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Thermodynamics

Index

Topics	Page
1. Basic Concepts & Zeroth Law of Thermodynamics	2
2. First Law of Thermodynamics	8
3. Second Law of Thermodynamics	10
4. Entropy Availability and Irreversibility	16
5. Properties of Pure Substances	25
6. Thermodynamic Relations & real Gas Mixtures	37

Basic Concepts & Zeroth Law of Thermodynamics

System

A system can be defined as a quantity of matter (control mass) or a region (control volume) in space selected for the study.

SURROUNDING- Everything external to the system is known as surrounding or the environment. Energy interaction is studied between the system and surroundings i.e. every energy leaving the system will be absorbed by the surrounding and vice versa.

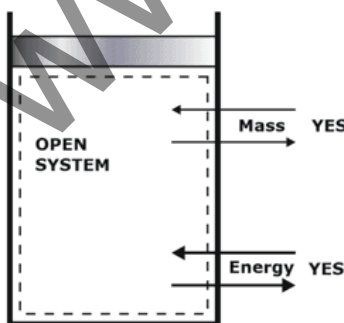
BOUNDARY- An imaginary or real surface that demarcates the system from its surroundings is known as the boundary. The boundary is the surface of contact between the system and surrounding, thus, shared by both the system and the surroundings. Mathematically, the boundary has no thickness, and can neither occupy any volume in space nor contain any mass. The boundary may either be moving or fixed.

Universe- A system and its surroundings together constitute the universe. Everything is contained in the universe, so everything occurring whether energy transfer or transformation or losses remains inside the universe.

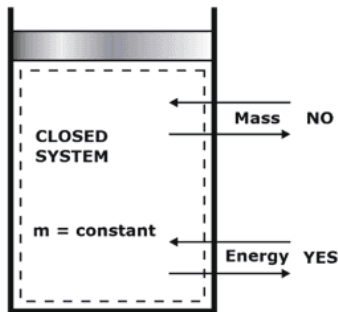
Types of System

Depending upon the mass and energy interaction.

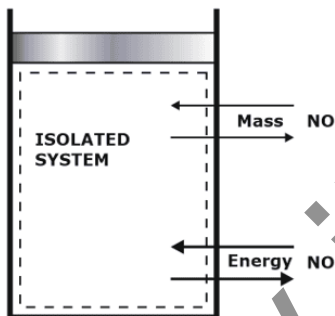
(i) **Open System** – When there is mass as well as energy transfer across the boundary, that type of system is called an Open system. Example - air compressor, boiler, pump, IC engine with valve open, etc. The majority of engineering devices come under this category.



(ii) closed system – When in a system, the mass remains fixed or constant but there may be energy transfer into or out of the system i.e. no mass transfer occurs across the system boundary but only energy transfer. Example – Tea in kettle, automobile engine with valve closed etc.



(iii) Isolated system - When there is no mass and energy interaction taking place between the system and the surroundings, such systems are called isolated systems. It is of fixed mass and energy, and there is no mass or energy interaction across the system boundary. Example – thermo-flask, Universe



Macroscopic v/s Microscopic Approach

Macroscopic Approach - When a certain quantity of matter is considered, without getting into molecular level, such systems are called Isolated systems (also called as **classical approach**). Every property will be the average of that property of each molecule passing through that space.

Microscopic Approach - When study is made on a molecular level as matter is composed of a large number of molecules, such approach is called a Microscopic approach. The behavior of the gas is determined by considering the behavior of each molecule.

CONCEPT OF CONTINUUM- The concept of the continuum is the idealization of the continuous description of matter where the properties of the matter are considered as continuous functions of space. The space between the molecules (mean free path) is almost zero or negligible when compared to the size of the system.

Extensive Properties v/s Intensive Properties

(i) Extensive Properties – The properties dependent on mass are known as extensive properties (sometimes known as extrinsic properties). Since, the mass of the specimen changes, the value of extensive properties will also change according to it.

Example – Volume, Enthalpy, Weight, etc.

(ii) Intensive Properties – Extrinsic properties per unit mass, are intensive properties. These properties are independent of the mass of the system (also known as intrinsic properties). It is a system property, independent of quantity.

Example – Pressure, Density, Viscosity, specific energy, specific enthalpy etc.

Thermodynamic Equilibrium

When no change in macroscopic properties is observed, a system is said to be in a state of thermodynamic equilibrium. A system will be in a state of thermodynamic equilibrium if the following conditions are met:

(i) Mechanical Equilibrium - without the presence of an unbalanced force within the system itself and also between the system and the surroundings.

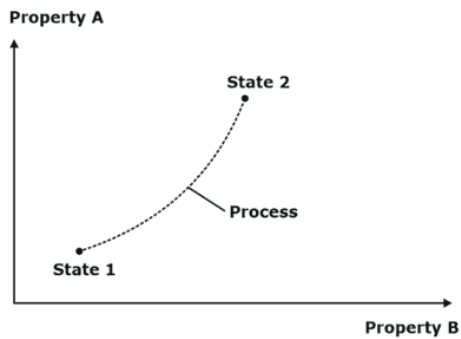
(ii) Chemical equilibrium - an absence of any chemical reaction or transfer of matter from one part of the system to another.

(iii) Thermal equilibrium - When a system exists in mechanical as well as a chemical equilibrium when separated from its surroundings by a diathermic wall (diathermic means 'which allows heat to flow').

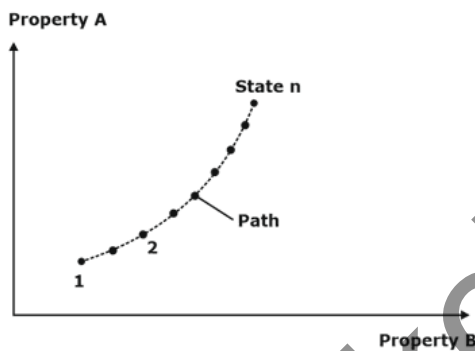
Even when one of these conditions is not met, the system can't be in thermodynamic equilibrium.

The thermodynamic properties are defined only for thermodynamic equilibrium states.

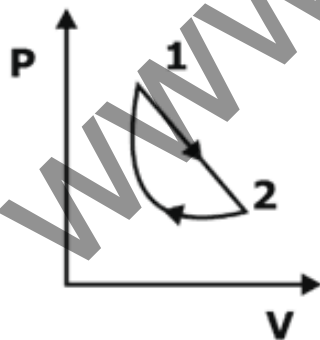
PROCESS - Any change of state that a system undergoes, from one equilibrium state to another equilibrium state is known as a process.



PATH - The succession of states passed through during a change of state from an initial condition to the final required condition, is called the path of the change of state.

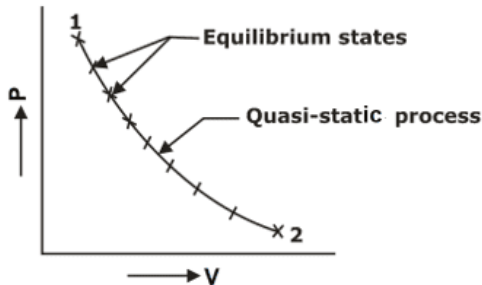


CYCLE - A series of changes in states of a system, such that the final point of the system coincides with the initial point is termed as a cycle.



QUASI-STATIC PROCESS- The meaning of 'Quasi' is 'almost' and the meaning of 'Static' is 'at rest'. The characteristic feature of a quasi-static process is its

infinite slowness. A process that is the locus of all the equilibrium states the system passes through from an initial condition to the final desired condition is known as a quasi-static process. Every state of the system through which it passes during this process is an equilibrium state.



Reversible and Irreversible Process

A reversible process is a process that can be reversed without causing any permanent change in the surroundings. That is, both the system and the surroundings are returned to their initial states if the given process is reversed. In the property diagrams, reversible processes are shown by continuous line or curve whereas irreversible processes are shown by dotted line or curve.

Reversible processes are actually only theoretical. They are a mere idealization of actual processes. Processes that are not reversible are termed irreversible processes.

PURE SUBSTANCE- A substance that has a uniform and invariable chemical composition throughout its mass is known as a pure substance.

Examples: Atmospheric air, steam-water mixture, ammonia, etc.

IDEAL GAS EQUATION - Ideal (perfect) gas equation is a unique equation of state, which is applicable specifically to ideal gases. The molecular forces of attraction between gas molecules are negligible in an ideal gas. The volume of the molecules should be negligible compared to the total volume for a perfect gas. Following is the perfect or ideal gas equation :

$$PV=nRT$$

Where:

P = Absolute Pressure = atmospheric pressure + Gauge pressure (in pascal)

V = Volume in m^3

R = Universal Gas constant = 8.314 KJ/Kmol-K

T = Absolute temperature in kelvin

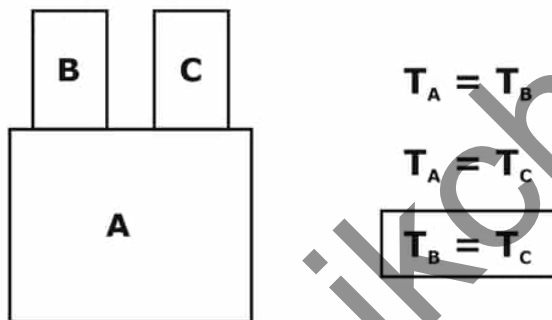
n = number of moles (in k-mol)

Boyle's Law- When the temperature is kept constant, the variation of pressure is such that for a volume of a given mass of gas it varies inversely.

Charles Law- When the pressure remains constant, then the volume occupied by a fixed amount of gas is directly proportional to its absolute temperature. It is the basis of temperature measurement.

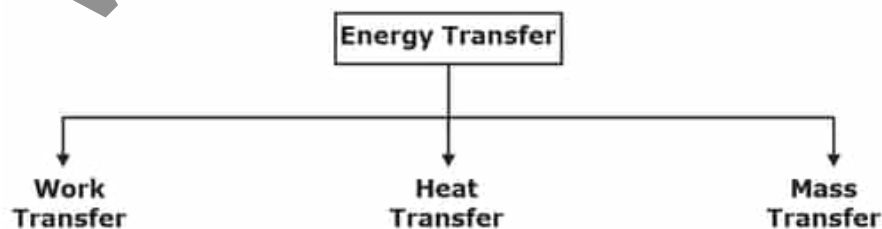
ZEROTH LAW OF THERMODYNAMICS

- It is the basic law of thermodynamics which defines the temperature.
- It defines that "If thermal equilibrium of body P exists with a body Q and body R separately, then there must be thermal equilibrium between Q and R also".



Energy

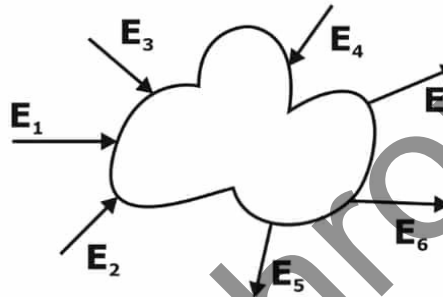
(i). In a thermodynamic system, Energy interaction can be in three ways namely work, heat, and by mass.



(ii). There is only work transfer and Heat transfer interaction between a closed system and surroundings without any mass transfer, while work, Heat, and mass transfer interaction all occur in the open system (because mass also carries energy).

First Law of Thermodynamics

- The first law of thermodynamics is to relate the various form of energy and energy interaction.
- Its states that “In a process the creation or destruction of energy is impossible but it can be changed from one form to another form” and it is known as the “Conservation of energy principle”.



- From the above statement, we can say that the energy leaving the system must be equal to the energy supplied to the system.

$$E_{in} = E_{out}$$

$$E_1 + E_2 + E_3 + E_4 = E_5 + E_6 + E_7$$

FIRST LAW FOR A CLOSED SYSTEM UNDERGOING A CYCLE

As per the first law for a closed system undergoing a cycle, net heat interaction in a cycle is equal to the net Work interaction.

where J is the Joule's equivalent. This is also expressed in the form

$$\oint dW = \oint dQ$$

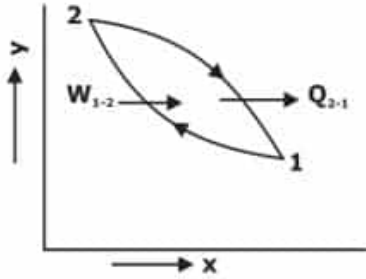


Fig.1: Closed System Undergoing A Cycle

1st LAW FOR A CLOSED SYSTEM UNDERGOING A CHANGE OF STATE (for a process):

The expression:

$$(\Sigma W)_{\text{cycle}} = J(\Sigma Q)_{\text{cycle}}$$

The above equation is applicable only to systems undergoing cycles, and the algebraic sum of all energy interaction across system boundaries is zero.

If both heat transfer and work transfer are involved in a change of state of the system, then the net energy transfer will be stored or accumulated within the system.

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

Then, net energy transfer ($Q - W$) will be stored in the system.

Energy in storage is not in the form of heat and work and it is simply the energy of the system, thus referred as the internal energy of the system.

Therefore: $Q - W = \Delta E$

where ΔE : Increase in the energy of the system.

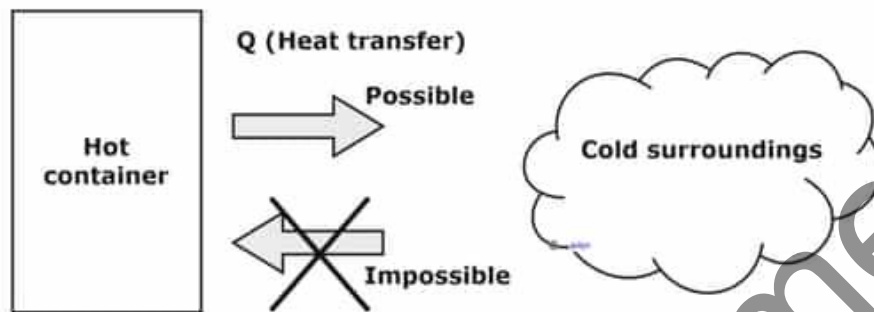
$$Q = \Delta E + W$$

Consequences of 1st Law of Thermodynamics

(i) Heat is a path function.

- (ii) Energy-a property of the system.
- (iii) Energy of isolated system is Constant.
- (iv) Perpetual motion machine of first kind-PMM1 is not possible.

Second Law of Thermodynamics



The figure shown above shows us that the heat transfer process can occur only when it satisfies both the first and the second laws of thermodynamics.

- The second law also asserts that energy has a quality attached to it and its preservation is a major concern of engineers. In the above example, it can be seen that the energy contained in the hot container (present at a higher temperature) has a higher quality (ability to work) compared to the energy stored (at a lower temperature) in the surroundings.
- The second law is also used in the determination of the theoretical limits of the performance of the general engineering systems like heat engines and refrigerators etc.

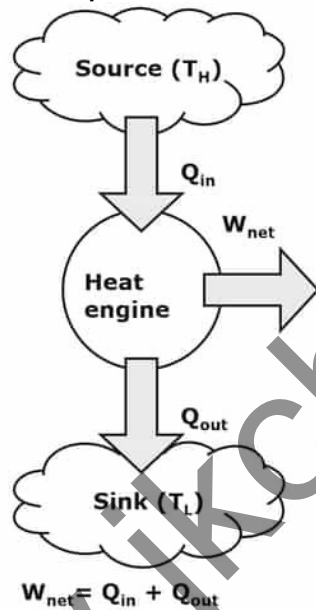
Thermal Energy Reservoirs

- Thermal energy reservoirs are hypothetical bodies that have a relatively large thermal energy capacity (mass \times specific heat). They can supply or absorb infinite amounts of heat without undergoing any change in temperature. Lakes, atmosphere, seas are examples of thermal reservoirs.
- As a two-phase can absorb and release large quantities of heat while remaining at a constant temperature, therefore it can be modeled as a reservoir.

- A reservoir that supplying energy in the form of heat is called a source and the one absorbing energy in the form of heat is known as the sink.

Heat Engines

- Heat engines perform the work of conversion of heat into work. The working of heat engines is described as follows :
 - receiving heat from a high-temperature source (oil furnace, nuclear reactor, etc.)
 - conversion of a part of this heat to work
 - rejection of the remaining waste heat to a low-temperature sink
 - cyclic operation



- Thermal efficiency: Ratio of the network generated to the total heat supplied to the engine.

$$\eta_{th} = \frac{W_{net,out}}{Q_{in}}$$

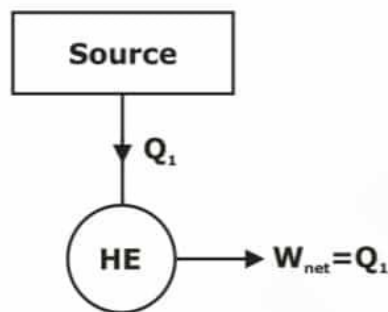
$$W_{net,out} = Q_{in} - Q_{out}$$

$$\eta_{th} = 1 - \frac{Q_{out}}{Q_{in}}$$

- The thermal efficiencies of work-developing systems are low. The thermal efficiency of ordinary spark-ignition automobile engines is about 20%, thermal efficiency of diesel engines is about 30%, and that of a power plant is in the range of 40%.

The Second Law: Kelvin-Planck Statement

- The Kelvin Planck statement is "it is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work." In other words, its impossible for a heat engine to attain a thermal efficiency of 100%.

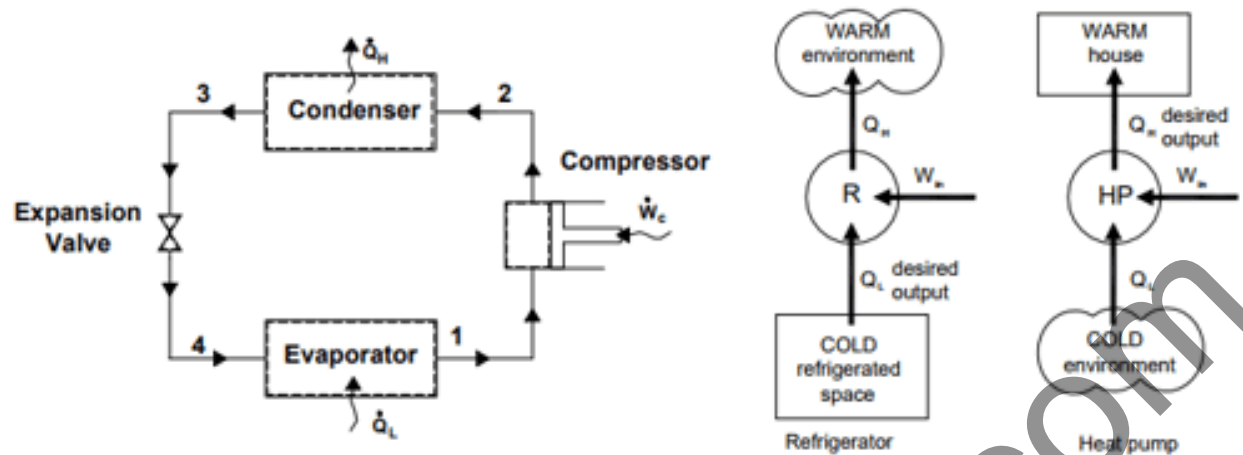


Impossible

The figure above shows a heat engine that violates the Kelvin-Planck statement of the second law and such a heat engine cannot be built.

Refrigerators and Heat Pumps

- Naturally, heat flows from higher temperature regions to lower temperature ones. It is not possible for the reversal of this process to occur by itself.
- Special devices are used for the transfer of heat from a lower temperature region to a higher temperature one namely refrigerators and heat pumps.
- Refrigerators and heat pumps are cyclic devices where the working fluids used in the cycles are called refrigerants.
- Refrigerators and heat pumps are more or less the same devices; differing in their objectives only. A refrigerator maintains the refrigerated space at a lower temperature whereas a heat pump absorbs heat from a lower temperature source and supplies the heat to a warmer medium.



Coefficient of Performance (COP)

- The performance of heat pumps and refrigerators is expressed in terms of the coefficient of performance (COP) which is expressed as:

$$(\text{COP})_R = \frac{\text{Desired Effect}}{\text{Work Input}} = \frac{q_L}{W_c}$$

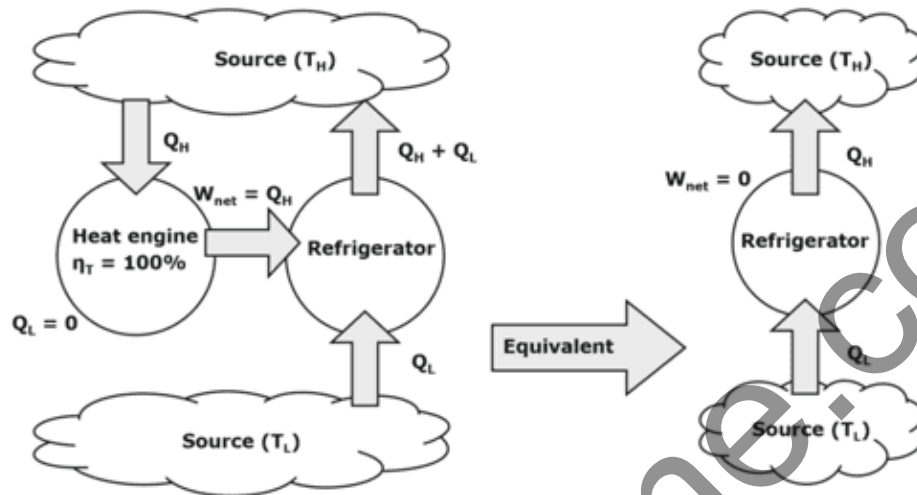
$$(\text{COP})_{HP} = \frac{\text{Desired Effect}}{\text{Work Input}} = \frac{q_H}{W_c}$$

- Mathematically, it can be seen that:
 $\text{COP}_{HP} = \text{COP}_R + 1$
- Air conditioners perform nearly the same task refrigerators perform but the refrigerated space is a room or a building.
- The Energy Efficiency Rating (EER) is the ratio of the quantity of heat removed from the cooled space to the power consumed by the unit.
- Most air conditioners have an EER in the range of 8 to 12 (with COP of 2.3 to 3.5).

The Second Law of Thermodynamics: Clausius Statement

- The Clausius statement is - "It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body."
- A refrigerator can only operate when its compressor is driven by an external power source.
- Kelvin-Planck and Clausius's statements of the second law both being negative statements, cannot be proved.

- The two statements of the second law are equivalent and therefore any device violating the Kelvin-Planck statement also violates the Clausius statement and vice versa.



The violation of the Kelvin-Planck statement leads to the violation of the Clausius statement is being shown in the above figure.

Note:

- A perpetual-motion machine of the first kind (**PMM1**) is a device that violates the **first law of thermodynamics** (by generating energy).
- A perpetual-motion machine of the second kind (**PMM2**) is a device that violates the second law of Thermodynamics.

Read also: Zeroth and First Law of Thermodynamics Notes for Mechanical Exams

Reversible and Irreversible Process

- A reversible process is a process that can be reversed without causing any permanent change in the surroundings. That is, both the system and the surroundings return to their initial states if the given process is reversed. In the property diagrams, reversible processes are shown by continuous line or curve whereas irreversible processes are shown by dotted line or curve.

Reversible processes are actually only theoretical. They are a mere idealization of actual processes. Processes that are not reversible are termed irreversible processes.

- Some of the factors causing irreversibility's in a process are listed below:
 - Friction
 - Unrestrained expansion and compression
 - mixing
 - Heat transfer (finite ΔT)
 - Inelastic deformation
 - Chemical reactions

The Carnot Cycle

- The execution of the processes that make up a heat engine cycle greatly affects the efficiency of the cycle.
- The maximum efficiency could be attained if all the processes involved are made reversible and the best known reversible cycle is the Carnot cycle.
- Reversible cycles are practically not possible due to the irreversibility's involved.
- The reversible cycles give us an idea of the upper limits on the performance of real cycles.
- The Carnot cycle has four processes:
 - **1-2 Reversible isothermal expansion**
 - **2-3 Reversible adiabatic expansion**
 - **3-4: Reversible isothermal compression**
 - **4-1: Reversible adiabatic compression**
- The thermal efficiency of a heat engine (reversible or irreversible) is provided by the following expression :

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

- For the Carnot cycle, it is:

$$\eta_{th,Carnot} = 1 - \frac{T_L}{T_H}$$

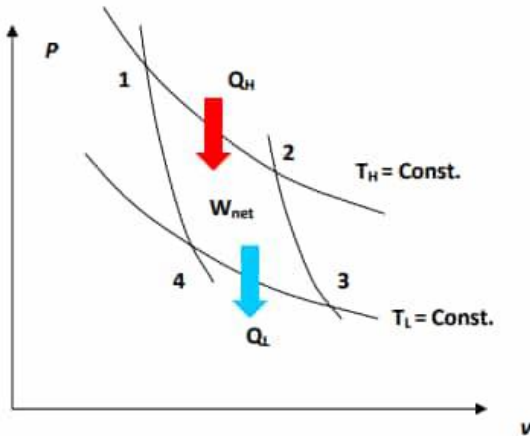


Fig above shows P-v diagram for the Carnot cycle.

- An irreversible (real) cycle operating between the same two thermal reservoirs has an efficiency which is always lesser than the Carnot cycle.

The Carnot Refrigeration and Heat Pump Cycle

- A refrigerator or heat pump operating on the reversed Carnot cycle is called a Carnot Refrigerator, or a Carnot heat pump.
- The COP (Coefficient of Performance) of any refrigerator or heat pump (reversible or irreversible) is given by:

$$(\text{COP})_R = \frac{1}{\frac{Q_H}{Q_L} - 1} \quad \text{and} \quad (\text{COP})_{HP} = \frac{1}{1 - \frac{Q_L}{Q_H}}$$

- COP of all reversible refrigerators or heat pumps can be calculated by:

$$(\text{COP})_{R,\text{rev}} = \frac{1}{\frac{T_H}{T_L} - 1} \quad \text{and} \quad (\text{COP})_{HP,\text{rev}} = \frac{1}{1 - \frac{T_L}{T_H}}$$

Also, similar to heat engine, one can conclude:

$$\left\{ \begin{array}{l} < \text{COP}_{R,\text{rev}} & \text{Irreversible refrigerator} \\ = \text{COP}_{th,\text{rev}} & \text{Reversible refrigerator} \\ > \text{COP}_{th,\text{rev}} & \text{Impossible refrigerator} \end{array} \right.$$

Entropy Availability and Irreversibility

Entropy

The Clausius Inequality

- The first law is just a balance of energy.
- The second law states an inequality ie an irreversible process is less efficient than a reversible process.
- One of such important inequalities is that of the Clausius inequality in Thermodynamics according to which the cyclic integral of $\delta Q / T$ is always less than or equal to zero.
- It is valid for all cycles, be it reversible or irreversible.
- The basis for the definition of a new property called entropy is formed by the Clausius inequality.
- For an internally reversible process, the cyclic integral of $\delta Q / T$ is zero.
- If the cyclic integral of a quantity is zero, it means that it depends on the state only and not the process path. Hence, it is a property.
- For an irreversible process, the value of entropy change for a closed system is greater than the value of integral of dQ/T evaluated for that process.
- If the energy exchange takes place, δQ will be the energy transfer from the surroundings to the system.

$$\oint \frac{\delta Q}{T} = 0 \rightarrow \text{Reversible}$$

$$\oint \frac{\delta Q}{T} < 0 \rightarrow \text{Irreversible}$$

$$\oint \frac{\delta Q}{T} > 0 \rightarrow \text{Impossible}$$

TEMPERATURE-ENTROPY PLOT

$$dS = \frac{dQ_{\text{rev}}}{T}$$

Now $dQ_{\text{rev}} = TdS$

$$Q_{\text{rev}} = \int_i^f T dS$$

Thus, area under the T -S plot on S axis will give the heat transfer in a reversible process.

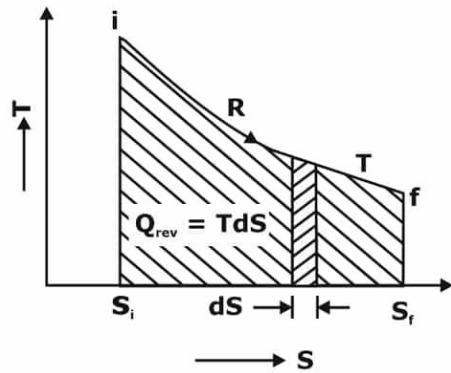


Fig.: Area under a reversible path on the T-s plot

THE INCREASE OF ENTROPY PRINCIPLE:

Let us assume a cycle that is made up of two processes as shown below:

process 1-2, which is an arbitrary process (reversible or irreversible),

and process 2-1, which is internally reversible in nature, as shown in the Figure below,

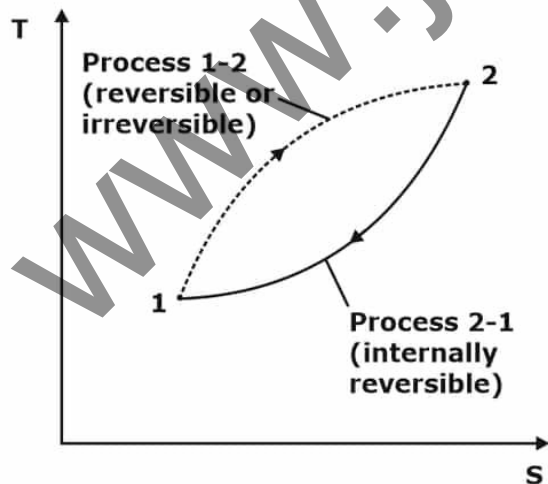


Fig.: Combination of reversible & irreversible process

$$S_2 - S_1 \geq \int_1^2 \frac{dQ}{T}$$

where the equality is for the internally reversible process and the inequality for the irreversible process.

It should be kept in mind that the entropy generation S_{gen} is always a positive quantity or zero. Its value is process-dependent, and thus it is not a property of the system.

$$S_{gen} \geq 0$$

$$S_{gen} < 0 \quad (\text{impossible Process})$$

For an isolated system,

$dQ = 0$ since no energy interaction occurs between the system and the surrounding.

Therefore, for an isolated system

$$dS_{iso} \geq 0$$

For a reversible process,

$$dS_{iso} = 0$$

implies, $S = \text{constant}$

For an irreversible process

$$dS_{iso} > 0$$

Entropy change of the system:

Entropy change of the system is summation entropy change due to internal irreversibility and entropy change due to external interaction

$$dS = (dS)_{irr} + (dS)_{EI}$$

$$dS = \frac{dQ}{T} + S_{\text{gen}}$$

T-dS EQUATION

$$s_2 - s_1 = C_v \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right) \dots\dots(1)$$

$$s_2 - s_1 = C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right) \dots\dots(2)$$

Note:

Equation (1) & (2) are applicable for both reversible process as well as the irreversible process because it contains all properties.

APPLICATIONS OF ENTROPY PRINCIPLE:

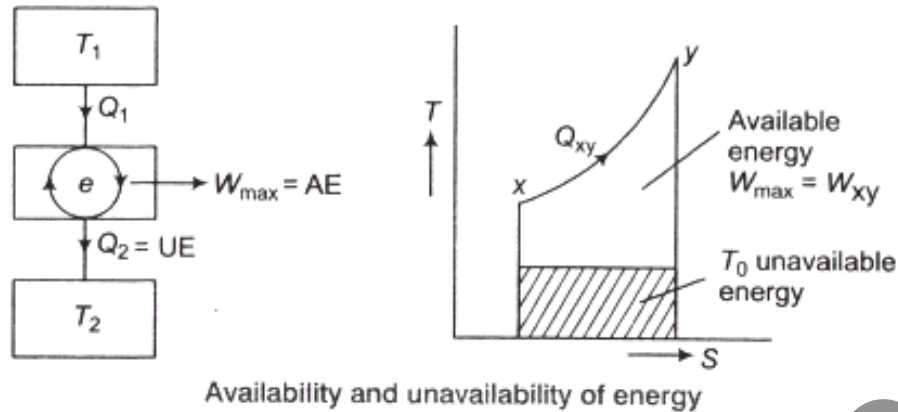
For every irreversible process, there is an increase of entropy of the universe, and this entropy increase determines the extent of the irreversibility of the process. The higher the entropy increase of the universe; the higher will be the irreversibility of the process.

Some of the applications of the entropy principle are illustrated in the following.

- (A) Heat transfer through a Finite Temperature Difference.
- (B) Two fluids mixing with each other.
- (C) Maximum Work that can be obtained from Two Finite Bodies at Temperatures T_1 and T_2 interacting in a reversible manner.

The sources of energy can be divided into two groups i.e., high grade energy (mechanical work, electrical energy, water power, wind power) and low grade energy (heat or thermal energy, heat derived from nuclear fission or combustion of fossil fuels). That part of the low grade energy which is available for, conversion is referred to as available energy, while the part which is not available is known as unavailable energy.

Availability: When a system is subjected to a process from its original state to dead state the maximum amount of useful work that can be achieved under ideal conditions is known as available energy or availability of the system.

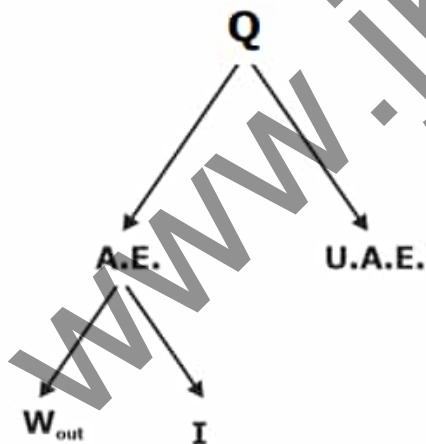


$$W_{\max} = AE = Q_{xy} - T_0(S_y - S_x)$$

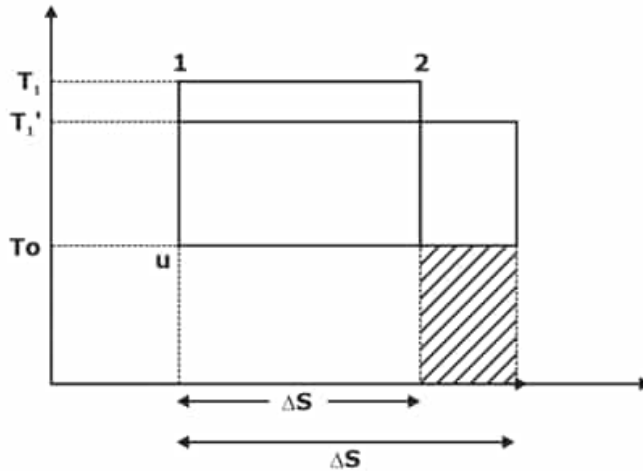
$$\text{Unavailable Energy: } UAE = T_0(S_y - S_x)$$

where, S_x and S_y are the entropy at x and y , respectively.

The Available Energy (AE) is also known as exergy and the Unavailable Energy (UAE) as anergy. The energy which cannot be utilised for doing useful work is called unavailable energy. Irreversibility is equivalent to energy destroyed, hence also known as energy destruction consider the example given below.



DECREASE IN AVAILABILITY WHEN HEAT TRANSFER THROUGH FINITE TEMPERATURE DIFFERENCE



Consider a reversible heat engine operating between T_1 and T_0 .

$$Q_1 = T_1 \cdot \Delta s$$

$$W = AE = (T_1 - T_0)\Delta s$$

Let us now consider heat Q_1 is transferred through a finite temperature difference.

$$Q_1 = T_1 \Delta s = T'_1 \cdot \Delta s'$$

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

$$Q_2 = T_0 \Delta s \rightarrow \text{Initial UAE}$$

$$Q'_2 = T_0 \Delta s' \Rightarrow \text{Afterward UAE}$$

$$Q'_2 > Q_2$$

$$W' = Q'_1 - Q'_2$$

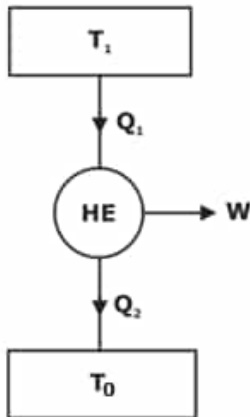
$$W' = T'_1 \Delta s' - T_0 \Delta s'$$

$$W' = (T'_1 - T_0) \Delta s'$$

$$W = (T_1 - T_0) \Delta s$$

Hence increase in UAE and the shaded portion represent increase in UAE.

SECOND LAW EFFICIENCY: Second law efficiency is the ratio of the exergy recovered to the exergy spent. OR It is the ratio of actual work produced to the max work produced under reversible condition. Consider the case of heat engine.



$$\text{Energy recovered} = Q_1 - Q_2 = W$$

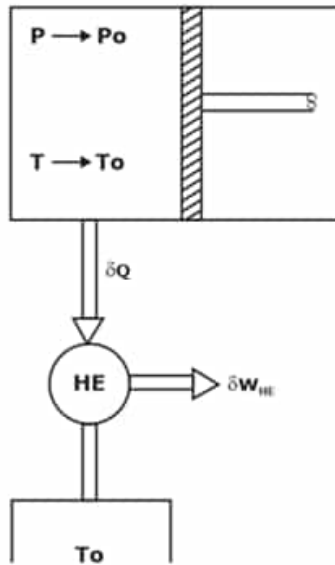
$$\text{Energy spent} = \left(1 - \frac{T_0}{T_1}\right) Q_1$$

$$\eta_{111} = \frac{W}{\left(1 - \frac{T_0}{T_1}\right) Q_1} = \frac{W | Q_1}{\left(1 - \frac{T_0}{T_1}\right) Q_1}$$

$$\eta_{111} = \frac{(\eta_{\text{thermal}})_{\text{act}}}{(\eta_{\text{thermal}})_{\text{Rev}}}$$

The second law efficiency is measure of the performance of a device relative to its performance under reversible conditions.

EXERGY OF A CLOSED SYSTEM : Consider a piston cylinder device that contains a fluid of mass m at temperature T and pressure P . The system is then allowed to undergo a differential change of state during which volume changes by dV and heat is transferred from the system to surroundings.



For change of exergy from state 1 to state 2.

$$\Phi_1 = (E_1 - E_0) + P_0(V_1 - V_0) - T_0(S_1 - S_0)$$

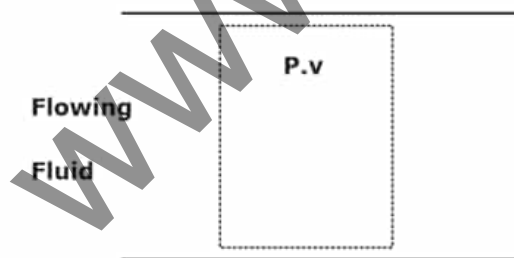
$$\Phi_2 = (E_2 - E_0) + P_0(V_2 - V_0) - T_0(S_2 - S_0)$$

$$\Phi_1 - \Phi_2 = \text{Energy at state 1} - \text{Energy at state 2}$$

$$\Phi_1 - \Phi_2 = (E_1 - E_2) + P_0(V_1 - V_2) - T_0(S_1 - S_2)$$

EXERGY OF OPEN SYSTEM: A flowing fluid has an additional form of energy, called flow energy, which is the energy needed to maintain flow in Pipe.

$$W_{\text{flow}} = PV$$



Exergy associated with system is

$$\Phi_{\text{flowing fluid}} = \Phi_{\text{non flow fluid}} + \Phi_{\text{flow}}$$

$$\Phi_{\text{flowing fluid}} = (E_1 - E_0) + P_0(V_1 - V_0) - T_0(S_1 - S_0) + P_1V_1 - P_0V_0$$

$$\Phi_{\text{flowing}} = U_1 - U_0 + (KE)_1 - (KE)_0 + (PE)_1 - (PE)_0 + P_1V_1 - P_0V_0 - T_0(S_1 - S_0)$$

$$\Phi_{\text{flowing fluid}} = (U_1 + P_1V_1) - (U_0 + P_0V_0) - T_0(S_1 - S_0) + (KE)_1 - (KE)_0 + (PE)_1 - (PE)_0$$

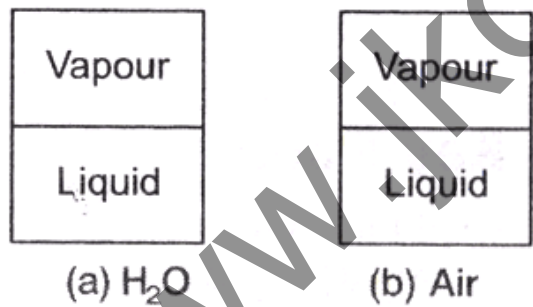
$$\Phi_{\text{flowing}} = (H_1 - H_0) - T_0(S_1 - S_0) + (KE)_1 - (KE)_0 + (PE)_1 - (PE)_0$$

Properties of Pure Substances

- A pure substance is a material with homogeneous and invariable composition.
- Pure substances can have multiple phases, an ice water mixture is still a pure substance but an air-steam is not a pure substance.

Pure Substance:

- A substance that has a fixed chemical composition throughout is called a pure substance i.e., water, nitrogen, helium, and CO₂.
- Substances which are mixture of various elements or compounds also qualifies as pure substances as long as mixture is homogeneous.



Saturation Temperature and Saturation Pressure:

- At given pressure, the temperature at which a pure substance changes phase is called the saturation temperature T_{sat} .
- Likewise at a given temperature, the pressure at which a pure substance changes phase is called the saturation pressure p_{sat} .

Example: For water at a pressure of 101.325 kPa, T_{sat} is 100°C, conversely at a temperature of 100°C, p_{sat} is 101.325 kPa.

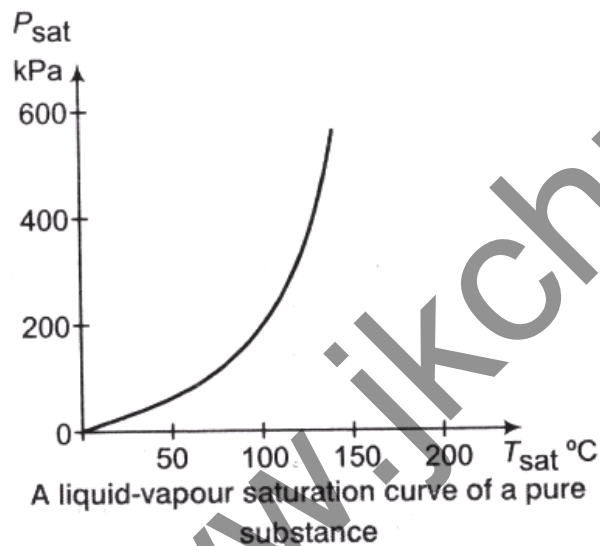
Latent Heat:

- The amount of energy absorbed or released during a phase change process is called the **latent heat**.
- The amount of energy absorbed during melting is called the latent heat of vaporization.
- Similarly, the amount of energy absorbed during vaporization is called latent heat of vaporization and is equivalent to the energy released during condensation.

Liquid-Vapour Saturation Curve:

From the following figure, it is clear that T_{sat} increases with p_{sat} . Thus, a substance at higher pressure will boil at higher temperatures.

$$T_{sat} = f(p_{sat})$$

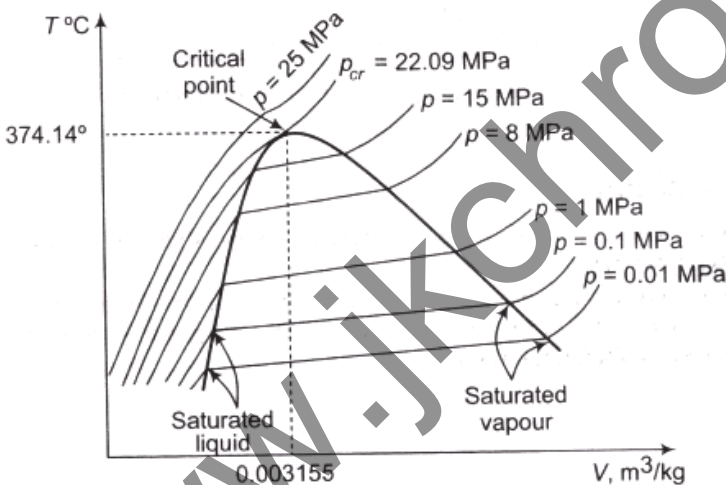


- In the kitchen, higher boiling temperature means shorter cooking time and energy saving.
- The atmospheric pressure, and thus the boiling temperature of water, decreases with elevation. Therefore, it takes longer time to cook at higher altitudes than it does at sea level.

Property Diagrams for Phase-change Process

The T-V Diagram:

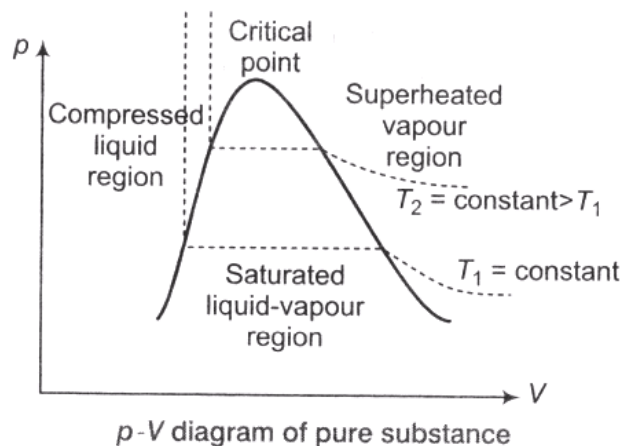
- The specific volume of the saturated liquid is larger and the specific volume of the saturated vapour is smaller than the corresponding values at 1 atm pressure. That is, the horizontal line that connects the saturated liquid and saturated vapour states is much shorter.
- As the pressure is increased further, this saturation line will continue to get shorter as shown in figure and it will become a point when the pressure reaches 22.09 MPa for the case of water. This point is called the critical point and it is defined as the point at which the saturated liquid and saturated vapour state are identical.
- At pressure above the critical pressure, there will not be a distinct phase change. Instead, the specific volume of the substance will continually increase and at all times there will be only one phase present. It is customary to refer to the substance as superheated vapour at temperature above the critical temperature and as compressed liquid at temperatures below the critical temperature.



T-V diagram of constant pressure phase-change process of a pure substances at various pressures.

Triple Phase:

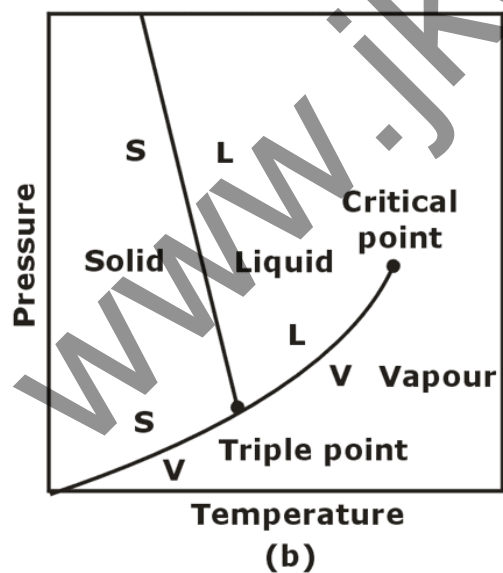
- When all three phases of a pure substance co-exist in equilibrium. It is called **triple phase**.
- Triple phase states form a line called the triple line.
- The triple line appears as a point on the p - T diagram and therefore is often called the **triple point**.



- No substance can exist in the liquid phase in stable equilibrium at pressure below the triple point pressure.
- The same can be said for temperature for substance that contract on freezing.
- Substances at high pressure can exist in the liquid phase at temperatures below the triple point temperature.

The p - T Diagram:

- Solid – Liquid = Fusion
- Liquid – Vapour = Vaporisation
- Solid – Vapour = Sublimation



Enthalpy

- Enthalpy is a measure of the total energy of a thermodynamic system.
- It includes energy required to create a system and the amount of energy required to make room for it by displacing its environment and establishing its volume and pressure.
- For certain type of processes particularly in power generation and refrigeration.
 - Enthalpy (H) = $U + pV$ (kJ) Or
 - per unit mass $h = u + pV$ (kJ/kg)

Saturated Liquid and Saturated Vapour States:

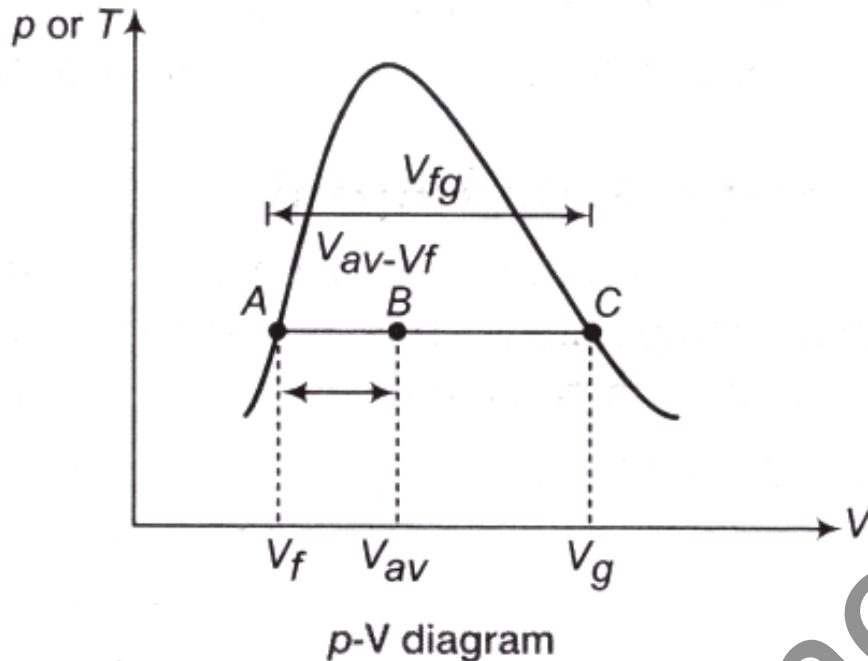
- Subscript f → properties of saturated liquid
- Subscript g → properties of saturated vapour
- V_f → specific volume of saturated liquid
- V_g → specific volume of saturated vapour
- V_{fg} → difference between V_g and V_f
- $V_{fg} = V_g - V_f$
- h_{fg} → enthalpy of vaporisation or latent heat of vaporisation (amount of energy need to vaporise a unit mass of saturated liquid at a given temperature of pressure).
- The magnitude of latent heat depends on temperature and pressure at which phase change occurs.
- For example at 1 atm pressure, the latent heat of fusion of water is 333.7 kJ/kg and latent heat of vaporization is 2257.1 kJ/kg.
- At below triple point pressure, substance begins to change directly gas.
- Enthalpy of vaporization decreases as the temperature or pressure increases and become zero at the critical point.

Saturated Liquid Vapour Mixture:

- During vaporisation process, a substance exists as part liquid and part vapour.
- A new property quality x is the ratio of mass of vapour to the total mass of the mixture.

Quality or dryness fraction:

$$x = \frac{m_{\text{vapour}}}{m_{\text{total}}}$$



$$m_{total} = m_{liquid} + m_{vapour} = m_f + m_g$$

where, m_f = mass of the saturated liquid, and m_g = mass of the saturated vapour

- Quality has significance for saturated mixtures only.
- It has no meaning in the compressed liquid or superheated region.
- Its value lie between 0 (saturated liquid) and 1 (saturated vapour).
- The properties of the saturated liquid are the same whether it exists alone or in a mixture with saturated vapour.
- During vaporization process, only the amount of saturated liquid changes not its properties. The same can be said about a saturated vapour.

Quality :

$$x = \frac{AB}{AC} \Rightarrow x = \frac{V_{av} - V_f}{V_{fg}}$$

- $V_{av} = (1-x)V_f + xV_g$ or $V_{av} = V_f + xV_g$
- $U_{av} = U_f + U_{fg}$
- $h_{av} = h_f + xh_{fg}$

Superheated Vapour :

Since, the superheated region is a single phase region (vapour phase only) temperature and pressure are no longer dependent properties and they can conveniently be used as the two independent properties.

Superheated vapour is characterised by:

- Lower pressures ($p < p_{sat}$ at a given T)
- Higher temperatures ($T < T_{sat}$ at a given p)
- Higher specific volumes ($U > V_g$ at a given p or T)
- Higher internal energies ($U > U_g$ at a given p or T)
- Higher enthalpies ($h > h_g$ at a given p or T)

Thermodynamic Relations & real Gas Mixtures

INTRODUCTION

The properties such as temperature pressure, volume and mass can be calculated directly.

The substances properties such as density (ρ) and specific volume(v) can be estimated using some simple relations.

However, energy, enthalpy (h) and entropy (s) are not very easy to determine because they are not measurable or can not be easily expressed in terms of measurable properties through some simple relations :

1. Maxwell's Equations

These are the set of equations that establish the relation between the partial derivatives of properties P , V , T , and S of a simple compressible system.

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

Helmholtz function

$$F = U - TS \text{ (availability of closed system)}$$

Gibb's function

$$G = H - TS \text{ (availability of open system)}$$

For all real processes, the value of the Helmholtz function & Gibbs function decreases & attains a min value at equilibrium.

Helmholtz function

$$F = U - TS \text{ (availability of closed system)}$$

Gibb's function

$$G = H - TS \text{ (availability of open system)}$$

For all real processes the value of Helmholtz function & Gibbs function decreases & attains a min value at equilibrium.

Hence Four Maxwell's relations are,

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

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial S}\right)_p$$

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

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

COEFFICIENT OF VOLUME EXPANSION (β)

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p$$

It is rate of change of volume with respect to temperature at constant pressure.

ISOTHERMAL COMPRESSIBILITY (K_T)

$$K_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$$

It shows the rate of change of volume with respect to pressure at a constant temperature or at isothermal conditions.

2. T-dS Equation

$$T dS = C_v dT + T \left(\frac{\partial P}{\partial T} \right)_v dV$$

This is known as the first Tds equation

$$T dS = C_p dT - T \left(\frac{\partial v}{\partial T} \right)_P dP$$

This is known as the second Tds equation.

$$C_p - C_v = -T \left(\frac{\partial v}{\partial T} \right)_P \left(\frac{\partial P}{\partial v} \right)_T$$

T = Positive

$$\left(\frac{\partial v}{\partial T} \right)_P \rightarrow \text{Positive}$$

$$\left(\frac{\partial p}{\partial v} \right)_T \rightarrow \text{Positive}$$

$$C_p - C_v = +ve$$

$$C_p > C_v$$

3. Energy Equation

$$dU = C_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dV$$

Joule Thompson Coefficient (μ)

When a fluid passes through the porous plug, capillary tube, or valve, its pressure decreases. The throttling process is isenthalpic in nature. The temperature behavior of the fluid during throttling is described by the joule Thompson coefficient(μ),

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

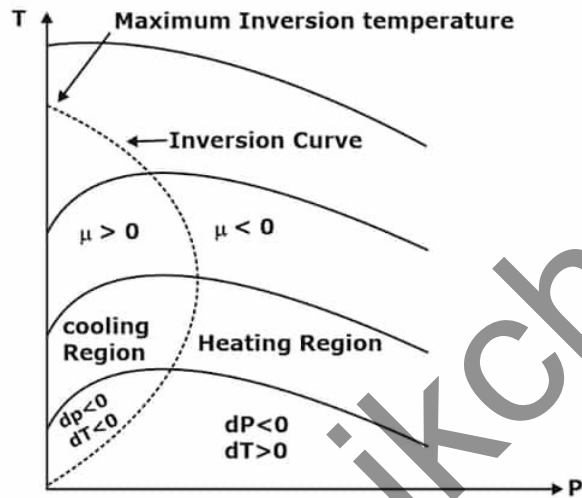


Fig:1

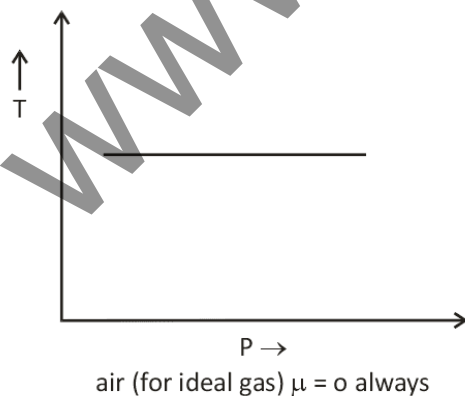


Fig:2

Important points:

1. Joule Thomson coefficient is +ve in cooling region i.e slope of isenthalpic curve on T – P diagram is +ve in cooling region,
2. μ is –ve in heating region i.e the slope of isenthalpic curve on T – P diagram is –ve in the heating region,
3. There is nothing as a heating or cooling region for an ideal gas & the value of the joule Thomson coefficient is zero everywhere.

4. Clausius Clapeyron Equations

Clausius Clapeyron equations is a relationship between saturation pressure, temperature, and enthalpy of vaporization and the specific volume of two phases involved. This equation helps in calculations of properties in two-phase regions.

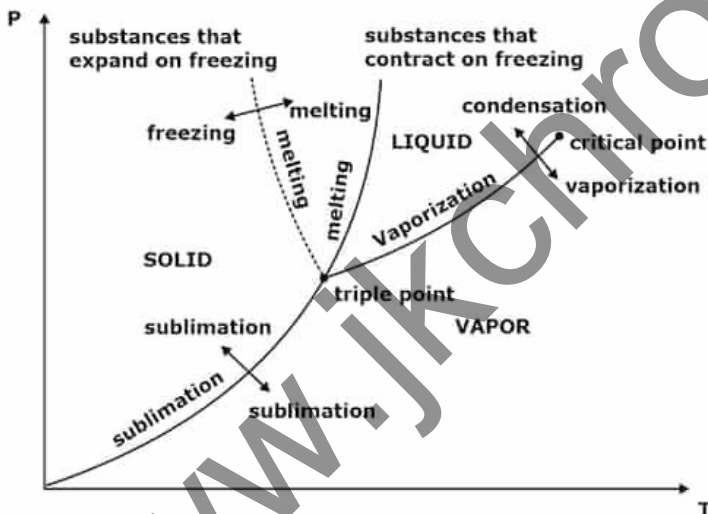


Fig:3

$$s_g - s_f = \frac{\text{Latent heat (LH)}}{T_{\text{sat}}} = \frac{(h_{fg}) \text{ or } (h_g - h_f)}{T_{\text{sat}}}$$

$$\boxed{\frac{dP}{dT} = \frac{(h_{fg})}{T_{\text{sat}}(v_g - v_f)}} \Rightarrow \text{Clausius Clapeyron Eq}^n$$

$$\frac{dP}{dT} = \frac{P_{\text{sat}} \text{ (L.H.)}}{RT_{\text{sat}}^2}$$

The above equation is called the Clausius Clapeyron equation. It helps to determine enthalpy change associated with phase change by measuring pressure, temperature, and volume.

Gas Constant

- It has been experimentally observed that the ideal gas relation given closely approximately the p-V-T behaviour of real gases at low densities.
- At low pressure and high temperature, the density of a gas decreases and the gas behaves as an ideal gas under these conditions.

$$R = \frac{R_u}{M}$$

where, R_u = Universal gas constant, M = Molar mass, R = Gas constant.

Compressibility Factor

- Compressibility factor (correction factor) is measurement of deviation of gases from ideal gas behaviour.
- Compressibility factor (z):

$$z = \frac{pV}{RT} \text{ or } pV = zRT$$

- It can also be expressed as

$$z = \frac{V_{\text{actual}}}{V_{\text{ideal}}}, \text{ where } V_{\text{ideal}} = \frac{RT}{p}$$

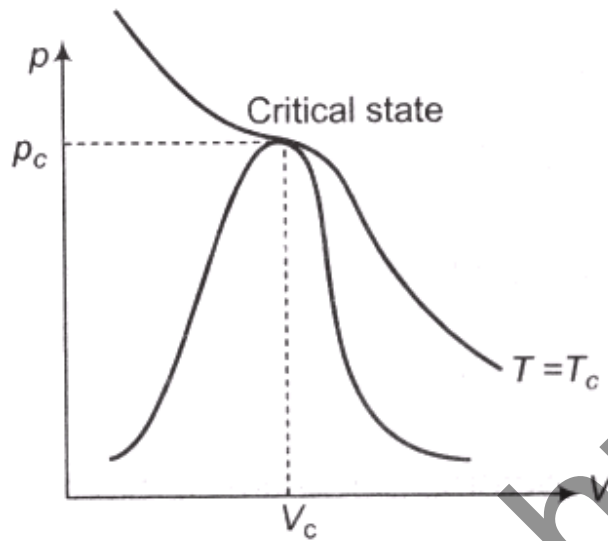
- For ideal gases $\Rightarrow z = 1$
- For real gases $\Rightarrow z$ is away from unity (> 1 or < 1)

Van der wall's Equation of State:

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

- Two effects: Inter molecular attraction forces:

$\frac{a}{V^2}$ and b accounts for volume occupied by the gas molecules.



Critical properties on p-V diagram



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