Cal. of K from ΔG^0

$\therefore \Delta G^0 = -RT \ln K$ gives us a way to evaluate the value of K (eq^n const!) from std-free energy ΔG^0 data

(1) From std. free energy calculations ΔG_f^0 of the reactants & Products $\Delta G^0 = \sum \Delta G_f^0 (P) - \sum \Delta G_f^0 (R)$ where ΔG_f^0 for elements in their std state is taken as zero

(2) From ΔH^0 obtain calorimetrically or from Hess's law ΔS^0 from third law entropies
$$\Delta G^0 = \Delta H^0 - T\Delta S$$

(3) using statistical mechanics & certain information about ¶ molecule obtained from spectroscopic data

(4) From emf data using $\Delta G^0 = -nFE^0$

Variation of Equilibrium Const! with Temp
The eq^n const! K_p & Standard free energy of a general reaction $aA + bB \rightleftharpoons mN + nN$ are related as
$\Delta G^0 = -RT \ln K_p$ & $\Delta G^0 = (m\mu_M^0 + n\mu_N^0) - (a\mu_A^0 + b\mu_B^0)$
$-RT \ln K_p = (m\mu_M^0 + n\mu_N^0) - (a\mu_A^0 + b\mu_B^0)$
Diff. w.r.t temp at const!
$$\frac{d\ln K_p}{dT} = -\frac{1}{R}\left[\frac{m}{T}\left(\frac{\partial \mu_M^0}{\partial T}\right) + \frac{n\partial}{\partial T}\left(\frac{\mu_N^0}{N}\right)\right] -$$
$$\left(a\frac{\partial}{\partial T}\left(\frac{\mu_A^0}{T}\right) + b\frac{\partial}{\partial T}\left(\frac{\mu_B^0}{}\right)\right.$$

From Gibbs Helmholtz eq. $\frac{\partial}{\partial T}\left(\frac{\Delta G^\circ}{\partial T}\right) = -\frac{H_{im}}{T^2}$ (19)

$\frac{H_{im}}{T}$ is partial molar enthalpy of the substance in the ith standard state

$$\frac{d\ln k_p}{dT} = -\frac{1}{RT^2}\left[(-m H_{c,m}^\circ - n H_{N,m}^\circ) - (-a H_{A,m}^\circ - b H_{B,m}^\circ)\right]$$

$$= \frac{1}{RT^2}\left[\Sigma H^\circ(P) - \Sigma H^\circ(R)\right]$$

$$\frac{d\ln k_p}{dT} = \frac{1}{RT^2}\Delta H^\circ \qquad\qquad ①$$

This eq is called referred as van't Hoff eq. It relates the rate of change of eq^n const with temp to the heat of reaction. Sign of heat of reaction. As per the rate of change of eq^n const with temp, whether K will ↑ or ↓ depends upon the nature of reaction whether it is exothermic, endothermic or athermic

(17)(a) For exothermic reaction ΔH° is negative. R.H.S of eq ① is negative so with increase of temp, dT is +ve therefore to make R.H.S. +ve $d\ln k_p$ and k_p should be $-ve$ ie decrease

(b) When ΔH° is +ve, then $\ln k_p$ and k_p should +ve,↑ that means increase in equilibrium const means in increase in conc^n of products. That mean in endothermic reactions, formation of products is favoured with lowering of temp. That is why NH_3 is synthesized at low temp
$N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\Delta H^\circ = a94 kJ$

(20)

reaction ΔH° is positive, R.HS

... when ΔH or ΔE, then $\ln K_p$ and K_p should ... the ↑ that means increase in equilibrium const means ... increase in conc" of products. That ... known as endothermic reaction, formation of products is favoured with decreasing of Temp that is why NH_3 is synthesized at low temp

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H^\circ = -92 \, kJ$$

(29)

(3) for endothermic reaction, ΔH° is positive, K us of eq" is positive. So with increase of temp ΔT is positive should be K_p should increase K_p increase. In endothermic reaction, the formation of product is favoured with increase of temp

(4) for athermic reaction, ΔH° is zero, the eq" const K_p is independent of temperature.

Variation of K_c with Temp

$$RT \ln \left[K_c \left(\frac{c^\circ RT}{p^\circ} \right)^{\Delta \nu} \right] = -\Delta G^\circ$$

$$\ln K_c + \Delta \nu \ln T + \Delta \nu \ln \frac{c^\circ R}{p^\circ} = -\frac{\Delta G^\circ}{RT}$$

on differentiating w.r.t. T

$$\frac{d \ln K_c}{dT} + \frac{\Delta \nu}{T} + 0 = -\frac{1}{R} \frac{\partial}{\partial T} \left[\frac{\Delta A^\circ}{T} \right]$$

$$\frac{d \ln K_c}{dT} + \frac{\Delta \nu}{T} = \frac{\Delta H^\circ}{RT^2}$$

$$\frac{d \ln K_c}{dT} = \frac{\Delta H^\circ}{RT^2} - \frac{\Delta \nu}{T}$$

$$\frac{d \ln K_c}{dT} = \frac{\Delta H^\circ - \Delta \nu RT}{RT^2}$$

$$\Delta H^\circ = \Delta E^\circ + \Delta n RT \quad \text{for an ideal gas}$$
$$\Delta E^\circ = \Delta H^\circ - \Delta n RT \text{ or } \Delta H^\circ - \Delta \nu RT$$

$$\frac{d \ln K_c}{dT} = \frac{\Delta E^\circ}{RT^2} \qquad \text{where } \Delta E^\circ \text{ is change of}$$

internal energy in a reaction and is heat change when reaction occurs at const T & V

Note: When $\Delta J = 0$ like $H_2 + J_2 = 2HJ$, $K_p = K_c$ [4]

$\Delta H^\circ = \Delta E^\circ$

When $\Delta J \neq 0$, then K_p & K_c have different leap coefficient

Variation of Equilibrium const with Pressure

K_p & K_c are independent of Pressure for ideal gases, but K_x is pressure dependent

(1) $RT \ln K_p = -\Delta G^\circ$ where ΔG° is Standard free energy of the reaction when the reactant & products of a chemical reaction are at standard state of 1 atm P and is the function of temperature only. K_p is function of Temp. only & independent of Pressure

$$\left(\frac{\partial \ln K_p}{\partial P}\right)_P = -\frac{\partial}{\partial P}\left(\frac{\Delta G^\circ}{RT}\right)_P = 0$$

It means that the amounts of reactants & Products at equilibrium do not change. There is change in the amounts so that K_p is not changed.

$N_2O_4 \rightleftharpoons 2NO_2$ with $\uparrow$ of P, $\propto N_2O_4$ degree of dissociation of N_2O_4 decreases, while $\downarrow$ of $P \uparrow \propto$

$$\therefore K_p = \frac{4\alpha^2 P}{1-\alpha^2}$$

lah → —

NPA

(2) K_c is independent of P

$$K_P = K_c \left(\frac{C^\circ RT}{P^\circ}\right)^{\Delta v}$$

$$\ln K_P = \ln K_c + \Delta v \ln \frac{C^\circ RT}{P^\circ}$$

Diff w.r.t P keeping T const

$$\left(\frac{\partial \ln K_P}{\partial P}\right)_T = \left(\frac{\partial \ln K_c}{\partial P}\right)_T + \frac{\partial}{\partial P}\left[\Delta v \ln \frac{C^\circ RT}{P^\circ}\right]$$

$$0 = \left(\frac{\partial \ln K_c}{\partial P}\right)_T + 0$$

$$\left(\frac{\partial \ln K_c}{\partial P}\right)_T = 0$$

(3) K_x is Pressure depends $\qquad K_P = K_x \left(P/P^\circ\right)^{\Delta v}$

$$\ln K_P = \ln K_x + \Delta v \ln P/P^\circ$$

$$\ln K_x = \ln K_P - \Delta v \ln P/P^\circ \qquad \text{Diff w.r.t } P \text{ at const } T$$

$$\left(\frac{\partial \ln K_x}{\partial P}\right)_T = \left(\frac{\partial \ln K_P}{\partial P}\right)_T - \frac{\Delta v}{(P/P^\circ)}$$

$$\left(\frac{\partial \ln K_x}{\partial P}\right)_T = \left(\frac{-\Delta v}{P/P^\circ}\right) \quad \text{(3)} \qquad \Delta v = \Sigma \text{ Moles of } P - \Sigma \text{ Moles of}$$

(1) when $\Delta v = 0$, $K_P = K_c = K_x$, K_P is independent of P

$$H_2 + I_2 \rightleftharpoons 2HI \qquad , \qquad CO_2 + H_2 \rightleftharpoons H_2O + CO$$

(2) when there is $\downarrow$ in mole nos. $\Delta v < 0$, K_x
$\uparrow$ with $\uparrow$ of P, ie more product is formed with $\downarrow$
of P, K_x will $\downarrow$, product will $\downarrow$

eg $N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta v = -2$

The reaction is carried out at high Pressure

(3) If $\Delta v > 0$, there is increase in no. of moles
$K_x \downarrow$ with $\uparrow$ in Pressure as

when $\Delta n = 0$, $K_p = K_c = K_x$, K_x is independent of P
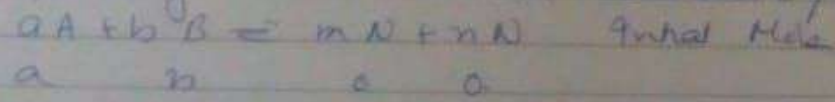$H_2 + I_2 \rightleftharpoons 2HI$
$CO_2 + H_2 \rightleftharpoons H_2O + CO$

(2) when there is ↗ in mole nos. $\Delta n \angle c a$, K_x with ↗ of P, K_x will ↓, product will ↓
i.e. more product is formed with ↓
eg $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\Delta n = -2$
The reaction is carried out at high Pressure

(3) If $\Delta n > 0$, there is increase in no of moles 23
$N_2O_4 \rightleftharpoons 2NO_2$, K_x ↓ with ↗ in Pressure as
R H S of eq (2) is -ve , & L H S should also
be -ve, with ↗ in Pressure, then K_x must
be -ve ie less than zero

Effect of Inert Gas on Reaction Equilibrium
$aA + bB \rightleftharpoons mM + nN$ Initial Mole
a b e o
$a(1-\xi)$ $b(1-\xi)$ $m\xi$ $n\xi$ At equilibrium
Let ξ be the extent of reaction. The moles nos of
different species at equilibrium
$n_A = a(1-\xi) = n_B = b(1-\xi)$, $n_M = m\xi$, $n_N = n\xi$
Total no. of moles $= n_t = n_A + n_B + n_M + n_N$
$\qquad = a(1-\xi) + b(1-\xi) + m\xi + n\xi$
$\qquad = (a+b) + \xi(m+n-a-b)$
$\qquad = (a+b) + \Delta v \xi$

$x_A = \dfrac{a(1-\xi)}{a+b+\Delta v\xi}$ $\qquad x_B = \dfrac{b(1-\xi)}{(a+b)+\Delta v\xi}$ $\qquad x_M = \dfrac{m\xi}{(a+b)+\Delta v\xi}$

$x_N = \dfrac{n\xi}{a+b+\Delta v\xi}$

Partial Pressures are given by Dalton law $P_i = x_i P$

$P_A = \dfrac{a(1-\xi)}{a+b+\Delta v\xi} P$, $\qquad P_B = \dfrac{b(1-\xi)}{a+b+\Delta v\xi} P$ $\qquad P_M = \dfrac{m\xi}{a+b+\Delta v\xi} P$

$P_N = \dfrac{n\xi}{a+b+\Delta v\xi} P$

$\qquad$ Eqⁿ Constt $K_p = \dfrac{(P_M)^m (P_N)^n}{(P_A)^a (P_B)^b}$