Chapter 8

Kinetic Theory of Gases and Thermodynamics

Pressure Exerted by the Gas

The pressure of the gas is due to continuous bombardment of the gas molecules against the walls of the container. According to kinetic theory, the pressure exerted by an ideal gas is given by

$$\boxed{P = \frac{1}{3}\frac{M}{V}\bar{v}^2}$$

M = Mass of the enclosed gas

V = Volume of the container

$\bar{v}^2$ = Mean square speed of molecules

or $P = \frac{1}{3}\frac{M}{V}v_{rms}^2$ v_{rms} = Root mean square velocity

or $P = \frac{1}{3}\frac{Nm}{V}\bar{v}^2$ N = Number of molecules

$$\boxed{P = \frac{\rho}{3}v_{rms}^2}$$

ρ = density of gas

m = Mass of the molecule

$\bar{v}^2$ = Mean square speed of molecules

Speeds of gas molecules :

(i) Root mean square speed,

$$v_{rms} = \sqrt{\frac{3RT}{M_w}} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + ... v_n^2}{n}}$$

Here, M_W is molecular weight in kg.

$$v_{rms} = \sqrt{\frac{3\,kT}{m}}$$, k = Boltzmann's constant, m = mass of one molecule in kg

(ii) Average speed $v_{avg} = \sqrt{\frac{8RT}{\pi M_w}} = \sqrt{\frac{8P}{\pi\rho}} = \frac{v_1 + v_2 + v_3 + ... + v_n}{n}$

(iii) v_{mp} = Most probable speed is defined as the speed corresponding to which there are maximum number of molecules.

$$v_{mp} = \sqrt{\frac{2RT}{M_w}} = \sqrt{\frac{2P}{\rho}} = \sqrt{\frac{2\,kT}{m}}$$

ρ = Density of gas
M_w = Molecular weight
R = Gas constant
P = Pressure of gas
m = Mass of one molecule

Order of magnitude : $v_{rms} > v_{avg} > v_{mp}$

$$v_{rms} : v_{av} : v_{mp} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} \simeq \sqrt{3} : \sqrt{2.5} : \sqrt{2}$$

Relation between C_P & C_V :

(i) $C_P - C_V = R \qquad (C_P > C_V)$

(ii) $\frac{C_P}{C_V} = \gamma$

(iii) $C_v = \frac{f}{2}R$

Gas	Degrees of freedom (f)	$\Delta U = \frac{f}{2}nR\Delta T$	$C_V = \frac{\Delta U}{n\Delta T}$	$C_P = C_V + R$	$\gamma = \frac{C_P}{C_V}$
Monoatomic	3 (Translational)	$\frac{3}{2}nR\Delta T$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$
Diatomic	3(Trans) + 2(Rot)	$\frac{5}{2}nR\Delta T$	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5}$
Non-Linear Poly atomic	3 (Trans) + 3 (Rot)	$3nR\Delta T$	$3R$	$4R$	$\frac{4}{3}$

For a mixture of two gases A and B containing n_A and n_B number of moles.

(i) $f_{mix} = \frac{(n_A f_A + n_B f_B)}{n_A + n_B}$

(ii) $\gamma_{mix} = 1 + \frac{2}{f_{mix}}$

$C_{v_{mix}} = \frac{f_{mix}R}{2}$

$C_{p_{mix}} = C_{v_{mix}} + R$

Thermodynamic Process

(1) Melting process : (Change of state, solid to liquid)

$Q = \Delta U + W$

$mL_f = \Delta U + 0$ [$W = 0$ as volume remains nearly constant]

(2) Boiling process : (Change of state, liquid to vapours)

$mL_v = \Delta U + P[V_2 - V_1]$

V_2 = volume of vapours

V_1 = volume of liquid

When 1 g of water vapourises isobarically at atmospheric pressure. ΔU = 2091 J, $P = 1.01 \times 10^5$ Pa, $V_1 = 1\ cm^3$, $V_2 = 1671\ m^3$.

(3) Isochoric process : Volume is constant

$dV = 0 \Rightarrow W = 0$ [dV = change in volume]

$Q = nC_V\Delta T = \Delta U$

$\Rightarrow \quad C_V = \dfrac{\Delta U}{n\Delta T}$

(4) Isobaric process : Pressure is constant

P = constant, $dW = PdV$

$\Rightarrow \quad W = P\Delta V = nR\Delta T$

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

$nC_P\Delta T = nC_V\Delta T + nR\Delta T$

$\Rightarrow \quad C_P = C_V + R$

$\dfrac{\Delta U}{f} = \dfrac{W}{2} = \dfrac{Q}{f+2}$ or $\dfrac{\Delta U}{1} = \dfrac{W}{\gamma - 1} = \dfrac{Q}{\gamma}$

Fraction of total heat converted to internal energy = $\dfrac{\Delta U}{Q} = \dfrac{1}{\gamma}$

Fraction of total heat converted to work is, $\dfrac{W}{Q} = \dfrac{\gamma - 1}{\gamma}$

(5) Isothermal process : Temperature is constant

$PV = K \Rightarrow dT = 0 \Rightarrow dU = 0,\ C = \infty$

as $PV = nRT$ (Constant)

So $P = \dfrac{nRT}{V}$

Work done in isothermal process

$$W = Q = nRT\log_e\left(\frac{V_2}{V_1}\right) = 2.303\ nRT\log_{10}\left(\frac{V_2}{V_1}\right) = 2.303\ nRT\log_{10}\left(\frac{P_1}{P_2}\right)$$

(6) Adiabatic process : Heat exchanged (Q) is zero

$PV^\gamma = K$ [Equation of adiabatic process]

As $Q = 0$, $nC\Delta T = 0$ or $C = 0$

Also, $0 = nC_V\Delta T + W$ [by first law of thermodynamics]

Now, $\boxed{W = -\Delta U}$ i.e. $W = -nC_V\Delta T = -\dfrac{nR}{\gamma - 1}(T_2 - T_1)$

(7) Polytropic Process

PV^x = Constant

$W = \dfrac{nR\Delta T}{1 - x}$

Molar heat capacity $\boxed{C = C_V + \dfrac{R}{1-x}}$

(8) Cyclic process : System returns to its initial state (P, V & T)

For the overall process $\Delta T = 0 \Rightarrow \Delta U = 0$

$\Rightarrow \quad \Delta Q = \Delta W$

(9) Adiabatic free expansion : It is sudden process, only initial and final states are defined.

For this process $\Delta Q = 0$, $\Delta T = 0$, $\Delta U = 0$, and $W = 0$

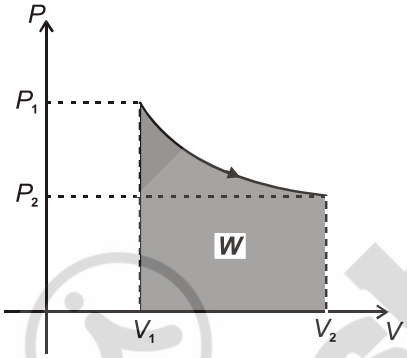
Indicator Diagram :

P-V graph of a process is called indicator diagram. Area under P-V graph represents the work done in a process.

Small work done, $dW = PdV$

Total work done, $W = \int dW = \int PdV$

= Area of curve ($P - V$) bounded with volume axis



CARNOT ENGINE

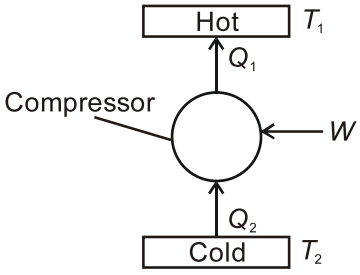
Heat supplied = Q_1

Heat rejected = Q_2 $\quad \Rightarrow \quad Q_1 - Q_2 = W$

% efficiency, $\eta = \dfrac{W}{Q_{supplied}} \times 100 = \dfrac{Q_1 - Q_2}{Q_1} \times 100\%$

If source temperature is T_1 and sink temperature is T_2, then

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



Refrigerator : In a refrigerator, W work is done on the working substance, Q_2 heat is absorbed from lower temperature T_2 and Q_1 heat is rejected to higher temperature T_1. ($T_1 > T_2$).

Coefficient of performance $\beta = \dfrac{\text{Heat extracted from cold reservoir}}{W_{total}} = \dfrac{Q_2}{Q_1 - Q_2}$

$$\Rightarrow \beta = \frac{T_2}{T_1 - T_2} = \frac{1-\eta}{\eta}$$

Heat pump :

Coefficient of performance (r) $= \dfrac{\text{Heat pumped to hot reservoir}}{\text{Total work}}$

$$r = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2}$$

$$r = \frac{T_1}{T_1 - T_2} = \frac{1}{\eta}$$

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