$

or we can write :-

$$(m_2 U_2 - m_1 U_1) = Q - m_s h_g \rightarrow ①$$

$$\left\{\text{change in internal energy}\right\} = \left\{\begin{matrix}\text{heat input}\\ \text{to the system}\\ \text{from external}\\ \text{source}\end{matrix}\right\} - \left\{\begin{matrix}\text{heat or energy leaving}\\ \text{with dry steam}\end{matrix}\right\}$$

At 1 Mpa = 10 bar from saturated steam table

$v_f = 0.001127$, $v_g = 0.1944$ m^3/kg , $h_g = 2778.1$ kJ/kg

To find m_s :-

~~To find m_s~~, The initial mass of saturated water & steam in the boiler is given by, at 10 bar $v_{f1} = 0.001127$ m^3/kg

$v_{g1} = 0.1944$ m^3/kg

$$m_{f1} = \frac{V_{f1}}{v_{f1}} = \frac{5}{0.001127} = 4436.5 \text{ kg}$$

$$m_{g1} = \frac{V_{g1}}{v_{g1}} = \frac{5}{0.1944} = 25.72 \text{ kg}$$

$\therefore$ The final mass of saturated water & steam in the boiler is given by

$\because$ pressure is constant

$\therefore$ at P = 10 bar

$v_{f2} = v_{f1}$

$v_{g2} = v_{g1}$

$$m_{f2} = \frac{V_{f2}}{v_{f2}} = \frac{4}{0.001127} = 3549.2 \text{ kg}$$

$$m_{g2} = \frac{V_{g2}}{v_{g2}} = \frac{6}{0.1944} = 30.86 \text{ kg}$$

Mass of steam taken out of the boiler (m_s)

= Total mass of mixture at state 1 − Total mass of mixture at state 2

$$= (m_{f1} + m_{g1}) - (m_{f2} + m_{g2})$$

m_s = ~~894.9 kg~~ 882.16 Kg

Equation ① can we written as

$$U_2 - U_1 = Q - m_s h_g$$

$$[U_{f2} + U_{g2}] - [U_{f1} + U_{g1}] = Q - m_s h_g$$

$$(m_{f2} u_{f2} + m_{g2} u_{g2}) - (m_{f1} u_{f1} + m_{g1} u_{g1}) = Q - m_s h_g \rightarrow ③$$

to find $u_{f2} = h_{f2} - p \cdot v_{f2} = 762.6 - 1.127 = 761.473$ KJ/kg

$u_{f1} = h_{f1} - p v_{f1} = 761.473$ KJ/kg

$u_{g2} = h_{g2} - p \cdot v_{g2} = 2776.2 - 0.1944 = 2581.8$ KJ/kg

$u_{g1} = h_{g1} - p \cdot v_{g1} = 2581.8$ KJ/kg

Substituting in ③ we get

$$(3549.2 \times 761.473 + 30.86 \times 2581.8) - (4436.5 \times 761.473 + 25.72 \times 2581.8) = Q - 882.16 \times 2778.1$$

$$\boxed{Q = 1752.676 \text{ MJ}} = 1.805 \text{ KJ}$$

MODULE V

IDEAL GAS AND REAL GAS MIXTURE

OBJECTIVE: **To Calculate Thermodynamics properties of real gases at all ranges of pressure, temperatures using modified equation of state including Vander Waals equation, Redlich Wong equation and Beattie-Bridgeman equation**

STRUCTURE:

5.1 Ideal gas laws:
5.2 Ideal gas equation (or) characteristic equation for the gases
5.3 Avogadro hypothesis:
5.4 Relations between properties of an ideal gas:
5.5 Relation between specific heat of gases and gas constant
5.6 Psychrometric properties
5.7 Psychrometric Chart
5.8 Ideal gas mixture
5.9 Gibbs daltons law
5.10 Amagats law of partial volume or additive volume:
5.11 Expressions for gas constant for mixture of perfect gas:
5.12 Expression for molecular weight (m) :
5.13 Enthalpy of gaseous mixture (h):
5.14 change in entropy of gaseous mixture (s):
5.15 Partial pressure ratio = mole fraction = volume fraction
5.16 Real gases
  5.17 Vanderwaals equation of state
  5.18 Compressibility ratio
  5.19 Compresibility chart
5.20 Critical Constants of the van der Waals Gas

IDEAL GAS

An ideal gas is an imaginary gas having no forces of intermolecular attraction so that the behavior of a molecule is not influenced by the presence of the other molecules and obeys the lay PV = RT at all pressures and temperatures. This relation Is called the ideal gas equation of state.

5.1 IDEAL GAS LAWS:

1) **BOYLE'S LAW :**The volume of a given gas is inversely proportional to the absolute pressure when temperature remains constant during the change of state"

$V \propto 1/P$ PV = Constant $P_1V_1 = P_2V_2$ = constant

2) **GAY LUSSACS LAW :** The volume of a given gas is directly proportional to the absolute temperature when pressure remains constant during the change of state

$V \propto T$ V/T = Constant $\frac{V_1}{T_1} = \frac{V_2}{T_2} = constant$

3) **CARLE'S LAW :** The pressure of a given gas is directly proportional to the absolute temperature when volume remains constant during the change of state

$P \propto T$ P/T = Constant $\frac{P_1}{T_1} = \frac{P_2}{T_2} = constant$

5.2 Ideal gas equation (or) characteristic equation for the gases:

The relation exist between all three variables P,V,T of the gas under consideration. This relationship is called characteristic gas equation This equation can be derived by combining boyle's and charle's law.

Fig shows that a gas undergoes an arbitrary change from state 1 to state 2 and follows a path 1 – A – 2, i.e a constant pressure process (1 – A) and a constant temperature process (A – 2)

Applying Charles law to the process 1- A , and assuming unit mass of gas

$$\frac{V_1}{V_A} = \frac{T_1}{T_A}$$

$$V_A = \frac{T_2 \times V_1}{T_1} \quad (T_A = T_2) \text{ ………… (1)}$$

Applying Boyle's law to the process A-2

$$\frac{V_2}{V_A} = \frac{P_1}{P_2} \quad (P_A = P_1)$$

$$V_A = \frac{P_2 \times V_2}{P_1} \text{ …………(2)}$$

equating equation (1) and (2) we get

$$\frac{T_2 \times V_1}{T_1} = \frac{P_2 \times V_2}{P_1}$$

$\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$

Since state 1 and 2 are arbitrarily selected, it follows that

$\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2} = \frac{P_3 \times V_3}{T_3} = \frac{P_4 \times V_4}{T_4}$ = constant …………(3)

The constant is known as the **CHARACTERISTIC GAS CONSTANT**

Equation 3 can be written as

$\frac{P \times V}{T} = R$ for unit mass

PV = mRT for mass m

5.3 Avagadro hypothesis:

It states that "**Equal volume of all ideal gases under identical conditions of temperature and pressure have equal number of molecules**"

that is 1 mole of any gas contains 6.022×10^{23} MOLECULES And the number is called asAVAGADRO'S NUMBER

He proved that at normal temperature and pressure (NTP) that is at $T = 0^0$ C 0R 273 K , P = 760 mm of Hg = 1.013×10^5 N/m^2 the volume of 1 Kg mole ($\overline{V}$) of the gas is equal to 22.416 m^3 .

The volume per mole of a substance is called MOLAR VOLUME denoted by $\overline{V}$

$$\overline{V} = \frac{V}{n}$$

where , n = number of moles = $\frac{m}{M}$

PV = mRT

PV = n m R T

$P\overline{V}$ n = n m R T

$P\overline{V}$ = M R T

The quantity " MR" is a UNIVERSAL GAS CONSTANT ($\bar{R}$)

$P\overline{V} = \bar{R}$ T

The universal gas constant is a Physical constant whose value is given by

$\bar{R} = \frac{P \times \overline{V}}{T} = 1.013 \times 10^5 \times \frac{22.416}{273} =$ 8.31773 K J / Kg mol K

$\bar{R}$ = 8.31773 K J / Kg mol K

5.4 Relation between properties of an ideal gas:

1) INTERNAL ENERGY AND ENTHALPY CHANGE OF AN IDEAL GAS:

i) Constant volume specific heat for an ideal gas

$C_V = \frac{du}{dT}$ where u = internal energy

ii) **Change in internal energy** = du = C_V . dT this equation hold good for an ideal gas for any process.

NOTE : For any other substance it is true only for the constant volume process

$$\int_1^2 du = C_V \int_1^2 dT$$

$u_2 - u_1 = C_v (T_2 - T_1)$ …….. (4)

iii) **constant pressure specific heat for an ideal gas**

$C_P = \frac{dh}{dT}$ where h = Enthalpy

Change in enthalpy = dh = C_P . dT this equation hold good for an ideal gas for any process.

NOTE : For any other substance it is true only for the constant pressure process

$$\int_1^2 dh = C_P \int_1^2 dT$$

$h_2 - h_1 = C_P (T_2 - T_1)$………..(5)

5.5 Relation between specific heat of gases and gas constant :

h = u + pv

where, h = enthalpy

u = internal energy

h = u + RT

in differential form

dh = du + RdT

Substituting for du and dh we get

C_p dT = $C_v$du +RdT

$C_p = C_v + R$

$R = C_p - C_v$

The ratio of specific heats C_p and C_v is again a constant and is a function of temperature only and is represented by γ (gama)

$\gamma = \frac{C_P}{C_V}$ ………(6)

$R = C_p - C_v$ ……..(7)

$\frac{R}{C_V} = \frac{C_P}{C_V} - 1$ (dividing by C_V)

by rearranging we get

$$C_V = \frac{R}{\gamma - 1}$$

Similarly by dividing equ (7) by C_P we get

$$C_P = \frac{R \times \gamma}{\gamma - 1}$$

Psychrometry

Psychrometry is the study of the properties of mixtures of air and water vapour.

5.6 Psychrometric properties:

Dry-bulb temperature (DBT)

The dry-bulb temperature is the temperature indicated by a thermometer exposed to the air in a place sheltered from direct solar radiation. The term dry-bulb is customarily added to temperature to distinguish it from wet-bulb and dewpoint temperature

Wet-bulb temperature (WBT)

The thermodynamic wet-bulb temperature is a thermodynamic property of a mixture of air and water vapor. The value indicated by a wet-bulb thermometer often provides an adequate approximation of the thermodynamic wet-bulb temperature.

Dew point temperature

The saturation temperature of the moisture present in the sample of air, it can also be defined as the temperature at which the vapour changes into liquid (condensation)

Specific Humidity

Specific humidity is defined as the proportion of the mass of water vapor and mass of the moist air sample (including both dry air and the water vapor); it is closely related to humidity ratio and always lower in value.

Absolute humidity

The mass of water vapor per unit volume of air containing the water vapor. This quantity is also known as the water vapor density.

Relative humidity

The ratio of the vapor pressure of moisture in the sample to the saturation pressure at the dry bulb temperature of the sample.

Specific enthalpy

Analogous to the specific enthalpy of a pure substance. In psychrometrics, the term quantifies the total energy of both the dry air and water vapour per kilogram of dry air

Specific volume

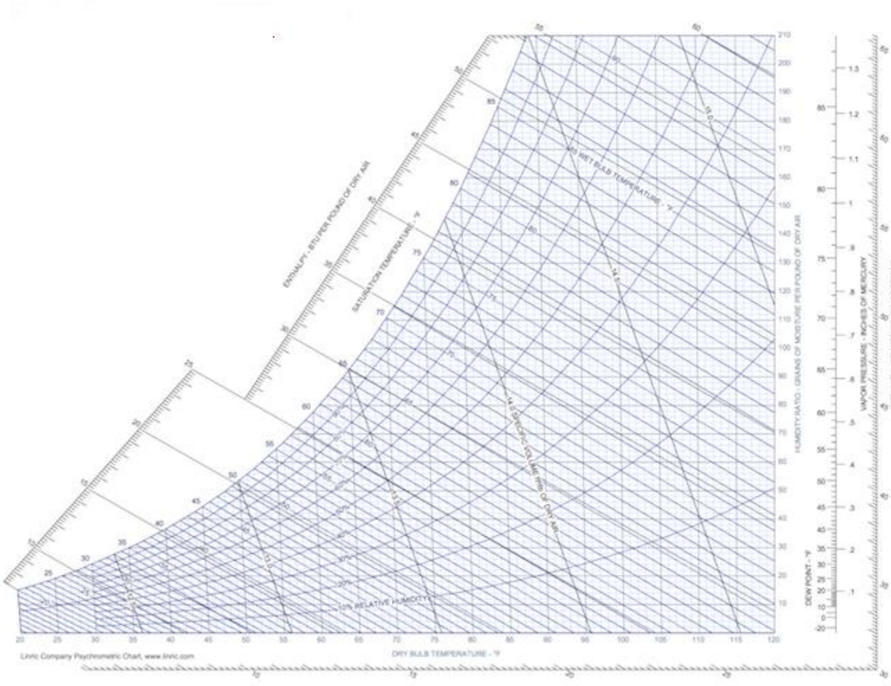
Analogous to the specific volume of a pure substance. However, in psychrometrics, the term quantifies the total volume of both the dry air and water vapour per unit mass of dry air.

Psychrometric ratio

The psychrometric ratio is the ratio of the heat transfer coefficient to the product of mass transfer coefficient and humid heat at a wetted surface. It may be evaluated with the following equation

5.7 Psychrometric chart

A Psychrometric chart raphically represents the thermodynamic properties of moist air. Standard psychrometric charts are bounded by the dry-bulb temperature line (abscissa) and the vapour pressure or humidity ratio (ordinate). The Left Hand Side of the psychrometric chart is bounded by the saturation line. Figur shows the schematic of a psychrometric chart. Psychrometric charts are readily available for standard barometric pressure of 101.325 kPa at sea level and for normal temperatures (0-50˚C).



- <u>Dry-bulb temperature</u> (*DBT*) is that of an air sample, as determined by an ordinary thermometer. It is typically plotted as the <u>abscissa (horizontal axis)</u> of the graph. The SI units for temperature are <u>kelvins</u> or <u>degrees Celsius</u>; other units are <u>degrees Fahrenheit</u> and <u>degrees Rankine</u>.
- <u>Wet-bulb temperature</u> (*WBT*) is that of an air sample after it has passed through a constant-pressure, ideal, adiabatic saturation process, that is, after the air has passed over a large surface of liquid water in an insulated channel. In practice this is the reading of a thermometer whose sensing bulb is covered with a wet sock evaporating into a rapid stream of the sample air (see <u>Hygrometer</u>). When the air sample is pre-saturated with water, the WBT will read the same as the DBT. The slope of the line of constant WBT reflects the heat of vaporization of the water required to saturate the air of a given relative humidity.

- Dew point temperature (*DPT*) is the temperature at which a moist air sample at the same pressure would reach water vapor "saturation." At this point further removal of heat would result in water vapor condensing into liquid water fog or, if below freezing point, solid hoarfrost. The dew point temperature is measured easily and provides useful information, but is normally not considered an independent property of the air sample as it duplicates information available via other humidity properties and the saturation curve.
- Relative humidity (*RH*) is the ratio of the mole fraction of water vapor to the mole fraction of saturated moist air at the same temperature and pressure. RH is dimensionless, and is usually expressed as a percentage. Lines of constant RH reflect the physics of air and water: they are determined via experimental measurement. The concept that air "holds" moisture, or that moisture "dissolves" in dry air and saturates the solution at some proportion, is erroneous see relative humidity for further details.
- Humidity ratio is the proportion of mass of water vapor per unit mass of dry air at the given conditions (DBT, WBT, DPT, RH, etc.). It is also known as the moisture content or mixing ratio. It is typically plotted as the ordinate (vertical axis) of the graph. For a given DBT there will be a particular humidity ratio for which the air sample is at 100% relative humidity: the relationship reflects the physics of water and air and must be determined by measurement. The dimensionless humidity ratio is typically expressed as grams of water per kilogram of dry air, or grains of water per pound of air (7000 grains equal 1 pound).
- Specific enthalpy, symbolized by *h*, is the sum of the internal (heat) energy of the moist air in question, including the heat of the air and water vapor within. Also called heat content per unit mass. In the approximation of ideal gases, lines of constant enthalpy are parallel to lines of constant WBT. Enthalpy is given in (SI) joules per kilogram of air, or BTU per pound of dry air.

5.8 Ideal gas mixture:

Consider a mixture of perfect gases A, B C etc existing in equilibrium at pressure P and occupying a volume V , at temperature T . Each constitutes occupies the same volume that the entire mixture occupies and each constituent is at same temperature of the mixture

Constituents	Properties	Mixture
A	P_a , V , T , m_a , n_a	P , V , T , m , n
B	P_b , V , T , m_b , n_b	
C	P_c , V , T , m_c , n_c	

From the table it can be seen that (taking mass as an example) the total mass of the mixture is equal to the sum of the masses of the individual gases, $m = m_a + m_b + m_c$

- **Mass fraction (x_i) :**

  Mass fraction of the constituent gas is the ratio of the mass of the constituent gas to the total mass of the mixture of perfect gases

$$\boldsymbol{x_a} = \frac{m_a}{m} , \boldsymbol{x_b} = \frac{m_b}{m} , \boldsymbol{x_c} = \frac{m_c}{m}$$

$$m = m_a + m_b + m_c$$

$$\frac{m}{m} = \frac{m_a}{m} + \frac{m_b}{m} + \frac{m_c}{m}$$

$$1 = \boldsymbol{x_a} + \boldsymbol{x_b} + \boldsymbol{x_c}$$

- **Mole (n) :** A mole of a substance has a mass numerically equal to the weight of the substance

- **Mole fraction (y_i) :** The total number of moles of the mixture is equal to the sum of the moles of the individual gas

$$n = n_a + n_b + n_c$$

The mole fraction of any component is the ratio of the number of moles of the constituent gas to the total number of moles of the mixture of perfect gases

mole fraction of gas A, B and C is given by $y_a = \frac{n_a}{n}$, $y_b = \frac{n_b}{n}$, $y_c = \frac{n_c}{n}$ respectively

$$n = n_a + n_b + n_c$$

$$\frac{n}{n} = \frac{n_a}{n} + \frac{n_b}{n} + \frac{n_c}{n}$$

$$1 = y_a + y_b + y_c$$

5.9 Gibbs daltons law:

The total pressure of a mixture of perfect gases is equal to the sum of the partial pressure of the constituent gases if each component exists separately at the same temperature and volume as that of the mixture. If this component pressure is denoted by p_i , then Daltons law can be written as

$$P = \sum_{i=1}^{j} P_i$$

Considering 3 gases A,B , C

GASES A, B, C	=	GAS A V, T, P_a , m_a , n_a	+	GAS B V, T, P_b , m_b, n_b	+	GAS C V, T, P_c , m_c , n_c
Schematic representation of Daltons law of partial pressure						

$$P = P_a + P_b + P_c$$

$$\frac{P}{P} = \frac{P_a}{P} + \frac{P_b}{P} + \frac{P_c}{P}$$

$$1 = P_{fa} + P_{fb} + P_{fc}$$

where P_f is pressure fraction

in general we can write $P_f = \sum_{i=1}^{j} P_{fi} = 1$

- **Partial pressure of a gas** (P_i) in a mixture of perfect gases is the pressure that it would exert if it alone occupied the whole volume of the mixture at same temperature.
-

5.10 Amagats law of partial volume or additive volume:

It states that "Total volume (V) of a mixture of gases is equal to the sum of the volume, each component would occupy if each component exists separately at the same temperature and pressure as that of the mixture". If its component is denoted by V_i , Amagats law can be written as

$$V = \sum_{i=1}^{j} V_{fi}$$

Considering 3 gases we can write $V = V_a + V_b + V_c$

GASES A, B, C	=	GAS A P, T, V_a , m_a , n_a	+	GAS B P, T, V_b , m_b, n_b	+	GAS C P, T, V_c , m_c , n_c
Schematic representation of Amagats law of partial volume						

$$V = V_a + V_b + V_c$$

$$\frac{V}{V} = \frac{V_a}{V} + \frac{V_b}{V} + \frac{V_c}{V}$$

$$1 = V_{fa} + V_{fb} + V_{fc}$$

where V_f is volume fraction

in general we can write $V_f = \sum_{i=1}^{j} V_{fi} = 1$

5.11 Expression for gas constant for mixture of perfect gas:

PV = mRT

For 3 gases A,B, C which are at same temperature and volume as the mixture we can write

$P_a V = m_a R_a T_a$

$P_b V = m_b R_b T_b$

$P_c V = m_c R_c T_c$

But from Daltons law of partial pressures

$P = P_a + P_b + P_c$

$$\frac{\mathrm{mRT}}{\mathrm{V}} = \frac{\mathrm{m_a R_a T_a}}{\mathrm{V}} + \frac{\mathrm{m_b R_b T_b}}{\mathrm{V}} + \frac{\mathrm{m_c R_c T_c}}{\mathrm{V}}$$

$$R = x_a . R_a + x_b . R_b + x_c . R_c$$

5.12 Expression for molecular weight (M) :

PV = mRT

wkt $n = \frac{m}{M}$ where $\bar{R} = Universal\ gas\ constant$, M = Molecular weight

PV = nMRT

PV = n $\bar{R}$ T where $\bar{R} = Universal\ gas\ constant = MR$

$P\bar{v} = \bar{R}\,T$ Where $\bar{v}$ = specific volume = $\frac{V}{n}$

Considering 3 gases A,B,C

$$R_a = \frac{\bar{R}}{M_a}, \quad R_b = \frac{\bar{R}}{M_b}, R_c = \frac{\bar{R}}{M_c}$$

Substituting in equation R we get

$$R = x_a \, . \, R_a + x_b \, . \, R_b + x_c \, . \, R_c$$

$$\frac{\bar{R}}{M} = x_a \frac{\bar{R}}{M_a} + x_b \frac{\bar{R}}{M_b} + x_c \frac{\bar{R}}{M_c}$$

$$\frac{1}{M} = \frac{x_a}{M_a} + \frac{x_b}{M_b} + \frac{x_c}{M_c}$$

$$M = \frac{1}{\frac{x_a}{M_a} + \frac{x_b}{M_b} + \frac{x_c}{M_c}}$$

Alternate expression for molecular weight

wkt, $m = n\,M$

for 3 gases we can write

$m_a = n_a \, . \, M_a$, $m_b = n_b \, . \, M_b$, $m_c = n_c \, . \, M_c$

$m = m_a + m_b + m_c = n_a \, . \, M_a + n_b \, . \, M_b + n_c \, . \, M_c = n.M$

$M = y_a M_a + y_b M_b + y_c M_c$

Internal energy of gaseous mixture (U) :

Internal energy of a mixture of ideal gases is equal to the sum of the individual energies of the constituent gases at the same pressure and temperature of the mixture.

$U = U_a + U_b + U_c$

$m.u = m_a u_a + m_b u_b + m_c u_c$

where u = specific internal energy = $\frac{U}{m}$

by differentiating we get

$m \, . \, du = m_a \, . \, du_a + m_b \, . \, du_b + m_c \, . \, du_c$

wkt $du = C_v \, dT$

$m\, C_v \, dT = m_a C_{va} \, dT + m_b C_{vb} \, dT + m_c C_{vc} \, dT$

$$C_V = \frac{m_a}{m} C_{Va} + \frac{m_b}{m} C_{Vb} + \frac{m_c}{m} C_{Vc}$$

$$C_v = x_a C_{va} + x_b C_{vb} + x_c C_{vc}$$

5.13 Enthalpy of gaseous mixture (h):

The enthalpy of a mixture of perfect gas is equal to sum of the enthalpies of the constituent gases

$H = H_a + H_b + H_c$

$m.h = m_a h_a + m_b h_b + m_c h_c$

where h = specific enthalpy = $\frac{H}{m}$

by differentiating we get

$m \,.\, dh = m_a \,.\, dh_a + m_b \,.\, dh_b + m_c \,.\, dh_c$

wkt $dh = C_p\, dT$

$m\, C_p\, dT = m_a C_{pa}\, dT + m_b C_{pb}\, dT + m_c C_{pc}\, dT$

$$C_p = \frac{m_a}{m} C_{Pa} + \frac{m_b}{m} C_{Pb} + \frac{m_c}{m} C_{Pc}$$

$$C_P = x_a C_{Pa} + x_b C_{Pb} + x_c C_{Pc}$$

5.14 Change in entropy of gaseous mixture (s):

$S = S_a + S_b + S_c$

$m.s = m_a s_a + m_b s_b + m_c s_c$

where s = specific entropy = $\frac{S}{m}$

by differentiating we get

$m \,.\, ds = m_a \,.\, ds_a + m_b \,.\, ds_b + m_c \,.\, ds_c$

$ds = x_a\, ds_a + x_b\, ds_b + x_c\, ds_c$

Change in entropy of a gas can be calculated using the equation , $ds_a = \left[C_P \ln\frac{T_2}{T_1} - R \ln\frac{P_2}{P_1}\right]_a$,for gas A . Similarly for all gases we can calculate.

5.15 For mixture of perfect gases show that partial pressure ratio = mole fraction = volume fraction

$PV = mRT$

$PV = nmRT$

$PV = n\bar{R}T$ for a mixture ……..(1)

Let us consider a GAS A

$P_aV = n_a\bar{R}T$ (applying Daltons law of partial pressure , i.e at same volume and temperature) … (2)

Dividing 2 by 1 we get

$$\frac{P_aV}{PV} = \frac{n_a\bar{R}T}{n\bar{R}T}$$

$$\frac{P_a}{P} = \frac{n_a}{n} = X_a$$

Again

$PV = n\bar{R}T$ for a mixture ……..(4)

$PV_a = n_a\bar{R}T$ (applying Amagats law , i.e at same pressure and temperature) … (5)

dividing 5 by 4 we get

$\frac{V_a}{V} = \frac{n_a}{n} = X_a$ ……….(6)

From equation (6) and (3)

$\frac{P_a}{P} = \frac{V_a}{V} = \frac{n_a}{n} = X_a$ Hence proved

5.16 REAL GASES:

I. Real gases doesn't obey ideal gas equation at all pressures and temperatures

II. Ideal gas equation is given by

- $PV = m\,RT$
- $PV = n\,\bar{R}\,T$, $\bar{R} = MR$
- $P\,v = RT$, where $v = V/m$
- $P\bar{v} = \bar{R}T$, where $\bar{v} = V/n$

III. A gas which follows gas laws at all ranges of pressure and temperature can be considered as an ideal gas. But no such gas exists in nature.

IV. The REAL GASES obey very closely to ideal gas or gas laws equation when the pressure is very small or temperature is very large

V. When the pressure increases the intermolecular forces of attraction and repulsion increases, and the volume of the molecules becomes appreciable compared to the total volume of the gases. Therefore the real gases deviate considerably from the ideal gas equation.

The behaviour of real gas approaches closely to that of the ideal gas provided the following assumptions are valid:

- Any finite volume of a gas consists of a very large number of molecules
- The molecules are separated by distances larger than compared to their own dimensions and are in a state of continuous motion.
- Molecules exert no force on one another except when they collide
- Collisions of molecules with one another and with the walls of the container are perfectly elastic.
- If the conditions of temperature and pressure are such that the assumptions are not valid then the real gases starts deviating from the ideal gas.

5.17 VANDERWAALS EQUATION OF STATE:

The ideal gas law treats the molecules of a gas as point particles with perfectly elastic collisions. This works well for dilute gases in many experimental circumstances. But gas molecules are not point masses, and there are circumstances where the properties of the molecules have an experimentally measurable effect. A modification of the ideal gas law was proposed by Johannes D. van der Waals in 1873 to take into account molecular size and molecular interaction forces. It is usually referred to as the van der Waals equation of state.

$$\left[P + a\left(\frac{n}{V}\right)^2\right]\left(\frac{V}{n} - b\right) = RT$$

The constants a and b have positive values and are characteristic of the individual gas. The van der Waals equation of state approaches the ideal gas law PV=nRT as the values of these constants approach zero. The constant a provides a correction for the intermolecular forces. Constant b is a correction for finite molecular size and its value is the volume of one mole of the atoms or molecules. R is universal gas constant

5.18 CRITICAL CONSTANTS OF THE VAN DER WAALS GAS:

We saw in our discussion of critical phenomena that the mathematical definition of the critical point is,

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \qquad (1)$$

and

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 \quad . \qquad (2)$$

In other words, the critical isotherm on a p-V diagram has a point of inflection. Equations (1) and (2) constitute a set of two equation in two unknowns, V, and T. One can test to see if an approximate equation of state gives a critical point by calculating these two derivatives for the equation of state and trying to solve the pair of equations. If a solution exists (and T and V are neither zero or infinity) then we say that the equation of state has a critical point.

Let's use this test to see if a van der Waals gas has a critical point. First we have to solve the van der Waals equation of state for pressure, p,

$$p = \frac{nRT}{V-nb} - a\frac{n^2}{V^2}. \qquad (3)$$

Now we can take the derivatives in Equations 1 and 2 and set them (independently) equal to zero.

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{nRT}{(V-nb)^2} + 2a\frac{n^2}{V^3} = 0 \qquad (4)$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2nRT}{(V-nb)^3} - 6a\frac{n^2}{V^4} = 0. \qquad (5)$$

In order to stress that from here on the problem is pure algebra, let's rewrite the simultaneous equations that must be solved for the two unknowns V and T (which solutions we will call V_C and T_C),

$$-\frac{nRT}{(V-nb)^2} + 2a\frac{n^2}{V^3} = 0 \qquad (6)$$

$$\frac{2nRT}{(V-nb)^3} - 6a\frac{n^2}{V^4} = 0. \qquad (7)$$

There are several ways to solve simultaneous equations. One way is to multiply Equation (6) by,

$$\frac{2}{V-nb}$$

to get

$$-\frac{2nRT}{(V-nb)^3} + 4a\frac{n^2}{V^3(V-nb)} = 0. \qquad (8)$$

Now add equations (7) and (8). Note that in this addition the terms containing T will cancel out leaving,

$$-\frac{6an^2}{V^4} + 4a\frac{n^2}{V^3(V-nb)} = 0. \qquad (9)$$

Divide Equation (9) by $2an^2$ and multiply it by V^3 (and bring the negative term to the other side of the equal sign) to get,

$$\frac{2}{(V-nb)} = \frac{3}{V}, \qquad (10)$$

which is easily solved to get

$$V = V_c = 3nb. \qquad (11)$$

To find the critical temperature, substitute the critical volume from Equation (11) into one of the derivatives (which equals zero) say Equation (6). This gives,

$$-\frac{nRT}{(3nb-nb)^2} + 2a\frac{n^2}{(3nb)^3} = 0, \qquad (12)$$

which "cleans up" to give,

$$\frac{RT}{4} = \frac{2a}{27b}, \qquad (13)$$

or

$$T = T_c = \frac{8a}{27bR}. \qquad (14)$$

The critical pressure is obtained by substituting V_C and T_C into the van der Waals equations of state as solved for p in Equation (3).

$$p_c = \frac{nRT_c}{V_c - nb} - a\frac{n^2}{V_c^2}$$
$$= \frac{nR\left(\dfrac{8a}{27bR}\right)}{3nb-nb} - a\frac{n^2}{(3nb)^2}. \qquad (15\ a,b)$$

This simplifies to,

$$p_c = \frac{a}{27b^2}. \qquad (16)$$

Our conclusion is that the van der Waals equation of state does give a critical point since the set of simultaneous equations (Equations (1) and (2)) has a unique solution.

The van der Waals equation of state is still an approximate equation of state and does not represent any real gas exactly. However, it has some of the features of a real gas and is therefore useful as the next best approximation to a real gas. We will be deriving thermodynamic relationships (equations) using the ideal gas approximation. We can rederive some of these equations using the van der Walls equation of state in order to see how these relationships are.

5.19 Compressibility factor:

The assumption of ideal gas relation implies that:

- the gas particles take up negligible volume
- the intermolecular potential energy between particles is small
- particles act independent of one another

However, real gases deviate from ideal gas behavior. This deviation at given temperature and pressure can be accurately accounted for by introduction of a correction factor called the compressibility factor Z.

$$Z = \frac{Pv}{RT} \qquad or \qquad Pv = ZRT$$

or Z = v_{actual} / v_{ideal}. Obviously, Z=1 for ideal gases.

Gases behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures.

$$P_R = \frac{P}{P_{cr}} \qquad and \qquad T_R = \frac{T}{T_{cr}}$$

Here P_R and T_R are called the reduced pressure and temperature, respectively.

By curve-fitting all the data, the general compressibility chart is obtained which can be used for all gases.

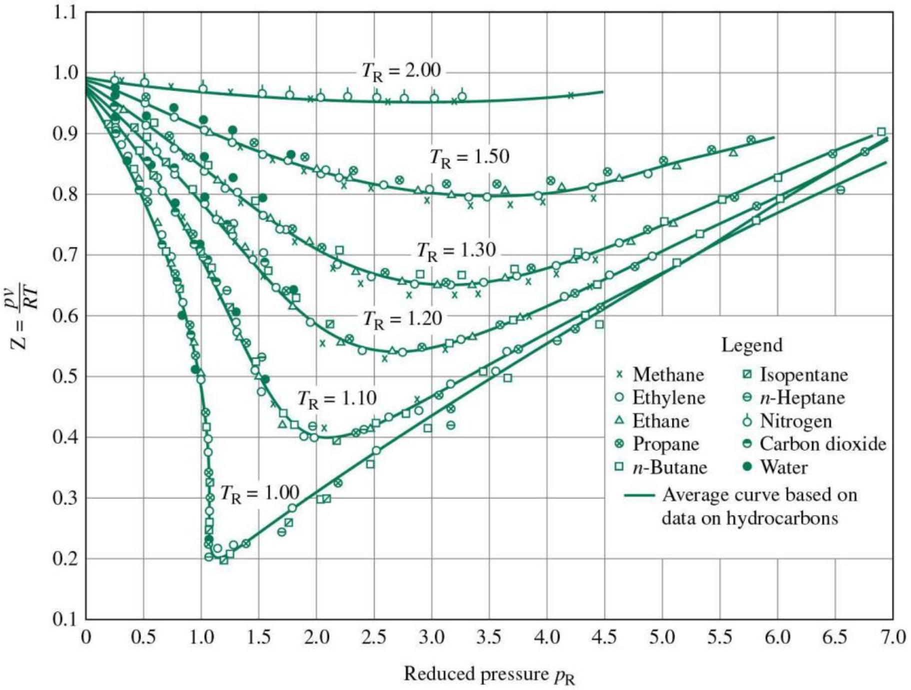
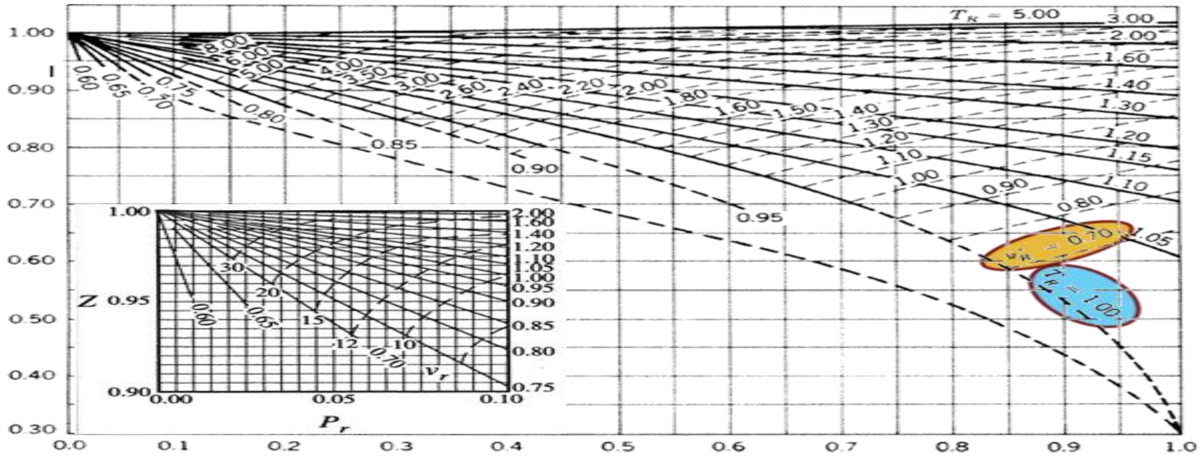


Fig. 6: Z factor, general compressibility chart.

From the Z chart, one can conclude:

- at very low pressure ($P_R <<1$), the gases behave as an ideal gas regardless of temperature
- at high temperatures ($T_R>2$), ideal gas behavior can be assumed.
- the deviation is highest in the vicinity of the critical point.

5.20 COMPRESSIBILITY CHART:



- This chart is the low-pressure chart, for reduced pressures between 0 and 1 as you can see on the x-axis.
- Z is plotted on the y-axis.
- The solid curves on this diagram are the family of curves for constant reduced temperature. These curves generally run from the upper left-hand corner downwards and towards the right-hand edge of the diagram.
- You can tell the solid curves represent constant TR by reading the labels on the curves for TR = 1.0 and TR = 5.0 highlighted on the chart with yellow circles.
- The dashed curves on this diagram are the family of curves for constant ideal reduced molar volume.
- You can tell the dashed curves represent constant VR-ideal by reading the label on the curve for VR-ideal = 0.07, highlighted on the chart with a light blue circle.
- Inset on this diagram and highlighted in pale green is a very handy enlargement of the top corner of the chart, where reduced pressure is between 0 and 0.1.

The Redlich–Kwong equation is formulated as:

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}\, V_m\,(V_m + b)}$$

where:

- P is the gas pressure
- R is the gas constant,
- T is temperature,
- V_m is the molar volume (V/n),
- a is a constant that corrects for attractive potential of molecules, and
- b is a constant that corrects for volume.

- **Beattie-Bridgeman Equation of State:**

The Beattie-Bridgeman equation of state was proposed in 1928. It has five experimentally determined constants.

$$P = \frac{R_u T}{\bar{v}^2}\left(1 - \frac{c}{\bar{v}T^3}\right)(\bar{v} + B) - \frac{A}{\bar{v}^2}$$

$$A = A_0\left(1 - \frac{a}{\bar{v}}\right) \quad B = B_0\left(1 - \frac{b}{\bar{v}}\right)$$

IMPORTANT QUESTIONS:

1. State Gibbs Daltons law of partial pressures and hence derive an expression for the gas R of a mixture of gas
2. Write a brief note on Compressibility factor and compressibility chart
3. Derive critical constants of the Van-der-Waals gas.
4. A cylinder of volume $1m^3$ is filled with a mixture of 1 Kg of CO_2 and 2 Kg of N_2 at 27 degree Celsius. Determine 1. Pressure of the mixture 2) gas constant for the mixture 4) Mole fraction of N_2 and CO_2 and 4) Molecular weight of the mixture
5. Determine the mass of nitrogen contained in a $35m^3$ vessel at 200bar and 200K by using ideal gas equation and Compressibility chart.
6. Determine the pressure exerted by CO_2 in a container of $1.5m^3$ capacity when it contains 5 Kg at 27 degree Celsius 1) using idea gas equation and 2) Van-der-Waal's equation

   Solution:

   i) Ideal gas equation PV = mRT

   $$p = \frac{m \times \overline{R} \times T}{V \times M} = \frac{5 \times 8.3143 \times 300}{1.5 \times 44}$$

   $$\mathbf{p = 188.96\ KN/m^2}$$

   ii) Vander Waal's Equation

   $(p - a/v^2)(v-b) = RT$

v =V/m =1.5/5 =0.3
a = 36.56kN $m^4/(kgmol)^2$
b= 0.0428 m^3/kg mol
after substituting we get
p = 187.48 kN/m^2

7. A mixture of gases has the following volumetric composition CO_2 = 12% , O_2 = 4% , N_2 = 82%, CO = 2% Calculate : i)Gravimetric Composition ii)Molecular Weight of mixture iii) R of mixture

Solution:

Gas	Volume fraction(y)	Molecular Weight(M)	Product(M×y)	Mass Fraction $(x = \frac{M\times y}{\sum M_i y_i})$
CO_2	0.12	44	5.28	0.1755
O_2	0.04	32	1.28	0.0425
N_2	0.82	28	22.96	0.7632
CO	0.02	28	0.56	0.0186
			Total	30.08

Molecular weight of the mixture = 30.08

R of mixture = $\overline{R}/M$ = 8.314/30.18 = 0.2764 kJ/kg K

LIST OF FORMULAS:

1. $m = m_1 + m_2 + \ldots$

2. $n = n_1 + n_2 + \ldots$

3. Mass fraction = $x_i = m_i / m_{mix}$

4. Mole fraction = $y_i = n_i/n_{mix}$

5. $P_i/P = V_i/V = n_i/n = y_i$

6. $M = \sum y_i M_i$

7. n = m/M

8. $R = \frac{\overline{R}}{M}$

9. $(P - a/v^2)(v-b) = RT$

10. $Z = \frac{PV}{RT}$

OUTCOME: Describe ideal gas mixture composition in terms of mass fractions or mole fractions. use the Dalton model to relate pressure, volume, and temperature and to calculate changes in U , H, and S for ideal gas mixtures. Apply mass, energy, and entropy balances to systems involving ideal gas mixtures, including mixing processes.

FURTHER READING:

- An Introduction to Thermodynamcis, Y.V.C.Rao, Wiley Eastern, 1993,
- B.K Venkanna, Swati B. Wadavadagi "Basic Thermodynamics'
- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
- http://www.nptel.ac.in/courses/112104113/4#