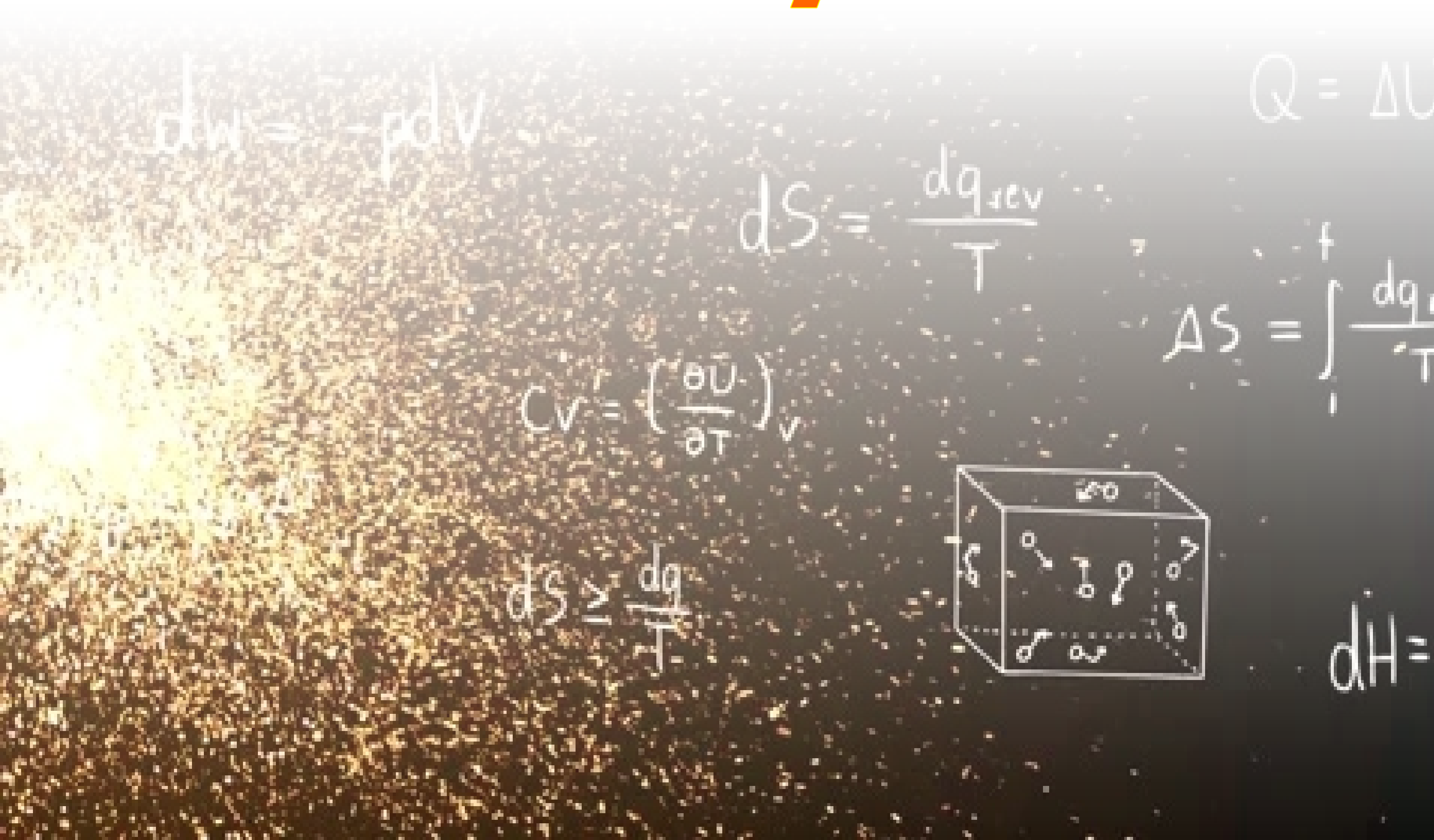
Basic Thermodynamics



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Thermodynamics

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1

BASIC CONCEPTS

1.1 Introduction

- Thermodynamics is the branch of science which deals with the energy interactions (heat & work interactions) and its effect on properties of the system.

1.2 System, Surrounding & Boundary

System: Quantity of matter or region in space which is under investigation.

Surrounding: Anything which is external to the system.

Boundary: Interface shared by system and surrounding.

Boundary can be Rigid (Fixed) or Flexible (Movable)

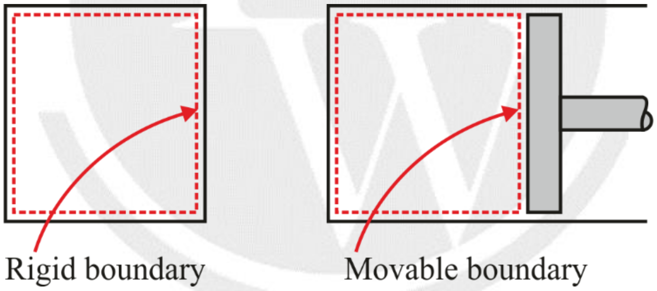


Fig. 1.1 Fixed and movable boundary

Mathematically, thickness of boundary is zero, hence it has neither volume nor mass.

Universe = System + Surroundings

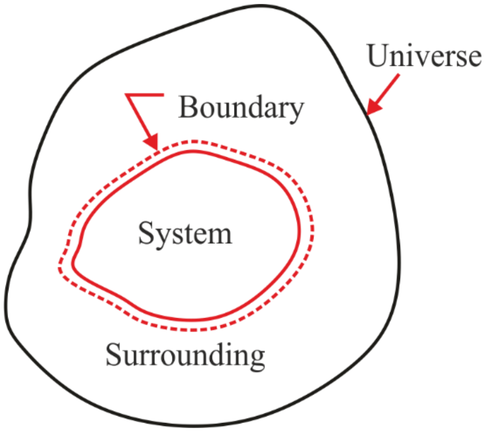


Fig. 1.2 System, boundary, surroundings and universe

1.2.1 Types of System

Closed System:-

- Closed System is the system in which mass interaction can’t take place but energy interactions can take place.
- The terms Control Mass is some times used in place of closed system.

eg. Air in rigid container, Air in piston cylinder arrangement (without valves)

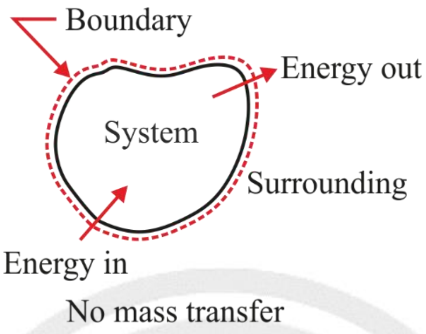


Fig. 1.3 Closed system

Isolated System:-

- Isolated system is the system in which neither mass nor energy interactions can take place.
- In isolated system, energy transfer can’t take place, but energy transformation can take place.

eg. Stationary well insulated thermo flask

Universe

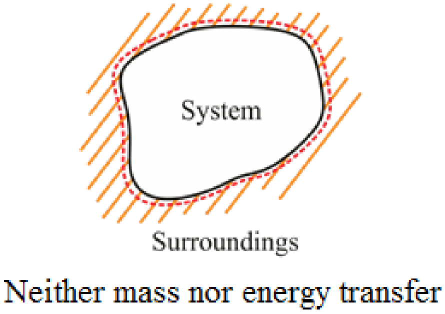


Fig. 1.4 Isolated system

Open System:-

- Open system is the system where both mass and energy interactions can take place.
- An open system is said to be steady flow open system if none of the properties change with time at a particular location.
- For steady flow open system

$$\left.\frac{dm}{dt}\right|_{cv} = 0 \ \& \ \left.\frac{dE}{dt}\right|_{cv} = 0$$

- The term control volume is sometimes used in place of open system.

- eg. Pump, Boiler, Super heater, Turbine, Condenser

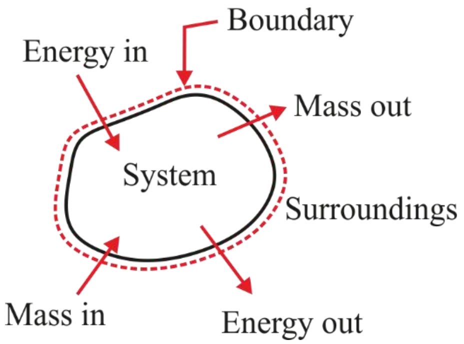


Fig. 1.5 Open system

1.3 Thermodynamic Equilibrium

- Two systems are said to be in thermodynamic equilibrium when they are in thermal, mechanical, chemical and phase equilibrium with each other.

1.4 Property

- Macroscopic characteristic of the system to which a numerical value can be assigned at any given instant of time is known as property.

1.4.1 Types of Property

1. Extensive Property ⇒ depends on the extent (Size) of the system.
2. Intensive Property ⇒ Independent of the extent (Size) of the system.

Mass (m) ⇒ Extensive

Volume (V) ⇒ Extensive

Pressure (P) ⇒ Intensive

Temperature, Viscosity, Thermal conductivity, Pressure, Velocity ⇒ Intensive properties

Density $(\rho) = \frac{\text{Mass (m)}}{\text{Volume (V)}}$

Density → Intensive

Specific Extensive Properties → Intensive properties

Kinetic energy, Potential energy, Internal energy (U), Enthalpy (H) and Entropy (S) are Extensive properties

1.4.2 Conclusions

- Density is an Intensive property.
- Ratio of two extensive properties is an intensive property.
- Specific properties are defined as extensive properties per unit mass.
- Specific properties such as specific volume, specific internal energy, specific enthalpy, specific entropy are intensive properties.

- In case of extensive property, its value for the overall system is the sum of its values for the parts in which system is divided, i.e. extensive properties are additive in nature.
- Intensive properties are not additive in nature.

1.5 Process

- A process is said to be occurred if the system undergoes from one equilibrium state to another equilibrium state.

1.5.1 Quasi-static process

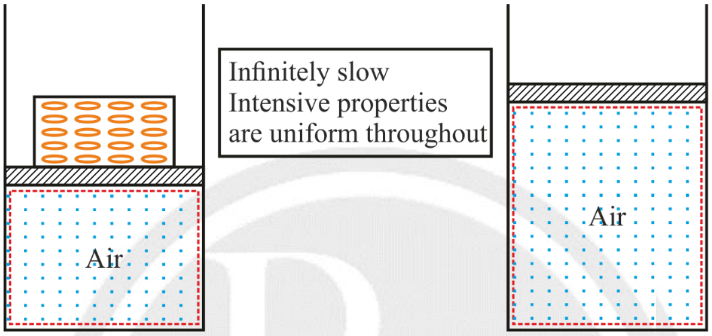


Fig. 1.6 Piston cylinder arrangement representing Quasi – static process

- Quasi-static process is infinitely slow process such that intensive properties are uniform throughout the system.
- All internally reversible processes are quasi-static process but all quasi-static processes need not to be internally reversible.

1.5.2 Internally Reversible Process

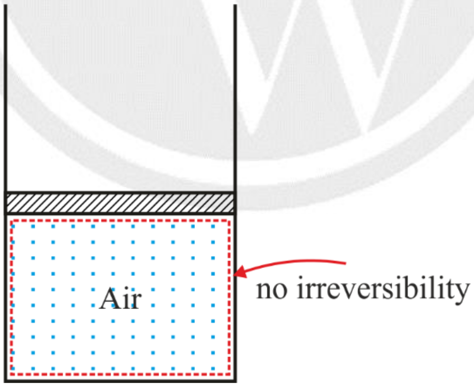


Fig. 1.7 A system undergoing an internally reversible process

- A process is said to be internally reversible process if no irreversibility occurs inside the boundary of the system.
- For closed system, at every intermediate state of an internally reversible process all intensive properties are uniform throughout i.e. closed system passes through series of equilibrium states.
- For closed system, any quasi-static process (neglecting viscous losses) is an internally reversible process.
- If we reverse the process, the system can pass through exactly the same equilibrium states while returning to its initial state i.e. the forward & reverse process can coincide for an internally reversible process.
- In general Phase change process can be considered as internally reversible process.

1.5.3 Externally Reversible Process

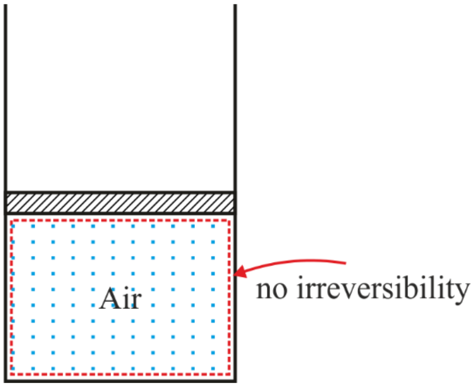


Fig. 1.8 A system undergoing an externally reversible process

- A process is said to be externally reversible process, if no irreversibility occurs outside of the boundary of the system.
- Heat transfer through negligible temperature difference is an externally reversible process whereas heat transfer through finite temperature difference is an externally irreversible process.

1.5.4 Totally Reversible Process

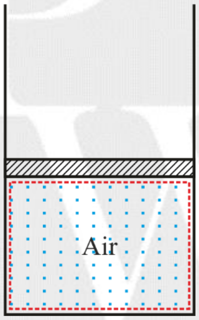


Fig. 1.9 A system undergoing a reversible process

- A process is said to be totally reversible process, if no irreversibility occurs inside & outside of the boundary of the system.
- Reversible Process = Internally Reversible Process + Externally Reversible Process
- For a totally reversible process, the system and its surroundings can be exactly restored to their respective initial states after the process has taken place.

1.6 Cyclic Process

- If a system undergoes number of processes such that the initial and final states are same, then the process is known as cyclic process.
- Cyclic processes are used to get continuous effect.

1.7 Characteristics of Properties

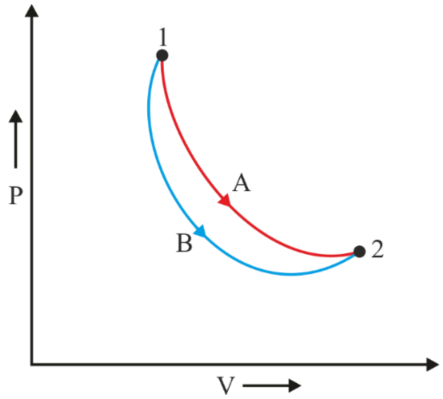


Fig. 1.10 Two processes with same end states

- Properties are independent of path followed by the process. They depend only on the state and hence properties are known as state functions.
- On property diagram state is represented by a point hence properties are also known as point functions.
- Whatever the path, internally reversible or internally irreversible, the difference of properties between two states is exactly same, hence properties are known as exact differentials. In differential form properties are represented by dB.
- Mathematically

  $dB = Mdx + Ndy$

  If B is an Exact differential

  $\left.\frac{\partial M}{\partial y}\right|_x = \left.\frac{\partial N}{\partial x}\right|_y$ (Test of Exactness)
- For a cyclic process change in property is always zero, $\oint dB = 0$
- For Cyclic Process $\Delta U = 0$

1.8 Zeroth Law of Thermodynamics

- When a body A is in thermal equilibrium with a body B, and also separately with a body C, then bodies B and C will be in thermal equilibrium with each other. This is known as the Zeroth law of thermodynamics.
- It is the basis of temperature measurement.

1.8.1 Thermodynamic Temperature Scale

$$\frac{T_I - I_I}{S_I - I_I} = \frac{T_{II} - I_{II}}{S_{II} - I_{II}}$$

Where, T_I = Temperature on first scale (in °C)

T_{II} = Temperature on second scale (in °C)

S_I = Steam point temperature on first scale

S_{II} = Steam point temperature on second scale

I_I = Ice point temperature on first scale

I_{II} = Ice point temperature on first scale

Temperature Conversion Formula:

$$\frac{°C}{5} = \frac{°F - 32}{9} = \frac{T - 273.15}{5}$$

Where, °C = Temperature in degree Celsius

°F = Temperature in degree Fahrenheit

T = Temperature in Kelvin.

Thermometer	Thermometric property	Symbol
1. Constant volume gas thermometer	Pressure	P
2. Constant pressure gas thermometer	Volume	V
3. Electrical resistance thermometer	Resistance	R
4. Thermocouple	Thermal e.m.f	ε
5. Mercury-in-glass thermometer	Length	L

1.9 Universal Gas Constant

$$\bar{R} = \lim_{P \to 0} \frac{PV}{nT}$$

$$\bar{R} = 8.314 \frac{kJ}{kmol - K}$$

$$\bar{R} = 8.314 \frac{J}{mol - K}$$

$$\bar{R} = 8314 \frac{J}{kmol - K}$$

Compressibility Factor (Z)

- Mathematically

$$Z = \frac{PV/nT}{\bar{R}}$$

Where $\bar{R} = \lim_{P \to 0} \frac{PV}{nT}$

Reduced property

- Reduced property at a given state is the value of property at that state divided by the value of property at critical point.
- Mathematically

$$B_r = \frac{B}{B_c}$$

- Reduced pressure $P_r = \frac{P}{P_c}$
- Reduced Temperature $T_r = \frac{T}{T_c}$

1.9.1 Generalized Compressibility Chart

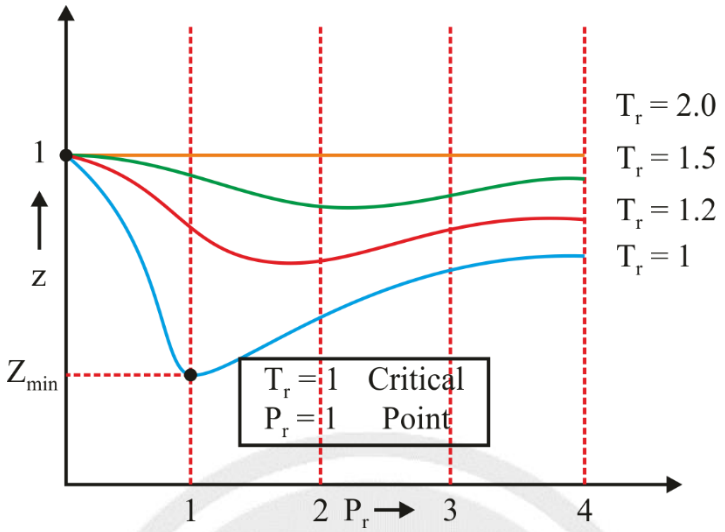


Fig. 1.11 Generalized compressibility chart

- At $P_r \rightarrow 0$ (low pressure) the value of compressibility factor approaches to unity irrespective of temperature.
- At $T_r \geq 2$ (high temperature) the value of compressibility factor approaches to unity up to $P_r = 4$.
- Compressibility factor is minimum at critical point ($P_r = 1$, $T_r = 1$).
- Compressibility factor is approximately same, at same reduced pressure and reduced temperature. This is known as principle of corresponding states.
- Generalised compressibility chart is extremely useful in situation where detailed data on a particular gas are lacking but critical properties are available.

1.10 Ideal Gas

- For Ideal Gas compressibility factor is unity
- Various forms of Ideal gas equation
  - $PV = n\overline{R}T$
  - $PV = mRT$
  - $P = \rho RT$
  - $Pv = RT$
  - $R = \frac{\overline{R}}{M}\left(\frac{kJ}{Kg-K}/\frac{J}{gm-K}\right)$
  - Units of characteristic gas constant is kJ/kg-K or J/kg-K.
  - Characteristic gas constant depends only on the molar mass of the gas and is independent of the temperature of the gases.
  - Characteristic gas constant is different for different gases. Higher the molar mass of the gas, lesser the characteristic gas constant.

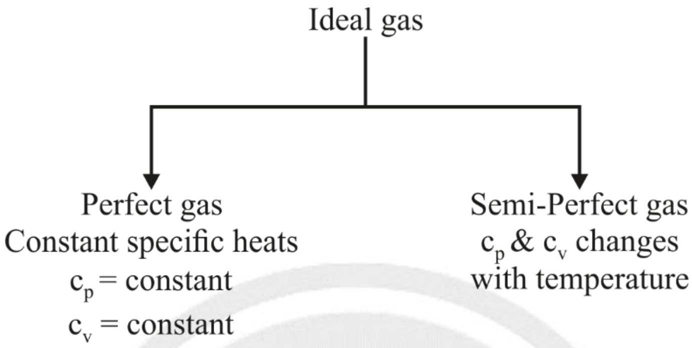
1.10.1 Physical Meaning of Ideal Gas

Ideal gas is having following characteristics

(i) Negligible intermolecular forces of attraction.

(ii) Volume of the gas molecules is negligible as compared to the container volume.

1.10.1.1 Ideal gas vs Perfect Gas



1.11 Analysis of Non-Reacting Ideal Gas Mixture

Case 1: Mole fractions ($\bar{x}$) of gases are given

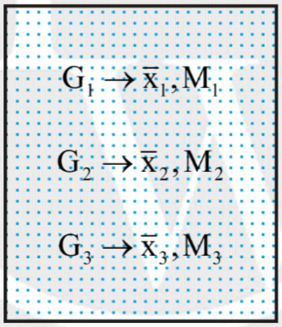


Fig. 1.12 Mole fraction of gases in a mixture

$$\bar{x}_1 + \bar{x}_2 + \bar{x}_3 = 1$$

$$M_{mix} = \bar{x}_1 M_1 + \bar{x}_2 M_2 + \bar{x}_3 M_3$$

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

Case 2: Mass fractions (x) of gases are given

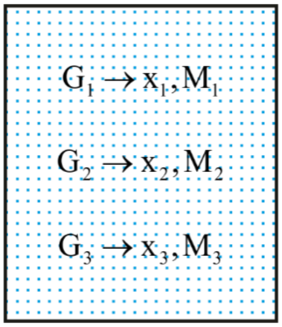


Fig. 1.13 Mass of fraction of gases in a mixture

$x_1 + x_2 + x_3 = 1$

$$M_{mix} = \frac{1}{\frac{x_1}{M_1} + \frac{x_2}{M_2} + \frac{x_3}{M_3}}$$

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

1.12 Van der Waals Equation of State

- $\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad (v \text{ in } m^3/kg)$
- $\left(P + \frac{\bar{a}}{\bar{v}^2}\right)(\bar{v} - \bar{b}) = \bar{R}T \quad (\bar{v} = \text{molar specific volume in } m^3/kmol)$
- $\frac{a}{v^2}$ accounts for intermolecular force of attraction.
- b accounts for volume of molecules.

1.12.1 Discussion on Critical Isotherm

- Critical isotherm passes through a point of inflection at the critical point.

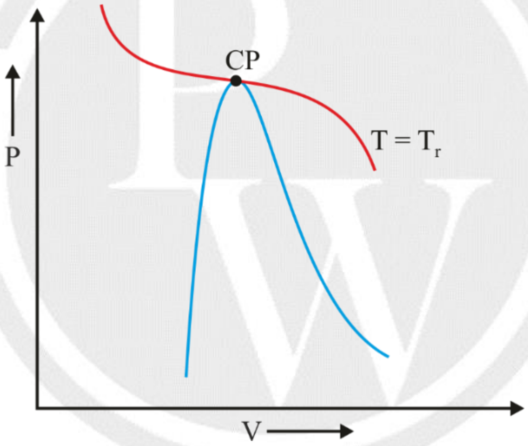


Fig. 1.14 Isotherm on P-v diagram

- $\left.\frac{\partial P}{\partial v}\right|_{cp} = 0$
- $\left.\frac{\partial^2 P}{\partial v^2}\right|_{cp} = 0$
- $\left.\frac{\partial^3 P}{\partial v^3}\right|_{cp} < 0$

1.12.2 Expressions of a & b in Van der Walls equation

$a = 3P_c v_c^2$

$b = \frac{v_c}{3}$

Where P_c & v_c are pressure and specific volume at critical point.

$Z_c = \frac{3}{8} = 0.375$

1.13 Various Process

1.13.1 Constant Volume Process / Isochoric Process / Isometric Process

V = Constant [Any Substance]

dV = 0 [Any Substance]

Physical representation for Isochoric heat addition process

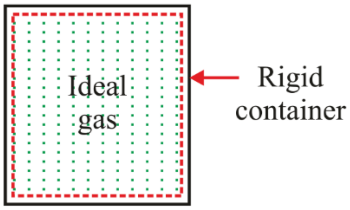


Fig. 1.15 Ideal gas in a rigid container

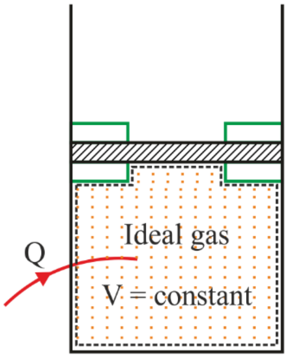
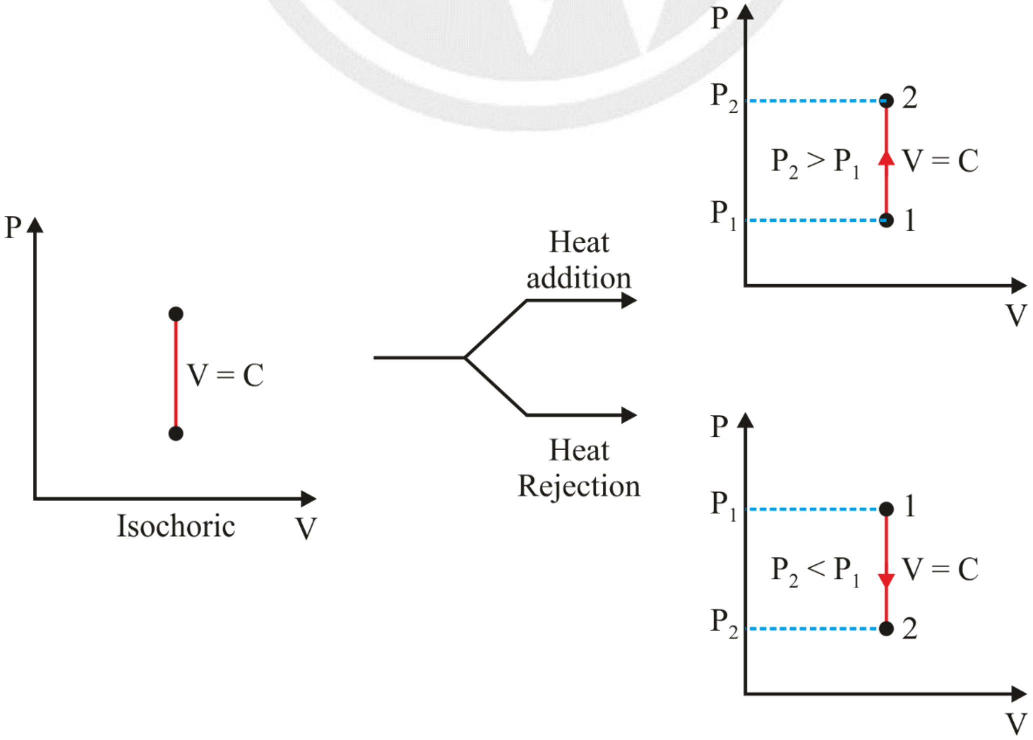


Fig. 1.16 Piston cylinder arrangement with stoppers

- For an ideal gas undergoing Isochoric heat addition process then both temperature and pressure increases.
- For an ideal gas undergoing isochoric process

  $\frac{P}{T} = \frac{mR}{V} = \text{constant}$
- According to Gay Lussac's law, for a given mass of an ideal gas undergoing isochoric process, absolute pressure is directly proportional to absolute temperature.



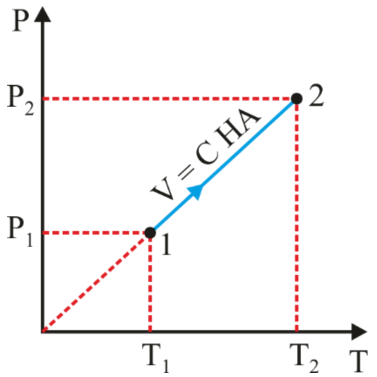


Fig. 1.17 Isochoric process on P – V and P – T diagram

1.13.2 Constant pressure process/ Isobaric Process/ Isopiestic Process

The pressure is constant at equilibrium states.

- P = constant
- dP = 0 [Any substance]

Physical representation for Isobaric heat addition process

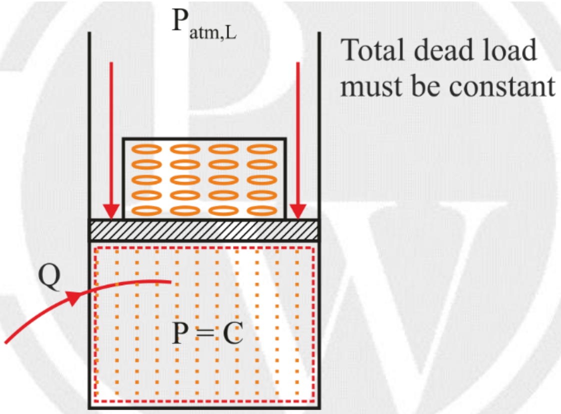


Fig. 1.18 Piston cylinder arrangement have constant total dead load

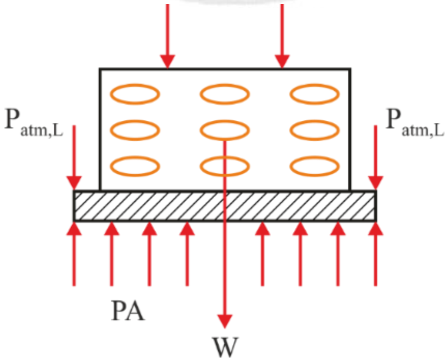


Fig. 1.19 Representation of different pressures on piston

- At equilibrium state for vertical piston cylinder arrangement

  $PA = P_{atm,L}\ A + W$

  $\Rightarrow P = P_{atm,L} + \frac{W}{A}$

- For an ideal gas undergoing isobaric heat addition process then both temperature and volume increases.

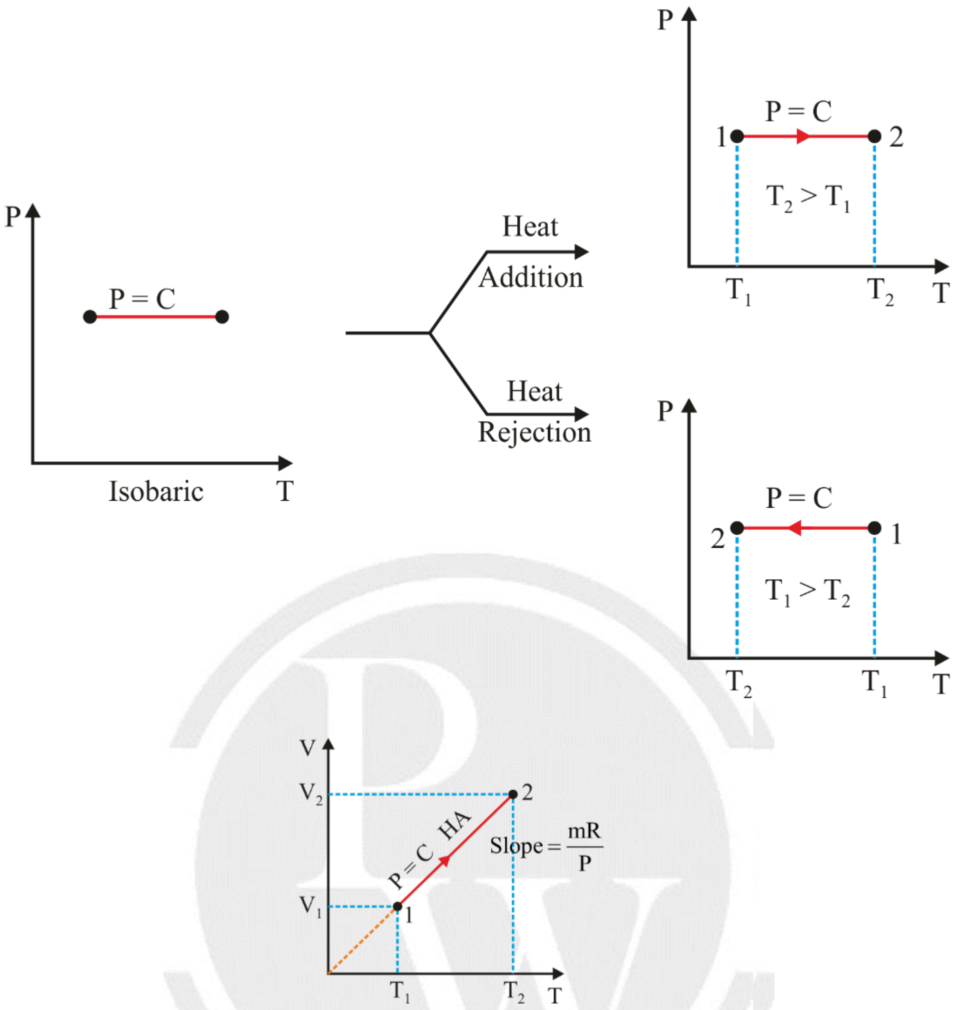


Fig. 1.20 Isochoric process on P – T and V – T diagram

- For an ideal gas, $\frac{V}{T} = \frac{mR}{P} = \text{constant}$
- According to Charles law, for a given mass of an ideal gas undergoing isobaric process, volume is directly proportional to absolute temperature.

1.13.3 Constant temperature process/Isothermal Process

- T = Constant [Any Substance]
  dT = 0 [Any Substance]

Physical representation for Isothermal heat addition process

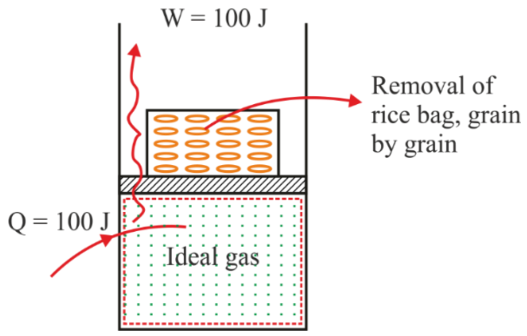


Fig. 1.21 Arrangement for Isothermal process

- For ideal gas, heat can be supplied at constant temperature.
- For an ideal gas undergoing isothermal process heat completely converts into work.
- Isothermal heat transfer to a closed system, neglecting friction can be considered as an internally reversible process.

Analysis for an Ideal gas

For an ideal gas undergoing isothermal heat addition process pressure decreases and volume increases.

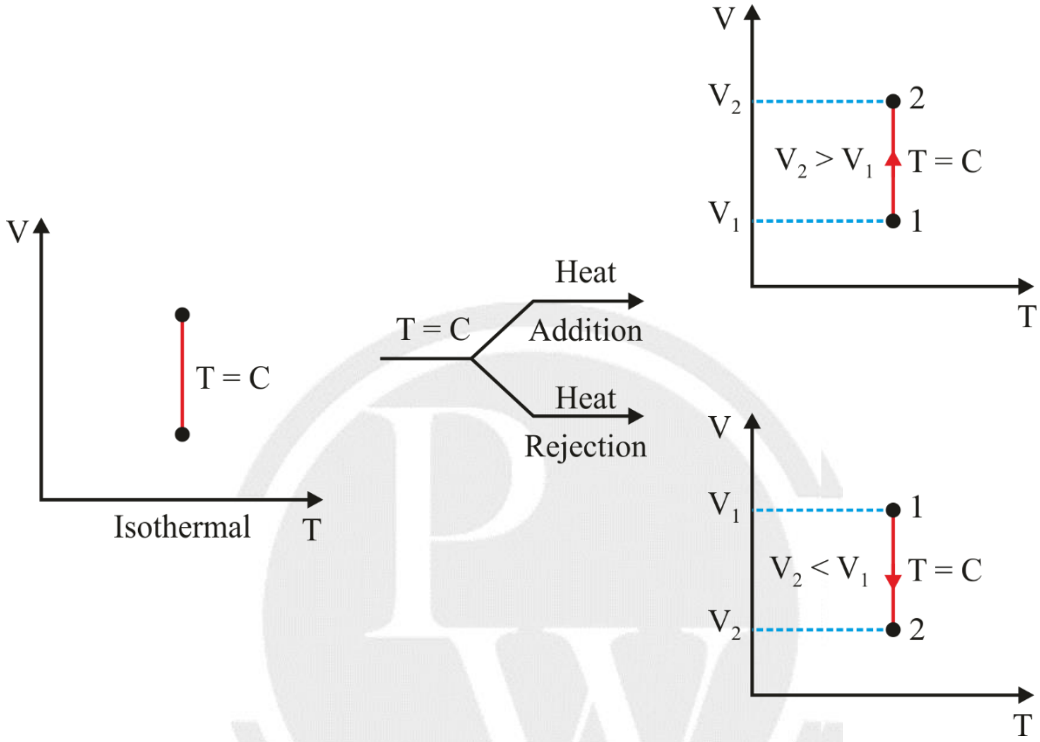


Fig. 1.22 Isothermal process on V – T diagram

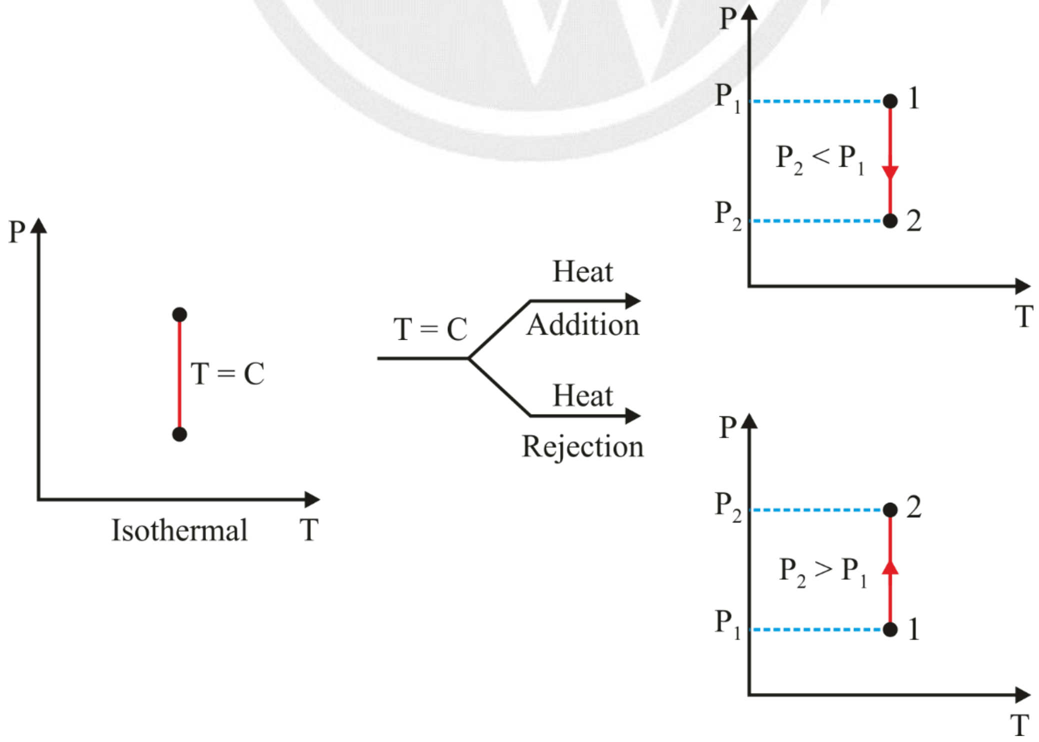


Fig. 1.23 Isothermal process on P-T diagrams

- For an Ideal gas
- PV = mRT = Constant

According to Boyle's law, for a given mass of an ideal gas undergoing isothermal process, absolute pressure is inversely proportional to volume.

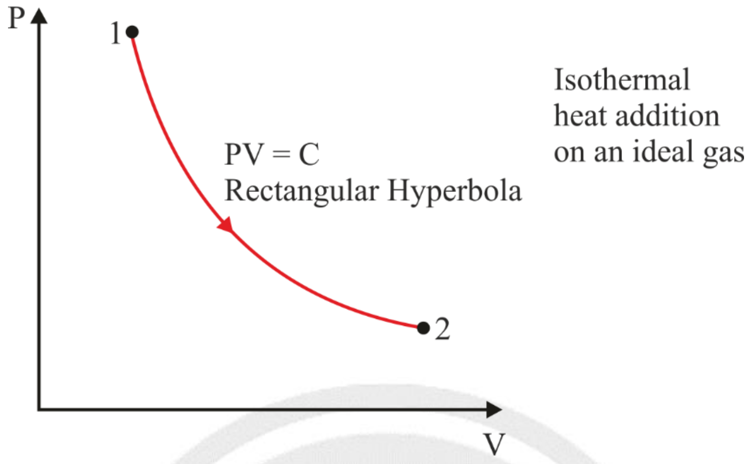


Fig. 1.24 Isothermal heat addition process on P-V diagram

Note:

For an ideal gas, Isothermal process on a P-V diagram is represented by a rectangular hyperbola which is symmetric to both pressure and volume axis.

1.13.4 Adiabatic process

- A process during which there is no heat interaction is called an adiabatic process.

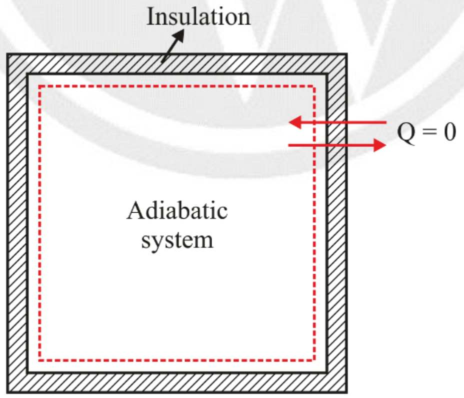


Fig. 1.25 Adiabatic system

- Q = 0 (Any Substance)

- For perfect gas undergoing Isentropic process following relations can be used

PV^{γ} = Constant

$TP^{\frac{1-\gamma}{\gamma}}$ = Constant

$TV^{\gamma-1}$=Constant

- For a perfect gas undergoing Isentropic Expansion process, Pressure decreases, volume increases, temperature decreases.

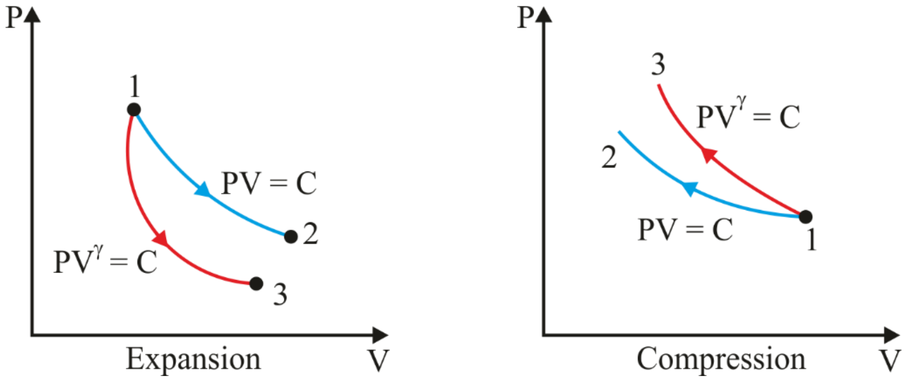


Fig. 1.26 Isothermal and adiabatic processes during expansion and compression

- $\left.\frac{\partial P}{\partial v}\right|_S = \gamma \left.\frac{\partial P}{\partial v}\right|_T$

Note:

- For perfect gas on P-V diagram, both isothermal and Isentropic (internally reversible adiabatic) processes have negative slopes.
- For perfect gas on the same P-V diagram, the slope of internally reversible adiabatic process is more (γ times) than the slope of isothermal process.

1.13.5 Polytropic Process

- For Polytropic process following equations can be used

PV^n = Constant (Any substance)

$TP^{\frac{1-n}{n}}$ = Constant (Ideal Gas)

TV^{n-1} = Constant (Ideal Gas)

Where n is known as polytropic index

Representation of various processes on same P-V diagram

- P-V diagram for expansion

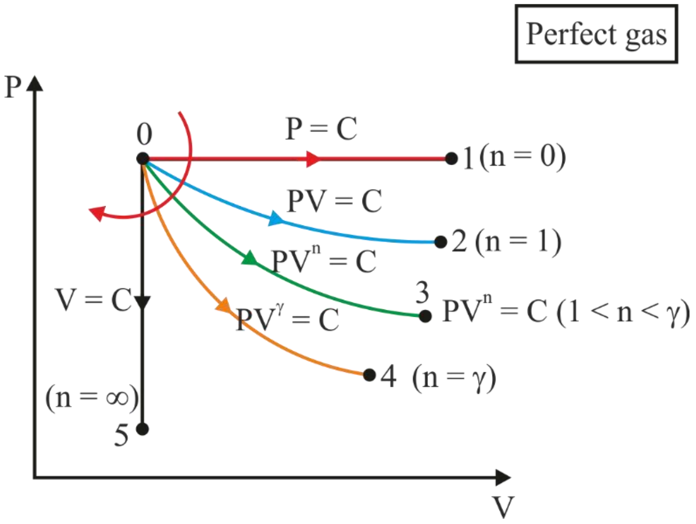


Fig. 1.27 P – V diagram for expansion

- P-V diagram for compression

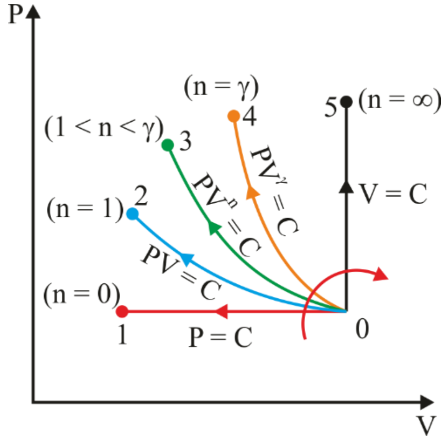


Fig. 1.28 P – V diagram for compression

1.14 Energy of A System

- E = Macroscopic Energy (KE + PE) + Microscopic energy (U)

  E = KE + PE + U

  ΔE = ΔKE + ΔPE + ΔU
- Internal energy depends on the size of the system. Larger the size of the system, higher will be the number of molecules hence higher will be the internal energy. Internal energy is an extensive property.

1.14.1 Stationary System

- A stationary system is a closed system having no change in kinetic energy & potential energy during a process.
- For a stationary system change in energy is equal to the change in internal energy.

❑❑❑

2

WORK INTERACTIONS

2.1 Thermodynamic Work

- Thermodynamic Work is done by the system if the sole effect on the surrounding (everything external to the system) could be raising of weights (real or imaginary).
- Thermodynamic Work is a

1. Form of Energy in transit
2. Boundary Phenomenon

Note:

Thermodynamic work is a form of energy in transit, since it is energy being transferred across the system boundary.

Thermodynamic work is a boundary phenomenon since it is observed only at the boundary.

2.1.1 Sign Convention

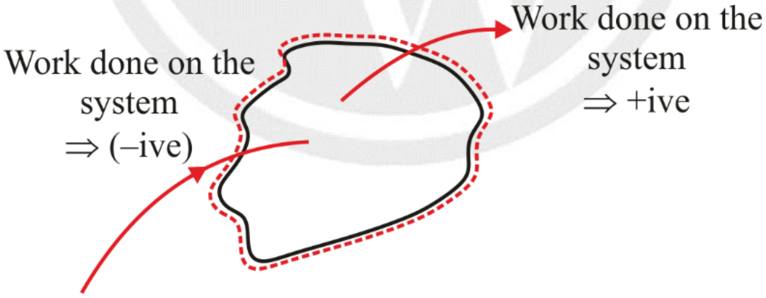


Fig.2.1 Sign convention of work

Work done by the system is taken as positive whereas work done on the system is taken as negative.

2.2 Heat Interaction

- Heat interaction is defined as the form of energy that is transferred across a boundary of a system by virtue of temperature difference between system and surrounding.

2.2.1 Sign Convention

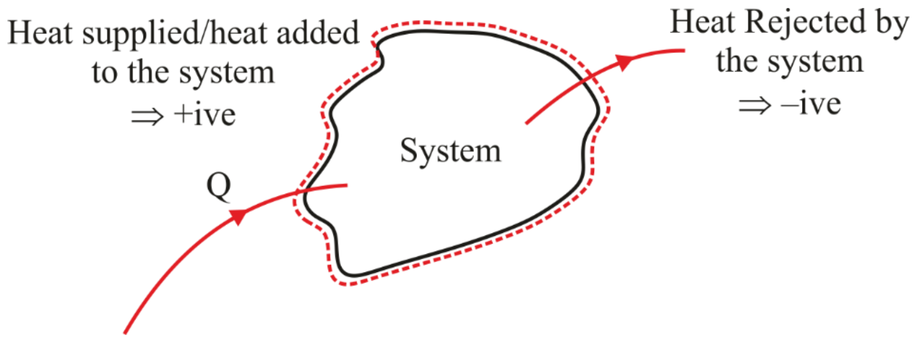


Fig. 2.2 Sign convention of heat interaction

Heat supplied to the system is taken as positive whereas heat rejected by the system is taken as negative.

2.3 Work Done at the moving boundary of a closed system (Displacement Work)

$\delta W_d = PdV$ [Closed system and Int. Rev. Process]

$W_{d_{1-2}} = \int_1^2 PdV$ [System undergoing a process 1 − 2]

2.4 Displacement Work on P-V Diagram

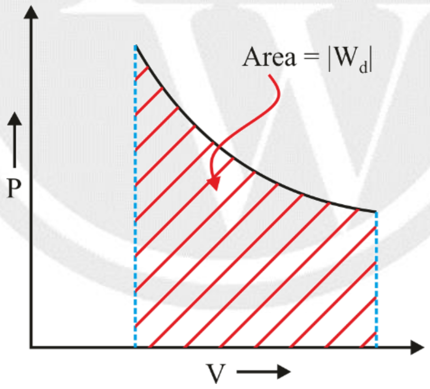


Fig. 2.3 Displacement work on P-V diagram

$\delta W_d = PdV$

- $dV = +ve \rightarrow \delta W_d = +ive$ (For expansion process) (Done by the system)
- $dV = -ve \rightarrow \delta W_d = -ive$ (For compression process) (Done on the system)

Note:

For a closed system undergoing internally reversible process,

- On P-V diagram area under the curve projected on volume axis gives the magnitude of displacement work.
- For expansion displacement work is positive while for compression displacement work is negative.

2.5 Observation for Work Interactions

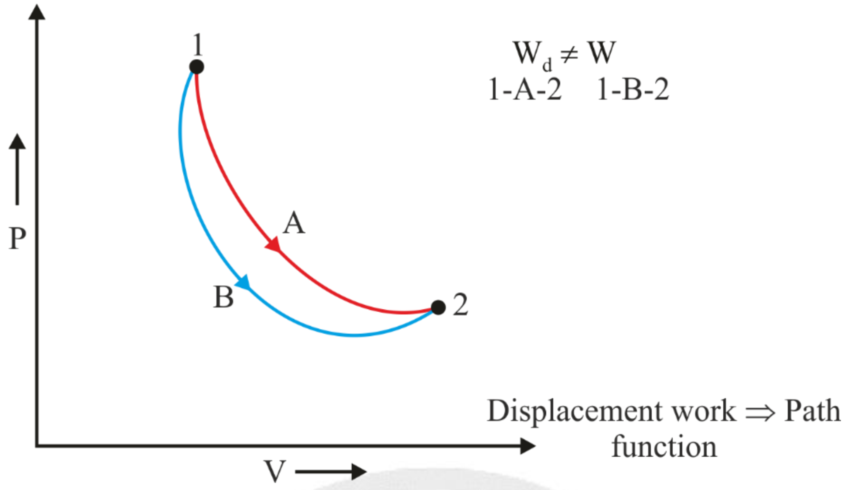


Fig.2.4 Two processes A and B with same end states

- Even though initial and final states are same for both the paths 1-A-2 and 1-B-2, but work interactions are different, hence work interaction is a path function.
- Work interaction is an inexact differential.

Note:

Heat and work are energy transfer mechanisms between a system and its surroundings, and there are many similarities between them:

I. Both are recognized at the boundaries of a system as they cross the boundaries. That is, both heat and work are boundary phenomena.

II. Systems possess energy, but not heat or work.

III. Both are associated with a process, not a state. Unlike properties, heat or work has no meaning at a state.

IV. Both are path functions (i.e., their magnitudes depend on the path followed during a process as well as the end states).

2.6 Displacement Work for Various Process

Isochoric process

Isobaric process

Isothermal process

Adiabatic process

Polytropic process

2.6.1 Isochoric Process

- For any substance consisting closed system undergoing Isochoric process
- $W_{d_{1-2}} = 0$

2.6.2 Isobaric Process

- For any substance, consisting closed system under goes an internally reversible isobaric process.

$$W_{d_{1-2}} = P(V_2 - V_1) = P\Delta V_{1-2}$$

- For an ideal gas, consisting closed system undergoing an internally reversible isobaric process

$$W_{d_{1-2}} = mR(T_2 - T_1)$$
$$W_{d_{1-2}} = n\overline{R}(T_2 - T_1)$$

2.6.3 Isothermal process

- For an ideal gas consisting closed system undergoing internal reversible isothermal process

$$W_{d_{1-2}} = C\ln\left(\frac{V_2}{V_1}\right) = C\ln\left(\frac{P_1}{P_2}\right)$$

Where C can be P_1V_1, P_2V_2, mRT or $n\overline{R}T$

2.6.4 Adiabatic Process

- For a perfect gas consisting closed system undergoing isentropic process.

$$W_{d_{1-2}} = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

$$W_{d_{1-2}} = \frac{mR(T_1 - T_2)}{\gamma - 1}$$

$$W_{d_{1-2}} = \frac{n\overline{R}(T_1 - T_2)}{\gamma - 1}$$

2.6.5 Polytropic process

- For any substance consisting closed system undergoing Internally reversible polytropic process

$$W_{d_{1-2}} = \frac{P_1V_1 - P_2V_2}{n - 1}$$

- For Ideal gas consisting closed system undergoing Internally reversible polytropic process

$$W_{d_{1-2}} = \frac{mR(T_1 - T_2)}{n-1} = \frac{n\overline{R}(T_1 - T_2)}{n-1}$$

- Finding of Polytropic Index (n)

$$PV^n = \text{Constant},\ n = \frac{\ln\left(\frac{P_2}{P_1}\right)}{\ln\left(\frac{V_1}{V_2}\right)}$$

$$TV^{n-1} = \text{Constant} \Rightarrow n - 1 = \frac{\ln\left(T_2/T_1\right)}{\ln\left(V_1/V_2\right)}$$

$$TP^{\frac{1-n}{n}} = \text{Constant} \Rightarrow \frac{1-n}{n} = \frac{\ln\left(P_2/T_1\right)}{\ln\left(P_1/P_2\right)}$$

Note:

Don't put –ve sign in front of formulas seeing compression in problem. Automatically answer will come negative for compression.

All formulas are derived with the sign convention that work done by the system is +ve while work done on the system is – ve.

If the sign conventions are reversed, then – ve sign must be placed before the formula.

2.7 Random Process

- If $P \propto V$

  $$W_{d_{1-2}} = \frac{1}{2}\frac{P_1}{V_1}(V_2^2 - V_1^2)$$

- If $P \propto D^3$

  $$W_{d_{1-2}} = \frac{\pi}{12}\frac{P_1}{D_1^3}(D_2^6 - D_1^6)$$

- $P \propto D$

  $$W_{d_{1-2}} = \frac{\pi}{8}\frac{P_1}{D_1}(D_2^4 - D_1^4)$$

2.8 Piston Cylinder Arrangement with Spring

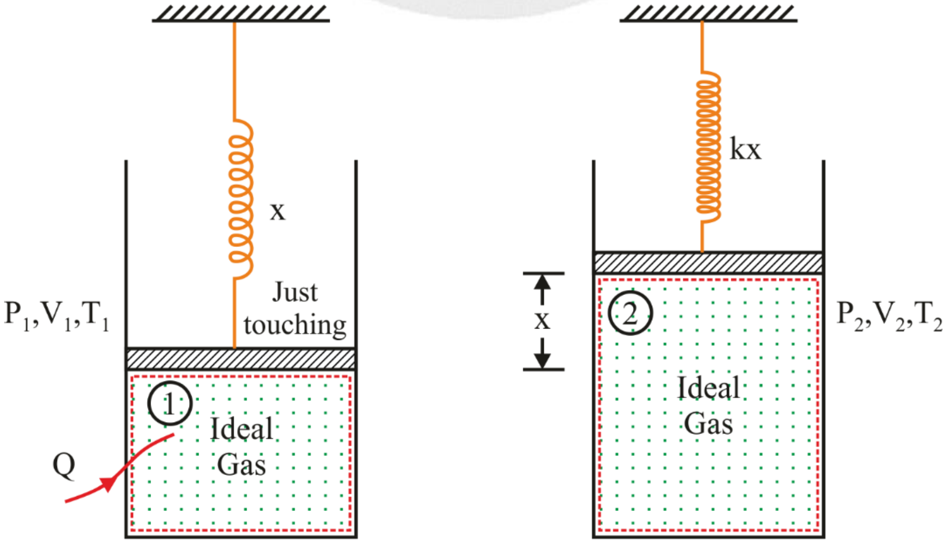


Fig. 2.5 Piston cylinder arrangement with springs

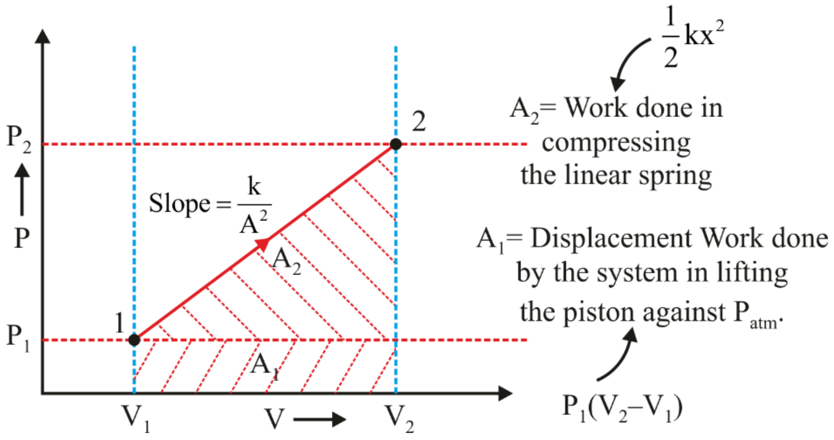


Fig. 2.6 Expansion process against spring force

Note:

- For an ideal gas enclosed by piston cylinder arrangement with spring heat addition leads to increase in pressure, volume and temperature.

2.9 Net Displacement Work for Cyclic Process

Net displacement work for a cyclic process is the sum of displacement work of all the processes consisting the cycle.

$$\sum W_d = W_{d_{1-2}} + W_{d_{2-3}} + W_{d_{3-4}} + W_{d_{4-1}}$$

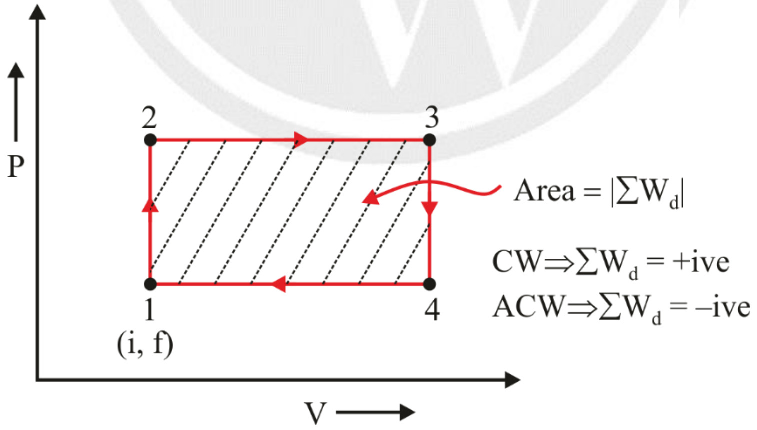


Fig.2.7 Cyclic process on P.V. Diagram

2.9.1 Conclusions

On a P-V diagram, the area enclosed by the cycle represents the magnitude of net displacement work of the cycle.

For clockwise cycles, on P-V diagram net displacement work is +ve. All power producing cycles are clock-wise on P-V diagram e.g. I.C. engine cycle

Otto, Diesel, Dual cycle

Gas power cycle (Brayton cycle)

Vapour power cycle (Rankine cycle)

For anti-clockwise cycles, on P-V diagram, net displacement work is negative. All power consuming cycles are anti-clockwise on P-V diagram.

e.g. Refrigeration cycles (Reversed Carnot cycle, Reversed Brayton cycle, Vapour Compression Refrigeration System cycle)

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3

FIRST LAW OF THERMODYNAMICS

3.1 Introduction

- First law of thermodynamics is based on experimental results.
- First law of thermodynamics is the law of conservation of energy.
- First law of thermodynamics gives the concept of internal energy.

3.2 Statement

- For a closed system undergoing a cyclic process, net heat interaction is equal to the net work interaction.
- For a closed system undergoing cyclic process

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

$$\text{or } \oint \delta Q = \oint \delta W \text{ (Any cycle)}$$

Note:

- For power producing cycles, both network interactions and net heat interactions are positive.
- For power consuming cycles, both network interactions and net heat interactions are negative.

3.3 Consequences of First Law of Thermodynamics

(1) Heat interaction is a path function.

(2) Energy of the system is the property of the system.

(3) Energy of an isolated system is constant.

(4) Perpetual motion machine of first kind (PMM-1) is impossible.

3.4 Heat Interaction is a Path Function

Heat interaction is a

- Path function
- Inexact differential
- Form of a energy in transit
- Boundary phenomena

3.5 Energy of the System is the Property of the System

Energy of the system is a

- Property
- State function
- Point function
- Exact differential
- $\oint dE = 0$

3.6 First Law of Thermodynamics for a Process

- $Q = W + \Delta E$

  Where $\Delta E = \Delta KE + \Delta PE + \Delta U$ and $W = W_e + W_s + W_d$
- $\delta Q = \delta W + dE$

  Q and W are inexact differential & E is an exact differential

3.6.1 For Simple compressible, Stationary system undergoing internally reversible process

- $Q = \int PdV + \Delta U$

  $\delta Q = PdV + dU$

3.7 Energy of an Isolated System is Constant

- $Q = 0, W = 0$

  $Q = W + \Delta E$

  $\Rightarrow \Delta E = 0$

  $E = \text{Constant}$

3.8 Perpetual Motion Machine of first kind (PMM-1) is impossible

- PMM-1 is fictitious machine which continuously produces the mechanical work without consuming any form of energy.

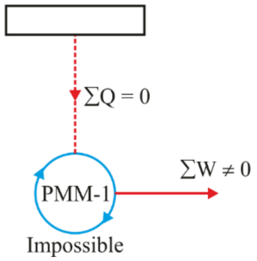


Fig. 3.1 PMM – 1

- PPM-1 is impossible as it violates first law of thermodynamics for a cycle.

* * *

4

HEAT INTERACTIONS

4.1 State Postulate

According to State postulate, state of a simple compressible system can be completely defined by 2 independent intensive properties.

- (P, v) ⇒ Always independent intensive properties
- (T, v) ⇒ Always independent intensive properties
- (T, P) ⇒ In single phase independent intensive properties

4.2 Internal Energy (U)

- Internal energy is an extensive property having unit J or kJ.
- Specific Internal energy is an intensive property having unit J/kg or kJ/kg.
- Internal energy of an Ideal gas depends on temperature only, if temperature of an ideal gas increases internal energy increases & vice versa.
- For an Ideal gas undergoing Isothermal process, change in internal energy is zero.
- For any substance undergoing Isochoric process (or) Ideal gas undergoing any process we can apply the following two equations,

$$du = c_v dT$$

$$\Delta u = \int c_v \, dT$$

- For any substance having constant c_v undergoing isochoric process or perfect gas undergoing any process, we can apply following three equations,

Change in specific Internal Energy is $\Delta u = c_v \Delta T \left(\frac{J}{kg} \text{ or } \frac{kJ}{kg}\right)$

Change in molar specific internal energy is $\Delta \bar{u} = \bar{c}_v \, \Delta T \left(\frac{J}{mol} \text{ or } \frac{kJ}{kmol}\right)$

Total internal energy change is $\Delta U = mc_v \Delta T$ (J or kJ)

4.3 Enthalpy (H)

- It was observed that in thermodynamics calculations, U + PV term was coming very frequently.
- For convenience, U + PV was named as "Enthalpy".
- Enthalpy is an extensive property having unit J & kJ.
- Specific enthalpy is an intensive property having unit J/kg & kJ/kg.
- Enthalpy of an Ideal gas depends on temperature only, if temperature of an ideal gas increases enthalpy increases & vice versa.
- For an Ideal gas undergoing isothermal process the change in Enthalpy is zero.
- For any substance undergoing Isobaric process (or) Ideal gas undergoing any process we can apply these two equations

  $dh = c_p dT$

  $\Delta h = \int c_p \, dT$
- For any substance having constant c_p undergoing isobaric process or perfect gas undergoing any process, we can apply following three equations.

  Change in specific Enthalpy is $\Delta h = c_p \Delta T \left(\frac{J}{kg} \text{ or } \frac{kJ}{kg}\right)$

  Change in molar specific Enthalpy is $\Delta \bar{h} = \bar{c}_p \, \Delta T \left(\frac{J}{mol} \text{ or } \frac{kJ}{kmol}\right)$

  Total Enthalpy change is $\Delta H = mc_p \Delta T$ (J or kJ)

4.4 Heat Interactions for Various Processes

(a) Isochoric process

(b) Isobaric process

(c) Isothermal process

(d) Adiabatic expansion

(e) Polytropic process

4.4.1 Isochoric process

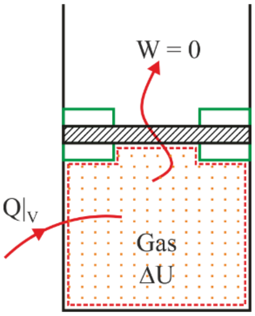


Fig. 4.1 Piston cylinder arrangement with stoppers

- $\mathbf{Q|_v = \Delta U_{1-2}}$
- If c_v is constant

  $Q|_v = m\, c_v \Delta T_{1-2}$
- For a simple compressible stationary system undergoing isochoric process, heat supplied is completely utilized to increase the internal energy.

4.4.2 Isobaric process

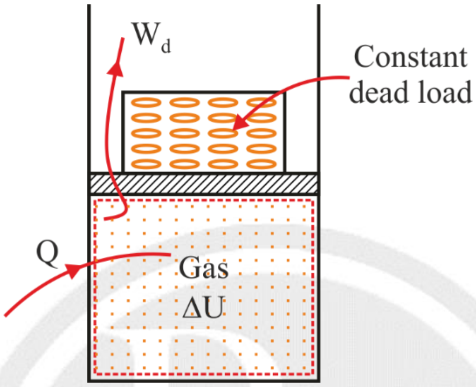


Fig. 4.2 Piston cylinder arrangement with constant dead load

- $Q|_P = \Delta H_{1-2}$
- If c_p is constant

  $Q|_P = m\, c_p \Delta T_{1-2}$
- For a simple compressible stationary system undergoing internally reversible Isobaric process, heat supplied is equal to the increase in enthalpy of the system.

4.4.2.1 Isobaric heat addition to perfect gas

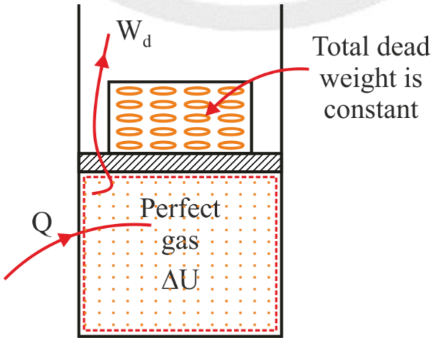


Fig.4.3 Isobaric heat addition to the perfect gas

If Q = +ive

then W_d = +ive, ΔU = +ive

- For simple compressible stationary system consisting of perfect gas, isobaric heat supplied partially converts into displacement work while remaining is stored as internal energy.

4.4.2.2 Analysis for an ideal gas

- $c_p - c_v = R \;\&\; \bar{c}_p - \bar{c}_v = \bar{R}$
- $c_v = \frac{R}{\gamma - 1} \;\&\; \bar{c}_v = \frac{\bar{R}}{\gamma - 1}$
- $c_p = \frac{R\gamma}{\gamma - 1} \;\&\; \bar{c}_p = \frac{\bar{R}\,\gamma}{\gamma - 1}$

4.4.2.3 Adiabatic Index

- $\gamma = \frac{c_p}{c_v} = \frac{\bar{c}_p}{\bar{c}_v}$
- For Monoatomic gas $\Rightarrow \gamma = \frac{5}{3} = 1.67$
- For Diatomic gas $\Rightarrow \gamma = \frac{7}{5} = 1.4$
- For Triatomic gas $\Rightarrow \gamma = \frac{4}{3} = 1.33$

Note:

For air, following values can be used for calculation purpose

- $c_p = 1.005$ kJ/kg-K
- $c_v = 0.718$ kJ/kg-K

4.5 Fraction of Isobaric Heat Supplied Converting into Displacement Work

$$\mathbf{W} = \left(1 - \frac{1}{\gamma}\right) Q|_P$$

$$\Delta U = \frac{1}{\gamma} Q|_P$$

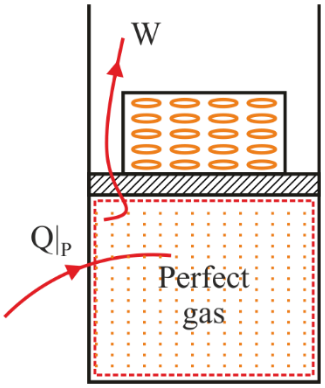


Fig. 4.4 Isobaric heat addition to a system

4.5.1 Relation between Isochoric & Isobaric heat addition for same temperature increase

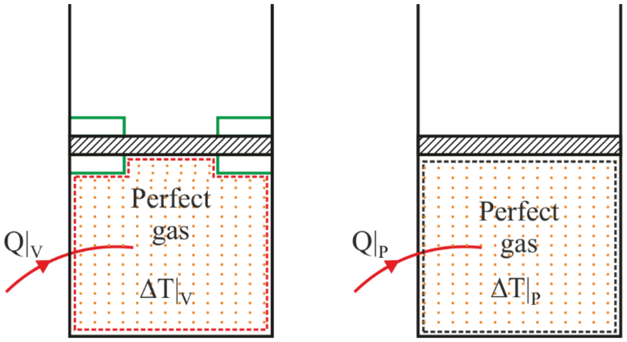


Fig.4.5 Isochoric and isobaric heat addition

- $Q|_P > Q|_v$
- $Q|_P = \gamma Q|_v$

Note:

For same increase in Internal Energy, Isobaric Heat addition will be more than Isochoric Heat addition since in Isobaric heat addition some part of the heat addition will convert into displacement work.

4.6 Isochoric & Isobaric Heat Interactions to Perfect gas in P-V Terms

- $Q|_v = \Delta U = mc_v\Delta T$

  $$Q|_v = \frac{V(P_2 - P_1)}{\gamma - 1}$$
- $Q|_p = \Delta H = mc_p\Delta T$

  $$Q|_p = \frac{\gamma P(V_2 - V)}{\gamma - 1}$$

4.7 Isothermal Process

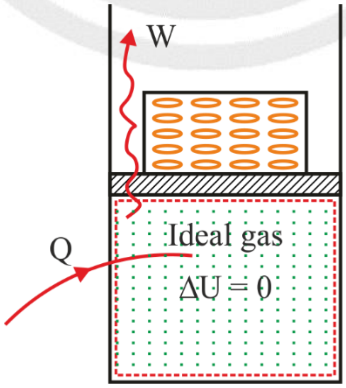


Fig. 4.6 Isothermal heat addition to the system

- $\mathbf{Q = W_d}$

  $$\mathbf{Q = C\ln\left(\frac{V_2}{V_1}\right) = C\ln\left(\frac{P_1}{P_2}\right)}$$

Where C can be $\mathbf{P_1V_1, P_2V_2, mRT, n\bar{R}T}$

- For simple compressible stationary system consisting of Ideal gas undergoing internally reversible isothermal process, heat completely converts into displacement work.

4.8 Adiabatic Process

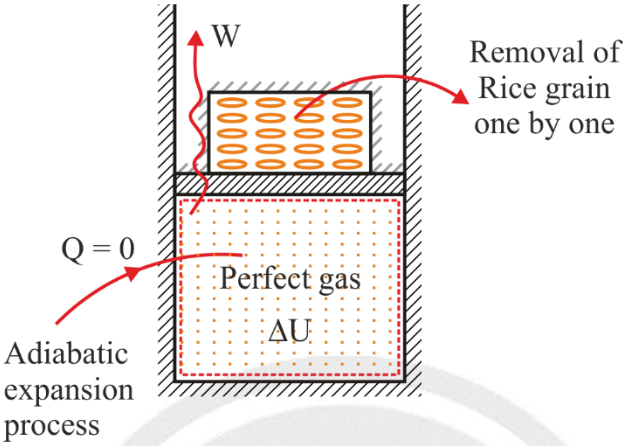


Fig. 4.7 Adiabatic expansion of perfect gas

$\mathbf{Q = 0}$

$\mathbf{W_d + \Delta U = 0}$

- For simple compressible stationary system, undergoing adiabatic expansion, displacement work is done at the expense of internal energy.

4.9 Polytropic Process

- $Q = \left(\frac{\gamma-n}{\gamma-1}\right) W_d$ (Perfect Gas)
- $C_{po} = -\frac{(\gamma-1)}{(n-1)} c_v$

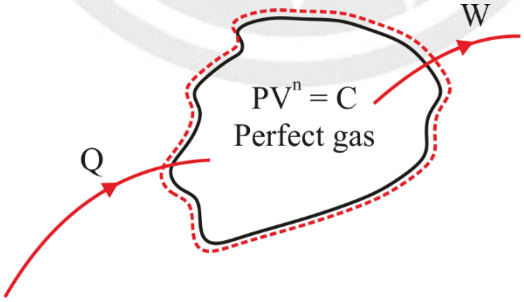


Fig. 4.8 A system undergoing polytropic process

- $W_d = \frac{P_1V_1 - P_2V_2}{n-1}$ (Any Gas)
- For polytropic heat addition to a perfect gas having polytropic index between 1 & γ
  (i) Displacement work is more than the heat supplied.
  (ii) The extra displacement work is done at the expense of internal energy.
- Polytropic heat addition to a perfect gas having polytropic index between 1 & γ leads to increase in volume but decrease in pressure & temperature.

4.10 Free Expansion

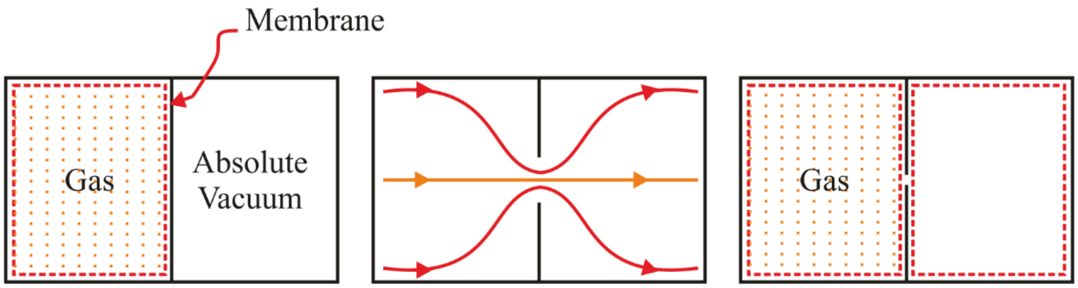
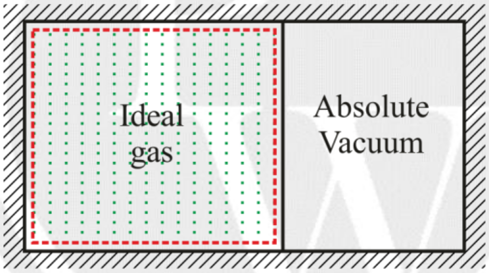


Fig. 4.9 Free expansion

- Expansion of a gas against absolute vacuum is known as free expansion.
- In free expansion, external resistance is zero, hence work interaction is also zero.
- In case of free expansion, although $\int PdV$ is non-zero, but it can't be applied for free expansion, since free expansion is non quasi-static process.

4.10.1 Free expansion of an Ideal gas inside an insulated chamber



$\Delta KE = 0$

$\Delta PE = 0$

Fig. 4.10 Ideal gas vacuum space separated by a membrane in an insulated chamber

- For an Ideal gas undergoing free expansion inside an insulated chamber,
  1. $\Delta U_{1-2} = \Delta T_{1-2} = \Delta H_{1-2} = 0$
  2. $P_1V_1 = P_2V_2$

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5

OPEN SYSTEM ANALYSIS

5.1 Introduction [Open System Overview]

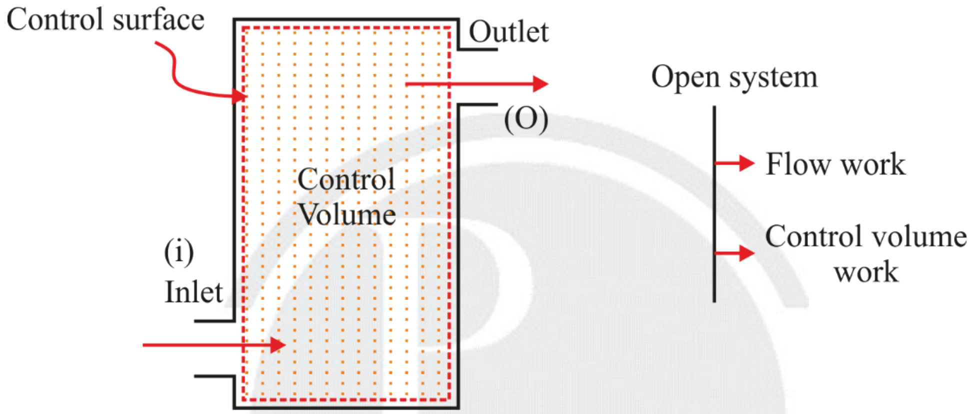


Fig.5.1 Open system

5.2 Flow Work

Flow work is the energy needed to push a fluid into (or) out of a control volume.

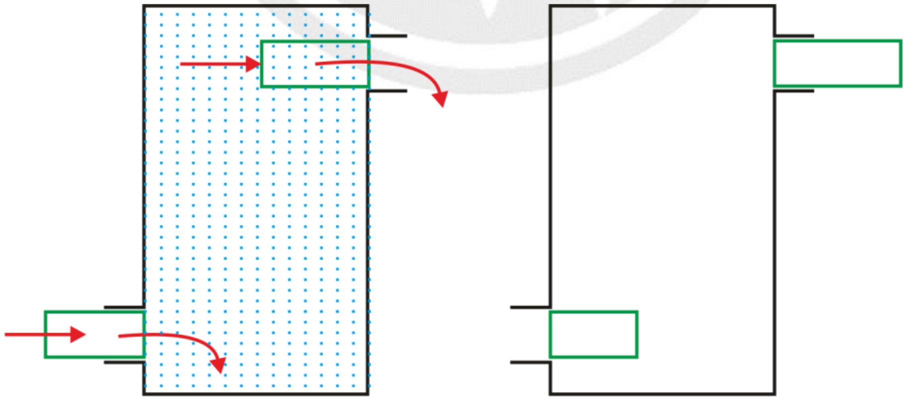


Fig.5.2 Fluid elements crossing the control surface

- The work involved in crossing the fluid element either to enter or to leave the control volume is known as flow work.

5.2.1 Expression of flow work

Specific flow work, $w_f = P_v$

Rate of flow work, $\dot{W}_f = mPv$

Note:

Unlike closed systems, control volumes involve mass flow across their boundaries, and some work is required to push the mass into or out of the control volume. This work is known as the flow work, or flow energy, and is necessary for maintaining a continuous flow through a control volume.

5.3 Control Volume Work (W_{cv})

- Closed system ⇒ Shaft Work

  Open System ⇒ Control Volume Work

5.3.1 Control Volume Work

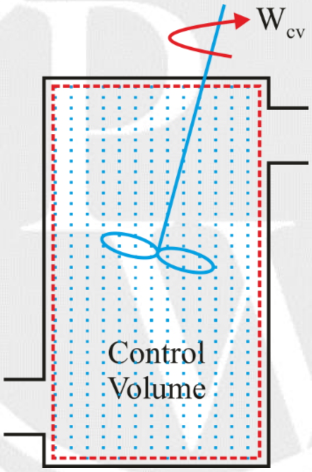


Fig. 5.3 An open system with control volume work

- Rotated from inside of CV ⇒ $W_{cv} = +ive$

  Rotated from outside of CV ⇒ $W_{cv} = -ive$
- Work interaction across the control surface for the open system is known as control volume work.

  For turbine ⇒ $W_{cv} = +ive$

  For compressor ⇒ $W_{cv} = -ive$

  For pump ⇒ $W_{cv} = -ive$

Note:

Expression for control volume work

- $w_{cv} = -\int vdP \qquad \begin{bmatrix}\text{Int. Rev. Steady Flow} \\ \Delta ke \cong 0, \Delta pe \cong 0\end{bmatrix}$
- $W_{cv} = -\dot{m}\int vdP$

5.3.1.1 Control Volume Work on P-v diagram

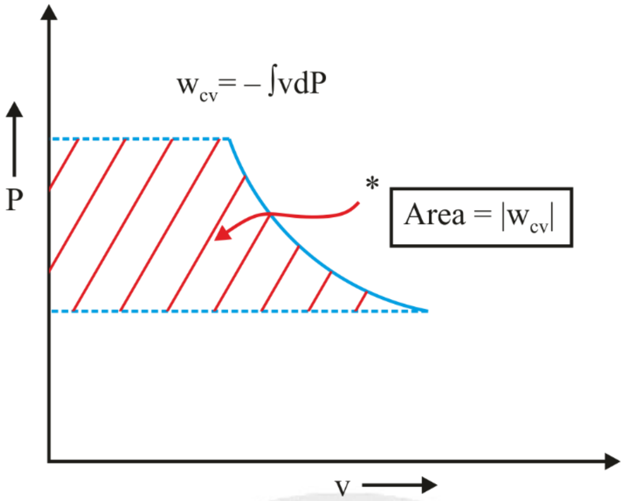


Fig. 5.4 Control volume work on P-v Diagram

5.3.1.2 Analysis for Pump work

- Pump ⇒ Vapour Power Plant
- $w_i = v(P_b - P_c)$

5.4 Conservation of Mass and Energy

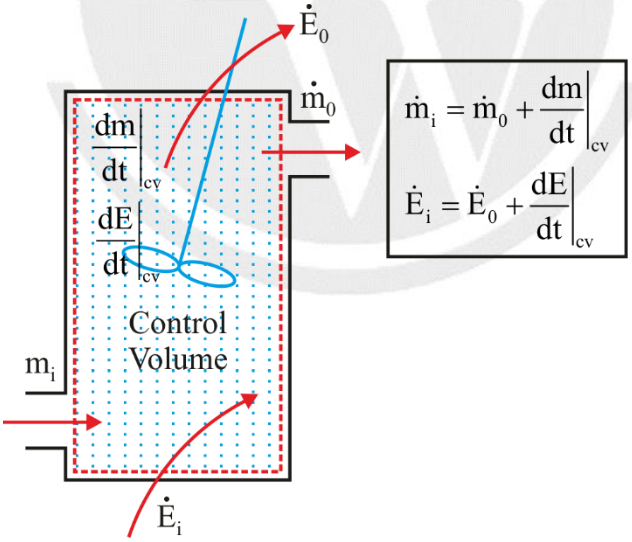


Fig. 5.5 Mass and energy conservation in an open system

5.4.1 Energy equation for an open system

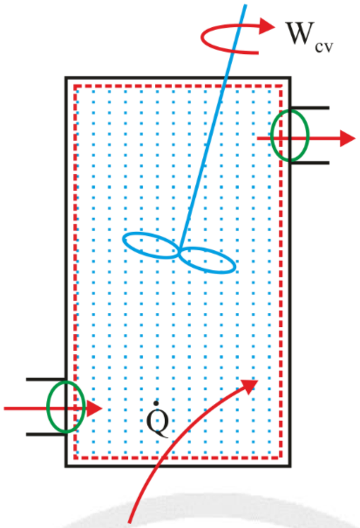


Fig.5.6 Heat and work interaction in open system

- $\dot{Q} = \dot{W}_{cv} + \Delta\dot{KE} + \Delta\dot{PE} + \Delta\dot{H} + \left.\frac{dE}{dt}\right|_{CV}$

Where

$\Delta\dot{KE} = \frac{1}{2}\dot{m}_o c_o^2 - \frac{1}{2}\dot{m}_i c_i^2$

$\Delta\dot{PE} = \dot{m}_O g z_O - \dot{m}_i g z_i$

$\Delta\dot{H} = \dot{m}_o h_o - \dot{m}_i h_i$

- Energy equation for an open system is also known as first law of thermodynamics for an open system.

5.4.1.1 Steady Flow

For steady flow

- A flow is said to be steady flow if thermodynamic properties don't change with time at a particular location.
- Thermodynamic properties may vary along the space coordinate but do not vary with time.
- $\left.\frac{dm}{dt}\right|_{cv} = 0, \dot{m}_i = \dot{m}_o = \dot{m}$
- $\left.\frac{dE}{dt}\right|_{cv} = 0$

5.4.1.2 Steady flow energy equation for an open system

- $\dot{Q} = \dot{W}_{cv} + \Delta\dot{KE} + \Delta\dot{PE} + \Delta\dot{H}$ (in W/kW)

Where

$\Delta\dot{KE} = \frac{1}{2}\dot{m}\left(c_o^2 - c_i^2\right)$

$\Delta\dot{PE} = \dot{m}g\,(z_o - z_i)$

$\Delta\dot{H} = \dot{m}(h_o - h_i)$

$q = w_{cv} + \Delta ke + \Delta pe + \Delta h$ (in J/kg / kJ/kg)

Where

$$\Delta ke = \frac{1}{2}(c_o^2 - c_i^2)$$

$$\Delta pe = g(z_o - z_i)$$

$$\Delta h = (h_o - h_i)$$

5.5 Nozzle

- Nozzle is the steady flow device which increases the kinetic energy. Nozzles are used in jet propulsion system and inlet of impulse turbine.

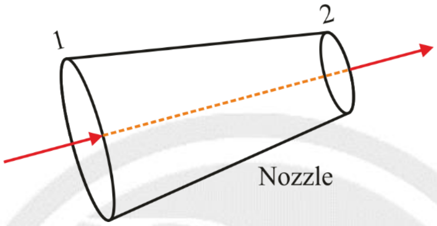


Fig.5.7 Nozzle for subsonic flow

- $c_o > c_i$
- $\dot{Q} = \Delta\dot{KE} + \Delta\dot{PE} + \Delta\dot{H}$

  $q = \Delta ke + \Delta pe + \Delta h$

5.5.1. Well Insulated Horizontal Nozzle

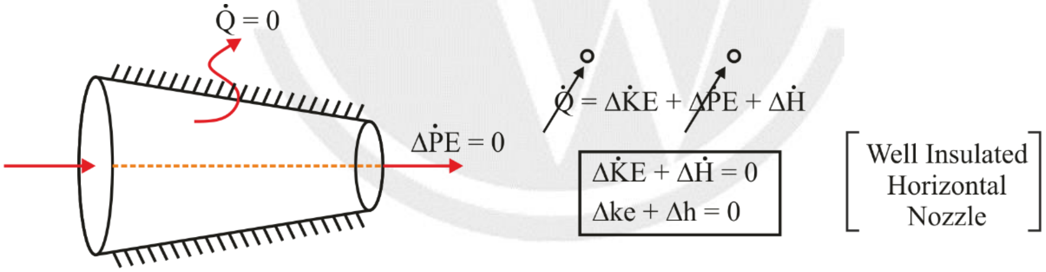


Fig. 5.8 Horizontal nozzle with insulation

5.5.1.2 Perfect gas is the working fluid

- $\Delta H = mc_p\Delta T$

  $\Delta h = c_p\Delta T$

  For perfect gas flowing through well insulated horizontal nozzle

  $\Delta ke + \Delta h = 0$

  $$\frac{1}{2}(c_o^2 - c_i^2) + c_p(T_o - T_i) = 0$$

Note:

- For perfect gas, flowing through perfectly insulated horizontal nozzle, temperature at the outlet is always less than the temperature at the inlet.
- value should be taken in J/kg-K (to write the equation in J/kg)
- $TP^{\frac{1-\gamma}{\gamma}} = C$ can be applied only when perfect gas is having internally reversible adiabatic flow.

  (Internal reversible flow means Ideal flow/Inviscid flow/Frictionless flow)

5.6 Diffuser

- Diffuser is a steady flow device which increases the pressure. It is used in centrifugal compressor.

Note:

Equations for the Diffuser are exactly same as Nozzle.

5.7 Turbine

- Turbine is the steady flow device which is used to produce power. It is used in gas turbine power plant, vapour power plant & hydroelectric power plant.
- For turbine, $\dot{W}_{cv} = +\text{ive}$

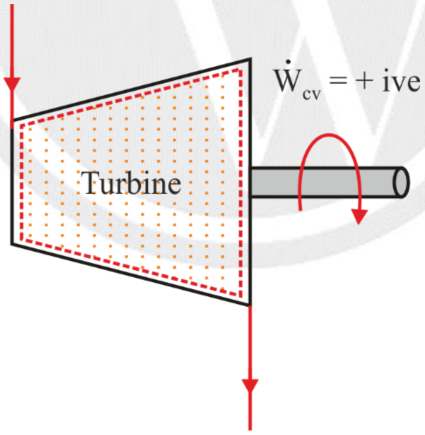
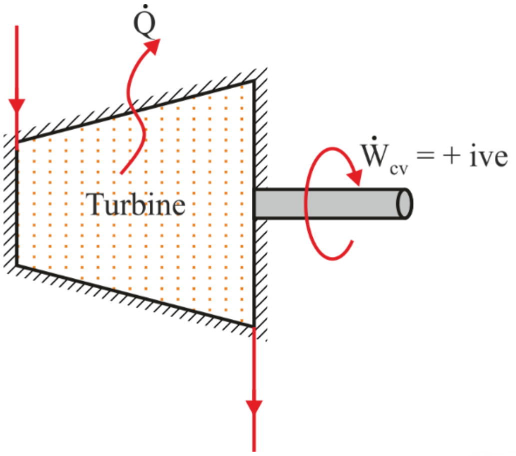


Fig.5.9 Turbine

- $\dot{Q} = \dot{W}_{CV} + \Delta\dot{KE} + \Delta\dot{PE} + \Delta\dot{H}$

5.7.1 Well Insulated turbine having negligible changes in KE & PE



$$\cancelto{0}{\dot{Q}} = \dot{W}_{cv} + \Delta \cancelto{0}{\dot{KE}} + \Delta \cancelto{0}{\dot{PE}} + \Delta \dot{H}$$

$$\boxed{\begin{array}{l} \dot{W}_{cv} + \Delta \dot{H} = 0 \\ \dot{W}_{cv} + \Delta h = 0 \end{array}}$$

Fig. 5.10 Insulated turbine producing work

- For perfectly insulated turbine, having negligible changes in kinetic and potential energies, control volume work is done at the expense of enthalpy.

5.7.1.1 Perfect gas is the working fluid

- $\Delta H = mc_p\Delta T$
  $\Delta h = c_p\Delta T$
- For perfect gas flowing through well insulated turbine having negligible changes in KE & PE.

  $w_{cv} + \Delta h = 0$

  $w_{cv} + c_p\Delta T = 0$

5.8 Compressor

- Compressor is the steady flow device, which is used to increase the pressure of the fluid. It is used in Gas power plant & Vapour compression refrigeration system.

Note:
Equations for Compressor are exactly same as Turbine.

5.9 Throttling Device

- Throttling device is a steady flow restricting device which causes pressure drop of the fluid.
- Throttling device produces a pressure drop without involving any control volume work.

5.9.1 Examples:

1. Orifice
2. Partially opened adjustable valve
3. Porous plug
4. Capillary tube

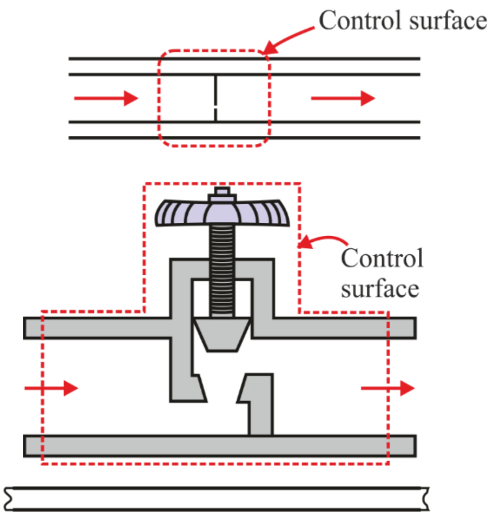


Fig. 5.11 Orifice and partially opened adjustable valve

Note:

- In VCRS throttling valve (throttling device) is used to reduce the pressure of refrigerant from condenser pressure to evaporator pressure while in Domestic refrigerator, same function is performed by capillary tubes.
- Throttling device is used in throttling calorimeter which is used to measure the dryness fraction (quality of two-phase liquid–vapour mixture).

5.9.2 Ideal gas undergoing throttling in small throttling device with negligible changes in KE and PE

- For an ideal gas undergoing throttling in a small throttling device with negligible changes in KE and PE following equations can be used,

$$\Delta h = \Delta T = \Delta u = 0$$

$$P_i v_i = P_o v_o$$

5.10 Mixing Chamber

- Mixing chamber is the steady device where mixing process takes place.

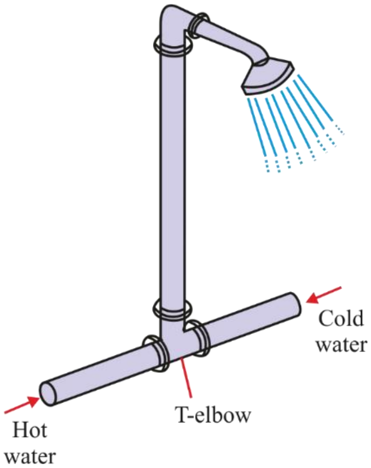


Fig. 5.12 A mixing chamber for hot and cold-water streams

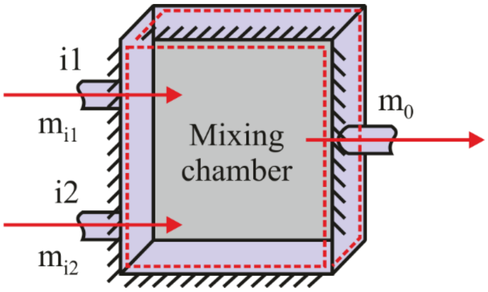


Fig. 5.13 An insulated mixing chamber

- $\dot{m}_{i1} + \dot{m}_{i2} = \dot{m}_0$
- $\dot{Q} = \Delta\dot{KE} + \Delta\dot{PE} + \Delta\dot{H}$
- Well insulated mixing chamber having negligible changes in KE and PE

  $\Delta\dot{H} = 0$

  $$h_0 = \frac{\dot{m}_{i1} h_{i1} + \dot{m}_{i2}\, h_{i2}}{\dot{m}_{i1} + \dot{m}_{i2}}$$

5.11 Unsteady Flow

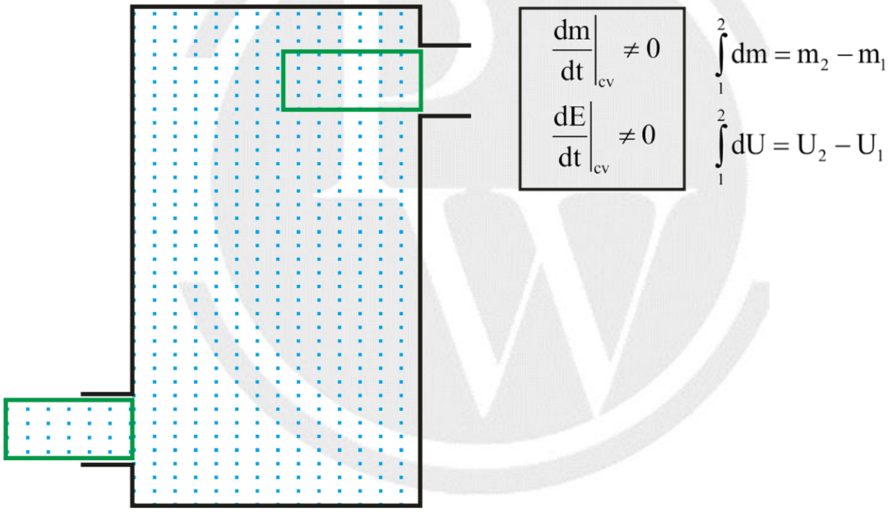
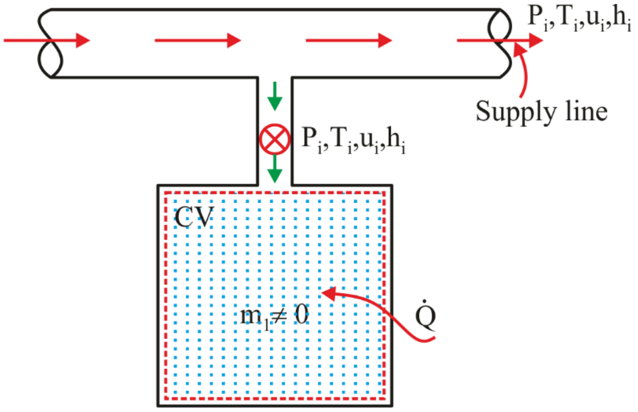


Fig. 5.14 Unsteady flow through a control volume

5.11.1 Charging of non-insulated tank having initial mass non-zero



- $U_2 - U_1 = (m_2 - m_1)h_i + Q$ (Any Fluid)
- $u_2 = \frac{m_1}{m_2}u_1 + \left(1 - \frac{m_1}{m_2}\right)h_i + \frac{Q}{m_2}$ (Any Fluid)
- $T_2 = \frac{\frac{m_1}{m_2}T_1 + \left(1 - \frac{m_1}{m_2}\right)\gamma T_i}{1 - \frac{(\gamma-1)Q}{P_2V_2}}$ (Perfect gas)

5.11.2 Charging of an insulated evacuated tank

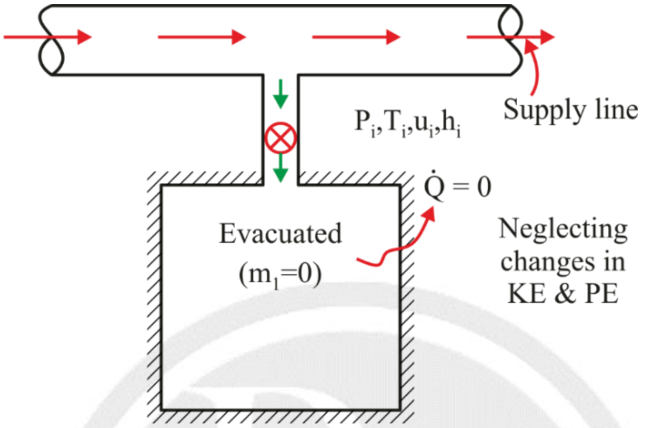


Fig.5.15 An evacuated tank connected to a supply pipeline with $m_1 = 0$

- $U_2 = m_2h_i$ (Any Fluid)
- $u_2 = h_i$ (Any Fluid)
- $T_2 = \gamma T_i$ (Perfect gas)

Conclusions

- Final specific internal energy of the fluid in the tank is equal to the specific enthalpy of the fluid flowing in supply pipeline.
- Final temperature of perfect gas in the tank is γ times of the temperature of the fluid flowing in the supply pipeline.
  (a) Well Insulated
  (b) Evacuated tank

5.11.3 Charging of a non-insulated evacuated tank

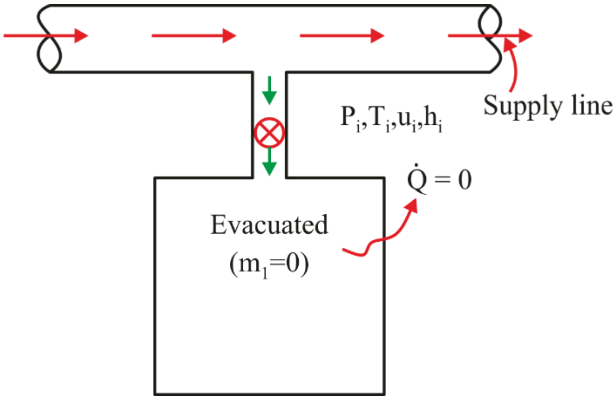


Fig.5.16 Charging of a non-insulated evacuated tank

- $U_2 = m_2h_i + Q$ (Any Fluid)
- $u_2 = h_i + \frac{Q}{m_2}$ (Any Fluid)

- $T_2 = \frac{\gamma T_i}{1 - \frac{(\gamma - 1)Q}{P_2 V_2}}$ (Perfect gas)

5.11.4 Charging of an insulated tank having initial mass non-zero

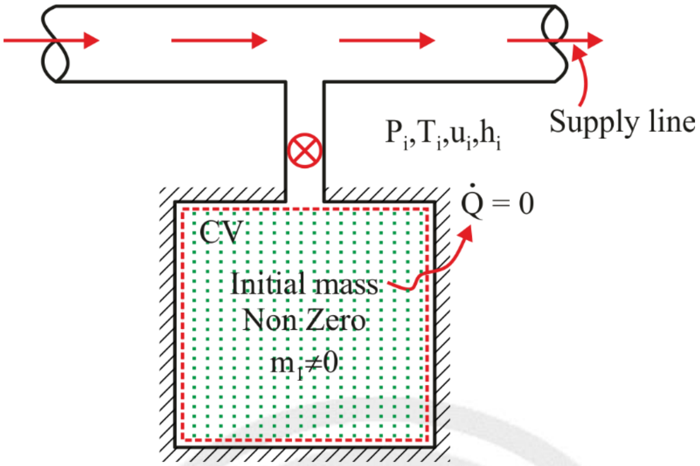
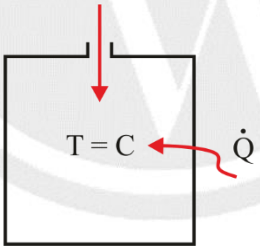


Fig. 5.16 An evacuated tank connected to a supply pipeline with $m_1 = 0$

- $U_2 - U_1 = (m_2 - m_1)h_i$ (Any Fluid)
- $u_2 = \frac{m_1}{m_2} u_1 + \left(1 - \frac{m_1}{m_2}\right) h_i$ (Any Fluid)
- $T_2 = \frac{\gamma T_i}{1 + \frac{P_1}{P_2}\left(\frac{\gamma T_i}{T_1} - 1\right)}$ (Perfect gas)

5.11.5 Charging of a non-insulated evacuated tank from tiny hole maintaining constant temperature of fluid in tank



- Total heat transfer during charging
  $Q = -P_2 V_2$

❑❑❑

6

SECOND LAW OF THERMODYNAMICS

6.1 Drawback of First Law of Thermodynamics

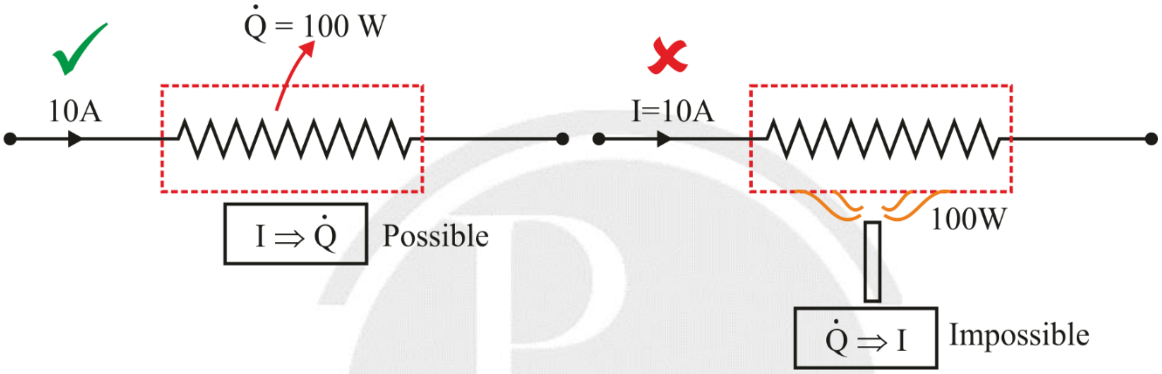


Fig. 6.1 Conversion of Electric energy into heat and vice - versa

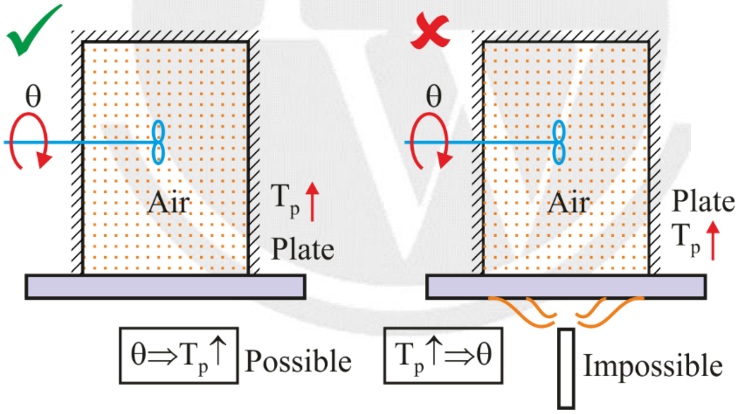


Fig. 6.2 Conversion of paddle work into heat and vice versa

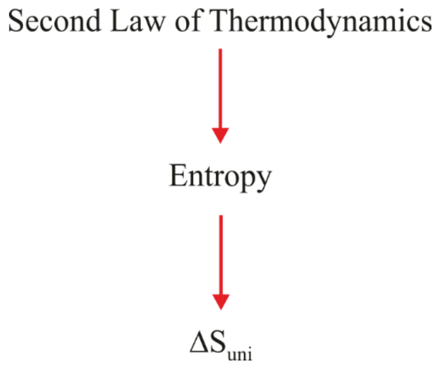
- First law of thermodynamics gives the information about the conservation of energy during a process, but it doesn't give any information about the feasibility & nature of the process.

Note:

- Second Law of thermodynamics tells the direction of a process, with the help of concept of entropy & is known as directional law.
- The process takes place in the direction in which $\Delta S_{\text{universe}} \geq 0$.

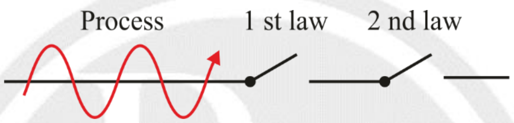
- $\Delta S_{\text{uni}} < 0 \rightarrow$ Impossible
- $\Delta S_{\text{uni}} = 0 \rightarrow$ Possible & Reversible

- $\Delta S_{uni} > 0 \rightarrow$ Possible & Irreversible



6.2 Remember

- A process cannot occur unless it satisfies both the first and the second laws of thermodynamics.



- The use of the second law of thermodynamics is not limited to identifying the direction of processes. The second law also asserts that energy has quality as well as quantity.

6.3 Thermal Energy Reservoirs

- A hypothetical body with a relatively large thermal energy capacity (mass × specific heat) that can supply or absorb finite amounts of heat without undergoing any change in temperature, such a body is called a thermal energy reservoir.

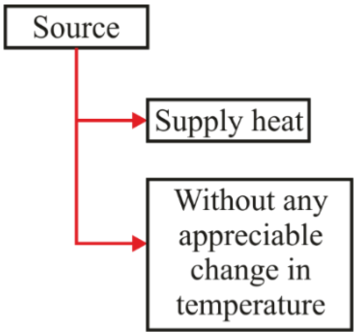
(i) Source

(ii) Sink

6.3.1 Source

- Source is the relatively large heat capacity body, which can supply finite amount of heat without undergoing any appreciable change in temperature.

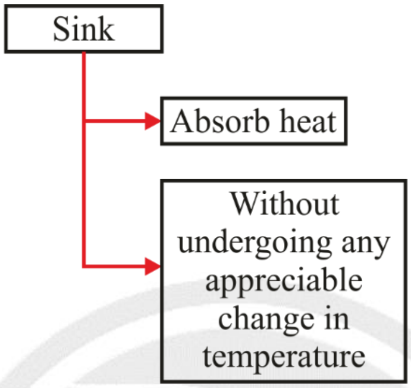
  e.g. Sun, industrial furnace, phase change from vapour to liquid.

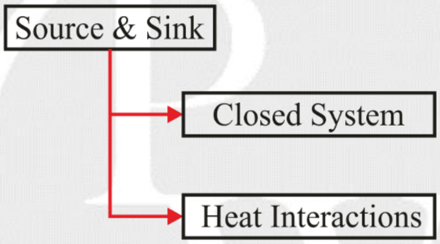


6.3.2 Sink

- Sink is the relatively large heat capacity body, which can absorb finite amount of heat without undergoing any appreciable change in temperature.

  e.g. Atmospheric air, lake, river, sea etc.





Note:

- For analysis purpose source and sink can be assumed as closed system having only heat interactions.
- The changes that take place in such large bodies are so slow and so minute that the process within it can be assumed as internally reversible.

6.4 Statements of Second Law of Thermodynamics

(1) Kelvin-Planck Statement

(2) Clausius Statement

6.4.1 Kelvin-Planck statement

- It is impossible for a system to operate in thermodynamic cycle and deliver net work to its surroundings while receiving heat from a single thermal energy reservoir.

6.4.2 Consequences of Kelvin – Planck statement

(1) Perpetual Motion Machine of Second Kind (PMM-2) is impossible

(2) Concept of Heat Engine

6.4.3 Perpetual Motion Machine of Second Kind (PMM-2) is impossible

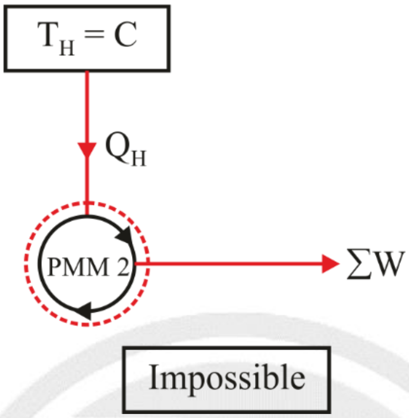


Fig. 6.3 PMM – 2

PMM-2 having 100% thermal efficiency is impossible.

6.5 CONCEPT OF HEAT ENGINE

- Heat engine is the power producing cyclic device which converts a part of heat into work and rejects remaining heat to the sink.

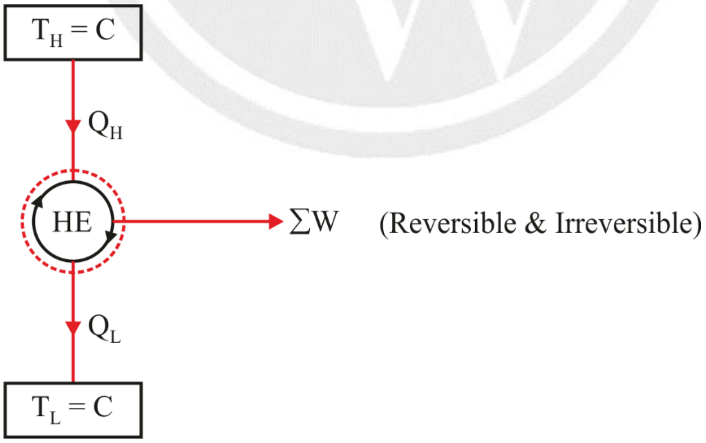


Fig. 6.4 A cyclic heat engine

- The fraction of the heat input that is converted to network output is a measure of the performance of a heat engine and is called the thermal efficiency.

  Thermal efficiency = $\dfrac{\text{Net work output}}{\text{Total heat supplied}}$

- $\eta_{th} = \dfrac{Q_H - Q_L}{Q_H}$

Note:
- In a cyclic process, Heat can't be completely converted into work hence "Heat" is known as "Low Grade Energy".

6.6 Heat Engine in Series

Sink of HE-1 = Source of HE-2

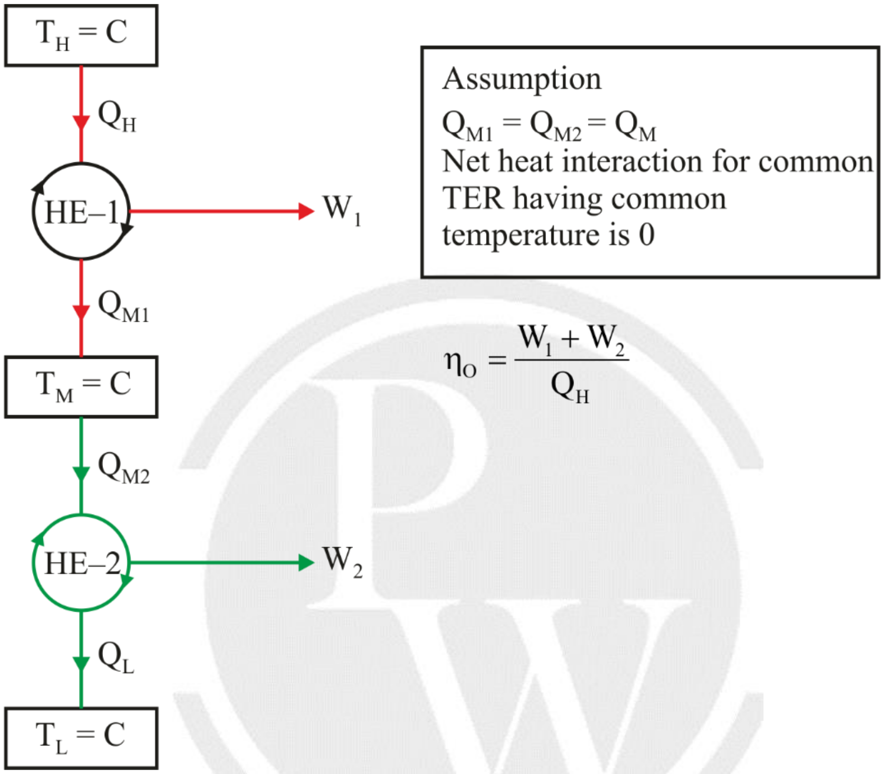


Fig. 6.5 Heat engines in series

- Overall efficiency

$$\eta_o = \frac{W_1 + W_2}{Q_H}$$

$$\eta_o = \eta_1 + \eta_2 - \eta_1\eta_2$$

Above formula valid for any Heat Engine Reversible or Irreversible

6.7 Clausius Statement

- It is impossible for a system to operate in such a way that the sole result could be heat transfer from a cooler body to a hotter body.

6.7.1 Consequences of Clausius Statement

1. Direction of Heat Transfer
2. Concept of Refrigerator
3. Concept of Heat pump

6.7.1.1 Direction of Heat Transfer

Naturally/Automatically

↓

Hotter body (High temperature body) To Cooler body (Low temperature body)

1. Naturally heat transfer take place from hotter body to cooler body.
2. Direction of heat transfer is given by the Second Law of Thermodynamics (Clausius statement)

6.7.1.2 Concept of Refrigerator

- The transfer of heat from a low-temperature medium to a high-temperature requires power consuming cyclic devices called refrigerators. Refrigerators, like heat engines, are cyclic devices.

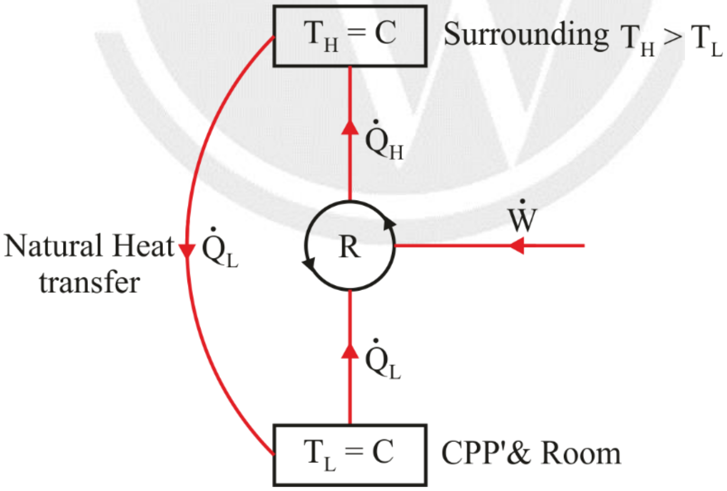


Fig. 6.6 A cyclic Refrigerator

- Here $\dot{Q}_L$ is the magnitude of the heat extracted from the refrigerated space at temperature T_L, $\dot{Q}_H$ is the magnitude of the heat rejected to the warm environment.
- Power consuming cyclic device, aim ⇒ to maintain the lower temperature of lower temperature body
- Desired effect ⇒ $\dot{Q}_L$

6.7.1.3 Concept of Heat pump

- The device which transfers heat from a low-temperature medium to a high-temperature one is the heat pump.

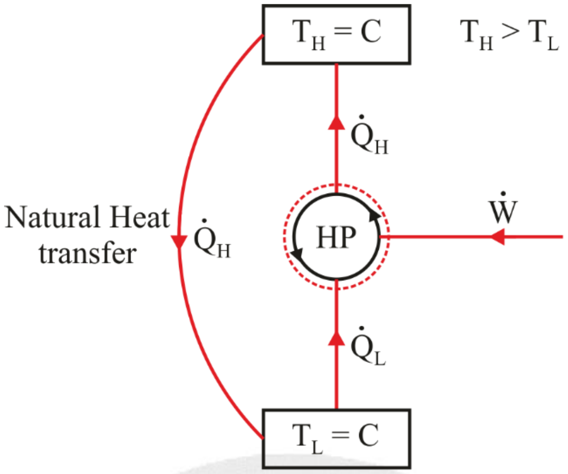


Fig. 6.7 A cyclic heat pump

- Power consuming cyclic device, aim ⇒ to maintain the high temperature of higher temperature body
- Desired effect ⇒ $\dot{Q}_H$

6.8 Coefficient of Performance (COP)

Kelvin-Plank Statement

Power Producing cyclic device

Heat Engine

Thermal Efficiency (η_{th})

Clausius Statement

Power consuming cyclic device

Refrigerator / heat pump

Coefficient of performance

- For power producing cyclic device (Heat Engine), the performance parameter was thermal efficiency (η). For power consuming cyclic devices, (Refrigerator and Heat Pump), the performance parameter was named as Coefficient of Performance (COP).
- $\mathrm{COP_R} = \frac{\dot{Q}_L}{\dot{W}} = \frac{\dot{Q}_L}{\dot{Q}_H - \dot{Q}_L} = \frac{Q_L}{Q_H - Q_L}$
- $\mathrm{COP_{HP}} = \frac{\dot{Q}_H}{\dot{W}} = \frac{\dot{Q}_H}{\dot{Q}_H - \dot{Q}_L} = \frac{Q_H}{Q_H - Q_L}$

6.8.1 Relation between $\mathrm{COP_R}$ & $\mathrm{COP_{HP}}$

Assumption:- Both refrigerator and heat pump are having same amount of heat and work interactions.

- $\mathrm{COP_{HP}} = \mathrm{COP_R} + 1$
- This relation implies that the coefficient of performance of a heat pump is always greater than unity since $\mathrm{COP_R}$ is a positive quantity.

6.9 Relation between Thermal Efficiency (η) & Coefficient of Performance (COP)

Assumption:- All devices Heat Engine, Refrigerator and Heat Pump are having same amount of heat & work interactions.

- $COP_{HP} = \frac{1}{\eta_{HE}}$ and $COP_R = \frac{1}{\eta_{HE}} - 1$

6.10 Carnot Cycle

6.10.1 Various processes of Carnot Cycle

1-2: Reversible Adiabatic compression

2-3: Reversible Isothermal heat addition

3-4: Reversible Adiabatic expansion

4-1: Reversible Isothermal heat rejection

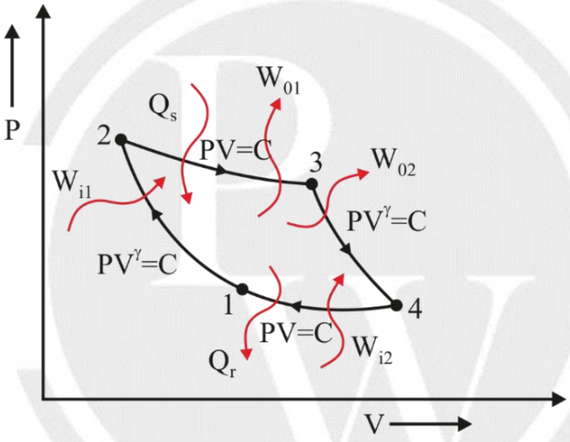


Fig. 6.8 P – V diagram of Carnot cycle

- For Carnot Cycle, all the processes are reversible (both internally & externally), hence Carnot cycle is a reversible cycle.
- For Carnot Cycle

  Heat interactions ⇒ 2 Processes

  Work interactions ⇒ 4 Processes

Analysis for Carnot cycle

- $V_1V_3 = V_2V_4$
- $r = \varepsilon$

  Here r = compression ratio, $r = \frac{V_1}{V_2}$ and ε = expansion ratio, $\varepsilon = \frac{V_4}{V_3}$

- $\eta_c = \frac{T_H - T_L}{T_H}$

  $\because \frac{T_L}{T_H} = \frac{1}{r^{\gamma-1}} = \frac{1}{\varepsilon^{\gamma-1}}$

  $\therefore \eta_c = 1 - \frac{1}{r^{\gamma-1}} = 1 - \frac{1}{\varepsilon^{\gamma-1}}$

Most effective way to increase the thermal efficiency of Carnot cycle

$$\eta_c = 1 - \frac{T_L}{T_H}$$

There are two ways of increasing the thermal efficiency.

(a) Decreasing T_L keeping T_H constant.

(b) Increasing T_H keeping T_L constant.

Out of the two option (a) is more effective.

6.11 Carnot Theorem

For different heat engines operating between same temperature limits, thermal efficiency of reversible heat engine is more than the efficiency of irreversible heat engine.

- For same Temperature limits

$$\eta_{RHE} > \eta_{IRHE}$$

6.12 Carnot Corollary

- For different reversible heat engines operating between same temperature limits, thermal efficiency of all reversible heat engines is equal.
- For same temperature limits

$$\eta_{RHE1} = \eta_{RHE2}$$

- Carnot, Stirling & Ericsson cycles are reversible cycles, hence heat engines operating on these cycles will have same thermal efficiency between same temperature limits.
- For reversible heat engine thermal efficiency is the function of temperature only. It is independent of construction working fluid and processes.

$$\eta_{RHE} = \frac{T_H - T_L}{T_H}$$

$$\eta_{RHE} = f\,(T_H\,,\,T_L)$$

6.13 Thermodynamic Temperature Scales

Temperature scales that are independent of the properties of the substances and are used to measure the temperature are known as thermodynamic temperature scales.

6.13.1 Thermodynamic Kelvin Scale

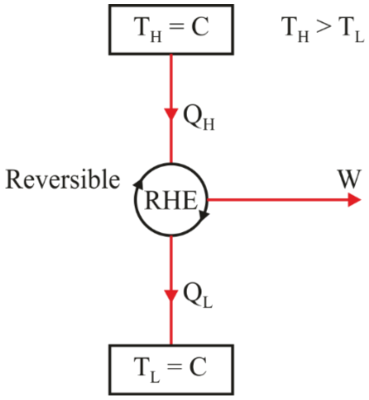


Fig. 6.9 A cyclic reversible heat engine

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

Note:

- Thermodynamic Kelvin scale is valid only for reversible cycles having single heat addition and single heat rejection.
- For Thermodynamic Kelvin scale, Temperature must be absolute temperature (in Kelvin) only.

6.14 Thermal Efficiency of Reversible Heat Engine

- $\eta_{HE} = \frac{Q_H - Q_L}{Q_H}$ (Reversible & Irreversible)
- $\eta_{RHE} = \frac{T_H - T_L}{T_H}$ (Reversible)

6.14.1 Reversible heat engines in series

- Sink of RHE – 1 = Source of RHE – 2
- Assumption:-
  - Net heat interaction for common TER having temperature T_M is 0.
  - $Q_{M1} = Q_{M2} = Q_M$.

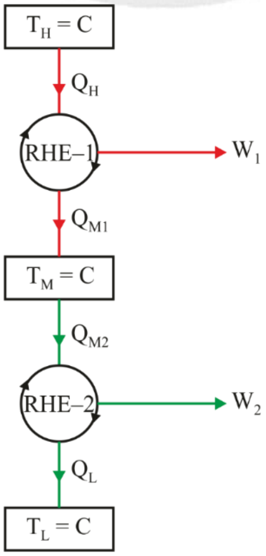


Fig. 6.10 Reversible heat engines in series

- $\frac{Q_H}{T_H} = \frac{Q_M}{T_M} = \frac{Q_L}{T_L}$

6.14.2 Different Cases

Case 1: Same thermal efficiency

- $T_M = \sqrt{T_H T_L}$

Case 2: Same network output

- $T_M = \frac{T_1+T_2}{2}$

6.15 COP of Reversible Refrigerator

- $COP_R = \frac{Q_L}{Q_H - Q_L}$ [Reversible & Irreversible]
- $COP_{RR} = \frac{T_L}{T_H - T_L}$ [Reversible]

6.16 COP of Reversible Heat Pump

- $COP_{HP} = \frac{Q_H}{Q_H - Q_L}$
- $COP_{RHP} = \frac{T_H}{T_H - T_L}$

6.17 Clausius Inequality

- Whether the cycle is reversible/irreversible can be known with the help of Clausius inequality.
- According to Clausius inequality

$$\oint \frac{\delta Q}{T} < 0 \rightarrow \text{Possible, Internally Irreversible cycle}$$
$$\oint \frac{\delta Q}{T} = 0 \rightarrow \text{Possible, Internally Reversible cycle}$$
$$\oint \frac{\delta Q}{T} > 0 \rightarrow \text{Impossible cycle}$$

6.17.1 Remember

- Clausius Inequality is valid only for cycles.
- Whenever in a given question, more than two thermal reservoirs are involved for a cyclic device we have to apply Clausius inequality.
- $\oint \frac{\delta Q}{T} \leq 0 \rightarrow$ Valid for all thermodynamic cycles, reversible/irreversible, including the power consuming cycles.

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7

ENTROPY

7.1 Mathematical feel of Entropy – Part A

- For a closed system, undergoing an internally reversible process, entropy change is given by the expression

$$\Delta S = \int \frac{\delta Q}{T}\bigg|_{\text{Int.Rev}}$$

- Entropy is a property. It is a state (point) function and an exact differential.
- In differential form entropy change is represented by $dS = \frac{\delta Q}{T}\Big|_{\text{Int.Rev}}$.
- For a closed system, undergoing an internally reversible process, entropy change takes place due to entropy transfer (associated with heat transfer) only.
- Since entropy is a state (point) function hence entropy change between two given states is always same whether the path is internally reversible or internally irreversible.

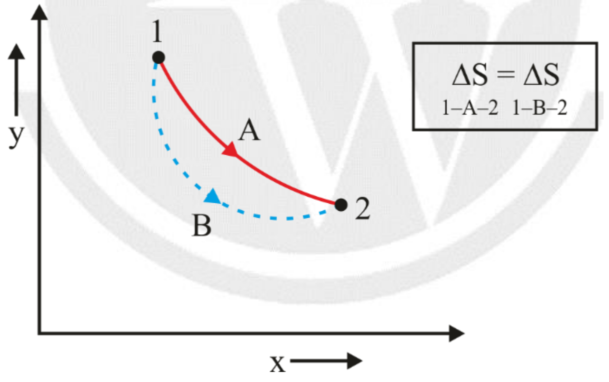


Fig. 7.1 Internally Reversible and Internally Irreversible processes with same initial & final states

7.2 Mathematical feel of Entropy – Part B

- Entropy change for a closed system undergoing internally irreversible process, is greater than entropy transfer for the process.
- $\Delta S > \int \frac{\delta Q}{T}\Big|_{\text{Int.Irr}}$
- For a closed system undergoing internally irreversible process

$$\Delta S = \int \frac{\delta Q}{T} + S_g$$

Here ΔS = Entropy change

$\int \frac{\delta Q}{T}$ = Entropy transfer (due to heat transfer)

S_g = Entropy generation (due to irreversibilities)

- Entropy generation within the system takes place only for internally irreversible process & it is always positive.
- For a closed system undergoing internally irreversible processes, entropy change takes place due to entropy transfer (associated with heat transfer) and entropy generation (associated with Irreversibility).
- For internally reversible processes, entropy generation within the system is "zero".
- Entropy generation depends upon the irreversibilities. Higher the irreversibilities, higher will be the entropy generation.
- Different paths have different irreversibilities, hence different magnitudes of entropy generation.
- Entropy generation is a path function & inexact differential represented by δS_g .

7.3 Entropy Change for a Closed System Undergoing Various Internally Reversible Heat Interactions

$$dS = \frac{\delta Q}{T}$$

- Heat Addition ⇒ Entropy increases
- Heat Rejection ⇒ Entropy decreases
- Adiabatic Process ⇒ Isentropic process

7.4 Entropy Change for a Closed System Undergoing Various Internally Irreversible Heat Interactions

- $dS = \frac{\delta Q}{T} + \delta S_{gen}$
- Heat addition ⇒ Entropy Increases
- Adiabatic Process ⇒ Entropy Increases
- Heat Rejection ⇒ Entropy may increase, decrease or remain same

Note:

- For a closed system undergoing heat addition process, entropy of the system always increases.
- For an insulated closed system, entropy of the system can never decrease. It is constant for internally reversible process and increases for internally irreversible process.
- For a closed system, heat rejection is the only way to decrease the entropy of the system.
- For a closed system, every internally reversible adiabatic process is isentropic process, but every isentropic process is not internally reversible adiabatic process.
- For a closed system an internally irreversible heat rejection process will be isentropic, if entropy decrease due to entropy transfer is exactly equal to the entropy increase due to entropy generation.
- Entropy of a closed system can increase, decrease & remains constant depending upon the type of process (Internally reversible/Internally Irreversible) and the type of heat interaction (heat addition/heat rejection/adiabatic process), but entropy of universe can never decrease.

7.5 Third Law of Thermodynamics

- It is based on low temperature chemical reaction observations.
- The entropy of a pure crystalline substance at nearly absolute zero temperature is “zero”.
- The entropy of a substance that is not pure crystalline (solid solution) is not zero at nearly absolute zero temperature since more than one molecular configuration exists for such substances, which introduces some uncertainty about the microscopic state of the substance.

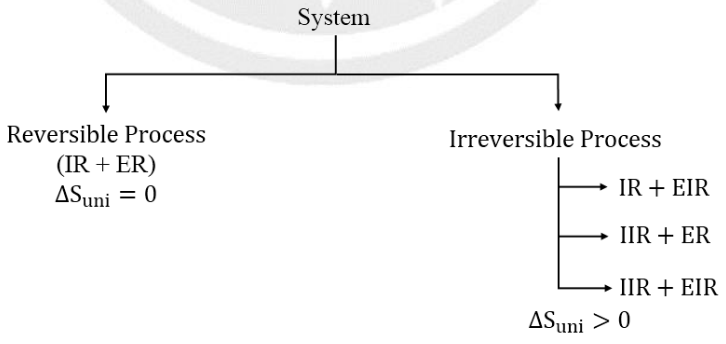
7.6 Discussion on Work Interaction

- Work interaction is organised form of energy. Work is free from disorderness or randomness and thus free of entropy.
- An energy interaction that is accompanied by entropy transfer is heat interaction and energy interaction that is not accompanied by entropy transfer is work interaction.

Note:

- Entropy is an extensive property.
- Entropy generation in the universe is equal to the entropy change of the universe which is further equal to the summation of entropy change of system and entropy change of surrounding.
- $S_{g,uni} = \Delta S_{uni}$
- Entropy change of Universe $\Delta S_{uni} = \Delta S_{sys} + \Delta S_{sur}$

7.7 Entropy change of Universe



Where

- IR:- Internally Reversible process, ER:- Externally Reversible process
- IIR = Internally Irreversible process, EIR = Externally Irreversible process
- Entropy of universe during an actual process (Irreversible process) always increases. In limiting case, for ideal process (Reversible process) entropy of universe remains constant. In other words, Entropy of universe can never decrease. This is known as “Increase of entropy principle”.

- Entropy of universe can never decrease but entropy of system may decrease during a process.
- Entropy is not a conserved property for actual process (Irreversible processes) however, it is conserved for ideal processes (Reversible processes). Mass & Energy are always conserved.

Note:

For a closed system, entropy change will be zero in the following cases

- System undergoing internally reversible adiabatic process.
- System undergoing internally irreversible heat rejection process such that entropy increase due to entropy generation is equal to the entropy decrease due to entropy transfer.
- Cyclic process
- Steady state heat interaction

7.7.1 Physical meaning of Entropy

- Entropy is related to the predictability of the position of the molecules. As the system molecules become more disordered, the position of molecules becomes less predictable and entropy increases.
- Entropy can be defined as the measure of molecular randomness or molecular disorderness.
- Entropy of a substance is minimum in solid phase while it is maximum in gaseous phase.
- When heat is supplied to an incompressible substance, the position of molecules becomes less predictable, hence entropy of the system increases.
- Temperature decrease → Oscillations decreases → Predictability Increases → Entropy decreases

7.7.2 Entropy transfer for closed system undergoing constant temperature heat interactions

- $S_t = \frac{Q}{T}$
- Entropy transfer for a closed system undergoing constant temperature heat interaction can be calculated by evaluating (Q/T).
- Entropy transfer to the system is taken as positive whereas entropy transfer from the system is taken as negative.

7.8 Entropy Change for a Closed System Undergoing Internally Reversible Constant Temperature Heat Interaction

7.8.1 Case 1: Source

(Closed system, T = constant)

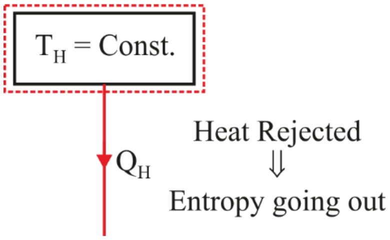


Fig. 7.2 Heat rejection from the source

- $S_{t,source} = -\frac{Q_H}{T_H}$
- $S_{out,source} = \frac{Q_H}{T_H}$

7.8.2 Case 2: Sink

(Closed system, T = constant)

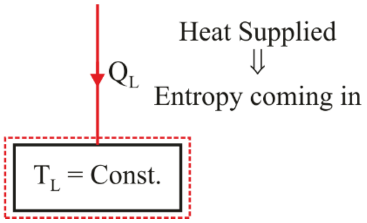


Fig. 7.3 Heat addition to the sink

- $\Delta S_{t,sink} = \frac{Q_L}{T_L}$
- $\Delta S_{in,sink} = \frac{Q_L}{T_L}$

7.8.3 Case 3: Plane wall

Assumption

Steady state heat conduction

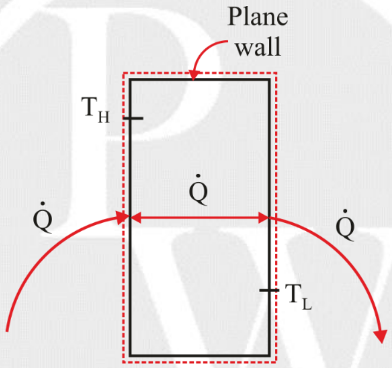


Fig. 7.4 Steady state heat conduction through a plane wall

- $\dot{S}_{g,sys} = \frac{(T_H - T_L)\,\dot{Q}}{T_H\ T_L}$

7.8.4 Phase change process

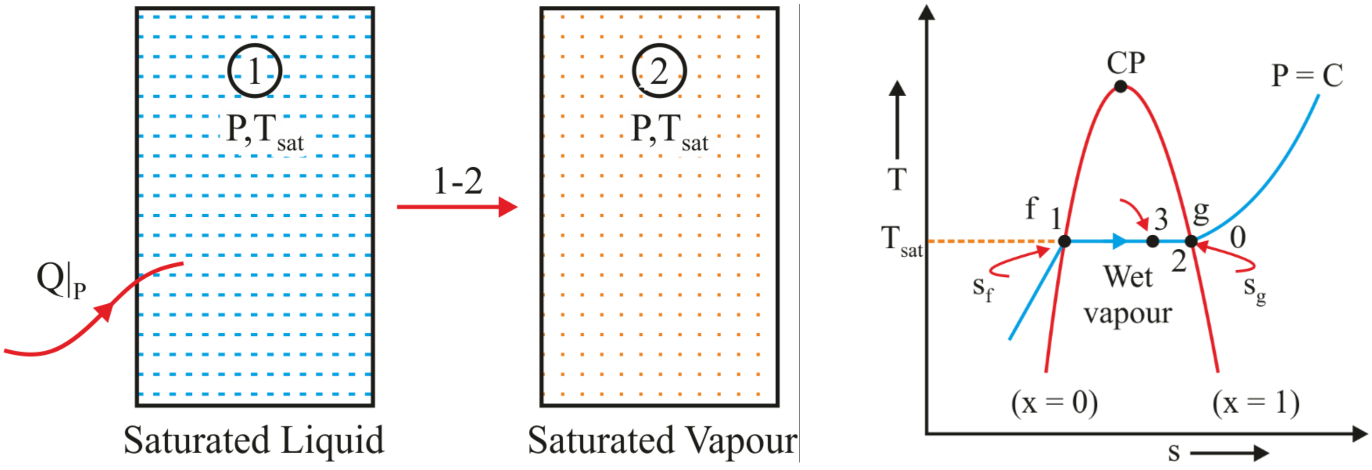


Fig. 7.5 Phase change from saturated liquid to saturated vapour on T-s diagram

Saturated Liquid ⇒ Saturated Vapour
(f) (g)

- $S_{fg} = \frac{H_{fg}}{T_{sat}}, \left[\frac{J}{K} \text{ or } \frac{kJ}{K}\right]$

  H_{fg} = Latent Heat [J or kJ]

  T_{sat} = Saturation Temperature (K)
- $s_{fg} = \frac{h_{fg}}{T_{sat}} \left[\frac{J}{kg-K} \text{ or } \frac{kJ}{kg-K}\right]$

  h_{fg} = Specific latent heat $\left[\frac{J}{kg} \text{ or } \frac{kJ}{kg}\right]$

  T_{sat} = Saturation Temperature (K)

7.8.5 Heat transfer between Source & Sink

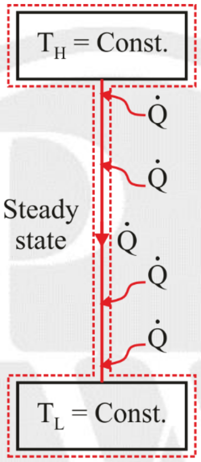


Fig. 7.6 Heat transfer between source and sink

- $\dot{S}_{g,sys} = \frac{(T_H - T_L)}{T_H T_L} \dot{Q}$

7.9 Tds Equations (Gibbs Equations)

- Tds = du + Pdv
- Tds = dh – vdP
- Tds equations are valid for any substance, any system and any process.

7.9.1 Specific entropy change calculation for a perfect gas

- $\Delta s_{1-2} = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right)$
- $\Delta s_{1-2} = c_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)$
- $\Delta s_{1-2} = c_v \ln\left(\frac{P_2}{P_1}\right) + c_p \ln\left(\frac{v_2}{v_1}\right)$
- Specific entropy change equations for a perfect gas are valid for both internally reversible & internally irreversible processes.
- Entropy of a perfect gas is not the function of temperature only.
- For finding total entropy change, specific entropy change equation must be multiplied by mass.

7.9.2 Entropy change of incompressible substances (Solid, Liquid)

- $\Delta s_{1-2} = c \ln\left(\frac{T_2}{T_1}\right)$;   assuming $c = c(T)$ only
- $\Delta S_{1-2} = mc \ln\left(\frac{T_2}{T_1}\right)$
- Entropy change for a perfect incompressible substance depend on temperature only.

7.10 Different Cases

7.10.1 Two finite bodies (having same heat capacities) at different temperatures are in contact with each other in an insulated chamber

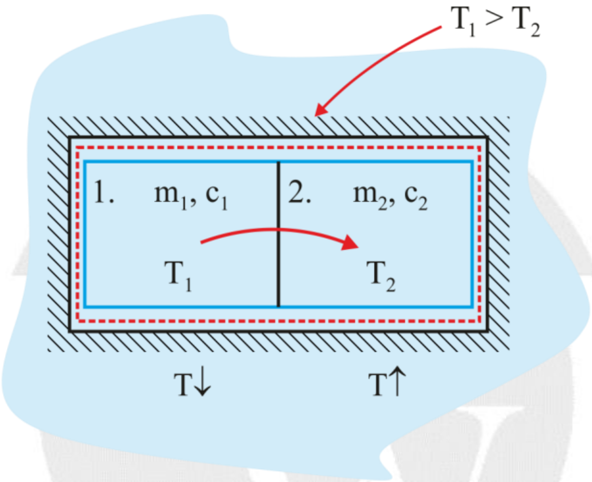


Fig. 7.7 Two finite bodies in an insulated chamber

- Assuming system is two finite bodies
- $T_f = \frac{T_1+T_2}{2}$
- $\Delta S_{sys} = 2\ mc \ln\left(\frac{AM}{GM}\right)$, here $AM = \frac{T_1+T_2}{2}$ and $GM = \sqrt{T_1\ T_2}$
- $\Delta S_{sys} = \Delta S_{uni} = S_{g,uni} = S_{g,sys} = 2\ mc \ln\left(\frac{AM}{GM}\right)$
- $\Delta S_{surr} = S_{g,surr} = 0$

7.10.2 Reversible heat engine is connected between two finite bodies (having same heat capacities) at different temperatures

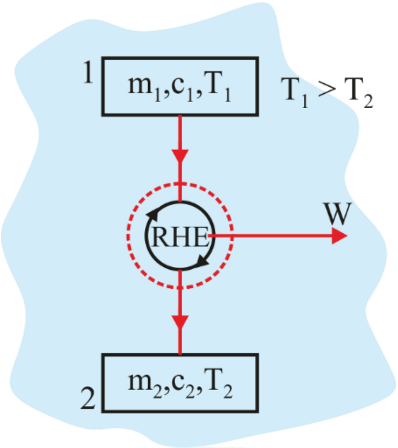


Fig. 7.8 A cyclic reversible heat engine between two finite bodies

- Assuming system is reversible heat engine
- $\Delta S_{sur} = 0$

  $T_f = \sqrt{T_1 T_2}$
- $W_{max} = 2\ mc\ (AM - GM)$; here $AM = \frac{T_1 + T_2}{2}$ and $GM = \sqrt{T_1\ T_2}$

7.10.3 Reversible Refrigerator connected between two finite bodies (having same heat capacities) at different temperatures

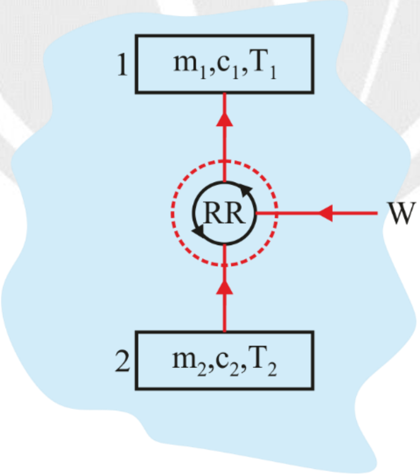


Fig. 7.9 A cyclic reversible refrigerator between two finite bodies

- Assuming system is a reversible refrigerator.
- $\Delta S_{sur} = 0$
- $T_{f1} T_{f2} = T_1 T_2$

  Where T_{f1} & T_{f2} are the final temperature of body 1 and body 2 respectively.

7.10.4 Entropy change of an Open System

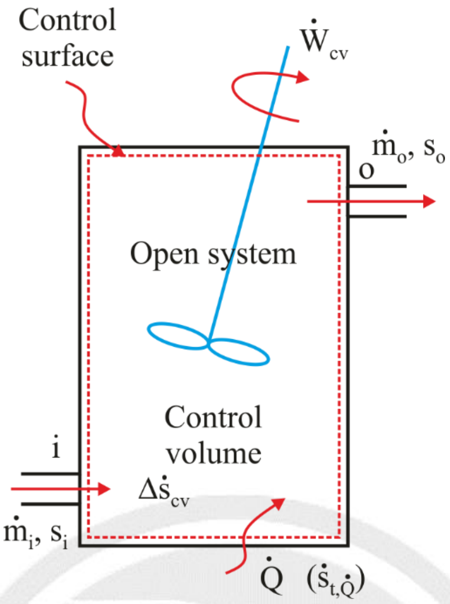


Fig. 7.10 Entropy change in a control volume

- $\Delta\dot{S}_{cv} = \dot{S}_{t,\dot{m}} + \dot{S}_{t,\dot{Q}} + \dot{S}_{g,cv}$
- The rate of entropy change within control volume during a flow is equal to the sum of the rate of entropy transfer into the control volume by mass transfer, the rate of entropy transfer into the control volume by heat transfer and the rate of entropy generation within control volume as a result of irreversibilities.
- For open system the rate of entropy changes of control volume and change of rate of entropy fluid are different things.
  $\Delta\dot{S}_{cv} \neq \Delta\dot{S}_f$

Note:

$$\Delta\dot{S}_{cv} + \Delta\dot{S}_f = \Delta\dot{S}_{t,\dot{Q}} + \dot{S}_{g,cv}$$

7.10.5 Steady Flow

- For steady flow $\mathbf{\Delta\dot{S}_{cv} = 0}$
- For adiabatic flow $\mathbf{\dot{S}_{t,\dot{Q}} = 0}$
- For Internally Reversible flow $\mathbf{\dot{S}_{g,cv} = 0}$

7.10.6 Throttling of ideal gas in small throttling device

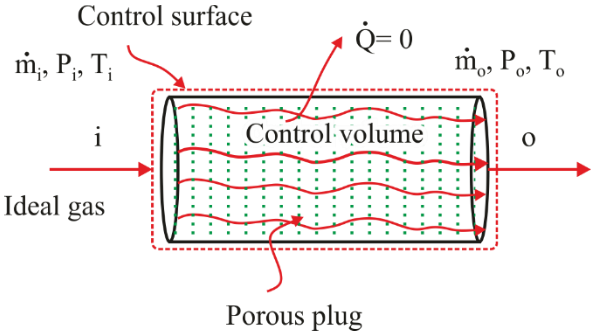


Fig. 7.11 Entropy generation in a throttling device

- $\dot{S}_{g,cv} = \Delta\dot{S}_f$
- $\Delta\dot{S}_f = -\dot{m}R\ln\left(\frac{P_o}{P_i}\right)$

7.10.7 T-s diagram

- On T-s diagram area under the curve projected on specific entropy axis gives the magnitude internally reversible heat interactions per unit mass.
- For heat addition process entropy increase while for heat rejection process entropy decreases.

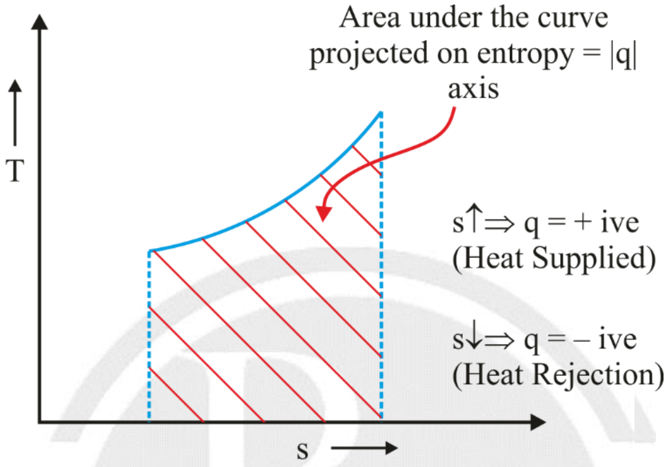


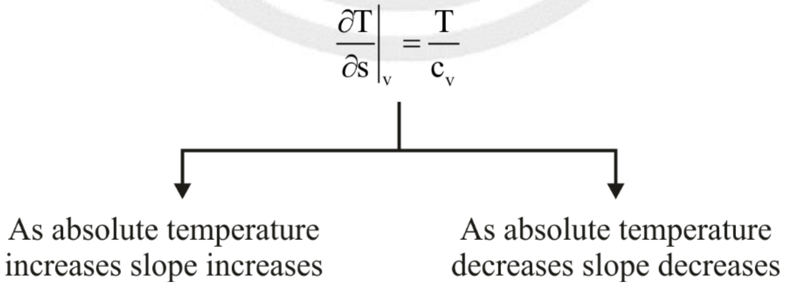
Fig. 7.12 Heat supplied on T-s diagram

7.11 T-s Diagram for Various Internally Reversible Processes

7.11.1 Isochoric process

Slope of Isochore on T-s diagram is given by

$$\left.\frac{\partial T}{\partial s}\right|_v = \frac{T}{c_v}$$



$$\left.\frac{\partial T}{\partial s}\right|_v = \frac{T}{c_v}$$

As absolute temperature increases slope increases

As absolute temperature decreases slope decreases

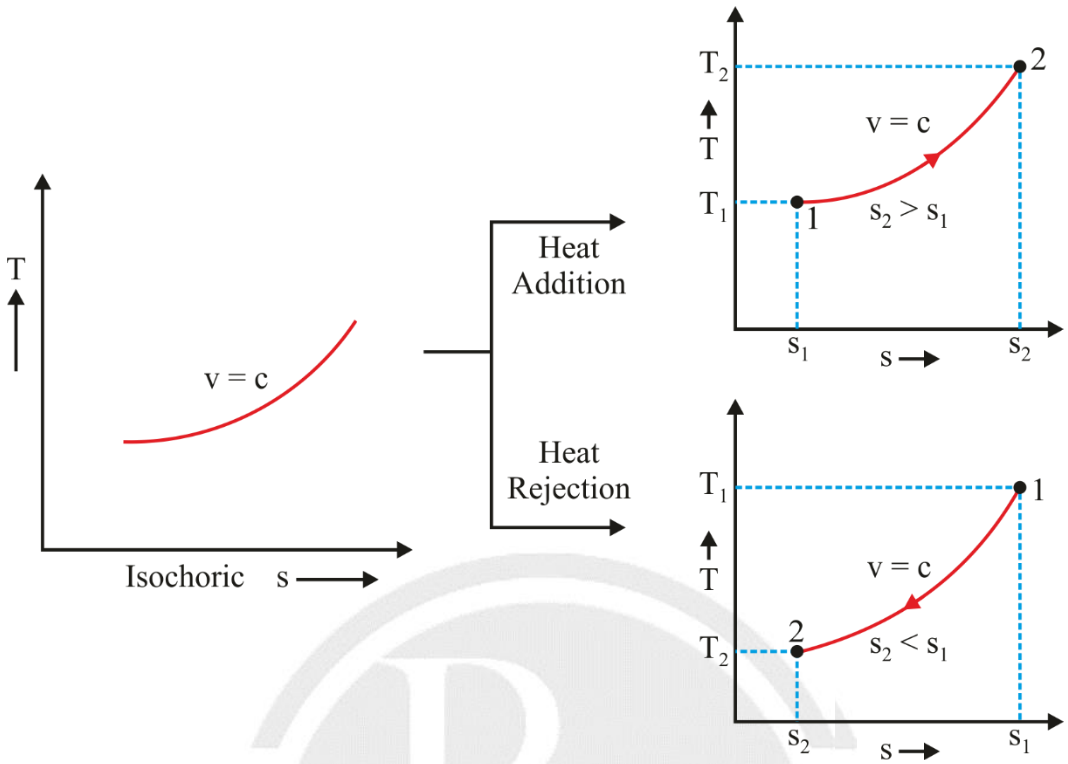


Fig. 7.13 T-s diagram of heat interactions in isochoric process

7.11.2 Isobaric process

Slope of Isobar on T-s diagram is given by

$$\left.\frac{\partial T}{\partial s}\right|_P = \frac{T}{c_P}$$

$$\left.\frac{\partial T}{\partial s}\right|_p = \frac{T}{c_p}$$

As absolute temperature increases slope increases

As absolute temperature decreases slope decreases

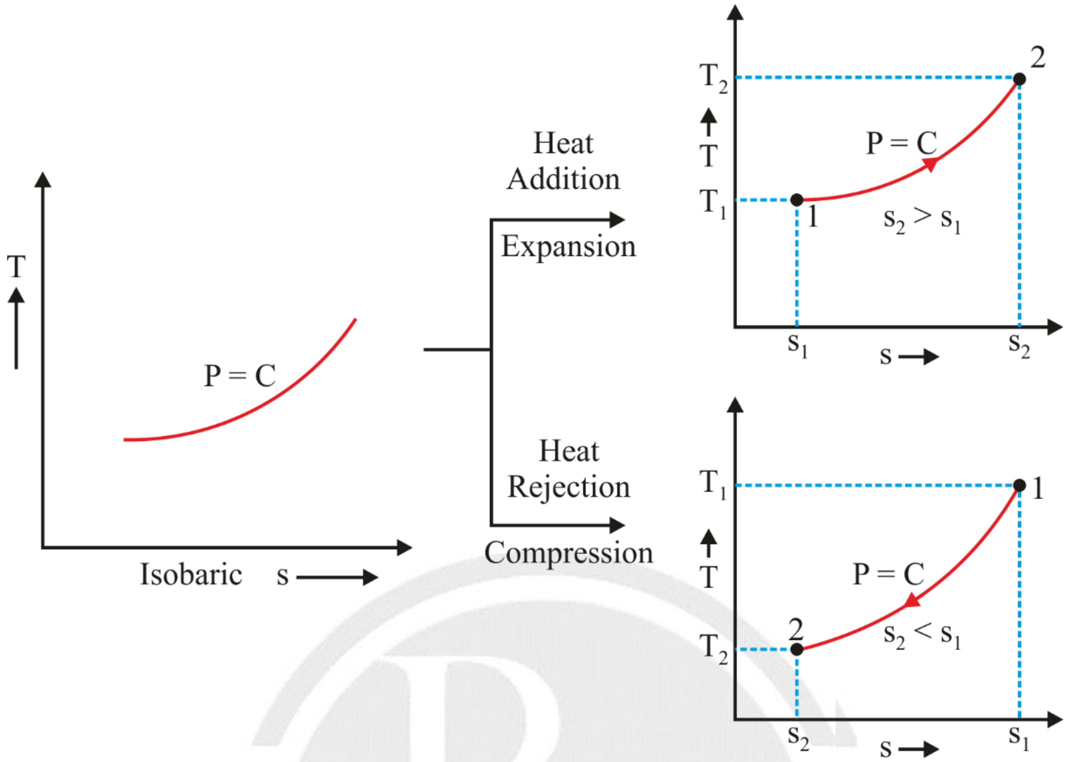


Fig. 7.14 T-s diagram of heat interactions in isobaric process

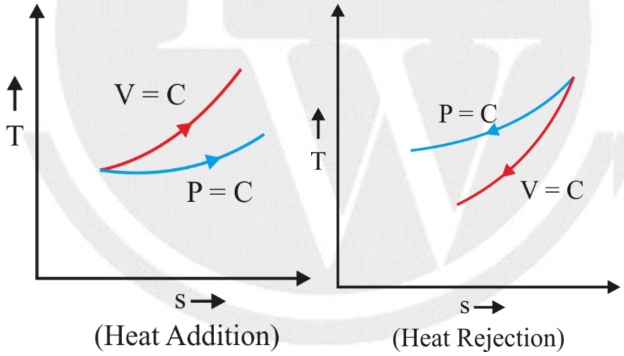


Fig. 7.15 T-s diagram of Isobaric and isochoric processes

- $\left.\frac{\partial T}{\partial s}\right|_V = \gamma \left.\frac{\partial T}{\partial s}\right|_P$

  $\gamma > 1$

  $\left.\frac{\partial T}{\partial s}\right|_V > \left.\frac{\partial T}{\partial s}\right|_P$
- On T-s diagram internally reversible isochoric and isobaric processes have positive slopes.
- On T-s diagram, slope of internally reversible isochoric process is more (γ times) than the slope of internally reversible isobaric process.
- On T-s diagram both internally reversible isochoric and isobaric processes are curves.

7.11.3 Isothermal process

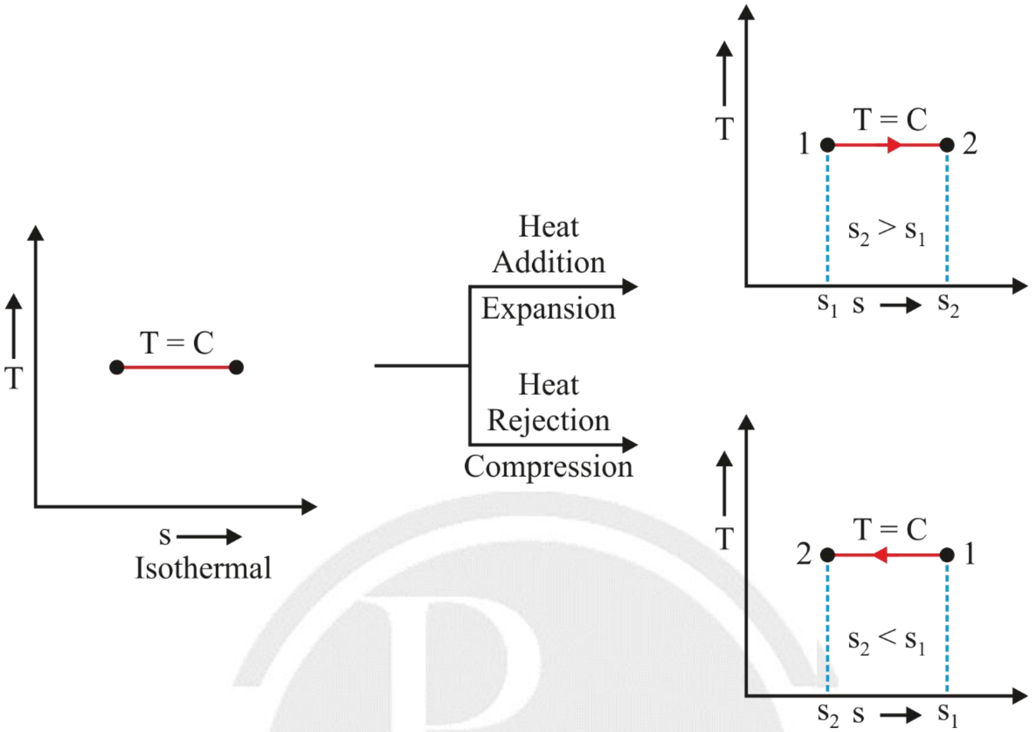
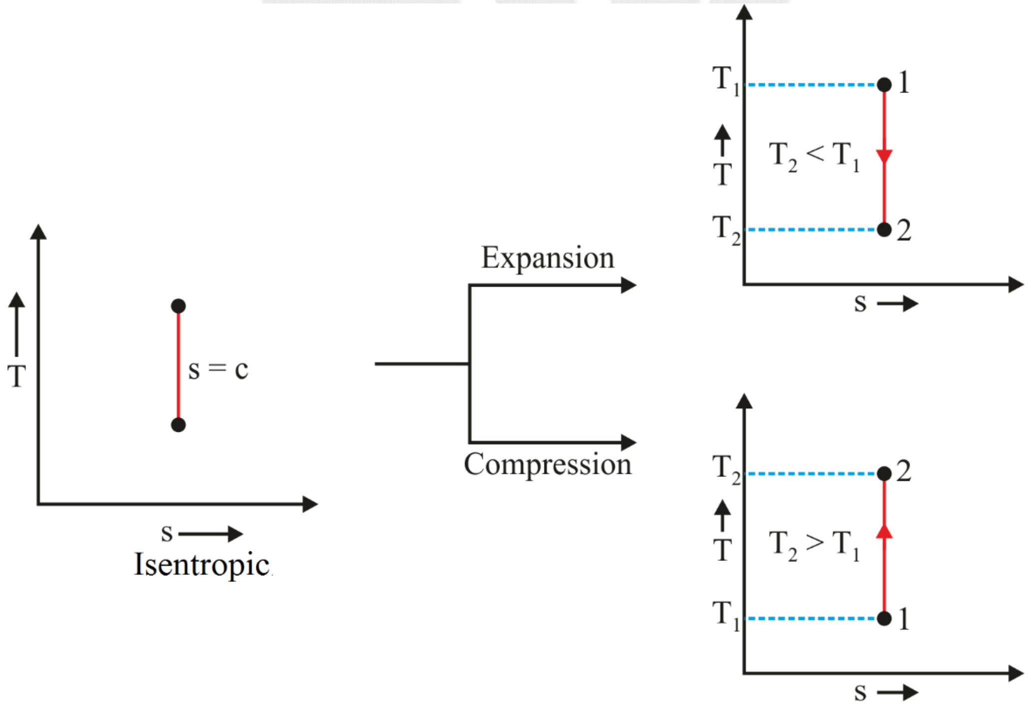


Fig. 7.16 T-s diagram of heat interactions in polytropic process

7.11.4 Adiabatic process



7.11.5 Net heat interaction for a cyclic process

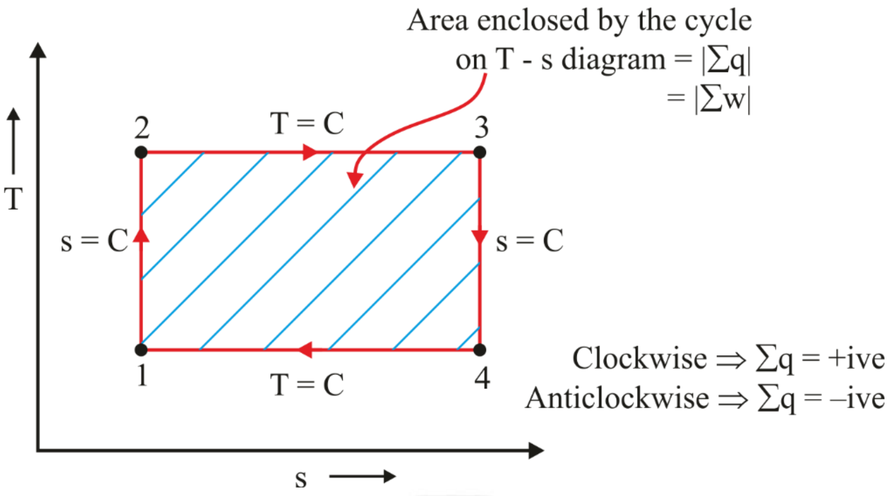


Fig. 7.17 T-s diagram of a cyclic process

- On **T-s** diagram area enclosed by the cycle represents the magnitude of net heat interaction per unit mass for the cycle.
- For clockwise cycle on **T-s** diagram net het interaction is positive while for anticlockwise cycle on **T-s** diagram net heat interaction is negative.
- Power producing cycles are clockwise on both P-V & **T - s** diagrams while power consuming cycles are anticlockwise on both P-V & **T-s** diagrams.
- From **T-s** diagram whatever is net heat interaction per unit mass that will be network interaction per unit mass.

7.11.6 Mixing of perfect gases

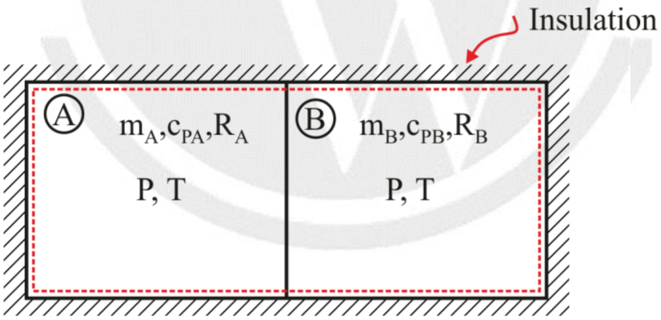


Fig. 7.18 Mixing of gases in an insulated cylinder

Assuming system is perfect gases and pressure after mixing is P only

- $S_{g,sys} = S_{g,uni} = \Delta S_{uni} = \Delta S_{sys} = +X,\ S_{g,sur} = \Delta S_{sur} = 0$
- $\Delta S_{sys} = -m_A R_A \ln\left(\frac{P_{2A}}{P}\right) - m_B R_B \ln\left(\frac{P_{2B}}{P}\right)$
- $\Delta S_{sys} = -\bar{R}[n_A \ln(\bar{x}_A) + n_B \ln(\bar{x}_B)]$

Note:

If two gases are same & initially at same temperature and pressure, then entropy increase is zero since we can't distinguish between the gases.

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8 EXERGY

8.1 Introduction

- Exergy is the maximum possible useful work obtainable from the system.
- In exergy analysis the initial state is specified, and thus it is not a variable.
- Exergy associated with heat is also known as available energy while exergy associated with state of system (closed system / open system) is also known as availability.

8.2 Available Energy Associated with Heat

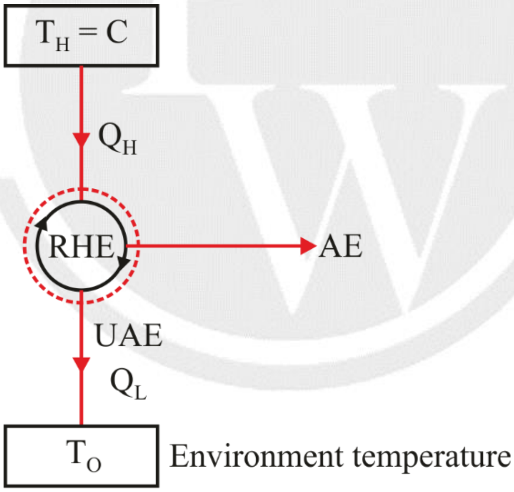


Fig. 8.1 AE and UAE in a reversible heat engine

- Available energy is the maximum possible useful work output obtainable from a certain heat input at a given temperature.
- The minimum heat that must be rejected to the environment is known as unavailable energy
- $\mathrm{AE} = \left(\frac{T_H - T_0}{T_H}\right) Q_H$
- $\mathrm{AE} + \mathrm{UAE} = Q_H$
- $\frac{\mathrm{UAE}}{T_0} = \frac{Q_H}{T_H}$

8.3 Representation of AE & UAE on T-S Diagram for Carnot Heat Engine (RHE)

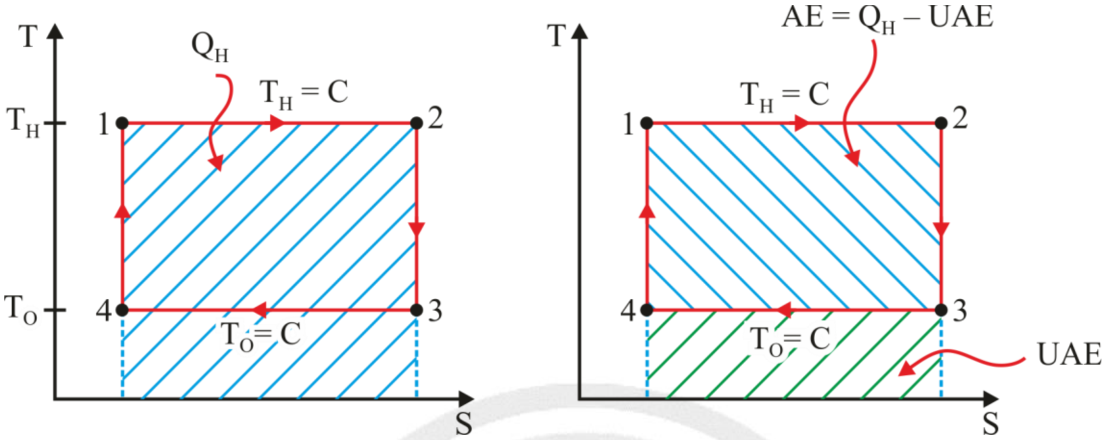
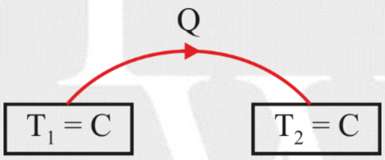


Fig. 8.2 AE and UAE on T-S diagram

8.4 Decrease in Available Energy When Heat is Supplied from A Finite Temperature Difference ($T_1 > T_2$ and T_0 = ambient)



$$\Delta AE = AE_1 - AE_2$$

- As the temperature of heat supplied decreases, available energy associated with the heat decreases leading to increase in unavailable energy.
- Whenever heat transfer takes place from a higher temperature body to lower temperature body, then the AE obtained from the heat provided by the lower temperature body decreases, due to heat transfer.
- If the heat is transferred to the environment then the complete AE is lost.

Note:
Decrease in AE & increase in UAE both are equal in magnitude

8.5 Available Energy Associated with the Heat Loss from Finite Body

- **Assumptions**

  Finite body is perfect incompressible substance.

  Heat is lost to environment.

- $AE = T_0\left[mc\ln\left(\frac{T_2}{T_1}\right) + \frac{mc(T_1 - T_2)}{T_0}\right]$
- $AE = T_0 \Delta S_{uni}$

8.6 Irreversibility

- $IR = W_{Idal} - W_{act}$
- If $T_L = T_o$, then $IR = AE - W_{act}$
- $IR = W_R - W_{IR}$
- The actual work done by a system is always less than the idealised reversible work and the difference between the two is called irreversibility.
- Irreversibility is always positive.
- The smaller the irreversibility associated with a process, the greater is the actual work produced.

8.7 Gouy – Stodola Theorem

- $IR = T_o \Delta S_{uni}$
- $IR = T_o, S_{g,uni}$
- According to Gouy – Stodola theorem irreversibility is directly proportional to the entropy generation in the universe.

8.8 Availability

- Maximum possible useful work output obtained from a given system when it comes in equilibrium with environment is known as Availability.
- When the system is in equilibrium and at rest relative to the environment then the system is said to the in dead state.

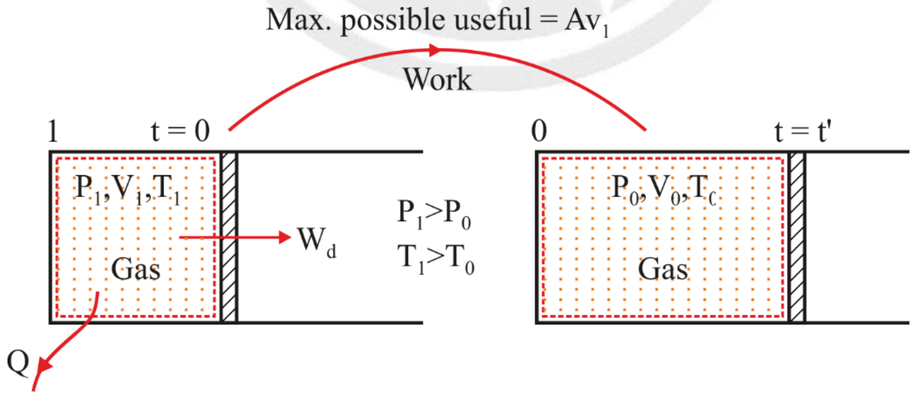


Fig. 8.3 Expansion of gas in a cylinder

- $AV_1 = \phi_1 - \phi_0$

  Where ϕ is availability function for closed system.
- $\phi = E + P_0 V - T_0 S$

  Neglecting changes in KE & PE, $\phi = U + P_0 V - T_0 S$
- $Av_1 = (E_1 - E_0) + P_0(V_1 - V_0) - T_0(S_1 - S_0)$

8.8.1 Availability Change for a Closed System

- $\Delta Av_{1-2} = \phi_2 - \phi_1$
- $\Delta Av_{1-2} = (E_2 - E_1) + P_o(V_2 - V_1) - T_O(S_2 - S_1)$

8.9 Specific Availability for Open System

- $av_i = \Psi_i - \Psi_d$

  Where Ψ is specific availability function for an open system
- $\Psi = \frac{c^2}{2} + gz + h - T_o s$
- $av_i = \frac{1}{2}(c_i^2) + g(z_i) + (h_i - h_d) - T_d(s_i - s_d)$

8.9.1 Specific availability changes for an Open System

(1) $\Delta av_{i-o} = \Psi_o - \Psi_i$

(2) $\Delta av_{i-o} = \frac{1}{2}(c_o^2 - c_i^2) + g(z_o - z_i) + (h_o - h_i) - T_d(s_o - s_i)$

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9

THERMODYNAMIC RELATIONS

9.1 Basic Mathematics

1. $dB = Mdx + Ndy$

If B is continuous point function having exact differential then

- $\left.\frac{\partial M}{\partial y}\right|_x = \left.\frac{\partial N}{\partial x}\right|_y$ (Test of Exactness)

2. If $x = x(y, z)$

$y = y(x, z)$ then

- $\left.\frac{\partial x}{\partial y}\right|_z = \frac{1}{\left.\frac{\partial y}{\partial x}\right|_z}$ (Reciprocity relation)
- $\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = -1$ (Cyclic Relation)

3. If $z = z(x, y, f)$ then

- $\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial f}\right|_z \left.\frac{\partial f}{\partial x}\right|_z = 1$

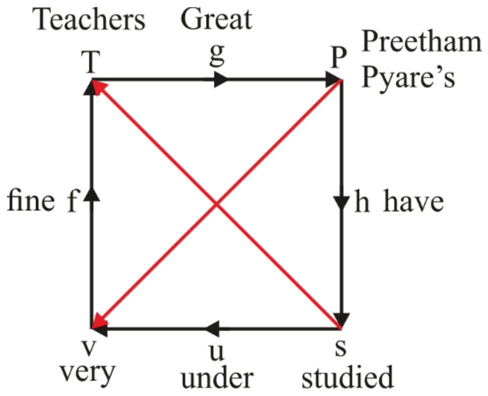
9.2 Gibbs Relations

$du = Tds - Pdv$ (Derived from $Tds = du + Pdv$)

$dh = Tds + vdP$ (Derived from $Tds = dh - vdP$)

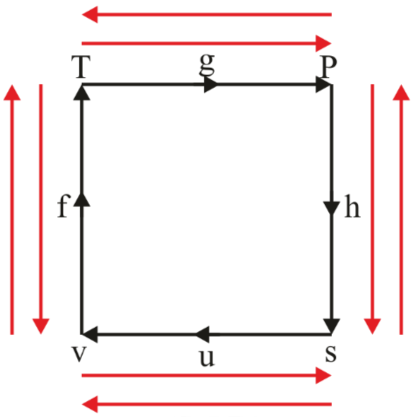
$df = -sdT - Pdv$ (Derived from $f = u - Ts$)

$dg = -sdT + vdP$ (Derived from $g = h - Ts$)



9.3 Maxwell Relations

- Maxwell relations are useful for finding specific change by measuring the changes in pressure, volume, temperature.



$$\left.\frac{\partial T}{\partial P}\right|_s = \left.\frac{\partial v}{\partial s}\right|_P ; \quad \left.\frac{\partial T}{\partial v}\right|_s = -\left.\frac{\partial P}{\partial s}\right|_v$$

$$\left.\frac{\partial P}{\partial T}\right|_v = \left.\frac{\partial s}{\partial v}\right|_T ; \quad \left.\frac{\partial v}{\partial T}\right|_P = -\left.\frac{\partial s}{\partial P}\right|_T$$

9.4 Volume Expansivity (α)

- Volume Expansivity is an indication of the change in volume that occurs when temperature changes while pressure remains constant.

$$\alpha = \frac{1}{v}\left.\frac{\partial v}{\partial T}\right|_P$$

Note:

- $\alpha_I = \frac{1}{T}$ (For ideal gas)
- For water at 1 atm pr & 4°C
  $\alpha_{H_2O} = 0$

9.5 Isothermal Compressibility (β_T)

- Isothermal compressibility is an indication of the change in volume that occurs when pressure changes while temperature remains constant.

$$\beta_T = -\frac{1}{v}\left.\frac{\partial v}{\partial P}\right|_T$$

Note:

- $\beta_{T,I} = \frac{1}{P}$ (For ideal gas)

9.6 Isentropic Compressibility (β_s)

- Isentropic compressibility is an indication of the change in volume that occurs when pressure changes while entropy remains constant.

$$\beta_s = -\frac{1}{v}\frac{\partial v}{\partial P}\bigg|_s$$

Note:

1. $\beta_{I,G} = \frac{1}{\gamma P}$
2. $\frac{\partial v}{\partial T}\Big|_P = \alpha v$
3. $\frac{\partial P}{\partial T}\Big|_v = \frac{\alpha}{\beta_T}$

9.7 Specific entropy change equations

$$ds = \frac{c_v}{T}dT + \frac{\alpha}{\beta_T}\,dv$$

$$\Delta s_{1-2} = \int_1^2 \frac{c_v}{T}\,dT + \int_1^2 \frac{\alpha}{\beta_T}\,dv$$

$$ds = \frac{c_p}{T}dT - \alpha v\,dp$$

$$\Delta s_{1-2} = \int_1^2 \frac{c_p}{T}\,dT - \int_1^2 \alpha\,v\,dP$$

9.8 Tds Equations

- $Tds = c_v dT + T\frac{\alpha}{\beta_T}dv$
- $Tds = c_p dT - T\alpha v dP$

9.9 Mayer's Equation

$$c_p - c_v = \frac{Tv\alpha^2}{\beta_T}$$

9.9.1 Conclusions

(1) In general c_p is always greater than c_v

(2) The difference between c_p and c_v approaches to zero as the absolute temperature approaches to zero Kelvin.

(3) For incompressible substances, the difference between c_p and c_v is negligible. Hence the two specific heats c_p and c_v are nearly identical for incompressible substance.

(4) For water at 1 atm pressure and 4°C, $c_p = c_v$

(5) For Ideal gas $c_p - c_v = R$

9.10 Specific Internal Energy Change Equation

$$du = c_v dT + \left(T\frac{\alpha}{\beta_T} - P\right) dv$$

$$\Delta u_{1-2} = \int_1^2 c_v dT + \int_1^2 \left(T\frac{\alpha}{\beta_T} - P\right) dv$$

9.11 Specific Enthalpy Change Equation

$$dh = c_p dT - (T\alpha v - v)dP$$

$$\Delta h_{1-2} = \int_1^2 c_p dT - \int_1^2 (T\alpha v - v)dv$$

9.12 Adiabatic Index

$$\gamma = \frac{c_p}{c_v} = \frac{\beta_T}{\beta_s}$$

Where β_T is Isothermal compressibility

β_s is Isentropic compressibility

9.13 Speed of Sound

$$c = \sqrt{\frac{v}{\beta_s}} \quad \text{(Any substance)}$$

$$c = \sqrt{\frac{\gamma v}{\beta_T}} \quad \text{(Any substance)}$$

$$c = \sqrt{\gamma RT} \quad \text{(Perfect gas)}$$

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10 PROPERTIES OF PURE SUBSTANCES

10.1 Introduction

Pure Substance

- Any substance having homogeneous chemical composition throughout is knows as pure substance.
- A mixture of various chemical elements or compounds will behave as pure substance as long as the mixture is homogeneous in chemical composition.
- A mixture of two or more phases of a pure substance will be a pure substance as long as chemical composition of all the phases is same.

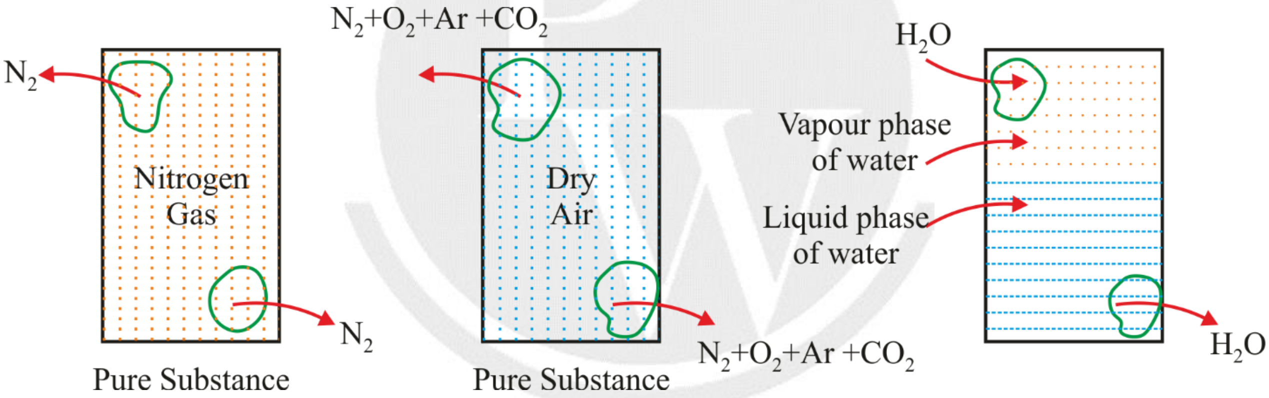


Fig.10.1 Nitrogen, dry air and two phases of water as a pure substance

10.2 Gibbs Phase Rule

F = C – P + 2

Where

C = number of components

P = number of phases (Solid /Liquid /Gas)

F = Degree of freedom

- Degree of freedom represents the number of independent intensive variables required to fix the intensive state of the system.
- For sub cooled liquid/Superheated vapour ⇒ F = 2 (T & P)
- For wet vapour ⇒ F = 1 (T or P)
- For triple phase state ⇒ F = 0

Note:

Triple phase state (Triple point)

It is the state at which all 3 phases (solid, liquid and vapour) can coexist together.

For water

$T_t = 0.01°C = 273.16\ K$

$P_t = 612\ Pa$

10.3 Temperature - Specific Heat Diagram

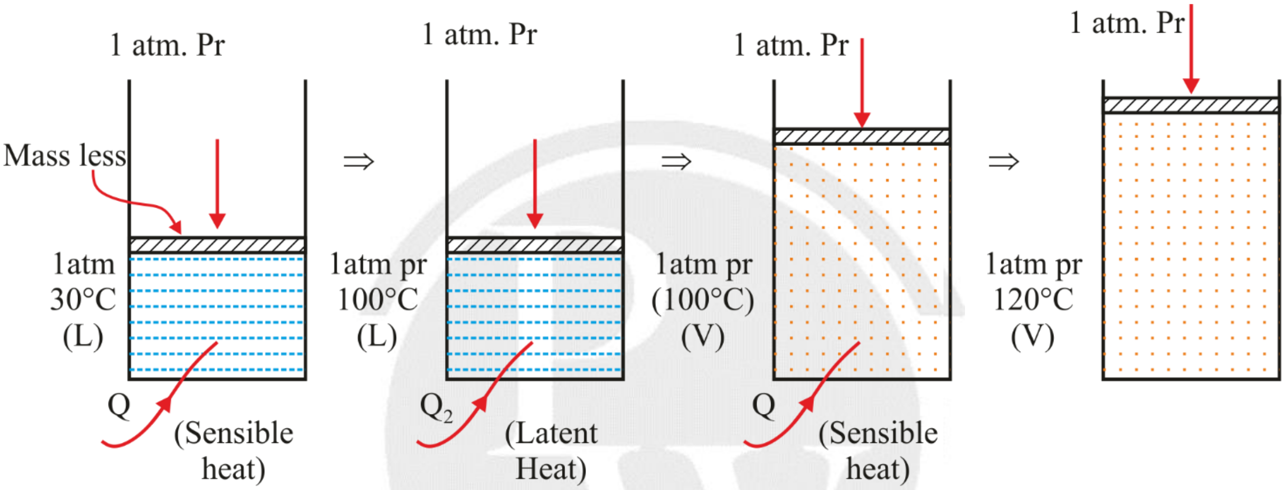


Fig.10.2 Sensible and latent heat addition to the water at 1 atm pr

10.3.1 Sensible heat

The heat which is used to change the temperature without any change in phase is known as sensible heat.

10.3.2 Latent heat

The heat which causes change in phase without any change in temperature is known as latent heat.

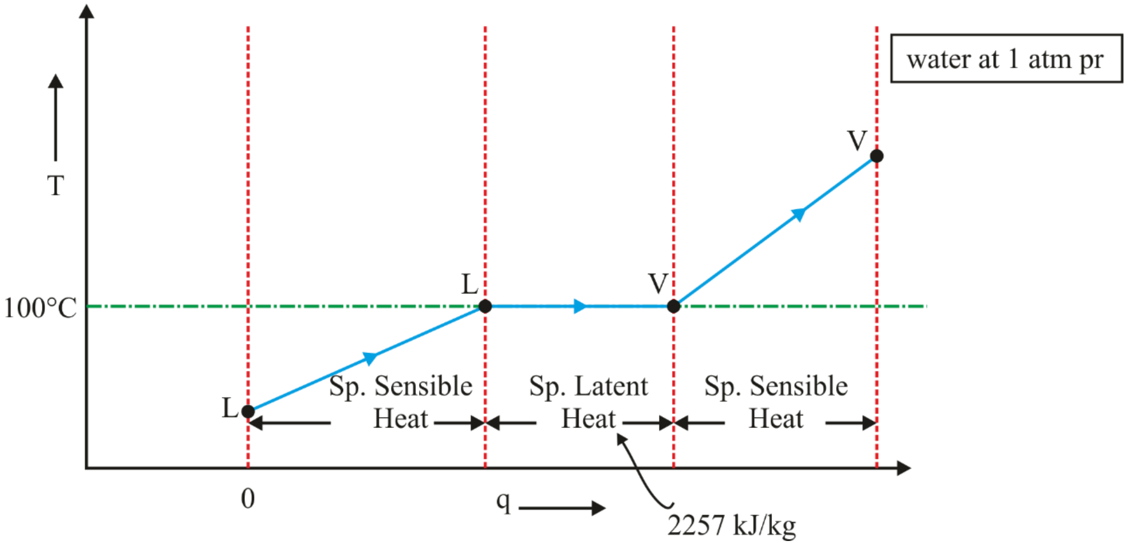


Fig.10.3 T-q diagram of sensible and latent heat addition to the water at 1 atm pr

For water

- Specific latent heat of fusion (L_f) = 334 kJ/kg
- Special latent heat of vaporisation (L_v) = 2257 kJ/kg

$\}$ at 1 atm pressure

10.4 Saturation Temperature

- Saturation temperature is the temperature at which phase change starts at a particular pressure.
- The saturation temperature of water for liquid to vapour phase change

  Corresponding to 1 atm pressure is 100°C

  Corresponding to 5 bar is 152°C

  Corresponding to 10 bar is 180°C

  Corresponding to 3.17 kPa is 25°C
- As the pressure changes, corresponding saturation temperature also changes, hence saturation temperature is always defined at a particular pressure.
- On increasing pressure, corresponding saturation temperature also increases.

10.5 Saturation Pressure

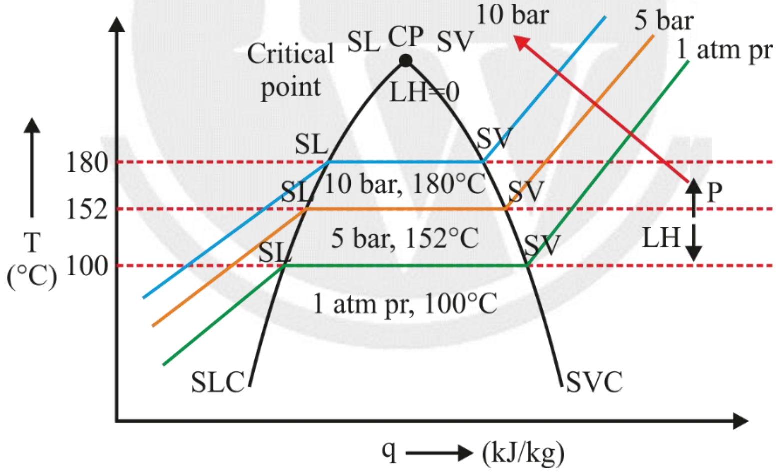


Fig.10.4 T-q diagram per saturation pressure

- Saturation pressure is the pressure at which phase change starts at particular temperature.
- The saturation pressure of water for liquid to vapour phase change

  Corresponding to 100°C is 1 atm pressure

  Corresponding to 152°C is 5 bar

  Corresponding to 180°C is 10 bar

  Corresponding to 25°C is 3.17 kPa

10.6 Saturated Liquid Curve

- It is the locus of all states where liquid starts converting into vapour at temperature equal to saturation temperature.
- A liquid that is about to vaporize is knows as Saturated liquid.

10.7 Saturated Vapour Curve

- It is the locus of all states where liquid completely converts into vapour at temperature equal to saturation temperature.
- A vapour that is about to condense is knows as saturated vapour.

Note:

Critical Point

It is defined as the state at which saturated liquid and saturated vapour states are identical.

At critical point Latent heat of vaporization is zero.

10.8 Subcooled Liquid Region

Subcooled liquid region is the region in which

- Actual temperature (T_{act}) is less than corresponding saturation temperature (T_{sat}) at a particular pressure (P).
- Actual pressure (P_{act}) is more than corresponding saturation pressure (P_{sat}) at a particular temperature (T).
- Subcooled liquid is the liquid which is not about to vaporise.
- For a given temperature subcooled liquid has higher pressure as compared to corresponding saturation pressure, hence it is known as compressed liquid also.

Note:

In Subcooled liquid region, at a given pressure $T_{act} < T_{sat}$ and at a given temperature $P_{act} > P_{sat}$.

10.9 Superheated Vapour Region

Superheated vapour region is the region in which

- Actual temperature (T_{act}) is more than corresponding saturation temperature (T_{sat}) at a particular pressure (P).
- Actual pressure (P_{act}) is less than corresponding saturation pressure (P_{sat}) at a particular temperature (T).
- Superheated vapour is the vapour, which is not about to condense.

Note: In superheated vapour region, at a given pressure $T_{act} > T_{sat}$ and at a given temperature $P_{act} < P_{sat}$.

10.10 Wet Vapour Region (Saturated Liquid – Saturated Vapour Mixture)

Wet vapour region is the region in which

- Actual temperature is exactly equal to the saturation temperature corresponding to a particular pressure (excluding saturated liquid curve and saturated Vapour curve).

- Actual pressure is exactly equal to the saturation pressure corresponding to a particular temperature (excluding saturated liquid curve and saturated Vapour curve).
- In wet region, saturated liquid and saturated vapour are at equilibrium.
- In wet region pressure and temperature are dependent variables. On changing one of the Variable, other variable changes automatically.

Note:

In Wet vapour region, at a given pressure $T_{act} = T_{sat}$ and at a given temperature $P_{act} = P_{sat}$.

10.11 Dryness Fraction

- Dryness fraction represents the fraction of saturated vapour present in wet vapour (saturated liquid – saturated vapour mixture)
- $x = \frac{m_v}{m_L + m_v}$

Where

m_v represents mass of saturated vapour

m_L represents mass of saturated liquid.

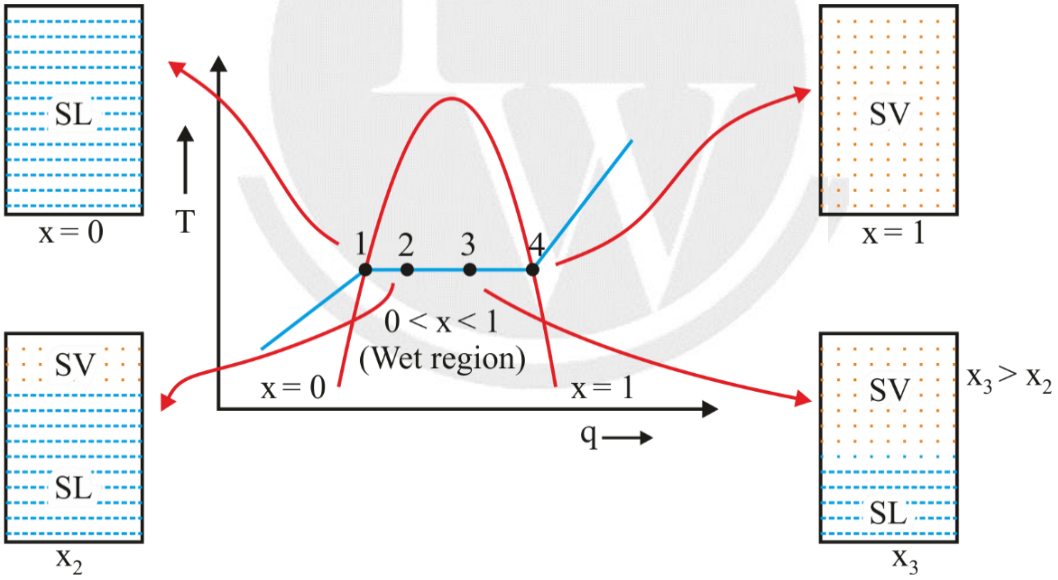


Fig.10.5 Dryness fraction at various states

- At critical point dryness fraction is not defined.

10.12 T-h and T-s Diagrams

Heat supplied at constant pressure increases the specific enthalpy and specific entropy. T-h and T-s diagram will be having same profile as that of T-q diagram for isobar.

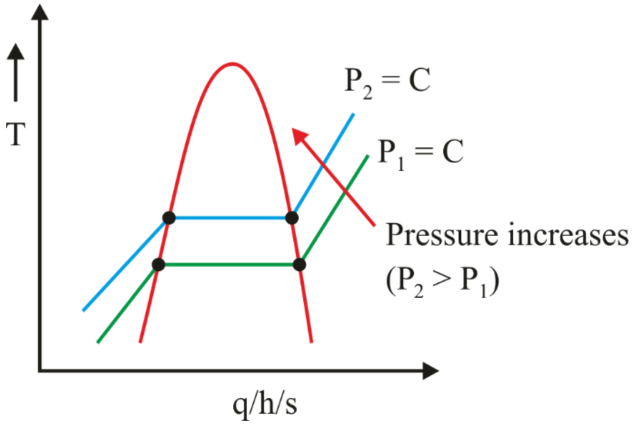


Fig.10.6 T-q/h/s diagrams of isobaric heat addition

10.13 Specific Enthalpy Calculation at Various States

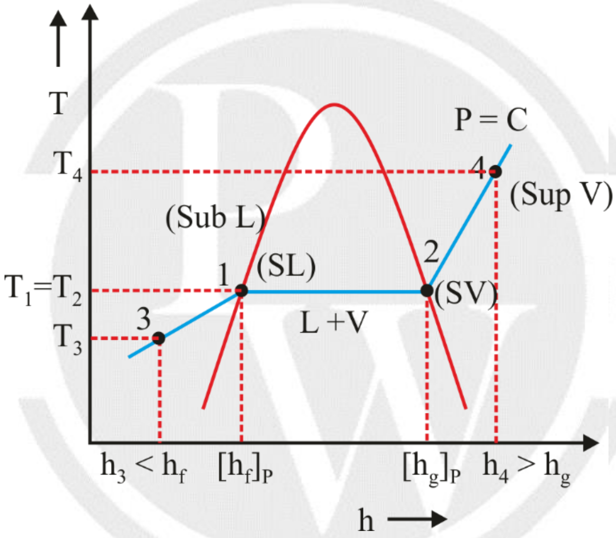


Fig.10.7 Isobar on T-h diagram

- 3For saturated liquid state: $h_1 = [h_f]_P$
- For saturated vapour state $h_2 = \left[h_g\right]_P$
- For subcooled liquid state $h_3 = [h]_{P,T_3}$
- For subcooled liquid state $h_3 = h_f - c(T_{sat} - T_{act})$, assuming subcooled liquid is behaving as perfect incompressible substance having constant specific heat.
- For superheated vapour state $h_4 = [h]_{P,T_4}$
- For superheated vapour state $h_4 = h_g + c_p\,\Delta T_{sup}$, assuming superheated vapour is behaving as perfect gas having constant specific heat.

10.14 Specific Entropy Calculation at Various States

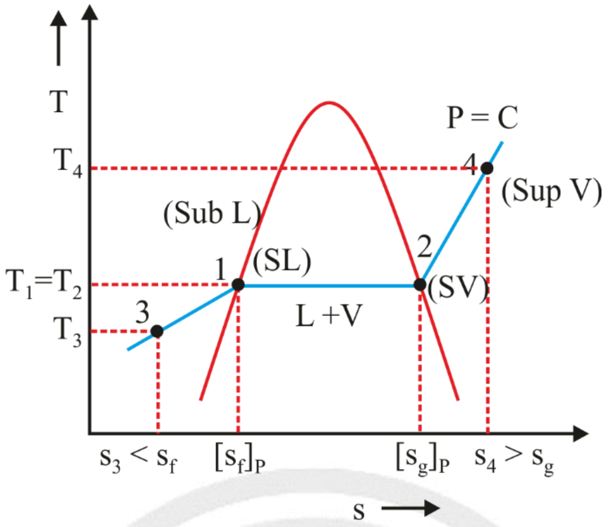


Fig.10.8 Isobar on T-s diagram

- For saturated liquid state: $s_1 = [s_f]_P$
- For saturated vapour state $s_2 = [s_g]_P$
- For subcooled liquid state $s_3 = [s]_{P,T_3}$
- For subcooled liquid state $s_3 = s_g - c\ln\left[\frac{T_{sat}}{T_{act}}\right]$, assuming subcooled liquid is behaving as perfect incompressible substance having constant specific heat.
- For superheated vapour state $s_4 = [s]_{P,T_4}$
- For superheated vapour state $s_4 = [s_g]_p + c_p \ln\left[\frac{T_{act}}{T_{sat}}\right]_p$, assuming superheated vapour is behaving as perfect gas having constant specific heat.

10.15 Properties Calculation in Wet Region

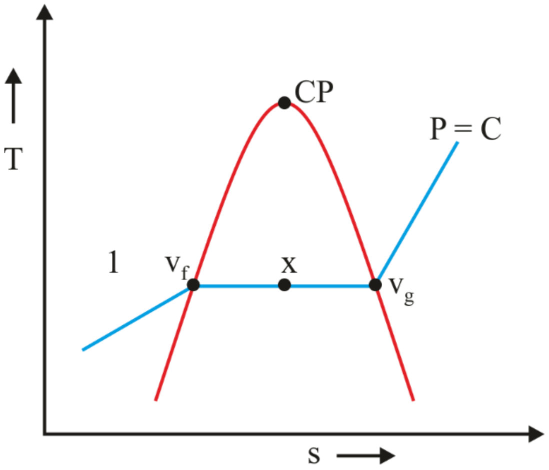


Fig.10.9 Isobar on T-s diagram

- $p = p_f + x\, p_{fg}$

  where p is specific extensive property

$v = v_f + xv_{fg}$, $u = u_f + xu_{fg}$

$h = h_f + xh_{fg}$, $s = s_f + xs_{fg}$

Remember: $\frac{1}{\rho} = \frac{1}{\rho_f} + x\left(\frac{1}{\rho_g} - \frac{1}{\rho_f}\right)$

10.16 Mollier Diagram

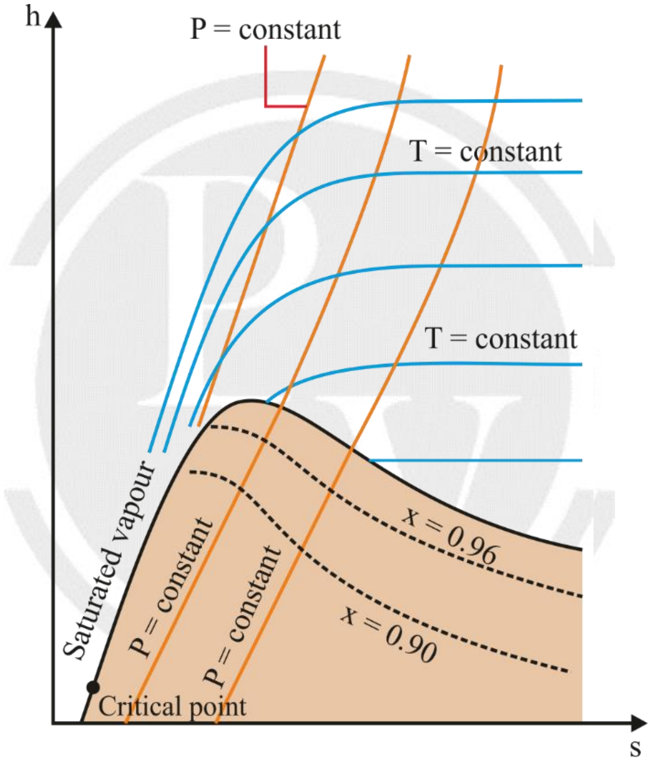


Fig.10.10 Specific enthalpy specific entropy (h-s) diagram

- Mollier diagram was named after Richard Mollier.
- It is specific enthalpy-specific entropy (h-s) diagram.
- Mollier diagram is used in vapour power plant for evaluating properties of superheated vapour region and high-quality wet vapour. Property of low-quality wet vapour data is seldom used.
- Slope of Isobar on Mollier diagram is constant and equal to absolute temperature.

$$\left.\frac{\partial h}{\partial s}\right|_P = T$$

- In wet region slope of isobar is constant and equal to saturation temperature corresponding to that constant pressure, hence on Mollier diagram isobars are straight lines in wet region.

- Higher the pressure, higher is the saturation temperature, hence higher the slope of isobar on Mollier diagram in wet region.
- In superheated region as temperature increases slope of isobar on Mollier diagram also increase.
- It is impossible to have negative slope of isobar on Mollier diagram since absolute temperature can never be negative.

10.17 Pressure-Specific Volume (P-v) Diagram

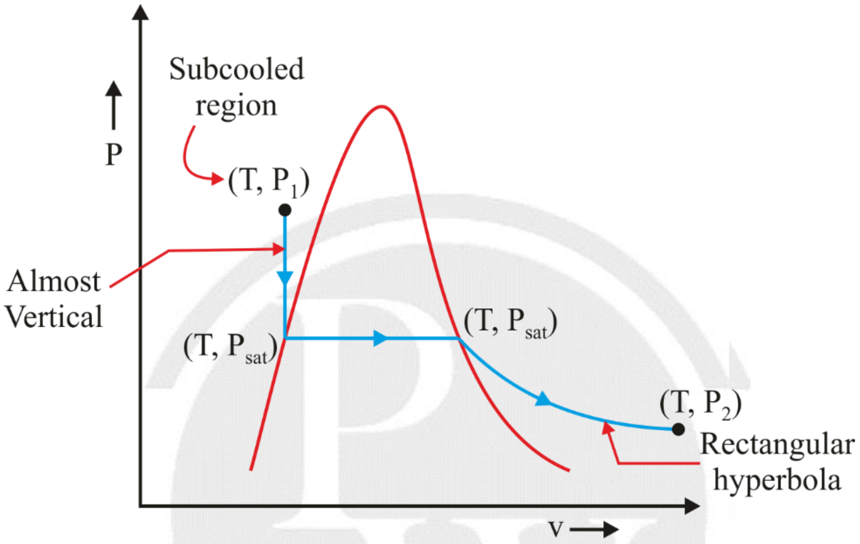


Fig.10.11 Isotherm on P-v diagram

- In subcooled region, liquid behaves as an incompressible substance.
- In subcooled region decrease in pressure, there is negligible increase in specific volume at constant temperature, hence isotherms are almost vertical in subcooled region on P-v diagram.
- In wet region, pressure and temperature are dependent intensive variables hence for constant temperature process pressure is also constant.
- In superheated region, superheated vapour behaves as compressible substance. With small decrease in pressure there is huge increase in volume.
- For sub cooled region, $v_{(T,P)} \cong v_{f(T)}$, $u_{(T,P)} \cong u_{f(T)}$, $s_{(T,P)} \cong s_{f(T)}$

10.18 Analysis for Isochoric Heat Addition

If the specific volume of wet vapour (saturated liquid – saturated vapour mixture) is

1. more than critical specific volume then isochoric heat addition (1-2) leads to the increase in dryness fraction & decrease in liquid level.
2. less than critical specific volume then isochoric heat addition (3-4) leads to the decrease in dryness fraction & increase in liquid level.

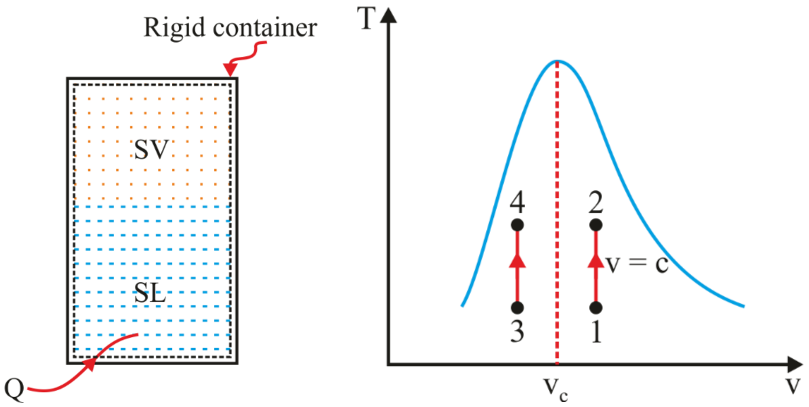


Fig.10.12 Isochoric heat addition to wet vapour

10.19 Pressure - Temperature (P-T) Diagram

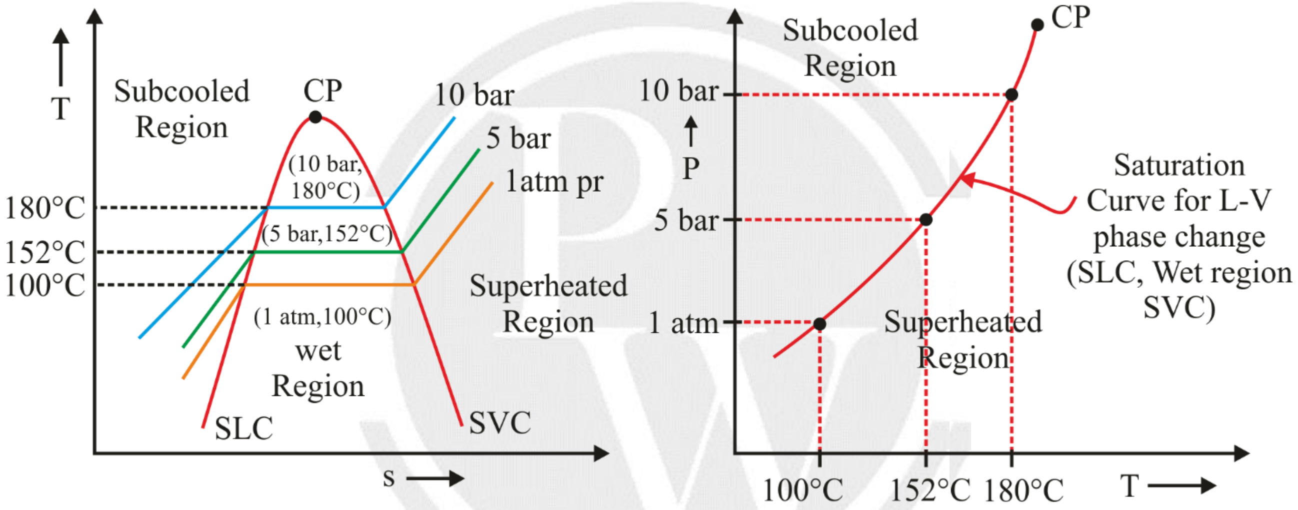


Fig.10.13 T-s and P-T diagrams during phase change

- The slope of fusion curve on P-T diagram for water is negative.
- If the pressure is less than triple pressure, then a pure substance can't exist in liquid phase.

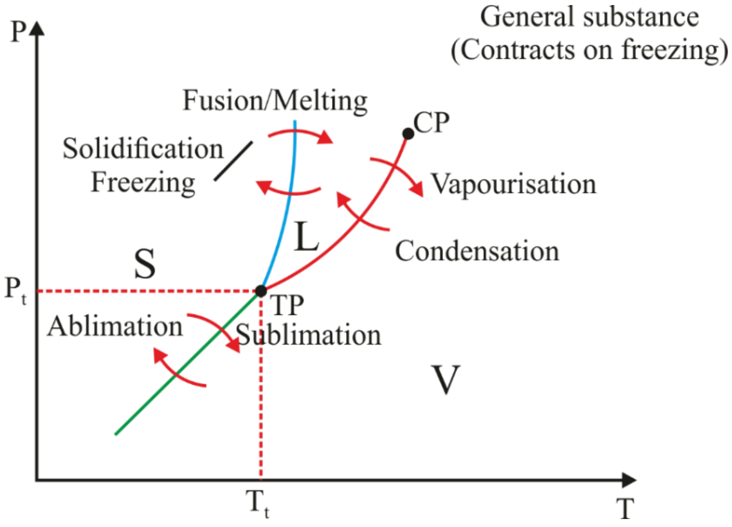


Fig.10.14 P-T diagram for general substance

For general substance

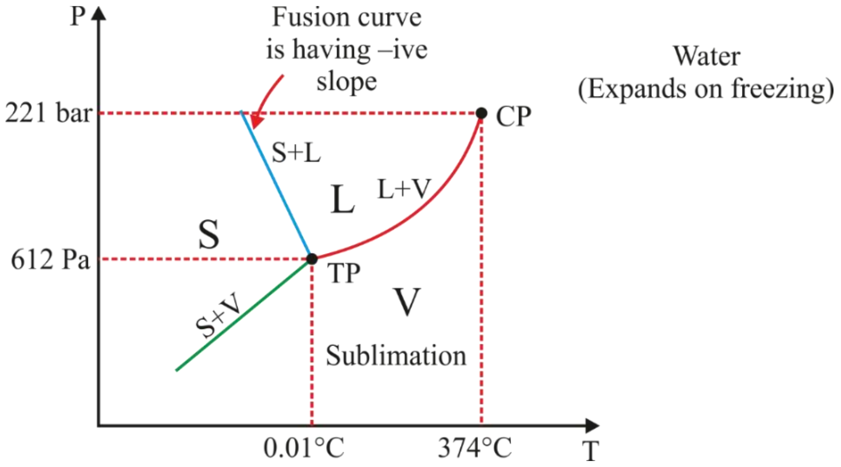


Fig.10.15 Triple point of water on P-T diagram

Note:

Triple phase state (Triple point). It is the state at which all the three phases, (solid, liquid & vapour) can co-exist together.

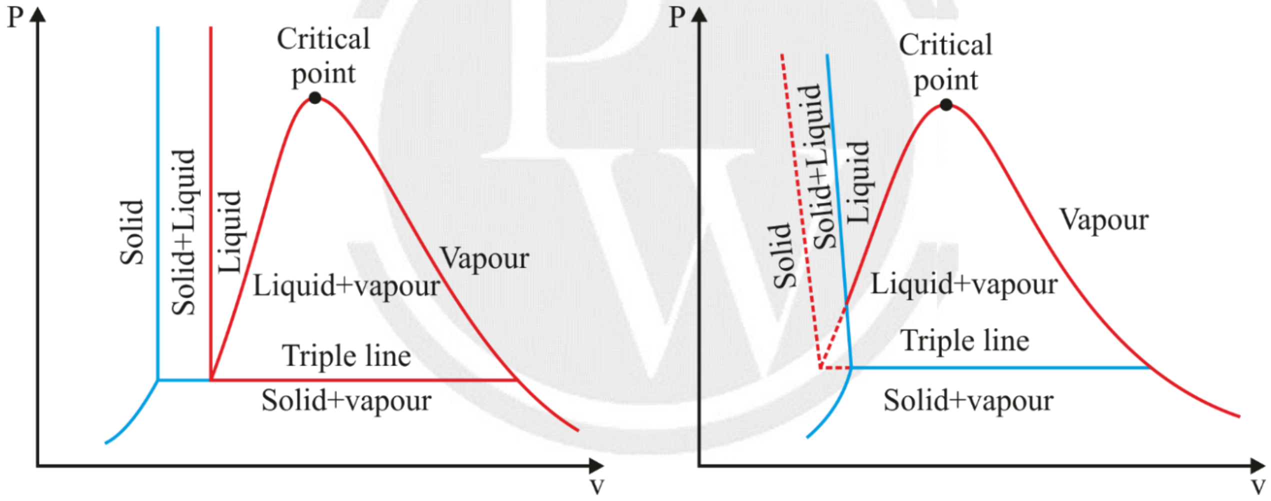
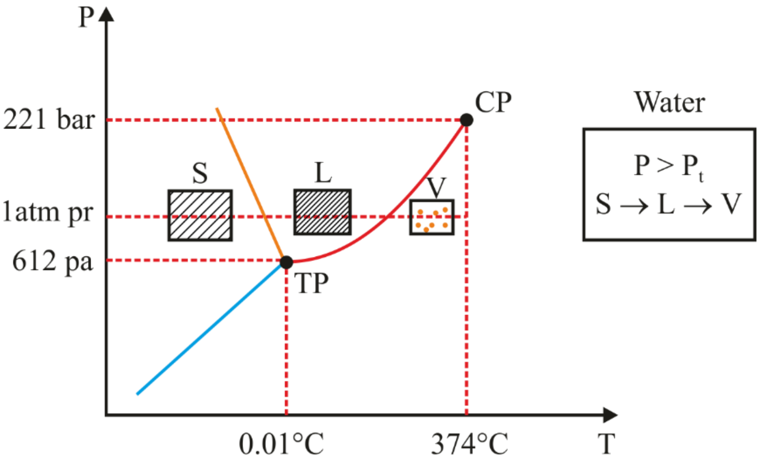


Fig.10.16 Triple phase state on P- v of a pure substance and water

- Triple phase state (Triple point) is a point on P-T diagram but it is line on P-v and T-v diagram.
- The Specific volume of the mixture at triple phase state (triple point) is not fixed and it depends on the composition of the mixture.

10.19.1 Isobaric process on P-T Diagram

- When heat is extracted by solid phase at constant pressure which is more than triple pressure then solid first melts and subsequently evaporates. Example: Heating of Ice at atmospheric pressure.
- When heat is extracted by solid phase at constant pressure, which is less than triple pressure, then solid directly sublimates (evaporates) without undergoing melting. Example: Sublimation of solid CO_2 at atmospheric pressure.



(Other Substances)

Fig.10.17 Solid, liquid and vapour states above triple point

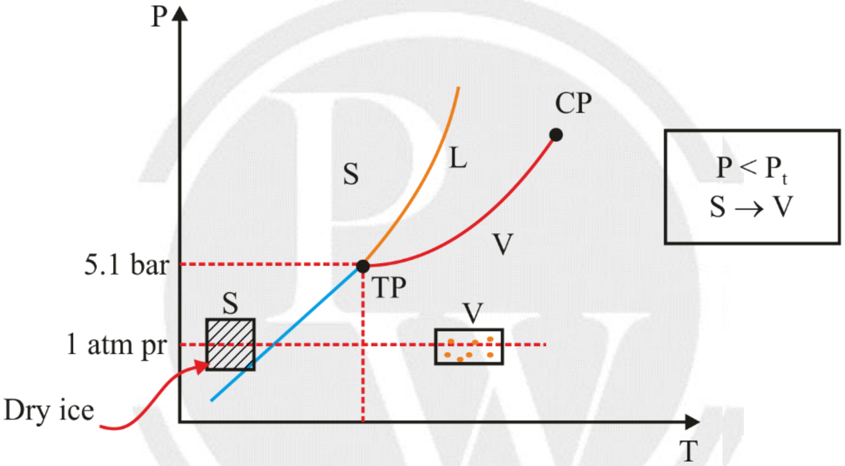


Fig.10.18 Solid and vapour states below triple point on P-T diagram

10.20 Critical Point

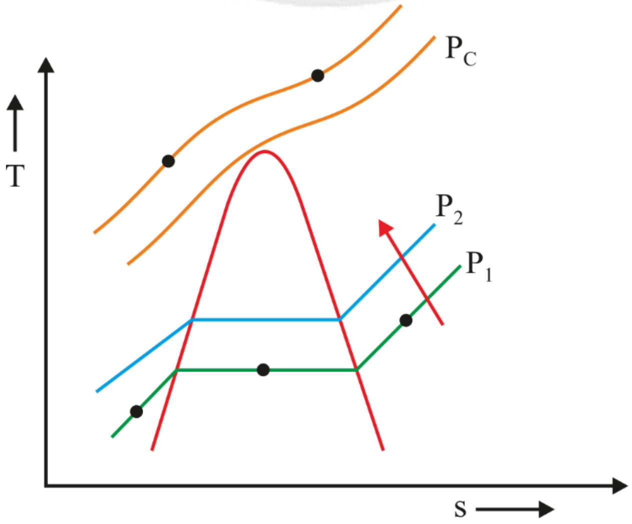


Fig.10.19 Critical point on T-s diagram

- Critical point is the state at which saturated liquid and saturated vapour states are identical.
- At pressure above critical pressure, there is no distinct phase change process. i.e., all the times there is only one phase.

Note:

A liquid is having pressure more than critical pressure doesn't undergo phase change in wet region, rather it directly converts into super critical fluid.

It is impossible to liquify a gas by compression which is having temperature more than critical temperature.

10.21 P-V-T Surface for Substance Which Contracts on Freezing (General Substance)

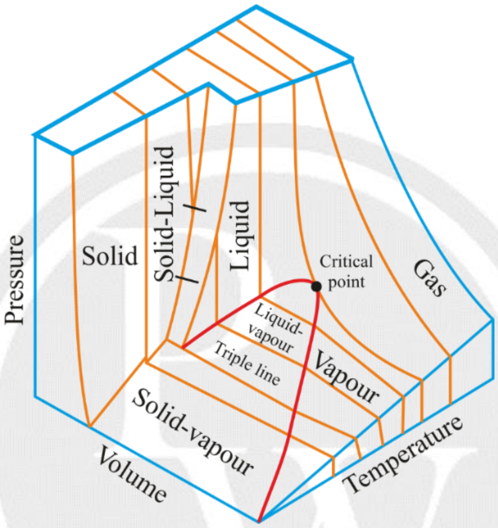


Fig.10.20 P – V – T surface of a substance contracting on freezing

10.22 P-V-T Surface for Substance Which Expands on Freezing (Water)

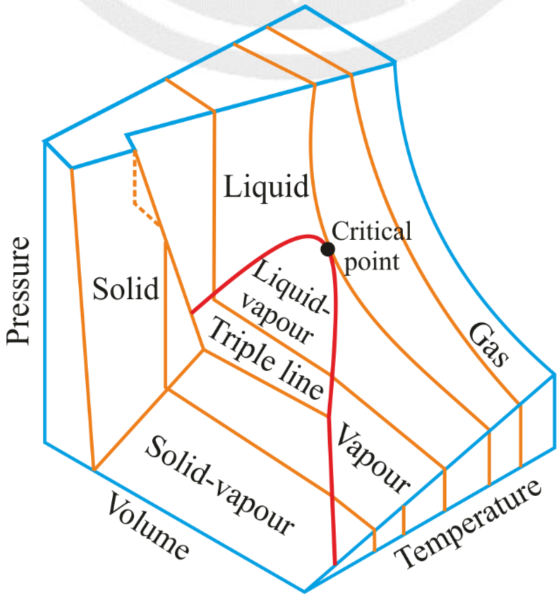


Fig.10.21 P-V-T surface of a substance expanding on freezing

10.23 Clapeyron Equation

- Clapeyron equation is used to find specific enthalpy change associated with phase change.
- The Clapeyron equation is applicable for any phase change process whether it is solid to liquid or liquid to vapour or solid to vapour.
- For liquid to vapour phase change.

$$\left.\frac{dP}{dT}\right|_{sat} = \frac{1}{T_{sat}}\frac{h_{fg}}{v_{fg}}$$

10.23.1 Clausius – Clapeyron equation

Assumptions: $v_f \lll v_g$

Saturated vapour is behaving as an Ideal gas

Differential form

$$\left.\frac{dP}{dT}\right|_{sat} = \frac{P_{sat}}{T_{sat}^2} \times \frac{h_{fg}}{R}$$

Integral form

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

10.24 Joule – Thomson Coefficient (μ)

- Joule – Thomson coefficient is used to evaluate specific heat at constant pressure.

  Mathematically, $\mu = \left.\frac{\partial T}{\partial P}\right|_h$

- Slope of isenthalpic curve on T-P diagram.

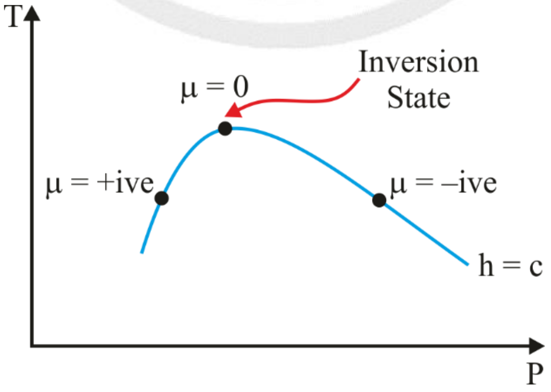


Fig.10.22 Isenthalpic curve on T-P diagram

- $\mu = \frac{v\,(T\alpha - 1)}{c_p}$

  Where α is volume expansivity

10.24.1 Experimental evaluation of Joule -Thomson coefficient

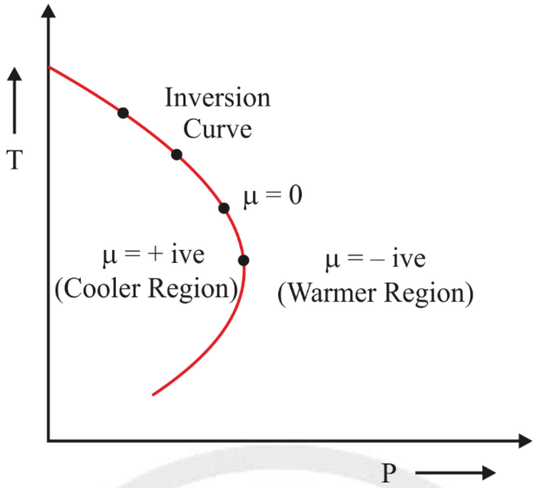


Fig.10.23 Inversion curve on T-P diagram

- The temperature behaviour of a real fluid for a given pressure drop is given by Joule – Thompson coefficient.
  μ = −ive, warmer region, on throttling Temperature increases.
  μ = +ive, cooler region, on throttling Temperature decreases
- For maximum temperature decrease, initial state must be inversion state.

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