KINETIC THEORY OF GASES

It related 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 comparision 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. (ie., 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 :

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

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

Ideal gas equation

$$PV = \mu RT \Rightarrow P = \frac{\mu RT}{V} = \frac{\mu N_A kT}{V} = \left(\frac{N}{V}\right)kT = nkT$$

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 $V \propto T$

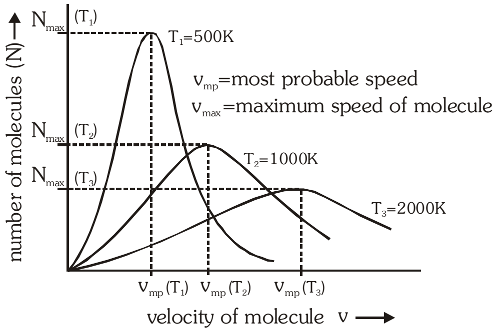
❒ **Gay–Lussac's law** For a given mass at constant volume $P \propto T$

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

Different speeds of molecules

$$v_{rms} = \sqrt{\frac{3RT}{M_W}} = \sqrt{\frac{3kT}{m}} \;;\; v_{mp} = \sqrt{\frac{2RT}{M_W}} = \sqrt{\frac{2kT}{m}}$$

$$v_{av} = \sqrt{\frac{8RT}{\pi M_W}} = \sqrt{\frac{8kT}{\pi m}}$$



Kinetic Interpretation of Temperature :

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

$$PV = \frac{1}{3}mNV_{rms}^2 \;\&\; PV = \mu RT \Rightarrow \frac{1}{2}mv_{rms}^2 = -kT$$

Degree of Freedom (F) :

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

At higher temperature, diatomic molecules have two more 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 $C = \frac{dQ}{\mu dT}$
- $C_V = \left(\frac{dQ}{\mu dT}\right)_{V=\text{constant}} = \frac{dU}{\mu dT}$
- $C_P = \left(\frac{dQ}{\mu dT}\right)_{dP=0} = C_V + R$ ← Mayer's equation

Atomicity	Translational	Rotational	Total (f)	$\gamma = \frac{C_P}{C_V}$	$C_V = \frac{f}{2}R$	$C_P=C_V+R$
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

For mixture of non-reacting gases

Molecular weight : $M_{W_{mix}} = \frac{\mu_1 M_{W_1} + \mu_2 M_{W_2} + \ldots.}{\mu_1 + \mu_2 + \ldots.}$

Specific heat at constant V: $C_{V_{mix}} = \frac{\mu_1 C_{V_1} + \mu_2 C_{V_2} + \ldots..}{\mu_1 + \mu_2 + \ldots.}$

Specific heat at constant P: $C_{P_{mix}} = \frac{\mu_1 C_{P_1} + \mu_2 C_{P_2} + \ldots...}{\mu_1 + \mu_2 + \ldots...}$

$$\gamma_{mix} = \frac{C_{P_{mix}}}{C_{V_{mix}}} = \frac{\mu_1 C_{P_1} + \mu_2 C_{P_2} + \ldots...}{\mu_1 C_{V_1} + \mu_2 C_{V_2} + \ldots..}$$

KEY POINTS

- Kinetic energy per unit volume

$$E_V = \frac{1}{2}\left(\frac{mN}{V}\right)v_{rms}^2 = \frac{3}{2}P$$

- 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 = 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
  - (d) Work done $= \Delta Q - \Delta U = \frac{nR}{1-x}dT$

    For any polytropic process PV^x = constant

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 (ΔQ) to a system is equal to algebraic sum of change in internal energy (ΔU) of the system and mechanical work (W) done by the system

  $\Delta Q = W + \Delta U$ [Here $W = \int PdV$; $\Delta U = nC_V\Delta T$]

  For differential change $\boxed{\underbrace{\delta Q = \delta W}_{\text{path dependent}} + \underbrace{dU}_{\text{path independent}}}$

  Area between P-V curve & V-axis gives work done by gas from one state to another state.
- **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** $\Delta U = 0 \Rightarrow \Delta Q = W$
- **For isochoric process**

  V = constant $\Rightarrow P \propto T$ & $W = 0$
  $\Delta Q = \Delta U = \mu C_V\Delta T$
  Isochoric $\Delta V = 0$ B = not defined.
  Bulc modulus
  Volume expansion coefficient = 0
- **For isobaric process**

  P = constant $\Rightarrow V \propto T$
  $\Delta Q = \mu C_P\Delta T$, $\Delta U = \mu C_V\Delta T$
  $W = P(V_2 - V_1) = \mu R\Delta T$
  Isobaric $\Delta P = 0$ Bulk modulus (B) = 0

  Volume Expansion coefficient = $\dfrac{1}{T}$

- **For adiabatic process** PV^{γ} = constant
  or $T^{\gamma}P^{1-\gamma}$ = constant
  or $TV^{\gamma-1}$ = constant
  In this process $\Delta Q = 0$ and

  $$W = -\Delta U = \mu C_V(T_1 - T_2) = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

  adiabatic Bulk modulus $B = -v\left(\dfrac{\partial P}{\partial v}\right)$

  $$B = \gamma P$$

  Volume Expansion coefficient = $\dfrac{1}{(1-\gamma)T}$

- **For Isothermal Process**

  T = constant or $\Delta T = 0 \Rightarrow PV$ = constant
  In this process $\Delta U = \mu C_V\Delta T = 0$

  So, $\Delta Q = W = \mu RT\,\ell n\left(\dfrac{V_2}{V_1}\right) = \mu RT\ell n\left(\dfrac{P_1}{P_2}\right)$

  Isothermal Bulk modulus $B = -v\left(\dfrac{\partial P}{\partial v}\right)_{T=\text{const}}$

  $B = -v\left(\dfrac{-P}{v}\right) = P$

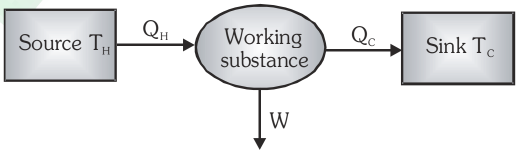
  $\Delta T = 0$
  Volume expansion coefficient not defined.
- **For any general polytropic process**

  PV^x = constant
  - Molar heat capacity $C = C_V + \dfrac{R}{1-x}$
  - 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 $\dfrac{dP}{dV} = -x\dfrac{P}{V}$)

  Polytropic Bulk modulus $B = xP$

Efficiency of a cycle



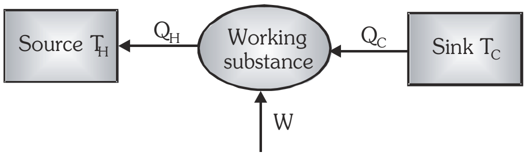
$$\eta = \frac{\text{Work done by working substance}}{\text{Heat supplied}}$$

$$= \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

For carnot cycle

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H} \text{ so } \eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

For refrigerator

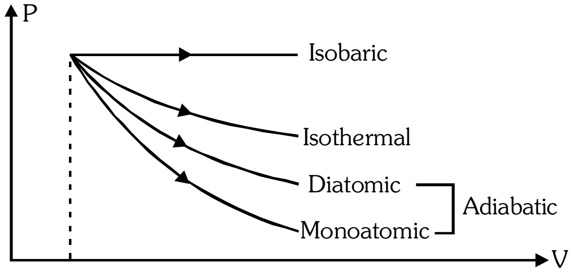


Coefficient of performance

$$\beta = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C} = \frac{T_C}{T_H - T_C}$$

KEY POINTS

Work done is least for monoatomic gas (adiabatic process) in shown expansion.



At a particular pressure and volume, magnitude of slope of P-V curve is greater for adiabatic $\left(\gamma\frac{P}{V}\right)$ then isothermal $\left(\frac{P}{V}\right)$

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.
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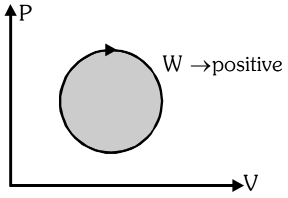

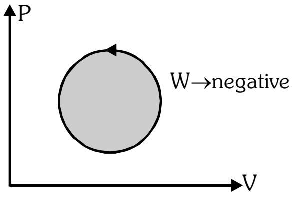

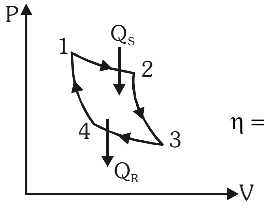

$$\eta = 1 - \frac{T_{3-4}}{T_{1-2}}$$

- **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.

Second Law :- First law is quantitative analysis while second law is qualitative analysis of thermodynamics processes. Second law tells us in what conditions best can be converted into useful work.

$$\boxed{ds = \frac{dQ}{T}}$$

ds → change in entropy, dθ → best exchanged.