Imp.

Gibb's energy and equilibrium constant :-

$$\Delta G = \Delta G^\circ + RT \ln Q$$
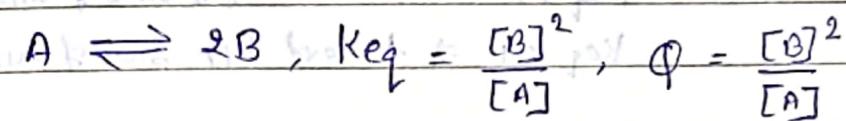
ΔG = Gibb's energy change at any condt.

ΔG° = G.E.C. under standard condition

R = U.G.C. $\longrightarrow \begin{cases} \frac{15}{3} \ (\Delta G = J) \\ 2 \ (\Delta G = cal.) \end{cases}$

T = Temp. (K)

Q = Reaction Quotient

$$A \rightleftharpoons 2B , \quad Keq = \frac{[B]^2}{[A]}, \quad Q = \frac{[B]^2}{[A]}$$

Keq	Q	Direction
① Constant	Variable	① $Q < keq \Rightarrow$ forward
② given	Calculate	② $Q = keq \Rightarrow$ eq.
③ Defined only at equilibrium	It is defined at any time.	③ $Q > keq \Rightarrow$ backward

at equilibrium $\quad \Delta G = 0 , \quad Q = keq.$
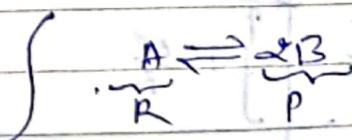
$$0 = \Delta G^\circ + RT \ln Keq$$

$$\boxed{\Delta G^\circ = -RT \ln Keq} \qquad \boxed{\Delta G^\circ = -2.303 \, RT \log keq}$$

$\begin{cases} \Delta G^\circ = 0 & keq = 1 \\ \Delta G^\circ < 0 & keq > 1 \\ \Delta G^\circ > 0 & keq < 1 \end{cases}$

$$\Delta G = -RT \ln keq + RT \ln Q$$

$$\boxed{\Delta G = RT \ln \left(\frac{Q}{keq}\right)}$$

$\begin{cases} A \rightleftharpoons 2B \\ \frac{}{R} \qquad P \end{cases}$
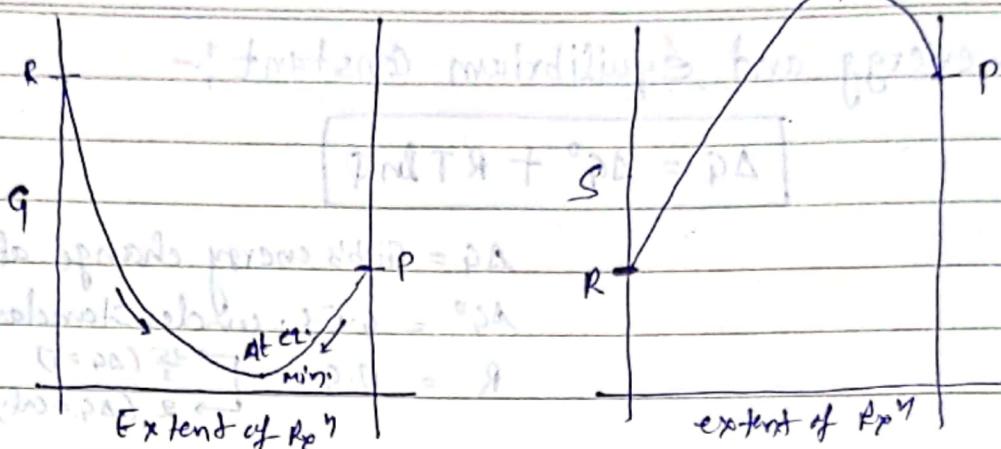
(i) $\quad Q = keq \Rightarrow \Delta G = 0$ (eq.)

(ii) $\quad Q < keq \Rightarrow \Delta G < 0$ (spontaneous)

(iii) $\quad Q > keq \Rightarrow \Delta G > 0$ (Non-spont.)

$K_{eq} = 1 \Rightarrow$ mid point (min/max.)

$K_{eq} > 1 \Rightarrow$ toward right side of mid (max/min)

$K_{eq} < 1 \Rightarrow$ toward left side of mid (min/max)

V.V. Imp.

Variation of K_{eq} with Temp :-

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad\text{———(1)}$$

$$\Delta G^0 = -RT \ln K_{eq} \quad\text{———(2)}$$

Compare.

$$-RT \ln K_{eq} = \Delta H^0 - T\Delta S^0$$

$$\ln K_{eq} = \frac{\Delta H^0}{-RT} - \frac{T\Delta S^0}{-RT}$$

$$\boxed{\underset{y}{\ln K_{eq}} = \underset{}{\frac{\Delta S^0}{R}} + \left(\frac{-\Delta H^0}{R}\right)\cdot\underset{x}{\frac{1}{T}}} \qquad y = c + mx$$

$\ln K_{eq}$
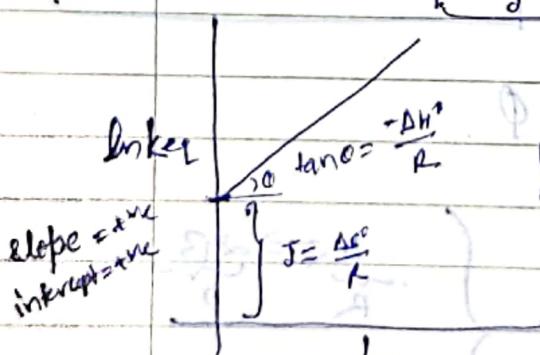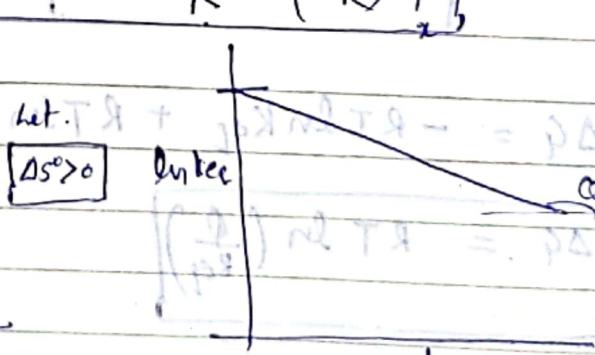
slope = +ve
intercept = +ve

$\tan\theta = \frac{-\Delta H^0}{R}$

$J = \frac{\Delta S^0}{R}$

$\frac{1}{T}$

(exothermic R^n)
($\Delta H < 0$)

Let. T ↑

$\Delta S^0 > 0$

$\ln K_{eq}$
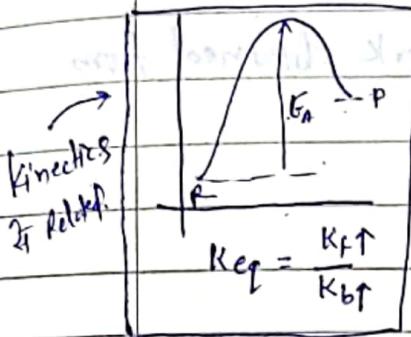
$\frac{1}{T}$

(endothermic R^n)
($\Delta H > 0$)

slope = -ve
Int = (+)ve
$\theta > 90°$

chemical equilibrium ⟹ Endo - high Temp $[T\uparrow, K_{eq}\uparrow]$

Exo - low temp. $[T\uparrow\ K_{eq}\downarrow]$

⟹ $\Delta S°$ and $\Delta H°$ are assumed to be independent from temp.

Kinetics & Related

$K_{eq} = \dfrac{K_f\uparrow}{K_b\uparrow}$

① $T = T_1$, $K_{eq} = K_1$

$$\ln k_1 = \frac{\Delta S°}{R} - \frac{\Delta H°}{R} \times \frac{1}{T_1} \quad\quad —(i)$$

② $T = T_2$, $K_{eq} = K_2$

$$\ln k_2 = \frac{\Delta S°}{R} - \frac{\Delta H°}{R} \times \frac{1}{T_2} \quad\quad —(ii)$$

$(ii) - (i)$

$$\ln k_2 - \ln k_1 = \left[\frac{\Delta S°}{R} - \frac{\Delta H°}{R} \times \frac{1}{T_2}\right] - \left[\frac{\Delta S°}{R} - \frac{\Delta H°}{R} \times \frac{1}{T_1}\right]$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{\Delta H°}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

(Kinetics से आयेगा) imp.

$$\boxed{\log \frac{k_2}{k_1} = \frac{\Delta H°}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

$\Delta H° \begin{cases} \nearrow\ cal\ (R=2) \\ \searrow\ J\ (R=\frac{25}{3}) \end{cases}$

Physical Significance of Gibb's Energy :-

$$\underbrace{G}_{\text{Useful energy}} = \underbrace{H}_{\substack{\text{Total}\\\text{energy}}} - \underbrace{TS}_{\text{useless energy}}$$

FLOT $dU = dq + (dw_{p-v} + \underline{dw_{non\,pv}})$

$dU - dq - dw_{pv} = dw_{non-pv}$

$dU - dq + Pdv = dw_{non-pv}$ $\boxed{dw_{p-v} = -Pdv}$

at const temp. and pressure for R.P.

$d(U+PV) - Tds = dw_{non-pv}$ $\left\{ds = \dfrac{dq_{rev.}}{T}\right\}$

$$dH - TdS = dW_{non-pv} \qquad [H = U + pv]$$

$$d(H - TS) = dW_{nm-pv}$$

$$\boxed{dG = dW_{nm-pv}} \qquad (G = H - TS)$$

Decrease in gibb's energy denotes useful work obtained from system.

formulae:-

$$\boxed{\begin{array}{l} \Delta G = \Delta G^\circ + RT \ln Q \\ \Delta G^\circ = -RT \ln K_{eq} \\ \Delta G = RT \ln \left(\dfrac{Q}{K_{eq}}\right) \end{array}}$$

Q. If eq. constant of a reversible Rₙ is 1 at 27°C then cal. ΔG° of the Rₙ?

$$\Delta G^\circ = -RT \ln K_{eq} = -2 \times 300 \times \ln 1$$

$$\boxed{\Delta G^\circ = 0}$$

at eq $\Delta G = 0$, $\Delta G^\circ = 0$ when $K_{eq} = 1$.

Q. If ΔG° of a Rev. Rₙ at 727°C is -4.606 K.cal/mole then cal value of K_{eq}.

Solⁿ

$$\begin{cases} \Delta G^\circ = 0 & K_{eq} = 1 \\ \Delta G^\circ < 0 & K_{eq} > 1 \\ \Delta G^\circ > 0 & K_{eq} < 1 \end{cases}$$

$$\boxed{\Delta G^\circ = -2.303 \, RT \log K_{eq}} \qquad \left\{ \ln x = 2.303 \log x \right\}$$

$$-4.606 \times 10^3 = -2.303 \times 2 \times 10^3 \log K_{eq}$$

$$\log K_{eq} = 1$$

$$K_{eq} = 10^1 = 10$$

Q. For a Rev. Rₙ $A_{(g)} \rightleftharpoons 2B_{(g)}$, $k_p = 100$ bar at 27°C if equilibrium constants P.P. of A and P.P. of B is 1 bar & 5 bar respectively then cal. value of ΔG and Predict the direction of Rₙ.

Sol? $Q_P = \dfrac{(P_B)^2}{P_A} = \dfrac{(5)^2}{1} = 25$ $Q_P < k_P \Rightarrow$ forward dir^n $(\Delta G, -ve \text{ मिलेगी})$

$$\Delta G = RT \ln\left(\dfrac{Q}{k_{eq}}\right)$$
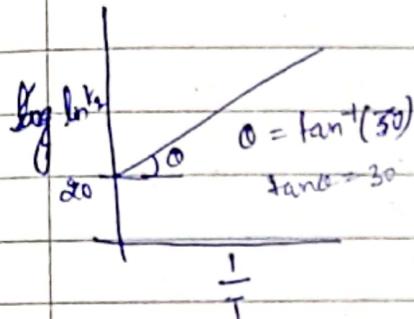
$$= 2 \times 300 \ln\left(\dfrac{25}{100}\right)$$ \qquad $\{\ln 2 = 0.693\}$

$$\Delta G = -600 \ln 4$$
$$\Delta G = -600 \times 2 \times 0.7 = -840 \text{ cal}$$

Q. Cal value of ΔS^0 and ΔH^0 from the following graph (in cal.)

Sol?

$$\ln k_{eq} = \underset{\underset{\underset{2}{m}}{c}}{\underset{y}{\dfrac{\Delta S^0}{R}}} + \left(\dfrac{-\Delta H^0}{R}\right) \times \dfrac{1}{T}$$

$\theta = \tan^{-1}(30)$

$\tan\theta = 30$

$\dfrac{\Delta S^0}{R} = 20 \Rightarrow \Delta S^0 = 20 \times 2 = 40 \text{ cal}$

$\dfrac{-\Delta H^0}{R} = 30 \Rightarrow -\Delta H^0 = 30 \times 2$

$\Delta H^0 = -30 \times 2 \text{ cal}$

(1) $A_{(g)} \rightleftharpoons 2B_{(g)}$ (2) $2B_{(g)} \rightleftharpoons A_{(g)}$
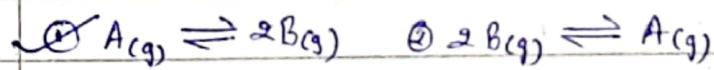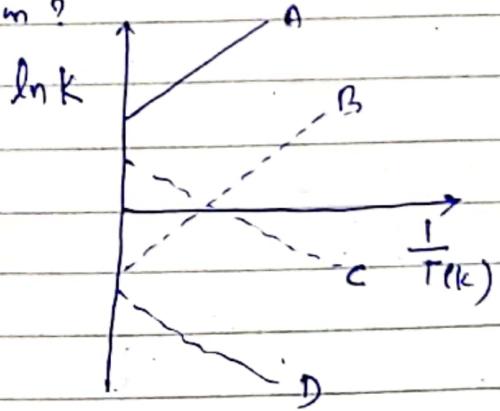
Q. which of the following lines correctly show the temp. dependence of equilibrium constant k for an exothermic Reaction?

(A) A and B
(B) B and C
(C) C and D
(D) A and D