HEAT AND THERMODYNAMICS (PART - II)

(KINETIC THEORY OF GAS & THERMODYNAMICS)

• ASSUMPTIONS OF KINETIC THEORY OF GASES

(i) A gas consists of a large number of identical, tiny spherical, neutral and elastic particles called molecules.

(ii) In a gas, molecules are moving in all possible directions with all possible speeds in accordance with Maxwell's distribution law.

(iii) The space occupied by the molecules is much smaller than the volume of the gas.

(iv) There is no force of attraction among the molecules.

(v) The pressure of a gas is due to elastic collision of gas molecules with the walls of the container.

(vi) The time of contact of a moving molecule with the walls of the container is negligible as compared to the time interval between two successive collisions.

PRESSURE EXERTED BY AN IDEAL GAS AND ROOT MEAN SQUARE SPEED

(i) Pressure P exerted by an ideal gas is given by

$$P = \frac{1}{3}\rho C^2 \qquad \Rightarrow P = \frac{mN}{3V}C^2$$

where C^2 is the mean square velocity , m, mass of each molecule and N, the total number of molecules in the vessel having volume V.

(ii) We define root mean square (rms) speed as

$$C = v_{rms} = \sqrt{\left(C^2\right)} = \sqrt{\frac{(v_1^2 + v_2^2 + ...)}{N}}$$

then equation (1) can be written as

$$v_{rms} = \sqrt{(3P/\rho)} \qquad \text{i.e. } v_{rms} \propto (1/\sqrt{\rho}) \text{ ; Hence } v_{rms} \text{ or rate of diffusion } \alpha \frac{1}{\sqrt{\rho}}$$

which is called Graham's Law of Diffusion

(iii) Also translational KE/volume $\quad E = \frac{1}{2}\frac{mN}{V}C^2 = \frac{1}{2}\rho C^2 = \frac{3}{2}P$

hence eq. (1) can be written as $\quad P = \frac{2}{3}\left(\frac{1}{2}\rho C^2\right) = \frac{2}{3}E$

i.e. Pressure of a gas is numerically equal to (2/3) of its K.E. per unit volume.

(iv) From eq. (1) $\quad PV = \frac{1}{3}mN(v_{rms})^2$

$$v_{rms} = \sqrt{\frac{3PV}{mN}} = \sqrt{\frac{3PV}{\text{total mass of gas}}}$$

(v) If M be the molecule weight of gas.

mass of gas = μM and $PV = \mu RT$

$$v_{rms} = \sqrt{\frac{3\mu RT}{\mu M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(N_A K)T}{N_A m}} = \sqrt{\frac{3KT}{m}}$$

- Most probable speed : It is the speed which maximum number of molecules in a gas have. For a gas of molecular weight M at temperature T is given by

$$v_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2}{3}}\,v_{rms} = 0.816\,v_{rms}$$

- Average speed : It is the arithmatic mean of the speed of molecules in a gas at a given temperature, i.e.

$$v_{av} = \frac{v_1 + v_2 + v_3 + \ldots\ldots v_n}{N}$$ and according to Kinetic theory of gases,

$$v_{av} = \sqrt{\frac{8RT}{\pi M}} = \left(\sqrt{\frac{8}{3\pi}}\right)v_{rms} = 0.92\,v_{rms}$$ It is thus, evident that $v_{rms} > v_{av} > v_{mp}$

Kinetic Interpretation of Temperature: Mean Kinetic Energy

According to kinetic theory of gases,

$$PV = \frac{1}{3}mNC^2 \quad \text{or} \quad PV = \mu RT$$

Translational KE of a molecule = $\frac{1}{2}mC^2 = \frac{3}{2}kT$

Further, mean kinetic energy per gm mole is given by

$$E_{mole} = \left(\frac{1}{2}mC^2\right)N_A = \frac{3}{2}kTN_A = \frac{3}{2}RT = \frac{3}{2}(PV) \Rightarrow \text{Energy per unit volume} = \frac{E_{mole}}{V} = \frac{3}{2}P$$

Note that, Average translational KE of a gas molecule depends only on its temperature and its independent of its nature i.e., molecules of different gases say He, H_2, and O_2 etc., at same temperature will have same translational kinetic energy though their rms speed are different.

Degrees of Freedom

(i) The term degrees of freedom of a system refers to the possible independent motions, a system can have or number of possible independent modes in which a system can have energy.

(ii) The independent motions of a system can be translational, rotational or vibrational or any combination of these.

(iv) If instead of particle, we consider a molecule of a monoatomic gas (like He, Ar, etc.), which consists of a single atom, the translational motion can take place in any direction in space i.e., it can be resolved along three co-ordinate axes and can have three independent motions and 3 degrees of freedom all translational. A monoatomic molecule can also rotate but due to its small moment of inertia, rotational KE is not significant. Therefore, it does not possess rotational degrees of freedom.

(v) The molecules of a diatomic gas such as (H_2, O_2 etc) are made of two atoms joined rigidly to one another through a bond. Not only this can move bodily, but also rotate about two of the three co-ordinate axes. However, its moment of inertia about the axis joining the two atoms is negligible compared to that about the other two axes. Hence, it can have only 2 rotational motions. Thus, a diatomic molecule has 5 degrees of freedom: 3 translational and 2 rotational. If vibration is effective then degree of freedom is 7.

Law of Equipartition of Energy

(i) According to law of equipartititon of energy, energy of a gas molecule is equally distributed among its various degrees of freedom and each degree of freedom is associated with energy $\frac{1}{2}KT$, where K is Boltzmann constant and T temperature of the gas in Kelvin.

(ii) According to equipartitition theorem, the mean internal energy of an ideal monoatomic gas molecule will be

(3/2)kT as it has 3 degrees of freedom. So energy per unit mole = $\left(\frac{3}{2}KT\right).\ N_A = \frac{3}{2}RT$

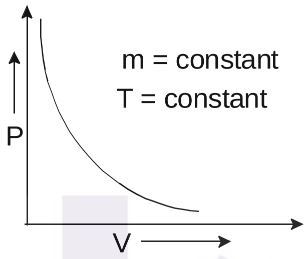
In general, the internal energy of μ moles of a gas in which each molecule has f degrees of freedom will be

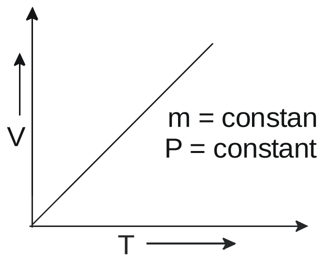
$\boxed{U = \frac{1}{2}\mu fRT}$ For example, for diatomic gas, $f = 5$, so $U = \frac{5}{2}\mu RT$

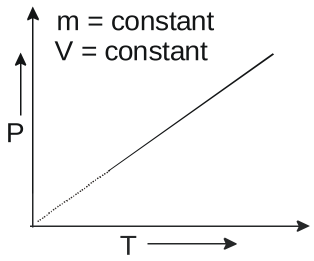
Gas-Laws

(i) Boyle's Law: According to it for a given mass of an ideal gas at constant temperature, the volume of a gas is inversely proportional to its pressure i.e.,

$V \propto \frac{1}{P}$ if mass of gas and T are constant ; Graphical forms of the law are as follows:







(ii) Charle's Law: According to it for a given mass of an ideal gas at constant pressure, volume of a gas its directly proportional to its absolute temperature i.e, $V \propto T$ if m and T = constant

(iii) Gay-Lussac's Law: According to it, for a given mass of an ideal gas at constant volume, pressure of a gas is directly proportional to its absolute temperature, i.e., $P \propto T$ if m and V = constant

(iv) Avogadro's Law: According to it, at same temperature and pressure equal volumes of all the gases contain equal number molecules, i.e., $N_1 = N_2$ if P, V and T are same

(v) Dalton's Law: According to it, the pressure exerted by a gaseous mixture is equal to the sum of partial pressure of each component present in the mixture, i.e., $P = P_1 + P_2 + ... P_n$

THERMODYNAMICS

(i) A system whose state is completely defined by the variables like pressure (P), volume (V), temperature (T) internal energy(U),is called thermodynamic system.

(ii) The variables P, V, T, U whose knowledge specifies the state of a thermodynamical system, are called as thermodynamic variables/parameters.

(iii) All the variables P, V, T, U are not independent as relations like $PV = \mu RT,\ U = (f/2)\mu RT,$ connecting these variables exist.

(iv) A P-V diagram for a system is called an indicator diagram. Each dot in a P-V diagram represents a possible state of the system.

(v) A curve drawn between two points on the indicator diagram shows a thermodynamic process obeying some rule.

(vi) The area under a curve on P-V diagram shows work done ON or BY the system.

(vii) Work done ON or BY a gas or system and heat exchange by a system depends upon both the initial state, final state and the path adopted between these two states.

(viii) Change in internal energy of a gas depends only upon initial and the final state but not on the path. It is a unique function of the point on the indicator diagram.So during isothermal process change in internal energy is zero.

Different Thermodynamical Processes

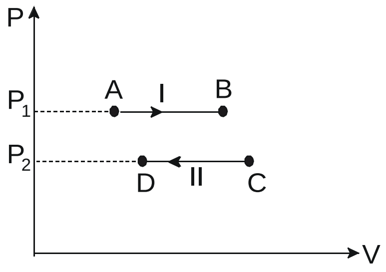
(i) Isobaric Process

(a) It is thermodynamic process in which pressure is kept constant. i.e. $\frac{V}{T} = \text{constant}$

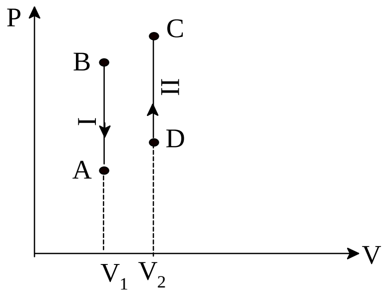
(b) The amount of heat energy transferred is given by $\Delta Q = \mu C_P \Delta T$ $(\mu = \text{number of moles})$

(c) In the adjoining figure, graphs I and II represent isobaric expansion and compression respectively.

Isobaric Process



Isochoric



ii) Isochoric (isometric) process

(a) It is thermodynamic process in which the volume of the system is kept constant i.e. (P/T) = constant.

(b) For increasing (decreasing) the pressure of a gas at constant volume, its temperature must be increased (decreased) by adding (taking out) heat energy into (from) the system.

(c) For isochoric process:

(d) In the adjoining figure, graphs I and II represents decrease in pressure at volume V_1 and isometric increase in pressure at volume V_2 respectively.

(iii) Isothermal Process

(a) It is a thermodynamic process in which the temperature of the system remains constant. (P.V = constant)

(b) During isothermal expansion of a gas, its volume increases while pressure decreases, while in isothermal compression, the volume decreases while pressure increases.

(c) The isothermal curve on P-V diagram is like a Hyperbola and the slope is given by: $\frac{dP}{dV} = -\left(\frac{P}{V}\right)$

(d) elasticity constant for isothermal process is B = P = Pressure

(iv) Adiabatic Process

(a) A process in which heat exchange between the system and the surroundings is zero ($PV^{\gamma} = \text{constant}$)

(b) The adiabatic curve on the PV diagram is shown in the figure. The slope of the curve at any point is given

by: $\frac{dP}{dV} = -\gamma\left(\frac{P}{V}\right)$ where $\gamma = \frac{C_P}{C_v}$ Hence $(\text{Slop})_{\text{Adiabatic}} = \gamma(\text{slope})_{\text{Isothermal}}$

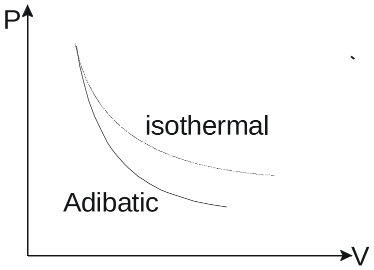
Slope of adiabatic curve is more in magnitude in comparison to the slope of the isothermal curve.

(e) Equation of state of the adiabatic process can be any of the following three types:

(i) $PV^{\gamma} = \text{constant}$

(ii) $TV^{\gamma-1} = \text{constant},$

(iii) $P^{1-\gamma}T^{\gamma} = \text{constant}$



(f) In adiabatic expansion, temperature decreases while in adiabatic compression, temperature increases.

(g) Isothermal and adiabatic Bulk modulus of a gas are given by $B_{\text{isothermal}} = P$ and $B_{\text{adiabatic}} = \gamma P$

Work done in Thermodynamic Process

(i) Total work done by a thermodynamic process in going from some initial state to final state is: $W = \int_{V_i}^{V_f} PdV$

This is equal to area under the curve on P-V diagram.

(ii) Work done by as gas during expansion is taken as positive (as is positive) while during compression it is taken as negative (as is negative).

(iii) Work done in various Thermodynamic processes

(a) Isobaric process: $W = P(V_f - V_1)$

(b) Isometric process: $W = O$ $(Q\,\Delta V = 0)$

(c) Isothermal process: $W = \mu RT\log_e\left(\frac{V_f}{V_i}\right) = \mu RT\log_e\left(\frac{P_i}{P_f}\right) = P_iV_i\log_e\left(\frac{V_f}{V_i}\right)$

(d) Adiabatic process: $W = \frac{P_iV_i - P_fV_f}{\gamma - 1} = \frac{\mu R(T_i - T_f)}{\gamma - 1} = \mu C_V(T_i - T_f)$ $\quad Q \quad C_V = \frac{R}{\gamma - 1}$

(e) Cyclic process: W = area enclosed in the cycle. This work done is positive when the cycle is traced out in clockwise direction and work is negative when the cycle is traced out in anti-clockwise direction.

Internal Energy of a Gas

In practice, we ignore potential energies of the molecules and neglect intermolecular forces. Thus, the total KE of all the molecules of the gas is equal to the internal energy of the gas. So, $U = \frac{f}{2}nRT$

Zeroth Law of Thermodynamics

When two bodies A and B are in thermal equilibrium with a third body C, then A and B are in thermal equilibrium mutually i.e, if $T_A = T_C$ and $T_B = T_C$, then $T_A = T_B$

First Law of Thermodynamics

(i) First law of thermodynamics is equivalent to law of conservation of energy.

(ii) According to this law, if heat ΔQ is added to a system then it will be used either as change in internal energy ΔU of the system and/or as work ΔW performed by the system i.e., $\Delta Q = \Delta U + \Delta W$

Specific Heats of a Gas

(i) Gases have infinite number of specific heats but two are mainly used,

(a) Specific heat of a gas at constant volume $(C_v) = \frac{(dQ)_v}{\mu dT}$; $dQ = \mu C_v dT = dU$ $(Q\, dW = PdV = 0)$

(b) Specific heat of a gas at constant pressure $(C_p) = \frac{(dQ)_p}{\mu dT}$; $dQ = \mu C_p dT = dU + dW = \mu C_v dT + nRdT$

hence $C_p = C_v + R$ $\Rightarrow$ $\boxed{C_p - C_v = R \text{ and } \frac{C_p}{C_v} = \gamma}$

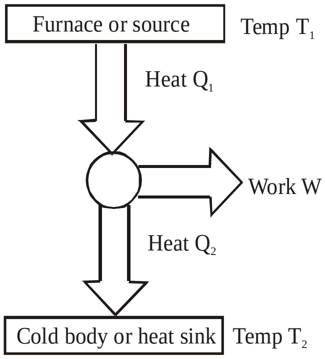
(ii) For any gas: $\gamma = 1 + (2/f) = \frac{f+2}{f}$ where f represents the degrees of freedom)

Second Law of Thermodynamics

(i) Kelvin’s statement: it is impossible for an engine operating in a cyclic process to extract heat from a reservoir and convert it completely into work.

(ii) Clausius statement: It is impossible for a self acting machine unaided by any external agency to transfer heat from a cold to hot reservoir i.e, heat by itself cannot pass from a colder to hotter body.

Heat Engine



(i) It is a device which converts heat into mechanical work continuously through a cyclic process.

(ii) In a heat engine working substance absorbs heat from the source at a higher temperature T_1 converts a part of it into useful work (motion of piston) and rejects the rest to the sink (usually atmosphere) at a lower temperature T_2 and comes back to its initial state (thus works in cyclic process).

(iii) Efficiency of a heat engine

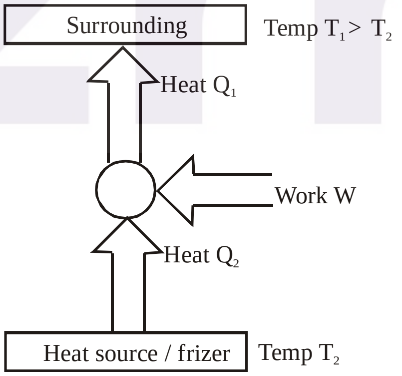
$$\eta = \frac{\text{work done}}{\text{heat absorbed}} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1};\ \text{as}\ \frac{Q_2}{Q_1} = \frac{T_2}{T_1} = \frac{T_{low}}{T_{High}}$$

(iv) A perfect heat engine is one which converts all heat into work i.e., $W = Q_1$ so that $Q_2 = 0$ and hence for it $\eta = 1$

Refrigerator or Heat Pump

(i) A refrigerator or heat pump is basically a heat engine running in reverse direction. In it working substances takes heat Q_2 from a body at lower temperature T_2 has a net amount of work done on it by an external agent (usually compressor) and gives out a larger amount of heat $Q_1 (= Q_2 + W)$ to a hot body at temperature T_1 (usually atmosphere).

(ii) A refrigerator or heat pump transfers heat from a cold to a hot body at the expense of mechanical energy supplied to it by an external agent. The working substance here is called Refrigerant and works in cyclic process.



(iii) The coefficient of performance of a refrigerator is defined as

$$\beta = \frac{\text{heat extracted from the reservoir at low temperature}\ T_2}{\text{Work done to transfer the heat}}$$

$$= \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} \Rightarrow \frac{1}{\beta} = \frac{Q_1}{Q_2} - 1 = \frac{1}{1-n} - 1$$

(iv) A perfect refrigerator is one which transfers heat from cold to hot body without doing any work i.e., W = 0 so that $Q_1 = Q_2$ and hence for it $\beta \to \infty$

Carnot Heat Engine

(i) Engine: It consists of four parts (a) A cylinder with perfectly insulating walls and a perfectly conducting base containing a perfect gas as working substance and fitted with a insulating frictionless piston; (b) A source of infinite thermal capacity maintained at a constant higher temperature T_H; (c) A sink of infinite thermal capacity maintained at constant lower temperature T_L and (d) A perfectly non-conducting stand for cylinder.

(ii) Carnot Cycle: It consist of four operations in succession: (a) isothermal expansion at higher temperature T_H (b) adiabatic expansion between temperatures T_H and T_L (c) isothermal compression at constant lower temperature T_L and (d) adiabatic compression between temperatures T_L and T_H.

(iii) Efficiency of the engine: $\eta = 1 - \dfrac{T_2}{T_1} = 1 - \dfrac{Q_2}{Q_1}$