

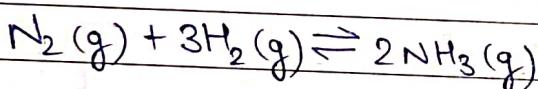
Chemical Eq.

Chemical Rxn of 2 types: Reversible & Irreversible

Reversible

- 1) Both forward & backward dirxn.

Eg: Haber's process



- 2) Occur in closed container.

- 3) Eq. is achieved.

- 4) All neutralisation rxns w/o (strong acid & base) together.

Irreversible

- 1) Only in forward dirxn.

Eg: Explosion, Combustion,...
Milk to Curd, ...

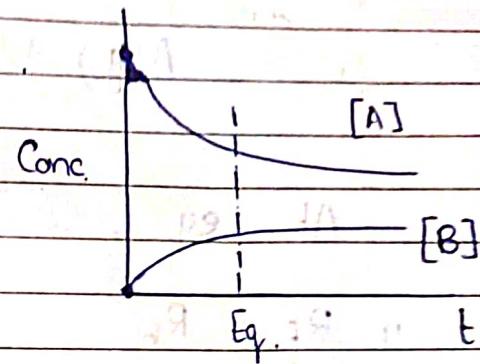
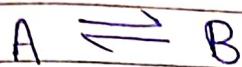
- 2) Occur in both area.

- 3) Eq. NOT achieved

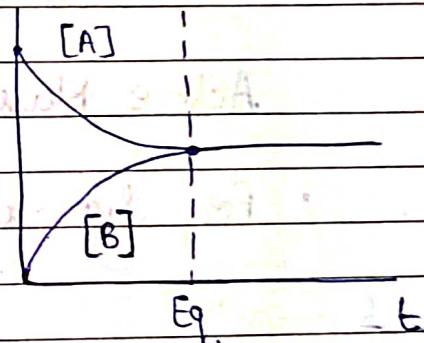
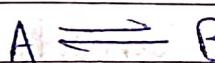
- 4) Strong Acid + Strong Base Rxns.

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

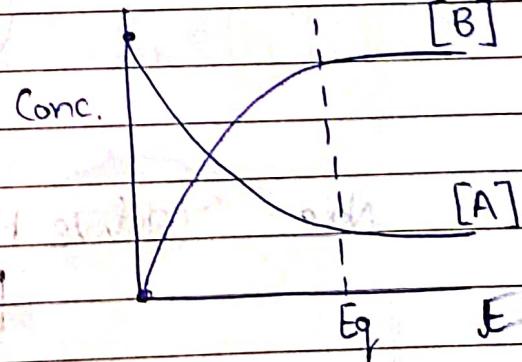
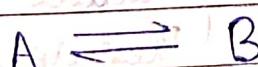
- C1: R_x^n goes little forward.



- C2: R_x^n goes exactly 50%



- C3: R_x^n goes very far.



- Note -

If no products initially present
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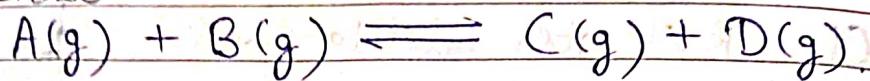
Rate of r_x^n

R_f t
 R_b

R_f - frwd 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. soln.,

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

For gases,

$$\begin{aligned} \text{(Active Mass)} &\rightarrow \boxed{\begin{array}{l} (\text{Molar Conc.}) \{[A]\} \\ (\text{Partial Pressure}) \{[P_A]\} \end{array}} \end{aligned}$$

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

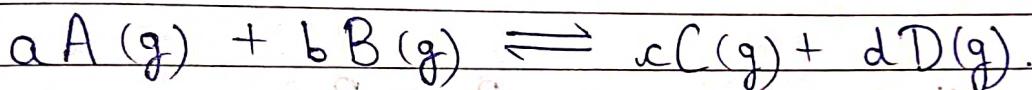
$$\frac{(\text{Density})}{(\text{Molar Mass})} = \frac{1}{(\text{Molar Mass})} \frac{(\text{Mass})}{(\text{Volume})}$$

For solids / pure liq., excess density = const.
 We assume active mass to be ①. $(\text{molar mass}) \text{volume} = \text{const.}$
 $\Rightarrow \text{active mass} = \text{const.}$

$\Rightarrow \text{Active Mass} = 1$

Law of Mass Action

Consider homogenous reversible $a \times^n$,



Acc. to the law,

$$R_f \propto [A]^a [B]^b \quad \text{st} \quad R_b \propto [C]^c [D]^d$$

$$\Rightarrow R_f = k_f [A]^a [B]^b \quad \text{st} \quad R_b = k_b [C]^c [D]^d$$

Rate const.
fwd \times^n Rate const.
back. \times^n

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

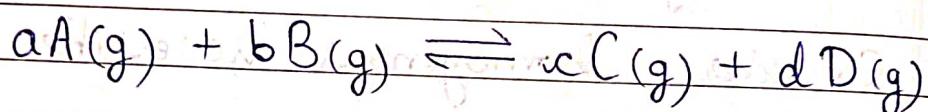
$$\text{Units of rate const.} = (\text{mol L}^{-1})^{1-(a+b)} \text{s}^{-1}$$

★ Rate const. depends only on :

Temp. & Catalyst.

Law of Chemical Eq.

Consider homogenous reversible rxn,



At eq.,

$$R_f = R_b$$

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

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

K_{eq}

In terms of conc.
(K_c)

$$\begin{aligned} (\text{Units of } K_{eq}) &= \frac{(\text{mol L}^{-1})^{(c+d)} \cdot (\text{atm})^{(a+b)}}{(\text{mol L}^{-1})^{(c+d)-(a+b)}} \\ &= (\text{mol L}^{-1})^{\Delta n_g} \end{aligned}$$

$\Delta n_g = (\text{Product gas mol}) - (\text{Reactant gas mol})$

In terms of partial pressure
(K_p)

$$(\text{Units of } K_{eq}) = p^{(\Delta n_g)}$$

In terms of mol frac. (K_x)
(Units of K_{eq}) = K_x

Imp. Pts on K_{eq} :

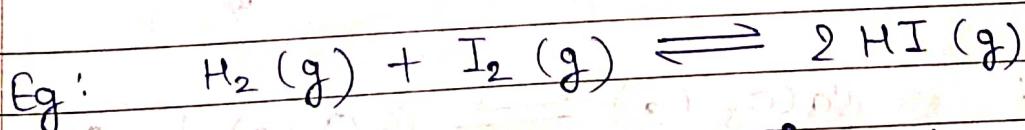
- 1) Def'n - It value of K_{eq} holds only at eq. cond'n.
- 2) It is fixed for a rxn at a particular temp., i.e. it is temp. dependent.
- 3) Indepⁿ of conc., pressure, vol., catalyst.

Types of Chemical Eq

1) Homogenous Chem. Eq

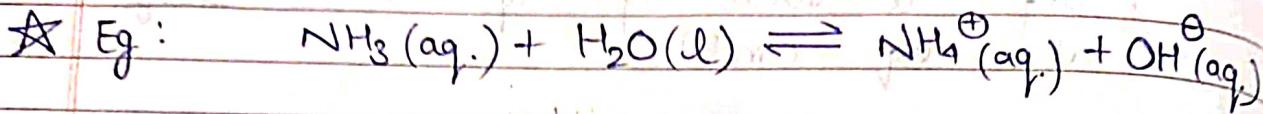
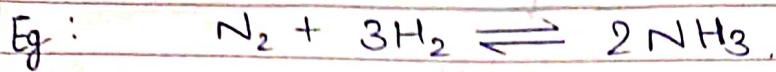
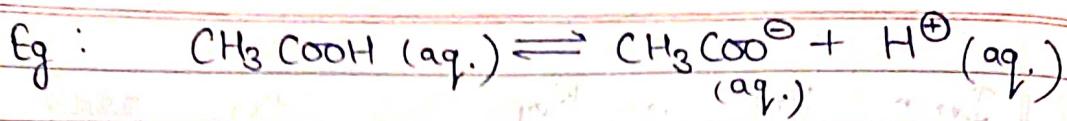
2) Heterogeneous Chem. Eq

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



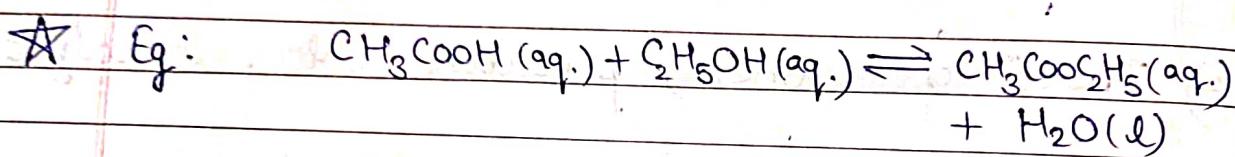
$$K_c = \frac{[HI]^2}{[H_2][I_2]}, \quad K_p = \frac{P_{HI}^2}{P_{H_2}[P_{I_2}]}, \quad K_x = \frac{[X_{HI}]^2}{[X_{H_2}][X_{I_2}]}$$

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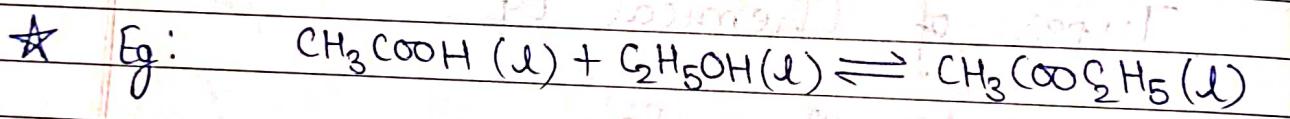
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$$K_c = \frac{[\text{NH}_4^\oplus][\text{OH}^\ominus]}{[\text{NH}_3][\text{H}_2\text{O}]} \Rightarrow K = [\text{NH}_4^\oplus][\text{OH}^\ominus]$$

Since in excess, $[\text{NH}_3]$
active mass = 1



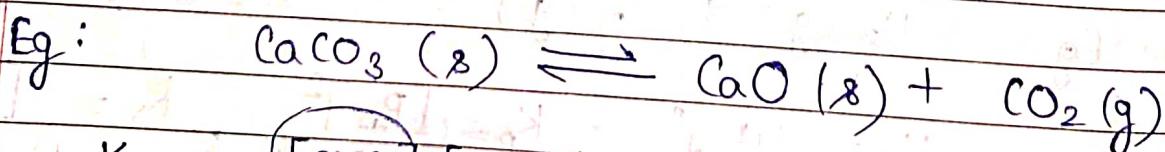
$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} \rightleftharpoons \frac{\text{active mass}}{\text{active mass}} = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$



$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} \rightleftharpoons +1 \text{ as}$$

NOT in excess.

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

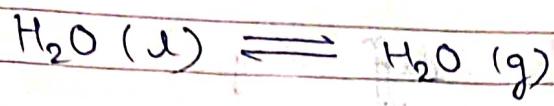


$$K_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]} \rightleftharpoons \text{Solids active mass} = 1 \Rightarrow K_c = [\text{CO}_2]$$

$$K_p = [\text{P}_{\text{CO}_2}]$$

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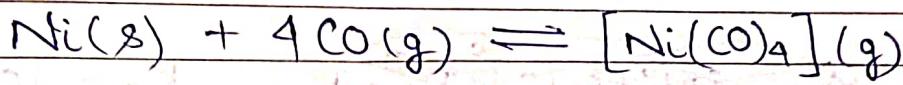
Eg:



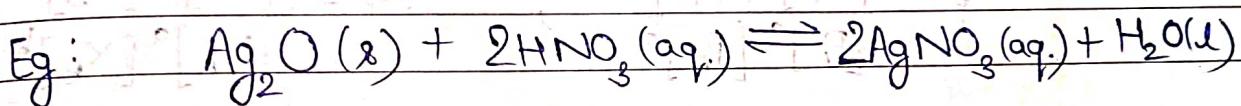
$$K_c = \frac{[\text{H}_2\text{O}(g)]}{[\text{H}_2\text{O}(\ell)]}$$

Liq. \Rightarrow Kc = [H₂O(g)]
active
mass = 1, if
gas present K_p = [P_{H₂O(g)}]

Eg:



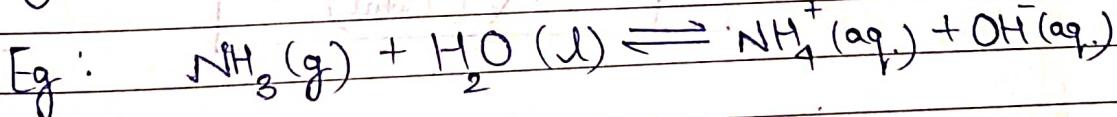
$$K_c = \frac{[\text{Ni(CO)}_4]}{[\text{CO}]^4}$$



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



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

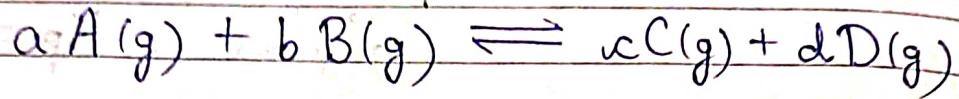


$$K_{pc} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[P_{\text{NH}_3}]}$$

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

Reln b/w diff. K_{eq} & K_p

Consider the homo. reversible rxn,



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

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

$$K_p = \frac{[P_c]^c [P_d]^d}{[P_A]^a [P_B]^b}; \quad K_x = \frac{[x_c]^c [x_d]^d}{[x_A]^a [x_B]^b}$$

Now by Dalton's law,

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

$$\Rightarrow K_p = \frac{x_c^c x_d^d}{x_A^a x_B^b} (P_{\text{Total}})^{(c+d)-(a+b)}$$

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

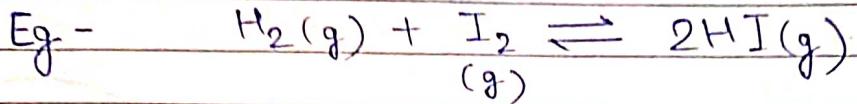
Now by Ideal gas eqn, $PV = nRT$

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

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

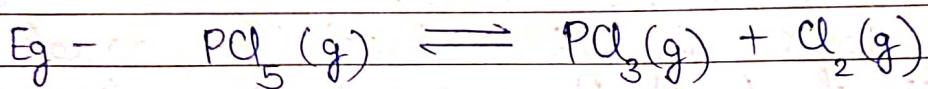
$$\Rightarrow K_p = K_c (RT)^{\Delta n}$$

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

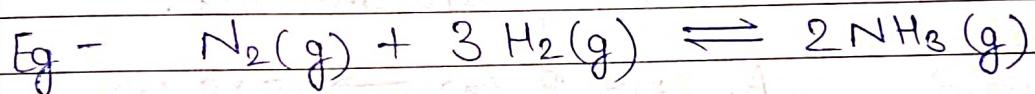


Both K_p & K_c dimensionless.

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



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



★ C4: $K_p = K_c$, if $\Delta n_g = 0$ if $T = \frac{1}{R}$

Q) A mix. of SO_3 , SO_2 & O_2 gases is maintained at eq. in 10L flask at temp. at which K_c for $2SO_2 + O_2 \rightleftharpoons 2SO_3$ is $100\text{ mol}^{-1}\text{L}$.

At eq,

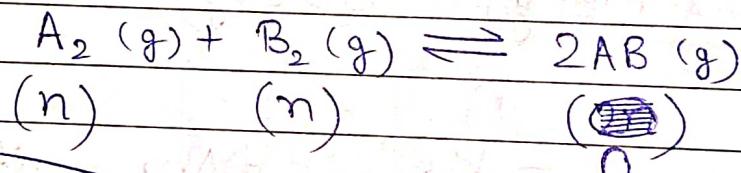
- a) if # mol(SO_2) = # mol(SO_3), find # mol(O_2)
- b) if # mol(SO_3) = 2 # mol(SO_2), find # mol(O_2)

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

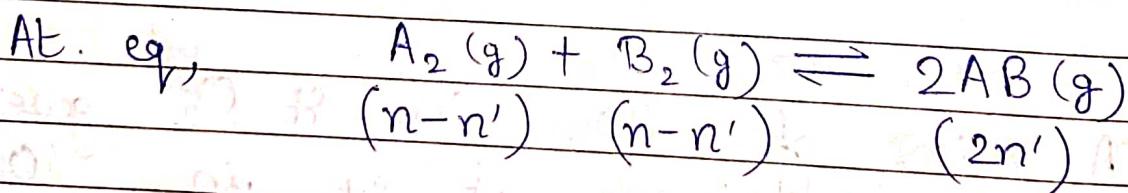
b) $K_c = 100 = \frac{(n_{SO_3}/10)^2}{(n_{SO_2}/10)^2(n_{O_2}/10)} \Rightarrow n_{O_2} = 0.4$

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

A) Let 'n' mol be present initially.



★ ~~$16 = \frac{(2n/2)^2}{(n/2)(n/2)}$~~ ← wrong. Can't apply at initial condn.

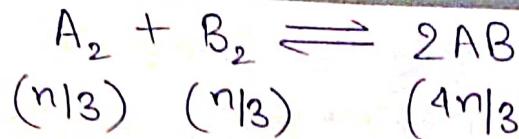


Now,

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

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

At eq.,



(n/3) (n/3)

(4n/3)

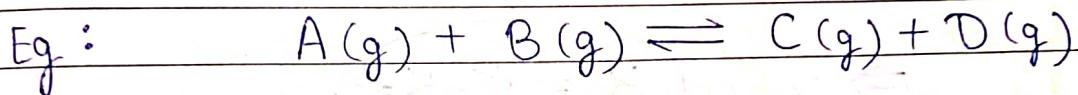
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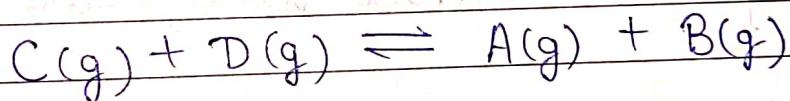
$$\left(\text{Mole \% of } A_2 \right) = \left(\frac{n/3}{n/3 + n/3 + 4n/3} \right) \cdot 100\% \Rightarrow \boxed{\left(\text{Mol \% of A} \right) = 16.6\%}$$

Factors affecting K_{eq}

1) Mode of representation :-



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

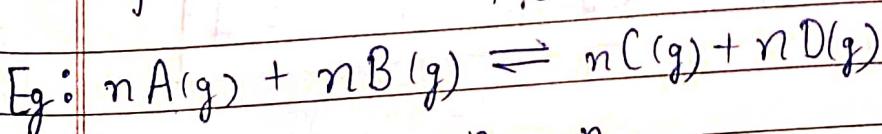


$$K'_c = \frac{[A][B]}{[C][D]}$$

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

2) Stoichiometry of \times^n :-

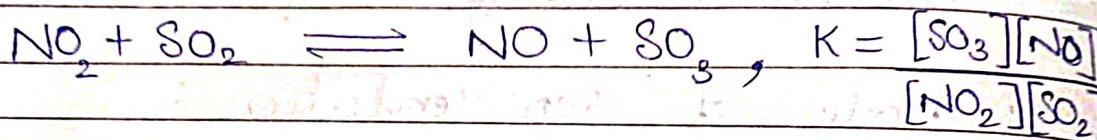
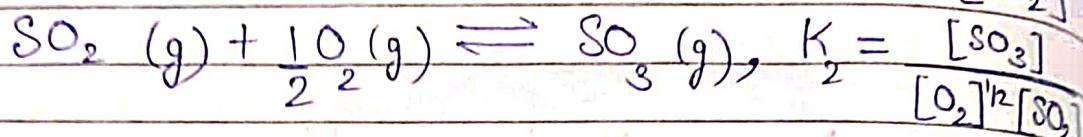
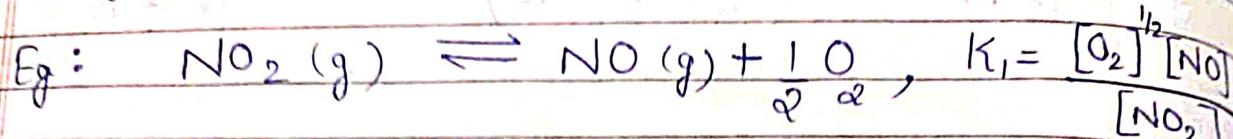
If we multiply \times^n by 'n'.



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

GOOD WRITE

3) By addⁿ & subⁿ of λx^n :



$$\Rightarrow K = K_1 K_2$$

If we subtract λx^n s, we get

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

4) Effect of Temp:

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

ΔS = Change in Entropy

ΔH = Change in Enthalpy

\Rightarrow

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

(Don't Read!)

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

If $T_2 > T_1$ (Temp \uparrow) $\Rightarrow K_1 > K_2$ (K_{eq.} dec.)

$\Rightarrow Rx^n$ shifts in back dirxⁿ.

$\Rightarrow Rx^n$ shifts towards Endothermic.

If $T_1 > T_2$ (Temp \downarrow) $\Rightarrow K_2 > K_1$ (K_{eq.} inc.)

$\Rightarrow Rx^n$ shifts frwd dirxⁿ

$\Rightarrow Rx^n$ shifts towards Exothermic

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

If $T_2 > T_1$ (Temp \uparrow) $\Rightarrow K_2 > K_1$ (K_{eq.} inc.)

$\Rightarrow Rx^n$ shifts towards Endothermic

If $T_1 > T_2$ (Temp \downarrow) $\Rightarrow K_1 > K_2$ (K_{eq.} dec.)

$\Rightarrow Rx^n$ shifts towards Exothermic

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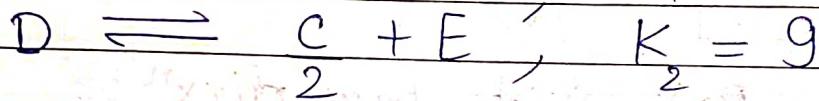
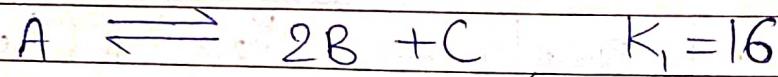
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In general, in any Rx^n

Temp. $\uparrow \Rightarrow Rx^n$ towards Endo.

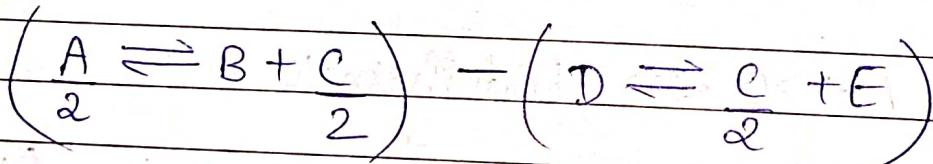
Temp. $\downarrow \Rightarrow Rx^n$ towards Exo.

(Q)



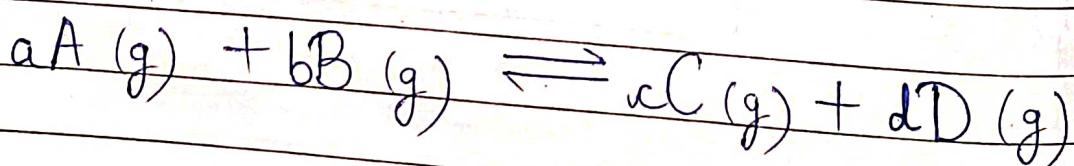
Find K_{eq} for, $\frac{1}{2} A + E \rightleftharpoons B + D$:

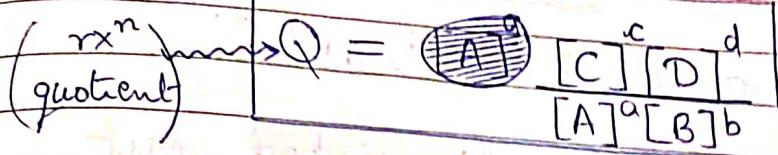
A)

 \Rightarrow

$$K_{eq} = \left(\frac{16}{9} \right)^{1/2} \Rightarrow \boxed{K_{eq} = \frac{4}{3}}$$

Rx^n Quotient (Q)



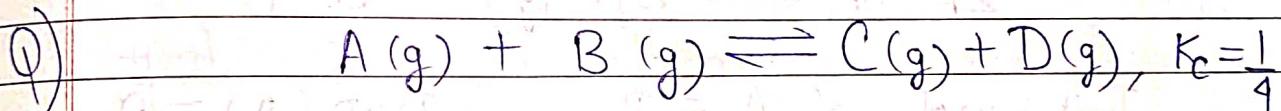


at any pt. of time.

C1: $Q > K_{\text{eq.}}$ \Rightarrow Rx^n shifts backward.

C2: $Q < K_{\text{eq.}}$ \Rightarrow Rx^n shifts forward

C3: $Q = K_{\text{eq.}}$ \Rightarrow Rx^n at eq..



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

- 1) direction of Rx^n 2) # mol. of each at eq.

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

	A	B	C	D
I:	1	1	1	1
E:	$1+x$	$1+x$	$1-x$	$1-x$
C:	$1+x$	$1+x$	$1-x$	$1-x$

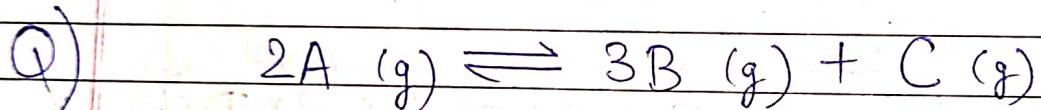
$K_c = \frac{(1-x)(1-x)}{(1+x)(1+x)} = \frac{1}{4} \Rightarrow \frac{(1-x)^2}{(1+x)^2} = \frac{1}{4} \Rightarrow x = \frac{1}{3}$

GOOD WORK

Degree of Dissociation (α)

No. of moles dissociated out of 1 mol of a species.

Eg:	Init. mol	Mol. diss.	D.O.D.
	1	a	a
	2	a	a/2
	a	α	α/a
★	a	$a\alpha$	α

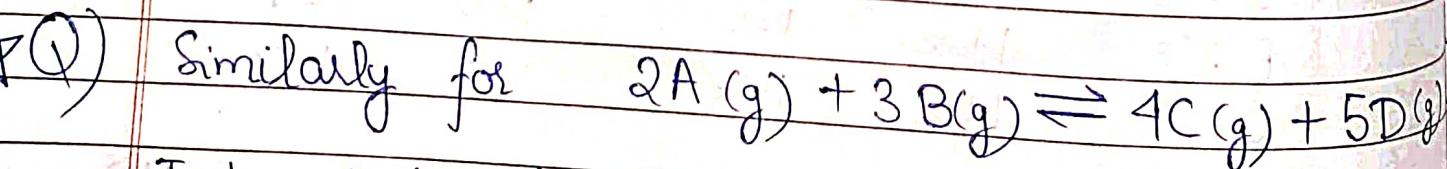


Init. mol. of A = 3. DOD(A) = α .

Calc. total no. of moles at eq.

A)	R:	$2A \rightleftharpoons 3B + C$
	I:	3 0 0
	E:	$3(1-\alpha)$ $\left(\frac{9\alpha}{2}\right)$ $\left(\frac{3\alpha}{2}\right)$

$$\text{(Total mol. at eq.)} = 3\alpha + 3$$



$$\text{Init mol (A, B)} = (3, 2) \quad \text{D.O.D. (A)} = 0.3$$

GOOD WRITE

A) *

Assume new variable to red. calc.

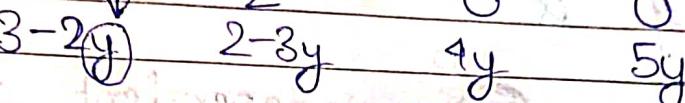
R:



I:



E:



$$(Total mol. at eq.) = 4y + 5 \quad \text{Now, } 2y = 3(0.3)$$

 \Rightarrow

$$\text{Req.} = 23$$

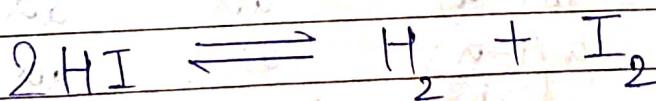
 \Rightarrow

$$y = 0.45$$

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

$$Cl: \Delta n_{\text{g}} = 0$$

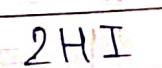
Q) 'a' mol of HI are taken in a container of vol 'V'. If DoD of HI is α , and total pressure at eq. is P , find K_c & K_p in terms of a , V , P , α .



(g)

A)

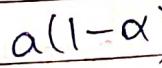
R:

Total
 a

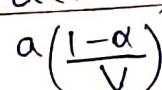
I:

Same
 a

E:



C:



GOOD WRITE

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Since $\Delta n_g = 0 \Rightarrow K_p = K_c$ SPP DATE: ___/___/___
PAGE ___

$$K_c = \frac{(\alpha/\nu)(\alpha'/\nu)}{\left(\frac{\alpha(1-\alpha)}{\nu}\right)^2} \Rightarrow K_c = \frac{\alpha^2}{2(1-\alpha)^2}$$

Const.

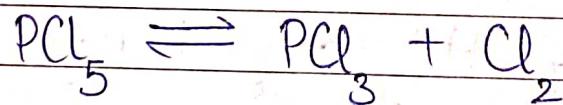


- If $\alpha \ll 1 \Rightarrow (1-\alpha) \approx 1$

- Since K_c is independent of init. mol. st. vol. taken, assume them to be $\nu = 1$

C2: $\Delta n_g > 0$

Q) 'a' mol PCl_5 taken in container of vol. V . If DoD of PCl_5 is α and total pressure at eq. is P find K_c, K_p in terms of a, V, P, α .



A) R:

	PCl_5	PCl_3	Cl_2	Total	Dif.
I:	a	0	0	a	
E:	$a(1-\alpha)$	$a\alpha$	$a\alpha$	$a + a\alpha$	
c:	$a\left(\frac{1-\alpha}{V}\right)$	$\left(\frac{a\alpha}{V}\right)$	$\left(\frac{a\alpha}{V}\right)$		

$$K_c = \frac{(a\alpha/V)(a\alpha/V)}{a\left(\frac{1-\alpha}{V}\right)}$$

Const.

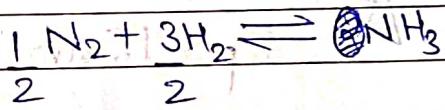
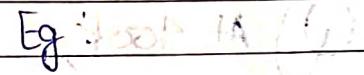
$$K_c = \frac{a\alpha^2}{V(1-\alpha)}$$

GOOD WRITE

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

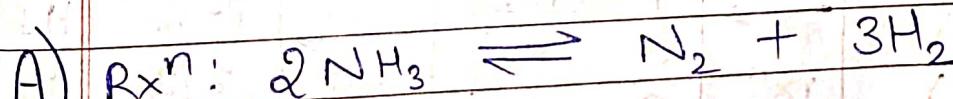
C3: $\Delta n_g < 0$

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



16/9/22

Q) $NH_3(g)$ at 15 atm is intro. in rigid vessel at 1.300 K. At eq., total presre of vessel is 40.11 atm. at 300°C. ~~The~~ find DoD of NH_3 .



Init: -n

Eq: $m(1-\alpha)$

$n\alpha$

$\frac{3n\alpha}{2}$

$n + n\alpha$

GOOD WRITE

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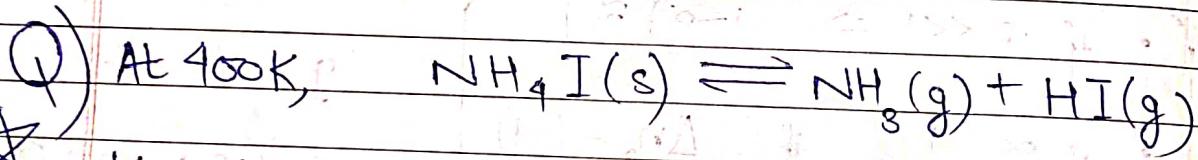
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$$\text{By } PV = nRT, \quad n = \frac{(15)}{(300)} \left(\frac{V}{R} \right)$$

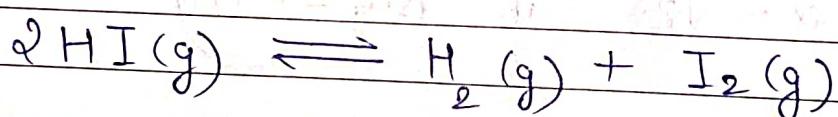
$$n(1+\alpha) = \frac{(40.11)}{573} \left(\frac{V}{R} \right)$$

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

$$\Rightarrow \alpha = 0.4$$



$K_p = 16 \text{ atm}$. Under catalyst,

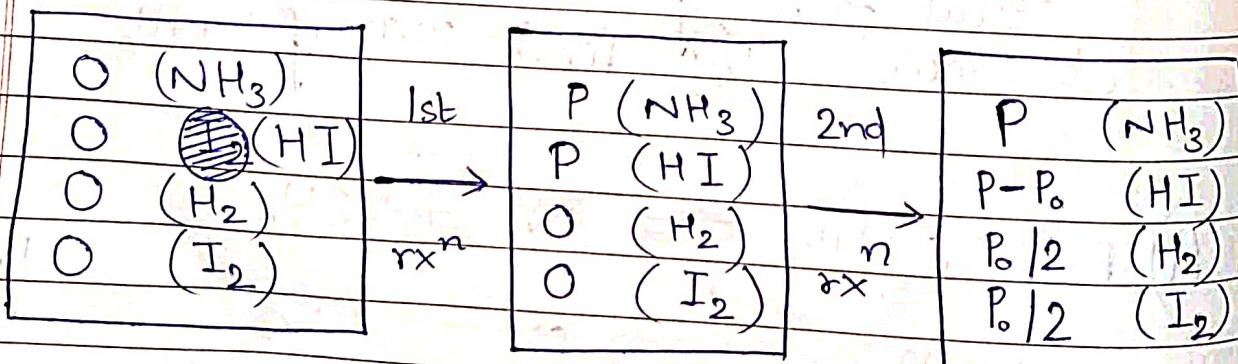


If partial presre of H_2 at this temp.

is 1 atm, when both eq. exist simultaneously

Calc. K_p of second rxn.

A)



Final
Composition.

GOOD WRITE

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for 1st rxn :

$$P(P - P_0) = 16 \Rightarrow P = 5.1$$

We know,

$$P_0/2 = 1 \quad (\text{for } H_2) \Rightarrow P_0 = 2$$

For 2nd rxn:

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

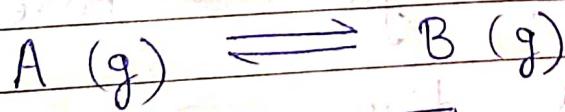
 \Rightarrow

$$K_p = 0.1$$

Le Chatlier's Principle

If system is 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.:

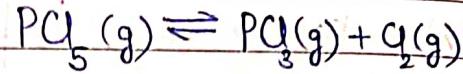


If $\boxed{\text{conc. } A \downarrow \text{ (or } \uparrow)}$ $\Rightarrow \text{conc. } B \downarrow \text{ (or } \uparrow)$

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

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

2) Effect of Pressure:



If $P \uparrow$ (or \downarrow) \Rightarrow (Total gaseous moles) \downarrow (or 1)
 so as to \downarrow (or \uparrow) P.

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

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

3) Effect of Vol.:

Vol. bada diya \Rightarrow Pressure ghatा diya.

Vol. ghatा diya \Rightarrow Pressure bāda diya.

Hence,

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

4) Addⁿ 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. Prsre

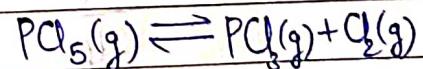
at

Const. Vol.

Inert gas added \Rightarrow Gaseous mol \uparrow \Rightarrow Rxⁿ shifts to ↓
no. of gds mol.

Case 3:

At. Const. Prsre

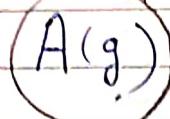
Movable
PistonInert gas added \Rightarrow Prsre $\uparrow \Rightarrow$ Vd \uparrow to nullify effect
 \Rightarrow Rxⁿ shifts to ↑
no. of gds mol.


If we add solid, then No Effect.

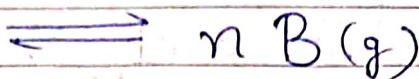
380

DATE: ___/___/___
PAGE ___Vapor Density

R:



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



I:

a

0

E:

a(1- α)n α

Initially, only A present. $\Rightarrow (V.D.)_{\text{of A}} = D'$ Theoretical

At Eq., both A & B present $\Rightarrow (V.D.)_{\text{of mix.}} = d$ Observed

for any pt. in rxn, mass consrv.

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

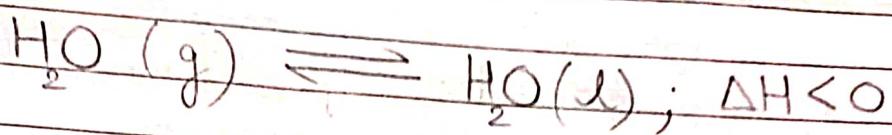
$$\Rightarrow \frac{n_i}{n_f} = \frac{M_f}{M_i} = \frac{d}{D} \Rightarrow \frac{a}{a + (n-1)\alpha} = \frac{d}{D}$$

\Rightarrow

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

Physical Eq. :-

Eg :



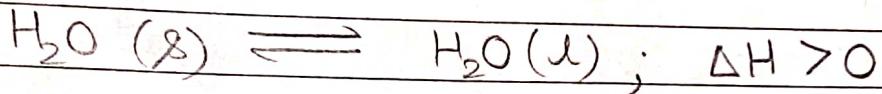
Favorable

Condts for : frwd rxn

Temp. ↓

Prsre ↑

Eg :



Favorable

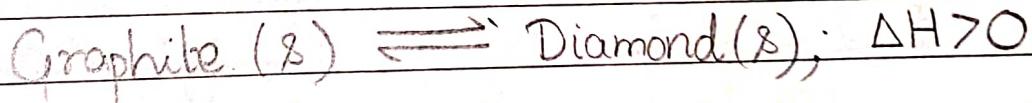
Condts for : frwd rxn

Temp. ↑

Prsre ↑

(as Vol. water < Ice)
prsre ↑ ⇒ vol. ↓

Eg :



Favorable

Condts for : frwd rxn

Temp. ↑

Prsre ↑

(as Vol. Diamond < Graphite)
prsre ↑ ⇒ vol. ↓

Imp. Pts —

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