CHAPTER

16

Kinetic Theory of Gases and Thermodynamics

- **Boyle's law:** If m and T are constant

$$V \propto \frac{1}{P}$$

$$P_1V_1 = P_2V_2$$

- **Charles's law:** If m and P are constant

$$V \propto T$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

- **Gay-Lussac's law:** If m and V are constant

$$P \propto T$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

- **Avogadro's law:** If P, V and T are same

$$N_1 = N_2$$

where, N_1 and N_2 are the number of molecules

$V \propto n$ (no. of molecules of gas)

$$\frac{\mathrm{V}_1}{\mathrm{n}_1} = \frac{\mathrm{V}_2}{\mathrm{n}_2}$$

- **Graham's law:** If P and T are constant

rate of diffusion $r \propto \frac{1}{\sqrt{\rho}}$

ρ is density

$$\frac{r_1}{r_2} = \sqrt{\quad}$$

- **Dalton's law:** $P = P_1 + P_2 + P_3$ ......

P = Total pressure

P_1, P_2, P_3 .... = Pressure exerted by each component present in the mixture.

- **Ideal gas equation:** $PV = nRT = k_BNT$

n = number of moles

N = number of molecules

R = universal gas constant

k_B = Boltzmann's constant

- Pressure exerted by ideal gas

$$P = \frac{1}{3}\frac{mN}{v}\overline{v^2}$$

$\overline{\mathrm{v}^2}$ = mean square velocity $\left\{\overline{v^2} = \frac{v_1^2 + v_2^2 + v_3^2 + \ldots\ldots}{N}\right\}$

m = mass of each molecule

or $P = \frac{1}{3}nm\overline{v^2}$

n = number density *i.e.*, $n = \frac{N}{V}$

- $V_{rms} = \left(\overline{v^2}\right)^{1/2}$

K.E. $= \frac{3}{2}k_BT = \frac{1}{2}m\overline{v^2}$

$$\overline{v^2} = \frac{3k_BT}{m}$$

$$\Rightarrow V_{\text{rms}} = \sqrt{\frac{3k_BT}{m}}$$

- $V_{av} = \sqrt{\frac{8K_BT}{\pi m}}$

- $V_{\text{mp}} = \sqrt{\frac{2K_BT}{m}}$

- Mean free path $(\bar{l}) = \frac{1}{\sqrt{2}n\pi d^2}$

n = number density

d = diameter of molecule

- $\gamma = \frac{C_p}{C_v}$

γ = ratio of specific heats

C_p = specific heat at constant pressure

C_v = specific heat at constant volume

$C_p - C_v = R$

R = universal gas constant

S.No.	Atomicity	No. of degree of freedom	C_P	C_v	$\gamma = C_P/C_v$
1	Monoatomic	3	$\frac{5}{2}R$	$\frac{3}{2}R$	$\frac{5}{3}$
2	Diatomic	5	$\frac{7}{2}R$	$\frac{5}{2}R$	$\frac{7}{5}$

❖ $C_{v(\text{mix})} = \dfrac{n_1 C_{v_1} + n_2 C_{v_2}}{n_1 + n_2}$

where n_1 and n_2 are number of moles of gases mixed together C_{v_1} and C_{v_2} are molar specific heat at constant volume of the two gas and $C_{v(\text{mix})}$: Molar specific heat at constant volume for mixture.

THERMODYNAMICS

❖ First law of themodynamics

$\Delta Q = \Delta U + \Delta W$

❖ Work done.

$\Delta W = P\Delta V$

$\therefore\ \Delta Q = \Delta U + P\Delta V$

❖ Relation between specific heats for a gas

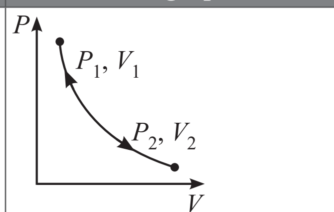
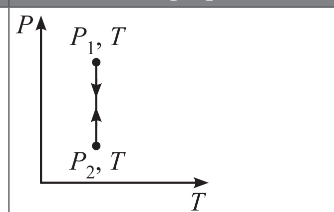
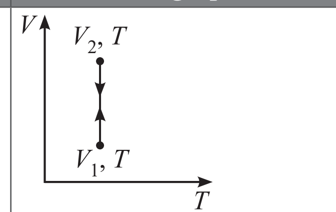
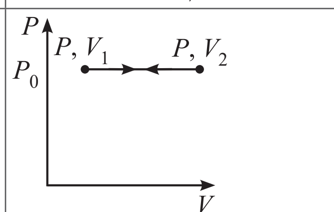
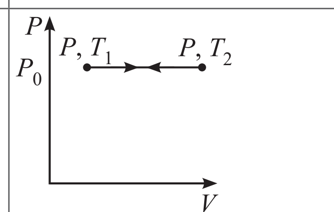
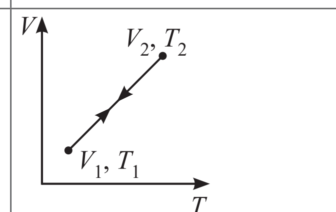
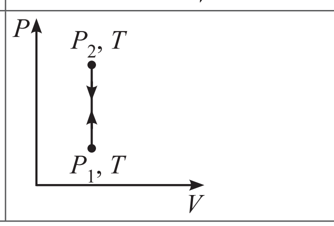
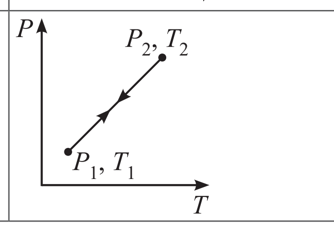
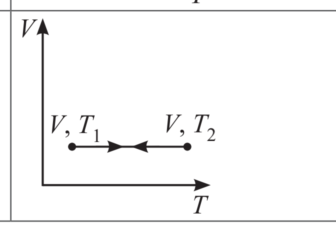
$C_p - C_v = R$

Polytropic Process

It is a thermodynamic process that can be expressed as follows:

$PV^x = \text{Constant}$

x (Polytropic exponent)	Type of standard process	Expression
0	Isobaric ($dP = 0$)	P = Constant
1	Isothermal ($dT = 0$)	PV = Constant
γ	Adiabatic ($dQ = 0$)	PV^{γ} = Constant
∞	Isochoric ($dV = 0$)	V = Constant

Process	Definition	P-V graph	P-T graph	V-T graph
Isothermal	Temperature constant			
Isobaric	Pressure constant			
Isochoric	Volume constant			

For Polytropic Process

$\Delta Q = \Delta U + W$

$\Rightarrow\ nC\Delta T = \dfrac{f}{2} nR\Delta T + \dfrac{nR\Delta T}{1-x}$

[$\because$ Work done in a general polytropic process = [$nR\Delta T/(1 - x)$]

$\Rightarrow\ C = \dfrac{f}{2} R + \dfrac{R}{1-x}$

For infinitesimal changes in Q, U, and W, we ca write,

$dQ = dU + dW$

$\Rightarrow\ nCdT = \dfrac{f}{2} nRdT + PdV$

$\Rightarrow\ C = \dfrac{f}{2} R + \dfrac{P}{n}\dfrac{dV}{dT}$

Process	Equation of State	W	ΔU
Isobaric ($dP = 0$)	$\frac{V}{T} = c$	$P(V_f - V_i) = nR(T_f - T_i)$	$\frac{f}{2}nR(T_f - T_i) = \frac{f}{2}P(V_f - V_i)$
Isochoric ($dV = 0$)	$\frac{P}{T} = c$	0	$\frac{f}{2}nR(T_f - T_i) = \frac{f}{2}V(P_f - P_i)$
Isothermal ($dT = 0$)	$PV = c$	$nRT\ \ln\left(\frac{V_f}{V_i}\right) = nRT\ \ln\left(\frac{P_i}{P_f}\right)$	0
Adiabatic ($dQ = 0$)	$PV^\gamma = c$	$\frac{f}{2}nR(T_i - T_f) = \frac{f}{2}(P_iV_i - P_fV_f)$	$\frac{f}{2}nR(T_f - T_i)$

Process	ΔQ
Isobaric ($dP = 0$)	$\left(\frac{f}{2}+1\right)nR\Delta T = \left(\frac{f}{2}+1\right)P(V_f - V_i)$
Isochoric ($dV = 0$)	$\frac{f}{2}nR(T_f - T_i) = \frac{f}{2}V(P_f - P_i)$
Isothermal ($dT = 0$)	$nRT\ \ln\left(\frac{V_f}{V_i}\right) = nRT\ \ln\left(\frac{P_i}{P_f}\right)$
Adiabatic ($dQ = 0$)	0

- Slope of adiabatic = γ (slope of isotherm)
- Carnot engine

  $\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$

  $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

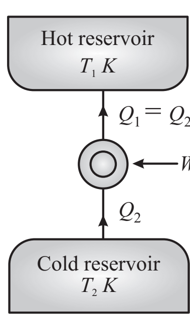
  $W = Q_1 - Q_2$

  (efficiency) $\eta = \frac{W}{Q_1}$
- Refrigerator

  Coefficient of performance is β

  $\beta = \frac{Q_2}{Q_1 - Q_2} = \frac{Q_2}{W}$; $\beta = \frac{1-\eta}{\eta}$
- Heat pump

  $\alpha = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} = \frac{1}{\eta}$



SUMMARY

- Zeroth law of thermodynamics states that 'two systems in thermal equilibrium with a third system are in thermal equilibrium with each other.
- Zeroth law leads to the idea of temperature.
- Heat and work are two modes of energy transfer to the system.
- Heat gets transferred due to temperature difference between the system and its environment (surroundings).
- Work is energy transfer which arises by other means, such as moving the piston of a cylinder containing the gas, by raising or lowering some weight connected to it.
- Internal energy of any thermodynamic system depends only on its state. The internal energy change in a process depends only on the initial and final states, not on the path, i.e. it is state function.
- The internal energy of an isolated system is constant.
- (*a*) For isothermal process $\Delta T = 0$

  (*b*) For adiabatic process $\Delta Q = 0$
- First law of thermodynamics states that when heat Q is added to a system while the system does work W, the internal energy U changes by an amount equal to $Q - W$. This law can also be expressed for an infinitesimal process.
- First law of thermodynamics is general law of conservation of energy.
- Second law of thermodynamics does not allow some processes which are consistent with the first law of thermodynamics.

  It states

  Clausius statement: No process is possible whose only result is the transfer of heat from a colder object to a hotter object.

  Kelvin-Plank statement: No process is possible whose only result is the absorption of heat from a reservoir and complete conversion of the heat into work.
- No engine can have efficiency equal to 1 or no refrigerator can have co-efficient of performance equal to infinity.
- Carnot engine is an ideal engine.
- The Carnot cycle consists of two reversible isothermal process and two reversible adiabatic process.
- If $Q > 0$, heat is added to the system.

  If $Q < 0$, heat is removed from the system.

  If $W > 0$, work is done by the system (Expansion).

  If $W < 0$, work is done on the system (Compression).