Ques. 1 Which of the following statement is TRUE regarding the pH of 10^{-6}M HCl aqueous solution?

a) pH=6

b) pH<6

c) pH>6

d) Insufficient data

Ques.2 What is the approximate value of pH for 10^{-9}M $HClO_4$ aqueous solution?

a) 9

b) 8

c) 7

d) 6

Ques.3 Which of the following is a buffer solution?

a) $HCl/NaCl$

b) CH_3COOH/CH_3COONa

c) $HClO_4/KClO_4$

d) HCN/HCl

WA / A^-

WB / BH^+

IfAS

Ques. 4 Which of the following solution is best buffer?

a) (0.50 mole of CH_3COOH + 0.30 mole of CH_3COONa) in 1L aqueous solution.

b) (1.00 mole of CH_3COOH + 0.500 mole of CH_3COONa) in 1L aqueous solution.

c) (0.50 mole of CH_3COOH + 1.00 mole of CH_3COONa) in 1L aqueous solution.

d) (1.00 mole of CH_3COOH + 1.00 mole of CH_3COONa) in 1L aqueous solution.

Ques. 5 Suppose 1 mole of Formic acid (HCOOH) is added with 1 mole of HCOONa in water and diluted up to 2 litre. What will the pH of the solution? (K_a of Formic acid $=1.77\times 10^{-4}$)

a) 1.14

b) 2.14

c) ~~1.14~~ 3.75

d) Can't predict

$[HCOOH]_0 = \frac{1}{2} = 0.5M \quad [HCOO^-]_0 = \frac{1}{2} = 0.5M$

$pH = pK_a + \log\frac{[A^-]}{[HA]}$

$pH = 3.75 + \log\frac{0.5}{0.5}$

Ionic Equilibrium

lec-5

IONIC EQUILIBRIUM

lecture - 5

Buffer sol^n

components of Buffer sol^n

pH of Buffer

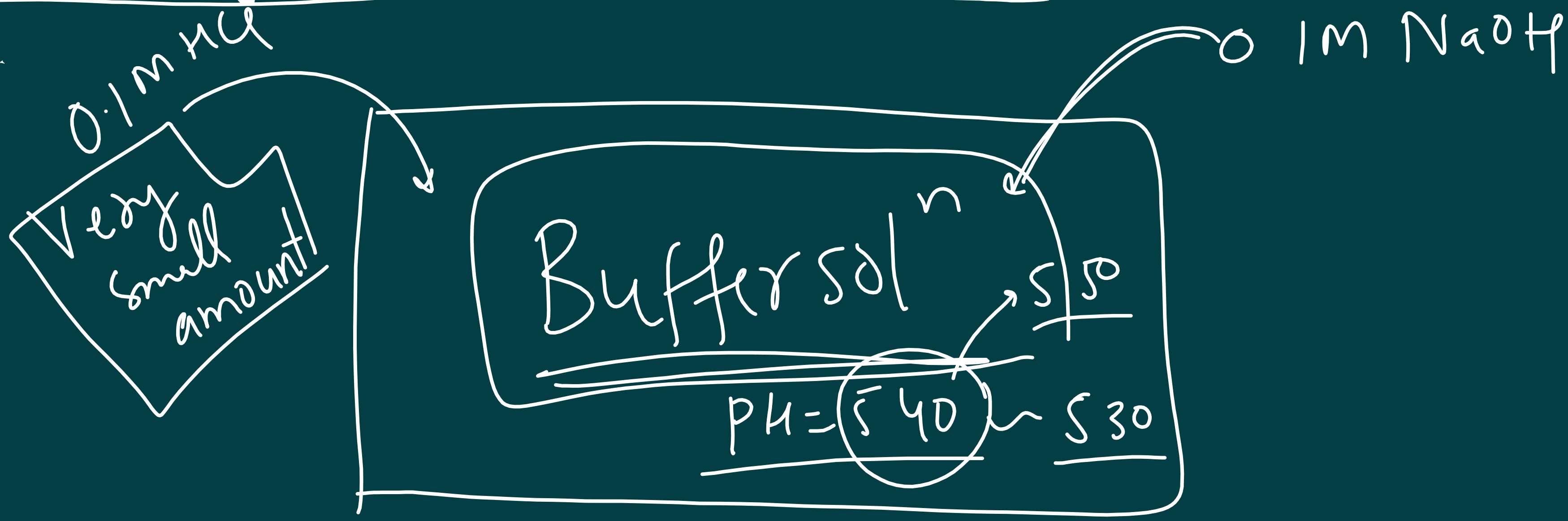
pH of Buffer if small $amou^n t$ of Acid & Base is added

Buffer Capacity ✓

Design a Buffer solution at desired pH

Buffered solutions (Buffer)

A buffered solution (or buffer) is any solution that maintains an approximately constant pH despite small addition of acid and base.



PH will altered significally

A buffer contains -

(i) Weak Acid + Salt of its conjugate Base. → ACIDIC

(CH_3COOH) + (CH_3COONa)

Weak Base + salt of its conjugate Acid → BASIC

[NH_3] NH_4^+Cl / $(NH_4)_2SO_3$

(ii) Both components have to be in approximately equal amounts (i.e their concentrations should be similar)

(iii) Should be in substential amounts (i.e higher concentration).

$$[CH_3COOH] \simeq 1M / 0.5M$$ / ~~0.00 M~~

IfAS

How does Buffer Work?

$[CH_3COOH] = 1M$

$[CH_3COO^-] = 1M$

0.1 M HCl = 0.1 M H_3O^+

$$CH_3COOH(aq) + H_2O(l) \underset{}{\overset{K_a}{\rightleftharpoons}} CH_3COO^-(aq) + H_3O^+(aq)$$

	CH_3COOH		CH_3COO^-	H_3O^+
I	1M		1M	–
C	$-x$		$+x$	$+x$
E	$(1-x) \approx 1$	$\frac{1}{1} \approx 1$	$(1+x) \approx 1$	x

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \Rightarrow [H_3O^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$$

const

Adding small amount of Acid :-

$$HCl \xrightarrow{H_2O} Cl^-(aq) + H_3O^+(aq)$$

0.1M → 0.1M, 0.1M

Neutral

$$CH_3COO^-(aq) + H_3O^+(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$$

(1M) 0.1M (1M)

− 1.1 / 0.9

Limiting reagent

After complete neutralis.

$1 - 0.1 = 0.9\,M$

$(1 + 0.1) = 1.1\,M$

Adding small amount of strong Base :

0.1 M NaOH ⟶ Na^+ + OH^-
0.1 M

Limiting reagent

$$OH^-_{(aq)} + CH_3COOH \longrightarrow CH_3COO^-(aq) + H_2O(l)$$

	OH^-	CH_3COOH	CH_3COO^-
	0.1 M	1 M	1 M
After complete rxn	0	(1 − 0.1) ≃ 0.9 M	(1 + 0.1) ≃ 1.1 M

IfAS

Ques. (a) Suppose 1.0 mol of HCOOH and 0.500 mole of HCOONa are added to water and diluted to 1.0 L. Calculate the pH of the solution. ($K_a = 1.77 \times 10^{-4}$)

$pH = 3.45$

(b) Suppose 0.1 mol of strong acid such as HCl is added to the above HCOOH/HCOONa solution. Calculate the pH of the resulting solution

$pH = 7$

$pH = 1$

$pH = 3.31$

IfAS

$1 - x \approx 1$

$0.5 - x \approx 0.5$

$K_a = 1.77 \times 10^{-4}$

$pH = -\log(3.54 \times 10^{-4}) = 3.45$

$$HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$$

	$HCOOH$		$HCOO^-$	H_3O^+
I	1M	1M	0.5M	—
C	$-x$		$+x$	$+x$
E	$(1-x)$		$(0.5+x)$	x

0.1M

$\approx 0.5 = [HCOO^-]_0$

$\approx 1 \approx [HCOOH]_0$

$$K_a = 1.77 \times 10^{-4} = \frac{[HCOO^-][H_3O^+]}{[HCOOH]} = \frac{(0.5+x)(x)}{(1-x)} = \frac{0.5x}{1}$$

$x = 3.54 \times 10^{-4} = [H_3O^+]$

$$H_3O^+_{(aq)} + HCOO^-_{(aq)} \longrightarrow HCOOH_{(aq)} + H_2O(l)$$

Add: $0.1M$ | $0.5M \rightarrow 0.1$ | $1M$

After complete rxn: 0 | $(0.5-0.1) = 0.4M$ | $(1+0.1) \simeq 1.1M$

$K_a = 1.77\times10^{-4}$

$$HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq.) + H_3O^+(aq)$$

	$HCOOH$	$HCOO^-$	H_3O^+
I	$1.1M$	$0.4M$	—
C	$-x$	$+x$	$+x$
E	$(1.1-x) \simeq 1.1M$	$(0.4+x) \simeq 0.4M$	x

$$K_a = 1.77 \times 10^{-4} = \frac{[HCOO^-][H_3O^+]}{[HCOOH]} = \frac{[0.4 + x](x)}{[1.1 - x]}$$

$$1.77 \times 10^{-4} = \frac{(0.4)(x)}{(1.1)}$$

$$\Rightarrow x = 4.87 \times 10^{-4} = [H_3O^+]$$

$$pH = -\log(4.87 \times 10^{-4})$$

$$= 3.31$$

Henderson- Hasselbalch Equation

Easy way to calculate the pH of Buffers.

$$HA(aq.) + H_2O(l) \underset{}{\overset{Ka}{\rightleftharpoons}} H_3O^+(aq.) + A^-(aq.)$$

(1M) (1M)

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

IfAS

$$\Rightarrow \quad K_a = \frac{[H_3O^+][A^-]}{[HA]} \longrightarrow K_a = \frac{[H_3O^+][A^-]_0}{[HA]_0}$$

$$[H_3O^+] = K_a \frac{[HA]_0}{[A^-]_0}$$

$$-\log[H_3O^+] = -\log\left(K_a \frac{[HA]_0}{[A^-]_0}\right)$$

$-\log[H_3O^+]$

$$pH = -\log\left(\frac{K_a [HA]_0}{[A^-]_0}\right)$$

$$\log(ab) = \log a + \log b$$

$$\log\left(\frac{a}{b}\right) = \log a - \log b$$

$$pH = -\log K_a - \log \frac{[HA]_0}{[A^-]_0}$$

$$pH = pK_a + \log \frac{[A^-]_0}{[HA]_0}$$

$[A^-]_0$ → Initial concn of Salt

$[HA]_0$ → Initial concn of Acid

$[HCOO]_0 = 1M$ $\quad$ $[HCOONa] = 0.5M$

Ques. (a) Suppose 1.0 mol of HCOOH and 0.500 mole of HCOONa are added to water and diluted to 1.0L. Calculate the pH of the solution. ($K_a = 1.77 \times 10^{-4}$)

$pK_a = -\log(K_a) = 3.75$

(b) Suppose 0.1 mol of strong acid such as HCl is added to the above HCOOH/HCOONa solution. Calculate the pH of the resulting solution.

$$pH = 3.75 + \log \frac{(0.4)}{(1.1)} = 3.31$$

(a) $pH = pK_a + \log \frac{[salt]}{[acid]} = 3.75 + \log \frac{[0.5]}{[1]}$

$= 3.49$

Ques. You prepare a buffer solution of 0.323 M NH_3 and $(NH_4)_2SO_4$. What molarity of $(NH_4)_2SO_4$ is necessary to have a pH of 8.6? The pK_b of NH_3 is 4.74.

IfAS

K_a ~ , $10^{-3}, 10^{-7}, -1$ $= 1.77 \times 10^{-4}$

10000

0.5M

1M

Assumptions in the Henderson-Hasselbalch Equation —

① ✓ $-1 < \log \frac{[A^-]}{[HA]} < 1$

② The molarity of buffer should be 100 times that of acid dissociation constant (K_a)

③ pK_a values must be in the range of 5 to 9.

④ Designing Buffers at specific pH

Example : Design a buffer at pH = 4.60

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$CH_3COOH \mid CH_3COO^-$

$$4.60 = 4.75 + \log \frac{[A^-]}{[HA]}$$

$$10^{-0.15} = \frac{[A^-]}{[HA]}$$

$$0.7 = \frac{[A^-]}{[HA]}$$

$$\frac{[HA]}{[A^-]} = \frac{1}{0.7} = 1.4$$

Name	Acid	Conjugate Base	K_a	pK_a
Hydroiodic	HI	I^-	$\sim 10^{11}$	~ -11
Hydrobromic	HBr	Br^-	$\sim 10^{9}$	~ -9
Perchloric	$HClO_4$	ClO_4^-	$\sim 10^{7}$	~ -7
Hydrochloric	HCl	Cl^-	$\sim 10^{7}$	~ -7
Chloric	$HClO_3$	ClO_3^-	$\sim 10^{3}$	~ -3
Sulfuric (1)	H_2SO_4	HSO_4^-	$\sim 10^{2}$	~ -2
Nitric	HNO_3	NO_3^-	~ 20	~ -1.3
Hydronium ion	**H_3O^+**	**H_2O**	**1**	**0.0**
Urea acidium ion	$NH_2CONH_3^+$	$(NH_2)_2CO$ (urea)	6.6×10^{-1}	0.18
Iodic	HIO_3	IO_3^-	1.6×10^{-1}	0.80
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}	1.23
Sulfurous (1)	H_2SO_3	HSO_3^-	1.54×10^{-2}	1.81
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92
Chlorous	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.96
Phosphoric (1)	H_3PO_4	$H_2PO_4^-$	7.52×10^{-3}	2.12
Arsenic (1)	H_3AsO_4	$H_2AsO_4^-$	5.0×10^{-3}	2.30
Chloroacetic acid	$CH_2ClCOOH$	CH_2ClCOO^-	1.4×10^{-3}	2.85
Hydrofluoric acid	HF	F^-	6.6×10^{-4}	3.18
Nitrous	HNO_2	NO_2^-	4.6×10^{-4}	3.34
Formic	$HCOOH$	$HCOO^-$	1.77×10^{-4}	3.75
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.46×10^{-5}	4.19
Oxalic (2)	$HC_2O_4^-$	$C_2O_4^{2-}$	6.4×10^{-5}	4.19
Hydrazoic	HN_3	N_3^-	1.9×10^{-5}	4.72
Acetic	CH_3COOH	CH_3COO^-	1.76×10^{-5}	4.75
Propionic	CH_3CH_2COOH	$CH_3CH_2COO^-$	1.34×10^{-5}	4.87
Pyridinium ion	$HC_5H_5N^+$	C_5H_5N	5.6×10^{-6}	5.25
Carbonic (1)	H_2CO_3	HCO_3^-	4.3×10^{-7}	6.37
Sulfurous (2)	HSO_3^-	SO_3^{2-}	1.02×10^{-7}	6.91
Arsenic (2)	$H_2AsO_4^-$	$HAsO_4^{2-}$	9.3×10^{-8}	7.03
Hydrosulfuric	H_2S	HS^-	9.1×10^{-8}	7.04
Phosphoric (2)	$H_2PO_4^-$	HPO_4^{2-}	6.23×10^{-8}	7.21
Hypochlorous	$HClO$	ClO^-	3.0×10^{-8}	7.53
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25
Hydrocyanic	HCN	CN^-	6.17×10^{-10}	9.21
Carbonic (2)	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32
Methylammonium ion	$CH_3NH_3^+$	CH_3NH_2	2.3×10^{-11}	10.64
Arsenic (3)	$HAsO_4^{2-}$	AsO_4^{3-}	3.0×10^{-12}	11.53
Hydrogen peroxide	H_2O_2	HO_2^-	2.4×10^{-12}	11.62
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	2.2×10^{-13}	12.67
Water	**H_2O**	**OH^-**	**1.0×10^{-14}**	**14.00**
Methanol	CH_3OH	CH_3O^-	$\sim 10^{-18}$	~ 18
Ammonia	NH_3	NH_2^-	$\sim 10^{-34}$	~ 34

Possible choices :

Buffer capacity ↑

$[CH_3COOH]_0$ ✓	$[CH_3COO^-]_0$ ✓
2.8 M	2.0 M
1.4 M	1.0 M
0.28 M	0.20 M
0.14 M	0.10 M
0.014 M	0.010 M

Buffer Capacity

The Buffer capacity is the ability of buffer to withstand the added Acid and Base.

THANK YOU