O-II

(1) $pH = 5 \Rightarrow [H^+] = 10^{-5} M$; V L

$pH = 3 \Rightarrow [H^+] = 10^{-3} M$: V L

finally $[H^+] = \dfrac{10^{-5} V + 10^{-3} V}{V + V}$

$= \dfrac{10^{-5} + 10^{-3}}{2} \simeq \dfrac{10^{-3}}{2} M$

$pH = 3 + \log 2 = 3.3$

(2)

$pH = 2 \Rightarrow [H^+] = 10^{-2} M = M_1$

$pH = 3 \Rightarrow [H^+] = 10^{-3} M = M_2$

moles of HCl removed = n_{H^+} (initial) (moles) $- n_{H^+}$ (final) (moles)

$= 10^{-2} \times 1 - 10^{-3} \times 1$

$= 9 \times 10^{-3} = 0.009$

(3)

(A) $K_{sp} = s^2 \Rightarrow s = \sqrt{8 \times 10^{-37}}$

(B) $K_{sp} = s^2 \Rightarrow s = \sqrt{7 \times 10^{-16}}$

(C) $K_{sp} = 108\, s^5 \Rightarrow s = \left(K_{sp}/108\right)^{1/5}$

(D) $K_{sp} = 27 s^5 \Rightarrow s = \left(K_{sp}/27\right)^{1/4} \Rightarrow$ Maximum

④ [common ion] ↑ ⇒ solubility ↓

max. concn. of common ion, $(Br^-) = 0.2$ in 0.1M $CaBr_2$

⑤ $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

a	$\frac{a}{4}$	–	–
$\frac{3a}{4}$	x	$(\frac{a}{4})$	

Buffer Soln.

$$pH = pK_a + \log\left(\frac{s}{a}\right) = 11 + \log\frac{(3a/4)}{(a/4)}$$

$$pH = 11 + \log 3$$

⑥

	HIn (Red)	In^- (Blue)	pH
1.)	80	20	$pK_{In} + \log(20/80)$
2.)	20	80	$pK_{In} + \log(80/20)$

$$\Delta pH = 2\log 4 = 4\log 2 = 4 \times 0.3 = 1.2$$

⑦ $[OH^-] = 10^{-7} + 10^{-7} = 2\times10^{-7} \Rightarrow pOH = 7 - \log 2$

$pH = 7 + \log 2$

$= 7.3$

(10^{-7} from H_2O (without common ion effect))

But Due to common ion effect for $H_2O \Rightarrow [OH^-] < 2\times10^{-7}$

Hence $pH < 7.3$

⑧ On increasing dilution (volume) concentration of H^+ ion decrease, although moles increase but volume increase more.

$$\text{Concn.} = \frac{\text{moles}}{\text{volume}} \propto \frac{\sqrt{v}}{V} \propto \frac{1}{\sqrt{v}}$$

(for dilute soln.)

(9)

(A) $[OH^-] = \sqrt{K_b \cdot C} = \sqrt{10^{-5} \times 0.1} = 10^{-3} M$

&

(B) $pOH = 3$; $pH = 14 - 3 = 11$

(C) Salt of S.A. & W.B. is acidic solution.

(D) for phenolphthalein indicator can be used when strong base is present.

(10) (A) $K_{eq.} = K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{2 \times 10^{-6}} = 5 \times 10^{-9}$

(B) $HA + NaOH \rightleftharpoons NaCl + H_2O$;

$K_{eq} = \frac{1}{K_h} = \frac{K_a}{K_w} = \frac{2 \times 10^{-6}}{10^{-14}} = 2 \times 10^{8}$

(C) $[H^+] = \sqrt{K_a \cdot C} = \sqrt{2 \times 10^{-6} \times 0.1} = \sqrt{20} \times 10^{-4}$

$pH = 4 - \frac{1}{2} \log 20 = 3.35$

(D) $A^- + H_2O \rightleftharpoons HA + OH^-$ ← Basic

(11)

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; K_{a_1}

$c - x$ $(x+y+z) \simeq x$ $(x-y) \simeq x$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$; K_{a_2}

$(x-y) \simeq x$ $(x+y+z) \simeq x$ $(y-z) \simeq y$

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$; K_{a_3}

$(y-z) \simeq y$ $(x+y+z) \simeq x$ z

(as $K_{a_1} >> K_{a_2} >> K_{a_3} \Rightarrow x >> y >> z$)

(A) $[H^+] = [H_2PO_4^-] = x$

(B) $K_{a_1} = \frac{x^2}{[H_3PO_4]} \Rightarrow x = [H^+] = \sqrt{K_1 [H_3PO_4]}$

(C) $K_2 = \frac{x \cdot y}{x} = y = [HPO_4^{2-}]$ (D) $[PO_4^{3-}] = z$

(12.) (A) No effect of dilution on pH of buffer

(B), (C) & (D) :- $pH = pK_b + \log(s/b)$

$(s) = [NH_4Cl] \uparrow \Rightarrow pOH \uparrow \Rightarrow pH \downarrow$

$(b) = [NH_4OH] \uparrow \Rightarrow pOH \downarrow \Rightarrow pH \uparrow$

(13.) when equal volumes are mixed concn. of each ion will be half of initial

For ppt. of AgCl,

$Q_{sp} = [Ag^+][Cl^-] > K_{sp} = 1.8 \times 10^{-10}$

(A) $Q_{sp} = \frac{10^{-4}}{2} \times \frac{10^{-4}}{2} = 2.5 \times 10^{-9} > K_{sp}$

(14.) $C = \frac{8 \times 1000}{80 \times 100} = 1\,M$

as $\frac{K_a}{C} < 10^{-3} \Rightarrow [H^+] = \sqrt{K_a \cdot C} = 10^{-2}\,M$

$\Rightarrow pH = 2$

(15.) $HX + NaOH \longrightarrow NaX + H_2O$

0.1 moles $\quad 0.1 = M_2V_2$, $M_2 = 0.25$

0.1 moles at equivalence point

(Salt of W.A & S.B.)

$C = \frac{0.1}{\frac{100}{1000} + 0.4} = \frac{1}{5} = 0.2\,M$

$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C = 8.65$

(16.)

Mixing of S.A (HCl) & W.A (HX)

$$[HCl] = \frac{10^{-3}}{(100/1000)} = 10^{-2}\ M$$

$$HX\ (aq.) \rightleftharpoons H^+\ (aq) + X^-\ (aq) : K_a = 10^{-4}$$

1 M	10^{-2}	—
$(1-x) \simeq 1$	$(10^{-2}+x)$	x

$$K_a = 10^{-4} = \frac{(10^{-2}+x)\,x}{1}$$

$$10^{-4} = 10^{-2}x + x^2$$

$$x^2 + 10^{-2}x - 10^{-4} = 0$$

$$x = 0.62 \times 10^{-2}$$

$$[H^+] = 10^{-2} + x = 1.62 \times 10^{-2}\ M$$

17.

(A) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

	100	25	—
	75	x	25

$$pH = pK_a + \log(S/a) = pK_a + \log\left(\frac{25}{75}\right)$$
$$= pK_a - \log 3$$

(B)

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

	100	50	—
	50	x	50

$$pH = pK_a + \log\left(\frac{50}{50}\right) = pK_a$$

(C) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

	100	75	—
	25	x	75

$$pH = pK_a + \log\left(\frac{75}{25}\right) = pK_a + \log 3$$

(D) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

	100	100	—
	x	x	100

$$C = \frac{100}{200} = \frac{1}{2}M$$

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$
$$= \frac{1}{2}[pK_w + pK_a - \log 2]$$

(18) (A) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

$\frac{0.2}{2} = 0.1\,M$ $\quad \frac{0.1}{2}\,M$ $\quad —$

$\frac{0.1}{2}\,M$ $\quad x$ $\quad \frac{0.1}{2}\,M$

$$pH = pK_a + \log(S/a) = pK_a = 5$$

(B) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+ ; \quad K_a$

$\frac{0.1}{2}\,M$ $\quad \frac{0.1}{2}\,M \leftarrow$ from HCl

$\left(\frac{0.1}{2} - x\right)$ $\quad x$ $\quad \left(\frac{0.1}{2} + x\right) \simeq \frac{0.1}{2}\,M$

(x is negligible as $\frac{K_a}{C} \leq 10^{-3}$)

$[H^+] = \frac{0.1}{2}\,M \Rightarrow pH = 1 + \log 2 = \underline{1.3}$

(C) $CH_3COOH + NH_4OH \longrightarrow CH_3COONH_4 + H_2O$

$\frac{0.1}{2}\,M$ $\quad \frac{0.1}{2}\,M$ $\quad \frac{0.1}{2}\,m$

x $\quad x$

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b = 7$$

(Salt hydrolysis)

(D) $NH_4Cl + NaOH \longrightarrow NH_4OH + NaCl$

20 $\quad 10$ $\quad —$ $\quad —$

10 $\quad x$ $\quad 10$

$$pOH = pK_b = 5 \Rightarrow pH = 9$$

as $[NH_4OH] = [NH_4Cl] \Rightarrow$ Buffer capacity is maximum.

(19) first strong acid will react with NaOH

$HCl + NaOH \longrightarrow NaCl + H_2O$

moles	0.1	0.15	—
	x	0.05	0.1

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

	0.1	0.05	—
	0.05	x	0.05

$$pH = pka + \log(S/a) = pka = 5$$

(20) $HCl + NaOH \longrightarrow NaCl + H_2O$

moles	0.1	0.1	—
	x	x	0.1

only CH_3COOH remain in soln. with $C = \frac{0.2}{2} = 0.1M$

$$[H^+] = \sqrt{ka \cdot C} = 10^{-3} M$$

$$pH = 3$$