

## Relation between S, U, H:-

From 1st law of TD,  $q = \Delta U + W$

For an infinitesimal small change,

$$dq = dU + dW$$

If only mechanical work is involved,

$$dq_{rev} = dU + pdV$$

$$\therefore \boxed{TdS = dU + pdV} \quad [\text{From 2nd law, } \frac{dq_{rev}}{T} = dS]$$

Now,  $H = U + PV$

$$dH = dU + pdV + Vdp$$

$$= dq_{rev} + Vdp$$

$$\boxed{dH = TdS + Vdp}$$

## Spontaneous process:-

A process which proceeds on its own accord, without any outside assistance, is called spontaneous process.

## Factors responsible for spontaneity of a rxn:-

### (a) Tendency to attain maximum randomness:-

$$\Delta S > 0$$

$$\Delta S < 0 \rightarrow \text{for non-spontaneous process}$$

example:- Solid  $\rightarrow$  Liquid ( $\Delta S > 0$ )

Liquid  $\rightarrow$  gas ( $\Delta S > 0$ )

Limitation:- Liquification of gas ( $\Delta S < 0$ )

Solidification of liquid ( $\Delta S < 0$ )

Hence, attaining maximum randomness is not the sole criteria for a spontaneous process.

### (b) Tendency to attain minimum ~~enthalpy~~ energy (enthalpy):-

Example:- Heat flows from hot body to ~~cold~~ cold body to attain minimum energy ( $\Delta H = -ve$ )

Exothermic rxn ( $\Delta H = -ve$ )

Limitations:- Endothermic rxns ~~(exothermic)~~

such as melting of ice ( $\Delta H = +ve$ )  
vap. of water ( $\Delta H = +ve$ )

Hence, attaining minimum enthalpy is not the sole criteria for spontaneity.

Thus, spontaneous process depends on two factors,

- ① tendency to attain minimum enthalpy
- ② " " " maximum randomness,

Free-energy Concept:-

- ① Work function or Helmholtz free energy

$$A = U - TS$$

- ② Gibb's free energy  $G = H - TS$

Property:- ① State function.

- ②  $dA, dG$  exact differentials.
- ③ Extensive property.
- ④  $\oint dA = 0 ; \oint dG \neq 0$
- ⑤ Absolute value can't be determined.

Relation between A and G and their changes:-

$$\begin{aligned} G &= H - TS \\ &= (U + PV) - TS = (U - TS) + PV \end{aligned}$$

$$\therefore \boxed{G = A + TS}$$

Let us consider, a system changes from state I to state II at constant ~~constant~~ temperature T.

$$\therefore \Delta G = G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1)$$

$$\boxed{\Delta G = \Delta H - T\Delta S} \quad [\text{at Const. } T]$$

$$\therefore \Delta G = (\Delta U + P\Delta V) - T\Delta S$$

[at constant temp. and pressure]

For a very small change,

$$dG = dH - TdS$$

(at constant temperature).

$$A = U - TS$$

Consider a system changes from State I to State II at constant temperature.

$$\therefore \Delta A = A_2 - A_1 = (U_2 - TS_2) - (U_1 - TS_1)$$

$$= \Delta U - T\Delta S$$

$$\therefore \boxed{\Delta A = \Delta U - T\Delta S}$$

For a very small change (rev. process).

$$dA = du - TdS$$

(at constant Temp.)

Meaning of A and G:-

$$\text{Now, } \Delta A_T = \Delta U - T\Delta S$$

$$= (q_{rev} + w_{rev}) - T\Delta S$$

$$= q_{rev} + w_{rev} - q_{rev}$$

From 1st law,

~~$q + w$~~

$$\Delta U = q + w$$

~~$\therefore \Delta A_T = -w_{rev} = +w_{rev}$~~

So, decrease in A at constant Temp. gives the maximum work done. as the process carried out reversibly. Hence, the function A is termed as work function.

$$\text{Now, } \Delta G_T = \Delta H - T\Delta S$$

$$= \Delta U + P\Delta V + V\Delta P - T\Delta S$$

$$= \Delta A + P\Delta V + V\Delta P$$

$$\therefore \Delta G_{T,P} = \Delta A + P\Delta V = -w_{rev} + P\Delta V, \text{ Hence,}$$

~~$\Rightarrow -\Delta G_{T,P} = w_{rev} - P\Delta V$~~

$$\therefore \Delta G_{T,P} = -w_{rev} - P\Delta V$$

Thus, decrease in free energy

$$\begin{aligned} &= \text{max work obtainable} - \text{mechanical work} \\ &\quad \text{done at constant pressure } P \\ &= \text{non-mechanical work} \end{aligned}$$

Thus,  $-AG$  is a measure of maximum net useful (non-mechanical work) from the system at const. T and P.

$$\text{Thus, net or useful work} = -AG = W_{rev} - P\Delta V$$

$$\text{If } P\Delta V = 0; \text{ mechanical work} = 0$$

$$\therefore \boxed{dA = AG}$$

### Variation of A with temp. and Volume

#### ① Variation of A with temp. T at Constant Volume

$$\text{We know, } A = U - TS$$

$$\therefore dA = dU - TdS - SdT$$

$$= dq_{rev} - dw - TdS - SdT$$

$$= TdS - Pdv - TdS - SdT \quad [\text{Consider only mechanical work done}]$$

$$\boxed{dA = -Pdv - SdT} \rightarrow ①$$

At Constant volume,  $dv = 0$

$$\therefore dA_V = -SdT$$

$$\Rightarrow \boxed{\left(\frac{\partial A}{\partial T}\right)_V = -S} \rightarrow ②$$

Change in A with temp. T at Isochoric condition represents the decrease in entropy of the system.

Variation of A with volume at constant Temp.  
at Constant temp.  $dT=0$

$$\therefore dA = -pdv$$

$$\Rightarrow \boxed{\left(\frac{\partial A}{\partial V}\right)_T = -p} \quad \rightarrow ③$$

Again from eqn ①,

$$dA = -pdv - SdT$$

$$dT = -pdv$$

$$\therefore \int dA_T = - \int_{V_1}^{V_2} pdv = - \int_{V_1}^{V_2} \frac{RT}{V} dv$$

$$\therefore \boxed{dA = RT \ln \frac{V_1}{V_2}} = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{P_2}{P_1}$$

Variation of G with temp. and pressure. → ④

④ ~~Varied~~

$$G = H - TS$$

//

$$dG = dH - TdS - SdT$$

$$= du + pdv + vdp - TdS - SdT$$

$$= dq_{rev} + vdp - TdS - SdT$$

$$\Rightarrow TdS + vdp - TdS - SdT$$

$$= vdp - SdT \rightarrow ⑤$$

At Constant pressure,  $dp = 0$

$$\therefore dG_p = - SdT$$

$$\Rightarrow \boxed{\left(\frac{\partial G}{\partial T}\right)_p = -S} \rightarrow ⑥$$

At Constant Temp,  $dT = 0$

$$\therefore dG_T = vdp$$

$$\Rightarrow \boxed{\left(\frac{\partial G}{\partial p}\right)_T = V} \rightarrow ⑦$$

Again from eqn ⑤.

$$dA = Vdp - SdT$$

$$dG_T = Vdp$$

$$\int_{G_1}^{G_2} dG_T = \int_{P_1}^{P_2} \frac{nRT}{P} dP$$

$$\therefore \Delta G = G_2 - G_1 = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2} \rightarrow ⑧$$

Now, we know,

$$-S = \left(\frac{\partial A}{\partial T}\right)_V ; \quad -S = \left(\frac{\partial G}{\partial T}\right)_P$$

Hence,

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

$$\frac{\partial A}{\partial T} = \frac{U}{T^2} + \frac{1}{T} \left(\frac{\partial A}{\partial T}\right)_V$$

$$\Rightarrow -\frac{\partial A}{\partial T} + \frac{1}{T} \left(\frac{\partial A}{\partial T}\right)_V = -\frac{U}{T^2}$$

$$\Rightarrow \boxed{\frac{d}{dT} \left(\frac{A}{T}\right)_V = -\frac{U}{T^2}}$$

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

$$\frac{\partial G}{\partial T} = \frac{H}{T^2} + \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P$$

$$\Rightarrow -\frac{\partial G}{\partial T} + \frac{1}{T} \cdot \left(\frac{\partial G}{\partial T}\right)_P = -\frac{H}{T^2}$$

$$\Rightarrow \boxed{\frac{d}{dT} \left(\frac{G}{T}\right)_P = -\frac{H}{T^2}}$$

$$\Delta A = \Delta U + T \left[ \frac{\partial(4A)}{\partial T} \right]_V$$

$$\frac{d}{dT} \left(\frac{\Delta A}{T}\right)_V = -\frac{\Delta U}{T^2}$$

$$\Delta G = \Delta H + T \left[ \frac{\partial(4G)}{\partial T} \right]_P$$

$$\frac{d}{dT} \left(\frac{\Delta G}{T}\right)_P = -\frac{\Delta H}{T^2}$$

Different form of Gibbs Helmholtz eqn

Maxwell relation :-

$$① dU = TdS - PdV \quad ② dA = \cancel{V} - PdV - SdT$$

$$③ dH = TdS + VdP \quad ④ dG = VdP - SdT$$

Using these equations, four relations known as Maxwell's relation can be derived.

From eqn ①

$$dU = TdS - PdV$$

$$\therefore \left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\therefore \frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_S \quad \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_V$$

Since,  $dU$  is an exact differential,

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$$

$$\therefore \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \rightarrow ①$$

From eqn ③

$$dH = TdS + VdP$$

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

$$\left(\frac{\partial H}{\partial P}\right)_S = V$$

$$\therefore \frac{\partial^2 H}{\partial P \partial S} = \left(\frac{\partial T}{\partial P}\right)_S$$

$$\frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial V}{\partial S}\right)_P$$

Since,  $dH$  is an exact differential,

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \rightarrow ②$$

From eq<sup>n</sup> ③

$$dA = -pdv - SdT$$

$$\therefore \underbrace{\left(\frac{\partial A}{\partial v}\right)_T}_{= -p} = -p \quad \left| \quad \underbrace{\left(\frac{\partial A}{\partial T}\right)_v}_{= -S} = -S$$

$$\frac{\partial^2 A}{\partial T \partial v} = -\left(\frac{\partial p}{\partial T}\right)_v \quad \left| \quad \frac{\partial^2 A}{\partial v \partial T} = -\left(\frac{\partial S}{\partial v}\right)_T$$

$$\boxed{\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial S}{\partial v}\right)_T} \rightarrow ③$$

From eq<sup>n</sup> ④,  $dG = vdp - SdT$

$$\therefore \underbrace{\left(\frac{\partial G}{\partial p}\right)_T}_{= v} = v \quad \left| \quad \underbrace{\left(\frac{\partial G}{\partial T}\right)_p}_{= -S} = -S$$

$$\therefore \frac{\partial^2 G}{\partial T \partial p} = \left(\frac{\partial v}{\partial T}\right)_p \quad \left| \quad \frac{\partial^2 G}{\partial p \partial T} = -\left(\frac{\partial S}{\partial p}\right)_T$$

$$\boxed{\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T} \rightarrow ④$$

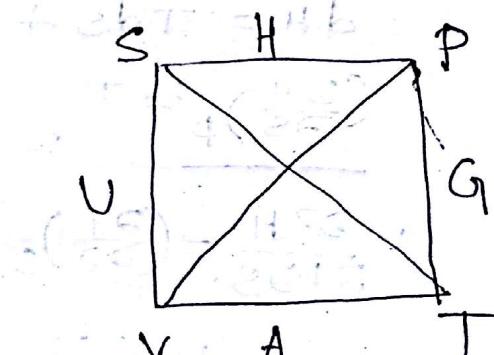
We get also different form

$$\left(\frac{\partial U}{\partial S}\right)_V = T = \left(\frac{\partial H}{\partial S}\right)_P$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P = \left(\frac{\partial A}{\partial V}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V = \left(\frac{\partial G}{\partial P}\right)_T$$

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



$$U = f(S, V)$$

$$H = f(S, P)$$

$$G = f(P, T)$$

$$A = f(V, T)$$

$$du = Tds - pdv$$

$$U = f(s, v)$$

$$dH = Tds + vdp$$

$$H = f(s, p)$$

$$dG = Vdp - sdt$$

$$G = f(p, t)$$

$$dA = -pdv - sdt$$

$$A = f(v, t)$$

Now,  $du = Tds - pdv$

$$\therefore \left(\frac{\partial U}{\partial S}\right)_V = \textcircled{1} \quad \left|\quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\therefore \frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial I}{\partial V}\right)_S \quad \left|\quad \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\text{since, } \frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

Hence,  $\boxed{\left(\frac{\partial I}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \rightarrow \textcircled{U}$

$$dH = Tds + vdp$$

$$\therefore \left(\frac{\partial H}{\partial S}\right)_P = \textcircled{1} \quad \left|\quad \left(\frac{\partial H}{\partial P}\right)_S = \textcircled{V}$$

$$\therefore \frac{\partial^2 H}{\partial P \partial S} = \left(\frac{\partial I}{\partial P}\right)_S \quad \left|\quad \frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial V}{\partial S}\right)_P$$

Hence,  $\boxed{\left(\frac{\partial I}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \rightarrow \textcircled{H}$

Now,  $dG = Vdp - sdt$

$$\therefore \left(\frac{\partial G}{\partial P}\right)_T = \textcircled{1} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\therefore \frac{\partial^2 G}{\partial T \partial P} = \left(\frac{\partial I}{\partial T}\right)_P \quad \left|\quad \frac{\partial^2 G}{\partial P \partial T} = -\left(\frac{\partial S}{\partial P}\right)_T$$

Hence,  $\boxed{\left(\frac{\partial I}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \rightarrow \textcircled{G}$

$$dT = -pdv - SdT$$

$$\therefore \left(\frac{\partial A}{\partial v}\right)_T = -P$$

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

$$\Rightarrow \frac{\partial^2 A}{\partial T \partial V} = -\left(\frac{\partial P}{\partial T}\right)_V \quad \left| \quad \frac{\partial^2 A}{\partial V \partial T} = -\left(\frac{\partial S}{\partial V}\right)_T$$

Hence,

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

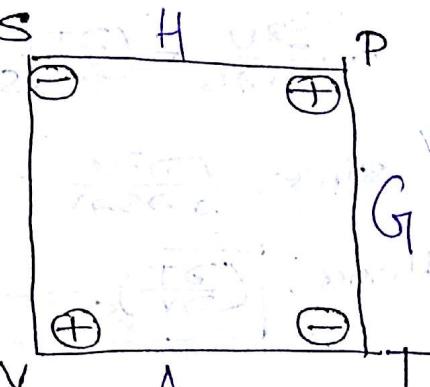
Thus, four Maxwell's relations are -

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

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

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

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



Here,

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

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

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

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

Tricks to keep  
remember the  
maxwell relation

we have also got the relation

$$\boxed{\left(\frac{\partial U}{\partial S}\right)_V = T = \left(\frac{\partial H}{\partial S}\right)_P}$$

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

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

$$\boxed{\left(\frac{\partial H}{\partial P}\right)_S = V = \left(\frac{\partial G}{\partial P}\right)_T}$$

$$\textcircled{b} \quad G = H - TS$$

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

$$\frac{G}{T^2} = \frac{H}{T^2} + \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_P$$

$$\Rightarrow \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_P - \frac{G}{T^2} = - \frac{H}{T^2}$$

$$\Rightarrow \boxed{\frac{d}{dT} \left( \frac{G}{T} \right)_P = - \frac{H}{T^2}}$$

$$A = V - TS$$

$$\boxed{A = V + T \cdot \left( \frac{\partial A}{\partial T} \right)_V}$$

$$\frac{A}{T^2} = \frac{V}{T^2} + \frac{1}{T} \left( \frac{\partial A}{\partial T} \right)_V$$

$$\frac{1}{T} \left( \frac{\partial A}{\partial T} \right)_V - \frac{A}{T^2} = - \frac{V}{T^2}$$

$$\Rightarrow \boxed{\frac{d}{dT} \left( \frac{A}{T} \right)_V = - \frac{V}{T^2}}$$

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

$$\frac{d}{dT} \left( \frac{\Delta G}{T} \right)_P = - \frac{\Delta H}{T^2}$$

↓

Gibbs-Helmholtz eqn

$$\textcircled{b} \quad \Delta A = \Delta V + T \cdot \left[ \frac{\partial (\Delta A)}{\partial T} \right]_V$$

$$\frac{d}{dT} \left( \frac{\Delta A}{T} \right)_V = - \frac{\Delta V}{T^2}$$

Gibbs-Helmholtz eqn.

Free energy change and Criteria of spontaneity of a process:- In a chemical system,

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$$\Delta G = \Delta H - T \Delta S \quad \textcircled{b}$$

$\Delta G < 0 \rightarrow$  spontaneous process

$\Delta G > 0 \rightarrow$  non-spontaneous

$\Delta G = 0 \rightarrow$  equilibrium

$\Delta H = -ve, \Delta S = +ve, \Delta G = -ve$

$\Delta H = +ve, \Delta S = +ve,$

$\Delta H = -ve, \Delta S = -ve,$

and  $\Delta A$  and  $\Delta S$

- ④ Calculate the free energy change when 5 moles of an ideal gas expands reversibly and isothermally at 300 K from 1 litre to 10 litres.

$$\text{Ans. } \Delta S = nR \ln \frac{V_2}{V_1} = 5 \times 8.314 \times \ln \frac{10}{1} \text{ J.K}^{-1}$$

$$= 95.718 \text{ J.K}^{-1}$$

$$\Delta G = nRT \ln \frac{V_1}{V_2} = 5 \times 8.314 \times 300 \ln \frac{1}{10} \text{ J.K}^{-1}$$

$$= -28.715 \text{ kJ}$$

$$\therefore \Delta A = nRT \ln \frac{V_1}{V_2} = -28.715 \text{ J}$$

- ④ Calculate the free energy change,  $\Delta A$  and  $\Delta S$  when two moles of an ideal gas expands reversibly and isothermally at 300 K from a pressure of 1 atm to 0.1 atm.

$$\text{Soln: } \Delta S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2} = 2 \times 8.314 \times \ln \frac{1}{0.1} \text{ J.K}^{-1}$$

$$= 38.287 \text{ J.K}^{-1}$$

$$\Delta G = nRT \ln \frac{P_2}{P_1} = 2 \times 8.314 \times 300 \ln \frac{0.1}{1} \text{ J.K}^{-1}$$

$$= -11.486 \text{ kJ}$$

$$\Delta A = nRT \ln \frac{P_2}{P_1} = 2 \times 8.314 \times 300 \ln \frac{0.1}{1} \text{ J.K}^{-1}$$

$$= -11.486 \text{ kJ}$$

- ⑤ Calculate change in entropy accompanying the heating of 1 mole of He gas. Assumed ideal behaviour. Temp. changes from 298 K to 1000 K at constant pressure.  $C_V = \frac{3}{2} R$

$$\Delta S = n\bar{C}_p \ln \frac{T_2}{T_1} = n(C_V + R) \ln \frac{T_2}{T_1} = n \cdot \frac{5}{2} R \ln \frac{T_2}{T_1}$$

$$= 1 \times \frac{5}{2} \times 8.314 \times \ln \frac{1000}{298} \text{ J.K}^{-1}$$

$$\approx 25.17 \text{ J.K}^{-1}$$

## Phase equilibria

①

### Clapeyron eqn.

When a pure substance is present in two phases at equilibrium.

$$\Delta G = 0$$

$$\Rightarrow G_2 - G_1 = 0$$

$$\Rightarrow G_2 = G_1$$

$$\Rightarrow dG_2 = dG_1$$

$$\Rightarrow V_2 dP - S_2 dT = V_1 dP - S_1 dT$$

$$\Rightarrow (V_2 - V_1) dP = (S_2 - S_1) dT$$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{4S}{4V}} \rightarrow \text{Clapeyron equation.}$$

This eqn can be applied to various phase equilibrium

### ① Liquid-vap. Equilibrium:-

$$\text{Liq} \rightleftharpoons \text{Vap.}$$

$$\frac{dp}{dT} = \frac{4S}{4V} = \frac{4H_{\text{vap}}}{T_b(V_g - V_l)} = +ve.$$

At this equilibrium, as the temp. increases, equilibrium vap. pressure of the liquid also increases.

### ② Solid-vap. Equilibrium:- Solid $\rightleftharpoons$ Vap.

$$\frac{dp}{dT} = \frac{4S}{4V} = \frac{4H_{\text{sub}}}{T_s(V_g - V_s)} = +ve.$$

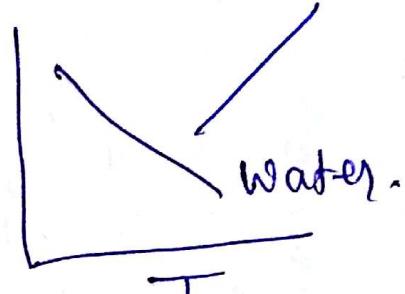
Hence, increase in temp. Increases the ~~to~~ equilibrium  
vap. pressure of the solid.

(2)

### (iii) Solid - liquid equilibrium:-

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H_{fus}}{T_{fus}(V_l - V_s)}$$

P



For most cases,  $\frac{dp}{dT} = \text{pos}$ , as  $V_l > V_s$ .

Hence, ~~an~~ increase in pressure increases the melting point of the solid.

For Water,  $V_s < V_l$ .  $\frac{dp}{dT} = -V_s$ .

Thus, increase in pressure ~~decreases~~ the melting point of ~~water~~ ice.

Damius - Clapeyron eqn:- Integrated form of Clapeyron eqn.

~~solid. liq~~  $\equiv$  vap.

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H_{vap}}{T_b(V_g - V_l)} \approx \frac{\Delta H_{vap}}{T_b, V_g}$$

~~not~~

$$= \frac{\Delta H_{vap}}{T \cdot \frac{nRT}{P}}$$

[vap behave ideally]

$$\Rightarrow \frac{dp}{P} = \frac{4H_{\text{vap}}}{nR} \cdot \frac{dT}{T^2} \rightarrow \textcircled{1} \quad (3)$$

$$\Rightarrow \int_{P_1}^{P_2} \frac{dp}{P} = \frac{4H_{\text{vap}}}{R} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Rightarrow \boxed{\ln \frac{P_2}{P_1} = \frac{4H}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]} \rightarrow \textcircled{1}$$

$$\Rightarrow \boxed{\frac{d \ln P}{dT} = \frac{4H}{RT^2}} \rightarrow \textcircled{III}$$

Bq<sup>n</sup>  $\textcircled{1}$  and  $\textcircled{III}$  are known as Clapeyron equation.

$\textcircled{9}$  The vap. pressure of water at  $95^\circ\text{C}$  is  $634 \text{ mm Hg}$  what would be the vap. pressure of water at  $100^\circ\text{C}$ ? The heat of vap. of water is  $40.593 \text{ KJ/mol}$ .

Sol<sup>n</sup>  $T_1 = 95^\circ\text{C} = 368 \text{ K}$   $4H_{\text{vap}} = 40.593 \text{ KJ/mol}$   
 $T_2 = 100^\circ\text{C} = 373 \text{ K}$   
 $P_1 = 634 \text{ mm Hg}$   $\therefore \ln \frac{P_2}{P_1} = \frac{40.593 \times 10^3}{8.314} \left[ \frac{5}{368 \times 373} \right]$   
 $P_2 = ?$   $\Rightarrow \boxed{P_2 = 759.8 \text{ mm Hg}}$

⑧ The vap. pressure of water at  $95^{\circ}\text{C}$  and  $100^{\circ}\text{C}$  were found to be 634 mmHg and 760 mmHg. What is the molar heat of vap. of water?

$$\underline{\text{Soln}} : \ln \frac{P_2}{P_1} = \frac{\bar{H}}{R} \cdot \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad (4)$$

$$\Rightarrow \ln \frac{760}{634} = \frac{\bar{H}}{8.314} \times \frac{5}{368 \times 373}$$

$$\Rightarrow \bar{H} = 40.593 \text{ kJ/mol.}$$

⑨ At  $100^{\circ}\text{C}$ , the sp. vol. of water and steam are 1 c.c. and 1673 c.c. respectively. Calculate the change in vap. pressure of the system if change in temp. of  $1^{\circ}$  takes place.

The molar heat of vap. of water is ~~40.589~~  $40.589 \text{ kJ/mol.}$

$$\underline{\text{Soln}} \quad \frac{dp}{dT} = \frac{\bar{H}_u}{T(V_g - V_l)} = \frac{40.589}{373 \times (18 - 1673)} = -\frac{40.589}{18 \times 10^{-3} \cdot 1673} \times 10^6 \text{ N/m}^2$$

$$dp = \frac{40589 \times 1}{373 \times (3014 - 18) \times 10^{-6}} = 0.00361 \times 10^6 \text{ N/m}^2$$

$$= 0.003561 \text{ atm} \quad (1 \text{ atm} = 101325 \text{ N/m}^2)$$

$$= 27.08 \text{ mmHg.}$$