

Kinetic Theory Of Gases

An ideal gas is collection of small, hard, randomly moving atoms that occasionally collide and bounce off each other but otherwise do not interact. Never the less, gases if two condition are met:

1. The density is low (i.e., the atoms occupy a volume much smaller than of the container), and
2. The temperature is well above the condensation point.

If the density gets too high, or the temperature too low, then the attractive forces between the atoms came interaction. These are the forces that are responsible under the right conditions, for the gas condensing into a liquid.

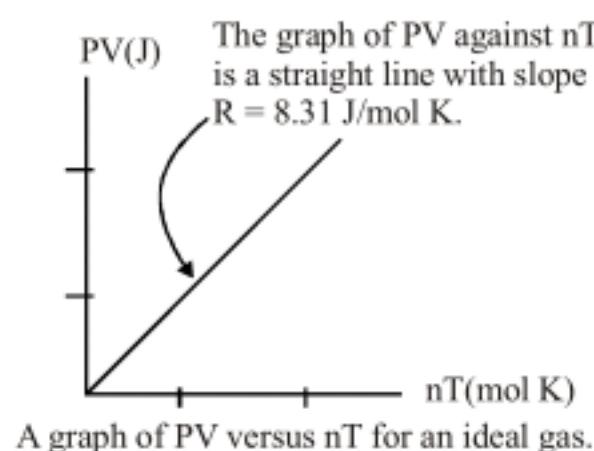


The Ideal-Gas Law

Experiments shown that there is a specific relationship between the state variables. (P, V, T)

There is a very clear proportionality between the quantity PV and the quantity nT. If we designate the slope of the line in this graph as R, then we can write relationship as

$$PV = R \times (nT)$$



It is customary to write the relationship in a slightly different form, namely

$$PV = nRT \quad (\text{ideal-gas law}) \quad \dots(i)$$

equation (i) is ideal gas law.

The constant R, which determined experimentally as the slope of the graph in figure is called the universal gas constant. Its value in SI units, is

$$R = 8.31 \text{ J-mol K}$$

If the gas is initially in state i, characterizes buy the state variables P_i , V_i and T_i and at some later time in a final in a final state f, the state variables for these two states are related by

$$\frac{P_f V_f}{T_f} = \frac{P_i V_i}{T_i} \quad (\text{ideal gas in a scaled container})$$

The mathematical relation between the state variables of a system is called the equation of state. Ideal gas will always follow ideal gas equation.

Symbols and constants :

P = Pressure of gas ; V = Volume of gas ; T = Temperature of gas
 n = no. of moles ; M = mol. wt. of gas ; m_0 = mass of each atom or molecule
 N = total no. of molecule ; N_0 = Avogadro no.
 K = Boltzmann gas constant = $1.38 \times 10^{-23} \text{ JK}^{-1}$
 R = Universal gas constant
 μ = Specific gas constant = $\frac{R}{M}$; m = mass of gas



Different forms of Ideal gas of equation

(a) $PV = nRT$

(b) $P = \frac{d RT}{M}$ (d is density of gas)

(c) $PV = NKT$ (per molecule)

(d) $PV = m\mu T$

* $n = \frac{m}{M} = \frac{N}{N_0}$

* $M = m_0 N_0$

* $K = \frac{R}{N_0}$

If mass of the gas is not constant then we can use

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2} = R \text{ (Universal gas constant)}$$

Illustration :

Two closed vessels of equal volume contain air at P_0 pressure, T_0 temperature and are connected through a narrow tube. If one of the vessels is now maintained at T_0 and other at T , what will be the pressure in the vessels?

Sol. Lets say volume of each vessel be V_0
 lets say initially n moles where present in each vessel

$$n = \frac{P_0 V_0}{R T_0}$$

$$\text{thus total no. of moles in the system} = \frac{2P_0 V_0}{R T_0}$$

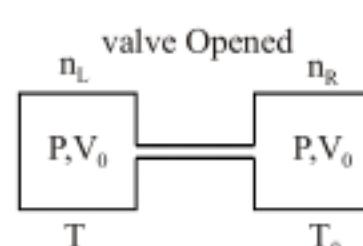
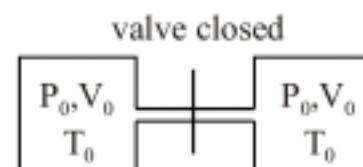
Finally lets say n_L moles where present in left vessel and n_R moles where present in right vessel.

$$n_L = \frac{P V_0}{R T} \quad \& \quad n_R = \frac{P V_0}{R T_0}$$

here P is the pressure in vessel

$$n_L + n_R = 2n \quad (\text{no. of moles is constant})$$

$$\frac{P V_0}{R T} + \frac{P V_0}{R T_0} = \frac{2P_0 V_0}{R T_0}$$



$$P = \frac{2P_0}{T_0 \left(\frac{1}{T} + \frac{1}{T_0} \right)}$$

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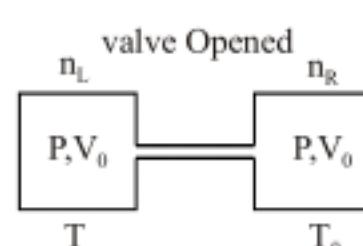
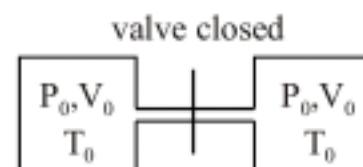
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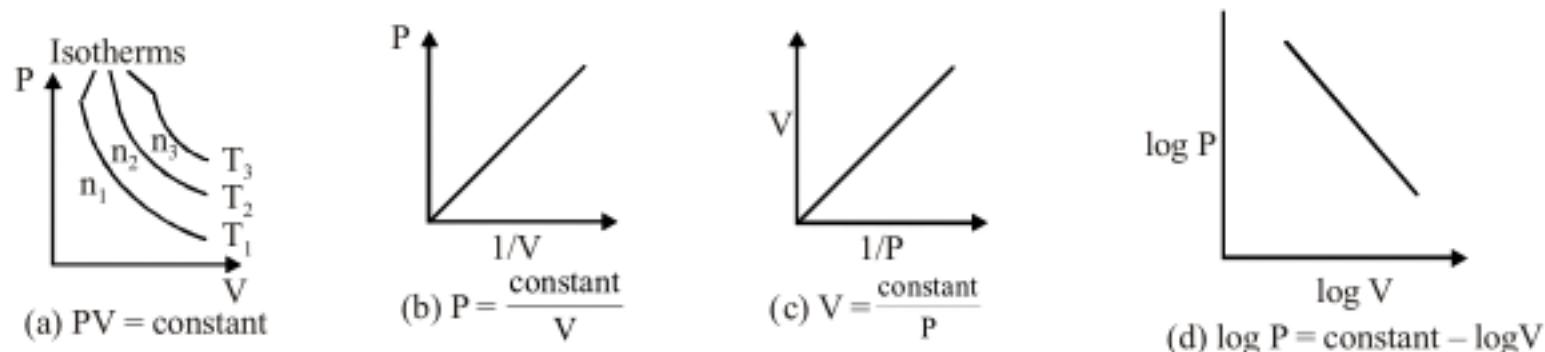
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$$P = \frac{2P_0}{T_0 \left(\frac{1}{T} + \frac{1}{T_0} \right)}$$

Boyle's Law : Relation Between Pressure and volume of a Gas

At constant temperature, volume of a fixed mass of a gas is inversely proportional to its pressure.



$$V \propto \frac{1}{P}$$

$$PV = \text{constant}$$

$$P_1 V_1 = P_2 V_2 \quad (\text{T, n are constant})$$

Charles' Law: Relation Between Temperature and volume of a Gas

When a gas is heated at constant pressure, its volume is a linear function of the temperature and can be expressed by the equation for a straight line

$$V = mt + C$$

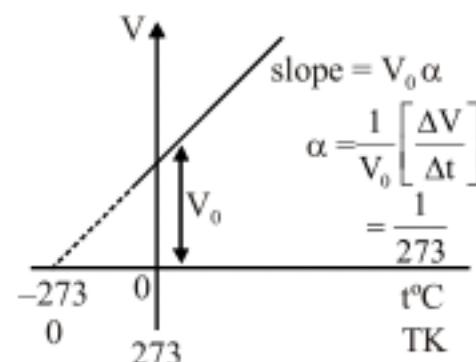
Where t is the temperature in $^{\circ}\text{C}$ and m and C are constants. The intercept on the vertical axis, C , is V_0 which is the volume at $t = 0^{\circ}\text{C}$. The slope of the line is $m = \frac{\Delta V}{\Delta t}$

Thus

$$V_t = V_0 + \left(\frac{\Delta V}{\Delta t} \right) t \quad (\text{n, p are constant})$$

$\frac{\Delta V}{\Delta t}$ = increase in volume per degree

$$\alpha = \frac{1}{V_0} \frac{\Delta V}{\Delta t} = \text{relative increase in volume per degree}$$

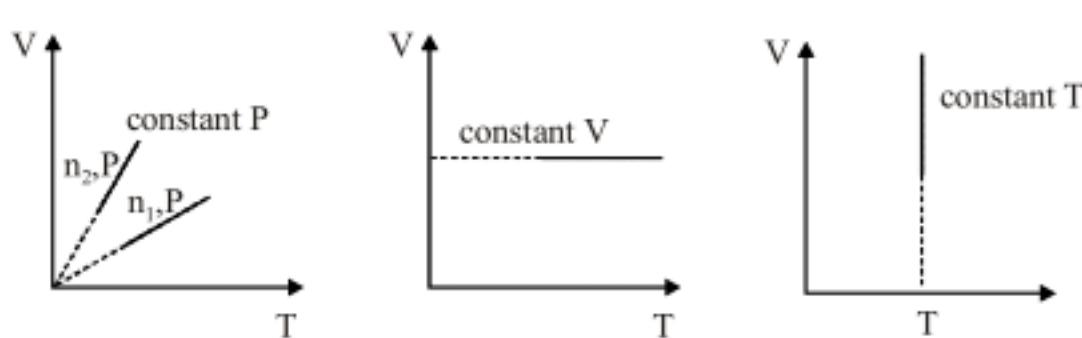


$$\text{Thus } V_t = V_0 + V_0 \alpha t = V_0 (1 + \alpha t)$$

α is called coefficient of expansion. It is approximately $\frac{1}{273}$ for all the gases.

$$V = V_0 \left(1 + \frac{t}{273} \right)$$

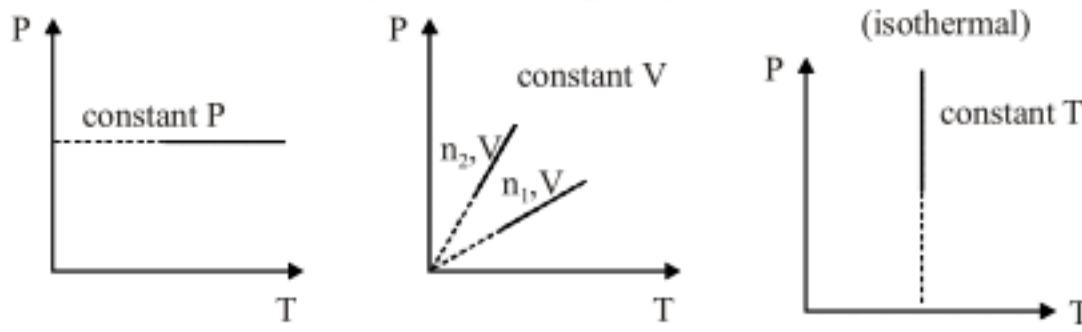
Thus, an increase in temperature of a fixed volume of a gas at constant pressure increases the volume by $\frac{1}{273}$ of the volume at 0°C.



$$\frac{V}{V_0} = \frac{T}{T_0} \quad (n, P \text{ are constants})$$

Gay-Lussac's Law

When the temperature of a gas is changed keeping the volume constant, the pressure of the gas changes. Similar to volume, the pressure changes by 1/273.



$$\beta = \frac{1}{P_0} \left[\frac{\Delta P}{\Delta t} \right] = \frac{1}{273}$$

$$P_t = P_0 \left[1 + \frac{t}{273} \right] = P_0 \left(\frac{273+t}{273} \right)$$

or $\frac{P_t}{P_0} = \frac{T}{T_0} \quad (n, V \text{ are constants})$

Dalton's Law of partial Pressures

This law states that the total pressure exerted by a mixture of non-reacting gases is equal to the sum of the pressure which each component would exert if placed independently in the container.

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots \quad (T, V \text{ are constants})$$

$$P_{\text{total}} = \sum_i P_i$$

Where the symbol \sum_i stands for the summation over all the components present in the mixture.

The partial pressure P_i of component i is defined as the pressure that the gas would exert if it were present alone in the same volume and the same temperature.

$$p_1 = \frac{n_1 RT}{V}$$

$$p_2 = \frac{n_2 RT}{V}$$

The total pressure of the system can be written as

$$\begin{aligned} P_{\text{total}} &= \sum_i p_i \\ &= \frac{RT}{V} \sum_i n_i = n_{\text{total}} \frac{RT}{V} \end{aligned}$$

and partial pressure of i^{th} component can be written as

$$P_i = P_{\text{total}} \frac{n_i}{n_{\text{total}}}$$

When $\frac{n_i}{n_{\text{total}}}$ is the mole fraction of the respective component

Equation of State :

The equation of state for an ideal gas :

$$PV = nRT$$

In this expression, known as the ideal gas law, R is a universal constant that is the same for all gases and T is the absolute temperature in kelvins. Experiments on numerous gases show that as the pressure approaches zero, the quantity PV/nT approaches the same value R for all gases. For the reason, R is called the universal gas constant. In SI units, in which pressure is expressed in pascals ($1 \text{ Pa} = 1 \text{ N/m}^2$) and volume in cubic meters, the product PV has units of newton meters, or joules, and R has the value

$$R = 8.315 \text{ J/mol K}$$

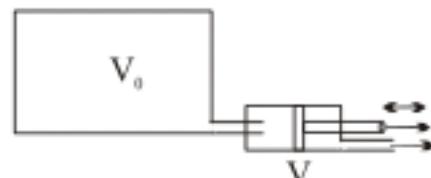
If the pressure is expressed in atmospheres and the volume in liters ($1 \text{ L} = 10^{-3} = 10^{-3} \text{ m}^3$), then R has the value

$$R = 0.08214 \text{ L atm/mol K}$$

Using this value of R we find that the volume occupied by 1 mol of any gas at atmospheric pressure and at 0°C (273 K) is 22.4 L.

Illustration :

A big container having ideal gas at pressure P and of volume V_0 is being evacuated by using vacuum pump of cylinder volume V . Find pressure in the big container after n strokes. Assume the whole process to be isothermal.



Sol. For first stroke, pressure becomes P_1 .

$$PV_0 = P_1 (V_0 + V)$$

$$P_1 = \frac{PV_0}{(V_0 + V)}$$

for 2nd stroke, pressure becomes P_2

$$P_1 V_0 = P_2 (V_0 + V)$$

$$P_2 = \frac{P_1 V_0}{(V_0 + V)}$$

$$P_2 = \frac{P V_0^2}{(V_0 + V)^2}$$

for n^{th} stroke, pressure becomes P_n

$$P_n = \frac{P V_0^n}{(V_0 + V)^n}$$



Illustration :

Consider the lung capacity to be 500 cm^3 and the pressure thereing to be equivalent of 761 mm of Hg ; estimate the number of molecules per breath.

Sol. From ideal gas equation,

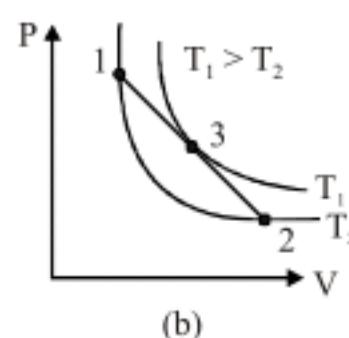
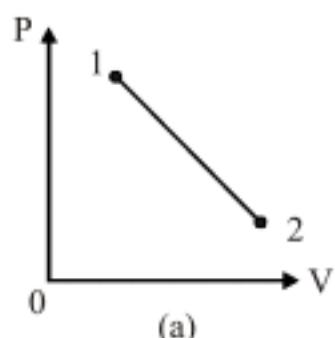
$$PV = NkT$$

Normal body temperature is $98.6^{\circ}\text{F} = 37^{\circ}\text{C} = 310 \text{ K}$.

$$\begin{aligned} N &= \frac{PV}{kT} \\ &= \frac{(101.46)(500 \times 10^{-6})}{(1.3807 \times 10^{-23} \times 310)} \\ &= 1.19 \times 10^{19} \text{ molecules} \end{aligned}$$

Illustration :

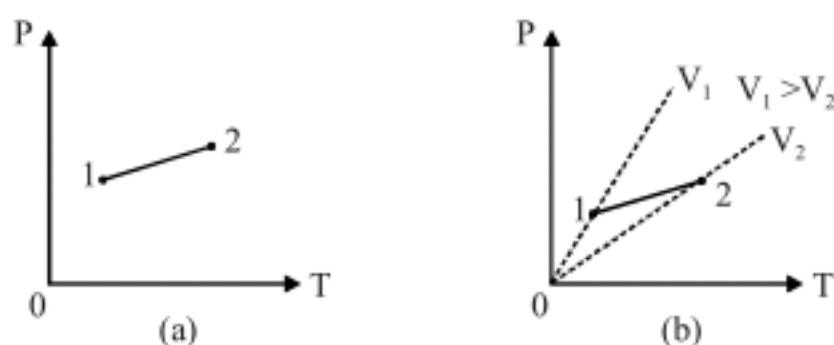
A gas is enclosed in a cylinder with a freely movable piston. The load on the piston is gradually decreased. The temperature of the gas can be changed by placing the cylinder on hot and cold heat reservoirs. The figure shown P-V graph of such a cylinder. What inference can be drawn the nature of change in the temperature of the gas ?



Sol. We draw two isotherms representing constant temperatures T_1 and T_2 , such that T_2 passes through initial and final points 1 and 2, and T_1 passes through certain intermediate point 3. The curve closer to origin represents lower temperature. Hence the gas is heated in the section 1 – 3 and cooled in the section 1–2.


Illustration :

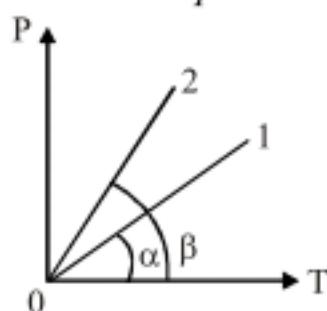
Figure (a) shows P-T curve of a ideal gas during a process. Does compression or expansion takes place when the gas is heated ?



Sol. We draw constant volume lines (isochores) through the initial and final points 1 and 2 (see example 71). The volume V_2 is greater than V_1 . Hence during heating of the gas expansion took place.

Illustration :

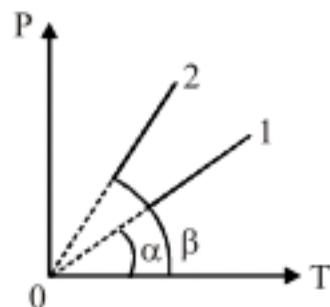
A certain mass of a gas was heated in a constant volume vessel; its P-T curve 3 is 1; similarly another mass of the gas was heated in the same vessel ; its P-T curve is 2. If $\tan \beta = 2 \tan \alpha$, what is the ratio of masses of gas in the two experiments ?



Sol. From ideal gas equation,

$$P = \left(\frac{nR}{V} \right) T = \left(\frac{mR}{MV} \right) T$$

The constant volume curves are straight lines with slope mR/MV . The slope of lines is proportional to the mass of the gas.



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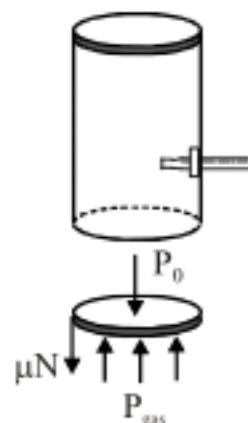
The constant volume curves are straight line with slope mR/MV . The slope of line is proportional to the mass of the gas.

$$\frac{(\text{slope})_1}{(\text{slope})_2} = \frac{m_1}{m_2} = \frac{\tan \alpha}{\tan \beta} = \frac{1}{2}$$

Hence the mass m_2 is twice of m_1

Illustration :

Figure shown a cylindrical tube of radius r and length l , fitted with a cork. The friction coefficient between the cork and the tube is μ . The tube contains an ideal gas at temperature T , and atmospheric pressure P_0 . The tube is slowly heated ; the cork pipe out when temperature is doubled. What is normal force per unit length exerted by the cork on the periphery of tube ? Assume uniform temperature throughout gas any instant.



Sol. Since volume of the gas is constant,

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

$$P_f = P \left(\frac{T_f}{T_i} \right) = 2P_i = 2P_0$$

The forces acting on the cork are shown in the figure in equilibrium.

$$P_0 \times A + \mu N = 2P_0 A$$

$$N = \frac{P_0 A}{\mu}$$

N is the total normal force exerted by the tube on the cork; hence contact force unit length is

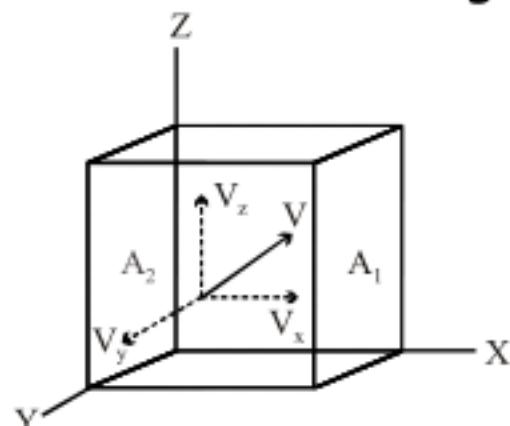
$$\frac{dN}{dl} = \frac{N}{2\pi r} = \frac{P_0 A}{2\pi \mu r}$$

Assumption of kinetic theory of gases

1. All gases are made of molecule moving randomly in all directions.
2. The size of a molecule is much smaller than the average separation between the molecules.
3. The molecules exert no force on each other or on the walls of the container except during collision.
4. All collisions between two molecules or between a molecule and a wall are perfectly elastic. Also, the time spent during a collision is negligibly small.
5. The molecules obey Newton's laws of motion.
6. When a gas is left for sufficient time, it comes to a steady state. The density and the distribution of position, direction and time. This assumption may be justified if the number of molecules is very large.



Calculation of the pressure of an ideal gas



Consider an ideal gas enclosed in a cubical vessel of edge L . Take a corner of the vessel as the origin O and the X -, Y -, Z -axes along the edges. Let A_1 and A_2 be the parallel faces perpendicular to the X -axis. Consider a molecule moving with velocity \vec{v} . The components of the velocity along the axes are v_x , v_y and v_z . When the molecule collides with the force A_1 , the x -component of the velocity is reversed whereas the y - and the z -components remain unchanged. This follows from our assumption that the collisions of the molecules with the wall are perfectly elastic. The change in momentum of the molecule is

$$\Delta p = (-mv_x) - (mv_x) = -2mv_x.$$

As the momentum remains conserved in a collision, the change in momentum of the wall is

$$\Delta p' = 2mv_x \quad \dots(i)$$

After rebound, this molecule travels towards A_2 with the x -component of velocity equal to $-v_x$. Any collision of the molecule with any other face (except for A_2) does not change the value of v_x . So, it travels between A_1 and A_2 with a constant x -component of velocity which is equal to v_x . Note that we can neglect any collision with the other molecules in view of the last assumption discussed in the previous section.

The distance travelled parallel to the x -direction between A_1 and A_2 is L . Thus, the time taken by the molecule to go from A_1 to A_2 is L/v_x . The molecule rebounds from A_2 , travels towards A_1 and collides with it after another time interval L/v_x . Thus, the time between two consecutive collisions of this molecule with A_1 is $\Delta t = 2L/v_x$. The number of collisions of this molecule with A_1 in unit time is

$$n = \frac{1}{\Delta t} = \frac{v_x}{2L} \quad \dots(ii)$$

The momentum imparted per unit time to the wall by this molecule is, from (i) and (ii),

The momentum imparted per unit time to the wall by this molecule is from (i) and (ii),

$$\Delta F = n\Delta p'$$

$$= \frac{v_x}{2L} \times 2mv_x = \frac{m}{L} v_x^2$$

This is also the force exerted on the wall A_1 due to this molecule. The total force on the wall A_1 due to all the molecules is

$$\begin{aligned} F &= \sum \frac{m}{L} v_x^2 \\ &= \frac{m}{L} \sum v_x^2 \end{aligned} \quad \dots(iii)$$

As all directions are equivalent, we have

$$\sum v_x^2 = \sum v_y^2 = \sum v_z^2$$

$$= \frac{1}{3} \Sigma (v_x^2 + v_y^2 + v_z^2)$$

$$= \frac{1}{3} \Sigma v^2$$

Thus, from (iii), $F = \frac{1}{3} \frac{m}{L} \Sigma v^2$.



If N is the total number of molecules in the sample, we can write

$$F = \frac{1}{3} \frac{mN}{L} \frac{\Sigma v^2}{N}$$

The pressure is force per unit area so that

$$p = \frac{F}{L^2}$$

$$= \frac{1}{3} \frac{mN}{L^3} \frac{\Sigma v^2}{N}$$

$$= \frac{1}{3} \frac{M}{L^3} \frac{\Sigma v^2}{N} = \frac{1}{3} \rho \frac{\Sigma v^2}{N}$$

where M is the total mass of the gas taken and ρ is its density. Also $\Sigma v^2/N$ is the average of the speeds squared. It is written as u^2 and is called mean square speed. Thus, the pressure is

$$p = \frac{1}{3} \rho u^2 \quad \dots(1)$$

or $pV = \frac{1}{3} Mu^2 \quad \dots(2)$

or, $pV = \frac{1}{3} Nm u^2 \quad \dots(3)$

RMS Speed

The square root of mean square speed is called root-square speed or rms speed. It is denoted by the symbol v_{rms} . Thus,

$$v_{rms} = \sqrt{\Sigma v^2 / N}$$

or, $v^2 = (v_{rms})^2$.

Equation (1) may be written as

$$p = \frac{1}{3} \rho v_{rms}^2$$

so that $v_{rms} = \sqrt{\frac{3p}{\rho}} = \sqrt{\frac{3pV}{M}} = \sqrt{\frac{3RT}{M}}$ (M → molecular weight)

$$\text{Avg. speed } v_{\text{avg}} = \sqrt{\frac{8KT}{\pi m_0}} = \sqrt{\frac{8RT}{\pi M}}$$

$$\text{Most probable speed } v_p = \sqrt{\frac{2KT}{m_0}} = \sqrt{\frac{2KT}{M}}$$



Translational kinetic energy of gas :

Kinetic energy of any molecule is k_1

$$k_1 = \frac{1}{2} m_0 V_1^2$$

Total K.E. of all molecular is k

$$k = \sum \frac{1}{2} m_0 V^2$$

$$= \frac{1}{2} m_0 \sum V^2 = \frac{1}{2} m_0 N \left(\frac{\sum V^2}{N} \right)$$

$$= \frac{m}{2} V_{\text{rms}}^2 = \frac{m}{2} \times \frac{3RT}{M}$$

$$k = \frac{3nRT}{2} \quad \left(\frac{m}{M} = n \right)$$

$$k = \frac{3 PV}{2}$$

$$\text{K.E. / volume} = \frac{3}{2} P$$

Illustration :

Calculate the rms speed of nitrogen at STP (pressure = 1 atm and temperature = 0°C). The density of nitrogen in these conditions is 1.25 kg/m³.

Sol. At STP, the pressure is $1.0 \times 10^5 \text{ N/m}^2$. The rms speed is

$$v_{\text{rms}} = \sqrt{\frac{3p}{\rho}}$$

$$= \sqrt{\frac{3 \times 10^5 \text{ N/m}^2}{1.25 \text{ kg/m}^3}}$$

$$= 490 \text{ m/s}$$

Translational Kinetic Energy of a Gas

The total translational kinetic energy of all the molecules of the gas is

$$K = \sum \frac{1}{2} mv^2 = \frac{1}{2} mN \frac{\sum v^2}{N} = \frac{1}{2} Mv_{rms}^2 \quad \dots(4)$$

The average kinetic energy of a molecule is

$$\frac{K}{N} = \frac{1}{2} \frac{M}{N} v_{rms}^2 = \frac{1}{2} mv_{rms}^2$$

From equation (2)

$$pV = \frac{2}{3} \frac{1}{2} Mv_{rms}^2$$

$$pV = \frac{2}{3} K$$

$$K = \frac{3}{2} pV$$

Illustration :

Assume that the temperature remains essentially constant in the upper part of the atmosphere.

Obtain an expression for the variation pressure in the upper atmosphere with height. The mean molecular weight of air is M .

Sol. Suppose the pressure at height h is p and the at $h + dh$ is $p + dp$. Then

$$dp = -\rho g dh. \quad \dots(i)$$

Now considering any small volume ΔV of air mass, Δm ,

$$p\Delta V = nRT = \frac{\Delta m}{M} RT$$

$$\text{or, } p = \frac{\Delta m}{\Delta V} \frac{RT}{M} = \frac{\rho RT}{M}$$

$$\text{or, } \rho = \frac{M}{RT}$$

Putting in (i)

$$dp = -\frac{M}{RT} \rho g dh$$

$$\text{or, } \int_{p_0}^p \frac{dp}{p} = \int_0^h -\frac{M}{RT} g dh$$

$$\text{or, } \ln \frac{p}{p_0} = -\frac{Mgh}{RT}$$

Where p_0 is the pressure at $h = 0$

$$\text{Thus, } p = p_0 e^{-\frac{Mgh}{RT}}.$$




Illustration:

A barometer tube contains a mixture of air and saturated water vapour in the space above the mercury column. It reads 70 cm when the actual atmospheric pressure is 76 cm of mercury. The saturation vapour pressure at room temperature is 1.0 cm of mercury. The tube is now lowered in the reservoir till space above the mercury column is reduced to half its original volume. Find the reading of the barometer. Assume that the temperature remains constant.

Sol. The pressure due to the air+vapour is $76\text{cm} - 70\text{cm} = 6\text{ m}$ of mercury. The vapour is saturated and the pressure due to it is 1 cm of mercury. The pressure due to the air is therefore, 5 cm of mercury.

As the tube is lowered and the volume above the mercury is decreased, some of the vapour will condense. The remaining vapour will again exert a pressure of the volume is halved. Thus, $p_{\text{air}} = 2 \times 5\text{ cm} = 10\text{ cm}$ of mercury. The pressure due to the air + vapour reading is $76\text{ cm} - 11\text{cm} = 65\text{ cm}$.

Internal Energy

Degree of freedom :

No of ways in which molecule can pass energy is known as degree of freedom.

S. N.	Gas	Translatory	Rotation	Vibration	Total
1.	Monoatomic	3	0	0	3
2.	Diatomeric	3	2	0	5

Law of equipartition of energy :

Statement : For an ideal gas average energy associated with its any molecule for each degree of freedom is $\frac{KT}{2}$. (Where temperature T in kelvin)

Let f be the degree of freedom for a gas. Average energy associated with its any molecule = $\frac{f KT}{2}$

$$\text{Total kinetic energy of a gas} = \frac{N f K T}{2}$$

$$\text{Kinetic energy of one mole of gas} = \frac{f R T}{2}$$

Value of internal energy of a gas

Internal energy of gas should be sum of K.E. and P.E. of its constitute molecules.

But for ideal gas we has assumed P.E. = 0 (Since force of interaction between molecules is zero)

Thus, I.E. of a gas = K.E. of molecules

If f is the degree of freedom of a gas molecules than total K.E. [Trans + Rotation of each molecule]

$$\text{for one mole } U = \frac{f R T}{2}$$

for n mole of gas and having f degree of freedom are at temperature T_1 kelvin and heated to temperature T_2 then

$$\text{at } T_1 \text{ kelvin} \quad U_1 = \frac{n f R T_1}{2}$$

$$\text{at } T_2 \text{ kelvin} \quad U_2 = \frac{n f R T_2}{2}$$

$$\text{change in I.E.} \quad \Delta U = \frac{n f R}{2} (T_2 - T_1)$$



Change in internal energy of ideal gas is a function of temperature and temperature only. It does not depend on how we carry out this change in temperature.

$\frac{f R}{2}$ is represented as C_v

$$C_v = \frac{f R}{2}$$

$$U = n C_v T$$

(i) For monoatomic gas ($f=3$)

$$U = \frac{n 3RT}{2} \quad \& \quad \Delta U = \frac{n 3R \Delta T}{2}$$

$$\text{or} \quad C_v = \frac{3R}{2}$$

(ii) For rigid diatomic molecule ($f=5$)

$$U = \frac{n 5RT}{2} \quad \& \quad \Delta U = \frac{n 5R \Delta T}{2}$$

$$C_v = \frac{5R}{2}$$

Illustration

The temperature of an ideal gas consisting of rigid diatomic molecules is $T = 300K$. Calculate the angular root mean square velocity of a rotating molecules if its moment of inertial is equal to

$$I = 2.1 \times 10^{-39} \text{ g.cm}^2$$

$$\text{Sol. K.E. associated with rotation} = \frac{1}{2} I \omega^2$$

Degree of freedom associated
with rotation = 2

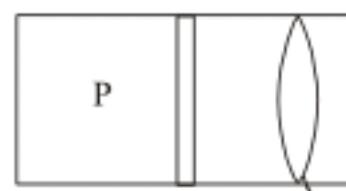
$$\frac{1}{2} I \omega^2 = 2 \times \frac{KT}{2}$$

$$\omega = \sqrt{\frac{2KT}{I}}$$

$$= 6.3 \times 10^{12} \text{ rad S}^{-1}$$



Calculation of work done by gas :



If the piston moves towards right a dx distance then work done by this force is dW .

$$dW = F \cdot dx$$

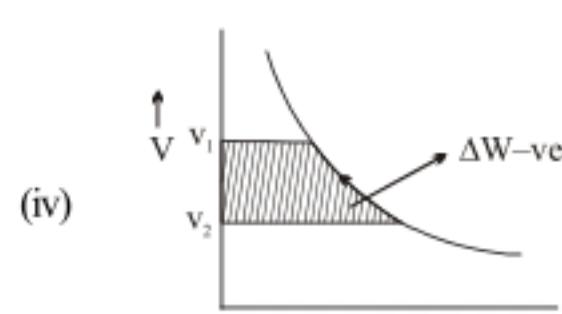
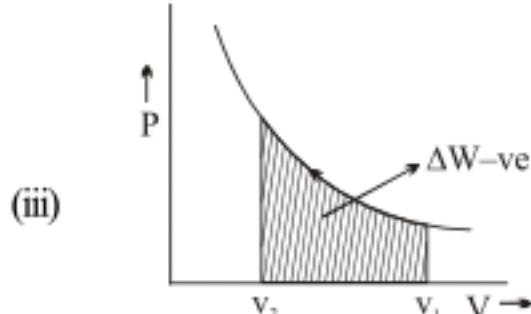
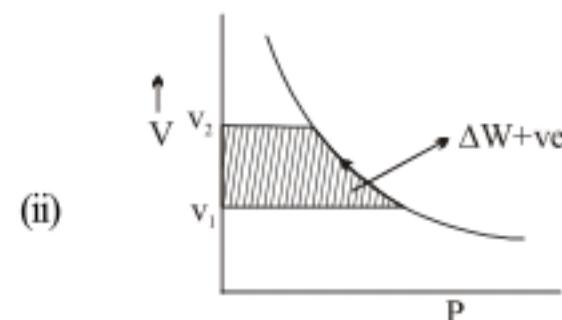
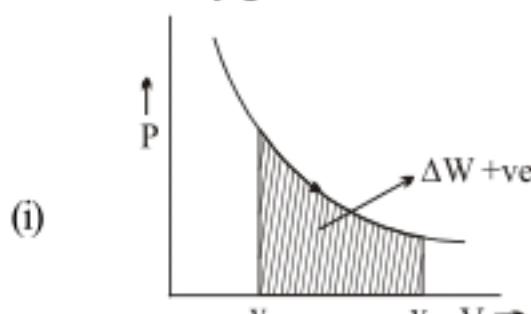
$$= P (A \cdot dx)$$

$$dW = PdV$$

$$dW = \int_{V_1}^{V_2} PdV$$

Graphical interpretation :

From above integral it can be understood that area enclosed by PV-curve and V-axis represents the work done by gas.



When volume decrease ΔW is $-ve$

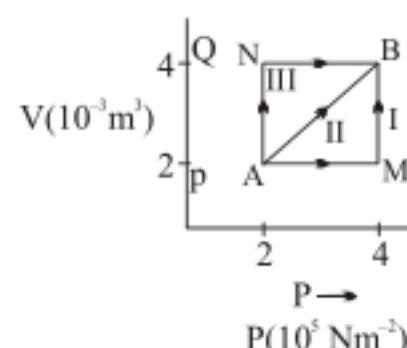
Illustration :

From the given curves find out the work done by the ideal for going from state A to state B. For all the three processes.

Sol. $W_1 = PAMBQNP = 800 J$

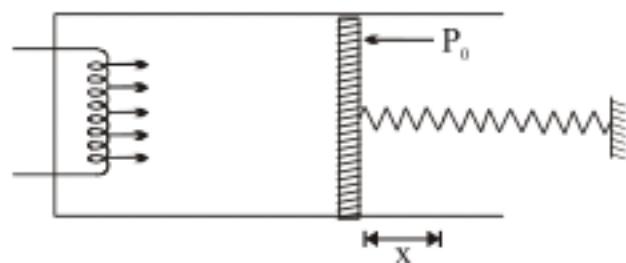
$W_2 = PABNQP = 600 J$

$W_3 = PANQP = 400 J$



Indirect technique(for quasistatic process) :

- Work done by gas + work done by all external agents = 0
 \Rightarrow Work done by gas = - (work done by all the external agents)



Work done by gas + WD by spring + W.D. by atm press = 0

W.D. by gas = - (W.D. by atm press + W.D. by spring)

$$= - [(-P_0Ax) + (-\frac{1}{2}kx^2 - 0)]$$

$$= P_0Ax + \frac{1}{2}kx^2$$

Heat & Thermodynamics

Definition :

Heat is defined as the amount of energy transfer from one body to another body or from one part of a body to other part of the body by virtue of temperature difference.

Important points :

- (a) When two bodies at different temperature are brought in contact the hotter body cools down and the cooler body warms up due to the transfer of heat from hotter body to cooler body.
- (b) "Heat is energy in transit due to temperature difference between the body" when heat is transferred from one body to another body then after the transfer this heat becomes part of internal energy or is used for doing work.

Unit & Dimension :

SI unit \rightarrow Joule
 Dimension \rightarrow ML^2T^{-2}

Specific heat of gas :

Types of specific heat of gas :

- (a) Molar specific heat : Unit mass is taken as one mole
 Units \rightarrow J / mole - k
- (b) Gram specific heat : Unit mass is taken as 1kg or 1 gm.
 Units \rightarrow J / kg-k or J / gm-k

$$C_{\text{gram}} = \frac{C_{\text{molar}}}{M}$$



Definition :

Amount of heat required to raise temperature of one unit amount (mass or mole) by one unit temperature through a given process is known as specific heat of that process.

$$C_{\text{process}} = \left(\frac{dQ}{n \Delta T} \right)_{\text{process}}$$

Note : Thus any gas can have infinite specific heats depending on the infinite different processes.

$$\Delta Q = \int_{T_1}^{T_2} n C dT \quad \text{where } C \text{ is the sp. heat for the process through which temperature from } T_1 \text{ to } T_2.$$

Note : C remains inside the integral because it may be a variable i.e. C may be a function of temperature (directly or indirectly).

Specific heat at constant volume :

Represented as C_v $C_v = \left(\frac{dQ}{n dT} \right)_{\text{const. volume}}$

Its experimental value is found to be very close to $\frac{f R}{2}$

thus $C_v = \frac{f R}{2}$

Specific heat at constant pressure :

Represented as C_p

$$C_p = \left(\frac{dQ}{n dT} \right)_{\text{const. pressure}}$$

its experimental value is found to be almost equal to $\frac{(f+2)R}{2}$

$$C_p = \frac{(f+2)R}{2}$$

Adiabatic exponent (γ) :

$$\gamma = \frac{C_p}{C_v}$$

$$\Rightarrow \gamma = 1 + \frac{2}{f} \quad \Rightarrow \quad C_v = \frac{R}{\gamma-1} \quad \Rightarrow \quad C_p = \frac{\gamma R}{\gamma-1}$$

First law of Thermodynamics



Statement : $dQ = dU + dW$ (For zero heat loss)

dQ = heat supplied to the system

dU = change in internal energy

dW = work done by the system

* This law is a form of energy conservation.

The first Law of Thermodynamics (derivation)

Let us introduce certain amount of heat energy dQ into a gas confined inside a cylinder fit with a piston.

The gas can either:

(i) store energy as random KE of its molecules (dU), or

(ii) use the energy to do work (dW) in the environment (such as raising a weight on the piston).

Thus, the first law of thermodynamics can be written : $dQ = dU + dW$

Note : In solving thermodynamics problems, always take gas as system.

Sign convention :

(i) Whenever heat is added to the system sign is +ve

(ii) Whenever system rejects the heat sign is -ve

Work (dW) :

(i) ($V \uparrow$) sign is +ve (ii) sign is -ve ($V \downarrow$)

Internal energy (dU) :

(i) When temperature increases sign is +ve

(ii) When temperature decreases sign is -ve

Application of first law of thermodynamics :

Isochoric process :

A process that takes place at constant volume is called isochoric process or isovolumetric process. (Gas will follow Gaylussac's Law)

(i) Conditions $\rightarrow V$ is constant

(ii) Process equation $\rightarrow \frac{P}{T} = \text{constant}$

(iii) If gas is taken from state A having pressure P_1 , temperature T_1 and volume V to state B having Pressure P_2 , temperature T_2 and volume V then

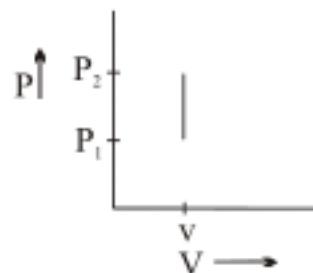
$$\begin{array}{ccc} A & \xrightarrow{\hspace{1cm}} & B \\ (P_1, V, T_1) & & (P_2, V, T_2) \end{array}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

[While $PV = nRT$ will relate variables in same state]



- (iv) P-V curve



- (v) $dW = 0$ since $dV = 0$
 (vi) $\Delta U = \frac{nfR}{2}(T_2 - T_1)$
 (vii) $\Delta Q = nC_v(T_2 - T_1)$
 (viii) Applying first law of thermodynamics (F.L.T.)

$$0 + \Delta U = \Delta Q$$

$$\Rightarrow n\left(\frac{fR}{2}\right)(T_2 - T_1) = nC_v(T_2 - T_1)$$

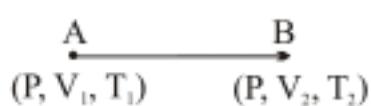
$$\Rightarrow C_v = \frac{fR}{2}$$

- (ix) Bulk modulus $= -\frac{dP}{(dV/V)} = -\infty$
 (x) sp. heat $= C_v$

Isobaric process :

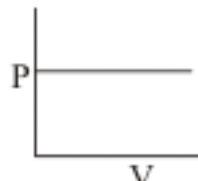
A process that takes place at constant pressure is called isobaric process. (Gas will follow Charle's Law)

- (i) Condition : P is constant
 (ii) Process equation $\rightarrow \frac{V}{T}$ is constant
 (iii) If gas is taken from state A having pressure P temperature T_1 and volume V_1 to state B having Pressure P temperature T_2 and volume V_2 then



$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad PV_1 = nRT_1 \quad PV_2 = nRT_2$$

- (iv) P – V curve





$$(v) \quad \Delta W = \int_{V_1}^{V_2} P \, dV$$

$$= P(V_2 - V_1)$$

$$= nR(T_2 - T_1)$$

$$(vi) \quad dU = nC_v \, dT$$

$$\Delta U = nC_v(T_2 - T_1)$$

$$(vii) \quad dQ = nC_p \, dT$$

$$\Delta Q = nC_p(T_2 - T_1)$$

(viii) Applying FLT

$$nC_p(T_2 - T_1) = nC_v(T_2 - T_1) + nR(T_2 - T_1)$$

$$\Rightarrow C_p - C_v = R$$

(known as meyer's relation)

Characteristic gas constant :

Gas constant expressed for particular gas in terms of mass is known as characteristic gas constant of that particular gas.

$$R_{\text{characteristic}} = \frac{R \text{ (universal gas const.)}}{M \text{ (mol. wt. of gas)}}$$

Units J / gm-k or J / kg-k

(ix) Bulk modulus

$$B = \frac{-dp}{(dV/V)} = 0$$

(x) Sp. heat capacity C_p

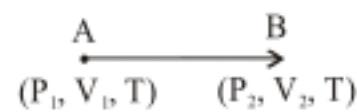
Isothermal process :

A process that takes place at constant temperature is called isothermal process. (Gas will follow Boyle's Law)

(i) Condition \rightarrow Temp. is constant

(ii) Process equation $\rightarrow PV = \text{const.}$

(iii) If gas is taken from state A having pressure P_1 , volume V_1 and temperature T to state B having Pressure P_2 , volume V_2 and temperature T then

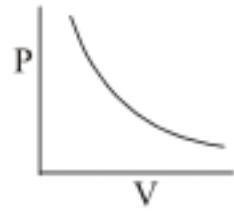


$$P_1 V_1 = P_2 V_2$$

$$P_1 V_1 = nRT$$

$$P_2 V_2 = nRT$$

(iv) P-V curve



$$\text{slope} = \frac{dP}{dV} = -\frac{P}{V}$$

$$(v) \Delta W = \int_{V_1}^{V_2} P dV = k \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= PV \ln \frac{V_2}{V_1}$$

$$= P_1 V_1 \ln \frac{V_2}{V_1} = P_1 V_2 \ln \frac{V_2}{V_1}$$

$$= nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$$

(vi) $dU = 0$

(vii) Using FLT

$$dQ = dW$$

$$\Delta Q = nRT \ln \frac{V_2}{V_1}$$

$$(viii) B = -\frac{dP}{(dV/V)} = P$$

$$(ix) \text{ Specific heat } = C = \left(\frac{dQ}{n dT} \right) = \infty$$

By adiabatic process :

Adiabatic Process (Derivation): For an adiabatic process ($\Delta Q = 0$)

$$0 = C_v + \frac{P}{n} \frac{dV}{dT} = \frac{R}{\gamma-1} + \frac{RT}{V} \frac{dV}{dT} \Rightarrow (\gamma-1) \int \frac{dV}{V} + \int \frac{dT}{T} = 0$$

$$(\gamma-1) \ln V + \ln T = \ln c' \therefore TV^{\gamma-1} = c'; \text{ Also, } T = \frac{PV}{nR} \therefore PV^{\gamma-1} = c'$$

$$P \left(\frac{T}{P} \right)^{\gamma} = c' \therefore \frac{T^{\gamma}}{P^{\gamma-1}} = c' \therefore P = T^{\gamma/\gamma-1}$$



In this process net heat supplied to the gas is zero

- (i) Condition $dQ = 0$
- (ii) Process equation $PV^\gamma = \text{const.}$
- (iii) If gas is taken from state A having pressure P_1 , volume V_1 and temperature T_1 to state B having Pressure P_2 , volume V_2 and temperature T_2 then

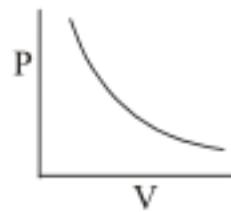
$$\begin{array}{ccc} A & \xrightarrow{\quad} & B \\ (P_1, V_1, T_1) & & (P_2, V_2, T_2) \end{array}$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$P_1 V_1 = nRT_1$$

$$P_2 V_2 = nRT_2$$

- (iv) P-V curve



$$\text{slope} = \frac{dP}{dV} = -\frac{\gamma P}{V}$$

$$(v) \Delta W = \int_{V_1}^{V_2} P dV \quad (\text{since } Pv^\gamma = k)$$

$$= k \int_{V_1}^{V_2} V^{-\gamma} dV = \frac{kV^{-\gamma+1}}{(-\gamma+1)} \Big|_{V_1}^{V_2} = \frac{P_2 V_2 - P_1 V_1}{1-\gamma}$$

$$(vi) \Delta V = nC_v(T_2 - T_1)$$

$$= \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

- (vii) Applying FLT we can see that

$$0 = \Delta W + \Delta U \Rightarrow \Delta U = -\Delta W$$

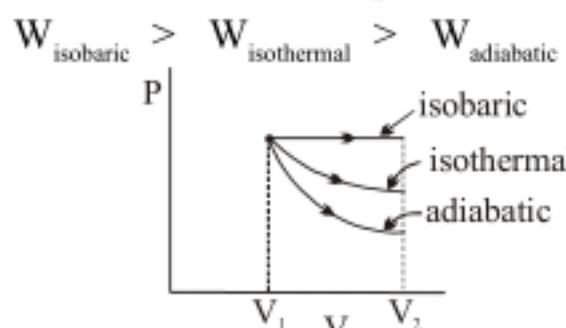
$$(viii) B = -\frac{dP}{(dV/V)} = \gamma P$$

- (ix) Sp. heat

$$C = \frac{dQ}{n dT} = 0$$

Results :

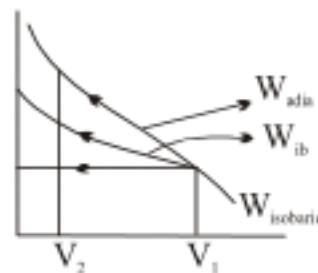
- (i) For expansion from same initial vol. & pressure to same final volume \rightarrow



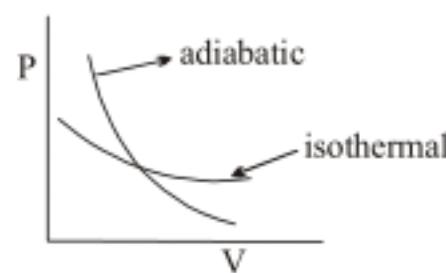
As the area under the P-V graph is largest for isobaric hence its work done is greater than isothermal and in similar manner we can say that work done in isothermal process will be greater than adiabatic process.



- (ii) For compression from same initial state to same final volume



- (iii) At pt. of interaction (slope of isothermal) $\times \gamma =$ slope of adiabatic.



Polytropic process :

It is a process in which molar heat capacity $C = \text{constant}$

$$C = C_v + \frac{P}{n} \frac{dV}{dT}; \quad PdV + VdP = n R dT$$

$$\Rightarrow C = C_v + \frac{PRdV}{PdV + VdP}$$

$$\Rightarrow \frac{R}{C - C_v} = 1 + \frac{VdP}{PdV}$$

$$\Rightarrow \frac{R - (C - C_v)}{C - C_v} = \frac{VdP}{PdV} = \frac{C - C_p}{C - C_v} = K$$

$$\Rightarrow \int \frac{dP}{P} + K \int \frac{dV}{V} = 0$$

$$\Rightarrow \ln P + K \ln V = \text{const}$$

$$\therefore PV^K = \text{const.} \quad K : \text{Polytropic constant}$$

$$\text{Isochoric: } K = \infty \quad [P^{1/K}V = \text{const.}]$$

$$C = C_v$$

$$\text{Isobaric: } K = 0$$

$$C = C_p$$

$$\text{Isothermal: } K = 1 \quad K = \frac{C - C_p}{C - C_v} = \frac{1 - C_p/C}{1 - C_v/C}$$

$$C = \infty$$

$$\text{Adiabatic: } K = \gamma \quad [\text{Put } C = 0 \text{ in the equation of } K]$$

$$C = 0$$

(i) Characteristic equation process

$$PV^x = \text{const.}$$

$$\begin{aligned} \text{(ii)} \quad \Delta W &= \int_{V_1}^{V_2} P dV \\ &= \int_{V_1}^{V_2} \frac{k}{V^x} dV = k \left(\frac{V_2^{-x+1} - V_1^{-x+1}}{-x+1} \right) \end{aligned}$$

$$\begin{aligned} &= \frac{\frac{k}{V^x} V_2 - \frac{k}{V_1^x} V_1}{1-x} = \frac{P_2 V_2 - P_1 V_1}{1-x} \\ &= \frac{n R (T_2 - T_1)}{1-x} \end{aligned}$$

$$\text{(iii)} \quad \Delta U = \frac{n R (T_2 - T_1)}{(\gamma - 1)}$$

(iv) From FLT

$$dQ = dW + dU$$

$$\Delta Q = nR(T_2 - T_1) \left[\frac{1}{1-x} + \frac{1}{\gamma-1} \right]$$

(v) Sp. heat

$$\Delta Q = nc(T_2 - T_1)$$

$$C = \frac{R}{1-x} + \frac{R}{\gamma-1}$$

Illustration*An ideal gas expands isothermally along AB and does 700 J of work.**(a) How much heat does the gas exchange along AB.**(b) The gas then expands adiabatically along BC and does 400 J of work.**When the gas returns to A along CA, it exhausts 100 J of heat to its surroundings. How much work is done on the gas along this path.*

Sol. (a) AB is an isothermal process. Hence,

$$\Delta U_{AB} = 0$$

$$\text{and } Q_{AB} = W_{AB} = 700 \text{ J}$$

(b) BC is an adiabatic process. Hence,

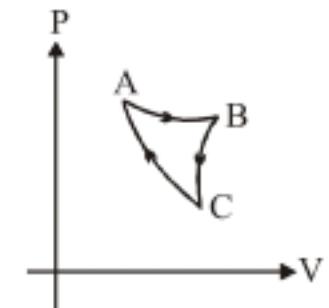
$$Q_{BC} = 0$$

$$W_{BC} = 400 \text{ J} \quad (\text{given})$$

$$\therefore \Delta U_{BC} = -W_{BC} = -400 \text{ J}$$

ABC is a cyclic process and internal energy is a state function. Therefore,

$$(\Delta U)_{\text{whole cycle}} = 0 = \Delta U_{AB} + \Delta U_{BC} + \Delta U_{CA}$$



and from first law of thermodynamics,

$$Q_{AB} + Q_{BC} + Q_{CA} = W_{AB} + W_{BC} + \Delta W_{CA}$$

Substituting the values,

$$700 + 0 - 100 = 700 + 400 + \Delta W_{CA}$$

$$\therefore \Delta W_{CA} = -500 \text{ J}$$

Negative sign implies that work is done on the gas.



Illustration

An ideal monoatomic gas at 300 K expands adiabatically to twice its volume. What is the final temperature.

Sol. For an ideal monoatomic gas,

$$\gamma = \frac{5}{3}$$

In an adiabatic process,

$$TV^{\gamma-1} = \text{constant}$$

$$\therefore T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$$

$$\text{or } T_f = T_i \left(\frac{V_i}{V_f} \right)^{\gamma-1}$$

$$= (300) \left(\frac{1}{2} \right)^{\frac{5}{3}-1}$$

$$= 189 \text{ K}$$

Illustration :

1 mole of an ideal monoatomic gas is expanded till the temperature of the gas is doubled under the process $V^2T = \text{constant}$. The initial temperature of the gas is 400 K. In terms of R, find total work done in the process.

Sol. Given $T_i = 400 \text{ K}$ and $T_f = 2T_i = 800 \text{ K}$

$$\Delta T = T_f - T_i = 400 \text{ K}$$

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

$$= (1) \left(\frac{3}{2} R \right) (400) = 600 R$$

The given process is $V^2T = \text{constant}$

$$\text{Putting } T = \frac{PV}{R} \text{ we get}$$

$$PV^3 = \text{constant}$$

Comparing this equation with $PV^x = \text{constant}$ we have $x = 3$ and molar heat capacity is

$$C = \frac{R}{\gamma-1} + \frac{R}{1-x} = \frac{R}{\frac{5}{3}-1} + \frac{R}{1-3}$$

$$\frac{3}{2}R - \frac{R}{2}$$

$$\therefore \Delta Q = nC\Delta T = (1) (R) (400) = 400 R$$

$$\text{Now, } \Delta W = \Delta Q - \Delta U = -200 R$$

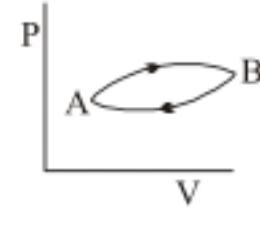


Cyclic process :

It is combination of two or more than two processes in which initial and final state of the system is same

(i) $dU = 0$

Total change in I.E. is zero because initial & final temp. is same



(ii) Applying FLT

$$dQ = dW$$

(iii) Net work done in a cyclic process is area bounded by process curve on PV diagram.



(iv) Efficiency of cyclic process :

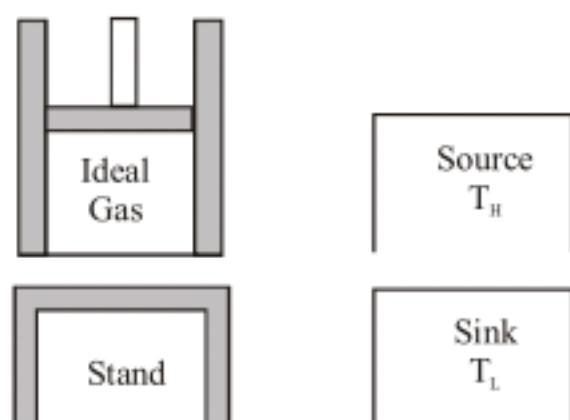
$$\eta = \frac{\text{Total work done (+ve and -ve both)}}{\text{Total heat supplied (only +ve heat) to the system}} \times 100$$

Carnot Heat Engine :

(A) The Engine :

As according to the second law of thermodynamics whole of heat can never be converted into work, the question then arises under what conditions the conversion of heat to work is these questions Carnot developed an ideal heat engine which is supposed to consist of the following four components :

- (1) A cylinder with perfectly non-conducting walls and a perfectly conducting base containing a perfect gas as working substance and fitted with a non-conducting frictionless piston'
- (2) A source of infinite thermal capacity maintained at constant higher temperature T_H ;
- (3) A sink of infinite thermal capacity maintained at constant lower temperature T_L ; and
- (4) A perfectly non-conducting stand for the cylinder.



Here it is worth mentioning that as all the above mentioned components cannot exist in reality, Carnot engine is an ideal (hypothetical) engine which can never be actually constructed.

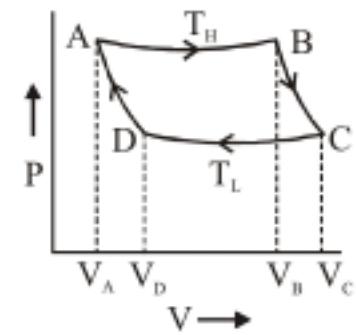


(B) Carnot Cycle [or Working of the Engine] :

The working substance in a Carnot engine is taken through a reversible cycle consisting of the following four steps :

- (i) The cylinder containing ideal gas is placed on the source and the gas is allowed to expand slowly at constant temperature T_H absorbing heat Q_H . This isothermal change is represented by the curve AB in the indicator diagram.
- (ii) The cylinder is then placed on the non-conducting stand and the gas is allowed to expand adiabatically till the temperature falls from T_H to T_L . This adiabatic expansion is represented by the curve BC.
- (iii) The cylinder is next placed on the sink and the gas is compressed at constant temperature T_L . This adiabatic compression is represented by the curve CD.
- (iv) Finally the cylinder is again placed on the non-conducting stand and the compression is continued so that the gas returns to its initial stage along DA.

The closed path ABCDA represents the so called **Carnot cycle** and the four stages taken together represent a cyclic process



(C) Efficiency of the Engine :

The efficiency of a engine is defined as the ratio of work done to the heat supplied, i.e.,

$$\eta = \frac{\text{Work done}}{\text{heat input}} = \frac{W}{W_H} \quad \dots(i)$$

But as for cyclic process $\Delta W =$ i.e., $W = Q_H - Q_L$

So eqn. (i) reduces to

$$\eta = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \quad \dots(ii)$$

Now as in an isothermal process internal energy remains constant, in accordance with first law

$$\Delta Q = \Delta W = nRT \log_e(V_F/V_I) \quad [\text{as } \Delta U = 0]$$

$$\text{So } Q_H = nRT_H \log_e\left(\frac{V_B}{V_A}\right)$$

$$\text{and } |Q_L| = nRT_L \log\left(\frac{V_C}{V_D}\right) \quad \dots(iii)$$

But as for adiabatics BC and DA respectively,

$$T_H V_B^{\gamma-1} = T_L V_C^{\gamma-1} \text{ and } T_H V_A^{\gamma-1} = T_L V_D^{\gamma-1}$$

Dividing these two results,

$$\left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1}, \text{ i.e., } \frac{V_B}{V_A} = \frac{V_C}{V_D} \quad \dots(iv)$$

Substituting the value of Q_H and Q_L from, equation (iii) in (ii) in the light of (iv), we get

$$\eta = 1 - \frac{T_L}{T_H} \quad \dots(v)$$

This is the required result and from this it is clear that :

- (1) Efficiency of a heat engine depends only on temperatures of source and sink and is independent of all other factors.
- (2) All reversible heat engines working between same temperatures are equally efficient and no heat engine can be more efficient than Carnot engine (as it is ideal).
- (3) As on Kelvin scale temperature can never be negative (as 0 K is defined as lowest possible temperature) and T_H and T_L are finite, efficiency of a heat engine is always lesser than unity, i.e., whole of heat can never be converted into work which is in accordance with second law.

The efficiency of actual engines is much lesser than that of ideal engine. Actually the practical efficiency of a steam engine is about (8-15)% while that of a petrol engine 40%. The efficiency of a diessel engine is maximum and is about (50-55)%.

Illustration :

An inventor claims to have developed an engine that during a certain time interval takes in 110 MJ of heat at 415 K, rejects 50 MJ of heat at 212 while manages to do 16.7kW of work. Do you agree with the inventor's claim ?

Sol. The claimed efficiency

$$\eta = \frac{W}{Q_H} = \frac{16.7 \text{ kWh}}{10 \text{ MJ}}$$

But as $1 \text{ kWh} = 10^3 \times (J/s) \times (60 \times 60s) = 3.6 \text{ MJ}$

$$\text{So } \eta = \frac{16.7 \times 3.6}{110} = 0.55 = 55\% \quad \dots(i)$$

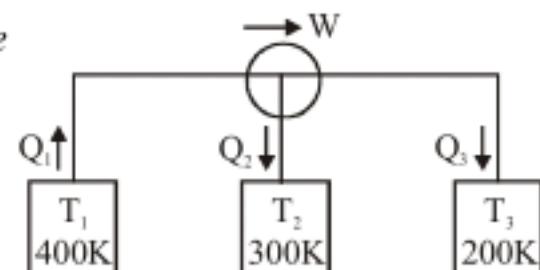
While maximum possible theoretical efficiency,

$$\begin{aligned} \eta_{max} &= -\frac{T_L}{T_H} = \frac{T_H - T_L}{T_H} = \frac{415 - 212}{415} \\ &= .49 = 49\% \end{aligned}$$

From eqns. (i) and (ii) it is clear that claimed efficiency is greater than maximum possible theoretical efficiency; so inventor's c claim does not appear to be correct.


Illustration :

During an integral number of complete cycles, a reversible engine (shown by a circle) absorbs 1200 joule from reservoir at 400 K and performs 200 joule of mechanical work,



(a) Find the quantities of heat exchanged with the other two reservoirs. State whether the reservoirs absorb or lose heat.

(b) Find the change of entropy of each reservoir.

(c) What is the change in entropy of the universe?

Sol. (a) By conservation of energy

$$Q_1 = W + Q_2 + Q_3$$

$$\text{i.e., } Q_2 + Q_3 = Q_1 - W = 1200 - 200 = 1000 \quad \dots(1)$$

And as change in entropy in a reversible-process is zero

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} = 0 \quad \text{i.e., } -\frac{200}{400} + \frac{Q_2}{300} + \frac{Q_3}{200} = 0$$

$$\text{i.e., } 2Q_2 + 3Q_3 = 1800$$

Solving equation (i) and (ii) for Q_2 and Q_3 , we get

$$Q_2 = 1200 \text{ J and } Q_3 = -200 \text{ J}$$

i.e., the reservoir at temperature T_2 absorbs 1200 J of heat while the reservoir at temperature T_3 , lose 200 J of heat

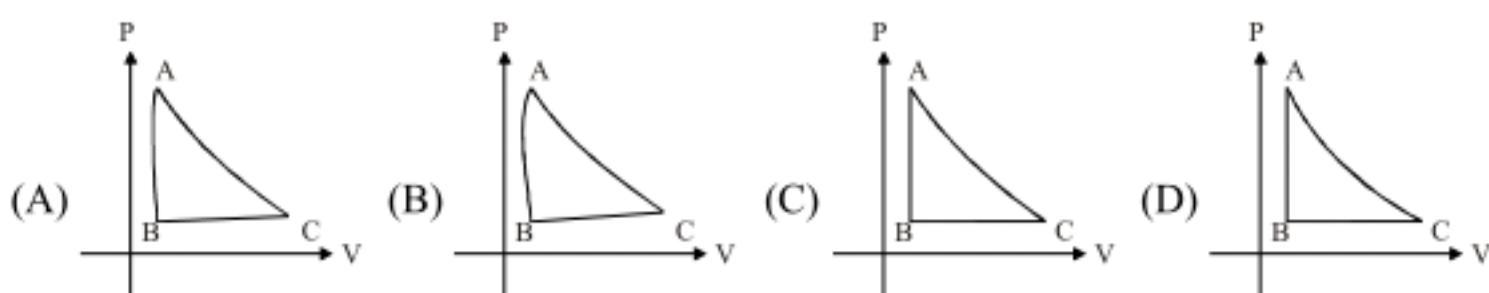
(b) Now as change in entropy at constant temperature is given by $\Delta S = (\Delta Q/T)$

So change in entropy of reservoir at temperatures T_1 , T_2 and T_3 will be respectively

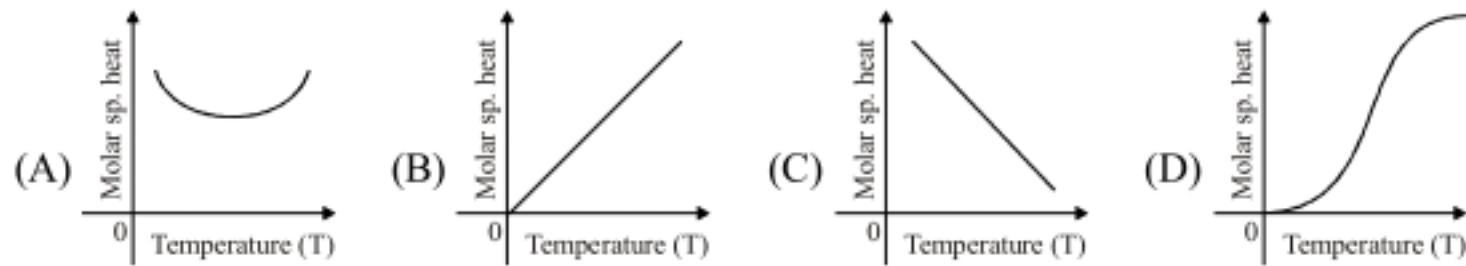
$$\frac{-1200}{400} = -3 \frac{\text{J}}{\text{K}}, \frac{1200}{300} = 4 \frac{\text{J}}{\text{K}} \text{ and } \frac{-200}{200} = -1 \frac{\text{J}}{\text{K}}$$

Practice Exercise

- Q.1 The average energy and the rms speed of molecules in a sample of oxygen gas at 300 K are $6.21 \times 10^{-21} \text{ J}$ and 484 ms^{-1} respectively. The corresponding values of 600 K are nearly
 (A) $12.42 \times 10^{-21} \text{ J}, 968 \text{ ms}^{-1}$ (B) $8.78 \times 10^{-21} \text{ J}, 684 \text{ ms}^{-1}$
 (C) $6.21 \times 10^{-21} \text{ J}, 968 \text{ ms}^{-1}$ (D) $12.42 \times 10^{-21} \text{ J}, 684 \text{ ms}^{-1}$
- Q.2 The P-T diagram for a ideal gas is shown in Figure where AC is an adiabatic process. The corresponding PV diagram is .



Q.3 Variation of molar specific heat of a metal with temperature is best depicted by



Answers

Q.1 D

Q.2 B

Q.3 D



Solved Example

$$\text{Sol. } \frac{C_p}{C_v} = \gamma = 1.4$$

$$\frac{(\Delta Q)_P}{(\Delta Q)_V} = \frac{nC_p\Delta T}{nC_v\Delta T} = \frac{C_p}{C_v} = 1.4$$

$$\therefore (\Delta Q)_v = \frac{(\Delta Q)_p}{1.4} = 50 \text{ cal}$$

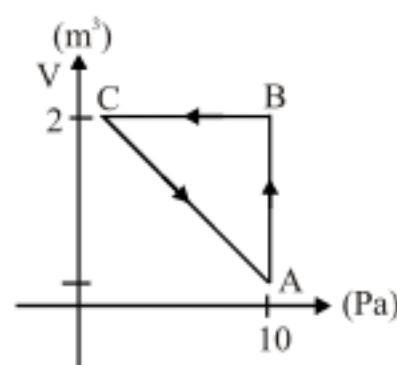
- Q.2 A vessel contains 1 mole of O₂ and 1 mole of He. The value of γ of the mixture is
(A) 1.4 (B) 1.50 (C) 1.53 (D) none of these

$$\text{Sol. } C_{\text{vmix}} = \frac{\frac{3}{4}R + \frac{5}{2}R}{2} = 2R$$

$$C_{\text{nmix}} = 2R + R = 3R$$

$$y_{\text{mix}} = \frac{C_p}{C_v} = \frac{3}{2}$$

- Q.3 An ideal gas taken through a cycle $A \rightarrow B \rightarrow C \rightarrow A$ as shown in Figure if the net heat supplied in the cycle is 5 J, then work done by the gas in the process $C \rightarrow A$ is



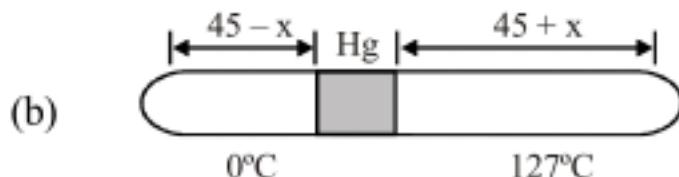
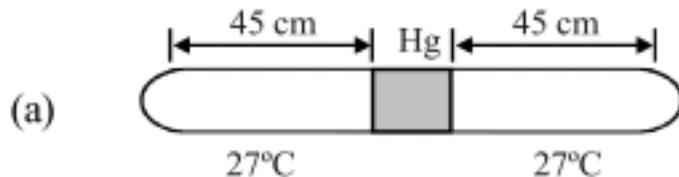
Sol. Work done = area under the curve 10 J; $5 = W_{CA} + 10$ or $W_{CA} = -5$ J

- Q.4 A glass tube scaled at both ends is 1 m long. It lies horizontally with the middle 10 cm containing Hg. The two ends of the tube, equal in length, contain air at 27°C and pressure 76 cm of Hg. The temperature at one end is kept 0°C and at the other end it 127°C . Neglect the change in length of Hg column. Then the change in length on two sides is

- (A) 12.3 cm (B) 10.311 cm (B) 9.9 cm (D) 8.49 cm

Sol. Initially $l = 45 \text{ cm}$ ($2l + 10 = 100 \text{ cm}$)

$$P_1 = P_2 = P \text{ (say)} \quad \dots(i)$$



Applying gas law at end A,

$$\frac{45AP}{300} = \frac{(45-x)AP_1}{273} \quad \dots(ii)$$

$$\text{At end B } \frac{45AP}{300} = \frac{(45+x)AP_2}{400} \quad \dots(iii)$$

From (i), (ii) and (iii)

$$\frac{(45-x)}{273} = \frac{45+x}{400} = 8.49 \text{ cm}$$

Q.5 Find the amount of work done to increase the temperature of one mole of an ideal gas by 30°C if it is expanding under the condition $V \propto T^{2/3}$.

- (A) 166.2 J (B) 136.2 J (C) 126.2 J (D) None of these

Sol. $PV = RT$ for 1 mole

$$W = \int PdV = \int \frac{RT}{V} dV$$

$$V = CT^{2/3}$$

$$\therefore dV = \frac{2}{3}CT^{2/3}dT$$

$$\text{or } \frac{dV}{V} = \frac{2}{3} \frac{dT}{T}$$

$$\therefore W = \int_{T_1}^{T_2} RT \left(\frac{2}{3} \right) \frac{dT}{T}$$

$$= \frac{2}{3} R(T_2 - T_1) = 166.2 \text{ J}$$



- Q.6 A mercury thermometer read 80°C when the mercury is at 5.2 cm mark and 60°C when the mercury is at 3.9 cm mark. Find the temperature when the mercury level is at 2.6 cm mark.

Sol. $\frac{l_1 - l_2}{l_1 - l_3} = \frac{\alpha l_0 (T_1 - T_2)}{\alpha l_0 (T_1 - T_3)} = \frac{T_1 - T_2}{T_1 - T_3}$

or $\frac{5.2 - 3.9}{5.2 - 2.6} = \frac{80 - 60}{80 - T_3}$

$1.3 (80 - T_3) = 2.6 (20)$ or $T_3 = 40^\circ\text{C}$

- Q.7 A vertical cylinder piston system has cross-section S. It contains 1 mole of an ideal monoatomic gas under a piston of mass M. At a certain instant a heater is switched on which transmits a heat q per unit time of the cylinder. Find the velocity v of the piston under the condition that pressure under the piston is constant and the system is thermally insulated.

Sol. Gas pressure $= P_0 + \frac{Mg}{S}$, Where M is mass of the piston.

As $C_V = \frac{3}{2}R$

$\therefore \Delta U = \frac{3}{2} R \Delta T = \frac{3}{2} P \Delta V$

$Q = P \Delta V + \Delta U = P \Delta V + \frac{3}{2} P \Delta V = \frac{5}{2} P \Delta V$

$\Delta V = S dx$

or $Q = q \cdot dt = \frac{5}{2} PS dx$

or $\frac{dx}{dt} = \frac{2q}{5PS} = \frac{2q}{5(P_0 + \frac{Mg}{S})S}$

- Q.8 A typer pumped to a pressure 3.3375 atm at 27°C suddenly bursts. What is the final temperature ($\gamma = 1.5$)?

(A) 27°C (B) -27°C (C) 0°C (D*) -73°

Sol. $T_1^\gamma P_1^{1-\gamma} = T_2^\gamma P_2^{1-\gamma}$

or $\left(\frac{T_1}{T_2}\right)^\gamma = \left(\frac{P_1}{P_2}\right)^{\gamma-1} = \left(\frac{300}{T_2}\right)^{3/2} = \left(\frac{3.375}{1}\right)^{3/2-1}$

or $T_2 = \frac{300}{(3.375)^{1/3}} = 200 \text{ K} = -73^\circ\text{C}$

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- Q.9 3 Moles of a gas mixture having volume V and temperature T is compressed to 1/5th of the initial volume. Find the change in its adiabatic compressibility if the gas obeys $PV^{19/13} = \text{constant}$ [$R = 8.3 \text{ J/mol-K}$]

Sol. Bulk modulus $B = \gamma P$



$$\text{Compressibility } C = \left(\frac{1}{B} \right) = \frac{1}{\gamma P}$$

$$\text{and } \Delta C = C - C$$

$$\text{or } \Delta C = \frac{1}{\gamma} \left[\frac{1}{P'} - \frac{1}{P} \right]$$

$$PV^\gamma = P' \left(\frac{V}{5} \right)^\gamma$$

$$\text{With } \gamma = \frac{19}{13} \text{ and } P' = 5^\gamma P, 11$$

$$\Delta C = \frac{1}{\gamma P} \left[\frac{1}{5^\gamma} - \frac{1}{1} \right] = \frac{13 \times 0.905}{19 P}$$

$$\text{But } PV = nRT \text{ or } P = \frac{nRT}{V}$$

$$\Delta C = \frac{13 \times 0.905 V}{19 \times 3 \times 8.317 T} = \frac{-0.0248 V}{T}$$

- Q.10 One mole of an ideal gas is contained under a weightless piston of a vertical cylinder at a temperature T. The space over the piston opens into the atmosphere. What work has to be performed in order to increase isothermally the gas volume under the piston η times

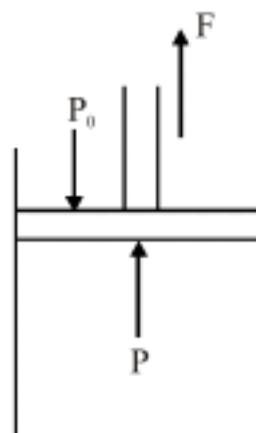
Sol. Let A be the area of cross-section

$$F + PA = P_0 A$$

$$F = (P_0 - P)A$$

Work done by the agent

$$W = \int_V^{\eta V} F dx = \int_V^{\eta V} (P_0 - P) A dx$$



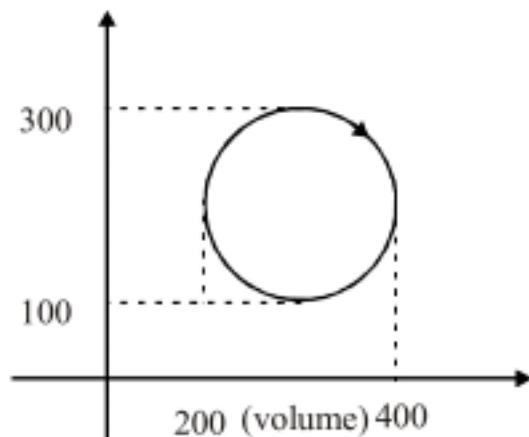
$$= \int_V^{\eta V} (P_0 - P) dV$$

$$= P_0 (\eta - 1)V - \int_V^{\eta V} nRT \frac{dV}{V}$$

$$= RT(\eta - 1) - n \log_e \eta$$



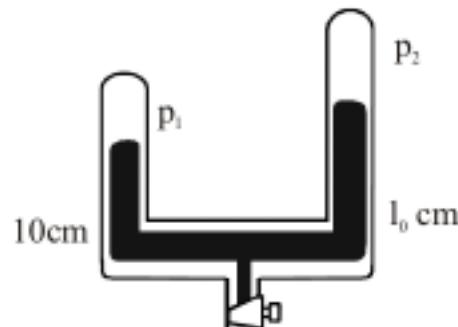
- Q.11 Calculate the heat absorbed by the system in going through the process shown in figure
 (A) 31.4 J (B) 3.14 J (C) 3.14×10^4 J (D) none



Sol. Heat absorbed = πr^2
 $= \pi (P_r)(V_r)$
 $= 3.14 (100 \times 10^3) (100 \times 10^{-6})$
 $= 31.4 \text{ J}$

- Q.12 A mercury manometer consists of two unequal arms of equal cross-section 1 cm^2 and lengths 100cm and 50cm. The two open ends are sealed with air in the tube at a pressure of 80 cm of mercury. Some amount of mercury is now introduced in the monometer through the stopcock connected to it. If mercury rises in the shorter tube to a length 10 cm in steady state, find the length of the mercury column risen in the longer tube.

Sol. Let p_1 and p_2 be the pressures in centimetre of mercury in the two arms after introducing mercury in the tube. Suppose the mercury column rises in the second arm to l_0 cm.



Using $pV = \text{constant}$ for the shorter arm,

$$(80\text{cm})(50\text{cm}) = p_1(50\text{cm} - 10\text{cm})$$

$$\text{or } p_1 = 100 \text{ cm.} \quad \dots(\text{i})$$

Using $pV = \text{constant}$ for the longer arm,

$$(80 \text{ cm})(100\text{cm}) = p_2(100 - l_0) \text{ cm} \quad \dots(\text{ii})$$

From the figure,

$$p_1 = p_2 + (l_0 - 10) \text{ cm.}$$

Thus by (i),

$$100 \text{ cm} = p_2 + (l_0 - 10) \text{ cm}.$$

$$\text{or } p_2 = 110 \text{ cm} - l_0 \text{ cm}$$

Putting in (ii),

$$(110 - l_0)(100 - l_0) = 8000$$

$$\text{or, } l_0^2 - 210 l_0 + 3000 = 0$$

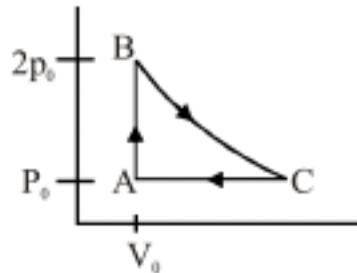
$$\text{or } l_0 = 15.5$$

The required length is 15.5 cm.



- Q.13 An ideal gas has pressure p_0 , volume V_0 and temperature T_0 . It is taken through an isochoric process till its pressure is doubled. It is now isothermally expanded to get the original pressure. Finally, the gas is isobarically compressed to its original volume V_0 . (a) Show the process on a p-V diagram. (b) What is the temperature in the isothermal part of the process? (c) What is the volume at the end of the isothermal part of the process?

Sol. (a) The process is shown in a p-V diagram in figure. The process starts from A and goes through ABCA.



(b) Applying $pV = nRT$ at A and B,

$$p_0 V_0 = nRT_0$$

$$\text{and } (2p_0)V_0 = nRT_B$$

$$\text{Thus, } T_B = 2T_0$$

This is the temperature in the isothermal part BC.

(c) As the process BC is isothermal, $T_C = T_B = 2T_0$.

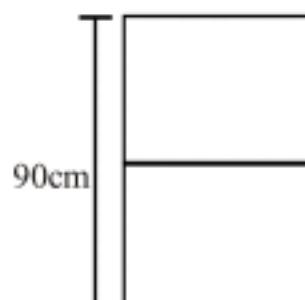
Applying $pV = nRT$ at A and C,

$$p_0 V_0 = nRT_0$$

$$\text{and } p_0 V_C = nR(2T_0)$$

$$V_C = 2V_0$$

- Q.14 Figure shown a vertical cylindrical vessel separated in two parts by a frictionless piston free to move along the length of the vessel. The length of the cylinder is 90 cm and the piston divides the cylinder in the ratio of 5 : 4. Each of the two parts of the vessel contains 0.1 mole of an ideal gas. The temperature of the gas is 300 K in each part. Calculate the mass of the piston.





Sol. Let l_1 and l_2 be the lengths of the upper part and the lower part of the cylinder respectively. clearly, $l_1 = 50 \text{ cm}$ and $l_2 = 40 \text{ cm}$. Let the pressures in the upper and lower parts be p_1 and p_2 respectively. Let the area of cross-section of the cylinder be A . The temperature in both parts is $T = 300 \text{ K}$.

Consider the equilibrium of the piston. The forces acting on the piston are

(a) its weight mg

(b) $p_1 A$ downward, by the upper part of the gas and (c) $p_2 A$ upward, by the lower part of the gas.

$$\text{Thus, } p_2 A = p_1 A + mg \quad \dots(\text{i})$$

Using $pV = nRT$ for the upper and the lower parts

$$p_1 l_1 A = nRT \quad \dots(\text{ii})$$

$$\text{and } p_2 l_2 A = nRT. \quad \dots(\text{iii})$$

Putting $p_1 A$ and $p_2 A$ from (ii) and (iii) into (i),

$$\frac{nRT}{l_2} = \frac{nRT}{l_1} + mg$$

$$\text{Thus, } m = \frac{nRT}{g} \left[\frac{1}{l_1} - \frac{1}{l_2} \right]$$

$$= \frac{(0.1 \text{ mol})(8.3 \text{ J/mol-K})(300 \text{ K})}{9.8 \text{ m/s}^2} \left[\frac{1}{0.4 \text{ m}} - \frac{1}{0.5 \text{ m}} \right]$$

$$= 12.7 \text{ kg.}$$

Q.15 Figure shows a cylindrical tube of volume V_0 divided in two parts by a frictionless separator. The walls of the tube are adiabatic but the separator is conducting. Ideal gasses are filled in the two parts. When the separator is kept in the middle, the pressures are p_1 and p_2 in the left part and the right part respectively. The separator is slowly slide and is released at a position where it can stay in equilibrium. Find the volume of the two parts.



Sol. As the separator is conducting, the temperatures in the two parts will be the same. Suppose the common temperature is T when the separator is in the middle. Let n_1 and n_2 be the number of moles of the gas in the left part and the right part respectively. Using ideal gas equation,

$$p_1 \frac{V_0}{2} = n_1 RT$$

$$\text{and } p_2 \frac{V_0}{2} = n_2 RT$$

$$\text{Thus, } \frac{n_1}{n_2} = \frac{p_1}{p_2} \quad \dots(\text{i})$$

The separator will stay in equilibrium at a position where the pressures on the two sides are equal. Suppose the volume of the left part is V_1 and of the right part is V_2 in this situation. Let the common pressure be p' . Also, let the common temperature in this situation be ' T '.

Using ideal gas equation

and $p'V_1 = n_1 RT'$
 $p'V_2 = n_2 RT'$

or, $\frac{V_1}{V_2} = \frac{n_1}{n_2} = \frac{p_1}{p_2}$ [using(i)]

Also, $V_1 + V_2 = V_0$

Thus, $V_1 = \frac{p_1 V_0}{p_1 + p_2}$ and $V_2 = \frac{p_2 V_0}{p_1 + p_2}$



Q.16 A gas is heated isobarically and the heat used for external work is W. Find the total amount of heat supplied.

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

$$\begin{aligned} &= nRT + nC_V \Delta T = nRT + \frac{nR\Delta T}{\gamma-1} = (nR\Delta T) \left(\frac{\gamma}{\gamma-1} \right) \\ &= \frac{W\gamma}{\gamma-1} \quad [\because W = nR\Delta T] \end{aligned}$$

Q.17 A vessel contains a mixture consisting of $m_1 = 7\text{ g}$ of nitrogen ($M_1 = 28$) and $m_2 = 11\text{ g}$ of carbon dioxide ($M_2 = 44$) at temperature $T = 300\text{ K}$ and pressure $p_0 = 1\text{ atm}$. Find the density of the mixture.

Sol. Let V be the volume of the vessel. Then $\rho_{\text{mis}} = \frac{m_1 + m_2}{V}$

Let p_1 and p_2 be the partial pressure

Then $p_1 V = \frac{m_1}{M_1} RT$ and $p_2 V = \frac{m_2}{M_2} RT$, $p_0 = p_1 + p_2$

$\therefore p_0 = \left(\frac{m_1}{M_1} + \frac{m_2}{M_2} \right) \frac{RT}{V}$

$\therefore \rho_{\text{mix}} = \frac{(m_1 + m_2) M_1 M_2}{m_1 M_2 + m_2 M_1} \times \frac{p_0}{RT}$

$$\begin{aligned} &= \frac{(7+11) \times 28 \times 44 \times 10^{-3}}{7 \times 44 + 11 \times 28} \times \frac{10^5}{8.3 \times 300} \\ &= 1.446 \text{ kg m}^{-3} = 1.446 \text{ per litre} \end{aligned}$$