

# Chemical Eq.

Chemical Rx<sup>n</sup> of 2 types: Reversible & Irreversible

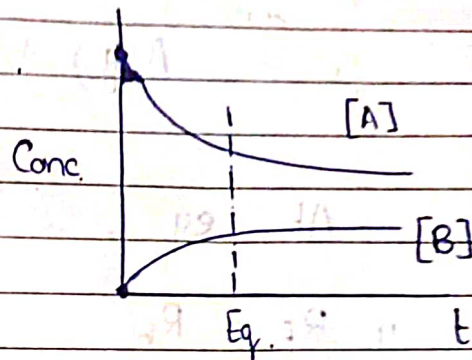
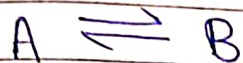
Reversible	Irreversible
1) Both forward & backward dirx <sup>n</sup> . Eg: Haber's process $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	1) Only in forward dirx <sup>n</sup> . Eg: Explosion, Combustion, ... Milk to Curd, ...
2) Occur in closed containers.	2) Occur in both area.
3) Eq. is achieved.	3) Eq. <u>NOT</u> achieved
4) All neutralisation rx <sup>n</sup> s w/o (strong acid & base) together.	4) Strong Acid + Strong Base Rx <sup>n</sup> s.

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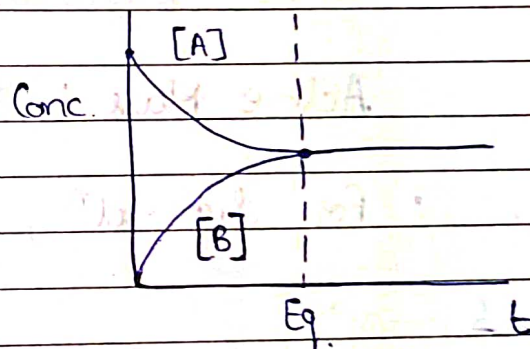
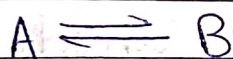


## Types of Equilibrium - (on basis of extent of rxn)

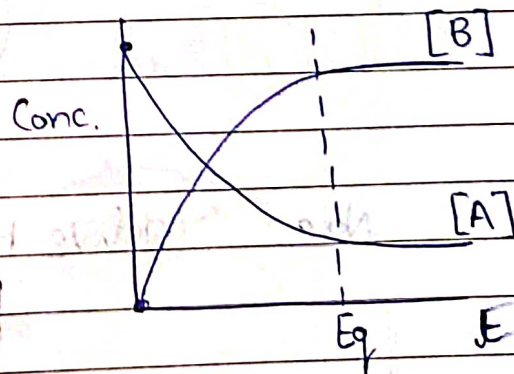
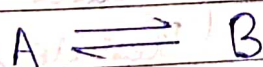
- C1:  $R \times^n$  goes little fwd.



- C2:  $R \times^n$  goes exactly 50%



- C3:  $R \times^n$  goes very fwd.

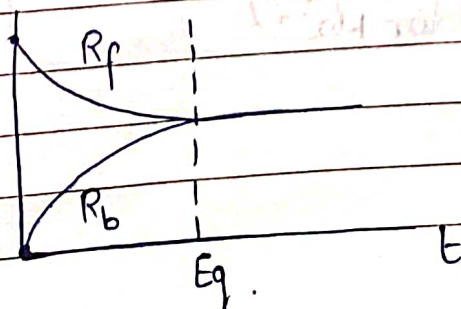


- Note -

(If no products initially present)

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Rate of rxn

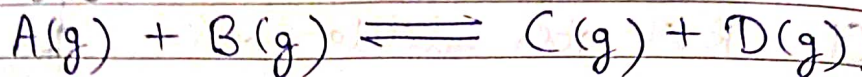


$R_f$  - fwd rate  
 $R_b$  - backward rate



Chemical Eq. & Active Mass

Consider homogenous reversible rxn,  
same phase



At eq.,

1)  $R_f = R_b$

2)  $[Reactant] = Const.$

$[Product] = Const.$

Active Mass ∴ Part of conc. involved in rxn

• For liq. sol<sup>n</sup>,

$$\text{(Active Mass)} = \text{(Molar Conc.)} \{ [A] \}$$

• For gases,

$$\text{(Active Mass)} \rightarrow \begin{cases} \text{(Molar Conc.)} \{ [A] \} \\ \text{(Partial Pressure)} \{ [P_A] \} \end{cases}$$

Note:  $\text{(Active Mass)} = \text{(Molar Conc.)} = \frac{\text{moles}}{\text{Volume}}$

$$\frac{\text{(Density)}}{\text{(Molar Mass)}} = \frac{1}{\text{(Molar Mass)}} \left( \frac{\text{Mass}}{\text{Volume}} \right)$$



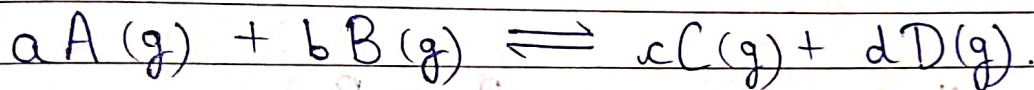
• For solids / <sup>excess</sup> pure liq.,

We assume active mass to be (1).  
density = const.  
(molar mass) volume = const.  
⇒ active mass = const.

⇒ Active Mass = 1

## Law of Mass Action

Consider homogenous reversible rxn,



Acc. to the law,

$$R_f \propto [A]^a [B]^b$$

$$\text{or } R_b \propto [C]^c [D]^d$$

$$\Rightarrow R_f = K_f [A]^a [B]^b$$

$$\text{or } R_b = K_b [C]^c [D]^d$$

Rate const.  
fwd rxn

Rate const.  
back rxn

Units of Rate =  $\text{mol L}^{-1} \text{s}^{-1}$

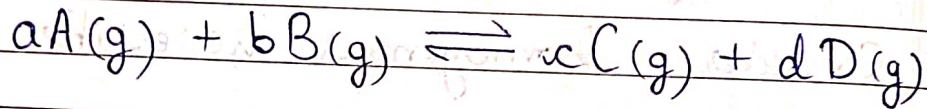
Units of rate const. =  $(\text{mol L}^{-1})^{1-(a+b)} \text{s}^{-1}$



★ Rate const. depends only on :  
Temp. & Catalyst.

## Law of Chemical Eq.

Consider homogenous reversible rxn,

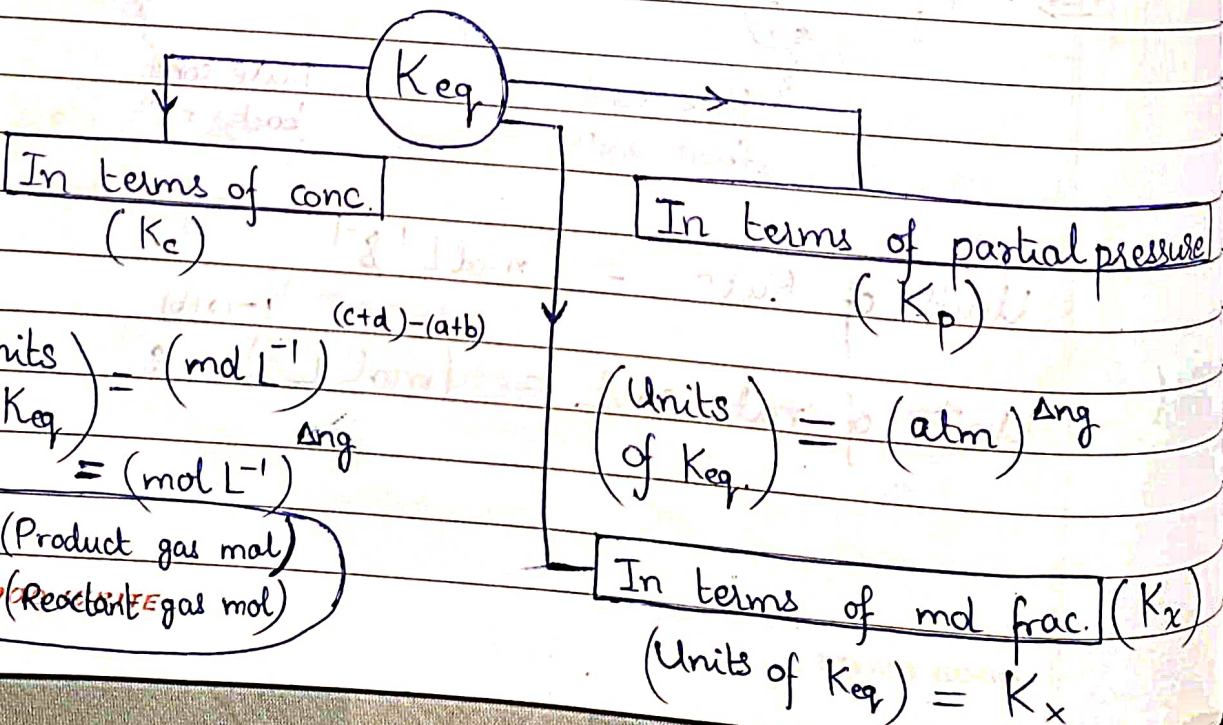


At eq.,

$$R_f = R_b$$

(All [ ] taken at eq.)  $\Rightarrow k_f [A]^a [B]^b = k_b [C]^c [D]^d$

Equilibrium Const.  $\Rightarrow K_{eq} = \left( \frac{k_f}{k_b} \right) = \frac{[C]^c [D]^d}{[A]^a [B]^b}$





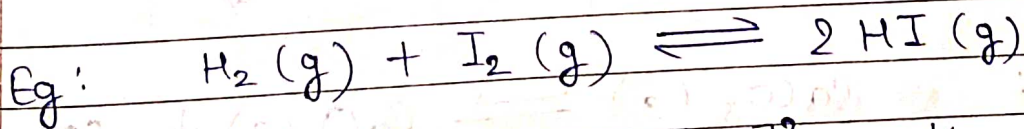
Imp. Pts on  $K_{eq}$  :-

- 1) Def<sup>n</sup> & value of  $K_{eq}$  holds only at eq. cond<sup>n</sup>.
- 2) It is fixed for a rx<sup>n</sup> at a particular temp.; i.e. it is only temp. dependent.
- 3) Indep<sup>n</sup> of conc., pressure, vol., catalyst.

Types of Chemical Eq.

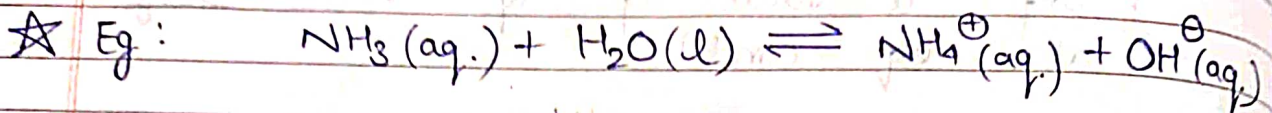
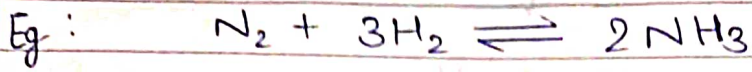
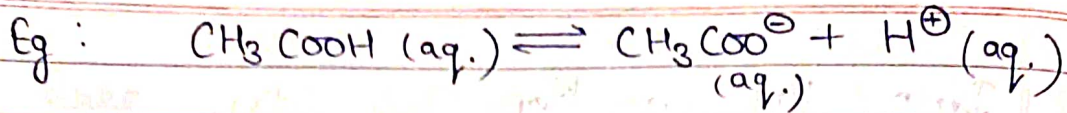
- 1) Homogenous Chem. Eq
- 2) Heterogenous Chem. Eq

1) Homo. Chem. Eq - Reactants and products in same phase.



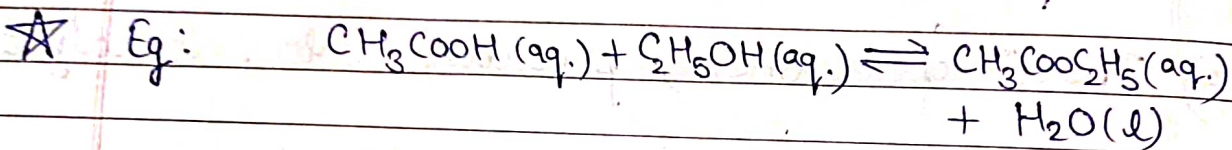
$$K_c = \frac{[HI]^2}{[H_2][I_2]}, \quad K_p = \frac{[P_{HI}]^2}{[P_{H_2}][P_{I_2}]}, \quad K_x = \frac{[X_{HI}]^2}{[X_{H_2}][X_{I_2}]}$$





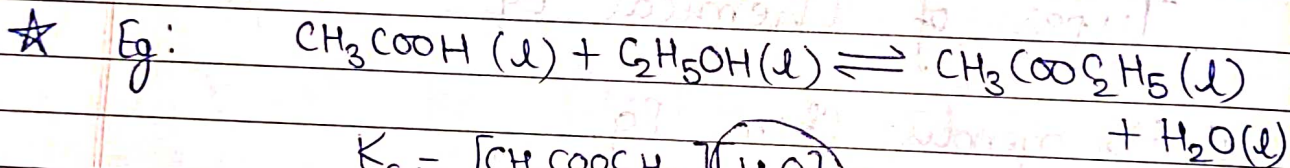
$$K_c = \frac{[\text{NH}_4][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]} \Rightarrow K = \frac{[\text{NH}_4][\text{OH}^-]}{[\text{NH}_3]}$$

Since in excess, active mass = 1



$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} \Rightarrow \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

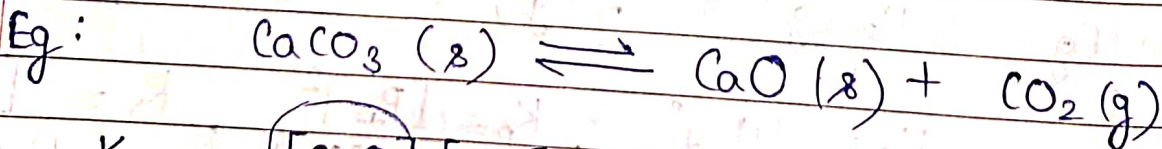
Since in excess, active mass = 1



$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

≠ 1 as NOT in excess.

2) Hetero. Chem. Eq - Reactants & products in diff. phase.

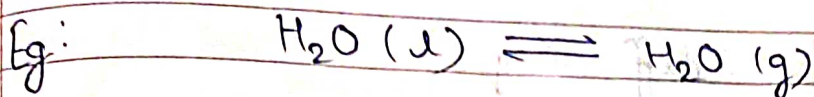


$$K_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]} \Rightarrow K_c = [\text{CO}_2]$$

Solids active mass = 1

$$K_p = [P_{\text{CO}_2}]$$

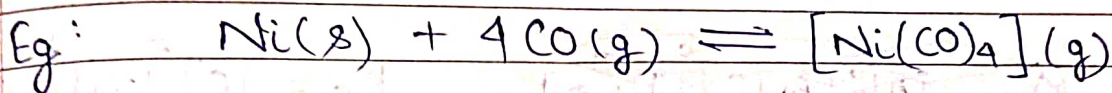




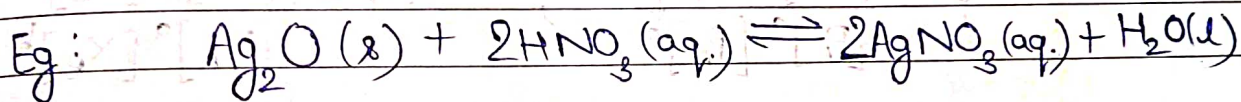
$$K_c = \frac{[\text{H}_2\text{O}(\text{g})]}{[\text{H}_2\text{O}(\text{l})]}$$

liq. active mass = 1, if gas present  $\Rightarrow K_c = [\text{H}_2\text{O}(\text{g})]$

$$K_p = [P_{\text{H}_2\text{O}(\text{g})}]$$

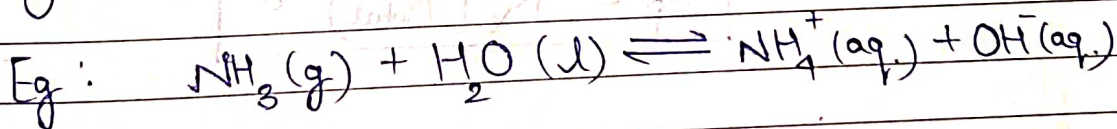


$$K_c = \frac{[\text{Ni}(\text{CO})_4]}{[\text{CO}]^4}$$



$$K_c = \frac{[\text{AgNO}_3]^2}{[\text{HNO}_3]^2}$$

★ When aq. species (solute / ions) of gaseous sub. are present together.



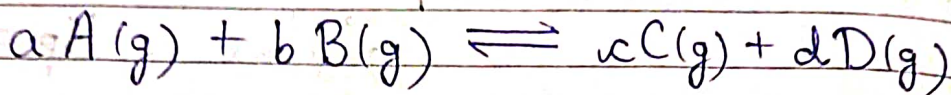
$$K_{pc} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[P_{\text{NH}_3}]}$$

Write conc. of aq. & partial pressure of gaseous.



Rel<sup>n</sup> b/w diff. Keq

Consider the homo. reversible rxn,



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

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

$$K_p = \frac{[P_c]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

$$K_x = \frac{[X_c]^c [X_D]^d}{[X_A]^a [X_B]^b}$$

Now by Dalton's law,

$$P_A = X_A P_{\text{Total}}$$

$$\Rightarrow K_p = \frac{[X_c]^c [X_D]^d}{[X_A]^a [X_B]^b} (P_{\text{Total}})^{(c+d)-(a+b)}$$

$$\Rightarrow K_p = K_x (P_{\text{Total}})^{\Delta n_g}$$

Now by Ideal gas eq<sup>n</sup>,  $PV = nRT$

$$\Rightarrow P = \left(\frac{n}{V}\right) RT$$

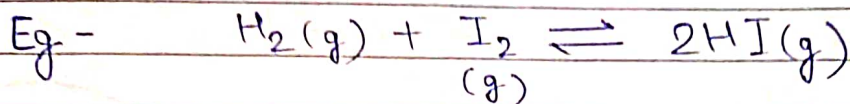
$$\Rightarrow K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d)-(a+b)}$$

$$\Rightarrow P = [\text{conc}] RT$$

$$\Rightarrow K_p = K_c (RT)^{\Delta n_g}$$

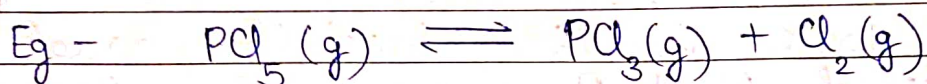


C1:  $K_p = K_c$ , when  $\Delta n_g = 0$ .

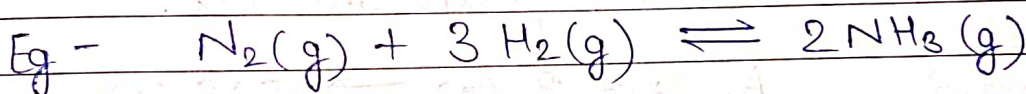


Both  $K_p$  &  $K_c$  dimensionless.

C2:  $K_p > K_c$ , when  $\Delta n_g > 0$  {  $RT > 1$  }



C3:  $K_p < K_c$ , when  $\Delta n_g < 0$  {  $RT > 1$  }



★ C4:  $K_p = K_c$ ,  $\forall \Delta n_g$  if  $T = \frac{1}{R}$

Q) A mix. of  $\text{SO}_3$ ,  $\text{SO}_2$  &  $\text{O}_2$  gases is maintained at eq. in 10L flask at temp. at which  $K_c$  for  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$  is  $100 \text{ mol}^{-1} \text{L}$ .

At eq,  
a) if  $\# \text{ mol}(\text{SO}_2) = \# \text{ mol}(\text{SO}_3)$ , find  $\# \text{ mol}(\text{O}_2)$   
b) if  $\# \text{ mol}(\text{SO}_3) = 2 \# \text{ mol}(\text{SO}_2)$ , find  $\# \text{ mol}(\text{O}_2)$

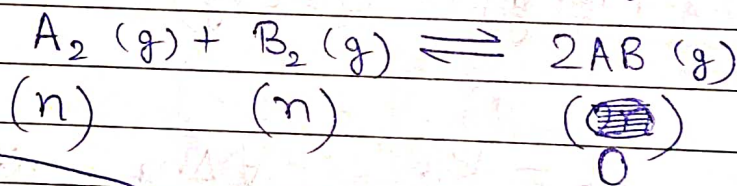


$$A) \ a) \ K_c = 100 = \frac{(n_{SO_3}/10)^2}{(n_{SO_2}/10)^2 (n_{O_2}/10)} \Rightarrow n_{O_2} = 0.1$$

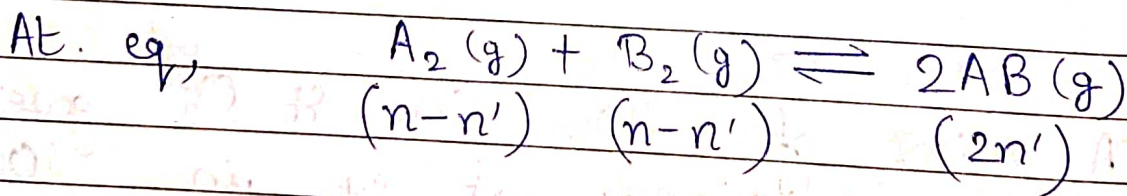
$$b) \ K_c = 100 = \frac{(n_{SO_3}/10)^2}{(n_{SO_2}/10)^2 (n_{O_2}/10)} \Rightarrow n_{O_2} = 0.4$$

★ Q) The eq. const. for  $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$  at  $100^\circ C$  is 16. Initially equal moles of  $A_2$  &  $B_2$  are taken in 2L container. Find mole % of  $A_2$  in eq. cond<sup>n</sup>.

A) Let 'n' mol be present initially.



★  ~~$16 = \frac{(2n/2)^2}{(n/2)(n/2)}$~~  ← Wrong. Can't apply at initial cond<sup>n</sup>.



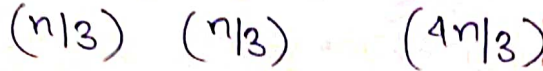
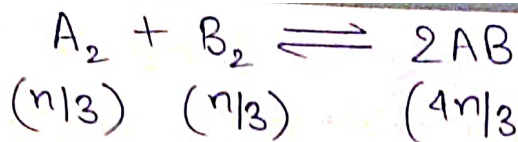
Now,

$$16 = \frac{(2n'/2)^2}{\left(\frac{n-n'}{2}\right)\left(\frac{n-n'}{2}\right)} = 4 \left(\frac{n'}{n-n'}\right)^2$$

$$\Rightarrow \left(\frac{n'}{n-n'}\right) = 2 \Rightarrow n' = \frac{2n}{3}$$



At eq.,



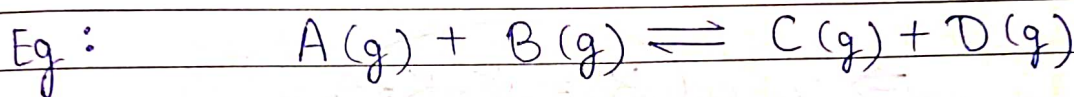
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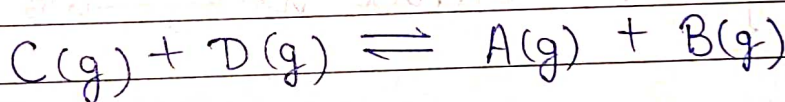
$$\left( \text{Mole \% of } A_2 \right) = \left( \frac{n/3}{n/3 + n/3 + 4n/3} \right) \cdot 100\% \Rightarrow \boxed{\left( \text{Mol \% of } A \right) = 16.6\%}$$

## Factors affecting $K_{eq}$

1) Mode of representation :-



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

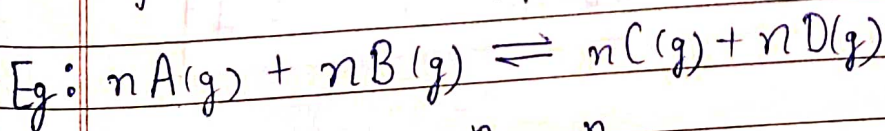


$$K'_c = \frac{[A][B]}{[C][D]}$$

$$\Rightarrow K'_c = \frac{1}{K_c}$$

2) Stoichiometry of  $n \times n$  :-

If we multiply  $n \times n$  by 'n'.



$$K''_c = \frac{[C]^n [D]^n}{[A]^n [B]^n}$$

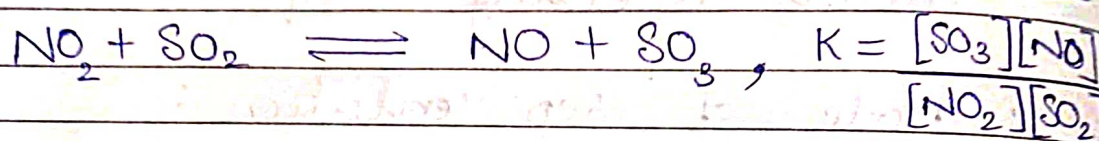
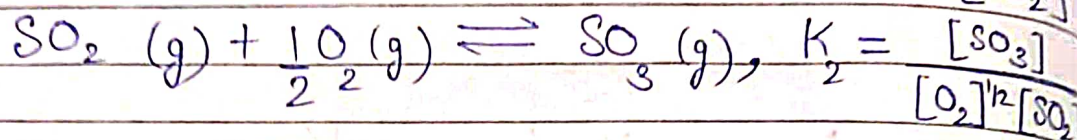
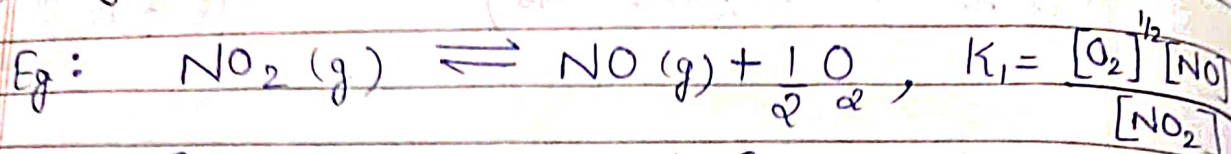
$\Rightarrow$

$$K''_c = K_c^n$$

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3) By add<sup>n</sup> & sub<sup>n</sup> of  $\times x^n$  :-



⇒

$$K = K_1 K_2$$

If we subtract  $\times x^n$ , we get

$$K = \frac{K_1}{K_2}$$

4) Effect of Temp :-

$$\log(K_{\text{eq}}) = \frac{\Delta S}{2.303 R} - \frac{\Delta H}{2.303 RT}$$

$\Delta S$  = Change in Entropy

$\Delta H$  = Change in Enthalpy

⇒

$$\log\left(\frac{K_2}{K_1}\right) = \left(\frac{\Delta H}{2.303 R}\right) \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$



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C1:  $\Delta H < 0 \Leftrightarrow$  Exothermic

• If  $T_2 > T_1$  (Temp  $\uparrow$ )  $\Rightarrow K_1 > K_2$  (Keq dec.)

$\Rightarrow$  Rxn shifts in back dirxn.

$\Rightarrow$  Rxn shifts towards Endothermic.

• If  $T_1 > T_2$  (Temp  $\downarrow$ )  $\Rightarrow K_2 > K_1$  (Keq inc.)

$\Rightarrow$  Rxn shifts fwd dirxn

$\Rightarrow$  Rxn shifts towards Exothermic

C2:  $\Delta H > 0 \Leftrightarrow$  Endothermic.

• If  $T_2 > T_1$  (Temp  $\uparrow$ )  $\Rightarrow K_2 > K_1$  (Keq inc.)

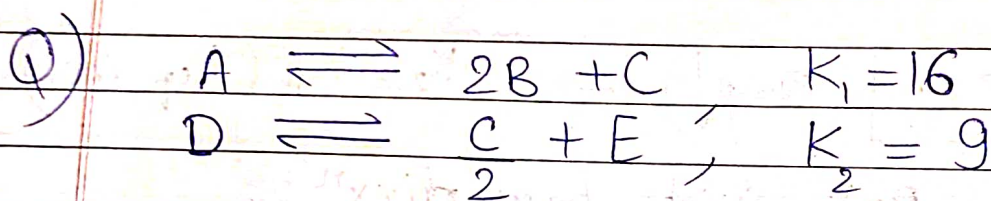
$\Rightarrow$  Rxn shifts towards Endothermic

• If  $T_1 > T_2$  (Temp  $\downarrow$ )  $\Rightarrow K_1 > K_2$  (Keq dec.)

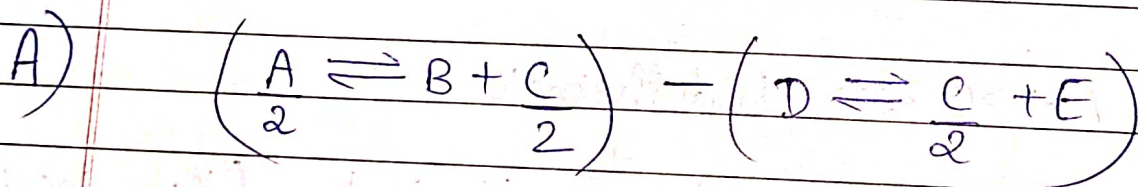
$\Rightarrow$  Rxn shifts towards Exothermic



★ In general, in any  $\text{rxn}$   
 Temp.  $\uparrow \Rightarrow \text{Rxn}$  towards Endo.  
 Temp.  $\downarrow \Rightarrow \text{Rxn}$  towards Exo.

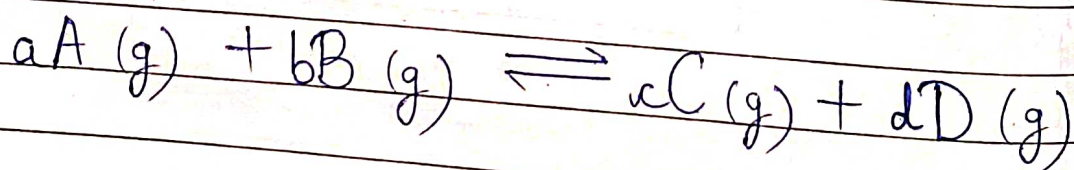


find  $K_{eq}$  for,  $\frac{1}{2}A + E \rightleftharpoons B + D$  :



$$\Rightarrow K_{eq} = \frac{16^{1/2}}{9} \Rightarrow \boxed{K_{eq} = \frac{4}{9}}$$

Rxn Quotient (Q)





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

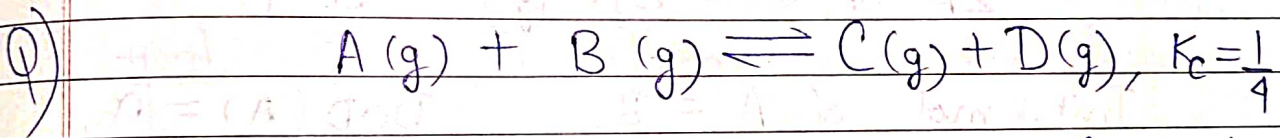
(quotient)  $R \times n$

at any pt. of time.

C1:  $Q > K_{eq} \Rightarrow R \times n$  shifts backward

C2:  $Q < K_{eq} \Rightarrow R \times n$  shifts forward

C3:  $Q = K_{eq} \Rightarrow R \times n$  at eq.



Init. mol. of A, B, C, D are 1 each and vol. of container is 1 L. Find -

- 1) dir  $R \times n$  of  $R \times n$       2) # mol. of each at eq.

A)  $Q = \frac{(1)(1)}{(1)(1)} = 1 > \frac{1}{4} = K_c \Rightarrow$  Backward

2) R:	A	+	B	$\rightleftharpoons$	C	+	D
I:	1		1		1		1
E:	$1-x$		$1-x$		$1-x$		$1-x$
C:	$1+x$		$1+x$		$1-x$		$1-x$

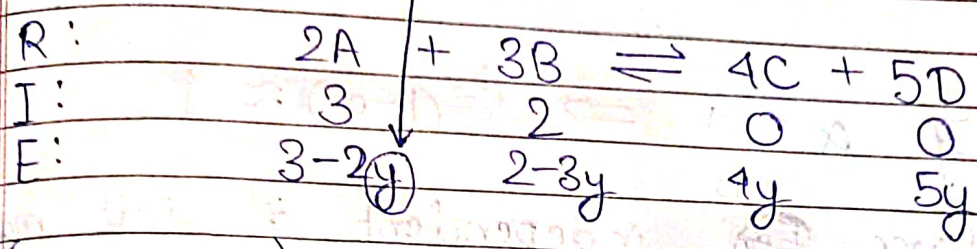
$$K_c = \frac{(1-x)(1-x)}{(1+x)(1+x)} = \frac{1}{4} \Rightarrow \frac{(1-x)}{(1+x)} = \frac{1}{2} \Rightarrow x = \frac{1}{3}$$







A) ★ Assume new variable to red. calc.



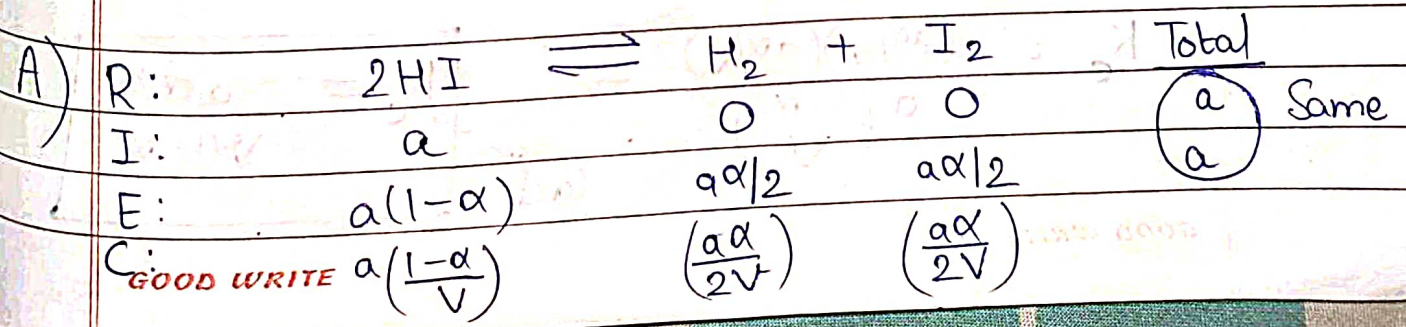
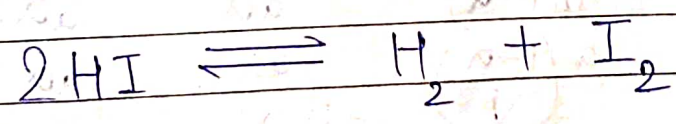
(Total mol. at eq.) =  $4y + 5$       Now,  $2y = 3(0.3)$

$\Rightarrow$  Req. = 23       $\Rightarrow$   $y = 0.45$

## Application of Chem Eq. (Don't learn)

Cl:  $\Delta n_g = 0$

Q) 'a' mol of HI are taken in a container of vol 'V'. If DoD of HI is  $\alpha$ , and total pressure at eq. is P, find  $K_c$  &  $K_p$  in terms of  $a, V, P, \alpha$ .



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Since  $\Delta n_g = 0 \Rightarrow K_p = K_c$ DATE: / /  
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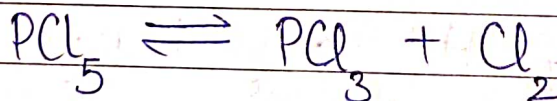
$$K_c = \frac{(a\alpha/V)(a\alpha/V)}{\left(\frac{a(1-\alpha)}{V}\right)^2} \Rightarrow K_c = \frac{\alpha^2}{2(1-\alpha)} \quad \text{Const.}$$



- If  $\alpha \ll 1 \Rightarrow (1-\alpha) \approx 1$
- Since  $K_{eq}$  independent of  $\text{DoD}$   $\text{init. mol.}$   $\text{ft. vol.}$  taken, assume them to be 1

C2:  $\Delta n_g > 0$ 

Q) 'a' mol  $\text{PCl}_5$  taken in container of vol.  $V$ . If  $\text{DoD}$  of  $\text{PCl}_5$  is  $\alpha$  and total pressure at eq. is  $P$ , find  $K_c, K_p$  in terms of  $a, V, P, \alpha$ .



A) R:	$\text{PCl}_5$	$\rightleftharpoons$	$\text{PCl}_3$	$+$	$\text{Cl}_2$	Total
I:	a		0		0	a
E:	$a(1-\alpha)$		$a\alpha$		$a\alpha$	$a + a\alpha$
e:	$a \frac{(1-\alpha)}{V}$		$\left(\frac{a\alpha}{V}\right)$		$\left(\frac{a\alpha}{V}\right)$	

$$K_c = \frac{(a\alpha/V)(a\alpha/V)}{a \left(\frac{1-\alpha}{V}\right)} \Rightarrow K_c = \frac{a\alpha^2}{V(1-\alpha)} \quad \text{Const.}$$





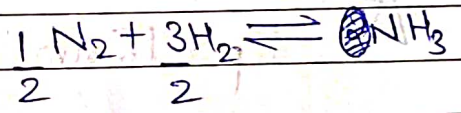
- If  $\alpha \ll 1 \Rightarrow (1-\alpha) \approx 1$
- $\alpha \propto \sqrt{V}$  if  $\Delta n_g = 1$
- $\alpha \propto \frac{1}{\sqrt{P}}$  if  $\Delta n_g = 1$

C3:  $\Delta n_g < 0$



- If  $\alpha \ll 1 \Rightarrow (1-\alpha) \approx 1$
- $\alpha \propto \frac{1}{\sqrt{V}}$  if  $\Delta n_g = (-1)$
- $\alpha \propto \sqrt{P}$  if  $\Delta n_g = (-1)$

Eg:



16/9/22

Q)  $NH_3(g)$  at 15 atm is intro. in rigid vessel at 300 K. At eq, total prsre of vessel is 40.11 atm. at 300°C. ~~The~~ find DoD of  $NH_3$ .

A) Rxn:  $2NH_3 \rightleftharpoons N_2 + 3H_2$

				Total
		0	0	n
Init:	-n			
Eq:	$n(1-\alpha)$	$n\alpha$	$\frac{3n\alpha}{2}$	$n + n\alpha$
		2	2	

GOOD WRITE

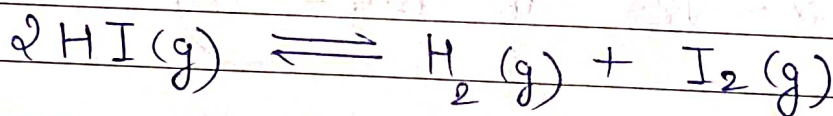
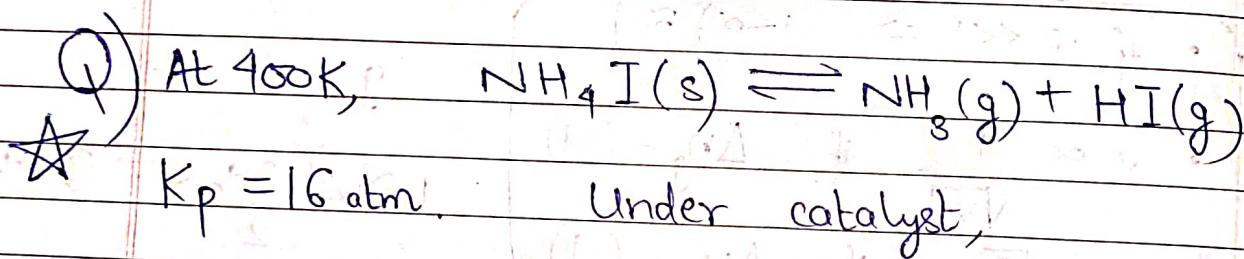


By  $PV = nRT$ ,  $n = \frac{(15)}{(300)} \left( \frac{V}{R} \right)$

$n(1+\alpha) = \left( \frac{40.11}{573} \right) \left( \frac{V}{R} \right)$

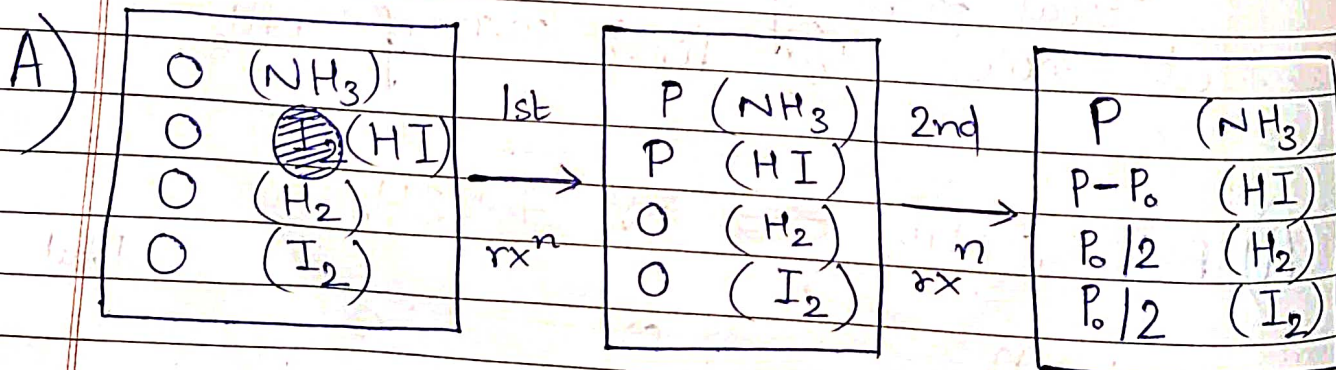
$\Rightarrow (1+\alpha) = \left( \frac{40.11}{573} \right) \left( \frac{300}{15} \right) = \frac{802.2}{573}$

$\Rightarrow \alpha = 0.4$



If partial pressure of  $H_2$  at this temp. is 1 atm, when both eq. exist simultaneously

Calc.  $K_p$  of second rxn.



Final Composition.



for 1st rxn :  $P(P - P_0) = 16 \Rightarrow P = 5.1$

We know,  $P_0/2 = 1$  (for  $H_2$ )  $\Rightarrow P_0 = 2$

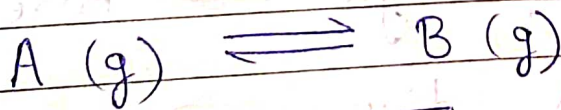
for 2nd rxn :  $K_p = \frac{(P_0/2)^2}{(P - P_0)^2} = 1$   
 $\frac{(2)^2}{(5.1 - 2)^2} = 1$

$\Rightarrow K_p = 0.1$

## Le Chatlier's Principle —

If system in eq. and subjected to external change (like conc., P, V, ...). then system will oppose it, and rxn will shift so as to nullify the external effect.

### 1) Effect of Conc :



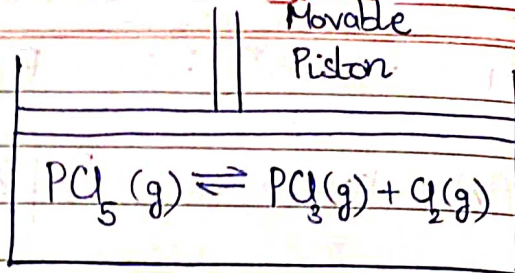
If  $\boxed{\text{conc. A} \downarrow \text{(or } \uparrow)}$   $\Rightarrow$   $\text{conc. B} \downarrow \text{(or } \uparrow)$

So as to  $\uparrow$  conc. of A!  
 (or  $\downarrow$ )

$\Rightarrow$   $\boxed{\text{Rxn shift backward (or fwd).}$



2) Effect of Pressure :



If  $P \uparrow$  (or  $\downarrow$ )  $\Rightarrow$  (Total gaseous moles)  $\downarrow$  (or  $\uparrow$ )  
so as to  $\downarrow$  (or  $\uparrow$ )  $P$ .

$\Rightarrow$  Rxn shifts to reduce (or inc.)  
no. of gaseous mols.

★ If  $\Delta n_g = 0$ , then no effect of  $P$   
on shifting rxn.

3) Effect of Vol. :

Vol. bada diya  $\Rightarrow$  Pressure ghata diya.

• Vol. ghata diya  $\Rightarrow$  Pressure bada diya.

Hence,

$V \uparrow$  (or  $\downarrow$ )  $\Rightarrow$  (Total no. of gas mol.)  $\uparrow$  (or  $\downarrow$ )



4) Add<sup>n</sup> of Inert gas :

Case 1: At const. Vol.

Since no. of mol. of react. & prod same  
 $\Rightarrow$  their conc. same  $\Rightarrow K_c, K_p, K_x$  same.

$\Rightarrow$  No Change

Case 2: At const. Presre & Const. Vol.

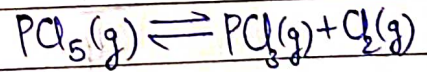
Inert gas added  $\Rightarrow$  Gaseous mol  $\uparrow$

$\Rightarrow$  Rx<sup>n</sup> shifts to  $\downarrow$   
no. of gas mol.

Case 3: At. const. Presre

Movable  
Piston

Inert gas added  $\Rightarrow$  Presre  $\uparrow \Rightarrow$  Vol  $\uparrow$  to nullify effect



$\Rightarrow$  Rx<sup>n</sup> shifts to  $\uparrow$   
no. of gas mol.

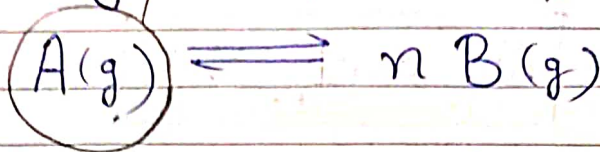
★ If we add solid, then NO EFFECT.



Vapor Density

(Formula valid only  
if 1 species with  
stoch. coeff = 1)

R:



I:

a

0

E:

 $a(1-\alpha)$  $na\alpha$ 

Initially, only A present.  $\Rightarrow$  (V.D. of A) =  $D$  <sup>Theoretical</sup>

At Eq., both A & B present  $\Rightarrow$  (V.D. of mix.) =  $d$  <sup>Observed</sup>

for any pt. in rxn, mass consrv.

$$\therefore n = \frac{W}{M} \text{ const.} \Rightarrow n \propto \frac{1}{M}$$

$$\Rightarrow \frac{n_i}{n_f} = \frac{M_f}{M_i} = \frac{d}{D} \Rightarrow \frac{a}{a+(n-1)a\alpha} = \frac{d}{D}$$

 $\Rightarrow$ 

$$\alpha = \frac{D-d}{(n-1)d}$$







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Imp. Pts —

- 1) In simultaneous eq., apply all formula using final values. (See Pg 376)