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.

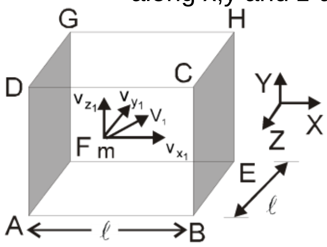
(e) The path travelled by a molecule between two collisions is called free path and the mean of this distance travelled by a molecule is called mean free path.

(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

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

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

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

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

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

where $< v^2_x >$ = 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 $< v^2 > = < v^2_x > + < v^2_y > + < v^2_z >$

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

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

Where ℓ^3 = volume of the container = V
M = total mass of the gas, $<c^2>$ = mean square velocity of molecules

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

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

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

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

Where v_{rms} is root mean square 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.

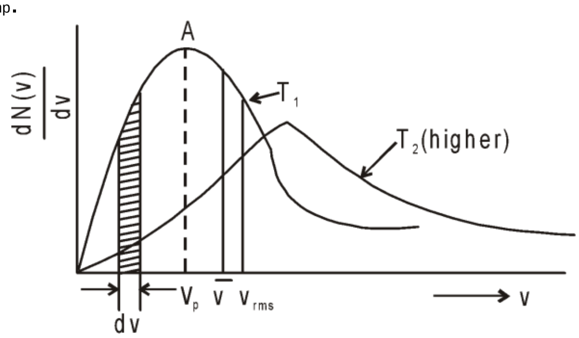
(c) At higher temperature and low pressure or at higher temperature and low density, a real gas behaves as an ideal gas.

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 distribution curve. The total area under the curve is given by the integral .

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

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 molecules have speed lying within a small range centered about the speed corresponding the peak (A) of the curve. This speed is called the 'most probable speed' v_p or v_{mp}.



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

Average (or Mean) Speed :

$\bar{v} = \sqrt{\frac{8}{\pi}\frac{kT}{m}} = 1.59\sqrt{kT/m}$.   (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

$v_{rms} > \bar{v} > v_p$.

DEGREE OF FREEDOM :

Total number of independent co-ordinates which must be known to completly 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 $U = \frac{1}{2}fkT$

INTERNAL ENERGY :

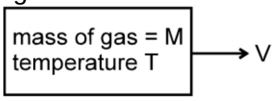
The internal energy of a system is the sum of kinetic and potential energies of the molecules of the system. It is denoted by U. Internal energy (U) of the system is the function of its absolute temperature (T) and its volume (V). i.e. U = f (T, V)

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

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

Solved Examples

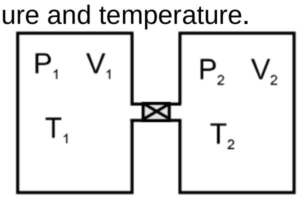
Example 1. A light container having a diatomic gas enclosed with in is moving with velocity v. Mass of the gas is M and number of moles is n.
(i) What is the kinetic energy of gas w.r.t. centre of mass of the system?
(ii) What is K.E. of gas w.r.t. ground?



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.

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

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

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

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

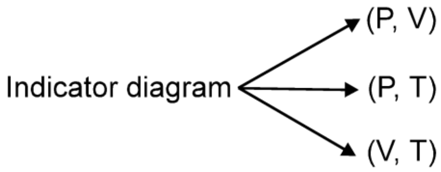
From energy conservation

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

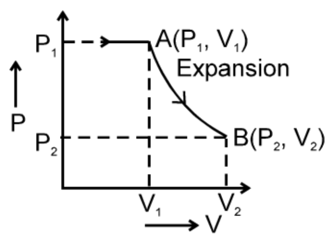
$$\Rightarrow \quad T = \frac{(3P_1V_1 + 5P_2V_2)T_1T_2}{3P_1V_1T_2 + 5P_2V_2T_1} \quad \Rightarrow P = \left(\frac{3P_1V_1 + 5P_2V_2}{3P_1V_1T_2 + 5P_2V_2T_1}\right)\left(\frac{P_1V_1T_2 + P_2V_2T_2}{V_1 + V_2}\right)$$

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 :

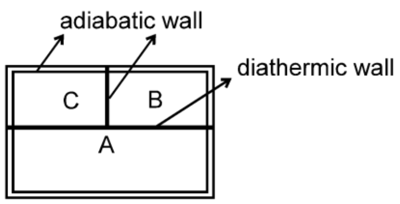
(a) **Open system :** A system is said to be an open system if it can exchange both energy and matter with its surroundings.

(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) :

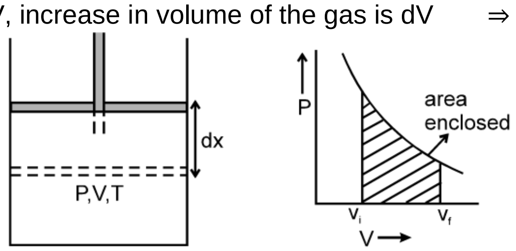
The relation between the thermodynamic variables (P, V, T) of the system is called equation of state. The equation of state for an ideal gas of n moles is given by $PV = nRT$,

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 $\Rightarrow$ $dW = P\,dV$



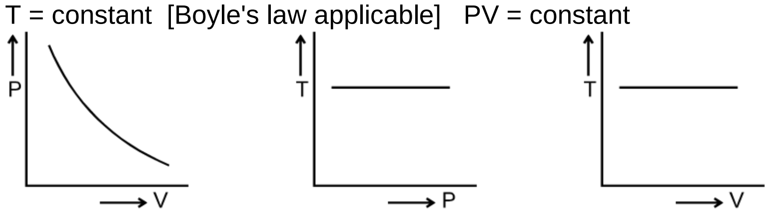
or $W = \int dW = \int P\,dV$

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.

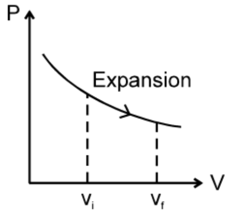
Slope of P–V curve in isothermal process:

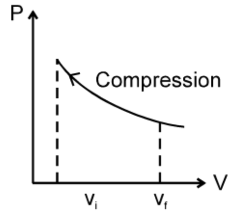
PV = constant = C $\Rightarrow$ $\frac{dP}{dV} = -\frac{P}{V}$

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

$\Rightarrow$ change in volume is zero

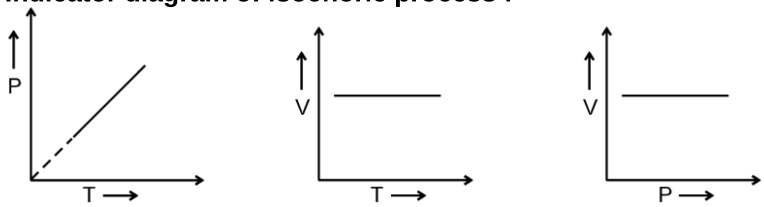
$\Rightarrow$ $\frac{P}{T}$ is constant

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

Work done in isochoric process :

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

Indicator diagram of isochoric process :



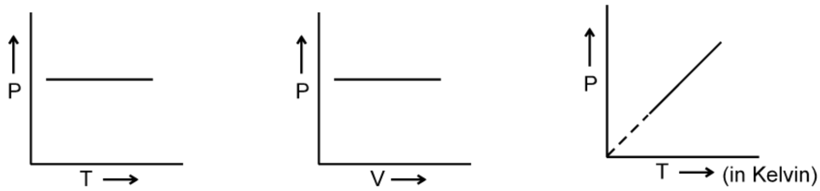
Change in internal energy in isochoric process : $\Delta U = n \frac{f}{2} R\, \Delta T$

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

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

Indicator diagram of isobaric process :



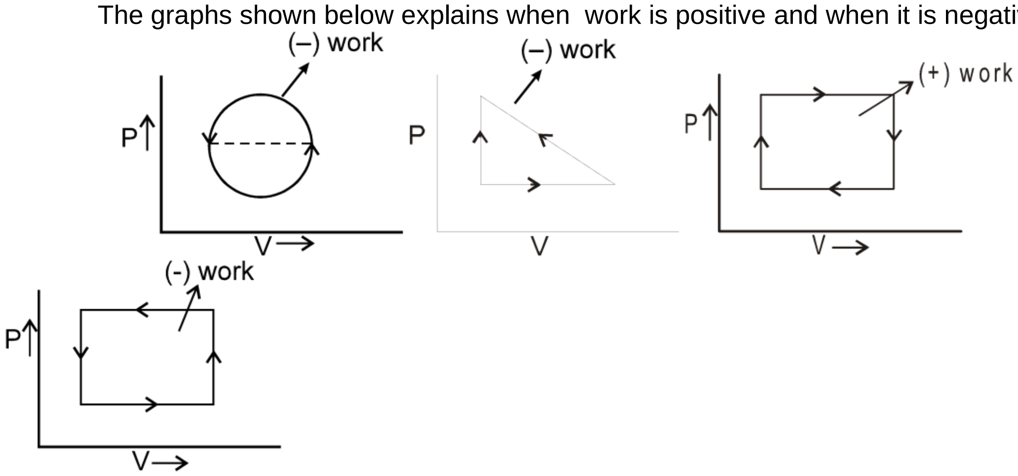
Work done in isobaric process :
$\Delta W = P\,\Delta V = P\,(V_{final} - V_{initial}) = nR\,(T_{final} - T_{initial})$

Change in internal energy in isobaric process : $\Delta U = n\,C_V\,\Delta T$
Heat given in isobaric process :
$\Delta Q = \Delta U + \Delta W$

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

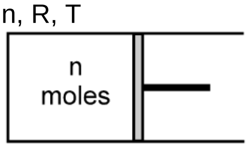
Above expression gives an idea that to increase temperature by ΔT in isobaric process heat required is more than in isochoric process.

(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 ΔU = 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

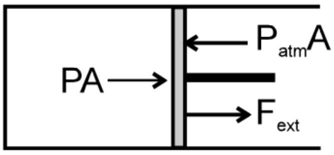


Solved Examples

Example 3. The cylinder shown in the figure has conducting walls and temperature of the sorrounding is T, the pistion is initially in equilibrium, the cylinder contains n moles of a gas. Now the piston is displaced slowly by an external agent to make the volume double of the initial. Find work done by external agent in terms of n, R, T



Solution : **1st Method :**
Work done by external agent is positive, because F_{ext} and displacement are in the same direction. Since walls are conducting therefore temperature remains constant.



Applying equilibrium condition when pressure of the gas is P

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

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

$W_{ext} = \int_0^d F_{ext}\, dx = \int_0^d P_{atm} A dx - \int_0^d PA\, dx$

$= P_{atm} A \int_0^d dx - \int_V^{2V} \frac{nRT}{V} dV = P_{atm} Ad - nRT \ln 2$

$= P_{atm} \cdot V_0 - nRT\ln 2 = nRT (1 - \ln 2)$

2nd Method

Applying work energy theorem on the piston

$\Delta k = 0$

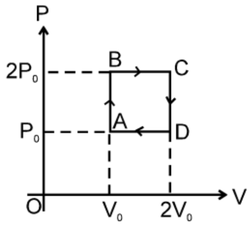
$W_{all} = \Delta k$

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

$nRT \ln \frac{V_f}{V_i} - nRT + W_{ext} = 0$

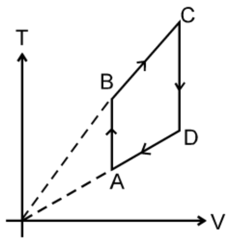
$W_{ext} = nRT (1 - \ln 2)$

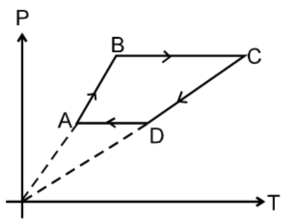
Example 4. Find out the work done in the given graph. Also draw the corresponding T-V curve and P-T curve.



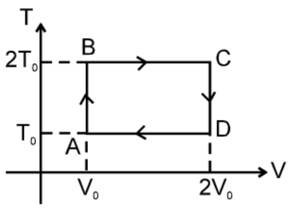
Solution : Since in P-V curves area under the cycle is equal to work done therefore work done by the gas is equal to $P_0 V_0$. Line A B and CD are isochoric line, line BC and DA are isobaric line.

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





Example 5. 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

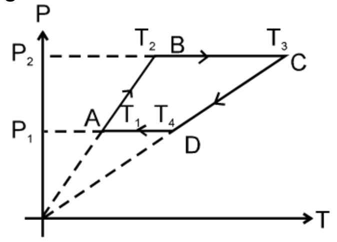
$W_{BC} = nR2T_0 \ln \frac{V_C}{V_B} = 2nRT_0 \ln 2$

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

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

$= nRT_0 \ln 2$

Example 6. 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 $W_{BC} = nR\Delta T = nR(T_3 - T_2)$

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

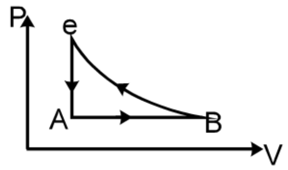
Total work done = $W_{BC} + W_{DA} = nR(T_1 + T_3 - T_4 - T_2)$

Example 7. 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 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 8. 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.)

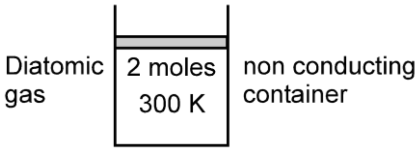
Solution : From first law of thermodynamic $\Delta Q = \Delta u + \Delta w$

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

$$\Delta W = P\Delta V = \frac{10^5(1671-1)\times10^{-6}}{4.2} = \frac{10^5\times1670)\times10^{-6}}{4.2} = 40 \text{ cal.}$$

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

Example 9. Two moles of a diatomic gas at 300 K are kept in a non-conducting container enclosed by a piston. Gas is now compressed to increase the temperature from 300 K to 400 K. Find work done by the gas



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

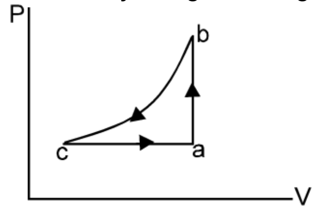
Since container is non-conducting therefore

$\Delta Q = 0 = \Delta u + \Delta w$

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

$= -5 \times 8.314 \times 100$ J $= -5 \times 831.4$ J $= -4157$ J

Example 10. 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

$\Delta U = \Delta Q = 50$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 $\Delta W = -40$J and no heat is given to the system. The increase in internal energy from b to c is

$\Delta U = -\Delta W = 40$ 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

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

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

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

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

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

Example 11. 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 2ºC, find the distance moved by the piston. Atmospheric pressure = 100 kPa.

Solution : The change in internal energy of the gas is

$$\Delta U = 1.5\, nR\, (\Delta T)$$
$$= 1.5\,(1\text{ mol})\,(8.3\text{ J/mol-K})\,(2K)$$
$$= 24.9\text{ J.}$$

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 12. 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

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

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

(b) The work done by the gas is

$$\Delta W = \Delta Q - \Delta U$$
$$= 140\text{ J} - 100\text{ J} = 40\text{ J.}$$

Effeciency of a cycle (η) :

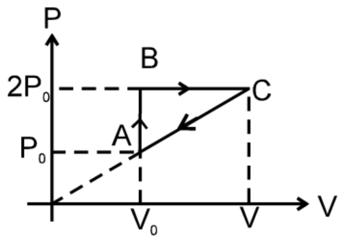
$$\eta = \frac{\text{total Mechanical work done by the gas in the whole process}}{\text{Heat absorbed by the gas (only + ve)}}$$

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

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

Solved Examples

Example 13. n moles of a diatomic gas has undergone a cyclic process ABC as shown in figure. Temperature at a is T_0. Find



(i) Volume at C ?

(ii) Maximum temperature ?

(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 similar therefore

$$\frac{2P_0}{V} = \frac{P_0}{V_0} \quad \Rightarrow V = 2V_0$$

(ii) Since process AB is isochoric hence

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

Since process BC is isobaric therefore $\frac{T_B}{V_B} = \frac{T_C}{V_C}$

$\Rightarrow \quad T_C = 2T_B = 4\,T_0$

(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

$\therefore$ 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 = $\frac{\text{work done by the gas}}{\text{heat injected}} = \eta = \frac{P_0V_0/2}{Q_{injected}} \times 100$

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

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

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

SPECIFIC HEAT :

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

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

The molar heat 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

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

$\Rightarrow \frac{C_P}{C_V} = \gamma = \frac{5}{3} = 1.67$

(ii) For a diatmoc gas f = 5

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

$\gamma = \frac{C_P}{C_V} = 1.4$

(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 14 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 $\Rightarrow$ dQ = $U_{final} - U_{initial}$ + dW

U_{final} = dQ – dW + $U_{initial}$ or U_{final} = –20 + 8 + 30 of U_{final} = 18 Joule

Example 15 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 ΔQ = 100 cal = 418 J.

Work done by the gas is ΔW = 40 J

The increase in internal energy is

ΔU = ΔQ – ΔW

= 418J – 40 J = 378 J

Example 16 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

δW = PdV = 6 × 50 = 300 J (Volume is decreasing, δQ = 100 J)

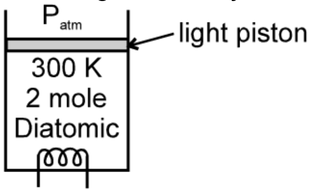
W = – 300 J

δQ = δW + dU

100 + 300 = dU

dU = increased by 400 J

Example 17. 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

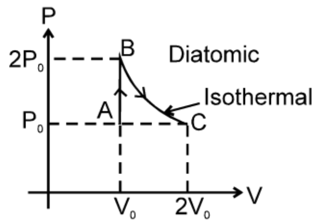
$\therefore\ \Delta W = 0$ and $\Delta Q = \Delta u$ (from first law)

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

(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 18. 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

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

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

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

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

Example 19. Calculate the value of mechanical equivalent of heat from the following data. Specific heat capacity of air at constant volume = 170 cal/kg-K, $\gamma = C_p/C_v = 1.4$ and the density of air at STP is 1.29 kg/m3. Gas consant R = 8.3 J/mol-K.

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

$V = \frac{nRT}{p} = \frac{(1\,\text{mol})\times(8.3\ \text{J/mol}-\text{K})\times(273\text{K})}{1.0\times10^5\,\text{N/m}^2} = 0.0224\text{m}^3.$

The mass of 1 mole is, therefore,

$(1.29\ \text{kg/m}^3) \times (0.0224\ \text{m}^3) = 0.029\ \text{kg}.$

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

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

Hence, $C_p = \gamma C_v = 1.4 \times 4.93$ cal/mol-K

or, $C_p - C_v = 0.4 \times 4.93$ cal/mol-K

= 1.97 cal/mol-K.

Also, $C_p - C_v = R = 8.3$ J/mol-K.

Thus, 8.3 J = 1.97 cal.

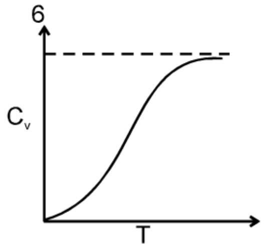
The mechanical equivalent of heat is

$\frac{8.3\ \text{J}}{1.97\ \text{cal}} = 4.2$ J/cal.

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

At room temperature average molar specific heat of all metals are same and is nearly equal to 3R

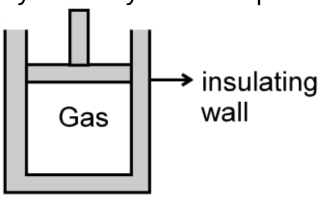
(6 cal. mol^{-1} K^{-1}).
[Note : Temp. above which the metals have constant C_V is called Debye temp.]



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

Adiabatic process :

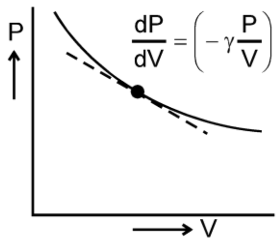
When no heat is supplied or extracted from the system the process is called adiabatic. Process is sudden so that there is no time for exchange of heat. If walls of a container are thermally insulated no heat can cross the boundary of the system and process is adibatic.



Equation of adiabatic process is given by
PV^{γ} = constant [Poission Law]
$T^{\gamma} P^{1-\gamma}$ = constant
$T V^{\gamma-1}$ = constant

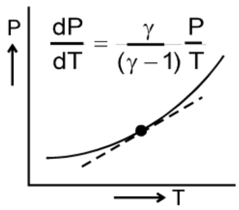
Slope of P–V–curve in adiabatic process :
Since PV^{γ} is a constant

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



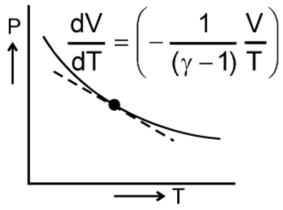
Slope of P–T–curve in adiabatic process : Since $T^{\gamma} P^{1-\gamma}$ is a constant

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



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 20. 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 temperature if the gas is compressed to 200cm^3 (a) in a short time (b) in a long time. Take γ = 1.4.

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

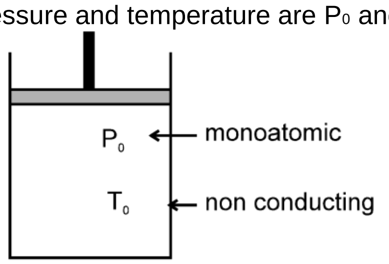
$T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$

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 21. 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

$P_0V^{\frac{5}{3}} = P_{final}\left(\frac{V}{8}\right)^{5/3}$. ⇒ $\gamma = \frac{C_P}{C_V} = \frac{5R}{2} / \frac{3R}{2} = \frac{5}{3}$

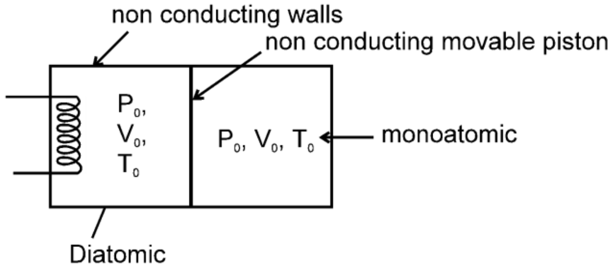
$P_{final} = 32\ P_0$.

Since process is adiabatic therefore

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

Example 22. A cylindrical container having nonconducting walls is partitioned in two equal parts such that the volume of the each parts is equal to V_0 . A movable nonconducting piston is kept between the two parts. Gas on left is slowly heated so that the gas on right is compressed upto volume $\frac{V_0}{8}$. Find pressure and temperature on both sides if initial pressure and temperature, were P_0

and T_0 respectively. Also find heat given by the heater to the gas. (number of moles in each part is n)



Solution : Since the process on right is adiabatic therefore

PV^{γ} = cosntant

⇒ $P_0 V_0^{\gamma} = P_{final} (V_0 / 8)^{\gamma}$ ⇒ $P_{final} = 32 P_0$

$T_0 V_0^{\gamma-1} = T_{final} (V_0/8)^{\gamma-1}$ ⇒ $T_{final} = 4T_0$

Let volume of the left part is V_1

⇒ $2V_0 = V_1 + \frac{V_0}{8}$ ⇒ $V_1 = \frac{15V_0}{8}$.

Since number of moles on the left parts remains constant therefore for the left part

$\frac{PV}{T}$ = constant.

Final pressure on both sides will be same

⇒ $\frac{P_0V_0}{T_0} = \frac{P_{final}V_1}{T_{final}}$ ⇒ $T_{final} = 60\ T_0$

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

$\Delta Q = n\frac{5R}{2}(60T_0 - T_0) + n\frac{3R}{2}(4T_0 - T_0)$ ⇒ $\Delta Q = \frac{5nR}{2} \times 59T_0 + \frac{3nR}{2} \times 3T_0$

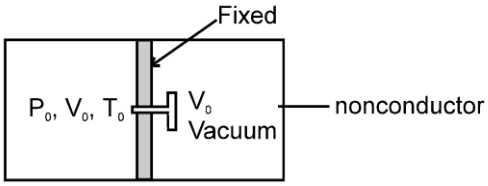
FREE EXPANSION

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 Example

Example 23. 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 $\Delta Q = 0$

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

$T_{final} = T_0$

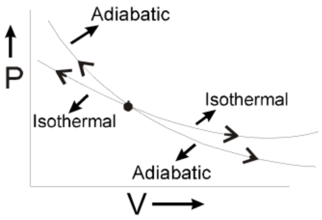
Since the process is isothermal therefore $P_0 \times V_0 = P_{final} \times 2V_0$ ⇒ $P_{final} = P_0/2$

Reversible and Irreversible Process

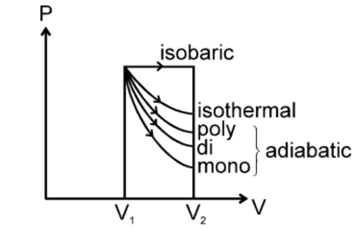
A process is said to be reversible when the various stages of an operation in which it is subjected can be traversed back in the opposite direction in such a way that the substance passes through exactly the same conditions at every step in the reverse process as in the direct process.

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 = $\frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$,
M_1 & M_2 are molar masses.

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

$C_P = \frac{n_1 C_{P_1} + n_2 C_{P_2}}{n_1 + n_2}$

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

Solved Examples

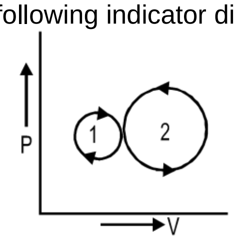
Example 24. 5 gm air is heated from 4ºC to 6ºC. If the specific heat of air at constant volume is 0.172 cal/gm/ºC, then increase in the internal energy of air will be -

Solution. $dU = mC_v dT$

$dU = 5 \times 0.172 \times 2$

$dU = 1.72$ calorie

Example 25. 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 26. 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. $W = 2.303\ \mu RT \log_{10} \frac{V_2}{V_1}$

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

$W = 2.303 \times 2 \times 8.7 \times 273 \times (\log_{10} - \log_{410})$
$\because\ \log_{410} = 0.6021$
$\therefore W = -6359$ Joule

Example 27. 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. $T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \Rightarrow T_2 = 300 \left(\frac{1}{2}\right)^{\frac{0.4}{1.4}} = 300 \left(\frac{1}{2}\right)^{2/7} = 300 \times 8.2 \Rightarrow T_2 = 246$ K

Example 28. One liter of air 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 29. In the following fig. the work done by the system in the closed path ABCA is
Solution. Work done in closed path ABCA

W_{ABCA} = Area of $\Delta ABC = \frac{1}{2} AB \times BC$

$W_{ABCA} = -\frac{1}{2} (P_2 - P_1)(V_2 - V_1)$

Example 30. According to the fig. if one mole of ideal gas in cyclic process the work done by the gas in the process will be
Solution. Work done W = area of PV curve

$= \frac{1}{2} [3P_0 - P_0][2V_0 - V_0] = P_0V_0$

Example 31. In above question, heat given by the gas is
Solution. $\delta Q = \mu C_p dT$, $\mu = 1$, $dT = T_A - T_C$, and for monoatomic ideal gas $C_P = 5/2\ R$

$\therefore$ $(\delta Q)_{CA} = \frac{5}{2} R [T_A - T_C] = \frac{5}{2} [P_AV_A - P_CV_C]$
But $P_A = P_0$, $V_A = V_0$, $V_C = 2V_0$, $P_C = P_0$
and $\frac{PV}{T} = R$

$\therefore$ $(\delta Q)_{CA} = \frac{5}{2} [P_0V_0 - P_0 2V_0] = -\frac{5}{2} P_0V_0$

Example 32. In above question, the heat taken by gas in the path AB will be
Solution. $(\delta Q)_{AB} = \mu C_v dT$ (process is on constant volume)

$C_V = \frac{3}{2} R$, $\mu = 1$

$(\delta Q)_{AB} = \frac{3}{2} R[T_B - T_A] = \frac{3}{2} [3P_0V_0 - P_0V_0]$
$= 3P_0V_0$

Example 33. In above question, the absorbed heat by gas in path BC will be
Solution. If the heat given for complete process is δQ then
$(\delta Q) = (\delta Q)_{AB} + (\delta Q)_{BC} + (\delta Q)_{CA}$
$dU = 0$ in cyclic process, thus by first law of thermodynamics $\delta Q = \delta W$
$\therefore$ $(\delta Q)_{AB} + (\delta Q)_{BC} + (\delta Q)_{AC} = \delta W$

$(\delta Q)_{BC} = \delta W - (\delta Q)_{AB} - (\delta Q)_{BC}$

$= P_0V_0 + \frac{5}{2} P_0 V_0 - 3P_0V_0$

$= \frac{P_0V_0}{2}$

Example 34. For a given cyclic process as shown in fig. the magnitude of absorbed energy for the system is

Solution. In cyclic process

$Q = W$ ($\because$ $dU = 0$)

Q = area of closed loop

$Q = 10_2\pi$ Joule

SECOND LAW OF THERMODYNAMICS

This law gives the direction of heat flow.

According to Classius : It is impossible to make any such machine that can transfer heat from an object with low temperature to an object with high temperature without an external source.

Accoding to Kelvin : It is impossible to obtain work continuously by cooling an object below the tempreature of its surroundings.

Statement of Kelvin-Planck : It is impossible to construct any such machine that works on a cyclic process and absorbs heat from a source, converts all that heat into work and rejects no heat to sink.

Heat engine :

The device, used to convert heat energy into mechanical energy, is called a heat engine.

For conversion of heat into work with the help of a heat engine, the following conditions have to be met with

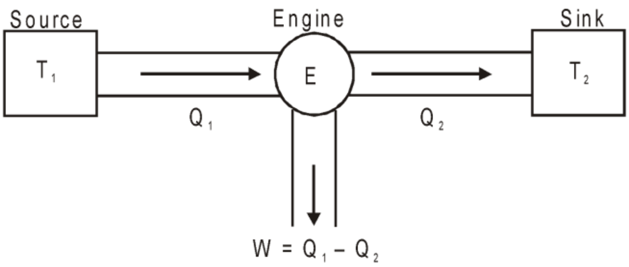
There should be a body at higher temperature 'T_1' from which heat is extracted. It is called the source.

Body of the engine containing working substance.

There should be a body at lower temperature 'T_2' to which heat can be rejected. This is called the sink.

Working of heat engine :

Schematic diagram of heat engine



Engine derives an amount 'Q_1' of heat from the source.

A part of this heat is converted into work 'W'.

Remaining heat 'Q_2' is rejected to the sink.

Thus $Q_1 = W + Q_2$

or the work done by the engine is given by $W = Q_1 - Q_2$

Efficiency of heat engine :

Efficiency of heat engine (η) is defined as the fraction of total heat, supplied to the engine which is converted into work.

Mathematically

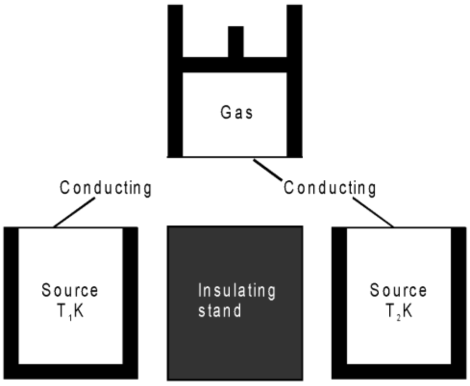
$\therefore$ $\eta = \frac{W}{Q_1}$ or $\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$

CARNOT ENGINE AND CARNOT CYCLE

Carnot engine :

Carnot engine is an ideal heat engine. It consists of the following parts.

Schematic diagram :



Source : It is a reservoir of heat energy with a condicting top maintained at a constant temperature T_1K. Source is so big that extraction of any amount of heat from it does not change its temperature.

Body of heat engine : It is a barrel having perfectly insulating walls and conducting bottom. It is fitted with an air tight piston capable of sliding within the barrel without friction. The barrel contains some quantity of an ideal gas.

Sink : It is a huge body at a lower temperature T_2 having a perfectly conducting top. The size of the sink is so large that any amount of heat rejected to it does not increase its temperature.

Insulating stand : It is a stand made up of perfectly insulating material such that the barrel when placed over it becomes thoroughly insulated from the surroundings.

Carnot cycle :

As the engine works, the working substance of the engine undergoes a cycle known as Carnot cycle. The Carnot cycle consists of the following four strokes.

Graphical representation of Carnot cycle :

First stroke (Isothermal expansion) :

In this stroke the barrel is placed over the source. The piston is gradually pushed back as the gas expands. Fall of temperature, due to expansion, is compensated by the supply of heat from the source and consequently temperature remains constant. The conditions of the gas change from A(P_1, V_1) to B(P_2, V_2). If W_1 is the work done during this process, then heat Q_1 derived from the source is given by

$Q_1 = W_1$ = Area ABGE = RT $\log_e \left(\frac{V_2}{V_1}\right)$

Second stroke (Adiabatic expansion) :

The barrel is removed from the source and is placed over the insulating stand. The piston is pushed back so that the gas expands adiabatically resulting in fall of temperature from T_1 to T_2. The conditions of the gas change from B(P_2, V_2) to C(P_3, V_3). If W_2 is the work done in this case then

$W_2 = \text{Area BCHG} = \frac{R}{\gamma - 1}(T_1 - T_2)$

Third stroke (isothermal compression) :

The barrel is placed over the sink. Piston is pushed down there by compressing the gas. The heat generated due to compression flows to the sink maintaining the temperature of the barrel constant. The state of the gas change from C(P_3, V_3) to D(P_4, V_4). If W_3 is the work done in this process and Q_2 is the heat rejected to the sink, then

$Q_2 = W_3$ = Area CDFH = $RT_2 \log_e \left(\frac{V_3}{V_4}\right)$

Fourth stroke (Adiabatic compression) :

The barrel is placed over the insulating stand. The piston is moved down thereby compressing the gas adibatically till the temperature of gas increases from T_2 to T_1. The state of gas changes from D(P_4, V_4) A(P_1, V_1). If W_4 is the work done in this process, then

W_4 = Area ADFE = $\frac{R}{\gamma - 1}(T_1 - T_2)$

Heat converted into work in Carnot cycle :

During the four strokes, W_1 and W_2 are the work done by the gas and W_3 and W_4 are the work done on the gas. Therefore the net, work performed by the engine

$W = W_1 + W_2 - W_3 - W_4$ = Area ABGE + Area BCHG – Area CDFH – Area ADEF = Area ABCD

Thus net work done by the engine during one cycle is equal to the area enclosed by the indicator diagram of the cycle. Analytically $W = R(T_1 - T_2)\log_e\left(\frac{V_2}{V_1}\right)$

Efficiency of Carnot engine :

Efficiency (η) of an engine is defined as the ratio of useful heat (heat converted into work) to the total heat supplied to the engine. Thus.

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} \quad \text{or} \quad \eta = \frac{R(T_1 - T_2)\log_e\left(\frac{V_2}{V_1}\right)}{RT_1\log_e\left(\frac{V_2}{V_1}\right)} = \frac{T_1 - T_2}{T_1} \quad \text{or} \quad \eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

Some important points regarding Carnot engine

Efficiency of an engine depends upon the temperatures between which it operates.

η is independent of the nature of working substance.

η is one only if $T_2 = 0$. Since absolute zero is not attainable, hence even an ideal engine cannot be 100 % efficient.

η is one only if $Q_2 = 0$. But η = 1 is never possible even for an ideal engine. Hence $Q_2 \neq 0$.

Thus it is impossible to extract heat from a single body and convert the whole of it into work.

If $T_2 = T_1$, then η = 0

In actual heat engines, there anr many losses due to friction etc. and various processes during each cyle are not quasistatic, so the efficiency of actual engines is much less than that of an ideal engine.

Solved Examples

Example 35. 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 $\frac{100}{500} = \frac{T}{900}$ ∴ T = 180K

Example 36. 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 η = 66.6 %

Example 37. 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 38. 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 $\frac{2}{5} = 1 - \frac{300}{T_1}$ ∴ $T_1 = 500K$

Example 39. 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 η = 50%

Example 40. 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 $T_1 = 560^{\circ}$K (temperature of source)

In the second state (i) $\frac{70}{100} = 1 - \frac{280}{T_1}$

$\therefore$ $T_1 = \frac{2800}{3} = 933.3$K

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

Example 41. A Carnot's engine work at 200ºC and 0ºC and another at 0ºC and –200ºC. The ratio of efficiency of the two is

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

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

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

Example 42. 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

Example 43. Work efficiency coefficient in above question

Solution. Work efficiency coefficient (cofficient of performance)

$\beta = \frac{Q_2}{Q_1 - Q_2} = \frac{800 \times 10^3}{(879 - 800) \times 10^3} = 10.13$

Example 44. A Carnot engine works as a refrigerator in between 250K and 300K. If it acquires 750 calories from heat source at low temperature, then the heat generated at higher temperature. (in calories) will be.

Solution . $\eta = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$ $\Rightarrow$ $\frac{750}{Q_1 - 750} = \frac{250}{300 - 250}$

$Q_1 = 900$ Calories

Solved Miscellaneous Problems

Problem 1. A vessel of volume 2×10^{-2} m^3 contains a mixture of hydrogen and helium at 47º C temperature and 4.15×10^5 N/m^2 pressure. The mass of the mixture is 10^{-2} kg. Calculate the masses of hydrogen and helium in the given mixture.

Solution: Let mass of H_2 is m_1 and He is m_2

$\therefore$ $m_1 + m_2 = 10^{-2}$ kg $= 10 \times 10^{-3}$ ....(1)

Let P_1, P_2 are partial pressure of H_2 and He

$P_1 + P_2 = 4.15 \times 10^5$ N/m^2

for the mixture

$(P_1 + P_2) V = \left(\frac{m_1}{n_1} + \frac{m_2}{n_2}\right) RT$

⇒ $4.15 \times 10^5 \times 2 \times 10^{-2} = \left(\frac{m_1}{2\times10^{-3}} + \frac{m_2}{4\times10^{-3}}\right) 8.31 \times 320$

⇒ $\frac{m_1}{2} + \frac{m_2}{4} = \frac{4.15\times2}{8.31\times320} = 0.00312 = 3.12 \times 10^{-3}$

⇒ $2m_1 + m_2 = 12.48 \times 10^{-3}$ kg .....(2)

Solving (1) and (2)

$m_1 = 2.48 \times 10^{-3}$ kg ≅ **2.5×10^{-3} kg**

and **$m = 7.5 \times 10^{-3}$ kg.**

Problem 2. The pressure in a monoatomic gas increases linearly from 4×10^5 N m^{-2} to 8×10^5 N m^{-2} when its volume increases from 0.2 m^3 to 0.5 m^3. Calculate the following:
(a) work done by the gas.
(b) increase in the internal energy.

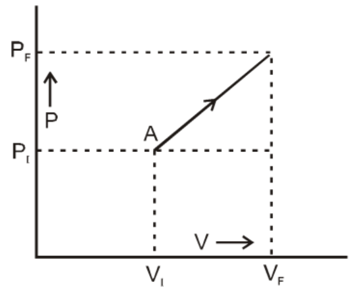
Solution : **(a)** As here pressure is varying linearly with volume, work done by the gas

$\Delta W = \int PdV$ = area under P-V curve

which in the light of figure 1 becomes:

$\Delta W = P_I (V_F - V_I) (P_F - P_I) \times (V_F - V_I)$

i.e., $\Delta W = P_I (V_F - V_I) + \frac{1}{2} (P_F - P_I) \times (V_F - V_I)$



i.e., $\Delta W = \frac{1}{2} (0.5 - 0.2) (8 + 4) \times 10^5$

i.e., **$\Delta W = 1.8 \times 10^5$ J**

(b) The change in internal energy of a gas is given by

$\Delta U = \mu C_V \Delta T = \frac{\mu R \Delta T}{(\gamma - 1)} = \frac{(P_F V_F - P_I V_I)}{(\gamma - 1)}$

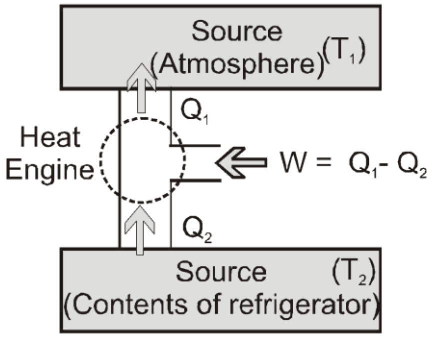
As the gas is monatomic γ = (5/3)

So, $\Delta U = \frac{10^5(8\times0.5 - 4\times0.2)}{[(5/3)-1]} = \frac{3}{2} \times 10^5(4 - 0.8)$.

i.e., **$\Delta U = 4.8 \times 10^5$ J**

Refrigerator or Heat Pump

A refrigerator or heat pump is basically a heat engine run in reverse direction.
It essentially consists of three parts
(1) **Source** : At higher temperature T_1.
(2) **Working substance :** It is called refregerant liquid ammonia and freon works as a working substance
(3) **Sink :** At lower temperature T_2.



The working substance takes heat Q_2 from a sink (contents of refrigerator) at lower temperature, has a net wmount of worj done W in it by an external agent (uaually compressor of refrigerator) and gives out a larger amount of heat Q_1 to a hot body at temperature T_1 (usally atmosphere) Thus, it transfers heat form a cold to a hot body at the expense of mechanical energy supplied to it by an external agent. The cold is thus cooled more and more.

The performance of a refrigerator is expressed by means of "coefficient of performance" β which is defined as the ratio of the heat extracted from the cold body to the needed to transfer it to the hot bdoy.

i.e $\beta = \frac{\text{Heat extraced}}{\text{Work done}} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$

A perfect refrigerator is one which transfers heat from cold to hot body with out doing work

i e. W = 0 so that $Q_1 = Q_2$ hence $\beta = \infty$

(1) **Carnot refrigerator:**

For Carnot refrigerator $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$ ⇒ $\frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2}$ or $\frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$

So Coefficient of performance $\beta = \frac{T_2}{T_1 - T_2}$

here T_1 = temperature of surrounding T_2 = temperature of cold body. It is clear that β = 0 when $T_2 = 0$ i.e the coefficient of performance will be zero if the cold body is at the temperature equal to absolute zero.

(2) Relation between coefficient of performance and efficiency of refrigerator

We know $\beta = \frac{Q_2}{Q_1 - Q_2} = \frac{Q_2 / Q_1}{1 - Q_2 - Q_1}$ ....(i)

But the efficiency $\eta = \frac{Q_2}{Q_1}$ or $\frac{Q_2}{Q_1} = 1 - \eta$ ....(ii)

Form (i) and (ii) we get , $\frac{1-\eta}{\eta}$

(3) Entropy

Entropy is measure of disoder of molecular motion of a system. Greater is the disorder, greater is the entropy.

The change in entropy i.e

$dS = \frac{\text{Heat absorbed by system}}{\text{Absolute temperature}}$ or $dS = \frac{dQ}{T}$

The realtion is called the mathematical form os Second Law of Thermodynamics.

(1) For solids and liquids

(i) When heat given to a substance change its state at constant temperature, then change in entropy

$dS = \frac{dQ}{T} = \pm \frac{mL}{T}$

where positive sign refers to heat absorption and negative sign to heat evolution.

(ii) When heat given to substance raises its temperature from T_1 to T_2 then change in entropy dS = $\int \frac{dQ}{T} = \int_{T_1}^{T_2} mc \frac{dT}{T} = mc \log_e\left(\frac{T_2}{T_1}\right)$ $\Rightarrow$ ΔS = 2.303 mc $\log_{10}\left(\frac{T_2}{T_1}\right)$

(2) For a perfect gas : Perfect gas equation for n moles is PV = nRT

$\Delta S = \int \frac{dQ}{T} = \int \frac{\mu C_V dT + P dV}{T}$ [As dQ = dU + dW]

$\Rightarrow \Delta S = \int \frac{\mu C_V dT + \frac{\mu RT}{V} dV}{T} = \mu C_V \int_{T_1}^{T_2} \frac{dT}{T} + \mu R \int_{V_1}^{V_2} \frac{dV}{V}$ [As PV = μ RT]

∴ $\Delta S = \mu C_V \text{long}_e \left(\frac{T_2}{T_1}\right) + \mu \log_e \left(\frac{V_2}{V_1}\right)$

In terms of T and P, $\Delta S = mC_P \text{lon}_g \left(\frac{T_2}{T_1}\right) - \mu R \log_e \left(\frac{P_2}{P_1}\right)$

and in terms of P and V $\Delta S = \mu C_V \log_e \left(\frac{P_2}{P_1}\right) + \mu C_p \log_e \left(\frac{V_2}{V_1}\right)$