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B.Sc. Chemistry Handwritten Notes

For 2nd Year Students

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Thermodynamics - I

Thermodyanamics -

The word thermodynamics means flow of heat.

The study of flow of heat into or out side it undergoes physical and chemical transformation is called thermodynamics.

Some imporent termology of thermodynamic is given below -

System -

The part of universe which undergoes thermodynamically study is called system.

Types of System -

These are three type of system -

1- Open system
2- Close system
3- Isolated system

Open System -

The system in which both energy and mass can exchange is called open system.

Example -

Hot water contain in open vessel.

Close system -

The system in which only energy can exchange from system to surrounding is called close system.

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Example - Hot water contain in close vessel.

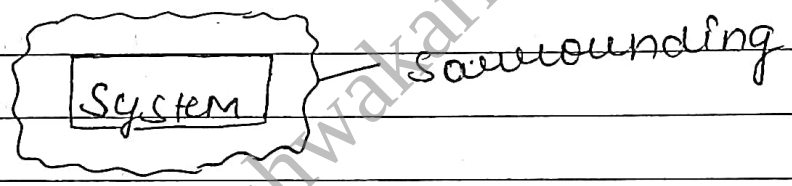
Isolated System -

The system in which nither energy nor mass can exchange b/w system and surrounding is called isolated system.

Example - Hot water contain in thermos.

Surrounding -

The rest of system the all atmospheric regards as surroundings.



Boundary -

Anything which seperate system and surrounding is called boundary.

Thermodynamic process -

When system change from one state to another state the operation is called thermodynamic process.

They are following types -

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Isothermal process –

The process in which temprature change in remains is called isothermal process.

For isothermal process –

$$\boxed{\Delta T = 0}$$

Isobaric process –

The process in which pressure is constants called isobaric process.

For isobaric process – $\boxed{\Delta P = 0}$

Isochoric process –

The process in which volume change in remains is called isochoric process. Depends on temp pressure law : Galisac law.

For isochoric process

$$\boxed{\Delta V = 0}$$

Adiabatic process –

The process in which heat change in remains is called adiabatic process.

For adiabatic process

$$\boxed{\Delta Q = 0}$$

Note –

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Note -

Cyclic process -

The process in which a system undergoes a number process and final returns in initial is called cyclic process.

Cyclic Process

- open cycle: Initial and Final state are not same ($CD \neq 0$)
- close cycle: Initial and Final state are same ($CD = 0$)

Intensive and Extensive properties -

The property of system which magnitude does not depend upon quantity of matter is called intesive property.

Example - Temperature, pressure, concentration density, Heat capacity.

Extensive property -

The property of system which magnitude depend on matter of quantity is called extensive property.

As- Entropy, Enthalpy, Internal energy, gives energy, mass, volume etc.

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Note -

The ratio of two extensive property to give intensive property.

$$d = \frac{m}{v}$$

m - Extensive
v - Extensive
d → Intensive

Path Function & state Function -

1- **Path Function -**

The function in which thermodynamic s variable system depend upon manner of path in which changes takes place. Whole the path is called path function.

1- **State Function -**

state function is a thermodynamic property system which does not depend upon manner of path. It only depend initial and final stages.

" The function in which thermodynamic variable changes takes place from initial and final state is called state function. "

Initial		Final	
(A)	———	(B)	
T_1	———	T_2	$\Delta T = T_2 - T_1$
S_1	———	S_2	$\Delta S = S_2 - S_1$
H_1	———	H_2	$\Delta H = H_2 - H_1$
E_1	———	E_2	$\Delta E = E_2 - E_1$
G_1	———	G_1	$\Delta G = G_2 - G_1$

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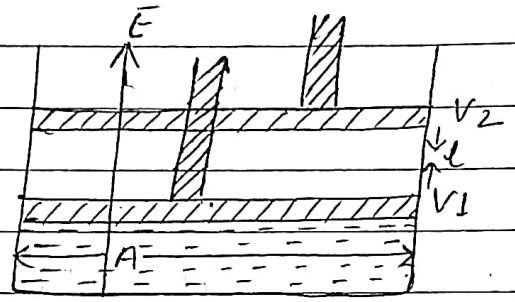
P-V work done -

A gas contain in a cylender vessels in which is fitted with in piston is external pressure applied on the gas by piston. Then force is balanced by internal gas which having opposite direaction than the piston. Due to gas it the gas travell (n. distance).



$W = F \times l$

we know that

$P = \frac{F}{A}$

$F = P \cdot A$

$W = P(A \times l)$

$W = P(V_2 - V_1)$

$\boxed{W = P\Delta V}$

Internal Energy -

The total possible energy present in an system is called internal energy. It is denoted by E/U

state (A) —— state (B)

E_A —— E_B

change in internal energy $\Delta E = E_B - E_A$

when $\Delta E = -ve$
or $E_A > E_B$

agains $\Delta E = +ve$
or $E_B > E_A$

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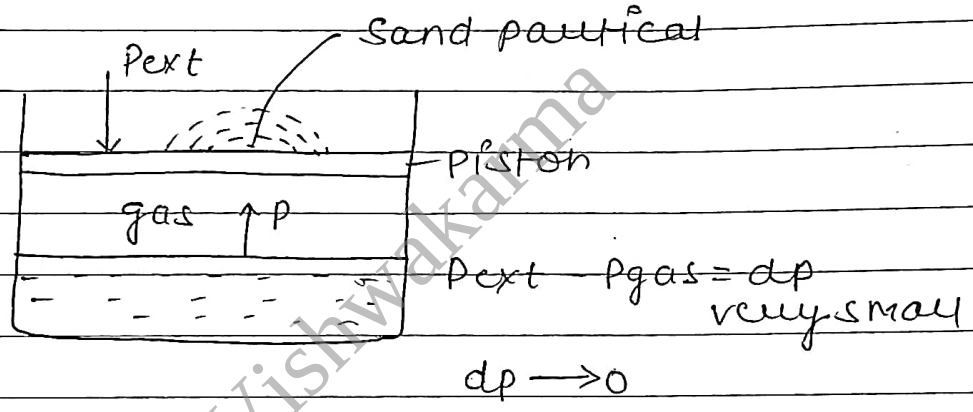
1- Reversibal and Irreversibal process-

In this process the reverse system easily occur at each step. It is time taken process it take place at slow form. The difference of driving force and opposing force is very small. In this process system is in equilibrium with surrounding through out process.

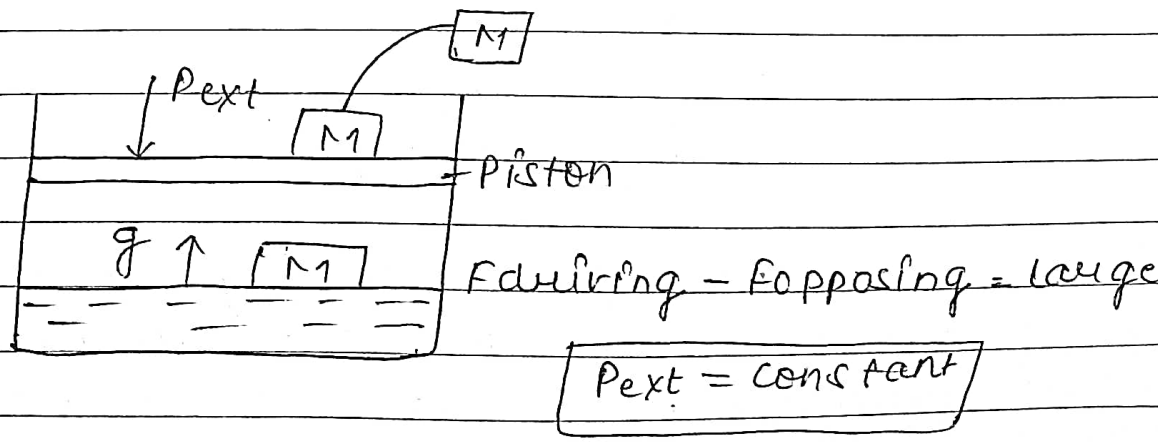
It's occur in ∞ step & ∞ time



Irreversible process-

In this process reverse system easily not occurs because the difference of driving force and opposing force large. It takes place in small time and high rate. The equilibrium exist in final and initial state.

It occur in difinite time and step.



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First law of thermodynamics –

It is based on law of conversation of energy.

According to this law,

"Energy can nither be created nor be destroyed it only tranfer one form to another form."

OR

"The total energy of a system and surrounding remains constant"

Mathmatical statement of first law of thermodynamics –

If Q heat given to a system which travell from state (A) to state (B) and the work done by system is W.

State (A) ———— State (B)

E_A ———— E_B

The internal energy change = Given heat − work done by system

$$E_B - E_A = Q - W$$

$$\Delta E = Q - W$$

$$Q = \Delta E + W$$

We know,

$$W = P\Delta V$$

$$\boxed{Q = \Delta E + P\Delta V}$$

If 500cal of heat energy are added to a system and the system does 350 calorij of work on the surrounding. What is the energy change of the system.

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$Q = \Delta E + W$

$\Delta E = Q + (-W)$

$\Delta E = 500 + (-350)$

$\Delta E = 500 - 350$

$\Delta E = 150$

If 100 cal of heat are added to the same system as in example one and a work of 50 cal is done on the system. Caculate the energy change on the system.

$Q = 100 cal$

$W = +50$

$\Delta E = Q + W$

$\Delta E = 100 + 50$

$\Delta E = 150$

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Heat contant –

The physical and chemical properties are carried out at constant volume and constant pressure.

Heat contant at constant volume –

At a constant volume change is zero is change then $\Delta V = 0$

According to first law of thermodynamics

$Q = \Delta E + W$

$Q = \Delta E + P \cdot \Delta V$ $\quad (W = P\Delta V)$

$Q = \Delta E + P \times 0$

$Q = \Delta E$

$\boxed{\Delta E = (Q)_V}$

hence the change internal energy of system is equal to given heat at constant volume.

Heat content at constant pressure or Enthalpy

The sum of internal energy work done (PV) of system is called enthalpy. It is denoted by H.

Enthalpy is a state function and extensive property.

$$\boxed{H = E + PV}$$

Change in Enthalpy –

If H_1 is enthalpy of initial state (E_1, V_1) and H_2 is enthalpy of final state (E_2, V_2) then,

At initial state –

$$H_1 = E_1 + PV_1 \quad \text{—— (I)}$$

At final state –

$$H_2 = E_2 + PV_2 \quad \text{—— (II)}$$

change in Enthalpy $= H_2 - H_1$

$$\Delta H = (E_2 + PV_2) - (E_1 + PV_1)$$
$$\Delta H = (E_2 - E_1) + (PV_2 - PV_1)$$
$$\Delta H = \Delta E + P(V_2 - V_1)$$
$$\Delta H = \Delta E + P\Delta V$$
$$\Delta E = \Delta H - P\Delta V \quad \text{—— (III)}$$

According to Ist law of thermodynamics

$$\Delta E = Q - P\Delta V \quad \text{—— (IV)}$$

comparission b/w eq (IV) and (III)

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$$\Delta H - \cancel{P\Delta V} = Q - \cancel{P\Delta V}$$

$$\boxed{\Delta H = (Q)_p}$$

hence the change of enthalpy is equal to given heat at constant pressure—

* Relation b/w ΔH and ΔE —

We know that —

$$\Delta H = \Delta E + P\Delta V \quad \text{— (1)}$$

$$\Delta H = H_P - H_R$$

Reactant —— Product

$$PV_R = n_R RT \quad \text{——} \quad PV_P = n_P RT$$

$$PV_P - PV_R = n_P RT - n_R RT$$

$$P(V_P - V_R) = RT(n_P - n_R)$$

$$P\Delta V = RT(\Delta n)$$

$$P\Delta V = \Delta n RT$$

Puting the value of $P\Delta V$ in equ (1)

$$\boxed{\Delta H = \Delta E + \Delta n_{(g)} RT}$$

$$\Delta n_{(g)} = n_P - n_R$$

Example - The heat of combustion of CO at constant volume and at 17°C is —20.3 kg/J calculate the heat of combousation at constant pressure when R = 8.314 J/°c/mole.

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$T = 17°C = 273 + 17 = 290K$

$R = 8.314 J/°C/mole$

$\Delta E = -283.3 KJ$

$CO(g) + 1/2\ O_2(g) \longrightarrow CO_2(g)$

$\Delta n = (1 - 3/2)$

$\Delta n = 1/2$

$\Delta H = ?$

$\Delta H = \Delta E + \Delta nRT$

$\Delta H = -283.3 + (-1/2) \times 8.314 \times 290$

$\Delta H = -283.3 + (-1/2) \times 2411.060$

$\Delta H = -283.3 + 1205.530$

$\Delta H = -1483.3 J$

✓ <u>Heat capacity</u>:-

The amount of heat required to raise the temperature of certain amount of substance through 1°C or 1K is called heat capacity. It is denoted by 'c'.

<u>OR</u>

It is heat required to raise temperature by 1°C

$Q = C \cdot \Delta T$

$C = \frac{Q}{\Delta T}$

$C = \frac{Q}{(t_f - t_i)}$

If $\Delta T = 1°C$ or $1K$

unit of $C = J/K$ or $J/C°$

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Note - Molar heat capcity -

It is heat required to raise temperature by 1°c for 1 mole substance.

$$Q = n\, C_M \times \Delta T$$

$$C_M = \frac{Q}{n\Delta T}$$

$$C_M = \frac{Q}{n(T_f - T_i)}$$

unit of C_M = J/mole k

Specific heat capacity -

It is heat required raise temperature by 1°c for 1 gram substance.

$$Q = m C_S \Delta t$$

$$C_S = \frac{Q}{m\Delta t}$$

unit of C_S = J/gram k

Heat capacity at constant volume -

The amount of energy required to raise temperature of system through 1°c at constant volum is called heat capacity at constant volume. It is denoted by C_V.

We know that

$$C = \frac{Q}{\Delta t}$$

According to definition of heat capacity at constant volume

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$$\boxed{C_V = \frac{(Q)_V}{\Delta T}}$$

Since heat contant at constant volume -

$$\Delta E = (Q)_V$$

$$\boxed{C_V = \frac{\Delta E}{\Delta T} = \left(\frac{\Delta E}{\Delta T}\right)_V}$$

Heat capacity at constant pressure -

The amount of energy required to raise temperature of system through 1°C at constant pressure is called heat capacity at constant pressure. It is denoted by C_p.

We know that -

$$C = \frac{Q}{\Delta T}$$

According to heat capacity at constant pressure -

$$C_p = \frac{(Q)_p}{\Delta T}$$

According to heat capacity at constant pressure

According to Ist law of thermodynamics at constant pressure

$$\Delta H = (Q)_p$$

$$C_p = \frac{\Delta H}{\Delta T}$$

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$$\boxed{C_p = \left(\frac{\Delta H}{\Delta T}\right)_p}$$

Relation b/w C_p & C_v (Mayer's formula) —

According to heat capacity at constant volume

$$C_v = \frac{dE}{dt} \quad \text{—— (I)}$$

According to heat capacity at constant pressure

$$C_p = \frac{dH}{dt} \quad \text{—— (II)}$$

From enthalpy difinition —

$$\boxed{H = E + PV} \quad \text{—— (III)}$$

Differentiating above equation with respt to t

$$\frac{dH}{dt} = \frac{dE}{dt} + \frac{d}{dt}(PV)$$

$$\frac{dH}{dt} = \frac{dE}{dt} + R\frac{dt}{dt}$$

$$C_p = C_v + R$$

$$\boxed{C_p - C_v = R}$$

Hence, the different of heat capacity at constant pressure, at constant volume is always to equal to gas constant.

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IUPAC convention –

Expension	compression
work done by the gas	work done on the gas
$V_2 > V_1$	$V_1 > V_2$
$w = -P\Delta V$	$w = -P\Delta V$
$w = -\Delta V$	$w = -P(-\Delta V)$
$w = \ominus ve$	$w = +PV$
	$w = \oplus ve$

In isothermal reversible expension –

1– calculation the work done in isothermal expension

work done by system –

$$w = -Pdv$$

$$w = -\int_{V_1}^{V_2} Pdv \quad \text{—— (1)}$$

from ideal gas equation –

$$PV = nRT$$

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

putting the value of P in equation (1)

$$w = -\int_{V_1}^{V_2} \frac{nRT}{V} dv$$

$$w = -nRT \int_{V_1}^{V_2} \frac{1}{V} dv$$

$$w = -nRT \left[\log_e V\right]_{V_1}^{V_2}$$

$$w = -2.303 nRT \left[\log_{10} V\right]_{V_1}^{V_2}$$

[~~wout~~ we know that $\log_e x = 2.303 \log_{10} x$]

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$$w = -2.303 nRT (\log_{10} V_2 - \log_{10} V_1)$$
$$w = -2.303 nRT (\log_{10} \frac{V_2}{V_1})$$

from boyle's law -

$$P \propto \frac{1}{V}$$
$$P = \frac{K}{V}$$
$$PV = K$$
$$P_1 V_1 = P_2 V_2$$
$$\boxed{\frac{P_1}{P_2} = \frac{V_2}{V_1}}$$

$$\boxed{w = 2.303 nRT [\log_{10} \frac{P_1}{P_2}]}$$

Example -

Calculate the work done when one mole of gas is allowed to expend reversibal and isothermal from 5 ATP to 1 ATM at 25°c.

$$W = -2.303 nRT [\log_{10} \frac{P_1}{P_2}]$$

$$W = -2.303 \cdot 8.314 \cdot 298 [\log_{10} \frac{5}{1}]$$

$$W = -2.303 \times 8.314 \times 298 [\log_{10} 5]$$
$$W = -2.303 \times 8.314 \times 298 \times 0.6991$$
$$W = -3988.21 \text{ Jule}$$

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Internal energy change (ΔE) –

$$\Delta E = E_f - E_i$$

or

$$\Delta E = E_2 - E_1$$

$$\boxed{\Delta E = 0}$$

Enthalpy change –

We know that

$$\Delta H = H_2 - H_1$$

$$\Delta H = [(E_2 + P_2V_2) + (E_1 + P_1V_1)] \quad (\text{since } H = E + PV)$$

$$\Delta H = [(E_2 - E_1) + (P_2V_2 - P_1V_1)]$$

$$\Delta H = [0 + (P_2V_2 - P_1V_1)] \quad \text{from boyles law } P_1V_1 = P_2V_2$$

$$\Delta H = [0 + (P_2V_2 - P_2V_2)]$$

$$\Delta H = [0 + 0]$$

$$\boxed{\Delta H = 0}$$

a- ## Heat change (q) –

From first law of thermodynamics

$$q = w_{rev} + \Delta E$$

$$q = w_{rev} + 0$$

$$q = w_{rev}$$

We know that

$$w = 2.303 nRT \log_{10} \frac{V_2}{V_1}$$

or

$$\boxed{q = -2.303 nRT \log_{10} \frac{V_2}{V_1}}$$

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Adiabatic process – As Before

Adiabatic expension of an ideal gas –

Under adiabatic expension the exchange of heat b/w the system and surroundings is 0.

$(q = 0)$

from 1st law of thermodynamics

$$\boxed{\Delta E = w = P\Delta V}$$

Temperature volume relationship –

$$q = dE + w$$
$$q = dE + P\Delta V$$
$$q = dE + P\Delta V$$
$$0 = dE + P\Delta V$$
$$-dE = P\Delta V$$

$$-nC_V dT = P\Delta V$$
$$-\cancel{n} C_V dT = \frac{\cancel{n}RT}{V} \Delta V$$

$$\frac{dT}{T} = -\frac{R}{C_V} \frac{\Delta V}{V}$$

Integrating on the both side

$$\int_{T_1}^{T_2} \frac{dT}{T} = -\frac{R}{C_V} \int_{V_1}^{V_2} \frac{\Delta V}{V}$$

$$\log_e [T]_{T_1}^{T_2} = -\frac{R}{C_V} \log_e [V]_{V_1}^{V_2}$$

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$$\log_e \frac{T_2}{T_1} = -\frac{R}{C_V} \log_e \frac{V_2}{V_1}$$

$$\log_e \frac{T_2}{T_1} = \frac{R}{C_V} \log_e \frac{V_1}{V_2}$$

We know that

$C_P - C_V = R$

dividing equ by C_V

$$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

$$\frac{C_P}{C_V} - \frac{\cancel{C_V}}{\cancel{C_V}} = \frac{R}{C_V}$$

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

$$(\gamma - 1) = \frac{R}{C_V}$$

γ = adibatic constant

Putting the value of $\frac{R}{C_V}$ in equ (1)

$$\log_e \frac{T_2}{T_1} = (\gamma - 1) \log_e \frac{V_1}{V_2}$$

$$\cancel{\log_e} \frac{T_2}{T_1} = \cancel{\log_e} \left[\frac{V_1}{V_2}\right]^{(\gamma-1)}$$

$$\frac{T_2}{T_1} = \frac{(V_1)^{(\gamma-1)}}{(V_2)^{(\gamma-1)}}$$

$$T_2 (V_2)^{(\gamma-1)} = T_1 (V_1)^{(\gamma-1)}$$

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

Temperature pressure relationship -

We know that

$$TV^{(\gamma-1)} = k \quad \text{—— (1)}$$

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For one mole of an ideal gas -

$$PV = RT$$

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

Putting the value of V in equ ① we get

$$T\left[\frac{RT}{P}\right]^{(\gamma-1)} = k$$

$$\frac{T(R)^{(\gamma-1)}(T)^{(\gamma-1)}}{P^{(\gamma-1)}} = k$$

$$\frac{T(T)^{(\gamma-1)}}{P^{(\gamma-1)}} = \frac{k}{R^{(\gamma-1)}}$$

$$\frac{T^{(\gamma-\cancel{1}+\cancel{1})}}{P^{(\gamma-1)}} = k$$

$$\boxed{T^{\gamma} P^{(\gamma-1)} = k}$$

III - Pressure - volume relationship -

We know that

$$TV^{(\gamma-1)} = k \quad \text{—} \quad ①$$

For one mole of an ideal gas

$$PV = RT$$

$$T = \frac{PV}{R}$$

Putting the value of T in equ ① we get

$$\frac{PV}{R} V^{(\gamma-1)} = k$$

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$$P\gamma\, V^{(\gamma-1)} = K \times R$$
$$PV^{(\gamma-1+1)} = K$$
$$\boxed{PV^{\gamma} = K}$$

a- **Adiabatic reversible expansion –**

We know that

$$W = -P\Delta V \quad \text{—— (I)}$$
$$n C_V \Delta T = -P\Delta V \quad \text{—— (II)}$$

For very small reversible process

$$C_V dT = -P dV \quad \text{—— (III)}$$

For one mole of an ideal gas

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

Putting the value of P in equ (III) we get

$$C_V dT = -\frac{RT}{V} dV$$

$$\frac{dT}{T} = -\frac{R}{C_V} \cdot \frac{dV}{V}$$

$$\int_{T_1}^{T_2} \frac{dT}{T} = -\frac{R}{C_V} \int_{V_1}^{V_2} \frac{dV}{V}$$

$$[\log_e T]_{T_1}^{T_2} = -\frac{R}{C_V} [\log_e V]_{V_1}^{V_2}$$

$$[\log_e T_2 - \log_e T_1] = -\frac{R}{C_V} [\log_e V_2 - \log V_1]$$

$$\log \frac{T_2}{T_1} = (\gamma-1) \log \frac{V_1}{V_2}$$

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$$\log_e \frac{T_2}{T_1} = \log_e \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

$$\boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}}$$

$C_V - C_P = R$ dividing by C_V in both side

$$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

$$(\gamma-1) = \frac{R}{C_V}$$

$$C_V = \frac{R}{(\gamma-1)} \quad \text{(IV)}$$

comparing equ (I) & (II) we get

$$W_{rev} = nC_V\Delta T$$

$$W_{rev} = \frac{nR}{(\gamma-1)}(T_2-T_1)$$

$$\boxed{W_{rev} = \frac{nR}{(\gamma-1)}(T_2-T_1)}$$

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<u>Conclusion</u> -

When $T_2 > T_1$ $W_{rev} = (+)ve$

When $T_2 > T_2$ $W_{rev} = (-)ve$

<u>Enthalpy change</u> -

$$\Delta H = H_2 - H_1$$

$$= [E_2 + P_2V_2] - [E_1 + P_1V_1]$$

$$= [E_2 - E_1] - [P_2V_2 - P_1V_1]$$

$$= \Delta E + nR(T_2 - T_1)$$

$$= C_V\Delta T + nR(T_2 - T_1)$$

$C_v (T_2 - T_1) + nR (T_2 - T_1)$ $\left\{ C_v = \frac{\Delta E}{\Delta T} \right\}$

$(T_2 - T_1)(C_v + nR)$

$$\boxed{\Delta H = \Delta T (C_v + nR)} \quad \text{— (I)}$$

We know that —

$$\Delta H = C_p \Delta T$$

For n mole of ideal gas —

$$\Delta H = n C_p \Delta T \quad \text{— (II)}$$

Comparing equation (I) and (II) we get —

$$\boxed{n C_p = (C_v + nR)}$$

OR

$$n C_p - nR = C_v$$

$$n (C_p - R) = C_v$$

$$\boxed{n = \frac{C_v}{(C_p - R)}}$$

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b- Adiabatic irreversible expension —

i- Work done (W_{irr}) —

Under the condition external pressure is constant and the work done is given by —

We know that —

$$W_{irr} = P_{ext} \times dV$$

$$W_{irr} = P_{ext} \times \int_{V_1}^{V_2} dV$$

$$W_{irr} = P_{ext} [V]_{V_1}^{V_2}$$

$$W_{irr} = P_{ext}\left[V_2 - V_1\right]$$

$P_{ext} = P_2 =$ final pressure

$$W_{irr} = P_2\left[V_2 - V_1\right]$$

$$W_{irr} = P_2\left[\left(\frac{nRT_2}{P_2}\right) - \left(\frac{nRT_1}{P_1}\right)\right]$$

$$W_{irr} = P_2\left[nR\left(\frac{T_2}{P_2} - \frac{T_1}{P_1}\right)\right]$$

$$W_{irr} = nR\left[\left(T_2 - \frac{T_1P_2}{P_1}\right)\right]$$

$$\boxed{W_{irr} = nRT_1\left[\frac{T_2}{T_1} - \frac{P_2}{P_1}\right]}$$

Energy change (ΔE) —

According to I^{st} law of thermodynamics —

$$\Delta E = W + q$$

for adiabatic process —

$$q = 0$$

$$\Delta E = W = P_2(V_1 - V_2) = C_v(T_2 - T_1)$$

$$P_2(V_1 - V_2) = C_v(T_2 - T_1)$$

$$C_v(T_2 - T_1) = P_2\left[\left(\frac{nRT_1}{P_1} - \frac{nRT_2}{P_2}\right)\right]$$

$$C_vT_2 - C_vT_1 = \frac{nRT_1P_2}{P_1} - nRT_2$$

$$C_vT_2 + nRT_2 = \frac{nRT_1P_2}{P_1} + C_vT_1$$

$$T_2(C_v + nR) = \left[\frac{nRP_2}{P_1} + C_v\right]T_1$$

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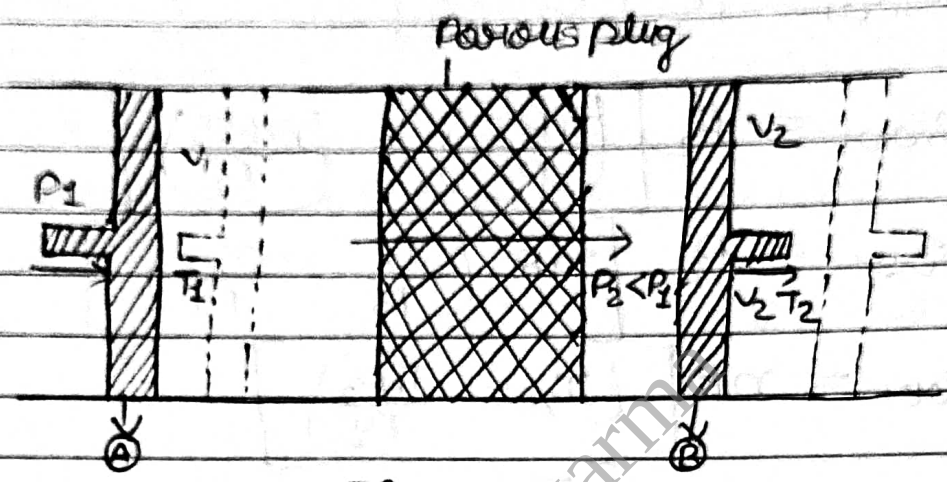
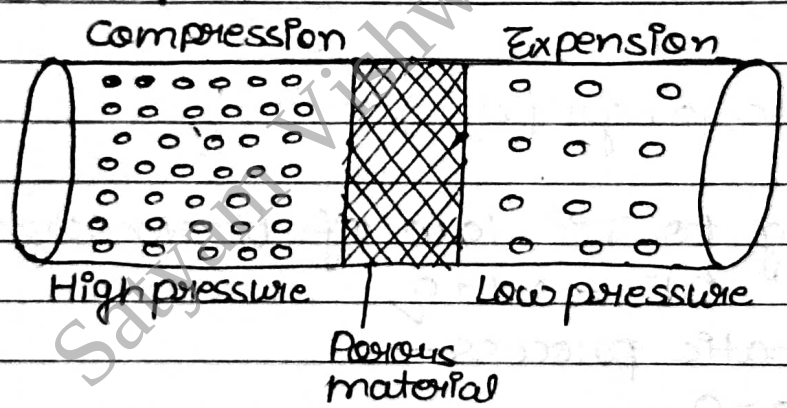
$$T_2 = \left[\frac{C_v + nR\,(P_2/P_1)}{C_v + nR} \right] T_1$$

Joule - Thomson effect



OR



Joule and Thomsan studied the behaviour of real gases and suggested a phenomenon known as Joule - Thomsan effect.

"when a gas is allowed to pass from a higher pressure to a lower pressure through a porous plug. It's temp. falls and fall in temperature is proportional to the different between pressure."

The apperatus use by Joule and Thomsan is show in figure. An insulated

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tube is fited with a porous plug in the middle and two frictionless piston A and B on the sides. A stream of gas of volume V_1 was forced at pressure P_1 to pass through the porous plug the gas in the right hand chamber is allowed to expend to volume V_2 and pressure P_2. The change in temperature is noted by talking reading on the true senstive thermamitter fited in the chamber.

Explanation—

Suppose volume V_1 of a gas is enclosed between piston A and porous plug at pressure P_1. This gas is slowly passed through plug by moving piston A inward and this gas is allowed to expend to lower pressure P_2 and volume V_2 by moving piston B outward.

Work done by the gas on piston (A) $= P_1V_1$
Work done by the gas on piston (B) $= P_2V_2$
Net work done by the gas (W) $= P_2V_2 - P_1V_1$

According to the Ist law of thermodynamics

$$\Delta E = q - W$$

for adiabatic process—

$$q = 0$$

$$\Delta E = -(P_2V_2 - P_1V_1)$$

$$\Delta E = P_1V_1 - P_2V_2$$

$$E_2 - E_1 = P_1V_1 - P_2V_2$$

$$E_2 + P_2V_2 = E_1 + P_1V_1$$

$$H_2 = H_1$$

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$H_2 - H_1 = 0$

$$\boxed{\Delta H = 0}$$

Joule - Thomson coefficient —

Joule - Thomson coefficient is defind as—

The change of temperature with pressure at constant enthalpy are called Joule - Thomson coefficient. It is denoted by 'μ_{JT}'.

$$\boxed{\mu_{JT} = \left(\frac{\Delta T}{\Delta P}\right)_H}$$

Inversion temperature —

The temperature at which Joule - Thomson coefficient becomes zero is known as Inversion temperature. It is denoted by T_i.

$$\boxed{T_i = \frac{2a}{Rb}}$$

where,

$a, b =$ Vander waal constant

$R =$ gas constant

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Thermochemistry

The study of heat change in chemical process is called thermochemistry.

Exothermic and Endothermic reaction —

Exothermic reaction —

Reaction in which heat is given out along with the product are called exothermic reaction.

As — Burning of coal

$$C + O_2 \rightarrow CO_2 + Heat$$

Endothermic reaction —

Reaction in which heat is absorbed are known as endothermic reaction.

As — $CaCO_3 \xrightarrow{Heating} CaO + CO_2$

Sign Convension —

	Δq	ΔE	ΔH
Exothermic reaction —	⊖	⊖	⊖
Endothermic reaction —	⊕	⊕	⊕

Difference between Exothermic and Endothermic reaction —

Exothermic	Endothermic
i- Heat is released by the system	i- Heat is absorbed by the system.
ii- Temperature of surrounding is increased	ii- Temperature of the surrounding is decreased

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iii- ΔH, ΔE, Δq all are negative iii- ΔH, ΔE, Δq all are positive.

Heat of reaction—

The amount of heat absorbed in a chemical reaction is called heat of reaction.

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow HCl(g) - 44\ Kcal$$

$$\Delta H = 44\ Kcal$$

Effect of temperature on heat of reaction—

Kirchoff's equation at constant pressure—

$$aA + bB \longrightarrow cC + dD$$

$$\Delta H = \Sigma H_{product} - \Sigma H_{reactant}$$

differentiating with respect to T at constant pressure

$$\frac{d(\Delta H)}{dT} = \left[c\left(\frac{dH_C}{dT}\right)_P + d\left(\frac{dH_D}{dT}\right)_P\right] - \left[a\left(\frac{dH_A}{dT}\right)_P + b\left(\frac{dH_B}{dT}\right)_P\right] \quad \text{--- (1)}$$

* $\left[c\left(\frac{dH_C}{dT}\right)_P + d\left(\frac{dH_D}{dT}\right)_P\right] = (C_P)_P$

* $\left[a\left(\frac{dH_A}{dT}\right)_P + b\left(\frac{dH_B}{dT}\right)_P\right] = (C_P)_R$

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from equation ① we have

$$\frac{d(\Delta H)}{dT} = (C_p)_P - (C_p)_R$$

$$\frac{d(\Delta H)}{dT} = \Delta C_p$$

$$d(\Delta H) = \Delta C_p dT$$

$$\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \Delta C_p \int_{T_1}^{T_2} dT$$

$$[\Delta H]_{\Delta H_1}^{\Delta H_2} = \Delta C_p [T]_{T_1}^{T_2}$$

$$\Delta H_2 - \Delta H_1 = \Delta C_p [T_2 - T_1]$$

$$(\Delta H)_{T_2} - (\Delta H)_{T_1} = \Delta C_p [T_2 - T_1]$$

$$\boxed{\Delta C_p = \left[\frac{(\Delta H)_{T_2} - (\Delta H)_{T_1}}{T_2 - T_1}\right]}$$

Kirchoff's equation at constant volume —

$$aA + bB \rightarrow cC + dD$$

$$\Delta E = \Sigma E_{Product} - \Sigma E_{reactant}$$

Differentiating with respect to T at constant volume —

$$\frac{d(\Delta E)}{dT} = \left[c\left(\frac{dE_C}{dT}\right)_V + d\left(\frac{dE_D}{dT}\right)_V\right] - \left[a\left(\frac{dE_A}{dT}\right)_V + b\left(\frac{dE_B}{dT}\right)_V\right]$$

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$$\frac{d(\Delta E)}{dT} = (C_V)_P - (C_V)_R$$

$$\frac{d(\Delta E)}{dT} = \Delta C_V$$

$$d(\Delta E) = \Delta C_V dT$$

$$\int_{\Delta E_1}^{\Delta E_2} d(\Delta E) = \Delta C_V \int_{T_1}^{T_2} dT$$

$$\left[\Delta E_2 - \Delta E_1\right] = \Delta C_V \left[T_2 - T_1\right]$$

$$(\Delta E)_{T_2} - (\Delta E)_{T_1} = \Delta C_V \left[T_2 - T_1\right]$$

$$\boxed{\Delta C_V = \frac{(\Delta E)_{T_2} - (\Delta E)_{T_1}}{T_2 - T_1}}$$

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Thermochemical equation ——

Physical state ——

The physical state are represented by the symbols s, l, g and aq. for solid, liquid, gas and aquoes state, respectively.

e.g.

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \quad \Delta H^\circ_{298} = -241.82\,KJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H^\circ_{298} = -285.82\,KJ$$

Fraction number of moles ——

A Thermochemical equation may be written form of fractional

number of moles of some reactant and products
e.g. —

$$C_6H_6(g) + \frac{15}{2} O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$$

$$\Delta H = -3301.5 \text{ KJ}$$

<u>Temperature and pressure</u> —

It is necessary to mention the temperature and pressure at which the reported enthalpy applies. e.g.

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow HCl(g)$$

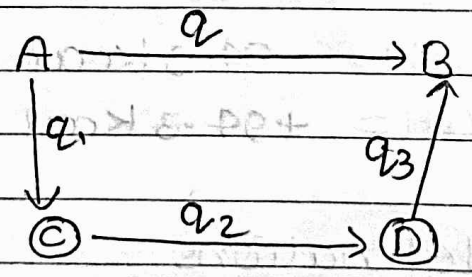
$$\Delta H^{\circ}_{298} = -92.31 \text{ KJ}$$

Note- 'o' indicates P = 1 atm and T = 25°C or 298 K

<u>Law of thermochemistry</u> —

<u>Hess's law</u> —

This law states that the amount of heat absorbed in a process including a physical change and chemical change is the same wheather the process takes place in one or several step.



$$q = q_1 + q_2 + q_3$$

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For example—
Formation of CO_2 —
First method—

$$C + O_2 \rightarrow CO_2 \quad \Delta H = -94.3\ KJ$$

Second method—

$$C + \frac{1}{2} O_2 \rightarrow CO \quad \Delta H = -26.3\ KJ$$

Third method—

$$C + \frac{1}{2} O_2 \rightarrow CO_2 \quad \Delta H = -68.0\ KJ$$

Application of Hess law —

i- Calculate of resonance energy.
ii- Calculation of enthalpy formation.
iii- Calculation of lattice energy
iv- Calculation of enthalpy of nutralization, Ionization, precipation, fission, vapourization.

B- Lavoisier and Laplace law —

According to this law,
Enthalpy of formation of compound is numerically equal to the enthalpy of decomposition of that compound with opposite sign.
As—

$$C + O_2 \rightarrow CO_2 \quad \Delta H = -94.3\ Kcal$$
$$CO_2 \rightarrow C + O_2 \quad \Delta H = +94.3\ Kcal$$

Note- Some important definations —

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Heat of formation

The process in which a compound is formed from its consitutent elements in their standered state is called formation.

The amount of heat absorbed when one mole of the substance is directly obtained from its consitutent elements is called heat of formation. It is denoted by ΔH_f.

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)} \quad \Delta H = -44.0 \text{ kcal}$$

Heat of neutralization

The heat of neutralization is defind as the heat evolved or decrease in ethalpy when one gram equivalent of an acid is neutralized by one gram equivalent of a base dilute solution.

Notation -

Acid + Base $\longrightarrow$ Salt H_2O

Step - I

Strong acid + strong base $\longrightarrow$ salt + H_2O

$\Delta H = -13.7$ KCal

$$HCl_{(g)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(aq)}$$

$\Delta H = -13.7$ KCal

Step - II -

Strong acid + weak base $\longrightarrow$ salt + H_2O

$\Delta H = -12.3$ KCal

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$HNO_3(aq) + NH_4OH(aq) \longrightarrow NH_4NO_3(aq) + H_2O(aq)$
$\Delta H = -12.3 \text{ KCal}$

Step - III -

Weak acid + weak base $\longrightarrow$ salt + H_2O
$\Delta H = -11.9 \text{ KCal}$

$CH_3COOH + NH_4OH \longrightarrow CH_3COONa + H_2O$
$\Delta H = -11.9 \text{ KCal}$

Enthalpy of solution or heat of solution -

The amount of heat evolved or absorbed when one mole solute is dissolved in excess of solvent is called heat of solution.

for example -

$H_2SO_4(l) + aq \longrightarrow H_2SO_4(aq)$
$\Delta H = -20.2 \text{ KCal}$

$KCl(s) + aq \longrightarrow KCl(aq)$ $\Delta H = 4.4 \text{ KCal}$

$KOH(s) + aq \longrightarrow KOH(aq)$ $\Delta H = -13.3 \text{ KCal}$

Bond dissociation energy -

The energy requir to break one mole of bond of particular type is termed bond dissociation energy.

Heat of reaction = Σ Bond energy of reactant − Σ bond energy of product.

Example -- Calculate the enthalpy of the following reaction

$CH_2=CH_2 + H_2 \longrightarrow CH_3CH_3$

Bond energy of C-H, C-C, C=C, H-H are 99, 83, 147, 104 kcal

Heat of Reaction = $[(4\Delta H_{C-H} + \Delta H_{C=C} + \Delta H_{(H-H)}) - (6\Delta H_{C-H} + \Delta H_{C-C})]$

$(4 \times 99 + 147 + 104) - (6 \times 99 + 83)$

$(396 + 147 + 104) - (594 + 83)$

$647 - 677 = -30 \text{ kcal}$

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Chemical Equilibrium

Irreversible Reaction -

The chemical reaction which proceed in such a way that reactants are completely converted into product i.e. the reaction which move in one direction are called irreversible reaction.

Example

I. Thermal decomposition of $KClO_3$

$$2KClO_3 \xrightarrow[Heat]{MnO_2} 2KCl + 3O_2$$

II- Decomposition of ammonium nitrite -

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

III- Neutralization -

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

IV- Precipation reaction -

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

V- Redox and combustion reaction

$$SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$$

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

Reversible reaction -

The chemical reaction which proceed in such both way i.e. reactant change into product and product change into reactant are called reversible reaction.

AS-

1- $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

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$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$RCOOH + R'OH \rightleftharpoons RCOOR + H_2O$

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Reversible chemical reaction are classified into two types –
Homogeneous and Heterogeneous reversible reaction.

Homogeneous –

The reversible reaction in which only one phase is present i.e. all the reactant and products are in same physical state.

Example –

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

Heterogeneous –

The reversible reaction in which more than one phase is present i.e. all the reactant and products are in the different physical state.

As –

$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

$3Fe(s) + 4H_2O(l) \longrightarrow Fe_3O_4(s) + 4H_2(g)$

Chemical equilibrium / equilibrium state –

The stage of the reversible reaction at which the concentrations of the reactants and products do not changes with time is called the equilibrium state.

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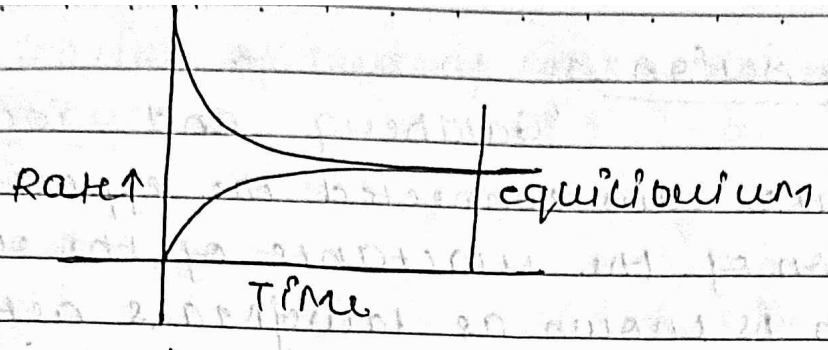

$A \rightleftharpoons P$

$R_f = R_b$

Characteristics of chemical equilibrium –

I- At equilibrium the concentration of each reactants and product are constant.

II- The rate of forward reaction is equal to rate of backward reaction.

$$R_f = R_b$$

III- At equilibrium the free energy change of the system is zero. ($\Delta G = 0$)

IV- At catalised does not change the equilibrium

V- A reversible reaction is the characteristic of equilibrium state.

Chemical equilibrium constant –

The equilibrium constant at a given temperature is the ratio of the rate constant of forward and backward reactions is represented by K_c.

$$K_c = \frac{K_f}{K_b}$$

Where, – K_f = velocity constant of forward reaction
K_b = velocity constant of backward reaction
K_c = Equilibrium constant.

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Law of Mass Action –

'Guldberg and waage' put forward a law connected the effect of concentration of the reactants of the reaction rate which is known as law of mass action.

'According to law of mass action,

"The rate at which a substance ~~reacts~~ reacts is proportional to its active mass and the rate of reaction is proportional to the products of the active mass."

Let's consider a general reaction in equilibrium.

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

Apply law of mass action

Rate of forward reaction-

$$R_f \propto [A][B]$$

$$R_f = K_f [A][B] \quad \text{—— (I)}$$

Again,

Rate of backward reaction

$$R_b \propto [C][D]$$

$$R_b = K_b [C][D] \quad \text{—— (II)}$$

At equilibrium

$$R_f = R_b$$

$$K_f [A][B] = K_b [C][D]$$

$$\frac{K_f}{K_b} = \frac{[C][D]}{[A][B]}$$

$$\boxed{\frac{K_f}{K_b} = K_c}$$

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Application of law of mass action of homogeneous equilibria –

Homogeneous gaseous reaction are of two type—

I- Those reaction in which the total number of reactants moles and product moles remain the same as a result of chemical reaction.
i.e. $\Delta n = 0$

formation of HI—

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$t=0$	a	b	0
$t=t$	$(a-x)$	$(b-x)$	$2x$

Let (a) moles of H_2 and (b) moles of I_2 are taken in a vessel of volume V. At equilibrium x mole of H_2 and x moles of I_2 react to form 2x moles of HI.

Molar concentration at equilibrium.

$$[H_2] = \frac{(a-x)}{V} \text{ M/l}$$

$$[I_2] = \frac{(b-x)}{V} \text{ M/l}$$

$$[HI] = \frac{2x}{V} \text{ mole/liter}$$

$$K_C = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_C = \frac{(2x/V)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$$

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$$K_C = \frac{4x^2/V^2}{(a-x)(b-x)/V^2}$$

$$\boxed{K_C = \frac{4x^2}{(a-x)(b-x)}}$$

Example –

16 ml of H_2 and 10 ml of I_2 combind togather to form 26 ml of HI at 444°c. Calculate the equilibrium constant of reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$K_C = \frac{4 \times 13 \times 13}{(16-13)(10-13)}$$

$$= \frac{4 \times 13 \times 13}{3 \times 5}$$

$$= \frac{4 \times 169}{15}$$

$$= \frac{676}{15}$$

$$= 45.06$$

At a certain temperature 0.1 mole H_2 and 0.1 mole of I_2 were placed in a 1 litre flask after some time the following equilibrium was stablised.

$$H_2 + I_2 \rightleftharpoons 2HI$$

at equilibrium it was found that the conc. of I_2 is decreased to 0.02 mole/litre calculate the value of K_C for the reaction at given temperature

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$$H_2 + I_2 \rightleftharpoons 2HI$$

$t=0$	0.1	0.1	0
$t=t$	$(0.1-x)$	$(0.1-x)$	$2x$

Given that

$[I_2] = (0.1-x) = 0.02$

$x = 0.1 - 0.02$

$x = 0.08$

$$K_C = \frac{4x^2}{(a-x)(b-x)}$$

$$K_C = \frac{4 \times (0.08)^2}{(0.1-0.08)(0.1-0.08)}$$

$$K_C \quad \frac{4 \times (0.0064)}{(0.02)(0.02)}$$

$$K_C = \frac{4 \times (0.\cancel{0064})\,16}{(0.\cancel{0004})}$$

$K_C = 64$

II- Let a moles of HI are taken in a ~~shield~~ sealed bulb of of volume v are heated at 444°c at equilibrium x moles of HI are dissociated to form x mole of H_2 and x mole of I_2.

$$2HI \rightleftharpoons H_2 + I_2$$

$t=0$	a	0	0
$t=t$	$(a-x)$	$x/2$	$x/2$

Molar concentration at equilibrium are-

$[H_2] = \frac{x}{2v}$ mole/litre

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$$[I_2] = \frac{x}{2V} \text{ mole/litre}$$

$$[HI] = \frac{(a-x)}{V} \text{ mole/litre}$$

Apply law of mass action—

$$K_C = \frac{[H_2][I_2]}{[HI]^2}$$

$$K_C = \frac{(x/2V)(x/2V)}{\left\{\frac{(a-x)}{V}\right\}^2}$$

$$\boxed{K_C = \frac{x^2}{4(a-x)^2}}$$

<u>Example</u>—

The degree of dissociation of HI at 440°c is 22% calculate the number of moles of HI, H_2 and I_2 at equilibrium if the number of moles at start is 2.4.

	$2HI \rightleftharpoons$	$H_2 + I_2$	
$t=0$	a	a	a
$t=t$	$(a-ax)$	$a(x/2)$	$a(x/2)$
	$a(1-x)$	$a(x/2)$	$a(x/2)$

$x = 22\%$

$x = \frac{22}{100} = 0.22$

$[HI] = a(1-x)$

$= 2.4(1-0.22)$

$= 2.4 \times 0.78$

$= 1.872$

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$[H_2] = a(x/2)$

$= 2.4\left(\frac{0.22}{2}\right)$

$= 2.4 \times 0.11$

$= 0.264$

$[I_2] = a(x/2)$

$= 2.4 \times 0.11$

$= 0.264$

Type II - 9 -

Reaction in which number of moles increase -

1- Dissociation Reaction -

Let one mole of PCl_5 is taken in a closed vessel of volume (V). If x is the degree of dissociation then the reaction may be written as follows -

$$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$$

$t=0$	1	0	0
$t=t$	$(1-x)$	x	x

Molar concentration at equilibrium

$[PCl_5] = \frac{(1-x)}{V}$ M/l

$[PCl_3] = \frac{x}{V}$ M/l

$[Cl_2] = \frac{x}{V}$ M/l

Apply law of mass action

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

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$$K_c = \frac{(x/V)(x/V)}{(1-x)/V}$$

$$K_c = \frac{x^2 V^2}{(1-x)V}$$

$$\boxed{K_c = \frac{x^2}{(1-x)V}}$$

Example –

1.2 mole of PCl_5 are heated at 50°c in flask of volume 2 liter at equilibrium the degree of dissociation of PCl_5 is 40% calculate the value of equilibrium constant K_c for the reaction.

$$PCl_5 \rightleftharpoons PCl_5 + Cl_2$$

$$[PCl_5] = \frac{0.72}{2} = 0.36\ M/l$$

$$[PCl_3] = \frac{0.48}{2} = 0.24\ M/l$$

$$[Cl_2] = \frac{0.48}{2} = 0.24\ M/l$$

We know that

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{(0.24)(0.24)}{(0.36)}$$

$$K_c = \frac{0.0576}{0.36}$$

$$K_c = 0.16$$

$$K_c = 1.6 \times 10^{-1}\ M/l$$

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Relation b/w Kp & Kc –

When active masses of reactants and products in a chemical reaction are expressed in a gram-mole/liter equilibrium constant is represented as Kc. Generally in gaseous reaction the active mass of reactant and products are expressed in term of their partial pressure and equilibrium constant is represented as Kp.

Now we consider following gaseous reaction.

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{—— (I)}$$

$$K_P = \frac{[P_C]^c (P_D)^d}{(P_A)^a (P_B)^b} \quad \text{—— (II)}$$

from ideal gas equation

$$PV = nRT$$

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

$$\frac{P}{RT} = \text{concentration}$$

Thus

$$\frac{P_A}{RT} = [A], \quad \frac{P_B}{RT} = [B]$$

$$\frac{P_C}{RT} = [C], \quad \frac{P_D}{RT} = [D]$$

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Putting the value of [A], [B], [C] and [D] in equ ① we get-

$$K_C = \frac{\left(\frac{P_C}{RT}\right)^c \left(\frac{P_D}{RT}\right)^d}{\left(\frac{P_A}{RT}\right)^a \left(\frac{P_B}{RT}\right)^b}$$

$$K_C = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \times \frac{(1/RT)^{c+d}}{(1/RT)^{a+b}}$$

$$K_C = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \cdot (RT)^{(a+b)-(c+d)}$$

$$K_C = K_p (RT)^{(a+b)-(c+d)} \quad \left\{ \text{from equ (11)} \right\}$$

$$K_p = K_C (RT)^{(c+d)-(a+b)}$$

$$\boxed{K_p = K_C (RT)^{\Delta n}}$$

Ex- The value of K_p at 400°c for the reaction $2H_2O + 2Cl_2 \rightleftharpoons 4HCl + O_2$ is 0.035 atm. Calculate the value of K_C for reaction.

$$K_p = K_C (\overset{0.0821}{RT})^{\Delta n}$$

$$0.035 = K_C (0.0821 \times 673)^1$$

$$\frac{0.035}{0.0821 \times 673} = K_C$$

$$K_C = \frac{0.035}{55.2383} \qquad K_C = 6.334 \times 10^{-4}$$

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Factor affecting equilibrium constant –

Effect of Temperature –

The value of equilibrium constant for any reaction is constant at constant temperature but changes with any change in temperature. The effect of temperature on equilibrium constant is represented by van't Hoff's equation

$$\log \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_2}{T_1 T_2}\right]$$

Where –

ΔH = Heat of reaction at constant ~~temperature~~ pressure.

K_{P_1} = equilibrium constant at constant temperature T_1

K_{P_2} = equilibrium constant at constant temp T_2

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11- Mode of representing the reaction –

The value of equilibrium constant also depends upon the method of expressing the reaction. e.g –

Let's consider the following general reversible reaction

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

Applying the law of mass action –

$$K_C = \frac{[C][D]}{[A][B]} \quad \text{——— (1)}$$

When –

$$C(g) + D(g) \rightleftharpoons A(g) + B(g)$$

Applying the law of mass action

$$K'c = \frac{[A][B]}{[C][D]} \quad \text{—— (II)}$$

comparing equ (I) & (II) we get

$$\boxed{K'c = \frac{1}{Kc}}$$

$N_2(g) + 3H_2 \rightleftharpoons 2NH_3(g)$ $K = 100$

$NH_3(g) \rightleftharpoons 1/2\, N_2(g) + 3/2\, H_2(g)$ $K'c = ?$

$$Kc = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \text{—— (I)}$$

$Kc = 100$

$$K'c = \frac{[N_2]^{1/2}[H_2]^{3/2}}{[NH_3]} \quad \text{—— (II)}$$

$$K'c = \frac{1}{\sqrt{Kc}}$$

$$K'c = \frac{1}{\sqrt{100}}$$

$$K'c = \frac{1}{10}$$

$K'c = 0.1$

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Mode of representing stoichiometry of the chemical reaction—

When a reversible reaction is a represented by two or more stoichometric equation the magnitude of their equilibrium constant are different. e.g—

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad \text{—— (I)}$$

$$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3 \quad \text{—— (II)}$$

equilibrium constant (Kc) for equation (I)

$$Kc = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} \quad \text{—— (III)}$$

thus

$$K'c = \frac{[SO_3]}{[SO_2] [O_2]^{1/2}} \quad \text{—— (IV)}$$

comparing equ (I) and (II) we get

$$\boxed{K'c = \sqrt{Kc}}$$

(4) The concentration or partial pressure units—

The value of equilibrium constant also depends upon units in which the concentration of reactants and products are expressed. Any change in the concentration units changes the value of equilibrium constant.

e.g - Let's consider the following gaseous reaction-

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$\Delta n = (-)$ forward reaction
$\Delta n = (+)$ backward reaction.

$$A + B \rightleftharpoons M + N$$

$$K_C = \frac{[M][N]}{[A][B]}$$

At a particular temperature concentration of a gaseous substance is proportional to it's partial pressure. Under such condition the equilibrium constant given by Kp i.e -

$$K_p = \frac{(P_M)(P_N)}{(P_A)(P_B)}$$

<u>Reaction quotient or Mass action ratio</u>—

Let's consider reaction

$$A + B \rightleftharpoons C + D$$

$$Q = \frac{[C][D]}{[A][B]}$$

<u>Note</u>-

I- $K_C = Q$ (equilibrium)
II- $Q < K_C$ (forward reaction)
III- $Q > K_C$ (Backward reaction)

<u>Le - Chatelier's Principle</u> - According to this principal,

"If a system at equilibrium is subjected to a change of concentration pressure or temperature. The equilibrium shift in the

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direction that tends to undo the effect of the change."

I- **Effect of pressure** –

An increase in pressure to apply to a system at equilibrium favours to the direaction that produced smaller number of moles of gases and a decreases in pressure favours the apposite reaction.

II- **Effect of temperature** –

$$2SO_2 + O_2 \underset{\text{Endothermic}}{\overset{\text{Exothermic}}{\rightleftharpoons}} 2SO_3$$

When temperature increase – backward
When temperature decrease – forward

The increase in temperature shifts the equilibrium in the direction of the endothermic reaction
The decrease in temperature shifts the equilibrium in the direction of the exothermic reaction.

$$N_2(g) + 3H_2 \underset{\text{Endothermic}}{\overset{\text{Exothermic}}{\rightleftharpoons}} 2NH_3(g)$$

Temperature increase – backward
Temperature decrease – forward.

III- **Change in concentration** –

The increase in conc of any of the reactants shifts the equilibrium

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towards forward direction.

The increase of the concentration of any of the products shift the equilibrium towards backward direction. e.g.

Formation of NH_3 –

$$N_2(g) + 3H(g) \rightleftharpoons 2NH_3$$

Reactant concentration

Application of le-Chatelier's principle –

1- Formation of NH_3 –

$$\underset{1\ Mole}{N_2(g)} + 3H(g) \underset{Endothermic}{\overset{Exothermic}{\rightleftharpoons}} 2NH_3(g) + 22.4\ Kcal$$

1- Effect of temperature –

When temperature at equilibrium is raised the equilibrium displaced in the direction which absorbs heat. every equilibrium system involves exothermic endothermic reaction. An increase in temperature will be favour the endothermic reaction. Thus for the above reaction the forward reaction is exothermic will backward

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reaction is endothermic.

11- Effect of pressure or change of volume -

According to this law.
Pressure increase or volume decrease equilibrime shift forward direction.
pressure decrease or volume increase - equilibrium shifts backward direction.

~~Formation of sulphur~~

Change in concentration -

Reactant concentration increase - Equilibrium shifts forward direction.

Reactant concentration decrease - Equilibrium shifts backward direction.

Formation of SO_3 -

$$2SO_{2(g)} + O_{2(g)} \underset{\text{Endothermic}}{\overset{\text{Exothermic}}{\rightleftharpoons}} 2SO_3 + 2k\,cal$$

1- Effect of temperature -

Temperature increase - Equilibrium shifts backward direction -

Temperature decrease - Equilibrium shifts forward direction.

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Effect of pressure or change in volume -

Pressure increase or volume decrease - Equilibrium shifts forward direction.

Pressure decrease or volume increase - Equilibrium shifts backward direction.

Effect of concentration -

Reactant concentration increase - Equilibrium shifts forward direction.

Reactant concentration decrease - Equilibrium shifts backward direction.

Effect of temperature of equilibrium constant - or Vant' Hoff equation or vant Hoff ~~exo~~ isochore

The effect of temperature on chemical equilibrium can be determind by using thermodynamics. The relation for the reaction isotherm when the reactants and products are gases and also in their standard state is represented by -

$$\Delta G^\circ = -RT\ln K_p \quad \text{—— (1)}$$

Differentiating equation (1) with respect to T at constant pressure

$$\left[\frac{d(\Delta G^\circ)}{dT}\right]_p = -R\ln K_p - RT\left[\frac{d(\ln K_p)}{dT}\right]_p \quad \text{—— (11)}$$

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multiplying equation (I) with (T)

$$T\left[\frac{d(\Delta G^\circ)}{dT}\right]_P = -RT\ln K_p - RT^2\left[\frac{d(\ln K_p)}{dT}\right]_P \quad \text{— (III)}$$

From equation (I) & (III) we get —

$$T\left[\frac{d(\Delta G^\circ)}{dT}\right]_P = \Delta G^\circ - RT^2\left[\frac{d(\ln K_p)}{dT}\right]_P \quad \text{— (IV)}$$

from Gibb's helmhotz energy

$$\Delta G^\circ = \Delta h^\circ + T\left[\frac{d(\Delta G^\circ)}{dT}\right]_P \quad \text{— (V)}$$

From equation (IV) & (V) we get

$$RT^2\left[\frac{d(\ln K_p)}{dT}\right]_P = \Delta h^\circ$$

$$\boxed{\frac{\Delta h^\circ}{RT^2} = \left[\frac{d(\ln K_p)}{dT}\right]_P}$$

This equ is also known as vant' hoff isochore.

<u>vant' hoff equation or vant' hoff isochore in terms of Kc</u> —

we know that

$K_p = K_c (RT)^{\Delta n}$

Taking logarithm of above equation

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$$\ln K_p = \ln K_c + \ln(RT)^{\Delta n}$$
$$\ln K_p = \ln K_c + \Delta n \ln RT$$

differentiating above equation

$$\frac{d(\ln K_p)}{dT} = \frac{d(\ln K_c)}{dT} + \frac{\Delta n}{T}$$

$$\frac{d(\ln K_c)}{dT} = \frac{d(\ln K_p)}{dT} - \frac{\Delta n}{T}$$

$$\frac{d(\ln K_c)}{dT} = \frac{\Delta n^\circ}{RT^2} - \frac{\Delta n}{T}$$

$$\frac{d(\ln K_c)}{dT} = \frac{\Delta n^\circ - \Delta n RT}{RT^2}$$

$$\left\{\begin{array}{l} \Delta n = \Delta E + \Delta n RT \\ \Delta n^\circ = \Delta E^\circ + \Delta n RT \\ \Delta n^\circ - \Delta n RT = \Delta E^\circ \end{array}\right\}$$

$$\boxed{\frac{d(\ln K_c)}{dT} = \frac{\Delta E^\circ}{RT^2}}$$

This equation is also known as van't hoff equ or van't hoff isochore with respect to Kc.

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Thermodynamics – II

Spontaneous process —

The process which proceed by their own accord without any external assitance are called spontaneous process. They are also known as positive or natural process.

As — (i) Candle burning

Non-spontaneous process —

The process which cannot proceed by themselves are called non-spontaneous process. Such process cannot proceed without any external assitance. They are also called negative or un-natural process.

As — (i) Dehydration of ethyl alcohol.

$$C_2H_5OH \xrightarrow[160-170°C]{Conc.\ H_2SO_4} C_2H_4 + H_2O$$

(ii) Pumping water out of the well.

Criteria of spontaneity —

i – A spontenous reaction may be takes place rapidly or slowly or very slowly that is for a spontenous change to occur time is no factor

ii – A spontenous change is one way or unidirectional for reverse change to take place some work has to be done.

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Second law of thermodynamics —

The second law of thermodynamics has been stated in various ways. All the statments have the same meaning.

I- All the spontaneous process occur in one direction only and can not be reversed

II- The energy of universe remain constant and entropy of universe increasing.

III- Clausius statment -

It's impossible for a self acting machine unaided by an external agency to carry heat from a body at lower temperature to another at higher temperature.

IV- Kelvin - plank statement —

It is impossible to construct a heat engine which operating in a cyclic process abstract heat from a single body or convert the whole of it into work without living in changes into working system

Carnot's cycle —

In order of zero of heat reversible cycle the system consist of mode of an ideal gas as the working system which is subjected to series of four operation b/w temperature T_2 and T_1 both adiabatic isothermal process are possible during the operation.

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The four operation in carnot cycle are—

Isothermal reversible expension.
Adiabatic " expension
Isothermal " compression
Adiabactic " compression

Isothermal reversible expension—

A gas is allow the expend isothermal at higher temperature at gas as volume increase of V_1 (state A) to V_2 (state B) so work done is by the system in this operation.

From first law of thermodynamics—

$$\Delta E = Q - W$$

$$0 = Q - W \quad [\because \Delta E = 0 \text{ is isothermal process}]$$

$$W = \int_{V_1}^{V_2} P_2 \, dV$$

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$$w_2 = \int_{V_1}^{V_2} (RT_2/V)\,dv$$ we know that

$$PV = RT$$

$$\left(P_2 = \frac{RT_2}{V}\right)$$

$$w_1 = RT_2 \int_{V_1}^{V_2} dv/v$$

$$w_1 = RT_2 \left[\log_e v\right]_{V_1}^{V_2}$$

$$\boxed{w_1 = RT_2 \log_e \frac{V_2}{V_1}}$$

Adiabatic reversible expension—

The gas is allow as to expend adiabatically from volume V_2 (state B) to V_3 (state C) the work done w_2 by the system in this operation.

From first law thermodynamics

$$\Delta E = Q - w_2$$

$$\Delta E = -w_2 \quad (\text{since } q = 0)$$

$$C_v dT = -w_2$$

$$C_v dT = -w_2$$

$$w_2 = -\int_{T_2}^{T_1} C_v dT$$

$$w_2 = C_v \int_{T_1}^{T_2} C_v dT$$

$$w_2 = C_v [T]_{T_1}^{T_2}$$

$$\boxed{w_2 = C_v [T_2 - T_1]}$$

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Isothermal reversible compression—

The gas is compressed isothermally at lower temperature T_1 from V_3 (state c) to before (state D) the workdone V_3 on the system in this operation

$$\boxed{W_3 = q_1 RT \log \frac{V_4}{V_3}} \text{ or}$$

$$\boxed{-Q = RT_1 \log \frac{V_4}{V_3}}$$

Adiabatic reversible compression—

By an adiabatic and reversible compression the gas is restarted to its original volume of temperature the work done w_4 on the system.

$$w_4 = -C_v (T_2 - T_1)$$

$$W_4 = C_v (T_1 - T_2)$$

Net work done in carnot cycle—

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

$$W = RT_2 \log \frac{V_2}{V_1} + C_v (T_2 - T_1) + RT_1 \log \frac{V_4}{V_3} + C_v (T_1 - T_2)$$

$$W = RT_2 \log \frac{V_2}{V_1} + T_2 \cancel{C_v} - \cancel{T_1 C_v} + RT_1 \log \frac{V_4}{V_3} + \cancel{T_1 C_v} - \cancel{T_2 C_v}$$

$$W = RT_2 \log \frac{V_2}{V_1} + RT_1 \log \frac{V_4}{V_3}$$

$$\boxed{W = R(T_2 \log \frac{V_2}{V_1} + T_1 \log \frac{V_4}{V_3})}$$

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Heat absorbed in one cycle –

Let 'q' is the heat absorbed in one cycle then

$$q = q_2 - q_1$$

$$q = RT_2 \log \frac{V_2}{V_1} + RT_1 \log \frac{V_4}{V_3}$$

$$q = RT_2 \log \frac{V_2}{V_1} - RT_1 \log \frac{V_3}{V_4} \quad \text{——— (I)}$$

for adiabatic changes we have

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \quad \text{——— (II)} \quad \{\text{for adiabatic expansion}\}$$

$$\frac{T_1}{T_2} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \quad \text{——— (III)} \quad \{\text{for adiabatic compression}\}$$

Comparing equation (II) & (III) we get

$$\frac{V_2}{V_3} = \frac{V_1}{V_4}$$

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Putting the value of $\frac{V_3}{V_4}$ in equation first we get –

$$q = RT_2 \log \frac{V_2}{V_1} - RT_1 \log \frac{V_2}{V_1}$$

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

$$\boxed{q = R(T_2 - T_1) \log \frac{V_2}{V_1}} \quad \text{——— (IV)}$$

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Calculate of thermodynamic efficiency -

Since the total workdone in a cycle is equal to the total heat absorbed. Thus from equation III we have

$$w = R(T_2 - T_1) \log \frac{V_2}{V_1} \quad \text{—— (IV)}$$

We know that

$$q_2 = RT_2 \log \frac{V_2}{V_1} \quad \text{—— (VI)}$$

Dividing equation (IV) by (VI) we have

$$\frac{w}{q_2} = \frac{\cancel{R}(T_2 - T_1) \cancel{\log \frac{V_2}{V_1}}}{\cancel{R} T_2 \cancel{\log V_2/V_1}}$$

$$\frac{w}{q_2} = \frac{(T_2 - T_1)}{T_2}$$

$$\frac{w}{q_2} = \left(1 - \frac{T_1}{T_2}\right)$$

$$\boxed{w = q_2\left(1 - \frac{T_1}{T_2}\right)}$$

The factor w/q_2 is called thermodynamic efficiency.

Efficiency of Carnot's Engine -

The fraction of heat absorbed engine which it can convert into work is called

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efficiency of carnot engine." It is denoted by η. Thus the efficiency of a carnot engine May be written as follows —

$$\eta = \frac{q_2 - q_1}{q_2}$$

$$\eta = \frac{RT_2 \log \frac{V_2}{V_1} - RT_1 \log \frac{V_3}{V_4}}{RT_2 \log \frac{V_2}{V_1}}$$

$$\eta = \frac{T_2 \log \frac{V_2}{V_1} - T_1 \log \frac{V_3}{V_4}}{T_2 \log \frac{V_2}{V_1}} \quad \text{—— (I)}$$

for adiabatic change —

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_3}\right)^{\gamma - 1} \quad \text{—— (II)}$$

thus $\frac{T_1}{T_2} = \left(\frac{V_1}{V_4}\right)^{\gamma - 1}$ —— (III)

Comparing equ (II) and (III) we get

$$\frac{V_2}{V_3} = \frac{V_1}{V_4}$$

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Putting the value of $\frac{V_3}{V_4}$ in equ (I)

$$\eta = \frac{T_2 \log \frac{V_2}{V_1} - T_1 \log \frac{V_2}{V_1}}{T_2 \log \frac{V_2}{V_1}}$$

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$$\boxed{\eta = \frac{T_2 - T_1}{T_2}}$$

Ex— Calculate the efficiency of steam engine operating b/w 110°c and 25°c?

$$T_L = 25 + 273$$
$$= 298K$$

$$T_2 = 110 + 273 = 383K$$

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

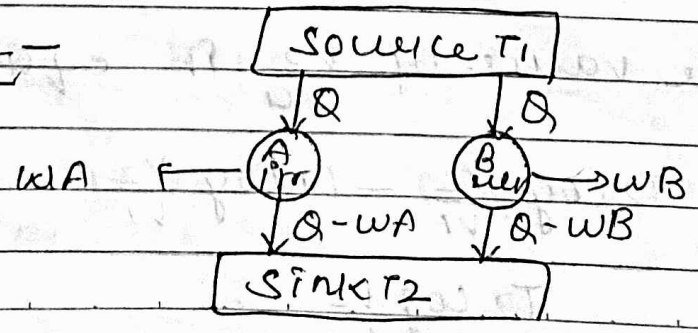
$$\eta = \frac{383 - 298}{383}$$

$$\eta = \frac{85}{383} = 0.222$$
or 22.2%

Carnot's theorem—

No heat engine working b/w to given temperature of source & sink can be more efficiency than a perfectly reversible engine working b/w the same two temperature.

Statement—



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Entropy –

The extent of dissorderd is expressed by a property known as entropy.

Or

Entropy is a thermodynamic state quantity which is a measure of dissorder of the molecules of the system.

Note –

The entropy is a state function and depend only on the intial and final state of the system.

$$\Delta S = S_{final} - S_{initial}$$

for chemical reaction –

$$\Delta S = S_{product} - S_{Reactant}$$

Mathmatical difinition of Entropy –

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged divided by the absolute temperature is also known as entropy.

$$\int dS = \frac{1}{T} \int dq_{rev}$$

$$\boxed{\Delta S = \frac{q}{T}}$$

or

$$\boxed{S_2 - S_1 = \frac{q}{T}}$$

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several factor influence the amount of entropy that a system has in particular state. In general—

(i) The value of entropy depends on the mass of the system. Hence it is an extensive property

(ii) A liquid has a higher entropy than the solid from which it is formed.

(iii) In a solid the atoms molecules or ions are fixed in position in the liquid these particle are free to move passed one another that liquid structure is more random and the solid more order.

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Unit of entropy—

We know that

$$\Delta S = \frac{q}{T}$$

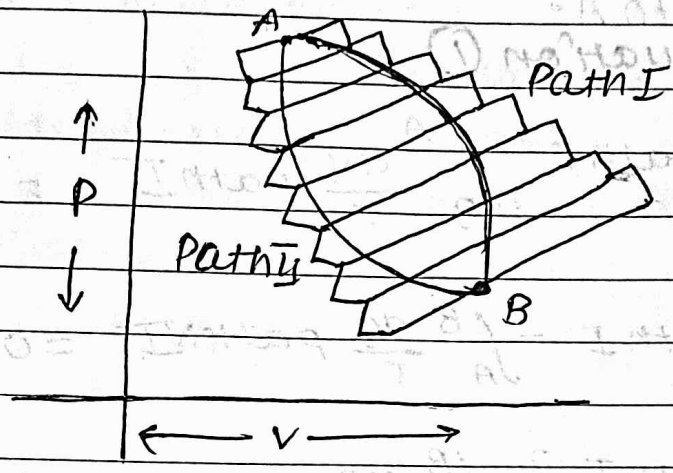
$$\Delta S = \frac{J}{K}$$

$$\boxed{\Delta S = JK^{-1}}$$

Derivation of entropy from carnot cycle—

In a carnot cycle q_2 heat is taken by a ~~tat~~ system at higher temperature and hence has a positive value while q_1 heat is given out at lower temperature at has a negative value.

Thus thermodynamics efficiency is given by –



$$\eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$\cancel{1} - \frac{q_1}{q_2} = \cancel{1} - \frac{T_1}{T_2}$$

$$-\frac{q_1}{q_2} = \frac{-T_1}{T_2}$$

$$\frac{q_1}{q_2} = \frac{T_1}{T_2}$$

Since heat absorbed that is q_2 is given positive sign and heat given out has negative (–) sign. Thus the above equation can be written as

$$-\frac{q_1}{q_2} + \frac{q_2}{T_2}$$

$$\frac{q_1}{q_2} + \frac{q_2}{T_2} = 0 \quad \text{—— (1)} \qquad \sum \frac{q}{T} = 0$$

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The cycle is ~~fenow~~ performed A to B and then back B to A.

from equation ①

$$\int_A^B \frac{dq}{T} \text{ path I} \quad \int_B^A \frac{dq}{T} \text{ path II} = 0$$

$$\int_A^B \frac{dq}{T} \text{ path I} - \int_A^B \frac{dq}{T} \text{ path II} = 0$$

$$\int_A^B \frac{dq}{T} \text{ path I} = \int_A^B \frac{dq}{T} \text{ path II}$$

It follows from the above that integration A to B $\frac{dq}{T}$ is a finite quantity

$$\Delta S = S_B - S_A \int_A^B \frac{dq}{T}$$

for each infinite simally small chang-

$$dS = \frac{dq}{T}$$

for finite change.

$$\boxed{\Delta S = \frac{q}{T}}$$

The entropy is defined as the change in entropy is equal to moment of heat absorbe an evolved divided by absolute temperature.

Physical significance of entropy -

<u>Entropy and unavitable energy</u> -

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When heat is supplied to a system a portion of it is used to do work.

This portion of heat is called unavailable energy.

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When reversible process is isothermal –

Let's consider an isothermal reversible process in which the system absorb heat q_{rev} from surroundings at temperature T. This increase the entropy of the system which is given by –

$$\Delta S_{system} = +\frac{q_{rev}}{T}$$

$$\Delta S_{surrounding} = -\frac{q_{rev}}{T}$$

Total change in entropy of the process =
$\Delta S_{system} + \Delta S_{surrounding}$

$$= \left(+\frac{q_{rev}}{T}\right) + \left(-\frac{q_{rev}}{T}\right)$$

$$= \cancel{+\frac{q_{rev}}{T}} - \cancel{\frac{q_{rev}}{T}}$$

$$= 0$$

When reversible process is adiabatic –

In this process no exchange of the heat takes place with the surrounding that is $q_{rev} = 0$
hence –

$$\Delta S_{system} = \frac{q_{rev}}{T} = \frac{0}{T} = 0$$

$$\Delta S_{surrounding} = \frac{q_{rev}}{T} = \frac{0}{T} = 0$$

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Total change in entropy of the process -

$$\Delta S_{system} + \Delta S_{surrounding}$$

$$0 + 0$$

$$= 0$$

Entropy change in an irreversible or spontaneous process →

Let's consider a system at higher temperature T_1 and its surroundings at lower temperature T_2. A small quantity of heat q_{irr} passes irreversibly from system to surroundings.

Decrease in entropy of system – $\frac{-q_{irr}}{T_1}$

Increase in entropy of surrounding – $+\frac{q_{irr}}{T_2}$

Total change in entropy of the process –

$$\frac{-q_{irr}}{T_1} + \frac{q_{irr}}{T_2}$$

$$= q_{irr}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

but $T_1 > T_2$ hence $T_1 - T_2$ is a positive quantity

Entropy change for ideal gas with change P, V and T →

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a- <u>When T and V are variables</u> -

Entropy is state function and it's value depends upon volume, pressure and temperature since temperature is take a one of the variable and second variable may be pressure and volume.
Thus variables are either volume and temperature or pressure and temperature

From defination of Entropy -

$$dS = \frac{dQ}{T} \quad \text{—— (I)}$$

From first law of thermodynamics -

$$dQ = dE + PdV \quad \text{—— (II)}$$

we know that

$$PV = RT$$

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

Again - $dE = C_v dT$

Putting the value of P & dE in equ (II)

$$dS = \frac{dE + PdV}{T}$$

$$dS = \frac{C_v dT + \frac{RT}{V} dV}{T}$$

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$$ds = C_v \frac{dT}{T} + R \frac{dV}{V}$$

integrating above equ with limits S_1 to S_2 T_1 to T_2 and V_1 to V_2.

$$\int_{S_1}^{S_2} ds = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$[S]_{S_1}^{S_2} = C_v [\log T]_{T_1}^{T_2} + R [\log V]_{V_1}^{V_2}$$

$$S_2 - S_1 = C_v [\log T_2 - \log T_1] + R [\log V_2 - \log V_1]$$

$$\Delta S = C_v \log \frac{T_2}{T_1} + R \log \frac{V_2}{V_1}$$

$$\boxed{\Delta S = 2.303\, C_v \log_{10} \frac{T_2}{T_1} + 2.303\, R \log_{10} \frac{V_2}{V_2}}$$

For n moles of gas

$$\boxed{\Delta S = 2.303\, n C_v \log_{10} \frac{T_2}{T_1} + 2.303\, n R \log \frac{V_2}{V_1}}$$

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<u>When T and P are variables</u> —

Suppose P_1 is the pressure of an ideal gas in the ~~def~~ initial state and P_2 in the final state then—

we know that

$$\Delta S = n C_v \log_e \frac{T_2}{T_1} + n R \log_e \frac{V_2}{V_1} \quad \text{——— (1)}$$

from gas equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \qquad \frac{V_2}{V_1} = \frac{P_1 T_2}{T_1 P_2}$$

putting the value of $\frac{V_2}{V_1}$ in equation (I) we get

$$\Delta S = nC_v \log_e \frac{T_2}{T_1} + nR \log_e \frac{P_1 T_2}{T_1 P_2}$$

$$\Delta S = nC_v \log_e \frac{T_2}{T_1} + nR \log_e \frac{P_1}{P_2} + nR \log_e \frac{T_2}{T_1}$$

$$\Delta S = n(C_v + R) \log_e \frac{T_2}{T_1} + nR \log_e \frac{P_1}{P_2}$$

$$\Delta S = nC_p \log_e \frac{T_2}{T_1} + nR \log_e \frac{P_1}{P_2} \quad \{\text{from } C_p - C_v = R\}$$

$$\Delta S = 2.303\, nC_p \log_{10} \frac{T_2}{T_1} + 2.303\, nR \log_{10} \frac{P_1}{P_2} \quad \text{--- (I)}$$

for 1 moles of the ideal gas $n = 1$ hence

$$\Delta S = 2.303\, C_p \log_{10} \frac{T_2}{T_1} + 2.303\, R \log_{10} \frac{P_1}{P_2}$$

from equ (II) and (III) abident that entropy change an ideal gas depends upon the initial and final temperatures as well as on pressure.

Calculate entropy change when one mole an ideal gas are allow to expand reversibly at 25°C. from a pressure of 1atm to 500 mm of mercury at 0°C. $C_v = \frac{3}{2R}$

Given that -

$n = 1$ mole

$T_1 = 25 + 273$

$= 298$

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$T_2 = 0 + 273$

$P_1 = 1 atm \quad 760 mm$

$P_2 = 500 mm$

$R = 8.314$

$$C_p = C_v + R$$

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

$$2.5R$$

$$2.5 \times 8.314 \text{ Joule/degree mole}$$

$$\Delta S = 2.303 n C_p \log \frac{T_2}{T_1} + 2.303 n R \log \frac{P_1}{P_2}$$

$$\Delta S = 2.303 \times 1 \times 2.5 \times 8.314 \log \frac{273}{298} + 2.303 \times 1 \times 8.314 \log \frac{760}{500}$$

$$\Delta S = 2.303 \times 8.314 \left[2.5 \times [\log_{10} 273 - \log_{10} 298] + [\log 38 - \log 25]\right]$$

$$\Delta S = 1.67 \text{ J/d/mole}$$

Entropy change of an ideal gas in different process —

We consider the following three types of process —

(A) <u>Isothermal process</u> —

$$\Delta S_T = 2.303 n R \log_{10} \frac{V_2}{V_1}$$

or

$$\boxed{\Delta S_T = 2.303 n R \log_{10} \frac{P_1}{P_2}}$$

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ii- Isobaric process -

$$\Delta S_p = 2.303\, n C_p \log_{10} \frac{T_2}{T_1}$$

iii- Isochoric process -

$$\Delta S_v = 2.303\, n C_v \log_{10} \frac{T_2}{T_1}$$

Entropy of a mixture of ideal gases

Entropy change in physical change -

Physical change taking place at constant temperature and pressure are as follows -

Solid — Liquid (melting)
Liquid — Vapour (vapourisation)
Solid — Vapour (sublimation)
Solid (α) — Solid (β) (transition)

① From solid to vapour phase -

1) $$\Delta S_f = \frac{\Delta H_f}{T_f}$$

where,

T_f = Temperature of fusion
ΔH_f = Enthalpy chang in fusion
ΔS_f = Entropy " " "

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Calculate the entropy change in the melting of 1 gm of ice at 0°C in calories as well as in S.I units. Heat of fusion of ice is equal to 80 calory/gm.

$$\Delta H_f = 80$$
$$T_f = 0 + 273$$
$$= 273\,K$$
$$\Delta S_f = \frac{\Delta H_f}{T_f}$$
$$\frac{80}{273}$$
$$= 0.29\ cal/K/gram$$

$$H_f = 80\ cal\,g^{-1}$$
$$H_f = 80 \times 4.2 \times 1000$$
$$H_f = 336000\ J\,kg^{-1}$$
$$\Delta S_f = \frac{\Delta H_f}{T_f}$$
$$\Delta S_f = \frac{336000}{273}$$
$$\Delta S_f = \boxed{1226.7\ J\,K^{-1}}$$

<u>From liquid phase to vapour phase -</u>

$$\boxed{\Delta S_v = \frac{\Delta H_v}{T_b}}$$

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(iii) From one crystalline form to another –

$$\Delta S_t = \frac{\Delta H_t}{T}$$

Standard Entropy – (S°) –

Entropy of 1 mole of a pure substance at 1 atm pressure and 25°c temperature is called the standard entropy. It is denoted by 'S°'.

Standard Entropy change –

A chemical reaction in which all the reactants and products are in their standard states, the entropy change is called the standard entropy change of the reaction. It is represented by 'ΔS°'. The standard entropy change of the any reaction is given by –

$$R \longrightarrow P$$

$$\Delta S^\circ = \Sigma S^\circ_{product} - \Sigma S^\circ_{reactant}$$

Standard entropy of formation – (ΔS°_f) –

The entropy change when 1 mole of a compound is formed from it's elements under standard condition is called the standard entropy of formation. It is denoted by 'ΔS°_f'.

$$\Delta S^\circ_f = S^\circ_{compound} - \Sigma S^\circ_{element}$$

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Helmholtz free energy or work Function (A)

The quantity (E − TS) is called helmholtz free energy or work function. It is represented by 'A'.

$$\boxed{A = E - TS}$$

Where,

A = work function
T = absolute temperature
S = Entropy
E = Internal energy

(a) change of work function for an isothermal process

Consider an isothermal change at temperature T from initial state (I) to final state (II) so that,

For initial state (I) $A_1 = E_1 - TS_1$

For Final state (II) $A_2 = E_2 - TS_2$

$$A_2 - A_1 = (E_2 - TS_2) - (E_1 - TS_1)$$
$$\Delta A = (E_2 - E_1) - T(S_2 - S_1)$$
$$\boxed{\Delta A = \Delta E - T\Delta S} \quad (1)$$

Where

ΔA = change in work function
ΔE = change in internal Energy
ΔS = change in entropy.

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since $\Delta S = \frac{Q}{T}$

$$Q = T\Delta S$$

Putting the value $T\Delta S$ in equation (I) we get

$$\Delta A = \Delta E - Q \quad \text{——— (II)}$$

From Ist law of thermodynamic's

$$Q = \Delta E + W \quad \text{——— (III)}$$

From equ (I) & (III) we get

$$\boxed{-\Delta A = W}$$

(b) variation of work function with temperature and volume —

we know that

$$A = E - TS$$

differentiating above equation with respect to T

$$\frac{dA}{dT} = \frac{dE}{dT} - \left[T\frac{dS}{dT} + \frac{S\,d(T)}{dT}\right]$$

$$\frac{dA}{dT} = \frac{dE}{dT} - \left\{T\frac{dS}{dT} + S\right.$$

$$dA = dE - TdS - SdT \quad \text{——— (I)}$$

Since $dS = \frac{dQ}{T}$

$$dQ = TdS \quad \text{——— (II)}$$

$$dQ = dE + PdV \quad \text{——— (III)}$$

comparing (II) and (III) we weget

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$TdS = dE + PdV$

Putting the value of TdS in equ (I)

$$dA = dE - (dE + PdV) - SdT$$

$$dA = \cancel{dE} - \cancel{dE} + PdV - SdT$$

$$\boxed{dA = -PdV - SdT}$$

$$\boxed{dA = -(PdV + SdT)} \quad \text{—— (IV)}$$

equation no (IV) represent the ~~ration~~ variation of work function with change in volume and temperature.

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Case I – At constant volume –

$$dV = 0$$

From equation (IV)

$$dA = -(PdV + SdT)$$

$$dA = -SdT$$

$$\boxed{\left(\frac{\partial A}{\partial T}\right)_V = -S}$$

Case II – At constant Temperature –

$$dT = 0$$

From equation (IV)

$$dA = -(PdV + SdT)$$

$$dA = -(PdV + S \times 0)$$

$$dA = -PdV$$

$$\boxed{\left(\frac{\partial A}{\partial T}\right)_T = -P}$$

Case III — At constant temperature and constant volume —

$$dT = 0, dV = 0$$

from equation (IV)

$$dA = -(PdV + SdT)$$

$$dA = -(P \times 0 + S \times 0)$$

$$dA = 0$$

$$\boxed{\left(\frac{\partial A}{\partial}\right)_{T,V} = 0}$$

Note — (1) From case I^{st} —

$$dA = -SdT \quad \text{—— (I)}$$

From case IInd

$$dA = -PdV \quad \text{—— (II)}$$

comparing equation (I) and (II) we get

$$dA = -PdV \quad \text{—— (III)}$$

From ideal gas equation

$$PV = nRT$$

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

Putting the value of P in equation (III) we get

$$dA = -nRT\frac{dV}{V}$$

on integrating we get

$$\int_{A_1}^{A_2} dA = -nRT\int_{V_1}^{V_2} \frac{dV}{V}$$

$$[A]_{A_1}^{A_2} = nRT\int_{V_2}^{V_1} \frac{dV}{V}$$

$$[A_2 - A_1] = nRT\,[\ln V]_{V_2}^{V_1}$$

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

$$\boxed{\Delta A = 2.303\, nRT \log_{10} \frac{V_1}{V_2}}$$

Gibb's Free energy Function –

The quantity H − TS or E + PV − TS is called ~~gives~~ Gibb's free energy function. It is represented by 'G'.

$$\boxed{G = h - TS} \qquad \{\because H = E + PV\}$$

$$\boxed{G = E + PV - TS}$$

Where, H = Enthalpy
T = absolute temperature
S = Entropy

Change in Free energy Function –

Let's consider isothermal process at constant temperature. The initial state represented by step-I and final state is represented by step-II.

hence
for initial state, $G_1 = H_1 - TS_1 \longrightarrow (I)$
for final state, $G_2 = H_2 - TS_2 \longrightarrow (II)$

from (II) − (I) we get

$$G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1)$$

$$\Delta G = (H_2 - H_1) - T(S_2 - S_1)$$

$$\boxed{\Delta G = \Delta H - T\Delta S} \longrightarrow (III)$$

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since

$$\Delta H = \Delta E + P\Delta V$$

$$\because \Delta S = \frac{Q}{T}$$

$$\boxed{Q = T\Delta S}$$

from Ist law of thermodynamics

$$\boxed{Q = \Delta E + W}$$

From equation (III)

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = \Delta E + P\Delta V - T\Delta S \quad \{\because \Delta H = \Delta E + P\Delta V\}$$

$$\Delta G = \Delta E + P\Delta V - (\Delta E + W) \quad \{T\Delta S = \Delta E + W\}$$

$$\Delta G = \cancel{\Delta E} + P\Delta V - \cancel{\Delta E} - W$$

$$\Delta G = P\Delta V - W$$

$$\boxed{-\Delta G = W - P\Delta V}$$

<u>Variation of free energy function with temp and pressure</u> —

According to defination of free energy function,

$$G = H - TS$$

$$G = E + PV - TS \quad \{H = E + PV\}$$

differentiating above equation w.r.t. T —

$$dG = dE + PdV + VdP - TdS - SdT \quad \text{—— (I)}$$

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

$$dQ = dST \quad \text{—— (II)}$$

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$$dQ = dE + PdV \quad \text{— (III)}$$

comparing equation (II) and (III) we get

$$dST = dE + PdV \quad \text{— (IV)}$$

putting the value of dST in equ (I)

$$dG = dE + PdV + VdP - TdS - SdT$$

$$dG = dE + PdV + VdP - (dE + PdV) - SdT$$

$$dG = \cancel{dE} + \cancel{PdV} + VdP - \cancel{dE} - \cancel{PdV} - SdT$$

$$\boxed{dG = VdP - SdT} \quad \text{— (V)}$$

equ (V) represents variation of free energy function (G) with temp. and pressure.
The following three case are show—

<u>Case I</u> – At constant pressure

$$dP = 0$$

from equation (V)

$$dG = VdP - SdT$$

$$dG = 0 - SdT$$

$$\Delta G = -SdT$$

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S}$$

<u>Case II</u> – At constant temperature

$$dT = 0$$

from equation (V)

$$dG = VdP - SdT$$

$$dG = VdP - 0$$

$$\Delta G = VdP$$

$$\boxed{\left(\frac{\partial G}{\partial P}\right)_T = -S}$$

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Case III – At constant temperature and pressure

$$dT = 0 \;,\; dP = 0$$

$$\Delta G = VdP - SdT$$

$$\Delta G = 0$$

$$\boxed{\left(\frac{\partial G}{\partial}\right)_{T,P} = 0}$$

Note – From case I –

$$dG = -SdT \quad \text{—— (I)}$$

From case – II

$$dG = -VdV \quad \text{—— (II)}$$

comparing equ (I) and (II)

$$dG = VdP$$

$$dG = VdP$$

$$\int_{G_1}^{G_2} dG = V\int_{P_1}^{P_2} dP \quad \text{—— (III)}$$

from 1 mole of an ideal gas

$$PV = RT$$

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

Putting the value of V in equ (III)

$$\int_{G_1}^{G_2} dG = RT\int_{P_1}^{P_2} \frac{dP}{P}$$

$$[G]_{G_1}^{G_2} = RT[\ln P]_{P_1}^{P_2}$$

$$G_2 - G_1 = RT[\ln P_2 - \ln P_1]$$

$$\Delta G = RT \ln \frac{P_2}{P_1}$$

$$\boxed{\Delta G = 2.303\, RT \log_{10} \frac{P_2}{P_1}}$$

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for n mole of an ideal gas

$$\boxed{\Delta G = 2.303\, nRT \log_{10} \frac{P_2}{P_1}}$$

Since T constant

$$P_1V_1 = P_2V_2$$

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

$$\boxed{\Delta G = 2.303\, nRT \log_{10} \frac{V_1}{V_2}}$$

Imp

Gibb's Halmhotz Equations —

Thiri are two equation which were derived by Gibb's and Halmhotz. These equation are known as Gibb's Halmhotz equation.

One equation can be expressed in terms of change of free energy (ΔG) and enthalpy (ΔH) while the other can be expressed in terms of change of work function (ΔA) and internal energy (ΔE).

a) In terms of change of free energy and enthalpy

We known that

$$G = H - TS$$

$$G = E + PV - TS \quad \{\because H = E + PV\}$$

Differentiating above equation, w.r.t T we get

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$\Delta G = dE + PdV + Vdp - SdT - TdS$

$\Delta G = dq + Vdp - SdT - TdS$ {from first law of Thermodynamic

$dG = \cancel{dq} + Vdp - SdT - (\cancel{dq})$ $\{\because TdS = dq\}$

$dG = Vdp - SdT$

At constant pressure

$dp = 0$

$dG = -SdT$

For initial state -1

$dG_1 = -S_1 dT$ —— (I)

For final state

$dG_2 = -S_2 dT$ —— (II)

change

$dG_2 - dG_1 = (-S_2 dT) - (-S_1 dT)$

$d(\Delta G) = -(S_2 - S_1) dT$

$d(\Delta G) = -\Delta S dT$

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = -\Delta S \quad \text{—— (III)}$$

We know that

$\Delta G = \Delta H - T\Delta S$ —— (IV)

Putting the value of ΔS in equation (IV) we get -

$$\boxed{\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P}$$

This equation is called Gibb's Helmholtz equation in terms of free energy and enthalpy change at constant pressure.

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(b) In terms of change of work function and internal energy —

we know that —

$$A = E - TS \quad \text{—— (I)}$$

for initial state - I -

$$A_1 = E_1 - TS_1 \quad \text{—— (II)}$$

for final state - II -

$$A_2 = E_2 - TS_2 \quad \text{—— (III)}$$

for change -

$$A_2 - A_1 = (E_2 - TS_1) - (E_1 - TS_1)$$

$$\Delta A = (E_2 - E_1) - T(S_2 - S_1)$$

$$\Delta A = \Delta E - T\Delta S \quad \text{—— (IV)}$$

From equ (I)

$$A = E - TS$$

differentiating equation (I) w.r.t, T —

$$dA = TdS - SdT \quad \text{—— (V)}$$

from first law of T.D -

$$dq = dE + PdV$$

thus second law of T.D

$$dq = TdS$$

$$TdS = dE + PdV$$

Putting the value of Tds in equation (V)

$$dA = \cancel{dE} - (\cancel{dE} + PdV) - SdT$$

$$dA = -PdV - SdT$$

At constant volume

$$dV = 0$$

$$dA = -SdT$$

$$\boxed{\left(\frac{\partial A}{\partial T}\right)_V = -S}$$

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for initial state I

$$\left[\frac{\partial A_1}{\partial T}\right]_V = -S_1 \quad \text{—— (VI)}$$

for final state II -

$$\left[\frac{\partial A_2}{\partial T}\right]_V = -S_2 \quad \text{—— (VII)}$$

for change

$$\left[\frac{\partial A_2}{\partial T}\right]_V - \left[\frac{\partial A_1}{\partial T}\right]_V = -(S_2 - S_1) \quad \text{—— V}$$

$$\left[\frac{\partial (\Delta A)}{\partial T}\right]_V = -\Delta S \quad \text{—— (VIII)}$$

We known that

$$\frac{\Delta A - \Delta E}{T} = -\Delta S \quad \text{—— (IX)}$$

$$\frac{\Delta A - \Delta E}{T} = \left[\frac{\partial (\Delta A)}{\partial T}\right]_V$$

$$\boxed{\Delta A = \Delta E + T\left[\frac{\partial (\Delta A)}{\partial T}\right]_V}$$

Nernst's Heat theorem —

Nernst's heat equation theorem is used to find out the condition which lead chemical reaction to completion According to Gibb's - Helmholtz equation -

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$$\boxed{\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P}$$

If $\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$ is a finite quantity, then at absolute zero, T = 0 kelvin

$$\Delta G = \Delta H$$

in other words

$$\lim_{T \to 0} \Delta G = \lim_{T \to 0} \Delta H$$

$$\boxed{\lim_{T \to 0} \Delta G - \lim_{T \to 0} \Delta H = 0}$$

This equation show that ΔG and ΔH are equal. Increases with lowering of temperature and becomes zero at 0 kelvin. This statement is known as Nernst's Heat theorem.

Mathmettically this theorem expressed at -

$$\boxed{\lim_{T \to 0}\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = \lim_{T \to 0}\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = 0}$$

<u>Consequences of Nernst's Heat theorem</u> -

1-

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Electrochemistry - I

The branch of chemistry which deals with the study of relationship b/w electrical energy, chemical energy and interconversion of these energy is called 'electrochemistry'.

Electrical conductance -

All substance donot conduct electrical current. The substance which allow the process of electrical current is called conductors.

The best conductors are metal such as Ag, Cu, Fe etc. On the other hand the substance which donot allow the process of electric current are called non-conductors or insulators.

Some common example of insulator are ~~gold~~ wood, plastic, rubber etc.

The electrode conected to positive terminal attracts the negative ions is called anode.

The other electrode conected to (-ve) the end of battery attract positive ion is called cathode.

Types of conductors -

The conductors are mainly two type -

(I) Metallic conducter
(II) Electrolytic conducter

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Metallic conductor –

These are metallic substances which allow the process of current without undergoing any chemical change.

Example – Ag, Cu, Al, Na etc.

Electrolytic conductors –

These are the conductors like aqu solution of acids, base and salt in which the flow of electric current is accompanied by chemical decomposition are known as electrolytic conductors.

Example – NaCl, KCl, LiCl. $CuSO_4$ etc.

Difference b/w metallic conductor and Electrolytic conductors –

Metallic Conductor	Electrolytic Conductor
1. It is carried out of by the movement of e⁻	1. It is carried out of by the movement of ions.
2. Ohm's law is followed	2. Ohm's law is followed.
3. Resistance increase with increase of temperature.	Resistance decrease with increase of temperature.
4. Metallic conductor do not follow Faraday	

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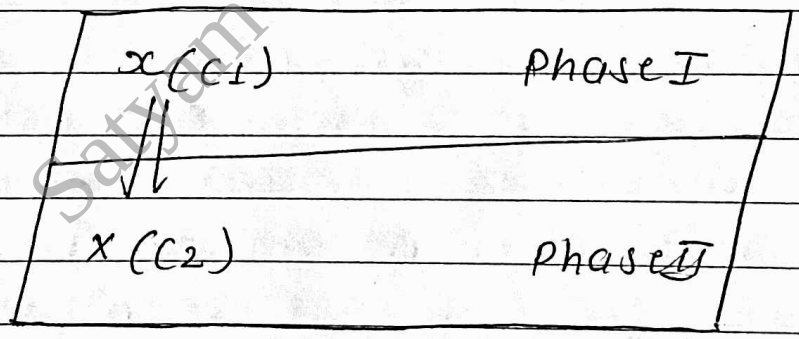
For section B Some important Question

(1) Nernst distribution law –

Nernst in 1891 studied the distribution of a large number of solutes between two immiscible solvents and generalised the result in the form of a law. This is called Nernst's distribution law or simply distribution law or partition law.

The Nernst distribution law may be stated as follows –

"A solute distributes itself between two immiscible solvents it contact with each other in such away that the ratio of the concentration of the same molecular spp in the two solvents is alway constant at constant temperature irrespective of the amount of solute.



Mathematically,

$$\frac{\text{Conc of solute (x) in phase I}}{\text{Conc of solute (x) in phase II}} = K$$

$$\frac{C_1}{C_2} = K$$

when K is a constant called distribution coffecient or :

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② Relation b/w ΔH and ΔE :-

We know that

$\Delta H = \Delta E + P\Delta V$ —— ①

$\Delta H = H_P - H_R$

~~Product - I~~

Reactant - Product

$PV_R = n_R RT$ — $PV_P = n_P RT$

$PV_P - PV_R = n_P RT - n_R RT$

$P(V_P - V_R) = RT(n_P - n_R)$

$P\Delta V = RT(\Delta n)$

$P\Delta V = \Delta n RT$

Putting the value of $P\Delta V$ in equ ①

$$\boxed{\Delta H = \Delta E + \Delta n_{(g)} RT}$$

③ Law of Mass action for the synthesis of HI :-

Goldberg and Waage put the formula law connected to the effect of conc of reactant and the rate of reaction is known as law of mass action.

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Those reaction in which total no of moles of reactant and product remain the same as a result of chemical reaction i.e $\Delta n = 0$

formation of HI-

$N_2 + 3H_2 \rightarrow 2NH_3$

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

$t=0$	a	b	$=0$
$t=t$	$(a-x)$	$(b-x)$	$=2x$

Let (a) mole of H_2 and (b) mole of I_2 is taken is a vessel volume(V) at equilibrium. x mole of H_2 and x mole of I_2 reacts to form two mole of HI.

Molar conc of equilibrium

$$[H_2] = \frac{(a-x)}{V} M/l$$

$$[I_2] = \frac{(b-x)}{V} M/l$$

$$[HI] = \frac{2x}{V}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$K = \frac{(2x/V)^2}{(a-x/V)(b-x/V)}$$

$$K_c = \frac{4x^2/V^2}{\frac{(a-x)(b-x)}{V^2}}$$

$$\boxed{K_c = \frac{4x^2}{(a-x)(b-x)}}$$

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(4) Prove $\Delta G^\circ = -RT \ln K_p$ — ~~Vant Hoff equation/isoch~~

The effect of temp. on chemical equilibrium can be determind by using thermodynamics.
The relation for the reaction isotherm when the reactant and products are gases and also in their standard state is represented by -

$$\Delta G^\circ = -RT \ln K_p \quad \text{—— (I)}$$

Differentiating equ (I) w.r.t T at constant P

$$\left[\frac{d(\Delta G^\circ)}{dt}\right]_P = -R \ln K_p - RT\left[\frac{d(\ln K_p)}{dt}\right]_P \quad \text{—— (II)}$$

multiplying equ (II) with T

$$T\left[\frac{d(\Delta G^\circ)}{dt}\right]_P = -RT \ln K_p - RT^2\left[\frac{d(\ln K_p)}{dt}\right]_P \quad \text{—— (III)}$$

From equ (I) and (III)

$$T\left[\frac{d(\Delta G^\circ)}{dt}\right]_P = \Delta G^\circ - RT^2\left[\frac{d(\ln K_p)}{dt}\right]_P \quad \text{—— (IV)}$$

From Gibb's helmhotz energy

$$\Delta G^\circ = \Delta h^\circ + T\left[\frac{d(\Delta G^\circ)}{dT}\right]_P \quad \text{—— (V)}$$

From equ (IV) and (V) we get

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$$\boxed{\frac{\Delta h^\circ}{RT^2} = \left[\frac{d(\ln K_p)}{dt}\right]_p}$$

(5) The Clapeyron - Clausius Equation —

The clapeyron - equ for liquid - vapour equilibrium may be written as follows -

$$\frac{dP}{dT} = \frac{\Delta H_v}{T_v(V_g - V_l)}$$

In this equilibrium V_l (mole volume of the liq state) may be neglected in comparison to V_g (mole volume of the gaseous state). Thus the above equ can be written as

$$\frac{dP}{dT} = \frac{\Delta H_t}{TV_g} \quad \text{——— (1)}$$

Here T is the normal boiling point of the liquid.

If the vapour obeys the ideal gas equ then

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

substituting the value of V_g in equ (1) we get

$$\frac{dP}{dT} = \frac{\Delta H_v P}{RT^2}$$

$$\frac{1}{P} \cdot \frac{dP}{dT} = \frac{\Delta H_v}{RT^2}$$

$$\boxed{\frac{d\ln P}{dT} = \frac{\Delta H_v}{RT^2}}$$

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This equ is known as clapeyron-clausius equ.

Application of clapeyron-clausius Equation—

I) Calculation of latent heat of vapourisation—

If the vapour pressure of a liquid as temp T_1 & T_2 are P_1 & P_2 respectively, the molar heat of vapourisation ΔH_v can be calculated by substituting these value is clapeyron-clausius equation.

Similarly latent heat of fusion can be calculated if the vapour pressure at two different temp of a solid in equilibrium with it's liq. phase are known.

II) Calculation of freezing point or boiling point—

If the freezing point or the boiling point of a liquid at one pressure is known, it is possible to calculate it at another pressure with the help of clayperon-clausius equation.

III) Calculation of vapour pressure—

The vapour pressure of a liquid at a given temperature can be calculated if the vapour pressure at another and heat of vaporisation are known.

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(6) **Ostwald's dilution law** –

According to Arrhenius theory of electrolytic dissociation, the molecules of an electrolyte in aqueous solution undergo dissociation to give positive and negative ions and setup a dynamic equilibrium betw ion and unionised molecule. Ostwald applied the law of mass action to such processes and suggested a law known as Ostwald's dilution law. This may be stated as follows –

"At constant temp the degree of dissociation of weak electrolyte is directly proportional to the square root of dilution or inversely proportional to the square root of it's concentration."

Derivation –

Let's consider aqu solution of a weak electrolyte AB whose conc is c gm mole per litre and it's degree of dissociation is α. At equilibrium, concentration of various spp can be written as –

$$AB \rightleftharpoons A^+ + B^-$$

c	0	0	Initial conc
$c(1-\alpha)$	$c\alpha$	$c\alpha$	equilibrium conc

Applying law of mass action we get –

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{(c\alpha) \times (c\alpha)}{c(1-\alpha)}$$

$$K = \frac{c\alpha^2}{(1-\alpha)} \quad \text{— (1)}$$

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Equ (1) is mathematical representation of Ostwald's dilution law. K is constant called dissociation constant of electrolyte AB. At constant temp, it has a constant value.

But for weak electrolyte, α is very small $\alpha << 1$.

Thus equ (1) may written as —

$$K = C\alpha^2$$

$$\alpha = \sqrt{\frac{K}{C}} = \sqrt{KV} \quad \text{—— (II)}$$

V = dilution which inversly proportional to conc. from equ (II) we get

$$\alpha \propto \frac{1}{\sqrt{C}}$$

$$\boxed{\alpha \propto \sqrt{V}}$$

or

(6) Arrhenius theory of Electrolytic Dissociation —

Arrhenius passed the electric current through the equ solution of different electrolytes and ~~conclu~~ conclude that the conductivity of solution was due to the presence of ions. In 1884 he put forward his theory which is known as Arrhenius theory of electrolytic dissociation

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Postulates - The main postulate of Arrhenius theory as follows-

(1) Neutral electrolyte molecule, when dissolved in H_2O split up into two types of charged particles which are called ions and this process was called ionisation. (+ve) cation and (-ve) anion

Now a-days the theory assumes that the ions are present in solid electrolytes. These ions are held together by electrostatic force of attraction. When dissolved in H_2O, these neutral molecule dissociate to give cation and anions. Thus,

$$AB \rightleftharpoons A^+ + B^-$$

$$A^+B^- \rightleftharpoons A^+ + B^-$$

$$AB \rightleftharpoons A^+ + B^-$$

$$K = \frac{[A^+][B^-]}{[AB]}$$

(7) Debye-Huckel-Onsagar theory of strong electrolytes-

P. Debye and E. Huckel (1923) put forward the modern theory of strong electrolytes considering the electrostatic force b/w the ions. This theory is known as Debye Huckel theory of interionic attraction. The treatment was later modified by L. Onsagar (1927). This theory is based on the following assumption:-

1- The strong electrolyte is completely ionised at all dilution. X-ray analysis of ionic solids of these electrolytes has shown that there is very small amount of unionised substance also present.

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II- The ratio $\frac{\lambda_r}{\lambda_\infty}$ does not correctly give the degree of dissociation α for strong electrolytes but only the conductance ratio.

III- The value of λ_r is much less λ_∞ even at almost complete ionisation.

(8) <u>Gibb's phase rule</u> -

The phase rule is important generalisation dealing with the behaviour of heterogeneous system. with the application of phase rule it is possible to predict equalitatively by means of a diagram the effect of change in pressure, temp and conc. on a heterogeneous system in equilibrium. Willard Gibbs (1876) put forward a rule which is known as Gibb's phase rule. This rule may be stated as follows -

In a heterogeneous system in equilibrium ~~then~~, the sum of the number of degrees of freedom and number of phase is equal to the number of components plus two

Mathematically,

$$F + P = C + 2$$

$$F = C - P + 2$$

F = No of degrees of freedom
C = No of component
P = No of phases.

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Phase diagram of consist of the following part -

(i) Three stable curves OA, OB and OC
(ii) One metastable curve OA
(iii) Triple point O
(iv) Area AOC, BOC and AOB.

(1.) curves -

Curve OA -

It is vapour pressure curve H_2O It represents the equilibrium b/w liquid H_2O and vapour at different temp. The vapour press

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Section B

Relation for entropy as a function v and T –

Entropy is a state function and its value depend upon the volume, pressure and temperature since temperature is take a one of the variable and second variable may be pressure and volume.
Thus variables are either volume and temp or pressure and temperature.

From defination of entropy –

$$ds = \frac{Q}{T} \quad \text{—— (I)}$$

From 1st law of T.D

$$dQ = dE + P\Delta V \quad \text{—— (II)}$$

we know that

$$PV = RT$$

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

again – $dE = C_v dT$

putting the value of P & dE in equ (II)

$$ds = \frac{dE + PdV}{T}$$

$$ds = \frac{C_v dT + \frac{RT}{V} dV}{T}$$

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$$ds = C_v \frac{dT}{T} + R\frac{dv}{V}$$

Integrating above equ with limits S_1 to S_2 – T_1 to T_2 and V_1 to V_2

$$\int_{S_1}^{S_2} ds = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R\int_{V_1}^{V_2} \frac{dv}{V}$$

$$[S]_{S_1}^{S_2} = C_v [\log T]_{T_1}^{T_2} + R[\log v]_{V_1}^{V_2}$$

$$S_2 - S_1 = C_v[\log T_2 - \log T_1] + R[\log V_2 - \log V_1]$$

$$\Delta S = C_v \log \frac{T_2}{T_1} + R \log \frac{V_2}{V_1}$$

$$\boxed{\Delta S = 2.303\, C_v \log_{10} \frac{T_2}{T_1} + 2.303\, R \log_{10} \frac{V_2}{V_1}}$$

For n moles of gas

$$\boxed{\Delta S = 2.303\, nC_v \log_{10} \frac{T_2}{T_1} + 2.303\, nR \log \frac{V_2}{V_1}}$$

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Prove that $C_p - C_v = R$

According to heat capacity at constant volume

$$C_v = \frac{dE}{dT} \quad \text{—— (I)}$$

According to heat capacity at constant pressure

$$C_p = \frac{dH}{dT} \quad \text{—— (II)}$$

From enthalpy difination

$$\boxed{H = E + PV} \quad \text{—— (III)}$$

Differenciate above equation with respect to T

$$H = E + PV$$

$$\frac{dH}{dT} = \frac{dE}{dT} + \frac{d}{dt} PV$$

$$\frac{dH}{dT} = \frac{dE}{dT} + R\frac{d}{dt}$$

$$C_p = C_v + R$$

$$\boxed{C_p - C_v = R}$$

Hence the difference b/w heat capacity at constant pressure and volume is always equal to gas constant.

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Kirchoff's equ. at constant pressure –

$$aA + bB \rightarrow cC + dD$$

$$\Delta H = \Sigma H_p - \Sigma H_R$$

differentiating with respect to T at constant pressure.

$$\frac{d(\Delta H)}{dt} = \left[c\left(\frac{dH_C}{dT}\right)_p + d\left(\frac{dH_P}{dt}\right)_p\right] - \left[a\left(\frac{dH_A}{dt}\right)_p + b\left(\frac{dH_B}{dt}\right)_p\right] \quad (1)$$

$$\left[c\left(\frac{dH_C}{dT}\right)_p + d\left(\frac{dH_P}{dT}\right)_p\right] = (C_p)_p$$

$$\left[a\left(\frac{dH_A}{dT}\right)_p + b\left(\frac{dH_B}{dT}\right)_p\right] = (C_p)_R$$

From equation (1) we have

$$\frac{d(\Delta H)}{dT} = (C_p)_p - (C_p)_R$$

$$\frac{d(\Delta H)}{dT} = \Delta C_p$$

$$d(\Delta H) = \Delta C_p \, dT$$

$$\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \Delta C_p \int_{T_1}^{T_2} dT$$

$$[\Delta H]_{\Delta H_1}^{\Delta H_2} = \Delta C_p [T]_{T_1}^{T_2}$$

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$$\Delta H_2 - \Delta H_1 = \Delta C_p [T_2 - T_1]$$

$$(\Delta H_2)_{T_2} - (\Delta H)_{T_1} = \Delta C_p [T_2 - T_1]$$

$$\boxed{\Delta C_p = \left[\frac{(\Delta H)_{T_2} - (\Delta H)_{T_1}}{[T_2 - T_1]}\right]}$$

Kirchoff equ at constant volume -

$$aA + bB \longrightarrow cC + dD$$

$$\Delta E = \Sigma E_P - \Sigma E_R$$

Differentiating w.r.t T at constant volume

$$\frac{d(\Delta E)}{dt} = \left[c\left(\frac{dE_C}{dT}\right)_V + d\left(\frac{dE_D}{dT}\right)_V\right] - \left[a\left(\frac{dE_A}{dT}\right)_V + b\left(\frac{dE_B}{dT}\right)_V\right]$$

$$\left[c\left(\frac{dE_C}{dT}\right)_V + d\left(\frac{dE_D}{dT}\right)_V\right] = (C_V)_P$$

$$\left[a\left(\frac{dE_A}{dT}\right)_V + b\left(\frac{dE_B}{dT}\right)_V\right] = (C_V)_R$$

From equ ① we have

$$\frac{d(\Delta E)}{dT} = (C_V)_P - (C_V)_R$$

$$\frac{d(\Delta E)}{dT} = \Delta C_V$$

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$$d(\Delta E) = \Delta C_v dT$$

$$\int_{\Delta E_1}^{\Delta E_2} d(\Delta E) = \Delta C_v \int_{T_1}^{T_2} dT$$

$$[\Delta E]_{\Delta E_1}^{\Delta E_2} = \Delta C_v [T]_{T_1}^{T_2}$$

$$\Delta E_2 - \Delta E_1 = \Delta C_v [T_2 - T_1]$$

$$(\Delta E)_{T_2} - (\Delta E)_{T_1} = \Delta C_v [T_2 - T_1]$$

$$\boxed{\Delta C_v = \left[\frac{(\Delta H)_{T_2} - (\Delta H)_{T_1}}{[T_2 - T_1}\right]}$$

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Gibb's halmholtz Equation –

There are two equ which were derived by Gibb's and halmholtz This equ are known as gibb's Halmholtz equation.

One equ can be expressed in term of change of free energy (ΔG) and enthalpy (ΔH) while the other can be expressed in term of change of work function (ΔA) and internal energy (ΔE)

(a) In term of change of free energy and enthalpy –

We know that

$$G = H - TS$$

$$G = E + PV - TS \quad \{H = E + PV\}$$

differenciate above equ w.r.t. T we get

$$G = E + PV - TS \qquad SdT - TdS$$

$$\Delta G = dE + PdV - VdP - \cancel{TdS - SdT}$$

$$\Delta G = dq + VdP - \cancel{TdS - SdT} \quad \{\text{from } I^{st} \text{ law of TD}\}$$

$$SdT - TdS$$

$$dG = \cancel{dq} + VdP - \cancel{(dq)} - SdT \quad \{\because TdS = dq\}$$

$$SdT - \cancel{dq}$$

$$dG = VdP - SdT$$

At constant pressure

$$dP = 0$$

$$dG = VdP - SdT$$

$$dG = 0 - SdT$$

$$dG = -SdT$$

~~For final state~~ initial

$$dG_1 = -S_1 dT \quad \text{—— (I)}$$

for final state

$$dG_2 = -S_2 dT \quad \text{—— (II)}$$

change

$$dG_2 - dG_1 = -(S_2 dT) - (-S_1 dT)$$

$$d(\Delta G) = -(S_2 - S_1) dT$$

$$d(\Delta G) = -\Delta S dT$$

$$\left(\frac{d(\Delta G)}{dT}\right)_P = -\Delta S \quad \text{—— (III)}$$

we know that

$$\Delta G = \Delta H - T\Delta S \quad \text{—— (IV)}$$

Putting the value of ΔS in equ (IV) we get

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$$\boxed{\Delta G = \Delta H + T\left(\frac{d(\Delta G)}{dT}\right)_P}$$

(6) In term of ~~wo~~ change of work function and internal energy -

we know that

$$A = E - TS \quad \text{—— (I)}$$

for initial state

$$A_1 = E_1 - TS_1 \quad \text{—— (II)}$$

for final state -

$$A_2 = E_2 - TS_2 \quad \text{—— (III)}$$

for change -

$$A_2 - A_1 = (E_2 - TS_2) - (E_1 - TS_1)$$

$$\Delta A = (E_2 - E_1) - T(S_2 - S_1)$$

$$\Delta A = \Delta E - T\Delta S \quad \text{—— (IV)}$$

From equ (I)

$$A = E - TS$$

differentiating equ w.r.t T

$$A = E - TS$$

$$\Delta A = dE + TdS - SdT \quad \text{—— (V)}$$

from I st law of T.D -

$$dq = dE + Pdv$$

Thus II sec law of T.D

$$dq = TdS$$

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$$TdS = dE + PdV$$

Putting the value of TdS in equ (V)

$$dA = dE - TdS - SdT$$
$$dA = \cancel{dE} - (\cancel{dE} + PdV) - SdT$$
$$dA = -PdV - SdT$$

At constant volume

$$dV = 0$$
$$dA = -PdV - SdT$$
$$dA = 0 - SdT$$
$$dA = -SdT$$

$$\boxed{\left(\frac{\partial A}{\partial T}\right)_V = -S}$$

for initial state -

$$\left(\frac{\partial A_1}{dT}\right)_V = -S_1 \quad \text{——— (VI)}$$

for final state -

$$\left(\frac{\partial A_2}{dT}\right)_V = -S_2 \quad \text{——— (VII)}$$

for change -

$$\left(\frac{\partial A_2}{\partial T}\right) - \left(\frac{\partial A_1}{dT}\right) = -S_2 - S_1$$

$$\left(\frac{\partial \Delta A}{dT}\right) = -\Delta S \quad \text{——— (VIII)}$$

we know that

$$\frac{\Delta A - \Delta E}{T} = -\Delta S \quad \text{——— (IX)}$$

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$$\frac{\Delta A - \Delta E}{T} = \left[\frac{\partial(\Delta A)}{\partial T}\right]_V$$

$$\boxed{\Delta A = \Delta E + T\left[\frac{\partial(\Delta A)}{\partial T}\right]_V}$$

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Short question –

(1) Degree of Freedom (F) –

The term degree of Freedom may be defind as follows :- The minimum number of independent variable temp, pressure and conc) which must be specified so that the ~~the~~ remaining variable are fixed automatically and the system is completely defined. It is denoted by F.

(2) Henry law –

The relation b/w pressure and solubility of a gas in a particular solvent was proposed by William Henry in the form of law known as Henry's law. It may be stated as follows –

"The mass of a gas dissolved in a solvent at constant temp is proportional to the pressure of the gas in equilibrium with the solution."

Mathematically

$$m \propto P$$

$$m = KP$$

m = mass of gas dissolved in unit volume of solvent

P = Pressure of the gas

K = Henry's constant

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Raoult's law -

F. Raoult's law studied the vapour pressure of binary solution of volatile liquid e.g. benzene and toluene at constant temp and gave a law which is known as raoult's law. According to this law:-

" At constant temp the partial pressure of any volatile component of solution is equal to the vapour pressure of the pure component multiplied by the mole fraction of that component in the solution."

Math -

$$P_A = X_A \cdot P_A^\circ$$

$$P_B = X_B \cdot P_B^\circ$$

Common Ion Effect -

The reduction of degree of dissociation of a salt by the addition of a common ion is called common ion effect.

Solubility Product -

suppose a saturated solution of sparingly soluble salt AB. In solution the following equilibrium.

$$AB \rightleftharpoons AB \rightleftharpoons A^+ + B^-$$

Applying law of mass action

$$K = \frac{[A^+][B^-]}{[AB]}$$

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$$K \times [AB] = [A^+][B^-]$$

Since active mass of a solid is constant at constant temp. the value of [AB] will be constant at constant temp. Thus the above equ may be written as

$$K \times \text{constant} = [A^+][B^-]$$

$$K_{sp} = [A^+][B^-]$$

Ksp is solubility product of AB. It may be defined as –

The product of the conc of ions in a saturated solution at a given temp is constant". It has a constant value at a particular temp.

Now let's consider a general salt A_xB_y which is in equilibrium in solⁿ as

$$A_xB_y \rightleftharpoons \overset{z+}{x}A + \overset{z-}{y}B$$

If solubility of salt is S mole/litre the conc of ion will be

$$A_xB_y \rightleftharpoons \overset{z+}{x}A + \overset{z-}{y}B$$

$$xS \quad yS$$

$$K_{sp} = [xS]^x \times [yS]^y$$

$$x^y(x+y)$$

$$K_{sp} = x^y \cdot y^y \cdot S$$

This is general equ of calculate solubility product of salt.

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Electronic theory of valency:-

Compound	Formula	Electronic Formula
Sodium chloride	NaCl	$Na^{+}[:\ddot{Cl}:]^{-}$
Magnesium chloride	$MgCl_2$	$[:\ddot{Cl}\times]\ Mg^{2+}\ [\times\ddot{Cl}:]$
Calcium oxide.	CaO	$[Ca]^{+2}\ [\times\ddot{O}:]^{-2}$

Compound	Formula	Structural Formula	Electronic Formula
Hydrogen			
Oxygen			
Nitrogen			
Chlorine			
Water			
Carbon monoxide			
Carbondioxide			
Ammonia			
Methane			
Ethane			
Ethylene			
Acetylene			
Hydrogen sulphide			
Hydrochloride			
Phosphene			
Nitric oxide			
Nitrous acid.			

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