## Lesson

 5 Review of fundamental principles Thermodynamics : Part II
## .The specific objectives are to:

1. State principles of evaluating thermodynamic properties of pure substances using:
a) Equations of State (Section 5.2)
b) Thermodynamic charts (Section 5.2)
c) Thermodynamic tables (Section 5.2)
2. Derive expressions for heat and work transfer in important thermodynamic processes such as:
a) Isochoric process (Section 5.3)
b) Isobaric process (Section 5.3)
c) Isothermal process (Section 5.3)
d) Isentropic process (Section 5.3)
e) Isenthalpic process etc. (Section 5.3)

At the end of the lesson the student should be able to:

1. Evaluate thermodynamic properties using equations of state, tables and charts
2. Identify various regimes on T-s and P-h charts
3. Estimate heat and work transferred in various thermodynamic processes

### 5.1. Thermodynamic relations

There are some general thermodynamic relations, which are useful for determination of several thermodynamic properties from measured data on a few properties. The following relationships are generally used for the evaluation of entropy change. These are called $T d s$ equations. They are obtained by applying first and second laws of thermodynamics

$$
\begin{array}{lll}
T & d s=d u+p & d v \\
T & d s=d h-v & d P
\end{array} \quad \begin{aligned}
& \text { first } T d s  \tag{5.1}\\
& \text { second }
\end{aligned} T d s \text { equation }
$$

Two more fundamental thermodynamic relations can be obtained by defining two new properties called Gibbs and Helmholtz functions.

### 5.2. Evaluation of thermodynamic properties

In order to perform thermodynamic calculations, one has to know various thermodynamic properties of the system. Properties such as internal energy, enthalpy and entropy cannot be measured directly. Thermodynamics gives mathematical relations using which one can obtain properties, which cannot be measured directly in terms of the measurable properties such as pressure, temperature, volume, specific heat etc.

In general thermodynamic properties can be evaluated from:

1. Thermodynamic equations of state
2. Thermodynamic tables
3. Thermodynamic charts
4. Direct experimental results, and
5. The formulae of statistical thermodynamics

An equation of state (EOS) is a fundamental equation, which expresses the relationship between pressure, specific volume and temperature. The simplest equation of state is that for an incompressible substance (e.g. solids and liquids), which states that the specific volume is constant. The next simplest EOS is that for an ideal gas.

Ideal (perfect) gas equation is a special equation of state, which is applicable to ideal gases. The molecular forces of attraction between gas molecules are small compared to those in liquids. In the limit when these forces are zero, a gas is called a perfect gas. In addition the volume of the molecules should be negligible compared to total volume for a perfect gas. The perfect or ideal gas equation of state is given by:

$$
\begin{equation*}
P v=R T \tag{5.2}
\end{equation*}
$$

$$
\begin{array}{rll}
\text { Where } P & = & \text { Absolute pressure } \\
V & = & \text { Specific volume } \\
R & = & \text { Gas constant } \\
T & = & \text { Absolute temperature }
\end{array}
$$

The gas constant $R$ is given by:

$$
\begin{equation*}
R=R_{u} / M \tag{5.3}
\end{equation*}
$$

Where $R_{u} \quad=\quad$ Universal gas constant
$M \quad=\quad$ Molecular weight
The ideal gas equation is satisfactory for low molecular mass, real gases at relatively high temperatures and low pressures. Ideal gas equation can be used for evaluating properties of moist air used in air conditioning applications without significant error.

For ideal gases, the change in internal energy and enthalpy are sole functions of temperature. Assuming constant specific heats ( $c_{p}, c_{v}$ ) in the temperature range $T_{1}$ to $T_{2}$, for ideal gases one can write the change in internal energy ( u ), enthalpy (h) and entropy (s) as:

$$
\begin{align*}
& \mathrm{u}_{2}-\mathrm{u}_{1}=\mathrm{c}_{\mathrm{v}}\left(\mathrm{~T}_{2}-\mathrm{T}_{1}\right) \\
& \mathrm{h}_{2}-\mathrm{h}_{1}=\mathrm{c}_{\mathrm{p}}\left(\mathrm{~T}_{2}-\mathrm{T}_{1}\right) \\
& \mathrm{s}_{2}-\mathrm{s}_{1}=\mathrm{c}_{\mathrm{v}} \ln \left(\frac{\mathrm{~T}_{2}}{\mathrm{~T}_{1}}\right)+\mathrm{R} \ln \left(\frac{\mathrm{v}_{2}}{\mathrm{v}_{1}}\right)  \tag{5.4}\\
& \mathrm{s}_{2}-\mathrm{s}_{1}=\mathrm{c}_{\mathrm{p}} \ln \left(\frac{\mathrm{~T}_{2}}{\mathrm{~T}_{1}}\right)-\mathrm{R} \ln \left(\frac{\mathrm{P}_{2}}{\mathrm{P}_{1}}\right) \\
& \mathrm{c}_{\mathrm{p}}-\mathrm{c}_{\mathrm{v}}=\mathrm{R}
\end{align*}
$$

The study of the properties of moist air is known as psychrometry. The psychrometric properties (temperature, humidity ratio, relative humidity, enthalpy etc.) are normally available in the form of charts, known as psychrometric charts. The psychrometric properties will be discussed in later chapters.
For gases with complex molecular structure or for real gases at high pressure and low temperatures or for gases approaching the saturated vapour region, the use of Ideal gas equation results in significant errors. Hence more complex but more realistic equations of states have to be applied. The accuracy of these EOS depend on the nature of the gas. Some of these EOSs are given below:
van der Waals equation:

$$
\begin{equation*}
\left(P+\frac{a}{v^{2}}\right)(v-b)=R T \tag{5.5}
\end{equation*}
$$

where $a$ and $b$ are constants that account for the intermolecular forces and volume of the gas molecules respectively.

Redlich-Kwong equation:

$$
\begin{equation*}
P=\frac{R T}{v-b}-\frac{a}{\sqrt{T} v(v+b)} \tag{5.6}
\end{equation*}
$$

A virial equation is more generalized form of equation of state. It is written as:

$$
\begin{equation*}
\mathrm{Pv}=\mathrm{RT}+\frac{\mathrm{A}}{\mathrm{v}}+\frac{\mathrm{B}}{\mathrm{v}^{2}}+\frac{\mathrm{C}}{\mathrm{v}^{3}}+\ldots \ldots . \tag{5.7}
\end{equation*}
$$

where $\mathrm{A}, \mathrm{B}, \mathrm{C}, \ldots$ are all empirically determined functions of temperature and are called as virial coefficients.

### 5.2.1. Properties Of Pure Substance

A pure substance is one whose chemical composition does not change during thermodynamic processes. Water and refrigerants are examples of pure substances. These days emphasis is on the use mixture of refrigerants. The properties of mixtures also require understanding of the properties of pure substances.

Water is a substance of prime importance in refrigeration and air-conditioning. It exists in three states namely, solid ice, liquid water and water vapour and undergoes transformation from one state to another. Steam and hot water are used for heating of buildings while chilled water is used for cooling of buildings. Hence, an understanding of its properties is essential for air conditioning calculations. Substances, which absorb heat from other substances or space, are called refrigerants. These substances also exist in three states. These also undergo transformations usually from liquid to vapour and vice-versa during heat absorption and rejection respectively. Hence, it is important to understand their properties also.

If a liquid (pure substance) is heated at constant pressure, the temperature at which it boils is called saturation temperature. This temperature will remain constant during heating until all the
liquid boils off. At this temperature, the liquid and the associated vapour at same temperature are in equilibrium and are called saturated liquid and vapour respectively. The saturation temperature of a pure substance is a function of pressure only. At atmospheric pressure, the saturation temperature is called normal boiling point. Similarly, if the vapour of a pure substance is cooled at constant pressure, the temperature at which the condensation starts, is called dew point temperature. For a pure substance, dew point and boiling point are same at a given pressure.

Similarly, when a solid is heated at constant, it melts at a definite temperature called melting point. Similarly cooling of a liquid causes freezing at the freezing point. The melting point and freezing point are same at same pressure for a pure substance and the solid and liquid are in equilibrium at this temperature.

For all pure substances there is a temperature at which all the three phases exist in equilibrium. This is called triple point.

The liquid-vapour phase diagram of pure substance is conveniently shown in temperatureentropy diagram or pressure-enthalpy diagram or $p$ - $v$ diagram. Sometimes, three dimensional $p$ $v$ - $t$ diagrams are also drawn to show the phase transformation. In most of the refrigeration applications except dry ice manufacture, we encounter liquid and vapour phases only. Thermodynamic properties of various pure substances are available in the form of charts and tables. Thermodynamic property charts such as Temperature-entropy (T-s) charts, pressureenthalpy (P-h) charts are very useful in evaluating properties of substances and also for representing the thermodynamic processes and cycles. Figures 5.1 and 5.2 show the P-h and T-s diagrams for pure substances.


Fig. 5.1. P-h diagram for a pure substance


Fig. 5.2. T-s diagram for a pure substance

## Critical point:

Figures 5.1 and 5.2 show the critical point. The temperature, pressure and specific volume at critical point are denoted by $T_{c}, P_{c}$ and $v_{c}$, respectively. A liquid below the critical pressure when heated first becomes a mixture of liquid and vapour and then becomes saturated vapour and finally a superheated vapour. At critical point there is no distinction between liquid state and vapour state; these two merge together. At constant pressure greater than critical pressure, $\mathrm{P}_{\mathrm{C}}$ when liquid is heated in supercritical region, there is no distinction between liquid and vapour; as a result if heating is done in a transparent tube, the meniscus of liquid and vapour does not appear as transformation from liquid to vapour takes place. At pressures below critical pressure, when a liquid is heated there is a clear-cut meniscus between liquid and vapour, until all the liquid evaporates.

For water: $\quad$ Triple point: $\quad 0.1^{\circ} \mathrm{C}, 0.006112$ bar
Critical point: 221.2 bar, 647.3 K and $0.00317 \mathrm{~m}^{3} / \mathrm{kg}$
For Dry Ice $\left(\mathrm{CO}_{2}\right)$ : $\quad$ Triple point: $\quad 5.18$ bar, $-56.6^{\circ} \mathrm{C}$
Critical point: 73.8 bar, $31^{\circ} \mathrm{C}$

## T-s and p-h diagrams for liquid-vapour regime

These are of great importance in refrigeration cycle calculations. Figure 5.3 and 5.4 show typical $T$-s diagram and $p$-h (Mollier) diagrams, respectively for a pure refrigerant. The $T$-s diagram
shows two constant pressure lines for pressures $\mathrm{P}_{1}$ and $\mathrm{P}_{2}$ where $\mathrm{P}_{1}>\mathrm{P}_{2}$. The constant pressure line 1-2-3-4 is for pressure $P_{1}$. The portion 1-2 is in the sub-cooled region, 2-3 is in wet region, that is mixture of liquid and vapour, and $3-4$ is in superheated region. A frequent problem in refrigeration cycle calculations is to find the properties of sub-cooled liquid at point $a$ shown in the figure. The liquid at pressure $\mathrm{P}_{1}$ and temperature $T_{a}$ is sub-cooled liquid. The liquid at state $a^{\prime}$ is saturated liquid at lower pressure $\mathrm{P}_{\mathrm{a}}$, but at the same temperature.


Fig. 5.3. $T$-s diagram of a pure substance


Fig. 5.4. P-h diagram of a pure substance

From $1^{\text {st }} \mathrm{T}$ ds equation , Eq. (5.1):

$$
\begin{equation*}
T \mathrm{ds}=\mathrm{du}+\mathrm{Pdv} \tag{5.1a}
\end{equation*}
$$

If the liquid is assumed to be incompressible then $\mathrm{dv}=0$ and

$$
\begin{equation*}
\mathrm{T} d \mathrm{~d}=\mathrm{du} \tag{5.8}
\end{equation*}
$$

For liquids, the internal energy may be assumed to be function of temperature alone, that is,

$$
\mathrm{u}_{\mathrm{a}}=\mathrm{u}_{\mathrm{a}^{\prime}} \text {, because } \mathrm{T}_{\mathrm{a}}=\mathrm{T}_{\mathrm{a}^{\prime}} \text { this implies that } \mathrm{s}_{\mathrm{a}}=\mathrm{s}_{\mathrm{a}^{\prime}}
$$

Therefore states $a$ and $a^{\prime}$ are coincident.
Also from the $2^{\text {nd }} \mathrm{T}$ ds equation, Eq. (5.1)
T ds=dh - vdP

The specific volume $v$ is small for liquids hence $v \mathrm{~d} p$ is also negligible, therefore $h_{a}=h_{a}$, That is, the enthalpy of sub-cooled liquid is equal to the enthalpy of saturated liquid at liquid temperature. For all practical purposes the constant pressure lines are assumed to be coincident with saturated liquid line in the sub-cooled region. This is a very useful concept.

T-s diagram gives a lot of information about the refrigeration cycle. It was observed in Chapter 4 that for a reversible process, the heat transfer is related to the change in entropy given by:

$$
\begin{equation*}
\mathrm{S}_{2}-\mathrm{S}_{1}=\left(\int_{1}^{2} \frac{\delta \mathrm{Q}}{\mathrm{~T}}\right)_{\mathrm{int}} \text {, this implies that }{ }_{1} \mathrm{Q}_{2}=\left(\int_{1}^{2} \text { T.ds }\right) \tag{5.9}
\end{equation*}
$$

The above equation implies that the heat transferred in a reversible process $1-2$ is equal to area under the line 1-2 on the T-s diagram.

Also, from Eq. (5.1b), T ds= $\mathrm{dh}-\mathrm{vdP}$, hence for a constant pressure process ( $\mathrm{dP}=0$ ), therefore, for a constant pressure process $\mathrm{Td}=\mathrm{dh}$, which means that for an isobaric process the area under the curve is equal to change in enthalpy on T-s diagram.

## Properties at Saturation

The properties of refrigerants and water for saturated states are available in the form of Tables. The properties along the saturated liquid line are indicated by subscript ' $f$ ' for example $v_{f}, u_{f}, h_{f}$ and $\mathrm{s}_{\mathrm{f}}$ indicate specific volume, internal energy, enthalpy and entropy of saturated liquid respectively. The corresponding saturated vapour states are indicated by subscript ' $g$ ' for example $\mathrm{v}_{\mathrm{g}}, \mathrm{u}_{\mathrm{g}}, \mathrm{h}_{\mathrm{g}}$ and $\mathrm{s}_{\mathrm{g}}$ respectively. All properties with subscript ' fg ' are the difference between saturated vapour and saturated liquid states. For example, $\mathrm{h}_{\mathrm{fg}}=\mathrm{h}_{\mathrm{g}}-\mathrm{h}_{\mathrm{f}}$, the latent heat of vaporization.

The specific volume, internal energy, enthalpy and entropy of the mixture in two-phase region may be found in terms of quality, ' $x$ ' of the mixture. The quality of the mixture denotes the mass
( kg ) of the vapour per unit mass ( kg ) of the mixture. That is there is x kg of vapour and (1-x) kg of liquid in one kg of the mixture.

Therefore the properties of the liquid-vapour mixture can be obtained by using the following equations:

$$
\begin{align*}
& \mathrm{v}=(1-\mathrm{x}) \mathrm{v}_{\mathrm{f}}+\mathrm{x} \cdot \mathrm{v}_{\mathrm{g}}=\mathrm{v}_{\mathrm{f}}+\mathrm{x} \cdot \mathrm{v}_{\mathrm{fg}} \\
& \mathrm{u}=(1-\mathrm{x}) \mathrm{u}_{\mathrm{f}}+\mathrm{x} \cdot \mathrm{u}_{\mathrm{g}}=\mathrm{u}_{\mathrm{f}}+\mathrm{u} \mathbf{u}_{\mathrm{fg}}  \tag{5.10}\\
& \mathrm{~h}=(1-\mathrm{x}) h_{\mathrm{f}}+\mathrm{x} \cdot \mathrm{~h}_{\mathrm{g}}=\mathrm{h}_{\mathrm{f}}+\mathrm{x} \cdot \mathrm{~h}_{\mathrm{fg}} \\
& \mathrm{~s}=(1-\mathrm{x}) \mathrm{s}_{\mathrm{f}}+\mathrm{x} \cdot \mathrm{~s}_{\mathrm{g}}=\mathrm{s}_{\mathrm{f}}+\mathrm{x} . \mathrm{s}_{\mathrm{fg}}
\end{align*}
$$

The table of properties at saturation is usually temperature based. For each temperature it lists the values of saturation pressure $\left(\mathrm{P}_{\mathrm{sat}}\right), \mathrm{v}_{\mathrm{f}}, \mathrm{v}_{\mathrm{g}}, \mathrm{h}_{\mathrm{f}}, \mathrm{h}_{\mathrm{g}}, \mathrm{s}_{\mathrm{f}}$ and $\mathrm{s}_{\mathrm{g}}$. Two reference states or datum or used in these tables. In ASHRAE reference $\mathrm{h}_{\mathrm{f}}=0.0 \mathrm{~kJ} / \mathrm{kg}$ and $\mathrm{s}_{\mathrm{f}}=1.0 \mathrm{~kJ} / \mathrm{kg} . \mathrm{K}$ at $-40^{\circ} \mathrm{C}$. In IIR reference $\mathrm{h}_{\mathrm{f}}=200.00 \mathrm{~kJ} / \mathrm{kg}$ and $\mathrm{s}_{\mathrm{f}}=1.0 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$ at $0^{\circ} \mathrm{C}$.

The properties in the superheated region are given in separate tables. The values of $v, h$ and $s$ are tabulated along constant pressure lines (that is, at saturation pressures corresponding to, say $0^{\circ} \mathrm{C}$, $1^{\circ} \mathrm{C}, 2^{\circ} \mathrm{C}$ etc.) at various values of degree of superheat.

## Clapeyron Equation

The Clapeyron equation represents the dependence of saturation pressure on saturation temperature (boiling point). This is given by,

$$
\begin{equation*}
\frac{\mathrm{dP}_{\mathrm{sat}}}{\mathrm{dT}}=\frac{\mathrm{s}_{\mathrm{fg}}}{\mathrm{v}_{\mathrm{fg}}}=\frac{\mathrm{h}_{\mathrm{fg}}}{\left(\mathrm{v}_{\mathrm{g}}-v_{\mathrm{f}}\right) \mathrm{T}} \tag{5.11}
\end{equation*}
$$

Some useful relations can be derived using Clapeyron equation. The specific volume of liquid is very small compared to that of vapour, hence it may be neglected and then perfect gas relation $\mathrm{pv}_{\mathrm{g}}=$ RT may be used to yield:

$$
\begin{equation*}
\frac{\mathrm{dP}_{\mathrm{sat}}}{\mathrm{dT}}=\frac{\mathrm{h}_{\mathrm{fg}}}{\left(\mathrm{v}_{\mathrm{g}}-\mathrm{v}_{\mathrm{f}}\right) \mathrm{T}}=\frac{\mathrm{h}_{\mathrm{fg}}}{\mathrm{v}_{\mathrm{g}} \mathrm{~T}}=\frac{\mathrm{P}_{\mathrm{sat}} \cdot \mathrm{~h}_{\mathrm{fg}}}{{R T^{2}}^{2}} \tag{5.12}
\end{equation*}
$$

This may be integrated between states 1 to an arbitrary state $\mathrm{P}_{\text {sat }}, \mathrm{T}$ to yield

$$
\begin{equation*}
\int_{\mathrm{p}_{1}}^{\mathrm{p}} \frac{\mathrm{dP}_{\text {sat }}}{\mathrm{P}_{\text {sat }}}=\frac{\mathrm{h}_{\mathrm{fg}}}{\mathrm{R}} \int_{\mathrm{T}_{\mathrm{T}}}^{\mathrm{T}} \frac{\mathrm{dT}}{\mathrm{~T}^{2}} \text { or } \ln \frac{\mathrm{P}_{\text {sat }}}{\mathrm{P}_{1}}=\frac{\mathrm{h}_{\mathrm{fg}}}{\mathrm{R}}\left(\frac{1}{\mathrm{~T}_{1}}-\frac{1}{\mathrm{~T}}\right) \tag{5.13}
\end{equation*}
$$

If $\mathrm{P}_{1}$ is chosen as standard atmospheric pressure of say $1 \mathrm{~atm} .(\ln (\mathrm{P} 1)=\ln (1)=0)$, and P is measured in atmospheres, then $\mathrm{T}_{1}=\mathrm{T}_{\mathrm{nb}}$ is the normal boiling point of the substance, then from Eq. (5.13), we obtain:

$$
\begin{equation*}
\ln \left(\mathrm{P}_{\mathrm{sat}}\right)=\frac{\mathrm{h}_{\mathrm{fg}}}{\mathrm{R}}\left(\frac{1}{\mathrm{~T}_{\mathrm{nb}}}-\frac{1}{\mathrm{~T}}\right) \tag{5.14}
\end{equation*}
$$

Therefore if $\ln (\mathrm{P})$ is plotted against $1 / T$, the saturated vapour line will be a straight line.
Also, it has been observed that for a set of similar substances the product of $\mathrm{Mh}_{\mathrm{fg}} / \mathrm{T}_{\mathrm{nb}}$ called Trouton number is constant. Here M is the molecular weight of the substance (kg/kmole). If we denote the Trouton number by $\mathrm{N}_{\text {trouton }}$, then

$$
\begin{align*}
& \mathrm{N}_{\text {trouton }}=\frac{\mathrm{Mh}_{\mathrm{fg}}}{\mathrm{~T}_{\mathrm{nb}}} \\
& \frac{\mathrm{~h}_{\mathrm{fg}}}{\mathrm{RT}_{\mathrm{nb}}}=\frac{\mathrm{N}_{\text {trouton }}}{\mathrm{MR}}=\frac{\mathrm{N}_{\text {trouton }}}{\overline{\mathrm{R}}}, \text { or }  \tag{5.15}\\
& \ln \mathrm{p}=\frac{\mathrm{h}_{\mathrm{fg}}}{\mathrm{RT}}+\frac{\mathrm{N}_{\text {trouton }}}{\overline{\mathrm{R}}}
\end{align*}
$$

For most of the substances, the Trouton number value is found to be about $85 \mathrm{~kJ} / \mathrm{kmol} . \mathrm{K}$

### 5.3. Thermodynamic processes

In most of the refrigeration and air conditioning systems, the mass flow rates do not change with time or the change is very small, in such cases one can assume the flow to be steady. For such systems, the energy balance equation ( $1^{\text {st }}$ law of thermodynamics) is known as steady-flow energy equation.


Fig. 5.5. Steady flow energy balance on a control volume

For the open system shown in Fig. 5.5, it is given by:

$$
\begin{equation*}
\mathrm{m}\left(\mathrm{~h}_{1}+\frac{\mathrm{v}_{1}^{2}}{2}+\mathrm{gz}_{1}\right)+\mathrm{Q}=\mathrm{m}\left(\mathrm{~h}_{2}+\frac{\mathrm{v}_{2}^{2}}{2}+\mathrm{gz}_{2}\right)+\mathrm{W} \tag{5.16}
\end{equation*}
$$

In many cases, compared to other terms, the changes in kinetic and potential energy terms, i.e., $\left(\mathrm{v}_{1}{ }^{2}-\mathrm{v}_{2}{ }^{2}\right) / 2$ and $\left(\mathrm{gz}_{1}-\mathrm{gz}_{2}\right)$ are negligible.

Heating and cooling: During these processes normally there will be no work done either on the system or by the system, i.e., $\mathrm{W}=0$. Hence, the energy equation for cooling/heating becomes:

$$
\begin{equation*}
\mathrm{Q}+\mathrm{mh}_{1}=\mathrm{mh}_{2} \quad \text { or } \mathrm{Q}=\mathrm{m}\left(\mathrm{~h}_{2}-\mathrm{h}_{1}\right) \tag{5.17}
\end{equation*}
$$

Some of the important thermodynamic processes encountered in refrigeration and air conditioning are discussed below.

Constant volume (isochoric) process: An example of this process is the heating or cooling of a gas stored in a rigid cylinder. Since the volume of the gas does not change, no external work is done, and work transferred $\Delta W$ is zero. Therefore from $1^{\text {st }}$ law of thermodynamics for a constant volume process:

$$
\begin{align*}
& { }_{1} \mathrm{~W}_{2}=0 \\
& { }_{1} \mathrm{Q}_{2}=\int_{1}^{2} \mathrm{dU}=\mathrm{U}_{2}-\mathrm{U}_{1}=\mathrm{mc}_{\mathrm{v}, \text { avg }}\left(\mathrm{T}_{2}-\mathrm{T}_{1}\right)  \tag{5.18}\\
& \mathrm{S}_{2}-\mathrm{S}_{1}=\mathrm{mc}_{\mathrm{v}, \text { avg }} \ln \left(\frac{\mathrm{T}_{2}}{\mathrm{~T}_{1}}\right)
\end{align*}
$$

The above equation implies that for a constant volume process in a closed system, the heat transferred is equal to the change in internal energy of the system. If ' $m$ ' is the mass of the gas, $\mathrm{C}_{\mathrm{v}}$ is its specific heat at constant volume which remains almost constant in the temperature range $\Delta \mathrm{T}$, and $\Delta \mathrm{T}$ is the temperature change during the process, then:

$$
\begin{equation*}
\Delta \mathrm{Q}=\Delta \mathrm{U}=\mathrm{m} \cdot \mathrm{C}_{\mathrm{v}} \cdot \Delta \mathrm{~T} \tag{5.19}
\end{equation*}
$$

Constant pressure (isobaric) process: If the temperature of a gas is increased by the addition of heat while the gas is allowed to expand so that its pressure is kept constant, the volume of the gas will increase in accordance with Charles law. Since the volume of the gas increases during the process, work is done by the gas at the same time that its internal energy also changes. Therefore for constant pressure process, assuming constant specific heats and ideal gas behaviour,

$$
\begin{align*}
& { }_{1} \mathrm{Q}_{2}=\left(\mathrm{U}_{2}-\mathrm{U}_{1}\right)+{ }_{1} \mathrm{~W}_{2} \\
& { }_{1} \mathrm{~W}_{2}=\int_{1}^{2} \mathrm{PdV}=\mathrm{P} \times\left(\mathrm{V}_{2}-\mathrm{V}_{1}\right) \\
& { }_{1} \mathrm{Q}_{2}=\mathrm{m}\left(\mathrm{~h}_{2}-\mathrm{h}_{1}\right)=\mathrm{m} \times \mathrm{C}_{\mathrm{p}, \mathrm{avg}} \times\left(\mathrm{T}_{2}-\mathrm{T}_{1}\right)  \tag{5.20}\\
& \mathrm{S}_{2}-\mathrm{S}_{1}=\mathrm{mc}_{\mathrm{p}, \mathrm{avg}} \ln \left(\frac{\mathrm{~T}_{2}}{\mathrm{~T}_{1}}\right)
\end{align*}
$$

Constant temperature (isothermal) process: According to Boyle's law, when a gas is compressed or expanded at constant temperature, the pressure will vary inversely with the volume. Since the gas does work as it expands, if the temperature is to remain constant, energy to do the work must be supplied from an external source. When a gas is compressed, work is done on the gas and if the gas is not cooled during the process the internal energy of the gas will increase by an amount equal to the work of compression. Therefore if the temperature of the gas is to remain constant during the process gas must reject heat to the surroundings. Since there is no temperature increase in the system change in internal energy becomes zero. And the amount of work done will be the amount of heat supplied. So for isothermal process

$$
\begin{align*}
& { }_{1} \mathrm{Q}_{2}=\left(\mathrm{U}_{2}-\mathrm{U}_{1}\right)+{ }_{1} \mathrm{~W}_{2} \\
& { }_{1} \mathrm{~W}_{2}=\int_{1}^{2} \mathrm{P} \cdot \mathrm{dV} \tag{5.21}
\end{align*}
$$

If the working fluid behaves as an ideal gas and there are no phase changes, then, the work done, heat transferred and entropy change during the isothermal process are given by:

$$
\begin{align*}
& { }_{1} \mathrm{Q}_{2}={ }_{1} \mathrm{~W}_{2}(\because \mathrm{U}=\mathrm{f}(\mathrm{~T})) \\
& { }_{1} \mathrm{~W}_{2}=\int_{1}^{2} \mathrm{P} \cdot \mathrm{dV}=\mathrm{mRT} \ln \left(\frac{\mathrm{v}_{2}}{\mathrm{v}_{1}}\right)=\mathrm{mRT} \ln \left(\frac{\mathrm{P}_{1}}{\mathrm{P}_{2}}\right)  \tag{5.22}\\
& \mathrm{S}_{2}-\mathrm{S}_{1}=\mathrm{mR} \ln \left(\frac{\mathrm{v}_{2}}{\mathrm{v}_{1}}\right)=\mathrm{mR} \ln \left(\frac{\mathrm{P}_{1}}{\mathrm{P}_{2}}\right)
\end{align*}
$$

Adiabatic process: An adiabatic process is one in which no heat transfer takes place to or from the system during the process. For a fluid undergoing an adiabatic process, the pressure and volume satisfy the following relation:

$$
\begin{equation*}
\mathrm{PV}^{k}=\text { constant } \tag{5.23}
\end{equation*}
$$

where $k$ is the coefficient of adiabatic compression or expansion. For an ideal gas, it can be shown that:

$$
\begin{equation*}
\mathrm{PV}^{\gamma}=\text { constant, where } \quad \gamma=\frac{C_{p}}{C_{v}} \tag{5.24}
\end{equation*}
$$

Applying first law of thermodynamics for an adiabatic process, we get:

$$
\begin{align*}
& { }_{1} \mathrm{Q}_{2}=\left(\mathrm{U}_{2}-\mathrm{U}_{1}\right)+{ }_{1} \mathrm{~W}_{2}=0 \\
& { }_{1} \mathrm{~W}_{2}=\int_{1}^{2} \mathrm{P} \cdot \mathrm{dV}=\left(\frac{\mathrm{k}}{\mathrm{k}-1}\right)\left(\mathrm{P}_{2} \mathrm{~V}_{2}-\mathrm{P}_{1} \mathrm{~V}_{1}\right)=\left(\mathrm{U}_{1}-\mathrm{U}_{2}\right) \tag{5.25}
\end{align*}
$$

If the process is reversible, adiabatic then the process is also isentropic:

$$
\begin{equation*}
{ }_{1} \mathrm{Q}_{2}=\int_{1}^{2} \mathrm{~T} . \mathrm{dS}=0 \Rightarrow \mathrm{~S}_{1}=\mathrm{S}_{2} \tag{5.26}
\end{equation*}
$$

The following P-V-T relationships can be derived for a compressible fluid undergoing an adiabatic process:

$$
\begin{equation*}
\frac{\mathrm{T}_{2}}{\mathrm{~T}_{1}}=\left(\frac{\mathrm{V}_{1}}{\mathrm{~V}_{2}}\right)^{k-1}=\left(\frac{\mathrm{P}_{2}}{\mathrm{P}_{1}}\right)^{(k-1) / k} \tag{5.27}
\end{equation*}
$$

If the adiabatic process is reversible, then from the definition of entropy, the process becomes an isentropic process or the entropy of the system does not change during a reversible adiabatic process. Hence all reversible, adiabatic processes are isentropic processes, however, the converse is not true, i.e., all isentropic processes need not be reversible, adiabatic processes.

Polytropic process: When a gas undergoes a reversible process in which there is heat transfer, the process frequently takes place in such a way that a plot of $\log \mathrm{P}$ vs $\log \mathrm{V}$ is a straightline, implying that:

$$
\begin{equation*}
\mathrm{PV}^{n}=\text { constant } \tag{5.28}
\end{equation*}
$$

The value of $n$ can vary from $-\infty$ to $+\infty$, depending upon the process. For example:
For an isobaric process, $\quad \mathrm{n}=0$ and $\mathrm{P}=$ constant
For an isothermal process,

$$
\mathrm{n}=1 \text { and } \mathrm{T}=\text { constant }
$$

For an isentropic process, $\mathrm{n}=\mathrm{k}$ and $\mathrm{s}=$ constant, and
For an isochoric process, $\quad \mathrm{n}=-\infty$ and $\mathrm{v}=$ constant
For a polytropic process, expressions for work done, heat transferred can be derived in the same way as that of a adiabatic process discussed above, i.e.,

$$
\begin{align*}
& { }_{1} \mathrm{~W}_{2}=\frac{\mathrm{n}}{(\mathrm{n}-1)}\left(\mathrm{P}_{2} \mathrm{~V}_{2}-\mathrm{P}_{1} \mathrm{~V}_{1}\right) \\
& \left(\mathrm{U}_{2}-\mathrm{U}_{1}\right)=\mathrm{mc}_{\mathrm{v}, \mathrm{avg}}\left(\mathrm{~T}_{2}-\mathrm{T}_{1}\right) \\
& { }_{1} \mathrm{Q}_{2}=\left(\mathrm{U}_{2}-\mathrm{U}_{1}\right)+\frac{\mathrm{n}}{(\mathrm{n}-1)}\left(\mathrm{P}_{2} \mathrm{~V}_{2}-\mathrm{P}_{1} \mathrm{~V}_{1}\right)  \tag{5.29}\\
& \mathrm{S}_{2}-\mathrm{S}_{1}=\int_{1}^{2} \frac{\mathrm{dU}}{\mathrm{~T}}+\int_{1}^{2} \frac{\mathrm{PdV}}{\mathrm{~T}}
\end{align*}
$$

The above expressions are valid for all values of n , except $\mathrm{n}=1$ (isothermal process)

Throttling (Isenthalpic) process: A throttling process occurs when a fluid flowing through a passage suddenly encounters a restriction in the passage. The restriction could be due to the presence of an almost completely closed valve or due to sudden and large reduction in flow area etc. The result of this restriction is a sudden drop in the pressure of the fluid as it is forced to flow through the restriction. This is a highly irreversible process and is used to reduce the pressure and temperature of the refrigerant in a refrigeration system. Since generally throttling occurs in a small area, it may be considered as an adiabatic process (as area available for heat transfer is negligibly small) also since no external work is done, we can write the $1^{\text {st }}$ law of thermodynamics for this process as:

$$
\begin{align*}
& \dot{\mathrm{Q}}=\dot{\mathrm{W}}=0 \\
& \mathrm{~h}_{1}+\frac{\mathrm{V}_{1}{ }^{2}}{2}=\mathrm{h}_{2}+\frac{\mathrm{V}_{2}{ }^{2}}{2} \tag{5.30}
\end{align*}
$$

where $V_{1}$ and $V_{2}$ are the inlet and exit velocities of the fluid respectively. The areas of inlet and outlet of a throttling device are designed in such a way that velocities at inlet and outlet become almost equal. Then the above equation becomes

$$
\begin{equation*}
\mathrm{h}_{1}=\mathrm{h}_{2} \tag{5.31}
\end{equation*}
$$

Thus throttling process is an isenthalpic process.

Though throttling is an expansion process, it is fundamentally different from expansion taking place in a turbine. The expansion of a fluid in a turbine yields useful work output, and can approach a reversible process (e.g. isentropic process), whereas expansion by throttling is highly irreversible. Depending upon the throttling conditions and the nature of the fluid, the exit temperature may be greater than or equal to or less than the inlet temperature.

## Questions:

1. Prove T dS equations starting from basic laws of thermodynamics? (Solution)
2. An interesting feature of the process of cooling the human body by evaporation is that the heat extracted by the evaporation of a gram of perspiration from the human skin at body temperature $\left(37^{\circ} \mathrm{C}\right)$ is quoted in physiology books as 580 calories/gm rather than the nominal 540 calories/gm at the normal boiling point. Why is it larger at body temperature? (Solution)
3. Find the saturation temperature, the changes in specific volume and entropy during evaporation, and the latent heat of vaporization of steam at 0.1 MPa ? (Solution)
4. Under what conditions of pressure and temperature does saturated steam have a entropy of $6.4448 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}$ ? State the specific volume and entropy under such conditions. (Solution)
5. Find the enthalpy of steam when the pressure is 2 MPa and the specific volume is $0.09 \mathrm{~m}^{3} / \mathrm{kg}$. (Solution)
6. A gas of mass 4 kg is adiabatically expanded in a cylinder from $0.2 \mathrm{~m}^{3}$ to $0.5 \mathrm{~m}^{3} \quad$ Initial pressure of the gas is 2 bar, and the gas follows the following pressure-volume relationship

$$
P V^{1.4}=\mathrm{K}(\mathrm{~K}=\text { constant })
$$

Find the decrease in the temperature of the gas? ( $\mathrm{C}_{\mathrm{V}}$ for the gas $\left.=0.84 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}\right)$ (Solution)
7. Air is contained in a vertical cylinder that is fitted with a frictionless piston. A set of stops is provided 0.5 m below the initial position of the piston. The piston cross-sectional area is $0.5 \mathrm{~m}^{2}$ and the air inside is initially at 100 kPa and 400 K . The air is slowly cooled as a result of heat transfer to the surroundings.

a) Sketch these two processes on P-V and T-V diagrams
b) What is the temperature of the air inside the cylinder when the piston reaches the stops?
c) After the piston hits the stops, the cooling is continued until the temperature reaches 100 K . What is the pressure at this state?
d) How much work is done by the system in the first cooling process?
e) How much work is done by the system in the second cooling process?

Assume air to be a thermally perfect gas and the first cooling is a quasi-static process. (Solution)
8. Consider a thermodynamic system containing air at $\mathrm{V}_{1}=1 \mathrm{~m}^{3} / \mathrm{kg}, \mathrm{P}_{1}=100 \mathrm{kPa}$. The system is compressed to $0.5 \mathrm{~m}^{3} / \mathrm{kg}$ via anyone of three quasi-static processes: isobaric, isothermal, or adiabatic. Assume that $\mathrm{C}_{\mathrm{v}}=0.7165 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$, and $\mathrm{R}=0.287 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$.
a) Sketch all three processes on the same P-V diagram.
b) For each process determine the pressure and temperature at the final state.
c) For each process determine the work done by the system and the heat transferred to the system. (Solution)

