Chapter

3 Kinetic Theory of Gases and Radiation

Quick Review

Ideal Gas

Boyle's Law
At constant Temperature, Volume is inversely proportional to Pressure.

Charles' Law
At constant Pressure, Volume is directly proportional to Temperature.

Gay-Lussac's Law
At constant Volume, Pressure is directly proportional to Temperature

Equation of state
Combining the three laws into a single relation for a fixed mass of gas yields ideal gas equation.

- $PV = nRT$
- $PV = Nk_BT$

As these quatities (P, V, T) describe the state of the gas, the equation relating them is known as *Equation of state.*

Kinetic Theorv of Gases

Mean Free Path
The average distance traversed by a molecule between two successive collisions
It varies:
- inversely with density ρ of the gas
- inversely with square of the diameter d of molecule

Pressure of the gas
Pressure exerted by gas is,
$$P = \frac{1}{3}\frac{MN}{V}\overline{v^2}$$

Kinetic energy
- In an ideal gas, the molecules are non-interacting, and hence there is no potential energy term. Thus, the internal energy of an ideal gas is purely kinetic.
- The average energy per molecule is proportional to the absolute temperature T of the gas.

R.M.S. Speed
Root mean squared value of speed
- It varies directly with the square root of the temperature of the gas.

Kinetic Energy

Law of equipartition of energy

- For a gas in thermal equilibrium at temperature T, the average energy for molecule associated with each quadratic term is $\frac{1}{2}k_BT$.
- **Translational K.E.:** $\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$
- **Rotational K.E.:** $\frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2 + \frac{1}{2}I\omega_z^2$
- **Vibrational K.E.:** $\frac{1}{2}mu^2 + \frac{1}{2}kr^2$

Degrees of Freedom

- The total number of coordinates or independent quantities required to describe the position and configuration of the system completely
- **Monoatomic Gas:** Translation dof : 3
- **Diatomic Gas:**
  Translation dof : 3
  Rotational dof : 2 or 3
  Vibrational dof : 0 or 2

Specific heat capacity

Mayer's Relation	Monoatomic Gas	Diatomic Gas (Rigid)	Diatomic Gas (non-rigid)	Polyatomic Gas
• $C_P - C_V = R$	• $C_P = \frac{5}{2}R$	• $C_P = \frac{7}{2}R$	• $C_P = \frac{9}{2}R$	• $C_P = (4 + f)R$
• $S_p - S_V = \frac{R}{M_0 J}$	• $C_V = \frac{3}{2}R$	• $C_V = \frac{5}{2}R$	• $C_V = \frac{7}{2}R$	• $C_V = (3 + f)R$
• $\frac{C_P}{C_V} = \gamma$	• $\gamma = \frac{5}{3}$	• $\gamma = \frac{7}{5}$	• $\gamma = \frac{9}{7}$	• $\gamma = \frac{(4+f)}{(3+f)}$

➢ Coefficients of absorption, reflection and transmission:

Coefficients	Definition	Formula	Relation
Absorptivity (a)	Ratio of heat absorbed to total heat incident on the surface of an object	$a = Q_a/Q$	$a + r + t_r = 1$
Reflectance (r)	Ratio of radiant energy reflected to the total energy incident on the surface of an object	$r = Q_r/Q$	
Transmittance (t_r)	Ratio of radiant energy transmitted to total energy incident on the surface of an object	$t_r = Q_t/Q$	

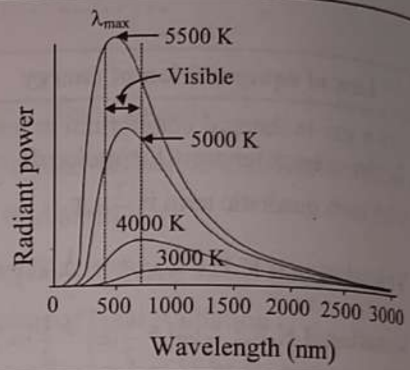
➢ Properties of Diathermanous and Athermanous Substances:

Substance	Type	Example
Diathermanous	Substances through which heat radiations can pass	Glass, Quartz, Sodium chloride, Hydrogen, Oxygen, Dry air, etc.
Athermanous	Substances which are largely opaque to thermal radiations	Water, Wood, Iron, Copper, Moist air, Benzene, etc.

➤ **Blackbody radiation:**

Perfect blackbody

- A body which absorbs the entire radiant energy incident on it.
- For perfect blackbody, a = 1
- In practice, Ferry's body is considered perfect blackbody as lampblack used in it absorbs 97% of incident energy.
- It appears black in light and glows in dark because good absorber is always a good emitter.



Prevost's theory of heat exchange	• All bodies at all temperatures above 0 K radiate thermal energy and at the same time, they absorb radiation received from surroundings.
Stefan-Boltzmann law	• The rate of emission of radiant energy per unit area or the power radiated per unit area of a perfect blackbody is directly proportional to the fourth power of its absolute temperature.
Kirchhoff's Law of radiation	• At a given temperature, the ratio of emissive power to coefficient of absorption of a body is equal to the emissive power of a perfect blackbody at the same temperature for all wavelengths
Wien's Displacement Law	• The wavelength, for which emissive power of a blackbody is maximum, is inversely proportional to the absolute temperature of the blackbody.

Formulae

1. Ideal gas equation:

i. $PV = nRT$

ii. $PV = Nk_BT$

where, $n = \dfrac{M}{M_0} = \dfrac{N}{N_A}$

2. Mean free path:

i. $\lambda = \dfrac{1}{\sqrt{2}\pi d^2\left(\dfrac{N}{V}\right)}$

ii. $\lambda = \dfrac{k_BT}{\sqrt{2}\pi d^2 P}$

3. Pressure exerted by gas:

$P = \dfrac{1}{3}\dfrac{N}{V}m\overline{v^2}$

4. Root mean square speed:

i. $v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\dfrac{3RT}{M_0}}$

ii. $v_{rms} = \sqrt{\dfrac{3P}{\rho}}$

iii. $v_{rms} = \sqrt{\dfrac{3}{2}k_BT}$

5. Average total energy:

$E_t = \dfrac{3}{2}Nk_BT = \dfrac{3}{2}PV$

6. Kinetic energy of gas molecule:

i. K.E of gas molecules $= \dfrac{3}{2}PV$

ii. K.E per unit mole $= \dfrac{3}{2}RT$

iii. K.E per unit mass $= \dfrac{3}{2}\dfrac{RT}{M_0}$

iv. K.E per molecule $= \dfrac{3}{2}k_BT$

7. Law of equipartition of energy:
Total energy,
$E = E_t + E_r + E_v$
Where E_t = Total translational K.E.
$= \left\langle \frac{1}{2}mv_x^2 \right\rangle + \left\langle \frac{1}{2}mv_y^2 \right\rangle + \left\langle \frac{1}{2}mv_z^2 \right\rangle = \frac{3}{2}k_BT$
E_r = Total rotational energy.
$= \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2$
....(considering all three rotational modes)
E_v = Total vibrational energy.
= K.E.(vibrational) + P.E. (vibrational)
$= \frac{1}{2}mu^2 + \frac{1}{2}kr^2$

8. Relation between molar specific heats:
i. $C_P - C_V = R$
When all quantities are expressed in same system of units.
ii. $\frac{C_P}{C_V} = \gamma$
When C_P, C_V are in heat units and R is in work unit.

9. Relation between principal specific heats:
$S_p - S_v = \frac{R}{M_0 J}$

10. Radiant energy incident on a surface:
$Q = Q_a + Q_r + Q_t$

11. Coefficient of radiation:
i. Coefficient of absorption, $a = \frac{Q_a}{Q}$
ii. Coefficient of reflection, $r = \frac{Q_r}{Q}$
iii. Coefficient of transmission,
$t_r = \frac{Q_t}{Q}$

12. Relation between a, r, and t_r:
$a + r + t_r = 1$

13. Coefficient of emission (Emissivity):
$e = \frac{R}{R_b} = a$

14. Emissive power/power radiated per unit area:
$R = \frac{Q}{At}$

15. Quantity of radiant heat emitted by a blackbody:
i. $Q = \sigma AT^4t$
When temperature of surrounding is not given
ii. $Q = \sigma A(T^4 - T_0^4)t$
When temperature of the surrounding is given

16. Radiant energy emitted by ordinary body:
i. $Q = eA\sigma T^4 t$
ii. $Q = eA\sigma(T^4 - T_0^4)t$

17. Rate of heat radiation:
$\frac{dQ}{dt} = eA\sigma(T^4 - T_0^4)$

18. Total radiant energy emitted from a body:
$Q = eAt\sigma(T^4 - T_0^4)$

19. Wien's law: $\lambda_{max} = \frac{b}{T}$

Shortcuts

1. Momentum imparted to the walls of the container of length l
$=$ Change in momentum × Frequency of collisions $= 2mu_1 \times \frac{u_1}{2l} = \frac{mu_1^2}{l}$

2. $S_p - S_v = r$ and $r = \frac{P}{\rho T}$
where, r = gas constant per unit mass of gas
P = pressure of gas
ρ = density of gas
T = absolute temperature of gas
This form of equation is true when all quantities are in the same system of units.

3. For any atom having f degrees of freedom (dof), the total internal energy is given as,
$E = \Delta U = \frac{f}{2}k_BT = \frac{f}{2}nRT$
Where, each dof contributes $\frac{1}{2}k_BT$ to the total internal energy.

4. Actually, γ is ratio of degree of freedoms and the real formula for γ is $\frac{f+2}{f}$, where f is number of degree of freedoms. $f = 3$ for monoatomic gas, 5 for diatomic gas and 6 for triatomic gas.

5. Whenever specific heat at constant volume is to be calculated, simply apply the formula, $C_v = \frac{R}{\gamma - 1}$ and to get C_p, just add R into it.

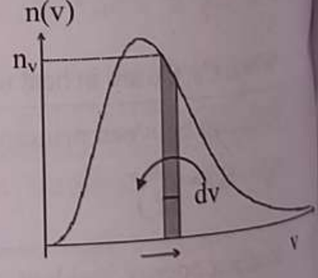
6. For any two bodies of radii R_1 and R_2, kept at temperatures T_1 and T_2, the power radiated or rate of loss of heat by them can be give as, $\frac{Q_1}{Q_2} = \left(\frac{R_1}{R_2}\right)^2 \times \left(\frac{T_1}{T_2}\right)^4$

   In case of non-spherical bodies, $\left(\frac{R_1}{R_2}\right)^2$ can be replaced by $\left(\frac{A_1}{A_2}\right)$ where A_1, A_2 are areas of the given bodies.

Mindbenders

7. The Maxwell speed distribution function gives us the number of molecules having speed between v and v + dv at a particular temperature.

   The peak of the curve however, does not mark average speed of gas but actually represents the most probable speed and not the average speed. Average speed is actually located more to the right of peak. This offset of average speed to the right of peak arises due to tails of graph being extended more towards right side than left.



   From Maxwell speed distribution function, we get,

   $v_{rms} = \sqrt{\frac{3k_BT}{m}}$; $v_{avg} = \sqrt{\frac{8k_BT}{\pi m}}$; $v_{mp} = \sqrt{\frac{2k_BT}{m}}$

   where, v_{mp} = most probable speed of gas molecules.

   At any particular temperature, we have,

   $v_{rms} > v_{avg} > v_{mp}$

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