VARSITY 'Ka' ADMISSION PROGRAM 2020

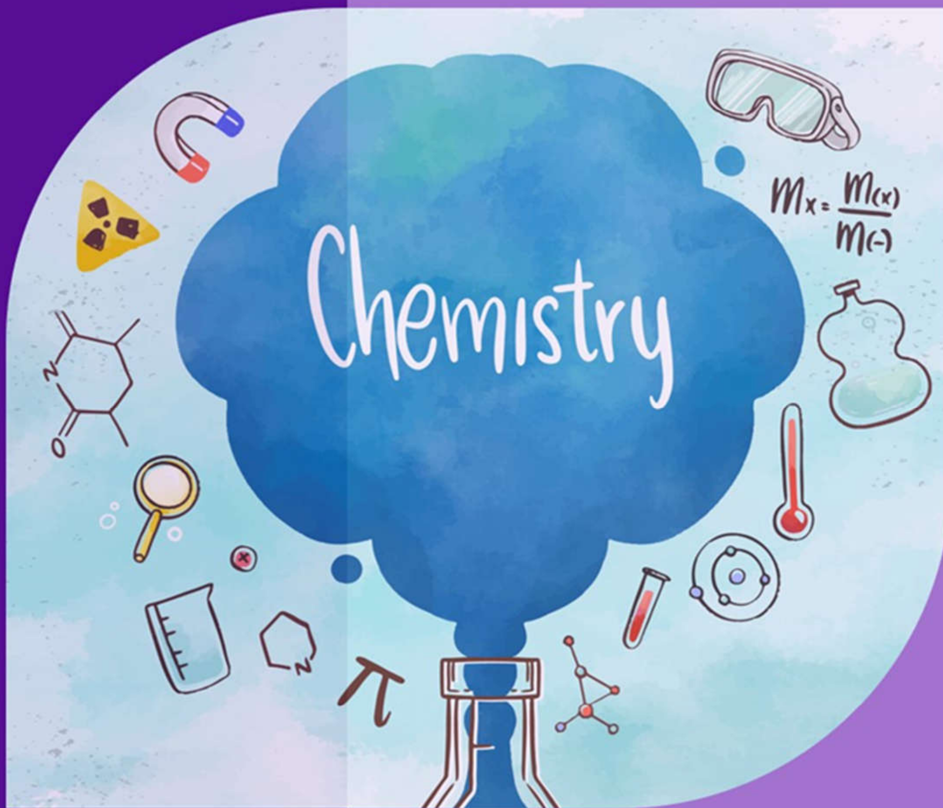
CHEMISTRY

LECTURE : C-03

CHAPTER 04 : CHEMICAL EQUILIBRIUM

Kp, Kc

Acid-Base eq.

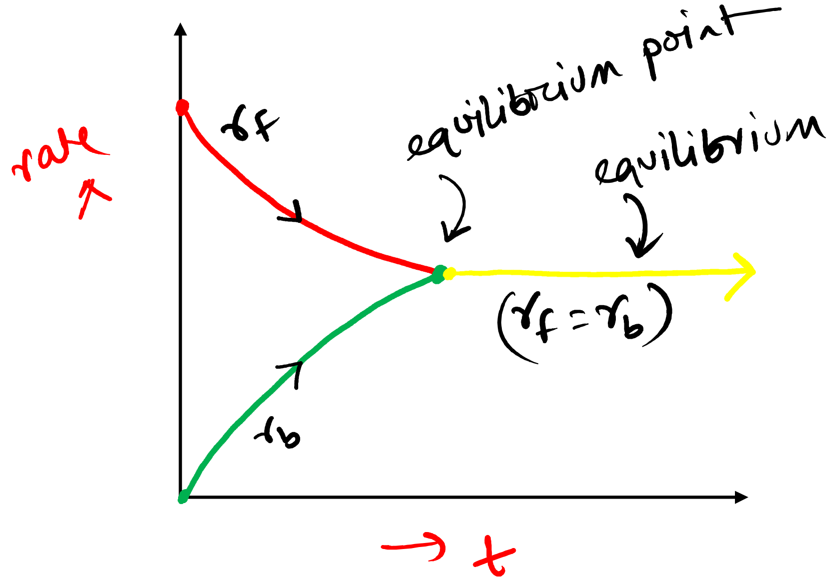


Time	[A]	[B]
0s	8	0
2s	6	2
4s	4	4
6s	3	5
8s	3	5
10s	3	5
5 years	3	5

$$A \rightleftharpoons B$$

Eq: $R_f = R_b$

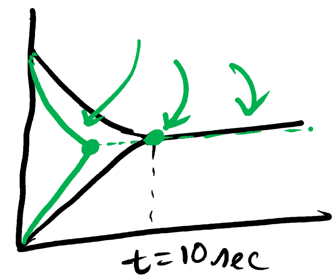
Rate vs time



$A \rightleftharpoons B$

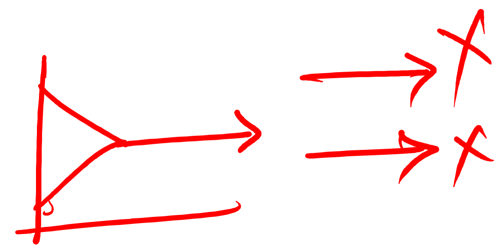
$r_f = -\frac{dA}{dt}$

$r_b = +\frac{dB}{dt}$



- positive catalyst:
  - r_f, r_b → time less
  - → eq. point (left)
- negative catalyst (eq. point → right)

- Equilibrium means the rate is equal not the amount.
- Equilibrium continues forever
- It is a dynamic state. And there is no role for the Catalyst
- A reversible reaction does not actually end, it reaches equilibrium. And this is what we often call the end.



Active mass

Aqueous: Molar Concentration (M)

Gas: Partial Pressure (atm)

Liquid : 1

Solid : 1

Partial pressure = Total Pressure × Mole Fraction

Concentration = Mole/ Volume (Litre)

Equilibrium Constant

Reactant ↓ product ↑ → eq. Reactant (unchanged) Product (")

↳ ratio between active mass of product & Reactant

active mass → unchanged (constant)

$K_{eq.} = \frac{\text{active mass of product}}{\text{active mass of reactant}} = \frac{\text{constant 1}}{\text{constant 2}} = \text{eq. constant}$

$aA + bB \rightleftharpoons cC + dD$

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

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

$A_{(aq.)} \rightleftharpoons B_{(aq.)}$

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

$A_{(aq.)} \rightleftharpoons 2B_{(aq.)}$ (B+B)

$K_c = \frac{[B].[B]}{[A]} = \frac{[B]^2}{[A]}$

$A_{(g)} \rightleftharpoons 2B_{(g)}$

$K_p = \frac{P_B^2}{P_A}$

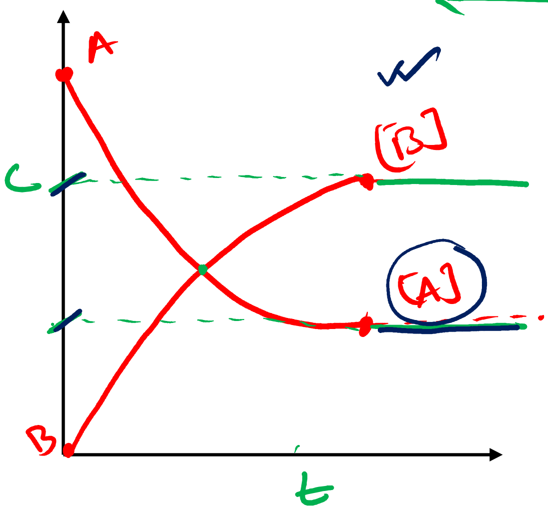
Only valid for equilibrium condition

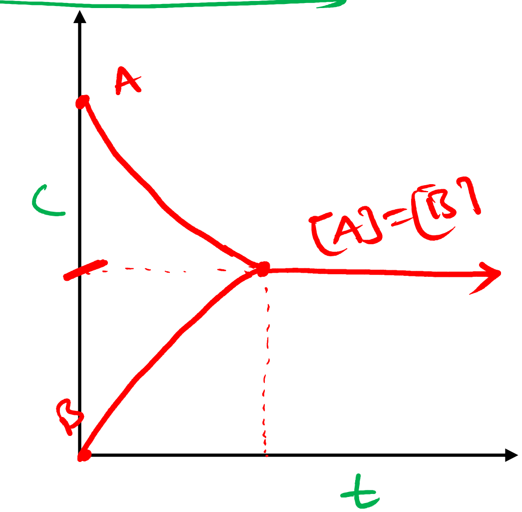
K_w

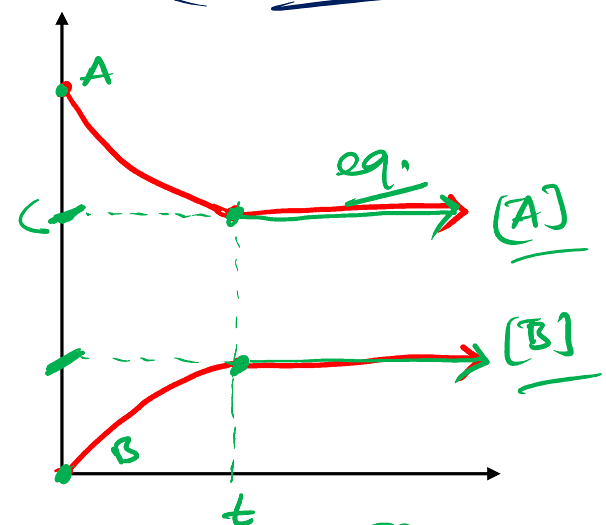
Conc vs time

(eq.): $A \rightleftharpoons B$; $K_c = \frac{[B]}{[A]}$

($K_c \uparrow$; profit $\uparrow$)







(1) $K_c > 1$

$\Rightarrow \frac{[B]}{[A]} > 1$

$\therefore [B] > [A]$ (at eq. state)

(2) When $K_c = 1$

$\therefore \frac{[B]}{[A]} = 1$

$\therefore [B] = [A]$ at eq.

(3) $K_c < 1$

$\Rightarrow \frac{[B]}{[A]} < 1$

$\therefore [B] < [A]$

Unit of K_P , K_C

active mass ↳ unitless

There is no UNIT, but is have unit in our EXAM (YEAH !!!) ← (অবশ্যই)

K_c = $(molL^{-1})^{\Delta n}$; Here, Δn= mole no of product- mole no of reactant (aq. + gas) ***

unit ↗ (conc^n → mol/L)

K_P = $(atm)^{\Delta n}$; Here, Δn= mole no of product- mole no of reactant (only gas) ***

(P. pressure ↳ atm)

$A(aq.) + 2B(g.) \rightleftharpoons 3C(aq.) + D(aq.) + E(s)$

K_c এর unit: $\Delta n = 4 - 3 = 1$

↳ $(mol\,L^{-1})^1$

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

K_p এর unit → $\Delta n = 2 - 1 = 1$

↳ $(atm)^1$

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Poll Question-01

- $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$; Find the unit of Kp of the given reaction?

(a) atm^{-1}

(b) atm^{-3}

(c) None of the above

(d) atm^{2}

$\Delta n = 2 - (1+1)$

$= 2-2$

$= 0$

$(atm)^{\Delta n}$

$= (atm)^{0}$

$= 1 \rightarrow$ No unit

K_P or K_C ?

If the toatall pressure of the system is not given, K_P can not be determined

- If the PRESSURE is given, then K_p
- If the VOLUME is given, then K_C
- If CONDITION is not given, then K_C

Type -01 (Equation Related)

If, $A \rightleftharpoons B$; K then.....

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

Δn= mole no of product - mole no of reactant

(only gas)

let, $K_c = \frac{[B]}{[A]} = 10$

$\rightarrow B \rightleftharpoons A$

$K_c = \frac{[A]}{[B]} = \frac{1}{10}$

$\rightarrow 2A \rightleftharpoons 2B$

$K_c = \frac{[B]^2}{[A]^2} = (10)^2 = 100$

$2B \rightleftharpoons 2A$

$\therefore K_c = \frac{1}{100} = (10)^{-2}$

$A \rightleftharpoons B$; $K_c = K$ ***

1. $B \rightleftharpoons A$; $K_c' = (K)^{-1}$
2. $nA \rightleftharpoons nB$; $K_c' = (K)^n$
3. $nB \rightleftharpoons nA$; $K_c' = (K)^{-n}$

eq. constant can be changed → via → Temp.
→ Reaction eq. changing

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Math Problem

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $K_P = \frac{1}{27}$ atm^{-2}

$\frac{2}{3}NH_3(g) \rightleftharpoons H_2(g) + \frac{1}{3}N_2(g)$; find K_P =?

[BUET 2017-18]

DU

modification (2) → side change; $\frac{1}{3}$ multiplication

3. $nB \rightleftharpoons nA$; $K_c' = (K)^{-n}$

$\therefore K_p' = (K_p)^{-\frac{1}{3}} = \left(\frac{1}{27}\right)^{-\frac{1}{3}} = \frac{1}{(27)^{-\frac{1}{3}}} = \frac{1}{\frac{1}{3}} = 3$

Poll Question-02

In a reversible reaction $\Delta n = \frac{1}{2}$, in which temperature K_P will be 8 times of K_C ?

(a) $32R^{-1}$
(b) $64R^{-1}$
(c) 32R
(d) 64R

$T = ?$

$K_p = 8 \cdot K_c$

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

$\Rightarrow 8K_c = K_c \cdot (RT)^{\Delta n}$

$\Rightarrow 8 = (RT)^{\frac{1}{2}}$

$\Rightarrow 64 = RT$

$\therefore T = \frac{64}{R} = 64R^{-1}$

Type-02 (Simple)

In 2L container, 12g H_2 reacts with 140g N_2 to form 34g NH_3 in equilibrium. How much is the equilibrium constant?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$K_c = ?$

$n = \frac{w}{M}$

$\frac{140}{28} = 5$, $\frac{12}{2} = 6$, $\frac{34}{17} = 2$

	N_2	$3H_2$	$2NH_3$
Initial mole:	5	6	0
eq. mole:	$5-x = 5-1 = 4$	$6-3x = 6-3 = 3$	$0+2x = 2x = 2$
eq. conc^n:	$4/2 = 2$	$3/2 = 3/2$	$2/2 = 1$

$2x = 2$, $x = 1$

$\Delta n = 2 - 4 = -2$

$$\therefore K_c = \frac{[NH_3]^2}{[N_2]\cdot[H_2]^3} = \frac{(1)^2}{2 \times (\frac{3}{2})^3} = \frac{2^3}{2 \times 3^3}$$

Unit: $(mol\,L^{-1})^{-2}$

off topic: $2A \rightleftharpoons 2B + C$ — Quantity

Type-03 (Initial amount is not given)

In a 2L container H_2 reacts with N_2 to form 1 mole NH_3 in equilibrium. What is the equilibrium constant?

coefficient → mole

1 : 3 : 2

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

	N_2	H_2	NH_3
initial mole:	1	3	0
eq. mole:	$1-x$	$3-3x$	$0+2x$
	$1-\frac{1}{2} = \frac{1}{2}$	$3-\frac{3}{2} = \frac{3}{2}$	$2\cdot\frac{1}{2} = 1$
eq. conc^n:	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{1}{2}$

$2x = 1$

$\therefore x = \frac{1}{2}$

$$\therefore K_c = \frac{\left(\frac{1}{2}\right)^2}{\left(\frac{1}{4}\right) \times \left(\frac{3}{4}\right)^3}$$

H.W. { = ☐ ; unit → ☐ }

Type-04 (Percentage amount is given is Equilibrium)

The 2L container has 20% (mol) N_2, 20% (mol) NH_3 in equilibrium. If the total pressure of the vessel is 10 atm, what is the constant?

→ K_p

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

%:

$N_2 = 20\% = 0.2$

$NH_3 = 20\% = 0.2$

$H_2 = 100 - 20 - 20 = 60\% = 0.6$

→ mole fraction

$\therefore P_{N_2} = 0.2 \times 10 = 2$

$P_{H_2} = 0.6 \times 10 = 6$

$P_{NH_3} = 0.2 \times 10 = 2$

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \cdot P_{H_2}^3} = \frac{(2)^2}{2 \times (6)^3}$$

→ = □ value

→ unit → $(atm)^{\Delta n} = (atm)^{2-4} = (atm^{-2})$

$(1-10)^2 ; (1-10)^3$

→ সুবিধা ; 6×6×6

Reaction Quotient (Q)

(K) ↓ ✓ ↓ at eq. state

(ratio between active mass of product and active mass of reactant)

↓ ✓ ↓ at any state

aA+ bB ⇌ cC+ dD

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

$$Q_p = \frac{P_C{}^c * PDd}{P_A{}^a * PB^b}$$

Q is at any state

but,

K is only valid in equilibrium state

A → B ; K = 10

when $Q_c = \frac{[B]}{[A]} = 5$

when, $Q_c = \frac{(B)}{(A)} = 20$

☐ comparison of K_c and Q_c:

1. $K_c = Q_c$; equilibrium state
2. $K_c < Q_c$; Backward Direction
3. $K_c > Q_c$; Forward Direction

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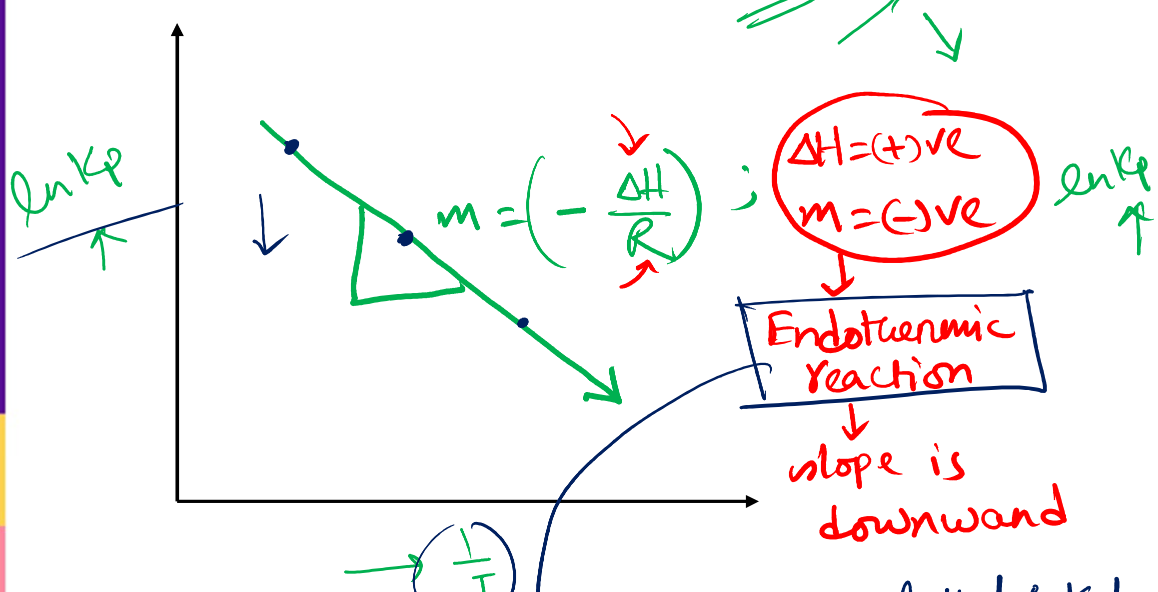
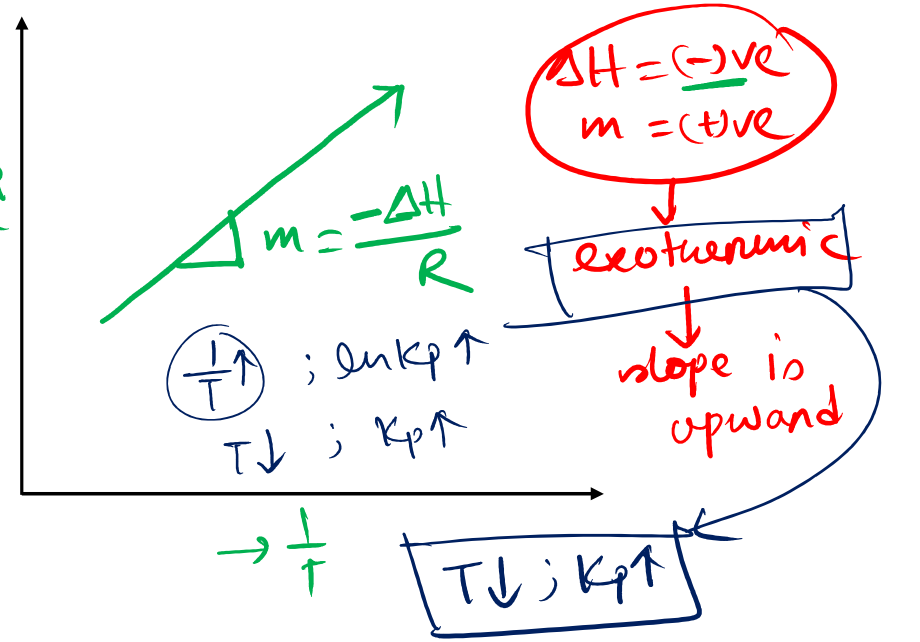
Type 05 (Van't Hoff equation)

Relation between temperature and eq. constant

$$\ln K_p = -\frac{\Delta H}{RT} + C$$





Math Problem

If the slope value of $\ln K_p$ vs T^{-1} graph is 10 K, then find ΔH?

slope, $m = \frac{-\Delta H}{R} = 10$

$\therefore \Delta H = -10R$

$= -10 \times 8.314$

$= -83.14$ J/mol

Reaction
↳ exothermic

Type – 06 : Dissociation

Amount of Dissociation

Quantity (x)

$x = N \times \alpha$

Percentage of Dissociation

percentage (α)

$\alpha = \frac{x}{N}$ — x: amount of Diss., N: Total amount

20 mol

4 mol

$4/20 = \frac{1}{5} = 0.2 = 20\%$

1 : 1 : 1

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

1 0 0

$1-\alpha$ α α ← amount

Math Problem

4mol H_2 and 2mol N_2 react in a container of 2L volume. 50% of N_2 is converted into NH_3. What is equilibrium constant ?

(1 : 3 : 2)

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

	N_2	$3H_2$	$2NH_3$
initial mol:	2	4	0
eq. mol:	2−1 = 1	4−3 = 1	0+2 = 2
eq. concn:	1/2	1/2	1

$K_c = \frac{[NH_3]^2}{[N_2]\cdot[H_2]^3} = ----$ H.W.

per. of dissociation

$x = N\alpha$

Quantity $= 2 \times 50\%$

$= 1$

Type - 07 (Two most popular reaction)

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$\left(K_p = \frac{\alpha^2}{1-\alpha^2} \cdot P\right)$

Remember

$N_2O_4 \rightleftharpoons 2NO_2$

$\left(K_p = \frac{4\alpha^2}{1-\alpha^2} \cdot P\right)$

10% PCl_5 is decomposed at a pressure of 1.5atm at a temperature of 30°C. What is equilibrium constant?

$\alpha = 10\% = 0.1$; $P = 1.5\,atm$

$K_p = \frac{(0.1)^2 (1.5)}{1-(0.1)^2}$

50% N_2O_4 decomposes at a pressure of 2atm at a temperature of 27°C. What is equilibrium constant?

$\alpha = 50\% = 0.5$; $P = 2\,atm$

$K_p = \frac{4 \times (0.5)^2}{1-(0.5)^2} \times 2$

$= \frac{8 \times 0.25}{1-0.25} = \frac{2}{0.75}$

$= \frac{2}{\frac{3}{4}} = \frac{8}{3}$

Acid-Base

Theory	Acid	Base
Arrhenius	Donates H^+ in aqueous solution HCl	Donates OH^- in aqueous solution $NaOH$
Bronsted & Lowry	Donates H^+ HCl	Accepts H^+ NH_3 $NH_3 + H^+ \rightarrow \overset{+}{N}H_4$
Lewis	Accepts a lone pair of electron $AlCl_3$	Donates a pair of electron $H_3N: \rightarrow H^+$ $\overset{+}{N}H_4$

** aq. solution must be needed.

(H^+ related)

Deals with e^-

Poll Question-03

Which is the strongest acid?

(a) H_2SO_4 (+6)

(b) HNO_3 (+5)

(c) H_2CO_3 (+4)

(d) $HClO_4$ (+7) ✓

Oxo-acid

strength ∝ ox. number of central atom

H → +1
O → −2

$(+1)\times1 + x\times1 + (-2)\times4 = 0$

$1 + x - 8 = 0$

$x = 8 - 1 = +7$

Conjugated acid-base

Bron.-Lowry (protonic concept)

$$\underset{\text{Base}}{NH_3} + \underset{\text{Acid}}{HCl} \longrightarrow \underset{\text{conj. acid}}{NH_4^+} + \underset{\text{conj. base}}{Cl^-}$$

conj. base (it can accept a proton)

conj. acid (it can donate a proton)

** Acid $-$ [H^+] = conj. base

Base + [H^+] = conj. acid

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pH Calculation

$c = \frac{K_a}{\alpha^2}$ $\alpha c = \alpha \times \frac{K_a}{\alpha^2}$

Strong

0.1M, 0.15M

(HCl, H_2SO_4, HNO_3)

$pH = -\log[H^+]$

$= -\log(n \times c)$

no. of proton donation → n; concentration → c

NaOH, $Ca(OH)_2$

↳ $pOH = -\log(OH^-)$

$= -\log(n \times c)$

Weak

(monoprotic)

↓ (Ostwald)

$K_a = \alpha^2 \cdot c$

$[H^+] = \alpha \cdot c$

$pH = -\log(\alpha c)$

$= -\log(\sqrt{K_a \cdot c})$

$= -\log\left(\frac{K_a}{\alpha}\right)$

Diluted

** condition: concentration(c) $\leq 10^{-5}$ M

* 10^{-6} M HCl → pH = ? (written)

$pH = -\log[H^+]$ ← From acid

$= -\log[10^{-6} + 10^{-7}]$ ← From H_2O

$H_2O \rightarrow H^+ + OH^-$

(10^{-7}) M

pH related maths

- Calculate the pH of 10^{-2}M HCl? ; $pH = -\log[H^+] = -\log(10^{-2}) = 2$
- Calculate the pH of 10^{-1}M NaOH? $pOH = -\log[OH^-] = -\log(10^{-1}) = 1$; $pH = 14 - 1 = 13$
- Calculate the pH of 10^{-8}M HCl ? $pH = -\log(10^{-7} + 10^{-8}) = \sim 6.9$
- Calculate the pOH of 0.02M CH_3COOH? $[K_{CH_3COOH} = 2 \times 10^{-4}]$ weak

$pH = -\log(\sqrt{Ka.c})$
$= -\log(\sqrt{0.02 \times 2 \times 10^{-4}}) = -\log\sqrt{4 \times 10^{-6}} = -\log(2 \times 10^{-3})$
$= -\log 2 + 3 = 3 - 0.3 = 2.7$

$pOH = 14 - 2.7 = 11.3$

log (1-10) (সুযোগ)

log 1 → 0
2 → 0.3
3 → 0.4
4 → 0.6
5 → 0.7
6 → 0.8
7 → 0.9
8 → 0.9
9 → 0.9
log 10 = 1

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Poll Question-04

What is the pH of 0.005M H_2SO_4 ?

$-\log(nc) = -\log(2 \times 0.005)$

$= -\log(0.01)$

$pH = 2$

(a) 14

(b) 12

(c) 2

(d) None

Buffer Solution

i. Adding a small amount of weak acid / alkali does not change the pH.

ii. Weak acid / alkali must be present.

iii. Buffer solutions are formed only when the amount of weak is much more in the misture of acid & alkali.

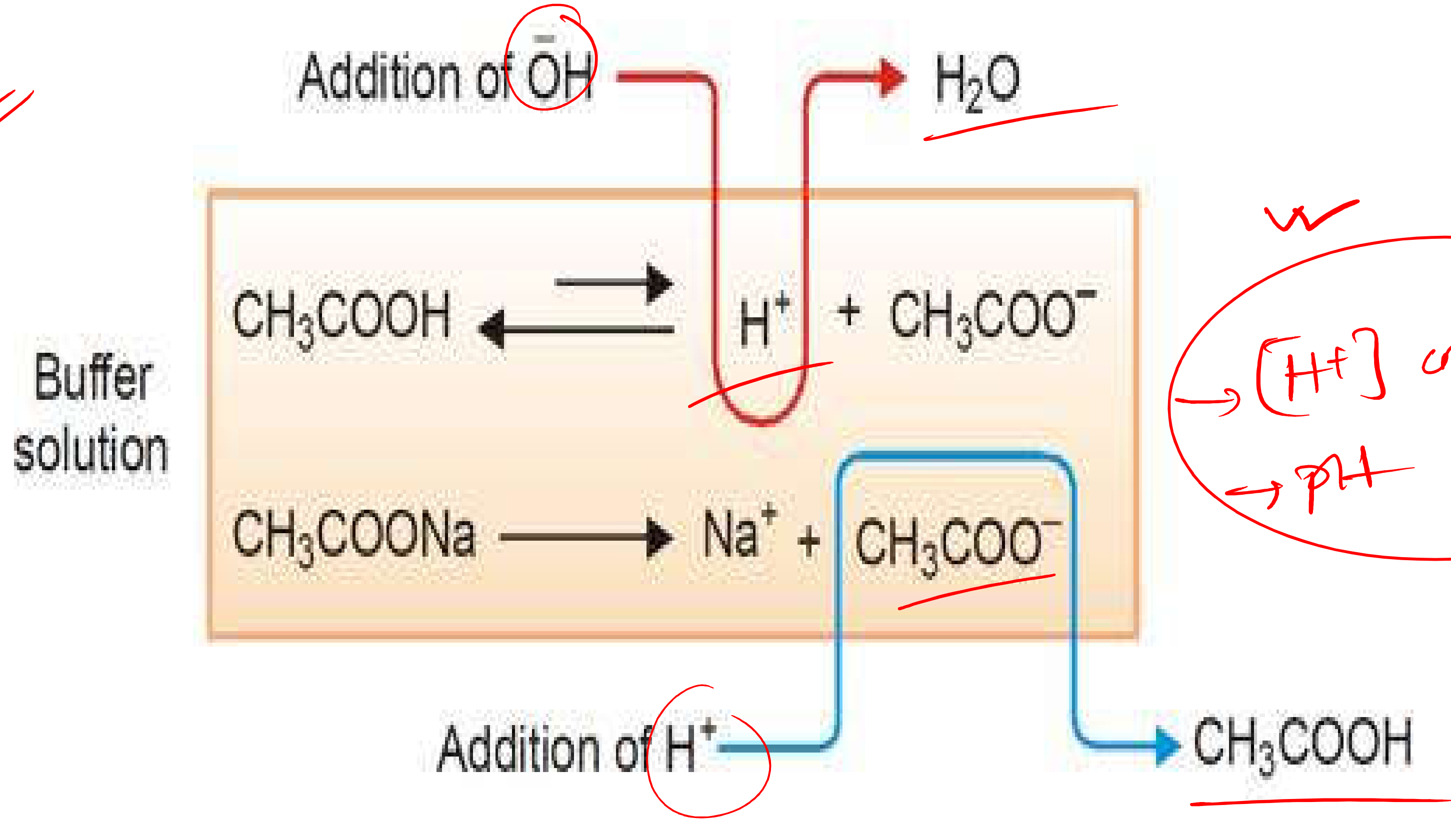
weak amount > strong amount

Poll Question-05

Which mixture will act as a buffer solution? **[DU'13-14]**

(a) 0.2 M 10 mL CH_3COOH + 0.2 M 10 mL NaOH
(b) 0.2 M 10 mL CH_3COOH + 0.1 M 10 mL NaOH
(c) 0.1 M 10 mL CH_3COOH + 0.2 M 10 mL NaOH
(d) 0.1 M 10 mL HCl + 0.2 M 10 mL NaOH

Mechanism



Addition of $\bar{O}H$
H_2O
Buffer solution
$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
$CH_3COONa \rightarrow Na^+ + CH_3COO^-$
Addition of H^+
CH_3COOH

pH of buffer

***

$S \times V = n$

$\log \frac{[salt] \times V}{[acid] \times V}$

Henderson- hasselbalch equation:

$$pH = pK_a + \log \frac{n_{salt}}{n_{acid}}$$

n ← mole number

$pK_a = -\log(K_a)$

$$pOH = pK_b + \log \frac{n_{salt}}{n_{base}}$$

$pK_b = -\log(K_b)$

weight/mass: $\therefore n = \frac{w}{M}$

concn & vol.: $n = S \times V_L$

Math Problem

A buffer solution was prepared by adding 20 mL 0.1 M CH_3COOH with 200mL 0.1M CH_3COONa. What is the pH of the buffer solution? $[pK_a = 4.8]$

acid

salt

$pH = pK_a + \log\left(\frac{n_{salt}}{n_{acid}}\right)$

$= 4.8 + \log\left(\frac{200 \times 0.1}{20 \times 0.1}\right)$

$= 4.8 + \log 10$

$= 4.8 + 1$

$= 5.8$ Ans.

$n_{salt} = 200 \times 0.1$

$K_a = ?$

$pK_a =$

Math Problem

Calculate pH of the mixture from 60gm CH_3COOH & 41gm CH_3COONa.
$[K_{CH_3COOH} = 10^{-5}]$

82

$n = \frac{w}{M}$

$pH = pK_a + \log\left(\frac{n_{CH_3COONa}}{n_{CH_3COOH}}\right)$

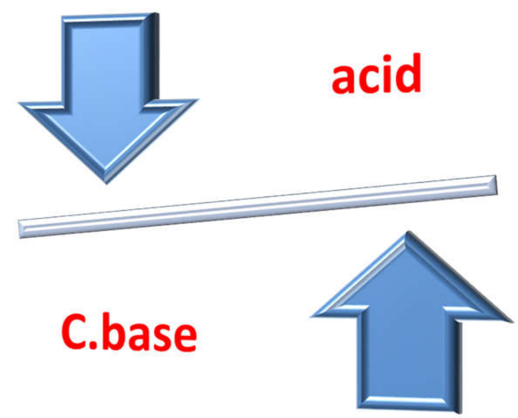
mole

$\Rightarrow pH = -\log(10^{-5}) + \log\left(\frac{\frac{41}{82_2}}{\frac{60}{60_1}}\right)$

$= 5 + \log\left(\frac{1}{2}\right)$

Name	Formula	K_a	pK_a
Hydrochloric acid	HCl	1.0×10^{7}	−7.00
Phosphoric acid	H_3PO_4	7.5×10^{-3}	2.12
Hydrofluoric acid	HF	6.6×10^{-4}	3.18
Lactic acid	$CH_3CH(OH)CO_2H$	1.4×10^{-4}	3.85
Acetic acid	CH_3CO_2H	1.8×10^{-5}	4.74
Carbonic acid	H_2CO_3	4.4×10^{-7}	6.36
Dihydrogenphosphate ion	$H_2PO_4^-$	6.2×10^{-8}	7.21
Ammonium ion	NH_4^+	5.6×10^{-10}	9.25
Hydrocyanic acid	HCN	4.9×10^{-10}	9.31
Hydrogencarbonate ion	HCO_3^-	5.6×10^{-11}	10.25
Methylammonium ion	$CH_3NH_3^+$	2.4×10^{-11}	10.62
Hydrogenphosphate ion	HPO_4^{2-}	4.2×10^{-13}	12.38

$$K_a \propto \frac{1}{K_b}$$



For Acid - K_a ↑ pK_a ↓ **Acid** ↑

For Base - K_b ↑ pK_b ↓ **Base** ↑

লেগে থাকো সৎ ভাবে,
স্বপ্ন জয় তোমারই হবে।