CHAPTER 14

Heat and Thermodynamics

Different Scale of Temperature

(i) **Celsius Scale** In this scale of temperature, the melting point of ice is taken as 0°C and the boiling point of water as 100°C and the space between these two points is divided into 100 equal parts.

(ii) **Fahrenheit Scale** In this scale of temperature, the melting point of ice is taken as 32°F and the boiling point of water as 212°F and the space between these two points is divided into 180 equal parts.

(iii) **Kelvin Scale** In this scale of temperature, the melting point of ice is taken as 273 K and the boiling point of water as 373 K and the space between these two points is divided into 100 equal parts.

Relation between Different Scales of Temperatures

$$\frac{C}{100} = \frac{F - 32}{180} = \frac{K - 273}{100}$$

Calorimetry

- $Q = ms\Delta\theta = c\Delta\theta$, when temperature varies without change in state.

Note *If specific heat s is a function of temperature* θ, *then* $Q = \int_{\theta_i}^{\theta_f} ms\,d\theta$

- $Q = mL$, when state changes without change in temperature.
- s = specific heat of any substance
  = heat required to increase the temperature of unit mass by 1°C or 1 K.
- c = heat capacity of a body = ms
  = heat required to increase the temperature of whole body by 1°C or 1 K.

- Specific heat of water is 1 cal/g-°C between 14.5°C and 15.5°C.
- L = latent heat of any substance
  = heat required to convert unit mass of that substance from one state to another state.
- **Water equivalent of a vessel** It is the mass of equivalent water which takes same amount of heat as taken by the vessel for same rise of temperature.

Thermal Expansion

- $\Delta l = l\,\alpha\,\Delta\theta$, $\Delta s = s\,\beta\,\Delta\theta$ and $\Delta V = V\,\gamma\Delta\theta$
- $\beta = 2\alpha$ and $\gamma = 3\alpha$ for isotropic medium.
- **Anomalous expansion of water** When temperature of water is increased from 0°C, then its volume decreases upto 4°C, becomes minimum at 4°C and then increases.

  So, volume of water at 4°C is minimum and density is maximum. This behaviour of water around 4°C is called, anomalous expansion of water.

Effect of Temperature on Different Physical Quantities

- **On density** With increase in temperature, volume of any substance increases while mass remains constant, therefore density should decrease.

  $$\rho' = \frac{\rho}{1 + \gamma\Delta\theta}$$

  or $$\rho' \approx \rho\,(1 - \gamma \cdot \Delta\theta), \quad \text{if } \gamma \cdot \Delta\theta << 1$$

- **In fluid mechanics**

  ***Case* 1** When a solid whose density is less than the density of liquid is floating, then a fraction of its volume remains immersed in liquid. This fraction is

  $$f = \frac{\rho_s}{\rho_l}$$

  When temperature is increased, ρ_s and ρ_l both will decrease. Hence, fraction may increase, decrease or remain same. At higher temperature,

  $$f' = f\left(\frac{1 + \gamma_l\Delta\theta}{1 + \gamma_s\Delta\theta}\right)$$

  If $\gamma_l > \gamma_s$, $f' > f$ or immersed fraction will increase.

  ***Case* 2** When a solid whose density is more than the density of liquid is immersed completely in a liquid, then upthrust will act on 100% volume of solid and apparent weight appears less than the actual weight.

  $$w_{\text{app}} = w - F$$

  Here, $$F = V_s\,\rho_l\,g$$

  With increase in temperature, V_s will increase and ρ_l will decrease, while g will remain unchanged.

  Therefore, upthrust may increase, decrease or remain same.

  At some higher temperature,

$$F' = F\left(\frac{1+\gamma_s\,\Delta\theta}{1+\gamma_l\Delta\theta}\right)$$

If $\gamma_s > \gamma_l$, upthrust will increase. Therefore, apparent weight will decrease.

- **Time period of pendulum**

$$T = 2\pi\sqrt{\frac{l}{g}} \quad \text{or} \quad T \propto \sqrt{l}$$

With increase in temperature, length of pendulum will increase. Therefore, time period will increase and pendulum clock will become slow and it loses the time. At some higher temperature,

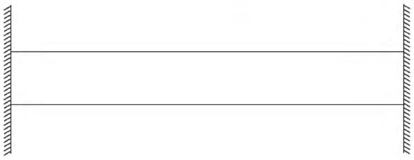
$$T' = T\,(1+\alpha\,\Delta\theta)^{\frac{1}{2}}$$

or $$T' \approx T\left(1+\frac{1}{2}\alpha\Delta\theta\right), \text{ if } \alpha\,\Delta\,\theta << 1$$

$$\Delta T = (T' - T) = \frac{1}{2}\,T\,\alpha\,\Delta\theta$$

Time lost/gained $$\Delta t = \frac{\Delta T}{T'} \times t$$

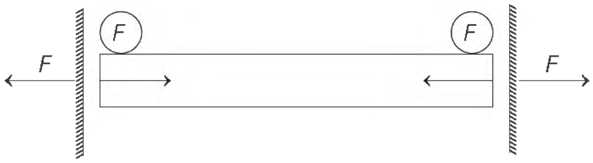
- **Thermal stress** If temperature of a rod fixed at both ends is increased, then thermal stresses are developed in the rod.



At some higher temperature, natural length of the rod should be more (by $\Delta l = l\alpha\Delta\theta$). We may assume that the rod has been compressed by a length,

$$\Delta l = l\,\alpha\,\Delta\theta$$

or $$\text{strain} = \frac{\Delta l}{l} = \alpha\,\Delta\theta$$



$$\text{stress} = Y \times \text{strain} = Y\,\alpha\,\Delta\theta$$

where, Y = Young's modulus of elasticity.

$\therefore$ $F = A \times \text{stress} = YA\alpha\Delta\theta$

Rod applies this much force on wall to expand. In turn, wall also exerts equal and opposite pair of encircled forces on rod. Due to this pair of forces only, we can say that rod is compressed.

Heat Transfer, Heat Conduction through a Rod

- Heat flow in steady state $Q = \frac{KA(\theta_1 - \theta_2)}{l} t$
- Rate of flow of heat = heat current

  or $$H = \frac{dQ}{dt} = \frac{\text{TD}}{R}$$

  Here, TD = temperature difference = $\theta_1 - \theta_2$

  and R = thermal resistance = $\frac{l}{KA}$

Radiation

- Absorptive power $a = \frac{\text{energy absorbed}}{\text{energy incident}}$

  $$a \leq 1$$

  $a = 1$ for perfectly black body.
- Spectral absorptive power a_λ = absorptive power of wavelength λ

  $$a_\lambda \leq 1$$

  $a_\lambda = 1$ for perfectly black body.
- **Emissive power *e*** Energy radiated per unit area per unit time is called emissive power of a body. Its SI units are $\text{Js}^{-1}\text{m}^{-2}$ or Wm^{-2}.
- **Spectral emissive power e_λ** Emissive power of wavelength λ is known as spectral emissive power of that wavelength λ.

  $$e = \int_0^\infty e_\lambda d_\lambda$$
- **Stefan's law** Emissive power of a body is given by

  $$e = e_r \sigma T^4$$

  Here, e_r = emissivity, emittance, relative emissivity or relative emittance.

  $e_r \leq 1$

  $e_r = 1$ for a perfectly black body.

  Sometimes emissivity is also denoted by e. In that case, differentiate them by their units. e_r is unitless while e has the units Wm^{-2}.
- Total energy radiated by a body,

  $$E = e_r \sigma T^4 At$$

  Here, A = surface area and t = time.

  Also, $a = e_r$ or absorptivity of a body

  = its emissivity.
- **Kirchhoff's law** If different bodies (including a perfectly black body) are kept at same temperature, then

  $$e_\lambda \propto a_\lambda \text{ or } \frac{e_\lambda}{a_\lambda} = \text{constant}$$

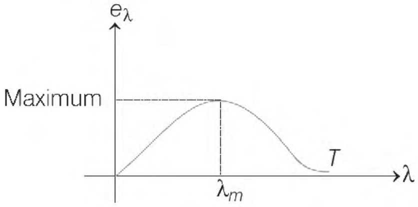
or
$$\left(\frac{e_\lambda}{a_\lambda}\right)_{\text{body-1}} = \left(\frac{e_\lambda}{a_\lambda}\right)_{\text{body-2}}$$
$$= \left(\frac{e_\lambda}{a_\lambda}\right)_{\text{perfectly black body}}$$
$$= (e_\lambda)_{\text{perfectly black body}}$$

From this law, following two conclusions can be drawn

(i) Good absorbers of a particular wavelength λ are also good emitters of same wavelength λ.

(ii) At a given temperature, ratio of e_λ and a_λ for any body is constant. This ratio is equal to e_λ of perfectly black body at that temperature.

- **Wien's displacement law**



$$\lambda_m \propto \frac{1}{T} \text{ or } \lambda_m T = \text{constant} = \text{Wien's constant } b$$

Here, $b = 2.89 \times 10^{-3}$ m-K

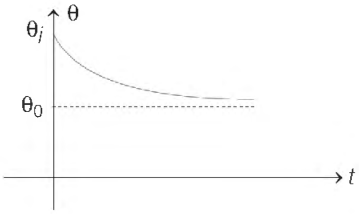
Further, area of this graph will give total emissive power which is proportional to T^4.

- **Cooling of a body by radiation**

(i) Rate of cooling
$$-\frac{dT}{dt} = \frac{e_r A\sigma}{ms}(T^4 - T_0^4) \quad \text{or} \quad -\frac{dT}{dt} \propto T^4 - T_0^4$$

(ii) **Newton's law of cooling** If temperature difference of a body with atmosphere is small, then rate of cooling ∝ temperature difference.

(iii) If body cools by radiation according to Newton, then temperature of body decreases exponentially.



In the figure,

θ_i = initial temperature of body

θ_0 = temperature of atmosphere.

Temperature at any time t can be written as

$$\theta = \theta_0 + (\theta_i - \theta_0)\, e^{-\alpha t}$$

(iv) According to Newton, if body is cooling, then to find temperature of a body at any time t, we will have to calculate $e^{-\alpha t}$. To avoid this, you can use a shortcut approximate formula given below

$$\left(\frac{\theta_1 - \theta_2}{t}\right) = \alpha\left[\frac{\theta_1 + \theta_2}{2} - \theta_0\right].$$

Kinetic Theory of Gases

Different equations used in kinetic theory of gases are listed below

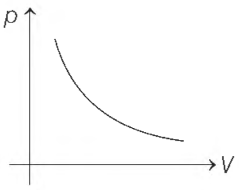
- $pV = nRT = \dfrac{m}{M} RT$ (where, m = mass of gas)
- Density, $\rho = \dfrac{m}{V}$ (General)

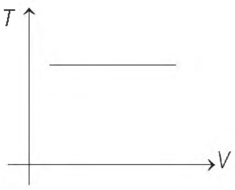
  $= \dfrac{pM}{RT}$ (For ideal gas)
- **Gas laws**

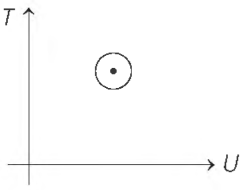
  (i) **Boyle's law** is applied when T = constant or process is isothermal. In this condition,

  $$pV = \text{constant or } p_1V_1 = p_2V_2 \text{ or } p \propto \frac{1}{V}$$

  In isothermal process, T, pV and U remain constant



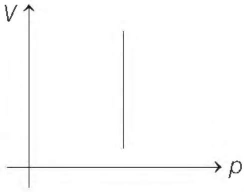


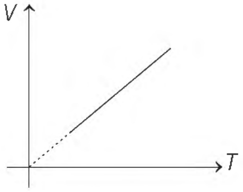


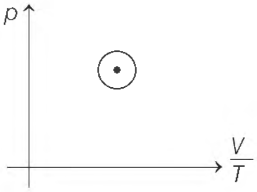
  (ii) **Charles' law** is applied when p = constant or process is isobaric. In this condition,

  $$\frac{V}{T} = \text{constant or } \frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ or } V \propto T$$

  In isobaric process, p and $\dfrac{V}{T}$ remain constant.







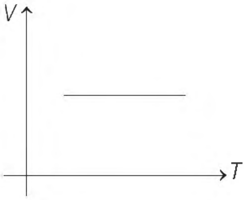
  (iii) **Pressure law or Gay-Lussac's law** is applied when V = constant or process is isochoric.

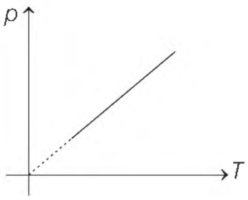
In this condition,

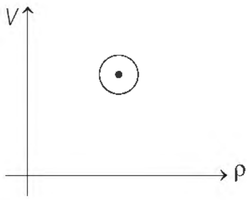
$$\frac{p}{T} = \text{constant}$$

or $$\frac{p_1}{T_1} = \frac{p_2}{T_2} \quad \text{or} \quad p \propto T$$

In isochoric process V, $\frac{p}{T}$ and ρ remain constant.







- For speeds, $v = \sqrt{\frac{ART}{M}} = \sqrt{\frac{AkT}{m}} = \sqrt{\frac{Ap}{\rho}}$

  Here, m = mass of one gas molecule.

  $A = 3$, for rms speed of gas molecules

  $A = \frac{8}{\pi} \approx 2.5$ for average speed of gas molecules

  $A = 2$, for most probable speed of gas molecules

- $p = \frac{1}{3}\frac{mn}{V} v_{\text{rms}}^2$

  Here, m is the mass of one gas molecule and n is total number of molecules.

- $p = \frac{2}{3}E.$

  Here, E = total translational kinetic energy per unit volume

- f = degree of freedom
  = 3 for monoatomic gas
  = 5 for diatomic and linear polyatomic gas
  = 6 for non-linear polyatomic gas

Note *(i) Vibrational degree of freedom is not taken into consideration.*
(ii) Translational degree of freedom for any type of gas is three.

- Total internal energy of a gas is

$$U = \frac{nf}{2}RT$$

  Here, n = total number of gram moles.

- $C_V = \frac{dU}{dT}$

  where, U = internal energy of one mole of a gas $= \frac{f}{2}RT$

$$\therefore \quad C_V = \frac{f}{2}R = \frac{R}{\gamma - 1}$$

- $C_p = C_V + R = \left(1 + \frac{f}{2}\right) R = \left(\frac{\gamma}{\gamma - 1}\right) R$
- $\gamma = \frac{C_p}{C_V} = 1 + \frac{2}{f}$
- Internal energy of 1 mole in one degree of freedom for any gas is $\frac{1}{2} RT$.
- Translational kinetic energy of one mole for any type of gas is $\frac{3}{2} RT$.
- Rotational kinetic energy of 1 mole of monoatomic gas is zero, for diatomic or linear polyatomic gas is $\frac{2}{2} RT$ or RT and for non-linear polyatomic gas is $\frac{3}{2} RT$.
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Nature of gas	Degree of freedom			Internal energy of 1 mole			Internal energy of 1 molecule		
	Total	Translational	Rotational	Total	Translational	Rotational	Total	Translational	Rotational
Monoatomic	3	3	0	$\frac{3}{2}RT$	$\frac{3}{2}RT$	0	$\frac{3}{2}kT$	$\frac{3}{2}kT$	0
Dia or linear polyatomic	5	3	2	$\frac{5}{2}RT$	$\frac{3}{2}RT$	RT	$\frac{5}{2}kT$	$\frac{3}{2}kT$	kT
Non-linear polyatomic	6	3	3	$3RT$	$\frac{3}{2}RT$	$\frac{3}{2}RT$	$3kT$	$\frac{3}{2}kT$	$\frac{3}{2}kT$

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Nature of gas	f	$U = \frac{f}{2}RT$	$C_V = dU/dT = \frac{f}{2}R$	$C_p = C_V + R$	$\gamma = \frac{C_p}{C_V} = 1 + \frac{2}{f}$
Monoatomic	3	$\frac{3}{2}RT$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{3} = 1.67$
Dia and linear polyatomic	5	$\frac{5}{2}RT$	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5} = 1.4$
Non-linear polyatomic	6	$3RT$	$3R$	$4R$	$\frac{4}{3} = 1.33$

- **Mixture of non-reactive gases**

  (i) $n = n_1 + n_2$

  (ii) $p = p_1 + p_2$

  (iii) $U = U_1 + U_2$

  (iv) $\Delta U = \Delta U_1 + \Delta U_2$

  (v) $C_V = \frac{n_1 C_{V_1} + n_2 C_{V_2}}{n_1 + n_2}$

  (vi) $C_p = \frac{n_1 C_{p_1} + n_2 C_{p_2}}{n_1 + n_2} = C_V + R$

  (vii) $\gamma = \frac{C_p}{C_V}$ or $\frac{n}{\gamma - 1} = \frac{n_1}{\gamma_1 - 1} + \frac{n_2}{\gamma_2 - 1}$

  (viii) $M = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$

- **Mean free path** Every gas consists of a very large number of molecules. These molecules are in a state of continuous rapid and random motion. They undergo perfectly elastic collisions against one another.

Therefore, path of a single gas molecule consists of a series of short *zig-zag* paths of different lengths.

The mean free path of a gas molecule is the average distance between two successive collisions. It is represented by λ.

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2\rho}$$

Here, σ = diameter of the molecule

and k = Boltzmann's constant.

- **Avogadro's hypothesis** At constant temperature and pressure, equal volumes of different gases contain equal number of molecules. In 1 g-mol of any gas, there are 6.02×10^{23} molecules of that gas. This is called Avogadro's number. Thus,

$$N = 6.02 \times 10^{23} \text{ per g-mol}$$

Therefore, the number of molecules in mass m of the substance

$$= nN = \frac{m}{M} \times N$$

- **Dalton' law of partial pressure** According to this law, if the gases filled in a vessel do not react chemically, then the combined pressure of all the gases is due to the partial pressure of the molecules of the individual gases.

If p_1, $p_2, \ldots$ represent the partial pressures of the different gases, then the total pressure is,

$$p = p_1 + p_2 \ldots$$

Thermodynamics

- **Molar heat capacity** = Heat required to raise the temperature of 1 mole of any substance by 1°C or 1 K.

$$C = \frac{Q}{n\Delta T}$$

$$\Rightarrow \qquad Q = nC\Delta T$$

Molar heat capacity of solids and liquids is almost constant.

In case of gases, C is process dependent. It varies from 0 to ∞.

In isothermal process, $C = \infty$ as $\Delta T = 0$

In adiabatic process, $C = 0$ as $Q = 0$

C_p (molar heat capacity of isobaric process) and C_V (molar heat capacity of isochoric process) are commonly used.

In a general process pV^x = constant, molar heat capacity is given by

$$C = \frac{R}{\gamma - 1} + \frac{R}{1 - x}$$

- **First law of thermodynamics** This is the law of conservation of energy is given by

$$Q = \Delta U + W$$

This law can be applied for any type of system (solid, liquid or gas) but in most of the cases, our system is an ideal gas.

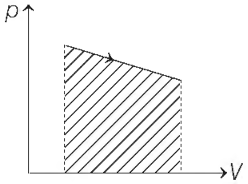
- **Detailed discussion of three terms of first law of thermodynamics**

  (i) **Work done** Following methods are generally used to find the work done.

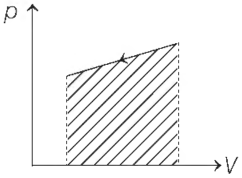
  Method 1 $W = \int_{V_i}^{V_f} p\,dV$ (because $dW = p\,dV$)

  Here, p should be either constant or function of V. If p is constant, it means process is isobaric, $W = p(V_f - V_i) = p\Delta V$.

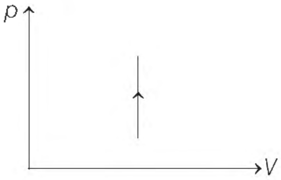
  Method 2 Work done can also be obtained by area under p-V diagram with projection on V-axis.



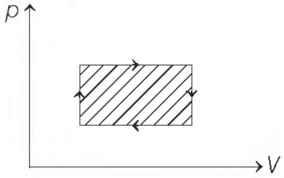
  W = + ve as volume is increasing



  W = – ve as volume is decreasing



  W = 0 as volume is constant



  W = +ve as cyclic process is clockwise with p on V-axis.

  (ii) **Change in internal energy** $\Delta U = nC_V \Delta T$ for all processes. For this, C_V (or nature of gas), n and ΔT should be known. If either of the three terms is not known, we can calculate ΔU by

$$\Delta U = Q - W$$

(iii) **Heat exchange** $Q = nC\Delta T$. For this, n, ΔT and molar heat capacity C should be known. C depends upon nature of gas and process. If either of the three terms (n, ΔT or C) is not known, we can calculate Q by,

$$Q = \Delta U + W$$

Name of the process	**Important points in the process**	$Q = nC\Delta T = W + \Delta U$	$\Delta U = nC_V \Delta T$	W
Isothermal	$T, pV, U =$ constant $\Delta T = \Delta(pV) = \Delta U = 0$ $p_1V_1 = p_2V_2$ or $p \propto \frac{1}{V}$	$Q = W$	0	$nRT \ln\left(\frac{V_f}{V_i}\right)$ $= nRT \ln\left(\frac{p_i}{p_f}\right)$
Isochoric	$V, \rho, \frac{p}{T} =$ constant $\Delta V = \Delta\rho = \Delta\left(\frac{p}{T}\right) = 0$ $\frac{p_1}{T_1} = \frac{p_2}{T_2}$ or $p \propto T$	$C = C_V$ $\therefore \; Q = nC_V\Delta T$	$nC_V\Delta T$	0
Isobaric	$p, \frac{V}{T} =$ constant $\Delta p = \Delta\left(\frac{V}{T}\right) = 0$ $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ or $V \propto T$	$C = C_p$ $\therefore \; Q = nC_p\Delta T$	$nC_V\Delta T$	$p\Delta V$ → For any system $Q - \Delta U = n(C_p - C_V)\Delta T$ $= nR\Delta T$ → for an ideal gas
Adiabatic process	$pV^{\gamma} =$ constant $TV^{\gamma-1} =$ constant $T^{\gamma}p^{1-\gamma} =$ constant	0	$nC_V\Delta T$	$W = -\Delta U$ $\therefore \; W = -nC_V\Delta T$ $= -n\left(\frac{R}{\gamma-1}\right)(T_f - T_i)$ $= \frac{p_iV_i - p_fV_f}{\gamma - 1}$
Cyclic process	$(p_i, V_i, T_i) = (p_f, V_f, T_f)$ Since, $T_i = T_f$ $\Rightarrow \; U_i = U_f$ or $\Delta T = \Delta U = 0$	$Q_{\text{net}} = W_{\text{net}}$	0	$W_{\text{net}} =$ area between cycle on p-V diagram
Polytropic process $pV^x =$ constant	$C = \frac{R}{\gamma - 1} + \frac{R}{1 - x}$ $= C_V + \frac{R}{1 - x}$	$nC\Delta T$	$nC_V\Delta T$	$Q - \Delta U = \frac{nR\Delta T}{1 - x}$ $= \frac{nR(T_i - T_f)}{1 - x}$ $= \frac{(p_iV_i - p_fV_f)}{1 - x}$
Free expansion in vacuum	$\Delta U = 0$ $\Rightarrow \; U, T$ and $pV =$ constant or $p \propto \frac{1}{V}$	0	0	0

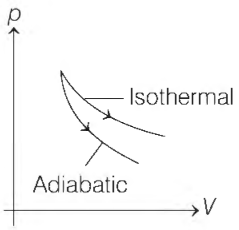
- $\frac{dp}{dV} = -\frac{xP}{V}$ or $pV^x =$ constant or slope of p-V graph $= -x\dfrac{p}{V}$

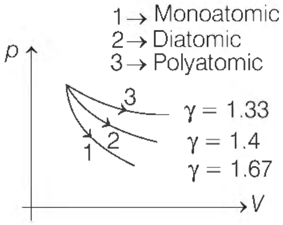
In isobaric process $x = 0$, therefore slope $= 0$

In isothermal process $x = 1$, therefore slope $= -\dfrac{p}{V}$

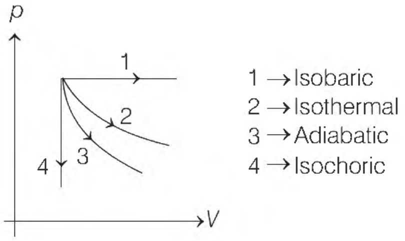
In adiabatic process $x = \gamma$, therefore slope $= -\gamma\dfrac{p}{V}$

Adiabatic and isothermal expansion of an ideal gas

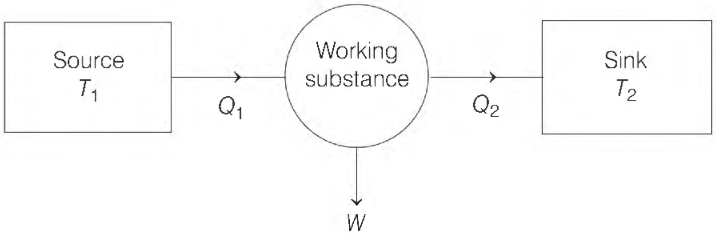




Adiabatic expansion of mono,dia and polyatomic gases.



Heat Engines



In general, $\eta = \dfrac{W}{Q_1} = \dfrac{Q_1 - Q_2}{Q_1} = 1 - \dfrac{Q_2}{Q_1}$

or
$$\eta = \left(\frac{\text{Work done by the working substance during a cycle}}{\text{Heat supplied to the gas during the cycle}} \right) \times 100$$

$$= \frac{W_{\text{Total}}}{|Q_{+\text{ve}}|} \times 100 = \frac{|Q_{+\text{ve}}| - |Q_{-\text{ve}}|}{|Q_{+\text{ve}}|} \times 100$$

$$= \left\{ 1 - \left| \frac{Q_{-\text{ve}}}{Q_{+\text{ve}}} \right| \right\} \times 100$$

Thus,
$$\eta = \frac{W_{\text{total}}}{|Q_{+\text{ve}}|} \times 100 = \left\{ 1 - \left| \frac{Q_{-\text{ve}}}{Q_{+\text{ve}}} \right| \right\} \times 100$$

Note *There cannot be a heat engine whose efficiency is 100%. It is always less than 100%. Thus,*

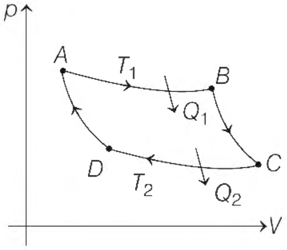
$$\eta \neq 100\%$$

or $W \neq Q_1$ *or* $W_{net} \neq Q_{+ve}$

or $Q_2 \neq 0$ *or* $|Q_{-ve}| \neq 0$

Carnot Engine

- Carnot cycle consists of the following four processes :
  (i) Isothermal expansion (process AB) at source temperature T_1
  (ii) Adiabatic expansion (process BC)
  (iii) Isothermal compression (process CD) at sink temperature T_2 and
  (iv) Adiabatic compression (process DA)
  The p-V diagram of the cycle is shown in the figure.



- In the whole cycle only Q_1 is the positive heat and Q_2 the negative heat. Thus,

$$Q_{+ve} = Q_1 \quad \text{and} \quad |Q_{-ve}| = Q_2$$

$\therefore$
$$\eta = \left(1 - \frac{Q_2}{Q_1} \right) \times 100$$

Specially for Carnot cycle, $\frac{Q_2}{Q_1}$ also comes out to be $\frac{T_2}{T_1}$.

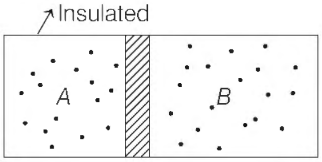
$$\therefore \qquad \eta = \left(1 - \frac{T_2}{T_1}\right) \times 100$$

- Efficiency of Carnot engine is maximum (not 100%) for given temperatures T_1 and T_2. But still Carnot engine is not a practical engine because many ideal situations have been assumed while designing this engine which can practically not be obtained.

Adiabatic and Diathermic Wall

- **Adiabatic wall** An insulating wall (can be movable also) that does not allow flow of energy (heat) from one chamber to another is called an adiabatic wall.

  If two thermodynamic systems A and B are separated by an adiabatic wall, then the thermodynamic state of A will be independent of the state of B and *vice-versa*, if wall is fixed or if the wall is movable, then only pressure will be same on both sides.



- **Diathermic wall** A conducting wall that allows energy flow (heat) from one chamber to another is called a diathermic wall. If two thermodynamic systems A and B are separated by a diathermic wall, then thermal equilibrium (same temperature) is attained in due course of time (if wall is fixed).

  If wall is movable, then temperature and pressure on both sides will become same.

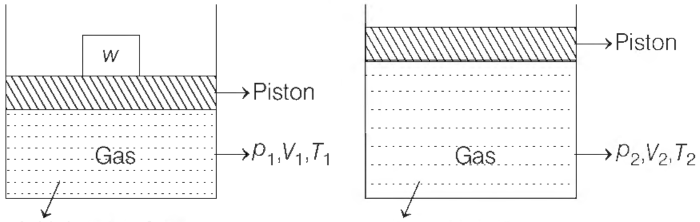
Note *In the above two cases, thermodynamic systems A and B are insulated from the external surroundings.*

Quasi-Static Process

Quasi means almost or near to. Quasi-static process means very nearly static process. Let us consider a system of gas contained in a cylinder. The gas is held by a moving piston and a weight w is placed over the piston. Due to the weight , the gas in cylinder is compressed.

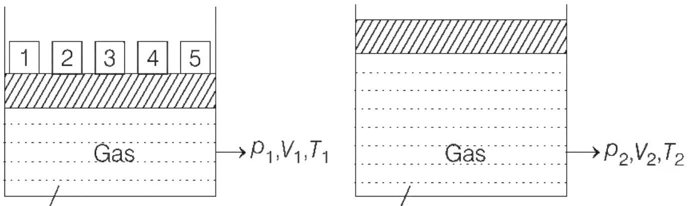
After the gas reaches equilibrium, the properties of gas are denoted by p_1, V_1 and T_1. The weight placed over the piston is balanced by upward force exerted by the gas. If the weight is suddenly removed, then there will be an unbalanced force between the system and the surroundings. The gas under pressure will expand and push the piston upwards.

The properties at this state after reaching equilibrium are p_2, V_2 and T_2. But the intermediate states passed through, when the system was in non-equilibrium states which cannot be described by thermodynamic coordinates. In this case, we only have initial and final states and do not have a path connecting them.



Initial state of gas Final state of gas

Sudden expansion of gas

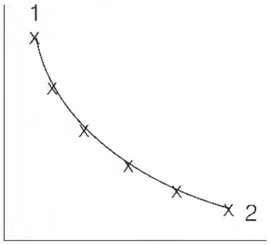


Initial state of gas Final state of gas

Quasi-static expansion of gas

Suppose, the weight is made of large numbers of small weights and one by one each of these small weights are removed and allowed the system to reach an equilibrium state. Then, we have intermediate equilibrium states and the path described by these states will not deviate much from the thermodynamic equilibrium state.

Such a process, which is the locus of all the intermediate points passed by the system is known as quasi-static process.

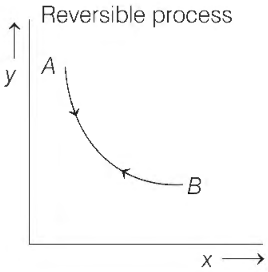


A quasi-static process

It means, this process is almost near to the thermodynamically equilibrium process. Infinite slowness is the characteristic feature of quasi-static process.

Reversible and Irreversible Process

- **Reversible process** The process in which the system and surroundings can be restored to the initial state from the final state without producing any changes in the thermodynamic properties of the universe is called a reversible process.
- In the figure below, let us suppose that the system has undergone a change from state A to state B. If the system can be restored from state B to state A and there is no change in the universe, then the process is said to be a reversible process.



- The reversible process can be reversed completely and there is no trace left to show that the system had undergone thermodynamic change.

  For the system to undergo reversible change, it should occur infinitely slowly or it should be quasi-static process. During reversible process, all the changes in state that occur in the system are in thermodynamic equilibrium with each other.

  Thus, there are two important conditions for the reversible process to occur.

  Firstly, the process should occur very slowly and secondly all of the initial and final states of the system should be in equilibrium with each other.

  For example, a quasi-static isothermal expansion of an ideal gas in a cylinder fitted with a frictionless movable piston is a reversible process.

  In actual practice, the reversible process never occurs, thus it is an ideal or hypothetical process.

- **Irreversible process** The process is said to be an irreversible process, if it cannot return the system and the surroundings to their original conditions when the process is reversed.

  The irreversible process is not at equilibrium throughout the process. Several examples can be cited. For examples,

  (i) When we are driving the car uphill, it consumes a lot of fuel and this fuel is not returned when we are driving down the hill.

  (ii) Cooking gas leaking from a gas cylinder in the kitchen diffuses to the entire room. The diffusion process will not spontaneously reverse and bring the gas back to the cylinder.

Triple Point of Water

The values of pressure and temperature at which water coexists in equilibrium in all three states of matter, i.e. ice, water and vapour is called triple point of water.

Triple point of water is 273 K temperature and 0.46 cm of mercury pressure.

Solar Constant

The amount of heat received from the sun by one square centimetre area of a surface placed normally to the sun rays at mean distance of the earth from the sun is known as solar constant. It is denoted by S.

$$S = \left(\frac{r}{R}\right)^2 \sigma T^4$$

Here, r is the radius of sun and R is the mean distance of earth from the centre of sun. Value of solar constant is 1.937 cal cm^{-2} min^{-1}.