



KINETIC THEORY OF GASES

It relates the macroscopic properties of gases to the microscopic properties of gas molecules.

Basic postulates of Kinetic theory of gases

Every gas consists of extremely small particles known as molecules. The molecules of a given gas are all identical but are different than those another gas.

The molecules of a gas are identical, spherical, rigid and perfectly elastic point masses.

The size is negligible in comparison to inter molecular distance (10^{-9} m)

Assumptions regarding motion

Molecules of a gas keep on moving randomly in all possible direction with all possible velocities.

The speed of gas molecules lie between zero and infinity (very high speed).

The number of molecules moving with most probable speed is maximum.

Assumptions regarding collision

The gas molecules keep colliding among themselves as well as with the walls of containing vessel. These collision are perfectly elastic. (i.e., the total energy before collision = total energy after the collisions.)

Assumptions regarding force

No attractive or repulsive force acts between gas molecules.

Gravitational attraction among the molecules is ineffective due to extremely small masses and very high speed of molecules.

Assumptions regarding pressure

Molecules constantly collide with the walls of container due to which their momentum changes. This change in momentum is transferred to the walls of the container. Consequently pressure is exerted by gas molecules on the walls of container.

Assumptions regarding density

The density of gas is constant at all points of the container.

Kinetic interpretation of pressure:

$$PV = \frac{1}{3}mNv_{\text{rms}}^2$$



[m = mass of a molecule, N = no. of molecules]

$$\text{Ideal gas equation } PV = \mu RT \Rightarrow P = \frac{\mu RT}{V} = \frac{\mu N_A k_b T}{V} = \left(\frac{N_A}{V}\right) k_b T = nk_b T$$

Where μ is the number of moles and $R = N_A \cdot k_b$ is a universal constant. Also, k_b is the Boltzmann constant having value $1.38 \times 10^{-23} \text{ J/K}$.

Gas laws

Boyle's law : For a given mass at constant temperature, $V \propto \frac{1}{P}$

Charles' law : For a given mass at constant pressure, $V \propto T$

Gay-Lussac's law For a given mass at constant volume, $P \propto T$

Avogadro's law: If P, V & T are same then no. of molecules $N_1 = N_2$

Graham's law : At constant P and T, Rate of diffusion $\propto \frac{1}{\sqrt{\rho}}$

Dalton's law : $P = P_1 + P_2 + \dots + P_n$

Total pressure = Sum of partial pressures

Real gas equation (Vander Waal's equation) $\left(P + \frac{\mu^2 a}{V^2}\right)(V - \mu b) = \mu RT$

where a & b are vander waal's constant and depend on the nature of gas.

Critical temperature $T_c = \frac{8a}{27Rb}$

The maximum temperature below which a gas can be liquefied by pressure alone.

Critical volume $V_c = 3b$

Critical pressure $P_c = \frac{a}{27b^2}$

Note :- For a real gas $\frac{P_c V_c}{RT_c} = \frac{3}{8}$

Different speeds of molecules

$$v_{rms} = \sqrt{\frac{3RT}{M_w}} = \sqrt{\frac{3kT}{m}} \quad v_{mp} = \sqrt{\frac{2RT}{M_w}} = \sqrt{\frac{2kT}{m}} \quad v_{av} = \sqrt{\frac{8RT}{\pi M_w}} = \sqrt{\frac{8kT}{\pi m}}$$

Kinetic Interpretation of Temperature :

Temperature of an ideal gas is proportional to the average KE of molecules.

$$PV = \frac{1}{3} m N v_{rms}^2 \quad \& \quad PV = \mu RT \Rightarrow \frac{1}{2} m v_{rms}^2 = \frac{3}{2} kT$$



Degree of Freedom (F) :

Number of minimum coordinates required to specify the dynamical state of a system.

- For monoatomic gas (He, Ar etc) $f = 3$ (only translational)
- For diatomic gas (H_2 , O_2 etc) $f = 5$ (3 translational + 2 rotational)
- At higher temperature, diatomic molecules have additional two degree of freedom due to vibrational motion (one for KE + one for PE)
- At higher temperature diatomic gas has $f = 7$

Maxwell's Law of equipartition of energy:

Kinetic energy associated with each degree of freedom of particles of an ideal gas is equal

to $\frac{1}{2}kT$

- Average KE of a particle having f degree of freedom = $\frac{f}{2}kT$
- Translational KE of a molecule = $\frac{3}{2}kT$
- Translational KE of a mole = $\frac{3}{2}RT$
- Internal energy of an ideal gas : $U = \frac{f}{2}\mu RT$

Specific heats (C_p and C_v) :

- Molar specific heat of a gas $C = \frac{dQ}{\mu dT}$
- $C_v = \left(\frac{dQ}{\mu dT} \right)_{v=\text{constant}} = \frac{dU}{\mu dT}$
- $C_p = \left(\frac{dQ}{\mu dT} \right)_{p=\text{constant}} = C_v + R \leftarrow \text{Mayer's equation}$

Atomicity	Translational	Rotational	Total (f)	$\gamma = \frac{C_p}{C_v}$	$C_v = \left(\frac{f}{2}\right)R$	$C_p = C_v + R$
Monoatomic [He, Ar, Ne...]	3	0	3	$\frac{5}{3} = 1.67$	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic [H_2, N_2 , ...]	3	2	5	$\frac{7}{5} = 1.4$	$\frac{5}{2}R$	$\frac{7}{2}R$
Triatomic (Linear CO_2)	3	2	5	$\frac{7}{5} = 1.4$	$\frac{5}{2}R$	$\frac{7}{2}R$
Triatomic Non-linear- NH_3 & Polyatomic	3	3	6	$\frac{4}{3} = 1.33$	$3R$	$4R$



Mean Free path :

Average distance between two consecutive collisions $\lambda_m = \frac{1}{\sqrt{2}\pi d^2 n}$

where d = diameter of molecule, n = molecular density = N/V

For mixture of non-reacting gases

1. Molecular weight	$M_{W_{mix}} = \frac{\mu_1 M_{W_1} + \mu_2 M_{W_2} + \dots + \mu_n M_{W_n}}{\mu_1 + \mu_2 + \dots + \mu_n}$
2. Specific heat at constant V	$C_{V_{mix}} = \frac{\mu_1 C_{V_1} + \mu_2 C_{V_2} + \dots + \mu_n C_{V_n}}{\mu_1 + \mu_2 + \dots + \mu_n}$
3. Specific heat at constant P	$C_{P_{mix}} = \frac{\mu_1 C_{P_1} + \mu_2 C_{P_2} + \dots + \mu_n C_{P_n}}{\mu_1 + \mu_2 + \dots + \mu_n}$
	$\gamma_{mix} = \frac{C_{P_{mix}}}{C_{V_{mix}}} = \frac{\mu_1 C_{P_1} + \mu_2 C_{P_2} + \dots + \mu_n C_{P_n}}{\mu_1 C_{V_1} + \mu_2 C_{V_2} + \dots + \mu_n C_{V_n}}$

KEY POINTS

- Kinetic energy per unit volume $E_v = \frac{1}{2} \left(\frac{m N}{V} \right) V_{rms}^2$
- At absolute zero, the motion of all molecules of the gas stops.
- At higher temperature and low pressure or at higher temperature and low density, a real gas behaves as an ideal gas.
- For any general process
 - (a) Internal energy change $\Delta U = nC_v dT$
 - (b) Heat supplied to a gas $\Delta Q = nCdT$

Where C for any polytropic process $PV^x = \text{constant}$ is $C = C_v + \frac{R}{1-x}$

(c) Work done for any process $\Delta W = P\Delta V$. It can be calculated as area under P-V curve

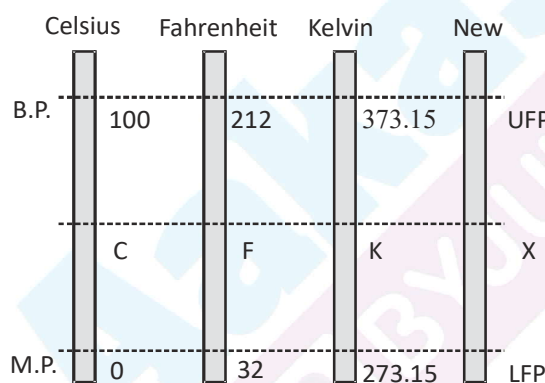
(c) Work done = $\Delta Q - \Delta U = \frac{nR}{1-x} dT$, For any polytropic process $PV^x = \text{constant}$



THERMOMETRY & CALORIMETRY

TEMPERATURE SCALES AND THERMAL EXPANSION

Name of the scale	Symbol for each degree	Lower fixed point (LFP)	Upper fixed point (UFP)	No of divisions on the scale
Celsius	°C	0°C	100°C	100
Fahrenheit	°F	32°F	212°F	180
Kelvin	K	273.15 K	373.15K	100



$$\frac{C - 0}{100 - 0} = \frac{F - 32}{212 - 32} = \frac{K - 273.15}{373.15 - 273.15} = \frac{X - \text{LFP}}{\text{UFP} - \text{LFP}}$$

$$\frac{\Delta C}{100} = \frac{\Delta F}{180} = \frac{\Delta K}{100} = \frac{\Delta X}{\text{UFP} - \text{LFP}}$$

Old thermometry

$$\frac{\theta - 0}{100 - 0} = \frac{X - X_0}{X_{100} - X_0}$$

[two fixed points - ice & steam points]

where X is thermometric property i.e., length, resistance etc.

Modern thermometry

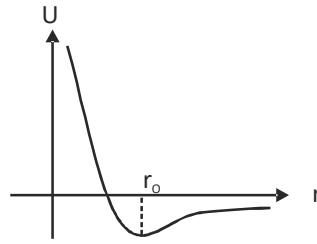
$$\frac{T - 0}{273.16 - 0} = \frac{X}{X_{tr}}$$

[Only one reference point - triple point of water is chosen]

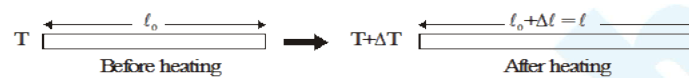


THERMAL EXPANSION

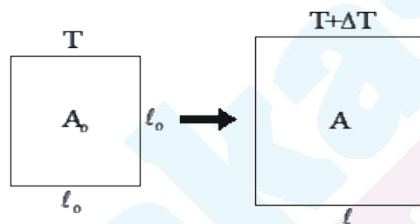
It is due to asymmetry in potential energy curve.



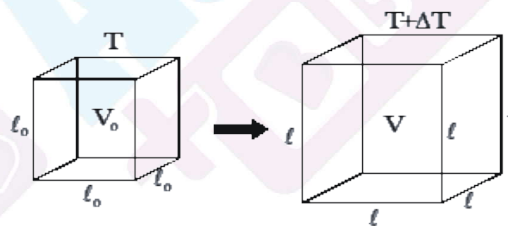
In solids → Linear expansion $l = l_0 (1 + \alpha \Delta T)$



In solids → Areal expansion $A = A_0 (1 + \beta \Delta T)$



In solids, liquids and gases → Volume expansion : $V = V_0 (1 + \gamma \Delta T)$



[For isotropic solids : $\alpha : \beta : \gamma : 1 : 2 : 3$]

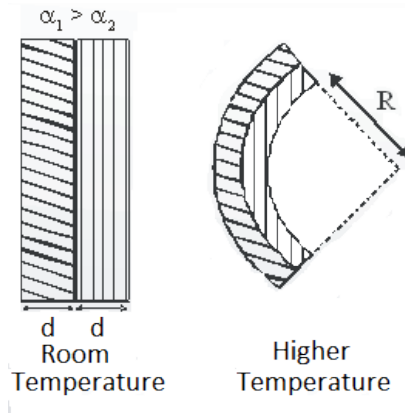
Thermal expansion of isotropic object may be imagined as photographic enlargement.

For anisotropic material $\beta_{xy} = \alpha_x + \alpha_y$ and $\gamma = \alpha_x + \alpha_y + \alpha_z$

If α is variable :
$$\Delta l = \int_{T_1}^{T_2} l_0 \alpha dT$$

Application of Thermal expansion in solids

1. Bi-metallic strip (used as thermostal or auto-cut in electric heating circuits)



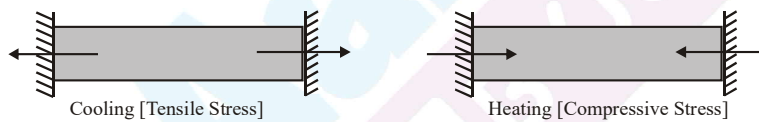
2. Simple pendulum : $T = 2\pi\sqrt{\frac{\ell}{g}} \Rightarrow T \propto \ell^{1/2} \Rightarrow \frac{\Delta T}{T} = \frac{1}{2} \frac{\Delta \ell}{\ell}$

Fractional change in time period = $\frac{\Delta T}{T} = \frac{1}{2} \alpha \Delta \theta$

3. Scale reading : Due to linear expansion / contraction, scale reading will be lesser / more than actual value.

If temperature increases then actual value = scale reading $(1 + \alpha \Delta \theta)$

4. Thermal stress



Thermal strain = $\frac{\Delta \ell}{\ell} = \alpha \Delta \theta$

As Young's modulus $Y = \frac{F/A}{\Delta \ell / \ell}$; So thermal stress = $Y \alpha \Delta \theta$

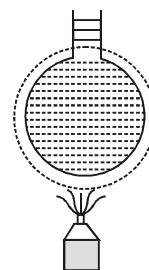
Thermal expansion in liquids (only volume expansion)

$\gamma_a = \frac{\text{Apparent increase in volume}}{\text{Initial volume} \times \text{Temperature rise}}$

$\gamma_r = \frac{\text{real increase in volume}}{\text{Initial volume} \times \text{Temperature rise}}$

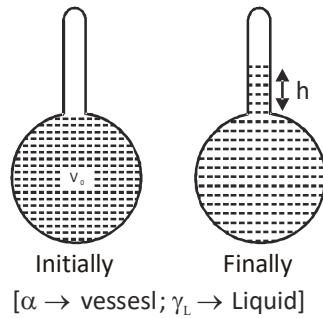
$\gamma_r = \gamma_a + \gamma_{\text{vessel}}$

Change in volume of liquid w.r.t. vessel $\Delta V = V_0 (\gamma_r - 3\alpha) \Delta T$





Expansion in enclosed volume.



Increase in height of liquid level in tube when bulb was initially completely filled.

$$h = \frac{\text{apparent change in volume of liquid}}{\text{area of tube}} = \frac{V_0(\gamma_L - 3\alpha)\Delta T}{A_0(1 + 2\alpha)\Delta T}$$

Anomalous expansion of water:

In the range 0°C to 4°C water contract on heating and expands on cooling.

At 4°C → density is maximum.

Aquatic life is able to survive in very cold countries as the lake bottom remains unfrozen at the temperature around 4°C.

Thermal expansion of gases :

Coefficient of volume expansion $\gamma_v = \frac{\Delta V}{V_0 \Delta T} = \frac{1}{T}$

PV = nRT at constant pressure $V \propto T \Rightarrow \frac{\Delta V}{V} = \frac{\Delta T}{T}$

Coefficient of pressure expansion $\gamma_p = \frac{\Delta P}{P_0 \Delta T} = \frac{1}{T}$

KEY POINTS :

- Liquids usually expand more than solids because the intermolecular forces in liquids are weaker than in solids.
- Rubber contract on heating because in rubber as temperature increases, the amplitude of transverse vibrations increases more than the amplitude of longitudinal vibrations.
- Water expands both when heated or cooled from 4°C because volume of water at 4°C is minimum.
- In cold countries, water pipes sometimes burst, because water expands on freezing.



Calorimetry

1 cal = 4.186 J ; 4.2 J

- **Thermal capacity of a body** = $\frac{Q}{\Delta T}$

Amount of heat required to raise the temp. of a given body by 1°C (or 1K).

- **Specific heat capacity** = $\frac{Q}{m\Delta T}$ (m = mass)

Amount of heat required to raise the temperature of unit mass of a body through 1°C (or 1K)

- **Molar heat capacity** = $\frac{Q}{n\Delta T}$ (n= number of moles)

- **Water equivalent:** If thermal capacity of a body is expressed in terms of mass of water, it is called water equivalent. Water equivalent of a body is the mass of water which when given same amount of heat as to the body, changes the temperature of water through same range as that of the body.

Therefore water equivalent of a body is the quantity of water, whose heat capacity is the same as the heat capacity of the body.

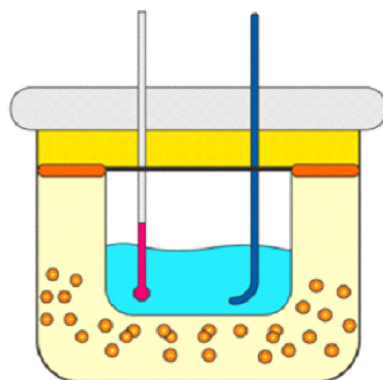
Water equivalent of the body,

$$W = \text{mass of body} \times \left(\frac{\text{specific heat of body}}{\text{specific heat of water}} \right)$$

Unit of water equivalent is g or kg.

- **Latent Heat (Hidden heat)** : The amount of heat that has to supplied to (or removed from) a body for its complete change of state (from solid to liquid, liquid to gas etc) is called latent heat of the body. Remember that phase transformation is an isothermal (i.e. temperature = constant) change.

Calorimeter principle



Calorimeter



When two bodies of different temperature (preferably a solid and a liquid) are placed in physical contact with each other, the heat is transferred from the body with higher temperature to the body with lower temperature until thermal equilibrium is attained between them. The body at higher temperature release heat while the body total heat lost by the hot body is equal to the total heat gained by the cold body.

Heat Lost = Heat Gained

The heat transfer in a system is calculated using the formula.

$$q = mc\Delta t$$

Where

q is the measure of heat transfer

m is the mass of the body

c is the specific heat of the body

Δt is the change in the temperature

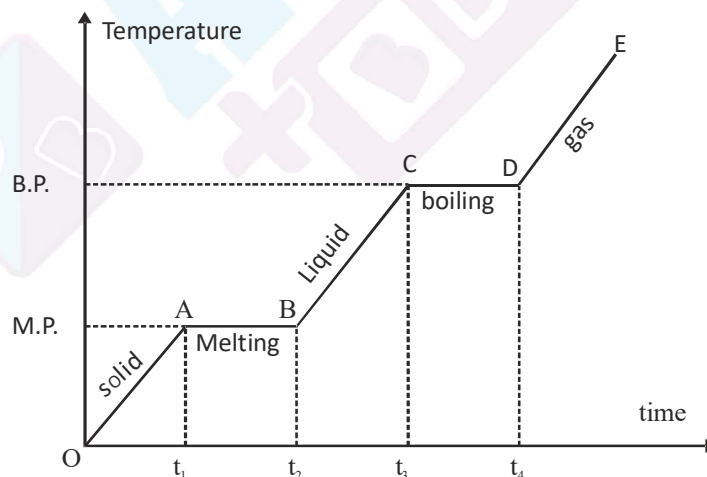
For phase change $Q = mL$

Where,

m is the mass of the body

L is the latent heat of the body.

- **Heating curve** : If t_0 is the initial temperature of a given mass (m) of a solid, heat is supplied at constant rate (Q) and a graph is plotted between temperature and time, the graph is called heating curve.



$$\text{Specific heat (or thermal capacity)} \propto \frac{1}{\text{slope of curve}}$$

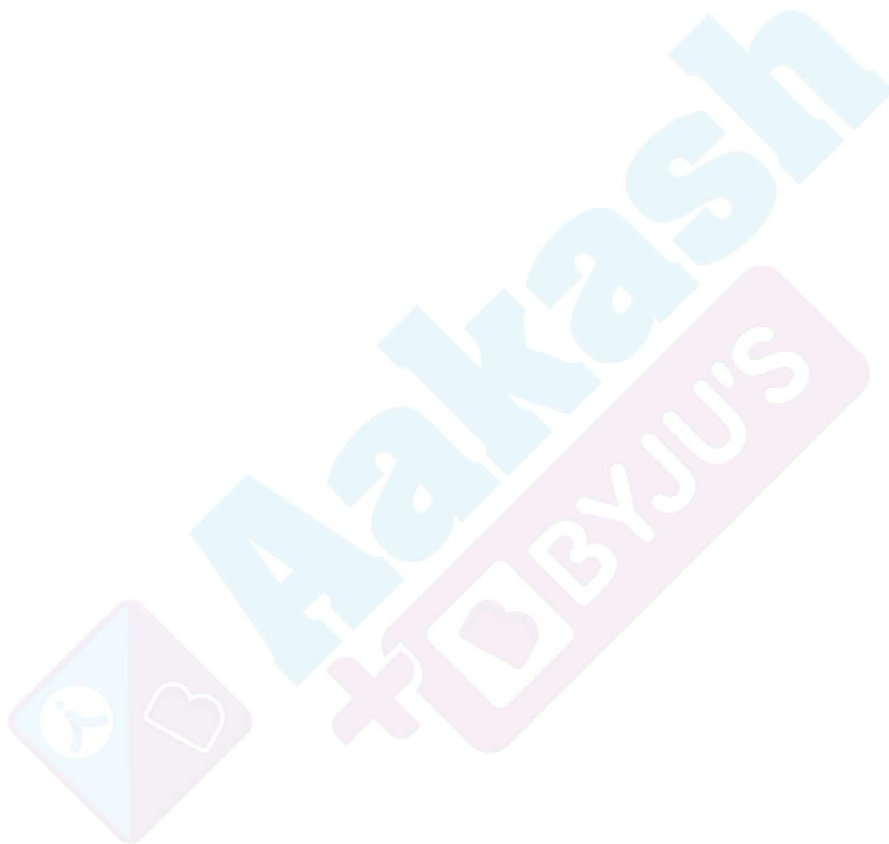
Latent heat \propto length of horizontal line.



KEY POINTS

- The steam at 100°C causes more severe burn to human body than the water at 100°C because steam has greater internal energy than water due to latent heat of vaporization.
- Heat is energy in transit which is transferred from hot body to cold body.
- One calorie is the amount of heat required to raise the temperature of one gram of water through 1°C (more precisely from 14.5 °C to 15.5°C).
- **Clausius & Clapeyron equation (effect of pressure on boiling point of liquids & melting point of solids related with latent heat).**

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$



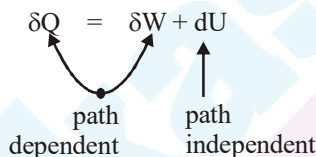


THERMODYNAMICS

THERMODYNAMICS

- **Zeroth law of thermodynamics** : If two systems are each in thermal equilibrium with a third, they are also in thermal equilibrium with each other.
- **First law of thermodynamics** : Heat supplied (Q) to a system is equal to algebraic sum of change in internal energy (ΔU) of the system and the mechanical work (W) done by the system.

$$Q = W + \Delta U \quad [\text{Here } W = \int PdV; \Delta U = nC_v\Delta T]$$



For differential change

- **Sign Convention**

- Heat absorbed by the system → positive
- Heat rejected by the system → negative
- Increase in internal energy (i.e., rise in temperature) → positive
- Decrease in internal energy (i.e., fall in temperature) → negative
- Work done by the system → positive
- Work done on the system → negative

- **For cyclic process** $\Delta U = 0 \Rightarrow Q = W$
- **For isochoric process** $V = \text{constant} \Rightarrow P \propto T \text{ \& } W = 0$
 $Q = \Delta U = \mu C_v \Delta T$
- **For isobaric process** $P = \text{constant} \Rightarrow V \propto T$
 $Q = \mu C_p \Delta T, \Delta U = \mu C_v \Delta T$
 $W = P(V_2 - V_1) = \mu R \Delta T$
- **For adiabatic process** $PV^\gamma = \text{constant}$
 or $T^\gamma P^{1-\gamma} = \text{constant}$
 or $TV^{\gamma-1} = \text{constant}$
 In this process $Q = 0$ and

$$W = -\Delta U = \mu C_v(T_1 - T_2) = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

- **For Isothermal Process** $T = \text{constant}$ or $\Delta T = 0 \Rightarrow PV = \text{constant}$
 In this process $\Delta U = \mu C_v \Delta T = 0$

$$\text{So, } Q = W = \mu RT \ln \left(\frac{V_2}{V_1} \right) = \mu RT \ln \left(\frac{P_1}{P_2} \right)$$



- For any general polytropic process $PV^x = \text{constant}$

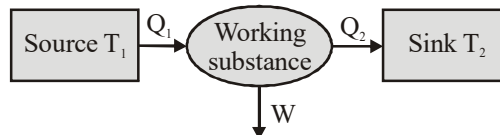
Molar heat capacity $C = C_v + \frac{R}{1-x}$

- Work done by gas $W = \frac{nR(T_1 - T_2)}{x-1} = \frac{(P_1V_1 - P_2V_2)}{x-1}$

- Slope of P-V diagram

(also known as indicator diagram at any point $\frac{dP}{dV} = -x \frac{P}{V}$)

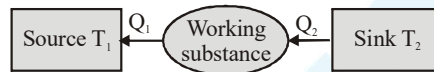
- Efficiency of a cycle



$$\eta = \frac{\text{Work done by working substance}}{\text{Heat Supplied}} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

- For Carnot cycle $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$ so $\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$

- For refrigerator



$$\text{Coefficient of performance } \beta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

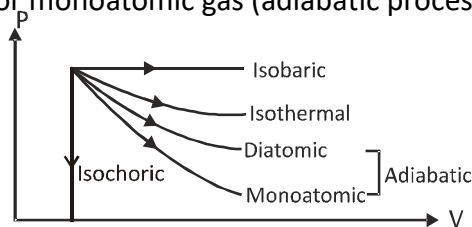
- Bulk modulus of gases : $B = \frac{\Delta P}{-\frac{\Delta V}{V}}$

Isothermal bulk modulus of elasticity, $B_{IT} = -V \left(\frac{\partial P}{\partial V} \right)_{T=\text{constant}}$

Adiabatic bulk modulus of elasticity $B_{AD} = -\gamma V \left(\frac{\partial P}{\partial V} \right) \Rightarrow B_{AD} = \gamma B_{IT}$

KEY POINTS

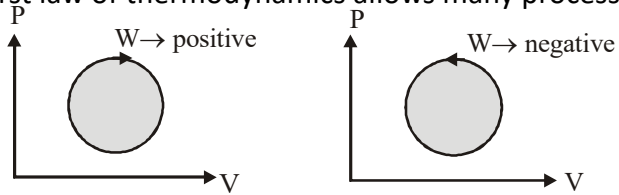
- Work done is least for monoatomic gas (adiabatic process).



- Air quickly leaking out of a balloon becomes cooler as the leaking air undergoes adiabatic expansion.
- First law of thermodynamics does not forbid flow of heat from lower temperature to higher temperature.



- First law of thermodynamics allows many processes which actually don't happen.

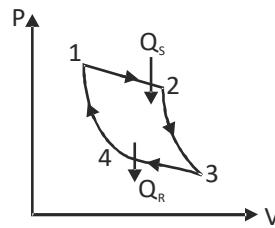


CARNOT ENGINE

It is a hypothetical engine with maximum possible efficiency

Process 1 → 2 & 3 → 4 are isothermal

Process 2 → 3 & 4 → 1 are adiabatic.



$$\eta = 1 - \frac{T_{3-4}}{T_{1-2}}$$