KINETIC THEORY OF GASES AND THERMODYNAMICS

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.

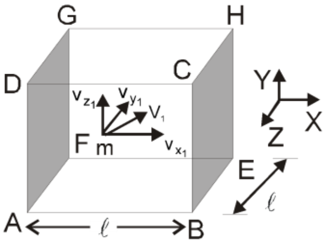
(d) The collision between molecules and the wall of the container is perfectly elastic. It means kinetic energy is conserved in each collision.

(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.

$$v_1^2 = v^2_{x_1} + v^2_{y_1} + v^2_{z_1}$$

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

$= m\, v_{x_1} - (-m\, v_{x_1}) = 2m\, v_{x_1}$

The time taken between the successive impacts on the face BCHE = $\dfrac{\text{distance}}{\text{velocity}} = \dfrac{2\ell}{v_{x_1}}$

Time rate of change of momentum due to collision = $\dfrac{\text{change in momentum}}{\text{time taken}} = \dfrac{2mv_{x_1}}{2\ell / v_{x_1}} = \dfrac{mv^2_{x_1}}{\ell}$

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

$$F_x = \frac{mv^2_{x_1}}{\ell} + \frac{mv^2_{x_2}}{\ell} + \frac{mv^2_{x3}}{\ell} + \ldots\ldots\ldots\ldots + \frac{mv^2_{x_n}}{\ell} = \frac{m}{\ell}\left(v^2_{x_1} + v^2_{x_2} + v^2_{x_3} + \ldots\ldots\ldots\ldots + v^2_{x_n}\right) = \frac{mN}{\ell} < v^2_x >$$

where = mean square velocity in x-direction. Since molecules do not favour any particular direction therefore $< v^2_x > = < v^2_y > = < v^2_z >$. But $< v^2 > = < v^2_x > + < v^2_y > + < v^2_z >$

$\Rightarrow \quad < v^2_x > = \dfrac{< v^2 >}{3}$ Pressure is equal to force divided by area.

$P = \dfrac{F_x}{\ell^2} = \dfrac{M}{3\ell^3} < v^2 > = \dfrac{M}{3V} < v^2 >$. Pressure is independent of x, y, z directions.

Where ℓ^3 = volume of the container = V

M = total mass of the gas, $<v^2>$ = mean square velocity of molecules ⇒ $P = \frac{1}{3}\rho <v^2>$

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

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 velocity of the gas.

Pressure exerted by the gas is $P = \frac{1}{3}\rho <v^2> = \frac{2}{3} \times \frac{1}{2}\rho <v^2>$ or $P = \frac{2}{3}E$, $E = \frac{3}{2}P$

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.

MAXWELL'S DISTRIBUTION LAW :

Distribution Curve – A plot of $\frac{dN(v)}{dv}$ (number of moleucles per unit speed interval) against c is known as Maxwell's distrubution curve. The total area under the curve is given by the integral .

$$\int_0^\infty \frac{dN(v)}{dv}dv = \int_0^\infty dN(v) = N$$

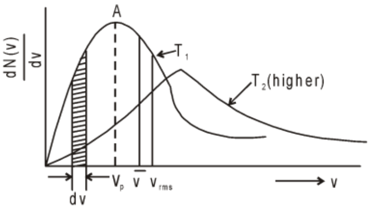


Figure shows the distribution curves for two different temperatures. At any temperature the number of molecules in a given speed interval dv is given by the area under the curve in that interval (shown shaded). This number increases, as the speed increases, upto a maximum and then decreases asymptotically toward zero. Thus, maximum number of the molecuels 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 : $\bar{v} = \sqrt{\frac{8}{\pi}\frac{kT}{m}} = 1.59\sqrt{kT/m}$ (derivation is not in the course)

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

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 probale speed is $v_p = \sqrt{\frac{2kT}{m}} = 1.41 . \sqrt{kT/m}$

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

DEGREE OF FREEDOM :

Total number of independent co-ordinates which must be known to complety 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. $\left(\frac{1}{2}mV_x^2 + \frac{1}{2}mV_y^2 + \frac{1}{2}mV_z^2\right)$

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 , 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 EQUPARTITION 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* = $\frac{1}{2}fkT$

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* = $\frac{f}{2}$ *nRT.***

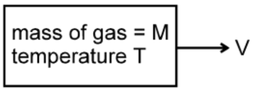
Solved Examples

Example 1. A light container having a diatomic gas enclosed with in 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?

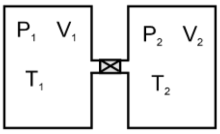
Solution : (i) K.E. = $\frac{5}{2}$ nRT



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

$$\text{K.E.} = \frac{1}{2}MV^2 + \frac{5}{2}nRT$$

Example 2. Two nonconducting containers having volume V_1 and V_2 contain monoatomic and dimatomic 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.



Solution : $n_1 = \frac{P_1V_1}{RT_1}$ $n_2 = \frac{P_2V_2}{RT_2}$

$n = n_1 + n_2$ (number of moles are conserved)

Finally pressure in both parts & temperature of the both the gases will be become equal.

$$\frac{P(V_1+V_2)}{RT} = \frac{P_1V_1}{RT_1} + \frac{P_2V_2}{RT_2}$$

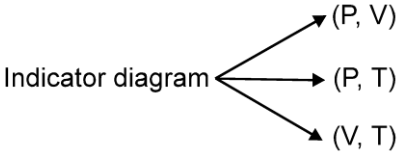
From energy conservation

$$\frac{3}{2}n_1RT_1 + \frac{5}{2}n_2RT_2 = \frac{3}{2}n_1RT + \frac{5}{2}n_2RT$$

$$\Rightarrow \quad T = \frac{(3P_1V_1+5P_2V_2)T_1T_2}{3P_1V_1T_2+5P_2V_2T_1} \quad \Rightarrow P = \left(\frac{3P_1V_1+5P_2V_2}{3P_1V_1T_2+5P_2V_2T_1}\right)\left(\frac{P_1V_1T_2+P_2V_2T_2}{V_1+V_2}\right)$$

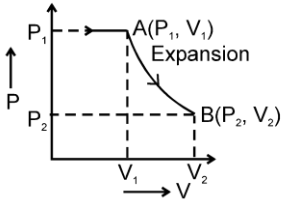
INDICATOR DIAGRAM :

A graph representing the variation of pressure or variation of tempeture or variation of volume with each other is called or 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.

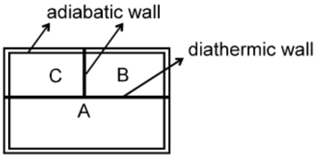
THERMODYNAMIC SYSTEM

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 nor matter with its surroundings.



ZEROTH LAW OF THERMODYNAMICS :

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

EQUATION OF STATE (FOR IDEAL GASES) :

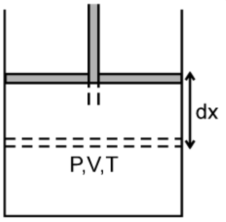
The relation between the thermodynamic variables (P, V, T) of the system is called equation of state. The equation of state for an ideal gas of n moles is given by $PV = nRT$,

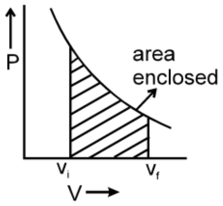
WORK DONE BY A GAS :

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 $dW = F\,dx = PA\,dx$

Since $A\,dx = dV$, increase in volume of the gas is dV ⇒ $dW = P\,dV$





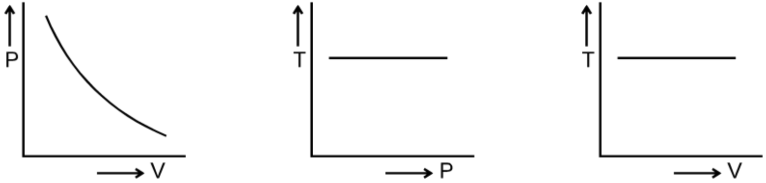
or $W = \int dW = \int P\,dV$

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.

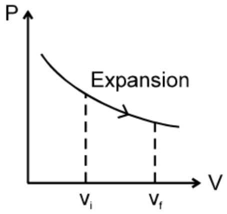
Slope of P-V curve in isothermal process:

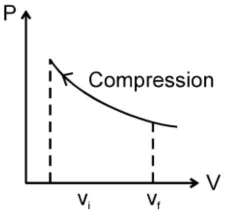
PV = constant = C ⇒ $\frac{dP}{dV} = -\frac{P}{V}$

Work done in isothermal process:

$W = nRT\,\ell n\,\frac{V_f}{V_i}$ $\begin{bmatrix} \text{If } v_f > v_i \text{ then W is positive} \\ \text{If } v_f < v_i \text{ then W is negative} \end{bmatrix}$

$W = \left[2.303\, nRT \log_{10} \frac{V_f}{V_i}\right]$





Internal energy in isothermal process :

$U = f(T) \Rightarrow \Delta U = 0$

(b) **Iso- Choric Process (Isometric Process) :**

V = constant

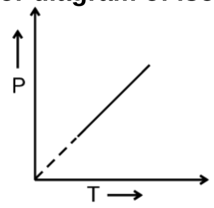
⇒ change in volume is zero ⇒ $\frac{P}{T}$ is constant

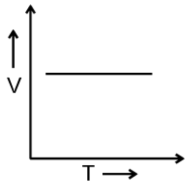
$\frac{P}{T} = \text{const.}$ (Galussac-law)

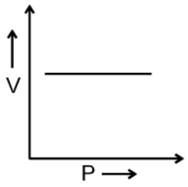
Work done in isochoric process :

Since change in volume is zero therefore $dW = p\ dV = 0$

Indicator diagram of isochoric process :







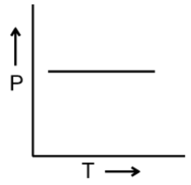
Change in internal energy in isochoric process : $\Delta U = n\frac{f}{2}R\ \Delta T$

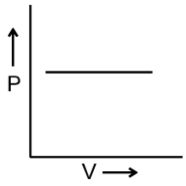
Heat given in isochoric process : $\Delta Q = \Delta U = n\frac{f}{2}R\ \Delta T$

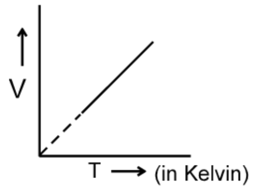
(c) **Isobaric Process :** Pressure remains constant in isobaric process

∴ P = constant ⇒ $\frac{V}{T}$ = constant

Indicator diagram of isobaric process :







Work done in isobaric process :

$\Delta W = P\ \Delta V = P\ (V_{\text{final}} - V_{\text{initial}}) = nR\ (T_{\text{final}} - T_{\text{initial}})$

Change in internal energy in isobaric process : $\Delta U = n\ C_V\ \Delta T$

Heat given in isobaric process :

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

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

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

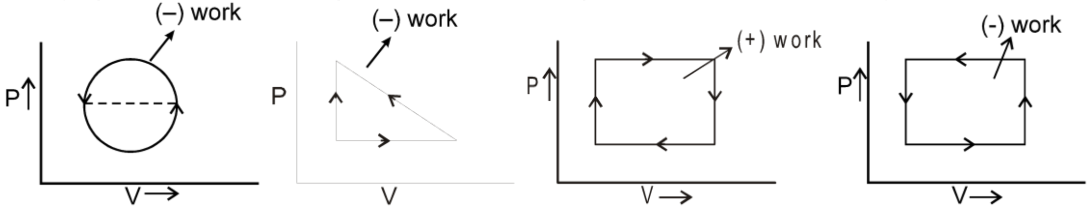
Work done = Area enclosed under P-V diagram.

Change in internal Energy $\Delta U = 0$

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

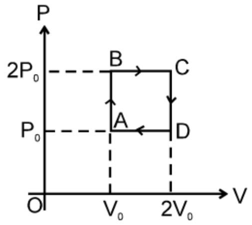
If the process on P-V curve is clockwise , then net work done is (+ve) and vice-versa.

The graphs shown below explains when work is positive and when it is negative



Solved Examples

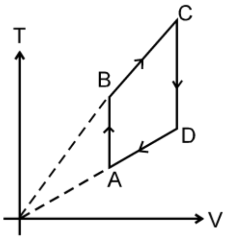
Example 3. Find out the work done in the given graph. Also draw the coresponding T-V curve and P-T curve.

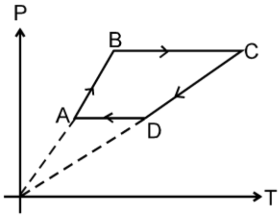


Solution : Since in P-V curves area under the cycle is equal to work done therefore work done by the gas is equal to P_0V_0.

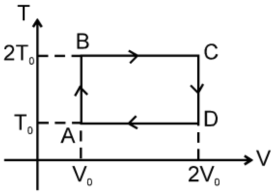
Line A B and CD are isochoric line, line BC and DA are isobaric line.

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





Example 4. 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.



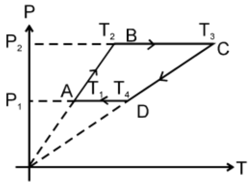
Solution : Since path AB and CD are isochoric therefore work done is zero during path AB and CD. Process BC and DA are isothermal, therefore

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

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

Total work done = $W_{BC} + W_{DA} = 2nRT_0 \ln 2 - nRT_0 \ln 2 = nRT_0 \ln 2$

Example 5. 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 $W_{BC} = nR\Delta T = nR(T_3 - T_2)$

$W_{DA} = nR(T_1 - T_4)$

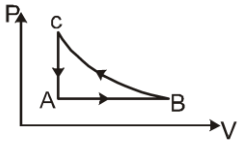
Total work done = $W_{BC} + W_{DA} = nR(T_1 + T_3 - T_4 - T_2)$

Example 6. Consider the cyclic process ABCA on a sample of 2.0 mol of an ideal gas as shown in figure. The temperatures of the gas at A and B are 300 K and 500 K respectively. A total of 1200 J heat is withdrawn from the sample in the process. Find the work done by the gas in part BC. Take R = 8.3J/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,

$W_{AB} + W_{BC} + W_{CA} = -1200$ J. ....(i)

The work done during the process AB is



$W_{AB} = P_A (V_B - V_A)$

$= nR(T_B - T_A)$

$= (2.0$ mol$)$ $(8.3$ J/mol–K$)$ $(200$ K$)$

$= 3320$ J

The work done by the gas during the process CA is zero as the volume remains constant. From (i),

3320 J $+ W_{BC} = -1200$ J or $W_{BC} = -4520$ J.$= -4520$ J.

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 + dW**.

But, $dW = P\,dV$ $\quad dQ = dU + P\,dV$

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.

Solved Examples

Example 7. 1 gm water at 100ºC is heated to convert into steam at 100ºC at 1 atm. Find out change in internal energy of water. It is given that volume of 1 gm water at 100ºC = 1 cc. volume of 1 gm steam at 100ºC = 1671 cc. Latent heat of vaporization = 540 cal/g. (Mechanical equivalent of heat J = 4.2J/cal.)

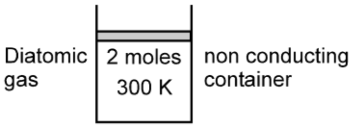
Solution : From first law of thermodynamic $\Delta Q = \Delta u + \Delta w$

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

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

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

Example 8. Two moles of a diatomic gas at 300 K are kept in a nonconducting 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



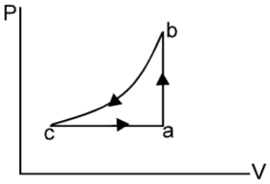
Solution : $\Delta Q = \Delta u + \Delta w$

Since container is nonconducting therefore

$$\Delta Q = 0 = \Delta u + \Delta w \quad \Rightarrow \quad \Delta W = -\Delta u = -n\frac{f}{2}R\ \Delta T = -2 \times \frac{5}{2}R\,(400 - 300)$$

$= -5 \times 8.314 \times 100\text{ J} = -5 \times 831.4\text{ J} = -4157\text{ J}$

Example 9. A sample of an ideal gas is taken through the cyclic process abca (figure. It absorbs 50 J of heat during the part ab, no heat during bc and rejects 70 J of heat during ca. 40 J of work is done on the gas during the part bc. (a) Find the internal energy of the gas at b and c if it is 1500 J at a. (b) Calculate the work done by the gas during the part ca.



Solution : (a) In the part ab the volume remains constant. Thus, the work done by the gas is zero. The heat absorbed by the gas is 50 J. The increase in internal energy from a to b is

$\Delta U = \Delta Q = 50\text{J}.$

As the internal energy is 1500 J at a, it will be 1550 J at b. In the part bc, the work done by the gas is $\Delta W = -40\text{J}$ and no heat is given to the system. The increase in internal energy from b to c is

$\Delta U = -\Delta W = 40\text{ J}.$

As the internal energy is 1550 J at b, it will be 1590 J at c.

(b) The change in internal energy from c to a is

$\Delta U = 1500\text{ J} - 1590\text{ J} = -90\text{ J}.$

The heat given to the system is $\Delta Q = -70\text{J}.$

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

$\Delta W_{ca} = \Delta Q - \Delta U$

$= -70\text{ J} + 90\text{ J} = 20\text{ J}.$

Example 10. The internal energy of a monatomic ideal gas is 1.5 nRT. One mole of helium is kept in a cylinder of cross-section 8.5 cm^2. The cylinder is closed by a light frictionless piston. The gas is heated slowly in a process during which a total of 42 J heat is given to the gas. If the temperature rises through 2^{o}C, find the distance moved by the piston. Atmospheric pressure = 100 kPa.

Solution : The change in internal energy of the gas is

$\Delta U = 1.5\text{ nR }(\Delta T)$

$= 1.5\text{ (1 mol) (8.3 J/mol-K) (2K)}$

$= 24.9\text{ J.}$

The heat given to the gas = 42 J

The work done by the gas is

$\Delta W = \Delta Q - \Delta U$

$= 42\text{ J} - 24.9\text{ J} = 17.1\text{ J.}$

If the distance moved by the piston is x, the work done is

$\Delta W = (100\text{ kPa})\ (8.5\text{ cm}^2)\ x.$

Thus, $(10^5\text{ N/m}^2)\ (8.5 \times 10^{-4}\text{ m}^2)\ x = 17.1\text{ J}$

or, $x = 0.2\text{m} = 20\text{ cm.}$

Example 11. A sample of ideal gas (f =5) is heated at constant pressure. If an amount 140 J of heat is supplied to the gas, find (a) the change in internal energy of the gas (b) the work done by the gas.

Solution : Suppose the sample contasins n moles. Also suppose the volume changes from V_1 to V_2 and the temperature changes from T_1 to T_2.

The heat supplied is

$$\Delta Q = \Delta U + P\Delta V = \Delta U + nR\Delta T = \Delta U + \frac{2\Delta U}{f}$$

(a) The change is internal energy is

$\Delta U = n\frac{f}{2}R$ $(T_2 - T_1) =$ $n\frac{f}{2}R$ $(T_2 - T_1)$

$= \frac{f}{2+f}\Delta Q = \frac{140J}{1.4} = 100$ J.

(b) The work done by the gas is

$\Delta W = \Delta Q - \Delta U$

$= 140$ J – 100 J $= 40$ J.

Effeciency of a cycle (η) :

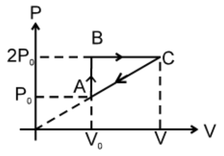
$$\eta = \frac{\text{total Mechanical work done by the gas in the whole process}}{\text{Heat absorbed by the gas (only + ve)}}$$

$$= \frac{\text{area under the cycle in P-V curve}}{\text{Heat injected into the system}}$$

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

Solved Examples

Example 12. n moles of a diatomic gas has undergone a cyclic process ABC as shwon in figure. Temperature at a is T_0. Find



(i) Volume at C ?

(ii) Maximum temprature ?

(iii) Total heat given to gas ?

(iv) Is heat rejected by the gas, if yes how much heat is rejected ?

(v) Find out the efficiency

Solution : (i) Since triangle O A V_0 and OC V are simillar therefore

$\frac{2P_0}{V} = \frac{P_0}{V_0}$ ⇒ $V = 2V_0$

(ii) Since process AB is isochoric hence

$\frac{P_A}{T_A} = \frac{P_B}{T_B}$ ⇒ $T_B = 2T_0$

Since process BC is isobaric therefore $\frac{T_B}{V_B} = \frac{T_C}{V_C}$ ⇒ $T_C = 2T_B = 4\,T_0$

(iii) Since process is cyclic therefore

$\Delta Q = \Delta W =$ area under the cycle $= \frac{1}{2}P_0V_0$.

(iv) Since Δu and ΔW both are negative in process CA

∴ ΔQ is negative in process CA and heat is rejected in process CA

$\Delta Q_{CA} = \Delta w_{CA} + \Delta u_{CA}$

$= \frac{1}{2}[P_0 + 2P_0]\,V_0 - \frac{5}{2}nR\,(T_c - T_a)$

$= -\frac{1}{2}[P_0 + 2P_0]\,V_0 - \frac{5}{2}nR\left(\frac{4P_0V_0}{nR} - \frac{P_0V_0}{nR}\right) = -9P_0V_0 =$ Heat injected.

(v) η = efficiency of the cycle $= \frac{\text{work done by the gas}}{\text{heat injected}} = \eta = \frac{P_0V_0/2}{Q_{\text{injected}}} \times 100$

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

$$= \left[\frac{5}{2}nR(2T_0 - T_0)\right] + \left[\frac{5}{2}nR(2T_0) + 2P_0(2V_0 - V_0)\right] = \frac{19}{2}P_0V_0. \quad \Rightarrow \quad \eta = \frac{100}{19}\ \%$$

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 susbstance 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 capacities of a gas are 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 C_V, 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,

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

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

$$C_V = \frac{3}{2}R\ , \quad C_P = \frac{5}{2}R \qquad \Rightarrow \quad \frac{C_P}{C_V} = \gamma = \frac{5}{3} = 1.67$$

(ii) For a diatmoc gas f = 5

$$C_V = \frac{5}{2}R,\ C_P = \frac{7}{2}R \qquad \gamma = \frac{C_P}{C_V} = 1.4$$

(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 CO_2; f = 5, it is linear]

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

$$C_V = \frac{f}{2}R,\quad C_P = \left(\frac{f}{2}+1\right)R,\qquad \gamma = \frac{C_P}{C_V} = \left[1+\frac{2}{f}\right]$$

Solved Examples

Example 13 In a thermodynamic process, the pressure of a certain mass of gas is changed in such a way that 20 Joule heat is released from it and 8 Joule work is done on the gas. If the initial internal energy of the system is 30 joule then the final internal energy will be

Solution. $dQ = dU + dW$

$dQ = U_{final} - U_{initial} + dW$

$U_{final} = dQ - dW + U_{initial}$

or $U_{final} = -20 + 8 + 30$

of $U_{final} = 18$ Joule

Example 14 A gas is contained in a vessel fitted with a movable piston. The container is placed on a hot stove. A total of 100 cal of heat is given to the gas & the gas does 40 J of work in the expansion resulting from heating. Calculate the increase in internal energy in the process.

Solution. Heat given to the gas is $\Delta Q = 100$ cal $= 418$ J.

Work done by the gas is $\Delta W = 40$ J

The increase in internal energy is

$\Delta U = \Delta Q - \Delta W = 418\text{J} - 40\text{ J} = 378\text{ J}$

Example 15 A gas is compressed from volume 10 m^3 to 4 m^3 at constant pressure 50N/m^2. Gas is given 100 J energy by heating then its internal energy.

Solution. $P = 50\ N/m^2$

$dV = 10 - 4 = 6\ m^3$

$\delta W = PdV = 6 \times 50 = 300$ J (Volume is decreasing, $\delta Q = 100$ J)

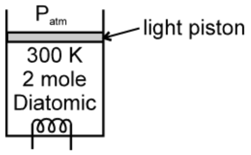
$W = -300$ J

$\delta Q = \delta W + dU$

$100 + 300 = dU$

dU = increased by 400 J

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

(iii) If piston is heavy and movable.

Solution : (i) Since pressure is constant

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

(ii) Since volume is constant

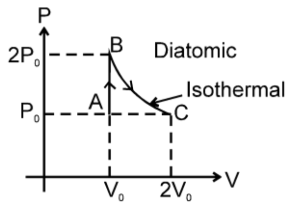
$\therefore\ \Delta W = 0$ and $\Delta Q = \Delta u$ (from first law)

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

(iii) Since pressure is constant

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

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



Solution : From first law of thermodynamics

$\Delta Q_{ABC} = \Delta u_{ABC} + \Delta W_{ABC}$

$\Delta W_{ABC} = \Delta W_{AB} + \Delta W_{BC} = 0 + nR\ T_B \ln \frac{V_C}{V_B} = nR\ T_B \ln \frac{2V_0}{V_0}$

$= nRT_B \ln 2 = 2P_0\,V_0 \ln 2$

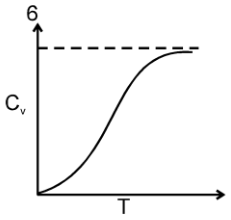
$\Delta u = nC_V\,\Delta T = \frac{5}{2}\,(2P_0V_0 - P_0V_0)$ $\Rightarrow$ $\Delta Q_{ABC} = \frac{5}{2}\,P_0V_0 + 2P_0V_0 \ln 2.$

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

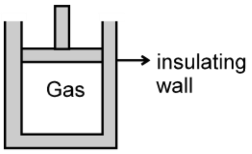
At room temperature average molar specifc heat of all metals are same and is nearly equal to 3R (6 cal. mol^{-1} K^{-1}).

[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 adibatic.

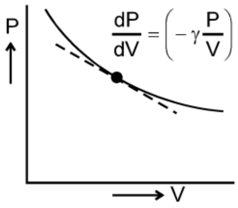
Equation of adiabatic process is given by

PV^{γ} = constant [Poission Law]

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

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

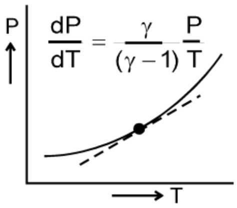
Slope of P-V-curve in adiabatic process : Since PV^{γ} is a constant



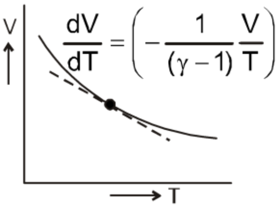
$$\therefore \quad \frac{dP}{dV} = -\gamma\left(\frac{P}{V}\right)$$

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

$$\therefore \quad \frac{dP}{dT} = -\frac{\gamma}{(1-\gamma)}\frac{P}{T} = \frac{(\gamma)}{(\gamma-1)}\frac{P}{T}$$



Slope of T-V-curve :



$$\frac{dV}{dT} = -\frac{1}{(\gamma-1)}\frac{V}{T}$$

Work done in adiabatic Process :

$$\Delta W = -\Delta U = nC_v(T_i - T_f) = \frac{P_iV_i - P_fV_f}{(\gamma-1)} = \frac{nR(T_i - T_f)}{\gamma - 1}$$

work done by system is (+ve) , if $T_i > T_f$ (hence expansion)

work done on the system is (-ve) if $T_i < T_f$ (hence compression)

Solved Examples

Example 18. A quantity of air is kept in a container having walls which are slightly conducting. The initial temperature and volume are 27ºC (equal to the temperature of the surrounding) and 800cm^3 respectively. Find the rise in the temparture if the gas is compressed to 200cm^3 (a) in a short time (b) in a long time. Take $\gamma = 1.4$.

Solution : (a) When the gas is compressed in a short time, the process is abiabatic. Thus,

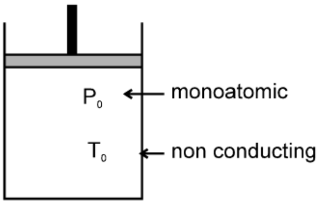
$T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$

or $T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$ = (300 K) × $\left[\frac{800}{200}\right]^{0.4}$ =522 K.

Rise in temperature = $T_2 - T_1$ = 222 K.

(b) When the gas is compressed in a long time, the process is isothermal. Thus, the temperature remains equal to the temperature of the surrounding that is 27ºC. The rise in temperature = 0.

Example 19. A monoatomic gas is enclosed in a nonconducting cylinder having a piston which can move freely. Suddenly gas is compressed to 1/8 of its initiall volume. Find the final pressure and temperature if initial pressure and temperature are P_0 and T_0 respectively.



Solution : Since process is adiabatic therefore

$P_0 V^{\frac{5}{3}} = P_{final}.\left(\frac{V}{8}\right)^{5/3}$ ⇒ $\gamma = \frac{C_P}{C_V} = \frac{5R}{2} / \frac{3R}{2} = \frac{5}{3}$ $P_{final} = 32\,P_0$.

Since process is adiabatic therefore

$T_1\,V_1^{\gamma-1} = T_2\,V_2^{\gamma-1}$ ⇒ $T_0\,V_0^{2/3} = T_{final}\left(\frac{V_0}{8}\right)^{2/3}$ ⇒ $T = 4T_0$

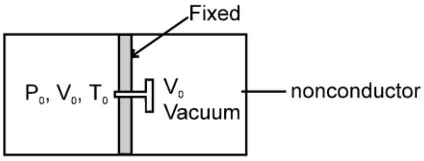
FREE EXPANSION

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.

Solved Examples

Example 20. A nonconducting cylinder having volume $2V_0$ is partitioned by a fixed nonconducting wall in two equal part. 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 finad the final pressure and temperature of the two parts.



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

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

$\Rightarrow$ $\Delta u = 0$ and temperature remains constant.

$T_{final} = T_0$

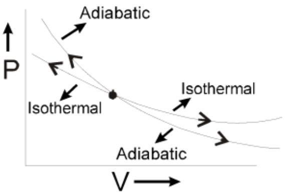
Since the process is isothermal therefore $P_0 \times V_0 = P_{final} \times 2V_0$ $\Rightarrow$ $P_{final} = P_0/2$

Reversible and Irreversible Process

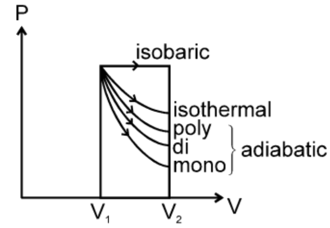
A process is said to be reversible when the various stages of an operation in which it is subjected can be traversed back in the opposite direction in such a way that the substance passes through exactly the same conditions at every step in the reverse process as in the direct process.

A process in which any one of the condition stated for reversible process are not fulfilled is called an irreversible process.

Comparison of slopes of Iso-thermal and Adiabatic Curve



$$\left|\frac{dP}{dV}\right|_{adia} > \left|\frac{dP}{dV}\right|_{isothermal}$$



$W_{mono} < W_{di} < W_{poly} < W_{isothermal} < W_{isobaric}$

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 weather some process is possible or not.

Mixture of non-reacting gases:

(a) Molecular weight = $\dfrac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$, M_1 & M_2 are molar masses.

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

(c) for mixture, $\gamma = \dfrac{C_{p_{mix}}}{C_{V_{mix}}} = \dfrac{n_1 C_{p_1} + n_2 C_{p_2} + ...}{n_1 C_{V_1} + n_2 C_{V_2} + ...}$

Reversible and Irreversible Process

A thermodynamical process taking a system from initial state i to final state f is reversible, if the process can be turned back such that both, the system and the surroundings return to their original states, with no other change anywhere else in the universe.

For a process to be reversible, the following conditions must be satisfied :

1. The process should proceed at an extremely slow rate, i.e., process is quasi-static so that the system is in equilibrium with surroundings at every stage, i.e.

(i) The system remains in mechanical equilibrium, i.e., there is no unbalanced force,

(ii) The system remains in thermal equilibrium, i.e., all parts of the system and the surroundings remain at the same temperature.

(iii) The system remains in chemical equilibrium, i.e., the internal structure of the system does not change.

2. The system should be free from dissipative forces like friction, inelasticity, viscosity, etc. This is because energy spent against such forces cannot be recovered.

As all the conditions mentioned above are of an idealized nature, no process in nature is truly reversible.

Infact, reversibility is an idealized concept which can never be attained. It can at best be approximated.

Some of the examples of approximately reversible processes are :

(i) An ideal gas allowed to expand slowly and then compressed slowly in a cylinder fitted with frictionless movable piston.

(ii) Electrolysis can be taken as a reversible process provided resistance offered by electrolyte is zero.

(iii) Slow compression and expansion of a spring can also be treated as a reversible process.

Now answer the following questions :

Q.1 What are irreversible process

Ans. A process, which does not satisfy any of the conditions for reversible process is called an irreversible process.

Infact, all spontaneous processes of nature are irreversible processes. For example, transfer of heat from a hot body to a cold body, ordinary expansion of a gas, diffusion of gases, stopping of moving body through friction etc. are all irreversible processes.

Q.2 What are fundamental cause of irreversibility ?

Ans. Irreversibility arises mainly from two causes :

(i) Many processes like free expansion or an explosive chemical reaction take the system to non equilibrium states.

(ii) Most processes involve friction, viscosity and other dissipative effects.

As the dissipative effects are present everywhere, and they can be minimised only and cannot be fully eliminated, therefore, most processes we deal with are irreversible processes.

Q.3 Give some example of irreversible process.

Ans. Examples of irreversible processes are :

(i) Most of the chemical reactions are irreversible, because they involve changes in the internal structure of the constituents.

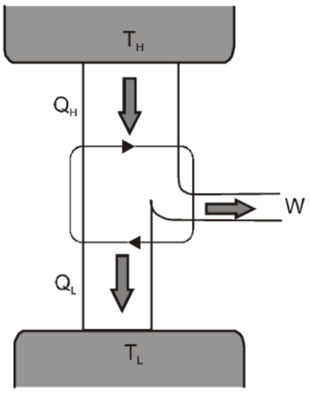
(ii) The decay of organic matter is an irreversible process.

(iii) Rusting of iron is an irreversible process.

(iv) Adiabatic (sudden) compression and expansion of a gas are irreversible processes.

HEAT ENGINES

We have seen that when mechanical work is done on a system, its internal energy increases (remember, we assume that the system does not have any systematic motion). The reverse process in which mechanical work is obtained at the expense of internal energy is also possible. Heat engines are devices to perform this task. The basic activity of a heat engine is shown in figure. It takes some heat from bodies at higher temperature, converts a part of it into the mechanical work and delivers the rest to bodies at lower temperature.



The substance inside the engine comes back to the original state. A process in which the final state of a system is the same as its initial state, is called a cyclic process. An engine works in cyclic process.

Efficiency

Suppose an engine takes an amount Q_H of heat from high-temperature bodies, converts a part W of it into work and rejects an amount Q_L of heat to low-temperature bodies. If the final state of the substance inside the engine is the same as the initial state, there is no change in its internal energy. By first law of thermodynamics, $W = Q_H - Q_L$.

The efficiency of the engine is defined as

$$\eta = \frac{\text{work done by the engine}}{\text{heat supplied to it}} = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

We now describe carnot engine

The significance of the concept of reversibility :

The main concern of thermodynamics is the efficiency with which heat can be converted into mechanical work. It turned out that a heat engine based on idealised reversible processes achieves the highest possible efficiency. All other engines involving irreversibility of some kind have much lower efficiency because there is energy loss in friction viscous forces etc. Therefore, reversibility is an important concept in thermodynamics.

Comprehension :

A steam engine delivers 5.4×10^8 J of work per mintue and take 3.6×10^9 J of heat per minute from its boiler.

Now answer the following questions :

1. Which engine have more efficiency ?

(A) Reversible engine
(B) Irreversible engine
(C) Both have same efficiency
(D) Can't say

Ans. **(A)**

2. What is the efficiency of the engine ?

(A) 10% (B) 15% (C) 20% (D) 25%

Ans. **(B)**

3. How much heat is wasted per minute ?

(A) 3.06×10^9 (B) 3.06×10^8 (C) 3.6×10^9 (D) 3.6×10^8

Ans. **(A)**

4. If this heat engine is used as water pump, then how much water per second can be transfered at a building of height 30 meter ?

(A) 1.8×10^6 Kg (B) 1.8×10^5 Kg (C) 5.4×10^4 Kg (D) 5.4×10^3 Kg

Ans. **(A)**

Sol. Work done per minute output = 5.4×10^8 J

Heat absorbed per minute, input = 3.6×10^9 J

Efficiency, $\eta = \frac{5.4 \times 10^8}{3.6 \times 10^9} = 0.15$

$\% \eta = 0.15 \times 100 = 15$

Heat energy wasted/minute = Heat energy absorbed/minute – Useful work done/minute

$= 3.6 \times 10^9 - 5.4 \times 10^8 = (3.6 \times 0.54) \times 10^9 = 3.06 \times 10^9$ J.

$mgh = W$

$m \times 10 \times 30 = 5.4 \times 10^8 \Rightarrow \quad m = 1.8 \times 10^6$ kg/s

Comprehension

The first law of thermodynamics establishes the essential equivalence between the heat energy and mechanical work and says that the two can be converted into each other. Further, 4.18 joule of mechanical work are required to produce one calorie of heat and vice-versa. However, this law has the following limitations :

1. The first law does not indicate the direction in which the change can occur.

For example (i) when two bodies at different temperatures are put in thermal contact with each other, heat flows from the body at higher temperature to the body at lower temperature. We now know that heat cannot flow from the body at lower temperature to the body at higher temperature, although first law of thermodynamics is not violated.

(ii) When a moving car is stopped by applying brakes, work done against friction is converted into heat. When the car cools down, it does not start moving with the conversion of all its heat energy into mechanical work.

(iii) When a bullet strikes a target, kinetic energy of the bullet is converted into heat energy. But heat energy developed in the target cannot be converted back into mechanical energy of the bullet enabling it to fly back.

2. The first law gives no ideal about the extent of change

Our observations and experience tell that there appears to be no restriction on conversion of mechanical work into heat. But there are severe restrictions on the reverse process, i.e, conversion of heat energy into mechanical energy.

We know that heat is not converted into mechanical energy all by itself. An external agency called heat engine is required for the purpose.

No heat engine can convert all the heat energy received from the source into mechanical energy. The first law of thermodynamics is silent about all this.

3. The first law of thermodynamics gives no information about the source of heat, i.e., whether it is a hot or a cold body.

These limitations lead to the formulation of another law called the "**second law of thermodynamics**".

SECOND LAW OF THERMODYNAMICS

This law specifies the conditions for the conversion of heat into work. There are several statements of this law but the following two are the most significant :

(i) Kelvin-Planck Statement

" It is impossible to construct an engine, operating in a cycle, which will produce no effect other than extracting heat from a reservoir and performing an equivalent amount of work ." In simple words, it is not possible to get a continuous supply of work from a body by cooling it to temperature lower than that of the surroundings.

This form of the law is applicable to heat engines. The working substance of a heat engine, operating in a cycle, cannot convert all the extracted heat into work. It must reject a part of the heat to the sink at a lower temperature. So, in order to convert heat into wrok, it is necessary to have both source and sink. Since all the heat extracted from the source can never be converted into work therefore the efficiency of the engine is never one.

(ii) Rudlope Classius Statement

"It is impossible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing external work on the working substance". In simple words, heat cannot by itself, flow from a body at a lower temperature to a body at a higher temperature.

This form of the law is applicable to ice plants and refrigerators. Ths refrigerant absorbs heat from inside the refrigerator and rejects a greater quantity of heat to the surroundings (at higher temperature) with the help of an external agency say an electric motor. In ammonia ice plant heat is absorbed from the brine solution at a lower temperature and rejected into water at a higher temperature. This is achieved with the help of an external agency like a pump.

Now answer the following questions :

1. What forbids the complete conversion of work into heat?

Ans. Second law of thermodynamics.

2. Can mechanical work be completely converted into heat. Is reverse also possible?

Ans. The mechanical work can be completely converted into heat but heat extracted from some body cannot be completely converted into useful work.

3. **Statement-1 :** It is not possible for a system unaided by any external agency to transfer heat from a body at lower temperature to another body at higher temperature.

Statement-2 : It is not possible to violate the second law of thermodynamics.

Then which of the combination is true.

(1*) T, T (2) T, F (3) F, T (4) F, F

4. "Heat cannot be itself flow from a body at lower temperature to a body at higher temperature” is a statement or consequence of :

(1*) second law of thermodynamics (2) conservation of momentum

(3) conservation of mass (4) first law of thermodynamics

Sol. Heat cannot flow itself from a lower temperature to a body of higher temperature. This corresponds to second law of thermodynamics.

Comprehension :

ENTROPY

Changes in energy within a closed system do not set the direction of irreversible processes. Rather that direction is set by another that we shall discuss hear that is change in entropy ΔS of the system.

Like pressure, volume temperature internal energy etc. we have another thermodynamic variable of a system named entropy. In a given equilibrium state, the system has a definite value of entropy. If the system has a temperature T (in absolute scale) and a small smount of heat ΔQ is given to it, we define the change in the entropy of the system as

$$\Delta S = \frac{\Delta Q}{T} \qquad \text{..........(i)}$$

In general, the temperature of the system may change during a process. If the process is reversible, the change in entropy is defined as

$$S_f - S_i = \int_i^f \frac{\Delta Q}{T} \qquad \text{........(ii)}$$

In an adiabatic reversible process, no heat is given to the system, The entropy of the system remains constant in such a process.

Entropy is related to the disorder in the system. Thus, if all the molecules in a given sample of a gas are made to move in the same direction with the same velocity, the entropy will be samller then that in the actual situation in which the molecules move randomly in all directions.

An interesting fact about entropy is that it is not a conserved quantity. More interesting is the fact that entropy can be created but cannot be destroyed. Once some entropy is created in a process, the universe has to carry the burden of that entropy for ever. The second law of thermodynamics may be stated in terms of entropy as follows.

It is not possible to have a process in which the entropy of an isolated system is decreased.

Now answer the following questions :

1. Which has more entropy a crowd or a militry force ?

Ans. Crowd has more entropy due to randomeness.

2. What is the change in entropy for an adiabatic process ?

Ans. Zero.

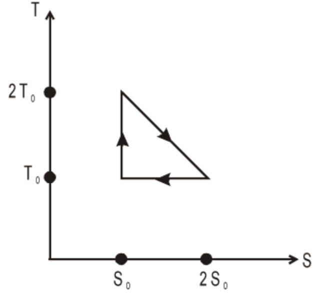
3. When you make ice cubes the entropy of water

(a) does not change (b) increases (c) decreases

(d) may either increase or decrease depending on the process used.

Ans. (b)

4. The temperature-entropy diagram of a reversible engine cycle is given in the figure. Its efficiency is :



(1) $\frac{1}{2}$ (2) $\frac{1}{4}$ (3) $\frac{1}{3}$ (4) $\frac{2}{3}$

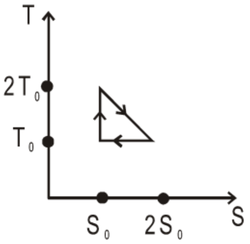
Sol. According to the figure

$Q_1 = T_0S_0 + \frac{1}{2}T_0S_0 = \frac{3}{2}T_0S_0$

$Q_2 = T_0(2S_0 - S_0) = T_0S_0$

$Q_3 = 0$

$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{2}{3} = \frac{1}{3}$



Comprehension

We cannot move a ship in an ocean by utilising the energy of the ocean. Why? Explanation is here.

CARNOT'S IDEAL HEAT ENGINE

It is an ideal heat engine which is free from all the imperfections of an actual engine. So, it cannot be realised in actual practice. It was conceived by Niolas Le'onard Sadi Carnot, a French Engineer. This engine serves us a standard by which the performance of actual engines can be judged. It consists essentially of the following parts.

(i) Source. It serves as source of heat. It is maintained at a constant high tempaerature T_1K. It has infinite thermal capacity i.e., any amount of heat may be extracted from it at a constant temperature T_1.

(ii) Sink. It is a cold body maintained at constant low temperature T_2K. It also has infinite thermal capacity, i.e., any amount of heat rejected to it will not affect its temperature.

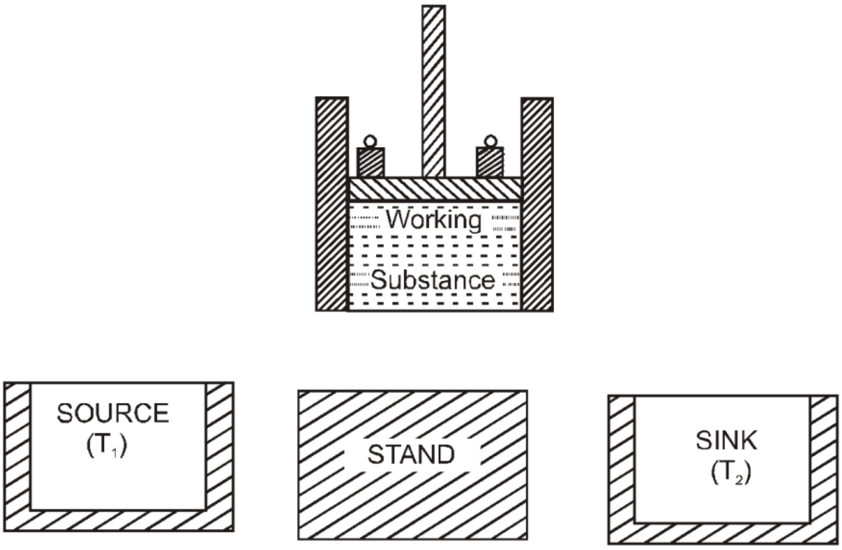


Fig. Carnot's ideal heat engine

(iii) Insulating stand. It is a perfectly non-conducting pad.

(iv) A cylinder : With perfectly non-conducting walls but with a perfectly conducting bottom. It is fitted with a perfectly non-conducting and frictionaless piston over which some weights are placed. One mole of an ideal gas is enclosed in the cylinder. The ideal gas acts as the working substance.

The working substance is subjected to the following four successive reversible operations so as to complete a reversible cycle. This cycle is called Carnot's cycle. The reversibility of operations is a very important assumption because our aim is to find out the maximum efficiency attainable by engine where all sources of irreversibilities are absent.

To begin with let the pressure, volume and temperature be P_1, V_1 and T_1 respectively. The state of the working substance is represented by the point a in the P-V diagram.

(1) Operation I (Isothermal Expansion). The cylinder is placed on the source. The piston is allowed to move out infinitely slowly by reducing very gradually the weights on the piston. The gas expands extremely slowly. As the gas expands, its temperature tends to fall. But since it is in thermal contact with the heat source therefore it will extract a certain amount of heat Q_1 from the source. In this way the temperature of the gas will remain T_1 throughout the process of expansion. In other words, the gas expands isothermally at temperature T_1K. This isothermal expansion is represented by the curve AB on the indicator diagram. Let W_1 be the work done by the gas in expanding from volume V_1 to volume V_2. The pressure decreases from P_1 to P_2.

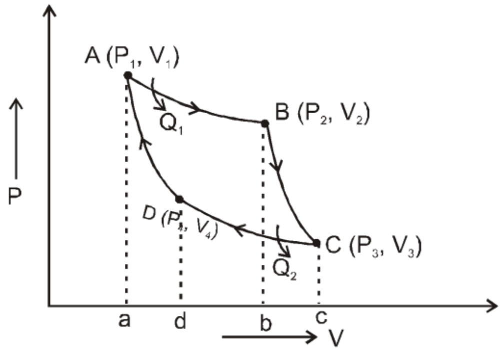


Fig. P-V Diagram of Carnot's cycle

Applying first law of thermodynamics,

$Q_1 = W_1 = \int_{V_1}^{V_2} PdV = RT_1 \log_e \frac{V_2}{V_1} = \text{Area AB ba A}$

(2) Operation II (Adiabatic Expansion). The cylinder is placed on the insulated stand and the piston is allowed to move out. The gas expands adiabatically from volume V_2 to volume V_3 till its temperature falls to T_2K.

The pressure falls from P_2 to P_3.

The adiabatic expansion is represented by the curve BC in the indicator diagram.

The work done by the gas is given by $W_2 = \int_{V_2}^{V_3} PdV = \frac{R}{\gamma - 1}(T_1 - T_2) = \text{Area BC cb B}$

(3) Operation III (Isothermal Compression) The cylinder is placed on the sink and the gas is isothermally compressed until the pressure and volume become P_4 and V_4 respectively. The operation is represented by the isothermal curve CD. The heat Q_2 developed in compression is absorbed by the sink. Let W_3 be the work done on the gas.

Applying first law of thermodynamics.

$Q_2 = W_3 = -\int_{V_3}^{V_4} PdV = -RT_2 \log_e \frac{V_4}{V_3} = RT_2 \log_e \frac{V_3}{V_4}$ = Area C cd DC

(4) Operation IV (Adiabatic Compression) The cylinder is placed on the insulating stand and the gas is compressed adiabatically till it attains its initial pressure P_1 volume V_1 and temperature T_1 . The adiabatic compression is represented by the curve DA in the indicator diagram. Let W_4 be the work done on the gas.

Then, $W_4 = -\int_{V_4}^{V_1} PdV = \frac{R}{\gamma - 1}(T_1 - T_2)$ = Area AD da A

Let W be the net external work done by the working substance during one cycle.

Then, W = Work done by the gas – Work done on the gas

$= W_1 + W_2 - W_3 - W_4 = W_1 - W_3 \qquad [\because W_2 = W_4]$

= area AB ba A – area C cd DC = area ABCDA

The working substance can be taken through the cycle again and again. In this way, more and more work can be done by the engine.

Thermal Efficiency of a Carnot engine is defined as the ratio of the external work done in one cycle to corresponding amount of heat extracted from the source.

Since the working substance is restored to its initial state therefore there is no change in its internal energy.

Applying first law of thermodynamics,

$W = Q_1 - Q_2$

W, Q_1 and Q_2 are all measured in the same units, i.e, either in units of heat or in units of work.

Thermal efficiency, $\eta = \frac{\text{external work done}}{\text{heat extracted}}$ or $\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$

Here, $Q_1 = W_1 = RT_1 \log_e \frac{V_2}{V_1}$ and $Q_2 = W_3 = RT_2 \log_e \frac{V_3}{V_4}$

Now, $\frac{Q_2}{Q_1} = \frac{RT_2 \log_e \left(\frac{V_3}{V_4}\right)}{RT_1 \log_e \left(\frac{V_2}{V_1}\right)}$ or $\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \frac{\log_e \left(\frac{V_3}{V_4}\right)}{\log_e \left(\frac{V_2}{V_1}\right)}$ ....(i)

The points B and C lie on the same adiabatic.

∴ $T_1V_2^{\gamma-1} = T_2V_3^{\gamma-1}$ ....(ii)

The points A and D lie on the same adiabatic.

∴ $V_1^{\gamma-1} = T_2V_4^{\gamma-1}$ ....(iii)

Dividing (2) by (3) be get

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$$ or $$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$ Put in eq. (i)

Then from equation (1), $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$ ⇒ $\eta = 1 - \frac{T_2}{T_1}$

Results (i) The efficiency of the Carnot's ideal engine is independent of the nature of the working substance. It depends only upon the temperatures of the source and sink. The greater the difference between the two temperatures, higher is the efficiency of the Carnot engine.

(ii) Efficiency is the same for all reversible engines working between temperatures T_1 and T_2.

(iii) η is always less than one. The value of η can be one only if $T_2 = 0$ i.e., if the sink is at absolute zero of temperature. Since the absolute zero of temperature cannot be attained therefore η cannot be equal to one.

(iv) When $T_2 = T_1$, then $\eta = 0$.

So, heat cannot be converted into work without a temperature difference. In other words, heat can be converted into work only if a sink at a lower temperature is available. This explains as to why the large amount of heat energy of sea water cannot be used for deriving mechanical work.

Solved Examples

SOLVED EXAMPLE

Example 21. How is the efficiency of a Carnot engine affected by the nature of the working substance?

Solution The efficiency is independent of the nature of the working substance.

Example 22. A Carnot engine operates between 227ºC and 127ºC. If it absorbs 60×10^4 calorie at higher temperature, how much work per cycle can the engine perform.

Solution $T_1 = (227 + 273)$ K = 500 K

$T_2 = (127 + 273)$ K = 400 K

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{400}{500} = \frac{100}{500} = \frac{1}{5}$$

But $\eta = \frac{W}{Q_1}$ or $W = \eta Q_1$ or $W = \frac{1}{5} \times 60 \times 10^4$ cal [∴ $Q_1 = 60 \times 10^4$ cal]

$= 12 \times 10^4$ cal $= 12 \times 10^4 \times 4.2$ J[∴ 4.2 J = 1 cal] $= 5.04 \times 10^5$ J

Example 23. A carnot cycle is performed by air initially at 927ºC. Each stage represents a compression or expansion in the ratio 1 : 32. Calculate (i) the lowest temperature (ii) efficiency of the cycle. Given : $\gamma = 1.4$.

Solution $T_1 = (927 + 273)$ K = 1200 K

$$\frac{V_1}{V_2} = \frac{1}{6}, \gamma = 1.4$$

(i) $T_2\, V_2^{\gamma-1} = T_1V_1^{\gamma-1}$ or $T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1}$ or $T_2 = 1200 = \left(\frac{1}{32}\right)^{1.4-1}$ 300 K

(ii) Efficiency, $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{1200} = 0.75$

% age $\eta = 0.75 \times 100 = 75\%$

Comprehension

REFRIGERATOR (HEAT PUMP)

An ideal refrigerator may be regarged as a carnot's ideal heat engine working in the reverse order.

In an actual refrigerator, the vapours of some low boiling point liquid (ammonia or freon – 12) act as the working substance. The working substance absorbs a certain quantity of heat Q_2 from the cold body or sink at lower temperature T_2. In a household refrigerator, the ice cubes in the freezer compartment and food constitute the cold body. A certain amount of work W is performed by the compressor of the refrigerator on the working substance. The compressor is operated by an electric motor. The quantity of heat Q_1 is rejected to the hot body (atmospher) at temperature T_1 K by the radiator (fixed at the back of the refrigerator).

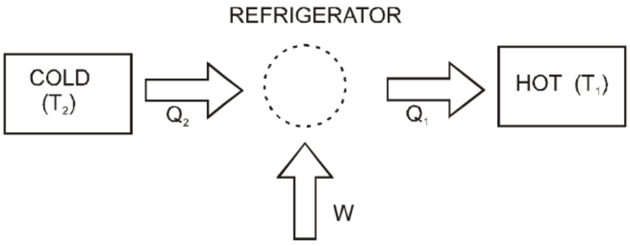


Fig. Refrigerator

Coefficient of performance. It measures the efficiency of a refrigerator.

It is defined as the ratio of the quantity of heat extracted per cycle from the contents of the refrigerator to the mechanical work W done by the external agency to do so.

It is denoted by β or K or ω.

$$\therefore \quad \beta = \frac{Q_2}{W}$$

Smaller the amount of mechanical work done in removing heat Q_2, greater will be the coefficient of performance.

$W = Q_1 - Q_2$ $\quad \therefore \quad \beta = \dfrac{Q_2}{Q_1 - Q_2}$ ....(i)

This expression may be put in another form also.

$$\beta = \frac{1}{\frac{Q_1}{Q_2} - 1}$$

[Dividing the numerator and denominator of equation (1) by Q_2.]

But $\dfrac{Q_1}{Q_2} = \dfrac{T_1}{T_2}$ $\quad \therefore \quad \beta = \dfrac{1}{\frac{T_1}{T_2} - 1}$ ....(ii) $\quad$ or $\quad \beta = \dfrac{T_2}{T_1 - T_2}$

Discussion (i) In actual practice, β varies from 2 to 6 . For an actual refrigerator, the value of β is less than that calculated from equations (1) or (2).

(ii) Lesser the difference in the temperatures of the cooling chamber and the atmosphere, higher is the coefficient of performance of the refrigerator.

(iii) In a heat engine the efficiency can never exceed 100%. But in the case of a refrigerator, the coefficient of performance may be much higher than 100%

(iv) As the refrigerator works, T_2 goes on decreasing due to formation of too much ice. There is practically no change in T_1 . This decreases the value of β. However, if the refrigerator is defrosted, T_2 shall increase and consequenctly the value of β. So, it is necessary to defrost the refrigerator.

Solved Example :

1. Refrigerator transfers heat from a cold body to a hot body. Does this not violate the second law of thermodynamics

Ans. No. This is because external work is being performed.

2. Is coefficient of performance of a refrigerator constant?

Ans. No, the coefficient of performance of refrigerator decreases with decrease in its inside temperature.

Now answer the following Questions :

1. Can we increase the coefficient of performance of a refrigerator by increasing the amount of working substance

(A) No (B) Yes

(C) some time yes, some time no (D) can't say

Ans. **(A)**

2. The door of an operating refrigerator is kept open in a closed room. Then temperature of room will be :

(A) increases slightly (B) decreases slightly

(C) may increase or decrease (D) can't say

Ans. The room will be slightly warmed.

3. A Carnot engine, having an efficiency of $\eta = 1/10$ as heat engine, is used as a refrigerator. If the work done on the system is 10 J, the amount of energy absorbed from the reservoir at lower temperature is

(1) 99 J (2) 90 J (3) 1 J (4) 100 J

Ans. **(2)**

Sol. For Carnot engine using as refrigerator $W = Q_2\left(\frac{T_1}{T_2} - 1\right)$

It is given $\eta = \frac{1}{10}$ ⇒ $\eta = 1 - \frac{T_2}{T_1}$ ⇒ $\frac{T_2}{T_1} = \frac{9}{10}$

So, $Q_2 = 90$ J (as W = 10 J)

The first law of thermodynamics given us an equivalence of the work done and the heat produced. It merely tells us that heat and work are inter convertible and the rate of exchange is fixed, i.e., 4.2 joule is required to produce 1 calorie of heat. This law suffers from the following limitations :

1. **It does not indicate the direction in which the change can proceed.**

Illustrations.

(i) When a hot body is brought in thermal contact with a cold body, heat always flows from the hot body to the cold body. Why heat does not flow from the cold body to the hot body? The first law of thermodynamics is silent about it. So, this law does not indicate the direction of heat transfer.

(ii) It is not possible for a ship to use the huge amounts of heat of the sea waters to operate its engine. What prevents the conversion of heat into work ? The first law is again silent about this. So, the first law of thermodynamics does not specify the conditions under which heat is converted into work.

2. **The first law of thermodynamics gives no idea about the extent to which the change takes place.** It has been observed that no heat engine can convert all the heat extracted from the source into mechanical energy. Why the whole of the heat cannot be converted into mechanical energy. The first law is silent about this question.

Solved Examples

Example 24. Three ideal engines operate between reservoir temperatures of (a) 400 K and 500 K; (b) 600 K and 800 K, and (c) 400 K and 600 K. Rank the engines according to their thermal efficiencies, greatest first.

Ans. c, b, a.

Solution (c) $\eta = 1 - \frac{400}{600} = 1 - \frac{2}{3} = \frac{1}{3}$ (b) $\eta = 1 - \frac{600}{800} = 1 - \frac{3}{4} = \frac{1}{4}$ (a) $\eta = 1 - \frac{400}{500} = 1 - \frac{4}{5} = \frac{1}{5}$

Example 25. Five moles of an ideal gas are taken in a Carnot engine working between 100ºC and 30ºC. The useful work done in one cycle is 420 joule. Calculate the ratio of the volume of the gas at the end and beginning of the isothermal expansion. Give : $R = 8.4$ J mol^{-1} K^{-1}.

Solution $T_1 = (100 + 273)$ K $= 373$ K

$T_2 = (30 + 273)\ K = 303\ K$

Useful work , $W = Q_1 - Q_2 = 420\ J$ ....(i)

Let W_1 and W_2 be the works done during isothermal expansion at T_1 and isothermal compression at T_2.

Now $\frac{Q_1}{Q_2} = \frac{W_1}{W_2} = \frac{T_1}{T_2} = \frac{373}{303}$ ∴ $Q_1 = \frac{373}{303}Q_2$

From equation $W = \frac{373}{303}Q_2 - Q_2$

or $420 = \left(\frac{373}{303} - 1\right)Q_2$ or $Q_2 = 1818\ J$

Again %, $Q_1 = \frac{373}{303}Q_2 = \frac{373}{303} \times 1818\,J = 2238\,J$

Heat used in isothermal expansion is given by

$$Q_1 = \mu RT \log_e \frac{V_2}{V_1} = 2.3026 \times \mu RT \log_{10} \frac{V_2}{V_1}$$

or $2238 = 2.3026 \times 5 \times 8.4 \times 373 \log_{10} \frac{V_2}{V_1}$

On simplification , $\frac{V_2}{V_1} = 1.15$

Example 26. A carnot engine takes in 1000 k cal of heat from a reservoir at 627ºC and exhausts heat to sink at 27ºC. What is its efficiency? When will its efficiency be 100% ?

Solution Temperature of source,

$T_1 = (627 + 273)\ K = 900\ K$

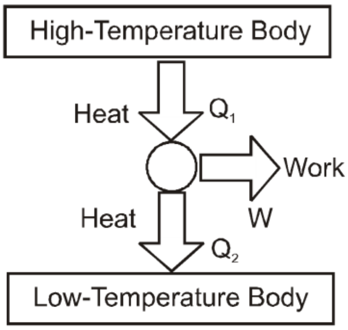
Temperature of sink

$T_2 = (27 + 273)\ K = 300\ K$

Efficiency $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{900} = \frac{2}{3}$

% age efficiency = $\frac{2}{3} \times 100 = 66.67$

The efficiency will be 100 % if $T_2 = 0$, i.e., if the sink is maintained at absolute zero of temperature.



Example 27. You wish to increase the coefficient of performance of an ideal refrigerator. You can be do so by (a) running the cold chamber at a slightly higher temperature, (b) running it at a slightly lower temperature, (c) moving the unit to a slightly warmer room, or (d) moving it to a slightly cooler room. The temperature changes are to be the same in all four cases. List the changes according to the resulting coefficients of performance, greatest first.

Ans. (a), (b), (c), (d)

Solution Closer the temperatures of the two reservoirs to each other higher is the value of coefficient of performance.

Example 28. Assuming a domestic refrigerator as reversible engine working between melting point of ice and the room temperature of 27ºC, calculate the energy in joule that must be supplied to freeze one kg of water. Given : temperature of water – 0ºC, L = 80 cal g^{-1}.

Solution T_1 = (27 + 273) K = 300 K

T_2 = (0 + 273) K = 273 K

Heat to be removed, $Q_2 = mL$

where m is the mass of water and L is the latent heat.

∴ $Q_2 = 1000 \times 80$ cal $= 8 \times 10^4$ cal [∴ m = 1 kg = 1000 g]

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \text{or} \quad Q_1 = \frac{T_1}{T_2} \times Q_2 \quad \text{or} \quad Q_1 = \frac{300}{273} \times 8 \times 10^4 \text{ cal} = 87912.1 \text{ cal}$$

Energy required to be supplied, $W = Q_1 - Q_2$

or W = (87912.1 – 80,000) cal = 9712.1 cal = 7912.1 × 4.2 J = 33230.8 J

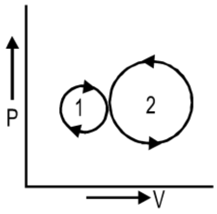
Example.29. 5 gm air is heated from 4ºC to 6ºC. If the specific heat of air at constant volume is 0.172 cal/gm/ºC, then increase in the internal energy of air will be -

Solution. $dU = mC_vdT$

$dU = 5 \times 0.172 \times 2$

dU = 1.72 calorie

Example.30 In the following indicator diagram, the net amount of work done will be -



Solution. The cyclic process 1 is clockwise and the process 2 is anti clockwise. Therefore W_1 will be positive and W_2 will be negative area 2 > area 1, Hence the net work will be negative .

Example.31 Two gram-mole of a gas, which are kept at constant temperature of 0ºC, are compressed from 4 liter to 1 liter. The work done will be

Solution. $W = 2.303\ \mu RT\ \log_{10}\frac{V_2}{V_1}$

$W = 2.303 \times 2 \times 8.4 \times 273 \log_{10}\frac{1}{4}$

$W = 2.303 \times 2 \times 8.7 \times 273 \times (\log_{10} - \log^{4}{}_{10})$ $\because\ \log^{4}{}_{10} = 0.6021$

$\therefore W = -6359$ Joule

Example.32 Air is filled in a motor car tube at 27ºC temperature and 2 atmosphere pressure. If the tube suddenly bursts then the final temperature will be $\left[\left(\frac{1}{2}\right)^{2/7} = 0.82\right]$

Solution. $T_2 = T_1\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$

$T_2 = 300\left(\frac{1}{2}\right)^{\frac{0.4}{1.4}} = 300\left(\frac{1}{2}\right)^{2/7} = 300 \times 8.2 \Rightarrow T_2 = 246$ K

Example.33 One liter of monoatomic gas at NTP is suddenly compressed to 1 c.c. the final pressure will be.

Solution. $P_2 = P_1\left(\frac{V_1}{V_2}\right)^{\gamma}$

$P_2 = 10^5 (10^3)^{5/3} = 10^5 \times 10^5$

$P_2 = 10^{10}$ Pascal

Example.34 A Carnot engine has same efficiency between (i) 100 K and 500K and (ii) Tk and 900 K. The value of T is

Solution. Efficiency $\eta = 1 - \frac{T_2}{T_1}$

or $\eta = 1 - \frac{100}{500} = 1 - \frac{T}{900}$ or $\frac{100}{500} = \frac{T}{900}$

$\therefore$ T = 180K

Example.35 A Carnot engine takes 10^3 kilocalories of heat from a reservoir at 627ºC and exhausts it to a sink at 27ºC. The efficiency of the engine will be.

Solution. Efficiency of Carnot engine

$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{900} = \frac{2}{3}$ or $\eta = 66.6\ \%$

Example. 36 In the above problem, the work performed by the engine will be

Solution. Work performed by the engine

$W = \eta Q_1 = \frac{2}{3} \times 10^6 \times 4.2$ or $W = 2.8 \times 10^6$ Joule

Example. 37 A Carnot engine has an efficiency of 40% when the sink temperature is 27ºC. The source temperature will be

Solution. $\eta_{\text{efficiency}} = 1 - \frac{T_2}{T_1}$ or $\frac{2}{5} = 1 - \frac{300}{T_1}$ $\therefore\ T_1 = 500$K

Example. 38 A reversible engine takes heat from a reservoir at 527ºC and gives out to the sink at 127ºC. The engine is required to perform useful mechanical work at the rate of 750 watt. The efficiency of the engine is

Solution. Efficiency $\eta = 1 - \frac{T_2}{T_1}$ or $\eta = 1 - \frac{400}{800} = \frac{1}{2}$ or $\eta = 50\%$

Example. 39 The efficiency of Carnot's engine is 50%. The temperature of its sink is 7ºC. To increase its efficiency to 70%. The increase in heat of the source will be

Solution. Efficiency in first state $\eta = 50\% = 1/2$

$T_2 = 273 + 7 = 280$ K

Formula $\eta = 1 - \frac{T_2}{T_1}$ $\frac{1}{2} = 1 - \frac{280}{T_1} \Leftrightarrow \frac{280}{T_1} = \frac{1}{2}$

or $T_1 = 560$ºK (temperature of source)

In the second state (i) $\frac{70}{100} = 1 - \frac{280}{T_1}$ $\therefore$ $T_1 = \frac{2800}{3} = 933.3\text{K}$

$\therefore$ Increase in source temperature = (933.3 – 560) = 373.3 K

Example. 40 A Carnot's engine work at 200ºC and 0ºC and another at 0ºC and –200ºC. The ratio of efficiency of the two is

Solution.

$$\eta = \frac{(T_1 - T_2)}{T_1}$$

$$\eta_1 = \frac{(473 - 273)}{473} = \frac{200}{473} \quad \text{and} \quad \eta_2 = \frac{(273 - 73)}{273} = \frac{200}{273}$$

$$\frac{\eta_1}{\eta_2} = \frac{273}{473} = 0.577$$

Example. 41 A Carnot engine work as refrigerator in between 0ºC and 27ºC. How much energy is needed to freeze 10 kg ice at 0ºC.

Solution. Heat absorbed by sink

$Q_2 = 10 \times 10^2 \times 80 = 800$ k.cal

Now $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$, $Q_1 = Q_2 \cdot \frac{T_1}{T_2}$

$\therefore$ $Q_1 = 800 \times \frac{300}{273}$ k.cal = 879 kcal