CHAPTER-16 KINETIC THEORY OF GASES AND

KINETIC THEORY OF GASES :

Kinetic theory of gases is based on the following basic assumptions.

- (a) A gas consists of very large number of molecules. These molecules are identical, perfectly elastic and hard spheres. They are so small that the volume of molecules is negligible as compared with the volume of the gas.
- (b) Molecules do not have any preferred direction of motion, motion is completely random.
- (c) These molecules travel in straight lines and in free motion most of the time. The time of the collision between any two molecules is very small.
- (d) The collision between molecules and the wall of the container is perfectly elastic. It means kinetic energy is conserved in each collision.
- (e) The path travelled by a molecule between two collisions is called free path and the mean of this distance travelled by a molecule is called mean free path.
- (f) The motion of molecules is governed by Newton's law of motion
- (g) The effect of gravity on the motion of molecules is negligible.

EXPRESSION FOR THE PRESSURE OF A GAS:

Let us suppose that a gas is enclosed in a cubical box having length ℓ . Let there are 'N' identical molecules, each having mass 'm'. Since the molecules are of same mass and perfectly elastic, so their mutual collisions result in the interchange of velocities only. Only collisions with the walls of the container contribute to the pressure by the gas molecules. Let us focus on a molecule having velocity v_1 and components of velocity v_{x_1},v_{y_1},v_{z_1} along x, y and z-axis as shown in

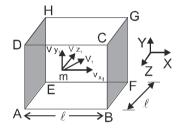


figure.

$$V_1{}^2 = V_{x_1}^2 + V_{y_1}^2 + V_{z_1}^2$$

The change in momentum of the molecule after one collision with wall BCGF

$$mv_{x_1} - (-mv_{x_1}) = 2 m v_{x_1}$$
.

The time taken between the successive impacts on the face BCGF = $\frac{\text{distance}}{\text{velocity}} = \frac{2\ell}{v_x}$

Rate of change of momentum due to collision =
$$\frac{\text{change in momentum}}{\text{time taken}} = \frac{2\text{mv}_{x_1}}{2\ell/v_{x_2}} = \frac{\text{mv}_{x_1}^2}{\ell}$$

Hence the net force on the wall BCGF due to the impact of n molecules of the gas is :

$$F_{x} = \frac{mv_{x_{1}}^{2}}{\ell} + \frac{mv_{x_{2}}^{2}}{\ell} + \frac{mv_{x_{3}}^{2}}{\ell} + \dots + \frac{mv_{x_{n}}^{2}}{\ell} = \frac{m}{\ell} \left(v_{x_{1}}^{2} + v_{x_{2}}^{2} + v_{x_{3}}^{2} + \dots + v_{x_{n}}^{2} \right) = \frac{mN}{\ell} < v_{x}^{2} > 0$$

where $\langle v_x^2 \rangle =$ mean square velocity in x-direction. Since molecules do not favour any particular direction therefore $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$. But $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$

$$\Rightarrow \langle v_x^2 \rangle = \frac{\langle v^2 \rangle}{3}$$
. Pressure is equal to force divided by area.

 $\mathsf{P}=\;\frac{\mathsf{F}_x}{\ell^2}=\frac{\mathsf{M}}{3\ell^3}< v^2>\;=\;\frac{\mathsf{M}}{3\mathsf{V}}< v^2>\;.\; \text{Pressure is independent of x, y, z directions.}$

Where $\ell^3 =$ volume of the container = V

M = total mass of the gas, $< v^2 > =$ mean square speed of molecules

$$\Rightarrow P = \frac{1}{3}\rho < V^2 >$$

As PV = n RT , then total translational K.E. of gas = $\frac{1}{2}$ M < v² > = $\frac{3}{2}$ PV = $\frac{3}{2}$ n RT

Translational kinetic energy of 1 molecule = $\frac{3}{2}$ kT (it is independent of nature of gas)

$$< v^2 > = \frac{3P}{\rho}$$
 or $v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3RT}{M_{mole}}} = \sqrt{\frac{3kT}{m}}$

Where v_{rms} is root mean square speed of the gas.

Pressure exerted by the gas is $P = \frac{1}{3} \rho \langle v^2 \rangle = \frac{2}{3} \times \frac{1}{2} \rho \langle v^2 \rangle$ or $P = \frac{2}{3} E$, $E = \frac{3}{2} P$. Thus, total, translational, kinetic energy, per unit volume (it is called energy density)

Thus total translational kinetic energy per unit volume (it is called energy density) of the gas is numerically equal to $\frac{3}{2}$ times the pressure exerted by the gas.

IMPORTANT POINTS :

(a)
$$v_{rms} \propto \sqrt{T}$$
 and $v_{rms} \propto \frac{1}{\sqrt{M_{mole}}}$

(b) At absolute zero, the motion of all molecules of the gas stops.

- (c) At higher temperature and low pressure or at higher temperature and low density, a real gas behaves as an ideal gas.
- (d) The mean free path ℓ is the average distance covered by a molecule between two successive collisions :

$$<\ell> = < v > \tau = \frac{1}{\sqrt{2} nd^2}$$

where n is the number density and d the diameter of the molecule.

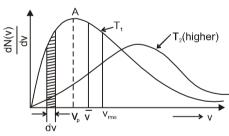
MAXWELL'S DISTRIBUTION LAW :

Distribution Curve – A plot of $\frac{dN(v)}{dv}$ (number of molecules per unit speed interval) against v is known as

Maxwell's distribution curve. The total area under the curve is given by the integral $\int_{0}^{\infty} \frac{dN(v)}{dv} dv = \int_{0}^{\infty} dN(v) = N$.

[Note : The actual formula of $\frac{dN(v)}{dv}$ is not in JEE syllabus.]

Figure shows the distribution curves for two different temperatures. At any temperature the number of molecules in a given speed interval dv is given by the area under the curve in that interval (shown shaded). This number increases, as the speed increases, upto a maximum and then decreases asymptotically towards zero. Thus, maximum number of the molecules have speed lying within a small range centered about the speed corresponding the peak (A) of the curve. This speed is called the 'most probable speed' v_p or v_{mp} .



The distribution curve is asymmetrical about its peak (the most probable speed v_p) because the lowest possible speed is zero, whereas there is no limit to the upper speed a molecule can attain. Therefore, the average speed \bar{v} is slightly larger than the most probable speed v_p . The root-mean-square speed, v_{rms} , is still larger ($v_{rms} > \bar{v} > v_p$).

Average (or Mean) Speed : $\overline{v} = \sqrt{\frac{8 \text{ kT}}{\pi \text{ m}}} = 1.59 \text{ }\sqrt{\text{kT/m}}$. (derivation is not in the course)

RMS Speed :
$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} = 1.73 \sqrt{\frac{kT}{m}}$$
.

Most Probable Speed : The most probable speed v_p or v_{mp} is the speed possessed by the maximum number of molecules, and corresponds to the maximum (peak) of the distribution curve. Mathematically, it is obtained by the condition.

 $\frac{dN(v)}{dv} = 0$ [by substitution of formula of dN(v) (which is not in the course)]

Hence the most probable speed is
$$v_p = \sqrt{\frac{2kT}{m}} = 1.41 \sqrt{kT/m}$$
.

From the above expression, we can see that $v_{rms} > \overline{v} > v_p$.

(a) Boyle's law

- (b) Charle's law
- (c) Avogadro's hypothesis
- (d) Graham's law of diffusion of gases
- (f) Dalton's Law of Partial Pressure
- (e) Regnault's or Gay Lussac's law(f)(g) Ideal Gas Equation or Equation of state

DEGREE OF FREEDOM :

Total number of independent co-ordinates which must be known to completely specify the position and configuration of dynamical system is known as "degree of freedom f". Maximum possible translational

degrees of freedom are three i.e. $\left(\frac{1}{2}\right)$

$$\left(\frac{1}{2}mv_{x}^{2}+\frac{1}{2}mv_{y}^{2}+\frac{1}{2}mv_{z}^{2}\right)$$

Maximum possible rotational degrees of freedom are three i.e. $\left(\frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2\right)$

Vibrational degrees of freedom are two i.e. (Kinetic energy of vibration and Potential energy of vibration) **Mono atomic :** (all inert gases Ex. He, Ar etc.) f = 3 (translational)

Diatomic : (gases like H_2 , N_2 , O_2 etc.)

f = 5 (3 translational + 2 rotational)

If temp < 70 K for diatomic molecules, then f = 3

If temp in between 250 K to 5000 K, then f = 5

If temp > 5000 K f = 7 [3 translational.+ 2 rotational + 2 vibrational]

MAXWELL'S LAW OF EQUIPARTITION OF ENERGY :

Energy associated with each degree of freedom = $\frac{1}{2}$ kT. If degree of freedom of a molecule is f, then

total kinetic energy of that molecule $U = \frac{1}{2} fkT$

INTERNAL ENERGY:

The internal energy of a system is the sum of kinetic and potential energies of the molecules of the system. It is denoted by U. Internal energy (U) of the system is the function of its absolute temperature (T) and its volume (V). i.e., U = f(T, V)

In case of an ideal gas, intermolecular force is zero. Hence its potential energy is also zero. In this case, the internal energy is only due to kinetic energy, which depends on the absolute temperature of

the gas. i.e. U = f (T). For an ideal gas internal energy U = $\frac{1}{2}$ nRT.

- **Example 1.** A light container having a diatomic gas enclosed within is moving with velocity V. Mass of the gas is M and number of moles is n.
 - (i) What is the kinetic energy of gas w.r.t. centre of mass of the system?
 - (ii) What is K.E. of gas w.r.t. ground?

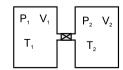
Solution :

(i) K.E. =
$$\frac{5}{2}$$
 nRT mass of gas = M
temperature T

(ii) Kinetic energy of gas w.r.t. ground = Kinetic energy of gas w.r.t. centre of mass + Kinetic energy of centre of mass w.r.t. ground.

K.E. =
$$\frac{1}{2}$$
 MV² + $\frac{5}{2}$ nRT

Example 2. Two non conducting containers having volume V_1 and V_2 contain mono atomic and diatomic gases respectively. They are connected as shown in figure. Pressure and temperature in the two containers are P_1 , T_1 and P_2 , T_2 respectively. Initially stop cock is closed, if the stop cock is opened find the final pressure and temperature.



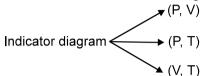
 $n_1 =$

$$\frac{P_1V_1}{RT_1} \quad n_2 = \frac{P_2V_2}{RT_2}$$

$$\begin{aligned} \frac{P(V_1 + V_2)}{RT} &= \frac{P_1V_1}{RT_1} + \frac{P_2V_2}{RT_2} \\ \text{From energy conservation } \frac{3}{2}n_1RT_1 + \frac{5}{2}n_2RT_2 &= \frac{3}{2}n_1RT + \frac{5}{2}n_2RT \\ \Rightarrow T &= \frac{(3P_1V_1 + 5P_2V_2)T_1T_2}{3P_1V_1T_2 + 5P_2V_2T_1} \Rightarrow P = \left(\frac{3P_1V_1 + 5P_2V_2}{3P_1V_1T_2 + 5P_2V_2T_1}\right) \left(\frac{P_1V_1T_2 + P_2V_2T_1}{V_1 + V_2}\right) \end{aligned}$$

INDICATOR DIAGRAM :

A graph representing the variation of pressure or variation of temperature or variation of volume with each other is called indicator diagram.



- (a) Every point of Indicator diagram represents a unique state (P, V, T) of gases.
- (b) Every curve on Indicator diagram represents a unique process.

THERMODYNAMICS

Thermodynamics is mainly the study of exchange of heat energy between bodies and conversion of the same into mechanical energy and vice-versa.

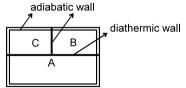
THERMODYNAMIC SYSTEM

Collection of an extremely large number of atoms or molecules confined within certain boundaries such that it has a certain value of pressure (P), volume (V) and temperature (T) is called a **thermodynamic system**. Anything outside the thermodynamic system to which energy or matter is exchanged is called its surroundings. Taking into consideration the interaction between a system and its surroundings thermodynamic system is divided into three classes :

- (a) **Open system :** A system is said to be an open system if it can exchange both energy and matter with its surroundings.
- (b) **Closed system :** A system is said to be closed system if it can exchange only energy (not matter with its surroundings).
- (c) **Isolated system :** A system is said to be isolated if it can neither exchange energy nor matter with its surroundings.

ZEROTH LAW OF THERMODYNAMICS :

If two systems (B and C) are separately in thermal equilibrium with a third one (A), then they themselves are in thermal equilibrium with each other.



EQUATION OF STATE (FOR AN IDEAL GASES) :

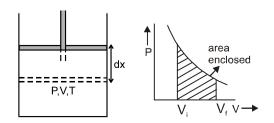
The relation between the thermodynamic variables (P, V, T) of the system is called equation of state. The equation of state for an ideal gas of n moles is given by

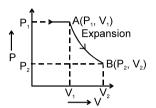
PV = nRT,

WORK DONE BY A GAS :

Let P and V be the pressure and volume of the gas. If A be the area of the piston, then force exerted by gas on the piston is, $F = P \times A$.

Let the piston move through a small distance dx during the expansion of the gas. Work done for a small displacement dx is dW = F dx = PA dx





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Since A dx = dV, increase in volume of the gas is dV

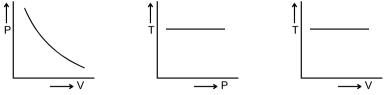
 \Rightarrow dW = P dV

or
$$W = \int dW = \int PdV$$

Area enclosed under P-V curve gives work done during process.

DIFFERENT TYPES OF PROCESSES :

(a) Isothermal Process : T = constant [Boyle's law applicable] PV = constant



There is exchange of heat between system and surroundings. System should be compressed or expanded very slowly so that there is sufficient time for exchange of heat to keep the temperature constant.

Slope of P–V curve in isothermal process:

$$PV = constant = C \implies \frac{dP}{dV} = -\frac{P}{V}$$

Work done in isothermal process:

W = nRT
$$\ell n \frac{V_f}{V_i}$$

- $\begin{bmatrix} If V_f > V_i & then W is positive \end{bmatrix}$
- If $V_f < V_i$ then W is negative

W =
$$\left[2.303 \text{ nRT } \log_{10} \frac{V_{f}}{V_{i}} \right]$$

Internal energy in isothermal process : U = f (T) $\Rightarrow \Delta U = 0$

(b) Iso- choric Process (Isometric Process) :

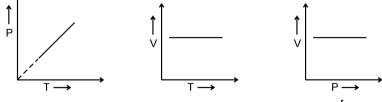
V = constant

 \Rightarrow change in volume is zero

$$\Rightarrow \frac{P}{T} \text{ is constant}$$
$$\frac{P}{T} = \text{const. (Gay lussac's law)}$$

Work done in isochoric process :

Since change in volume is zero therefore dW = P dV = 0Indicator diagram of isochoric process :



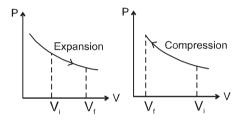
Change in internal energy in isochoric process : $\Delta U = n \frac{f}{2} R \Delta T$

Heat given in isochoric process : $\Delta Q = \Delta U = n \frac{f}{2} R \Delta T$

(c) Isobaric Process : Pressure remains constant in isobaric process

$$\therefore$$
 P = constant $\Rightarrow \frac{V}{T}$ = constant

Indicator diagram of isobaric process :



$$\begin{array}{c}
\uparrow \\
P \\
\hline \\
T \rightarrow \end{array}$$

$$\begin{array}{c}
\uparrow \\
P \\
\hline \\
V \rightarrow \end{array}$$

$$\begin{array}{c}
\uparrow \\
V \\
\hline \\
T \rightarrow (in \text{ Kelvin}) \end{array}$$

Work done in isobaric process : $\Delta W = P \Delta V = P (V_{final} - V_{initial}) = nR (T_{final} - T_{initial})$ Change in internal energy in isobaric process : $\Delta U = n C_V \Delta T$ Heat given in isobaric process : $\Delta Q = \Delta U + \Delta W$

$$\Delta Q = n \frac{f}{2} R \Delta T + P [V_f - V_i] = n \frac{f}{2} R \Delta T + n R \Delta T$$

Above expression gives an idea that to increase temperature by ΔT in isobaric process heat required is more than in isochoric process.

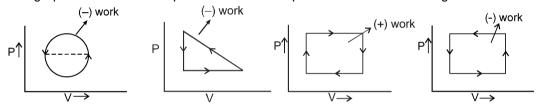
(d) Cyclic Process : In the cyclic process initial and final states are same therefore initial state = final state Work done = Area enclosed under P-V diagram.

Change in internal Energy $\Delta U = 0$

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

$$\therefore \Delta Q = \Delta W$$

If the process on P-V curve is clockwise, then net work done is (+ve) and vice-versa. The graphs shown below explains when work is positive and when it is negative



- **Example 3.** The cylinder shown in the figure has conducting walls and temperature of the surrounding is T, the piston is initially in equilibrium, the cylinder contains n moles of a gas. Now the piston is displaced slowly by an external agent to make the volume double of its initial value. Find work done by external agent in terms of n, R, T
- n moles
- Solution :1st Method : Work done by external agent is positive, because Fext and displacement are in the
same direction. Since walls are conducting therefore temperature remains constant.

Applying equilibrium condition when pressure of the gas is P

$$PA + F_{ext} = P_{atm} A$$

$$F_{ext} = P_{atm} A - PA$$

$$W_{ext} = \int_{0}^{d} F_{ext} dx$$

$$= \int_{0}^{d} P_{atm} A dx - \int_{0}^{d} P A dx = P_{atm} A \int_{0}^{d} dx - \int_{V}^{2V} \frac{nRT}{V} dV$$

$$= P_{atm} A d - nRT In2 = P_{atm} \cdot V_{0} - nRTIn2 = nRT (1 - In2)$$

$$2^{nd} Method : Applying work energy theorem on the piston$$

$$As W_{all} = \Delta K.E$$

$$\Delta K.E = 0 \quad (given)$$

$$W_{gas} + W_{atm} + W_{ext} = 0$$

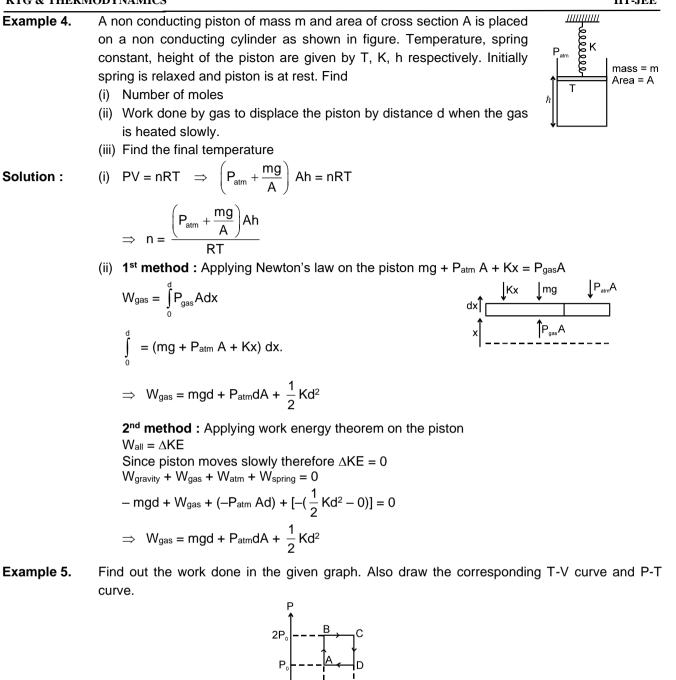
$$nRT ln \frac{V_{f}}{V_{i}} - nRT + W_{ext} = 0$$

PA→	$ \begin{array}{c} \leftarrow P_{atm} A \\ \hline \hline F_{ext} \end{array} $

 $W_{ext} = nRT (1 - ln2)$

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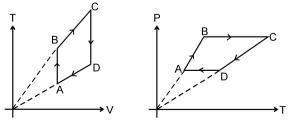
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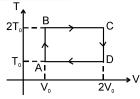
- Since in P-V curves area under the cycle is equal to work done therefore work done by the gas Solution : is equal to P₀ V₀.

Line A B and CD are isochoric line, line BC and DA are isobaric line.

:. the T-V curve and P-T curve are drawn as shown.



Example 6. T-V curve of cyclic process is shown below, number of moles of the gas are n find the total work done during the cycle.



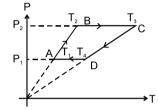
Solution : Since path AB and CD are isochoric therefore work done is zero during path AB and CD. Process BC and DA are isothermal, therefore

$$W_{BC} = nR2T_0 \ \ell n \ \frac{V_C}{V_B} = 2nRT_0 \ \ell n \ 2$$

$$W_{DA} = nRT_0 \ \ell n \ \frac{V_A}{V_D} = -nRT_0 \ \ell n \ 2$$

Total work done = W_{BC} + W_{DA} = $2nRT_0~\ell n~2 - nRT_0~\ell n~2$

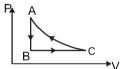
Example 7. P-T curve of a cyclic process is shown. Find out the work done by the gas in the given process if number of moles of the gas are n.



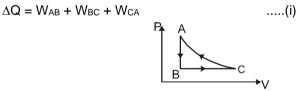
Solution : Since path AB and CD are isochoric therefore work done during AB and CD is zero. Path BC and DA are isobaric.

Hence $W_{BC} = nR\Delta T = nR(T_3 - T_2)$ $W_{DA} = nR(T_1 - T_4)$. Total work done = $W_{BC} + W_{DA} = nR(T_1 + T_3 - T_4 - T_2)$

Example 8. In figure, a cyclic process ABCA of 3 moles of an ideal gas is given. The temperatures of the gas at B and C are 500 K and 1000 K respectively. If the work done on the gas in process CA is 2500 J then find the net heat absorbed or released by an ideal gas. Take R = 25/3 J/mol–K.



Solution : The change in internal energy during the cyclic process is zero. Hence, the heat supplied to the gas is equal to the work done by it. Hence,



The work done during the process AB is zero

 $W_{BC} = P_B (V_C - V_B) = nR(T_C - T_B) = (3 \text{ mol}) (25/3 \text{ J/mol}-\text{K}) (500 \text{ K}) = 12500 \text{ J}$ As $W_{CA} = -2500 \text{ J} (given)$

∴ $\Delta Q = 0 + 12500 - 2500$ [from(i)] $\Delta Q = 10 \text{ kJ}$

FIRST LAW OF THERMODYNAMICS :

The first law of thermodynamics is the law of conservation of energy. It states that if a system absorbs heat dQ and as a result the internal energy of the system changes by dU and the system does a work dW, then dQ = dU + W. But, W = P dV

$$dQ = dU + P dV$$

which is the mathematical statement of first law of thermodynamics.



Heat gained by a system, work done by a system and increase in internal energy are taken as positive. Heat lost by a system, work done on a system and decrease in internal energy are taken as negative.

Example 9. 1 gm water at 100°C is heated to convert into steam at 100°C at 1 atm. Find out change in internal energy of water. It is given that volume of 1 gm water at 100° C = 1 cc, volume of 1 gm steam at 100° C = 1671 cc. Latent heat of vaporization = 540 cal/g. (Mechanical equivalent of heat J = 4.2J/cal.)

Solution :

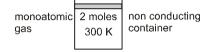
 $\Delta Q = mL = 1 \times 540$ cal. = 540 cal.

From first law of thermodynamic $\Delta Q = \Delta U + W$

W = P
$$\Delta$$
V = $\frac{10^{5}(1671-1)\times10^{-6}}{4.2}$ = $\frac{10^{5}\times(1670)\times10^{-6}}{4.2}$ = 40 cal.

 $\Delta U = 540 - 40 = 500$ cal.

Example 10. Two moles of a monoatomic gas at 300 K are kept in a non conducting container enclosed by a piston. Gas is now compressed to increase the temperature from 300 K to 400 K. Find work done by the gas ($R = \frac{25}{2}$ J/mol–K)



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

Since container is non conducting therefore $\Delta Q = 0 = \Delta U + W$

$$\Rightarrow W = -\Delta U = -n \frac{f}{2} R \Delta T = -2 \times \frac{3}{2} R (400 - 300) = -3 \times \frac{25}{3} \times 100 J = -2500 J$$

Example 11. In figure, a sample of an ideal gas is taken through the cyclic process abca. 800 J of work is done by the gas during process ab. If gas absorb no heat in process ab, rejects 100 J of heat during bc and absorb 500 J of heat during process ca. Then (a) find the internal energy of the gas at b and c if it is 1000 J at a. (b) Also calculate the work done by the gas during the part bc.

Solution : (a) In process $ab \Delta Q = \Delta U + W$ $0 = U_B - 100 + 800$

 $0 = U_B - 100 + 800$ $U_B = 200 \text{ J}$ for Cyclic process $\Delta Q = \Delta U + W$

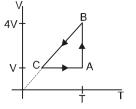
$$\begin{array}{l} 400 = 0 + 800 + W_{BC} \\ W_{BC} = -400 \ J \\ \text{for process bc} \ ; \ \Delta Q = \Delta U + W \\ -100 = -400 + U_{C} - 200 \\ \therefore \quad U_{C} = 500 \ J \end{array}$$

Example 12. Two moles of nitrogen gas is kept in a cylinder of cross-section area 10 cm². The cylinder is closed by a light frictionless piston. Now the gas is slowly heated such that the displacement of piston during process is 50 cm, find the rise in temperature of gas when 200 J of heat is added in it. (Atmospheric pressure = 100 kPa, R = 25/3 J/mol-K)

Solution :

ion : The change in internal energy of the gas is $\Delta U = 5/2 \text{ nR } (\Delta T) = 5/2 \times 2R \times (\Delta T) = 5R \times \Delta T$ The heat given to the gas = 200 J The work done by the gas is $W = \Delta Q - \Delta U = 200 \text{ J} - 5R \Delta T$ As the distance moved by the piston is 50 cm, \therefore the work done is $\Delta W = P\Delta V = PA\Delta x = 10^5 \times 10 \times 10^{-4} \times 50 \times 10^{-2}$(ii) From (i) and (ii) $\Delta T = 18/5 \text{ K} = 3.6 \text{ K}$

Example 13. An ideal gas initially has pressure P volume V and temperature T. It is isothermally expanded to four times of its original volume, then it is compressed at constant pressure to attain its original volume V. Finally, the gas is heated at constant volume to get the original temperature T. (a) Draw V-T curve (b) Calculate the total work done by the gas in the process. (given ℓn2 = 0.693)



Solution : (a) V-T curve for all process is shown in figure. The initial state is represented by the point A. In the first step, it is isothermally expanded to a volume 4V. This is shown by AB. Then the pressure is kept constant and the gas is compressed to the initial volume V. From the ideal gas equation, V/T is constant at constant pressure (PV = nRT). Hence, the process is shown by a line BC which passes through the origin. At point C, the volume is V. In the final step, the gas is heated at constant volume to a temperature T. This is shown by CA. The final state is the same as the initial state.

(b) Total work done by gas,
$$W_{Total} = W_{AB} + W_{BC} + W_{CA}$$

$$W_{AB} = nRT \ln \frac{4V}{V} = 2nRT \ln 2 = 2PV \ln 2.$$

Also $P_A V_A = P_B V_B$ (As AB is an isothermal process) or, $P_B = \frac{P_A V_A}{V} = \frac{PV}{4V} = \frac{P}{4V}$

In the step BC, the pressure remains constant. Hence the work done is,

$$W_{BC} = \frac{P}{4} (V - 4V) = -\frac{3PV}{4}$$

In the step CA, the volume remains constant and so the work done is zero. The net work done by the gas in the cyclic process is

$$W = W_{AB} + W_{BC} + W_{CA} = 2PV \ln 2 - \frac{3PV}{4} + 0$$

Hence, the work done by the gas 0.636 PV.

Example 14. A diatomic gas is heated at constant pressure. If 105 J of heat is given to the gas, find (a) the change in internal energy of the gas (b) the work done by the gas.

Solution : Suppose the volume changes from V_1 to V_2 and the temperature changes from T_1 to T_2 . The

heat supplied is $\Delta Q = \Delta U + P\Delta V = \Delta U + nR\Delta T = \Delta U + \frac{2\Delta U}{f} \left[\Delta U = \frac{nfR\Delta T}{2} \right]$

(a) The change in internal energy is $\Delta Q = \Delta U \left[1 + \frac{2}{f} \right]$

$$105 = \Delta U \left[1 + \frac{2}{5} \right], \ \Delta U = 75 \text{ J}$$

(b) The work done by the gas is $W = \Delta Q - \Delta U$ = 105 J - 75 J = 30 J.

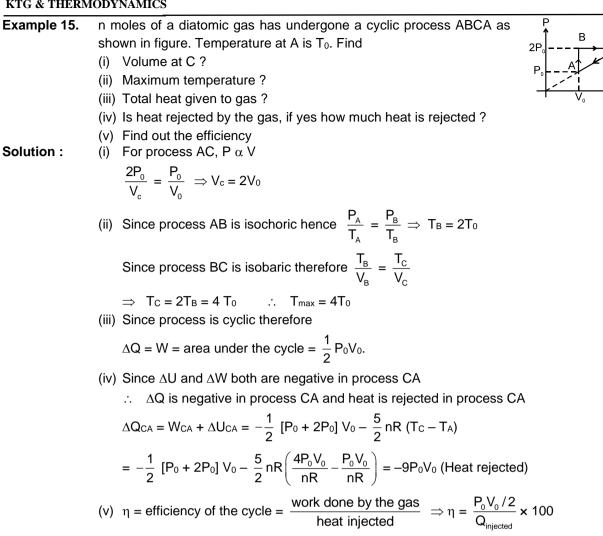
Efficiency of a cycle (η) :

Heat absorbed by the gas (only + ve)

area under the cycle in P-V curve

Heat injected into the system

$$\eta = \left(1 - \frac{Q_2}{Q_1}\right) \text{ for Heat Engine,}$$
$$\eta = \left(1 - \frac{T_2}{T_1}\right) \text{ for Carnot cycle}$$



$$\Delta Q_{inj} = \Delta Q_{AB} + \Delta Q_{BC}$$

$$= \left[\frac{5}{2}nR(2T_0 - T_0)\right] + \left[\frac{5}{2}nR(2T_0) + 2P_0(2V_0 - V_0)\right] = \frac{19}{2}P_0V_0.$$

$$\eta = \frac{100}{19}\%$$

SPECIFIC HEAT :

The specific heat capacity of a substance is defined as the heat supplied per unit mass of the substance per unit rise in the temperature. If an amount ΔQ of heat is given to a mass m of the substance and its temperature rises by ΔT , the specific heat capacity s is given by equation

$$s = \frac{\Delta Q}{m\Delta T}$$

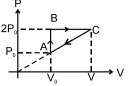
The molar heat capacity of a gas is defined as the heat given per mole of the gas per unit rise in the temperature. The molar heat capacity at constant volume, denoted by Cv, is :

$$C_v = \left(\frac{\Delta Q}{n \ \Delta T}\right)_{\text{constant volume}} \ = \ \frac{f}{2} \ R$$

and the molar heat capacity at constant pressure, denoted by C_p is,

$$C_{P} = \left(\frac{\Delta Q}{n \ \Delta T}\right)_{\text{constant pressure}} = \left(\frac{f}{2} + 1\right)R$$

where n is the amount of the gas in number of moles and f is degree of freedom. Quite often, the term specific heat capacity or specific heat is used for molar heat capacity. It is advised that the unit be carefully noted to determine the actual meaning. The unit of specific heat capacity is J/kg-K whereas that of molar heat capacity is J/mol-K.



MOLAR HEAT CAPACITY OF IDEAL GAS IN TERMS OF R :

(i) For a monoatomic gas f = 3

$$C_V = \frac{3}{2}R, \ C_P = \frac{5}{2}R \implies \gamma = \frac{C_P}{C_V} = \frac{5}{3} = 1.67$$

(ii) For a diatmoc gas f = 5

$$C_{V} = \frac{5}{2}R, C_{P} = \frac{7}{2}R, \gamma = \frac{C_{P}}{C_{V}} = 1.4$$

(iii) For a Triatomic gas f = 6 $C_{V} = 3R$, $C_{P} = 4R$

$$\gamma = \frac{C_{P}}{C_{V}} = \frac{4}{3} = 1.33$$
 [Note for CO₂; f = 5, it is linear]

In general if f is the degree of freedom of a molecule, then,

$$C_{V} = \frac{f}{2}R$$
, $C_{P} = \left(\frac{f}{2}+1\right)R$, $\gamma = \frac{C_{P}}{C_{V}} = \left\lfloor 1+\frac{2}{f} \right\rfloor$

Example 16. Two moles of a diatomic gas at 300 K are enclosed in a cylinder as shown in figure. Piston is light. Find out the heat given if the gas is slowly heated to 400 K in the following three cases.

- (i) Piston is free to move
- (ii) If piston does not move

(i) Since pressure is constant

- (iii) If piston is heavy and movable.
- Solution :

:
$$\Delta Q = nC_P \Delta T = 2 \times \frac{7}{2} \times R \times (400 - 300) = 700 R$$

(ii) Since volume is constant

 \therefore W = 0 and $\Delta Q = \Delta U$ (from first law)

$$\Delta Q = \Delta U = nC_V \Delta T = 2 \times \frac{5}{2} \times R \times (400 - 300) = 500 R$$

(iii) Since pressure is constant

:
$$\Delta Q = nC_P \Delta T = 2 \times \frac{7}{2} \times R \times (400 - 300) = 700 R$$

Example 17. P-V curve of a diatomic gas is shown in the figure. Find the total heat given to the gas in the process AB and BC

$$P_0$$
 B Diatomic
 P_0 C Isothermal
 V_0 $2V_0$ V

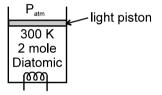
Solution : From first law of thermodynamics $\Delta Q_{ABC} = \Delta U_{ABC} + W_{ABC}$

$$\begin{split} W_{ABC} &= W_{AB} + W_{BC} = 0 + nR \ T_B \ In \ \frac{V_C}{V_B} = nR \ T_B \ In \ \frac{2V_0}{V_0} \\ &= nRT_B \ In \ 2 = 2P_0 \ V_0 \ In \ 2 \\ \Delta U &= nC_V \ \Delta T = \ \frac{5}{2} \ (2P_0V_0 - P_0V_0) \quad \Rightarrow \quad \Delta Q_{ABC} = \ \frac{5}{2} \ P_0V_0 + 2P_0V_0 \ In \ 2. \end{split}$$

Example 18. From given data, calculate the value of mechanical equivalent of heat. The specific heat capacity of air at constant volume 170 cal/kg-K, $\gamma = C_p/C_v = 1.4$ and the density of air at STP is 1.29 kg/m³. Gas constant R = 8.3 J/mol-K.

Solution : Using pV = nRT, the volume of 1 mole of air at STP is

$$V = \frac{nRT}{p} = \frac{(1 \text{ mol}) \times (8.3 \text{ J/mol} - \text{K}) \times (273 \text{ K})}{1.01 \times 10^5 \text{ N/m}^2} = 0.0224 \text{ m}^3.$$



The mass of 1 mole is, therefore, $(1.29 \text{ kg/m}^3) \times (0.0224 \text{ m}^3) = 0.029 \text{ kg}$.

The number of moles in 1 kg is $\frac{1}{0.029}$. The molar heat capacity at constant volume is

 $C_v = \frac{170 \text{ cal}}{(1/0.029) \text{ mol} - \text{K}} = 4.93 \text{ cal/mol-K}.$

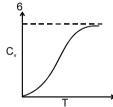
Hence, $C_p = \gamma C_v = 1.4 \times 4.93$ cal/mol-K or, $C_p - C_v = 0.4 \times 4.93$ cal/mol-K = 1.97 cal/mol-K. Also, $C_p - C_v = R = 8.3$ J/mol-K. Thus, 8.3 J = 1.97 cal.

The mechanical equivalent of heat is $\frac{8.3J}{1.97cal} = 4.2 \text{ J/cal}.$

Average Molar Specific Heat of Metals : [Dulong and Petit law]

At room temperature average molar specific heat of all metals are same and is nearly equal to 3R (6 cal. mol⁻¹ K⁻¹).

[Note : Temp. above which the metals have constant C_V is called Debye temp.]



MAYER'S EQUATION : $C_P - C_V = R$ (for ideal gases only)

Adiabatic process : When no heat is supplied or extracted from the system the process is called adiabatic. Process is sudden so that there is no time for exchange of heat. If walls of a container are thermally insulated no heat can cross the boundary of the system and process is adiabatic. Equation of adiabatic process is given by

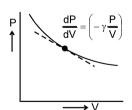
 $PV^{\gamma} = constant$ [Poisson Law]

 $T^{\gamma} P^{1-\gamma} = constant$

T V^{γ -1} = constant

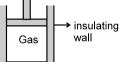
Slope of P–V–curve in adiabatic process : Since PV^{γ} is a constant

 $\therefore \quad \frac{dP}{dV} = -\gamma \left(\frac{P}{V}\right)$

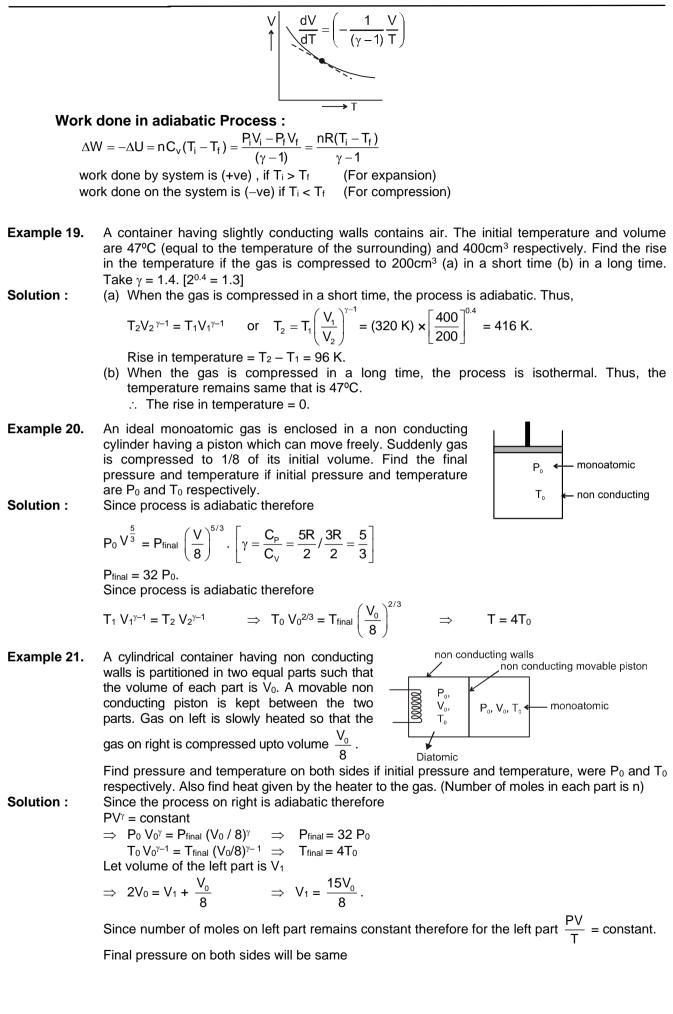


Slope of P–T–curve in adiabatic process : Since T $^{\gamma}$ P^{1- γ} is a constant

Slope of T–V–curve : $\frac{dV}{dT} = -\frac{1}{(\gamma - 1)} \frac{V}{T}$



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$$\Rightarrow \frac{P_0 V_0}{T_0} = \frac{P_{\text{final}} V_1}{T_{\text{final}}} \Rightarrow T_{\text{final}} = 60 \text{ T}_0$$

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

$$\Delta Q = n \frac{5R}{2} (60T_0 - T_0) + n \frac{3R}{2} (4T_0 - T_0)$$

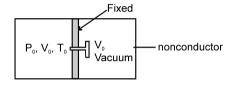
$$\Delta Q = \frac{5nR}{2} \times 59T_0 + \frac{3nR}{2} \times 3T_0 = 152 \text{ nRT}_0$$

FREE EXPANSION

If a system, say a gas expands in such a way that no heat enters or leaves the system and also no work is done by or on the system, then the expansion is called the "free expansion".

 $\Delta Q = 0$, $\Delta U = 0$ and $\Delta W = 0$. Temperature in the free expansion remains constant.

Example 22. A non conducting cylinder having volume $2V_0$ is partitioned by a fixed non conducting wall in two equal parts. Partition is attached with a valve. Right side of the partition is a vacuum and left part is filled with a gas having pressure and temperature P_0 and T_0 respectively. If valve is opened find the final pressure and temperature of the two parts.



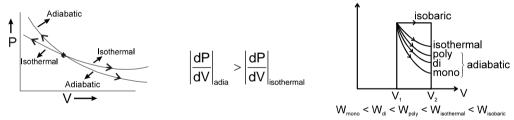
Solution : From the first law thermodynamics $\Delta Q = \Delta U + W$

Since gas expands freely therefore W = 0, since no heat is given to gas $\Delta Q = 0$

$$\Rightarrow \Delta U = 0 \text{ and temperature remains constant.} T_{final} = T_0$$

Since the process is isothermal therefore $P_0 \times V_0 = P_{\text{final}} \times 2V_0 \implies P_{\text{final}} = P_0/2$

Comparison of slopes of an Iso-thermal and Adiabatic Curve



In compression up to same final volume: | W_{adia} |> | W_{isothermal} | In Expansion up to same final volume: W_{isothermal} > W_{adia}

Limitations of Ist Law of Thermodynamics :

The first law of thermodynamics tells us that heat and mechanical work are interconvertible. However, this law fails to explain the following points :

- (i) It does not tell us about the direction of transfer of heat.
- (ii) It does not tell us about the conditions under which heat energy is converted into work.

(iii) It does not tell us whether some process is possible or not.

Mixture of non-reacting gases :

(a) Molecular weight = $\frac{n_1M_1 + n_2M_2}{n_1 + n_2}$, M₁ & M₂ are molar masses.

(b) Specific heat
$$C_V = \frac{n_1 C_{V_1} + n_2 C_{V_2}}{n_1 + n_2}$$
, $C_P = \frac{n_1 C_{P_1} + n_2 C_{P_2}}{n_1 + n_2}$

(c) for mixture,
$$\gamma = \frac{C_{p_{mix}}}{C_{v_{mix}}} = \frac{n_1 C_{p_1} + n_2 C_{p_2} + \dots}{n_1 C_{v_1} + n_2 C_{v_2} + \dots}$$

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Problem 1.	A vessel of volume 2 x 10^{-2} m ³ contains a mixture of hydrogen and helium at 47° C temperature	
	and 4.15 x 10 ⁵ N/m ² pressure. The mass of the mixture is 10 ⁻² kg. Calculate the masses of	
	hydrogen and helium in the given mixture.	
Solution :	Let mass of H_2 is m_1 and He is m_2	
	$\therefore m_1 + m_2 = 10^{-2} \text{ kg} = 10 \times 10^{-3} \text{ kg} \qquad \dots \dots (1)$	
	Let P_1 , P_2 are partial pressure of H_2 and H_2	
	$P_1 + P_2 = 4.15 \times 10^5 \text{ N/m}^2$	
	for the mixture (P ₁ + P ₂) V = $\left(\frac{m_1}{M_1} + \frac{m_2}{M_2}\right)$ RT	
	$\Rightarrow 4.15 \times 10^5 \times 2 \times 10^{-2} = \left(\frac{m_1}{2 \times 10^{-3}} + \frac{m_2}{4 \times 10^{-3}}\right) 8.31 \times 320$	
	$\Rightarrow \frac{m_1}{2} + \frac{m_2}{4} = \frac{4.15 \times 2}{8.31 \times 320} = 0.00312 = 3.12 \times 10^{-3}$	
	$\Rightarrow 2m_1 + m_2 = 12.48 \times 10^{-3} \text{ kg}$ (2)	
	Solving (1) and (2)	
	$m_1 = 2.48 \times 10^{-3} \text{ kg}, \ 2.5 \times 10^{-3} \text{ kg}$	
	and $m_2 = 7.5 \times 10^{-3} \text{ kg}.$	
Problem 2.	The pressure in a monoatomic gas increases linearly from 4×10^5 N m ⁻² to 8×10^5 N m ⁻² when its volume increases from 0.2 m ³ to 0.5 m ³ . Calculate the following:	
	(a) work done by the gas. (b) increase in the internal energy.	
Solution :	(a) As here pressure is varying linearly with volume,	
	work done by the gas	
	$W = \int PdV = area under P-V curve$	
	$W = P_{I} \left(V_{F} - V_{I} \right) + \frac{1}{2} \left(P_{F} - P_{I} \right) \times \left(V_{F} - V_{I} \right) \qquad P_{I} = P_{I} \left(P_{F} - P_{I} \right) + \frac{1}{2} \left(P_{F} - P_{I} \right) + \frac{1}$	
	i.e., W = 4 × 10 ⁵ × 0.3 + $\frac{1}{2}$ × 4 × 10 ⁵ × 0.3	
	i.e., $W = 1.8 \times 10^5 \text{ J}$ $V_{_{\rm F}}$	
	(b) The change in internal energy of a gas is given by	
	$\Delta U = nC_V \Delta T = \frac{nR\Delta T}{(\gamma - 1)} = \frac{(P_F V_F - P_1 V_1)}{(\gamma - 1)}$	
	As the gas is monoatomic $\gamma = (5/3)$	
	So, $\Delta U = \frac{10^5 (8 \times 0.5 - 4 \times 0.2)}{[(5/3) - 1]} = \frac{3}{2} \times 10^5 (4 - 0.8).$	
	i.e., $\Delta U = 4.8 \times 10^5 \text{ J}$	
Problem 3.	There are two vessels. Each of them contains one mole of a monoatomic ideal gas. Initial	
	volume of the gas in each vessel is $8.3 \times 10^{-3} \text{ m}^3$ at 27° C. Equal amount of heat is supplied to each vessel. In one of the vessels, the volume of the gas is doubled without change in its internal energy, whereas the volume of the gas is held constant in the second vessel. The vessels are now connected to allow free mixing of the gas. Find the final temperature and	
	pressure of the combined gas system.	
Solution :	According to 1st law of thermodynamics, $\Delta Q = \Delta U + W$	
	So for the vessel for which internal energy (and hence, temperature) remains constant.	
	$\Delta Q_1 = W = nRT \log_e (V_F/V_I)$	

$$\Delta Q_1 = 1 \times R \times 300 \log_e(2) = 0.693 \times 300 R = 207.9 R$$

and for the vessel for which volume is kept constant.

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 $\Delta Q_2 = \Delta U = nC_V \Delta T$ [as W = 0] i.e., $\Delta Q_1 = 1(3/2)R \Delta T$ According to given problem $\Delta Q_1 = \Delta Q_2$ i.e., $207.9R = (3/2)R\Delta T$, i.e. $\Delta T = 138.6$ i.e., $T_F - T_I = 138.6$ $T_{I} = 300 \text{ K}$ with So, T_F = 300 + 138.6 = **438.6 K** Now when the free mixing of gases is allowed $U_1 + U_2 = U$ $n_1(C_V)_1T_1 + n_2(C_V)_2T_2 = nC_VT$ with $n = n_1 + n_2$ Here $n_1 = n_2 = 1$ and $(C_V)_1 = (C_V)_2 = C_V$ So 1 × 300 + 1 × 438.6 = 2T, i.e., T = 369.3 K Further for the mixture from PV = nRT with V = V + 2V = 3V and n = $n_1 + n_2 = 2$, we have $\mathsf{P} = \frac{\mathsf{n}\mathsf{R}\mathsf{T}}{\mathsf{3}\mathsf{V}} = \frac{2 \times 8.3 \times 369.3}{3 \times 8.3 \times 10^{-3}} = 2.462 \times 10^5 \,\mathsf{N/m^2}$

Problem 4.

A gaseous mixture enclosed in a vessel of volume V consists of one gram mole of a gas A with $\gamma = \frac{C_p}{C} = \frac{5}{3}$ and another gas B with $\gamma = \frac{7}{5}$ at a certain temperature T. The gram molecular

weights of the gases A and B are 4 and 32 respectively. The gases A and B do not react with each other and are assumed to be ideal. The gaseous mixture follows the equation; $PV^{19/13}$ = constant in adiabatic processes.

- (a) Find the number of gram moles of the gas B in the gaseous mixture.
- (b) Compute the speed of sound in the gaseous mixture at T = 300 K.
- (c) If T is raised by 1 K from 300 K, find the percentage change in the speed of sound in the gaseous mixture.

Solution :

(a) As for ideal gas $C_P - C_V = R$ and $\gamma = (C_P/C_V)$,

So
$$\gamma - 1 = \frac{R}{C_{\gamma}}$$
 or $C_{V} = \frac{R}{(\gamma - 1)}$
 $\therefore \quad (C_{V})_{1} = \frac{R}{(5/3) - 1} = \frac{3}{2}R$; $(C_{V})_{2} = \frac{R}{(7/5) - 1} = \frac{5}{2}R$

and $(C_V)_{mix} = \frac{R}{(19/13) - 1} = \frac{13}{6}R$

Now from conservation of energy, i.e., $\Delta U = \Delta U_1 + \Delta U_2$,

$$(n_{1} + n_{2}) (C_{V})_{mix} \Delta T = [n_{1}(C_{V})_{1} + n_{2}(C_{V})_{2}]\Delta T$$

i.e., $(C_{V})_{mix} = \frac{n_{1}(C_{V})_{1} + n_{2}(C_{V})_{2}}{n_{1} + n_{2}}$
We have $\frac{13}{6}R = \frac{1 \times \frac{3}{2}R + n \times \frac{5}{2}R}{1 + n} = \frac{(3 + 5n)}{2(1 + n)}$

or, 13 + 13n = 9 + 15n, n = 2 mole.

(b) Molecular weight of the mixture will be given by

$$M = \frac{n_A M_A + n_B M_B}{n_A + n_B} = \frac{(1)(4) + 2(32)}{1+2}$$
$$M = 22.67$$

Speed of sound in a gas is given by

$$v = \sqrt{\frac{\gamma RT}{M}}$$

Therefore, in the mixture of the gas

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$$v = \sqrt{\frac{(19/13)(8.31)(300)}{22.67 \times 10^{-3}}} m/s$$

$$v \approx 401 m/s$$
(c) $v \propto \sqrt{T}$
or $v = KT^{1/2}$ (2)
$$\Rightarrow \frac{dv}{dT} = \frac{1}{2}KT^{-1/2} \Rightarrow dv = K\left(\frac{dT}{2\sqrt{T}}\right)$$

$$\Rightarrow \frac{dv}{v} = \frac{K}{v}\left(\frac{dT}{2\sqrt{T}}\right) \Rightarrow \frac{dv}{v} = \frac{1}{\sqrt{T}}\left(\frac{dT}{2\sqrt{T}}\right) = \frac{1}{2}\left(\frac{dT}{T}\right)$$

$$\Rightarrow \frac{dv}{v} \times 100 = \frac{1}{2}\left(\frac{dT}{T}\right) \times 100 = \frac{1}{2}\left(\frac{1}{300}\right) \times 100 = 0.167 = \frac{1}{6}$$

Therefore, percentage change in speed is 0.167%.