Thermodynamic system -

A system may be defined as a definite quantity of matter (solid, liquid or gases) bounded by some closed surface.

When a system is completely uniform throughout, such as gas or mixture of gases or a pure solid or a liquid or a solⁿ is called as homogenous system.

When a system consists of two or more phases, which are separated ~~by~~ from one another by definite boundary surfaces, it is said to be a hetrogenous system.

Anything outside the system which can exchange energy with it and has direct effect on the behaviour of the system is called as surroundings.

There are three classes of system

① Open system -

A system which can exchange matter and energy with surroundings is called as open system.

② Closed system -

A system which can exchange only energy but not matter is called as closed system.

③ Isolated system -

A system which can exchange neither energy nor matter with the surroundings is called as isolated system.

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Thermodynamic equilibrium -

(1) Mechanical equilibrium - for a system to be in mechanical equilibrium, there should be no movement (ie no unbalanced forces acting) on the system with respect to its surroundings

(2) Thermal equilibrium - for a system to be in thermal equilibrium, there should no temperature difference between the parts of the system and surroundings.

(3) Chemical equilibrium - for a system to be in chemical equilibrium there should be no chemical reaction within the system and also no movement of any chemical constituent from one part of the system to the other.

Zeroth law of thermodynamics -

The zeroth law of thermodynamics states that if two bodies A and B are each separetly in thermal equilibrium with a third body C, then A and B are also in thermal equilibrium with each other.

First law of thermodynamics -

When a certain amount of heat Q is supplied to a system which does external work W in passing from state 1 to state 2, the amount of heat is equal to sum of increase in internal energy of the system and the external work done by the system.

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

For a very small change in the system,

$$\delta q = dU + \delta w.$$

where δq and δw are not perfect differentials but dU is perfect differential because U is a function of the state of the system.

Isochoric process -

If a system undergoes a change in which the volume remains constant, the process is called as isochoric process.

ie at constant volume, no work is done.

ie $\delta w = 0$.

$\therefore \delta q = dU$.

$$\delta q = dU + \delta w$$
$$\delta q = dU + P.dV$$
$$\because dV = 0$$
$$\therefore \delta q = dU$$

Isobaric process -

If a system undergoes a change in which the pressure is kept constant, the process is called as isobaric process.

Suppose q is the heat absorbed by a system at a constant pressure P and suppose its volume increases from V_1 to V_2.

Then from law of thermodynamics.

$$q = (U_2 - U_1) + W$$
$$= (U_2 - U_1) + P(V_2 - V_1)$$
$$= (U_2 + PV_2) - (U_1 + PV_1)$$
$$q = H_2 - H_1 \quad \text{where } H = U + PV$$

Hence, the heat absorbed at constant pressure is equal to the increase in quantity H, called as enthalpy.

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Isothermal process -

If a system is perfectly conducting to the surroundings & temperature remains constant throughout the process, it is called as isothermal process.

Adiabatic process -

When a system undergoes from an initial state to a final state in such a way that no heat leaves or enters the system, the process is called as adiabatic process.

Adiabatic equation of a perfect gas -

Considering one gram of the working substance (ideal gas) perfectly insulated from the surroundings.
Let, the external work done by the gas be dW.

Applying the first law of thermodynamics.

$$\delta Q = dU + dW \quad —(1)$$

but $\delta Q = 0$ for an adiabatic process.

$$\therefore dW + dU = 0.$$

$$P \cdot dv + dU = 0$$

where P is the pressure of the gas and dv is the change in volume.

$$\therefore dU + \frac{P \cdot dv}{J} = 0 \quad —(2)$$

where J is the mechanical equivalent of heat.

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As the external work is done by the gas at the cost of its internal energy, there is fall in temperature by dT.

$\therefore dU = 1 \times C_v \cdot dT$ put in eqn. 2

$$\therefore C_v \cdot dT + \frac{P \cdot dv}{J} = 0 \quad \text{— (3)}$$

For an ideal gas of 1 mole $(n=1)$

$PV = RT$. R - constant

differentiating

$P \cdot dv + v \cdot dP = R \cdot dT$

put this value of dT in eqn 3

$$\therefore \left[\frac{P \cdot dv + v \cdot dP}{R}\right] C_v + \frac{P \cdot dv}{J} = 0$$

$$\Rightarrow (P \cdot dv + v \cdot dP) C_v + \frac{R}{J} P \cdot dv = 0$$

but $\frac{R}{J} = C_p - C_v$.

$$\Rightarrow (P \cdot dv + v \cdot dP) C_v + (C_p - C_v) \cdot P \cdot dv = 0$$

$$\Rightarrow \cancel{C_v \cdot P \cdot dv} + C_v \cdot v \cdot dP + C_p \cdot P \cdot dv - \cancel{C_v \cdot P \cdot dv} = 0$$

$$\Rightarrow C_v \cdot v \cdot dP + C_p \cdot P \cdot dv = 0$$

dividing by $C_p \cdot P \cdot V$ we get.

$$\frac{dP}{P} + \frac{C_p}{C_v} \cdot \frac{dv}{v} = 0$$

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

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$$\therefore \frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

integrating

$$\int \frac{dP}{P} + \gamma \int \frac{dV}{V} = \int 0.$$

$$\log P + \gamma \log V = \text{constant}$$

$$\log P + \log V^{\gamma} = \text{constant}$$

$$\log (PV^{\gamma}) = C$$

$$PV^{\gamma} = e^{C} = \text{constant}$$

$$\therefore \boxed{PV^{\gamma} = \text{constant}} \quad (4)$$

This equation is known as Poisson's law.

Taking $PV = nRT$

$$\Rightarrow P = \frac{nRT}{V} \qquad \text{for 1 mole of gas } n=1$$

$$P = \frac{RT}{V}$$

$\therefore$ eqn (4) becomes

$$\left(\frac{RT}{V}\right) V^{\gamma} = C$$

$$RTV^{\gamma-1} = C$$

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

$$\therefore \boxed{TV^{\gamma-1}\ \text{constant}}$$

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also, $V = \frac{RT}{P}$. put in eqn 4

$$\therefore PV^{\gamma} = C$$

$$P \left(\frac{RT}{P} \right)^{\gamma} = C$$

$$R^{\gamma} T^{\gamma} P^{1} P^{-\gamma} = C$$

$$R^{\gamma} T^{\gamma} P^{1-\gamma} = C$$

$$\therefore \boxed{\frac{P^{1-\gamma}}{T^{\gamma}} = C}$$

Second law of thermodynamics

Kelvin- Planck statement -

It is impossible to construct an engine which, operating in a cycle, has the sole effect of extracting heat from a reservoir and performing an equivalent amount of work.

Clausius statement -

Heat cannot flow ~~fr~~ of itself from a colder body to a hotter body.

Heat engine –

Any practical machine which converts heat into mechanical work is called as heat engine.

Heat engines in their operation absorb heat at higher temperature, converts part of it into mechanical work and rejects the remaining amount of heat at a low temperature.

Efficiency –

The efficiency η of heat engine is defined as the ratio of the mechanical work done by the engine in one cycle to the heat absorbed from the high temperature source.

Thus, $\eta = \dfrac{Q_1 - Q_2}{Q_1}$

where Q_1 – heat absorbed from the source at high temperature

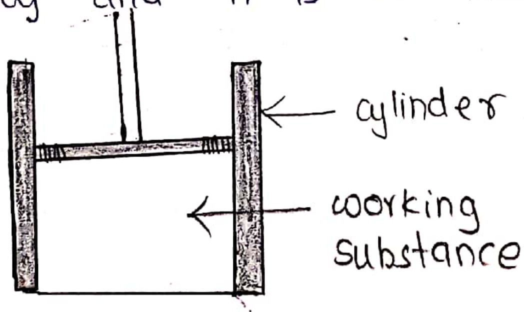
Q_2 – heat rejected to sink at low temperature

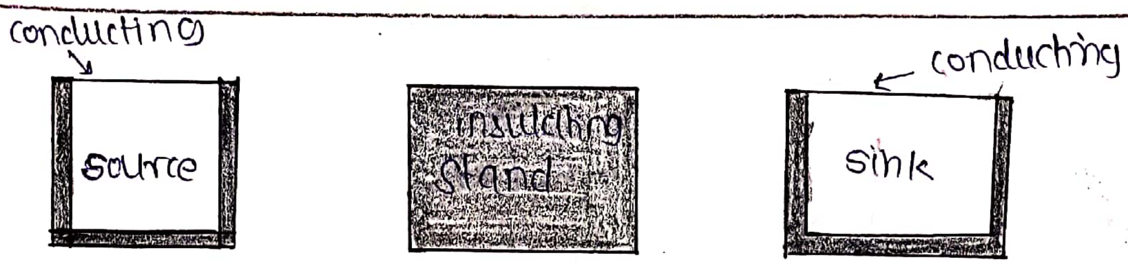
$(Q_1 - Q_2)$ – mechanical work done by engine in one cycle.

Carnot's ideal heat engine -

Such an engine can not be realised in practice. It has maximum efficiency and it is an ideal heat engine.

① Cylinder





② ③ ④

① Cylinder having perfectly non-conducting (insulating) walls and a conducting base and is provided with a perfect non conducting piston which moves without friction in the cylinder. The cylinder contains one mole of perfect gas as the working substance.

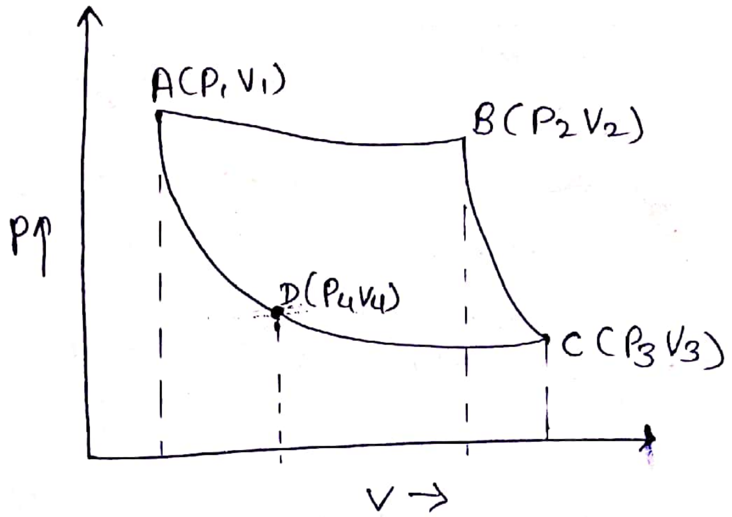
② Source - A reservoir maintained at a constant temperature T_1 from which the engine can draw heat by perfect conduction.

③ Insulating stand - A perfectly non conducting platform acts as a stand for adiabatic processes.

④ Sink - A reservoir maintained at a constant lower temperature to which heat engine can reject any amount of heat.

Carnot's cycle -

In order to obtain a continuous supply of work, the working substance is subjected to the following cycle of quasi - static operation known as Carnot's cycle.



① Isothermal expansion-

The cylinder is first placed on source, so that the gas acquires temperature T_1 of the source. It is then allowed to undergo quasi-static expansion. As the gas expands, its temperature tends to fall. Heat passes into the cylinder through perfectly conducting base which is in contact with source. The gas therefore undergoes slow isothermal expansion at a constant temperature (T_1).

Let, the working substance during isothermal expansion goes from its initial state $A(P_1 V_1 T_1)$ to the state $B(P_2, V_2, T_2)$ at constant temperature T_1 along AB. In this process, the substance absorbs heat Q_1 from the source T_1 and does work W_1 is given by,

$$Q_1 = W_1 = \int_{V_1}^{V_2} P.dV \qquad \because PV = RT, \quad P = RT/V$$

$$= \int_{V_1}^{V_2} \frac{RT_1}{V} dV$$

$$= RT_1 \left[\log V\right]_{V_1}^{V_2}$$

$$= RT_1 \log\left(\frac{V_2}{V_1}\right)$$

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(2) Adiabatic expansion - The cylinder is now removed from the source and is placed on the insulating stand. The gas is allowed to undergo slow adiabatic expansion. Therefore performing external work at the expense of its internal energy, until its temperature falls to T_2, same as that of the sink.

This operation is represented by the adiabatic BC curve. starting from $B(P_2 V_2 T_2)$ to the state $C(P_3 V_3 T_2)$. In this process, there is no transfer of heat. ∴ the temperature falls to T_2 and it does some external work W_2 which is given by,

$$W_2 = \int_{V_2}^{V_3} p\,dV$$

for an adiabatic process $PV^\gamma = \text{constant} = K$.

$\therefore P = K/V^\gamma$

$$= \int_{V_2}^{V_3} \frac{K}{V^\gamma}\,dV$$

$$= \int_{V_2}^{V_3} K V^{-\gamma}\,dV$$

$$= K\left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V_2}^{V_3}$$

$$= \frac{K}{1-\gamma}\left[V_3^{1-\gamma} - V_2^{1-\gamma}\right]$$

$$= \frac{1}{1-\gamma}\left[K V_3^1 V_3^{-\gamma} - K V_2 V_2^{-\gamma}\right]$$

$$= \frac{1}{1-\gamma}\left[\frac{K}{V_3^\gamma} V_3 - \frac{K}{V_2^\gamma} V_2\right]$$

$P_3 V_3^\gamma = P_4 V_4^\gamma = K$

$\frac{K}{V_3^\gamma} = P_3 \qquad P_4 = \frac{K}{V_4^\gamma}$

$$W_2 = \frac{1}{1-\gamma}\left[P_3 V_3 - P_2 V_2\right]$$

$\because PV = RT$

$$= \frac{1}{1-\gamma}\left[RT_3 - RT_2\right]$$

$$= \frac{R}{1-\gamma}\left[T_3 - T_2\right]$$

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③ Isothermal compression –

The cylinder is now removed from the insulating stand and is placed on the sink which is at temperature T_2. The piston is now very slowly moved inwards so that the work is done on the gas.

The operation is represented by the isothermal curve CD, starting from the state $C(P_3 V_3 T_2)$ to the state $D(P_4 V_4 T_2)$. The work done is given by,

$$Q_3 = W_3 = \int_{V_3}^{V_4} p.dv = RT_2 \log\left(\frac{V_4}{V_3}\right)$$

④ Adiabatic compression –

The cylinder is now removed from sink and is again placed on the insulating stand. The piston is slowly moved inwards so that the gas is adiabatically compressed and the temperature rises.

The adiabatic compression is represented by adiabatic curve DA, starting from $D(P_4 V_4 T_2)$ to the final state $A(P_1 V_1 T_1)$. In this process, workdone W_4 is given by,

$$W_4 = \int_{V_4}^{V_1} p.dv = \int_{V_4}^{V_1} kV^{-\gamma} dv$$

$$= k\left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V_4}^{V_1}$$

$$= \frac{1}{1-\gamma}\left[V_1^{1-\gamma} - V_4^{1-\gamma}\right]$$

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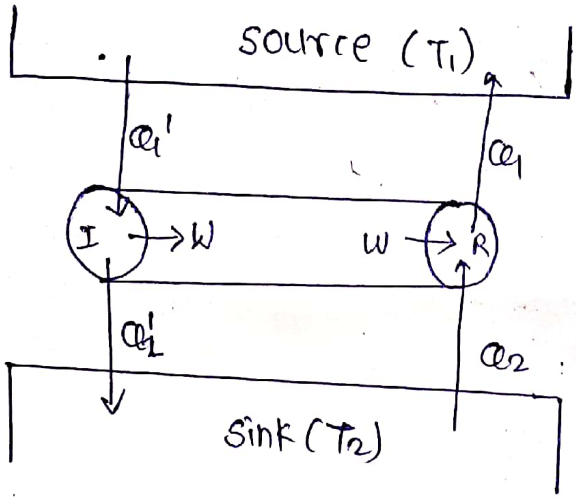
Workdone by the gas engine per cycle -

During the above cycle, the working substance absorbs an amount of heat Q_1 from the source and rejects Q_2 heat to the sink.

The net workdone by the engine per cycle

$$W = W_1 + W_2 + W_3 + W_4.$$

Carnot's theorem-



I : irreversible
R : Reversible

From the second law of thermodynamics, two important results are derived, these conclusions are taken together to constitute Carnot's theorem which may be stated in the following forms.

1. No engine can be more efficient than a perfectly reversible engine working between the same two temperatures.
2. The efficiency of all reversible engines, working between the same two temperatures is the same, whatever the working substance.

Suppose I is more efficient than R. suppose in each cycle, R absorbs the quantity of heat Q_1 from the source at T_1 and rejects the quantity of heat Q_2 to the sink at T_2. Suppose in each cycle I absorbs the quantity of heat Q_1' from the source at T_1 and gives up the quantity of heat Q_2' to the sink at T_2.

Let the two engines do the same amount of work W in each cycle.

Assumption $\therefore$ $$\frac{Q_1'-Q_2'}{Q_1'} > \frac{Q_1-Q_2}{Q_1}$$

$$\frac{W}{Q_1'} > \frac{W}{Q_1}$$

$$Q_1 > Q_1'$$

$$Q_1'-Q_2' = Q_1 - Q_2$$

$$Q_2 - Q_2' = Q_1 - Q_1'$$

Suppose the two engines are coupled together so that I drive R backwards and suppose they use the same source and sink.

new variable is entropy. The quantity entropy found to remain constant in adiabatic process just as temperature remains constant in an isothermal process. Thus, the entropy can be defined as the thermal property of a working substance which remains constant during an adiabatic process.

5.2 Change in Entropy

Let us consider reversible Carnot's cycles bounded by the same two adiabatics L and M and isothermals T_1, T_2 and T_3 as shown in an indicator diagram (Fig. 5.1) for an ideal gas. Then all along the adiabatics L and M, there is a change in volume and temperature with change in pressure. Let $ABCD$ and $DCEF$ represent the Carnot's reversible cycles. During Carnot's cycle $ABCD$, an amount of heat Q_1 is absorbed in going from A to B at constant temperature T_1 and an amount of heat Q_2 is rejected at constant temperature T_2. Then efficiency of Carnot's engine is given by

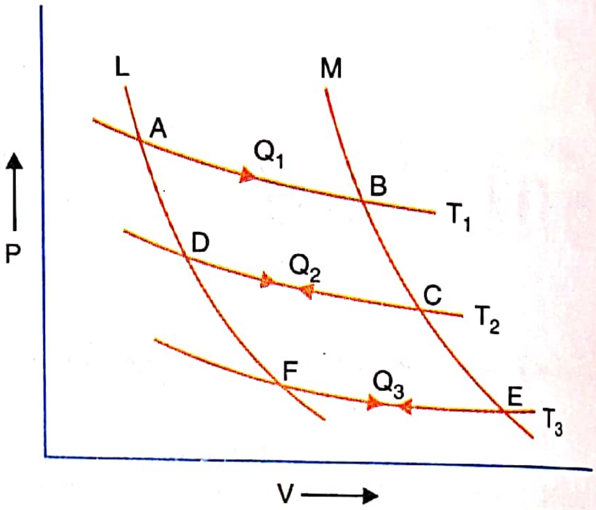


Fig. 5.1

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

$$1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

$$\therefore \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \qquad \text{...(5.1)}$$

Similarly considering the Carnot's cycle $DCEF$ in which an amount of heat Q_2 is absorbed at constant temperature T_2 and heat Q_3 is rejected at constant temperature T_3.

$$\therefore \quad \frac{Q_2}{T_2} = \frac{Q_3}{T_3} \qquad \text{...(5.2)}$$

From equations (5.1) and (5.2) we have

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{Q_3} = \text{......... constant.}$$

In general, if Q is the amount of heat absorbed or rejected at a temperature T in going from one adiabatic to the other, then

$$\frac{Q}{T} = \text{constant}$$

If the two adiabatics are very close to each other and if δQ is the small quantity of heat absorbed at constant temperature T in going from one adiabatic to another, then

$$\frac{\delta Q}{T} = \text{constant}$$

This constant ratio is called the 'change in entropy' between the states represented by the two adiabatics. It is denoted by δS

$$\therefore \quad \delta S = \frac{\delta Q}{T}$$

Third law of thermodynamics -

The heat capacities of all the solids tend to zero as the absolute zero of temperature is approached so that the internal energies and entropies of all the substances become equal there, approaching their common value asympotically tending to zero.

Thermodynamic potentials -

The state of a system can be described by two of the five state variables P, V, T, S and U. out of these, U the internal energy state variable is determined by using the remaining four. as follows.

According to first law of thermodynamics.

$$\delta Q = dU + \delta W \quad \Rightarrow \quad \delta Q = dU + P.dV$$

and from the second law of thermodynamics,

$$\delta Q = T.dS$$

$$dU + P.dV = T.dS$$

$$\therefore dU = T.dS - P.dV$$

Thus, there are four thermodynamic potentials.

① Internal energy U

② Helmboltz free energy ~~free~~ $F = U - TS$

③ Enthalpy $H = U + PV$

④ Gibbs function $G = H - TS$.

Each of Maxwell's four thermodynamical relation can be derived from one of these thermodynamic potentials U, F, H and G.

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① Internal energy -

The internal energy or the intrinsic energy is total energy of a system. according to first law of thermodynamics

$$dq = dU + dw$$
$$= dU + P \cdot dV.$$

$$dU = dq - P \cdot dV. \quad — (1)$$

and from second law of thermodynamics

$$dq = T \cdot ds.$$

$\therefore$ (1) becomes

$\therefore$ ~~dU~~

$$\boxed{dU = T \cdot ds - P \cdot dV}$$

This equation gives the change in internal energy of the system in terms of four thermodynamical variables P, V, T and S.

② Helmholtz free energy - (F).

Helmholtz free energy can be defined as

$$F = U - TS$$

as U, T and S are state variables. F is also a state variable.

$$dU = T \cdot ds - dw \qquad \text{from first law}$$

$F = U - TS$ is the Helmholtz free energy

$$dF = dU - T \cdot dS - S \cdot dT.$$
$$\& \; dU = T \cdot ds - dw = T \cdot ds - P \cdot dV$$
$$\therefore dF = T \cdot ds - P \cdot dV - T \cdot ds - S \cdot dT$$

$$\boxed{dF = -P \cdot dV - S \cdot dT}$$

This gives the change in ~~...~~ Helmholtz free energy during an infinitesimal reversible process.

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③ Enthalpy (H) - This is known as the total heat and is given by,

$$H = U + PV$$

as U, P and V are state variables. H is also a state variable.

change in enthalpy, $dH = dU + P.dV + V.dP$

but, $dU = T.ds - P.dV$

$$dH = T.ds - P.dV + P.dV + V.dP$$

$$\boxed{dH = T.ds + V.dP}$$

④ Gibbs function (G) or Gibbs free energy -

$G = H - TS$ but $H = U + PV$

$= U + PV - TS = U - TS + PV$

but $F = U - TS$

$\therefore G = F + PV$

$$dG = dU - T.ds - S.dT + P.dV + V.dP$$

$dU = T.ds - P.dV$ from first law.

$$\therefore dG = \cancel{T.ds} - \cancel{P.dV} - \cancel{T.ds} - S.dT + \cancel{P.dV} + V.dP$$

$$\boxed{dG = -S.dT + V.dP}$$

Maxwell's thermodynamical relations -

From first law of thermodynamics, maxwell was able to derive six fundamental relations. The state of a system can be specified by any pair of qualities ie pressure, volume, temp and entropy.

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from the first law of thermodynamics.

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

$$\delta Q = dU + P \cdot dV$$

$$dU = \delta Q - P \cdot dV \quad \text{— (1)}$$

from second law of thermodynamics

$$dQ = T \cdot dS. \quad \text{— (2)}$$

$\therefore$ eqn (1) becomes.

$$dU = T \cdot dS - P \cdot dV \quad \text{— (3)}$$

considering U, S and V to be functions of two independent variables x and y.

$$\left.\begin{aligned} \therefore dU &= \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy \\ dS &= \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \\ \& \ dV &= \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy \end{aligned}\right\}$$

put all these values in eqn (3)

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

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

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

Compairing the coefficients of dx and dy.

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

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For the second law of thermodynamics,

$$dS = \frac{\delta Q}{T}$$

or

$$\delta Q = TdS$$

Substituting this value of δQ, we get

$$\delta U = TdS - PdV \qquad \text{...(6.1)}$$

Considering U, S and V to be function of two independent variables x and y [here, in general, x and y can be any two variables out of P, V, T and S],

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

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

and

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

Substituting these values in equation (6.1), we get

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

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

Comparing the coefficients of dx and dy, we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \qquad \text{...(6.2)}$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \qquad \text{...(6.3)}$$

Differentiating equation (6.2) with respect to y and equation (6.3) with respect to x,

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

and

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

The change in internal energy brought about by changing V and T, whether V is changed by dV first and T by dT later or vice versa is the same.

It means dU is a perfect differential.

∴

$$\frac{\partial^2 U}{\partial y.\partial x} = \frac{\partial^2 U}{\partial x.\partial y} \text{ and}$$

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

$$= \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x.\partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial y.\partial x} \qquad \text{...(6.4)}$$

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Since dS and dV are also perfect differentials, we have

$$\frac{\partial^2 S}{\partial x.\partial y} = \frac{\partial^2 S}{\partial y.\partial x} \quad \text{and} \quad \frac{\partial V}{\partial x.\partial y} = \frac{\partial V}{\partial y.\partial x}$$

Equation (6.4), therefore reduces to

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x \quad ...(6.5)$$

This is the general expression for Maxwell's thermodynamical relations. In place of the independent variables x and y, any two of the four variables S, T, P and V can be substituted so that there may be one mechanical variable (P or V) and one thermal variable (S or T). Thus, there may be four sets of possible substitutions (S, V), (T, V), (S, P) and (T, P), providing the four Maxwell's thermodynamical relations.

First Relation:

Put $x = S$ and $y = V$ in equation (6.5), so that

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

and

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

Substituting in equation (6.5), we get

$$\left(\frac{\partial T}{\partial y}\right)_x = -\left(\frac{\partial P}{\partial x}\right)_y$$

But $\partial y = \partial V$ (as $y = V$) and $\partial s = \partial S$ (as $x = S$). Hence

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad ...(6.6)$$

This is Maxwell' first thermodynamical relation.

Second Relation :

Put $x = T$ and $y = V$ in equation (6.5),

then

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

and

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

Substituting in equation (6.5), we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad ...(6.7)$$

This is Maxwell's second thermodynamical relation.

Third Relation:

Put $x = S$ and $y = P$, in equation (6.5) then

$$\frac{\partial S}{\partial x} = 1, \frac{\partial P}{\partial y} = 1, \frac{\partial S}{\partial y} = 0, \frac{\partial P}{\partial x} = 0$$

Substituting these in equation (6.5), we get

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad ...(6.8)$$

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This is Maxwell's third thermodynamical relation

Fourth Relation:

Put $x = T$ and $y = P$, then equation (6.5) gives

$$\frac{\partial T}{\partial x} = 1, \frac{\partial P}{\partial y} = 1, \frac{\partial T}{\partial y} = 0 \text{ and } \frac{\partial P}{\partial x} = 0$$

Substituting these values in equation (6.5), we get

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad ...(6.9)$$

This is Maxwell's fourth thermodynamical relation. These are the four Maxwell's fundamental thermodynamic relations.

Further there are two more relations within the mechanical variables (*P, V*) and thermal variables (*T, S*).

Fifth Relation:

Put $x = P$ and $y = V$

$$\frac{\partial P}{\partial x} = 1, \frac{\partial V}{\partial y} = 1, \frac{\partial P}{\partial y} = 0 \text{ and } \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (6.5), we get

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1 \quad ...(6.10)$$

Sixth Relation:

Put $x = T$ and $y = S$

$$\frac{\partial T}{\partial x} = 1, \frac{\partial S}{\partial y} = 1, \frac{\partial T}{\partial y} = 0 \text{ and } \frac{\partial S}{\partial x} = 0$$

Substituting in equation (6.5), we get

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1 \quad ...(6.11)$$

Out of these six thermodynamic relations, the one suited for a particular problem is used and the problem is solved. Let us see, some of the important applications of these Maxwell's thermodynamic relations.

6.4 Applications of Maxwell's Thermodynamic Relations

6.4.1 Specific Heat Equation

The specific heat at constant pressure is given

as

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \qquad (\because \partial Q = T.\partial S)$$

and the specific heat at constant volume is

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Now, if the entropy S is regarded as a function of T and V and since dS is a perfect differential,

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

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anticlockwise order. In the clockwise direction, the right hand side expression is with a + sign and
the anticlockwise direction, it is – *ve*. These equations are

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

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

Similarly to write the other equations, ∂S is written in the denominator of the right hand side of equation and the other quantities are written (*i*) in the anticlockwise direction and (*ii*) in the clock direction. These equations are

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

6.8 Relation between C_P, C_V and μ

The specific heat at constant pressure C_P, the specific heat at constant volume C_V and the J
Kelvin coefficient μ are defined as follows:

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

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h$$

These three quantities are defined in terms of the thermodynamic properties *viz.* pressure, vol temperature, internal energy and enthalpy. Hence C_P, C_V and μ are also thermodynamic propertie a substance.

6.9 The *T. dS* Equations

1. ***First T.dS Equation.*** The entropy *S* of a pure substance can be taken as a functio temperature and volume.

∴
$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Multiplying both sides by *T*

$$T.dS = T\left(\frac{\partial S}{\partial T}\right)_V dV + T\left(\frac{\partial S}{\partial V}\right)_T dV$$

∴ But

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

dQ= T.dS

and from Maxwell's relations

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

Substituting these values in equation (*ii*)

$$T\,dS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad ...(6.4$$

Equation (6.42) is called the first *T. dS* equation.

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2. ***Second T.dS Equation.*** The entropy S of a pure substance can also be regarded as a function of temperature and pressure

$$\therefore \quad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Multiplying both sides by T

$$T.dS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

But

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

and from Maxwell's relations

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

Substituting these values in equation (v)

$$T.dS = C_P\, dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{...(6.43)}$$

Equation (6.43) is called the second $T.dS$ equation.

6.10 Clapeyron's Latent Heat Equation using Maxwell's Thermodynamical Relations

From Maxwell's second thermodynamical relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad (\because \text{ eqn. } 6.36)$$

Multiplying by T, we get

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

$$\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \qquad (\because T\,\partial S = \partial Q)$$

Here $\left(\frac{\partial Q}{\partial V}\right)_T$ represents the quantity of heat absorbed per unit increase in volume at constant temperature. This quantity of heat asborbed at constant temperature is the latent heat (L).

Thus, $\partial Q = L$ and $\partial V = V_2 - V_1$, for unit mass of a substance.

Substituting,

$$\left(\frac{L}{V_2 - V_1}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

or

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

or

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \qquad \text{...(6.44)}$$

This is **Clapeyron's latent heat equation.**

6.11 Cl...

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