

**ME6301****ENGINEERING THERMODYNAMICS****L T P C**  
**3 0 0 3****UNIT I BASIC CONCEPTS AND FIRST LAW****9**

Basic concepts - concept of continuum, comparison of microscopic and macroscopic approach. Path and point functions. Intensive and extensive, total and specific quantities. System and their types. Thermodynamic Equilibrium State, path and process. Quasi-static, reversible and irreversible processes. Heat and work transfer, definition and comparison, sign convention. Displacement work and other modes of work .P-V diagram. Zeroth law of thermodynamics – concept of temperature and thermal equilibrium– relationship between temperature scales – new temperature scales. First law of thermodynamics –application to closed and open systems – steady and unsteady flow processes.

**UNIT II SECOND LAW AND AVAILABILITY ANALYSIS****9**

Heat Reservoir, source and sink. Heat Engine, Refrigerator, Heat pump. Statements of second law and its corollaries. Carnot cycle Reversed Carnot cycle, Performance. Clausius inequality. Concept of entropy, T-s diagram, Tds Equations, entropy change for - pure substance, ideal gases - different processes, principle of increase in entropy. Applications of II Law. High and low grade energy. Available and non-available energy of a source and finite body. Energy and irreversibility. Expressions for the energy of a closed system and open systems. Energy balance and entropy generation. Irreversibility. I and II law Efficiency.

**UNIT III PROPERTIES OF PURE SUBSTANCE AND STEAM POWER CYCLE****9**

Formation of steam and its thermodynamic properties, p-v, p-T, T-v, T-s, h-s diagrams. p-v-T surface. Use of Steam Table and Mollier Chart. Determination of dryness fraction. Application of I and II law for pure substances. Ideal and actual Rankine cycles, Cycle Improvement Methods - Reheat and Regenerative cycles, Economiser, preheater, Binary and Combined cycles.

**UNIT IV IDEAL AND REAL GASES, THERMODYNAMIC RELATIONS****9**

Properties of Ideal gas- Ideal and real gas comparison- Equations of state for ideal and real gases- Reduced properties-.Compressibility factor-.Principle of Corresponding states. - Generalised Compressibility Chart and its use-. Maxwell relations, Tds Equations, Difference and ratio of heat capacities, Energy equation, Joule-Thomson Coefficient, Clausius Clapeyron equation, Phase Change Processes. Simple Calculations.

**UNIT V GAS MIXTURES AND PSYCHROMETRY****9**

Mole and Mass fraction, Dalton's and Amagat's Law. Properties of gas mixture – Molar mass, gas constant, density, change in internal energy, enthalpy, entropy and Gibbs function. Psychrometric properties, Psychrometric charts. Property calculations of air vapour mixtures by using chart and expressions. Psychrometric process –adiabatic saturation, sensible heating and cooling, humidification, dehumidification, evaporative cooling and adiabatic mixing. Simple Applications.

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## UNIT –I

# BASIC CONCEPTS AND DEFINITIONS

Thermodynamics is the science of energy transfer which deals with the relations among heat, work and properties of systems.

The name ‘thermodynamics’ is derived from the Greek words therme, meaning ‘heat’ and dynamis meaning power. Thus, thermodynamics is basically the study of heat and power.

### Application Area of Thermodynamics

Energy transfer is present in almost all the engineering activities. Hence, the principles of thermodynamics are playing vital role in designing all the engineering equipments such as internal combustion engines, rockets, jet engines, thermal and nuclear power plants, refrigerators etc.

### 1.1 Statistical and Classical Thermodynamics

Statistical Thermodynamics is microscopic approach in which, the matter is assumed to be made of numerous individual molecules. Hence, it can be regarded as a branch of statistical mechanics dealing with the average behaviour of a large number of molecules.

Classical thermodynamics is macroscopic approach. Here, the matter is considered to be a continuum without any concern to its atomic structure.

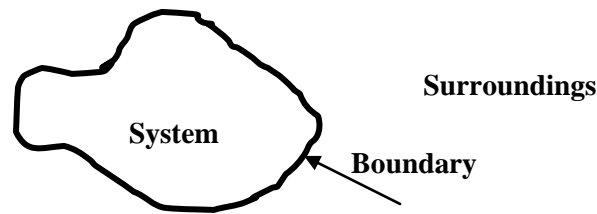
Consider a gas in a container. Pressure exerted at the wall of the container is the average force per unit area due to the collision of the gas molecules on the wall surface. To determine this pressure, we need not know the behaviour of individual molecules of the gas. This approach is macroscopic approach. However, the results obtained from macroscopic and statistical study of matter.

### Thermodynamic Systems and Surroundings

A Thermodynamic system is defined as a quantity of matter or a region in space whose behaviour is being investigated.

Everything external to the system is defined as surroundings. In its usual context the term ‘surroundings’ is restricted to the regions in the immediate vicinity which has a detectable influence on the system.

Boundary is the surface which separates the system from its surroundings. It may be fixed or moving and real or imaginary.



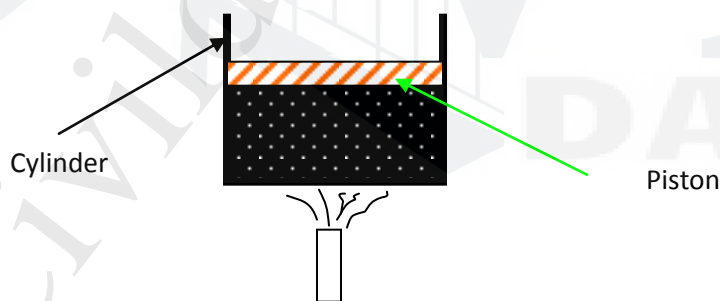
**Fig.1.1 Thermodynamic System, boundary, surroundings**

### 1.2 Types of Thermodynamic Systems

There are three types of thermodynamic systems :

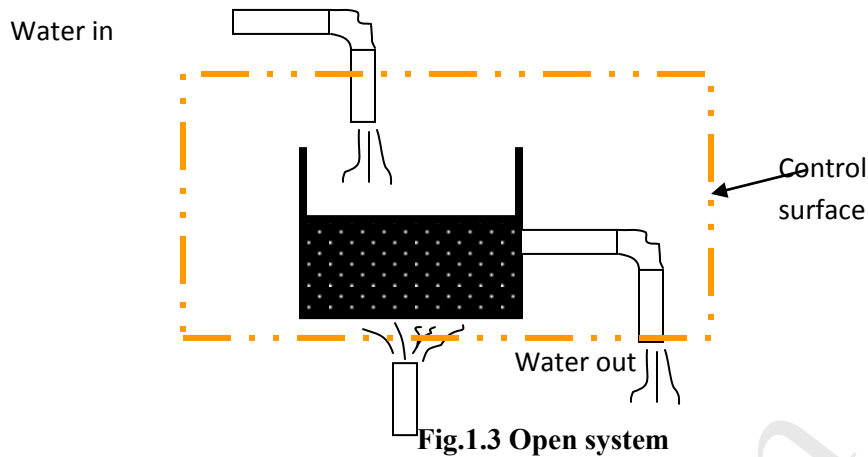
- a) Closed System
- b) Open System and
- c) Isolated System

In closed system, attention is focused on a fixed mass. Energy in the form of heat and work (*The terms heat and work will be defined in the chapter 2.*) can cross the boundary of the system. But there is no mass flow across the boundary. Hence, the possibility of change in volume is always there in the closed systems.

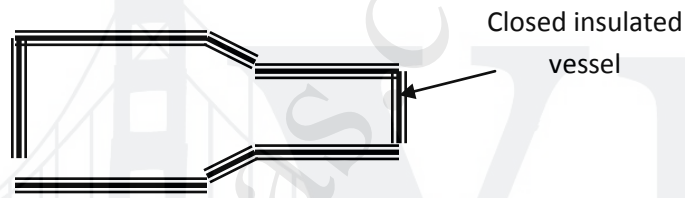


**Fig.1.2 Closed system**

In open system, both matter and energy can cross the boundary. Here, the behaviour of a fixed region in space called control volume is investigated and hence, there is no change in volume. The surface of the control volume is known as control surface.



A system that exchanges neither energy nor matter with its surroundings is known as an isolated system.



**Fig.1.2 Isolated system**

### 1.3 Thermodynamic Properties

In all thermodynamic problems energy transfer to or from the system is observed. To receive, store and deliver energy a working substance is present within the system. The characteristics which can be used to describe the condition of the system are known as properties.

Thermodynamic properties are classified into two categories : intensive and extensive. Intensive properties are independent of quantity of matter or mass whereas extensive properties are dependent on mass

Consider a vessel containing air. If a membrane is assumed to be introduced into the vessel, such that it is divided into two equal parts. The properties remaining unchanged such as pressure and temperature are intensive properties. Volume of air will be reduced to half of its initial value. Hence, it is an extensive property.

### 1.4 Thermodynamic State and Equilibrium

When a system does not undergo any change, all the properties have fixed values. This condition is known as a thermodynamic state.

The word equilibrium means balance. An equilibrium state of a thermodynamic system is a state that can not be changed without any interaction with its surroundings. The factors that cause a change without any interactions with its surroundings are:

1. Pressure difference
2. Temperature difference
3. Chemical reaction

If a system is balanced in all respects, it is in a state of thermodynamic equilibrium. Balanced in all respects means :

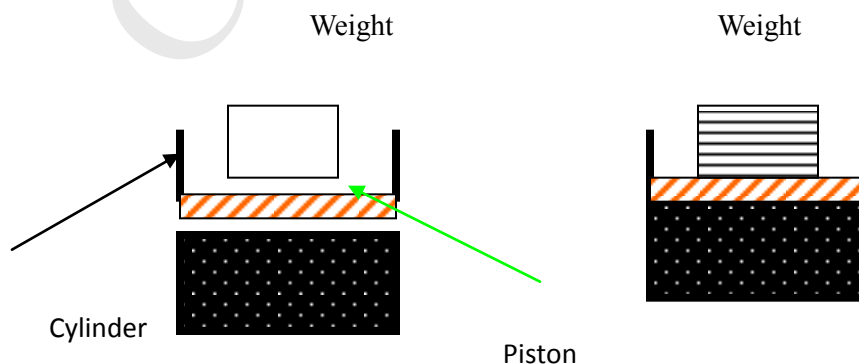
- There should not be any temperature difference within the system, so that the system is thermally balanced.
- No pressure difference exists between any two points within the system (Neglecting gravitational effects) and between the system and surroundings, so that it is mechanically balanced.
- No chemical reaction is taking place, so that it is chemically balanced.
- If two phases are involved, mass of each phase remains constant so that phase equilibrium is achieved.

Hence, for a system in a state of thermodynamic equilibrium, there is no change in any macroscopic property.

## 1.5 Processes and Cycles

When a system is taken from one equilibrium state to another, the change is known as process. The series of intermediate states through which a system passes during a process is called the path of the process. If all these intermediate states are equilibrium states, the process is known as quasi equilibrium or quasi-static process.

Consider a certain quantity of gas taken in a frictionless piston cylinder arrangement as shown in Fig 1.5. The system is in thermodynamic equilibrium so that there is no unbalanced force acting on piston.





(a)

(b)

Fig.1.5 Illustration for thermodynamic equilibrium

The moment the weight is removed from the piston, mechanical equilibrium does not exist and as a result the piston is moved upward until mechanical equilibrium is restored again. Therefore the actual process occurs only when equilibrium does not exist.

As shown in Fig.1.5.a, if the entire weight on the piston is removed at once, the deviation from the equilibrium is high and the expansion is rapid. For such a process the intermediate states are not equilibrium states and hence the process would be non-quasi-equilibrium.

If the weight is assumed to be made of a large number of small pieces as shown in Fig.1.5.b and taken off one by one, the deviation from equilibrium is less. The process could be considered quasi-equilibrium.

A thermodynamic system is said to undergo a cycle, if it is taken through a number of processes such that, the final state of the last process is identical with the initial state of the first process in all respects. For cycles net change in any property is zero.

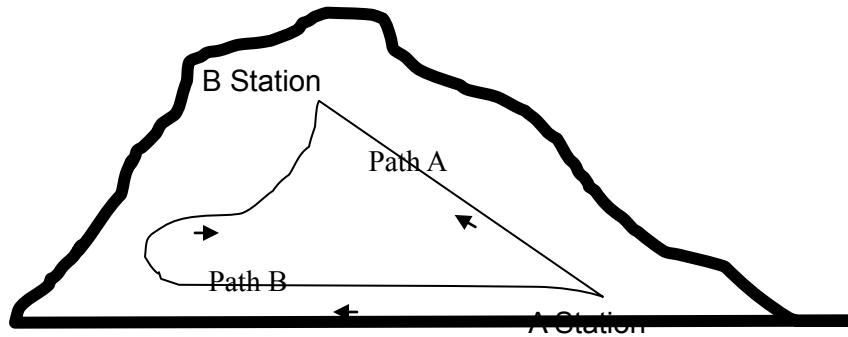
## 1.6 Point and Path Functions

Thermodynamic functions are classified into two categories namely point and path functions. Point functions are those for which the change depends on only the end states and not on the path followed. Hence point functions are inexact differentials

Path functions are those for which the change depends not only on the end states but also on the path followed. Hence path functions are exact differentials

It can be observed the change in any property during a process depends only on end states. Therefore all the properties are point functions.

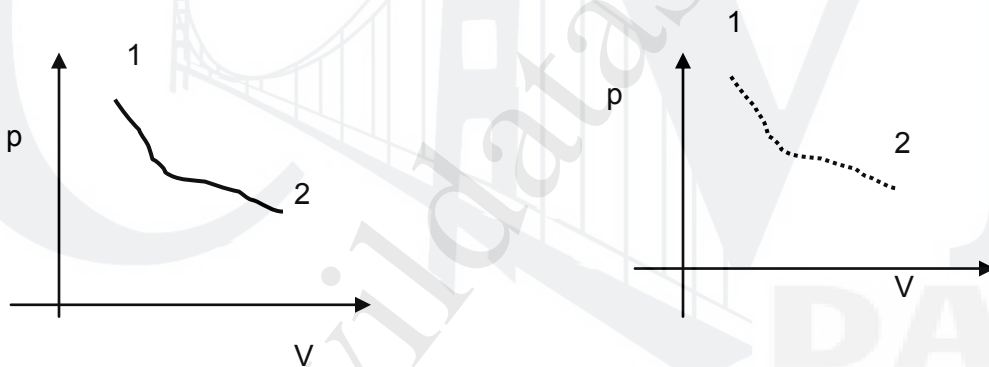
To demonstrate path and point functions, let us consider two stations A and B on a hill as shown in the Fig.1.6. While moving from station A to station B, let the distance traveled and increase in height from the mean sea level are observed. Distance traveled in path 1 is different from that in path 2. Hence it may be regarded as path function. But the change in height is same in both path 1 and path 2, therefore it is a point function.



**Fig.1.6 Illustration of point and path functions**

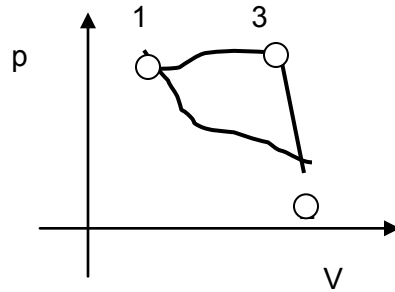
### State Postulate and Property Diagrams

As mentioned earlier, properties are meant for describing the state of a system. To fix a state, all the properties need not be specified. If any two independent intensive properties are specified, rest of the properties automatically assumes certain values. This is known as state postulate.



**Fig.1.7 property diagram of equilibrium and non equilibrium processes**

Consider pressure and specific volume (*Volume per unit mass*) are the two independent, intensive properties, describing the state of a compressible system. On a p-V diagram the state will assume a point as represented in the Fig.1.7(a). Let the system be taken to another state such that all the intermediate states are equilibrium states. The curve connecting the initial state and final state, passing through all the intermediate states is indicating the path of the process. In non-quasi-equilibrium process as the intermediate status can not be defined, the path is denoted by dashed line as given in Fig.1.7(b)



**Fig. 1.8 Thermodynamic cycle on a property diagram**

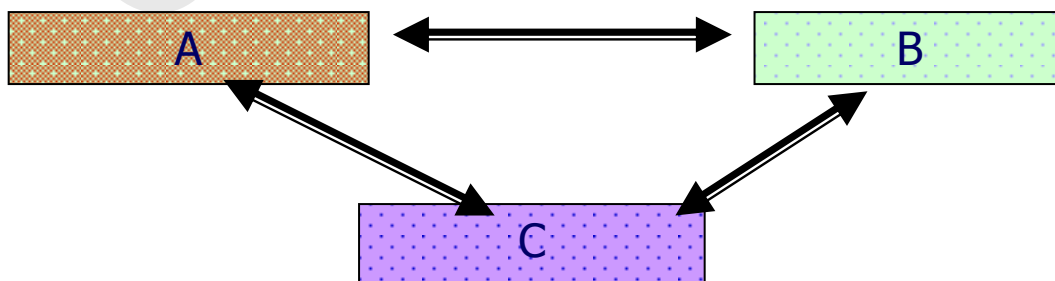
Fig.1.8 indicates a system undergoing a cycle consisting of three quasi-equilibrium processes.

### 1.7 Temperature and Zeroth Law

Maxwell defined the temperature of a system as *its Thermal state considered with reference to its ability to communicate heat to other bodies.*

When a hot body is brought into contact with a cold body, the hot body becomes cooler and the cold body becomes hotter. After sufficient time, the temperature of both the bodies will be equal. At that point, the two bodies are said to have reached thermal equilibrium.

*Consider three bodies A, B and C. If the bodies A and B are in thermal equilibrium with C when brought into contact separately, they are also in thermal equilibrium with each other. This concept is known as zeroth law of thermodynamics.*



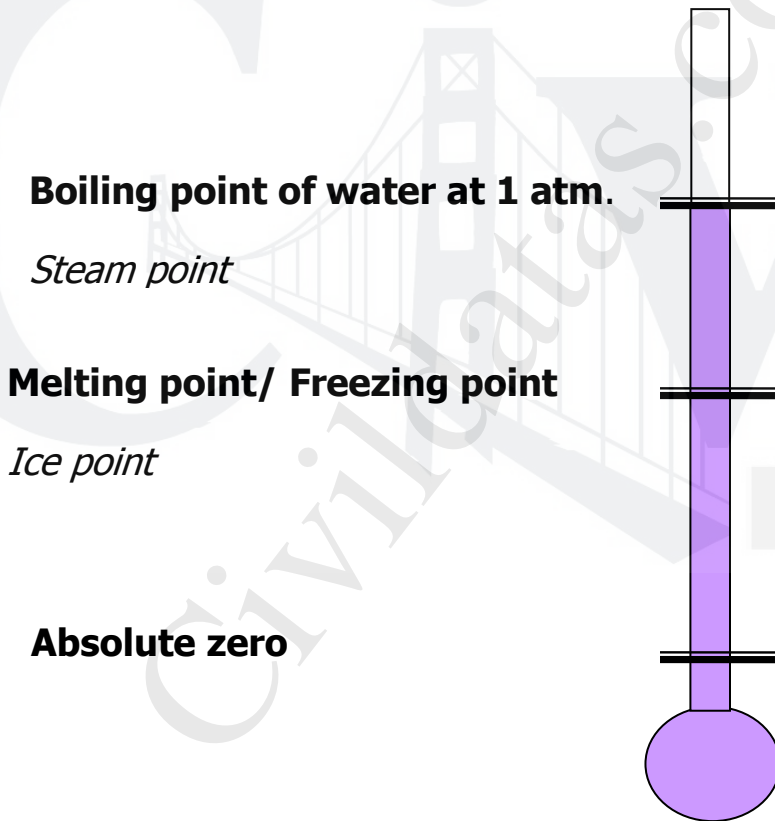
Several properties of materials are found to be varying with temperature in a predictable way. This variation is used to measure temperature. In mercury thermometers, expansion of mercury with temperature is used for temperature measurement.

### 1.8 Temperature Scales

Freezing point of water known as *ice point* and boiling point of water known as *steam point* are taken as the reference states for all types of temperature scales.

The various types as temperature scales in use are :

- a) Celsius scale
- b) Fahrenheit scale
- c) Kelvin scale
- d) Rankine scale



Reference state	Celsius	Kelvin	Fahrenheit	Rankine

Steam point	<b>100</b>	<b>373</b>	<b>212</b>	<b>672</b>
Ice point	<b>0</b>	<b>273</b>	<b>32</b>	<b>492</b>
Absolute Zero	<b>-273</b>	<b>0</b>	<b>- 460</b>	<b>0</b>

## Homogeneous and Heterogeneous Systems

Matter can exist in any one of the three phases namely solid, liquid and gas. A system consisting of a single phase is known as homogeneous systems. If the matter exists in more than one phase, the system is known as heterogeneous system.

### 1.9 Pure Substances

Substances of fixed chemical composition throughout are known as pure substances.

That is, pure substances have homogenous and invariable chemical composition irrespective of the phase or phases in which they exist.

#### Example

- a. Atmosphere air
- b. Water
- c. Nitrogen
- d. Water-steam mixture
- e. Product of combustion.

Though, mixture of water and steam is considered a pure substance, air and liquid air cannot be, since, the chemical composition of liquid air differs from that of gaseous air.

### The Ideal Gas

Based on the experimental work carried out by Boyle, Charles and Gay-Lussac, pressure, temperature and specific volume of many gases at low pressure and moderate temperature are related by the following equation.

$$pv = RT \text{ where } R =$$

This equation is known as equation of state of an ideal gas. The term R is known as characteristic gas constant and  $R_u$  universal gas constant. In SI unit  $R_u = 8.314 \text{ kJ/kgmol.K}$ .

## 1.10 Concept of continuum

In microscopic approach the substance is assumed to be continuously distributed, ignoring the space between the molecules. This is known as continuum hypothesis.

Since the matter is treated as continuous, the density at a point can be defined as

$$\rho = \lim_{v \rightarrow v'} \left( \frac{m}{v} \right)$$

Where  $v'$  is the smallest volume for which a definite value of the ratio exists. Below the limiting value of  $v'$ , the fluctuation in average density will be high and a definite value for the ratio becomes impossible, with the *mean free path*\* of the molecules approaching the order of magnitude of the dimension of the vessel

## 1.11 WORK AND HEAT

In the previous chapter, the different thermodynamic systems and their characteristics were discussed. To undergo a change of state, the system has to interact with its surroundings. Work and heat transfers across the boundaries cause these changes. In this chapter various forms of work and modes of heat transfers are discussed.

### Work as Defined in Mechanics

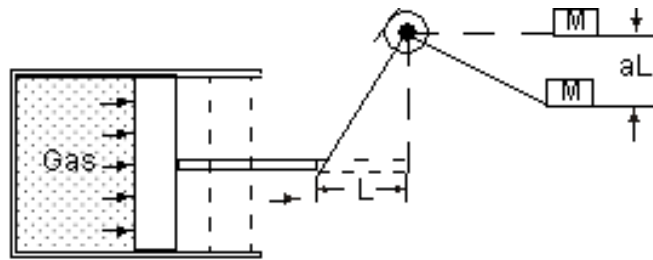
work is done when the point of application of a force moves in the direction of the force. The product of the force and the distance moved in the direction of the force is equal to the amount of the work done.

This simple definition of work confines only to the area of mechanics and can not be extended to the more complex problems in thermodynamics. Hence a new definition should be introduced to cover mechanical as well as the other forms of work.

### The Thermodynamic Definition of Work

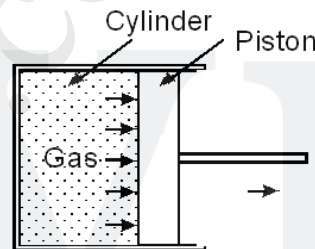
*Positive work is done by a system, during a given process, when sole effect external to the system could be reduced to the lifting of a mass.*

Consider a gas expanding in a piston cylinder arrangement as given in Figure 2.1. Here no mass is actually lifted against gravity. But if the existing surroundings is fitted with an arrangement as given in the Figure 2.2, there is a possibility of lifting the mass. Hence work is said to be done by the system.



**Figure 2.2 Expansion with actual lifting of mass**

While exploring the possibility of lifting a mass the effects that are external to the system alone must be taken into account. For example, a lift with a person and a suitcase is considered as a system. If the person lifts the suitcase, it should not be taken into account, because this event occurs within the system.



**Figure 2.1 Expansion without actual lifting of mass**

### 1.12 Units of Work and Power

In the international system (SI), the unit of force is Newton (N) and that of distance is metre (m). Hence the unit of work is Nm which is also given a special name Joule. In most of the applications large quantity of work is involved. Therefore kJ is commonly used.

Rate of doing work is known as power. Hence its unit is Nm/S or J/S which is again given a special name Watts(W).

### 1.13 Sign Convention of Work

- Work done by the system on the surroundings is considered as positive work.
- Work done on the system by the surroundings is taken as negative work.

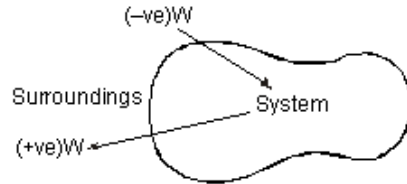


Figure 2.3 Sign Convention of work

### 1.14 Displacement Work

Consider a piston cylinder arrangement as given in the Figure 2.4. If the pressure of the fluid is greater than that of the surroundings, there will be an unbalanced force on the face of the piston. Hence, the piston will move towards right.

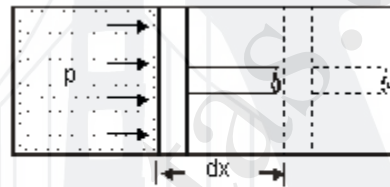


Figure 2.4 Displacement work

Force acting on the piston = Pressure  $\times$  Area

$$= pA$$

$\therefore$  Work done = Force  $\times$  distance

$$= pA \times dx$$

$$= pdV$$

where  $dV$  - change in volume.

This work is known as displacement work or  $pdV$  work corresponding to the elemental displacement  $dx$ . To obtain the total work done in a process, this elemental work must be added from the initial state to the final state. Mathematically, .

### Evaluation of Displacement Work

#### Constant Pressure Process



Figure 2.5 shows a piston cylinder arrangement containing a fluid. Let the fluid expands such that the pressure of the fluid remains constant throughout the process. Figure 2.6 shows the process in a p-V diagram.

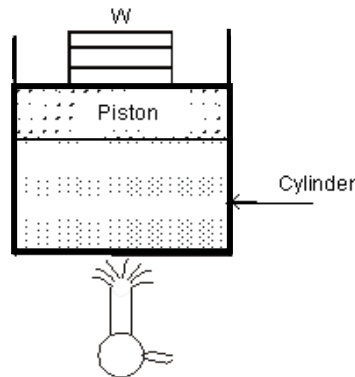


Figure 2.5

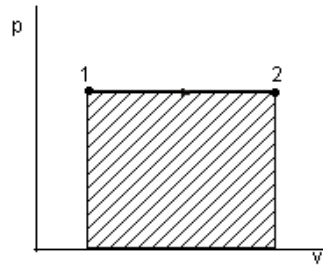


Figure 2.6

The mathematical expression for displacement work can be obtained as follows:

$$= p(V_2 - V_1) \quad \dots(2.1)$$

This expression shows that the area under a curve in a p-V diagram gives work done in the process.

### Constant volume process

Consider a gas contained in a rigid vessel being heated. Since there is no change in volume, the displacement work .

### Hyperbolic process

Let the product of pressure and volume remains constant at all the intermediate states of a process. In the p-V diagram it will be a hyperbola as given in Figure 2.7.

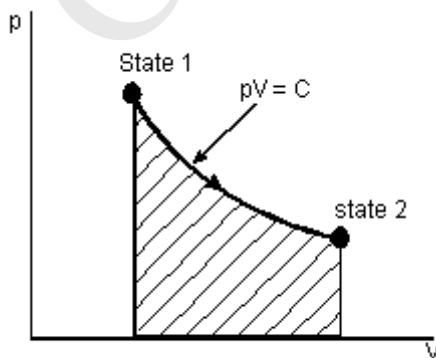


Figure 2.7

$$\begin{aligned}
 {}_1W_2 &= \int_1^2 p dV \\
 &= \int_1^2 C dV \text{ where } C=pV \\
 &= C \int_1^2 \frac{1}{V} dV \\
 &= C \ln (V_2/V_1) \\
 &= p_1 V_1 \ln(V_2/V_1) \text{ (or) } p_2 V_2 \ln (V_2/V_1) \dots(2.2)
 \end{aligned}$$

For Ideal gases when temperature remains constant, pV will be constant i.e., isothermal process are hyperbolic processes for an ideal gas.

### Polytropic Process

Any process can be represented by the general form  $pV^n = \text{constant}$ . Based on the value of  $n$ , the process differs as given below; For other values of  $n$ , the process is known as polytropic process. Figure 2.8 shows the polytropic process of various possible polytropic index 'n' on p-V coordinates. Expression for displacements work for a polytropic process can be obtained as follows :

$$\begin{aligned}
 {}_1W_2 &= \int_1^2 p dV \\
 &= \int_1^2 \frac{C}{V^n} dV \text{ where } C = pV^n \\
 &= C \int_1^2 V^{-n} dV \\
 &= C \left[ \frac{V^{-n+1}}{-n+1} \right]_1^2 \\
 &= \left[ \frac{CV_2^{-n+1} - CV_1^{-n+1}}{-n+1} \right]_1^2 \\
 &= \left[ \frac{p_2 V_2^n V_2^{-n+1} - p_1 V_1^n V_1^{-n+1}}{-n+1} \right] \text{ since } C = p_1 V_1^n = p_2 V_2^n
 \end{aligned}$$

$$= \left[ \frac{p_2 V_2 - p_1 V_1}{-n + 1} \right]$$

## Work is a Path Function

Consider a working substance initially occupying  $0.2 \text{ m}^3$  at 1 bar as represented by state 1 in the Figure 2.9. Let the system changes its state such that the final volume is  $0.05 \text{ m}^3$  and pressure 2 bar. The change of state may occur along the paths 1A2, 1B2 or 1C2. As mentioned earlier, area under the curve representing the process in a p-V diagram gives the work done in the process. Comparing the area under the paths 1A2, 1B2 and 1C2, it is clear that the work done in these paths are different. Hence it can be concluded that the amount of work done is not only a function of the end states of a process, but also the path followed between the states. Therefore work is a path function.

## Additivity of Work Over Processes

If a system is taken through two or more number of processes, the total work done is the sum of work done in the individual processes.

Let a system executes three processes as shown in Figure 2.10. The total work done,

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

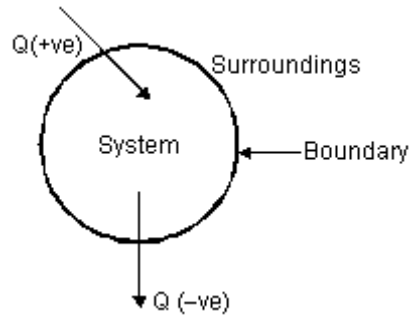
## 1.15 Heat

Heat is the interaction between systems which occurs by virtue of their temperature difference when they communicate.

If a system, at a given temperature is brought in contact with another system (or surroundings) at a lower temperature, it can be observed that heat is transferred from the system at the higher temperature to the system at lower temperature. This heat transfer occurs solely because of the temperature difference between the two systems. Another important aspect of the definition of heat is that a body never contains heat. Rather, heat can be identified only as it crosses the boundary. Similar to work, heat is also a form of energy transfer occurring at the boundary of the system and is a path function.

## Sign Convention of Heat

- Heat given into a system is positive
- Heat coming out of the system is negative



**Fig. 2.8 Sign convention of work**

### Modes of Heat Exchange

Conduction, convection and radiation are the three possible modes of heat transfer between systems and between system and its surroundings.

Conduction occurs without bulk movement of molecules. Energy transfer in conduction is due to lattice vibration and free electron movement. It is the predominant mode of heat transfer in solids.

Convection occurs with bulk movement of molecules and therefore, occurs in gases and liquids. If the bulk movement or flow is due to an external device, it is known as forced convection. In the absence of an external device the flow is due to the difference in density caused by the temperature difference. This mode is known as natural convection.

Bodies separated by a distance may exchange heat in the form of electromagnetic waves without the participation of the intervening medium. It is known as radiation. It is generally a surface phenomenon. Sometimes as in the case of gas mixtures containing carbon dioxide and water vapour it is a volume phenomenon.

### 1.16 Sensible and Latent Heat

It is known that a substance can exist in three phases namely solid, liquid and gas. When a substance is heated or cooled temperature of the substance increases or decreases respectively unless there is any phase change. Quantity of heat added or removed to change the temperature by unit degree is known as specific heat. For solids and liquids same quantity of heat is required to cause unit degree rise for both constant pressure heating as well as constant volume heating as they are incompressible. But for gases there is appreciable difference in the quantity of heat required to cause unit difference in temperature between constant volume and constant pressure processes. Accordingly, they are known as specific heat at constant volume ( $C_v$ ) and specific heat at constant pressure ( $C_p$ ). Thus to increase the temperature of  $m$  kg of the given substance by  $\Delta T$  degree, amount of heat required is given by

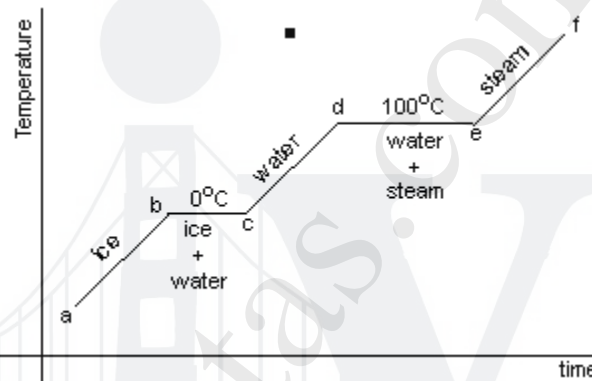
$$Q = mC_v\Delta T \text{ at Constant Volume} \quad \dots(2.5)$$

$$Q_1 = mC_p\Delta T \text{ at Constant Pressure} \quad \dots(2.6)$$

If a certain single component system is undergoing phase change at constant pressure, temperature of the system remains constant during heating or cooling. Quantity of heat removed or added to cause the change of phase of unit mass of the substance is known as latent heat. For example latent heat of fusion of water is the amount of heat to be removed to solidify 1 kg of water into 1 kg of ice at a given temperature.

Let us consider a process of converting 1 kg of ice at  $-30^{\circ}\text{C}$  to system to steam at  $250^{\circ}\text{C}$  at atmospheric pressure. We know that ice melts at  $0^{\circ}\text{C}$  and water evaporates at  $100^{\circ}\text{C}$  at atmospheric pressure.

For a constant rate of heating, if temperature at different instants are plotted we will get a graph as shown in Figure 2.9.



**Figure 2.9 Illustration for sensible and latent heat**

The total heat required can be obtained as follows:

$$Q = Q_{ab} + Q_{bc} + Q_{cd} + Q_{de} + Q_{ef} \quad \dots(2.7)$$

$$Q_{ab} = mC_{ice} (t_b - t_c) \quad \dots(2.8)$$

$$Q_{bc} = \text{Latent heat of melting of ice at } 0^{\circ}\text{C}$$

$$Q_{cd} = mC_{water} (t_d - t_c) \quad \dots(2.9)$$

$$Q_{de} = \text{Latent heat of evaporation of water at } 100^{\circ}\text{C}$$

$$Q_{ef} = mC_{P\text{Steam}} (t_f - t_e) \quad \dots(2.10)$$

Where  $C_{ice}$  = Specific heat of ice

$C_{water}$  = Specific heat of water

$C_{p\text{steam}}$  = Specific heat of steam at constant pressure

## Reversible Adiabatic Process

A reversible process during which, the system and the surroundings do not exchange any heat across the boundary is known as reversible adiabatic process. For such a process, pressure and volume variation is governed by the law :

$$pV^\gamma = \text{constant} \quad \dots(2.11)$$

Where

$C_p$  is the specific heat at constant pressure

$C_v$  is the specific heat at constant volume

Detailed discussion on these specific heats is presented in the next chapter.

A wall which does not permit the heat flow across it is known as adiabatic wall, whereas the wall that permits the heat is known as diathermic wall. In an adiabatic process the only possible energy interaction across the boundary of the system is work transfer to or from the system.

Displacement work involved in a reversible adiabatic process can be expressed as

$$W = \left[ \frac{p_2 V_2 - p_1 V_1}{-\gamma + 1} \right] \quad \dots(2.12)$$

## Comparison between work and heat

- Both heat and work are boundary phenomena, that is, they occur only at the boundary.
- The interaction due to the temperature difference is heat and all other interactions are to be taken as work.
- Both work and heat are path functions, that is, they are inexact differentials.

## 1.17 THE FIRST LAW OF THERMODYNAMICS

Energy interactions between a system and its surroundings across the boundary in the form of heat and work have been discussed separately in the previous chapter. So far, no attempt has been made to relate these interactions between themselves and with the energy content of the system.

First law of thermodynamics, often called as law of conservation of energy, relating work, heat, and energy content of the system will be discussed in detail in this chapter.

### First Law of Thermodynamics

In its more general form, the first law may be stated as follows

“When energy is either transferred or transformed, the final total energy present in all forms must precisely equal the original total energy”.

It is based on the experimental observations and can not be proved mathematically. All the observations made so far, confirm the correctness of this law.

### First Law of Thermodynamics for a Closed System Undergoing a Process

First law can be written for a closed system in an equation form as

$$\left[ \begin{array}{l} \text{Energy entered} \\ \text{into the system} \end{array} \right] + \left[ \begin{array}{l} \text{Energy left} \\ \text{the system} \end{array} \right] = \left[ \begin{array}{l} \text{Change in the energy} \\ \text{content of the system} \end{array} \right]$$

For a system of constant mass, energy can enter or leave the system only in two forms namely work and heat.

Let a closed system of initial energy  $E_1$  receives  $Q$  units of net heat and gives out  $W$  units of work during a process. If  $E_2$  is energy content at the end of the process as given in Figure 3.1, applying first law we get

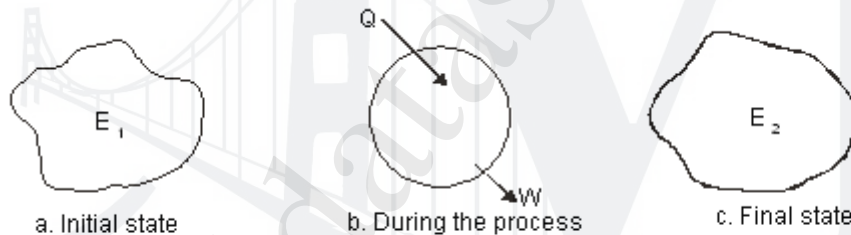


Figure 3.1 First Law for a closed system

$$Q - W = (E_2 - E_1)$$

Where the total energy content

$$E = \text{Internal Energy} + \text{Kinetic energy} + \text{Potential energy}$$

$$= U + \frac{1}{2} \frac{mC^2}{g_c} + mgz$$

The term internal energy usually denoted by the letter  $U$  is the energy due to such factors as electron spin and vibrations, molecular motion and chemical bond.

Kinetic energy term is due to the system movement with a velocity  $C$ . For stationary systems this term will be zero. The term  $g_c$  is a constant of value 1 in SI unit. It will be dropped here after since SI unit is followed throughout the book.

Potential energy term is due to the location of the system in the gravitational field. It remains constant for a stationary system. The unit of energy in SI is kJ.

## The Thermodynamic Property Enthalpy

---

Consider a stationary system of fixed mass undergoing a quasi-equilibrium constant pressure process

Applying first law

$$Q_{12} - {}_1W_2 = E_2 - E_1$$

$$\text{where } E_2 - E_1 = (U_2 - U_1) + m(C_2^2 - C_1^2) + mg(Z_2 - Z_1)$$

$$= U_2 - U_1 \quad \text{since it is a stationary system.}$$

$$\text{also } {}_1W_2 = p(V_2 - V_1)$$

$$= p_2V_2 - p_1V_1$$

$$\therefore Q_{12} = (p_2V_2 - p_1V_1) + (U_2 - U_1)$$

$$= (U_2 + p_2V_2) - (U_1 + p_1V_1)$$

The terms within brackets are all properties depending on the end states. This combination of properties may be regarded as a single property known as enthalpy. It is usually denoted by the letter H.

$$\text{ie } H = U + pV$$

$$\text{(or) } h = u + pv$$

Where  $h$  is specific enthalpy in kJ/kg

$u$  is specific internal energy in kJ/kg and

$v$  is specific volume in  $\text{m}^3/\text{kg}$

## Flow Energy

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Flow energy is defined as the energy required to move a mass into the a control volume against a pressure. Consider a mass of volume  $V$  entering into a control volume as given in the Figure 3.2 against a pressure  $p$ .



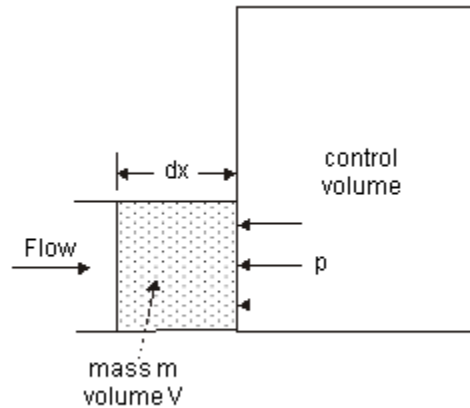


Figure 3.2 Flow energy

$$\begin{aligned}
 \text{The Flow energy} &= \text{Work done in moving the mass} \\
 &= \text{Force} \times \text{distance} \\
 &= pA \times dx \\
 &= p \times (Adx) \\
 &= pV
 \end{aligned}$$

Therefore, Enthalpy = Internal energy + Flow energy

### First Law of Thermodynamics for a Control Volume

Mass simultaneously entering and leaving the system is a very common phenomenon in most of the engineering applications. Control volume concept is applied to these devices by assuming suitable control surfaces.

To analyze these control volume problems, conservation of mass and energy concepts are to be simultaneously considered.

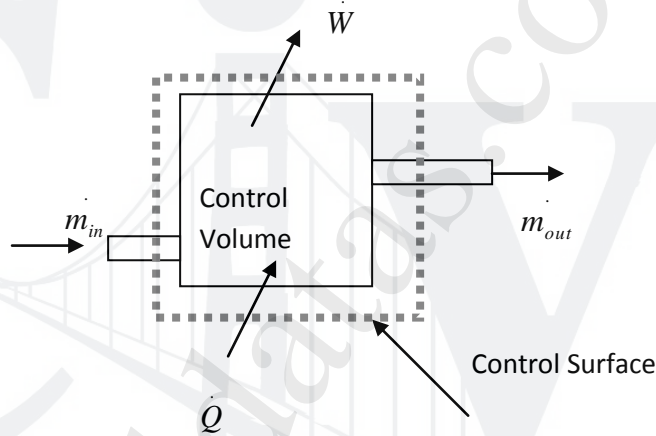
Energy may cross the control surface not only in the form of heat and work but also by total energy associated with the mass crossing the boundaries. Hence apart from kinetic, potential and internal energies, flow energy should also be taken into account.

### Conservation of mass

$$\left[ \begin{array}{l} \text{Total mass} \\ \text{entering the} \\ \text{control volume} \end{array} \right] + \left[ \begin{array}{l} \text{Total mass} \\ \text{leaving the} \\ \text{control volume} \end{array} \right] = \left[ \begin{array}{l} \text{Net change in the} \\ \text{mass content of the} \\ \text{control volume} \end{array} \right]$$

**Conservation of energy**

$$\left[ \begin{array}{l} \text{Net energy crossing the} \\ \text{boundary in the} \\ \text{form of heat} \\ \text{and work} \end{array} \right] + \left[ \begin{array}{l} \text{Total energy} \\ \text{associated with the} \\ \text{mass entering} \\ \text{the control volume} \end{array} \right] - \left[ \begin{array}{l} \text{Total energy} \\ \text{associated with the} \\ \text{mass leaving} \\ \text{the control volume} \end{array} \right] = \left[ \begin{array}{l} \text{Net change} \\ \text{in the energy} \\ \text{content of the} \\ \text{control volume} \end{array} \right]$$



**Figure 3.3 First Law of Thermodynamics Applied to a control Volume**

As a rate equation, it becomes

$$\left[ \dot{Q} - \dot{W} \right] + \sum_{in} m_{in} \left[ h + \frac{C^2}{2} + Zg \right] - \sum_{out} m_{out} \left[ h + \frac{C^2}{2} + Zg \right] = \left[ \Delta E_{CV} \right]$$

**1.18 The Steady-state Flow Process**

When a flow process is satisfying the following conditions, it is known as a steady flow process.

1. The mass and energy content of the control volume remains constant with time.
2. The state and energy of the fluid at inlet, at the exit and at every point within the control volume are time independent.
3. The rate of energy transfer in the form of work and heat across the control surface is constant with time.

Therefore for a steady flow process

$$\sum m_{in} = \sum m_{out}$$

also

$$[\Delta E_{CV}] = 0$$

$$[\dot{Q} - \dot{W}] + \sum_{in} m_{in} \left[ h + \frac{C^2}{2} + Zg \right] - \sum_{out} m_{out} \left[ h + \frac{C^2}{2} + Zg \right] = 0$$

For problem of single inlet stream and single outlet stream

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

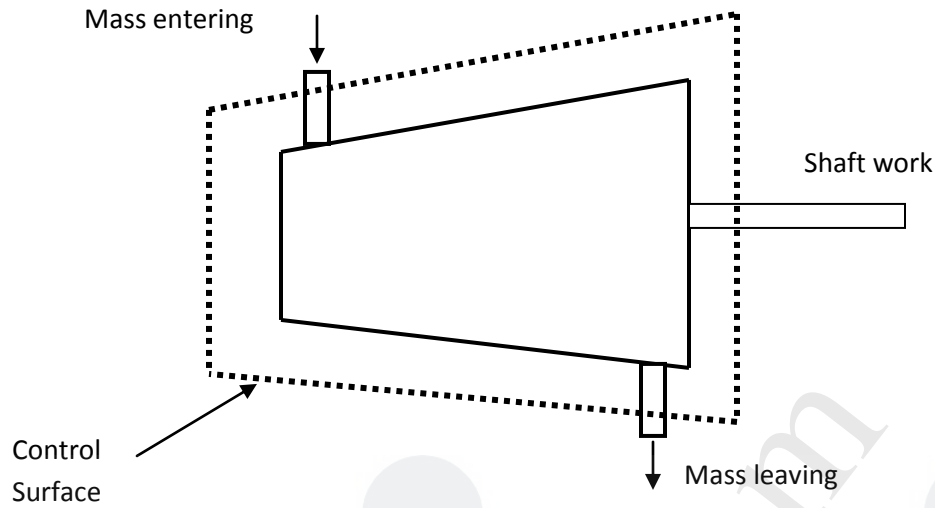
This equation is commonly known as steady flow energy equation (SFEE).

## Application of SFEE

SFEE governs the working of a large number of components used in many engineering practices. In this section a brief analysis of such components working under steady flow conditions are given and the respective governing equations are obtained.

### Turbines

Turbines are devices used in hydraulic, steam and gas turbine power plants. As the fluid passes through the turbine, work is done on the blades of the turbine which are attached to a shaft. Due to the work given to the blades, the turbine shaft rotates producing work.



**Figure 3.4 Schematic Representation of a Turbine**

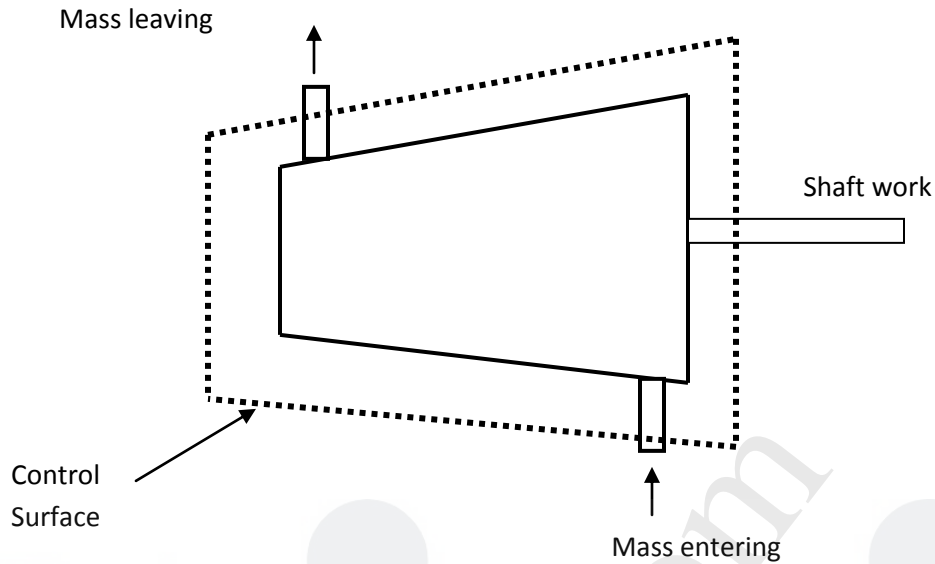
**General Assumptions**

1. Changes in kinetic energy of the fluid are negligible
2. Changes in potential energy of the fluid are negligible.

$$[\dot{Q} - \dot{W}] = \dot{m}(h_2 - h_1)$$

**Compressors**

Compressors (fans and blowers) are work consuming devices, where a low-pressure fluid is compressed by utilising mechanical work. Blades attached to the shaft of the turbine imparts kinetic energy to the fluid which is later converted into pressure energy.



**Figure 3.5 Schematic Representation of a Compresso**

**General Assumptions**

1. Changes in the kinetic energy of the fluid are negligible
2. Changes in the potential energy of the fluid are negligible

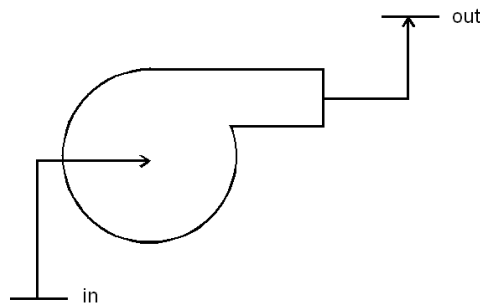
**Governing Equation**

Applying the above equations SFEE becomes

$$[\dot{Q} - \dot{W}] = \dot{m}[(h_2 - h_1)]$$

**Pumps**

Similar to compressors pumps are also work consuming devices. But pumps handle incompressible fluids, whereas compressors deal with compressible fluids.



**Figure 3.6 Schematic diagram of a pump**

**General Assumptions**

1. No heat energy is gained or lost by the fluids;
2. Changes in kinetic energy of the fluid are negligible.

**Governing Equation**

$$[-\dot{W}] = \dot{m}[(h_2 - h_1) + (Z_2 - Z_1)g] \quad \dots(3.13)$$

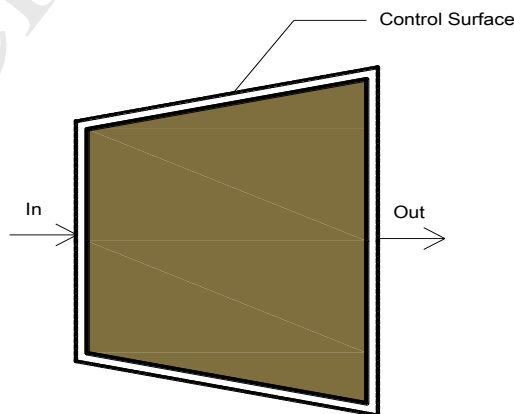
As the fluid passes through a pump, enthalpy of the fluid increases, (internal energy of the fluid remains constant) due to the increase in pv (flow energy). Increase in potential energy of fluid is the most important change found in almost all pump applications.

**Nozzles**

Nozzles are devices which increase the velocity of a fluid at the expense of pressure. A typical nozzle used for fluid flow at subsonic\* speeds is shown in Figure 3.7.

**General Assumptions**

1. In nozzles fluids flow at a speed which is high enough to neglect heat lost or gained as it crosses the entire length of the nozzle. Therefore, flow through nozzles can be regarded as adiabatic. That is  $Q = 0$ .
2. There is no shaft or any other form of work transfer to the fluid or from the fluid; that is  $\dot{W} = 0$ .
3. Changes in the potential energy of the fluid are negligible.



### Governing Equation

$$\left[ (h_2 - h_1) + \left( \frac{C_2^2 - C_1^2}{2} \right) \right] = 0$$

$$\left( \frac{C_2^2 - C_1^2}{2} \right) = (h_1 - h_2)$$

### Diffusers

Diffusers are (reverse of nozzles) devices which increase the pressure of a fluid stream by reducing its kinetic energy.

### General Assumptions

Similar to nozzles, the following assumptions hold good for diffusers.

1. Heat lost or gained as it crosses the entire length of the nozzle. Therefore, flow through nozzles can be regarded as adiabatic. That is  $\dot{Q} = 0$
2. There is no shaft or any other form of work transfer to the fluid or from the fluid; that is  $\dot{W} = 0$ .
3. Changes in the potential energy of the fluid are negligible

### Governing Equation

$$\left[ (h_2 - h_1) + \left( \frac{C_2^2 - C_1^2}{2} \right) \right] = 0$$

$$(h_2 - h_1) = \left( \frac{C_1^2 - C_2^2}{2} \right)$$

### Heat Exchangers

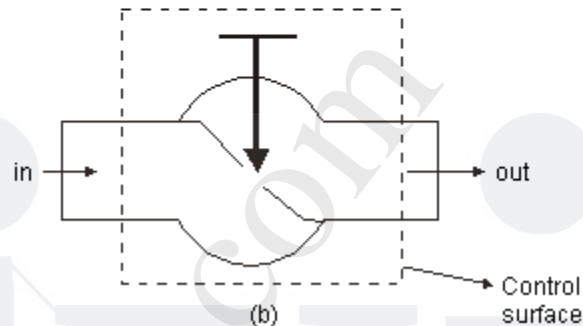
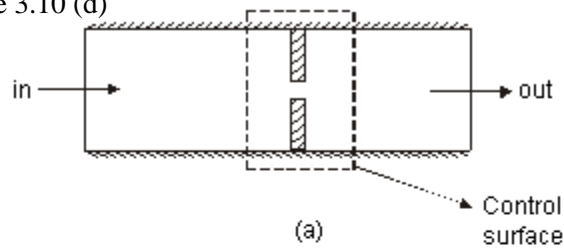
Devices in which heat is transferred from a hot fluid stream to a cold fluid stream are known as heat exchangers.

### Throttling

A throttling process occurs when a fluid flowing in a line suddenly encounters a restriction in the flow passage. It may be

- a plate with a small hole as shown in Figure 3.10 (a)
- a valve partially closed as shown in Figure 3.10 (b)

- a capillary tube which is normally found in a refrigerator as shown in Figure 3.10 (c)
- a porous plug as shown in Figure 3.10 (d)



### First Law for a Cyclic Process

In a cyclic process the system is taken through a series of processes and finally returned to its original state. The end state of a cyclic process is identical with the state of the system at the beginning of the cycle. This is possible if the energy level at the beginning and end of the cyclic process are also the same. In other words, the net energy change in a cyclic process is zero.

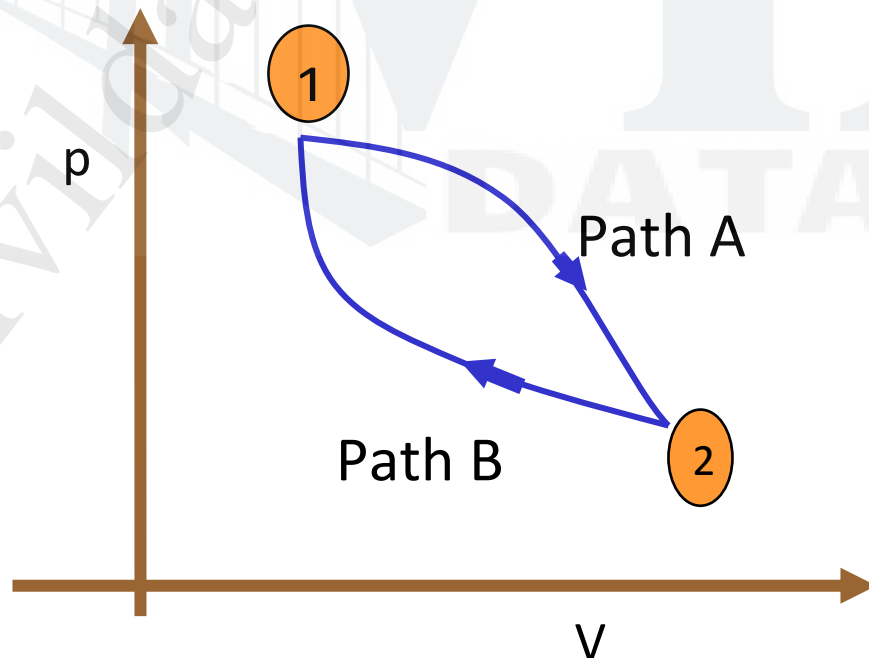


Figure 3.11 First Law for a Cyclic Process



Consider a system undergoing a cycle consisting of two processes A & B as shown in Figure 3.11  
 Net energy change

$$\Delta E_A + \Delta E_B = 0 \quad \dots(3.17)$$

$$(Q_A - W_A) + (Q_B - W_B) = 0 \quad \dots(3.18)$$

ie  $Q_A - Q_B = W_A - W_B \quad \dots(3.19)$

(or)  $\oint dQ = \oint dW \quad \dots(3.20)$

Hence for a cyclic process algebraic sum of heat transfers is equal to the algebraic sum of work transfer.

This was first proved by Joule, based on the experiments he conducted between 1843 and 1858, that were the first quantitative analysis of thermodynamic systems.

### Energy is a property of a system

Consider a system undergoing a process from state 1 to state 2 along path A as shown in Figure 3.12. Let the system be taken back to the initial state 1 along two possible paths B and C. Process A, combined separately with process B and C forms two possible cycles.

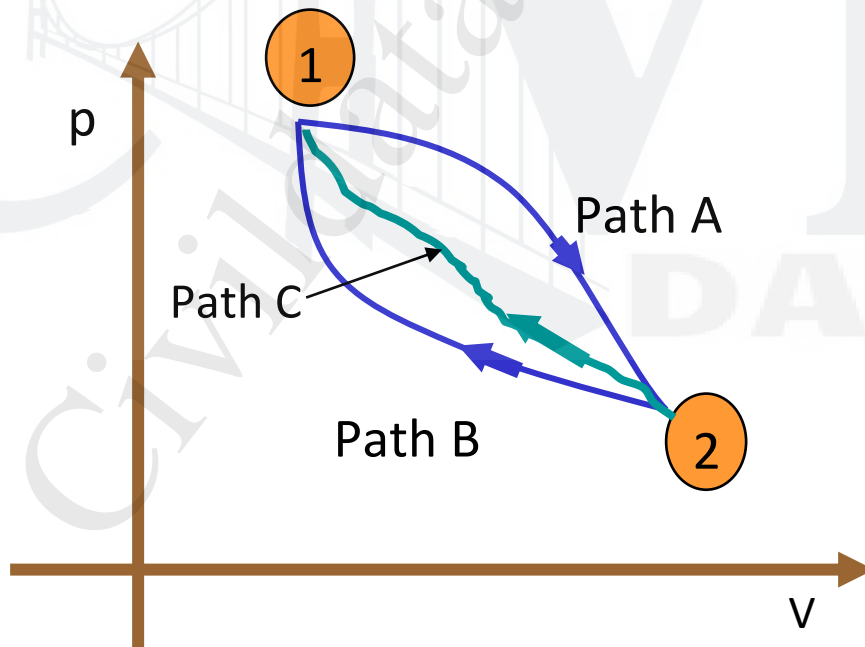


Figure 3.12 Illustration to show that energy is property

**Cycle 1A2B1**

$$Q_A + Q_B = [W_A + W_B]$$

$$Q_A - W_A = -[Q_B - W_B]$$

$$\Delta E_A = -\Delta E_B \quad \dots(3.21)$$

**Cycle 1A2C1**

$$Q_A + Q_C = [W_A + W_C]$$

$$Q_A - W_A = -[Q_C - W_C]$$

$$\Delta E_A = -\Delta E_C \quad \dots(3.22)$$

From Equation (3.21) and (3.22) it can be concluded that energy change in path B and path C are equal and hence energy is a point function depending only on the end states.

It has been already shown that all the properties are point functions and hence energy is also a property of the system.

**Specific Heat at Constant Volume and at Constant Pressure**

Specific heat at constant volume of a substance is the amount of heat added to rise the temperature of unit mass of the given substance by 1 degree at constant volume

From first law for a stationary closed system undergoing a process

$$dQ = pdV + dU \text{ or } dq = pdv + du$$

For a constant volume process

$$dQ = dU \text{ or } dq = du$$

∴

$$\text{or } du = C_v dT \quad \dots(3.23)$$

Similarly specific heat at constant pressure is the quantity of heat added to rise the temperature of unit mass of the given substance by 1 degree at constant pressure

$$\begin{aligned} \text{where } dQ &= pdV + dU \\ &= pdV + d(H - PV) \end{aligned}$$

$$dQ = pdV + dH - Vdp - pdV$$

$$dQ = dH - Vdp$$

For a constant pressure process  $dp = 0$

Hence  $dQ = dH$  or  $dq = dh$

$\therefore$

$$\text{or } dh = C_p dT$$

- The difference in specific heats  $C_p - C_v = R$
- The ratio of sp. heat  $\gamma = C_p/C_v$
- Since  $h$  and  $u$  are properties of a system,  $dh = C_p dT$  and  $du = C_v dT$ , for all processes.

### Work Interaction in a Reversible Steady Flow Process

In a steady flow process the work interaction per unit mass between an open system and the surroundings can be expressed in differential form as

$$dq - dw = dh + CdC + gdz$$

$$dw = dq - (dh + CdC + gdz)$$

Also,  $dq = du + pdv$  (or)  $dh - vdp$

Therefore,  $dw = dh - vdp - (dh + CdC + gdz)$

$$= -vdp - (CdC + gdz)$$

For a stationary  $W = -\int_1^2 vdp - \left( \frac{C_2^2 - C_1^2}{2} \right) - g(z_2 - z_1)$  system

$$W = -\int_1^2 vdp$$

3.26)

### First law for an open system under unsteady flow conditions

Many processes of engineering interest involve unsteady flow, where energy and mass content of the control volume increase or decrease.

Example for such conditions are:

- 1) Filling closed tanks with a gas or liquid.
- 2) Discharge from closed vessels.
- 3) Fluid flow in reciprocating equipments during an individual cycle.

To develop a mathematical model for the analysis of such systems the following assumptions are made.

- 1) The control volume remains constant relative to the coordinate frame.
- 2) The state of the mass within the control volume may change with time, but at any instant of time the state is uniform throughout the entire control volume.
- 3) The state of the mass crossing each of the areas of flow on the control surface is constant with time although the mass flow rates may be time varying.

Unlike in steady flow system, duration of observation  $\Delta t$  plays an important role in transient analysis. Let mass of the working fluid within the control volume before and after the observation be  $m_1$  and  $m_2$  respectively. Applying mass balance we get,

$$(m_2 - m_1)_{cv} = \Sigma m_i - \Sigma m_o \quad \dots(3.27)$$

Where  $\Sigma m_i$  is the mass entered the control volume during the interval  $\Delta t$  seconds.

$\Sigma m_o$  is the mass left the control volume during the interval  $\Delta t$  seconds.

By applying energy balance we get,

$$[Q_{cv} - W_{cv}] + \sum_{in} m_{in} \left[ h + \frac{C^2}{2} + Zg \right] - \sum_{out} m_{out} \left[ h + \frac{C^2}{2} + Zg \right] = \Delta E_{cv} \quad \dots(3.28)$$

Where  $E_{cv}$  is the change in energy content of the control volume in  $\Delta t$  seconds.

$Q_{cv}$  is the heat energy entered into the control volume in  $\Delta t$  seconds.

$W_{cv}$  is the work energy left the control volume in  $\Delta t$  seconds.

$h_i$  &  $h_o$  are specific enthalpy of the inlet and outlet streams respectively.

are the kinetic energy of the inlet and outlet streams respectively.

$Z_i g$  &  $Z_o g$  are the potential energy of inlet and outlet streams respectively.

### **Perpetual Motion Machine - I**

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An engine which could provide work transfer continuously without heat transfer is known as perpetual motion machine of first kind. It is impossible to have such an engine as it violates first law of thermodynamics.

# UNIT II

## THE SECOND LAW OF THERMODYNAMICS

### Limitations of First Law of Thermodynamics

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If a well insulated tank of fluid is stirred by a rotating paddle wheel, the energy of the fluid increases. If the stirrer is stopped, however the energy of the fluid will not decrease and cause the stirrer to rotate in the opposite direction. The possibility of this process proceeding in the opposite direction is not excluded by the first law of Thermodynamics. *Hence first law of thermodynamics does not allow us to predict whether a proposed conceived energy conversion is possible or not.*

In all the internal combustion engines fuel and air mixture is supplied at room temperature. This mixture undergoes combustion inside the engine and gives out work. Exhaust gases coming out of the engine are always at higher temperature, indicating that some heat is taken away into atmosphere. Hence, in all the IC engines only a part of the heat is converted into work. From our experience we know that if any attempt is made to convert all the heat into work, our effort will go in vain. *This limitation in the extent of energy conversion has also not been addressed in first law of thermodynamics.*

### 2.1 The Second law of Thermodynamics

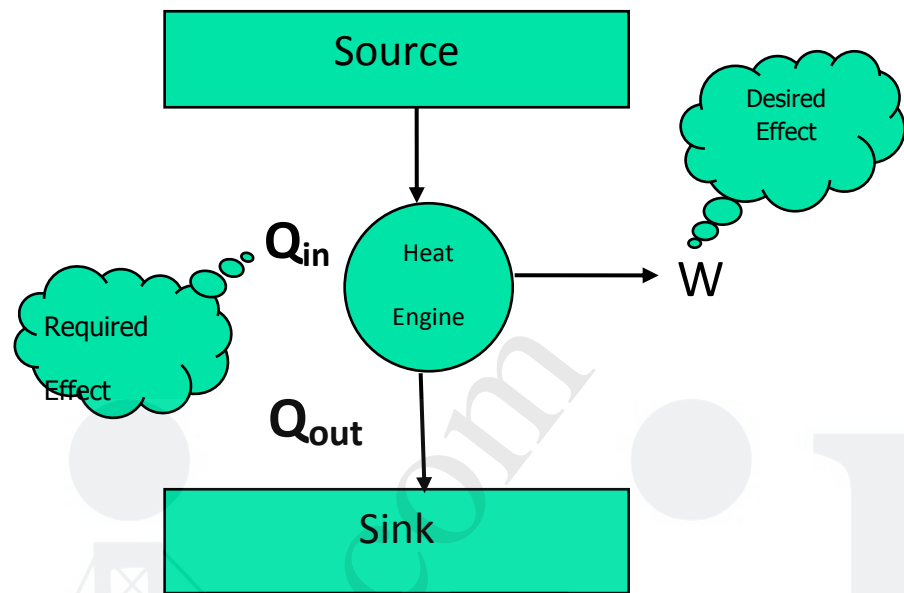
**Kelvin Planck's statement :** *It is impossible to construct a device that, operating continuously, will produce no effect other than transfer of heat from a single thermal reservoir and performance of an equal amount of work.*

The term thermal reservoir refers to a very large system in stable equilibrium, to which or from which, any amount of heat can be transferred at constant temperature.

A thermal reservoir supplying heat continuously at constant temperature is known as source. (Example : Sun)

A thermal reservoir receiving heat continuously at constant temperature is known as sink. (Examples : River, Sea)

From Kelvin-Planck statement it is clear that for any system to operate in a cycle and to give out work continuously it should interact with a minimum of two reservoirs at different temperatures. The system will receive heat from the high temperature reservoir and reject heat to the low temperature reservoir. Such devices are known as heat engines. Performance (or) Efficiency of a heat engine can be expressed as the ratio of desired output to the required input. In a heat engine the desired output is net work output and the required input is total heat input



**Figure 4.1 Heat Engine**

$$\eta = \frac{W_{net}}{Q_{in}}$$

From first law of thermodynamics

$$\Sigma Q = \Sigma W$$

$$Q_{in} - Q_{out} = W_{net}$$

**Clausius statement :** *Unaided by an external agency heat can not be transferred from a body at lower temperature to a body at higher temperature.*

Devices that are used to transfer heat from a body at lower temperature to a body at higher temperature are known as refrigerators (or) heat pumps. If the high temperature side is atmosphere it is a refrigerator. If the low temperature side is atmosphere it is known as a heat pump. The performance index here is called coefficient of performance (COP). In refrigerator (and heat pumps) the performance is the ratio of two independent parameters and hence the possibility of getting the value more than unity is always there. But the term efficiency is restricted to a maximum of unity. Hence the term efficiency is not used here.

$$COP = \frac{\text{Desired Effect}}{\text{Required Effect}}$$

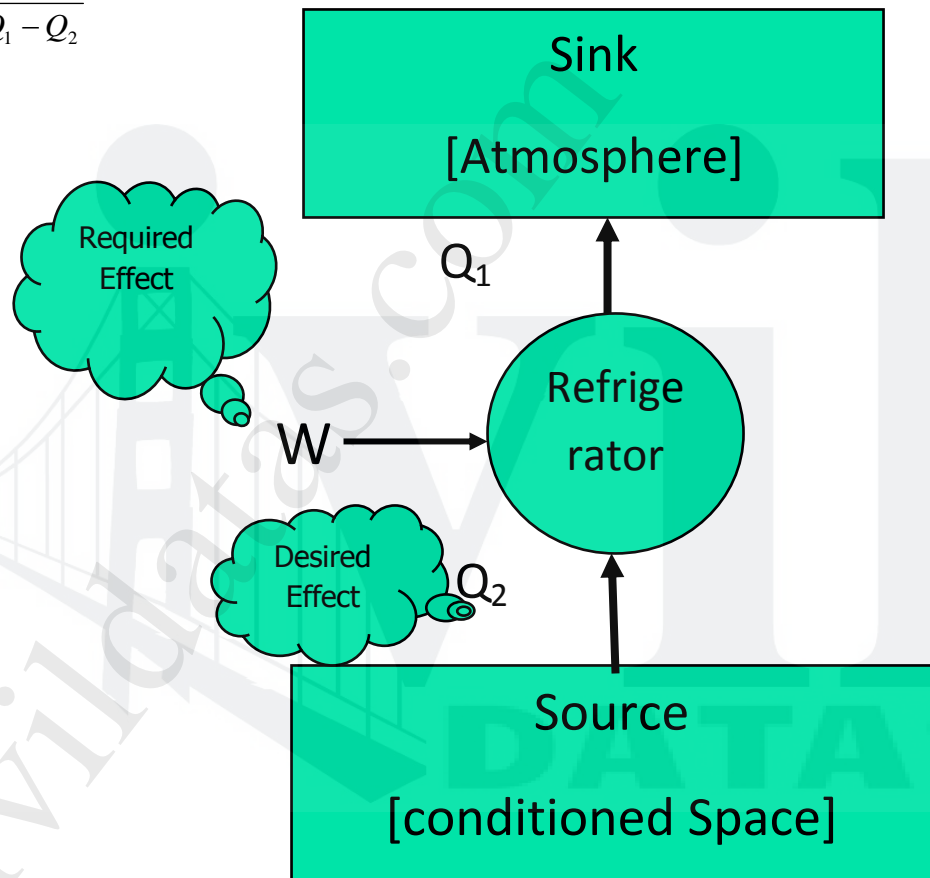
Taking work as external agency, for refrigerators (Figure 4.2)

From first law

$$\Sigma Q = \Sigma W$$

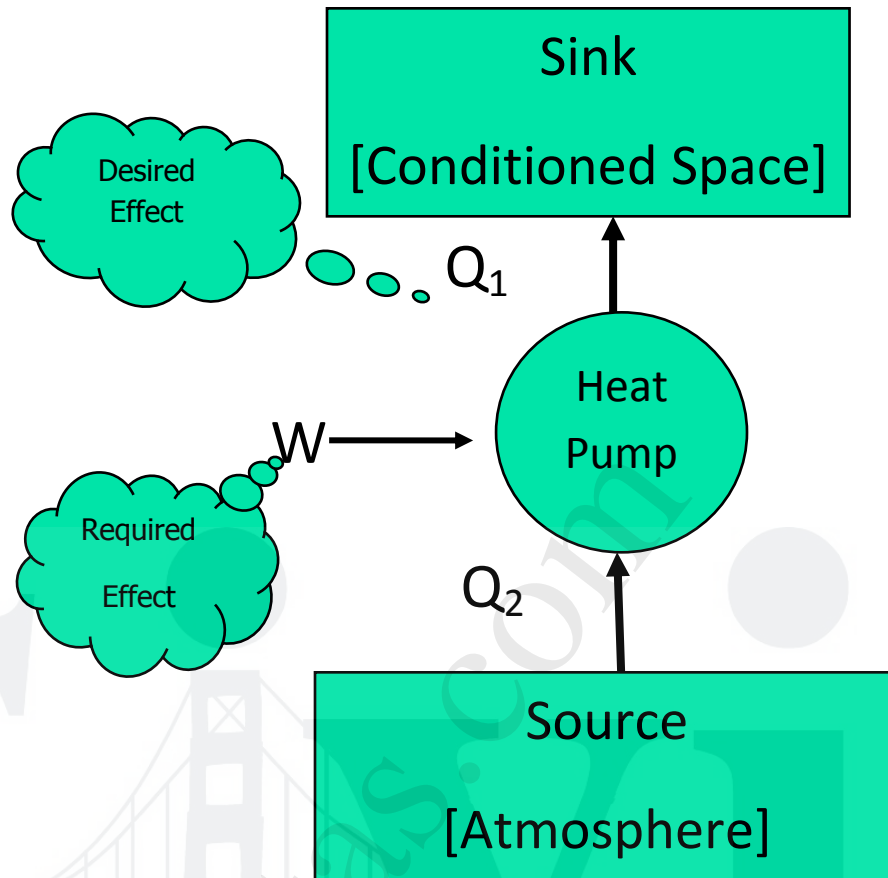
$$Q_1 - Q_2 = W$$

$$COP = \frac{Q_2}{Q_1 - Q_2}$$



**Figure 4.2 Refrigerator**





**Figure 4.3 Heat Pump**

Similarly for a heat pumps (Figure 4.3)

$$COP = \frac{\text{Desired Effect}}{\text{Required Effect}}$$

$$COP = \frac{Q_1}{W}$$

Since,  $Q_1 + Q_2 = W$

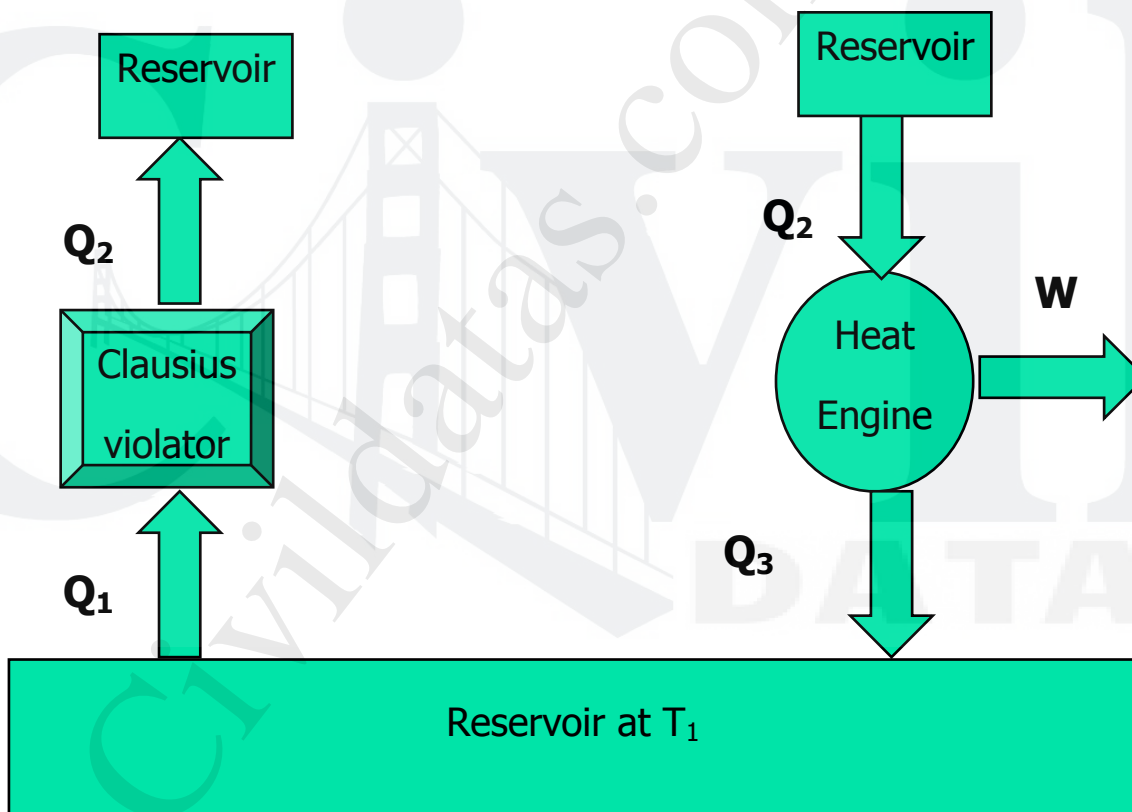
$$COP = \frac{Q_1}{Q_1 - Q_2}$$

## 2.2 Equivalence of Kelvin-Planck and Clausius Statements

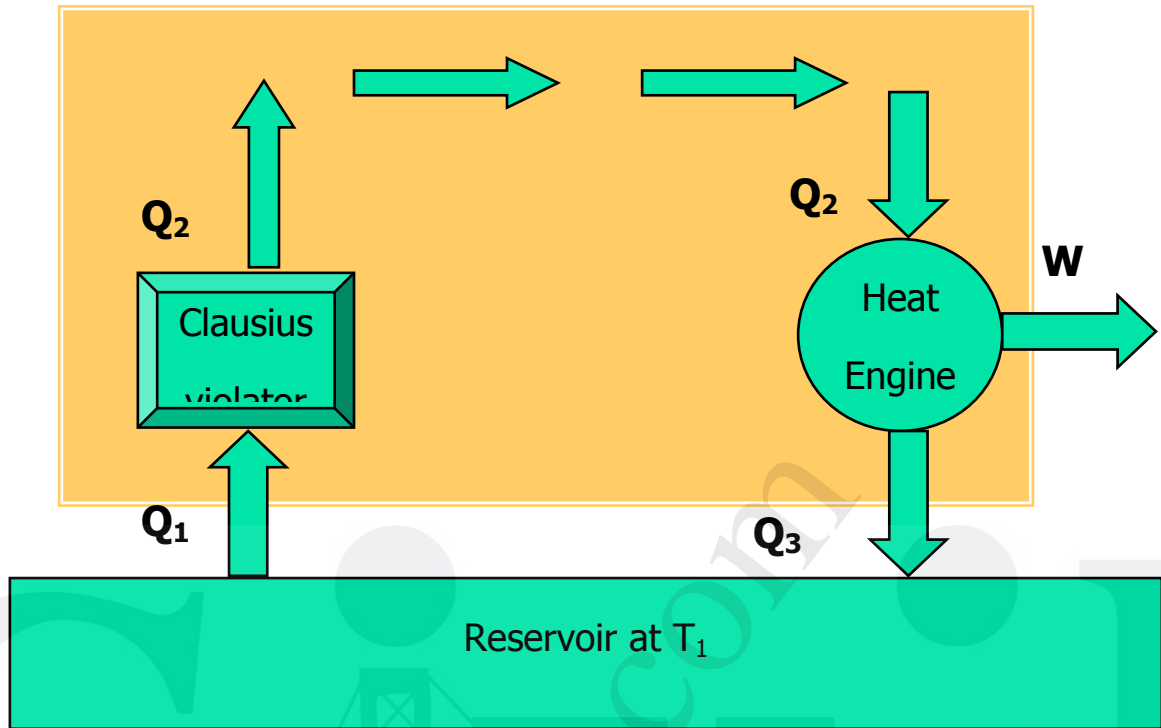
The Clausius and Kelvin-Planck statements of the second law are entirely equivalent. This equivalence can be demonstrated by showing that the violation of either statement can result in violation of the other one.

Referring to Figure 4.4(a) the device marked Clausius violator is pumping  $Q_1$  amount of heat from a low temperature reservoir at  $T_1$  to a high temperature reservoir at  $T_2$  without the aid of any external agency. This is an impossible arrangement.

If such an arrangement is possible it would also violate Kelvin-Planck statement. Let a heat engine operating between the same reservoirs at  $T_2$  and  $T_1$  take in  $Q_2$  as heat input at  $T_2$ . It converts a part of this heat into work and rejects heat  $Q_3$  to the sink at  $T_1$ . Since the Clausius violator is rejecting the same quantity  $Q_2$  at  $T_2$ , it can be supplied directly into the heat engine so that the reservoir at  $T_2$  can be eliminated. This combination as shown in Figure 4.4 (b) is producing continuous work with a single reservoir at  $T_1$ . Hence it violates the Kelvin-Planck statement.



(a)



(b)

Figure 4.4 Illustration of the equivalence of Clausius and Kelvin-Planck's statement

Referring to Figure 4.5 a Kelvin-planck violator is converting all heat  $Q_H$  taken from the reservoir at  $T_H$  into work. If such an impossible heat engine is assumed to exist it will violate the Clausius statement. Consider a refrigerator pumping  $Q_L$  heat from the low temperature reservoir at  $T_L$  to the reservoir at higher temperature  $T_H$ . Combined with the Kelvin-Planck violator, the arrangement is pumping  $Q_L$  heat from  $T_L$  to  $T_H$ , without any external agency. Hence it violate the Clausius statement.

### 2.3 Reversible Process

A process is said to be reversible if it can be reversed without leaving any trace on the surroundings.

For example, let a system be taken from state 1 to state 2 with a work transfer of +5 kJ and heat transfer of -10 kJ. If the process is reversible, while taking the system from state 2 to state 1, the work transfer must be -5 kJ and heat transfer must be +10 kJ. So that, both the system and surroundings are returned to their initial states at the end of the process 2 to 1.

## Irreversibility and Causes of Irreversibility

---

The factors that make a process irreversible are known as irreversibilities. Various forms of irreversibilities are listed below.

- a) Friction** : Friction occurs at the interface of two bodies moving relative to each other. It is the main cause of irreversibility in many processes. Energy spent in overcoming friction is dissipated in the form of heat which can never be restored.
- b) Heat transfer:** Once heat is transferred from a body at higher temperature to a body at lower temperature, it can never be reversed without the aid of an external agency.
- c) Unresisted expansion:** Consider a vessel with two chambers as given in the arrangement as shown in Fig. 4.6. If the members separating the gas from vacuum is removed, gas will expand and occupy the entire space. Since the expansion has no influence on the surroundings, there is no work output in this process. But to restore the initial arrangement, a definite work input is required.
- d) Mixing of two gases:** Consider a vessel with two chambers, one with  $O_2$  and the other with  $N_2$ . When the member separating  $O_2$  &  $N_2$  is removed, uniform mixing is taking place without any work output. But such a process cannot be reversed without any work input.
- e) Throttling:** It is a totally irreversible process. Gas or vapour will expand through a restricted passage with its pressure decreasing rapidly without any work output. Such an expansion cannot be reversed.

## Externally and internally reversible processes

---

As mentioned earlier if no irreversibilities occur outside the system boundaries during the process, it is known as externally reversible.

If no irreversibilities occur within the boundary of the system during a process, it is known as internally reversible process. For such a process, the path of the reverse process will follow exactly that of the forward process in any property diagram.

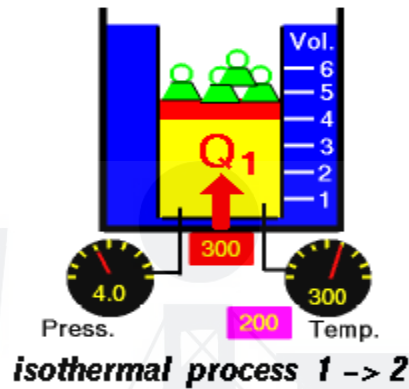
To be totally reversible or simply reversible both external and internal reversibilities must be ensured.

## The Carnot Cycle

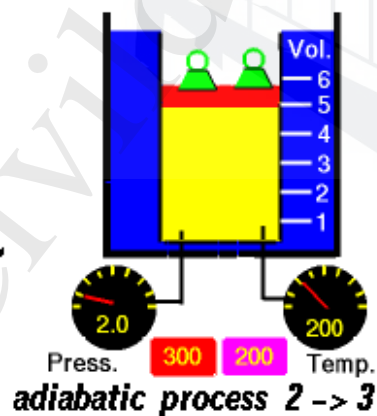
In 1824, Nicholas Sadi Carnot proposed a classical ideal cycle consisting of four processes. All processes are individually reversible and hence the cycle as a whole is a reversible cycle. The processes that make up the Carnot cycle are :

Process 1-2

The working substance is taken in a piston cylinder arrangement as given in Figure 4.8(a). Heat is added reversibly and isothermally from a high



temperature reservoir at  $T_H$ . Since the process is to be reversible, the temperature  $T_H$  of the reservoir should be equal to or infinitesimally greater than that of the working substance.



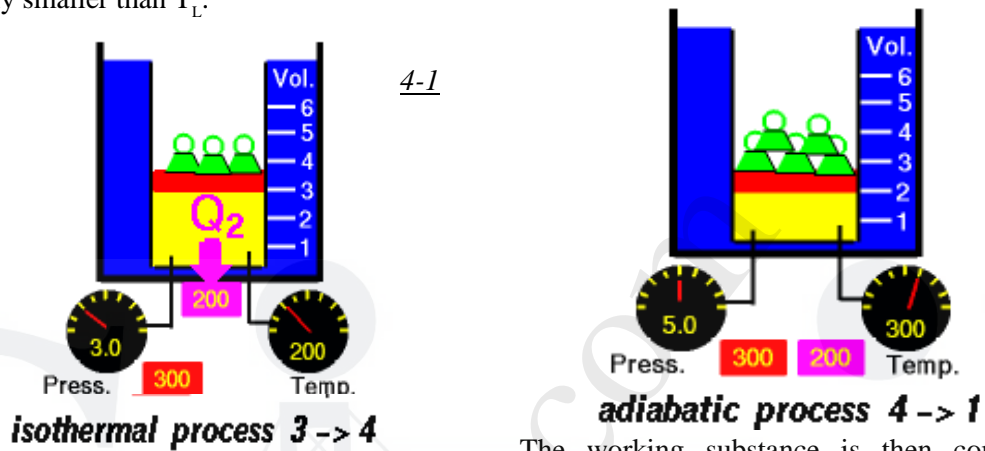
Process 2-3

The working substance is allowed to expand reversibly and adiabatically until its temperature falls down to  $T_L$ . The process is represented by Figure 4.8(b)

Process 3-4

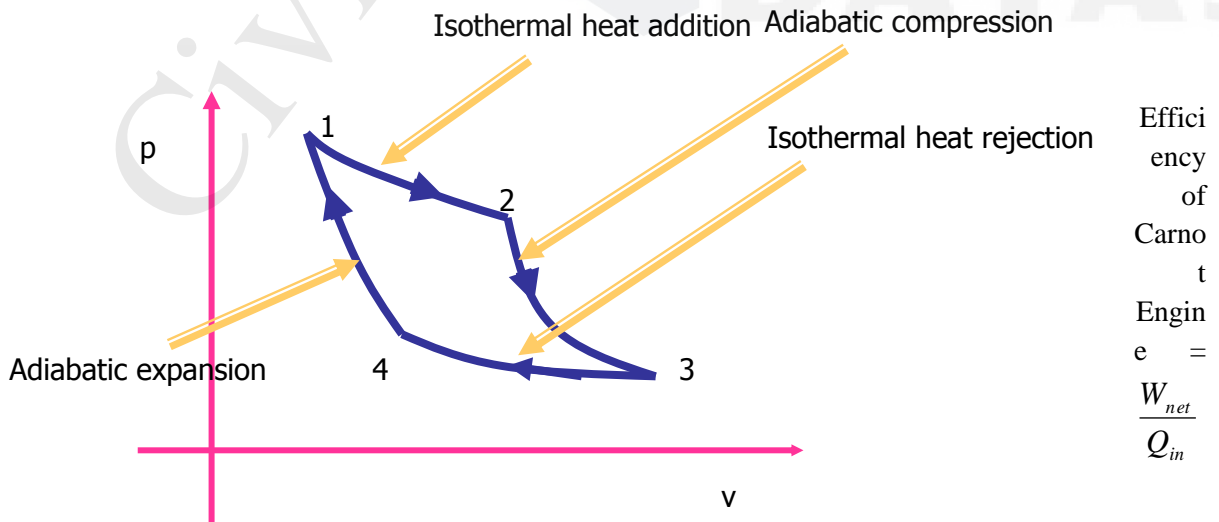
Heat is rejected by the working substance to a low temperature reservoir kept  $T_L$  or at temperature infinitesimally smaller than  $T_L$ .

Process



The working substance is then compressed reversibly and adiabatically until its temperature becomes  $T_H$  and the cycle continues.

The cycle has been represented in a p-V diagram in Figure 4.9. The included area represents the net work done in the cycle. From first law of thermodynamics net workdone is equal to net heat transfer in the cycle. Since  $Q_H$  is the heat added to system and  $Q_L$  is the heat rejected by the system, the net heat transfer is  $Q_H - Q_L$ .



$$= \frac{Q_H - Q_L}{Q_{in}}$$

$$= 1 - \frac{Q_L}{Q_{in}}$$

Where

$$Q_L = {}_3W_4 + U_4 - U_3$$

Since the process is isothermal  $U_4 = U_3$

$$\therefore Q_L = {}_3W_4$$

$$= P_3 V_3 \ln \left[ \frac{p_3}{p_4} \right]$$

$$= mRT_L \ln \left[ \frac{p_3}{p_4} \right]$$

Similarly  $Q_H = mRT_H \ln \left[ \frac{p_2}{p_1} \right]$

Process 2-3 is reversible adiabatic

$$\frac{T_2}{T_3} = \left[ \frac{p_2}{p_3} \right]^{\left( \frac{\gamma-1}{\gamma} \right)} = \frac{T_H}{T_L}$$

$\therefore$

Process 4-1 is also reversible adiabatic

$$\therefore \frac{T_1}{T_4} = \left[ \frac{p_1}{p_4} \right]^{\left( \frac{\gamma-1}{\gamma} \right)} = \frac{T_H}{T_L}$$

From the above two expressions,

$$\frac{p_2}{p_3} = \frac{p_1}{p_4}$$

$$\frac{p_2}{p_1} = \frac{p_3}{p_4}$$

Substituting the above condition we get

$$\begin{aligned} \eta_{Carnot} &= 1 - \frac{Q_L}{Q_{in}} = 1 - \frac{mRT_L \ln\left(\frac{p_3}{p_4}\right)}{mRT_L \ln\left(\frac{p_2}{p_1}\right)} \\ &= 1 - \frac{T_L}{T_H} \end{aligned}$$

It shows that efficiency of carnot engine is purely a function of  $T_H$  and  $T_L$ .

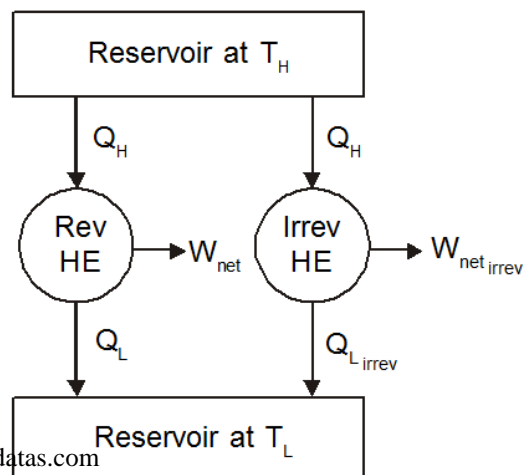
Since the carnot cycle being completely reversible, if carried out in reverse direction, the magnitudes of all energy transfers remain the same but their sign change. This reversed carnot cycle can be applied for a refrigerator or a heat pump. Figure 4.10 shows the p-V diagram of a reversed carnot cycle.

## 2.4 ENTROPY

The first law of thermodynamics deals with the property energy and the conservation of energy. The second law introduced in the previous chapter, leads to the definition of a new property called entropy. Entropy is defined in terms of a calculus operation, and no direct physical picture of it can be given. In this chapter, Clausius inequality, which forms the basis for the definition of entropy will be discussed first. It will be followed by the discussion of entropy changes that take place during various processes for different working fluids. Finally, the reversible steady-flow work and the isentropic efficiencies of various engineering devices such as turbine and compressors will be discussed.

### The Clausius Inequality

Consider two heat engines operating between two reservoirs kept at temperature  $T_H$  and  $T_L$  as shown in the Figure 5.1. Of the two heat engines, one is reversible and the other is irreversible.





For the reversible heat engine it has already been proved that

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L}$$

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

$$\oint \left( \frac{dQ}{T} \right)_{rev} = 0$$

As discussed earlier, the work output from the irreversible engine should be less than that of the reversible engine for the same heat input  $Q_H$ . Therefore  $Q_{L,Irrev}$  will be greater than  $Q_{L,Rev}$ . Let us define

$$Q_{L,Irrev} = Q_{L,Rev} + dQ$$

then

$$\oint \left( \frac{dQ}{T} \right)_{Irrev} = \frac{Q_H}{T_H} - \frac{Q_{L,Irrev}}{T_L}$$

$$= \frac{Q_H}{T_H} - \frac{Q_{L,rev}}{T_L} - \frac{dQ}{T_L}$$

$$= 0 - \frac{dQ}{T_L}$$

$$< 0$$

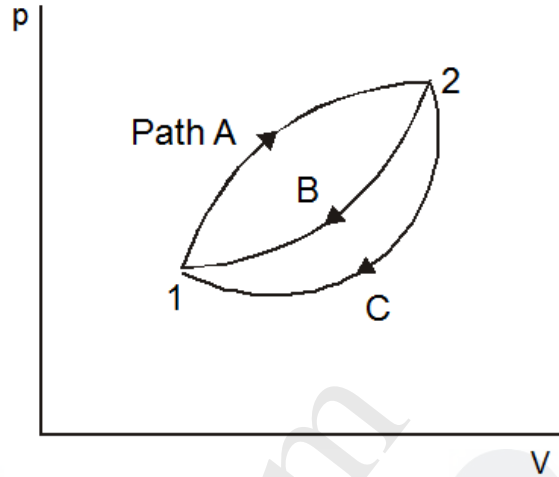
By combining this result with that of a reversible engine we get

$$\oint \left( \frac{dQ}{T} \right)_{Irrev} \leq 0$$

This is known as *Clausius inequality*.

Clausius inequality forms the basis for the definition of a new property known as entropy.

Consider a system taken from state 1 to state 2 along a reversible path A as shown in Figure 5.2. Let the system be brought back to the initial state 1 from state 2 along a reversible path B. Now the system has completed one cycle. Applying Clausius inequality we get



$$\oint \frac{dQ}{T} = 0$$

$$\int_1^2 \left( \frac{dQ}{T} \right)_A + \int_2^1 \left( \frac{dQ}{T} \right)_B = 0$$

...(5.2)

Instead of taking the system from state 2 to state 1 along B, consider another reversible path C. Then for this cycle 1-A-2-C-1, applying Clausius inequality :

$$\oint \frac{dQ}{T} = 0$$

$$\int_1^2 \left( \frac{dQ}{T} \right)_A + \int_2^1 \left( \frac{dQ}{T} \right)_C = 0$$

...(5.3)

Comparing 5.2 & 5.3

Hence, it can be concluded that the quantity is a point function, independent of the path followed. Therefore it is a property of the system. Using the symbol S for entropy we can write

...(5.4)

upon integration we get

$$S_2 - S_1 = \dots \quad (5.5)$$

For a reversible process.

### Entropy change for an irreversible process

The relationship between the entropy change and heat transfer across the boundary during an irreversible processes can be illustrated with a simple cycle composed of two processes, one of which is internally reversible and the other is irreversible, as shown in Figure 5.3. The Clausius inequality applied to this irreversible cycle can be written as

Since the process B is internally reversible, this process can be reversed, and therefore

or

$$\dots \quad (5.6)$$

As defined in equation 5.5, since the process B being reversible the integral on the left hand side can be expressed as

$$\dots \quad (5.7)$$

### 2.5 Temperature - Entropy diagram

In a T-s diagram consider a strip of thickness ds with mean height T as shown in Figure 5.4. Then Tds gives the area of the strip.

For a reversible process the elemental heat transfer

$$dQ = Tds = \text{Area of the strip}$$

To get the total heat transfer the above equation should be integrated between the limits 1 and 2, so that, we get

$$\dots \quad (5.8)$$

This is equivalent to the area under a curve representing the process in a T-S diagram as shown in the Fig 5.4.

**Note:** • For an isothermal process  $S_2 - S_1 = \dots$

• For reversible adiabatic process  $S_2 - S_1 = 0$ .

## 2.6 Change in Entropy

### a) Solids and Liquids

Change in entropy

$$\text{Where } dq = du + pdv$$

For solids and liquids

$$pdv = 0$$

Where c- is the specific heat

...(5.9)

### b) For ideal gases change in entropy

Substituting

$$du = C_v dT$$

We get ,Upon integration

Substituting  $dh = C_p dT$

and

We get

Upon integration

## 2.7 Principle of Increase in Entropy

Applying Clausius inequality,

For an isolated system undergoing a process

Consider a system interacting with its surroundings. Let the system and its surroundings are included in a boundary forming an isolated system. Since all the reactions are taking place within the combined system, we can express

or

Whenever a process occurs entropy of the universe (System plus surroundings) will increase if it is irreversible and remain constant if it is reversible. Since all the processes in practice are irreversible, entropy of universe always increases

$$\text{ie., } (\Delta s)_{\text{universe}} > 0$$

This is known as principle of increase of entropy.

### Adiabatic Efficiency of Compressors and Turbines

---

In steady flow compressors and turbines reversible adiabatic process is assumed to be the ideal process. But due to the irreversibilities caused by friction between the flowing fluid and impellers, the process is not reversible though it is adiabatic. Percentage deviation of this process from the ideal process is expressed in terms of adiabatic efficiency.

#### (a) Compressors :

Since compressors are work consuming devices actual work required is more than ideal work. For compressors handling ideal gases

#### (b) Turbines :

In turbine due to irreversibilities the actual work output is less than the isentropic work.

## 2.8 Solved Problems

**Prob : 5.1** A body at 200°C undergoes an reversible isothermal process. The heat energy removed in the process is 7875 J. Determine the change in the entropy of the body.

*System* : Closed system

*Known* :

$$T_1 = T_2$$

$$= 200^\circ\text{C}$$

$$= 473 \text{ K}$$

$$Q_{\text{rejected}} = 7875 \text{ J}$$

*Process* : Isothermal

*To find* :  $\Delta s$

*Analysis* :  $S_2 - S_1 =$  for an isothermal process

$$=$$

$$= -16.65 \text{ J/K.}$$

*Comment* : Entropy decreases as heat is removed from the system.

**Prob : 5.2** A mass of 5 kg of liquid water is cooled from 100°C to 20°C. Determine the change in entropy.

*System* : Closed system

*Known* : Mass of water = 5kg

$$T_1 = 100^\circ\text{C} = 373 \text{ K}$$

$$T_2 = 20^\circ\text{C} = 293 \text{ K}$$

*Process* : Constant pressure

*To find* : Change in entropy

*Assumptions* : 1) The process is reversible

2) The specific heat of liquid water is constant

*Analysis* :  $S_2 - S_1 = m$

For this problem

$$p_2 = p_1 \text{ \& } C_p = 4.186$$

$$\begin{aligned} \therefore S_2 - S_1 &= 5 \\ &= -5.053 \end{aligned}$$

*Comment* : Entropy decreases as heat is removed from the system.

**Prob : 5.3** Air is compressed isothermally from 100 kPa to 800 kPa. Determine the change in specific entropy of the air.

*System* : Closed/Open

*Known* :  $p_1 = 100 \text{ kPa}$

$p_2 = 800 \text{ kPa}$

*To find* :  $\Delta S$  - change in Specific entropy

*Analysis* :  $\Delta S = -R \ln$  [Since the process is isothermal]

$$\begin{aligned} &= -0.287 \times \ln \\ &= -0.597 \text{ kJ/kgK.} \end{aligned}$$

**Prob : 5.4** A mass of 5 kg of air is compressed from 90 kPa, 32°C to 600 kPa in a polytropic process,  $pV^{1.3} = \text{constant}$ . Determine the change entropy.

*System* : Closed / Open

*Known* :  $p_1 = 90 \text{ kPa}$

$T_1 = 32^\circ\text{C} = 305 \text{ K}$

$p_2 = 600 \text{ kPa}$

$m = 5 \text{ kg}$

*Process* :  $pV^{1.3} = \text{Constant}$

*To find* :  $\Delta S$  - Change in entropy

*Analysis* :  $S_2 - S_1 = m$

Where  $T_2 = T_1$

$= 305$

$= 473 \text{ K}$

$$\begin{aligned} \therefore S_2 - S_1 &= 5 \\ &= -0.517 \text{ kJ/K.} \end{aligned}$$

*Comment* : For air the ratio of  $C_p$  and  $C_v$  is equal to 1.4. Therefore the polytropic index  $n = 1.3 (< 1.4)$  indicates that some heat is removed from the system resulting in negative entropy.

**Prob : 5.5** A rigid insulated container holds 5 kg of an ideal gas. The gas is stirred so that its state changes from 5 kPa and 300 K to 15 kPa. Assuming  $C_p = 1.0 \text{ kJ/kgK}$  and  $\gamma = 1.4$ , determine the change of entropy of the system.

*System* : Closed

*Process* : Constant volume since the gas is stirred in a rigid container

*Known* :  $p_1 = 5 \text{ kPa}$        $p_2 = 15 \text{ kPa}$   
 $m = 5 \text{ kg}$        $C_p = 1.0 \text{ kJ/kgK}$   
 $T_1 = 300 \text{ K}$        $\gamma = 1.4$

*To find* : Change in entropy

*Analysis* :  $S_2 - S_1 = m$

By applying the state equation.

Since  $V_2 = V_1$

$$\begin{aligned} \text{Also } R &= C_p - C_v \\ &= \\ &= \\ &= \\ &= 0.286 \text{ kJ/kgK} \end{aligned}$$

Substituting these values we get

$$S_2 - S_1 = 5$$



$$= 3.922 \text{ kJ/K}$$

*Comment :* Though this process is adiabatic it is not isentropic since the process of stirring is an irreversible process.

**Prob : 5.6** An insulated rigid vessel is divided into two chambers of equal volumes. One chamber contains air at 500 K and 2 MPa. The other chamber is evacuated. If the two chambers are connected and, what would be the entropy change ?

*System :* Closed system

*Process :* Unresisted expansion

*Known :*  $T_1 = 500 \text{ K}$

$$p_1 = 2 \times 10^3 \text{ kPa}$$

*To find :* Entropy change

*Diagrams :*

*Analysis :*  $s_2 - s_1 =$

$$s_2 - s_1 =$$

After expansion air will occupy the entire volume of the container.

$$\therefore V_2 = 2V_1$$

Also  ${}_1W_2 = 0$  since it is an unresisted expansion

$Q_{12} = 0$  since the vessel is insulated

Applying the first law of thermodynamics

$$Q_{12} = \Delta U + {}_1W_2$$

Therefore  $\Delta u = 0$

For air

$$mc_v(T_2 - T_1) = 0$$

$$\text{i.e. } T_2 = T_1$$

Hence  $s_2 - s_1 = C_v \ln + R \ln$

$$= 0.287 \ln$$

$$= 0.199 \text{ kJ/kgK}$$

*Comment* : Though the process is adiabatic entropy increases as the process involving unresisted expansion is an irreversible process. It also proves the fact that

**Prob : 5.7** An adiabatic chamber is partitioned into two equal compartments. On one side there is oxygen at 860 kPa and 14°C. On the other side also, there is oxygen, but at 100 kPa and 14°C. The chamber is insulated and has a volume of 7500 cc. The partition is abruptly removed. Determine the final pressure and the change in entropy of the universe.

*System* : Closed

*Process* : Adiabatic Mixing

*Known* :

Subsystem I	Subsystem II	
Fluid	Oxygen	Oxygen
Initial pressure	850 kPa	100 kPa
Initial Temperature	14°C	14°C
Initial volume		

*Diagrams* :

*Analysis* : Here the energy interaction is taking place only between the two fluids and therefore the energy lost by one fluid should be equal to the energy gained by the other fluid. Taking  $t_f$  as the final temperature we get

Since the same fluid is stored in both the systems at the same temperature

$$C_1 = C_2 \text{ and}$$

$$t_1 = t_2 = 14^\circ\text{C}$$

Therefore the final temperature will also be 14°C

After removing partition total mass of oxygen is occupying the entire 7500cc at 14°C. Hence the final pressure can be computed as given below :

$$= 0.0427 \text{ kg}$$

$$= 0.00503 \text{ kg}$$

To find the final pressure

$$= m_1 + m_2$$

$$= 475 \text{ kPa}$$

$$\Delta S_{\text{system}} = \Delta S_1 + \Delta S_2$$

$$\Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{universe}} = 8.596$$

**Prob : 5.8** A closed system is taken through a cycle consisting of four reversible processes. Details of the processes are listed below. Determine the power developed if the system is executing 100 cycles per minutes.

Process	Q (kJ)	Temperature (K)	
		Initial	Final
1 - 2	0	300	1000
2 - 3	+1000	1000	1000
3 - 4	0	1000	300
4 - 1	-	300	300

*System* : Closed

*Process* : The system is executing cyclic process.

*Known* : Heat transfer in process 12, 23 and 34 and temperature change in all the process.

No of cycles per minute.

*To find* : Power developed.

*Analysis* : To find the power developed  $W_{\text{net}}$  per cycle must be known.

From I Law  $W_{\text{net}} = Q_{\text{net}}$  which can be computed from the following table

Process	Q (kJ)	Temperature (K)		$\Delta S$
		Initial	Final	
1 - 2	0	300	1000	0

2 - 3	1000	1000	1000	
3 - 4	0	1000	300	0
4 - 1	-	300	300	$\Delta S_{41}$

For a cyclic process  $\Sigma \Delta \phi = 0$

where  $\phi$  is any property

$$\therefore \Sigma \Delta S = 0$$

(i.e.,)  $\Delta S_{12} + \Delta S_{23} + \Delta S_{34} + \Delta S_{41} = 0$

$$0 + 1 + 0 + \Delta S_{41} = 0$$

$$\Delta S_{41} = -1$$

Since the process 4-1 is isothermal

$$= -1$$

$$Q_{41} = -300 \text{ kJ}$$

Therefore

$$Q_{\text{net}} = Q_{12} + Q_{23} + Q_{34} + Q_{41}$$

$$= 0 + 1000 + 0 - 300$$

$$= 700 \text{ kJ per cycle}$$

$$\therefore W_{\text{net}} = Q_{\text{net}} = 700 \text{ kJ}$$

and power developed =

$$= 700$$

$$= 1166.7 \text{ kW}$$

## 2.9 AVAILABLE ENERGY, AVAILABILITY AND IRREVERSIBILITY

From second law of thermodynamics we found that complete conversion of heat into work is not possible in a continuous process. Also it has been proved that the most efficient cycle to produce work is a reversible power cycle (Carnot cycle). Even in Carnot cycle, the efficiency of conversion can never be

unity and hence to establish a comparison of the work-energy conversion in actual processes, the maximum theoretical work obtainable with respect to some datum must be determined. This chapter is dedicated for this objective.

### Available and Unavailable Energy

The energy content of a system can be divided into two parts

- Available energy, which under ideal conditions may be completely converted into work
- Unavailable energy which is usually rejected as waste.

Consider Q units of heat energy available at a temperature T. Available part of energy can be obtained by assuming that the heat is supplied to a Carnot engine. Work obtained from the Carnot engine  $\left(\frac{T - T_o}{T}\right)Q$  is the available part. The quantity  $\left(\frac{T_o}{T}\right)Q$  is the unavailable part. In a T-S diagram these quantities can be represented as shown in the fig 6.1. The term  $T_o$  is the ambient temperature. Hence it can be concluded that the available and unavailable part of energy content of a system depends on the ambient conditions also.

### Reversible Work In A Non-flow Process

From first law of thermodynamics

$$Q_{sys} - W = U_2 - U_1 \quad \dots 6.1$$

From second law of thermodynamics for a reversible process

$$\begin{aligned} (\Delta s)_{universe} &= (\Delta s)_{system} + (\Delta s)_{surroundings} \\ &= 0 \end{aligned} \quad \dots 6.2$$

Where  $(\Delta s)_{system} = S_2 - S_1$

$$(\Delta s)_{surroundings} = \frac{Q_{surr}}{T_{Surr}} = \frac{-Q_{Sys}}{T_o}$$

where,

$$Q_{system} = T_o(S_2 - S_1) \quad \dots 6.3$$

substituting in 6.1 we get

$$\begin{aligned} T_o(S_2 - S_1) - W &= U_2 - U_1 \\ \therefore W &= (U_2 - U_1) - (S_1 - S_2) \end{aligned}$$

since the process is reversible W can be represented  $W_{rev}$

$$\therefore W_{rev} = (U_1 - U_2) - T_o(S_1 - S_2) \quad \dots 6.4$$

This is also the maximum work in the process.

For a closed system, when undergoing change in volume, the work done against the atmospheric pressure:

$$W_{atm} = p_o(V_2 - V_1)$$

But this work is not an useful work and hence

$$\begin{aligned} W_{max,useful} &= W_{max} - W_{atm} \\ &= [(U_1 - U_2) - T_o(S_1 - S_2)] - p_o(V_2 - V_1) \\ &= (U_1 - U_2) + P_o(V_1 - V_2) - T_o(S_1 - S_2) \quad \dots 6.5 \end{aligned}$$

### Reversible Work In A Steady-state Control Volume

Steady flow energy equation for a constant volume is

$$\dot{Q} - \dot{W}_{rev} = \sum_{out} \dot{m}_{out} \left( h + \frac{C^2}{2} + gZ \right) - \sum_{in} \dot{m}_{in} \left( h + \frac{C^2}{2} + gZ \right)$$

for a single inlet and outlet

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

...6.6

From Second law of thermodynamics

$$\Delta s_{universe} = (\Delta s)_{cv} + (\Delta s)_{surr}$$

$$= 0$$

where

$$\Delta s_{CV} = \dot{m}[(s_2 - s_1)]$$

$$\Delta s_{Sur} = \frac{-\dot{Q}}{T_o}$$

Substituting these values we get

$$\dot{m}(s_2 - s_1) = \frac{\dot{Q}}{T_o}$$

$$\dot{Q} = T_o \dot{m}(s_2 - s_1)$$

From eqn 6.6 neglecting kinetic and potential energy changes

$$\dot{W}_{rev} = \dot{m}[(h_1 - h_2) - T_o(s_1 - s_2)]$$

In an open system a fixed volume in space known as control volume is taken for analysis. Hence the atmospheric work term  $p_o(V_1 - V_2)$  should not be considered. Therefore

$$W_{rev} = W_{max,useful} \text{ for an open system}$$

## 2.10 Availability

*The maximum useful work that can be obtained from the system such that the system comes to a dead state, while exchanging heat only with the surroundings, is known as availability of the system. Here the term dead state means a state where the system is in thermal and mechanical equilibrium with the surroundings.*

Therefore for a closed system availability can be expressed as

$$\phi = (U - U_o) + p_o(V - V_o) - T_o(S - S_o)$$

similarly for an open system

$$\psi = (H - H_o) - T_o(S - S_o)$$

In steady flow systems the exit conditions are assumed to be in equilibrium with the surroundings. The change in availability of a system when it moves from one state to another can be given as:

for a closed system

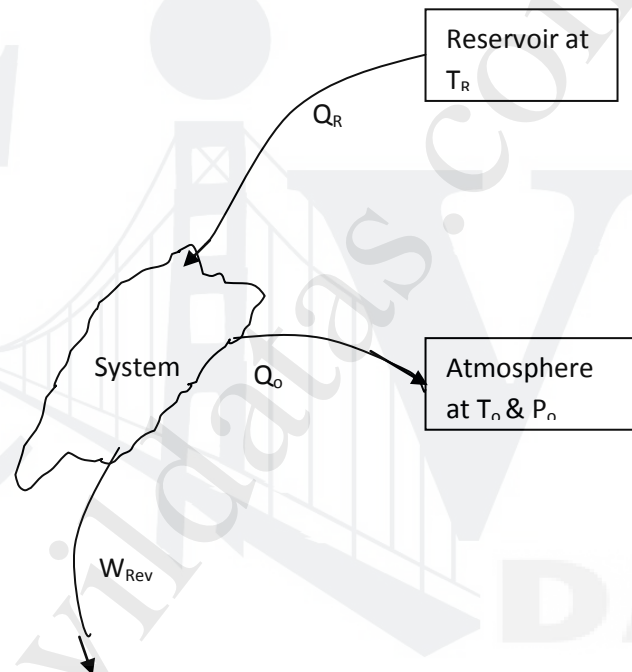
$$\phi_1 - \phi_2 = (U_1 - U_2) + p_o(V_1 - V_2) - T_o(S_1 - S_2) \quad \dots 6.10$$

for an open system

$$\psi_1 - \psi_2 = (H_1 - H_2) - T_o(S_1 - S_2). \quad \dots 6.11$$

### Availability Change Involving Heat Exchange with Reservoirs

Consider a system undergoing a change of state while interacting with a reservoir kept at  $T_R$  and atmosphere at pressure  $p_o$  and temperature  $T_o$ . Net heat transfer to the system



$$Q_{net} = Q_R - Q_o.$$

From first law of thermodynamics

$$Q_{net} - W_{rev} = U_2 - U_1 \quad \dots 6.12$$

From second law of thermodynamics, assuming the process to be reversible

$$(\Delta s)_{Res} + (\Delta s)_{atm} + (\Delta s)_{sys} = 0$$



$$\frac{-Q_R}{T_R} + \frac{Q_o}{T_o} + (S_2 - S_1) = 0$$

The negative sign for  $Q_R$  shows that the heat is removed from the reservoir.

By rearranging We get

$$Q_o = Q_R \frac{T_o}{T_R} + T_o(S_1 - S_2)$$

Net heat transferred

$$Q_{net} = Q_R - Q_o$$

$$Q_{net} = Q_R - Q_R \frac{T_o}{T_R} - T_o(S_1 - S_2) \quad \dots 6.13$$

Substituting 6.13 in 6.12 we get

$$Q_R - Q_R \frac{T_o}{T_R} - T_o(S_1 - S_2) - W_{rev} = U_2 - U_1$$

$$W_{rev} = U_1 - U_2 - T_o(S_1 - S_2) + Q_R \left( 1 - \frac{T_o}{T_R} \right) \quad \dots 6.14$$

$$W_{max,useful} = U_1 - U_2 + p_o(V_1 - V_2) - T_o(S_1 - S_2) + Q_R \left( 1 - \frac{T_o}{T_R} \right) \quad \dots 6.15$$

## 2.11 Irreversibility

*Work obtained in an irreversible process will always be less than that of a reversible process. This difference is termed as irreversibility (i.e) the difference between the reversible work and the actual work for a given change of state of a system is called irreversibility.*

$$I = W_{rev} - W_{act}$$

Let a stationary closed system receiving  $Q$  kJ of heat is giving out  $W_{act}$  kJ of work. From first law of thermodynamics.

$$Q - W_{act} = U_2 - U_1$$

$$\begin{aligned}
 W_{act} &= U_1 - U_2 + Q \\
 W_{rev} &= (U_1 - U_2) - T_0(S_1 - S_2) \\
 &= (U_1 - U_2) + T_0(\Delta S)_{system} \\
 \therefore I &= W_{rev} - W_{act} \\
 &= (U_1 - U_2) + T_0(\Delta S)_{system} - (U_1 - U_2) - Q \\
 &= T_0(\Delta S)_{system} - Q \quad \text{Where } Q = -Q_{surroundings} = T_0(\Delta S)_{surroundings} \\
 &= T_0(\Delta S)_{system} + T_0 \Delta S_{surroundings} \\
 &= T_0(\Delta S)_{universe}
 \end{aligned}$$

Since  $(\Delta S)_{universe}$  will be positive for an irreversible flow, irreversibility will be zero for a reversible process and will never be negative.

$$I \geq 0$$

Similarly for a steady flow system

$$I = W_{rev} - W_{act}$$

Where

$$\dot{W}_{rev} = \dot{m}[(h_1 - h_2) - T_0(s_1 - s_2)]$$

$$W_{act} = \dot{m}[(h_1 - h_2)] + Q_{sys}$$

$$Q_{sys} = Q_o = T_0 \Delta S_{surroundings}$$

Therefore  $I = T_0(S_1 - S_2) + T_0 \Delta S_{surroundings}$

$$= T_0[\Delta S_{sys} + \Delta S_{surroundings}]$$

$$= T_0[\Delta S_{universe}]$$

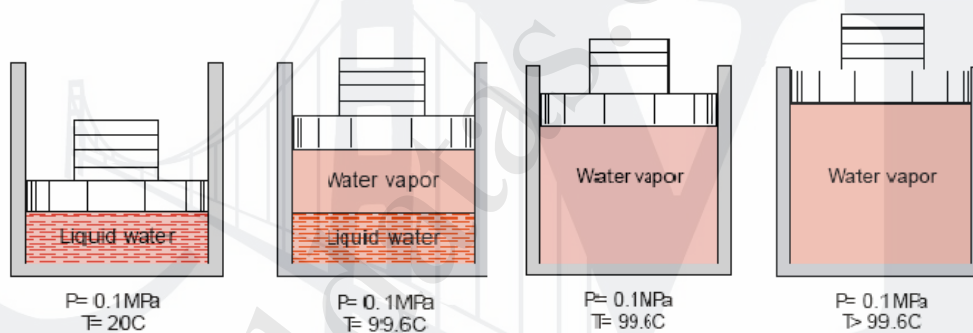
## UNIT-III

### PROPERTIES OF A PURE SUBSTANCE AND STEAM POWER CYCLE

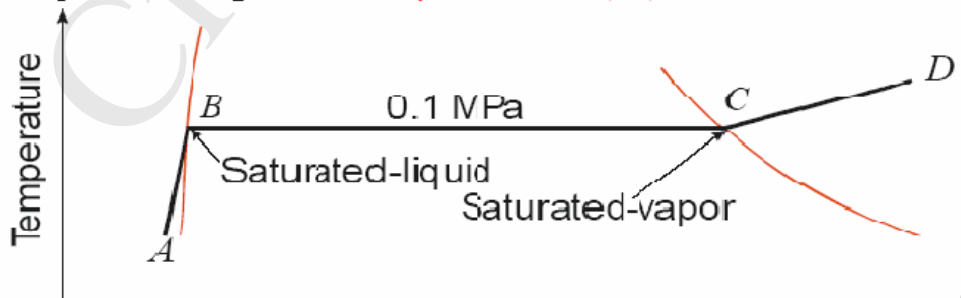
#### 3.1 PURE SUBSTANCE

A pure substance is one that has homogeneous and invariable chemical composition. It may exist in more than one phase, but chemical composition is same for all the phases. Thus, water, mixture of water and ice and water and steam are all examples of pure substance. Sometimes a mixture of gases e.g. air is considered as pure substance.

We have seen that two independent properties are sufficient to determine thermodynamic state of a fluid when it is in equilibrium. Any other thermodynamic property is a function of the chosen pair of independent properties. We shall first consider the relation between the primary properties  $p$ ,  $v$  and  $T$ , the equation expressing this relation for any particular fluid being called the equation of state or characteristic equation of the fluid.



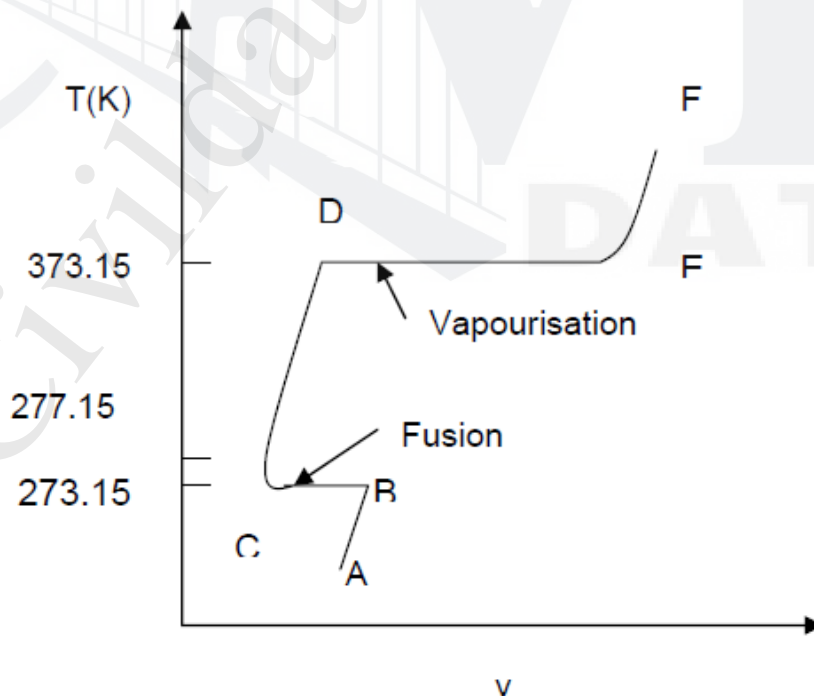
1. **Compressed or subcooled liquid** – *not ready to vaporize (AB)*
2. **Saturated liquid** – *just ready to vaporize (B)*
3. **Saturated liquid/vapor mixture** – *liquid vaporizing, vapor condensing (equil)*
4. **Saturated vapor** – *just ready to condense (C)*
5. **Superheated vapor** – *not ready to condense (CD)*



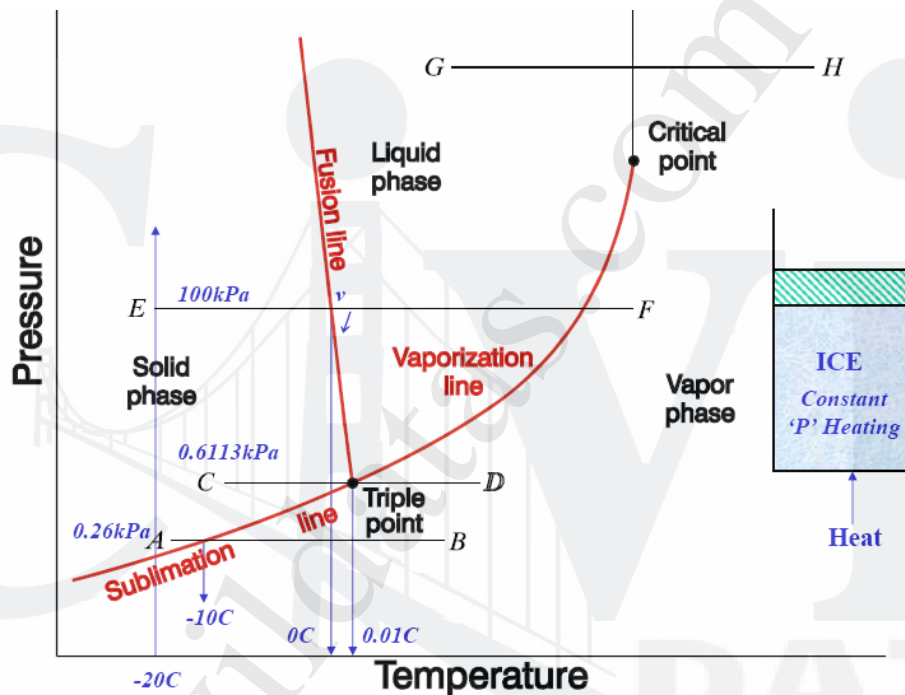
Since we have three variables to consider, the obvious procedure is to measure the variation of one with another while the third is kept constant and repeat this for a range of values of the third variable.

### 3.2 FORMATION OF STEAM AND PROPERTIES

Imagine unit mass of ice below the freezing point, enclosed in a cylinder by a piston under a constant load of 1 atmosphere (1 atm. = 1.01325 bar = 101.325 kPa). If heat is added to the cylinder while keeping the pressure constant, the temperature rises and ice expands until a temperature of 273.15 K (00C) is reached (AB) as shown in Fig. Further heating does not raise the temperature of ice but causes a change to the liquid phase (BC). The change of phase occurs at a constant temperature and by reduction of specific volume. The heat required for this process is known as *latent heat of fusion*. Further heating results in a rise of temperature of liquid and a further contraction in volume until the temperature is about 40C and subsequent expansion until a temperature of 373.15 K (1000C) is reached (point D). At this point a second phase change occurs at constant temperature with a large increase in volume until the liquid has been vaporised (point E). The heat required in this case is called the *latent heat of vaporisation*. When vaporisation is complete, the temperature rises again on heating (line EF). The heat transferred to a substance while the temperature changes is sometimes referred to as *sensible heat*. This constant pressure lines are called *isobars*.

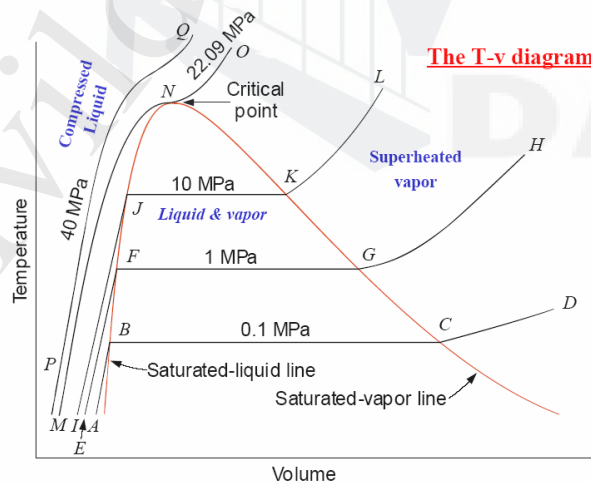
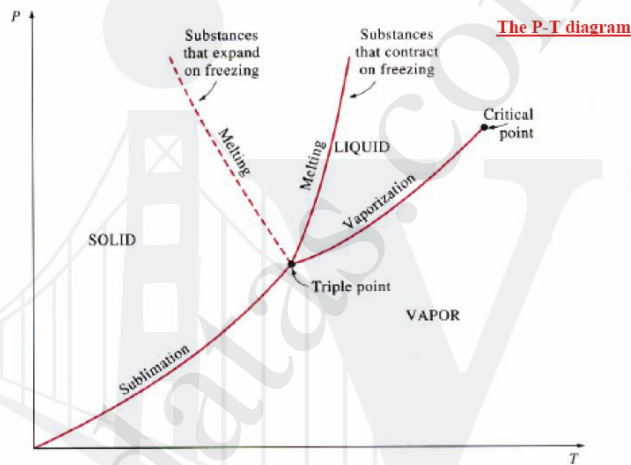
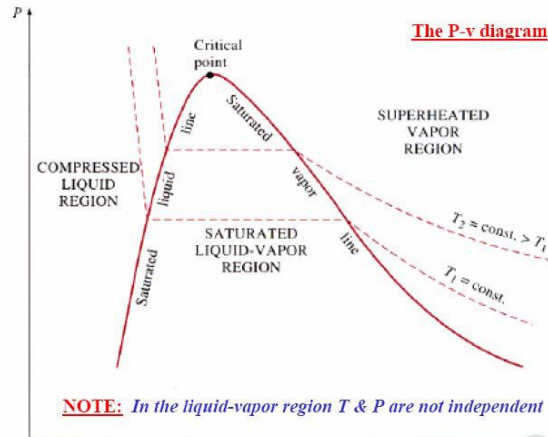


If the pressure is reduced, there is a slight rise in the melting point and also there is a marked drop in the boiling point of water and a marked increase in the change in volume, which accompanies evaporation. When the pressure is reduced to 0.006113 bar (0.6113 kPa), the melting point and boiling point temperatures become equal and change of phase, ice-water-steam, are represented by a single line. The temperature at which this occurs has been accepted internationally as a fixed point for the absolute temperature scale and is by definition 273.16 K. Only at this temperature and pressure of 0.6112 kPa, can ice, water and steam coexist in thermodynamic equilibrium in a closed vessel and is known as **triple point**. If the pressure is reduced further, the ice, instead of melting, sublimates directly into steam.



### 3.3 p-v, p-T, T-v, T-s, h-s DIAGRAMS

Consider now the behaviour at pressure above atmospheric. The shape of the curve is similar to that of the atmospheric isobar, but there is a marked reduction in the change in volume accompanying evaporation. At a sufficiently high pressure, this change in volume falls to zero and the horizontal portion of the curve reduces to a point of inflexion. This is referred to critical point. The values pressure and temperature of water at which critical point reached are  $p_c = 221.2 \text{ bar} = 22.12 \text{ MPa}$  ;  $T_c = 647.3 \text{ K}$  ;  $v_c = 0.00317 \text{ m}^3/\text{kg}$ .



The pressure at which liquid vaporises or condenses is called **saturation pressure** corresponding to a given temperature. Alternately, the temperature at which this phenomena occur is called **saturation temperature** corresponding to the given pressure. A vapour in a state lying along the saturated vapour line is also

called *dry saturated vapour* and the vapour lying right of this line is called *superheated vapour*.

### 3.4 DEFINITION AND APPLICATIONS

- **Saturation temperature:** *Temperature at which a pure substance changes phase at a given pressure.*
- **Saturation pressure:** *Pressure at which a pure substance changes phase at a given temperature.*
- **Latent heat:** *The amount of energy absorbed or released during a phase-change.*
- Melting/freezing:** *Latent heat of fusion.*
- Evaporation/condensation:** *Latent heat of vaporization.*
- **Temperature at which water starts boiling depends on the pressure => if the pressure is fixed, so is the boiling temperature.**

### 3.5 SLOVED PROBLEMS

1. A vessel of volume  $0.04 \text{ m}^3$  contains a mixture of saturated water and steam at a temperature of  $250^\circ\text{C}$ . The mass of the liquid present is  $9 \text{ kg}$ . Find the pressure, mass, specific volume, enthalpy, entropy and internal energy. [April/May 2012,2015]

**Given Data:**

Volume,  $V = 0.04 \text{ m}^3$

Temperature,  $T = 250^\circ\text{C}$

Mass,  $m = 9 \text{ kg}$

**To find:**

- 1)  $p$ , 2)  $m$ , 3)  $v$ , 4)  $h$ , 5)  $S$ , 6)  $\Delta U$

**Solution:**

From the Steam tables corresponding to  $250^\circ\text{C}$ ,

$$v_f = v_l = 0.001251 \text{ m}^3/\text{kg}$$

$$v_g = v_s = 0.050037 \text{ m}^3/\text{kg}$$

$$p = 39.776 \text{ bar}$$

Total volume occupied by the liquid,

$$\begin{aligned}V_1 &= m_1 \times v_1 \\ &= 9 \times 0.001251 \\ &= 0.0113 \text{ m}^3.\end{aligned}$$

Total volume of the vessel,

$$\begin{aligned}V &= \text{Volume of liquid} + \text{Volume of steam} \\ &= V_1 + V_s\end{aligned}$$

$$0.04 = 0.0113 + V_s$$

$$V_s = 0.0287 \text{ m}^3.$$

$$\begin{aligned}\text{Mass of steam, } m_s &= V_s / v_s \\ &= 0.0287 / 0.050037 \\ &= 0.574 \text{ kg.}\end{aligned}$$

$$\begin{aligned}\text{Mass of mixture of liquid and steam, } m &= m_1 + m_s \\ &= 9 + 0.574 \\ &= 9.574 \text{ kg.}\end{aligned}$$

Total specific volume of the mixture,

$$\begin{aligned}v &= V/m \\ &= 0.04 / 9.574 \\ &= 0.00418 \text{ m}^3 / \text{kg.}\end{aligned}$$

We know that,

$$v = v_f + x v_{fg}$$

$$0.00418 = 0.001251 + x (0.050037 - 0.001251)$$

$$x = 0.06$$

From Steam table corresponding to 250 °C,

$$h_f = 1085.8 \text{ KJ / kg}$$



$$h_{fg} = 1714.6 \text{ KJ / kg}$$

$$s_f = 2.794 \text{ KJ / kg K}$$

$$s_{fg} = 3.277 \text{ KJ / kg K.}$$

Enthalpy of mixture,

$$\begin{aligned} h &= h_f + x h_{fg} \\ &= 1085.8 + 0.06 \times 1714.6 \\ &= 1188.67 \text{ KJ / kg} \end{aligned}$$

Entropy of mixture,

$$\begin{aligned} S &= S_f + X S_{fg} \\ &= 2.794 + 0.06 \times 3.277 \\ &= 2.99 \text{ kJ / kg K.} \end{aligned}$$

Internal energy,  $u = h - p v$

$$\begin{aligned} &= 1188.67 - 39.776 \times 10^2 \times 0.00418 \\ &= 1172 \text{ KJ / kg.} \end{aligned}$$

**Result:**

- 1)  $p = 39.776 \text{ bar}$
- 2)  $m = 9.574 \text{ kg}$
- 3)  $v = 0.00418 \text{ m}^3 / \text{kg}$
- 4)  $h = 1188.67 \text{ KJ / kg}$
- 5)  $S = 2.99 \text{ KJ / kg K}$
- 6)  $\Delta U = 1172 \text{ KJ / kg.}$

**2). A steam power plant uses steam at boiler pressure of 150 bar and temperature of 550°C with reheat at 40 bar and 550 °C at condenser pressure of 0.1 bar. Find the quality of steam at turbine exhaust, cycle efficiency and the steam rate. [May/June 2014]**

**Given Data:**

$$p_1 = 150 \text{ bar}$$

$$T_1 = 550^\circ\text{C}$$

$$p_2 = 40 \text{ bar}$$

$$T_3 = 550 \text{ }^\circ\text{C}$$

$$p_3 = 0.1 \text{ bar}$$

**To find:**

1. The quality of steam at turbine exhaust, ( $x_4$ )
2. cycle efficiency and
3. The steam rate.

**Solution:****1. The quality of steam at turbine exhaust, ( $x_4$ ):**

Properties of steam from steam tables at 150 bar & 550°C

$$h_1 = 3445.2 \text{ KJ/kg.}$$

$$S_1 = 6.5125 \text{ KJ/kg K}$$

At 40 bar & 550°C

$$h_3 = 3558.9 \text{ KJ/kg.}$$

$$S_3 = 7.2295 \text{ KJ/kg K}$$

At 40 bar

$$T_{\text{sat}} = 250.3^\circ\text{C} = 523.3 \text{ K}$$

$$h_f = 1087.4 \text{ KJ/kg.} \quad h_{fg} = 1712.9 \text{ KJ/kg.}$$

$$S_f = 2.797 \text{ KJ/kg K} \quad S_{fg} = 3.272 \text{ KJ/kg K}$$

At 0.1 bar

$$h_f = 191.8 \text{ KJ/kg.} \quad h_{fg} = 2392.9 \text{ KJ/kg.}$$

$$S_f = 0.649 \text{ KJ/kg K} \quad S_{fg} = 7.502 \text{ KJ/kg K}$$

1-2 = isentropic

$$S_1 = S = 6.5125 \text{ KJ/kg K}$$

$$S_2 = S_g \text{ at 40 bar}$$

Therefore,

Exit of HP turbine is superheat

$$T_{\text{sup}} = 332^{\circ}\text{C}$$

$$h_2 = 3047.18 \text{ KJ/kg}$$

$$S_3 = S_g \text{ at } 0.1 \text{ bar}$$

Steam is at wet condition.

$$S_4 = S_3 = 7.2295 \text{ KJ/kg K}$$

$$S_4 = S_{f4} + x_4 S_{fg4}$$

$$7.2295 = 0.649 + x_4 \times 7.502$$

$$x_4 = 0.877$$

$$h_4 = h_{f4} + x_4 h_{fg4}$$

$$= 191.8 + 0.877 \times 2392.9$$

$$h_4 = 2290.37 \text{ KJ/kg K}$$

2) Cycle efficiency:

$$\begin{aligned} \eta &= \frac{(h_1 - h_2) + (h_3 - h_4)}{(h_1 - h_{f4}) + (h_3 - h_2)} \\ &= \frac{(3445.2 - 3047.15) + (3558.9 - 2290.37)}{(3445.2 - 191.8) + (3558.9 - 3047.18)} \\ &= 0.4426 \times 100 \\ &= 44.26\% \end{aligned}$$

3) Steam rate:

$$\begin{aligned} &= \frac{3600}{(h_1 - h_2) + (h_3 - h_4)} \\ &= \frac{3600}{(3445.2 - 3047.15) + (3558.9 - 2290.37)} \end{aligned}$$

$$= 2.16 \text{ kg/Kw-hr.}$$

**Result:**

1. The quality of steam at turbine exhaust,  $(x_4) = 0.877$
2. cycle efficiency = 44.26%
3. The steam rate = 2.16 kg/Kw-hr.

**3). Ten kg of water 45 °C is heated at a constant pressure of 10 bar until it becomes superheated vapour at 300°C. Find the change in volume, enthalpy, internal energy and entropy.**

**Given Data:**

$$m = 10 \text{ kg}$$

$$p_1 = p_2 = 10 \text{ bar}$$

$$T_2 = 300^\circ\text{C}$$

**To find:**

- 1) Change in volume,
- 2) Change in Enthalpy,
- 3) Change in Internal energy,
- 4) Change in Entropy.

**Solution:**

From steam tables, corresponding to 45°C,

$$v_1 = v_{f1} = 0.001010 \text{ m}^3 / \text{kg}; \quad h_1 = h_{f1} = 188.4 \text{ KJ/kg};$$

$$s_1 = s_{f1} = 0.638 \text{ KJ/kg K}$$

From steam tables, corresponding to 10 bar and 300°C,

$$h_2 = 3052.1 \text{ KJ/kg}; \quad s_2 = 7.125 \text{ KJ/kg K};$$

$$v_2 = 0.258 \text{ m}^3 / \text{kg};$$

Change in Volume,  $\Delta V = m (v_2 - v_1)$

$$= 10 (0.258 - 0.001010)$$

$$= 2.5699 \text{ m}^3.$$

$$\begin{aligned}\text{Change in Enthalpy, } \Delta h &= m (h_2 - h_1) \\ &= 10 (3052.1 - 188.4) \\ &= 28637 \text{ KJ.}\end{aligned}$$

$$\begin{aligned}\text{Change in Entropy, } \Delta S &= m (s_2 - s_1) \\ &= 10 (7.125 - 0.638) \\ &= 64.87 \text{ KJ/K.}\end{aligned}$$

$$\begin{aligned}\text{Change in Internal energy, } \Delta U &= m (u_2 - u_1) \\ &= m [(h_2 - h_1) - (p_2 v_2 - p_1 v_1)] \\ &= m [(h_2 - h_1) - p_1 (v_2 - v_1)] \\ &= 10 [(3052.1 - 188.4) - 1000 (0.258 - 0.001010)] \\ &= 26067.1 \text{ KJ.}\end{aligned}$$

**Result:**

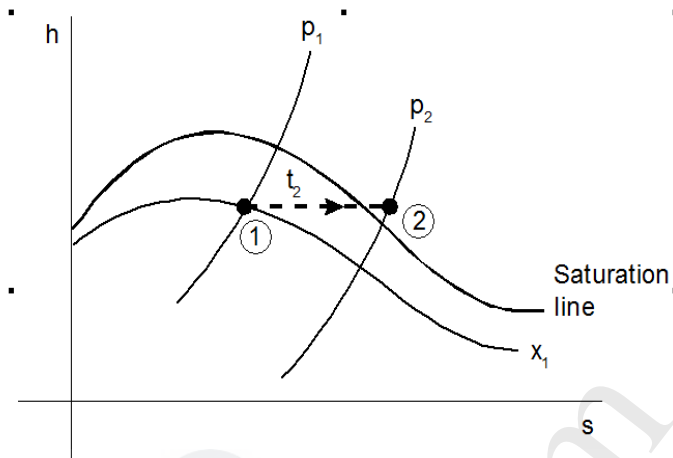
- 1) Change in volume,  $\Delta V = 2.5699 \text{ m}^3$ .
- 2) Change in Enthalpy,  $\Delta h = 28637 \text{ KJ}$ .
- 3) Change in Internal energy,  $\Delta U = 26067.1 \text{ KJ}$ .
- 4) Change in Entropy,  $\Delta S = 64.87 \text{ KJ/K}$ .

### 3.6 THE MEASUREMENTS OF DRYNESS FRACTION

Dryness fraction of wet steam, representing the fraction of steam in the mixture of water and steam can be measured by using (i) Throttling calorimeter and (ii) Separating and Throttling calorimeter.

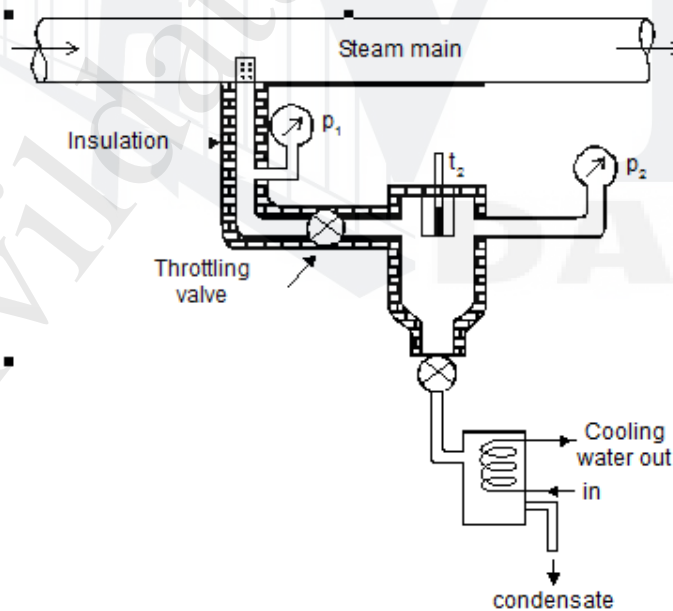
**(i) Throttling calorimeter:**

Let us consider a wet steam as represented by state 1 in the h-s diagram. When it undergoes a throttling process to state 2, it enters into the superheated region. By measuring the temperature and pressure after throttling the specific enthalpy can be obtained. As mentioned earlier during throttling enthalpy remains constant. Therefore the initial state can be completely fixed since the pressure before throttling and the corresponding specific enthalpy are known.



**Fig. h-s diagram**

Steam from the main is extracted through a perforated tube projecting into it as shown in the Figure. Pressure of the steam is measured. It is then throttled into a chamber where the necessary pressure and temperature measurements are made. From the chamber the expanded steam is then condensed by circulating cooling water and discharged.



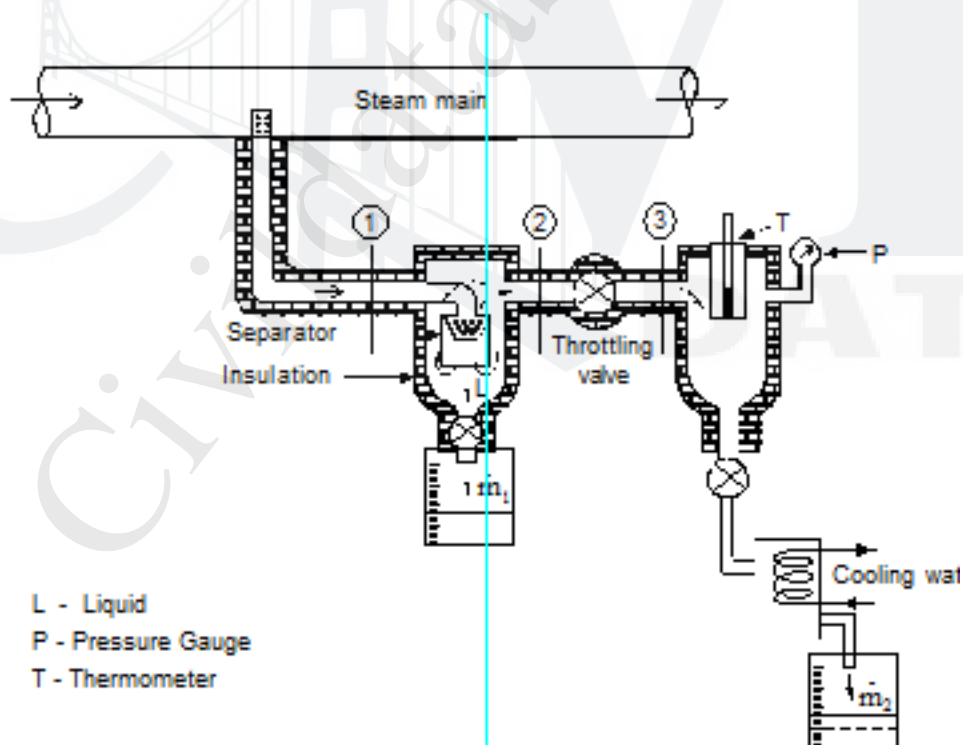
**Fig . Throttling Calorimeter**

**(ii) Separating and Throttling calorimeter:**

When the dryness fraction of the steam is very low, it becomes superheated vapour only at very low end pressure on throttling. In general, the pressure after throttling for dryness fraction measurement is preferred to be above atmospheric. In such applications, separating and throttling calorimeters are used for dryness fraction measurement.

Wet steam, when subjected to sudden change in the direction of flow, a portion of the liquid falls due to gravity and gets separated from the main stream. Thus the remaining steam becomes rich in vapour, which upon throttling will become superheated vapour even at a pressure higher than atmospheric pressure. This principle is employed in the separating and throttling calorimeter.

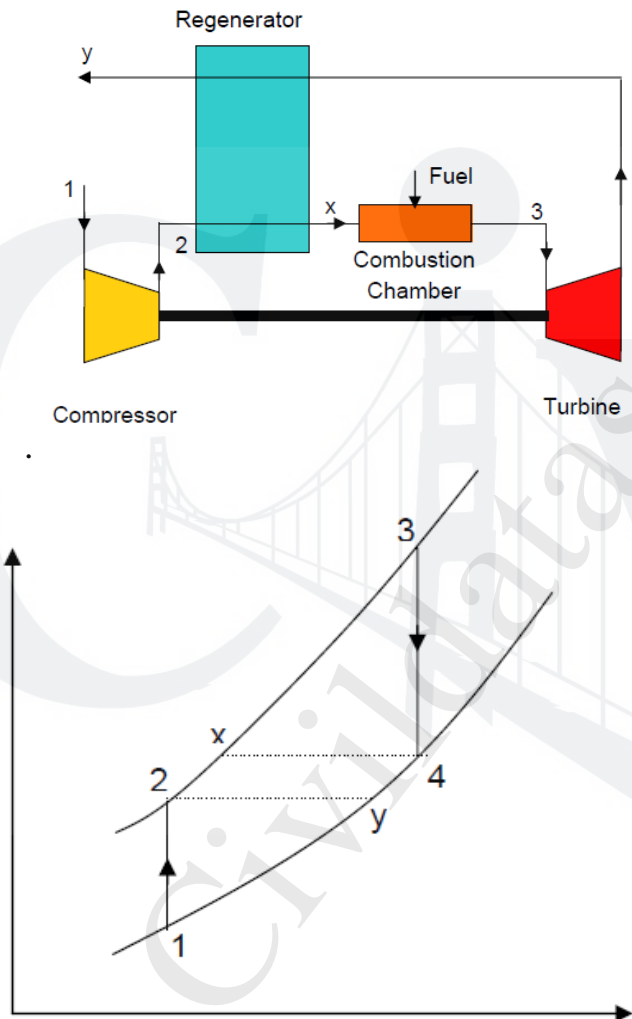
The wet steam from the steam main is extracted through a perforated tube and sent to the separator where a portion of the liquid is separated due to sudden change in the direction. The remaining steam is throttled into a chamber where the required pressure and temperature measurements are made. Mass flow rate of liquid separated in the separator is collected and measured. Mass of the remaining steam is also measured by condensing the throttled steam and collecting it. Let be the mass of liquid separated in the separator and be the mass of steam throttled.



**Fig. Separating and Throttling calorimeter**

### 3.7 REGENERATIVE BRAYTON CYCLE

The temperature of the exhaust gases of simple gas turbine is higher than the temperature of air after compression. If the heat energy in the exhaust gases instead of getting dissipated in the atmosphere is used in heating air after compression, it will reduce the energy requirement from the fuel, thereby increasing the efficiency of the cycle



Air is drawn from the atmosphere into compressor and compressed isentropically to state 2. It is then heated at constant pressure in the regenerator to state x by hot burnt gases from the turbine. Since the temperature of air is increased before it reaches the combustion chamber, less amount of fuel will be required to attain the designed turbine inlet temperature of the products of combustion. After the combustion at constant pressure in the combustion chamber, the gas enters the



turbine at state 3 and expands to state 4 isentropically. It then enters the counter-flow regenerator, where it gives up a portion of its heat energy to the compressed air from the compressor and leaves the regenerator at state y.

The effectiveness of regenerator is given by

$$\eta_R = \frac{h_{x'} - h_2}{h_x - h_2}$$

Assuming constant specific heat

$$\eta_R = \frac{T_{x'} - T_2}{T_x - T_2}$$

The thermal efficiency of an ideal gas turbine cycle with regenerator is

$$\eta_{th} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{h_y - h_1}{h_3 - h_x} = 1 - \frac{T_y - T_1}{T_3 - T_x}$$

Since for ideal condition

$$T_x = T_4 \text{ and } T_y = T_2$$

Therefore,

$$\eta_{th} = \frac{T_2 - T_1}{T_3 - T_4} = 1 - \frac{T_1 \left[ \frac{T_2}{T_1} - 1 \right]}{T_3 \left[ 1 - \frac{T_4}{T_3} \right]}$$

Since

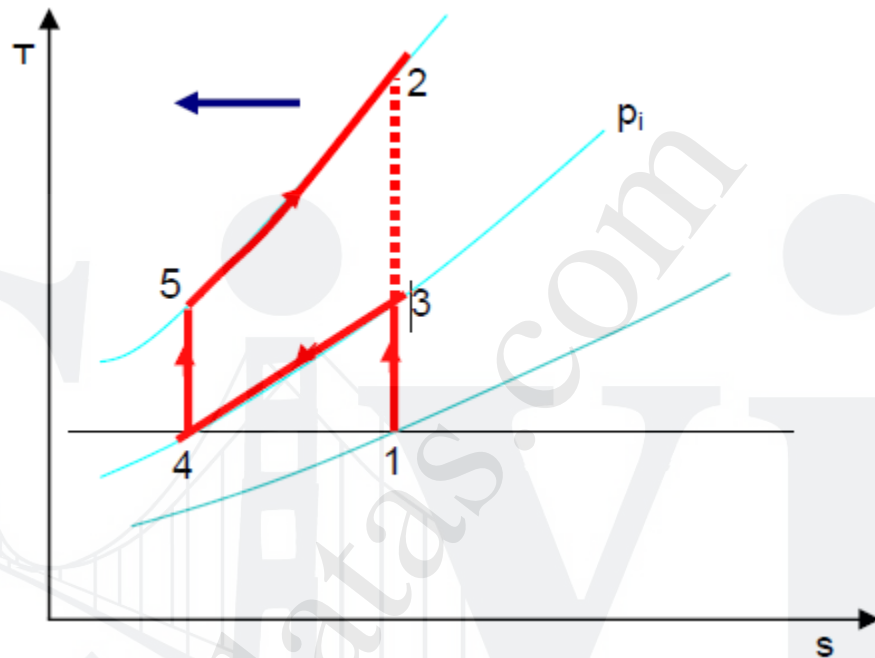
$$\frac{T_2}{T_1} = \left( \frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} \text{ and } \frac{T_4}{T_3} = \left( \frac{p_4}{p_3} \right)^{\frac{\gamma-1}{\gamma}} = \left( \frac{p_1}{p_2} \right)^{\frac{\gamma-1}{\gamma}}$$

$$\therefore \eta_{th} = 1 - \frac{T_1 \left[ \left( \frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right]}{T_3 \left[ 1 - \frac{1}{\left( \frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}}} \right]}$$

$$= 1 - \frac{T_1}{T_3} \left( \frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}}$$

### 3.8 INTERCOOLING AND REHEATING

The addition of regenerator improves the ideal efficiency but does not improve the work ratio. The latter may be reduced by reducing the compressor work or increasing the turbine work.



Consider the compressor work first. The curvature of the constant pressure lines on T-s diagram is such that the vertical distance between them reduces as we go towards the left (shown by the arrow). Therefore, further to the left the compression process 1-2 takes place, smaller is the work required to drive the compressor. State 1 is determined by the atmospheric pressure and temperature. But if the compression is carried out in two stages, 1-3 and 4-5 with the air is being cooled at constant intermediate pressure  $p_i$  between the stages; some reduction of compression work can be achieved. The sum of temperature rises  $(T_3 - T_1)$  and  $(T_5 - T_4)$  will be clearly less than  $(T_2 - T_1)$ . Ideally, it is possible to cool the air to atmospheric condition i.e.  $T_4 = T_1$ , and in this case Intercooling is complete.

4). A steam boiler generates steam at 30 bar, 300 °C at the rate of 2 kg/s. This steam is expanded isentropically in a turbine to a condenser pressure of 0.05 bar, condensed at constant pressure and pumped back to boiler.

- Find the heat supplied in the boiler per hour.
- Determine the quality of steam after expansion.
- What is the power generated by the turbine?
- Estimate the Ranking efficiency considering pump work.

**Given Data:**

$$p_1 = 30 \text{ bar}$$

$$p_2 = 0.05 \text{ bar}$$

$$T_1 = 300^\circ\text{C}$$

$$m = 2 \text{ kg / s}$$

**To find:**

- Find the heat supplied in the boiler per hour ( $Q_S$ )
- Determine the quality of steam after expansion ( $x_2$ )
- What is the power generated by the turbine ( $W_T$ )
- Estimate the Ranking efficiency considering pump work ( $\eta$ )

**Solution:**

**1. Heat supplied in the boiler per hour ( $Q_S$ ):**

Properties of steam from the steam table

At 30 bar & 300°C

$$h_1 = 2995.1 \text{ KJ/kg};$$

$$S_1 = 6.542 \text{ KJ/kg K};$$

At 0.05 bar

$$h_{f2} = 137.8 \text{ KJ/kg};$$

$$h_{fg2} = 2423.8 \text{ KJ/kg};$$

$$S_{f2} = 0.476 \text{ KJ/kg K};$$

$$S_{fg2} = 7.920 \text{ KJ/kg K};$$

$$V_{f2} = 0.001005 \text{ m}^3/\text{kg}.$$

1-2 = Isentropic expansion in the turbine

$$S_1 = S_2 = 6.542 \text{ KJ/ kg K}$$

$$S_2 = S_{f2} + x_2 \times S_{fg2}$$

$$6.542 = 0.476 + x_2 \times 7.92$$

$$x_2 = 0.766$$

Therefore, Quality of steam after expansion = 0.766 dry.

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

$$= 137.81 + 0.766 \times 2423.8$$

$$= 1994.43 \text{ KJ/kg.}$$

$$h_3 = h_{fg2} = 137.8 \text{ KJ/kg.}$$

Considering the pump work,  $h_4 - h_3 = v_{f2} (p_1 - p_2)$

$$h_4 = h_3 + v_{f2} (p_1 - p_2)$$

$$= 137.8 + 0.001005 \times (30 - 0.05) \times 10^2$$

$$= 140.81 \text{ KJ/kg.}$$

**Heat supplied in the boiler:**

$$Q_s = m \times (h_1 - h_4)$$

$$= 2 \times (2995.1 - 140.81)$$

$$= 5708.58 \text{ KJ/s}$$

$$= 20.55 \times 10^6 \text{ KJ /hr.}$$

**Power generated by the turbine:**

$$W_T = m \times (h_1 - h_2)$$

$$= 2 \times (2995.1 - 1994.43)$$

$$= 2001.34 \text{ KW.}$$

**Rankine efficiency by the plant:**

$$\frac{(h_1 - h_2) - (h_4 - h_3)}{h_1 - h_4}$$

$$\begin{aligned} & \frac{(h_1 - h_4)}{=} \\ & = \frac{(2995.1 - 1994.43) - (140.81 - 137.8)}{(2995.1 - 140.81)} \\ & = 35 \% \end{aligned}$$

**Result:**

1. Find the heat supplied in the boiler per hour ( $Q_s$ ) =  $20.55 \times 10^6$  KJ /hr
2. Determine the quality of steam after expansion ( $x_2$ ) = 0.766 dry
3. What is the power generated by the turbine ( $W_T$ ) = 2001.34 KW.
4. Estimate the Ranking efficiency considering pump work ( $\eta$ ) = 35%

**3.9 GAS POWER / AIR STANDARD CYCLES.**

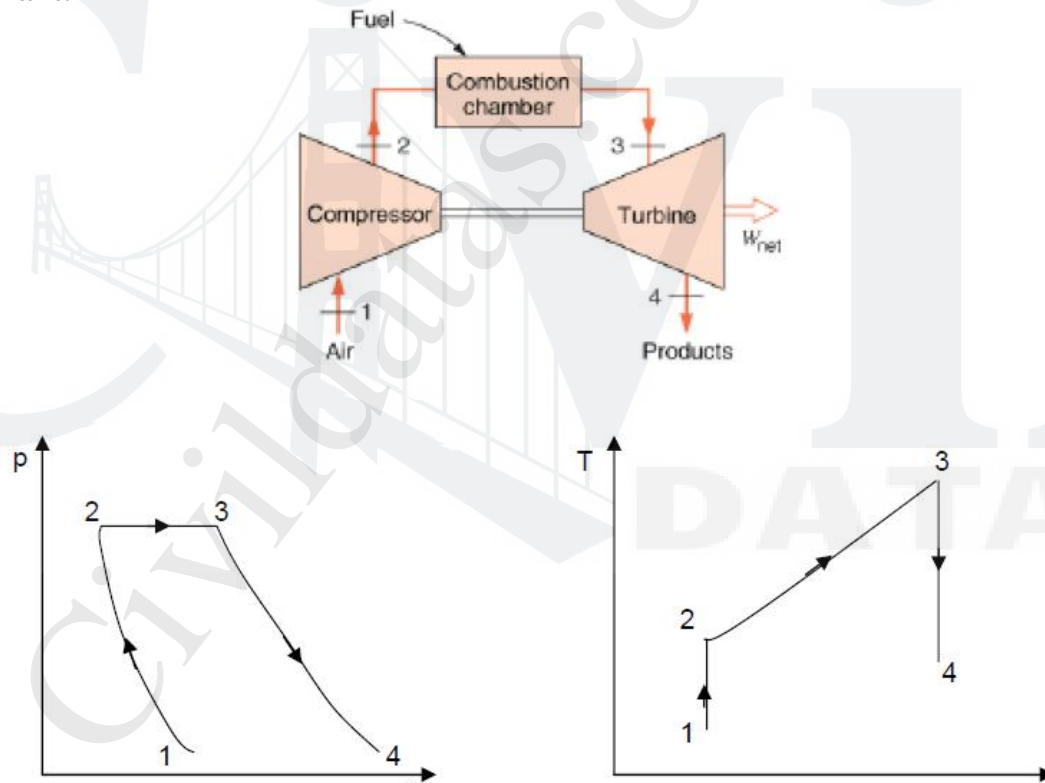
For small power plants, gas is ideally preferred as the working fluid. The gasoline engines, diesel engines and gas turbines are common examples. The analysis of the air-standard cycle is based on the assumptions that are far from real. In actual internal combustion (IC) engines, chemical reaction occurs inside the engine cylinder as a result of combustion of air-fuel mixture and. The IC engines are actually operated on Open cycles in which the working fluid does not go through a cycle. The accurate analysis of IC engine is very complicated. However, it is advantageous to analyse the performance of an ideal closed cycle that closely approximates the real cycle. One such approach is air-standard cycle, which is based on certain assumptions. The assumptions for idealized air-standard cycles are:

- 1) The working fluid, air, is assumed to be an ideal gas. The equation of state is given by the equation  $pv = RT$  and the specific heats are assumed to be constant.
- 2) All processes that constitute the cycle are reversible.
- 3) No chemical reaction occurs during the cycle. Heat is supplied from a high temperature reservoir (instead of chemical reaction) and some heat is rejected to the low temperature reservoir during the cycle.
- 4) The mass of air within the system remains constant throughout the cycle.

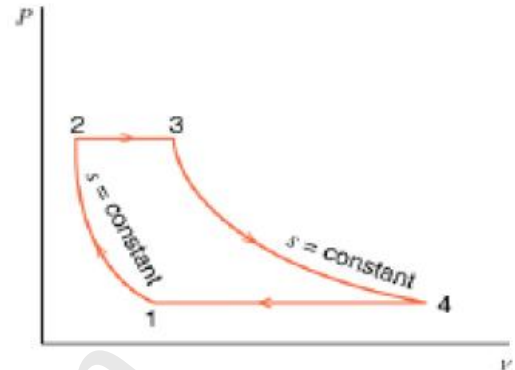
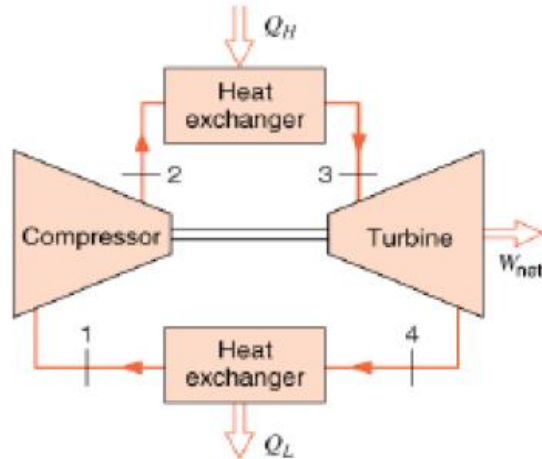
5) Heat losses from the system to the atmosphere are assumed to be zero. In this we shall discuss about the Brayton cycle, Otto cycle and Diesel cycle.

### 3.10 BRAYTON CYCLE

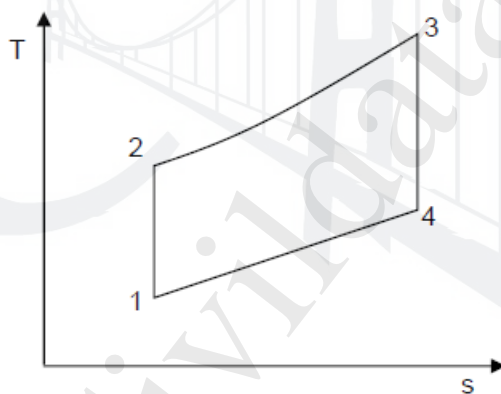
The Brayton cycle is widely used as the basis for the operation of Gas turbine. A schematic diagram of a simple gas turbine (open cycle) and the corresponding p-v and T-s diagrams are shown below. Air is drawn from the atmosphere into compressor, where it is compressed reversibly and adiabatically. The relative high pressure air is then used in burning the fuel in the combustion chamber. The air-fuel ratio quite high (about 60:1) to limit the temperature burnt gases entering the turbine. The gases then expand isentropically in the turbine. A portion of the work obtained from the turbine is utilised to drive the compressor and the auxiliary drive and the rest of the power output is the net power of the gas turbine plant.



Simple gas turbine Brayton cycle with closed cycle consists of



- 1 – 2 Isentropic compression in the compressor.
- 2 – 3 Constant pressure heat addition.
- 3 – 4 Isentropic expansion in the turbine.
- 4 – 1 Constant pressure heat rejection.



Assuming constant specific heats, the thermal efficiency of the cycle

$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

$$\text{or } \eta_{th} = 1 - \frac{h_4 - h_1}{h_3 - h_2}$$

$$= 1 - \frac{C_p (T_4 - T_1)}{C_p (T_3 - T_2)}$$

The thermal efficiency can be written as

$$\eta_{th} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

$$= 1 - \frac{T_1 \left[ \frac{T_4}{T_1} - 1 \right]}{T_2 \left[ \frac{T_3}{T_2} - 1 \right]}$$

Now  $\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$  and  $\frac{T_3}{T_4} = \left(\frac{p_3}{p_4}\right)^{\frac{\gamma-1}{\gamma}}$

Since,  $p_2 = p_3$  and  $p_1 = p_4$ , it follows

$$\frac{T_2}{T_1} = \frac{T_3}{T_4} \quad \text{or} \quad \frac{T_4}{T_1} = \frac{T_3}{T_2}$$

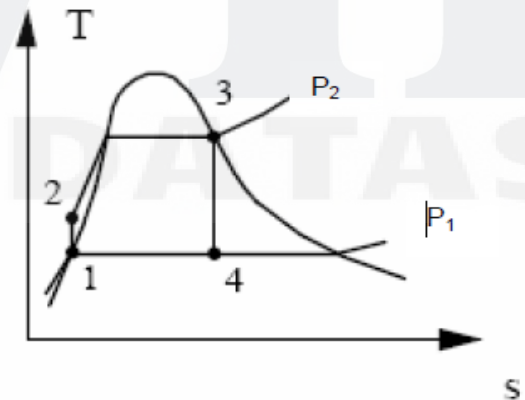
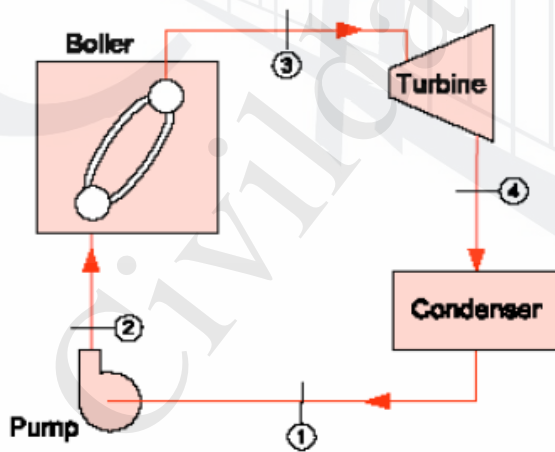
Hence, 
$$\eta_{th} = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{\left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}} = 1 - \left(\frac{1}{r_p}\right)^{\frac{\gamma-1}{\gamma}}$$

Where  $r_p$  is the pressure ratio.

It can be seen that increasing the pressure ratio can increase the efficiency of the Brayton cycle.

**RANKINE CYCLE**

The simplest way of overcoming the inherent practical difficulties of Carnot Cycle without deviating too far from it is to keep processes 2-3 and 3-4 of Carnot Cycle unchanged and to continue the process 4-1 in the condenser until all vapour is converted to liquid water. Water is then pumped into Boiler till its pressure is raised to



the pressure corresponding to state 2 and the cycle is completed. Such a cycle is known as Rankine Cycle.



where  $W_T$  and  $W_P$  are the turbine work and pump work respectively per kg of steam flow through the cycle and  $h_1, h_2, h_3, h_4$  are the specific enthalpies of the working fluid.

We know that the efficiency of the Carnot cycle depends only on the temperature levels of high and low temperature reservoirs. Efficiency of the Rankine cycle similarly depends on the average temperature at which the heat is transferred to and from the working fluid. Any change that increases the average temperature at which heat is transferred to the working fluid will increase the efficiency of the Rankine cycle. Similarly, any change that decreases the average temperature at which heat is transferred from the working fluid will increase the efficiency of the Rankine cycle.

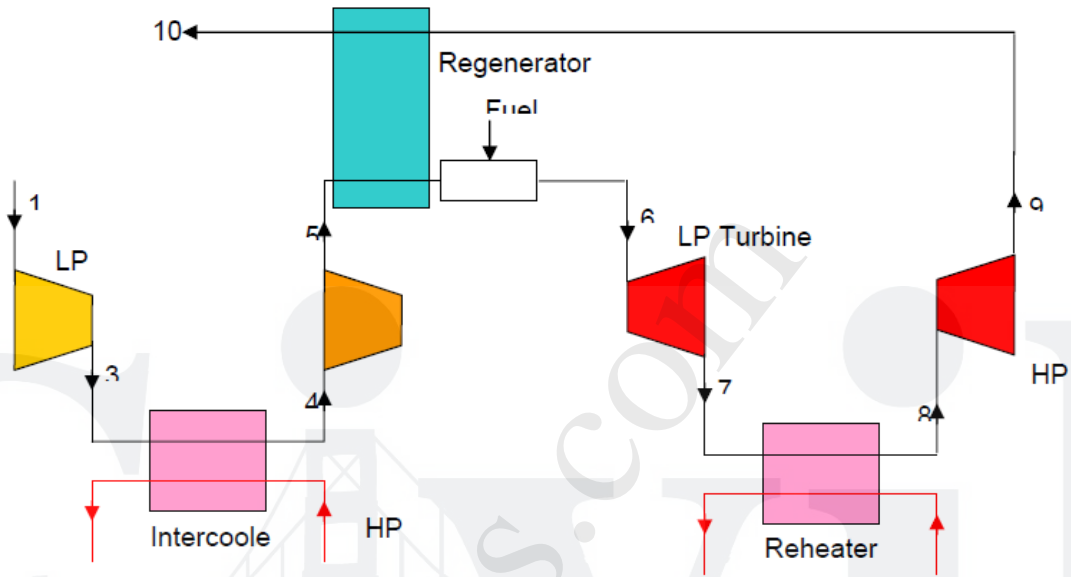
An advantage of the Rankine cycle over all other power cycles is its low back work ratio, which is expressed as the ratio of the pump work to the turbine work, i.e.

$$\text{Back work ratio} = \frac{W_P}{W_T}$$

If changes in kinetic and potential energies are neglected, the area under the curve 2-3 i.e. area 2-2'-3-5-6-2 represents the heat transfer to the working fluid in Boiler, which is equal to  $(h_3 - h_2)$  and area under the curve 1-2 i.e. area 1-4-5-6-1 represents the heat transferred from the working fluid in condenser, which is equal to  $(h_4 - h_1)$ . The difference between the two areas, namely area 1-2-2'-3-4-1, represents the work obtained from the cycle. The thermal efficiency of the cycle is given by

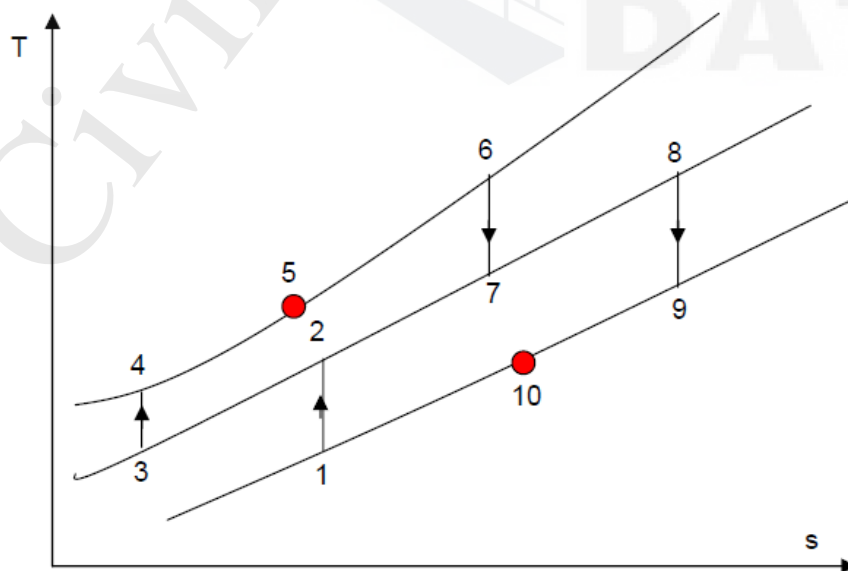
$$\begin{aligned} \eta_{th} &= \frac{W_{net}}{Q_H} = \frac{\text{area } 1-2-2'-3-4-1}{\text{area } 2-2'-3-5-6-2} \\ &= \frac{(h_3 - h_2) - (h_4 - h_1)}{(h_3 - h_2)} \\ &= \frac{(h_3 - h_4) - (h_2 - h_1)}{(h_3 - h_2)} = \frac{W_T - W_P}{Q_H} \end{aligned}$$

### 3.11 COMBINED CYCLE



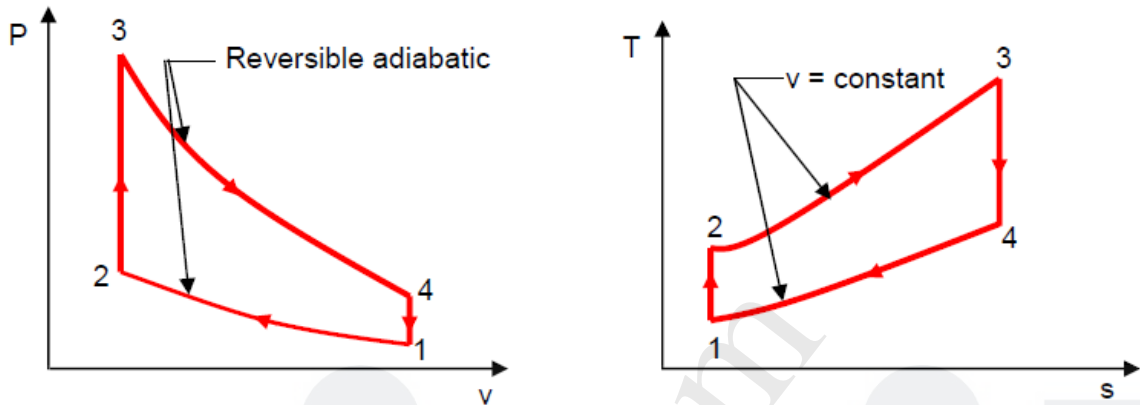
Thermal Efficiency is given by

$$\eta_{th} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{(h_{10} - h_1) + (h_2 - h_3)}{(h_6 - h_5) + (h_8 - h_7)}$$



### OTTO CYCLE

The air standard Otto Cycle is an idealised cycle which closely approximates the operation of Spark Ignition (SI) Engine.



Process 1-2 is reversible adiabatic (isentropic) compression of air when the piston moves from crank-end dead centre (BDC) to cylinder head dead centre (TDC). During the process 2-3, heat is transferred reversibly to the system at constant volume (this process corresponds to the spark ignition of the actual engine). The curve 3-4 represents the reversible adiabatic expansion process when piston moves from TDC to BDC and the curve 4-1 represents the heat rejected by the system reversibly at constant volume.

The thermal efficiency

$$\begin{aligned} \eta_{th} &= \frac{Q_{added} - Q_{rejected}}{Q_{added}} = 1 - \frac{Q_{rejected}}{Q_{added}} \\ &= 1 - \frac{u_4 - u_1}{u_3 - u_2} = 1 - \frac{C_v (T_4 - T_1)}{C_v (T_3 - T_2)} \\ &= 1 - \frac{T_4 - T_1}{T_3 - T_2} \end{aligned}$$

## UNIT IV

### IDEAL AND REAL GASES, THERMODYNAMIC RELATIONS

#### 4.1 IDEAL GAS

An **ideal gas** is a theoretical gas composed of a set of randomly-moving point particles that interact only through elastic collisions. The ideal gas concept is useful because it obeys the ideal gas law, a simplified equation of state, and is amenable to analysis under statistical mechanics.

At normal ambient conditions such as standard temperature and pressure, most real gases behave qualitatively like an ideal gas. Generally, deviation from an ideal gas tends to decrease with higher temperature and lower density, as the work performed by intermolecular forces becomes less significant compared with the particles' kinetic energy, and the size of the molecules becomes less significant compared to the empty space between them.

#### EQUATION TABLE FOR AN IDEAL GAS

Quantity	General Equation	Isobaric $\Delta p = 0$	Isochoric $\Delta V = 0$	Isothermal $\Delta T = 0$	Adiabatic $Q = 0$
Work $W$	$\delta W = pdV$	$p\Delta V$	0	$nRT \ln \frac{V_2}{V_1}$	$C_V(T_1 - T_2)$
Heat Capacity $C$	(as for real gas)	$C_p = \frac{5}{2}nR$	$C_V = \frac{3}{2}nR$		
Internal Energy $\Delta U$	$\Delta U = \frac{3}{2}nR\Delta T$	$\frac{Q - W}{C_p - p\Delta V}$	$\frac{Q}{C_V(T_2 - T_1)}$	$Q = W$	$C_V \frac{-W}{(T_2 - T_1)}$
Enthalpy $\Delta H$	$H = U + pV$	$C_p(T_2 - T_1)$	$Q_V + V\Delta p$	0	$C_p(T_2 - T_1)$
Entropy $\Delta S$	$ds = c_p \frac{dT}{T} - R \frac{dp}{p}$ <sup>[2]</sup>	$C_p \ln \frac{T_2}{T_1}$	$C_V \ln \frac{T_2}{T_1}$	$nR \ln \frac{V_2}{V_1}$ $\frac{Q}{T}$	$C_p \ln \frac{V_2}{V_1} + C_V \ln \frac{p_2}{p_1} = 0$

#### 4.2 REAL GAS

**Real gas**, as opposed to a Perfect or Ideal Gas, effects refers to an assumption base where the following are taken into account:

- Compressibility effects
- Variable heat capacity
- Van der Waals forces
- Non-equilibrium thermodynamic effects
- Issues with molecular dissociation and elementary reactions with variable composition.

For most applications, such a detailed analysis is "over-kill" and the ideal gas approximation is used. Real-gas models have to be used near condensation point of gases, near critical point, at very high pressures, and in several other less usual cases.

### 4.3 VAN DER WAALS MODELISATION

Real gases are often modeled by taking into account their molar weight and molar volume

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

Where P is the pressure, T is the temperature, R the ideal gas constant, and V<sub>m</sub> the molar volume. a and b are parameters that are determined empirically for each gas, but are sometimes estimated from their critical temperature (T<sub>c</sub>) and critical pressure (P<sub>c</sub>) using these relations:

$$a = \frac{27R^2T_c^2}{64P_c}$$

$$b = \frac{RT_c}{8P_c}$$

### 4.4 REDLICH-KWONG MODELISATION

The Redlich-Kwong equation is another two-parameters equation that is used to modelize real gases. It is almost always more accurate than the Van der Waals equation, and often more accurate than some equation with more than two parameters. The equation is

$$RT = P + \frac{a}{V_m(V_m + b)T^{\frac{1}{2}}}(V_m - b)$$

## 4.5 THERMODYNAMICS RELATIONS

### Fundamental Equation of Thermodynamics

$$\bullet U = TS - pV + \mu N$$

### Enthalpy

$$\bullet H \equiv U + pV = \mu N + TS$$

### Helmholtz free energy

$$\bullet A \equiv U - TS = \mu N - pV$$

### Gibbs free energy

$$\bullet G \equiv U + pV - TS = H - TS = \mu N$$

### Maxwell relations

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}$$

$$\left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N}$$

$$\left(\frac{\partial T}{\partial V}\right)_{p,N} = -\left(\frac{\partial p}{\partial S}\right)_{T,N}$$

$$\left(\frac{\partial T}{\partial p}\right)_{V,N} = \left(\frac{\partial V}{\partial S}\right)_{T,N}$$

### Maxwell relations.

The Maxwell's equations relate entropy to the three directly measurable properties p, v and T for pure simple compressible substances.

From first law of thermodynamics,

$$Q = W + \Delta U$$

Rearranging the parameters

$$Q = \Delta U + W \quad \text{since } [ds = \frac{Q}{T}, W = pdv]$$

$$\therefore Tds = du + pdv$$

$$du = Tds - pdv \quad \text{----- (1)}$$

We know that,  $h = u + pv$

$$\begin{aligned} dh &= du + d(pv) \\ &= du + vdp + pdv \quad \text{----- (2)} \end{aligned}$$

Substituting the value  $du$  in equation (2),

$$\begin{aligned} dh &= Tds + pdv + vdp - pdv \\ dh &= Tds + vdp \quad \text{----- (3)} \end{aligned}$$

By Helmotz's function,

$$\begin{aligned} a &= u - Ts \\ da &= du - d(Ts) \\ &= du - Tds - sdT \quad \text{----- (4)} \end{aligned}$$

Substituting the values of  $du$  in equation (4),

$$\begin{aligned} da &= Tds - pdv - Tds - sdT \\ T &= - pdv - sdT \quad \text{----- (5)} \end{aligned}$$

By Gibbs functions,

$$\begin{aligned} G &= h - Ts \\ dg &= dh - d(Ts) \end{aligned}$$

$$dg = dh - Tds - sdT \quad \text{----- (6)}$$

Substituting the value of dh in equation (6),

So, dg becomes

$$dg = Tds + vdp - Tds - sdT$$

$$dg = vdp - sdT \quad \text{----- (7)}$$

By inverse exact differential we can write equation (1) as,

$$du = Tds - pdv$$

$$\left(\frac{\partial T}{\partial v}\right)_s = - \left(\frac{\partial p}{\partial s}\right)_v \quad \text{----- (8)}$$

Similarly, equation (3) can be written as,

$$dh = Tds + vdp$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \quad \text{----- (9)}$$

Similarly, equation (5) can be written as,

$$- \left(\frac{\partial p}{\partial T}\right)_v = - \left(\frac{\partial s}{\partial v}\right)_T$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad \text{----- (10)}$$

Similarly, equation (7) can be written as,

$$dg = vdp - sdT$$

$$\left(\frac{\partial v}{\partial T}\right)_p = - \left(\frac{\partial s}{\partial p}\right)_T \quad \text{----- (11)}$$

These equations 8, 9, 10 and 11 are Maxwell's equation.



### Incremental processes

- $dU = T dS - p dV + \mu dN$
- $dA = -S dT - p dV + \mu dN$
  
- $dG = -S dT + V dp + \mu dN = \mu dN + N d\mu$
- $dH = T dS + V dp + \mu dN$

#### Proof #1

An example using the above methods is:

$$\begin{aligned} \left(\frac{\partial T}{\partial p}\right)_H &= -\frac{1}{C_p} \left(\frac{\partial H}{\partial p}\right)_T \\ \left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial p}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_p &= -1 \\ \left(\frac{\partial T}{\partial p}\right)_H &= -\left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial T}{\partial H}\right)_p \\ &= \frac{-1}{\left(\frac{\partial H}{\partial T}\right)_p} \left(\frac{\partial H}{\partial p}\right)_T; \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p \\ \Rightarrow \left(\frac{\partial T}{\partial p}\right)_H &= -\frac{1}{C_p} \left(\frac{\partial H}{\partial p}\right)_T \end{aligned}$$

**Tds relations in terms of temperature and pressure changes and temperature and volume changes.**

The entropy (s) of pure substance can be expressed as a function of temperature (T) and pressure (p).

$$s = f(T,p)$$

We know that,

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp \text{ and}$$

$$C_p = T \left(\frac{\partial s}{\partial T}\right)_p$$

$$\left(\frac{\partial s}{\partial T}\right)_p = \frac{C_p}{T}$$

From Maxwell equation, we know that

$$\left(\frac{\partial s}{\partial p}\right)_T = - \left(\frac{\partial v}{\partial T}\right)_p$$

Substituting in ds equation,

$$ds = \frac{C_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp$$

Multiplying by T on both sides of the equation,

$$Tds = C_p dT - T \left(\frac{\partial v}{\partial T}\right)_p dp$$

This is known as the first form of entropy equation or the first Tds equation.

By considering the entropy of a pure substance as a function of temperature and specific volume,

i.e.  $s = f(T,v)$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv \text{ and}$$

$$C_v = T \left(\frac{\partial s}{\partial T}\right)_v$$

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T}$$

From the Maxwell Equations, we know that

$$\left(\frac{\partial s}{\partial T}\right)_v = \left(\frac{\partial p}{\partial T}\right)_v$$

Substituting in ds Equation,

$$ds = \frac{c_v}{T} dT + \left(\frac{\partial p}{\partial T}\right)_v dv$$

Multiplying by T,

$$Tds = C_v dT + T \left(\frac{\partial p}{\partial T}\right)_v dv$$

This is known as the second form of entropy equation or the second Tds equation

#### 4.6 THE JOULE-THOMSON COEFFICIENT OF AN IDEAL GAS IS ZERO

The Joule-Thomson coefficient is defined as the change in temperature with change in pressure, keeping the enthalpy remains constant. It is denoted by,

$$\mu = \left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{c_p} \left[ T \left(\frac{\partial v}{\partial T}\right)_p - v \right]$$

We know that the equation of state as,

$$pV=RT$$

Differentiating the above equation of state with respect to T by keeping pressure, p constant.

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} = \frac{v}{T}$$

$$\mu = \frac{1}{c_p} \left[ T \frac{v}{T} - v \right]$$

$$\mu = 0.$$

It implies that the Joule-Thomson coefficient is zero for ideal gas.

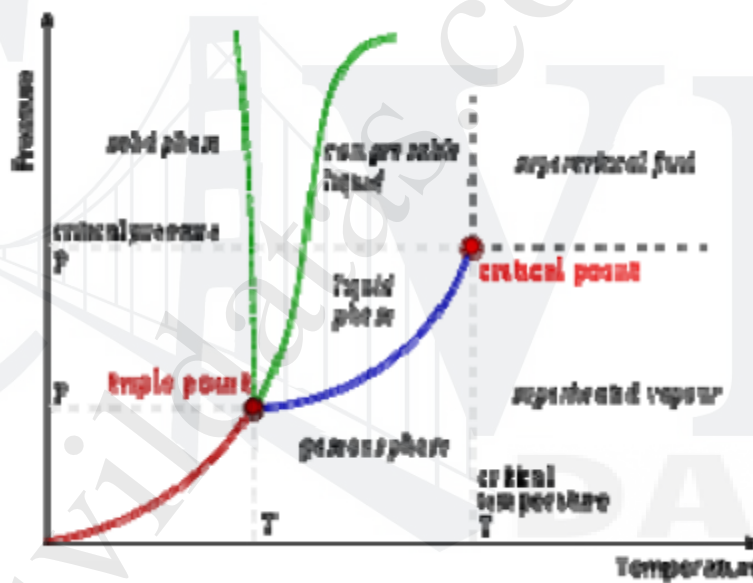
### 4.7 CLAUSIUS–CLAPEYRON RELATION

The **Clausius–Clapeyron relation**, named after Rudolf Clausius and Émile Clapeyron, who defined it sometime after 1834, is a way of characterizing the phase transition between two phases of matter, such as solid and liquid. On a pressure– temperature (P–T) diagram, the line separating the two phases is known as the coexistence curve. The Clausius–Clapeyron relation gives the slope of this curve. Mathematically,

$$\frac{dP}{dT} = \frac{L}{T \Delta V}$$

where  $dP / dT$  is the slope of the coexistence curve,  $L$  is the latent heat,  $T$  is the temperature, and  $\Delta V$  is the volume change of the phase transition.

#### Pressure Temperature Relations



A typical phase diagram. The dotted line gives the anomalous behavior of water. The Clausius–Clapeyron relation can be used to (numerically) find the relationships between pressure and temperature for the phase change boundaries. Entropy and volume changes (due to phase change) are orthogonal to the plane of this drawing

#### Derivation

Using the state postulate, take the specific entropy,  $s$ , for a homogeneous substance to be a function of specific volume,  $v$ , and temperature,  $T$ .

$$ds = \frac{\partial s}{\partial v} dv + \frac{\partial s}{\partial T} dT.$$

During a phase change, the temperature is constant, so

$$ds = \frac{\partial s}{\partial v} dv.$$

Using the appropriate Maxwell relation gives

$$ds = \frac{\partial P}{\partial T} dv.$$

Since temperature and pressure are constant *during a phase change*, the derivative of pressure with respect to temperature is not a function of the specific volume. Thus the partial derivative may be changed into a total derivative and be factored out when taking an integral from one phase to another,

$$s_2 - s_1 = \frac{dP}{dT} (v_2 - v_1),$$

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\Delta s}{\Delta v}.$$

$\Delta$  is used as an operator to represent the change in the variable that follows it—final (2) minus initial (1) For a closed system undergoing an internally reversible process, the first law is

$$du = \delta q + \delta w = Tds - Pdv.$$

This leads to a version of the Clausius–Clapeyron equation that is simpler to integrate:

$$\frac{dP}{P} = \frac{\Delta h}{R} \frac{dT}{T^2},$$

$$\ln P = -\frac{\Delta h}{R} \frac{1}{T} + C,$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta h}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right).$$

$C$  is a constant of integration

These last equations are useful because they relate saturation pressure and saturation temperature to the enthalpy of phase change, *without* requiring specific volume data. Note that in this last equation, the subscripts 1 and 2 correspond to different locations on the pressure versus temperature phase lines. In earlier equations, they corresponded to different specific volumes and entropies at the same saturation pressure and temperature.

**The Joule–Thomson (Kelvin) coefficient**

The rate of change of temperature  $T$  with respect to pressure  $P$  in a Joule–Thomson process (that is, at constant enthalpy  $H$ ) is the Joule–Thomson (Kelvin) coefficient  $\mu_{JT}$ . This coefficient can be expressed in terms of the gas's volume  $V$ , its heat capacity at constant pressure  $C_p$ , and its coefficient of thermal expansion  $\alpha$  as

$$\mu_{JT} \equiv \left( \frac{\partial T}{\partial P} \right)_H = \frac{V}{C_p} (\alpha T - 1)$$

See the Appendix for the proof of this relation. The value of  $\mu_{JT}$  is typically expressed in °C/bar (SI units: K/Pa) and depends on the type of gas and on the temperature and pressure of the gas before expansion.

All real gases have an inversion point at which the value of  $\mu_{JT}$  changes sign. The temperature of this point, the Joule–Thomson inversion temperature, depends on the pressure of the gas before expansion. In a gas expansion the pressure decreases, so the sign of is always negative. With that in mind, the following table explains when the Joule–Thomson effect cools or warms a real gas:

If the gas temperature is	then $\mu_{JT}$ is	since $\partial P$ is	thus $\partial T$ must be	so the gas
below the inversion temperature	positive	always negative	negative	cools
above the inversion temperature	negative	always negative	positive	warms

Helium and hydrogen are two gases whose Joule–Thomson inversion temperatures at a pressure of one atmosphere are very low (e.g., about 51 K (–222 °C) for helium). Thus, helium and hydrogen warm up when expanded at constant enthalpy at typical room temperatures. On the other hand nitrogen and oxygen, the two most abundant gases in air, have inversion temperatures of 621 K (348 °C) and 764 K (491 °C) respectively: these gases can be cooled from room temperature by the Joule–Thomson effect.

## Derivation of the Joule–Thomson (Kelvin) coefficient

A derivation of the formula

$$\mu_{JT} \equiv \left( \frac{\partial T}{\partial P} \right)_H = \frac{V}{C_p} (\alpha T - 1)$$

for the Joule–Thomson (Kelvin) coefficient.

The partial derivative of T with respect to P at constant H can be computed by expressing the differential of the enthalpy dH in terms of dT and dP, and equating the resulting expression to zero and solving for the ratio of dT and dP. It follows from the fundamental thermodynamic relation that the differential of the enthalpy is given by:

$$dH = TdS + VdP$$

$$dH = C_p dT + \left[ V + T \left( \frac{\partial S}{\partial P} \right)_T \right] dP$$

The remaining partial derivative of S can be expressed in terms of the coefficient of thermal expansion via a Maxwell relation as follows. From the fundamental thermodynamic relation, it follows that the differential of the Gibbs energy is given by:

$$dG = -SdT + VdP$$

The symmetry of partial derivatives of G with respect to T and P implies that:

$$\left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P = -V\alpha$$

where  $\alpha$  is the coefficient of thermal expansion. Using this relation, the differential of H can be expressed as

$$dH = C_p dT + V(1 - T\alpha) dP$$

Expressing  $dS$  in terms of  $dT$  and  $dP$  gives:

$$dH = T \left( \frac{\partial S}{\partial T} \right)_P dT + \left[ V + T \left( \frac{\partial S}{\partial P} \right)_T \right] dP$$

Using

$$C_P = T \left( \frac{\partial S}{\partial T} \right)_P \text{ (see Specific heat capacity), we can write:}$$

#### 4.8 SOLVED PROBLEMS

1. A mixture of ideal gases consists of 7kg of  $N_2$  and 2kg of  $O_2$  at a pressure of 4bar and a temperature of  $27^\circ\text{C}$ . Determine:
  - i. Mole fraction of each constituent,
  - ii. Equivalent molecular weight of the mixture,
  - iii. Equivalent gas constant of the mixture,
  - iv. The partial pressure and partial volumes,
  - v. The volume and density of the mixture

**Given data:**

$$m_{N_2} = 7\text{kg}$$

$$m_{O_2} = 2\text{kg}$$

$$p = 4\text{bar}$$

$$T = 27^\circ\text{C}$$

**Solution:**

- i. Mole fraction of  $N_2$ ,

$$x_{N_2} = \frac{\left(\frac{7}{28}\right)}{\left(\frac{7}{28}\right) + \left(\frac{2}{32}\right)} = 0.8$$



Mole fraction of  $O_2$ ,

$$x_{O_2} = \frac{\left(\frac{2}{32}\right)}{\left(\frac{7}{28}\right) + \left(\frac{2}{32}\right)} = 0.2$$

ii. Equivalent molecular weight of the mixture,

$$\begin{aligned} M &= x_{N_2}M_{N_2} + x_{O_2}M_{O_2} \\ &= (0.8 \times 28) + (0.2 \times 32) = 28.8 \text{ kg/kg mol} \end{aligned}$$

$$\text{Total mass, } m = m_{N_2} + m_{O_2} = 7 + 2 = 9 \text{ kg}$$

iii. Equivalent gas constant of the mixture,

$$\begin{aligned} R &= \frac{m_{N_2}R_{N_2} + m_{O_2}R_{O_2}}{m} \\ &= \frac{7\left(\frac{8.314}{28}\right) + 2\left(\frac{8.314}{32}\right)}{9} = 0.2886 \text{ kJ/kgK} \end{aligned}$$

iv. The partial pressure and partial volumes,

$$p_{N_2} = x_{N_2}p = (0.8 \times 4) = 3.2 \text{ bar}$$

$$p_{O_2} = x_{O_2}p = (0.2 \times 4) = 0.8 \text{ bar}$$

$$V_{N_2} = \frac{m_{N_2}R_{N_2}T}{p} = \frac{7\left(\frac{8.314}{28}\right) \times 300}{400} = 1.558 \text{ m}^3$$

$$V_{O_2} = \frac{m_{O_2}R_{O_2}T}{p} = \frac{2\left(\frac{8.314}{32}\right) \times 300}{400} = 0.389 \text{ m}^3$$

v. The volume and density of the mixture,

$$\text{Density of } N_2 = \frac{m_{N_2}}{V_{N_2}} = \frac{7}{1.558} = 4.492 \text{ kg/m}^3$$

$$\text{Density of } O_2 = \frac{m_{O_2}}{V_{O_2}} = \frac{2}{0.389} = 5.141 \text{ kg/m}^3$$

### Describe Joule Kelvin effect with the help of T-p diagram

The Joule Kelvin effect or Joule Thomson effect is an efficient way of cooling gases. In this, a gas is made to undergo a continuous throttling process. A constant pressure is

maintained at one side of a porous plug and a constant lower pressure at the other side. The apparatus is thermally insulated so that the heat loss can be measured.

Joule – Thomson coefficient is defined as the change in temperature with change in pressure, keeping the enthalpy remains constant. It is denoted by,

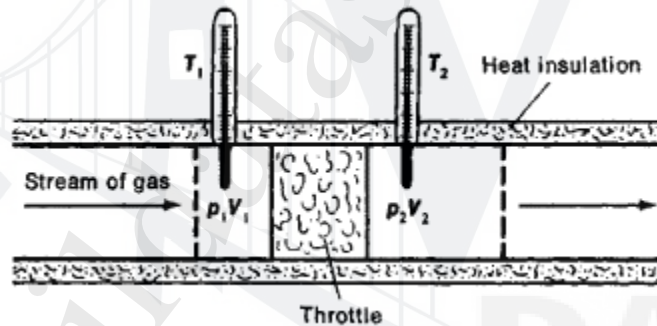
$$\mu = \left( \frac{\partial T}{\partial p} \right)_h$$

**Throttling process:**

It is defined as the fluid expansion through a minute orifice or slightly opened valve. During this process, pressure and velocity are reduced. But there is no heat transfer and no work done by the system. In this process enthalpy remains constant.

**Joule Thomson Experiment:**

The figure shows the arrangement of porous plug experiment. In this experiment, a stream of gas at a pressure  $p_1$  and temperature  $T_1$  is allowed to flow continuously through a porous plug. The gas comes out from the other side of the porous plug at a pressure  $p_2$  and temperature  $T_2$ .



The whole apparatus is insulated. Therefore no heat transfer takes place.  $Q = 0$ .

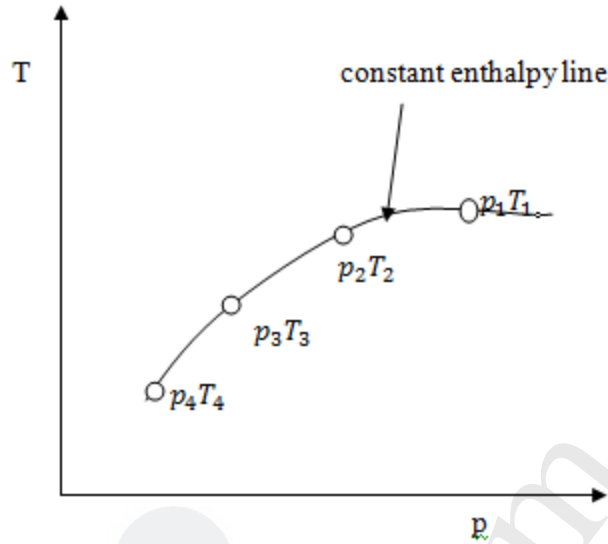
The system does not exchange work with the surroundings.

So,  $W=0$  from steady flow energy equation we know that

$$gz_1 + \frac{C_1^2}{2} + (U_1 + P_1 V_1) + Q = gz_2 + \frac{C_2^2}{2} + (U_2 + P_2 V_2) + W$$

Since there is no considerable change velocity,  $V_1 = V_2$  and  $z_1 = z_2$ ,  $Q=0, W=0$ , are applied in steady flow energy equation. Therefore,  $h_1 = h_2$

It indicates that the enthalpy is constant for throttling process.



It is assumed that a series of experiments performed on a real gas keeping the initial pressure  $p_1$  and temperature  $T_1$  constant with various down stream pressures ( $p_2, p_3 \dots$ ). It is found that the down stream temperature also changes. The results from these experiments can be plotted as enthalpy curve on T-p plane.

The slope of a constant enthalpy is known as Joule Thomson Coefficient. It is denoted by  $\mu$ .

$$\mu = \left( \frac{\partial T}{\partial p} \right)_h$$

For real gas,  $\mu$  may be either positive or negative depending upon the thermodynamic state of the gas.

2. A mixture of 2kg oxygen and 2kg Argon is in an insulated piston cylinder arrangement at 100kPa, 300K. The piston now compresses the mixture to half its initial volume. Molecular weight of oxygen is 40. Ratio of specific heats for oxygen is 1.39 and for argon is 1.667.[Nov 2004]

**Given data:**

$$m_{O_2} = 2\text{kg}$$

$$m_{Ar} = 2\text{kg}$$

$$p_1 = 100\text{kPa}$$

$$T_1 = 300\text{K}$$

$$V_2 = \frac{V_1}{2}$$

$$M_{O_2} = 32$$

$$M_{Ar} = 40$$

$$\gamma_{O_2} = 1.39$$

$$\gamma_{Ar} = 1.667$$

**Solution:**

$$\text{Mass fraction, } x_{O_2} = \frac{\left(\frac{2}{32}\right)}{\frac{2}{32} + \frac{2}{40}} = 0.56$$

$$p_{O_2} = x_{O_2} p = 55.6 \text{ kPa}$$

Similarly,

$$x_{Ar} = \frac{\left(\frac{2}{40}\right)}{\frac{2}{32} + \frac{2}{40}} = 0.44$$

$$p_{Ar} = p x_{Ar} = 44.4 \text{ kPa}$$

From equation of state,

$$V_{O_2} = \frac{m_{O_2} R_{O_2} T}{p_{O_2}} = \frac{2 \left(\frac{8.314}{32}\right) \times 300}{55.6} = 2.804 \text{ m}^3$$

$$V_{Ar} = \frac{m_{Ar} R_{Ar} T}{p_{Ar}} = \frac{2 \left(\frac{8.314}{40}\right) \times 300}{44.4} = 2.81 \text{ m}^3$$

Volume of mixture before expansion,

$$V_1 = V_{O_2} + V_{Ar} = 5.61 \text{ m}^3$$

Volume after expansion,

$$V_2 = \frac{V_1}{2} = \frac{5.61}{2} = 2.807 \text{ m}^3$$

Ratio of specified heat of mixture,

$$\gamma = x_{O_2} \gamma_{O_2} + x_{Ar} \gamma_{Ar} = 1.513$$

Insulated process refers reversible adiabatic process

$$p_1 V_1^\gamma = p_2 V_2^\gamma$$

$$p_2 = p_1 \frac{V_1^\gamma}{V_2^\gamma} = 100(2)^{1.513} = 285.4 \text{ kPa}$$

Similarly,

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$$

$$\frac{T_2}{300} = \left(\frac{285.4}{100}\right)^{\frac{1.513-1}{1.513}}$$

$$T_2 = 2040.19K$$

Piston work,

$$W = \frac{p_1V_1 - p_2V_2}{n-1} = \frac{(100 \times 5.61) - (285.4 \times 2.807)}{1.513 - 1} = -1000.23kJ$$

$$W = -1MJ$$

(Negative sign indicates the work input to piston)

## UNIT V

### GAS MIXTURES AND PSYCHROMETRY

#### 5.1 GAS MIXTURES

*Pure substance is defined as a substance which means that it is homogeneous and unchanging in chemical composition.*

#### COMPOSITION OF A GAS MIXTURE:

##### MASS AND MOLE FRACTIONS

To determine the properties of a mixture, we need to know the composition of the mixture as well as the properties of the individual components. There are two ways to describe the composition of a mixture: either by specifying the number of moles of each component, called molar analysis, or by specifying the mass of each component, called gravimetric analysis.

Consider a gas mixture composed of k components. The mass of the mixture  $m_m$  is the sum of the masses of the individual components, and the mole number of the mixture  $N_m$  is the sum of the mole numbers of the individual components.

$$m_m = \sum_{i=1}^k m_i \quad \text{and} \quad N_m = \sum_{i=1}^k N_i$$

The ratio of the mass of a component to the mass of the mixture is called the mass fraction  $mf$ , and the ratio of the mole number of a component to the mole number of the mixture is called the mole fraction

$$mf_i = \frac{m_i}{m_m} \quad \text{and} \quad y_i = \frac{N_i}{N_m}$$

Dividing (1) by  $m_m$  or (2) by  $N_m$ , we can easily show that the sum of the mass fractions or mole fractions for a mixture is equal to 1

$$\sum_{i=1}^k mf_i = 1 \quad \text{and} \quad \sum_{i=1}^k y_i = 1$$

The mass of a substance can be expressed in terms of the mole number  $N$  and molar mass  $M$  of the substance as  $m = NM$ . Then the apparent (or average) molar mass and the gas constant of a mixture can be expressed as

$$M_m = \frac{m_m}{N_m} = \frac{\sum m_i}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum_{i=1}^k y_i M_i \quad \text{and} \quad R_m = \frac{R_u}{M_m}$$

The molar mass of a mixture can also be expressed as

$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i / M_i} = \frac{1}{\sum m_i / (m_m M_i)} = \frac{1}{\sum_{i=1}^k \frac{mf_i}{M_i}}$$

Mass and mole fractions of a mixture are related by

$$mf_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m}$$

### EXAMPLE 13-1 Mass and Mole Fractions of a Gas Mixture

Consider a gas mixture that consists of 3 kg of  $O_2$ , 5 kg of  $N_2$ , and 12 kg of  $CH_4$ , as shown in Fig. 13-4. Determine (a) the mass fraction of each component, (b) the mole fraction of each component, and (c) the average molar mass and gas constant of the mixture.

**Solution** The masses of components of a gas mixture are given. The mass fractions, the mole fractions, the molar mass, and the gas constant of the mixture are to be determined.

**Analysis** (a) The total mass of the mixture is

$$m_m = m_{O_2} + m_{N_2} + m_{CH_4} = 3 + 5 + 12 = 20 \text{ kg}$$

Then the mass fraction of each component becomes

$$mf_{O_2} = \frac{m_{O_2}}{m_m} = \frac{3 \text{ kg}}{20 \text{ kg}} = 0.15$$

$$mf_{N_2} = \frac{m_{N_2}}{m_m} = \frac{5 \text{ kg}}{20 \text{ kg}} = 0.25$$

$$mf_{CH_4} = \frac{m_{CH_4}}{m_m} = \frac{12 \text{ kg}}{20 \text{ kg}} = 0.60$$

(b) To find the mole fractions, we need to determine the mole numbers of each component first:

$$N_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{3 \text{ kg}}{32 \text{ kg/kmol}} = 0.094 \text{ kmol}$$

$$N_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{5 \text{ kg}}{28 \text{ kg/kmol}} = 0.179 \text{ kmol}$$

$$N_{CH_4} = \frac{m_{CH_4}}{M_{CH_4}} = \frac{12 \text{ kg}}{16 \text{ kg/kmol}} = 0.750 \text{ kmol}$$

Thus,

$$N_m = N_{O_2} + N_{N_2} + N_{CH_4} = 0.094 + 0.179 + 0.750 = 1.023 \text{ kmol}$$

and

$$y_{O_2} = \frac{N_{O_2}}{N_m} = \frac{0.094 \text{ kmol}}{1.023 \text{ kmol}} = \mathbf{0.092}$$

$$y_{N_2} = \frac{N_{N_2}}{N_m} = \frac{0.179 \text{ kmol}}{1.023 \text{ kmol}} = \mathbf{0.175}$$

$$y_{CH_4} = \frac{N_{CH_4}}{N_m} = \frac{0.750 \text{ kmol}}{1.023 \text{ kmol}} = \mathbf{0.733}$$

(c) The average molar mass and gas constant of the mixture are determined from their definitions,

$$M_m = \frac{m_m}{N_m} = \frac{20 \text{ kg}}{1.023 \text{ kmol}} = \mathbf{19.6 \text{ kg/kmol}}$$

or

$$\begin{aligned} M_m &= \sum y_i M_i = y_{O_2} M_{O_2} + y_{N_2} M_{N_2} + y_{CH_4} M_{CH_4} \\ &= (0.092)(32) + (0.175)(28) + (0.733)(16) \\ &= 19.6 \text{ kg/kmol} \end{aligned}$$

Also,

$$R_m = \frac{R_u}{M_m} = \frac{8.314 \text{ kJ}/(\text{kmol} \cdot \text{K})}{19.6 \text{ kg/kmol}} = \mathbf{0.424 \text{ kJ/kg} \cdot \text{K}}$$

**Discussion** When mass fractions are available, the molar mass and mole fractions could also be determined directly from Eqs. 13-4 and 13-5.

## 5.2 P-v-T BEHAVIOR OF GAS MIXTURES: IDEAL AND REAL GASES

An ideal gas is defined as a gas whose molecules are spaced far apart so that the behavior of a molecule is not influenced by the presence of other molecules—a



situation encountered at low densities. We also mentioned that real gases approximate this behavior closely when they are at a low pressure or high temperature relative to their critical-point values. The P-v-T behavior of an ideal gas is expressed by the simple relation  $Pv = RT$ , which is called the ideal-gas equation of state. The P-v-T behavior of real gases is expressed by more complex equations of state or by  $Pv = ZRT$ , where Z is the compressibility factor.

When two or more ideal gases are mixed, the behavior of a molecule normally is not influenced by the presence of other similar or dissimilar molecules, and therefore a nonreacting mixture of ideal gases also behaves as an ideal gas. Air, for example, is conveniently treated as an ideal gas in the range where nitrogen and oxygen behave as ideal gases. When a gas mixture consists of real (nonideal) gases, however, the prediction of the P-v-T behavior of the mixture becomes rather involved.

The prediction of the P-v-T behavior of gas mixtures is usually based on two models: Dalton's law of additive pressures and Amagat's law of additive volumes. Both models are described and discussed below.

***Dalton's law of additive pressures:***

**Dalton's law** (also called **Dalton's law of partial pressures**) states that the total pressure exerted by a gaseous mixture is equal to the sum of the partial pressures of each individual component in a gas mixture. This empirical law was observed by John Dalton in 1801 and is related to the ideal gas laws. Mathematically, the pressure of a mixture of gases can be defined as the summation

$$P_{total} = \sum_{i=1}^n p_i \quad \text{or} \quad P_{total} = p_1 + p_2 + \dots + p_n$$

where  $p_1, p_2, p_n$  represent the partial pressure of each component.

***Amagat's law of additive volumes:***

**Amagat's law** or the **Law of Partial Volumes** of 1880 describes the behavior and properties of mixtures of ideal (as well as some cases of non-ideal) gases. Of use in chemistry and thermodynamics, Amagat's law states that the volume  $V_m$  of a gas mixture is equal to the sum of volumes  $V_i$  of the  $K$  component gases, if the temperature  $T$  and the pressure  $p$  remain the same:

$$V_m(T, p) = \sum_{i=1}^K V_i(T, p)$$

This is the experimental expression of volume as an extensive quantity. It is named after Emile Amagat. Both Amagat's and Dalton's Law predict the properties of gas mixtures. Their predictions are the same for ideal gases. However, for real (non-ideal) gases, the results differ. Dalton's Law of Partial Pressures assumes that the gases in the mixture are non-interacting (with each other) and each gas independently applies its own **pressure**, the sum of which is the total pressure. Amagat's Law assumes that the **volumes** of each component gas (same temperature and pressure) are additive; the interactions of the different gases are the same as the average interactions of the components.

### **Heat capacity**

The heat capacity at constant volume of an ideal gas is:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \hat{c}_V Nk = \hat{c}_V nR.$$

It is seen that the constant is just the dimensionless heat capacity at constant volume. It is equal to half the number of degrees of freedom per particle. For moderate temperatures, the constant for a monoatomic gas is  $\hat{c}_V = 3/2$  while for a diatomic gas it is  $\hat{c}_V = 5/2$ . It is seen that macroscopic measurements on heat capacity provide information on the microscopic structure of the molecules.

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p = (\hat{c}_V + 1)Nk$$

where  $H = U + pV$  is the enthalpy of the gas. It is seen that is also a constant and that the dimensionless heat capacities are related by:

$$\hat{c}_p - \hat{c}_V = 1.$$

### **5.3 ENTROPY**

Using the results of thermodynamics only, we can go a long way in determining the expression for the entropy of an ideal gas. This is an important step since, according to the theory of thermodynamic potentials, of which the internal energy  $U$  is one, if we can express the entropy as a function of  $U$  and the volume  $V$ , then we will have a complete statement of the thermodynamic behavior of the ideal gas. We will be able to derive both the ideal gas law and the expression for internal energy from it. Since the entropy is an exact differential, using the chain rule, the change in entropy when going from a reference state 0 to some other state with entropy  $S$  may be written as  $\Delta S$  where:

$$\Delta S = \int_{S_0}^S dS = \int_{T_0}^T \left( \frac{\partial S}{\partial T} \right)_V dT + \int_{V_0}^V \left( \frac{\partial S}{\partial V} \right)_T dV$$

$$\frac{\Delta S}{Nk} = \ln \left( \frac{VT^{\hat{c}_v}}{N\phi} \right)$$

This is about as far as we can go using thermodynamics alone. Note that the above equation is flawed — as the temperature approaches zero, the entropy approaches negative infinity, in contradiction to the third law of thermodynamics. In the above "ideal" development, there is a critical point, not at absolute zero, at which the argument of the logarithm becomes unity, and the entropy becomes zero.

## 5.4 PSYCHROMETRY

**psychrometry** is a term used to describe the field of engineering concerned with the determination of physical and thermodynamic properties of gas-vapor mixtures. The term derives from the Greek *psuchron* meaning "cold" and *metron* meaning "means of measurement"

### Common applications

The principles of psychrometry apply to any physical system consisting of gasvapor mixtures. The most common system of interest, however, are mixtures of water vapor and air because of its application in heating, ventilating, and air-conditioning and meteorology.

### Psychrometric ratio

The **psychrometric ratio** is the ratio of the heat transfer coefficient to the product of mass transfer coefficient and humid heat at a wetted surface. It may be evaluated with the following equation

$$r = \frac{h_c}{k_y c_s}$$

where:

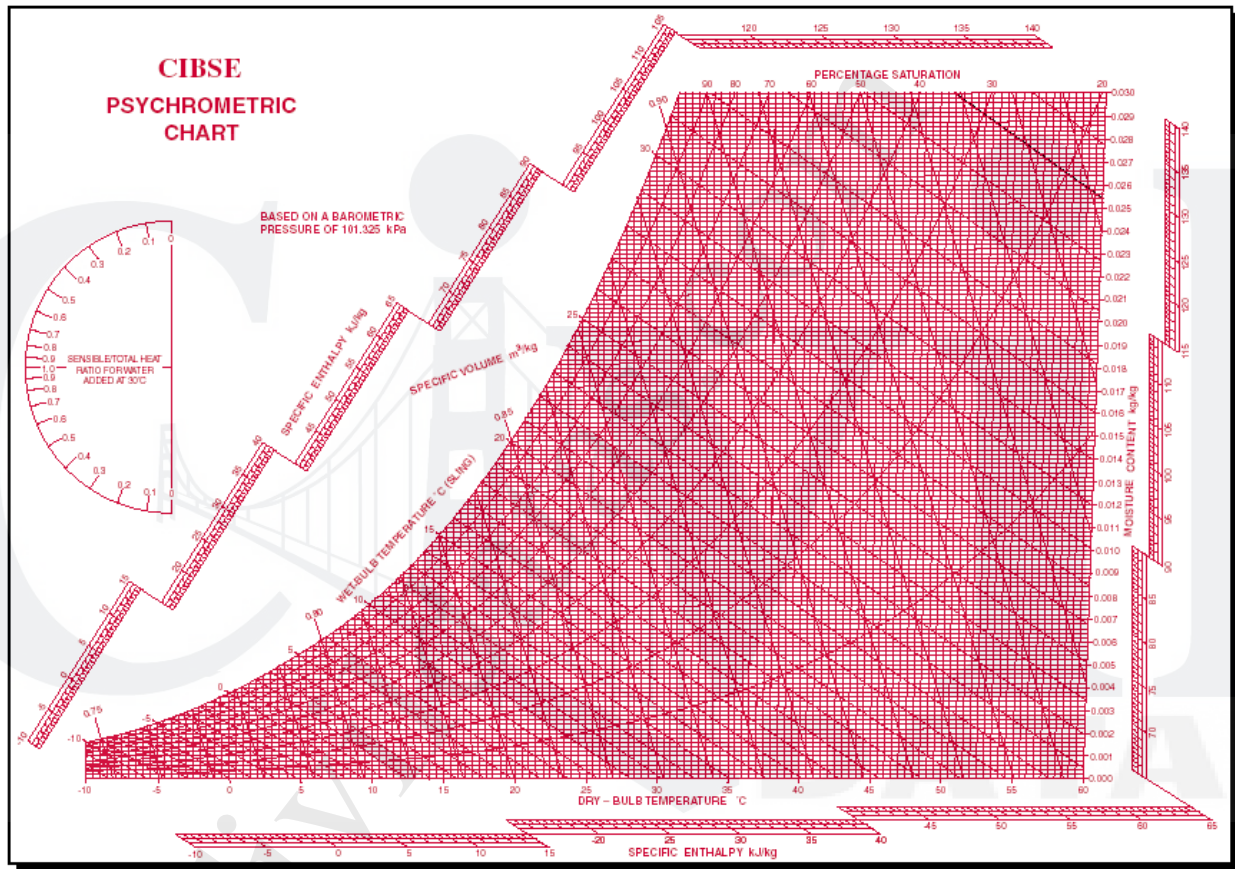
- $r$  = Psychrometric ratio, dimensionless
- $h_c$  = convective heat transfer coefficient, W m<sup>-2</sup> K<sup>-1</sup>
- $k_y$  = convective mass transfer coefficient, kg m<sup>-2</sup> s<sup>-1</sup>
- $c_s$  = humid heat, J kg<sup>-1</sup> K<sup>-1</sup>

**Humid heat** is the constant-pressure specific heat of moist air, per unit mass of dry air.

The psychrometric ratio is an important property in the area of psychrometrics as it relates the absolute humidity and saturation humidity to the difference between the

dry bulb temperature and the adiabatic saturation temperature. Mixtures of air and water vapor are the most common systems encountered in psychrometry. The psychrometric ratio of air-water vapor mixtures is approximately unity which implies that the difference between the adiabatic saturation temperature and wet bulb temperature of air-water vapor mixtures is small. This property of air-water vapor systems simplifies drying and cooling calculations often performed using psychrometric relationships.

### PSYCHROMETRIC CHART



A psychrometric chart is a graph of the physical properties of moist air at a constant pressure (often equated to an elevation relative to sea level). The chart graphically expresses how various properties relate to each other, and is thus a graphical equation of state. The thermophysical properties found on most psychrometric charts are:

- **Dry-bulb temperature (DBT)** is that of an air sample, as determined by an ordinary thermometer, the thermometer's bulb being dry. It is typically the x-axis,

the horizontal axis, of the graph. The SI units for temperature are Kelvin; other units are Fahrenheit.

- **Wet-bulb temperature (*WBT*)** is that of an air sample after it has passed through a constant-pressure, ideal, adiabatic saturation process, that is, after the air has passed over a large surface of liquid water in an insulated channel. In practice, this is the reading of a thermometer whose sensing bulb is covered with a wet sock evaporating into a rapid stream of the sample air. The WBT is the same as the DBT when the air sample is saturated with water. The slope of the line of constant WBT reflects the heat of vaporization of the water required to saturate the air of a given relative humidity.

- **Dew point temperature (*DPT*)** is that temperature at which a moist air sample at the same pressure would reach water vapor saturation. At this saturation point, water vapor would begin to condense into liquid water fog or (if below freezing) solid hoarfrost, as heat is removed. The dewpoint temperature is measured easily and provides useful information, but is normally not considered an independent property. It duplicates information available via other humidity properties and the saturation curve.

- **Relative humidity (*RH*)** is the ratio of the mole fraction of water vapor to the mole fraction of saturated moist air at the same temperature and pressure. RH is dimensionless, and is usually expressed as a percentage. Lines of constant RH reflect the physics of air and water: they are determined via experimental measurement. Note: the notion that air "holds" moisture, or that moisture dissolves in dry air and saturates the solution at some proportion, is an erroneous (albeit widespread) concept (see relative humidity for further details).

- **Humidity ratio** (also known as moisture content, mixing ratio, or specific humidity) is the proportion of mass of water vapor per unit mass of dry air at the given conditions (DBT, WBT, DPT, RH, etc.). It is typically the y-axis, the vertical axis, of the graph. For a given DBT there will be a particular humidity ratio for which the air sample is at 100% relative humidity: the relationship reflects the physics of water and air and must be measured. Humidity ratio is dimensionless, but is sometimes expressed as grams of water per kilogram of dry air or grains of water per pound of air.

- **Specific enthalpy** symbolized by  $h$ , also called heat content per unit mass, is the sum of the internal (heat) energy of the moist air in question, including the heat of the air and water vapor within. In the approximation of ideal gases, lines of

constant enthalpy are parallel to lines of constant WBT. Enthalpy is given in (SI) joules per kilogram of air or BTU per pound of dry air.

- **Specific volume**, also called *inverse density*, is the volume per unit mass of the air sample. The SI units are cubic meters per kilogram of dry air; other units are cubic feet per pound of dry air.

### Specific humidity

*Specific humidity* is the ratio of water vapor to air (including water vapor and dry air) in a particular mass. Specific humidity ratio is expressed as a ratio of kilograms of water vapor,  $m_w$ , per kilogram of air (including water vapor),  $m_t$ .

$$SH = \frac{m_w}{m_t}$$

$$MR = \frac{SH}{1 - SH}$$

### Relative Humidity

The relative humidity of an air-water mixture is defined as the ratio of the partial pressure of water vapor in the mixture to the saturated vapor pressure of water at a prescribed temperature. Relative humidity is normally expressed as a percentage and is defined in the following manner

$$RH = \frac{P_{(H_2O)}}{P_{(H_2O)}^*} \times 100\%$$

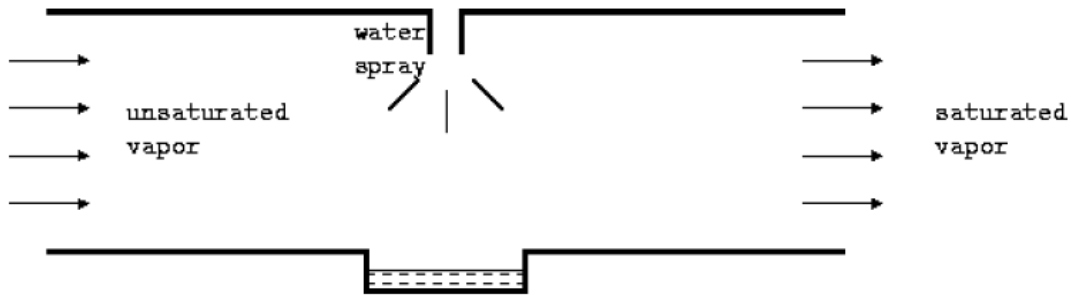
$RH$  is the relative humidity of the mixture being considered;

$P_{(H_2O)}$  is the partial pressure of water vapor in the mixture; and

$P_{(H_2O)}^*$  is the saturated vapor pressure of water at the temperature of the mixture.

The international symbols  $U$  and  $U_w$ , expressed in per cent, are gaining recognition.

### Adiabatic Saturation

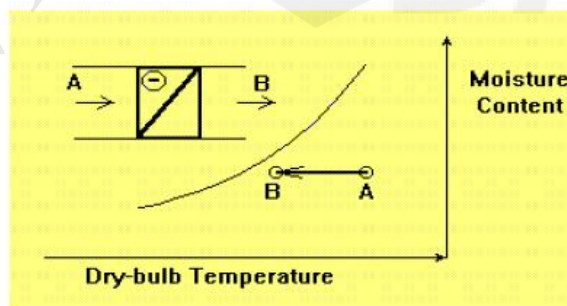


Consider an unsaturated mixture entering a chamber. Suppose water was sprayed into the stream, so that the humidity increases and it leaves as a saturated mixture. This is accompanied by a loss of temperature due to heat being removed from the air which is used for vaporization. If the water supplied is at the temperature of exit of the stream, then there is no heat transfer from the water to the mixture. The final temperature of the mixture is called *adiabatic saturation temperature*.

increased. The process occurs at constant moisture content. The air passes over a hot and dry surface which might be pipe coil using steam or hot water, electrical resistance or an air-to-air heat recovery unit. The load on the heater is:

$$Q = m \cdot (h_B - h_A)$$

### Sensible Cooling Process



Sensible cooling process at constant moisture content is a process during which

### 5.5 SOLVED PROBLEMS

1. Atmospheric air at 1.0132bar has a DBT of 30°C and a WBT of 25°C. Compute
- i. The partial pressure of water vapour,
  - ii. The specific humidity,
  - iii. The dew point temperature,
  - iv. The relative humidity,
  - v. The degree of saturation,
  - vi. The density of air in the mixture,
  - vii. The density of vapour in the mixture and
  - viii. The enthalpy of the mixture. Use thermodynamic table. [April/May - 2015]

**Given data:**

Dry bulb temperature, ( $t_{d1}$ ) = 30°C

Wet bulb temperature, ( $t_{d2}$ ) = 25°C

Atmospheric pressure, ( $p_b$ ) = 1.0132bar

**Solution:**

1. Humidity ratio,  $\omega = 0.622 \frac{p_v}{p_b - p_v}$

Partial pressure vapour,  $p_v = p_{sw} - \frac{(p_b - p_{sw})(t_d - t_w)}{1527.4 - 1.3t_w}$

Where,

$p_{sw}$  - saturation pressure corresponding to WBT

$p_b$  - barometric pressure = 1bar

$t_d$  - Dry bulb temperature

$t_w$  - Wet bulb temperature

From steam table, for 25°C WBT, corresponding pressure is 0.03166bar

i.e.  $p_{sw} = 0.03166\text{bar}$

$$p_v = 0.0336 - \frac{(1.013 - 0.03166)(32 - 26)}{1527.4 - (1.3 \times 25)}$$

Partial pressure of vapour,

$$p_v = 0.0296\text{bar}$$

Substituting  $p_v$  and  $p_b$  value in equation  $\omega$ ,

$$\omega = 0.622 \times \frac{0.0296}{1 - 0.0296}$$



Specific humidity,  $\omega = 0.0189 \text{ kJ/kg}$  of air

2. Dew point temperature ( $t_{dp}$ )

From steam table, we find that partial vapour pressure,  $p_v = 0.03 \text{ bar}$ , corresponding temperature is  $24.1^\circ\text{C}$ .

So, the dew point temperature  $t_{dp} = 24.1^\circ\text{C}$

3. Relative humidity

$$\phi = \frac{p_v}{p_s}$$

Where,  $p_s$  – Saturation pressure corresponding DBT

From steam table,

For  $30^\circ\text{C}$  DBT, corresponding pressure is  $0.04242 \text{ bar}$

$$\text{i.e. } p_s = 0.04242 \text{ bar}$$

$$\phi = \frac{0.0296}{0.04242}$$

$$\phi = 0.6977 = 69.77\%$$

4. Degree of saturation,  $\mu = \frac{p_v}{p_s} \left( \frac{p_b - p_s}{p_b - p_v} \right)$

$$\mu = \frac{0.0296}{0.04242} \left( \frac{1.013 - 0.04242}{1.013 - 0.0296} \right)$$

$$\mu = 0.6886$$

5. Specific volume ( $v_a$ ) of air:

From gas law,

$$p_a v_a = R_a T_a$$

Where,

Gas constant,  $R = 0.287 \text{ kJ/kg}$

$$T_a = t_d + 273 = 30 + 273 = 303 \text{ K}$$

$$p_a = p_b - p_v = 1.013 - 0.0296$$

$$p_a = 0.9834 \text{ bar}$$

$$v_a = \frac{R_a T_a}{p_a} = \frac{0.287 \times 303}{0.9834} = 88.428 \text{ m}^3/\text{kg}$$

Density of air,

$$\rho_a = \frac{1}{v_a} = \frac{1}{88.428} = 0.011 \text{ kg/m}^3$$

6. Density of water vapour ( $\rho_v$ )

From steam table, corresponding to 30°C DBT, specific volume ( $v_g$ ) is

$$32.929 \text{ m}^3/\text{kg}$$

$$\rho_v = \frac{1}{v_g} = \frac{1}{32.929} = 0.0303 \text{ kg/m}^3$$

Vapour density of relative humidity,

$$\phi = 0.6977$$

Vapour density,  $\rho_v = 0.0303 \times 0.6977$

$$\rho_v = 0.0211 \text{ kg/m}^3$$

7. Total enthalpy

$$\text{Enthalpy, } h = C_p t_d + \omega h_g$$

Where,  $C_p$  - Specific heat = 1.005 kJ/kgK

$h_g$  - Specific enthalpy of air corresponding DBT

From steam table,

For 30°C DBT, corresponding specific enthalpy is 2430.7 kJ/kg

$$h = (1.005 \times 30) + (0.0189 \times 2430.7)$$

$$h = 76.09 \text{ kJ/kg}$$

**2. Air at 20°C, 40% relative humidity is mixed adiabatically with air at 40°C, 40% RH in the ratio of 1kg of former with 2kg of latter (on dry basis). Find the final condition (humidity and enthalpy) of air. [May/June - 2012]**

**Given data:**

Dry bulb temperature,  $t_{d1} = 20^\circ\text{C}$

Relative humidity,  $\phi_1 = 40\%$

Dry bulb temperature,  $t_{d2} = 40^\circ\text{C}$

Relative humidity,  $\phi_2 = 40\%$

$$\frac{m_1}{m_2} = \frac{1}{2}$$

**Solution:**

We know that mass balance,

$$m_1 + m_2 = m_3 \quad \text{----- (1)}$$

$$m_1 \omega_1 + m_2 \omega_2 = m_3 \omega_3 \quad \text{----- (2)}$$

By energy balance,

$$m_1 h_1 + m_2 h_2 = m_3 h_3 \quad \text{----- (3)}$$

Substituting the value of  $m_3$  in equation (2),

$$m_1\omega_1 + m_2\omega_2 = (m_1 + m_2)\omega_3$$

$$m_1\omega_1 - m_1\omega_3 = m_2\omega_3 - m_2\omega_2$$

$$m_1(\omega_1 - \omega_3) = m_2(\omega_3 - \omega_2)$$

$$m_1\omega_1 - m_2\omega_3 = m_2\omega_3 - m_1\omega_3$$

$$\frac{m_1}{m_2} = \frac{\omega_3 - \omega_2}{\omega_1 - \omega_3} \quad \text{----- (4)}$$

From psychrometry chart,

$$\omega_1 = 0.0058 \text{ kg/kg of dry air}$$

$$\omega_2 = 0.0187 \text{ kg/kg of dry air}$$

$$\frac{1}{2} = \frac{\omega_3 - 0.0187}{0.0058 - \omega_3}$$

$$\omega_3 = 0.01440187 \text{ kg/kg of dry air}$$

Similarly,

$$m_1h_1 + m_2h_2 = (m_1 + m_2)h_3$$

$$m_1h_1 - m_1h_3 = -m_2h_2 + m_2h_3$$

$$\frac{m_1}{m_2} = \frac{h_3 - h_2}{h_1 - h_3} \quad \text{----- (5)}$$

From psychrometry,

$$h_1 = 35 \text{ kJ/kg}$$

$$h_2 = 90 \text{ kJ/kg}$$

$$\frac{1}{2} = \frac{h_3 - 90}{35 - h_3}$$

$$h_3 = 71.67 \text{ kJ/kg.}$$

3. An air conditioning system is to take in outdoor air at 283K and 30percent relative humidity at a steady rate of  $45 \text{ m}^3/\text{min}$  and to condition it to 298K and 60% relative humidity. The outdoor air is first heated to 295K in the heating section and then humidified by the injection of hot steam in the humidifying

section. Assuming the entire process takes place at a pressure of 100kPa, determine (i) the rate of heat supply in the heating section and (ii) the mass flow rate of the steam required in the humidifying section. [Nov/Dec 2009]

**Given data:**

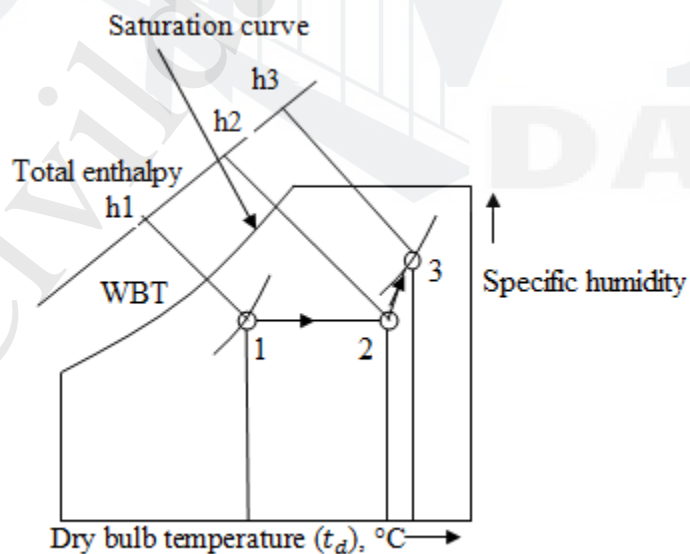
- $t_{d1} = 10^\circ\text{C}$
- $\phi_1 = 30\%$
- $t_{d3} = 25^\circ\text{C}$
- $\phi_2 = 60\%$
- $t_{d2} = 22^\circ\text{C}$
- $v = 45\text{m}^3/\text{min}$
- $p = 100\text{kPa}$

**Solution:**

Step 1:

The dry of air i.e  $10^\circ\text{C}$  of dry bulb temperature and 30% relative humidity is marked on the psychrometric chart at point

1. The horizontal line is drawn up to  $22^\circ\text{C}$  to obtain point
2. The dry of air i.e.  $25^\circ\text{C}$  dry bulb temperature and 60% relative humidity is marked on the psychrometric chart at point
- 3.



Step 2:

Draw an inclined line from point 1 to 2. Read enthalpies and specific humidity values at point 1,2 and 3 from psychrometric chart.

At point 1, enthalpy  $h_1 = 16.5 \text{ kJ/kg}$

At point 2, enthalpy  $h_2 = 28 \text{ kJ/kg}$

Mass of air,  $m_a = \frac{pv}{RT}$

$$m_a = \frac{100 \left( \frac{45}{60} \right)}{0.287 \times 283} = 0.923 \text{ kg/s}$$

Heated added,

$$\begin{aligned} Q &= m(h_2 - h_1) \\ &= 0.923 \times (28 - 16.5) \\ &= 10.615 \text{ kJ} \end{aligned}$$

Specific humidity,

$$\begin{aligned} \omega_2 &= 0.003 \text{ kg/kg of dry air} \\ \omega_3 &= 0.012 \text{ kg/kg of dry air} \end{aligned}$$

Moisture added,

$$\omega = \omega_3 - \omega_2 = 0.012 - 0.003 = 0.009 \text{ kg/kg of dry air}$$

We know that,

$$\text{Specific humidity, } \omega = \frac{m_v}{m_a}$$

$$0.009 = \frac{m_v}{0.923}$$

Mass of steam  $m_v = 0.0083 \text{ kg/s}$

4. (i) What is the lowest temperature that air can attain in an evaporative cooler, if it enters at 1atm, 302K and 40% relative humidity? [Nov/Dec 2008]

**Given data:**

$$p = 1 \text{ bar}$$

$$T = 302 \text{ K}$$

$$\phi = 40\%$$

**Solution:**

From steam table, corresponding to dry bulb temperature  $29^\circ\text{C}$ , saturation pressure is  $4.004 \text{ kPa}$

Relative humidity,

$$\phi = \frac{p_v}{p_s}$$

$$0.4 = \frac{p_v}{4.004}$$

$$p_v = 1.601\text{kPa}$$

Lowest temperature that air attain in an evaporative cooler = 113.6°C which is corresponding to  $p_v = 1.601\text{kPa}$ .

(ii) Consider a room that contains air at 1atm, 308K and 40% relative humidity. Using the psychrometric chart, determine: the specific humidity, the enthalpy, the wet bulb temperature, the dew point temperature and the specific volume of air.

**Given data:**

Pressure,  $p = 1\text{atm}$

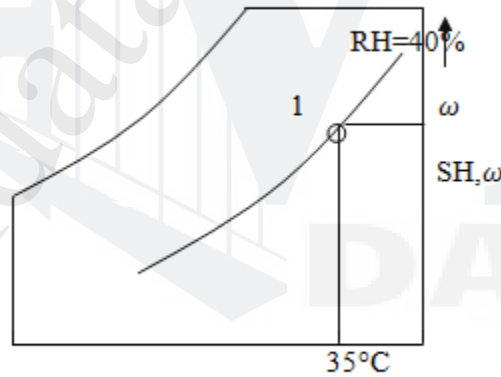
Relative humidity,  $\phi = 40\%$

Temperature,  $T = 308\text{K} = 35^\circ\text{C}$

**Solution:**

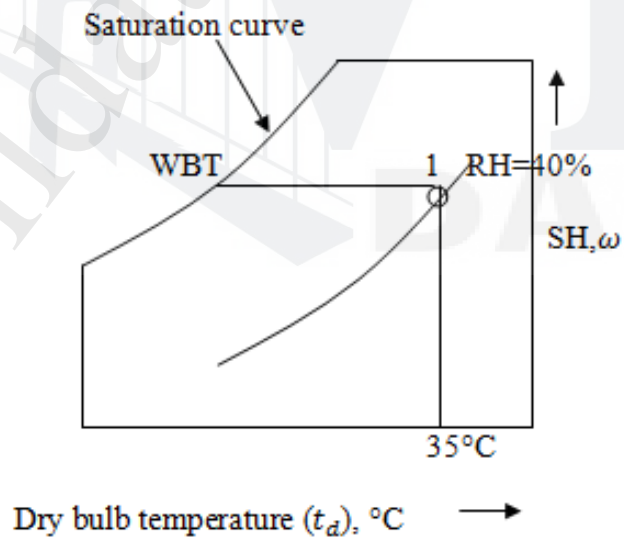
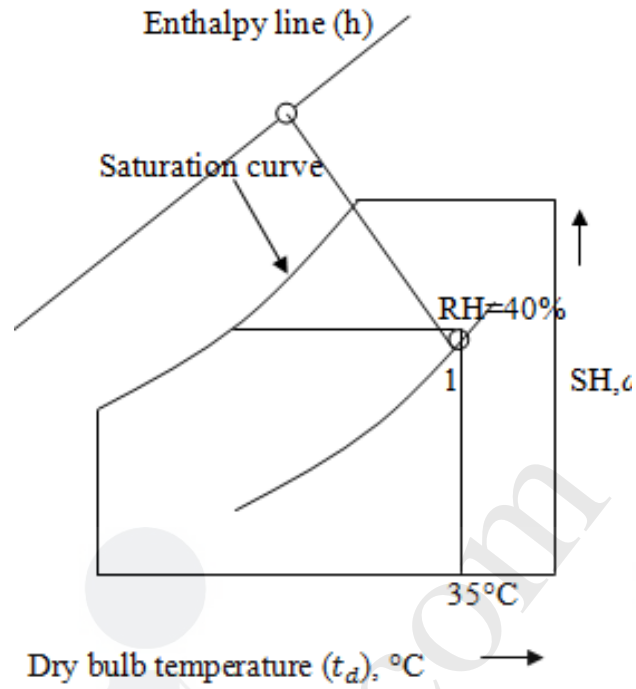
- Specific humidity,  $\omega$

From the point 1, draw a horizontal line with respect to temperature and relative humidity. At this point specific humidity is 0.0138kJ/kg. i.e.  $\omega = 0.0138\text{kJ/kg}$

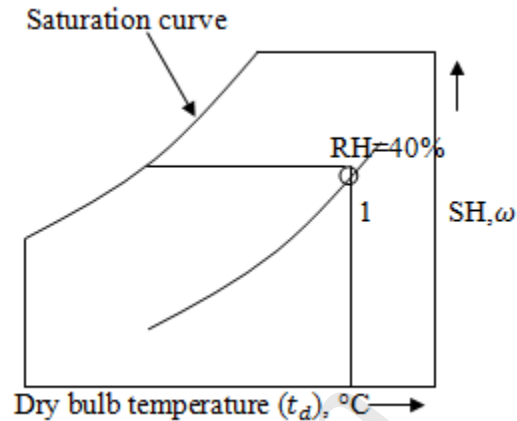


- Enthalpy,  $h$  and Wet bulb temperature,  $t_w$

From the point 1, draw a inclined line along the constant wet bulb temperature line till it cuts enthalpy line. At this point, enthalpy is 52.5kJ/kg and wet bulb temperature is 23.9°C. i.e.  $h = 52.5\text{kJ/kg}$  and  $t_w = 23.9^\circ\text{C}$



- Dew point temperature,  $t_{dw}$  and specific volume,  $v$



Mark point 1 on the psychrometric chart by given dry bulb temperature ( $35^\circ\text{C}$ ) and relative humidity 40%.

From point 1, draw a horizontal line to the left till it cuts saturation curve. At that point, temperature is  $20^\circ\text{C}$  and specific volume is  $0.89\text{m}^3/\text{kg}$ . i.e.  $t_{dw} = 20^\circ\text{C}$  and  $v = 0.89\text{m}^3/\text{kg}$ .

**5.  $30\text{m}^3/\text{min}$  of moist air at  $15^\circ\text{C}$  DBT and  $13^\circ\text{C}$  WBT are mixed with  $12\text{m}^3/\text{min}$  of moist air at  $25^\circ\text{C}$  DBT and  $18^\circ\text{C}$  WBT. Determine DBT and WBT of the mixture assuming barometric pressure is one atmosphere. [Nov/Dec 2008]**

**Given data:**

- First steam of air,  
 Dry bulb temperature,  $t_{d1} = 15^\circ\text{C}$   
 Wet bulb temperature,  $t_{w1} = 13^\circ\text{C}$   
 Flow rate,  $v_1 = 30\text{m}^3/\text{min}$
- Second steam of air,  
 Dry bulb temperature,  $t_{d2} = 25^\circ\text{C}$   
 Wet bulb temperature,  $t_{w2} = 18^\circ\text{C}$   
 Flow rate,  $v_2 = 12\text{m}^3/\text{min}$

**Solution:**

Step 1:

The first steam of air  $15^\circ\text{C}$  DBT and  $13^\circ\text{C}$  WBT is marked on the psychrometric chart at point 1.

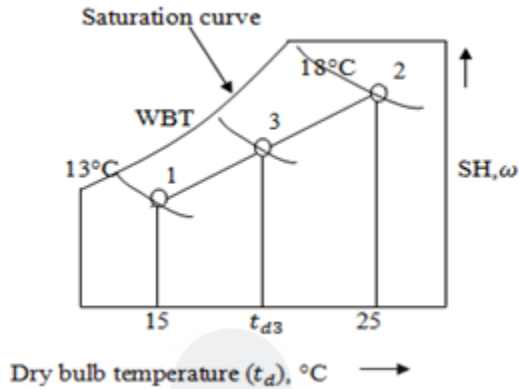
Step 2:



The second stream of air 25°C DBT and 18°C WBT is marked on the psychrometric chart at point 2.

Join the points 1 and 2 from psychrometric chart.

Step 3:



We know that,

Specific humidity of first steam of air,

$$\omega_1 = 0.007 \text{ kg/kg of dry air}$$

Specific humidity of second steam of air,

$$\omega_2 = 0.014 \text{ kg/kg of dry air}$$

Step 4:

First steam flow rate,

$$V_1 = \frac{30}{60} = 0.5 \text{ m}^3/\text{s}$$

From psychrometric chart we specific volume  $v_1 = 0.835 \text{ m}^3/\text{kg}$  passing through point 1.

$$\text{Mass, } m_1 = \frac{V_1}{v_1} = \frac{0.5}{0.835} = 0.6 \text{ kg/s}$$

Second stream flow rate,

$$V_2 = \frac{12}{60} = 0.2 \text{ m}^3/\text{s}$$

From psychrometric chart we specific volume  $v_2 = 0.845 \text{ m}^3/\text{kg}$  passing through point 2.

$$\text{Mass, } m_2 = \frac{V_2}{v_2} = \frac{0.2}{0.845} = 0.24 \text{ kg/s}$$

We know that,

$$\frac{m_1}{m_2} = \frac{\omega_3 - \omega_2}{\omega_1 - \omega_3}$$

Substituting  $m_1$  and  $m_2$  values,

$$\frac{0.6}{0.24} = \frac{\omega_3 - 0.014}{0.0076 - \omega_3}$$

$$\omega_3 = 0.00943 \text{ kg/kg of dry air}$$

Specific humidity after mixing,

$$\omega_3 = 0.00943 \text{ kg/kg of dry air}$$

Step 5:

Draw a horizontal line from  $\omega_3 = 0.00943$  till it cuts 1 – 2 line.

Name the point 3.

From psychrometric chart, at point 3

Dry bulb temperature,  $t_{d3} = 24.02^\circ\text{C}$

Wet bulb temperature,  $t_{w3} = 18.2^\circ\text{C}$