DEPARTMENT OF MECHANICAL ENGINEERING

## SUBJECT NOTES

## SUB NAME: AAPLIED THERMODYNAMICS

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## UNIT - 1

## OBJECTIVE :

To familiarize the students with the fundamentals of thermodynamics. so it will be useful to study about the thermodynamics in detail manner.

## REAL GAS EQUATION:

At high pressures, the gases start to deviate from ideal -gas behavior. So the deviation should be accounted. For accounting this deviation a factor called compressibility is introduced. So the state equation for real gases is given as,

$$
p v=Z R T
$$

where, $Z=$ compressibility factor.
The compressibility factor, $\mathbf{Z}=\mathbf{p v} / \mathbf{R T}$
The compressibility factor can also be expresses as

$$
Z=V_{\text {actual }} / V_{\text {ideal }}
$$

Where, Vactual - Specific volume of real gases.
V Ideal-Specific Volume of Ideal gases.
For ideal gases $Z=1$. But for Real gases, $Z$ is greater than or less than unity.

## IDEAL GAS:

An ideal gas is an imaginary substance that obeys the relation $\mathrm{pV}=\mathrm{RT}$ or $\mathrm{pv}=\mathrm{RT}$ . so, the equation of state is also known as ideal- gas equation. At low pressures and high temperature, the density of a gas decreases. At that time, the gas behaves as an ideal gas. A factor is introduced to account the deviation of ideal gas behavior known as compressibility factor. It means a measure of deviation of the ideal gas behaviour At normal condition $\mathrm{H}_{2}, \mathrm{O}_{2}, \mathrm{~N}_{2}$ and air behave as ideal gas.
"A Perfect gas may be defined as a state of a substance, whose evaporation from its liquid state is complete and strictly obeys all the gas laws under all conditions of temperature and pressure.

- No Real or actual gas strictly obey the gas laws.
- Real gases which are ordinarily difficult to liquify, such as oxygen, $\mathrm{N}_{2}, \mathrm{H}_{2}$ and air.


## Difference Between Ideal Gas \& Real Gas

| IDEAL GAS | REAL GAS |
| :--- | :--- |
| The behaviour of ideal gases is <br> SIMPLE. | The behaviour of ideal gases is <br> COMPLEX. |
| Mass is considered as a "point <br> mass". It means that the particle is <br> extremely small where its mass is <br> almost zero. So, it does not have <br> volume. | Real gases are made up of <br> molecules or atoms which occupies <br> some space. It has a definite volume <br> even they are extremely small. |
| Only air is considered as ideal gas. | lll gases are considered as real gas <br> except air. |
| The pressure of ideal gas is more | The pressure of a real gas is lesser <br> as compared to ideal gas |
| It follows pV = nRT. This is the <br> equation of ideal gas | It does not follow idea gas equation. <br> So the equation of state for real <br> gases become pv = ZRT or <br> $\left(p+a / V^{2}\right)(V-b)=n R T$. |

## LAW OF PERFECT GASES:

## Types of Laws :

1. Boyle's Law : (Robert Boyle in 1662)
"The Absolute pressure of a given mass of a perfect gas varies inversely as its volume, when the temperature remains constant"

Mathematically,

$$
P \propto 1 / v \quad \text { or } P v=\text { constant }
$$

Then, $\mathrm{P}_{1} \mathrm{~V}_{1}=\mathrm{P}_{2} \mathrm{~V}_{2}=\mathrm{P}_{3} \mathrm{~V}_{3}=\ldots . . . .=$ const.

## 2. Charles' Law : (Frechman Jacques A.C. Charles in 1787)

"The volume of a given mass of a perfects gas varies directly as its absolute temperature, when the absolute pressure remains constant."

Mathematically

$$
\begin{aligned}
\mathrm{V} & \propto \mathbf{T} \\
\mathrm{~V} / \mathrm{T} & =\text { Constant } \\
\text { Then, } \mathrm{V}_{1} / T_{1} & =\mathrm{V}_{2} / T_{2}=\mathrm{V}_{3} / T_{3}=\ldots . . . . . .=\text { const. }
\end{aligned}
$$

## 3. Gay-Lussac Law :

"The Absolute pressure of a given mass of a perfect gas varies directly as its absolute temperature, when the volume remains constant"

Mathematically,

$$
\begin{aligned}
& \mathbf{P} \propto \mathbf{T} \\
& \mathrm{P} / \mathrm{T}=\text { constant } \\
\text { then, } & \mathrm{P}_{1} / \mathrm{T}_{1}=\mathrm{P}_{2} / \mathrm{T}_{2}=\mathrm{P}_{3} / \mathrm{T}_{3}=\ldots \ldots \ldots .=\text { Const. }
\end{aligned}
$$

## 4. Joule's Law :

"The change of internal energy of a perfect gas is directly proportional to the change of temperature."

Mathematically

$$
\begin{aligned}
& \mathbf{d E} \propto \mathbf{d T} \\
& \mathrm{dE}=\mathrm{mc} \mathrm{dt}
\end{aligned}
$$

constant proportionality known as spefic heat

$$
\mathrm{dE}=\mathrm{mc}\left(\mathrm{~T}_{2}-\mathrm{T}_{1}\right)
$$

Temp. of a given mass $m$ of a gas changes from $T_{1}$ to $T_{2}$, then Internal Energy changes from $E_{1}$ to $E_{2}$ and change in internal energy $\left(E_{2}-E_{1}\right)$ will be same irrespective of the manner how the pressure ( $P$ ) and volume ( $v$ ) of the gas have changed.

## 5. Regnaut's Law :

"The two specific heats Cp and Cv of a gas do not change with the change of temperature and pressure."

Eg., $c_{p}$ and $c_{v}$ always constant.
It is only an approximate one, because the sphefic heats of a gas vary with temperature

## 6. Avogador's Law :

- "avogadro's law states that equal volumes of different perfect gases at the same temperature and pressure contain equal number of molecules.
- It can also be stated, "the volume of one gram mole of all gases at the pressure of 760 mm Hg and temperature of $0^{\circ} \mathrm{C}$ is same and equal to 22.4 litres.

Kg mole of a gass $=22.4 \times 10^{-3} \mathrm{~cm}^{3}=22.4 \mathrm{~m}^{3 .}$

## 7. Characteristic Gas Equation:

The general gas equaton for ideal gas is given by
pV / T = Constant
Where, p - Pressure in $\mathbf{N} / \mathbf{m}^{\mathbf{3}}$
V - Volume in $\mathbf{m}^{\mathbf{3}}$
T - Temperature ${ }^{\circ} \mathbf{C}$
Taking R as Constant

$$
\begin{aligned}
& \mathrm{pV} / \mathrm{T}=\mathrm{R} \\
& \mathrm{pV}=\mathrm{RT}
\end{aligned}
$$

If the mass of gas ' $m$ ' is considered, the equation of state becomes

$$
\mathrm{pV}=\mathrm{mRT}
$$

This equation is known as Characteristic gas equation.

## EQUATION OF STATE FOR REAL GAS:

## 1. Vandar Waal's Equation :

The equation of state for real gases is given by

$$
\left[P+\frac{a}{v^{2}}\right](v-b)=R T
$$

For ideal gas, the constants $a$ and $b$ are zero. The values of $a$ and $b$ are dependent on the type of fluid or gases used.

If molar volume is considered in the analysis, the equation of state becomes

$$
\left[\mathrm{P}+\frac{\mathrm{a}}{\bar{V}^{2}}\right](\bar{V}-\mathrm{b})=\bar{R} \mathrm{~T}
$$

Where, $\quad \bar{V}=$ molar volume

$$
\bar{R}=\text { Universal Gas Constant }=8.314 \mathrm{Nm} / \mathrm{KgmolK}
$$

The value of $a \& b$ is theoretically determined by

$$
\mathrm{a}=\frac{27 \mathrm{R}^{2}\left(\mathrm{~T}_{c}\right)^{2}}{64 \mathrm{P}_{c}} \quad \& \quad \mathrm{~b}=\frac{\mathrm{R} T_{c}}{8 \mathrm{P}_{c}}
$$

Where, $T_{c}$ - critical Temperature

$$
P_{c} \text { - Critical Pressure. }
$$

## 2. Redlich - kwong equtaion

$$
\begin{gathered}
p=\frac{R T}{V_{m-b}}-\frac{a}{\sqrt{T} V_{m\left(V_{m}+b\right)}} \\
\mathrm{a}=\frac{0.42748 \mathrm{R}^{2} \mathrm{~T}_{\mathrm{c}}^{5 / 2}}{\mathrm{p}_{\mathrm{c}}} \quad ; \quad b=\frac{0.08664 R T_{c}}{P_{c}}
\end{gathered}
$$

This equation gives good restult at high pressure and is fairly accurate for temperature abare the oritical value

## 3. Dieterici equation :

$$
P(V-b)=R T e^{-a / R T V}
$$

It does not give accurate value of the properties

## PROPERTIES OF PURE SUBSTANCES

## DEFINITION OF THE PURE SUBSTANCE

A pure substance is a system which is (i) homogeneous in composition, (ii) homogeneous in chemical aggregation, and (iii) invariable in chemical aggregation.

- "Homogeneous in composition" means that the composition of each part of the system is the same as the composition of every other part. "Composition means the relative proportions of the chemical elements into which the sample can be analysed. It does not matter how these elements are combined.

For example in Fig. 1 system (a), comprising steam and water, is homogeneous in composition, since chemical analysis would reveal that hydrogen and oxygen atoms are presents in the ratio $2: 1$ whether the sample be taken from the steam or from the water. The same is true of system (b)


Fig. 1 Illustrating the definition of a pure substance.

Containing uncombined hydrogen and oxygen gas in the atomic ratio 2: 1 in the upper part, and water in the lower part. System (c) however, is not homogeneous in composition, for the hydrogen and oxygen are present in the ratio 1:1 in the upper part, but in the ratio 2:1 (as water) in the lower part.
_ "Homogeneous in chemical aggregation" means that the chemical elements must be combined chemically in the same way in all parts of the system. Consideration of Fig. 1 again shows that the system (a) satisfies this condition also; for steam and water consist of identical molecules. System (b) on the other hand is not homogeneous in chemical aggregation since in the upper part of the system the hydrogen and oxygen are not combined chemically (individual atoms of $H$ and $O$ are not uniquely associated), whereas in the lower part of the system the hydrogen and oxygen are combined to form water.

Note however that a uniform mixture of steam, hydrogen gas, and oxygen gas would be regarded as homogeneous in both composition and chemical aggregation whatever the relative proportions of the components.
_"Invariable in chemical aggregation" means that the state of chemical combination of the system does not change with time (condition (ii) referred to variation with position). Thus a mixture of hydrogen and oxygen, which changed into steam during the time that the system was under consideration, would not be a pure substance.

## PHASE CHANGE OF A PURE SUBSTANCE

Let us consider 1 kg of liquid water at a temperature of $20^{\circ} \mathrm{C}$ in a cylinder fitted with a piston, which exerts on the water a constant pressure of one atmosphere (1.0132 bar) as shown in Fig 2 (i).

As the water is heated slowly its temperature rises until the temperature of the liquid water becomes $100^{\circ} \mathrm{C}$. During the process of heating, the volume slightly increases as indicated by the line 1-2 on the temperature - specific volume diagram (Fig.3). The piston starts moving upwards.


Fig. 2 Phase change of water at content pressure

## From liquid to vapour phase.

If the heating of the liquid, after it attains a temperature of $100^{\circ} \mathrm{C}$, is continued it undergoes a change in phase. A portion of the liquid water changes into vapour as shown in Fig 2 (ii). This state is described by the line 2-3 in Fig. 3 The amount of heat


Fig. 3
required to convert the liquid water completely into vapour under this condition is called the heat of vaporization. The temperature at which vaporization takes place at a given pressure is called the saturation temperature and the given pressure is called the saturation pressure.During the process represented by the line 2-3 (Fig.3) the volume increases rapidly and piston moves upwards Fig. 2 (iii).

For a pure substance, definite relationship exists between the saturation pressure and saturation temperature as shown in Fig. 4, the curve so obtained is called vapour pressure curve.


Fig. 4 Vapour pressure curve for water.

It may be noted that if the temperature of the liquid water on cooling becomes lower than the saturation temperature for the given pressure, the liquid water is called a sub cooled liquid. The point ' 1 ' (in Fig. 3.3) illustration, when the liquid water is cooled under atmospheric pressure to a temperature of $20^{\circ} \mathrm{C}$, which is below the saturation temperature $\left(100^{\circ} \mathrm{C}\right)$.

Further, at point ' 1 ' the temperature of liquid is $20^{\circ} \mathrm{C}$ and corresponding to this temperature, the saturation pressure is 0.0234 bar, which is lower than the pressure on the liquid water, which is 1 atmosphere. Thus the pressure on the liquid water is greater than the saturation pressure at a given temperature. In this condition, the liquid water is known as the compressed liquid.

The term compressed liquid or sub cooled liquid is used to distinguish it from saturated liquid. All points is the liquid region indicate the states of the compressed liquid.

When all the liquid has been evaporated completely and heat is further added, the temperature of the vapour increases. The curve 3-4 in Fig. 3 describes the process. When the temperature increases above the saturation temperature (in this case $100^{\circ} \mathrm{C}$ ), the vapour is known as the superheated temperature. There is rapid increase in volume and the piston moves upwards [Fig. 2 (iii)].

The difference between the superheated temperature and the saturation temperature at the given pressure is called the degree of superheat.

If the above mentioned heating process is repeated at different pressures a number of curve similar to 1-2-3-4 are obtained. Thus, if the heating of the liquid water in the piston cylinder arrangement takes place under a constant pressure of 12 bar with an initial temperature of $20^{\circ} \mathrm{C}$ until until the liquid water is converted into superheated steam, then curve 5-6-7-8 will represent the process.

In the above heating process, it may be noted that, as the pressure increases the length of constant temperature vaporizations gets reduced.

From the heating process at a constant pressure of 225 bar represented by the curve $9-10-11$ in Fig. 3, it can be seen that there is no constant temperature vaporizations line. The specific volume of the saturated liquid and of the saturated vapour is the same, i.e. $=\mathrm{vg}$. Such states are called critical parameters.

The curve 12-13 (Fig. 3) represents a constant pressure heating process, when the pressure is greater than the critical pressure. At this state, the liquid water is directly converted into superheated steam. As there is no definite point at which the liquid water changes into superheated steam, it is generally called liquid water when the temperature is less than the critical temperature and superheated steam when the temperature is above the critical temperature.

## P-T (Pressure - Temperature) DIAGRAM FOR A PURE SUBSTANCE

If the vapour pressure of a solid is measured at various temperatures until the triple point is reached and then that of the liquid is measured until the critical point is reached, the result when plotted on a P-T diagram appears as in Fig. 5.

If the substance at the triple point is compressed until there is no vapour left and the pressure on the resulting mixture of liquid and solid is increased, the temperature will have to be changed for equilibrium to exist between the solid and the liquid.

Measurements of these pressures and temperatures give rise to a third curve on the P T diagram, starting at the triple point and continuing indefinitely.

The points representing the coexistence of (i) solid and vapour lie on the 'sublimation curve', (iii) liquid and solid lie on the 'fusion curve'. In the particular case of water, the sublimation curve is called the frost line, the vaporizations curve is called the steam line, and the fusion curve is called the ice line.


Fig .5 P-T diagram for a substance such as water
The slopes of sublimation and the vaporizations curves for all substances are positive. The slope of the fusion curve however may be positive or negative. The fusion curves of most substances have a positive slope. Water is one of the important exceptions.

## Triple point

The triple point is merely the point of intersection of sublimation and vaporizations curves. It must be understood that only on P -T diagram is the triple point represented by a point. On $\mathrm{P}-\mathrm{V}$ diagram it is a line, and on a $\mathrm{U}-\mathrm{V}$ diagram it is a triangle.

The pressure and temperature at which all three phases of a pure substance coexist may be measured with the apparatus that is used to measure vapour pressure.

Triple-point data for some interesting substances are given in table 3.1.
Table 3.1 Triple-point Date

| S. <br> No. | Substance | Temp., $\boldsymbol{K}$ | Pressure, $\mathbf{m m} \mathbf{H g}$ |
| :---: | :---: | :---: | :---: |
| 1. | Hydrogen (normal) | 13.96 | 54.1 |
| 2. | Deuterium (normal) | 18.63 | 128 |
| 3. | Neon | 24.57 | 324 |
| 4. | Nitrogen | 63.18 | 94 |
| 5. | Oxygen | 54.36 | 1.14 |
| 6. | Ammonia | 195.40 | 45.57 |
| 7. | Carbon dioxide | 216.55 | 3,880 |
| 8. | Sulphur dioxide | 197.68 | 1.256 |
| 9. | Water | 273.16 | 4.58 |

## P-V-T (Pressure-Volume-Temperature) SURFACE

A detailed study of the heating process reveals that the temperature of the solid rises and then during the change of phase from solid to liquid (or solid to vapour) the temperature remains constant. This phenomenon is common to all phase changes. Since the temperature is constant, pressure and temperature are not independent properties and cannot be used to specify state during a change of phase.

The combined picture of change of pressure, specific volume and temperature may be shown on a three dimensional state model. Fig 6, illustrate the equilibrium states for a pure substance which expands on fusion. Water is an example of a substance that exhibits this phenomenon.


Fig. 6 A Pressure-Volume-Temperature ( $P-V-T$ )
All the equilibrium states lie on the surface of the model. States represented by the space above or below the surface are not possible. It may be seen that the triple point appears as a line in this representation. The point C.P. is called the critical point and no liquid phase exists at temperatures above the isotherms through this point. The term evaporation is meaningless in this situation.

At the critical point the temperature and pressure are called the critical temperature and the critical pressure respectively and when the temperature of a substance is above the critical value, it is called a gas. It is not possible to cause a phase change in a gas unless the temperature is lowered to a value less than the critical temperature. Oxygen and nitrogen are examples of gases that have critical temperatures below normal atmospheric temperature.

## PHASE CHANGE TERMINOLOGY AND DEFINITIONS

## Suffices: Solid i <br> Liquid $\quad f$ <br> Vapour $g$

Phase change
Process suffix

1. Solid-liquid
if
2. Solid-vapour
ig
3. Liquid-vapour
fg


Phase change terminology.

Triple point: The only state at which the solid, liquid and vapour phases coexist in equilibrium.

Critical point (C.P): The limit of distinction between a liquid and vapour.
Critical pressure: The pressure at the critical point.
Critical temperature: The temperature at the critical point.
Gas - A vapour whose temperature is greater than the critical temperature.

## Liquid-Vapour terms:

Saturation temperature: The phase change pressure.
Compressed liquid: Liquid whose temperature is lower than the saturation temperature Sometimes called a sub cooled liquid.
Saturated liquid: Liquid at the saturation temperature corresponding to the saturation pressure. That is liquid about to commence evaporating, represented by the point $f$ on a diagram.

Saturated vapour: A term including wet and dry vapour.

Dry (saturated) vapour: Vapour which has just completed evaporation. The pressure and temperature of the vapour are the saturation values. Dry vapour is represented by a point g on a diagram.
Wet vapour: The mixture of saturated liquid and dry vapour during the phase change.
Superheated vapour: Vapour whose temperature is greater than the saturation temperature corresponding to the pressure of the vapour.

Degree of superheat: The term used for the numerical amount by which the temperature of a superheated vapour exceeds the saturation temperature.

## FORMATION OF STEAM AND ITS PROPERTIES

## INTRODUCTION

For any system we need a working substance to convert a heat energy which is produced by a fuel into mechanical work. In the previous article we considered an ideal gas as a working substance. But in practice, there is no ideal gases exist. In this article, we consider steam as a working substance because of its following unique properties
> Steam can be produced from water which is cheap and readily available in large quantity.
> It can carry large amount of heat.
> It can be used for some other purposed after its duty as a working substance is completed.


## STEAM FORMATION

Consider one kg of water in a closed vessel under a pressure of $p \mathrm{n} / \mathrm{m}^{2}$ ant at a temperature of $-20^{\circ} \mathrm{C}$. If we heat the water gradually when pressure remains constant, the following changes will occur:
(a) The temperature of the ice will increase till it reaches the freezing temperature of water i.e. $0^{\circ} \mathrm{C}$. This shown by the line 1-2 in fig.
(b) When we add more heat after the point 2, the ice starts melting at the same time. There is no rise in temperature till the whole of the ice has been melted and converted into water. This process is represented by a line 2-3 in fig The heat added during this period is called Latent heat of fusion of fusion of ice or Latent heat of ice.
(c) On further heating, the water reaches its boiling point or saturation point4. This saturation temperature varies with pressure. At the atmospheric pressure, boiling point of water is $100^{\circ} \mathrm{C}$. The amount of heat added during heating of water from $0^{\circ} \mathrm{C}$ to saturation temperature of $100^{\circ} \mathrm{C}$ is known as sensible heat or Latent heat of water. It is denoted by $\mathrm{h}_{\mathrm{f}}$.

Mathematically, $\mathrm{h}_{\mathrm{f}}=m C_{p}\left(T_{2}-T_{1}\right)$
(d) On further heating beyond 4 , the water will gradually be converted into steam, when the temperature remains constant. At this stage, the steam will have some water particles in suspension and is called wet steam. The same process continues till all the water particles converted into wet steam. The line 4-5 in fig. represents this process.
(e) If the water is heated further the water particles in suspension will be converted into steam. The same without any water suspension is called as dry steam or dry saturated steam.

The amount of heat added during heating of water from boiling point to dry saturated stage is called as Latent heat of vaporization or Enthalpy of vaporization or Latent heat of steam. It is denoted by ' $h_{f g}$ '.
(f) When the dry steam is further heated, the temperature rises again. This process is called 'Superheating' and the steam obtained is known as superheated Steam.

The heat supplied to the dry steam at saturation temperature $T_{s}$ (i.e. $100^{\circ} \mathrm{C}$ ), to convert it into superheated steam at the temperature $T_{\text {sup }}$ is called heat of super heat of Superheat enthalpy. It is denoted by ' $h_{\text {sup }}$ '.

Mathematically, $\mathrm{h}_{\text {sup }}=h_{g}+C_{p}\left(T_{\text {sup }}-T_{s}\right) \mathrm{kJlkg}$

## Dryness Fraction

It is defined as the ratio of the mass of the dry steam to the mass of wet steam actually Present. It is denoted by ' $x$ '.

$$
\text { Dryness fraction, } \quad \mathrm{X}=\frac{\mathrm{m}_{\mathrm{g}}}{\mathrm{~m}_{\mathrm{f}}+\mathrm{m}_{\mathrm{g}}}
$$

where,

$$
\begin{aligned}
& m_{g} \text { - mass of dry steam in } \mathrm{kg} \\
& \mathrm{~m}_{\mathrm{f}} \text { - mass of water vapour in suspension. }
\end{aligned}
$$

This dryness fraction when expressed in percentage (i.e $100 x$ ) is called the quality of system.

## _PROPERTIES OF STEAM

Various properties of water at various conditions of steam.

1. Enthalpy of steam(h);

It is the amount of heat added to the water from freezing point to till the water becomes wet of dry or superheated steam.

For wet steam, $h_{\text {wet }}=h_{f}+\mathrm{xhfg}_{\mathrm{fg}} \mathrm{kJ} / \mathrm{kg}$
For dry steam, $h_{\text {dry }}=h_{g}=h_{f}+h_{f g} \mathrm{~kJ} / \mathrm{kg}$
For superheated steam, $h_{\text {sup }}=h_{g}+C_{p}\left(T_{\text {sup }}-T_{\text {sat }}\right) k J / k g$
Where,

$$
\left(T_{\text {sup }}-T_{\text {sat }}\right) \text { is called as'degree of superheat'. }
$$

2. Specific volume of steam (v):

It is defined as the volume occupied by the unit mass of the steam at the given pressure and temperature.

For wet steam, $\mathrm{v}_{\text {wet }}=\mathrm{Xvg}_{\mathrm{g}} \mathrm{m}^{3} / \mathrm{kg}$
For dry steam, $\mathrm{v}_{\text {dry }}=\mathrm{v}_{\mathrm{g}} \mathrm{m}^{3} / \mathrm{kg}$
For superheated steam, $\mathrm{v}_{\text {sup }}=\mathrm{v}_{\mathrm{g}} \mathrm{T}_{\text {sup }} / \mathrm{T}_{\text {sat }} \mathrm{m}^{3} / \mathrm{kg}$
3. Density of steam ( $\rho$ );

It is defined as the ratio of mass to the unit volume of the steam at given pressure and temperature. Its value for wet, dry and superheated steam is the reciprocal of the specific volume of the steam.
4. Workdone during expansion(W):

During the evaporation process, there is a considerable increase in the volume when pressure remains constant. Thus some amount of external work is done during evaporation. In other words, it is the energy required for absorption of latent heat for increasing volume of the steam.

For wet steam, $\mathrm{W}_{\text {wet }}=100 \mathrm{Pxv}_{\mathrm{g}} \mathrm{kJ}$
For dry steam, $\mathrm{W}_{\text {dry }}=100 \mathrm{P}_{\mathrm{g}} \mathrm{kJ}$

For superheated steam, $\mathrm{W}_{\text {sup }}=100 \mathrm{Pv}_{\text {sup }} \mathrm{kJ}$
Where p - pressure at which evaporation takes place in bar.
5. Internal energy of steam (U):

Internal energy of steam is defined as the actual heat energy stored in the steam above the freezing point of water at the given conditions. It is the difference between enthalpy of steam and the external work done.

$$
\begin{aligned}
& \mathrm{h}=\mathrm{W}+\Delta \mathrm{u} \\
& \Delta \mathrm{u}=\mathrm{h}-\mathrm{W}
\end{aligned}
$$

For wet steam, $u_{\text {wet }}=\left(h_{f+}+h_{f g}\right)-\left(100 \mathrm{pxv}_{g}\right) \mathrm{kJ} / \mathrm{kg}$
For dry steam, Udry= $\left(h_{f}+h_{f g}\right)-\left(100 p v_{g}\right) \mathrm{kJ} / \mathrm{kg}$
For superheated steam, usup $=h_{\text {sup }}-\left(100 p v_{\text {sup }}\right) \mathrm{kJ} / \mathrm{kg}$
6. Entropy of steam(s):

It is the property of the steam which increases with increase in temperature and decrease with decrease in temperature.

For wet steam, $\mathbf{S}_{\text {wet }}=\mathrm{Sf}_{\mathrm{f}}+\mathrm{XStg} \mathrm{KJ} / \mathrm{kg} \mathrm{K}$
For dry steam, $\mathrm{S}_{\mathrm{dr}}=\mathrm{Sf}+\mathrm{Stg}_{\mathrm{kJ}} / \mathrm{kg} \mathrm{K}$
For superheated steam, $\mathrm{S}_{\text {sup }}=\mathrm{S}_{\mathrm{g}}+\mathrm{C}_{\mathrm{ps}} \log _{\mathrm{e}}\left(\mathrm{T}_{\text {sup }} / \mathrm{T}_{\mathrm{s}}\right) \mathrm{kJ} / \mathrm{kg} \mathrm{K}$

## T - S DIAGRAM FOR WATER AND STEAM

$T$-s is the plot of the saturation temperature of water and steam corresponding to the various absolute against the entropies at those saturation temperatures. It is shown in fig.. It is very much useful to solve the numerical problems on steam as it considerably reduces time and labour in making calculations.

In the $T$-s diagram, the region left of the water line, the water exists as liquid. In the right of the dry steam line, the water exists as a wet steam. Therefore the dryness fraction lines are represented in these regions as shown in fig. 3.2. The value of various quantities can be directly read form the diagram.

It can be noted from the figure that the water line and steam line are converging with the increase in temperature. At a particular point, the water is directly converted into dry steam without formation of wet steam. This point is called 'critical Point'.

The critical temperature is the temperature above which a substance can not exist as a liquid. The corresponding pressure is called critical pressure. The critical pressure and temperature of water are 221.2 bar and $374.15^{\circ} \mathrm{C}$ respectively.


An isothermal process is represented by a horizontal line and a reversible adiabatic or isentropic is represented by a vertical line as shown in fig. In the diagram, constant volume lines are plotted in the wet region and constant pressure lines are plotted in the superheated region.

The $T$-s diagram represents the whole cycle of heat addition and rejection whereas the $p-V$ diagram represents only the work done.

## USE OF STEAM TABLES

In practice, it is very tedious to calculate the relations between various quantities like pressure, temperature, specific volume, specific volume, enthalpy, and entropy of steam at various stages. These properties have been determined experimentally and tabulated in a specific manner is known as steam tables. The values of the various quantities given in these tables are for 1 kg of steam which is dry steam which is dry saturated. The calculation for wet steam can be easily made by making suitable use of such table. The following three main divisions present in the steam tables.

Table I shows the various quantities like specific volume, specific enthalpy, and specific entropy for various pressures. If the required pressure is not directly included in a steam tables it is obvious that it would be lying between two consecutive pressures. Such a data can be calculated by simple interpolation.

Table Il shows the various quantities for various saturation temperatures since there is only one saturation temperature for each saturation pressure.

Table III shows the superheated steam table. Here the various quantities like specific volume, specific enthalpy and specific entropy for various pressure and temperature are shown in tabular from.

It can be noted from the properties of a saturated steam that the increase of pressure results in gradual increase of sensible heat and decrease of latent heat of vaporization. But the enthalpy of dry steam increases up to a certain pressure (approximately 33.5 bar) and then it decreases.

## USE OF MOLLIER CHART

It is also called as Enthalpy-Enthalpy (h-s) diagram. In Mollier chart, the vertical ordinate represents the total heat while the base represents the entropy as shown in fig

In Mollier chart, the dry steam line divides this chart into two regions. The region which is below the dry steam line represents the wet condition of steam. Here, the dryness fraction lines are shown parallel to dry steam line. The region above the dry steam line represents the superheated condition of steam. In this region, constant temperature lines are shown. It should be noted that the lines at constant pressure are straight in the wet steam region but curved in the superheated region.


PROBLEMS:

1. Find the saturation temperature, the changes in specific volume and entropy during evaporation, and the latent heat of vaporization of steam at 1 MPa .
Solution At 1 MPa, from steam table

$$
\begin{array}{rlr}
t_{\mathrm{sat}} & =179.91^{\circ} \mathrm{C} & \\
v_{\mathrm{f}} & =0.001127 \mathrm{~m}^{3} / \mathrm{kg} \\
& v_{\mathrm{g}} & =0.19444 \mathrm{~m}^{3} / \mathrm{kg} \\
& v_{\mathrm{fg}} & \text { Ans. } \\
\therefore \quad v_{\mathrm{g}}-v_{\mathrm{f}}=0.1933 \mathrm{~m}^{3} / \mathrm{kg} & \\
& s_{\mathrm{f}} & =2.1387 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K} \\
& s_{\mathrm{g}} & =6.5855 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K} \\
& s_{\mathrm{fg}} & =s_{\mathrm{g}}-s_{\mathrm{f}}=4.4478 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K} \\
h_{\mathrm{fg}} & =h_{\mathrm{g}}-h_{\mathrm{f}}=2015.3 \mathrm{~kJ} / \mathrm{kg} & \\
\therefore \quad & \text { Ans. } & \text { Ans. }
\end{array}
$$

2. Find the enthalpy, entropy, and volume of steam at 1.4 MPa , $380^{\circ} \mathrm{C}$.
Solution At $p=1.4 \mathrm{MPa}$, in Table A.1(b), $t_{\text {sat }}=195.07^{\circ} \mathrm{C}$. Therefore, the state of steam must be in the superheated region. In Table A.2, for properties of superheated steam, at $1.4 \mathrm{MPa}, 350^{\circ} \mathrm{C}$

$$
\begin{aligned}
v & =0.2003 \mathrm{~m}^{3} / \mathrm{kg} \\
h & =3149.5 \mathrm{~kJ} / \mathrm{kg} \\
s & =7.1360 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K} \\
v & =0.2178 \mathrm{~m}^{3} / \mathrm{kg} \\
h & =3257.5 \mathrm{~kJ} / \mathrm{kg} \\
s & =7.3026 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K}
\end{aligned}
$$

and at $1.4 \mathrm{MPa}, 400^{\circ} \mathrm{C} \quad v=0.2178 \mathrm{~m}^{3} / \mathrm{kg}$
$\therefore$ By interpolation at $1.4 \mathrm{MPa}, 380^{\circ} \mathrm{C}$

$$
\begin{aligned}
v & =0.2108 \mathrm{~m}^{3} / \mathrm{kg} \\
h & =3214.3 \mathrm{~kJ} / \mathrm{kg} \\
s & =7.2360 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K}
\end{aligned}
$$

Ans.
3. A vessel of volume $0.04 \mathrm{~m}^{3}$ contains a mixture of saturated water and saturated steam at a temperature of $250^{\circ} \mathrm{C}$. The mass of the liquid present is 9 kg . Find the pressure, the mass, the specific volume, the enthalpy, the entropy, and the internal energy.
Solution From Table A. 1(a), at $250^{\circ} \mathrm{C} \quad p_{\text {sat }}=3.973 \mathrm{MPa}$

$$
\begin{array}{ll}
v_{\mathrm{f}}=0.0012512 \mathrm{~m}^{3} / \mathrm{kg}, & v_{\mathrm{g}}=0.05013 \mathrm{~m}^{3} / \mathrm{kg} \\
h_{\mathrm{f}}=1085.36 \mathrm{~kJ} / \mathrm{kg}, & h_{\mathrm{ff}_{\mathrm{f}}}=1716.2 \mathrm{~kJ} / \mathrm{kg} \\
s_{\mathrm{f}}=2.7927 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K}, & s_{\mathrm{fg}}=3.2802 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K}
\end{array}
$$

Volume of liquid,

$$
V_{f}=m_{f} v_{f}
$$

$$
=9 \times 0.0012512
$$

$$
=0.01126 \mathrm{~m}^{3}
$$

Volume of vapour, $\quad V_{g}=0.04-0.01126$

$$
=0.02874 \mathrm{~m}^{3}
$$

$\therefore$ Mass of vapour

$$
m_{\mathrm{g}}=\frac{V_{\mathrm{g}}}{v_{\mathrm{g}}}=\frac{0.02874}{0.05013}=0.575 \mathrm{~kg}
$$

## $\therefore$ Total mass of mixture,

$$
m=m_{\mathrm{f}}+m_{\mathrm{g}}=9+0.575=9.575 \mathrm{~kg} \quad \text { Ans. }
$$

Quality of mixture,

$$
\begin{aligned}
& x=\frac{m_{\mathrm{g}}}{m_{\mathrm{f}}+m_{\mathrm{g}}}=\frac{0.575}{9.575}=0.06 \\
& \therefore \quad v=v_{f}+x v_{\mathrm{fs}} \\
& =0.0012512+0.06(0.05013-0.0012512) \\
& =0.00418 \mathrm{~m}^{3} / \mathrm{kg} \\
& h=h_{f}+x h_{\mathrm{fk}} \\
& =1085.36+0.06 \times 1716.2 \\
& =1188.32 \mathrm{~kJ} / \mathrm{kg} \\
& s=s_{f}+x s_{\mathrm{fg}} \\
& =2.7927+0.06 \times 3.2802 \\
& =2.9895 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K} \\
& u=h-p v \\
& =1188.32-3.973 \times 10^{3} \times 0.00418 \\
& =1171.72 \mathrm{~kJ} / \mathrm{kg} \\
& \text { Also, at } 250^{\circ} \mathrm{C}, \quad u_{\mathrm{f}}=1080.39 \text { and } u_{\mathrm{fg}}=1522.0 \mathrm{~kJ} / \mathrm{kg} \\
& \therefore \quad u=u_{\mathrm{f}}+x u_{\mathrm{fg}} \\
& =1080.39+0.06 \times 1522 \\
& =1071.71 \mathrm{~kJ} / \mathrm{kg} \\
& \text { Also, at } 250^{\circ} \mathrm{C} \text {, } \\
& \text { Ans. }
\end{aligned}
$$

4. Steam initially at $0.3 \mathrm{MPa}, 250^{\circ} \mathrm{C}$ is cooled at constant volume.
(a) At what temperature will the steam become saturated vapour? (b) What is the quality at $80^{\circ} \mathrm{C}$ ? What is the heat transferred per kg of steam in cooling from $250^{\circ} \mathrm{C}$ to $80^{\circ} \mathrm{C}$ ?
Solution At $0.3 \mathrm{MPa}, t_{\text {sat }}=133.55^{\circ} \mathrm{C}$
Since $t>t_{\text {sat }}$, the state would be in the superheated region (Fig) r properties of superheated steam, at $0.3 \mathrm{MPa}, 250^{\circ} \mathrm{C}$

$$
v=0.7964 \mathrm{~m}^{3} / \mathrm{kg}
$$

$h=2967.6 \mathrm{~kJ} / \mathrm{kg}$


$$
\therefore \quad v_{1}=v_{3}=v_{2}=0.7964 \mathrm{~m}^{3} / \mathrm{kg}
$$

In Table A. 1
when

$$
\begin{aligned}
& v_{\mathrm{g}}=0.8919, t_{\mathrm{sat}}=120^{\circ} \mathrm{C} \\
& v_{\mathrm{g}}=0.7706, t_{\mathrm{sat}}=125^{\circ} \mathrm{C}
\end{aligned}
$$

Therefore, when $v_{g}=0.7964, t_{\text {sat }}$, by linear interpolation, would be $123.9^{\circ}$.
Steam would become saturated vapour at $t=123.9^{\circ} \mathrm{C}$
Ans. (a)
At $80^{\circ} \mathrm{C}, v_{\mathrm{f}}=0.001029 \mathrm{~m}^{3} / \mathrm{kg}, v_{\mathrm{g}}=3.407 \mathrm{~m}^{3} / \mathrm{kg}$,

$$
\begin{align*}
h_{\mathrm{f}}=334.91 \mathrm{~kJ} / \mathrm{kg}, h_{\mathrm{fg}} & =2308.8 \mathrm{~kJ} / \mathrm{kg}, p_{\mathrm{cat}}=47.39 \mathrm{kPa} \\
v_{1} & =v_{2}=0.7964 \mathrm{~m}^{3} / \mathrm{kg}=v_{\mathrm{fg} 0^{\circ} \mathrm{C}}+x_{2} v_{\mathrm{fg} 80^{\circ} \mathrm{C}} \\
& =0.001029+x_{2}(3.407-0.001029) \\
\therefore \quad x_{2} & =\frac{0.79539}{3.40597}=0.234  \tag{b}\\
& h_{2}
\end{align*}
$$

From the first law of thermodynamics

$$
\begin{aligned}
\mathrm{d} Q & =\mathrm{d} u+p \mathrm{~d} v \\
\therefore \quad(\AA Q)_{\mathrm{v}} & =\mathrm{d} u \\
\text { or } \quad & \\
Q_{1-2} & =u_{2}-u_{1}=\left(h_{2}-p_{2} v_{2}\right)-\left(h_{1}-p_{1} v_{1}\right) \\
& =\left(h_{2}-h_{1}\right)+v\left(p_{1}-p_{2}\right) \\
& =875.9-2967.6)+0.7964(300-47.39) \\
& =2091.7+201.5 \\
& =-1890.2 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

Ans. (c)
5. Steam initially at $1.5 \mathrm{MPa}, 300^{\circ} \mathrm{C}$ expands reversibly and adiabatically in a steam turbine to $40^{\circ} \mathrm{C}$. Determine the ideal work output of the turbine per kg of steam.
Solution The steady flow energy equation for the control volume, as shown in Fig. gives (other energy terms being neglected)

$$
\begin{array}{ll} 
& h_{1}=h_{2}+W \\
\therefore & W=h_{1}-h_{2}
\end{array}
$$



Work is done by steam at the expense of a fal in its enthalpy value. The process is reversible and adiabatic, so it is isentropic. The process is shown on the $T-s$ and $h$-s diagrams

From Table A.1(a), at $40^{\circ} \mathrm{C}$

$$
\begin{aligned}
p_{\text {sat }} & =7.384 \mathrm{kPa}, s_{\mathrm{f}}=0.5725, \text { and } s_{\mathrm{fg}}=7.6845 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K} \\
h_{\mathrm{f}} & =167.57, \text { and } h_{\mathrm{fg}}=2406.7 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

At $p=1.5 \mathrm{MPa}, t=300^{\circ} \mathrm{C}$, from the tabulated properties of superheated steam (Table A.2)

$$
\begin{aligned}
& s_{1}=6.9189 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K} \\
& h_{1}=3037.6 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$


(a)

(b)

$$
\begin{aligned}
& \text { Since } \\
& \begin{aligned}
s_{1} & =s_{2} \\
6.9189 & =s_{\mathrm{f}}+x_{2} s_{\mathrm{fg}} 40^{\circ} \mathrm{C}
\end{aligned} \\
& =0.5725+x_{2} \times 7.6845 \\
& x_{2}=\frac{6.3464}{7.6845}=0.826 \text { or } 82.6 \% \\
& \therefore \quad h_{2}=h_{\mathrm{f} 40^{\circ} \mathrm{C}}+x_{2} h_{\mathrm{ff} 40^{\circ} \mathrm{C}} \\
& =167.57+0.826 \times 2406.7 \\
& =2152.57 \mathrm{~kJ} / \mathrm{kg} \\
& \therefore \quad W=h_{1}-h_{2}=3037.6-2152.57 \\
& =885.03 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

6.Steam flows in a pipeline at 1.5 MPa . After expanding to 0.1 MPa in a throttling calorimeter, the temperature is found to be $120^{\circ} \mathrm{C}$. Find the quality of steam in the pipeline. What is the maximum moisture at 1.5 MPa that can be determined with this set-up if at least $5^{\circ} \mathrm{C}$ of superheat is required after throttling for accurate readings?
Solution At state 2 when $p=0.1 \mathrm{MPa}, t=120^{\circ} \mathrm{C}$ by inter-polation


$$
\begin{aligned}
& h_{2}=2716.2 \mathrm{~kJ} / \mathrm{kg}, \text { and at } p=1.5 \mathrm{MPa} \\
& h_{\mathrm{f}}=844.89 \text { and } h_{\mathrm{fg}}=1947.3 \mathrm{~kJ} / \mathrm{kg} \\
& h_{1}=h_{2} \\
& h_{\mathrm{ff} .5 \mathrm{MPa}}+x_{1} h_{\mathrm{fg} 1.5 \mathrm{MPa}}=h_{2} \\
& 844.89+x_{1} \times 1947.3=2716.2 \\
& x_{1}=\frac{1871.3}{1947.3}=0.963
\end{aligned}
$$

Now
or

Ans.
When $p=0.1 \mathrm{MPa}$ and $t=99.63+5=104.63^{\circ} \mathrm{C}$

Since

$$
h_{3}=2685.5 \mathrm{~kJ} / \mathrm{kg}
$$

$$
h_{3}=h_{4}
$$

$$
2685.5=844.89+x_{4} \times 1947.3
$$

$$
\therefore \quad x_{4}=\frac{1840.6}{1947.3}=0.948
$$

The maximum moisture that can be determined with this set-up is only $5.2 \%$.

## UNIT-II

## OBJECTIVE:

To familiarize the students with the topics of energy and Entropy and know learn about the $1^{\text {st }}$ Law \& $2^{\text {nd }}$ law of thermodynamics and its applications.

## THERMODYNAMICS ANALYSIS OF A SYSTEMS

Work is defined as energy in transition between system and surroundings, without transfer of mass. Work is said to be done by a system on its surroundings if the sole effect external to the system could be the raising of a weight.

## Examples:


$\Rightarrow$ Let as consider a system which induces a battery and a motor as shown in figure (a). The motor drives a fan (b) the effect of work transfer from the system are driving the fan.
Work is done by the system taken as positive quantity.
Let us consider a system which include paddle wheel with stirrer. To raise or lower the weight, the work is given to the system.
Work is done on the system taken as negative quantity.

## SIGN CONVENTION FOR WORK:

Work done by the system on its surroundings is considered as positive. When work is done on the system as negative.


## HEAT TRANSFER:

It is defined as the form of energy. (i.e) transfer between two systems (or a system and its surroundings) by virtue of temperature difference. The transfer of heat into the system is referred as heat addition and transfer of heat out of the stem as heat rejection.

Heat is energy in transition. It is recognized only as it crosses the boundary of the system. The term heat is denoted by $\phi$. Heat simply means Heat transfer. Heat flow into the system is taken as positive and heat flow out of the system is taken as negative.


Heat addition $\phi$ (+ve)
Heat rejection $\phi$ (-ve)

## DISPLACEMENT WORK - PDV WORK:




Displacement Work - Pdv Work:-

Consider a gas enclosed in a piston and cylinder arrangement as shown in figure. The system is in thermodynamic equilibrium in initial position ( $p_{1} V_{1}$ ) and the piston moves to final position, which is also a thermodynamic equilibrium state specified by $\mathrm{P}_{2} \mathrm{~V}_{2}$.

$$
\begin{aligned}
d w & =\text { force } x \text { distance } & & \\
& =F \times d x & & \text { But } F=P \times A \\
\Rightarrow \quad & =P A \times d x & & \text { But } d v=A d x
\end{aligned}
$$

For any process chanting, cooling, expansion, compression

$$
\mathrm{Dw}=\mathrm{pdv}
$$

$\Rightarrow$ Work done is
$\int_{1}^{2} d w=\int_{1}^{2} p d v$
$\int_{1}^{\mathrm{W}} 1-2=$
$\int_{1}^{2} p d v n m$

Area under the curve in pv-diagram gives the work done under the process.

## POINT AND PATH FUNCTIONS:

The quantities pressure, volume, heat, work etc... can be grouped under two classes namely point and path functions.

## POINT FUNCTION:

Thermodynamic properties are point function. Since for a given state there is a definite value for each property.

They depend only on the state and not on how the system reaches that state. They have exact differentials.

A small change in Volume is represented by $d V$ and the total change in volume during a process

$$
\int d v=V_{2}-V_{1}
$$

For a cyclic process, the initial and final states are same and bench, the change in any property is zero is

$$
\oint d p=0, \oint d v=0, \oint d T=0
$$

## PATH FUNCTION:



Path Function
Heat and work are path functions. The system from which state 1 to state 2 along many quasi - static process such as $A, B$ and $C$. Since the curve represents the work for each process.

The amount of work involved in each case is not a function of end state of the process and it depends on the path of the system follows from state 1 to state 2. For this reason, work is called path function and dw is an in - exact differential

$$
\int d w \neq w 2-w 1==>\int d w=W 1-2
$$

## FIRST LAW OF THERMODYNAMICS:

First law of thermodynamics states that, "when a system undergoes a cyclic process, then the net heat transfer is equal to the net work transfer".

Mathematically,

$$
\oint s w=\oint \theta Q
$$

(or)

$$
\oint s w-\oint \theta \phi=0
$$

According to law of conservation of energy, "Energy can be neither created nor destroyed but it can transferred to one form to another". In general for any Thermodynamic systems, the first law of Thermodynamics can be written in the form of following equation.

Heat transfer = Work done + change in Internal Energy.

$$
Q=W+\Delta U
$$

## FIRST LAW FOR A SYSTEM UNDERGOING A CYCLE:

## JOULE'S PADDLE WHEEL EXPERIMENT (CLOSED SYSTEM)



Energy which enters the system has heat may leave the system as work or energy which enters the system as work may leave the system as heat.

Let us consider an insulated system which consists of a liquid at a temperature " $\mathrm{T}_{1}$ "and pressure " $\mathrm{P}_{1}$ " maintained at atmospheric pressure. A paddle wheel which is placed in the system with weight W . A thermometer is placed in the system to measure the temperature differences.

When the weight falls down, this drives the paddle wheel to pulley. A quantity work can be measured by the fall of weight. During this fall, the paddle wheel stirs the liquid: the temperature of the liquid is increased and taken as " $\mathrm{T}_{2}$ ". Work transfer: 1-2

Now the insulations is removed such that system and surrounding are interacted by heat transfer till the system returns to its original temperature attaining the condition of Thermal equilibrium with Atmospheric. Heat transfer: 2-1

The system thus executes the cycle which says that an infinite amount of work transfer into a system equal to amount of heat transfer from system. Hence work done during process $1-2$ is always proportional to heat transfer during process 2-1

$$
\mathrm{W}_{1-2}^{\alpha \phi 2-1} \begin{gathered}
W=J Q
\end{gathered}
$$

Where J - Joule equivalent / mechanical equivalent of heat
If no. of cycles are involved
$(\in W)$ cycle $=(\in \phi)$ cycle
(or)
$\oint d w=\oint d Q$.

## ENERGY - THE PROPERTY OF THE SYSTEM:



Consider a system changes from state 1 to state 2 by following path A and returns from state 2 to state 1 by path $B$.

For path A

$$
\begin{aligned}
& Q A=\triangle E A+W A \\
& ==>Q A-W A=\Delta E A
\end{aligned}
$$

For path B

$$
\begin{aligned}
& Q B=\Delta E B+W B \\
& ==>Q B-W B=\Delta E B
\end{aligned}
$$

The process $A$ and $B$ together constitute a cycle, for which

$$
\begin{aligned}
& (\in W) \text { cycle }=(\in \phi) \text { cycle } \\
& W A+W B=\phi A+\phi B \\
& ==>W A-\phi A=\phi B-W B \\
& W A-\phi A=-[W B-\phi B] \quad \text { From 1 \& } 2 \\
& \Delta E A=-\Delta E B
\end{aligned}
$$

Similarly had the system returned from state 2 to state 1 by following the path C instead of path $B$.

For path A,
$\phi A=\Delta E A+W A$
$\phi A-W A=\Delta E A$
ForpathC

$$
\begin{aligned}
& \phi c=\Delta E C+W c \\
& \phi c-W c=\Delta E c
\end{aligned}
$$

The process A and C together constitute a cycle, for which
$\left(\sum W\right)$ cycle $=\left(\sum \phi\right)$ cycle
$W A+W C=\phi A+\phi C$
From $4 \& 5$ from 3 and 6
$\phi A-W A=W C-\phi c$
$\Delta E A=-E C$

$$
\Delta E B=\Delta E C
$$

Therefore it is seen that the change in energy between two states of a system is same, whatever path the system follows undergoing that change of state. Hence it is a point function and the property of the system. The energy $E$ is an extensive property.

## ENERGY OF AN ISOLATED SYSTEM:

An Isolated system is one in which there is no intersection of the system with the surrounding.

$$
\begin{aligned}
& d \phi=0: \\
& d W=0:
\end{aligned}
$$

According to first law $\mathrm{dE}=0$; or $\mathrm{E}=$ constant Energy of an isolated system is always constant

## SPECIFIC HEAT CAPACITY (C):

The specific heat capacity or heat capacity of a substance is defined as the quantity of heat transfer required to raise or lower the temperature of the unit mass of the substance through one degree.

This is denoted by the symbol 'C'. Its unit is given as $\mathrm{J} / \mathrm{kgk}$ or $\mathrm{kJ} / \mathrm{kgk}$.

## SPECIFIC HEAT CAPACITY AT CONSTANT VOLUME [Cv]:-

It is defined as, the quantity of heat transfer required to raise or lower the temperature of unit ma of the substance through one degree when the Volume remain constant. It is denoted by the symbol ' $\mathrm{c}_{\mathrm{v}}$ '

When the gas is heated or cooled at constant volume, the heat transfer is given by

$$
\phi=m c v(T 2-T 1) k J
$$

Where, $\phi$ - Heat transfer (kJ) ; m-mass of the gas (kg)
$\mathrm{C}_{\mathrm{v}}$ - Specific heat capacity at constant Volume (kj / lgk)
$\mathrm{T}_{1}$-Initial temperature of the gas $(\mathrm{k})$
$\mathrm{T}_{2}$ - Final temperature of the gas (k)

## SPECIFIC HEAT CAPACITY AT CONSTANT PRESSURE [Cp]:

It is defined as the quantity of heat transfer required to raise or lower the temperature of unit mass of the substance through one degree when the pressure is kept constant. It is denoted by the symbol $\mathrm{c}_{\mathrm{p}}$.

When the gas is heated or cooled at constant pressure, the heat transfer is given by

$$
\phi=m c p(T 2-T 1) J
$$

Cp is always greater than $\mathrm{C}_{v}$
The ratio of two specific heats ( $\mathrm{cp} / \mathrm{c}_{\mathrm{v}}$ ) remains constant and it is denoted by the symbol $/ \mathrm{v}$. It is also called adiabatic index. $v=\frac{c p}{c v}$ For air $\mathrm{cp}=1.005 \mathrm{~kJ} / \mathrm{kg} . \mathrm{K}=1.4 \mathrm{C}_{\mathrm{v}}=0.718 \mathrm{~kJ}$ / kg.K

## PERPETUAL MOTION MACHINE (PMM) OF FIRST KIND:

There can be no machine which would continuously supply mechanical work without some other form of energy disappearing simultaneously. Such a fictitious machine is called PMM of first kind.

Thus, a PMM1 is impossible.

## INTERNAL ENERGY (U):

Internal energy of a gas is the heat energy stored in the gas at a given temperature. It is denoted by the letter ' U '.

Where

$$
\mathrm{U}=\mathrm{mcv} \mathrm{kj}
$$

m - Mass of gas (kg)
$\mathrm{c}_{\mathrm{v}}$ - Specific heat at constant volume (kJ / kgk)
t - Temperature of the gas ( ${ }^{\circ} \mathrm{c}$ )

## CHANGE IN INTERNAL ENERGY ( $\Delta U$ )

When heat is supplied to a certain mass of gas a) the temperature of the gas may increase (or) b) the volume of the gas may increase doing external work (or) c) it may do both.

The increase in heat energy stored in the gas due to rise in temperature is known as increase of internal energy or change in internal energy.

$$
\Delta U=m c v(T 2-T 1) k J
$$

m - Mass of the gas (kg)
$\mathrm{c}_{v}$ - Specific heat capacity at constant Volume (kJ / kgk)
$\mathrm{T}_{1}$ - Initial temperature of the gas before heating (k)
$\mathrm{T}_{2}$ - Final Temperature of the gas after heating (k)

## FIRST LAW APPLIED TO FLOW PROCESSES

## STEADY FLOW PROCESS

Steady flow means that the rates of flow of mass and energy across the control surface are constant.

At the steady state of a system, any thermodynamic property will have a fixed value at a particular location and will not alter with time.

## STEADY FLOW ENERGY EQUATION (SFEE):

Consider a thermodynamic system in which a fluid is flowing at a steady steady state. Fluid enters the system at point 1. And leaves the system at point 2 . The space under consideration between entry and exit is known as control volume.

Assumptions made in the system analysis.

1. The mass rate of flow through the control volume is constant.
2. Only potential, kinetic, Internal and flow energies are considered. Other forms of energy are not considered.
3. The interaction between the system and the surroundings are only work and heat. The rate at which work and heat cross the boundary is constant.
4. The state of fluid at any point remains constant at all times.

| Let | A+ entry | A+ exit |
| :--- | :---: | :--- |
| Intensity of pressure $\left(\mathrm{N} / \mathrm{m}_{2}\right)$ | $\mathrm{P}_{1}$ | $\mathrm{P}_{2}$ |
| Internal energy | $(\mathrm{J} / \mathrm{kg})$ | $\mathrm{u}_{1}$ |
| Velocity of flow | $(\mathrm{m} / \mathrm{s})$ | $\mathrm{V}_{1}$ |
| Height above datum $(\mathrm{m})$ | $\mathrm{Z}_{1}$ | $\mathrm{u}_{2}$ |
| Specific Volume $\left(\mathrm{m}^{3} / \mathrm{kg}\right)$ | $\mathrm{V}_{1}$ | $\mathrm{Z}_{2}$ |
| Enthalpy of working fluid $(\mathrm{J} / \mathrm{kg})$ | $\mathrm{h}_{1}$ | $\mathrm{~V}_{2}$ |
| Areas $(\mathrm{m} 2)$ | $\mathrm{A}_{1}$ | $\mathrm{~h}_{2}$ |
| Mass (kg) | $\mathrm{m}_{1}$ | $\mathrm{~A}_{2}$ |
| M |  | $\mathrm{m}_{2}$ |

Q - Heat transfer during the flow through the system ( $\mathrm{J} / \mathrm{kg}$ ) W- Work transfer during the flow through the system ( $\mathrm{J} / \mathrm{kg}$ )


## MASS BALANCE:

By the conservation of mass, if there is no accumulation of mass within the control volume, the mass flow rate entering must equal the mass flow rate leaving

$$
M_{1}=M_{2}
$$

$$
\begin{aligned}
& \frac{\mathrm{A}_{1} \mathrm{~V}_{1}}{\mathrm{~V}_{1}}=\frac{\mathrm{A}_{2} \mathrm{~V}_{2}}{\mathrm{~V}_{2}} \\
& \frac{A_{1}}{A_{2}}=\frac{V_{2}}{V_{1}} \cdot \frac{V_{1}}{V_{2}}
\end{aligned}
$$

$$
\frac{\frac{\pi}{4} d_{1}^{2}}{\frac{\pi}{4} d_{2}^{2}}=\frac{V_{2}}{V_{1}} \cdot \frac{V_{1}}{V_{2}}
$$

$$
\frac{\mathrm{d}_{1}^{2}}{\mathrm{~d}_{2}^{2}}=\sqrt{\frac{\mathrm{v}_{2}}{\mathrm{v}_{1}} \cdot \frac{\mathrm{v}_{1}}{\mathrm{v}_{2}}}
$$

## ENERGY BALANCE:

By the conservation of energy, the total rate of flow of all energy streams entering the control volume must equal the total rate of flow of cull energy streams leaving the control volume.

Total energy entering the system = potential energy+ kinetic energy
+Internal energy + flow energy

+ Heat transfer.
$\Rightarrow$ Total energy entering the system $=\mathrm{g} \mathrm{Z}_{1}+\frac{V_{1}^{2}}{2}+u_{1}+p_{1} Q_{1}+Q$

Total energy leaving the system = potential energy + kinetic energy + Internal energy

+ Flow energy + Work transfer.

Total energy leaving the system $=\mathrm{g} \mathrm{Z}_{2}+\frac{V_{2}^{2}}{2}+u_{2}+p_{2} Q_{2}+W$
By low of conservation of energy.
Energy Entering the system = Energy leaving the system From 1 \& 2

$$
\begin{align*}
& \Rightarrow g Z_{1}+\frac{V_{1}^{2}}{2}+h_{1}+Q=g Z_{2}+\frac{V_{2}^{2}}{2}+h_{2}+W \\
& \Rightarrow Q-W=g\left(Z_{2}-Z_{1}\right)+\frac{V_{2}^{2}-V_{1}^{2}}{2}+\left(h_{2}-h_{1}\right)
\end{align*}
$$

" $m$ " is mass flow rate of the fluid, Eqn. 4 becomes
$4 \rightarrow Q-W=m\left[g\left(Z_{2}-Z_{1}\right)+\frac{V_{2}^{2}-V_{1}^{2}}{2}+\left(h_{2}-h_{1}\right)\right]$
If $\mathrm{h}, \mathrm{Q}$ and W are expressed in $\mathrm{KJ} / \mathrm{kg}$, Eqn. 5 becomes
$5 \rightarrow \mathrm{Q}-\mathrm{W}=\mathrm{m}\left[\mathrm{g}\left(\frac{\mathrm{Z}_{2}-\mathrm{Z}_{1}}{1000}\right)+\frac{\mathrm{V}_{2}^{2}-\mathrm{V}_{1}^{2}}{2000}+\left(\mathrm{h}_{2}-\mathrm{h}_{1}\right)\right]$
And finally,

$$
\mathbf{m}\left(\frac{\mathrm{gz}_{1}}{1000}+\frac{\mathrm{v}_{1}^{2}}{2000}+\mathbf{h}_{1}\right)+\mathbf{Q}=\mathbf{m}\left(\frac{\mathrm{gz}_{2}}{1000}+\frac{\mathrm{v}_{2}^{2}}{2000}+\mathbf{h}_{2}\right)+\mathbf{W}
$$

## APPLICATIONS OF STEADY FLOW ENERGY EQUATION:-

The steady flow energy equation is applied in
a. Steam generators (boilers)
b. Steam condensers
c. Steam nozzles
d. Air compressors
e. Steam or gas turbines
f. Air heaters.

## a) Steam Generator (Or) Boiler:-

Boiler is equipment which generates steam. Water is supplied to the boiler. This water is heated by burning fuel ad steam is generated. This steam is supplied to machines for doing work.

$\Rightarrow$ No mechanical work
Is $\mathrm{W}=0$
$\Rightarrow$ Fluid velocity at the inlet and exit is small. There is no change in kinetic energy
$\Rightarrow V_{1}=V_{2}$
Potential energy between inlet and exit is also negligible
$Z_{1}=Z_{2}$
For SFEE,

$$
\begin{aligned}
& Q-W=m\left[g\left(\frac{\mathrm{Z}_{2}-\mathrm{Z}_{1}}{1000}\right)+\frac{\mathrm{V}_{2}^{2}-\mathrm{V}_{1}^{2}}{2000}+\left(\mathrm{h}_{2}-\mathrm{h}_{1}\right)\right] \\
\Rightarrow & Q=\mathrm{h}_{2}-\mathrm{h}_{1} \mathrm{j} / \mathrm{kg}
\end{aligned}
$$

## b) Steam Condenser:-

A steam condenser condenses steam into water. The main function of a condenser is to transfer the heat out of the steady flow system.
$\Rightarrow$ No work is done $\mathrm{W}=0$
$\Rightarrow$ No change in K.E V1 = V2
$\Rightarrow$ No change in potential energy $Z_{1}=Z_{2}$
SFEE,

$$
\mathrm{Q}-\mathrm{W}=\mathrm{m}\left[\mathrm{~g}\left(\frac{\mathrm{Z}_{2}-\mathrm{Z}_{1}}{1000}\right)+\frac{\mathrm{V}_{2}^{2}-\mathrm{V}_{1}^{2}}{2000}+\left(\mathrm{h}_{2}-\mathrm{h}_{1}\right)\right]
$$



## Steam Condenser

Heat transfer, $\Rightarrow Q=h_{2}-h_{1} \mathrm{j} / \mathrm{kg}$
c) Steam Nozzles:-

Nozzle is a device used for increasing the velocity of flowing fluid at the cost of pressure drop.


## Steam Nozzles

$$
\Rightarrow \mathrm{Q}-\mathrm{W}=\mathrm{m}\left[\mathrm{~g}\left(\frac{\mathrm{Z}_{2}-\mathrm{Z}_{1}}{1000}\right)+\frac{\mathrm{V}_{2}^{2}-\mathrm{V}_{1}^{2}}{2000}+\left(\mathrm{h}_{2}-\mathrm{h}_{1}\right)\right]
$$

$$
\frac{\mathrm{V}_{2}^{2}-\mathrm{V}_{1}^{2}}{2000}+\left(\mathrm{h}_{2}-\mathrm{h}_{1}\right)=0
$$

$$
\frac{\mathrm{V}_{2}^{2}-\mathrm{V}_{1}^{2}}{2000}=\left(\mathrm{h}_{1}-\mathrm{h}_{2}\right)
$$

$$
V_{2}^{2}-V_{1}^{2}=2000\left(\mathrm{~h}_{1}-\mathrm{h}_{2}\right)
$$

$$
V_{2}^{2}=V_{1}^{2}+2000\left(\mathrm{~h}_{1}-\mathrm{h}_{2}\right)
$$

$$
V_{2}=\sqrt{V_{1}^{2}+2000\left(\mathrm{~h}_{1}-\mathrm{h}_{2}\right)} \mathrm{m} / \mathrm{s}
$$

$\mathrm{h}_{1}, \mathrm{~h}_{2}$ are in kj/kg.

## d) Air compressors:-

Air compressor is a machine used to produce high pressure air. It takes in atmospheric air and compresses it to a high pressure. It may be broadly classified as i) rotary compressor ii) reciprocating compressors.

## Rotary Compressor:-

Rotary compressor has a rotor to develop pressure. In this type of compressors, the rate off low is very high. Hence this process is treated as reversible adiabatic or isentropic.

SFEE,
Work input, $\quad W=h_{1}-h_{2} \mathrm{~J} / \mathrm{kg}$

## Reciprocating Compressor:-

It has a cylinder in which a piston reciprocates. In this type, the rate of flow is comparatively low and large area is in contact with the surroundings. Hence heat transfer is in contact with the surroundings. Hence heat transfer is appreciably more and cannot be neglected.

## SFEE,

$$
\text { Work input, } \mathrm{W}=\phi+\left(\mathrm{h}_{1}-\mathrm{h}_{2}\right) \mathrm{J} / \mathrm{kg}
$$

## e) Steam turbines:-

A steam turbine is a device which converts the energy of steam into mechanical work. Steam is expanded thru a nozzle and a certain amount of head energy is converted into kinetic energy. The steam with high velocity flows over curved blades and its direction of motion is changed. This causes a change of momentum and force thus developed drives the turbine shaft,

SFEE
Work output, $\mathrm{W}=\left(\mathrm{h}_{1}-\mathrm{h}_{2}\right) \mathrm{J} / \mathrm{kg}$


## PROBLEMS:

1. When a system is taken from state $a$ to state $b$, in Fig. Ex. 4.2, along path acb, 84 kJ of heat flow into the system, and the system does 32 kJ of work. (a) How much will the heat that flows into the system along path adb be, if the work done is 10.5 kJ ? (b) When the system is returned from $b$ to $a$ along the curved path, the work done on the system is 21 kJ . Does the system absorb or liberate heat, and how much of the heat is absorbed or liberated? (c) If $U_{\mathrm{a}}=0$ and $U_{\mathrm{d}}=42 \mathrm{~kJ}$, find the heat absorbed in the processes $a d$ and $d b$.


Solution

$$
\begin{aligned}
& Q_{\mathrm{acb}}=84 \mathrm{~kJ} \\
& W_{\mathrm{acb}}=32 \mathrm{~kJ}
\end{aligned}
$$

We have

$$
\begin{aligned}
& Q_{\mathrm{acb}}=U_{\mathrm{b}}-U_{\mathrm{a}}+W_{\mathrm{acb}} \\
& \therefore \quad U_{\mathrm{b}}-U_{\mathrm{a}}=84-32=52 \mathrm{~kJ} \\
& Q_{\mathrm{adb}}=U_{\mathrm{b}}-U_{\mathrm{a}}+W_{\mathrm{adb}} \\
& =52+10.5 \\
& =62.5 \mathrm{~kJ} \\
& Q_{\mathrm{b}-\mathrm{a}}=U_{\mathrm{a}}-U_{\mathrm{b}}+W_{\mathrm{b}-\mathrm{a}} \\
& =-52-21 \\
& =-73 \mathrm{~kJ} \\
& \text { (b) }
\end{aligned}
$$

Ans.

Ans.
2. A piston and cylinder machine contains a fluid system which passes through a complete cycle of four processes. During a cycle, the sum of all heat transfers is -170 kJ . The system completes 100 cycles per min. Complete the following table showing the method for each item, and compute the net rate of work output in kW .

| Process | $Q(k J / m i n)$ | $W(k J / m i n)$ | $\Delta E(k J / m i n)$ |
| :---: | :---: | :---: | :---: |
| a-b | 0 | 2,170 | - |
| $\mathrm{b}-\mathrm{c}$ | 21,000 | 0 | - |
| c-d | $-2,100$ | - | $-36,600$ |
| d-a | - | - | - |

## Solution Process $\boldsymbol{a}-\boldsymbol{b}$ :

$$
\begin{array}{rlrl} 
& Q & =\Delta E+W \\
& 0 & =\Delta E+2170 \\
\therefore \quad \Delta E & =-2170 \mathrm{~kJ} / \mathrm{min}
\end{array}
$$

Process $b-c$ :

$$
\begin{aligned}
Q & =\Delta E+W \\
21,000 & =\Delta E+0
\end{aligned}
$$

$$
\therefore \quad \Delta E=21,000 \mathrm{~kJ} / \mathrm{min}
$$

Process c-d:

$$
\begin{array}{rlrl}
Q & =\Delta E+W \\
& & -2100 & =-36,600+W \\
\therefore & W & =34,500 \mathrm{~kJ} / \mathrm{min}
\end{array}
$$

Process $d-a$ :

$$
\sum_{\text {eycle }} Q=-170 \mathrm{~kJ}
$$

The system completes 100 cycles $/ \mathrm{min}$.

$$
\begin{array}{rlrl} 
& \because & Q_{\mathrm{ab}}+Q_{\mathrm{bc}}+Q_{\mathrm{cd}}+Q_{\mathrm{da}} & =-17,000 \mathrm{~kJ} / \mathrm{min} \\
& 0+21,000-2,100+Q_{\mathrm{da}} & =-17,000 \\
& \therefore \quad Q_{\mathrm{da}} & =-35,900 \mathrm{~kJ} / \mathrm{min}
\end{array}
$$

Now $\oint \mathrm{d} E=0$, since cyclic integral of any property is zero.

$$
\begin{array}{rlrl}
\therefore \quad \Delta E_{\mathrm{a}-\mathrm{b}}+\Delta E_{\mathrm{b}-\mathrm{c}}+\Delta E_{\mathrm{od}}+\Delta E_{\mathrm{d}-\mathrm{a}} & =0 \\
& -2,170+21,000-36,600+\Delta E_{\mathrm{d}-\mathrm{a}} & =0 \\
\therefore & \Delta E_{\mathrm{d}-\mathrm{a}} & =17,770 \mathrm{~kJ} / \mathrm{min} \\
\therefore & W_{\mathrm{d}-\mathrm{a}} & =Q_{\mathrm{d}-\mathrm{a}}-\Delta E_{\mathrm{d}-\mathrm{a}} \\
& & =-35,900-17,770 \\
& & =-53,670 \mathrm{~kJ} / \mathrm{min}
\end{array}
$$

The table becomes

| Process | $Q(\mathrm{~kJ} / \mathrm{min})$ | $W(\mathrm{~kJ} / \mathrm{min})$ | $\Delta E(\mathrm{~kJ} / \mathrm{min})$ |
| :---: | :---: | :---: | :---: |
| a-b | 0 | 2,170 | $-2,170$ |
| b-c | 21,000 | 0 | 21,000 |
| c-d | $-2,100$ | 34,500 | $-36,600$ |
| d-a | $-35,900$ | $-53,670$ | 17,770 |

Since
Rate of work output

$$
\begin{aligned}
& \sum_{\text {cycle }} Q=\sum_{\text {cycle }} W \\
& =-17,000 \mathrm{~kJ} / \mathrm{min} \\
& =-283.3 \mathrm{~kW}
\end{aligned}
$$

Ans.
3. A fluid is confined in a cylinder by a spring-loaded, frictionless piston so that the pressure in the fluid is a linear function of the volume ( $p=a+b V$ ). The internal energy of the fluid is given by the following equation

$$
U=34+3.15 p V
$$

where $U$ is in $\mathrm{kJ}, p$ in kPa , and $V$ in cubic metre. If the fluid changes from an initial state of $170 \mathrm{kPa}, 0.03 \mathrm{~m}^{3}$ to a final state of $400 \mathrm{kPa}, 0.06 \mathrm{~m}^{3}$, with no work other than that done on the piston, find the direction and magnitude of the work and heat transfer.
Solution The change in the internal energy of the fluid during the process.

$$
\begin{aligned}
& U_{2}-U_{1}= 3.15\left(p_{2} V_{2}-p_{1} V_{1}\right) \\
&= 315(4 \times 0.06-1.7 \times 0.03) \\
&= 315 \times 0.189=59.5 \mathrm{~kJ} \\
& p=a+b V \\
& 170=a+b \times 0.03 \\
& 400=a+b \times 0.06
\end{aligned}
$$

From these two equations

$$
\begin{aligned}
& a=-60 \mathrm{kN} / \mathrm{m}^{2} \\
& b=7667 \mathrm{kN} / \mathrm{m}^{5}
\end{aligned}
$$

Work transfer involved during the process

$$
\begin{aligned}
W_{1-2} & =\int_{V_{1}}^{V_{2}} p \mathrm{~d} V=\int_{V_{1}}^{V_{2}}(a+b V) \mathrm{d} V \\
& =a\left(V_{2}-V_{1}\right)+b \frac{V_{2}^{2}-V_{1}^{2}}{2} \\
& =\left(V_{2}-V_{1}\right)\left[a+\frac{b}{2}\left(V_{1}+V_{2}\right)\right] \\
& =0.03 \mathrm{~m}^{3}\left[-60 \mathrm{kN} / \mathrm{m}^{2}+\frac{7667}{2} \frac{\mathrm{kN}}{\mathrm{~m}^{5}} \times 0.09 \mathrm{~m}^{3}\right] \\
& =8.55 \mathrm{~kJ}
\end{aligned}
$$

Work is done by the system, the magnitude being 8.55 kJ .
$\therefore$ Heat transfer involved is given by

$$
\begin{aligned}
Q_{1-2} & =U_{2}-U_{1}+W_{1-2} \\
& =59.5+8.55 \\
& =68.05 \mathrm{~kJ}
\end{aligned}
$$

68.05 kJ of heat flow into the system during the process.
4.Air flows steadily at the rate of $0.5 \mathrm{~kg} / \mathrm{s}$ through an air compressor, entering at $7 \mathrm{~m} / \mathrm{s}$ velocity, 100 kPa pressure, and $0.95 \mathrm{~m}^{3} / \mathrm{kg}$ volume, and leaving at $5 \mathrm{~m} / \mathrm{s}, 700 \mathrm{kPa}$, and $0.19 \mathrm{~m}^{3} / \mathrm{kg}$. The internal energy of the air leaving is $90 \mathrm{~kJ} / \mathrm{kg}$ greater than that of the air entering. Cooling water in the compressor jackets absorbs heat from the air at the rate of 58 kW . (a) Compute the rate of shaft work input to the air in kW . (b) Find the ratio of the inlet pipe diameter to outlet pipe diameter.
Solution Figure shows the details of the problem.

(a) Writing the steady flow energy equation, we have

$$
\begin{gathered}
w\left(u_{1}+p_{1} v_{1}+\frac{V_{1}^{2}}{2}+Z_{1} g\right)+\frac{\mathrm{d} Q}{\mathrm{~d} \tau} \\
= \\
w\left(u_{2}+p_{2} v_{2}+\frac{\mathrm{V}_{2}^{2}}{2}+Z_{2} g\right)+\frac{\mathrm{d} W_{\mathrm{x}}}{\mathrm{~d} \tau} \\
\therefore \frac{\mathrm{~d} W_{\mathrm{x}}}{\mathrm{~d} \tau}=-w\left[\left(u_{2}-u_{1}\right)+\left(p_{2} v_{2}-p_{1} v_{1}\right)+\frac{\mathrm{V}_{2}^{2}-\mathrm{V}_{1}^{2}}{2}+\left(Z_{2}-Z_{1}\right) g\right]+\frac{\mathrm{d} Q}{\mathrm{~d} \tau} \\
\begin{aligned}
& \frac{\mathrm{d} W_{\mathrm{X}}}{\mathrm{~d} \tau}=-0.5 \frac{\mathrm{~kg}}{\mathrm{~s}}\left[90 \frac{\mathrm{~kJ}}{\mathrm{~kg}}+(7 \times 0.19-1 \times 0.95) 100 \frac{\mathrm{~kJ}}{\mathrm{~kg}}\right. \\
&\left.+\frac{\left(5^{2}-7^{2}\right) \times 10^{-3}}{2} \frac{\mathrm{~kJ}}{\mathrm{~kg}}+0\right]-58 \mathrm{~kW} \\
&=-0.5[90+38-0.012] \mathrm{kJ} / \mathrm{s}-58 \mathrm{~kW} \\
&=-122 \mathrm{~kW}
\end{aligned}
\end{gathered}
$$

Ans. (a)
Rate of work input is 122 kW .
(b) From mass balance, we have

$$
\begin{array}{ll}
\therefore & w=\frac{A_{1} \mathbf{V}_{1}}{v_{1}}=\frac{A_{2} V_{2}}{v_{2}} \\
\therefore & \frac{A_{1}}{A_{2}}=\frac{v_{1}}{v_{2}} \cdot \frac{\mathbf{V}_{2}}{\mathbf{V}_{1}}=\frac{0.95}{0.19} \times \frac{5}{7}=3.57 \\
\therefore & \frac{d_{1}}{d_{2}}=\sqrt{3.57}=1.89
\end{array}
$$

5. In a steady flow apparatus, 135 kJ of work is done by each kg of nuid. The specific volume of the fluid, pressure, and velocity at the inlet are $0.37 \mathrm{~m}^{3} / \mathrm{kg}, 600 \mathrm{kPa}$, and $16 \mathrm{~m} / \mathrm{s}$. The inlet is 32 m above the floor, and the discharge pipe is at floor level. The discharge conditions are $0.62 \mathrm{~m}^{3} / \mathrm{kg}, 100 \mathrm{kPa}$, and $270 \mathrm{~m} / \mathrm{s}$. The total heat loss between the inlet and discharge is $9 \mathrm{~kJ} / \mathrm{kg}$ of fluid. In flowing through this apparatus, does the specific internal energy increase or decrease, and by how much?
Solution Writing the steady flow energy equation for the control volume,


$$
\begin{gathered}
u_{1}+p_{1} v_{1}+\frac{\mathbf{V}_{1}^{2}}{2}+Z_{1} g+\frac{đ Q}{\mathrm{~d} m}=u_{2}+p_{2} v_{2}+\frac{\mathbf{V}_{2}^{2}}{2}+Z_{2} g+\frac{\mathrm{d} W_{\mathrm{x}}}{\mathrm{~d} m} \\
\therefore u_{1}-u_{2}=\left(p_{2} v_{2}-p_{1} v_{1}\right)+\frac{\mathbf{V}_{2}^{2}-V_{1}^{2}}{2}+\left(Z_{2}-Z_{1}\right) g+\frac{đ W_{\mathrm{x}}}{\mathrm{~d} m}-\frac{₫ Q}{\mathrm{~d} m} \\
=(1 \times 0.62-6 \times 0.37) \times 10^{2}+\frac{\left(270^{2}-16^{2}\right) \times 10^{-3}}{2} \\
+\left(-32 \times 9.81 \times 10^{-3}\right)+135-(-9.0) \\
=-160+36.45-0.314+135+9 \\
=20.136 \mathrm{~kJ} / \mathrm{kg}
\end{gathered}
$$

Specific internal energy decreases by 20.136 kJ .
6. Air at a temperature of $15^{\circ} \mathrm{C}$ passes through a heat exchanger at a velocity of $30 \mathrm{~m} / \mathrm{s}$ where its temperature is raised to $800^{\circ} \mathrm{C}$. It then enters a turbine with the same velocity of $30 \mathrm{~m} / \mathrm{s}$ and expands until the temperature falls to $650^{\circ} \mathrm{C}$. On leaving the turbine, the air is taken at a velocity of $60 \mathrm{~m} / \mathrm{s}$ to a nozzle where it expanas untu the temperature nas ralien to $\operatorname{suv}^{-}$C. If the air now rate is $2 \mathrm{~kg} / \mathrm{s}$, calculate (a) the rate of heat transfer to the air in the heat exchanger, (b) the power output from the turbine assuming no heat loss, and (c) the velocity at exit from the nozzle, assuming no heat loss. Take the enthalpy of air as $h=c_{\mathrm{p}} t$, where $c_{\mathrm{p}}$ is the specific heat equal to $1.005 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}$ and $t$ the temperature.
Solution As shown in Fig. writing the S.F.E.E. for the heat exchanger and eliminating the terms not relevant,

Solution As shown in Fig. writing the S.F.E.E. for the heat exchanger and eliminating the terms not relevant,

$$
\begin{array}{rlrl} 
& & w\left(h_{1}+\frac{\mathbf{v}_{1}^{2}}{2}+Z_{1} g\right)+Q_{1-2} & =w\left(h_{2}+\frac{\mathbf{v}_{2}^{2}}{2}+Z_{2} g\right)+W_{1-2} \\
\therefore \quad w h_{1}+Q_{1-2} & =w h_{2} \\
\therefore \quad Q_{1-2} & =w\left(h_{2}-h_{1}\right)=w c_{\mathrm{p}}\left(t_{2}-t_{1}\right) \\
& & =2 \times 1.005(800-15) \\
& =2.01 \times 785 \\
& =1580 \mathrm{~kJ} / \mathrm{s}
\end{array}
$$

Ans. (a).


Energy equation for the turbine gives

$$
\begin{aligned}
& w\left(\frac{\mathbf{V}_{2}^{2}}{2}+h_{2}\right)=w h_{3}+w \frac{V_{3}^{2}}{2}+W_{\mathrm{T}} \\
& \frac{\mathbf{V}_{2}^{2}-\mathbf{V}_{3}^{2}}{2}+\left(h_{2}-h_{3}\right)=W_{\mathrm{T}} / w \\
& \frac{\left(30^{2}-60^{2}\right) \times 10^{-3}}{2}+1.005(800-650)=W_{\mathrm{T}} / w
\end{aligned}
$$

$$
\begin{array}{rlrl}
\therefore & \frac{W_{T}}{w} & =-1.35+150.75 \\
& & =149.4 \mathrm{~kJ} / \mathrm{kg} \\
\therefore & & W_{\mathrm{T}} & =149.4 \times 2 \mathrm{~kJ} / \mathrm{s} \\
& & =298.8 \mathrm{~kW}
\end{array}
$$

Ans. (b)
Writing the energy equation for the nozzle

$$
\begin{aligned}
\frac{\mathbf{v}_{3}^{3}}{2}+h_{3} & =\frac{\mathbf{v}_{4}^{2}}{2}+h_{4} \\
\frac{\mathbf{v}_{4}^{2}-\mathbf{v}_{3}^{2}}{2} & =c_{\mathrm{p}}\left(t_{3}-t_{4}\right) \\
\mathbf{v}_{4}^{2}-\mathbf{V}_{3}^{2} & =1.005(650-500) \times 2 \times 10^{3} \\
& =301.50 \times 10^{3} \mathrm{~m}^{2} / \mathrm{s}^{2} \\
& =30.51 \times 10^{4} \mathrm{~m}^{2} / \mathrm{s}^{2}
\end{aligned}
$$

$\therefore$ Velocity at exit from the nozzle

$$
\begin{equation*}
V_{4}=554 \mathrm{~m} / \mathrm{s} \tag{c}
\end{equation*}
$$

7. A cyclic heat engine operates between a source temperature of $800^{\circ} \mathrm{C}$ and a sink temperature of $30^{\circ} \mathrm{C}$. What is the least rate of heat rejection per kW net output of the engine?
Solution For a reversible engine, the rate of heat rejection will be minimum


$$
\begin{aligned}
\eta_{\max }=\eta_{\mathrm{rev}} & =1-\frac{T_{2}}{T_{1}} \\
& =1-\frac{30+273}{800+273} \\
& =1-0.282=0.718
\end{aligned}
$$

Now $\quad \frac{W_{\text {net }}}{Q_{1}}=\eta_{\max }=0.718$
$\therefore \quad Q_{1}=\frac{1}{0.718}=1.392 \mathrm{~kW}$
Now

$$
\begin{aligned}
Q_{2} & =Q_{1}-W_{\text {net }}=1.392-1 \\
& =0.392 \mathrm{~kW}
\end{aligned}
$$

This is the least rate of heat rejection.
8. A reversible heat engine in a satellite operates between a hot reservoir at $T_{1}$ and a radiating panel at $T_{2}$. Radiation from the panel is proportional to its area and to $T_{2}^{4}$. For a given work output and value of $T_{1}$ show that the area of the panel will be minimum when $\frac{T_{2}}{T_{1}}=0.75$.

Determine the minimum area of the panel for an output of 1 kW if the constant of proportionality is $5.67 \times 10^{-8} \mathrm{~W} / \mathrm{m}^{2} \mathrm{~K}^{4}$ and $T_{1}$ is 1000 K .
Solution For the heat engine (Fig. Ex. 6.7), the heat rejected $Q_{2}$ to the panel (at $T_{2}$ ) is equal to the energy emitted from the panel to the surroundings by radiation. If $A$ is the area of the panel, $Q_{2} \propto A T_{2}^{4}$, or $Q_{2}=K A T_{2}^{4}$, where $K$ is a constant.


Fig. Ex. 6.7
Now $\quad \eta=\frac{W}{Q_{1}}=\frac{T_{1}-T_{2}}{T_{1}}$
or $\quad \frac{W}{T_{1}-T_{2}}=\frac{Q_{1}}{T_{1}}=\frac{Q_{2}}{T_{2}}=\frac{K A T_{2}^{4}}{T_{2}}$
$=K A T_{2}^{3}$
$\therefore \quad A=\frac{W}{K T_{2}^{3}\left(T_{1}-T_{2}\right)}=\frac{W}{K\left(T_{1} T_{2}^{3}-T_{2}^{4}\right)}$
For a given $W$ and $T_{1}, A$ will be minimum when

$$
\frac{\mathrm{d} A}{\mathrm{~d} T_{2}}=-\frac{W}{K}\left(3 T_{1} T_{2}^{2}-4 T_{2}^{3}\right) \cdot\left(T_{1} T_{2}^{3}-T_{2}^{4}\right)^{-2}=0
$$

Since $\quad\left(T_{1} T_{2}^{3}-T_{2}^{4}\right)^{-2} \neq 0,3 T_{1} T_{2}^{2}=4 T_{2}^{3}$
$\therefore \quad \frac{T_{2}}{T_{1}}=0.75$ Proved.

$$
\begin{aligned}
\because \quad A_{\min } & =\frac{W}{K(0.75)^{3} T_{1}^{3}\left(T_{1}-0.75 T_{1}\right)} \\
& =\frac{W}{K \frac{27}{256} T_{1}^{4}}=\frac{256 W}{27 K T_{1}^{4}}
\end{aligned}
$$

Here

$$
\begin{array}{ll}
\text { Here } & W=1 \mathrm{~kW}, K=5.67 \times 10^{-8} \mathrm{~W} / \mathrm{m}^{2} \mathrm{~K}^{4}, \text { and } T_{1}=1000 \mathrm{~K} \\
\therefore & A_{\min }=\frac{256 \times 1 \mathrm{~kW} \times \mathrm{m}^{2} \mathrm{~K}^{4}}{27 \times 5.67 \times 10^{-8} \mathrm{~W} \times(1000)^{4} \mathrm{~K}^{4}} \\
& =\frac{256 \times 10^{3}}{27 \times 5.67 \times 10^{-8} \times 10^{12}} \mathrm{~m}^{2} \\
= & 0.1672 \mathrm{~m}^{2} \quad \text { Ans. }
\end{array}
$$

## UNIT III

## OBJECTIVE:

To familiarize the students with the topic of exergy and to learn about the practical applications of second law efficiencies

## DEAD STATE:

A system exchanges work, heat and mass with its surroundings during the process. If the system reaches a state which is in equilibrium with its surrounding then the system cannot exchanges the work heat and mass with its surroundings. This state is called a dead state and its properties are denoted by subscript $O$, such as pressure $P_{o}$ and temperature $T_{0}$.

At the dead state:

- A system is at the temperature and pressure of it's surroundings.
- It has no kinetic (or) potential energy relative to it's surroundings
- It does not react with the surroundings
- There are no unbalanced magnetic, electrical and surface tension effects b/w the system and it's surroundings.


## AVAILABLITY:

The availability of a given system is defined as the maximum useful work (total work -PdV work) that is obtainable in a process in which the system comes to equilibrium with its surrounding availability is thus a composite property depending on the state of system and surroundings.

Whenever useful work is obtained during a process in which a finite system undergoes a change of state, the process must terminated.

Therefore for a closed system availability can be expressed as

$$
\varnothing=\left(U-U_{0}\right)+P_{0}\left(v-V_{0}\right)-T_{0}\left(S-S_{0}\right)
$$

Similarly for an open system

$$
\not ¥=\left(\mathrm{H}-\mathrm{H}_{0}\right)-\mathrm{T}_{\mathrm{o}}\left(\mathrm{~S}-\mathrm{S}_{\mathrm{o}}\right)
$$

In steady flow system the exit condition 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 closed system

$$
\varnothing_{1}-\varnothing_{2}=\left(\mathrm{U}_{1}-\mathrm{U}_{2}\right)+\mathrm{P}_{0}\left(\mathrm{~V}_{1}-\mathrm{V}_{2}\right)-\mathrm{T}_{\mathrm{o}}\left(\mathrm{~S}_{1}-\mathrm{S}_{2}\right)
$$

For an open system

$$
¥_{1}-\not ¥_{2}=\left(\mathrm{H}_{1}-\mathrm{H}_{2}\right)-\mathrm{T}_{0}\left(\mathrm{~S}_{1}-\mathrm{S}_{2}\right)
$$

## IRREVERSIBILITY:

In thermodynamics, a change in the thermodynamic state of a system and all of its surroundings cannot be precisely restored to its initial state by infinitesimal changes in some property of the system without expenditure of energy. A system that undergoes an irreversible process may still be capable of returning to its initial state; however, the impossibility occurs in restoring the environment to its own initial conditions. An irreversible process increases the entropy of the universe. However, because entropy is a state function, the change in entropy of the system is the same whether the process is reversible or irreversible. The second law of thermodynamics can be used to determine whether a process is reversible or not

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

$$
\mathrm{I}=\mathrm{W}_{\max }-\mathrm{W}
$$

This is also some time referred to as degradiate or dissipation. For a non-flow process between the equilibrium states, when the system exchanges heat only with the environment.
$\mathrm{I}=\left[\left(\mathrm{U}_{1}-\mathrm{U}_{2}\right)-\mathrm{To}\left(\mathrm{S}_{1}-\mathrm{S}_{2}\right)\right]-\left[\left(\mathrm{U}_{1}-\mathrm{U}_{2}\right)+\mathrm{Q}\right]$

$$
=\left[\mathrm{T}_{0}\left(\mathrm{~S}_{2}-\mathrm{S}_{1}\right)-\mathrm{Q}\right]
$$

$$
=\mathrm{T}_{0}(\Delta \mathrm{~S})_{\text {system }}+\mathrm{T}_{0}(\Delta \mathrm{~S})_{\text {surrounding }}
$$

$$
=T_{0}\left[(\Delta \mathrm{~S})_{\text {system }}+\mathrm{T}_{0}(\Delta \mathrm{~S})_{\text {surrounding }}\right]=\mathrm{T}_{0}(\Delta \mathrm{~S})_{\text {universe }}
$$

Similarly, for the steady flow process

$$
\mathrm{I}=\mathrm{W}_{\max }-\mathrm{W}
$$

$$
=T_{0}\left(S_{2}-S_{1}\right)-Q
$$

$=T_{0}(\Delta S)_{\text {system }}+T_{0}(\Delta S)_{\text {surrounding }}$

$$
=T_{0}\left[(\Delta S)_{\text {system }}+\mathrm{T}_{0}(\Delta \mathrm{~S})_{\text {surrounding] }}=\mathrm{T}_{0}(\Delta \mathrm{~S})\right. \text { universe }
$$

The same expression for irreversibility applies to both flow \& non - flow process.

## REVERSIBLE FOR IN STEADY FLOW PROCESS:

Let us consider and open system exchange energy only with the surrounding at constant temperature $T_{o}$ and at constant pressure $\mathrm{P}_{\mathrm{o}}$. A mass $\mathrm{d}_{\mathrm{m} 1}$ enters the system at state 1 , a mass $d_{m 2}$ leaves the system at sate 2 , an account of heat $d Q$ is absorbed by the system an amount of work dw is delivered by the system, and the energy of the system changes by an amount $d(E) \sigma$ applying the first law, wehave,


For a steady flow process
and

$$
\begin{aligned}
& \mathrm{d} m_{1}=\mathrm{d} m_{2}=\mathrm{d} m \\
& \mathrm{~d}\left[U-T_{0} S+\frac{m V^{2}}{2}+m g z\right]_{\sigma}=0
\end{aligned}
$$

Equation (8.24) reduces to

$$
₫ W_{\max }=\mathrm{d} m\left[\left(h_{1}-T_{0} s_{1}+\frac{V_{1}^{2}}{2}+g z_{1}\right)-\left(h_{2}-T_{0} s_{2}+\frac{V_{2}^{2}}{2}+g z_{2}\right)\right]
$$

For total mass flow, the integral form of Eq. (8.25) becomes

$$
W_{\max }=\left(H_{1}-T_{0} S_{1}+\frac{m \mathbf{V}_{1}^{2}}{2}+m g z_{1}\right)-\left(H_{2}-T_{0} S_{2}+\frac{m \mathbf{V}_{2}^{2}}{2}+m g z_{2}\right)
$$

The expression ( $H-T_{0} S$ ) is called the Keenan function, B.

$$
\begin{aligned}
\therefore \quad W_{\max }=\left(B_{1}+\frac{m \mathbf{V}_{1}^{2}}{2}+\right. & \left.m g z_{1}\right)-\left(B_{2}+\frac{m \mathbf{V}_{2}^{2}}{2}+m g z_{2}\right) \\
& =\psi_{1}-\psi_{2}
\end{aligned}
$$

where $\psi$ is called the availability function of a steady flow process given by

$$
\psi=B+\frac{m \mathbf{V}^{2}}{2}+m g z
$$

On a unit mass basis,

$$
\begin{aligned}
W_{\max }= & \left(h_{1}-T_{0} s_{1}+\frac{\mathbf{V}_{1}^{2}}{2}+g z_{1}\right)-\left(h_{2}-T_{0} s_{2}+\frac{\mathbf{V}_{2}^{2}}{2}+g z_{2}\right) \\
& =\left(b_{1}+\frac{\mathbf{V}_{1}^{2}}{2}+g z_{1}\right)-\left(b_{2}+\frac{\mathbf{V}_{2}^{2}}{2}+g z_{2}\right)
\end{aligned}
$$

If K.E. and P.E. changes are neglected

$$
\begin{aligned}
W_{\max } & =B_{1}-B_{2} \\
& =\left(H_{1}-T_{0} S_{1}\right)-\left(H_{2}-T_{0} S_{2}\right) \\
& =\left(H_{1}-H_{2}\right)-T_{0}\left(S_{1}-S_{2}\right)
\end{aligned}
$$

## REVERSIBLE WORK IN A CLOSED SYSTEM:

$$
\begin{aligned}
\mathrm{d} m_{1} & =\mathrm{d} m_{2}=0 \\
\mathrm{~d} W_{\max } & =-\mathrm{d}\left[U-T_{0} S+\frac{m V^{2}}{2}+m g z\right]_{\sigma} \\
& =-\mathrm{d}\left(E-T_{0} S\right)_{\sigma}
\end{aligned}
$$

where

$$
E=U+\frac{m \mathbf{V}^{2}}{2}+m g z
$$

For a change of state of the system from the initial state 1 to the final state 2,

$$
\begin{aligned}
W_{\max } & =E_{1}-E_{2}-T_{0}\left(S_{1}-S_{2}\right) \\
& =\left(E_{1}-T_{0} S_{1}\right)-\left(E_{2}-T_{0} S_{2}\right)
\end{aligned}
$$

If the K.E. and P.E. changes are neglected, Eq. (8.31) reduces to

$$
W_{\max }=\left(U_{1}-T_{0} S_{1}\right)-\left(U_{2}-T_{0} S_{2}\right)
$$

For unit mass of fluid,

$$
\begin{aligned}
W_{\max } & =\left(u_{1}-u_{2}\right)-T_{0}\left(s_{1}-s_{2}\right) \\
& =\left(u_{1}-T_{0} s_{1}\right)-\left(u_{2}-T_{0} s_{2}\right)
\end{aligned}
$$

## USEFUL WORK:

All of the work w of the system would not be available for delivery, since a certain portion of it would be spent in pushing out the atmosphere. The useful work is defind as the actual work delivered by a system less the work performed on the atmosphere if $\mathrm{V}_{1}$ and $V_{2}$ are the initial and final volumes of the system and $P_{0}$ is the atmospheric pressure, then the work done on the atmosphere is $\mathrm{P}_{\mathrm{o}}\left(\mathrm{V}_{2}-\mathrm{V}_{1}\right)$. therefore , the useful work $\mathrm{W}_{\mathrm{u}}$ becomes

$$
W_{u}=W_{\mathrm{act}}-P_{\mathrm{o}}\left(\mathrm{~V}_{2}-\mathrm{V}_{1}\right)
$$



Work done by a closed system in pushing out the atmosphere

Similarly, the maximum useful work will be

$$
\left(W_{u}\right)_{\max }=W_{\max }-p_{0}\left(V_{2}-V_{1}\right)
$$

In differential form

$$
\left(\mathrm{d} W_{0}\right)_{\max }=\mathrm{d} W_{\max }-p_{0} \mathrm{~d} V
$$

In a steady flow system, the volume of the system does not change. Hence, the maximum useful work would remain the same, i.e., no work is done on the atmosphere, or

$$
\left(đ W_{w}\right)_{\max }=\mathrm{d} W_{\max }
$$

But in the case of an unsteady-flow open system or a closed system, the volume of the system changes. Hence, when a system exchanges heat only with the atmosphere, the maximum useful work becomes

$$
\left(\varangle W_{u}\right)_{\max }=\varangle W_{\max }-p_{0} \mathrm{~d} V
$$

Substituting $\mathrm{d} W_{\max }$ from Eq.

$$
\begin{aligned}
\left(\mathrm{d} W_{\mathrm{v}}\right)_{\max }= & \mathrm{d} m_{1}\left(h_{1}-T_{0} s_{1}+\frac{\mathrm{V}_{1}^{2}}{2}+g z_{1}\right)-\mathrm{d} m_{2}\left(h_{2}-T_{0} s_{2}+\frac{\mathbf{V}_{2}^{2}}{2}+g z_{2}\right) \\
& -\mathrm{d}\left[U+p_{0} V-T_{0} S+\frac{m \mathrm{~V}^{2}}{2}+m g z\right]_{\sigma}
\end{aligned}
$$

This is the maximum useful work for an unsteady open system.
For the closed system

$$
\begin{aligned}
\left(\mathrm{d} W_{v}\right)_{\max } & =-\mathrm{d}\left[U+p_{0} V-T_{0} S+\frac{m \mathrm{~V}^{2}}{2}+m g z\right]_{\sigma} \\
& =-\mathrm{d}\left[E+p_{0} V-T_{0} S\right]_{\sigma} \\
\therefore \quad\left(W_{u}\right)_{\max } & =E_{1}-E_{2}+p_{0}\left(V_{1}-V_{2}\right)-T_{0}\left(S_{1}-S_{2}\right)
\end{aligned}
$$

If K.E. and P.E. changes are neglected

$$
\left(W_{0}\right)_{\max }=U_{1}-U_{2}+p_{0}\left(V_{1}-V_{2}\right)-T_{0}\left(S_{1}-S_{2}\right)
$$

This can also be written in the following form

$$
\begin{aligned}
\left(W_{0}\right)_{\max } & =\left(U_{1}+p_{0} V_{1}-T_{0} S_{1}\right)-\left(U_{2}+p_{0} V_{2}-T_{0} S_{2}\right) \\
& =\phi_{1}-\phi_{2}
\end{aligned}
$$

where $\phi$ is called the availability function for a closed system given by

$$
\phi=U+p_{0} V-T_{0} S
$$

The useful work per unit mass becomes

$$
\left(W_{u}\right)_{\max }=\left(u_{1}+p_{0} v_{1}-T_{0} s_{1}\right)-\left(u_{2}+p_{0} v_{2}-T_{0} s_{2}\right)
$$

## EXERGY BALCNE OF CLOSED AND OPEN SYSTEM:

## CLOSED SYSTEM:

For a closed system, availability or exergy transfer occurs through heat and worl interactions


Exergy balance for a closed system

1st law:

$$
E_{2}-E_{1}=\int_{1}^{2} ₫ Q-W_{1-2}
$$

2nd law:

$$
S_{2}-S_{1}-\int_{1}^{2}\left[\frac{d Q}{T}\right]=S_{\mathrm{gen}}
$$

$$
\text { or } \quad T_{0}\left(S_{2}-S_{1}\right)-T_{0} \int_{1}^{2}\left[\frac{\mathrm{~d} Q}{T}\right]_{\sigma}=T_{0} S_{\mathrm{gen}}
$$

Subtracting

$$
\begin{aligned}
E_{2}-E_{1}-T_{0}\left(S_{2}-S_{1}\right) & =\int_{1}^{2} \mathrm{~d} Q-W_{1-2}-T_{0} \int_{1}^{2}\left[\frac{\mathrm{~d} Q}{T}\right]-T_{0} S_{\mathrm{gen}} \\
& =\int_{1}^{2}\left[1-\frac{T_{0}}{T_{\sigma}}\right] d Q-W_{1-2}-T_{0} S_{\mathrm{gen}}
\end{aligned}
$$

Since,

$$
\begin{aligned}
& A_{2}-A_{1}=E_{2}-E_{1}+p_{0}\left(V_{2}-V_{1}\right)-T_{0}\left(S_{2}-S_{1}\right) \\
& A_{2}-A_{1}=\int_{1}^{2}\left(1-\frac{T_{0}}{T_{\sigma}}\right) d Q-\left[W_{1-2}-p_{0}\left(V_{2}-V_{1}\right)\right]-T_{0} S_{\text {gen }} \\
& \begin{array}{c}
\text { Change } \\
\text { in exergy }
\end{array} \\
& \begin{array}{c}
\text { Exergy transfer } \\
\text { with heat }
\end{array} \\
& \begin{array}{c}
\text { Exergy transfer } \\
\text { with work }
\end{array}
\end{aligned} \begin{gathered}
\text { Exergy } \\
\text { destruction }
\end{gathered}
$$

## OPENSYSTEM:

1st law:

$$
\begin{aligned}
& H_{1}+\frac{m V_{1}^{2}}{2}+m g Z_{1}+Q_{1-2} \\
= & H_{2}+\frac{m V_{2}^{2}}{2}+m g Z_{2}+W_{1-2}
\end{aligned}
$$

2nd law:

$$
S_{1}+\int_{1}^{2}\left(\frac{\mathrm{dQ}}{T}\right)-S_{2}=S_{\mathrm{gen}}
$$

or

$$
T_{0}\left(S_{1}-S_{2}\right)+T_{0} \int_{1}^{2}\left(\frac{\mathrm{~d} Q}{T}\right)_{\sigma}=T_{0} S_{\mathrm{gen}}=I
$$



> Exergy balance for a steady flow system

From Eqs

$$
\begin{gathered}
H_{2}-H_{1}-T_{0}\left(S_{2}-S_{1}\right)+m \frac{V_{2}^{2}-V_{1}^{2}}{2}+m g\left(Z_{2}-Z_{1}\right) \\
=\int_{1}^{2}\left(1-\frac{T_{0}}{T_{\sigma}}\right) \mathrm{d} Q-W_{1-2}-I \\
A_{2}-A_{1}=\int_{1}^{2}\left(1-\frac{T_{0}}{T_{\sigma}}\right) \mathrm{d} Q-W_{1-2}-I
\end{gathered}
$$

In the form of rate equation at steady state:

$$
\sum_{\mathrm{j}}\left(1-\frac{T_{0}}{T_{\mathrm{j}}}\right) \dot{Q}_{\mathrm{j}}-\dot{W}_{\mathrm{C} . \mathrm{V} .}+\dot{m}\left(a_{\mathrm{f}_{1}}-a_{\mathrm{f}_{2}}\right)-\dot{I}_{\mathrm{C} . \mathrm{v}}=0
$$

where $a_{\mathrm{f}_{1}}-a_{\mathrm{f}_{2}}=\left(h_{1}-h_{2}\right)-T_{0}\left(s_{1}-s_{2}\right)+\frac{V_{1}^{2}-V_{2}^{2}}{2}+g\left(Z_{1}-Z_{2}\right)$ and $\left[1-T_{0} / T_{j}\right] \dot{Q}_{j}$
= time rate of exergy transfer along with heat $\dot{Q}_{\mathrm{j}}$ occurring at the location on the boundary where the instantaneous temperature is $T_{\mathrm{j}}$.

For a single stream entering and leaving, the exergy balance gives

$$
\left[1-\frac{T_{0}}{T_{\sigma}}\right] \frac{\dot{Q}}{\dot{m}}+a_{\mathrm{f}_{1}}-\frac{\dot{W}}{\dot{m}}-a_{\mathrm{f}_{2}}=\frac{\dot{I}}{\dot{m}}
$$

Exergy in Exergy out Exergy loss

## SECOND LAW EFFICIENCIES OF THERMAL EQUIPMENTS:

## 1. TURBINE:

The steady state exergy balance gives:

$$
\frac{\dot{\mathrm{q}}}{\dot{\mathrm{~m}}}\left[1-\frac{\mathrm{T}_{\mathrm{O}}}{\mathrm{~T}_{\sigma}}\right]+\mathrm{a}_{\mathrm{f} 1}=\frac{\dot{\mathrm{W}}}{\dot{\mathrm{~m}}}+\mathrm{a}_{\mathrm{f} 2}+\frac{\dot{\mathrm{I}}}{\dot{\mathrm{~m}}}
$$



If there is no heat loss,

$$
\mathrm{af}_{1}-\mathrm{af}_{2}=\frac{\dot{\mathrm{W}}}{\dot{\mathrm{~m}}}+\frac{\dot{\mathrm{I}}}{\dot{\mathrm{~m}}}
$$

the second law efficiency,

$$
\eta_{I I}=\frac{w \dot{m}}{a f_{1}-a_{f 2}}
$$

## 2.COMPRESSOR AND PUMP:

Similarly for a compressor or pump,

$$
\frac{\dot{\mathrm{w}}}{\dot{\mathrm{~m}}}=\mathrm{af}_{1}-\mathrm{af}_{2}+\frac{\dot{\mathrm{I}}}{\dot{\mathrm{~m}}}
$$

And

$$
\eta_{I I}=\frac{a_{f 2}-a_{f 1}}{-w / \dot{m}}
$$

## PROBLEMS:

Calculate the decrease in available energy when 25 kg of water at $95^{\circ} \mathrm{C}$ mix with 35 kg of water at $35^{\circ} \mathrm{C}$, the pressure being taken as constant and the temperature of the surroundings being $15^{\circ} \mathrm{C}\left(c_{\mathrm{p}}\right.$ of water $\left.=4.2 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}\right)$.
Solution The available energy of a system of mass $m$, specific heat $c_{p}$, and at temperature $T$, is given by
A.E. $=m c_{\mathrm{p}} \int_{\mathrm{T}_{0}}^{\mathrm{T}}\left(1-\frac{T_{0}}{T}\right) \mathrm{d} T$
$\therefore \quad(\text { A.E. })_{25}=$ Available energy of 25 kg of water at $95^{\circ} \mathrm{C}$

$$
\begin{aligned}
& =25 \times 4.2 \int_{273+15}^{273+95}\left(1-\frac{288}{T}\right) \mathrm{d} T \\
& =105\left[(368-288)-288 \ln \frac{368}{288}\right] \\
& =987.49 \mathrm{~kJ}
\end{aligned}
$$

$(\text { A.E. })_{35}=$ Available energy of 35 kg of water at $35^{\circ} \mathrm{C}$
$=147\left[(308-288)-288 \ln \frac{308}{288}\right]$
$=97.59 \mathrm{~kJ}$
Total available energy

$$
\begin{aligned}
(\text { A.E. })_{\text {total }} & =(\text { A.E. })_{25}+(\text { A.E. })_{35} \\
& =987.49+97.59 \\
& =1085.08 \mathrm{~kJ}
\end{aligned}
$$

After mixing, if $t$ is the final temperature

$$
25 \times 4.2(95-t)=35 \times 4.2(t-35)
$$

$$
\therefore \quad t=\frac{25 \times 95 \times 35 \times 35}{25+35}
$$

$$
=60^{\circ} \mathrm{C}
$$

Total mass after mixing $=25+35=60 \mathrm{~kg}$
(A.E.) $)_{60}=$ Available energy of 60 kg of water at $60^{\circ} \mathrm{C}$

$$
\begin{aligned}
& =4.2 \times 60\left[(333-288)-288 \ln \frac{333}{288}\right] \\
& =803.27 \mathrm{~kJ}
\end{aligned}
$$

$\therefore$ Decrease in available energy due to mixing

$$
\begin{aligned}
= & \text { Total available energy before mixing } \\
& - \text { Total available energy after mixing } \\
= & 1085.08-803.27 \\
= & 281.81 \mathrm{~kJ}
\end{aligned}
$$

Ans.
2. The moment of inertia of a flywheel is $0.54 \mathrm{~kg} \cdot \mathrm{~m}^{2}$ and it rotates at a speed 3000 RPM in a large heat insulated system, the temperature of which is $15^{\circ} \mathrm{C}$. If the kinetic energy of the flywheel is dissipated as frictional heat at the shaft bearings which have a water equivalent of 2 kg , find the rise in the temperature of the bearings when the flywheel has come to rest. Calculate the greatest possible amount of this heat which may be returned to the flywheel as high-grade energy, showing how much of the original kinetic energy is now unavailable. What would be the final RPM of the flywheel, if it is set in motion with this available energy?
Solution Initial angular velocity of the flywheel

$$
\omega_{1}=\frac{2 \pi N_{1}}{60}=\frac{2 \pi \times 3000}{60}=314.2 \mathrm{rad} / \mathrm{s}
$$

Initial available energy of the flywheel

$$
\begin{aligned}
& =(\text { K.E. })_{\text {initial }}=\frac{1}{2} I \omega_{1}^{2} \\
& =0.54 \mathrm{~kg} \mathrm{~m}^{2} \times(314.2)^{2} \frac{\mathrm{rad}^{2}}{\mathrm{~s}^{2}} \\
& =2.66 \times 10^{4} \mathrm{Nm}=26.6 \mathrm{~kJ}
\end{aligned}
$$

When this K.E. is dissipated as frictional heat, if $\Delta t$ is the temperature rise of the bearings, we have
water equivalent of the bearings $\times$ rise in temperature $=26.6 \mathrm{~kJ}$

$$
\therefore \quad \Delta t=\frac{26.6}{2 \times 4.187}=3.19^{\circ} \mathrm{C}
$$

Ans.

## $\therefore$ Final temperature of the bearings

$$
t_{f}=15+3.19=18.19^{\circ} \mathrm{C}
$$

The maximum amount of energy which may be returned to the flywheel as high-grade energy is

$$
\begin{aligned}
\text { A.E. } & =2 \times 4.187 \int_{288}^{291.19}\left(1-\frac{288}{T}\right) \mathrm{d} T \\
& =2 \times 4.187\left[(291.19-288)-288 \ln \frac{291.19}{288}\right] \\
& =0.1459 \mathrm{~kJ}
\end{aligned}
$$

The amount of energy rendered unavailable is

$$
\begin{aligned}
\text { U.E. } & =(\text { A.E. })_{\text {initiail }}-(\text { A.E. })_{\text {retumable as high energy }} \\
& =26.6-0.1459 \\
& =26.4541 \mathrm{~kJ}
\end{aligned}
$$

Since the amount of energy returnable to the flywheel is 0.146 kJ , if $\omega_{2}$ is the final angular velocity, and the flywheel is set in motion with this energy

$$
\begin{array}{ll} 
& 0.146 \times 10^{3}=\frac{1}{2} \times 0.54 \omega_{2}^{2} \\
\therefore & \omega_{2}^{2}=\frac{146}{0.27}=540.8 \\
\therefore & \omega_{2}=23.246 \mathrm{rad} / \mathrm{s}
\end{array}
$$

If $N_{2}$ is the final RPM of the flywheel
or

$$
\begin{aligned}
& \omega_{2}=23.246=\frac{2 \pi N_{2}}{60} \\
& N_{2}=\frac{23.246 \times 60}{2 \times \pi}=222 \mathrm{RPM}
\end{aligned}
$$

Ans.
3. Two kg of air at $500 \mathrm{kPa}, 80^{\circ} \mathrm{C}$ expands adiabatically in a closed system until its volume is doubled and its temperature becomes equal to that of the surroundings which is at $100 \mathrm{kPa}, 5^{\circ} \mathrm{C}$. For this process, determine (a) the maximum work, (b) the change in availability, and (c) the irreversibility. For air, take $c_{\mathrm{v}}=0.718 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}, u=c_{\mathrm{v}} T$ where $c_{\mathrm{v}}$ is constant, and $p V=m R T$ where $p$ is pressure in $\mathrm{kPa}, V$ volume in $\mathrm{m}^{3}, m$ mass in $\mathrm{kg}, R$ a constant equal to $0.287 \mathrm{~kJ} / \mathrm{kg}$ K , and $T$ temperature in K .
Solution From the property relation

$$
T \mathrm{~d} S=\mathrm{d} U+p \mathrm{~d} V
$$

the entropy change of air between the initial and final states is

$$
\int_{1}^{2} \mathrm{~d} S=\int_{1}^{2} \frac{m c_{\mathrm{v}} \mathrm{~d} T}{T}+\int_{1}^{2} \frac{m R \mathrm{~d} V}{V}
$$

or

$$
S_{2}-S_{1}=m c_{v} \ln \frac{T_{2}}{T_{1}}+m R \ln \frac{V_{2}}{V_{1}}
$$

From Eq.

$$
\begin{aligned}
W_{\max } & =\left(U_{1}-U_{2}\right)-T_{0}\left(S_{1}-S_{2}\right) \\
& =m\left[c_{\mathrm{v}}\left(T_{1}-T_{2}\right)+T_{0}\left(c_{\mathrm{v}} \ln \frac{T_{2}}{T_{1}}+R \ln \frac{V_{2}}{V_{1}}\right)\right] \\
& =2\left[0.718(80-5)+278\left(0.718 \ln \frac{278}{353}+0.287 \ln \frac{2}{1}\right]\right. \\
& =2[53.85+278(-0.172+0.199)] \\
& =2(53.85+7.51)
\end{aligned}
$$

$$
=122.72 \mathrm{~kJ}
$$

Ans. (a)
From Eq the change in availability

$$
\begin{aligned}
& =\phi_{1}-\phi_{2} \\
& =\left(U_{1}-U_{2}\right)-T_{0}\left(S_{1}-S_{2}\right)+p_{0}\left(V_{1}-V_{2}\right) \\
& =W_{\max }+p_{0}\left(V_{1}-V_{2}\right) \\
& =122.72+p_{0}\left(V_{1}-2 V_{1}\right) \\
& =122.72-100 \times \frac{2 \times 0.287 \times 353}{500} \\
& =82.2 \mathrm{~kJ}
\end{aligned}
$$

Ans. (b)
The irreversibility

$$
I=W_{\text {max, useful }}-W_{\text {act }}
$$

From the first law,

$$
\begin{aligned}
\quad W_{\text {act }} & =Q-\Delta U=-\Delta U=U_{1}-U_{2} \\
I & =U_{1}-U_{2}-T_{0}\left(S_{1}-S_{2}\right)-U_{1}+U_{2} \\
& =T_{0}\left(S_{2}-S_{1}\right) \\
& =T_{0}(\Delta S)_{\text {system }}
\end{aligned}
$$

For adiabatic process, $(\Delta S)_{\text {sur }}=0$

$$
\begin{aligned}
I & =T_{0}\left[m c_{\mathrm{v}} \ln \frac{T_{2}}{T_{1}}+m R \ln \frac{V_{2}}{V_{1}}\right] \\
& =278 \times 2\left[0.718 \ln \frac{278}{353}+0.287 \ln 2\right] \\
& =278 \times 2(-0.172+0.199) \\
& =15.2 \mathrm{~kJ}
\end{aligned}
$$

Ans. (c)
4. Air expands through a turbine from $500 \mathrm{kPa}, 520^{\circ} \mathrm{C}$ to 100 kPa , $300^{\circ} \mathrm{C}$. During expansion $10 \mathrm{~kJ} / \mathrm{kg}$ of heat is lost to the surroundings which is at $98 \mathrm{kPa}, 20^{\circ} \mathrm{C}$. Neglecting the K.E. and P.E. changes, determine per kg of air (a) the decrease in availability, (b) the maximum work, and (c) the irreversibility.

For air, take $c_{\mathrm{p}}=1.005 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}, h=c_{\mathrm{p}} T$ where $c_{\mathrm{p}}$ is constant, and the $p, V$ and $T$ relation
Solution From the property relation

$$
T \mathrm{~d} S=\mathrm{d} H-V \mathrm{~d} p
$$

the entropy change of air in the expansion process is
or

$$
\int_{1}^{2} \mathrm{~d} S=\int_{1}^{2} \frac{m c_{\mathrm{p}} \mathrm{~d} T}{T}-\int_{1}^{2} \frac{m R \mathrm{~d} p}{p}
$$

$$
S_{2}-S_{1}=m c_{\mathrm{p}} \ln \frac{T_{2}}{T_{1}}-m R \ln \frac{p_{2}}{p_{1}}
$$

For 1 kg of air,

$$
s_{2}-s_{1}=c_{p} \ln \frac{T_{2}}{T_{1}}-R \ln \frac{p_{2}}{p_{1}}
$$

From Eq. the change in availability

$$
\begin{aligned}
\psi_{1}-\psi_{2} & =b_{1}-b_{2} \\
& =\left(h_{1}-T_{0} s_{1}\right)-\left(h_{2}-T_{0} s_{2}\right) \\
& =\left(h_{1}-h_{2}\right)-T_{0}\left(s_{1}-s_{2}\right) \\
& =c_{\mathrm{p}}\left(T_{1}-T_{2}\right)-T_{0}\left(R \ln \frac{p_{2}}{p_{1}}-c_{\mathrm{p}} \ln \frac{T_{2}}{T_{1}}\right) \\
& =1.005(520-300)-293\left(0.287 \ln \frac{1}{5}-1.005 \ln \frac{573}{793}\right) \\
& =1.005 \times 220-293(0.3267-0.4619) \\
& =221.1+39.6 \\
& =260.7 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

The maximum work is

$$
\begin{aligned}
W_{\max } & =\text { change in availability }=\psi_{1}-\psi_{2} \\
& =260.7 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

Ans. (b)
From S.F.E.E.,

$$
\begin{aligned}
Q+h_{1} & =W+h_{2} \\
W & =\left(h_{1}-h_{2}\right)+Q \\
& =c_{p}\left(T_{1}-T_{2}\right)+Q \\
& =1.005(520-300)-10 \\
& =211.1 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

The irreversibility

$$
\begin{aligned}
I & =W_{\max }-W \\
& =260.7-211.1 \\
& =49.6 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

Ans. (c)
Alternatively,

$$
\begin{aligned}
I & =T_{0}\left(\Delta S_{\text {system }}+\Delta S_{\text {surr }}\right) \\
& =293\left[1.005 \ln \frac{573}{793}-0.287 \ln \frac{1}{5}+\frac{10}{293}\right] \\
& =293 \times 0.1352+10 \\
& =49.6 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

5.An air preheater is used to cool the products of combustion from a furnace while heating the air to be used for combustion. The rate of flow of products is $12.5 \mathrm{~kg} / \mathrm{s}$ and the products are cooled from 300 to $200^{\circ} \mathrm{C}$, and for the products at this temperature $c_{\mathrm{p}}=1.09 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}$. The rate of air flow is $11.5 \mathrm{~kg} / \mathrm{s}$, the initial air temperature is $40^{\circ} \mathrm{C}$, and for the air $c_{\mathrm{p}}=1.005 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}$. (a) Estimate the initial and final availability of the products. (b) What is the irreversibility for the process? (c) If the heat transfer from the products occurs reversibly through heat engines, what is the final temperature of the air? What is the power developed by the heat engine? Take $T_{0}=300 \mathrm{~K}$ and neglect pressure drop for both the fluids and heat transfer to the surroundings.

## Solution

(a)

$$
\begin{aligned}
\psi_{1} & =\text { initial availability of the products } \\
& =\left(h_{1}-h_{0}\right)-T_{0}\left(S_{1}-S_{0}\right) \\
& =c_{\mathrm{p}_{\mathrm{g}}}\left(T_{\mathrm{g}_{1}}-T_{0}\right)-T_{0} c_{\mathrm{p}_{\mathrm{g}}} \ln \frac{T_{\mathrm{g}_{1}}}{T_{0}} \\
& =1.09(573-300)-300 \times 1.09 \ln \frac{573}{300} \\
& =297.57-211.6=39.68 \mathrm{~kJ} / \mathrm{kg} \\
\psi_{2} & =\text { final availability of the products } \\
& =\left(h_{2}-h_{0}\right)-T_{0}\left(s_{2}-s_{0}\right) \\
& =1.09(473-300)-300 \times 1.09 \ln \frac{473}{300} \\
& =188.57-148.89=39.68 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

(b) Decrease in availability of the products

$$
\begin{aligned}
& =\psi_{1}-\psi_{2} \\
& =\left(h_{1}-h_{2}\right)-T_{0}\left(s_{1}-s_{2}\right) \\
& =1.09(573-473)-300 \times 1.09 \ln \frac{573}{473} \\
& =109-62.72=46.28 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

By making an energy balance for the air preheater

$$
\begin{aligned}
\dot{m}_{\mathrm{g}} c_{\mathrm{p}_{2}}\left(T_{\mathrm{g}_{1}}-T_{\mathrm{g}_{2}}\right) & =\dot{m}_{\mathrm{a}} c_{\mathrm{p}_{4}}\left(T_{\mathrm{a}_{2}}-T_{\mathrm{a}_{1}}\right) \\
12.5 \times 1.09(573-473) & =11.15 \times 1.005\left(T_{\mathrm{a}_{2}}-313\right) \\
\therefore \quad T_{\mathrm{a}_{2}} & =\frac{12.5 \times 109}{11.5 \times 1.005}+313=430.89 \mathrm{~K}
\end{aligned}
$$

Increase in availability for air

$$
\begin{aligned}
& =\psi_{2}-\psi_{1} \\
& =\left(h_{2}-h_{1}\right)-T_{0}\left(s_{2}-s_{1}\right)
\end{aligned}
$$

Products of Combustion


$$
\begin{aligned}
& =c_{\mathrm{p}_{4}}\left(T_{\mathrm{a}_{2}}-T_{\mathrm{a}_{1}}\right)-T_{0} c_{\mathrm{p}_{4}} \ln \frac{T_{\mathrm{a}_{2}}}{T_{\mathrm{a}_{1}}} \\
& =1.005 \times(430.89-313)-300 \times 1.005 \ln \frac{430.89}{313} \\
& =118.48-96.37=22.11 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

$\therefore$ Irreversibility of the process

$$
\begin{aligned}
& =12.5 \times 46.28-11.5 \times 22.11 \\
& =578.50-254.27 \\
& =324.23 \mathrm{~kW}
\end{aligned}
$$

(c) Let us assume that heat transfer from the products to air occurred through heat engines reversibly as shown in Fig. ${ }^{-}$


For reversible heat transfer,

$$
\begin{aligned}
\Delta \dot{S}_{\text {univ }} & =0 \\
\Delta \dot{S}_{\text {sys }}+\Delta \dot{S}_{\text {surr }} & =0 \\
\Delta \dot{S}_{\mathrm{gas}}+\Delta \dot{S}_{\text {air }} & =0 \\
\Delta \dot{S}_{\mathrm{gas}} & =-\Delta \dot{S}_{\text {air }} \\
\dot{m}_{\mathrm{g}} c_{\mathrm{p}_{\mathrm{g}}} \ln \frac{T_{\mathrm{g} 2}}{T_{\mathrm{g} 1}} & =-\dot{m}_{\mathrm{a}} c_{\mathrm{pas}} \ln \frac{T_{\mathrm{a} 2}}{T_{\mathrm{a} 1}}
\end{aligned}
$$

$$
12.5 \times 1.09 \ln \frac{473}{573}=-11.5 \times 1.005 \ln \frac{T_{\mathrm{n} 2}}{313}
$$

$$
\therefore \quad T_{\mathrm{a} 2}=392.41 \mathrm{~K}
$$

Rate of heat supply from the gas to the working fluid in the heat engine,

$$
\begin{aligned}
\dot{Q}_{1} & =\dot{m}_{\mathrm{g}} c_{\mathrm{p}_{\mathrm{g}}}\left(T_{\mathrm{g} 1}-T_{\mathrm{g}}\right) \\
& =12.5 \times 1.09(573-473) \\
& =1362.50 \mathrm{~kW}
\end{aligned}
$$

Rate of heat rejection from the working fluid in the heat engine to the air,

$$
\begin{aligned}
\dot{Q}_{2} & =\dot{m}_{\mathrm{a}} c_{\mathrm{p}_{\mathrm{a}}}\left(T_{\mathrm{n} 2}-T_{\mathrm{a}}\right) \\
& =11.5 \times 1.005(392.41-313) \\
& =917.78 \mathrm{~kW}
\end{aligned}
$$

Total power developed by the heat engine

$$
\begin{aligned}
\dot{W} & =\dot{Q}_{1}-\dot{Q}_{2}=1362.50-917.78 \\
& =444.72 \mathrm{~kW}
\end{aligned}
$$

## UNIT - IV

## OBJECTIVE:

To familiarize the students with the thermodynamics properties and its relations and uses of this thermodynamics relations

## HELM HOLTZ AND GIBBS FUNCTIONS:

The combination of properties (U-TS) is also a Thermodynamic properly. It is named as the Helmholtz function. It is denoted an A and a .

$$
\mathrm{A}=\mathrm{U}-\mathrm{TS} \quad \mathrm{a}=\mathrm{u}-\mathrm{Ts}
$$

Another combination of properties $(\mathrm{H}-\mathrm{Ts})$ is also a Thermodynamic property. It is named as Gibbs function. It is denoted as $G$ and $g$.

$$
\begin{array}{l|l|l}
\mathrm{G}=\mathrm{H}-\mathrm{TS} & \mathrm{~g}=\mathrm{h}-\mathrm{Ts}
\end{array}
$$

## Mathematical Conditions for Exact Differentials (Properties)

Properties are mathematically exact differentials. These are point functions and their differences between two points do not depend upon the path of integration.

Let $Z$ is function of two variables $x$ and $y$

$$
\begin{align*}
& \mathrm{Z}=\mathrm{Z}(\mathrm{x}, \mathrm{y}) \\
& \mathrm{dz}=\left(\frac{\partial z}{d x}\right)_{\mathrm{y}} \mathrm{dx}+\left(\frac{\partial z}{d y}\right)_{\mathrm{x}} \mathrm{dy}  \tag{1}\\
& \text { But }\left(\frac{\partial z}{d x}\right)_{\mathrm{y}=\mathrm{M}} \mathrm{M} \text { and } \mathrm{dx}+--\left(\frac{\partial z}{d y}\right)_{\mathrm{x}=\mathrm{N}} \mathrm{~N} .
\end{align*}
$$

Then Eq. (1) Becomes

$$
\begin{equation*}
d z=M d x+N d y \tag{2}
\end{equation*}
$$

If $x, y, z$ are all pint functions. Is there are state variable representing properties which do not depend on the path, then dx , dy and dz are exact differentials. Two mathematical conditions apply,
a) $\left(\frac{\partial m}{\partial y}\right)_{x}=\left(\frac{\partial n}{\partial x}\right)_{y}$
b) $\left(\frac{\partial x}{\partial y}\right)_{z}=\left(\frac{\partial y}{\partial z}\right)_{x}\left(\frac{\partial z}{\partial x}\right)_{y}=-1$

Among the variable $x, y$ and $z$, any one variable may be considered as a function of the other two

$$
\begin{align*}
& \mathrm{x}=\mathrm{x}(\mathrm{y}, \mathrm{z}) . \\
& \mathrm{dx}=\left(\frac{\partial x}{\partial y}\right)_{\mathrm{z}} \mathrm{dy}+\left(\frac{\partial y}{\partial z}\right)_{\mathrm{y}} \mathrm{dz}-  \tag{1}\\
& \mathrm{dz}=\left(\frac{\partial x}{\partial x}\right)_{\mathrm{z}} \mathrm{dx}+\left(\frac{\partial z}{\partial y}\right)_{\mathrm{x}} \mathrm{dy}- \tag{2}
\end{align*}
$$

From (1) \& (2)

$$
\begin{align*}
& \mathrm{dx}=\left(\frac{\partial x}{\partial y}\right)_{\mathrm{z}} \mathrm{dy}+\left(\frac{\partial z}{\partial z}\right)_{\mathrm{y}} \mathrm{dz}\left[\left(\frac{\partial z}{\partial x}\right)_{\mathrm{y}} \mathrm{dx}+\left(\frac{\partial z}{\partial x}\right)_{\mathrm{x}} \mathrm{dy}\right] \\
&=\left[\left(\frac{\partial x}{\partial y}\right)_{\mathrm{z}}+\left(\frac{\partial x}{\partial z}\right)_{\mathrm{y}}\left(\frac{\partial z}{\partial y}\right)_{\mathrm{x}}\right]_{\mathrm{dy}+}\left(\frac{\partial x}{\partial z}\right)_{\mathrm{y}}\left(\frac{\partial z}{\partial x}\right)_{\mathrm{y}} \mathrm{dx} \\
&=\left[\left(\frac{\partial x}{\partial y}\right)_{\mathrm{z}}+\left(\frac{\partial x}{\partial z}\right)_{\mathrm{y}}\left(\frac{\partial z}{\partial y}\right)_{\mathrm{x}}\right]_{\mathrm{dy}+\mathrm{dx}} \\
& \Rightarrow \quad\left(\frac{\partial x}{\partial y}\right)_{\mathrm{z}}+\left(\frac{\partial x}{\partial z}\right)_{\mathrm{y}}\left(\frac{\partial z}{\partial y}\right)_{\mathrm{x}}=0 \\
&(\mathrm{OR}) \\
&\left(\frac{\partial x}{\partial y}\right)_{\mathrm{z}}+\left(\frac{\partial z}{\partial x}\right)_{\mathrm{y}}\left(\frac{\partial y}{\partial z}\right)_{\mathrm{x}}=-1 \tag{3}
\end{align*}
$$

Among the thermodynamic variable $\mathrm{P}, \mathrm{V}$ and T , the following relation holds good

$$
\begin{equation*}
\left(\frac{\partial p}{\partial v}\right)_{\mathrm{z}}+\left(\frac{\partial v}{\partial T}\right)_{\mathrm{y}}\left(\frac{\partial T}{\partial P}\right)_{\mathrm{v}=-1} \tag{4}
\end{equation*}
$$

## Maxwell Relations:

Consider a simple compressible control mass of fixed chemical composition. The Maxwell relations, which can be written for such a system, are four equations relating the properties $\mathrm{P}, \mathrm{V}, \mathrm{T}$ and S .

The Maxwell relations are most easily derived by considering the different forms of the thermodynamic property relation.

$$
\begin{equation*}
\mathrm{du}=\mathrm{Tds}-\mathrm{pdv} \tag{1}
\end{equation*}
$$

and

$$
\begin{equation*}
d h=T d s+v d p \tag{2}
\end{equation*}
$$

The above expressions are of the form
$\mathrm{U}=\mu(\mathrm{s}, \mathrm{v}), \mathrm{h}=\mathrm{h}(\mathrm{s}, \mathrm{p})$ in both of which entropy is used as one of the two independent properties.

To eliminate entropy as an independent property by introducing two new properties and thereby two new forms of the thermodynamic property relations.

The first of there is the helmholtz function A,

$$
\begin{equation*}
A=U-T s, a=u-T s \tag{3}
\end{equation*}
$$

Differentiate eq (3) we get

$$
\begin{equation*}
d a=d u-T d s-s d T \tag{4}
\end{equation*}
$$

Put eqn (1) in (4) we get

$$
\begin{align*}
\Rightarrow d a & =T d / s-p d v-T d / s-s d T \\
& =-s d T-p d v \tag{5}
\end{align*}
$$

The above expression is a form of the property relation utilizing $T$ and $v$ as the independent properties.

The second new property is the Gibbs function G.

$$
\begin{equation*}
G=H-T S \quad, \quad g=h-T s \tag{6}
\end{equation*}
$$

Differentiate eq (2) we get

$$
\begin{equation*}
d g=d h-T d s-s d T \tag{7}
\end{equation*}
$$

put eq (7) in eq (2) we get

$$
\begin{align*}
\Rightarrow d g & =T d s+v d p-T d s-s d T \\
& =-s d T+v d p \tag{8}
\end{align*}
$$

Eq. (1), (2), (5), (8) all relations involving only properties. We conclude that these are exact differentials.

$$
d z=m d x+n d y
$$

The coefficient $M$ and $n$ are

$$
\left(\frac{\partial m}{\partial y}\right)_{x=}\left(\frac{\partial n}{\partial x}\right)_{y}
$$

## From

Eq.(1) we get

$$
\begin{equation*}
\left(\frac{\partial T}{\partial u}\right)_{s=-}\left(\frac{\partial p}{\partial s}\right)_{v} \tag{9}
\end{equation*}
$$

Eq.(2) we get

$$
\begin{equation*}
\left(\frac{\partial T}{\partial u}\right)_{\mathrm{s}=}\left(\frac{\partial v}{\partial s}\right)_{\mathrm{p}} \tag{10}
\end{equation*}
$$

Eq.(5) we get

$$
\begin{equation*}
\left(\frac{\partial p}{\partial T}\right)_{v=}\left(\frac{\partial v}{\partial s}\right)_{T} \tag{11}
\end{equation*}
$$

Eq.(8) we get

$$
\begin{equation*}
\left(\frac{\partial v}{\partial T}\right)_{\mathrm{P}=}\left(\frac{\partial s}{\partial p}\right)_{\mathrm{T}} \tag{12}
\end{equation*}
$$

These four equations are known as Maxwell relations for a simple compressible mass.

## Clausius Clapeyron Equation:

An important application of one of the Maxwell relations is in the derivation of the clapeyron equation. This equation relates the enthalpy of vaporization of a substance with the slope of its vapour pressure curve.

During phase transitions like melting, vaporization and sublimation the temperature and pressure remain constant while the entropy and volume changes. If $x$ is the fraction of initial phase $i$ which has been transformed into final phase $f$.

$$
\left.\begin{array}{c}
S=(1-x) s(i)+s(f) \\
V=(1-x) v(i)+v(f) \tag{9}
\end{array}\right\}
$$

where $s$ and $v$ are

Linear functions of x .

This is used to find the value of the property which is not measurable for pure substances. This equation provides a basis for calculation of properties in a two phase region.

Consider a change of phase of pure substances from saturated liquid to saturated vapour. During the vaporization process both temperature and pressure remains constant, but specific volume and entropy changes.

$$
\begin{align*}
& \mathrm{S}=\mathrm{f}(\mathrm{~T}, \mathrm{~V}) \\
& \Rightarrow \mathrm{ds}=\left(\frac{\partial s}{\partial T}\right)_{\mathrm{v}} \mathrm{dT}+\left(\frac{\partial s}{\partial v}\right)_{\mathrm{T}} \mathrm{dv} \tag{1}
\end{align*}
$$



## P-T diagram for a pure substance

When the phase is changing from saturated liquid to Sat.vapour, temperature relations const.

Eq. (1) becomes.

$$
\begin{equation*}
\mathrm{ds}=\left(\frac{\partial s}{\partial v}\right)_{\mathrm{v}} \mathrm{dT} \tag{2}
\end{equation*}
$$

From Maxwell equation gives.

$$
\begin{equation*}
\left(\frac{\partial s}{\partial v}\right)_{\mathrm{T}=}\left(\frac{\partial p}{\partial T}\right)_{v} \tag{3}
\end{equation*}
$$

Put (3) in (2) we get

$$
\begin{equation*}
\Rightarrow \quad d s=\left(\frac{\partial p}{\partial t}\right)_{v} d v \tag{4}
\end{equation*}
$$

$\left(\frac{\partial p}{\partial T}\right)$ is the slope of the saturation curve.
During a phase change process, the pressure is a sat. Pressure which depends on temperature ( T ) only and independent of specific volume (v)

Integrating the eq.(4) we get

$$
\begin{align*}
\int_{s f}^{s g} d s & =\frac{\partial p}{\partial t} \int_{v f}^{v g} d v \\
\mathrm{sg}-\mathrm{sf} & =\frac{d p}{d T} \quad(\mathrm{vg}-\mathrm{vf}) \\
\Rightarrow \quad \frac{d p}{d T} & =\frac{s g-s f}{v g-v f} \\
\Rightarrow \quad & \frac{d p}{d T} \tag{5}
\end{align*}
$$

From second law of thermodynamics.

$$
\begin{align*}
\mathrm{ds} & =\frac{d Q}{T} \\
\Rightarrow \quad \mathrm{ds} & =\frac{d H}{T} \tag{6}
\end{align*}
$$

but $\mathrm{dQ}=\mathrm{dH}$ for const. press. process.
$\qquad$

Integrating we get

$$
\begin{align*}
& \int_{\mathrm{sf}}^{\mathrm{sg}} \mathrm{ds}=\int_{\mathrm{hf}}^{\mathrm{hg}} \frac{\mathrm{dH}}{\mathrm{~T}} \\
& \mathrm{sg}-\mathrm{sf}=\frac{1}{\pi}[\mathrm{hg}-\mathrm{hf}] \\
& \mathrm{sfg}=\frac{\mathrm{hfg}}{T} \tag{7}
\end{align*}
$$

put eq (7) in (5)

$$
\begin{equation*}
\left(\frac{\partial \mathbf{p}}{\partial \mathrm{T}}\right)_{\text {sat }}=\frac{\mathbf{h f g}}{\mathrm{Tvfg}} \tag{8}
\end{equation*}
$$

The above equation is known as clapeyron equation. This equation can be used to determine the enthalpy of evaporation at a given temp if the slope of the saturation curve on a put diagram for the given fluid is known.

For very low pressure, $\mathrm{u} f$ is very small

$$
\mathrm{vf} \ll \mathrm{vg}
$$

Eq.(8) $=>\left(\frac{\mathrm{dp}}{\mathrm{dT}}\right)_{\text {sat }}=\frac{\mathrm{hfg}}{\mathrm{Tvfg}}$

$$
\begin{gather*}
\Rightarrow\left(\frac{\mathrm{dp}}{\mathrm{dT}}\right)_{\text {sat }}=\frac{\mathrm{hg}-\mathrm{hf}}{\mathrm{~T}(\mathrm{vg}-\mathbf{v f})} \\
\mathrm{Vf}=0 \\
\Rightarrow\left(\frac{\mathrm{dp}}{\mathrm{dT}}\right)_{\text {sat }}=\frac{\mathrm{hg}-\mathbf{h f}}{\mathrm{Tvg}} \tag{9}
\end{gather*}
$$

For ideal gas $\mathrm{pv}=\mathrm{RT}$

$$
\begin{align*}
\mathrm{V} & =\frac{R T}{p} \\
\Rightarrow \quad \mathrm{Vg} & =\frac{R T}{p} \tag{10}
\end{align*}
$$

Put (10) in (9)
(9) $\quad=>\left(\frac{d p}{d T}\right)_{\text {sat }}=\left(\frac{\mathrm{hg}-\mathbf{h f}}{\frac{\mathrm{RT}}{\mathrm{P}}}\right) \frac{\mathbf{1}}{\mathbf{T}}$

$$
\begin{gather*}
\frac{\mathrm{dp}}{\mathrm{dT}}=\frac{\mathrm{Phfg}}{\mathrm{RT}^{2}} \\
\frac{\mathrm{dp}}{\mathrm{dT}}=\frac{\mathrm{dThfg}}{\mathrm{RT}^{2}} \\
\int_{P_{1}}^{P 2} \frac{d P}{P}=\int_{T 1}^{T z} \frac{d P}{\mathrm{RT}^{2}} \mathrm{hfg} \\
\int_{P_{1}}^{P 2} \frac{d P}{P}=\frac{\mathrm{hfg}}{\mathrm{R}} \int_{T 1}^{T z} \frac{d T}{\mathrm{~T}^{2}} \\
\ln \left(\frac{\mathrm{~d} \mathbf{p}}{\mathrm{dT}}\right)=\frac{\mathrm{hfg}}{\mathrm{R}}\left[\frac{-1}{T}\right]_{\mathrm{T} 2} \\
\ln \left(\frac{\mathrm{~d} \mathbf{p}}{\mathrm{dT}}\right)=\frac{\mathrm{hfg}}{\mathrm{R}}\left[\frac{1}{T 1}-\frac{1}{T 2}\right] \tag{11}
\end{gather*}
$$

The above equation is known an clausius - clapeyron equation. It is also used to determine the variable in saturation pressure with temperature.

## T-D Relations:

(i) Let entropy s be imagined as a function T and V then.

$$
\begin{align*}
& \mathrm{ds}=\left(\frac{\partial s}{\partial T}\right)_{\mathrm{v}} \mathrm{dT}+\left(\frac{\partial s}{\partial v}\right)_{\mathrm{T}} \mathrm{dv} \\
& \Rightarrow \mathrm{Tds}=\mathrm{T}\left(\frac{\partial s}{\partial T}\right)_{\mathrm{v}} \mathrm{dT}++\left(\frac{\partial s}{\partial v}\right)_{\mathrm{T}} \mathrm{dv}  \tag{1}\\
& \Rightarrow \mathrm{~T}\left(\frac{\partial s}{\partial T}\right)_{\mathrm{v}}=\mathrm{C}_{\mathrm{v}} \tag{2}
\end{align*}
$$

$\mathrm{C}_{\mathrm{v}}$ - specific heat at const.volume
And $\left(\frac{\partial s}{\partial v}\right)_{\mathrm{T}=}\left(\frac{\partial p}{\partial T}\right)_{\mathrm{V}}$
Maxwell's third equation
put eq (2), (3) in eq (1)

$$
\Rightarrow \quad \mathrm{Tds}=\mathrm{C}_{\mathrm{v}} \mathrm{dT}+\mathrm{T}\left(\frac{\partial p}{\partial T}\right)_{\mathrm{v}} \mathrm{dP}
$$

(4)

This equation is known as first Tds equation.
(ii) If entropy S is considered as a function T and P .

Then

$$
\mathrm{ds}=\left(\frac{\partial s}{\partial T}\right)_{\mathrm{p}} \mathrm{dT}+\left(\frac{\partial s}{\partial p}\right)_{\mathrm{T}} \mathrm{dp}
$$

$$
\begin{equation*}
\mathrm{Tds}=\mathrm{T}\left(\frac{\partial s}{\partial T}\right)_{\mathrm{p}} \mathrm{dT}+\left(\frac{\partial s}{\partial p}\right)_{\mathrm{T}} \mathrm{Tdp} \tag{5}
\end{equation*}
$$

$$
\begin{equation*}
\Rightarrow \quad \mathrm{T}\left(\frac{\partial s}{\partial T}\right)_{\mathrm{p}}=\mathrm{C}_{\mathrm{p}} \tag{6}
\end{equation*}
$$

Cp - Specific heat at const. pressure.
And $\left(\frac{\partial s}{\partial p}\right)_{T}=-\left(\frac{\partial v}{\partial T}\right)_{p}$

Maxwell's fourth equation.
Put (6) \& (7) in eq (5) we get

$$
\begin{equation*}
\mathrm{Tds}=\operatorname{cpdT}-\mathrm{T}\left(\frac{\partial v}{\partial T}\right)_{\mathrm{p}} \mathrm{dP} \tag{8}
\end{equation*}
$$

## Specific Heat Relations:

$$
\begin{align*}
& \mathrm{Tds}=\mathrm{CvdT}+\mathrm{T}\left(\frac{\partial p}{\partial T}\right)_{\mathrm{v}} \mathrm{dP}  \tag{1}\\
& \mathrm{Tds}=\mathrm{cpdT}-\mathrm{T}\left(\frac{\partial v}{\partial T}\right)_{\mathrm{p}} \mathrm{dP} \tag{2}
\end{align*}
$$

$\qquad$
---------------------------------------------

Equation eq (1) \& (2) we get

$$
\begin{equation*}
\mathrm{Cp}-\mathrm{Cv}=-\mathrm{T}\left(\frac{\partial v}{\partial T}\right)_{\mathrm{p}}\left(\frac{\partial p}{\partial v}\right) \tag{3}
\end{equation*}
$$

This relation can be expressed in terms of two other thermodynamic properties called the volume expressivities B and the isothermal compressibility $\partial$.

$$
\left.\begin{array}{r}
\beta=\frac{1}{v}\left(\frac{\partial v}{\partial T}\right) p \\
\propto=-\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)^{T} \tag{4}
\end{array}\right\}
$$

Put (4) in (3) we get

$$
\begin{equation*}
\mathrm{Cp}-\mathrm{Cv}=v t \beta^{2} / \infty \tag{5}
\end{equation*}
$$

- The isothermal compressibility $\propto$ is a positive quality for all substances in all phases.
- The volume expansivity could be negative for some substances, but in square is always positive
- The constant - pressure specific heat is always greater than or equal to the constant volume specific heat.
- $\mathrm{Cp} \geq \mathrm{Cv}$
- The difference between Cp and Cv approached Zero as the absolute temperature approaches zero.


## GIBBS PHASE RULE:

$f=c-\varnothing+2$
the above equation is known as the Gibbs phase rule for a non reactive system
where,

$$
\begin{aligned}
& f=\text { degree of freedom } \\
& c=\text { chemical constituents } \\
& \varnothing=\text { phase }
\end{aligned}
$$

## UNIT - V

## OBJECTIVE:

To familiarize the students with the topics of combustion, chemical reactions of fuels combustion analysis.

## COMBUSTION:

Combustion is the chemical combination of the combustible constituents of a fuel with oxygen. During this chemical reaction carbon, hydrogen and sulphur present in the fuel combine vapidly with oxygen to form carbon dioxide (or) carbon monoxide (co), sulphur dioxide $\left(\mathrm{SO}_{2}\right)$ and water $\left(\mathrm{H}_{2} \mathrm{O}\right)$ with the release of large amount of energy. To begin this process, temperature of the fuel must be raised to a certain value known as ignition point of the fuel. The fuel and oxidizer which supplies the necessary oxygen are known as reactants and the constituents resulting from the combustion process are called the proudest.

## STOICHIOMETRY:

The minimum amount of air which provides sufficient oxygen for the complete combustion of all the elements like carbon, hydrogen etc. which may oxidize is called the theoretical or stoichiometric air. There is no oxygen in the products when complete combustion oxidation is a achieved with this theoretical air.

Theoretical or minimum air required for complete combustion of 1 kg of fuel

$$
=\frac{100}{23}\left[\left(\frac{8}{3} c+8 H 2+S\right)-o\right] k g .
$$

## ENTHALPY OF FORMATION:

Let us consider the steady state steady flow combustion of carbon and oxygen to form $\mathrm{CO}_{2}$ as shown in figure.


- Let the carbon and oxygen enter the control volume at $25^{\circ} \mathrm{C}$ and 1 atm , pressure and the heat transfer be such that the product $\mathrm{CO}_{2}$ leaves at $25^{\circ} \mathrm{C}$, 1atm pressure
- The measure value of heat transfer is $-393,522 \mathrm{KJ}$ per kg of $\mathrm{CO}_{2}$ formed
- If $H_{R}$ and $H_{P}$ refer to the total enthalpy of the reactants and products respectively.

Then the first law applied to the reaction

$$
\mathrm{C}+\mathrm{O}_{2} \longrightarrow \mathrm{CO}_{2} \text { gives }
$$

$$
\mathbf{H}_{\mathrm{R}}+\mathbf{Q}_{\mathrm{c} . \mathrm{v}}=\mathbf{H}_{\mathrm{p}}
$$

Generally all the reactants and products in a reaction, the equation may be written as

$$
\sum_{R} \boldsymbol{n}_{i} \overline{\boldsymbol{h}_{\boldsymbol{l}}}+\mathbf{Q}_{\mathrm{c} . \mathrm{v}}=\sum_{p} \boldsymbol{n}_{\boldsymbol{e}} \overline{\boldsymbol{h}_{\boldsymbol{e}}}
$$

Where R and P refer to the reactants and products respectively.

- The enthalpy of all the elements at the standard reference state of $25^{\circ} \mathrm{C}, 1$ atm is assigned the value of zero
- In carbon- oxygen reaction, $\mathrm{H}_{\mathrm{R}}=0$
i.e. $\quad H P=Q_{c . v}=-393522 \mathrm{KJ} / \mathrm{Kgmol}$

It is also denoted by $\overline{\boldsymbol{h}}^{\circ}$

$$
\Rightarrow \bar{h}_{\mathrm{f}} 0=-393522 \mathrm{KJ} / \mathrm{Kgmol}
$$

But in most cases, the reactants and products are not at $25^{\circ} \mathrm{c}, 1 \mathrm{~atm}$. Therefore, the change in enthalpy between $25^{\circ} \mathrm{C}$, 1 atm and the given state must be known. Thus the enthalpy at any temperature and pressure, $\overline{\boldsymbol{h}}_{\mathrm{T}, \mathrm{p}}$ is

$$
\overline{\boldsymbol{h}}_{\mathrm{T}, \mathrm{p}}=\overline{\boldsymbol{h}}_{\mathrm{f}}^{\circ}+\Delta \bar{n}
$$

Where $\boldsymbol{\Delta} \overline{\boldsymbol{n}}$ referents the difference in enthalpy between any given state and the enthalpy at 298.15 K , 1 atm .

## ADIABATIC FLAME TEMPERATURE:

Consider a given combustion process that takes place adiabatically and with no work or changes in K.E or potential energy involved. The temperature of the products is referred to as the adiabatic Flame temperature.

With the assumption of no work and no changes in kinetic or potential energy, this is the maximum temperature that can be achieved for the given reactants because any heat transfer from the reacting substances and any incomplete combustion would tend to lower the temperature of the products.

For a given fuel and given pressure and temp of reactants, the maximum adiabatic flame temperature that can be achieved is with a stoichiometric mixture. The Adiabatic flame temperature can be controlled by the amount of excess air that is used.

The energy equation is

$$
\begin{gathered}
\mathrm{H}_{\mathrm{R}}=\mathrm{H}_{\mathrm{p}} \\
\sum_{\boldsymbol{R}} \boldsymbol{n}_{\boldsymbol{i}} \overline{\boldsymbol{h}_{\boldsymbol{\imath}}}=\sum_{\boldsymbol{p}} \boldsymbol{n}_{\boldsymbol{e}} \overline{\boldsymbol{h}_{\boldsymbol{e}}}
\end{gathered}
$$

$$
\begin{gathered}
\text { Or } \\
\sum_{R} n_{i}\left[\bar{h}_{f^{\circ}}^{\circ}+\Delta \bar{h}\right]_{\mathrm{i}}=\sum_{p} \boldsymbol{n}_{e}\left[\overline{\boldsymbol{h}}_{\mathrm{f}}{ }^{\circ}+\Delta \bar{h}\right]_{\mathrm{e}}
\end{gathered}
$$

## For example:

In gas turbine, where the maximum permissible temperature is determined by metallurgical consideration in the turbine is determine by metallurgical consideration in the turbine and close control of the temp. Of the products is essential.

## ENTHALPY OF REACTION AND HEATING VALUE:

The enthalpy of combustion is defined as the difference between the enthalpy of the products and the enthalpy of reactants when complete combustion occurs at a given temperature and pressure

$$
\begin{aligned}
& \bar{h}_{\mathrm{RP}}=\mathrm{H}_{\mathrm{p}}-\mathrm{H}_{\mathrm{R}} \\
& \quad \mathrm{Or} \\
& \bar{h}_{\mathrm{RP}}=\sum_{R} n_{e}\left[\bar{h}_{\mathrm{f}}^{\circ}+\Delta \bar{h}\right] \mathrm{e}-\sum_{p} n_{i}\left[\bar{h}_{\mathrm{f}}^{\circ}+\Delta \bar{h}\right]_{\mathrm{i}}
\end{aligned}
$$

Where $\overline{\boldsymbol{h}_{\boldsymbol{R P}}}$ is the enthalpy of combustion $(\mathrm{KJ} / \mathrm{Kg}$ or $\mathrm{KJ} / \mathrm{mol})$ of the fuel
The internal energy of combustion, $\boldsymbol{U}_{\boldsymbol{R}}$ is defined in

$$
\bar{u}_{R P}=U_{p}-U_{R}
$$

$$
=\sum_{R} n_{e}\left[\bar{h}_{\mathrm{f}}^{\circ}+\Delta \bar{h}\right] \mathrm{e}-\sum_{p} n_{i}\left[\bar{h}_{\mathrm{f}}^{\circ}+\Delta \bar{h}\right]_{\mathrm{i}}
$$

If all the gaseous constituent are considered ideal gases and the volume of liquid and solid considered is assume to be negligible compared to gaseous volume.

$$
\overline{\boldsymbol{U}}_{\mathrm{RP}}=\bar{h}_{\mathrm{RP}}-\bar{R} \mathbf{T}\left(\boldsymbol{\eta}_{\text {gaseous products }}-\boldsymbol{\eta}_{\text {gaseous Reactants })}\right.
$$

- In the case of a constant pressure or steady flow process, the negative of the enthalpy of combustion is frequently called the heating value at constant pressure, which represents the heat transferred from the chamber during combustion at const. pressure.
- Similarly, the negative of the internal energy of combustion is called as the heating value at constant volume in the case of combustion, because it represents the amount of heat transfer in the const volume process.
- The higher heating value (HHV) or higher calorific value (HCV) is the heat transferred when $\mathrm{H}_{2} \mathrm{O}$ in the products is in the liquid phase.
- The lower heating value (LHV) or lower calorific value (LCV) is the heat transferred when $\mathrm{H}_{2} \mathrm{O}$ in the products is in the vapour phase.

$$
\mathrm{LHV}=\mathrm{HHV}-\mathrm{m} \mathrm{H}_{2} \mathrm{O} . \mathrm{hfg}
$$

Where $\mathrm{mH}_{2} \mathrm{O}$ is the mass of water formed in the reaction.

## AIR - FUEL RATIO

Air - fuel ratio is the main quantity in the analysis of combustion process. It is defined as the ratio of the mass of air to the mass of fuel during a combustion process. That is

$$
\text { Air }- \text { fuel Ratio }=\frac{\text { Mair }}{\text { Mfuel }}
$$

## EFFECTS ON SUPPLY OF EXCESS AIR:

If the air supply is less than the stoichiometric amount, some of the carbon will become carbon monoxide or will remain as carbon particle in the product gas.

If the air supply is greater than the stoichimometric amount, the product of combustion will contain free oxygen.

## COMBUSTION REACTION:

During combustion, the fuel is oxidized so that the carbon becomes $\mathrm{CO}_{2}$ or co , Hydrogen becomes $\mathrm{H}_{2} \mathrm{O}$ and sculpture becomes $\mathrm{SO}_{2}$.

Consider 1 kmol of carbon combining with 1 kmd of oxygen to form 1 kmol of carbon dioxide.

$$
C+O_{2}=>\operatorname{co} 2
$$

In terms of main
1 kmol of $\mathrm{c}=>12 \mathrm{~kg}, 1 \mathrm{kmol}$ of $02=>32 \mathrm{~kg}$
1 kmol of $\mathrm{CO}_{2}=>44 \mathrm{~kg}$
Consider carbon combining with oxygen to for carbon monoxide.

$$
2 c+02=>2 c o
$$

2 kmol of carbon combines with 1 kmol of oxygen to form 2 kmol of carbon monoxide.

2 kmol of $\mathrm{c}=>24 \mathrm{~kg}, 1 \mathrm{kmol}$ of $\mathrm{O}_{2}=>32 \mathrm{~kg}$
2 kmol of $\mathrm{CO}=>56 \mathrm{~kg}$.
Oxidation of sulphur gives.
$\mathrm{S}+\mathrm{O}_{2}=>\mathrm{SO}_{2}$
1 kmol of sulphur combines with 1 kmol of oxygen to form of sculpture dioxide.
1 kmol of $\mathrm{s}=>32 \mathrm{~kg}, 1 \mathrm{~km}$ of $\mathrm{o}_{2}=>32 \mathrm{~kg}$.
$1 \mathrm{km01}$ of sO2 => 64 kg .

## ENTHALPY OF COMBUSTION:

The internal energy of combustion is defined as the difference between the internal energy of the product and the internal energy of reactants when complete combustion occurs at a given temperation and pressure.

$$
\begin{aligned}
\mathrm{URP} & =\mathrm{U}_{\mathrm{p}}-\mathrm{U}_{\mathrm{R}} \\
& =\sum_{P} n e[h \circ f+\Delta h-p \nu]-\sum_{R} n i[h f \circ+\Delta h-p v]
\end{aligned}
$$

## heating Valve of fuels:

The heating value of a fuel is the amount of heat transferred from the fuel when it is burned in stochiometric proportions of air in a steady - flow process such that the reactants are at the standard reference state and the products are returned to the standard reference state.

The heating value is numerically equal to the enthalpy of combustion, but it has the opposite sign.

There two types of calorific values namely:-
a) Higher calorific value
b) Lower calorific value

## HIGHER CALORIFIC VALUE: (HCV)

Higher calorific value (HCV) is the quantity of heat obtained by the complete combustion of unit mass of the fuel, when the products of combustion are cooled down to the temperature of the surroundings. In this case any water vapour formed by combustion is condensed and the heat is recovered from the products of combustion.

## LOWER CALORIFIC VALUE: (LCV)

Lower calorific value is the quantity of heat abstained by the complete combustion of unit mass of the fuel, when the products of combustion are not sufficiently cooled down to condense the steam formed during combustion.

$$
\begin{aligned}
& \text { LUV }=\text { HCV - Latent heat of steam formed } \\
& \text { HCV - } 2442 \times \text { steam formed (kj/kg) }
\end{aligned}
$$

## ADIABATIC FLAME TEMPERATURE:

The maximum temperature that products can reach during a combustion process which is adiabatic involving no work and negligible changes is kinetic and potential energy. Mathematically the energy balance gives

$$
\begin{aligned}
& \phi=W+H p-H R \\
& \text { But } \phi-W=0 \\
& ==>H P=H R \\
& (o r) \\
& \sum_{R} n i k i=\sum_{P} n e h e \\
& ==>\sum_{R} n i[h f \circ+\Delta h]=\sum_{P} n e[h f \circ+\Delta h] e
\end{aligned}
$$

## CHEMICAL EXERGY:

The chemical exergy is thus defined as the maximum theoretical work that could be developed by the combine system. Thus for a given system at a specific state.

Total exergy $=$ thermo chemical exergy + chemical exergy.

## SECOND LAW EFFICIENCY OF A REACTIVE SYSTEM.

For a fuel at To, Po, the chemical exergy is the maximum theoretical work that could be obtained through reaction with environmental substances. However due to various irreversibility like friction and heat loss, the actual work obtained is only a fraction of this maximum theoretical work.

The second law efficiency may thus be defined as the ratio of.

$$
\begin{aligned}
& \eta I I=\frac{\text { ActualWorkdone }}{\text { Maximumtheoreticalwork }} \\
& =\frac{\text { Wcv }}{m f u e l ~} \times \text { ach }
\end{aligned}
$$

## PROBLEMS:

1. The products of combustion of an unknown hydrocarbon $\mathrm{C}_{x} \mathrm{H}_{y}$ have the following composition as measured by an orsat apparatus:
$\mathrm{CO}_{2} 8.0 \%, \mathrm{CO} 0.9 \%, \mathrm{O}_{2} 8.8 \%$, and $\mathrm{N}_{2} 82.3 \%$
Determine : a) the composition of the fuel, b) the air fuel ratio, C) the \% of excess air used

## SOLUTION:

Let a moles of oxygen be supplied per mole of fuel. The chemical reaction can be written as follows.

$$
\begin{aligned}
& \mathrm{C}_{x} \mathrm{H}_{y}+\mathrm{aO}_{2}+3.76 \mathrm{a} \mathrm{~N}_{2} \\
= & 8 \mathrm{CO}_{2}, 0.9 \mathrm{CO}, 8.8 \mathrm{O}_{2} \text {, and } 82.3 \mathrm{~N}_{2}+\mathrm{y} / 2 \mathrm{H}_{2} \mathrm{O}
\end{aligned}
$$

Oxygen balance gives

$$
2 a=16+0.9+17.6+y / 2
$$

$\qquad$1

Nitrogen balance gives

$$
\begin{array}{r}
3.76 \mathrm{a}=82.3 \\
\mathrm{a}=21.89
\end{array}
$$

by substituting the value of a in eqn 1

$$
y=18.5
$$

carbon balance gives $x=8+0.9=8.9$
therefore, the chemical formula of the fuel is $\mathrm{C}_{8.9} \mathrm{H}_{18.5}$ The composition of the fuel is
$\%$ carbon $=\frac{8.9 \times 12}{8.9 \times 12+18.5 \times 1} \times 100=85.23 \%$
$\%$ of Hydrogen = $14.77 \%$
B) air fuel ratio $=\frac{32 a+3.76 a \times 28}{12 x+y}$

$$
=\frac{21.89(32+3.76 \times 28)}{12 \times 8.9+18.5}=\frac{3005}{125.3}=24
$$

C) Excess air used:

$$
\frac{8.8 \times 32}{21.89 \times 32-8.8 \times 32} \times 100=67.22 \%
$$

2. Determine the heat transfer per kg mol of fuel for the following reaction

$$
\mathrm{CH}_{4}+2 \mathrm{O}_{2} \longrightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}
$$

The reactants and products are each at a total pressure of 100 Kpa and $25^{\circ} \mathrm{C}$

## SOLUTION:

By the first law

$$
Q_{C . V}+\sum_{P} n_{i} \bar{h}_{i}=\sum_{P} n_{e} \bar{h}_{e}
$$

From table C in the appendix

$$
\begin{aligned}
& \sum_{R} n_{e} \bar{h}_{e}=\left(\bar{h}_{F}\right)_{C O 2}+2\left(\overline{\left.h_{f}\right)} H_{2} O\right. \\
& =-393,522+2(-285,838)=-965,198 \mathrm{KJ} \\
& \mathbf{Q}_{\mathrm{c.v}}=-890,325 \mathrm{KJ}
\end{aligned}
$$

