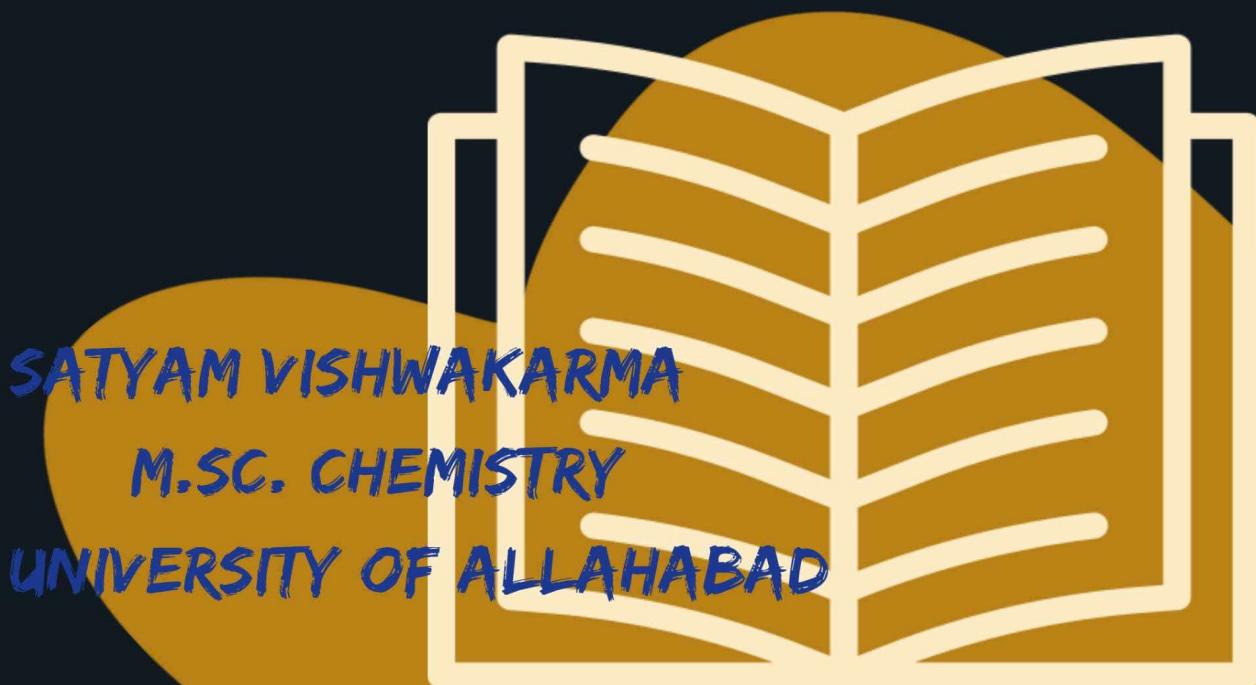


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B.Sc. Chemistry Handwritten Notes

For 2nd Year Students



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Thermodynamics - I

Thermodynamics -

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 important terminology 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.

Example - Hot water contain in close vessel.

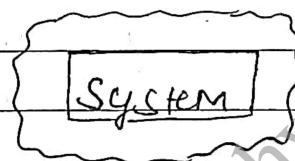
Isolated System -

The system in which neither energy nor mass can exchange b/w system and surrounding is called isolated system.

Example - Hot water contain in thermos.

Surrounding -

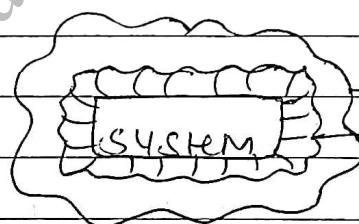
The rest of system the all atmospheric regards as surroundings.



Surrounding

Boundary -

Anything which separate system and surrounding is called boundary.



Surrounding

boundary

Thermodynamic process -

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

They are following types -

Isothermal process -

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

For isothermal process -

$$[\Delta T = 0]$$

Isobaric process -

The process in which pressure is constants called isobaric process.

For isobaric process - $[\Delta P = 0]$

Isochoric process -

The process in which volume change in remains is called isochoric process.

Depends on temp pressure law : Gay-Lussac law

For isochoric process

$$[\Delta V = 0]$$

Adiabatic process -

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

For adiabatic process

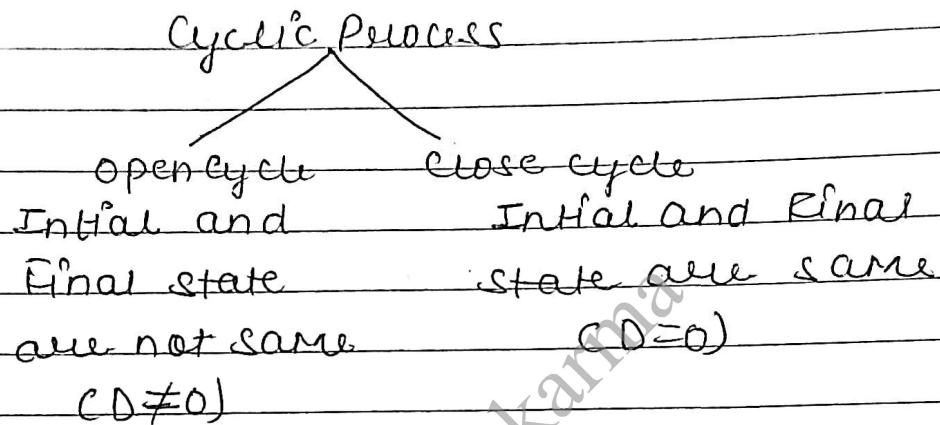
$$[\Delta Q = 0]$$

Note -

Note -

Cyclic process -

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



Intensive and Extensive properties -

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

Note-

The ratio of two extensive property to give intensive property.

$$d = \frac{m - \text{Extensive}}{v - \text{Extensive}}$$

↓
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's property system which does not depend upon manner of path. It only depend initial and final stages.

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

Initial

(A)

T_1

S_1

H_1

E_1

G_1

Final

(B)

$T_2 = \Delta T = T_2 - T_1$

$\Delta S = S_2 - S_1$

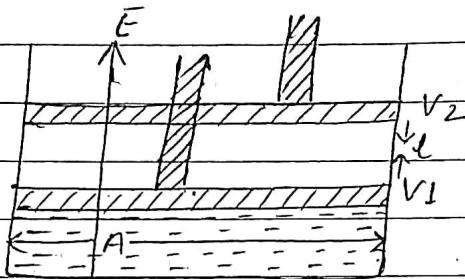
$\Delta H = H_2 - H_1$

$\Delta E = E_2 - E_1$

$\Delta G = G_2 - G_1$

P-V work done -

A gas contained in a cylinder vessel in which is fitted with a piston. An external pressure applied on the gas by piston. Then force is balanced by internal gas which has opposite direction than the piston. Due to gas it the gas moves (in 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 a system is called internal energy. It is denoted by E/U .

state — state

(A)

(B)

E_A — E_B

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

when $\Delta E = \ominus ve$

or $E_A > E_B$

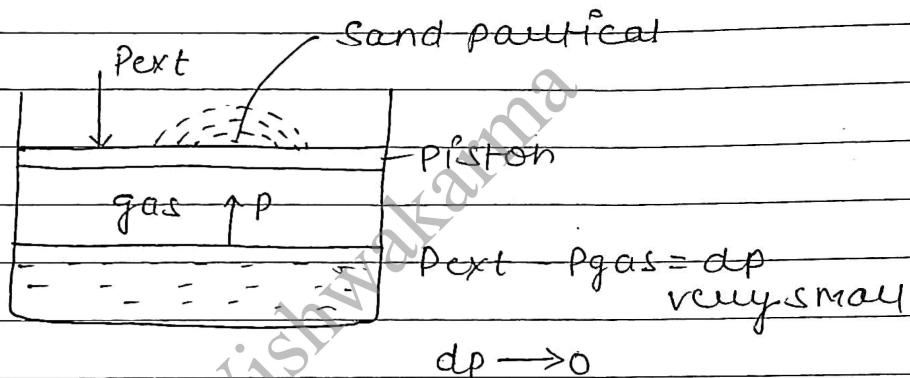
against $\Delta E = + ve$

or $E_B > E_A$

1- Reversible and Irreversible process

In this process the reverse system easily occurs 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 throughout the process.

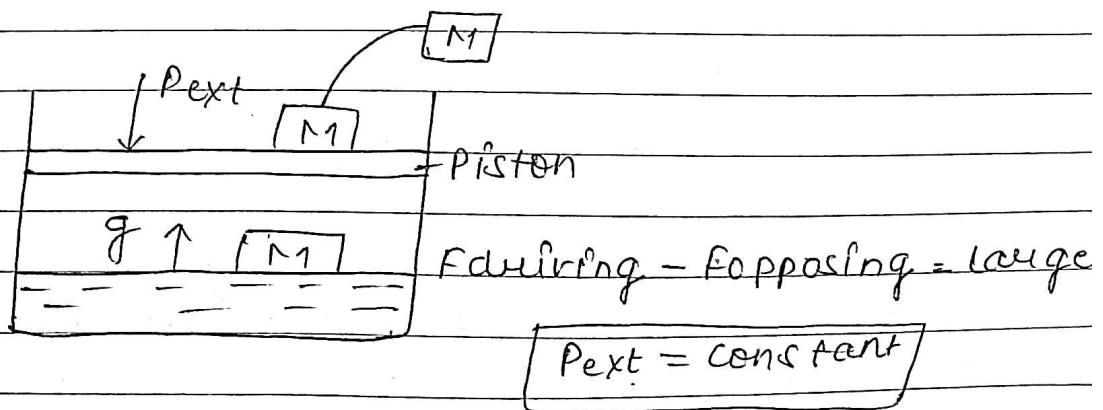
It's occur in ∞ step & ∞ time



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 definite time and step.



First law of thermodynamics

It is based on law of conservation of energy.

According to this law,

"Energy can neither be created nor be destroyed it only transfer one form to another form."

OR

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

Mathematical statement of first law of thermodynamics

S -

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

State (A)

E_A

State (B)

E_B

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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,

$$w = P\Delta V$$

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

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

$$Q = \Delta E + W$$

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

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

$$\Delta E = 500 - 350$$

$$\Delta E = 150$$

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. Calculate the energy change on the system.

$$Q = 100 \text{ cal}$$

$$W = +50$$

$$\Delta E = Q + W$$

$$\Delta E = 100 + 50$$

$$\Delta E = 150$$

Heat content -

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

✓ Heat content at constant volume -

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

According to first law of thermodynamics

$$Q = \Delta E + W$$

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

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

$$Q = \Delta E$$

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

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:

$$H = E + PV$$

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 -

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

$$\text{change in Enthalpy} = H_2 - H_1$$

$$\Delta H = (E_2 + PV_2) - (E_1 + PV_1)$$

$$\Delta H = (E_2 - E_1) + (PV_2 - PV_1)$$

$$\Delta H = \Delta E + P(V_2 - V_1)$$

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

$$\Delta E = \Delta H - P\Delta V \quad \text{--- (III)}$$

According to 1st law of thermodynamics

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

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

$$\Delta H - P\Delta V = Q - P\Delta V$$

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

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

$$PV_R = nRRT \quad \text{--- } PV_p = n_pRT$$

$$PV_p - PV_R = n_pRT - nRRT$$

$$P(V_p - V_R) = RT(n_p - nR)$$

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

$$P\Delta V = nRT$$

Putting 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 $17^\circ C$ is -20.3 kJ/J calculate the heat of combustion at constant pressure where $R = 8.314 \text{ J}/^\circ \text{C/mole}$.

$$T = 17^\circ\text{C} = 273 + 17 = 290\text{ K}$$

$$R = 0.314 \text{ J}/^\circ\text{C} / \text{mole}$$

$$\Delta E = -203.3 \text{ kJ}$$



$$\Delta n = (1 - \frac{1}{2})$$

$$\Delta n = \frac{1}{2}$$

$$\Delta H = ?$$

$$\Delta H = \Delta E + \Delta n RT$$

$$\Delta H = -203.3 + (-\frac{1}{2}) \times 0.314 \times 290$$

$$\Delta H = -203.3 + (-\frac{1}{2}) \times 2411.060$$

$$\Delta H = -203.3 + 1205.530$$

$$\Delta H = -1403.3 \text{ J}$$

✓ Heat capacity:-

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

OR

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 $\Delta T = 1^\circ\text{C}$ or 1K

unit of $c = \text{J/K}$ or J/C°

Note:- Molar heat capacity -

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

$$Q = n \cdot C_m \times \Delta T$$

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

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

unit of $C_m = \text{J/mole.K}$

Specific heat capacity -

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

$$Q = m \cdot c_s \cdot \Delta t$$

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

unit of $c_s = \text{J/gрамK}$

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Heat capacity at constant volume -

The amount of energy required to raise temperature of system through 1°C at constant volume 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

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

since heat constant at constant volume -

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

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

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 1st law of thermodynamics at constant pressure

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

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

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

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

According to heat capacity at constant volume

$$C_V = \frac{dE}{dt} \quad \textcircled{I}$$

According to heat capacity at constant pressure

$$C_P = \frac{dH}{dt} \quad \textcircled{II}$$

From enthalpy definition -

$$H = E + PV \quad \textcircled{III}$$

Differentiating above equation with respect to

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

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

$$C_p = C_v + R$$

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

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

IUPAC CONVENTION -

Expansion compression
work done work done on
by the gas the gas

$$V_2 > V_1$$

$$V_1 \rightarrow V_2$$

$$W = -P\Delta V$$

$$W = -P\Delta V$$

$$W = -nV$$

$$W = -P(-nV)$$

$$W = \text{Ave}$$

$$W = +PV$$

$$W = +\text{Ave}$$

In Isothermal reversible expansion -

1- calculation the work done in Isothermal expansion

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 off in equation (1)

$$W = - \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$W = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

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

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

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

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

$$W = -2.303 nRT \left(\log_{10} \frac{V_2}{V_1} \right)$$

from boyles law -

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

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

$$PV = k$$

$$P_1 V_1 = P_2 V_2$$

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

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

Example -

Calculate the work done when one mole of gas is allowed to expand reversibly and isothermally from 5 ATM to 1 ATM at 25°C.

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

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

$$W = -2.303 \times 8.314 \times 298 \left[\log_{10} 5 \right]$$

$$W = -2.303 \times 8.314 \times 298 \times 0.6991$$

$$W = -3980.21 \text{ Jules}$$

$$W = -3980.21 \text{ Jules}$$

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

$$\Delta H = H_2 - H_1$$

$$\Delta H = [CE_2 + P_2 V_2] + [E_1 + P_1 V_1] \quad (\text{since } H = E + PV)$$

$$\Delta H = [CE_2 - E_1] + [P_2 V_2 - P_1 V_1]$$

$$\Delta H = [0 + (P_2 V_2 - P_1 V_1)] \quad \text{from Boyle's law}$$

$$\Delta H = [0 + (P_2 V_2 - P_2 V_2)] \quad P_1 V_1 = P_2 V_2$$

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

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

σ - 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

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

Adiabatic process - As Before

Adiabatic expansion of an ideal gas -

under adiabatic expansion the exchange of heat b/w the system and surroundings is 0.

$(q=0)$
from 1st law of thermodynamics

$$\Delta E = w = P\Delta V$$

Temperature volume relationship -

$$q = \Delta E + w$$

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

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

$$0 = \Delta E + P\Delta V$$

$$-\Delta E = P\Delta V$$

$$-nC_V \Delta T = P\Delta V$$

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

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

Integrating on the both side

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

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

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

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

We know that

$$C_P - C_V = R$$

dividing equ by C_V

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

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

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

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

r = adiabatic constant

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

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

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

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

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

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

Temperature pressure relationship -

We know that

$$TV^{(r-1)} = K \quad \text{--- ①}$$

For one mole of an ideal gas -

$$PV = RT$$

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

Putting the value of V in equ ① we get

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

$$\frac{T(R)^{(r-1)}}{P^{(r-1)}} \cdot \frac{(T)^{(r-1)}}{R^{(r-1)}} = K$$

$$\frac{T(T)^{(r-1)}}{P^{(r-1)}} = \frac{K}{R^{(r-1)}}$$

$$\frac{T(r-x+x)}{P^{(r-1)}} = K$$

$$T \cdot P^{(r-1)} = K$$

III - Pressure - volume relationship -

We know that

$$TV^{(r-1)} = K \quad \text{①}$$

for one mole of an ideal gas

$$PV = RT$$

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

Putting the value of T in equ ① we get

$$\frac{PV}{R} \cdot V^{(r-1)} = K$$

$$P_r V(r^{-1}) = k \times R$$

$$P_r V(r^{-1} + r) = k$$

$$\boxed{PV = k}$$

Q- Adiabatic reversible expansion -

We know that

$$W = -P dV \quad \text{--- (1)}$$

$$n C_v dT = -P dV \quad \text{--- (2)}$$

for very small reversible process

$$C_v dT = -P dV \quad \text{--- (3)}$$

for one mole of an ideal gas

$$PV = RT$$

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

Putting the value of P in equ (3) we get

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

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

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

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

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

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

$$\log_e \frac{T_2}{T_1} = \log_e \left(\frac{v_1}{v_2} \right)^{(r-1)}$$

$$\boxed{\frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{(r-1)}}$$

$$cv - cp = R \quad \text{dividing by } cv \text{ in both sides}$$

$$\frac{cp}{cv} - 1 = \frac{R}{cv}$$

$$(r-1) = \frac{R}{cv}$$

$$\text{neg } cv = \frac{R}{(r-1)} \quad \text{IV}$$

comparing equ ① & ④ we get

$$w_{re} = ncv\Delta T$$

$$w_{re} = \frac{nR}{(r-1)} (T_2 - T_1)$$

$$\boxed{w_{re} = \frac{nR}{(r-1)} (T_2 - T_1)}$$

Conclusion -

when $T_2 > T_1$ $w_{re} = +ve$

when $T_2 < T_1$ $w_{re} = -ve$

Enthalpy change -

$$\Delta H = H_2 - H_1$$

$$= [E_2 + P_2 V_2] - [E_1 + P_1 V_1]$$

$$= [E_2 - E_1] - [P_2 V_2 - P_1 V_1]$$

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

$$- cv \Delta T + R(T_2 - T_1)$$

$$C_V(T_2 - T_1) + nR(T_2 - T_1) \quad \left\{ C_V = \frac{\partial E}{\partial T} \right\}$$

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

$$\boxed{\Delta H = \Delta T(C_V + nR)} \quad \text{--- (1)}$$

We know that —

$$\Delta H = C_P \Delta T$$

For n mole of ideal gas —

$$\Delta H = nC_P \Delta T \quad \text{--- (2)}$$

Comparing equation (1) and (2) we get —

$$\boxed{nC_P = (C_V + nR)}$$

OR

$$nC_P - nR = C_V$$

$$n(C_P - R) = C_V$$

$$\boxed{n = \frac{C_V}{(C_P - R)}}$$

b- Adiabatic irreversible expansion —

c- Work done ($W_{P_{ext}}$) —

Under the condition

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

We know that —

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

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

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

$$W_{\text{isoch}} = P_{\text{ext}} [V_2 - V_1]$$

$P_{\text{ext}} = P_2 = \text{final pressure}$

$$W_{\text{pump}} = P_2 [V_2 - V_1]$$

$$W_{\text{pump}} = P_2 \left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right]$$

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

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

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

Energy change (ΔE) —

According to 1st law of thermodynamics —

$$\Delta E = W + q$$

for adiabatic process —

$$q = 0$$

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

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

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

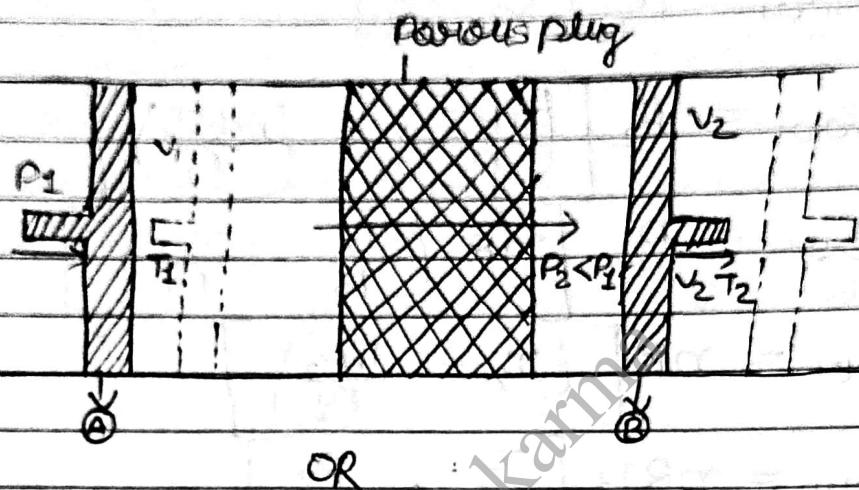
$$C_V T_2 - C_V T_1 = \frac{nRT_1 P_2}{P_1} - nRT_2$$

$$C_V T_2 + nRT_2 = \frac{nRT_1 P_2}{P_1} + C_V T_1$$

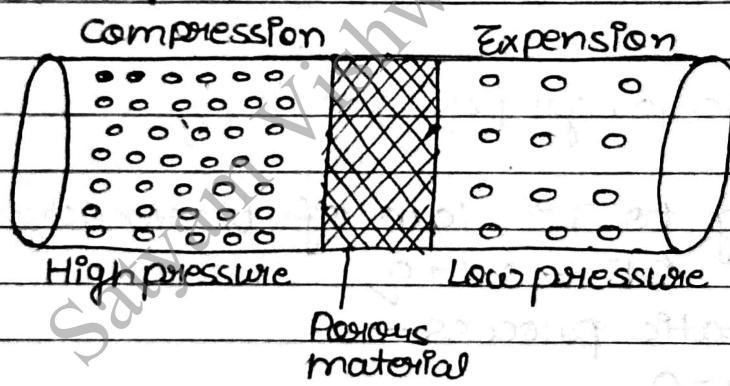
$$T_2 (C_V + nR) = \left[\frac{nRP_2}{P_1} + C_V \right] T_1$$

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

Joule - Thomson effect



OR



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

"When a gas is allowed to pass from a higher pressure to a lower pressure through a porous plug. Its temp. falls and fall in temperature is proportional to the difference between pressure."

The apparatus used by Joule and Thomson is shown in figure. An insulated

tube is fitted 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 expand to volume V_2 and pressure P_2 . The change in temperature is noted by taking reading on the true sensitive thermamitter fitted 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 expand to lower pressure P_2 and volume V_2 by moving piston B outward.

$$\text{Work done by the gas on piston (A)} = P_1 V_2$$

$$\text{Work done by the gas on piston (B)} = P_2 V_2$$

$$\text{Net work done by the gas (W)} = P_2 V_2 - P_1 V_2$$

According to the 1st law of thermodynamics

$$\Delta E = q - W$$

for adiabatic process—

$$q = 0$$

$$\Delta E = -(P_2 V_2 - P_1 V_1)$$

$$\Delta E = P_1 V_1 - P_2 V_2$$

$$E_2 - E_1 = P_1 V_1 - P_2 V_2$$

$$E_2 + P_2 V_2 = E_1 + P_1 V_1$$

$$H_2 = H_1$$

$H_1, H_2 = 0$

$$\Delta H = 0$$

Joule-Thomson coefficient

Joule-Thomson coefficient is defined as -

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

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

Inversion temperature -

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

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

where,

$a, b = \text{Vander waal constant}$

$R = \text{gas constant}$

Thermochemistry

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

Exothermic and Endothermic reaction

Exothermic reaction —

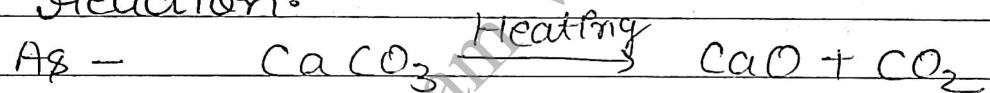
10 Reaction in which heat
is given out along with the product are
called exothermic reaction.

As — Burning of coal



Endothermic reaction —

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



Sign Convention —

Exothermic reaction — $\ominus \quad \Delta E \quad \Delta H$

Endothermic reaction — $\oplus \quad \oplus \quad \oplus$

Difference between Exothermic and Endothermic reaction —

Exothermic

Endothermic

i - Heat is released by the system

ii - Heat is absorbed by the system

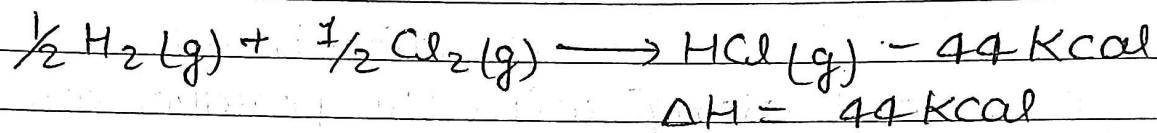
iii - Temperature of surrounding is increased

iv - Temperature of the surrounding is decreased

iii^o - ΔH , ΔE , Δq all are negative
iv^o - ΔH , ΔE , Δq all are positive.

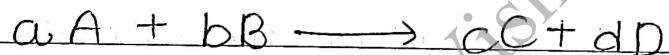
Heat of reaction —

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



Effect of temperature on heat of reaction —

Kirchhoff's equation at constant pressure —



$$\Delta H = \sum H_{\text{product}} - \sum H_{\text{reactant}}$$

differentiating with respect to T at constant pressure

$$\frac{d(\Delta H)}{dT} = \left[c \left(\frac{dH_c}{dT} \right)_P + d \left(\frac{dH_d}{dT} \right)_P \right] - \left[a \left(\frac{dH_A}{dT} \right)_P + b \left(\frac{dH_B}{dT} \right)_P \right]$$

$$* \quad \left[c \left(\frac{dH_c}{dT} \right)_P + d \left(\frac{dH_d}{dT} \right)_P \right] = (c_p)_P$$

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

from equation ① we have

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

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

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

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

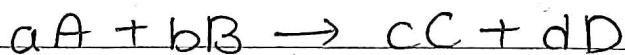
$$[\Delta H]_{\Delta H_2}^{\Delta H_2} = \Delta C_p [T]_{T_1}^{T_2}$$

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

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

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

Kirchhoff's equation at constant volume —



$$\Delta E = \Sigma E_{\text{Product}} - \Sigma E_{\text{Reactant}}$$

Differentiating with respect to T at constant volume —

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

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

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

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

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

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

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

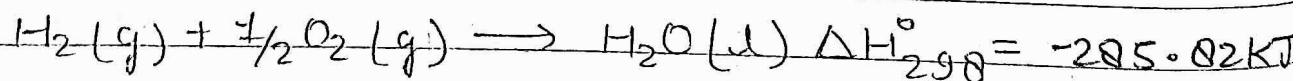
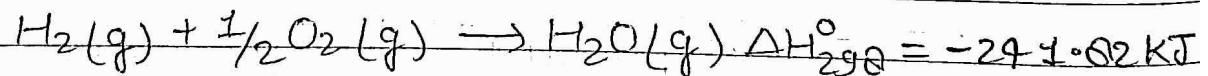
$$\Delta C_V = \frac{(\Delta E)_{T_2} - (\Delta E)_{T_1}}{T_2 - T_1}$$

Thermochemical equation

Physical state

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

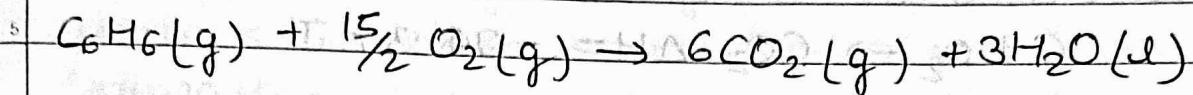
e.g.



Fraction number of moles

A Thermochemical equation may be written form of fractional

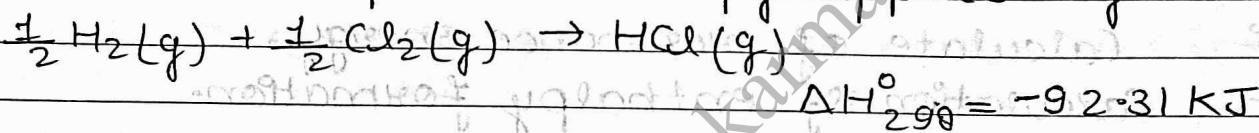
number of moles of some reactant and products
e.g. —



T.D.S. - $\Delta H = -3301.5 \text{ kJ}$

Temperature and pressure —

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

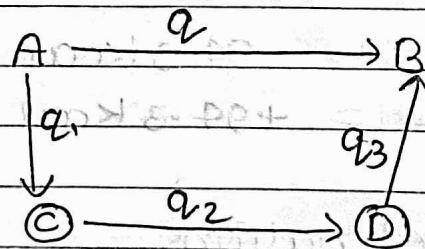


15 Note- '0' indicates $P = 1 \text{ atm}$ and $T = 25^\circ\text{C}$ or 298 K

Law of thermochemistry —

Hess's law —

20 This law states that the amount of heat absorbed in a process (including a physical change and chemical change) is the same whether the process takes place in one or several steps.

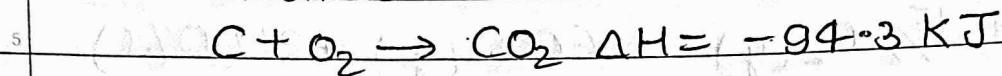


30 $q = q_1 + q_2 + q_3$

For example —

Formation of CO_2 —

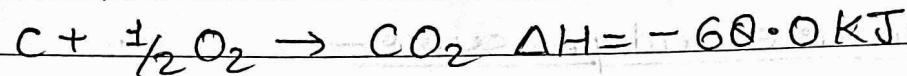
First method —



Second method —



Third method —



Application of Hess law —

i Calculate of resonance energy.

ii Calculation of enthalpy formation.

iii Calculation of lattice energy.

iv Calculation of enthalpy of neutralization,

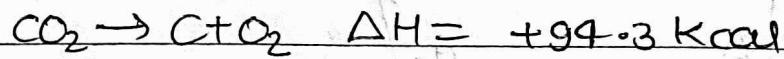
Ionization, precipitation, fission, Vapourization.

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 —



Note- Some important definitions —

Heat of formation

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

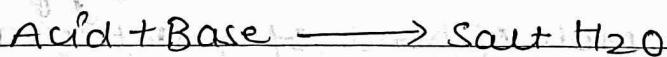
The amount of heat absorbed when one mole of the substance is directly obtained from its constituent elements is called heat of formation. It is denoted by ΔH_f .



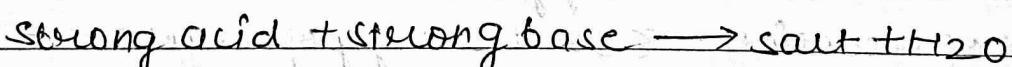
Heat of neutralization

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

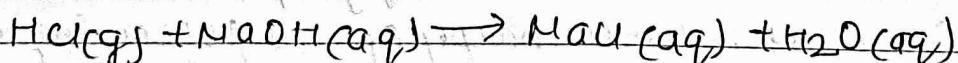
Notation -



Step - I

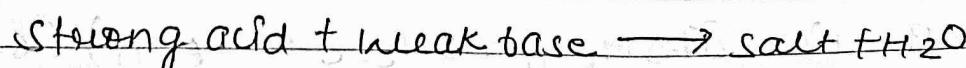


$$\Delta H = -13.7 \text{ kcal}$$

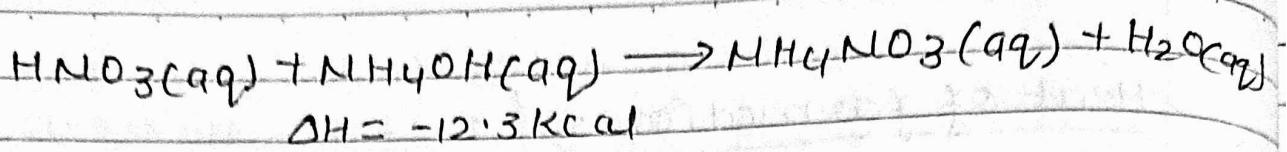


$$\Delta H = -13.7 \text{ kcal}$$

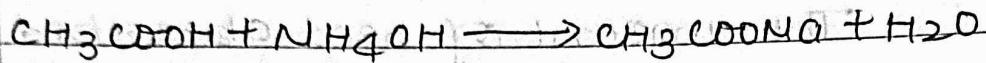
Step - II -



$$\Delta H = -12.3 \text{ kcal}$$



Step - II. (i) more general of both two
Weak acid + weak base \rightarrow salt + H₂O
 $\Delta H = -11.9 \text{ kcal}$



$$\Delta H = -11.9 \text{ kcal}$$

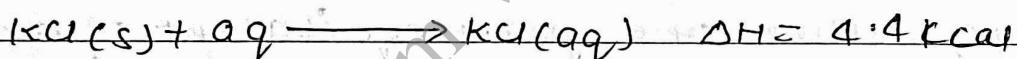
Enthalpy of solution or heat of solution

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

For example -



$$\Delta H = -20.2 \text{ kcal}$$

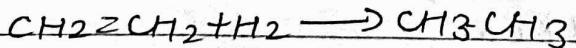


Bond dissociation energy -

The energy required 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



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

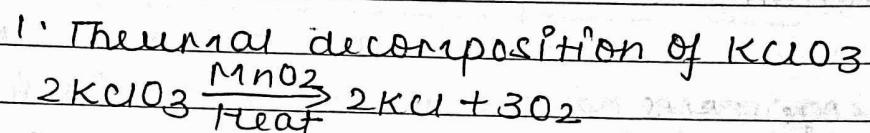
$$\begin{aligned} \text{Heat of Reaction} &= [(4 \Delta H_{\text{C}-\text{H}} + \Delta H_{\text{C}=\text{C}} + \Delta H_{\text{H}-\text{H}}) - (6 \Delta H_{\text{C}-\text{H}} + \Delta H_{\text{C}-\text{C}})] \\ &= (4 \times 99 + 147 + 104) - (6 \times 99 + 83) \\ &= (396 + 147 + 104) - (594 + 83) \\ &= 647 - 677 = -30 \text{ kcal} \end{aligned}$$

Chemical Equilibrium

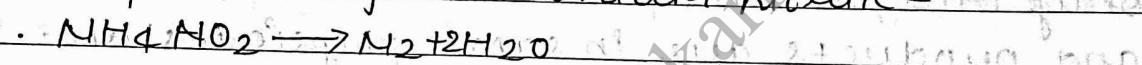
Inversible Reaction -

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



II- Decomposition of ammonium nitrate -



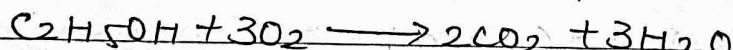
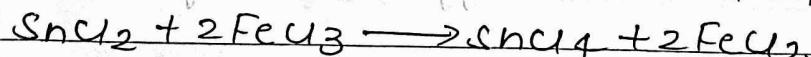
III- Neutralization -



IV- Precipitation reaction-



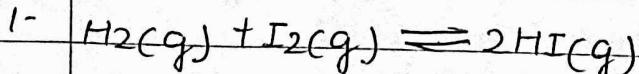
V- Redox and combustion reaction

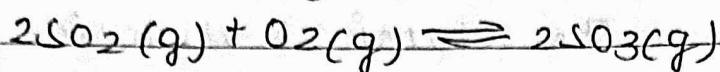
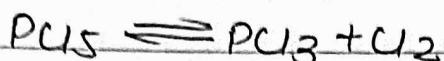
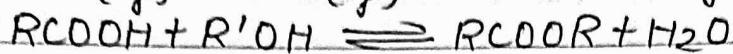
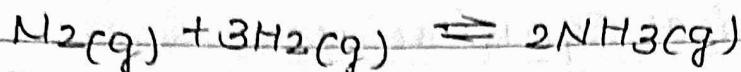


Reversible reaction -

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 - ~~the building of molecular organization in H₂I₂ mixture~~





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.

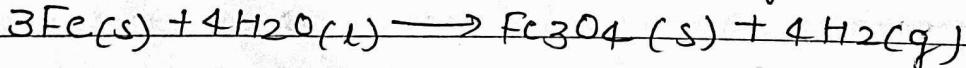
Example -



Heterogeneous

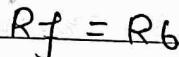
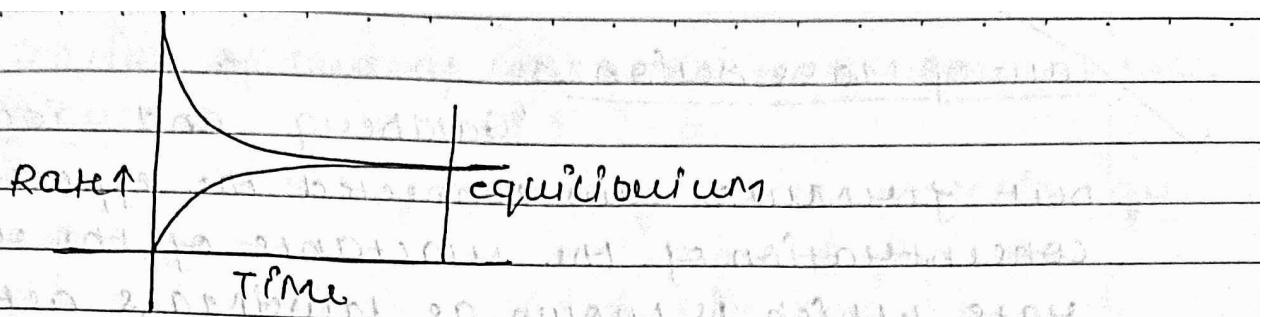
The reversible reaction in which more than one phase is present i.e. all the reactant and products are in the different physical state.

AS -



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.



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

Law of Mass Action

'Guldberg and Waage'

put forward a law connecting 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 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.



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

$$R_f = R_b$$

$$k_f [A][B] = k_b [C][D]$$

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

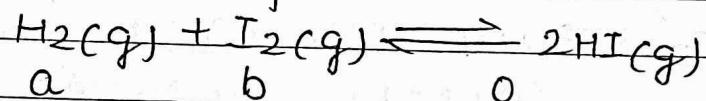
$$\boxed{\frac{k_f}{k_b} = K_c}$$

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 -



$t=0 \quad a \quad b \quad 0$

$2x \quad (a-x) \quad (b-x)$

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 mole of I_2 react to form $2x$ mole of HI .

Molar concentration at equilibrium.

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

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

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

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

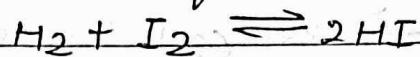
$$K_C = \frac{(2x/V)^2}{(a-x)/V \cdot (b-x)/V}$$

$$\frac{(a-x)(b-x)}{V^2}$$

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

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

Example - 16 ml of H_2 and 18 ml of I_2 combined together to form 26 ml of HI at $444^\circ C$. Calculate the equilibrium constant of reaction.



$$K_C = \frac{4 \times 13 \times 13}{(16-13)(18-13)}$$

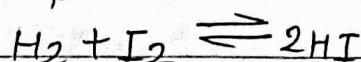
$$= 4 \times 13 \times 13 / (3 \times 5)$$

$$= 4 \times 169 / 15$$

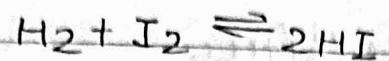
$$= 676 / 15$$

$$= 45.06$$

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 established.



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.



$$t=0 \quad 0.1 \quad 0 \quad 0$$

$$t=t \quad (0.1-x) \quad (0.1-x) \quad 2x$$

Given that

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

$$x = 0.1 - 0.02$$

$$x = 0.08$$

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

$$(a-x)(b-x)$$

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

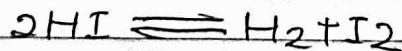
$$K_C = \frac{4x(0.0064)}{(0.02)(0.02)}$$

$$K_C = \frac{4x(0.0064)}{(0.0004)}$$

$$K_C = 64$$

Sealed

II- Let a moles of HI are taken in a shield bulb of volume V are heated at $444^\circ C$. At equilibrium x moles of HI are dissociated to form x mole of H_2 and x mole of I_2 .



$$t=0 \quad a \quad 0 \quad 0$$

$$t=t \quad (a-x) \quad x/2 \quad x/2$$

Molar concentration at equilibrium are-

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

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

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

5. Apply law of mass action -

$$K_C = [H_2][I_2]$$

$$[HI]^2$$

$$K_C = \left(\frac{x}{2v}\right) \left(\frac{x}{2v}\right)$$

$$\left(\frac{x(a-x)}{v}\right)^2$$

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

Example -

The degree of dissociation of HI at 400°C is 22% calculate the number of moles of HI, H₂ and I₂ at equilibrium if the number of moles at start is 2.4.



$$\begin{array}{l} t = t \\ t = t \\ t = t \end{array} \quad \begin{array}{l} (a-x) \\ a(x/2) \\ a(x/2) \end{array} \quad \begin{array}{l} a(1-x) \\ a(x/2) \\ a(x/2) \end{array}$$

$$x = 22\%$$

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

$$[HI] = 0(1-x)$$

$$= 2.4(1-0.22)$$

$$= 2.4 \times 0.78$$

$$= 1.872$$

$$\begin{aligned}
 [H_2] &= a(x/2) \\
 &= 2 \cdot 4 \left(\frac{0.22}{2} \right) \\
 &= 2 \cdot 4 \times 0.11 \\
 &= 0.264
 \end{aligned}$$

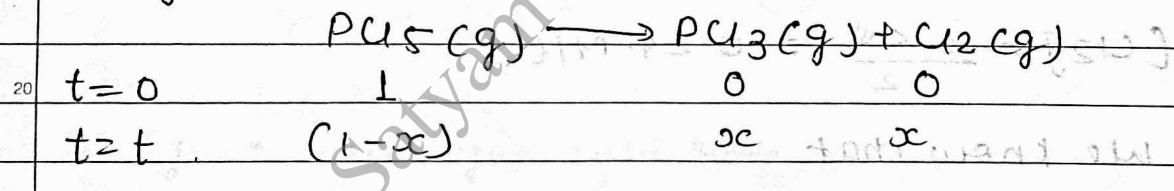
$$\begin{aligned}
 [I_2] &= a(x/2) \\
 &= 2 \cdot 4 \times 0.11 \\
 &= 0.264
 \end{aligned}$$

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 -



Molar concentration at equilibrium

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

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

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

Apply law of mass action

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

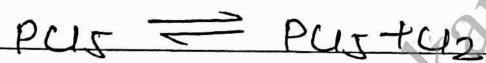
$$K_C = \frac{(x/V)(x/V)}{P_C(1-x)/V}$$

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

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

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.



$$[\text{PCl}_5] = \frac{0.72}{2} = 0.36 \text{ M/l}$$

$$[\text{PCl}_3] = \frac{0.48}{2} = 0.24 \text{ M/l}$$

$$[\text{Cl}_2] = \frac{0.48}{2} = 0.24 \text{ M/l}$$

We know that

$$K_C = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

$$= \frac{(0.24)(0.24)}{0.36} = [0.97]$$

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

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

$$K_C = 0.16$$

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

Relation b/w K_p & K_c -

When active masses of reactants and products in a chemical reaction are expressed in a gram-mole/liter equilibrium constant is represented as K_c . 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 K_p .

Now we consider following gaseous reaction.



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \textcircled{1}$$

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad \textcircled{2}$$

from ideal gas equation

$$PV = nRT$$

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

Thus

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

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

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

$$K_C = \frac{(PC)^c}{(RT)} \frac{(PD)^d}{(RT)}$$

$$\frac{(PA)^a}{(RT)} \frac{(PB)^b}{(RT)}$$

$$K_C = \frac{(PC)^c}{(PA)^a} \frac{(PD)^d}{(PB)^b} \times \frac{(1/RT)^{c+d}}{(1/RT)^{a+b}}$$

$$K_C = \frac{(PC)^c}{(PA)^a} \frac{(PD)^d}{(PB)^b} \cdot (RT)^{(a+b)-(c+d)}$$

$$K_C = K_P (RT)^{(c+d)-(a+b)} \left\{ \text{from eq 4} \right\}$$

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

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

Ex- The value of K_p at $400^\circ C$ for the reaction $2H_2O + 2Cl_2 \rightleftharpoons 4HCl + O_2$ is 0.035 atm. Calculate the value of K_c for reaction.

$$0.0821$$

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

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

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

$$K_C = \frac{0.035}{55.2883}$$

$$K_C = 6.334 \times 10^{-4}$$

Factors 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

$$\log \frac{K_P_2}{K_P_1} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

where —

ΔH = Heat of reaction at constant temperature

K_P_1 = equilibrium constant at constant temperature T_1

K_P_2 = equilibrium constant at constant temperature T_2

Mode of representing the reaction

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

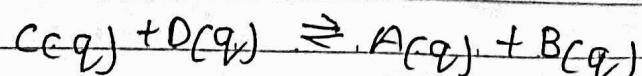
Let's consider the following general reversible reaction



Applying the law of mass action —

$$K_C = \frac{[C][D]}{[A][B]} \quad \textcircled{1}$$

When —



Applying the law of mass action

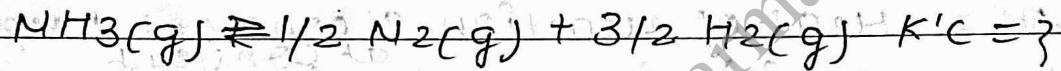
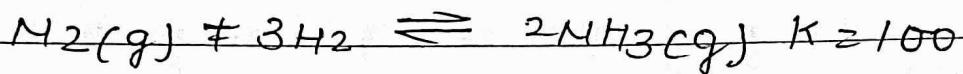
$$K'c = [A][B]$$

$$[C][D]$$

(11)

comparing equ ① & ⑪ we get

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



$$Kc = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad (1)$$

$$Kc = 100$$

$$K'c = \frac{[N_2]^{1/2}[H_2]^{3/2}}{[NH_3]} \quad (11)$$

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

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

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

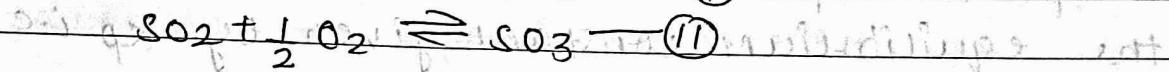
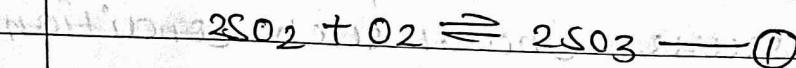
$$K'c = 0.1$$

$$\frac{[O_2][F_2]}{[OF_2]^2}$$

$$(p_B + p_A) \leq (p_B + p_C)$$

Mode of representing stoichiometry of the chemical reaction -

When a reversible reaction is represented by two or more stoichiometric equations the magnitude of their equilibrium constants are different. e.g -



equilibrium constant (K_C) for equation $\textcircled{1}$

$$K_C = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} \quad \textcircled{111}$$

thus

$$K'_C = \frac{[\text{SO}_3]}{[\text{SO}_2] [\text{O}_2]^{1/2}} \quad \textcircled{1111}$$

Comparing eqn $\textcircled{1}$ and $\textcircled{1111}$ we get

$$K'_C = \sqrt{K_C}$$

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 -

$\Delta n = -$ forward reaction
 $\Delta n = +$ backward reaction



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

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

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

Reaction quotient or mass action ratio

Let's consider reaction



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

Note -

i - $K_C = Q$ (equilibrium)

ii - $> K_C$ (forward reaction)

iii - $< K_C$ (backward reaction)

Le Chatelier's Principle

According to this principle,

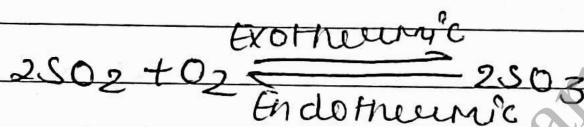
If a system at equilibrium is subjected to a change of concentration pressure or temperature. The equilibrium shift in the

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 the direction that produced smaller number of moles of gases and a decrease in pressure favours the opposite reaction.

II - Effect of temperature -

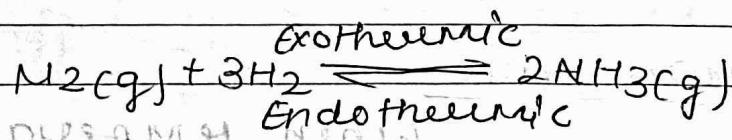


When temperature increase - backward

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.



Temperature increase - backward

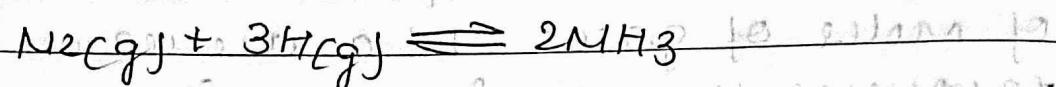
Temperature decrease - forward

III - Change in concentration -

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

towards forward direction.

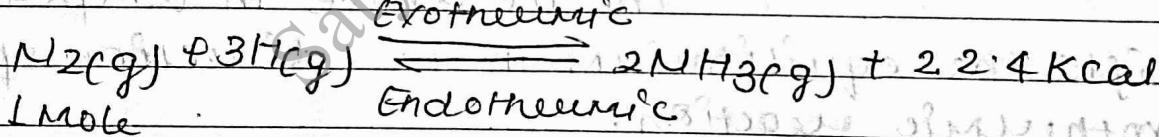
The increase of the concentration of any of the products shift the equilibrium towards backward direction. e.g. in the formation of NH_3 -



10 Reactant concentration

Application of Le Chatelier's principle -

Formation of SO_3 -



1 Mole

1- Effect of temperature -

When temperature at equilibrium is raised the equilibrium is placed 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 with backward

reaction is endothermic.

11- Effect of pressure on change of volume -

According to this law-

Pressure increase or volume decrease equilibrium shifts forward direction.

Pressure decrease or volume increase equilibrium shifts backward direction.

10

Formation of sulphur di-

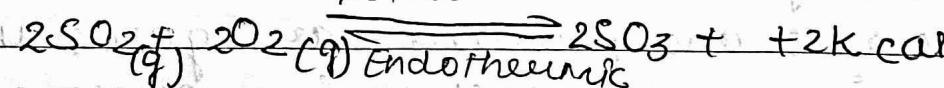
change in concentration -

15 Reactant concentration increase - Equilibrium shifts forward direction.

Reactant concentration decrease - Equilibrium shifts backward direction.

20

Formation of SO_3 -



25

1- Effect of temperature -

Temperature increase - Equilibrium shifts backward direction -

30

Temperature decrease - Equilibrium shifts forward direction.

Effect of pressure on change in volume

Pressure increase on volume decrease —

Equilibrium shifts forward direction.

Pressure decrease on 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 on vant Hoff exo-thermic

The effect of temperature on chemical equilibrium can be determined 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 —

$$\Delta G^\circ = -R \ln K_B T \quad \text{--- (1)}$$

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

$$\left[\frac{d(\Delta G^\circ)}{dT} \right]_P = -R \ln k_P - RT \left[\frac{d(\ln k_P)}{dT} \right]_P \quad \text{--- (1)}$$

multiplying equation ① with (T)

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

From equation ① & ② we get —

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

from gibb's helmholtz energy

$$\Delta G^\circ = \Delta H^\circ + T \left[\frac{d(\Delta G^\circ)}{dT} \right]_P \quad \text{--- (IV)}$$

From equation ③ & ④ we get

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

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

This equ is also known as vant' Hoff Isochores.

Vant' Hoff equation or vant' Hoff Isochore in terms of K_C —

we know that

$$K_P = K_C (RT)^{\Delta H}$$

taking logarithm of above equation

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

$$\ln K_p = \ln K_c + \Delta n \ln RT$$

Differentiating above equation

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

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

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

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

$$\left. \begin{aligned} \Delta h &= \Delta E + \Delta n RT \\ \Delta h^\circ &= \Delta E^\circ + \Delta n RT \\ \Delta h^\circ - \Delta n RT &= \Delta E^\circ \end{aligned} \right\}$$

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

This equation is also known as van't Hoff equation or van't Hoff isochore with respect to K_c .