

CHEMICAL EQUILIBRIUM.

Consider the reaction, $aA + bB \rightleftharpoons cC + dD$
Equilibrium Constant: -

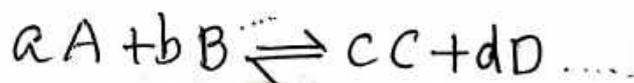
(a) In terms of Concⁿ: -

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

(b) In terms of Partial pressures: - (K_p)

In the case of gaseous reactions, eqbm const can be expressed in terms of partial pressures.

For a general reaction,



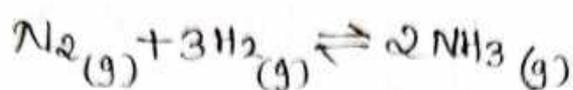
For this reaction, K in terms of partial pressure is given by,

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

eg: * formation of HI : $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$K_p = \frac{P_{HI}^2}{P_{H_2} \times P_{I_2}}$$

* Formⁿ of NH_3 :



$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3}$$

• The values of the eqbm const K_c & K_p for a particular "sea" at const. T are independent of,

(i) the actual quantities of the reactants taken

(ii) presence of a catalyst.

(iii) presence of inert materials &

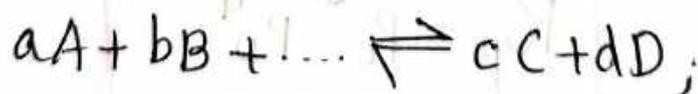
(iv) The overall pressure of the system.

Note:

* K_p & K_c vary only with T .

(c) In terms of mole fractions :-

For a "sea",



$$\text{then } K_x = \frac{x_c^c \times x_d^d}{x_a^a \times x_b^b}$$

where $x \Rightarrow$ mole fractions of the concerned species

Mole fraction:

If u have a mixture of gases (A, B, C etc), then the mole fraction of gas A is worked out by dividing the number of moles of gas.

The mole fraction of gas A,

$$X_A = \frac{\text{no: of moles of gas A}}{\text{total no: of moles of gas}}$$

eg: In a mixture of 1 mole of N_2 , 3 moles of H_2 , there are a total of 4 moles of gas.

$$\text{Then, mole fraction of } N_2 = \frac{1}{4} (0.25)$$

$$\text{" " " } H_2 = \frac{3}{4} (0.75)$$

Partial pressure

The partial pressure of one of the gases in a mixture is the pressure which it would exert if it alone occupied the whole container.

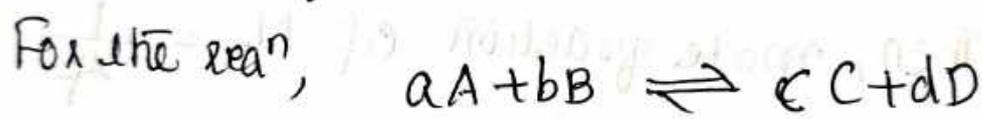
$$\text{Total pressure } P = P_A + P_B + P_C + \dots$$

$$\left\{ \begin{array}{l} P_A = \text{mole fraction of A} \times \text{Total P} \\ = X_A \times P \end{array} \right.$$

* K_p & K_c - vary only with T , K_c also depends on P :
 when the change in the no. of molecules in the reaction
 $(\Delta n) \neq 0$.

(d) Eqbm const. in terms of activities: (K)
 ↓ a measure of the effective concⁿ of a species in a reaction

"It is the ratio of the product of the eqbm activities of the products to the prod of the eqbm activities of the reactants, the activities of the concerned species being raised to the powers equal to their respective stoichiometric coefficients in the chemical eqⁿ."



$$K = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

a = activities of the constituents.

Note:-

* The thermodynamic eqbm const (K) depends only on T / Independent of all factors except T .

Relⁿ b/w K_p & K_c

Consider the following reversible reaction,



$$\text{Then } K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \quad \text{--- (1)}$$

Let, 'p' be the partial pressure of 'n' moles of certain gas in a mixture of ideal gases occupying a total volume 'v' at 'T', Applying the ideal gas eqⁿ,

$$PV = nRT \quad \text{--- (2)}$$

where, $R \Rightarrow$ universal gas const.

$$\text{Then, } P = (n/v)RT.$$

$n/v =$ no. of moles of the gas / unit volume
 $=$ Molar concⁿ 'C' of gas.

$$\therefore P = CRT \quad \text{--- (3)}$$

(3) in (1) \Rightarrow

$$K_p = \frac{(C_C RT)^c \cdot (C_D RT)^d}{(C_A RT)^a \cdot (C_B RT)^b}$$

$$K_p = \frac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b} \times \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

mm

$$\Rightarrow K_p = K_c \times \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

$$= K_c \cdot (RT)^{(c+d)-(a+b)}$$

$$a^m \cdot a^n = a^{m+n}$$

$$\frac{a^m}{a^n} = a^{m-n}$$

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

R = gas const [= 0.0821
lit atm mol⁻¹ K⁻¹]
T = temp in Kelvin (K)

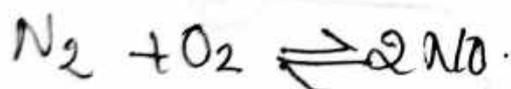
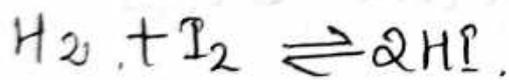
(4)

where, Δn = number of product molecules
- number of reactant molecules

Note:-

For those gaseous reactⁿ for which $\Delta n = 0$, the value of K_p will be equal to that of K_c .

eg:



$$\Delta n = 2 - 2 = 0 //$$

$$K_c = \frac{C_{HI}^2}{C_{H_2} \cdot C_{I_2}}$$

$$K_p = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}}$$

Here $K_p = K_c$ since $\Delta n = 0$.

b) Relⁿ B/w (i) K_p & K_x ; (ii) K_c & K_x .

The partial pressure (P) of any gas in a mixture of ideal gases is related to the total pressure (P) as

W.K.T.
$$P = P_A + P_B + P_C \dots$$

$$P = x P$$

where x = mole fraction in the mixture.

\therefore substitute ' xP ' for each p (partial pressure term) in the expression for K_p .

$$\Rightarrow K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

$$\Rightarrow = \frac{(x_C P)^c \cdot (x_D P)^d}{(x_A P)^a \cdot (x_B P)^b}$$

$$= \frac{x_C^c \times x_D^d}{x_A^a \times x_B^b} \times P^{(c+d) - (a+b)}$$

OR
$$K_p = K_x \times P^{\Delta n}$$

————— (5)

where

$$\Delta n = (c+d) - (a+b) \dots \Rightarrow$$

no. of prod molecules - no. of reactant molecules.

ii) $K_c \neq K_x$

w.k.t, $K_p = K_c (RT)^{\Delta n}$

Compare this eqⁿ with eqⁿ (5)

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

$$K_p = K_x \cdot P^{\Delta n}$$

$$\Rightarrow K_c (RT)^{\Delta n} = K_x \cdot P^{\Delta n}$$

$$K_x = K_c \left(\frac{RT}{P} \right)^{\Delta n}$$

w.k.t, $PV = RT$ (for $n=1$)

$$\text{OR } V = RT/P$$

$$\Rightarrow K_x = K_c \times V^{\Delta n} \quad \text{--- (6)}$$

Note:-

* when $\Delta n = 0$, they are all equal, otherwise they differ.

* ~~From~~ From eqⁿ (5) & (6),

$\Rightarrow K_x$ depends upon the total 'P' or 'V' of the system.

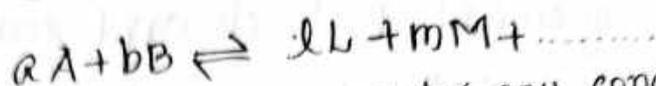
In general,

* K_p & K_c vary only with temp

* K_x depends also on the 'P' when $\Delta n \neq 0$.

Derivation of the Van't Hoff sea' Isotherm & the law of chemical eq^m:-

Consider the general sea',



that p can be used to calculate the maximum of reversible work under any conditions of P & T

The total Gibbs energy of the reactants ($G_{\text{reactants}}$) consisting of 'a' moles of A, 'b' moles of B etc is given by,

$$G_{\text{reactants}} = a\mu_A + b\mu_B + \dots \quad \text{--- (1)}$$

The total Gibbs energy of the pds (G_{pds}) consisting of 'l' moles of L, 'm' moles of M, etc is given by

$$G_{\text{products}} = l\mu_L + m\mu_M + \dots \quad \text{(2)}$$

In eqⁿ (1) & (2), μ -terms represent the chemical potentials of the indicated species.

The energy that can be absorbed or released due to a change of the particle numbers of the given species in a chemical sea'.

At const. T & P, the change in Gibbs energy (ΔG) is given by,

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

$$= (l \mu_L + m \mu_M + \dots) - (a \mu_A + b \mu_B + \dots) \quad \text{--- (3)}$$

w.k.t, chemical potential of (μ) each species is related to its activity (a) as,

$$\mu = \mu^\circ + RT \ln a \quad \text{--- (4)}$$

eqⁿ (3) can be written in terms of the activities (a)

& std chemical potentials (μ° terms) as;

$$\Delta G = \left[l (\mu_L^\circ + RT \ln a_L) + m (\mu_M^\circ + RT \ln a_M) + \dots \right]$$

$$- \left[a (\mu_A^\circ + RT \ln a_A) + b (\mu_B^\circ + RT \ln a_B) + \dots \right]$$

--- (5)

OR $\Delta G =$ ~~std~~

$$(l \mu_L^\circ + m \mu_M^\circ + \dots) - (a \mu_A^\circ + b \mu_B^\circ + \dots) +$$

$$\left[RT \ln a_L^l + RT \ln a_M^m + \dots \right] - \left(RT \ln a_A^a + RT \ln a_B^b + \dots \right)$$

--- (6)

The 1st term in eqⁿ (6) gives, ΔG° ,

$$\therefore \Delta G = \Delta G^\circ + RT \ln \left[\frac{a_L^l \times a_M^m \times \dots}{a_A^a \times a_B^b \times \dots} \right] \quad (7)$$

(7) \Rightarrow reaⁿ Isotherm :- bcuz it gives gibbs energy change in terms of activities at const T.

(7) \Rightarrow Act

$$\Delta G = \Delta G^\circ + RT \ln Q. \quad (7a)$$

where $Q = \frac{a_L^l \times a_M^m \times \dots}{a_A^a \times a_B^b \times \dots}$, it is the activity quotient / reaⁿ Quotient, under condⁿ (need not be eq^l condⁿ).

Now, activities are replaced by partial pressures,

$$(7) \Rightarrow \Delta G = \Delta G^\circ + RT \ln \frac{P_L^l \times P_M^m \times \dots}{P_A^a \times P_B^b \times \dots} \quad (7b)$$

$$\text{OR } \Delta G = \Delta G^\circ + RT \ln Q_p \quad (7c)$$

where $Q_p = \frac{P_L^l \times P_M^m}{P_A^a \times P_B^b}$ is the pressure quotient (or reaⁿ quotient).

eqⁿ (7) or any of its alternative forms (7a), (7b), (7c) is known as **van't Hoff seaⁿ isotherm**.
 When the seaⁿ is in a state of eq^l_b^m, $\Delta G = 0$. Then the activity terms in eqⁿ (7) become the eq^l_b^m activities & eqⁿ (7) becomes,

$$0 = \Delta G^{\circ} + RT \ln \left[\frac{a_L^l \times a_M^m \times \dots}{a_A^a \times a_B^b \times \dots} \right]_{\text{eq}l_b^m} \quad \text{--- (8)}$$

$$\Delta G^{\circ} = -RT \ln \left[\frac{a_L^l \times a_M^m \times \dots}{a_A^a \times a_B^b \times \dots} \right]_{\text{eq}l_b^m} \quad \text{--- (9)}$$

$\therefore \Delta G^{\circ}$ for the seaⁿ is a const at const. T,

$$\Rightarrow \left[\frac{a_L^l \times a_M^m \times \dots}{a_A^a \times a_B^b \times \dots} \right]_{\text{eq}l_b^m} = K, \text{ const} \quad \text{--- (10)}$$

where, $K =$ Thermodynamic eq^l_b^m const.

- This eqⁿ represents the law of chemical eq^l_b^m.

Since activity \propto molar concⁿ (c) & partial pressure (p) at const T & P.

$$\left[\frac{C_L^l \times C_M^m \times \dots}{C_A^a \times C_B^b \times \dots} \right]_{\text{eqibm}} = K_c, \text{ a const.} \quad (11)$$

$$\left[\frac{P_L^l \times P_M^m \times \dots}{P_A^a \times P_B^b \times \dots} \right]_{\text{eqibm}} = K_p, \text{ a const.} \quad (12)$$

The van't Hoff seaⁿ Isotherm :-

$$\Delta G = \Delta G^\circ + RT \ln \left[\frac{a_L^l \times a_M^m \times \dots}{a_A^a \times a_B^b \times \dots} \right]$$

It is under eqibm condⁿ (ie, $\Delta G = 0$)

$$\Rightarrow \Delta G^\circ = -RT \ln \left[\frac{a_L^l \times a_M^m \times \dots}{a_A^a \times a_B^b \times \dots} \right]_{\text{eqibm}} \quad (13)$$

$$\text{or } \Delta G^\circ = -RT \ln K. \quad (13)$$

where, $K =$ Thermodynamic eqibm const.

For gaseous reactants, (assuming ideal behavior), activities can be replaced by partial pressures.

So, K is replaced by K_p

(13) becomes \Rightarrow

$$\Delta G^\circ = -RT \ln K_p \quad \text{--- (14)}$$

$$\text{or } \Delta G^\circ = -2.303RT \log K_p \quad \text{--- (15)}$$

Temp dependence of eq^b constant - van't Hoff eqⁿ:-

The value of 'K' varies with change in T .

Now, we want to derive a relⁿ showing the quantitative variation of K_p with T .

w.k.t,

$$\Delta G^\circ = -RT \ln K_p.$$

Differentiating w.r.t T at const. P ,

we get,

$$\left(\frac{\partial (\Delta G^\circ)}{\partial T} \right)_P = -R \ln K_p - RT \frac{d \ln K_p}{dT}.$$

* Multiplying throughout by T,
we get,

$$T \left(\frac{\partial(\Delta G^\circ)}{\partial T} \right)_p = -RT \ln K_p - RT^2 \frac{d \ln K_p}{dT}$$

Put, $-RT \ln K_p = \Delta G^\circ$,

$$\Rightarrow T \left[\frac{\partial(\Delta G^\circ)}{\partial T} \right]_p = \Delta G^\circ - RT^2 \frac{d \ln K_p}{dT} \quad \text{--- (1)}$$

w.k.t, Gibbs Helmholtz eqⁿ is,

$$\Delta G = \Delta H + T \left[\frac{\partial(\Delta G)}{\partial T} \right]_p \quad \text{--- (2)}$$

under a condⁿ, when all the substances are in their standard states, Gibbs Helmholtz eqⁿ modifies as,

$$\Delta G^\circ = \Delta H^\circ + T \left[\frac{\partial(\Delta G^\circ)}{\partial T} \right]_p \quad \text{--- (3)}$$

where $\Delta H^\circ =$ Standard enthalpy of reactⁿ.

$$T \left[\frac{\partial(\Delta G^\circ)}{\partial T} \right]_p = \Delta G^\circ - \Delta H^\circ \quad \text{--- (4)}$$

From eqⁿ ① & ④, we get,

$$RT^2 \frac{d \ln K_p}{dT} = \Delta H^\circ \quad \text{--- ⑤}$$

or $\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$ --- ⑥

\Rightarrow Van't Hoff eqⁿ.

[This eqⁿ is known as Van't Hoff reⁿ Isochore, bcoz, Van't Hoff is deduced it for a const. volume system] Now it is not used.

* For an ideal gas, ΔH° replaced with ΔH without specifying standard states.

$$\text{⑥} \Rightarrow \frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2} \quad \text{--- ⑥a}$$

Integrated form of Van't Hoff eqⁿ:-

w.k.T, Van't Hoff eqⁿ is,

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

$$\Rightarrow d \ln K_p = \frac{\Delta H^\circ}{RT^2} dT \quad \text{--- ⑦}$$

Let, $(K_p)_1$ & $(K_p)_2$ represent values of the eq'lbr const at two temperatures T_1 & T_2 respectively.

Then, the integration of eqⁿ (7) b/w appropriate limits,

$$\Rightarrow \int_{(K_p)_1}^{(K_p)_2} d \ln K_p = \int_{T_1}^{T_2} \frac{\Delta H^\circ}{RT^2} dT \quad \text{--- (8)}$$

Assume that, ΔH° remains const in the narrow temp range from T_1 to T_2 ,

$$\text{(8)} \Rightarrow \int_{(K_p)_1}^{(K_p)_2} d \ln K_p = \frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT \quad \text{--- (9)}$$

$$\left[\frac{1}{T^2} dT = -\frac{1}{T} \right] \quad \left[\frac{-1}{T} \right]_{T_1}^{T_2}$$

$$\ln \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H^\circ}{R} \left[-\frac{1}{T_2} - \left(-\frac{1}{T_1} \right) \right]$$

$$= \frac{\Delta H^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \text{--- (10)}$$

$$= \frac{\Delta H^\circ}{R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right] \quad \text{--- (11)}$$

$\ln \frac{(K_p)_2}{(K_p)_1} = \log \frac{(K_p)_2}{(K_p)_1}$

$$\log \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right] \quad \text{--- (12)}$$

eqⁿ (10) to (12) are the various forms of the integrated Van't Hoff equation.

- * It permits the calculⁿ of the eq^lbm const. at one T^{mp} if its value for another T^{mp} & ΔH° (std. enthalpy of rxnⁿ) are known.
- * Also used to calculate ΔH° from known values of K_p at two T^{mp}'s.
- * For approximate purpose, ΔH° can be replaced with ΔH (when difference is too small),

$$\text{then, } \log \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right] \quad \text{--- (13)}$$