

(vii) $R T_c / P_c V_c$ for a gas obeying Van der Waal's equation is:

d) 2.66

(vii) Gibb's function is defined as:

a) $G = U - TS + PV$

(ix) The opposite faces of cubical block of iron of cross section 4cm^2 are kept in contact with steam and melting ice. The quantity of ice melted at the end of 10 minutes will be:

b) 300 gm

$$mL = \frac{KA(\Delta T)t}{l}$$

$$\Rightarrow m = \frac{KA(\Delta T)t}{LL} = \frac{0.2 \times 4 \times (100) \times 10 \times 60}{2 \times 80} = 300 \text{ gm}$$

(x) Let K be thermal conductivity for a certain metal, whose electrical conductivity is σ and T is absolute temperature, then three are related as:

b) $\frac{K}{\sigma T} = \text{constant}$

2. First law of thermodynamics: When a certain amount of heat Q is supplied to a system, the heat is used to do work in passing from state 1 to state 2 and the rest is used to increase in the internal energy of the system. That is,

$$Q = (U_2 - U_1) + W.$$

For a very small change in the state of the system, the law is expressed in the differential form as

$$\delta Q = dU + \delta W$$

where, δQ and δW are not perfect differential.

The amount of heat is taken positive, if heat is supplied to the system and negative, if heat is removed from it.

The work is positive when the external work is done by the system in expansion and negative if the work is done on it in compression.

The internal energy is taken positive when it increases and negative when it decreases.

Importance of the first law of thermodynamics: It is applicable to any process by which a system undergoes a physical or chemical change. It introduces the concept of internal energy. It provides a method for determining the

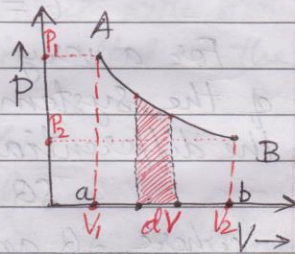
change in internal energy.

Work done in adiabatic process: During an adiabatic process, the system is thermally insulated from the surroundings. The gas expands from volume V_1 to V_2 as shown by indicator diagram.

The work done by the gas for an increase in volume dV is $= PdV$.

\therefore Work done when the gas expands from V_1 to V_2

is given by $W = \int_{V_1}^{V_2} PdV = \text{Area}(ABba)$.



During an adiabatic process, $PV^\gamma = \text{const} = K$
 $\Rightarrow P = \frac{K}{V^\gamma}$

$$\therefore W = K \int_{V_1}^{V_2} \frac{dV}{V^\gamma} = \frac{K}{1-\gamma} \left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right]$$

Since A and B lie on the same adiabatic,

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

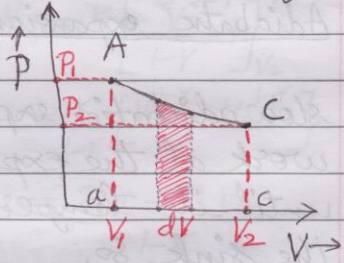
$$W = \frac{1}{1-\gamma} [P_2 V_2 - P_1 V_1]$$

Taking T_1 and T_2 as the temperatures at points A and B respectively, for 1 gm mole of the gas, $P_1 V_1 = RT_1$ and $P_2 V_2 = RT_2$

$$\text{Hence, } W = \frac{R}{1-\gamma} [T_2 - T_1]$$

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Work done in isothermal process: Let the initial and final volumes be V_1 and V_2 respectively when a gas is allowed to expand isothermally as shown in the indicated diagram.



Work done in isothermal expansion is given by

$$W = \int_{V_1}^{V_2} P dV = \text{Area}(ACca)$$

Considering 1 gm mole of the gas, $PV = RT$

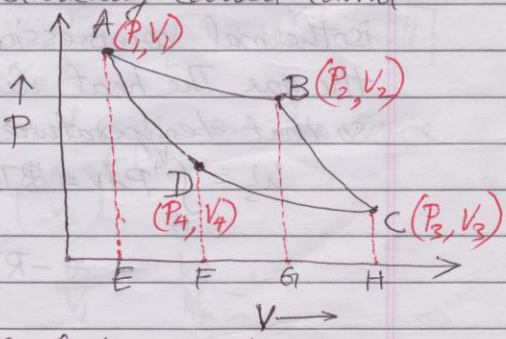
$$\therefore W = \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \times 2.303 \log_{10} \frac{V_2}{V_1}$$

Since A and C lie on the same isotherm,

$$P_1 V_1 = P_2 V_2$$

Hence, $W = RT \times 2.303 \log_{10} \frac{P_1}{P_2}$

3. Carnot cycle: In 1824, Sadi Carnot gave the idea of a theoretical ^{heat} engine having maximum efficiency. In order to obtain a continuous work, the working substance undergoes through a set of operations quasi-statically called Carnot cycle. Carnot cycle involves the following operations:



Isothermal expansion:

Let the working substance goes from its initial state $A(P_1, V_1, T_1)$ to state $B(P_2, V_2, T_1)$ at constant temperature T_1 along curve AB. In this process, the working

substance absorbs Q_1 heat from the source at T_1 temperature and does work given by

$$W_1 = \int_{V_1}^{V_2} P dV = RT_1 \log \frac{V_2}{V_1} = \text{area}(ABGEA).$$

Adiabatic expansion: The working substance is allowed to undergo slow adiabatic expansion performing external work at the expense of its internal energy, until its temperature falls to T_2 , that of the sink. So,

$$\begin{aligned} W_2 &= \int_{V_2}^{V_3} P dV = K \int_{V_2}^{V_3} \frac{dV}{V^\gamma} \quad (\because PV^\gamma = K = \text{constant}) \\ &= K \left[\frac{V^{1-\gamma}}{1-\gamma} \right]_{V_2}^{V_3} \\ &= \frac{K}{1-\gamma} [V_3^{1-\gamma} - V_2^{1-\gamma}] \\ &= \frac{P_3 V_3 - P_2 V_2}{1-\gamma} \quad (\because P_2 V_2^\gamma = P_3 V_3^\gamma = K) \\ &= \frac{R}{\gamma-1} (T_1 - T_2) = \text{Area}(BCHGB) \end{aligned}$$

Isothermal compression: The working substance undergoes isothermal compression when work is done on the gas. The heat developed is given to the sink so that temperature remains constant at T_2 . So

$$\begin{aligned} W_3 &= \int_{V_3}^{V_4} P dV = RT_2 \log \frac{V_4}{V_3} \\ &= -RT_2 \log \frac{V_3}{V_4} = \text{area}(CHFDC). \end{aligned}$$

Adiabatic compression: The working substance undergoes till adiabatic
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compression till it comes back to its original state A, thus completing one full cycle. In this process, work done on the working substance is given by

$$\begin{aligned}
 W_4 &= \int_{V_4}^{V_1} P \cdot dV = K \int_{V_4}^{V_1} \frac{dV}{V^\gamma} = K \left[\frac{V^{1-\gamma}}{1-\gamma} \right]_{V_4}^{V_1} \\
 &= \frac{K}{1-\gamma} [V_1^{1-\gamma} - V_4^{1-\gamma}] \\
 &= \frac{P_1 V_1 - P_4 V_4}{1-\gamma} \\
 &= \frac{-R}{\gamma-1} (T_1 - T_2) = \text{area(DFEAD)}.
 \end{aligned}$$

Hence, net amount of heat absorbed by the working substance per cycle = $Q_1 - Q_2$.

$$\begin{aligned}
 \text{and net work done per cycle} &= W_1 + W_2 + W_3 + W_4 \\
 &= W_1 + W_3 \\
 &= \text{area(ABCD)}.
 \end{aligned}$$

In the cyclic process,

$$\begin{aligned}
 Q_1 - Q_2 &= W_1 + W_3 \\
 &= RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_3}{V_4}.
 \end{aligned}$$

Since the points A and D lie on the same adiabatic, $\frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1}$ [$\because TV^{\gamma-1} = \text{const.}$]

Similarly, the points B and C lie on the same adiabatic, $\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$

$$\text{From above equations, } \frac{V_2}{V_1} = \frac{V_3}{V_4}.$$

$$\text{Hence, net work done} = Q_1 - Q_2 = W = R(T_1 - T_2) \log \frac{V_2}{V_1}.$$

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$$\text{Efficiency, } \eta = \frac{\text{useful output}}{\text{input}} = \frac{W}{Q}$$

$$= \frac{R(T_1 - T_2) \log(V_2/V_1)}{RT_1 \log(V_2/V_1)}$$

$$\Rightarrow \eta = 1 - \frac{T_2}{T_1}$$

We conclude that the efficiency depends only upon the temperature of the source (T_1) and that of sink (T_2) in Kelvin. And Carnot cycle is independent of the working substance.

Let the temperature of source is T_1 and that of sink be T_2 . Given that the efficiency of Carnot engine = 25% = $25/100 = 1/4$.

$$\text{That is, } \eta = \frac{25}{100} = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \frac{T_2}{T_1} = 1 - \frac{25}{100} = 1 - \frac{1}{4} = \frac{3}{4}$$

$$\Rightarrow T_1 = \frac{4}{3} T_2 \quad \text{--- (1)}$$

Again on reducing the temperature of sink by 50%, the efficiency = 50% = $50/100 = 1/2$.

$$\text{That is, } \eta = \frac{50}{100} = 1 - \frac{T_2/2}{T_1} = 1 - \frac{T_2}{2T_1}$$

$$\Rightarrow \frac{T_2}{2T_1} = 1 - \frac{50}{100} = 1 - \frac{1}{2} = \frac{1}{2}$$

$$\Rightarrow T_2 = T_1 \quad \text{--- (2)}$$

This equ. (2) implies that the temperatures of source and sink are equal which is not possible.

\therefore from equ. (1), source temp. = $\frac{4}{3}$ x sink temp.

4. Entropy: In addition to volume, pressure, temperature and internal energy, entropy is also a thermodynamic variable required to describe the condition of a working substance. Entropy is defined as the thermal property of a working substance which remains constant during an adiabatic process.

The change in entropy for a finite reversible change from state A to state B of working substance is given by

$$S_B - S_A = \int_A^B \frac{dQ}{T}$$

That means, the ^{ratio of the} amount of heat absorbed or rejected, dQ at constant temperature T in going from one adiabatic to another with the temperature is constant. This constant ratio is called the change in entropy between two adiabatic states.

Physical significance of entropy: From the expression of entropy change, it is clear that the unit of entropy is Cal/K or J/K . In other words, heat has the same dimensions as the product of entropy and absolute temperature. Since the gravitational potential energy of a body is proportional to the product of its mass and height above some zero level, similarly we may consider temperature analogous to height and entropy as analogous to mass (inertia). Thus, we may take entropy as

thermal inertia which establishes relation with heat motion in the similar way, as mass bears with linear motion or moment of inertia bears with rotational motion.

Microscopically, entropy is a measure of disorderness of a system. Molecules are in order in the equilibrium state of each system. When heat is imparted to the system, molecules get disordered and entropy of the system increases.

Let us consider an engine ^(with perfect gas as the working substance) performing ir-reversible cycle of changes. If the working substance absorbs heat Q_1 at temperature T_1 from the source and rejects heat Q_2 to the sink at temperature T_2 , then the efficiency of the engine is $\eta' = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$.

But according to Carnot's theorem, this efficiency is less than that of a reversible engine working betⁿ the same temperatures T_1 and T_2 , given by $\eta = 1 - \frac{T_2}{T_1}$.

Thus, $\eta' < \eta$

$$\Rightarrow 1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \frac{Q_2}{Q_1} > \frac{T_2}{T_1} \Rightarrow \left(\frac{Q_2}{T_2}\right) > \left(\frac{Q_1}{T_1}\right) \Rightarrow \frac{Q_2}{T_2} - \frac{Q_1}{T_1} > 0.$$

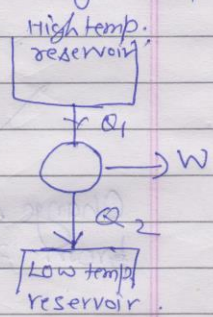
sink source

\therefore the net change in entropy for the whole system is positive (as source loses and sink gains entropy). Overall there is inc. in entropy in ir-reversible process of a perfect gas.
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5) Second law of thermodynamics: One of law of thermodynamics is based upon the heat engines.

No heat engine has ever been developed that converts the heat extracted from a reservoir at a high temperature into work without rejecting some heat to reservoir at a lower temperature.

This negative statement result which is the result of everyday experience, constitute the second law of thermodynamics and has been formulated in several ways:



① Kelvin Statement: "It is impossible to get a continuous supply of work from a body by cooling it to a temp lower than that of its surroundings"

② Clausius Statement: "It is impossible to make heat flow from a body at a lower temperature to a body at a higher temp. without doing external work on the working substance"

If we combine these statement into one equivalent statement, to which we shall refer as Kelvin-Planck statement of Second Law.

"It is impossible to construct a heat engine that operating in a cycle, will produce no effect other than the extraction of heat from a reservoir and the performance of equivalent amount of work."

Here, $m_1 = 50 \text{ gm.}$, $T_1 = 273 \text{ K}$
 $m_2 = 50 \text{ gm}$, $T_2 = 356 \text{ K.}$

Let the ^{final} temperature of mixture be $T \text{ K}$

$$m_1 S (T - T_1) = m_2 S (T_2 - T)$$

⑤ $\Rightarrow 50 \times 1 \times (T - 273) = 50 \times 1 \times (356 - T)$

$\Rightarrow T = \underline{\quad\quad\quad} 314.5 \text{ K.}$

Change in entropy by 50 gm of water when its temp. rises from 273 K to 314.5 K

$$\begin{aligned} &= \frac{\delta Q}{T} = ms \int_{T_1}^T \frac{dT}{T} \\ &= 50 \times 1 \times \log_e \frac{314.5}{273} \\ &= 50 \times 1 \times 2.303 \log_{10} \frac{314.5}{273} \\ &= 7.07 \text{ cal/K.} \end{aligned}$$

Change in entropy by 50 gm of water when temp falls from 356 to 314.5 K

$$\begin{aligned} &= ms \int_{T_2}^T \frac{dT}{T} \\ &= 50 \times 1 \times \log_e \frac{314.5}{356} \\ &= 50 \times 2.303 \log_{10} \frac{314.5}{356} \\ &= -6.19 \end{aligned}$$

$$\begin{aligned} \text{Gain in entropy} &= 7.07 - 6.19 \\ &= 0.88 \text{ cal/K.} \end{aligned}$$

Q.6 Maxwell's Relations: From the two laws of thermodynamics Maxwell's derived six fundamental relations -

From 1st Law of thermodynamics -

$$\begin{aligned} \delta Q &= du + \delta w = du + PdV \\ \therefore du &= \delta Q - PdV \quad \text{--- (1)} \end{aligned}$$

From Second Law of thermodynamics.

$$\begin{aligned} dS &= \frac{\delta Q}{T} \quad \text{---} \\ \delta Q &= T \cdot ds \quad \text{--- (2)} \\ du &= Tds - PdV \quad \text{--- (3)} \end{aligned}$$

considering S, U and V to be function of two independent variable x and y :-

$$\therefore ds = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$du = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$

Substituting these values in eqn (3) we have —

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T \left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \right] - P \left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy \right]$$

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = \left[T \left(\frac{\partial S}{\partial x}\right)_y - P \left(\frac{\partial V}{\partial x}\right)_y \right] dx + \left[T \left(\frac{\partial S}{\partial y}\right)_x - P \left(\frac{\partial V}{\partial y}\right)_x \right] dy$$

Comparing the coeff of dx and dy —

$$\left(\frac{\partial U}{\partial x}\right)_y = T \left(\frac{\partial S}{\partial x}\right)_y - P \left(\frac{\partial V}{\partial x}\right)_y \quad \text{--- (4)}$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T \left(\frac{\partial S}{\partial y}\right)_x - P \left(\frac{\partial V}{\partial y}\right)_x \quad \text{--- (5)}$$

Diff. eqn (4) w.r.t. y and (5) w.r.t. x . we have —

$$\frac{\partial^2 U}{\partial y \partial x} = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T \frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P \frac{\partial^2 V}{\partial y \partial x}$$

$$\text{and } \frac{\partial^2 U}{\partial x \partial y} = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T \frac{\partial^2 S}{\partial x \partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P \frac{\partial^2 V}{\partial x \partial y}$$

Since du is a perfect differential —

$$\therefore \frac{\partial^2 U}{\partial y \partial x} = \frac{\partial^2 U}{\partial x \partial y}$$

$$\Rightarrow \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T \frac{\partial^2 S}{\partial x \partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P \frac{\partial^2 V}{\partial x \partial y} = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T \frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P \frac{\partial^2 V}{\partial y \partial x}$$

$$\Rightarrow \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x \quad \text{--- (6)}$$

Here x and y can be any two variables out of P, V, T and S .

① Taking T and V as independent variables -

$$x = T, \quad y = V$$

$$\therefore \frac{\partial T}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these values in eqn (5) -

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{--- (1)}$$

but, $ds = \frac{\partial Q}{T}$

② Taking T and P as independent variables -

$$x = T, \quad y = P$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial P}{\partial y} = 1$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial P}{\partial x} = 0$$

Substituting these in eqn (6)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{--- (2)}$$

Ques 7

Enthalpy is an extensive thermodynamic variable and is defined as sum of the internal energy and the product of pressure and volume -

$$H = U + PV$$

$$\therefore dH = dU + PdV + V.dP$$

Since $\delta Q = dU + PdV$

$$\therefore dH = \delta Q + VdP$$

dividing by dT -

$$\frac{dH}{dT} = \frac{\delta Q}{dT} + V \frac{dP}{dT}$$

At constant P , $\left(\frac{\delta Q}{dT}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$

$$\therefore \left(\frac{\partial H}{\partial T}\right)_P = C_p$$

Latent heat of steam = 537 cal/g

Sp. volume of steam = 1674 cm³

$$\therefore dP = 2.712 \times 13.6 \times 980 \text{ dyne/cm}^2$$

$$T = 100 + 273 = 373 \text{ K}$$

$$L = 537 \times 4.2 \times 10^7 \text{ ergs}$$

$$V_1 = 1 \text{ cm}^3 \text{ \& } V_2 = 1674 \text{ cm}^3$$

~~V_2~~

From Clausius - Clapeyron - eqn -

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dT = \frac{dP \times T \cdot (V_2 - V_1)}{L}$$

$$= \frac{2.712 \times 13.6 \times 980 \times 373 \times 1673}{537 \times 4.2 \times 10^7 \text{ ergs}}$$

$$= 1^\circ \text{C or}$$

$$= 1 \text{ K}$$

Q. 8:

Consider a cube of side x cm and area of each face A sq. cm.

The opposite faces of the cube are maintained at temp. θ_1 and θ_2

Quantity of heat conducted across the two opposite faces -

$$Q \propto A$$

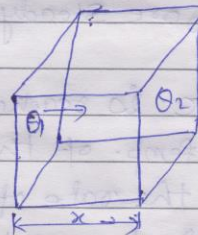
$$Q \propto (\theta_1 - \theta_2)$$

$$Q \propto t$$

$$Q \propto \frac{1}{x}$$

$$Q \propto \frac{A(\theta_1 - \theta_2)t}{x}$$

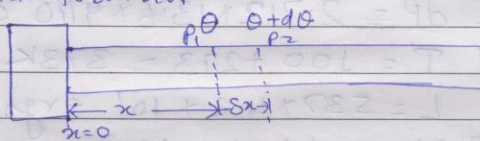
$$Q = \frac{K A (\theta_1 - \theta_2) t}{x}$$



Here, K is constant called the coefficient of thermal conductivity and is defined as the amount of heat flowing in one sec.

across the opposite faces of a cube of side one cm maintained at a difference of temp. of 1°C .

Consider a rod of uniform area of cross-section which is heated at one end and heat is flowing along the length of bar. Consider two plane P_1 and P_2 along the length of bar at a distance x & $x + \delta x$ from hot end.



The temp. gradient at $P_1 = \frac{d\theta}{dx}$. The excess of temp at $P_2 = \theta + \frac{d\theta}{dx} \delta x$

The temp. gradient at $P_2 = \frac{d}{dx} (\theta + \frac{d\theta}{dx} \delta x)$

Heat flowing through P_1 in 1 sec -

$$Q_1 = -KA \frac{d\theta}{dx} \quad \text{--- (1)}$$

Heat flowing through P_2 in 1 sec -

$$Q_2 = -KA \frac{d}{dx} (\theta + \frac{d\theta}{dx} \delta x) \quad \text{--- (2)}$$

Heat gained per second by the rod between the plane P_1 & P_2

$$Q = Q_1 - Q_2$$

$$Q = -KA \frac{d\theta}{dx} + KA \frac{d}{dx} (\theta + \frac{d\theta}{dx} \delta x)$$

$$Q = KA \cdot \frac{d^2\theta}{dx^2} \cdot \delta x \quad \text{--- (3)}$$

Before steady state: The quantity of heat Q is used in two ways before the steady state is reached. Partly the heat is used to raise the temp. of the rod and rest is lost due to radiation.

Let the rate of rise of temp. of the bar be $\frac{d\theta}{dt}$ -

The heat used per sec to raise the temp. of the rod -

$$= \text{mass} \times \text{sp. heat} \times \frac{d\theta}{dt}$$

$$= (A \times \delta x) \rho \times S \times \frac{d\theta}{dt} \quad \text{--- (4)}$$

Where A is area of cross-section. ρ - density of material.

S - sp. heat.

Heat lost per sec. due to radiation.

$$= Ep \delta x \cdot \theta \quad \text{--- (5)}$$

where, $E \rightarrow$ emissive power of surface,

$P \rightarrow$ perimeter,

$\theta \rightarrow$ Av. excess of temp. of the bar between plane P_1 & P_2

$$Q = A \cdot \delta x \cdot P \times S \cdot \frac{d\theta}{dx} + Ep \cdot \delta x \cdot \theta$$

From Eqn. (3), we have -

$$k \cdot A \frac{d^2\theta}{dx^2} \delta x = A \cdot \delta x \cdot P \cdot S \frac{d\theta}{dx} + Ep \cdot \delta x \cdot \theta.$$

$$\Rightarrow \frac{d^2\theta}{dx^2} - \frac{PS}{k} \frac{d\theta}{dx} + \frac{EP}{kA} \theta = 0.$$

This is general eqn of one-dimensional heat flow -