

Equilibrium & Chemical Kinetics

Equilibrium

Static:

→ Motions are ceased

Dynamic

→ Motions are not ceased

Chemical Equilibrium:

→ It is; rate of forward rxn equal to backward rxn.

$$R_f = R_r$$

∴ It is only applicable on reversible reactions

→ Concentration of products and reactants become equal.

→ The graph of concentration and time parallel to x-axis

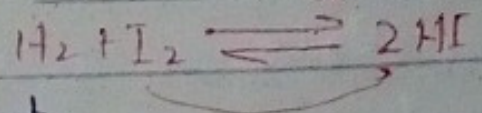
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Characteristics Of EQ:

→ Should be ⁱⁿ closed system otherwise the rxn will become irreversible

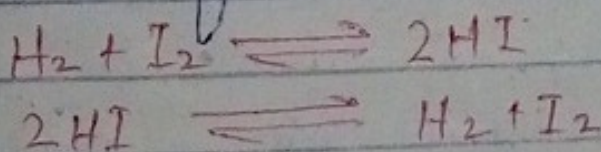
→ Dynamic

→ Microscopic Motion Continue.



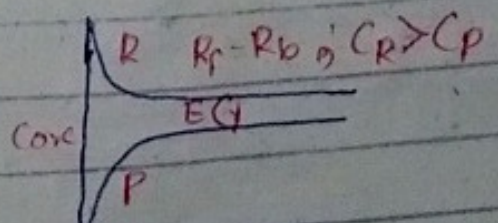
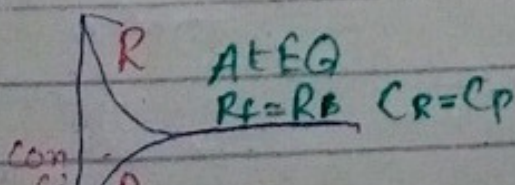
→ Doesnot depend upon catalyst.

→ Achieved from either side.

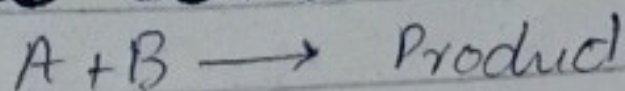


∴ EQ is not direction dependant

Graph:



Rate Constant:



$$\text{Rate} = k[A][B]$$

Temp

P/V/conc/catalyst

$$[A] = [B] = \text{Unity (1)}$$

Rate = $k \rightarrow$ velocity or specific rate.

Unit:

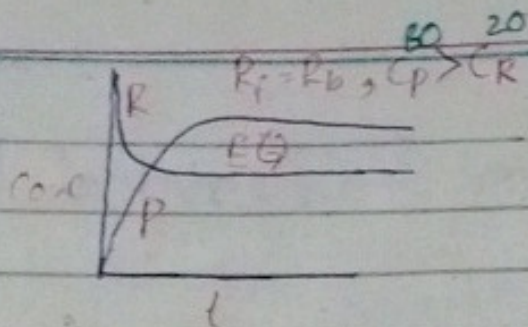
$$k = (\text{mol dm}^{-3})^{1-n} \text{ s}^{-1}$$

a: $\text{mol dm}^{-3} \text{ s}^{-1}$ ($n=0$) \rightarrow Zero order

b: s^{-1} ($n=1$) \rightarrow First order

c: $\text{mol}^{-2} \text{ dm}^3 \text{ s}^{-1}$ ($n=2$) \rightarrow Second Order

d: $\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ ($n=3$) \rightarrow Third Order



∴ Concentration will remain constant at EQ.

At EQ C_p & C_r always?

- a: Maximum
- b: Equal
- c: Minimum
- d: Constant (always)

C_r and C_p can be? on equilibrium?

- a: $C_p = C_r$
- b: $C_p > C_r$
- c: $C_r > C_p$
- d: All

Types of Chemical EQ:

Homogenous
 → Same phase of reactants and products
 $\text{solid} + \text{solid} \rightleftharpoons \text{solid}$

Heterogenous
 → Different phase of reactants & products.
 $\text{solid} + \text{solid} \rightleftharpoons \text{Liquid}$

Law of Mass Action:

Rate \propto Conc. of Reactant

\propto Active mass of reactant

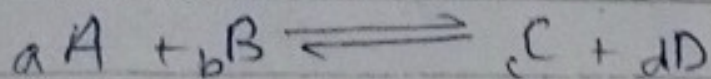
$\propto \frac{n}{V}$ } conc. solution > Dilute solution

Equilibrium Constant Expression:

K_c	K_p	K_x	K_n
mol/dm ³	Partial pressure	mole fraction	No. of mole

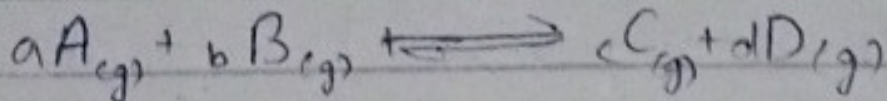
Partial Pressure & Concentration

General Reaction:



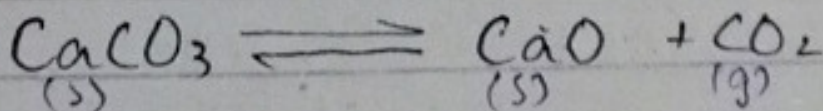
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Gases:



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

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$$a) K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

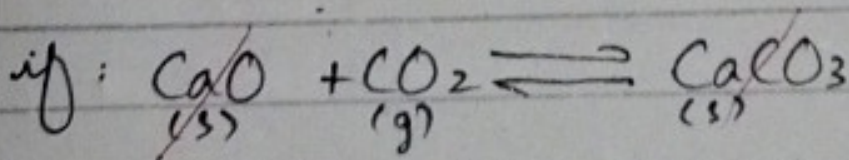
$$b) K_c = \frac{[CaO_3]}{[CaO][CO_2]}$$

$$c) K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

(d): None

$$\therefore K_c = [CO_2]$$

$$K_p = P_{CO_2}$$



$$K_c = \frac{1}{[CO_2]}$$

$$K_p = \frac{1}{P_{CO_2}}$$

$\therefore K_c$ is only for gases.

Characteristics of K_c :

Depends:

→ Temperature

Endo:

↑T \propto K_c ↑ → product ↑

Exo:

↓ K_c \propto $\frac{1}{T}$ ↑ → product ↓

Not Depends

→ Pressure

→ Volume

→ Catalyst

→ Direction

→ Initial Conc. of reactants

Units of K_c :

↳ It can have units and const.

No units: (1) $\Delta n = n_p - n_r$

$\Delta n = 0$

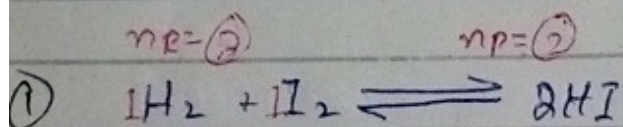
↓
no. of moles
of products

Units:

$\Delta n \neq 0$

$K_c = (\text{mol dm}^{-3})^{\Delta n}$

$K_p = (\text{atm})^{\Delta n}$



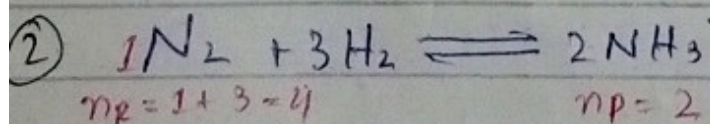
$n_r = 2$ $n_p = 2$

$$\Delta n = n_p - n_r$$

$$\Delta n = 2 - 2$$

$$\Delta n = 0$$

$$K_c = (\text{mol dm}^{-3})^0 = 1 \rightarrow \text{No units}$$



$n_r = 1 + 3 = 4$

$n_p = 2$

$$\Delta n = n_p - n_r$$

$$= 2 - 4$$

$$\Delta n = -2$$

$$K_c = (\text{mol dm}^{-3})^{-2}$$
$$= \text{mol}^{-2} \text{dm}^6$$

$$K_p = (\text{atm})^{-2}$$

$$K_p = \text{atm}^{-2}$$

$$K_p = \frac{1}{\text{atm}^2}$$

$$K_p = (\text{atm})^{\Delta n}$$

$$\Delta n = 0$$

$$K_p = K_c = K_x = K_n$$

Relation b/w K_p & K_c :

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

Equation balanced.

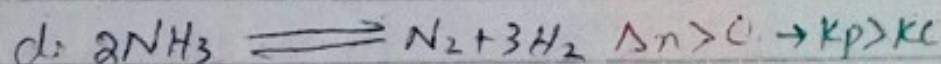
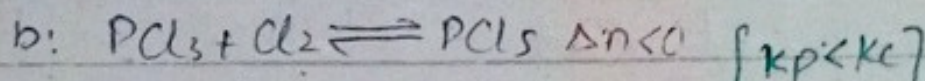
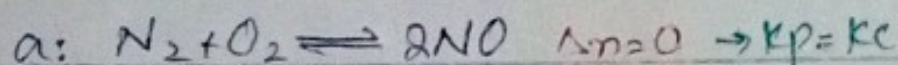
$$\Delta n = 0 \quad n_R = n_P \quad K_p = K_c$$

$$\Delta n > 0 \quad n_P > n_R \quad K_p > K_c$$

$$\Delta n < 0 \quad n_R > n_P \quad K_p < K_c$$

Questions:

$$\frac{K_p}{K_c} = ? \quad \frac{K_c}{K_p} = ?$$



MCG:

W.O.F is correct for $2SO_2 + O_2 \rightleftharpoons 2SO_3$

a: $K_p = K_c (RT)^{-1}$

b: $K_c = K_p (RT)^1$

$\Delta n = n_P - n_R$

c: $K_p = \frac{1}{K_c (RT)^2}$

Ⓐ All of these

$\Delta n = 2 - 3 = -1$

∴ ratio can also divide from these options.

Application Of K_c :

Extent of reaction

Large

$$K_c = 10^{30}$$

→ R almost completed in forward direction

→ Product → max

→ Reactant → min

→ Product → stable

→ Reactant → unstable

Small

$$K_c = 10^{-30}$$

→ Reaction is just started

→ R → maximum

→ R → stable

→ P → minimum

→ P → unstable

Neither small nor large

$$K_c = 100$$

At equilibrium both reactants and

products are in considerable amount

It is attained on equilibrium $\leftarrow K_c = \frac{[P]}{[R]}$ equilibrium

It is just ratio and can be taken any time. $\leftarrow Q_c = \frac{[P]}{[R]}$

Direction of Reaction:

$$Q_c = K_c$$

(At Equilibrium) - (Not Equilibrium).

→ Reaction should move in backward direction to attain equilibrium

→ Product > Reactant

$$Q_c > K_c$$

$$Q_c < K_c$$

(Not Equilibrium)

→ Rn should move in forward direction to attain equilibrium

Reactants > Product

Le-Chatlier's:

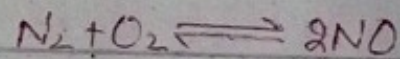
Applicable:

- Physical Equilibrium
- Chemical Equilibrium

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Statement: If stress is applied on a reaction at EQ then it will oppose by moving in opposite direction.

Factors Effecting EQ:



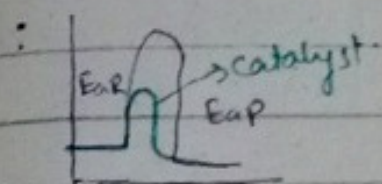
→ Effect of Concentration:

Concentration	Direction	EQ Position (Q_c)	Equilibrium Constant (K_c)
→ Add Reactants $N_2 \uparrow$ $O_2 \uparrow$	forward	change	Doesn't change
→ Remove Products $NO \downarrow$	forward	change	Doesn't change
→ Remove Reactants $N_2 \downarrow$ $O_2 \downarrow$	backward	change	Doesn't change
→ Add Products $NO \uparrow$	backward	change	Doesn't change

Effect of Catalyst:

Changes:

- Rate of reactions for both forward and backward.
- Path of mechanism
- Activation energy decreases



Not Changes:

- Position (Q_c)
- Equilibrium constant (K_c)
- Yield of product:

with
Products:
with catalyst → 35%
without catalyst → 35%
yield doesn't change

$$\uparrow \text{Rate} \propto \frac{1}{E_a \downarrow}$$

Effect of Temperature:

	Direction	Q_c	K_c
Endothermic:			
$T \uparrow$	forward	changes	$\uparrow K_c \propto T \uparrow \Rightarrow \text{Product} \uparrow$
$T \downarrow$	Backward	changes	$\downarrow K_c \propto T \downarrow \Rightarrow \text{Product} \downarrow$

Exothermic:

$T \uparrow$	Backward	changes	$\downarrow K_c \propto \frac{1}{T \uparrow} \Rightarrow \text{Product} \downarrow$
$T \downarrow$	forward	changes	$\uparrow K_c \propto \frac{1}{T \downarrow} \Rightarrow \text{Product} \uparrow$

Effect of pressure:

→ If EG mixture contains liquid and solid there will be no effect of pressure.

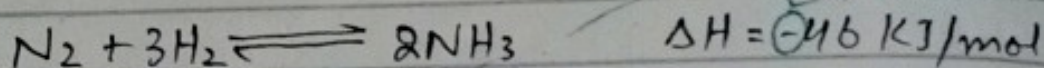
→ If EG mixture is gaseous then;

$\Delta n = 0$
→ No effect of pressure

$\Delta n \neq 0$
→ Effect of pressure.

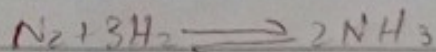
→ By increasing Pressure the reaction will move from high moles to lower moles.

Effect of pressure	Direction	EQ Position (Qc)	EQ Constant (Kc)
$n_R > n_P$ P↑V↓	forward	change	X
$n_R > n_P$ P↓V↑	backward	change	X
$n_R < n_P$ P↑V↓	Backward	change	X
$n_R < n_P$ P↓V↑	forward	change	X



- a: High P, low T, Add Reactants When will
 b: Low P, High T, Remove Product NH_3 produce $^{+}$ large
 c: High P, Low T, Remove Reactants
 d: None

Haber Process



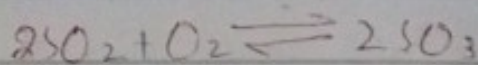
• Optimum:

→ Pressure → 200-300 atm

→ Temp = 450°C

→ Catalyst = Fe

Contact Process:



Optimum:

→ Pressure → 1 atm

→ Temp → 480-500°C

→ Catalyst → V_2O_5

Common Ion Effect:

↳ suppression / Decrease of weak electrolyte by adding strong electrolyte having common ion.

Common Ion

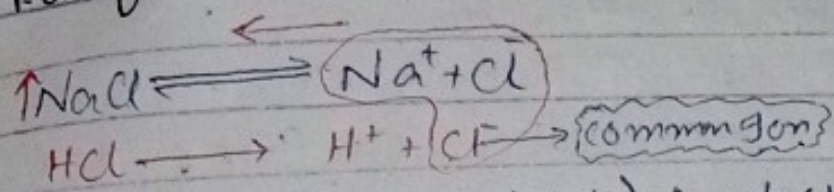
↑ Common Ion \propto 1 \propto 1

↓ Solubility Dissociation of weak electrolyte

C-I \propto Association of ions & Formation of solid & Crystallization & ppt

Strong Electrolytes:
 → Strong acid and bases & their salts
 Weak Electrolytes:
 → Weak acid & bases and their salts

Purification of NaCl:



- Adding HCl (strong electrolyte) in NaCl.
- NaCl amount will increase
- Cl⁻ conc. will increase
- Na⁺ conc. will decrease.

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Buffer Solution:

- Solution having almost constant pH.
- Solution Resist on changing pH.

Types Of Buffer:

Acidic:
 → pH < 7
 → Weak acid + salt of strong base
 → CH₃COOH + CH₃COONa⁺

Basic:
 → pH > 7
 → W. Base + salts of s. Acid.
 → NH₄OH + NH₄Cl⁺

WOF is not Buffer?

- a: HF / NaF
- b: H₂CO₃ / Na₂CO₃
- c: HCOOH / HCOONa⁺ (W.A / s.H.W.B)
- d: NH₄OH / NH₄NO₃

pH Calculation:

$$\text{pH} = \text{pKa} + \log \frac{[\text{salt}]}{[\text{Acid}]}$$

$$\text{pOH} = \text{pKb} + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

K_a & Acidity

pKa ∝ $\frac{1}{\text{acidity}}$

pH = ? [S] = 0.1, [A] = 0.01
 pKa = 4.74

$$\text{pH} = 4.74 + \log \frac{0.1}{0.01}$$

$$\text{pH} = 4.74 + \log \frac{\frac{1}{10}}{\frac{1}{100}}$$

$$\text{pH} = 4.74 + \log \frac{1}{10} \times \frac{100}{1}$$

$$\text{pH} = 4.74 + \log 10$$

$$\text{pH} = 4.74 + 1 = 5.74$$

$$\log_{10} 10 = 1, \log_{10} 100 = 2, \log_{10} 1000 = 3, \log_{10} 1 = 0$$
$$\log 2 = 0.3, \log 3 = 0.4, \log 4 = 0.6$$

$$[S] = 0.1, [A] = 0.1, pK_b = 9.26, pH = ?$$

$$pK_a = 14 - pK_b$$

$$pK_a = 14 - 9.26 = \boxed{4.74}$$

Now use formula:

$$pH = pK_a + \log \frac{[S]}{[A]} \rightarrow$$

$$pH = pK_a \quad [S] = [A]$$

$$pH > pK_a \quad [S] > [A]$$

$$pH < pK_a \quad [S] < [A]$$

Buffer Capacity:

→ Ability to resist change in pH is called buffer capacity.

WOF has higher buffer capacity?

a: $[A] = 0.1$ $[S] = 0.1$

B: $[A] = 0.1$ $[S] = 0.2$

C: $[A] = 0.2$ $[S] = 0.1$

D: $[A] = 0.2$ $[S] = 0.2$

∴ Equal and higher will have higher buffer capacity.

Solubility Product:

↳ product of ions at equilibrium
→ Applicable on sparingly soluble. \hookrightarrow solubility $\leq 0.01M$

$K_{sp} \propto T \uparrow$
 $K_{sp} \propto \text{Solubility}$
 $K_{sp} \propto \text{Number of ions}$

Applications:

① Precipitation:
Saturated:

Ionic product = K_{sp} (No precipitates)

Unsaturated:

Ionic product $< K_{sp}$ (No ppt)

Super Saturated:

Ionic product $> K_{sp}$ (ppt will form)

②: Solubility from K_{sp} :

Salt	No. of ions	Formula
AB (AgCl)	2	$K_{sp} = s^2$
AB ₂ or A ₂ B (PbCl ₂)	3	$K_{sp} = s^3$
AB ₃ or A ₃ B (AlCl ₃)	4	$K_{sp} = 27s^4$

What is ② → solubility of Ag^{+2} ions in AgCl

if its solubility 4×10^{-4}

a: 4×10^{-4}

b: 1×10^{-4}

③: 2×10^{-2}

d: 1×10^{-2}

$$K_{sp} = s^2$$

$$\sqrt{4 \times 10^{-4}} = \sqrt{s^2}$$

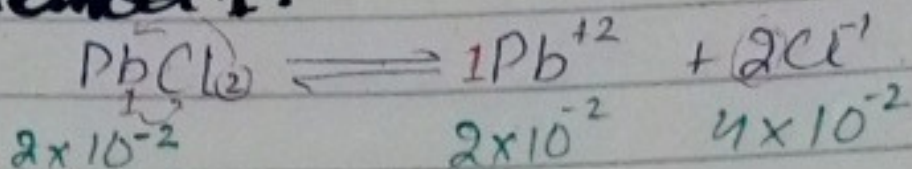
$$\sqrt{(2 \times 10^{-2})^2} = \sqrt{s^2}$$

$$s = 2 \times 10^{-2}$$

③ K_{sp} from Solubility:

What K_{sp} of $PbCl_2$ if its solubility $2 \times 10^{-2} \text{ mol/dm}^3$.

Method 1:



$$\begin{aligned} K_{sp} &= [\text{Pb}^{+2}] [\text{Cl}^-]^2 \\ &= [2 \times 10^{-2}] [4 \times 10^{-2}]^2 \\ &= [2 \times 10^{-2}] [16 \times 10^{-4}] \end{aligned}$$

$$K_{sp} = 32 \times 10^{-6}$$

Method 2:

$$K_{sp} = 4s^3$$

$$K_{sp} = 4(2 \times 10^{-2})^3$$

$$K_{sp} = 4(8 \times 10^{-6})$$

$$K_{sp} = 32 \times 10^{-6}$$