



# Basic Thermodynamics BME304

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**Introduction and Review of fundamental concepts:** Thermodynamic definition and scope, Microscopic and Macroscopic approaches. Characteristics of system boundary and control surface, examples. Thermodynamic properties; definition and units, intensive, extensive properties, specific properties, pressure, specific volume, Thermodynamic state, state point, state diagram, path and process, quasi-static process, cyclic and non-cyclic; processes; Thermodynamic equilibrium; definition, mechanical equilibrium; diathermic wall, thermal equilibrium, chemical equilibrium (*The topics are Only for Self-study and not to be asked in SEE. However, may be asked for CIE*)

**Zeroth law of thermodynamics**, Temperature; concepts, scales, international fixed points and measurement of temperature. Constant volume gas thermometer, constant pressure gas thermometer, mercury in glass thermometer, thermocouples, electrical resistance thermometer. Numerical.

**Work and Heat**: Mechanics, definition of work and its limitations. Thermodynamic definition of work; examples, sign convention. Displacement work; as a part of a system boundary, as a whole of a system boundary, expressions for displacement work in various processes through p-v diagrams. Shaft work; Electrical work. Other types of work. Heat; definition, units and sign convention. Problems





**First Law of Thermodynamics:** Joules experiments, equivalence of heat and work. Statement of the First law of thermodynamics, extension of the First law to non - cyclic processes, energy, energy as a property, modes of energy, Problems.

**Extension of the First law to control volume**; steady flow energy equation (SFEE), Problems





**Second Law of Thermodynamics:** Limitations of first law of thermodynamics, Thermal reservoir, heat engine and heat pump: Schematic representation, efficiency and COP. Reversed heat engine. Kelvin - Planck statement of the Second law of Thermodynamics; PMM I and PMM II, Clausius statement of Second law of Thermodynamics, Equivalence of the two statements; Carnot cycle, Carnot principles. Problems

**Entropy:** Clausius 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. Problems





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. Problems

**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. Problems

**Ideal gases:** Ideal gas mixtures, Daltons law of partial pressures, Amagat's law of additive volumes, evaluation of properties of perfect and ideal gases, Air- Water mixtures and related properties (*Processes are not to be asked for SEE*).

**Real gases** – Introduction, Van-der Waal's Equation of state, Van-der Waal's constants in terms of critical properties, Beattie-Bridgeman equation, Law of corresponding states, compressibility factor; compressibility chart. Difference between Ideal and real gases.

**Thermodynamic relations:** Maxwell's equations, TdS equation. Ratio of Heat capacities and Energy equation, Joule-Kelvin effect, Clausius-Clapeyron equation.





### **<u>MODULE 1</u> FUNDAMENTAL CONCEPTS & DEFINITIONS**

What is Thermodynamics?

Thermodynamics is the branch of physics that deals with the relationships between heat and other forms of energy. In particular, it describes how thermal energy is converted to and from other forms of energy and how it affects matter.









## System, System boundary & Surroundings:

### **SYSTEM:**

A Thermodynamics System is a prescribed region in space or a finite quantity of matter considered for the study.









### **SYSTEM BOUNDARY :**

- It is an real (that surrounds the matter considered for the study) or imaginary surface (that surrounds the region considered for the study) which surrounds the system.
- > The System Boundary may be Fixed (Rigid Walls of cylinder) or Movable (Piston head reciprocating motion)



Piston Cylinder Arrangement Department of Mechanical Engineering Compressor / Turbine





### **SURROUNDINGS:**

The region or matter outside the system is called as surroundings or Environment.







## **Types of Systems:**

	OPEN SYSTEM	CLOSED SYSTEM	ISOLATED SYSTEM
ENERGY TRANSFER	YES	YES	NO
MASS TRANSFER	YES	NO	NO
EXAMPLES	Pumps , Compressors , turbine , Valves and Heat Exchanger etc.	Sealed Tank ,Piston cylinder devices without valves etc.	Universe, Hot coffee in a well insulated flask, Thermo flask









## **Control volume & Control surface:**

#### **CONTROL VOLUME:**

- > Control volume in thermodynamics is basically defined as one fixed area in space upon which the study will be focused
- > A mass or matter will enter in to the system and will leave the system continuously. Example Turbine , Compressor etc.
- > Control volume system will interact with its surrounding in terms of heat energy and work energy.
- Hence Open System is also termed as Control volume System (Mass transfer)

#### **CONTROL SURFACE:**

- The real or imaginary surface that is fixed in shape, position and orientation Surrounding the Control Volume is called as Control Surface
- ➢ Boundary of OPEN SYSTEM is usually called as Control surface







### **Microscopic & Macroscopic Approach**

#### Microscopic Approach :

- > This approach considers that matter is composed of molecules.
- Each of these molecules have definite velocity & energy at a given instant.
- > Thus Microscopic viewpoint focus on molecules , atoms of even an electron and nucleus individually.

### In Microscopic approach:

•Molecular theory of matter is assumed.

•Many parameters are required to specify the state of a system.

•For every molecule,3-position Coordinates & 3-velocity Coordinates are required.

•For 1 mole of a gas,(6\*6.023\*10^23) coordinates are required.

•They can't be easily measured.

•They can't be felt by sense perceptions.









#### Macroscopic Approach:

It considers the effect of the action **of many molecules** instead of single molecules.

#### In Macroscopic approach:

•No assumptions are to be made regarding the structure of matter.

•Very few parameters are required to specify the **STATE** of a system like Pressure & Volume, Volume & Temp, Temperature & Pressure.

•They can be easily measured.

•They can be felt by sense perceptions.





= velocity, momentum

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### **Difference between Microscopic and Macroscopic Approach**

Sr. No.	Microscopic Approach	Macroscopic Approach	
1	This approach considers that the system is made up of a very large numbers of the 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 substances.	
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 molecule cannot be easily measured by instruments.	The properties like temperature and pressure are required to describe the system can be easily measured.	
4	Large number of variables is needed to describe such a system. So approach is complicated.	Only few properties are needed to describe such a system.	





Phase: A quantity of matter which is homogeneous in chemical composition and in physical structure.



State : Condition of system defined by certain set of properties is called State of a system.

**Property:** Any characteristic of a system is called Property.

**Example**: Pressure, Volume, Temperature Viscosity, Thermal Conductivity etc.

#### **Property is Classified into 3 types:**

- i) Intensive Property: Any thermodynamic property of a system that is INdependent of the system mass. Ex. Pressure Temperature , Density etc ( $\rho = m/V$  both mass and volume are extensive property).
- ii) Extensive Property: Any thermodynamic property of a system that is dependent on the system mass. Ex. Mass, Volume, Kinetic energy and Potential Energy etc.
- **iii)** Specific Property : Any thermodynamic property obtained by dividing Extensive Property by unit mass is called specific property. Ex. Specific Volume, Specific enthalpy, Specific energy etc.







**<u>Path</u>**: A thermodynamic process path is the series of states through which a system passes from an initial equilibrium state to a final equilibrium state



**Process:** Thermodynamic process is a passage of a thermodynamic system from an initial to a final state of thermodynamic equilibrium **OR** the path through which the system reaches the final state from its initial state.

- ✓ Constant Pressure or Isobaric Process
- ✓ Constant Volume or Isochoric Process
- ✓ Constant temperature or Isothermal Process
- $\checkmark$  Adiabatic Process or isentropic process , Q = 0
- $\checkmark\,$  Polytropic process or general process







### **Reversible & Irreversible Process**

<b>REVERSIBLE PROCESS</b>	<b>IRREVERSIBLE PROCESS</b>
A Reversible process is a process that can be reversed in order to obtain the initial state of a system without leaving any traces either in system or surrounding	As irreversible process is a thermodynamic process that cannot be reversed in order to obtain the initial state of a system
Can be reversed	Cannot be Reversed
Infinite (very small) changes occurs in the system	Finite changes occur in the system
There is an equilibrium between the initial state and the final state of the system	There is no equilibrium in the system









### **Thermodynamic cycle:**

A thermodynamic cycle consists of a **linked sequence of thermodynamic processes** that involve transfer of heat and work into and out of the system, while varying pressure, temperature, and other state variables within the system, and that eventually returns the system to its initial state.







### **Thermodynamic Equilibrium:**

A system is said to be in Thermodynamic equilibrium if it does not have the capacity to <u>spontaneously change its state after it has been isolated.</u>

There should not be any <u>unbalanced potential</u> which trigger the change of state.

The unbalanced potential may be

Mechanical

Thermal

Chemical

**Electrostatic or any combination of these conditions** 





## Mechanical Equilibrium

There is no UNBALANCED FORCE within the system and between the system and the surroundings (nor at the boundaries) the system is said to be in Mechanical Equilibrium







## **Chemical Equilibrium**

There is no CHEMICAL REACTION or a Process such as DIFFUSION within the system or between the system and the surroundings (nor at the boundaries) the system is said to be in Chemical Equilibrium









## **Thermal Equilibrium**

There is no **TEMPERATURE GRADIANT** within the system or between the system and the surroundings (nor at the boundaries) the system is said to be in Thermal Equilibrium









## **Electrical Equilibrium**

There is no **ELECTRICAL POTENTIAL** within the system or between the system and the surroundings (nor at the boundaries) the system is said to be in Electrical Equilibrium









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"When all the Conditions of Mechanical Equilibrium, Thermal Equilibrium, Electrical Equilibrium & Chemical Equilibrium then the system is said to be in Thermodynamic Equilibrium"



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Heterogeneous System: A system consisting of more than one phase is called Heterogeneous System. Example: Ice in liquid water.



## EQUALITY OF TEMPERATURE

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- $L_3 \& L_4$  Becomes Constant after some time when the system reaches equilibrium state.
- In THERMOMETER the length of mercury column remains same and the physical properties of the substance will not change furture then one can say that the two objects are at same 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 of the system remains constant. This concept is called **Equality of Temperature.**"

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## **Quasi-static process**



No Intermediate equilibrium state points Hence Path Cant be defined



"In thermodynamics, a quasi-static process (also known as quasi-equilibrium) is a thermodynamic process that happens slowly enough for the system to remain in internal equilibrium" OR "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"

Example: Quasi-static Expansion or Compression, where the volume of a system changes at a slow rate enough to allow the pressure to remain uniform and constant throughout the system.





### **ZEROTH LAW OF THERMODYNAMICS**



### TEMPERATURE

It is the measure of the average heat or thermal energy of the particles in a substance (**OR**) it is a measure of degree of hotness and coldness of the body.





## TEMRMOMETRIC PROPERTY

The characteristics or physical properties of 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	Р
Constant Pressure Gas Thermometer	Volume	V
Electrical Resistance Thermometer	Resistance	R
Thermocouple	Thermal emf	3
Liquid in Glass Thermometer	Length	L





## **TEMPERATURE SCALE**

- While using a thermometer, we need to mark a scale on the tube wall with numbers on it.
- We have to define a temperature scale.
- A temperature scale is a way to measure <u>temperature</u> relative to a starting point (0 or zero) and a unit of measurement.
- These numbers are arbitrary, and historically many different schemes have been used to fix that.







### **DIFFERENT TYPES OF SCALES**

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





## 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  $T(^{\circ}C) = \left[\frac{L - L_{I}}{L_{S} - L_{I}}\right] \times 100$ 

Similarly, for Fahrenheit, Rankine and Kelvin scale we get

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




## Cont..

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

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

**Relation between scales:** 

$$T(^{\circ}C) = \frac{5}{9}[T(^{\circ}F) - 32]$$
  

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

$$T(^{\circ}C) = [T(K) - 273.15]$$
  

$$T(R) = T(^{\circ}F) + 459.67 = 1.8 \times T(K)$$

Generally we can write

$$T = \left[\frac{L - L_I}{L_S - L_I}\right] \times (BP - FP) + FP$$







#### PROBLEMS

#### **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°C and thermometer 'B' indicates 50°C. Determine the values of L,M,N and also find the reading on 'A' if 'B' reads 25°C.

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

at Ice point : 
$$t_A = 0^{\circ}C$$
,  $t_B = 0^{\circ}C$   
 $t_A = L + M.t_B + N.t_B^2$   
 $0 = L + 0 + 0$   
 $L = 0$ 

at Steam point:  $t_A = 100^{\circ}C$ ,  $t_B = 100^{\circ}C$   $t_A = L + M.t_B + N.t_B^2$   $100 = L + M.100 + N.100^2$ M = 1 - 100.N







when 'A' indicates 55°C , 'B' indicates 50°C hence  $t_A = L + M.t_B + N.t_B^2$  55 = 50.M + 2500.N11 = 10.M + 500.N

Substituting for 'M' in the above equation we get

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

From equation M = 1 - 100.NM = 6/5

When thermometer 'B' reads 25°C , thermometer 'A' reads  $t_A = L + M.t_B + N.t_B^{\ 2}$ 

 $t_A = 28.75^{\circ}C$ 

Thus when 'B' reads 25°C, 'A' reads 28.75°C





2) The temperature 'T' on Celsius thermometer scale is defined interms of property 'p' by the relation T = A. ln (p) + B, where A and B are constants. At ice point and steam point the value of 'p' is 1.86 and 6.81 respectively. Find the value of 'T' for p = 2.5.

Given relation is 
$$T = A \cdot ln(P) + B \rightarrow \textcircled{1}$$
  
at ice point :-  $T = 0^{\circ}c$ ,  $P = 1.8c$   
 $T = A \cdot ln(P) + B$   
 $0 = A \cdot ln(P) + B$   
 $0 = A \cdot ln(P) + B$   
 $100^{\circ}C$   
 $T = A \cdot ln(P) + B$   
 $100 = A \cdot ln(C(B)) + B \rightarrow \textcircled{3}$   
Solving equation (a) 5 (a) we get  
 $A = 77.053$   
 $B = -47.82$   
Substituting in equation (b) we get  
 $T = A \cdot ln(P) + B$   
 $T = 77.053 \cdot ln(2:5) + (-47.82)$   
 $T = 22.78^{\circ}C$  when  $P = 2.5$ 

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3) The e.m.f in a thermocouple with the test junction at t°C on gas thermometer scale and reference junction at ice point is given by  $\varepsilon = 0.20.t - 5 \times 10^{-4}.t^2$  mV. The millivoltmeter is calibrated at ice and steam points. What will this thermometer read in a place where the gas thermometer reads 50°C.

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

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

 $\epsilon_{s} = 15 \text{ mV}$ 

When gas thermometer reading is 50 °C the e.m.f on thermocouple value will be

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

The value of Temperature corresponding to  $\varepsilon = 8.75$ mV can be obtained as For linear scale we have

 $t(^{\circ}C) = \left[\frac{\varepsilon - \varepsilon_{I}}{\varepsilon_{S} - \varepsilon_{I}}\right] \times 100$ 

Thus when gas thermometer reads 50°C, thermocouple reads 58.33°C

When ε = 8.75 m.V t(°C) = 58.33°C











4) In 1709, Sir Issac Newton proposed a linear temperature scale. Wherein the ice point and normal human body temperature were assumed as the two fixed points and assigned the values 0°N and 12°N resp. If the temperature of the human body on the Fahrenheit scale is 98°F, obtain the relation between Newton scale and Fahrenheit scale.

Let the temperature be a linear function Let t' = temperature on Newton scale

Then t' = a.X + bAt ice point  $X = X_i$ ,  $t' = 0^{\circ}N$  $0 = a.X_i + b$ 

At Normal human body temperature  $X = X_b$ , t' = 12°N 12 =  $a.X_b$ +b

Solving for a and b we get  $a = \frac{12}{X_b - X_i}$   $b = \frac{-12X_i}{X_b - X_i}$ 

Substituting this we get  $\mathbf{t'} = \frac{12}{X_b - X_i} \cdot \mathbf{X} - \frac{12X_i}{X_b - X_i} = \frac{12(X - X_i)}{(X_b - X_i)}$ 

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Let t= temperature on Fahrenheit scale The t =  $a_1.X + b_1$ At ice point X =  $X_i$ , t =  $32^{\circ}F$  $32 = a_1.X_i + b_1$ 

At Steam body temperature  $X = X_s$ ,  $t = 212^{\circ}F$  $212 = a_1 \cdot X_s + b_1$ 

Solving for a and b we get  $a_1 = \frac{180}{X_s - X_i}$   $b_1 = 32 - \frac{180X_i}{X_s - X_i}$ 

 $t = 32 + \frac{180 (X - X_i)}{(X_s - X_i)}$  $\frac{(X - X_i)}{(X_s - X_i)} = (t - 32) / 180$ 

at 
$$X_b$$
 ,  $t = 98^{\circ}F$ 

$$\frac{(X_b - X_i)}{(X_s - X_i)} = 66/180$$









$$T = \left[\frac{L - L_I}{L_S - L_I}\right] \times (BP - FP) + FP$$

Let the temperature be a linear function

Let t' = temperature on Newton scale

Then t' = a.X + b

At ice point t' =  $0^{\circ}$ N

At Normal human body temperature t' = 12°N In general Formula BP & FP are two FIXED Points in Newton scale given the two fixed points are ice point & Normal human body temperature, hence

$$t' = = \frac{(X - X_i)}{(X_b - X_i)} \times 12$$

Substituting this in t' equation we get  $t' = \frac{12(X - X_i) (X_S - X_i)}{(X_S - X_i) (X_b - X_i)}$  Let t= temperature on Fahrenheit scale

The  $t = a_1 \cdot X + b_1$ At ice point  $t = 32^{\circ}F$ 

At Steam body temperature  $t = 212^{\circ}F$ Solving for a and b we get  $t = \frac{(X - X_i)}{(X_s - X_i)} \times 180 + 32$ at X<sub>b</sub>, t = 98°F

$$\frac{(X_b - X_i)}{(X_s - X_i)} = 66/180$$

 $t' = \frac{2(t-32)}{11}$ 



N(t') F(t)





5) The resistance of the winding of a motor **at room temperature 28**°C and **at full load under steady state conditions** is given as **75 ohm and 90 ohm respectively**. The windings are made of copper with temperature t °C is given by ,  $R_{tp} = R_0 (1 + 0.004.t)$ . If  $R_0$  is the resistance at 0°C, find the temperature of the coil at Full Load.

At room temperature  $t = 28^{\circ}C$  we can write  $R_{tp} = R_o (1 + 0.004.t)$   $75 = R_o (1 + 0.004 x28)$  $R_o = 67.44$  ohm

At full load conditions , the temperature is given by  $90=67.44\ (\ 1+0.004.t\ )$  t = 83.63  $^\circ\mathrm{C}$ 





#### CONSTANT VOLUME GAS THERMOMETER

- Firstly the gas tube which has constant amount of gas is brought in contact with the system whose temperature needs to be measured.
- Due to change in temperature of the gas, the gas inside the bulb will expand(if the temperature of the system is higher than the gas) or compress (if the temperature of the system is lower than the gas)
- > Due to change in pressure, the level of mercury column in the right limb changes from point A
- To maintain CONSTANT VOLUME of the gas, the level of mercury column in left limb at point A, the Flexible tube (Right limb) needs to be moved up and down physically to keep the level fixed.
- $\succ$  By doing this the height of the mercury column changes
- > Note down the new value of "h" in the right limb and calculate the pressure using the formulae  $P = P_{atm} + \rho gh$
- > To calculate Temperature of the system we have  $T(K) = 273.16 \frac{P}{P_{tp}}$

Where  $T_{tp} = 273.16 \text{ K} = \text{triple point temperature of water}$  $P_{tp} = \text{Pressure of gas at Triple point temperature}$ 

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#### CONSTANT VOLUME GAS THERMOMETER





#### CONSTANT PRESSURE GAS THERMOMETER

- Firstly the gas tube which has constant amount of gas is brought in contact with the system whose temperature needs to be measured.
- Due to change in temperature of the gas, the gas inside the bulb will expand(if the temperature of the system is higher than the gas) or compress (if the temperature of the system is lower than the gas)
- > Due to change in pressure, the level of mercury column in the right limb changes from point A
- To maintain CONSATNT PRESSURE of the gas, the level of mercury in the RIGHT limb that is "h" value has to be kept constant, for this the Flexible tube (Right limb) needs to be moved up and down physically to keep the level fixed.
- By doing this the level of mercury column in the left limb will change that is the volume of gas will change.
- ➢ Note down the volume(V) of the gas
- > To calculate Temperature of the system we have  $T(K) = 273.16 \frac{V}{V_{tp}}$

Where  $T_{tp} = 273.16 \text{ K} = \text{triple point temperature of water}$  $V_{tp} = \text{Volume of gas at Triple point temperature}$ 

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## THERMOCOUPLE

- When two wires of different materials are joined at their ends with different temperatures existing at the two junctions an e.m.f is generated.
- The generated e.m.f may be used as a measure of the temperature of one junction, if the temperature at the other junction is known. Such a thermometer is known as thermocouple.
- The e.m.f generated (E) when two dissimilar metal A and B are joined at their ends with respective temperatures T1 and T2

Thus

$$T(K) = 273.16 \frac{E}{E_{tp}}$$







# MODULE 2 WORKAND HEAT

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## MODULE 2

**Work and Heat :** Mechanics, definition of work and its limitations. Thermodynamic definition of work; examples, sign convention. Displacement work; as a part of a system boundary, as a whole of a system boundary, expressions for displacement work in various processes through p-v diagrams. Shaft work; Electrical work. Other types of work. Heat; definition, units and sign convention. Problems

**CO1 Explain** fundamentals of thermodynamics and **evaluate** energy interactions across the boundary of thermodynamic systems.

**CO2 Evaluate** the feasibility of cyclic and non-cyclic processes using 2nd law of thermodynamics





## WORK

#### **MECHANICS DEFINITION**

### **THERMODYNAMIC DEFINITION**

Work is a distance moved by the force in the direction of the force or simply force acting through a distance W = F.dx Work is the energy transfer across the system boundary in an organized manner such that its sole use could be reduced to lift a weight (mass) against gravitational effect







## WORK

- From mechanics, W = ∫F.ds
- $\delta W = F_s ds$ , generalized force and generalized displacement
- All forms fully inter-convertible, and ultimately reducible to the raising (or lowering) of a weight in the earth's gravitational field (not necessarily actually the case)





## HEAT

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

## **DIFFERENCE BETWEEN HEAT & TEMPERATURE**







## **SIGN CONVENTION OF WORK & HEAT**

- Heat added into the system(Rejected from the surroundings) is Positive
- Heat Rejected from the system(added to the Surroundings) is Negative

- WORK done on the system( by the surrounding) Negative
- WORK done by the system(on the surrounding) Positive







#### **DISPLACEMENT WORK or P.dV Work**



Note: Area of Rectangle =  $B \cdot dL$ Comparing work done equation B – P, dL – dV, hence the area under the P-v diagram (Curves) gives Work done value



## **POINT & PATH FUNCTION**

**POINT FUNCTIONS:** A quantity say 'x' that have a value at every point within its domain of definition is called Point function. Its derivative is given by 'dx' and its integral is  $c^2$ 

$$\int_{1}^{2} \mathrm{d} \mathbf{x} = x_2 - x_1$$

Example: All properties (Pressure , volume , temperature etc)

Note: All point functions are Exact Differentials hence its differential is denoted by 'd'



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**PATH FUNCTIONS:** A quantity say 'y' whose value depends on the mathematical path taken between two points within its domine of definition is called path function.

- It is an inexact differential hence denoted by  $\delta$
- Thus we can write between two states 1 & 2 its integral as

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

**Example: Work, Heat** 







## **WORK IS A PATH FUNCTION**

- Consider the P-V diagram as shown in the figure. It is possible to reach final state(state B) from initial state (state A) or vice versa by following different paths 1,2 & 3.
- > As the area under the curve represents the work for each process  $\delta W = \int_1^2 P \, dV$  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









## **HEAT IS A PATH FUNCTION**

- Consider the T-s diagram as shown in the figure. It is possible to reach final state(state B) from initial state (state A) or vice versa by following different paths 1,2 & 3.
- As the area under the curve of T-s diagram represents the Heat for each process  $\delta q = \int_1^2 T ds$  it is evident that the amount of Heat 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 Heat is a path function. Thus









#### CONSTANT PRESSURE PROCESS (V/T = Const)

$$\frac{V_1}{V_2} = \frac{\mathrm{T}_1}{\mathrm{T}_2}$$

Derivation for work done during Constant Pressure process

W.K.T  $\int_{1}^{2} \delta W = W_{1-2} = \int_{1}^{2} P. dV$  $W_{1-2} = P(V_2 - V_1) kJ$ 

From First law,

$$\int_{1}^{2} \partial Q = \int_{1}^{2} \partial W + \int_{1}^{2} dU$$

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

$$= (U_2 + P_2 V_2) - (U_1 - P_1 V_1)$$

$$Q_{1-2} = (H_2 - H_1) \qquad \text{.....Change in Enthalpy}$$

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



 $dh = C_p/dT$ 



#### CONSTANT VOLUME PROCESS (**P/T = Const**)

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$
$$\int_1^2 \delta W = W_{1-2} = \int_1^2 P \cdot dV$$

 $W_{1-2} = 0$  for a constant volume process since 'dV=0' (Area under the curve is ZERO) From First law, 2

$$\int_{1}^{2} \partial \mathbf{Q} = \int_{1}^{2} \partial W + \int_{1}^{2} dU$$

or,  $Q_{1-2} = W_{1-2} + (U_2 - U_1)$ 

 $Q_{1-2} = U_2 - U_1 \dots$  Change in Internal energy

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

 $du = C_V/dT$ 

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#### CONSTANT TEMPERATURE PROCESS (**PV = Const**)

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

$$\int_1^2 \delta \mathbf{W} = \mathbf{W}_{1-2} = \int_1^2 \mathbf{P} \cdot \mathbf{dV}$$

$$\mathbf{W}_{1-2} = \int_1^2 \left(\frac{C}{V}\right) \cdot \mathbf{dV} = \mathbf{C} \cdot \int_1^2 \frac{1}{V} \cdot \mathbf{dV}$$

$$W_{1-2} = P_1 V_1 \ln \frac{V_2}{V_1} = P_2 V_2 \ln \frac{V_2}{V_1}$$
From First law, 
$$\int_1^2 \partial \mathbf{Q} = \int_1^2 \partial W + \int_1^2 dU$$

$$Q_{1-2} = P_1 V_1 \ln(V_2/V_1) + mC_v(T_2 - T_1)$$
but, 
$$T_1 = T_2$$
Therefore,
$$\mathbf{Q}_{1-2} = \mathbf{P}_1 \mathbf{V}_1 \ln(\mathbf{V}_2/\mathbf{V}_1) = \mathbf{Work \ done}$$







REVERSIBLE ADIABATIC PROCESS or ISENTROPIC PROCESS (**PV**<sup> $\gamma$ </sup> = **Constant**) (**Q** = **0**)  $\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$ 

$$\int_{1}^{2} \delta W = W_{1-2} = \int_{1}^{2} P_{.} dV$$

$$W_{1-2} = \int_{1}^{2} \left(\frac{c}{v^{\gamma}}\right) \cdot dV = C \cdot \int_{1}^{2} \frac{1}{v^{\gamma}} \cdot dV = C \cdot \int_{1}^{2} V^{-\gamma} \cdot dV = \frac{C \cdot [V_{2}^{(1-\gamma)} - V_{1}^{(1-\gamma)}]}{(1-\gamma)}$$
$$P_{1}V_{1}^{\gamma} = P_{2}V_{2}^{\gamma} = C$$

$$W_{1-2} = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} \qquad W_{1-2} = \frac{mR(T_1 - T_2)}{\gamma - 1}$$
  
From First law,  $\int_1^2 \partial Q = \int_1^2 \partial W + \int_1^2 \partial U$   
But,  $Q_{1-2} = 0$   
Therefore,  $0 = W_{1-2} + (U_2 - U_1)$ 

$$W_{1-2} = (U_1 - U_2) = m(u_1 - u_2) KJ$$

**Work done = Change in Internal energy** 





POLYTROPIC PROCESS (General Process) **PV**<sup>n</sup> = **Constant** We Know that, Work done =  $W_{1-2} = \frac{mR(T_1 - T_2)}{n-1}$  and  $dU = mC_v(T_2 - T_1)$ From First law of TD,  $\int_{1}^{2} \partial Q = \int_{1}^{2} \partial W + \int_{1}^{2} dU = \frac{mR(T_1 - T_2)}{n} + mC_v(T_2 - T_1)$ WKT  $C_P - C_V = R$  $C_P$  = Specific Heat of gas at constant Pressure  $C_{V}(\frac{C_{P}}{C_{V}} - 1) = R$  $C_{V} = \frac{R}{(\frac{C_{P}}{C_{V}} - 1)}$  $C_v$  = Specific Heat of gas at constant Volume R = Characteristic Gas constant for a gas But  $\gamma$  = Ratio of specific Heats =  $\frac{C_P}{C_V}$  $C_V = \frac{R}{V - 1}$ Substituting in main equation we get



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$$Q_{1-2} = \frac{mR(T_1 - T_2)}{n-1} + m\frac{R}{\gamma - 1}(T_2 - T_1)$$
$$Q_{1-2} = \frac{[(\gamma - 1)mR(T_1 - T_2)] - [(n-1)mR(T_1 - T_2)]}{(n-1)(\gamma - 1)} = \frac{mR(T_1 - T_2)(\gamma - 1 - n + 1)}{(n-1)(\gamma - 1)}$$

R

BY simplifying we get,

 $mR(T_4 - T_a)$ 

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

$$\mathbf{Q_{1-2}} = rac{\gamma-n}{\gamma-1} imes \mathbf{Polytropic}$$
 Work

done

#### When

n = 0, Constant Pressure process  $n = \infty$ , Constant Volume process n = 1, Constant Temperature process  $n = \gamma$ , Adiabatic process

## $\mathbf{PV^n} = \mathbf{Constant}$

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 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

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



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

Shaft power = 
$$P = \int_{1}^{2} T \cdot \frac{d\theta}{dT} = T \cdot \omega$$

Where  $\omega$  = 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

$$\begin{split} \delta W &= V.\,dC\\ \delta W &= V.\,I.\,dt \end{split}$$
 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 =  $\sigma = \frac{F}{A} = E.\epsilon...(2)$ 

Where, A = Cross sectional area of the wire, E = Modulus of elasticity,  $\varepsilon$  = Strain d $\varepsilon = \frac{dL}{L}$ .....(3) Substituting 2,3 in 1 we get

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

For finite changes in length

W = -A. E. L 
$$\int_{1}^{2} \varepsilon d\varepsilon = \frac{-A. E. L}{2} (\varepsilon_{2}^{2} - \varepsilon_{1}^{2})$$

L

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#### 4) Surface film work or stretching liquid film:

Work done by the wire frame is given by

$$\delta W = -\sigma_s . dA$$

 $\sigma_s$  = Surface tension of a film, dA = Change in area due to sliding of the wire frame

for finite changes, 
$$W_{1-2} = -\int_1^2 \sigma_s . dA$$



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NBA



5) Flow work:

- work is needed to push the fluid into or out of the boundary of a control volume if 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 the 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 =  $w_{flow} = P.v$  ( v = V/m)  $W_{Flow in} = W_{Flow out}$ 



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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 =  $P = P_m.L.A.N$ 

**NOTE:** The Mean effective pressure means the simply average pressure acting on the piston during the complete thermodynamic cycle in a Reciprocating internal combustion Engine.







### **SPECIAL CASES**

#### 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.






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#### 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 that means 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.





 $-m^2$ 

A battery is charged with a battery charger. The charger operates 1 hour at 15 V and a current of 30 A. Calculate the work done on the battery.

Solution :

Work done by the battery is given by

$$W = \int_{l}^{2} Eidt$$

Given data Voltage = E = 15VCurrent = i = 30 ATime = 1hr = = 3600 sec

The potential difference and current are taken to be constants during the charging period.

$$_{1}W_{2} = Ei(t_{2} - t_{1})$$
  
out  $1 V = \text{kg-m}^{2}/\text{C.s}^{2}$   
 $1 A = 1 \text{ Columb/sec}$   
 $\therefore _{1}W_{2} = 15 \times 30 \times 3600 = 1.62 \times 10^{6} \text{ J}$   
 $= 1.62 \text{ MJ}$ 

$$\frac{\mathrm{Kg}-m^2}{C.s^2} \times \frac{C}{Sec} \times sec = \frac{\mathrm{Kg}}{Sec}$$

Work is positive hence charger does work on the battery.





The pressure inside the cylinder is related to volume by p = C/V. (a) If the initial pressure is 200 kPa the initial volume is 0.018 m<sup>3</sup> and the final volume is 0.078 m<sup>3</sup>. Find (a) the work done. (b) Is work done by the system or on the system?

Solution :

a) Work done during the process,

$${}_{I}W_{2} = \int_{I}^{2} p dV = C \int_{I}^{2} \frac{dV}{V} \qquad \text{p.V}$$
Init  
Since  $p = \frac{C}{V}$ 

$${}_{I}W_{2} = C ln \left(\frac{V_{2}}{V_{I}}\right)$$

$$C = pV = p_{I}V_{I}$$

$${}_{I}W_{2} = P_{I}V_{I} ln \left(\frac{V_{2}}{V_{I}}\right)$$

$${}_{I}W_{2} = 200(0.018) ln \left(\frac{0.078}{0.018}\right) = 5.279 \text{ kJ}$$

b) The work is positive indicating that the system did work on the surroundings.

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#### GIVEN DATA

p.V = constant ( Constant Temperature or Isothermal process)

Initial Pressure =  $p_1 = 200$ kPa Initial Volume =  $V_1 = 0.018$  m<sup>3</sup> Final Volume =  $V_2 = 0.078$  m<sup>3</sup>



**ISOTHERMAL EXPANSION PROCESS** 





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 and 3. *Solution* :

In the Fig 1-2 is a constant pressure process and 2-3 is a constant temperature process work done during the process p.







Froblems:-  
An engine cylinder has a piston of area 
$$0.12m^2$$
 zs contains  
gas at a prevue of 1.5 MPa. The gas expands according to a  
process colvich is prepresented by a straight line on p-V drogram.  
The final prevuence is 0.15 Mpa. Determine the magnitude z direction  
of work transfer if the priston strake is 0.30m  
P<sub>1</sub> = 1.5 MPA  
P<sub>2</sub> = 0.15 MPA  
L = 0.30m  
Workdone =  $W_a = W_{1-2} = Area under the wave 1-2$   
 $= \frac{1}{2}(V_2 - V_1)(P_1 - P_2) + (V_2 - V_1)P_2$   
 $= \frac{1}{2}(V_2 - V_1)\left[\frac{P_1}{P_1} - \frac{P_2}{P_2} + \frac{P_2}{P_2}\right]$   
 $W_{1-2} = -\frac{1}{2}(P_1 + P_2)(V_2 - V_1) = -\frac{1}{2}[1-5+0.15] X1000 X(0.12+0.5)$ 

 $W_{1-2} = 29.7 \text{ KJ}$ 





3) A spherical balloon of 1m diameter contains a gas ... 250 kpa and 300K. The gas inside the balloon is hear until the pressure reaches to 500 kpa. During the proce of heating, the poressure of gas inside the balloon is propositional to the diameter of the balloon. Calculate the workdone by the gas, invide the balloon. => Given :- D= 1m D = 1mP. = asokpa P = 500 kPaP = 250 kPaT, = 300 K T = 300 KP2 = 500kpa PXD STATE 1 M = 2STATE 2 As percessure is propositional to diameter of the balloon PZD P= CD where 'C' is a constant ~> () Substituting given values in equation () 250 = C×1 ~ C = 250 kpa/m/ Now P2 = C.D2 500 = 250×02 · · P2 = 2m //









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 40 cm and the piston is held against the fluid due to atmospheric pressure equal to 100kPa. The stirrer turns 7000 Revolutions with an average torque of 1Nm. If the piston slowly moves outwards by 50cm determine the net work transfer to the system

Given data:

```
Diameter of cylinder = d = 40 \text{ cm} = 0.4 \text{m}
```

Atmospheric pressure = p = 100 k Pa

Number of revolutions = N = 7000

Torque = T = 1 N-m

Stroke Length = L = 50 cm = 0.5 m

#### Work done by the STIRRER or PADDLE Work

 $W_s = (2. \pi. N. T) = (2. \pi. 7000.1) = 43.98 \text{ kJ}$ 

 $W_{s} = -43.98 \text{ kJ}$ 

#### **IMPORTANT NOTE:**

Since Stirrer or Paddle work is done on the system that is FLUID hence it is taken as NEGATIVE

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Work done by the stirrer on the system = SHAFT WORK

W = F.s s= displacement

$$T = F.r$$
  

$$s = 2. \pi. r. N$$
  

$$W = \frac{T}{r} \times 2. \pi. r. N$$







#### Cont.

Work done by the system due to outward piston movement or displacement

$$W_d = p. dV = p. A. L$$
  
= 100 ×  $\frac{\pi}{4}$ . (0.4)<sup>2</sup> × 0.5  
 $W_d = 6.28 \text{ kJ}$ 

Net Work Transfer to the System

 $W_{net} = W_s + W_d$ = -43.98 + 6.28  $W_{net} = -37.69 \text{ kJ}$  Since the system(FLUID) does work in pushing the piston outwards ... Work is done by the system... hence W<sub>d</sub> is taken as Positive

-ve Sign indicates that Work output is less than Work input to the system





STA piston is cylinder machine containing a find system has a stirring device as shown. The put to almo spheric preusure of 101.3 kpa. The Stisving device is turned 9500 revolutions with an ano tosque 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 regitern. -> Work done by the stirring device upon the System = Shapt P=101.31400; work T= F. 8 W, S= STIX. N W= F.S = STINT = WI ->cy Under Lastinver [W] = 74.622KJ, negative work ? done On system [] W W1 = 2. TT. 9500. 1.25 = 74622 N.M. Work done by the System upon the Surroundings W2= F.L= p.A.L where, p= 101.3 kpa, A = I × (0.65)<sup>2</sup>= 0.3318 m<sup>2</sup>, L= 0.6 m W2 = 101.3×0.3318×0.6 = 20.167 KJ/ + Ve Work -Horce Net work transfer for the system Whet = W,+W2 = -74:622+20.167-Wnet = - 54.455 KJ





Determine the work done by the air which enters into a evacuated vessel from atmosphere when the valve is opened. The atmospheric pressure is 1.013 bar and 1.5 m<sup>3</sup> of air at atmospheric condition enters into the vessel

## **Solution:**

No work is done by the boundary in contact with the vessel as boundary does not move.

Work is done by the external boundary at constant pressure

$$W_{1-2} = \int_{1}^{2} p \cdot dV = p(V_{2} - V_{1})$$
  
= p(0 - V\_{1})  
= 1.013 × 100 × (0 - 1.5)

#### = - 151.95 kJ

• Since the boundary of vessel is fixed during filling of air inside the vessel, the work that is happening can be considered as Flow Work (that is filling of air into the vessel)

hence  $W_{1-2} = p.V$ 

Work is negative because the air is getting compressed during filling into the vessel hence work is done on the system







A Fluid undergoes the following process in sequence to complete a cycle:

- i) Heated reversibly at constant pressure of 1.05 bar until it has a volume of 0.02m<sup>3</sup>
- ii) It is then compressed reversibly according to a **law pv =Constant** to a pressure of 4.2 bar
- iii) It is then allowed to expand reversibly according to a law  $pv^{1.3} = Constant$
- 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 the cycle . Sketch also the cycle on a p-V diagram

#### GIVEN DATA

 $P_2 = 1.05 \text{ bar}$   $P_3 = 4.2 \text{ bar}$   $V_2 = 0.02 \text{ m3}$  $W_{1-2} = 515 \text{ N-m}$ 

 $W_{net} = W_{1-2} + W_{2-3} + W_{3-4} + W_{4-1}$ 

Work done during process 1-2 (P = Constant)
W<sub>1-2</sub> = 515 N-m







**Work done during process 2-3 (PV = Constant)(T = Constant)** 

$$W_{2-3} = P_2 V_2 \ln \frac{V_3}{V_2}$$

$$P_2 V_2 = P_3 V_3$$

$$V_3 = \frac{P_2 V_2}{P_3} = \frac{1.05 \times 0.02}{4.2} = 5 \times 10^{-3} \text{m}^3$$

$$W_{2-3} = 1.05 \times 10^5 \times 0.02 \times \ln \left(\frac{5 \times 10^{-3}}{0.02}\right)$$

$$W_{2-3} = -2911.2 \text{ J}$$



**Work done during process 3-4 (PV<sup>1.3</sup> = Constant)(Polytropic)** 

$$W_{3-4} = \frac{P_3 V_3 - P_4 V_4}{n-1}$$
  

$$P_3 V_3^{1.3} = P_4 V_4^{1.3}$$
  

$$P_4 = P_3 \left(\frac{V_3}{V_2}\right)^{1.3} = 4.2 \left(\frac{5 \times 10^{-3}}{0.0151}\right)^{1.3} = 0.998 \text{ bar}$$

From Process 1-2  $W_{1-2} = P_1 (V_2 - V_1)$   $515 = 1.05 \times 10^5 (0.02 - V_1)$  $V_1 = 0.0151 \text{ m}^3 = V_4$ 





$$W_{3-4} = \frac{(4.2 \times 10^5 \times 5 \times 10^{-3}) - (0.998 \times 10^5 \times 0.0151)}{1.3 - 1}$$

W<sub>3-4</sub> = + 1976.7 J

➢ Work done during process 4 − 1 (V = Consatnt)

 $W_{4-1} = 0$ 

> Net Work done

$$W_{net} = W_{1-2} + W_{2-3} + W_{3-4} + W_{4-1}$$

= 515 - 2911.2 + 1976.7 + 0

 $W_{net} = -419.5 J$ 







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







Substituting,

and  

$$p_1 = 200 \text{ kPa}, p_2 = 600 \text{ kPa}$$
  
 $V_1 = 0.1 \text{ m}^3; V_2 = 2 V_1 = 0.2 \text{ m}^3, \text{ we have}$   
Work done by the gas  $= (0.2 - 0.1) \left[ \frac{200 + 600}{2} \right]$   
 $= 40 \text{ kJ}$ 





# FIRST LAW OF THERMODYNAMICS



Joules Law Of Internal Energy States That " Internal Energy (U) Of A Perfect Gas Is A Function Of Temperature Change Only And Is Not Affected By The Change In Pressure And Volume"





# FIRST LAW OF THERMODYNAMICS

## **STATEMENTS**

"When a closed system executes a cyclic process the algebraic sum of work transfer is proportional to the algebraic sum of heat transfer"

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

"When a system undergoes a thermodynamic cycle then the net heat supplied to the system from the surroundings is equal to net work done by the system on its surroundings"

"Heat and work are mutually convertible but since energy can neither be created nor destroyed , the total energy associated with an energy conversion remains constant"





# FIRST LAW OF THERMODYNAMICS

## JOULES EXPERIMENT



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Work input to the paddle wheel is measured by fall of weight or change in potential energy. The work transfer caused a rise in temperature of the liquid

The temperature rise of Fluid in the insulated container is measured by the thermometer

Then the system is placed in the water bath so that the heat was transferred from the fluid to the water until the original state of fluid was reestablished

## This way the system(fluid) was taken through a cycle.

It is observed that the amount of heat rejected by the fluid to the water was proportional to the increase of energy of the water bath which could be easily determined by measuring the rise in temperature of the water bath.

Joule found that the net work input W to the system was always proportional to the net heat transfer Q by the system regardless of the rate of Work and heat.





#### PROVE THAT ENERGY IS A POINT FUNCTION

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

For this cycle we can write  

$$\int_{IA}^{2A} \delta Q + \int_{2B}^{IB} \delta Q = \int_{IA}^{2A} \delta W + \int_{2B}^{IB} \delta W$$
(A) IC (2A) IC

(Considering A-C)

$$\int_{2B}^{IB} \delta Q - \int_{2C}^{IC} \delta Q = \int_{2B}^{IB} \delta W - \int_{2C}^{IC} \delta W$$

 $\int \delta Q + \int \delta Q = \int \delta W + \int \delta W$ 

$$\int_{2B}^{IB} (\delta Q - \delta W) = \int_{2C}^{IC} (\delta Q - \delta W)$$

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Since B and C are two arbitrary processes between states 2 & 1, the quantity  $(\delta Q - \delta W)$  remains same for all processes between the two states

The value  $(\delta Q - \delta W)$  does not depends on path followed hence point function and it is property of the system.

This property is known as INTERNAL ENERGY or ENERGY denoted by E

$$(\delta Q - \delta W) = dE$$
  
 $\delta Q = dE + \delta W$ 





# **Physical Significance of "E"**

- Th property "E" represents the Sum of energy transfers across the system boundary known as STORED ENERGY
- > This energy might be in variety of forms
  - Kinetic Energy (KE)
  - Potential energy (PE)
  - Chemical energy (CE)
  - Electrical energy (EE)
  - Energy associated with the movement and position of molecules

Kinetic Energy Potential energy **Internal Energy ( All other forms of Stored Energy)** 







In the absence of motion and gravity effect we can write the above equation as

$$\delta Q = dU + \delta W$$

First law of thermodynamics equation for a CLOSED SYSTEM

# **This is NFEE (Non Flow Energy Equation)**





## **ENTHAPLY:**

**Enthalpy is a thermodynamic quantity equivalent to the total heat content of a system** & it is given by the sum of internal Energy and the Flow work (Product of pressure and volume) It is an Extensive property and denoted by symbol "H"

H = U + p.V kJ

$$h = u + p.v$$
 kJ/kg Where  $h = \frac{H}{m}$ ,  $u = \frac{U}{m}$ ,  $v = \frac{Total Volume}{m}$ 

#### **APPLICATION OF FIRST LAW TO A CLOSED SYSETM:**

Derivation of WORK AND HEAT TRANSFER Equations for different processes discussed in WORK & Heat chapter





- Specific heat (C) is the amount of heat required to change the temperature of a mass unit of a substance by one degree
- Specific heat (C<sub>P</sub>) is the amount of heat required to change the temperature of a mass unit of a substance by one degree at constant Pressure

$$c_{p} = \frac{dh}{dT}$$
  $Q_{1-2} = m(h_{2} - h_{1}) = mC_{p}(T_{2} - T_{1})$ 

Specific heat  $(C_V)$  is the amount of heat required to change the temperature of a mass unit of a substance by one degree at Constant Volume

$$\mathbf{c}_{\mathbf{V}} = \frac{\mathbf{d}\mathbf{u}}{\mathbf{d}\mathbf{T}} \qquad \qquad \mathbf{Q}_{1-2} = \mathbf{m}(\mathbf{u}_2 - \mathbf{u}_1) = \mathbf{m}\mathbf{C}_{\mathbf{V}} \left(\mathbf{T}_2 - \mathbf{T}_1\right)$$







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NBA

It is an Engine working in a cycle without receiving heat from any source , but delivering work to the surrounding

# **PMM-1 is IMPOSSIBLE**

## **STEADY FLOW ENERGY EQUATION** FIRST LAW OF THERMODYNAMICS FOR OPEN SYSTEM

Let,

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

 $\vartheta_1$  = Specific volume of the working substance in m<sup>3</sup>/kg.  $V_1$  or  $C_1$  = 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.

 $P_2$ ,  $\vartheta_2$ ,  $V_2$  or  $C_2$ ,  $u_2$ , and  $Z_2$  = corresponding values for the working substance leaving the control volume.

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Abitrary datum line





 $Q_{1-2}$  = 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.

 $e_1 = Internal energy + Displacement work + Kinetic energy + Potential energy + Heat supplied.$ 

$$e_1 = u_1 + P_1 \vartheta_1 + \frac{V_1^2}{2} + gZ_1 + q_{1-2}$$
 in kJ/kg

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

$$e_2 = u_2 + P_2 \vartheta_2 + \frac{V_2^2}{2} + gZ_2 + W_{1-2}$$
 in kJ/kg

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

 $e_1 = e_2$ 

$$u_1 + P_1\vartheta_1 + \frac{v_1^2}{2} + gZ_1 + q_{1-2} = u_2 + P_2\vartheta_2 + \frac{v_2^2}{2} + gZ_2 + W_{1-2}$$





We know that,

 $u_1 + P_1 v_1 = h_1 =$  Enthalpy of the working substance entering the control volume in kJ/kg.  $u_2 + P_2 v_2 = h_2 =$  Enthalpy of the working substance leaving the control volume in kJ/kg.

Therefore,  $h_1 + \frac{v_1^2}{2} + gZ_1 + q_{1-2} = h_2 + \frac{v_2^2}{2} + gZ_2 + W_{1-2}$ 

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,

$$m\left(h_{1}+rac{V_{1}^{2}}{2}+gZ_{1}+q_{1-2}
ight) = m\left(h_{2}+rac{V_{2}^{2}}{2}+gZ_{2}+W_{1-2}
ight)$$





## WORK ABSORBING SYSTEM

## **1. ROTARY COMPRESSOR**

- Work is done on the system ie., W<sub>1-2</sub> is Negative.
- Heat rejected by the system, ie., Q<sub>1-2</sub> is Negative
- **Change in Potential Energy and Kinetic Energy is negligible.** Applying the above conditions to SEEE we get.

$$m\left(h_{1} + \frac{V_{1}^{2}}{2} + gZ_{1} + q_{1-2}\right) = m\left(h_{2} + \frac{V_{2}^{2}}{2} + gZ_{2} + W_{1-2}\right)$$

$$m\left(h_{1} + \frac{V_{1}^{2}}{2} + gZ_{1}\right) + Q_{1-2} = m\left(h_{2} + \frac{V_{2}^{2}}{2} + gZ_{2}\right) + W_{1-2}$$

$$m\left(h_{1} + \frac{V_{1}^{2}}{2} + gZ_{1}\right) - Q_{1-2} = m\left(h_{2} + \frac{V_{2}^{2}}{2} + gZ_{2}\right) - W_{1-2}$$

$$m\left(h_{1} + \frac{V_{1}^{2}}{2} - \frac{V_{2}^{2}}{2} + gZ_{1} - gZ_{2}\right) - Q_{1-2} = m(h_{2}) - W_{1-2}$$

$$m(h_{1}) - Q_{1-2} = m(h_{2}) - W_{1-2}$$

$$W_{1-2} = m(h_{2} - h_{1}) + Q_{1-2}$$



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If the surface of the system is INSULATED (Q = 0)

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





## 2. BLOWER:

- Compression is isentropic and Heat Transfer is Zero, ie.,  $Q_{1-2} = 0$ ,
- Work done on the system is negative,
- Change in Potential Energy and Internal Energy is negligible,
- V<sub>1</sub> is very small when compared to V<sub>2</sub>
- **p**<sub>1</sub>**v**<sub>1</sub> approximately equal to **p**<sub>2</sub>**v**<sub>2</sub>

$$m\left(h_{1} + \frac{V_{1}^{2}}{2} + gZ_{1}\right) + Q_{1-2} = m\left(h_{2} + \frac{V_{2}^{2}}{2} + gZ_{2}\right) + W_{1-2}$$
$$m\left(u_{1} + p_{1}\vartheta_{1} + \frac{V_{1}^{2}}{2}\right) = m\left(u_{2} + p_{2}\vartheta_{2} + \frac{V_{2}^{2}}{2}\right) - W_{1-2}$$
$$W_{1-2} = m(u_{1} - u_{2}) + m\left(\frac{V_{1}^{2}}{2} - \frac{V_{2}^{2}}{2}\right)$$

In case of fans , temperature rise is negligible and heat lost is small Hence,  $\Delta u = 0$  and Q = 0 & if  $V_2 >> V_1$  we can write

$$(W_{1-2})_{fan} = m\left(\frac{V_1^2}{2} - \frac{V_2^2}{2}\right)$$
  $W_{1-2} = \frac{V_2^2}{2}$ 

# **Control Surface** Air out ∠ W Blower Air in





#### **<u>3. RECIPROCATING COMPRESSOR:</u>**

- Work is done on the system ie., W<sub>1-2</sub> is Negative.
- Heat rejected from the system, ie., Q<sub>1-2</sub> is Negative
- Change in Potential Energy and Kinetic Energy is negligible.

Applying the above conditions to SFEE we get,

$$m\left(u_{1} + p_{1}\vartheta_{1} + \frac{V_{1}^{2}}{2}\right) - Q_{1-2} = m\left(u_{2} + p_{2}\vartheta_{2} + \frac{V_{2}^{2}}{2}\right) - W_{1-2}$$
$$m(h_{1}) - Q_{1-2} = m(h_{2}) - W_{1-2}$$
$$W_{1-2} = m(h_{2} - h_{1}) + Q_{1-2}$$







## **4. CENTRIFUGAL PUMP:**

- Work is done on the system which is considered as negative.
- Heat transfer is Zero
- Change in internal energy (du = 0) is Zero due to no change in temperature of water

Applying the above conditions to SFEE we get,

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

$$m \left( u_1 + p_1 \vartheta_1 + \frac{V_1^2}{2} \right) = m \left( u_2 + p_2 \vartheta_2 + \frac{V_2^2}{2} \right) - W_{1-2}$$

$$m \left( p_1 \vartheta_1 + \frac{V_1^2}{2} + gZ_1 \right) = m \left( p_2 \vartheta_2 + \frac{V_2^2}{2} + gZ_2 \right) - W_{1-2}$$

**Note:** Usually we take inlet at datum , hence  $Z_1 = 0$  while  $Z_2$  we have to take outlet distance from the datum line Or else we have to substitute NEGATIVE VALUE for  $Z_1$  since it is below the axis of the pump and POSITIVE VALUE for  $Z_2$  Since it is above the axis of the pump







## **APPLICATION OF STEADY FLOW ENERGY EQUATION**

## WORK DEVELOPING SYSTEM

#### **1. TURBINE:**

- Work done is Positive,
- Change in KE and PE is negligible.
- Heat transfer is negligible

Applying the above conditions to SFEE we get,

$$m\left(h_{1} + \frac{V_{1}^{2}}{2} + gZ_{1}\right) + Q_{1-2} = m\left(h_{2} + \frac{V_{2}^{2}}{2} + gZ_{2}\right) + W_{1-2}$$
$$m(h_{1}) = m(h_{2}) + W_{1-2}$$
$$W_{1-2} = m(h_{1} - h_{2})$$







## **2. IC ENGINE:**

- Work done is Positive,
- Change in KE and PE is negligible.
- Heat transfer is negligible and assumed to be Zero

Applying the above conditions to SFEE we get,

 $m_1(h_1) + Q_{1-2} = m_2(h_2) + W_{1-2}$ 

- $m_1$  (h<sub>1</sub>) =  $m_2$ (h<sub>2</sub>) + W<sub>1-2</sub>
  - $W_{1-2} = m_1 h_1 m_2 h_2$

 $m_1 = mass of air fuel mixture$  $m_2 = mass of combustion products$ 







## **3. HYDRAULIC TURBINE:**

- Work done is Positive
- Change in temperature of water is negligible hence change in internal energy is taken as zero.
- Heat transfer is negligible and assumed to be Zero

$$m\left(h_{1} + \frac{V_{1}^{2}}{2} + gZ_{1}\right) + Q_{1-2} = m\left(h_{2} + \frac{V_{2}^{2}}{2} + gZ_{2}\right) + W_{1-2}$$

$$m(u_1 + p_1\vartheta_1 + \frac{V_1^2}{2} + gZ_1) + Q_{1-2} = m(u_2 + p_2\vartheta_2 + \frac{V_2^2}{2} + gZ_2) + W_{1-2}$$

$$m\left(p_1\vartheta_1+\frac{V_1^2}{2}+gZ_1\right)=\ m\left(p_2\vartheta_2+\frac{V_2^2}{2}+gZ_2\right)+W_{1-2}$$







#### **APPLICATION OF STEADY FLOW ENERGY EQUATION**

#### NON WORK ABSORBING AND NON WORK DEVELOPING SYSTEM

- **1. HEAT EXCHANGER(CONDENSER)**
- Change in KE and PE is negligible
- Work done is zero
- Heat transfer to the surroundings is also negligible (Perfect insulation)

Applying the above conditions to SFEE we get,

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

#### **Considering Steam as system:** Heat is lost by steam hence Q is negative $m(h_{s1}) - Q_s = m(h_{s2})$ $Q_{S} = m(h_{s1} - h_{s2})$

**Considering Water as system:** Heat added to water hence Q is positive  $m(h_{w1}) + Q_w = m(h_{w2})$  $Q_{S} = m(h_{w2} - h_{w1})$ 

Heat lost by steam( $Q_S$ ) = Heat gained by water( $Q_W$ )

$$m_s(h_{s1} - h_{s2}) = m_W(h_{w2} - h_{w1})$$

$$Q = m C_p \Delta T = m.\Delta h$$






### **2. EVAPORATOR**

- Change in KE and PE is negligible
- Work done is zero

Applying the above conditions to SFEE we get,

$$m\left(h_{1} + \frac{V_{1}^{2}}{2} + gZ_{1}\right) + Q_{1-2} = m\left(h_{2} + \frac{V_{2}^{2}}{2} + gZ_{2}\right) + W_{1-2}$$
$$Q_{1-2} = m(h_{2} - h_{1}) kJ$$



Liquid refrigerant absorbs heat from the cooling space and gets converted into vapour refrigerant hence the value heat transfer here will be positive





## **OTHER CASES**

### **1. THROTTLING PROCESS**

- Work done is ZERO
- Change in KE & PE is negligible
- Heat transfer is Zero



Applying the above conditions to SFEE we get,

$$m\left(h_{1} + \frac{V_{1}^{2}}{2} + gZ_{1}\right) + Q_{1-2} = m\left(h_{2} + \frac{V_{2}^{2}}{2} + gZ_{2}\right) + W_{1-2}$$
$$m(h_{1}) = m(h_{2})$$
$$h_{1} = h_{2}$$

During Throttling process pressure decreases and Enthalpy remains constant across the valve





## **2. FLOW THROUGH PIPES**

- Work done is zero
- Heat Transfer is Zero
- Since Temperature change is ignored, Change in INTERNAL ENERGY is zero

Applying the above conditions to SFEE we get,

$$m\left(h_{1} + \frac{V_{1}^{2}}{2} + gZ_{1}\right) + Q_{1-2} = m\left(h_{2} + \frac{V_{2}^{2}}{2} + gZ_{2}\right) + W_{1-2}$$



$$m(u_1 + p_1\vartheta_1 + \frac{V_1^2}{2} + gZ_1) + Q_{1-2} = m(u_2 + p_2\vartheta_2 + \frac{V_2^2}{2} + gZ_2) + W_{1-2}$$

$$m(P_1\vartheta_1 + \frac{V_1^2}{2} + gZ_1) = m(P_2\vartheta_2 + \frac{V_2^2}{2} + gZ_2)$$
$$m(\frac{P_1}{\rho_1} + \frac{V_1^2}{2} + gZ_1) = m(\frac{P_2}{\rho_2} + \frac{V_2^2}{2} + gZ_2)$$

Since Specific volume =  $\vartheta = \frac{1}{\rho}$ 





For incompressible Fluid  $\rho_1 = \rho_2 = \rho$ 

$$m(\frac{P_1}{\rho} + \frac{V_1^2}{2} + gZ_1) = m(\frac{P_2}{\rho} + \frac{V_2^2}{2} + gZ_2)$$

# This is known as BERNOULLI'S EQUATION for IDEAL FLUID FLOW

If h<sub>f</sub> is the frictional loss, then for a REAL FLUID we have

$$m(\frac{P_1}{\rho} + \frac{V_1^2}{2} + gZ_1) = m(\frac{P_2}{\rho} + \frac{V_2^2}{2} + gZ_2) + h_f$$
 This is known as MODIFIED BERNOULLI'S EQUATION for REAL FLUID FLOW





$$m\left(h_{1} + \frac{V_{1}^{2}}{2} + gZ_{1}\right) + Q_{1-2} = m\left(h_{2} + \frac{V_{2}^{2}}{2} + gZ_{2}\right) + W_{1-2} \quad (OR) \quad m\left(h_{1} + \frac{C_{1}^{2}}{2} + gZ_{1}\right) + Q_{1-2} = m\left(h_{2} + \frac{C_{2}^{2}}{2} + gZ_{2}\right) + W_{1-2}$$

In some text books they use 'C' instead of 'V' for Velocity

$$kg\left(\frac{kJ}{kg} + \frac{m^2}{s^2} + \frac{m^2}{s^2}\right) + kJ = kg\left(\frac{kJ}{kg} + \frac{m^2}{s^2} + \frac{m^2}{s^2}\right) + kJ$$

$$kg\left(\frac{kJ}{kg} + \frac{m^2}{s^2} + \frac{m^2}{s^2}\right) + kJ = kg\left(\frac{kJ}{kg} + \frac{m^2}{s^2} + \frac{m^2}{s^2}\right) + kJ$$

$$\frac{m^2}{s^2} = \frac{kg \times m^2}{kg \times s^2} = \frac{kg \times m \times m}{kg \times s^2} = \frac{N-m}{kg} = \frac{J}{kg} = \frac{10^{-3} \, kJ/kg}{10^{-3} \, kJ/kg} \qquad 1N = \frac{kg-m}{s^2}$$
$$\frac{1 \frac{m^2}{s^2}}{1 \frac{m^2}{s^2}} = \frac{10^{-3} \, kJ/kg}{10^{-3} \, kJ/kg}$$

Hence to get Heat transfer and work done in kJ/kg multiply KE and PE by 10<sup>-3</sup>





#### **Important Note**

• If 'm' is in 'kg' and h , KE . PE are in 'kJ/kg' we get Work done and heat transfer in 'kJ'

$$m\left(h_{1}+\frac{V_{1}^{2}}{2}+gZ_{1}\right)+Q_{1-2}=\ m\left(\ h_{2}+\frac{V_{2}^{2}}{2}+gZ_{2}\right)+W_{1-2}$$

• If 'm = 1kg' and h , KE . PE are in 'kJ' we get Work done and heat transfer in 'kJ/kg'

$$1kg \times \left(h_1 + \frac{V_1^2}{2} + gZ_1\right) + Q_{1-2} = 1kg \times \left(h_2 + \frac{V_2^2}{2} + gZ_2\right) + W_{1-2}$$

• If **'m'** is in 'kg/s' and h , KE . PE are in 'kJ/kg' we get POWER(P) instead of Work done and rate of heat transfer ( Q ) instead of heat transfer in 'kJ/s' or 'KW'

$$\dot{\mathbf{m}}\left(\mathbf{h}_{1}+\frac{\mathbf{V}_{1}^{2}}{2}+\mathbf{g}\mathbf{Z}_{1}\right)+\dot{\mathbf{Q}}_{1-2}=\dot{\mathbf{m}}\left(\mathbf{h}_{2}+\frac{\mathbf{V}_{2}^{2}}{2}+\mathbf{g}\mathbf{Z}_{2}\right)+\mathbf{P}_{1-2}$$

$$\dot{\mathbf{M}}=\text{Rate of mass transfer in }\frac{\mathbf{kg}}{\mathbf{k}}$$

$$\dot{\mathbf{Q}}=\text{Rate of heat transfer in }\mathbf{kJ/s}$$







**Example 4.12.** A fluid system, contained in a piston and cylinder machine, passes through a complete cycle of four processes. The sum of all heat transferred during a cycle is -340 kJ. The system completes 200 cycles per min.

PROBLEMS

Complete the following table showing the method for each item, and compute the net rate of work output in kW.

Process	Q(kJ/min)	W(kJ/min)	$\Delta E (kJ/min)$
1-2	0	4340	
2_3	42000	0	
3-4	-4200		- 73200
4-1	and the second - and the second second	n s 10 knopb <del>- s</del> hrantarith	

Solution. Sum of all heat transferred during the cycle = -340 kJ. Number of cycles completed by the system = 200 cycles/min.

Process 1-2:

 $Q = \Delta E + W$  $0 = \Delta E + 4340$  $\Delta E = -4340 \text{ kJ/min.}$ 

Process 2-3:

 $Q = \Delta E + W$   $42000 = \Delta E + 0$   $\Delta E = 42000 \text{ kJ/min.}$ 

Process 3-4:

 $Q = \Delta E + W$ - 4200 = - 73200 + W W = 69000 kJ/min.



or



Process 4-1:

 $\Sigma Q = -340 \text{ kJ}$ cycle

The system completes 200 cycles/min

∴  $Q_{1-2} = Q_{2-3} + Q_{3-4} + Q_{4-1} = -340 \times 200 = -68000 \text{ kJ/min}$ 0 + 42000 + (-4200) +  $Q_{4-1} = -68000$  $Q_{4-1} = -105800 \text{ kJ/min}.$ 

Now,  $\int dE = 0$ , since cyclic integral of any property is zero.

$$\begin{split} \Delta \ E_{1-2} + \Delta E_{2-3} + \Delta \ E_{3-4} + \Delta \ E_{4-1} &= 0 \\ - 4340 + 42000 + (-73200) + \Delta \ E_{4-1} &= 0 \\ \Delta \ E_{4-1} &= 35540 \text{ kJ/min.} \\ W_{4-1} &= Q_{4-1} - \Delta \ E_{4-1} \\ &= -105800 - 35540 = -141340 \text{ kJ/min} \end{split}$$

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#### PROBLEMS

10 kg of fluid per minute goes through a reversible steady flow process . The properties of fluid at the inlet are :  $p_1 = 1.5 \text{ bar}$ ,  $\rho_1 = 26 \text{ kg/m3}$ ,  $C_1 = 110 \text{ m/s}$  &  $u_1 = 910 \text{ kJ/kg}$  and at the exit are  $p_2 = 5.5 \text{ bar}$ ,  $\rho_2 = 5.5 \text{ kg/m3}$ ,  $C_2 = 190 \text{ m/s}$  &  $u_2 = 710 \text{ kJ/kg}$ . During the passage the fluid rejects 55 kJ/s and rises through 55 m. Determine

- i) The change in enthalpy  $(\Delta h)$
- ii) Work done during the process

 $p_1 = 1.5 \text{ bar} = 1.5 \times 100 \text{kpa} = 150 \text{kp}, \rho_1 = 26 \text{ kg/m3}, C_1 = 110 \text{ m/s} \& u_1 = 910 \text{ kJ/kg}$ 

$$p_2 = 5.5 \text{ bar} = 550 \text{kpa}, \rho_2 = 5.5 \text{ kg/m3}, C_2 = 190 \text{ m/s} \& u_2 = 710 \text{ kJ/kg}$$

$$Q_{1-2} = -55 \ kJ/s$$
  $z_2 = 55 \ m$   $m = 10 \frac{kg}{min} = \frac{10}{60} \ kg/s$   
(Heat rejection)

$$h_1 = u_1 + p_1 v_1 = 910 + (150 / 26) = 915.77 \text{ kJ /kg}$$

$$h_2 = u_2 + p_2 v_2 = 710 + (550 / 5.5) = 810 \text{ kJ/kg}$$

$$\Delta h = h_2 - h_1 = -105.76 \, kJ/kg$$

Since we need work done in kJ/kg we need to convert Q from kJ/s to kJ/kg , hence we have

$$q_{1-2} = rac{\dot{\mathbf{Q}} = \dot{\mathbf{m}}. \mathbf{q}}{\left[rac{10}{60}\right] kg/s} = -330 kJ/kg$$







$$\mathbf{m} \left( \mathbf{h}_{1} + \frac{\mathbf{V}_{1}^{2}}{2} + \mathbf{g} \mathbf{Z}_{1} \right) + \mathbf{Q}_{1-2} = \mathbf{m} \left( \mathbf{h}_{2} + \frac{\mathbf{V}_{2}^{2}}{2} + \mathbf{g} \mathbf{Z}_{2} \right) + \mathbf{W}_{1-2}$$
$$\mathbf{m} \left( \mathbf{h}_{1} + \frac{\mathbf{V}_{1}^{2}}{2} + \mathbf{g} \mathbf{Z}_{1} + \mathbf{q}_{1-2} \right) = \mathbf{m} \left( \mathbf{h}_{2} + \frac{\mathbf{V}_{2}^{2}}{2} + \mathbf{g} \mathbf{Z}_{2} + \mathbf{W}_{1-2} \right)$$

Mass flow rate or mass are equal in steady state condition

Because in problem we have Q in kJ/kg

$$\left(h_{1} + \frac{V_{1}^{2}}{2} + gZ_{1} + q_{1-2}\right) = \left(h_{2} + \frac{V_{2}^{2}}{2} + gZ_{2} + W_{1-2}\right)$$

$$15.77 + \frac{110^{2}}{2} + \frac{9.81 \times 0}{2.20} = \left(9.10 + \frac{190^{2}}{2} + \frac{9.81 \times 55}{2}\right)$$

$$\left(915.77 + \frac{110^2}{2 \times 1000} + \frac{9.81 \times 0}{1000} - 330\right) = \left(810 + \frac{190^2}{2 \times 1000} + \frac{9.81 \times 55}{1000} + W_{1-2}\right)$$

Work done during the process =  $W_{1-2} = -236.77 kJ/kg$ 

For work done per second or Power= (-236.77) kJ/kg ×  $\left(\frac{10}{60}\right)$  kg/s = -39.46 kW



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**Example 4.39.** A turbine, operating under steady-flow conditions, receives 4500 kg of steam per hour. The steam enters the turbine at a velocity of 2800 m/min, an elevation of 5.5 m and a specific enthalpy of 2800 kJ/kg. It leaves the turbine at a velocity of 5600 m/min, an elevation of 1.5 m and a specific enthalpy of 2300 kJ/kg. Heat losses from the turbine to the surroundings amount to 16000 kJ/h.

**Control Surface** Determine the power output of the turbine. **Solution.** Quantity of steam supplied to the turbine, m = 4500 kg/h  $C_1 = 2800 \text{ m/min}$ Steam velocity at the entrance to the turbine, Insulation  $Z_1 = 5.5 \text{ m}$ Elevation at the entrance,  $h_1 = 2800 \text{ kJ/g}$ Specific enthalpy at the entrance,  $C_2 = 5600 \text{ m/min}$ Steam velocity at the exit, W  $Z_2 = 1.5 \text{ m}$ Elevation at the exit,  $h_2 = 2300 \text{ kJ/kg}$ Specific enthalpy at the exit, Q = -16000 kJ/hTurbine Heat losses from the turbine to the surroundings, Applying the steady flow energy equation at entry (1) and exit (2) $m\left(h_{1}+\frac{C_{1}^{2}}{2}+Z_{1}g\right)+Q=m\left(h_{2}+\frac{C_{2}^{2}}{2}+Z_{2}g\right)+W$ 

$$Q - W = m \left[ (h_2 - h_1) + \left( \frac{C_2^2 - C_1^2}{2} \right) + (Z_2 - Z_1)g \right]$$









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Considering the nozzle as an open system, it is evident that :

- there is no work transfer across the boundary of the system (i.e., W = 0)
- there is no heat transfer because the nozzle is insulated (i.e., Q = 0).
- the change in potential energy is negligible since there is no significant difference elevation between the entrance and exit of the nozzle [i.e.  $(Z_2 - Z_1)g = 0$ ]. Thus eqn. (i) reduces to

$$h_1 + \frac{C_1^2}{2} = h_2 + \frac{C_2^2}{2}$$

$$\therefore \qquad (h_2 - h_1) + \frac{C_2^2 - C_1^2}{2} = 0$$
From steam table corresponding to 6.87 bar,  $h_1 = 2850$  kJ/k  

$$\therefore \qquad (h_2 - 2850) + \frac{(500)^2 - (50)^2}{2 \times 1000} = 0$$
 $h_2 - 2850 + 123.75 = 0$  or  $h_2 = 2726.25$  kJ  
Hence final enthalpy of steam = 2726.25 kJ  
(Ans.)

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or





Example 4.43. 12 kg of air per minute is delivered by a centrifugal air compressor. The inlet and outlet conditions of air are C<sub>1</sub> = 12 m/s, p<sub>1</sub> = 1 bar, v<sub>1</sub> = 0.5 m<sup>3</sup>/kg and C<sub>2</sub> = 90 m/s, p<sub>2</sub> = 8 bar, v<sub>2</sub> = 0.14 m<sup>3</sup>/kg. The increase in enthalpy of air passing through the compressor is 150 kJ/kg and heat loss to the surroundings is 700 kJ/min. Find : (i) Motor power required to drive the compressor ; (ii) Ratio of inlet to outlet pipe diameter.

Assume that inlet and discharge lines are at the same level.







$$(h_2 - h_1) = 150 \text{ kJ/kg}$$

Heat lost to the surroundings,

$$Q = -700 \text{ kJ/min} = -11.67 \text{ kJ/s}.$$

(i) Motor power required to drive the compressor : Applying energy equation to the system,

$$m\left(h_1 + \frac{C_1^2}{2} + Z_1g\right) + Q = m\left(h_2 + \frac{C_2^2}{2} + Z_2g\right) + W$$

Now

...



$$= 0.2 \left[ -150 + \frac{12^2 - 90^2}{2 \times 1000} \right] + (-11.67)$$

= -42.46 kJ/s = -42.46 kW

: Motor power required (or work done on the air) = 42.46 kW. (Ans.)

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(ii) Ratio of inlet to outlet pipe diameter,  $\frac{d_1}{d_2}$ : The mass of air passing through the compressor is given by

$$m = \frac{A_1 C_1}{v_1} = \frac{A_2 C_2}{v_2}$$
$$\frac{A_1}{A_2} = \frac{C_2}{C_1} \times \frac{v_1}{v_2} = \frac{90}{12} \times \frac{0.5}{0.14} = 26.78$$
$$\left(\frac{d_1}{d_2}\right)^2 = 26.78 \quad \text{or} \quad \frac{d_1}{d_2} = 5.175$$

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Hence ratio of inlet to outlet pipe diameter = 5.175. (Ans.)





**Example 4.48.** A centrifugal pump delivers 50 kg of water per second. The inlet and outlet pressures are 1 bar and 4.2 bar respectively. The suction is 2.2 m below the centre of the pump and delivery is 8.5 m above the centre of the pump. The suction and delivery pipe diameters are 20 cm and 10 cm respectively.

Determine the capacity of the electric motor to run the pump.

Quantity of water delivered by the pump,  $m_w = 50$  kg/s Inlet pressure,  $p_1 = 1$  bar  $= 1 \times 10^5$  N/m<sup>2</sup> Outlet pressure,  $p_2 = 4.2$  bar  $= 4.2 \times 10^5$  N/m<sup>2</sup> Suction-below the centre of the pump = 2.2 m Delivery-above the centre of the pump = 8.5 m Diameter of suction pipe,  $d_1 = 20$  cm = 0.2 m Diameter of delivery pipe,  $d_2 = 10$  cm = 0.1 m







#### **Capacity** of electric motor :

Steady flow energy equation is given by

$$m_{w}\left(u_{1}+p_{1}v_{1}+\frac{C_{1}^{2}}{2}+Z_{1}g\right)+Q=m_{w}\left(u_{2}+p_{2}v_{2}+\frac{C_{2}^{2}}{2}+Z_{2}g\right)+W$$

Considering the datum from suction 1, as shown

$$Z_1 = 0, Z_2 = 8.5 + 2.2 = 10.7 m$$
  
 $u_2 - u_1 = 0; Q = 0$ 

Thus eqn. (i) reduces to

$$W = m_w \left[ (p_1 v_1 - p_2 v_2) + (Z_1 - Z_2)g + \left(\frac{C_1^2 - C_2^2}{2}\right) \right]$$

As water is incompressible fluid.

2

$$v_2 = v_1 = v = \frac{1}{\rho} = \frac{1}{1000}$$

The mass flow through inlet and exit pipe is given by

$$m_{w} = \frac{\pi}{4} \times d_{1}^{2} \times C_{1} \times \rho = \frac{\pi}{4} \times d_{2}^{2} \times C_{2} \times \rho \text{ as } \rho_{1} = \rho_{2} = \rho \text{ (for water}}$$
  

$$\therefore \qquad 50 = \frac{\pi}{4} \times (0.2)^{2} \times C_{1} \times 1000$$
  

$$\therefore \qquad C_{1} = \frac{50 \times 4}{\pi \times (0.2)^{2} \times 1000} = 1.59 \text{ m/s}$$
  

$$C_{2} = \frac{50 \times 4}{\pi \times (0.1)^{2} \times 1000} = 6.37 \text{ m/s}$$
  
Substituting the values in eqn. (*ii*), we get  

$$W = 50 \left[ \left( 1 \times 10^{5} \times \frac{1}{1000} - 4.2 \times 10^{5} \times \frac{1}{1000} \right) + (0 - 10.7) \times 9.81 + \left( \frac{1.59^{2} - 6.37^{2}}{2} \right) \right]$$
  

$$= 50[-320 - 104.96 - 19.02]$$
  

$$= 22199 \text{ J/s or } 22.199 \text{ kJ/s} \simeq 22.2 \text{ kW.}$$
  
Hence capacity of electric motor = **22.2 kW.** (Ans.)

and

...

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## MODULE 3

## **SECOND LAW OF THERMODYNAMICS**

#### 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.





#### STEAM POWER PLANT







#### **REFRIGERATION CYCLE**







#### HEAT PUMP







#### **Device converting Heat to Work:**

#### HEAT ENGINE:

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.



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** 

$$\mathbf{Q_1} - \mathbf{Q_2} = \mathbf{W}$$

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

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





#### **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.







#### **Devices converting work to heat (Reversed Heat Engine):**

### 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.



temperature

source

Surroundings

(atmosphere)





#### **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"



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## **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"







**Equivalence of Kelvin Planck and Clausius Statements** 

**1.** Violation of Clausius statement leads to violation of Kelvin Planck statement



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- 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.

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2. Violation of Kelvin Planck statement leads to Violation of Clausius statement



**IMPORTANT NOTE:** WORK DEVELOPED BY HEAT ENGINE(W) IS COMPLETELY USED TO RUN THE HEAT PUMP IN COMBINED SYSTEM

HENCE THE NET WORKOUT FROM(OUT OF THE) COMBINED SYSTEM WILL BE ZERO

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- 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 clausius 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.

## <u>HENCE WE CAN CONCLUDE THAT BOTH KELVIN PLANCK AND CLAUSIUS STATEMENTS</u> <u>ARE EQUIVALENT IN SENSE.</u>





#### **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.







#### **CARNOT CYCLE**



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#### Carnot cycle consists of four reversible processes

1-2: Adiabatic compression  

$$W_{1-2} = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} = \frac{-(P_2 V_2 - P_1 V_1)}{\gamma - 1} = -m. R. (T_1 - T_2)/(\gamma - 1)$$

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

## 2-3: Isothermal Expansion $W_{2-3} = P_2 V_2 \ln \frac{V_3}{V_2} = m. R. T_2 \ln \frac{V_3}{V_2}$ $Q_{2-3} = W_{2-3} = m. R. T_2 \ln \frac{V_3}{V_2}$

3-4: Adiabatic Expansion  

$$W_{3-4} = \frac{P_3 V_3 - P_4 V_4}{\gamma - 1} = m. R. (T_3 - T_4)/(\gamma - 1)|$$
  
 $Q_{3-4} = 0$ 

4-1: Isothermal Compression  $W_{4-.1} = P_4 V_4 \ln \frac{V_1}{V_4} = -P_4 V_4 \ln \frac{V_4}{V_1} = -m. R. T_4 \ln \frac{V_4}{V_1}$  $Q_{4-1} = W_{4-1} = -m. R. T_4 \ln \frac{V_4}{V_1}$ 

Net Work done /cycle = 
$$\oint W = -m$$
. R.  $\ln \frac{v_3}{v_2} (T_2 - T_1)$ 

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"





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

Net Work done /cycle = 
$$\oint \mathbf{W} = -\mathbf{m} \cdot \mathbf{R} \cdot \ln \frac{\mathbf{v}_3}{\mathbf{v}_2} (\mathbf{T}_2 - \mathbf{T}_1)$$

## 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"

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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.



Total Heat supplied Q = W + Heat rejected = 600 + 412Q = 1012kJ/min

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 $Q_4 = 412 \text{ kJ/min}$


As engine is reversible, Clausius theorem becomes,

$$\oint \frac{dQ}{T} = 0 = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} - \frac{Q_4}{T_4}$$
$$\oint \frac{dQ}{T} = 0 = \frac{(0.6 \times Q3)}{1000} + \frac{(1012) - [(0.6 \times Q3) + Q3]}{800} + \frac{Q_3}{600} - \frac{412}{300}$$

Substituting the values in the above equation we get

$$Q_3 = 405 \text{ kJ/min}$$
  
 $Q_2 = 364 \text{ kJ/min}$   
 $Q_1 = 218.4 \text{ kJ/min}$ 

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# MODULE 5

#### **IDEAL GAS AND REAL GAS MIXTURE**

**Ideal gases:** Ideal gas mixtures, Daltons law of partial pressures, Amagat's law of additive volumes, evaluation of properties of perfect and ideal gases, Air- Water mixtures and related properties.

**Real gases –** Introduction, Van-der Waal's Equation of state, Van-der Waal's constants in terms of critical properties, Beattie-Bridgeman equation, Law of corresponding states, compressibility factor; compressibility chart. Difference between ideal and real gases.





## **IDEAL GAS**

An ideal gas is an imaginary gas having no forces of intermolecular attraction so that the behaviour of a molecule is not influenced by the presence of the other molecules and obeys the law PV = mRT at all pressures and temperatures. This relation Is called the ideal gas equation of state.

**IDEAL GAS MIXTURE** is the homogenous mixture of ideal gases which do not react with one another.

### **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 pressure of a given gas is directly proportional to the<br/>absolute temperature when volume remains constant during the change of state

 $P \propto T$  P/T = Constant  $\frac{P_1}{T_1} = \frac{P_2}{T_2} = constant$ 

3) **CARLE'S LAW :** The volume of a given gas is directly proportional to the absolute temperature when pressure remains constant during the change of state

$$V \propto T$$
  $V/T = Constant$   $\frac{V}{T_1} = \frac{V_2}{T_2} = constant$ 





#### **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

$$\frac{V_1}{V_A} = \frac{T_1}{T_A}$$

$$V_A = \frac{T_2 \times V_1}{T_1} \quad (T_A = T_2) \dots \dots (1)$$
Applying Boyle's law to the process A-2
$$\frac{V_2}{V_A} = \frac{P_1}{P_2} \quad (P_A = P_1)$$

$$V_A = \frac{P_2 \times V_2}{P_1} \dots \dots (2)$$







$$V_{A} = \frac{T_{2} \times V_{1}}{T_{1}}$$
 (T<sub>A</sub> = T<sub>2</sub>) .....(1)

equating equation (1) and (2) we get

$$\frac{\overline{T_2 \times V_1}}{\overline{T_1}} = \frac{\overline{P_2 \times V_2}}{\overline{P_1}}$$
$$\frac{\overline{P_1 \times V_1}}{\overline{T_1}} = \frac{\overline{P_2 \times V_2}}{\overline{T_2}}$$

Since state 1 and 2 are arbitrarily selected, it follows that

The constant is known as the CHARACTERISTIC GAS CONSTANT (R)

The value of "R " depends on type of GAS

Equation 3 can be written as

$$\frac{P \times V}{T} = R \quad \text{for unit mass}$$

PV = mRT for mass m







where , n = number of moles = 
$$\frac{m}{M}$$

Where m = mass of gas, M = molecular weight of the gas

We know that

PV = mRT

PV = n M R T

 $P \overline{\vartheta} = M R T$  Where ,  $\vartheta = \text{specific volume} = V/m kg/m^3$ 

PV = mRT

 $P\vartheta = RT$ 

where, Molar Specific Volume = 
$$\overline{\vartheta} = \frac{V}{n}$$
  
The quantity "MR" is a UNIVERSAL GAS CONSTANT ( $\overline{R}$ )  
 $\overline{P_{\vartheta}} = \overline{R}$  T

The universal gas constant is a Physical constant whose value is given by

 $\overline{R} = \frac{P \times \overline{\vartheta}}{T} = 1.013 \times 10^5 \times \frac{22.416}{273} = 8.31773 \text{ K J / Kg mol K}$ 

 $\overline{R} = 8.31773 \text{ K J} / \text{Kg mol K}$ 

1) 
$$n = \frac{m}{M}$$
  
2)  $V = n \cdot \overline{\vartheta} = m \cdot \vartheta$   
3)  $R = \frac{\overline{R}}{M}$   
4)  $PV = mRT$   
5)  $P \overline{\vartheta} = M R T$   
6)  $P \overline{\vartheta} = \overline{R} T$   
7)  $P\vartheta = RT$ 





#### **Relation between specific heat of gases and gas constant :**

h = u + pvwhere, h = enthalpyu = internal energy

h = u + RTin differential form dh = du + RdTR = constantSubstituting for 'du' and 'dh' we get

 $C_p dT = C_v dT + RdT$ 

 $C_p = C_v + R$ 

$$\mathbf{R} = \mathbf{C}_{\mathbf{p}} - \mathbf{C}_{\mathbf{v}}$$

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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  $\gamma$  (gama)

 $\frac{R}{C_V} = \frac{C_P}{C_V} - 1 \text{ (dividing by } C_V)$ by rearranging we get

 $C_V = \frac{R}{\gamma - 1}$ 

Similarly by dividing equ (7) by  $C_P$  we get

$$C_{P} = \frac{R \times \gamma}{\gamma - 1}$$





# **PARTIAL PRESSURE**

**Partial pressure of a gas** (P<sub>i</sub>) 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.







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 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

$$\boldsymbol{x_a} = \frac{m_a}{m}, \, \boldsymbol{x_b} = \frac{m_b}{m}, \, \boldsymbol{x_c} = \frac{m_c}{m}$$
$$\boldsymbol{m} = \boldsymbol{m_a} + \boldsymbol{m_b} + \boldsymbol{m_c}$$
$$\frac{m}{m} = \frac{m_a}{m} + \frac{m_b}{m} + \frac{m_c}{m}$$
$$\boldsymbol{1} = \boldsymbol{x_a} + \boldsymbol{x_b} + \boldsymbol{x_c}$$

• <u>Mole (n)</u> : A mole of a substance has a mass numerically equal to the weight of the substance

For a particular gas it is given by

$$n_i = \frac{m_i}{M_i}$$





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The total number of moles of the mixture is equal to the sum of the moles of the individual gas

 $n = n_a + n_b + n_c$ 

Mole fraction of gas A, B and C is given by

$$y_{a} = \frac{n_{a}}{n} \qquad y_{b} = \frac{n_{b}}{n} \qquad y_{c} = \frac{n_{c}}{n}$$
$$n = n_{a} + n_{b} + n_{c}$$
$$\frac{n}{n} = \frac{n_{a}}{n} + \frac{n_{b}}{n} + \frac{n_{c}}{n}$$
$$\mathbf{1} = \mathbf{y}_{a} + \mathbf{y}_{b} + \mathbf{y}_{c}$$

NOTE: Mass Fraction or Mole fraction of a IDEAL GAS MIXTURE is always equal to UNITY (**or**) Sum of Mass fraction or Mole fraction of individual gas components in an IDEAL GAS NMIXTURE is equal UNITY





### DALTONS LAW OF PARTIAL PRESSURE

- 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 GAS A , B , C we can write according to Daltons law that

For 'i' components generally we can write  $P = \sum_{i=1}^{j} P_i$ 

Dividing equation (1) by P we get

$$\frac{P}{P} = \frac{P_a}{P} + \frac{P_b}{P} + \frac{P_c}{P}$$
$$1 = P_{fa} + P_{fb} + P_{fc}$$

where  $P_{fi}$  is pressure fraction of a particular gas

$$\sum_{i=1}^{j} P_{fi} = 1$$

in general we can write

Pressure Fraction of Ideal gas Mixture =  $P_f = \sum_{i=1}^{j} P_{fi} = 1$ 





#### **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<sub>i</sub>, Amagats law can be written as

$$V = \sum_{i=1}^{j} V_i$$

Considering 3 gases A, B & C







Considering GAS A , B , C we can write according to Amagats law that

Total Volume of the Mixture of ideal gases =  $V = V_a + V_b + V_c$  .....(1)

For 'i' components generally we can write  $V = \sum_{i=1}^{j} V_i$ 

Dividing equation (1) by V we get

$$V = V_a + V_b + V_c$$
$$\frac{V}{V} = \frac{V_a}{V} + \frac{V_b}{V} + \frac{V_c}{V}$$

 $1 = V_{fa} + V_{fb} + V_{fc}$ 

where  $V_{fi}$  is volume fraction of a particular gas in general we can write

Volume Fraction of Ideal gas Mixture =  $V_f = \sum_{i=1}^{J} V_{fi} = 1$ 





#### **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

 $P_a V = m_a R_a T.... Gas A$  $P_b V = m_b R_b T.... Gas B$  $P_c V = m_c R_c T.... Gas C$ 

But from Daltons law of partial pressures the total pressure of Ideal gas mixture is given by  $P = P_a + P_b + P_c$ 

$$\frac{\mathbf{m}\mathbf{R}\mathbf{T}}{\mathbf{V}} = \frac{\mathbf{m}_{\mathbf{a}}\mathbf{R}_{\mathbf{a}}\mathbf{T}}{\mathbf{V}} + \frac{\mathbf{m}_{\mathbf{b}}\mathbf{R}_{\mathbf{b}}\mathbf{T}}{\mathbf{V}} + \frac{\mathbf{m}_{\mathbf{c}}\mathbf{R}_{\mathbf{c}}\mathbf{T}}{\mathbf{V}}$$
$$\mathbf{R} = \mathbf{x}_{\mathbf{a}} \cdot \mathbf{R}_{\mathbf{a}} + \mathbf{x}_{\mathbf{b}} \cdot \mathbf{R}_{\mathbf{b}} + \mathbf{x}_{\mathbf{c}} \cdot \mathbf{R}_{\mathbf{c}}$$





### **Expression for molecular weight (M) :**

PV = mRT

wkt n = 
$$\frac{m}{M}$$
 where  $\overline{R}$  = Universal gas constant, M = Molecular weight PV = nMRT

 $PV = n \overline{R} T \text{ where } \overline{R} = \text{Universal gas constant} = MR$   $P\overline{\vartheta} = \overline{R} T \text{ Where } \overline{\vartheta} = \text{molar specific volume} = V/n$ Considering 3 gases A,B,C

$$R_{a} = \frac{\overline{R}}{M_{a}}, \qquad R_{b} = \frac{\overline{R}}{M_{b}}, \qquad R_{c} = \frac{\overline{R}}{M_{c}}$$

Substituting in equation R we get

$$R = x_a \cdot R_a + x_b \cdot R_b + x_c \cdot R_c$$
$$\frac{\overline{R}}{M} = x_a \frac{\overline{R}}{M_a} + x_b \frac{\overline{R}}{M_b} + x_c \frac{\overline{R}}{M_c}$$
$$\frac{1}{M} = \frac{x_a}{M_a} + \frac{x_b}{M_b} + \frac{x_c}{M_c}$$

Molecular Weight of the Mixture  $M = \frac{1}{\frac{x_a}{M_a} + \frac{x_b}{M_b} + \frac{x_c}{M_c}}$ 



Alternate expression for molecular weight wkt, m = n Mfor 3 gases we can write

$$m_a = n_a \cdot M_a$$
 ,  $m_b = n_b \cdot M_b$  ,  $m_c = n_c \cdot M_c$ 

$$m = m_a + m_b + m_c$$
  

$$n.M = n_a \cdot M_a + n_b \cdot M_b + n_c \cdot M_c$$
  

$$M = y_a M_a + y_b M_b + y_c M_c$$

Where,  $y_a = \frac{n_a}{n}$   $y_b = \frac{n_b}{n}$   $y_c = \frac{n_c}{n}$  ISO





### **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<sub>a</sub> u<sub>a</sub> + m<sub>b</sub> u<sub>b</sub> + m<sub>c</sub> u<sub>c</sub> where u = specific internal energy =  $\frac{U}{m}$ 

by differentiating we get  $m \cdot du = m_a \cdot du_a + m_b \cdot du_b + m_c \cdot du_c$ 

wkt du = 
$$C_v dT$$
  
m  $C_v dT = m_a C_{va} dT + m_b C_{vb} dT + m_c C_{vc} dT$   
 $C_V = \frac{m_a}{m} C_{Va} + \frac{m_b}{m} C_{Vb} + \frac{m_c}{m} C_{Vc}$   
 $C_{vmix} = x_a C_{va} + x_b C_{vb} + x_c C_{vc}$ 





#### **Enthalpy of gaseous mixture (h<sub>mix</sub>):**

The enthalpy of a mixture of perfect gas is equal to sum of the enthalpies of the constituent gases

 $H = H_a + H_b + H_c$  $m.h = m_a h_a + m_b h_b + m_c h_c$  ..... (1)  $h_{mix} = x_a h_a + x_b h_b + x_c h_c$ where h = specific enthalpy =  $\frac{H}{m}$ by differentiating equation (1) we get  $\mathbf{m} \cdot \mathbf{dh} = \mathbf{m}_{a} \cdot \mathbf{dh}_{a} + \mathbf{m}_{b} \cdot \mathbf{dh}_{b} + \mathbf{m}_{c} \cdot \mathbf{dh}_{c}$ wkt dh =  $C_p dT$  $m C_p dT = m_a C_{pa} dT + m_b C_{pb} dT + m_c C_{pc} dT$  $C_{p} = \frac{m_{a}}{m}C_{Pa} + \frac{m_{b}}{m}C_{Pb} + \frac{m_{c}}{m}C_{Pc}$ 

$$\mathbf{C}_{\mathbf{Pmix}} = \mathbf{x}_{\mathbf{a}} \mathbf{C}_{\mathbf{Pa}} + \mathbf{x}_{\mathbf{b}} \mathbf{C}_{\mathbf{Pb}} + \mathbf{x}_{\mathbf{c}} \mathbf{C}_{\mathbf{Pc}}$$





#### **Change in entropy of gaseous mixture (s):**

 $\mathbf{S} = \mathbf{S}_{a} + \mathbf{S}_{b} + \mathbf{S}_{c}$ 

 $m.s=m_a\,s_a+m_b\,s_b+m_c\,s_c$ 

where s = specific entropy =  $\frac{s}{m}$ 

by differentiating we get

$$m \cdot ds = m_a \cdot ds_a + m_b \cdot ds_b + m_c \cdot ds_c$$

 $ds = x_a ds_a + x_b ds_b + x_c ds_c$ 

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.





For mixture of perfect gases show that partial pressure ratio( $p_{fi}$ ) = mole fraction ( $y_i$ ) = volume fraction( $v_{fi}$ )

PV = mRT

PV = nMRT

 $PV = n\overline{R}T$  for a mixture .....(1)

Let us consider a GAS A

 $P_a V = n_a \overline{R}T$  (applying Daltons law of partial pressure , i.e at same volume and temperature ) ... (2)

Dividing 2 by 1 we get

 $\frac{P_a V}{PV} = \frac{n_a \overline{R} T}{n \overline{R} T}$ 





Again

 $PV = n\overline{R}T$  for a mixture .....(4)

 $PV_a = n_a \overline{R}T$  (applying Amagats law , i.e at same pressure and temperature ) ... (5) dividing 5 by 4 we get

From equation (6) and (3)

$$\frac{V_a}{V} = \frac{n_a}{n} = y_a$$
 .....(6)  $\frac{P_a}{P} = \frac{n_a}{n} = y_a$  .....(3)

 $\frac{P_a}{P} = \frac{V_a}{V} = \frac{n_a}{n} = y_a$  Hence proved





#### **AIR- WATER MIXTURES AND RELATED PROPERTIES**

#### **Psychrometry**

Psychrometry is the study of the properties of mixtures of air and water vapour.

### **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 <u>thermodynamic property</u> 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.





#### PROBLEMS

A Perfect gas mixture consists of 1.4kg of nitrogen and 2.3 kg of carbon dioxide at a pressure of 3 bar and a temperature of 22°C, Find

- i) The mole fraction of each constituent
- ii) The equivalent molecular weight of the mixture
- iii) The equivalent gas constant of the mixture
- iv) The partial pressure and the partial volume
- v) The Volume and density of the mixture

<u>Solution</u>		N <sub>2</sub>	CO <sub>2</sub>
	m	1.4 kg	2.3 kg

$$\Gamma = 22^{\circ}C$$

i) Mole fraction of each constituent

$$y_{N_2} = \frac{n_{N_2}}{\sum_{i=1}^{j} n_i} \quad y_{co_2} = \frac{n_{co_2}}{\sum_{i=1}^{j} n_i}$$

$$n_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{1.4}{28} = 0.05$$
  $n_{CO_2} = \frac{m_{CO_2}}{M_{CO_2}} = \frac{2.3}{44} = 0.0523$ 

# $n_{mix} = n_{N_2} + n_{CO_2} = 0.05 + 0.0523 = 0.1023$

$$y_{N_2} = \frac{n_{N_2}}{\sum_{i=1}^j n_i} = \frac{0.05}{0.1023} = 0.489$$

$$y_{CO_2} = \frac{n_{CO_2}}{\sum_{i=1}^{j} n_i} = \frac{0.0523}{0.1023} = 0.511$$





- ii) Equivalent Molecular weight of the mixture
  - $M_{\text{mix}} = y_{\text{N2}} M_{\text{N2}} + y_{\text{CO2}} M_{\text{CO2}}$ = (0.05 x 28) + (0.0523 x 44)

= 0.4 + 2.3012

= **36.176 kg/kg.mol** iii) Equivalent Gas constant of the mixture

$$R_{mix} = \frac{\overline{R}}{M_{mix}} = \frac{8.3143}{36.176} = 0.2298 \frac{kJ}{kg. mol. K} \qquad R_{N_2} = \frac{R}{M_{N_2}} = \frac{8.3143}{28} = 0.297 R_{CO_2} = \frac{R}{M_{CO_2}} = \frac{8.3143}{44} = 0.189$$

iv) Partial pressure and partial volume

 $p_{N_2} = 0.489 X 3 = 1.467 bar$  $p_{CO_2} = 0.511 X 3 = 1.533 bar$  $\frac{P_a}{P} = \frac{V_a}{V} = \frac{n_a}{n} = y_a$ 

$$PV_{N_2} = m_{N_2}R_{N_2}T \qquad (\text{ Considering Amagats law})$$
$$V_{N_2} = \frac{m_{N_2}R_{N_2}T}{P} = \frac{1.4 \text{ X0. } 297 \text{ X } 295}{3\text{ X100}} = 0.4088 \text{ } m^3$$
$$V_{CO_2} = \frac{m_{CO_2}R_{CO_2}T}{P} = \frac{2.3 \text{ X0. } 189 \text{ X } 295}{3\text{ X100}} = 0.4274 m^3$$





<u>Volume of the mixture</u>

 $V_{\text{mix}} = \frac{m_{\text{mix}} R_{\text{mix}} T}{p_{\text{mix}}} = \frac{(2.3 + 1.4) X \, 0.2298 \, X \, 295}{3X100} = 0.836 \, m^3$ 

Density of the mixture

 $\rho_{\rm mix} = \rho_{\rm N_2} + \rho_{\rm CO_2}$ 

$$\rho_{\text{mix}} = \frac{m_{N_2}}{V_{N_2}} + \frac{m_{CO_2}}{V_{CO_2}} = \frac{m_{\text{mix}}}{V_{\text{mix}}} = \frac{3.7}{0.836}$$
$$= 4.426 \text{ kg/m3}$$

NOTE: Partial Volume can also be calculated after finding volume of mixture

$$\frac{P_a}{P} = \frac{V_a}{V} = \frac{n_a}{n} = y_a$$
$$V_{N_2} = 0.489 X 0.836 = 0.408 m^3$$

 $V_{CO_2} = 0.511 X 0.836 = 0.427 m^3$ 





 $\overline{\mathbf{D}}$ 

### The **GRAVIMETRIC ANALYSIS** of air and other data are as follows

Constituents	Percentage	Molecular Weight
Oxygen	23.14	32
Nitrogen	75.53	28
Argon	1.28	40
Carbon dioxide	0.05	44

Calculate i) Gas constant of air ii) Apparent Molecular Weight

Solution:

W.K.T  

$$R_{O_{2}} = \frac{\overline{R}}{M_{O_{2}}} = \frac{8.314}{32} = 0.2598 \text{ kJ/kgK} \qquad R_{Ar} = \frac{R}{M_{Ar_{2}}} = 0.2078 \text{ kJ/kgK}$$

$$R_{N_{2}} = \frac{\overline{R}}{M_{N_{2}}} = 0.2969 \text{ kJ/kgK} \qquad R_{CO_{2}} = \frac{\overline{R}}{M_{CO_{2}}} = 0.1889 \text{ kJ/kgK}$$





### i) Gas Constant for air

WKT

$$\mathbf{R} = \mathbf{x}_{a} \cdot \mathbf{R}_{a} + \mathbf{x}_{b} \cdot \mathbf{R}_{b} + \mathbf{x}_{c} \cdot \mathbf{R}_{c}$$
$$\mathbf{R} = \sum \mathbf{x}_{i} \cdot \mathbf{R}_{i}$$

Considering 1kg of the mixture

Where, 
$$\mathbf{x_i} = \frac{m_i}{m}$$

 $\mathbf{R} = \mathbf{x}_{o2} \cdot \mathbf{R}_{o2} + \mathbf{x}_{N2} \cdot \mathbf{R}_{N2} + \mathbf{x}_{Ar} \cdot \mathbf{R}_{Ar} + \mathbf{x}_{CO2} \cdot \mathbf{R}_{CO2}$ 

 $\mathbf{x_{02}} = \frac{m_{02}}{m} = \frac{23.14}{100} = 0.2314$  Similarly for all gases

 $\mathbf{R} = (0.2314 \text{ X } 0.2596) + (0.7553 \text{ X } 0.2969) + (0.0128 \text{ X } 0.2078) + (0.0005 \text{ X } 0.1889)$ 

R = 0.2871 kJ/kgK

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GRAVIMETRIC ANALYSIS Means MASS Percentage If you divide the value by 100 we get MASS FRACTION  $(x_i)$  of individual component in a GAS MIXTURE

VOLUMETRIC ANALYSIS Means VOLUME Percentage If you divide the value by 100 we get Mole FRACTION( $y_i$ ) or Volume Fraction of individual component in a GAS MIXTURE

> 100% -----23.14% 1kg-----?

Mass of oxygen in kg in a mixture = (23.14 / 100) = 0.2314 kg





### ii) Apparent Molecular Weight

Nothing but Molecular weight of mixture

$$M_{mix} = \frac{\bar{R}}{R_{mix}} = \frac{8.314}{0.2871}$$

= 28.96 kg/kg.mol





### The **VOLUMETRIC ANALYSIS** of a natural gas is as follows

 $CH_4 = 85.8\% C_2H_6 = 13.2\% CO_2 = 0.9\% N_2 = 0.1\%$ 

Determine for this natural gas

- i) The average molecular weight
- ii) The gravimetric analysis
- iii) The average gas constant

### **Solution:**

**NOTE:** Since VOLUMETRIC ANALYSIS Of gases is given that means it is % Volume of gas in 100% of mixture you can directly consider it as Volume Fraction or MOLE FRACTION  $(y_i)$  of gas

$y_{\rm CH_4} = 0.858$	i) The average molecular weight
$y_{C_2H_4} = 0.132$	
$y_{\rm CO_2} = 0.009$	$M_{mix} = \sum y_i M_i = (0.858x16) + (0.132x30) + (0.009x44) + (0.001x28)$
$y_{N_2} = 0.001$	M <sub>mix</sub> = 18.11 kg/kg mol





ii) The gravimetric analysis(Means we have to find mass fraction of gases)

GAS	y <sub>i</sub>	M <sub>i</sub>	$x_i = y_i \times \frac{M_i}{M_{mix}}$
CH <sub>4</sub>	0.858	16	0.7580
$C_2H_6$	0.132	30	0.2187
CO <sub>2</sub>	0.009	44	0.0218
N <sub>2</sub>	0.001	28	0.0015

$$\frac{\frac{P_{a}}{P} = \frac{V_{a}}{V} = \frac{n_{a}}{n} = y_{a}}{\frac{V_{CH_{4}}}{N}} = \frac{\left(\frac{m_{CH_{4}}}{M_{CH_{4}}}\right)}{\left(\frac{m_{mix}}{M_{mix}}\right)} = \left(\frac{m_{CH_{4}}}{M_{CH_{4}}} \times \frac{M_{mix}}{m_{mix}}\right) = \left(\frac{m_{CH_{4}}}{m_{mix}} \times \frac{M_{mix}}{M_{CH_{4}}}\right) = \left(x_{CH_{4}} \times \frac{M_{mix}}{M_{CH_{4}}}\right)$$
$$y_{CH_{4}} = \frac{n_{CH_{4}}}{n} = \left(x_{CH_{4}} \times \frac{M_{mix}}{M_{CH_{4}}}\right)$$
$$x_{CH_{4}} = y_{CH_{4}} \times \frac{M_{CH_{4}}}{M_{mix}} = 0.858 \times \frac{16}{18.11} = 0.7580$$





iii) The average gas constant

$$R_{mix} = \frac{\overline{R}}{M_{mix}} = \frac{8.314}{18.11} = 0.4591 kJ/kgK$$





A vessel of 0.35 m<sup>3</sup> capacity contains 0.4 kg of carbon monoxide (CO) and 1kg of air at 20°C. Calculate

- i) Partial pressure of each component
- ii) The total pressure in the vessel

The **GRAVIMETRIC ANALYSIS** of air may be taken as 23.3% oxygen ( $O_2$ ) and 76.7 % Nitrogen( $N_2$ )

	Solution. Capacity of the vessel, V	$= 0.35 \text{ m}^3$
	Mass of carbon monoxide	= 0.4  kg
	Mass of air	= 1  kg
	Temperature, T	= 20°C or 293 K
	Mass of oxygen present in 1 kg of air	$=\frac{23.3}{100}$ × 1 = 0.233 kg
	Mass of nitrogen present in 1 kg of air	$r = \frac{76.7}{100} \times 1 = 0.767 \text{ kg}$
	But, characteristic gas constant,	
	$R = \frac{R_0}{M}$	
nere,	$R_0$ = Universal gas constant (= 8.314) M = Molecular weight.	4 kJ/kg K), and



i.e.,



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**NB**A

...(*iv*)

Hence, for a constituent,

$$p_i = \frac{m_i R_0 T}{M_i V} \qquad \dots (v)$$

Substituting the values, we get the partial pressures as follows : (i) Partial pressures :

MV

For 
$$O_2$$
,  $p_{O_2} = \frac{0.233 \times (8.314 \times 10^3) \times 293}{32 \times 0.35 \times 10^5} = 0.5068$  bar. (Ans.)  
For  $N_2$ ,  $p_{N_2} = \frac{0.767 \times (8.314 \times 10^3) \times 293}{28 \times 0.35 \times 10^5} = 1.9065$  bar. (Ans.)  
For CO,  $p_{CO} = \frac{0.40 \times (8.314 \times 10^3) \times 293}{28 \times 0.35 \times 10^5} = 0.9943$  bar. (Ans.)  
(*ii*) Total pressure in the vessel, p:  
 $p = \Sigma p_i = P_{O_2} + P_{N_2} + p_{CO}$   
 $= 0.5068 + 1.9065 + 0.9943 = 3.4076$  bar

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(Ans.) ar. 0 17




### **REAL GASES**

1. Real gases doesn't obey ideal gas equation at all pressures and temperatures

- 2. Ideal gas equation is given by
- PV = m RT
- $PV = n \overline{R} T$ ,  $\overline{R} = MR$
- P v = RT, where v = V/m
- $P\overline{v} = \overline{R}T$ , where  $\overline{v} = V/n$

3. 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.

4. The REAL GASES obey very closely to ideal gas or gas laws equation when the pressure is very small or temperature is very large

5. 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.





# VANDERWAALS EQUATION OF STATE

$$\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = \bar{R}T$$

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

$$p_i v_i = RT$$

Where,

p = pressure

v =specific volume

 $\bar{v}$  = Molar specific volume

R = Characteristic gas constant

 $\overline{R}$  = universal gas constant

T = absolute Temperature

a & b are specific constants

# Why coefficient 'a'

It is introduced to account for the existence of mutual attraction between the molecules. The force due to mutual attraction is directly proportional to square of density  $F \propto \rho^2$ 

 $F \propto 1/v^2$ 

$$F = \frac{a}{v^2}$$

# Why coefficient 'b'

It is introduced to account for the volumes of molecules which was neglected in IDEAL GAS equation. And it is known as CO-VOLUME





#### **DERIVATION OF EQUATION FOR VANDERWAALS CONSTANTS**

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \dots \dots \dots (1)$$

$$\left(\frac{\delta p}{\delta v}\right)_{T_C} = 0 \dots \dots (2)$$

$$\left(\frac{\delta^2 p}{\delta v^2}\right)_{T_C} = 0 \dots \dots (3)$$

Solving equation (1) for p , we get

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \dots \dots \dots (4)$$



Differentiating equation(4) with respect to 'v' twice at critical point where  $p = p_c$ ,  $T = T_c$ ,  $v = v_c$  we get

$$\left(\frac{\delta p}{\delta v}\right)_{T_{c}} = 0 = \frac{-RTc}{(v_{c}-b)^{2}} + \frac{2a}{v_{c}^{3}}\dots(5) \qquad \left(\frac{\delta^{2}p}{\delta v^{2}}\right)_{T_{c}} = 0 = \frac{2RTc}{(v_{c}-b)^{3}} - \frac{6a}{v_{c}^{4}}\dots(6)$$





$$\left(\frac{\delta p}{\delta v}\right)_{T_{c}} = 0 = \frac{-RTc}{(v_{c} - b)^{2}} + \frac{2a}{v_{c}^{3}}....(5)$$

$$RT_{c} = \frac{2a}{v_{c}^{3}}(v_{c} - b)^{2}....(7)$$

$$\begin{pmatrix} \frac{\delta^2 p}{\delta v^2} \end{pmatrix}_{T_C} = 0 = \frac{2RTc}{(\overline{v_c} - b)^3} - \frac{6a}{\overline{v_c}^4} \dots \dots (6)$$
$$RT_C = \frac{3a}{v_c^4} (v_c - b)^3 \dots \dots (8)$$

From equation (7) and (8) we get

$$\frac{2a}{v_c^3} (v_c - b)^2 = \frac{3a}{v_c^4} (v_c - b)^3$$

$$v_c = 3b$$
.....(9)

Substituting equation (9) in equation (7) we get

 $v_{c} = 3b \qquad b = \frac{v_{c}}{3}$   $RT_{C} = \frac{2a}{v_{c}^{3}} (v_{c} - b)^{2} \dots \dots (7)$   $T_{c} = \frac{8a}{27. b. R} \dots (10)$ Department of Mechanical Engineering





Substituting (9) and (10) in equation (4) we get

$$v_c = 3b \text{ or } b = v_c/3 \dots (9)$$
  
 $T_c = \frac{8a}{27.b.R} \dots (10)$   
 $p = \frac{RT}{v-b} - \frac{a}{v^2} \dots (4)$   
 $p_c = \frac{a}{27.b^2} \dots (11)$ 

So equation (9) (10) and (11) are the critical pressure, critical temperature and critical volume equations

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#### NOW TO FIND SPECIFIC CONSTANTS "a" and "b" IN TERMS OF CRITICAL PROPERTIES

From equ(9) and (10)

$$b = \frac{v_c}{3}$$
$$T_c = \frac{8a}{27.b.R}$$

By substituting (9) in (10) we get

$$a = \frac{9}{8}R.T_C.v_c\dots\dots(12)$$

From equation (9) and 11)

$$b = \frac{v_c}{3} \dots \dots (9)$$
$$p_c = \frac{a}{27 \cdot b^2} \dots \dots (11)$$

Substituting (9) in (11)

$$a = 3p_c v_c^2 \dots \dots \dots (13)$$

From equation (10) and 11)

$$T_c = \frac{8a}{27.b.R}$$
$$b = \frac{8a}{27.T_cR}$$
$$p_c = \frac{a}{27.b^2}\dots(11)$$

Substituting (10) in (11)

$$a = \frac{27}{64} \frac{R^2 \cdot T_c^2}{p_c} \dots (14)$$

Hence in terms of critical properties

$$a = \frac{9}{8}R.T_{C}.v_{c} = 3p_{c}v_{c}^{2} = \frac{27}{64}\frac{R^{2}.T_{C}^{2}}{p_{c}}$$





To express constant "b" in terms of critical properties

WKT from equation (9)

$$b=rac{v_c}{3}$$

from equation (10)

$$T_c = \frac{8a}{27.b.R}$$

$$b=\frac{8a}{27.T_cR}$$

Substituting equation (14) in 
$$b = \frac{8a}{27.T_c R}$$

$$a = \frac{27}{64} \frac{R^2 \cdot T_c^2}{p_c} \dots \dots (14)$$
  $b = \frac{RT_c}{8P_c}$ 

from equation (11) and (12)

$$p_{c} = \frac{a}{27.b^{2}}....(11)$$

$$b = \sqrt{\frac{a}{27.p_{c}}}$$

$$a = \frac{9}{8}R.T_{c}.v_{c}....(12)$$

$$b = \sqrt{\frac{R.T_c v_c}{24.p_c}}$$

## Hence in terms of critical properties

$$b = \frac{v_c}{3} = \frac{RT_c}{8P_c} = \sqrt{\frac{R.T_cv_c}{24.p_c}}$$

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#### **COMPRESSIBILITY FACTOR (Z)**

- The specific volume of a gas becomes very large when the pressure is LOW and Temperature is HIGH.
- Thus it is not possible to conveniently represent the behavior of real gas es at low pressure and high temperature.
- In order to overcome this difficulty the properties of each Real gas is represented by means of a compressibility factor.
- The factor which expresses the extent if deviation of the gas from a perfect gas is known as COMPRESSIBILITY FACTOR

For ideal gas from the law we haven pv = RT

Dividing the above equation by "RT"

 $\frac{pv}{RT} = 1$ 

But for REAL GAS the number 1 is replaced by some other number "Z" Hence  $\frac{pv}{RT} = Z$ 

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- The compressibility factor of a perfect gas has a value of unity under all conditions
- As the pressure if reduced , the REAL GAS behaves as an IDEAL GAS and hence, at low pressure , for any gas compressibility factor tends to UNITY

$$\lim_{p\to 0} \mathbf{Z} = \mathbf{1}$$

The value of "Z" for a REAL GASES is finite and it may be LESSER or MORE than UNITY, depending in the temperature and pressure of the gas





### **REDUCED PROPERTIES:**

1) REDUCED PRESSURE : It is the ratio of the existing pressure to the critical pressure of the substance

$$\mathbf{p_r} = \frac{\mathbf{p}}{\mathbf{p_c}}$$

2) REDUCED TEMPERATURE : It is the ratio of the existing Temperature to the critical temperature of the substance

$$T_r = \frac{T}{T_c}$$

3) REDUCED VOLUME : It is the ratio of the existing Volume to the critical volume of the substance

$$\mathbf{v}_{\mathbf{r}} = \frac{\mathbf{v}}{\mathbf{v}_{\mathbf{c}}}$$

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#### LAW OF CORRESPONDING STATES:

If any two gases have equal values of Reduced pressure and reduced temperature then they will have same values of Reduced Volume

Or

The compressibility of any one component substance is a function of only two properties, usually temperature and pressure so that

 $Z = f(T_r, p_r)$ 

This equation is called Law of corresponding States





#### GENERALIZED COMPRESSIBILITY CHART

In generalized compressibility chart , the compressibility factor "Z" is plotted as a function of reduced pressure and reduced temperature. According to these charts , one component substance which are at same reduced pressure and temperature have the same compressibility factor

The generalized chart provide one of the best means of expressing deviation from ideal behavior and gives results with an accuracy of within 5%

A gas which has a compressibility factor less than unity is more compressible than a perfect gas. The chart shows both temperature and pressure introduce deviation from Ideal behavior







# **BEATTIE – BRIDGEMAN EQUATION OF STATE**

$$p = \frac{\bar{R}T}{\bar{v}^2} \left(1 - \frac{c}{\bar{v}^2}\right) (\bar{v} + B) - \frac{A}{\bar{v}^2}$$

# where

$$A = A_O \left( 1 - \frac{a}{\bar{v}} \right) \qquad B = B_O \left( 1 - \frac{b}{\bar{v}} \right)$$

The constants  $A_0$ , a,  $B_0$ , b & C are given in steam table

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Determine specific volume of helium at 200kpa and 300K using the vanderwaals equation and the ideal gas equation of state . The molecular weight of helium is 4 and constants in the vanderwaals equation a = 3.4 and b = 0.0234 from steam table

Solution

Using IDEAL GAS Equation

pv = RT

$$v = \frac{RT}{p} = \frac{\overline{RT}}{Mp} = \frac{8.314 \times 300}{4 \times 200} = 3.117 \ m^3/kg$$

Using Vanderwaals equation

$$\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = \bar{R}T$$

$$\left(200 + \frac{3.4}{\bar{v}^2}\right)(\bar{v} - 0.0234) = 8.314 X 300$$

By trial and error method we get

 $\bar{v} = 12.5 \ m^3/kg$ mol

$$\frac{V}{n} = 12.5 \qquad \frac{V}{\left(\frac{m}{M}\right)} = 12.5$$
$$\frac{VM}{m} = 12.5$$
$$v = \frac{12.5}{M} = \frac{12.5}{4} = 3.125 \ m^3/kg$$

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Calculate the reduced temperature and reduced pressure of a gas which is at a pressure of 7 Mpa and a temperature of  $150^{\circ}$ C. Also calculate the specific volume of the gas if Z=0.54. Compare this with the specific volume given by the ideal gas equation of state . Use the following values : critical pressure = 4.26 Mpa , critical temperature =  $370^{\circ}$ C , R = 0.189 kJ / kg °C

## To find reduced pressure and reduced temperature

$$p_{r} = \frac{p}{p_{c}} = \frac{7}{4.26} = 1.643$$
$$T_{r} = \frac{T}{T_{c}} = \frac{150}{370} = 0.06576$$

## **Using IDEAL GAS EQUATION**

Pv = RT

$$v = \frac{RT}{p} = \frac{0.189 \, X \, 423}{7000} = 0.0114 \, m^3 / kg$$

# Using COMPRESSIBILITY FACTOR

Pv = ZRT

$$v = \frac{ZRT}{p} = \frac{0.54 X \ 0.189 X \ 423}{7000} = 0.00616 \ m^3/kg$$

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Determine the pressure in a steel vessel having a volume of 15liters and containing 3.4kg nitrogen at 400<sup>o</sup>C by using i)ideal gas equation ii) vanderwaals equation

Also calculate the compressibility factor by using the answer obtained from vanderwaals equation

To find pressure using ideal gas equation

PV = mRT

$$p = \frac{m\bar{R}T}{VM} = \frac{3.4X\ 8.314\ X673}{0.015\ X\ 28} = \mathbf{45295}.\mathbf{46}\ \mathbf{kPa}$$

Using vanderwaals equation

$$\left(p+\frac{a}{v^2}\right)(v-b) = RT$$
  $p = \frac{\left(\frac{\overline{R}}{M}\right)T}{(v-b)} - \frac{a}{v^2}$ 

$$a = 136.4 \text{ KNm}^{4}/(\text{kg.mol})^{2}$$
  
 $b = 0.0386 \text{ m}^{3}/\text{kgmol}$ 

P = 56961.91 kPa

v = V/m

To find "Z" by using value of "p" from vanderwaals equation

Pv = ZRT

$$Z = \frac{pv}{RT} = \frac{56961.9 X(\frac{0.015}{3.4})}{\frac{\overline{R}}{M} \cdot T} = 1.25$$

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Compute the pressure of 2 mol of air at 400K with a total volume of  $0.5m^3$ . Using the ideal gas law and the Vanderwaals equation of state take a = 135.8 kpa (m<sup>3</sup>/kgmol)<sup>2</sup> and b = 0.0364 m<sup>3</sup>/kgmol

To find pressure using ideal gas equation

 $PV = n\overline{R}T$ 

$$p = \frac{n\overline{R}T}{V} = \frac{2X\,8.314\,X400}{0.5} = \mathbf{13302.4}kPa$$

#### Using vanderwaals equation

Since number of moles is given we can use  $\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = \bar{R}T$  $\bar{v} = \frac{V}{n} = \frac{0.5}{2} = 0.25$  P = 13396.48 kPa

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Determine the specific volume of  $H_2$  gas when its pressure is 60bar and temperature is 100K.

- a) By using compressibility chart
- b) By using Vanderwaals equation

Take for  $H_2$   $T_c = -239.76^{\circ}C$   $P_c = 12.92$  bar = 12.92 x 100 kpa  $a = 0.25105 x 10^5 Nm^2/kgmol^4$  $b = 0.0262 m^3/kgmol$ 

Given: p = 60 bar = 6000 kpa, T = 100 K,  $M_{\text{H2}} = 2 \text{ kg/kgmol}$ 

a) By using compressibility chart

 $P_r = P / P_c = 60 / 12.92 = 4.65$ 

 $T_r = T / T_c = 100/33.24 = 3.008$ 

From chart corresponding to the values  $P_r$  and  $T_r$  we get Z = 1.035

$$P\vartheta = ZRT$$
  

$$\vartheta = 0.0717 \text{ m}3/\text{kg}$$
  

$$P\vartheta = Z(\frac{\overline{R}}{M})T$$

# Using vanderwaals equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

$$\vartheta = 0.07 \text{ m}3/\text{kg}$$

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#### Difference between ideal gases and real gases

- 1. Ideal gas has no definite volume while real gas has definite volume
- 2. Ideal gas has no mass where as real gas has mass
- 3. Collision of ideal gas particles is elastic while non elastic for real gas
- 4. No energy transfer is involved during collision of particles in ideal gas but in real gas has attracting energy
- 5. Pressure is high in IDEAL GAS compared to real gas since the particles do not have the attractive forces that enable the molecules to held back when they will collide at an impact. Hence particles collide with less energy
- 6. Ideal gas follows the equation pV = mRT. Real gas follows Vander waals equation