Ionic S-1

(1) $[H^+] = 10^{-pH} = 10^{-13}$ mol/L

no. of $H^+ = \frac{10^{-13}}{1000} \times N_A = \frac{10^{-13}}{1000} \times 6.023 \times 10^{23}$

$= 6.023 \times 10^{7}$

(2) (i) $[H^+] = \sqrt{K_w} = 3 \times 10^{-7}$

pH at $60^\circ C = 7 - \log 3 = 6.53$

(ii) Neutral pH at $60^\circ C = 6.53$ (from (i) part)

(a) pH (6.7) > Neutral pH (6.53) ⇒ Basic

(b) pH (6.35) < Neutral pH (6.53) ⇒ Acidic

(3) $[H^+] = \sqrt{K_w} = 1.6 \times 10^{-7} = 16 \times 10^{-8}$

$pH = 8 - 4\log 2 = 6.8$

(4) (a) $[H^+] = 10^{-1}$ M ⇒ pH = 1

(b) $\frac{K_a}{C} < 10^{-3} \Rightarrow [H^+] = \sqrt{K_a \cdot C} = \sqrt{1.8 \times 10^{-5} \times 0.1}$

$= \sqrt{1.8} \times 10^{-3}$

$pH = 3 - \log\sqrt{1.8} = 2.87$

(c) $\frac{K_b}{C} < 10^{-3} \Rightarrow [OH^-] = \sqrt{K_b . C} = \sqrt{1.8 \times 10^{-5} \times 0.1}$

$= \sqrt{1.8} \times 10^{-3}$

$pOH = 3 - \log \sqrt{1.8} = 2.87$

$pH = 14 - pOH = 14 - 2.87 = 11.83$

(d) $HCl_{(aq.)} \longrightarrow H^+_{(aq.)} + Cl^-_{(aq.)}$

10^{-8} 0   0 $(10^{-8} + x)$ 10^{-8}

$H_2O \rightleftharpoons H^+_{(aq.)} + OH^-_{(aq.)}$

$(x + 10^{-8})$ x

$K_w = [H^+][OH^-]$

$10^{-14} = (x + 10^{-8})\, x$

$x^2 + 10^{-8} x - 10^{-14} = 0$

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2}$$

$[H^+] = x + 10^{-8} = 1.051 \times 10^{-7}$

$pH = 7 - \log 1.051 \Rightarrow 6.97$

(e) $[OH^-] = 10^{-10} + 10^{-7} \simeq 10^{-7}$

$pOH \simeq 7 \Rightarrow pH = 14 - 7 \simeq 7$

(f) $\frac{K_a}{C} > 10 \Rightarrow$ Behave like strong acid

$[H^+] = 10^{-6} \Rightarrow pH = 6$

(g) $\frac{K_a}{C} = \frac{1.8 \times 10^{-5}}{10^{-8}} > 10 \Rightarrow$ Behave like strong acid

So 10^{-8} M CH_3COOH is like 10^{-8}M HCl (as part (d))

$CH_3COOH\ (aq) \longrightarrow \underset{10^{-8}}{CH_3COO^-} + \underset{(10^{-8}+x)}{H^+}$;

$H_2O\ (l) \rightleftharpoons \underset{(x+10^{-8})}{H^+} + \underset{x}{OH^-}$

$K_w = 10^{-14} = (x+10^{-8})\, x$

Solving quadratic x can be calculated

$[H^+] = 10^{-8} + x = 1.051 \times 10^{-7}$

$pH = 7 - \log 1.051 = 6.97$

(h) $[OH^-] = 2 \times M_{final}$

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

$M_{final} = \frac{M_{initial}}{100}$

$= \frac{1/10}{100} = 10^{-3}$

$pOH = 3 - \log 2 = 2.7 \Rightarrow pH = 14 - 2.7 = \underline{11.30}$

(i) $[OH^-] = \frac{10^{-3}}{100} = 10^{-5}$ M $\Rightarrow pOH = 5$

$\Rightarrow pH = 14 - 5 = 9$

(j) $M_1 = 10^{-4} M$: $M_2 = 19 \times 10^{-4} M$

Let V litre of both the two are mixed

$$[H^+]_{final} = \frac{M_1V_1 + M_2V_2}{V_1+V_2} = 10^{-3} M$$

$pH = 3$

⑤ (a) $Ka = \frac{x^2}{c}$; $x = [H^+] = 10^{-4.5}$

$$= \frac{(10^{-4.5})^2}{0.1} = 10^{-8}$$

(b) $Kb = \frac{x^2}{c}$; $x = [OH^-] = 10^{-pOH} = 10^{-3.5}$

$$= \frac{(10^{-3.5})^2}{0.1} = 10^{-6}$$

⑥ $\alpha = \sqrt{\frac{Ka}{c}} \Rightarrow \frac{\alpha_2}{\alpha_1} = \sqrt{\frac{c_1}{c_2}} = \sqrt{\frac{c_1}{(c_1/100)}} = 10$

⑦ $\alpha = \sqrt{\frac{Ka}{c}} \Rightarrow \frac{\alpha_2}{\alpha_1} = \sqrt{\frac{Ka_1}{Ka_2}} = \sqrt{\frac{1.8 \times 10^{-5}}{6 \times 10^{-10}}}$

$$= \frac{1.732 \times 100}{1} = 173.2 : 1$$

⑧ H^+ removed = moles of H^+ initially − finally

$= M_1V_1 - M_2V_2$

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

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

(9.) $K_b = \dfrac{x^2}{c-x}$ | $x = [OH^-] = 10^{-4}$

$10^{-5} = \dfrac{(10^{-4})^2}{c-10^{-4}} \Rightarrow c = 1.1 \times 10^{-3}\,M$

(10) $K_a = \dfrac{x^2}{c-x} = \dfrac{(10^{-3})^2}{(10^{-2}-10^{-3})} = 1.11 \times 10^{-4}$

(11) $\dfrac{K_a}{c} < 10^{-3} \Rightarrow [H^+] = \sqrt{K_a \cdot C} = \sqrt{8 \times 10^{-10} \times 0.5}$

$= 2 \times 10^{-5}$

$pH = 5 - \log 2 = 4.7$

(12) when equal volume are mixed

$[H^+]_{final} = \dfrac{10^{-5} \times V + 10^{-3} \times V}{V+V} = 50.5 \times 10^{-5}\,M$

$pH = 5 - \log(50.5) = \underline{3.3}$

(13) (a) $[H^+]_{final} = \dfrac{0.1 \times 50 \times 2 + 0.4 \times 50 \times 1}{(50+50)} = 0.3$
$= 3 \times 10^{-1}$

$pH = 1 - \log 3 = 0.522$

(b) $[H^+]_{final} = \sqrt{K_{a_1}C_1 + K_{a_2}C_2}$ (Mixing of weak acids)

$= 3 \times 10^{-3}\,M$

$pH = 3 - \log 3 = 2.522$

(14)

$$HCl \longrightarrow H^+ + Cl^-$$

$$\begin{array}{ccc} 0 & \begin{pmatrix} 0.1\,M \\ +x \end{pmatrix} & 0.1\,M \end{array}$$

$$HA\,(aq.) \rightleftharpoons H^+\,(aq.) + A^-\,(aq.)$$

$$\begin{array}{ccc} 0.1 & - & - \\ (0.1-x) \simeq 0.1 & (x+0.1) & x \\ & \simeq 0.1 & \end{array}$$

as $\frac{Ka}{C} < 10^{-3} \Rightarrow x$ can be neglected

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

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(15) $H_2C_2O_4 (aq.) \rightleftharpoons H^+(aq) + HC_2O_4^-{}_{(aq)} \; : \; Ka_1$

0.1

$0.1-x$ $\qquad (x+y) \simeq x \quad (x-y) \simeq x$

$HC_2O_4^- (aq.) \rightleftharpoons H^+(aq) + C_2O_4^{2-}(aq) : Ka_2$

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

(as $Ka_1 >> Ka_2 \Rightarrow x >> y$)

$10^{-2} = Ka_1 = \dfrac{x^2}{0.1-x} \Rightarrow x^2 + 10^{-2}x - 10^{-3} = 0$

$\Rightarrow x = 2.7 \times 10^{-2}$ M (solving quadratic)

$Ka_2 = 10^{-5} = \dfrac{x.y}{x} = y$

$[H^+] = x = 0.027M = [HC_2O_4^-]$

$[C_2O_4^{2-}] = y = 10^{-5}M$; $[H_2C_2O_4] = 0.1 - x = 0.073M$

(16.) Diacidic weak base gives OH^- mainly due to I step

$Kb_1 = \dfrac{x^2}{c} \Rightarrow 2\times10^{-5} = \dfrac{x^2}{0.2}$

$x = [OH^-] = \sqrt{2\times10^{-5}\times0.2} = 2\times10^{-3}$ M

$pOH = 3 - \log 2 \Rightarrow pH = 14 - pOH = 11 + \log 2$

$= 11.3$

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

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8\times10^{-5}} = \frac{x^2}{C}$$

$$x = [OH^-] = \sqrt{\frac{10^{-14}}{1.8\times10^{-5}} \times 0.18} = 10^{-5} M$$

(18) $pH = 7 - \frac{1}{2} pK_b - \frac{1}{2}\log C$ (Salt of S.A & W.B.)

$$= 7 - \frac{1}{2}\times(5-\log 2) - \frac{1}{2}\log 2 = 4.5$$

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

$$K_h = \frac{10^{-14}}{K_b} = \frac{x^2}{C}$$

$x = [H^+] = 10^{-pH}$

$= 2\times10^{-3}$

$C = 0.25$

$$K_b = 6.25\times10^{-10}$$

(20) $pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$ (Salt of W.A & W.B.)

$= 7$ (as $K_a = K_b$)

$$\% h = \sqrt{\frac{10^{-14}}{K_a\times K_b}} \times 100 = 0.56\%$$

(21) $$\% h = \sqrt{\frac{K_h}{C}}\times100 = \sqrt{\frac{10^{-14}}{K_a\times C}}\times 100 = 1.667\%$$

Salt of W.A & S.B.

(22) Amphiprotic anion

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{7 - \log 5 + 11 - \log 5}{2} = 8.3$$

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(23) a) $K_h = \frac{x^2}{C} \Rightarrow x = [H^+] = \sqrt{K_h \cdot C}$

$$= \sqrt{10^{-9} \times 0.001} = 10^{-6} M$$

$\Rightarrow pH = 6$

b) $K_h = \frac{10^{-14}}{K_{b_2}} \Rightarrow K_{b_2} = \frac{10^{-14}}{K_h} = \frac{10^{-14}}{10^{-9}} = 10^{-5}$

(24) $pH = pK_a + \log\left(\frac{S}{a}\right) = 9 + \log\left(\frac{0.1}{0.1}\right) = 9$

(25) $pOH = pK_b + \log\left(\frac{S}{b}\right) = 5 - \log 1.8 + \log\left(\frac{0.1}{0.2}\right)$

$pH = 14 - pOH = 9.56$

(26) $pH = pKa + \log\left(\frac{S}{a}\right) = 5 - \log 1.8 + \log\left(\frac{0.4}{0.4 \times \frac{500}{1000}}\right)$

$= 5.04$

(27) $(NH_4)_2SO_4 \longrightarrow 2NH_4^+ + SO_4^{2-}$

x mol	$-$	$-$
0	$2x$	x

$pOH = pK_b + \log\left(\frac{S}{b}\right)$

$(14 - 9.26) = 4.74 + \log\left(\frac{2x}{0.1}\right)$

$x = \frac{0.1}{2} = 0.05$

(28) $K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_4OH]} = \frac{[0.1]\,[OH^-]}{0.05}$

$K_b = 1.8 \times 10^{-5}$

$[OH^-] = 9 \times 10^{-6}$ M

(29) $pH = pKa_{(HCO_3^-)} + \log\frac{[CO_3^{2-}]}{[HCO_3^-]} = 11 - \log 4 + \log\left(\frac{0.1}{0.2}\right)$

$= 10.1$

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

$50 \times 0.2 = 10$	$5\ (50 \times 0.1)$	$-$	
5	0	5	

for acidic buffer formed

$pH = pKa + \log\left(\frac{S}{a}\right) = 4.74 + \log\left(\frac{5}{5}\right) = 4.74$

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

$75\times0.1 = 7.5 \quad 50\times0.1 = 5 \quad - \quad -$

$2.5 \quad \times \quad 5 \quad 5$

Basic buffer

$$pOH = pK_b + \log\left(\frac{S}{b}\right) = (14-9.26) + \log\left(\frac{2.5}{5}\right)$$

$$= 14 - 9.26 - \log 2$$

$$pH = 14 - pOH = 9.26 + \log 2 = 9.56$$

(32) $NH_3 + HCl \longrightarrow NH_4Cl$

$20 \quad 15 \quad -$

$5 \quad \times \quad 15$

Basic Buffer

$$pOH = pK_b + \log\left(\frac{S}{b}\right) = 4.74 + \log\left(\frac{15}{5}\right) = 4.74 + \log 3$$

$$pH = 14 - pOH = 8.7782$$

(33) Let b millimoles of NaOH are added

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

initially $\quad 10 \quad b \quad 10$

After reaction $\quad 10-b \quad \times \quad 10+b$

$$pH_1 = pK_a + \log\left(\frac{10}{10}\right) = pK_a$$

$$pH_2 = pK_a + \log\left(\frac{10+b}{10-b}\right)$$

on solving

$$pH_2 - pH_1 = \log\left(\frac{10+b}{10-b}\right) = 0.3 = \log 2 \Rightarrow b = \frac{10}{3} = 3.33$$

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

$\frac{0.2}{2} = 0.1M \quad \frac{0.2}{2} = 0.1M \quad - \quad -$

$\times \quad \times \quad 0.1M$

(at equivalence point equal volumes are added so concentration becomes half)

for salt of S.B + W.A.

$$K_h = \frac{10^{-14}}{K_a} = \frac{x^2}{\cancel{c}\ 0.1}$$

$$x = [OH^-] = \sqrt{\frac{10^{-14}}{K_a} \times c} = 10^{-5}\ M$$

(35) at equivalence point CH_3COONa forms, $c = \frac{0.1}{2}M$

$$K_h = \frac{10^{-14}}{K_a} = \frac{x^2}{c} \quad \Big| \quad x = [OH^-]$$

$$[OH^-] = x = \sqrt{\frac{10^{-14}}{2\times10^{-5}} \times \frac{0.1}{2}} = \frac{10^{-5}}{2}$$

$$[H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{(10^{-5}/2)} = 2\times10^{-9}$$

$$pH = 9 - \log 2 = 8.7$$

(36) at equivalence point NH_4Cl forms, $C = \frac{0.4}{2} = 0.2M$

$$K_h = \frac{10^{-14}}{K_b} = \frac{x^2}{c} \Rightarrow x = [H^+] = 10^{-5}\ M$$

$$pH = 5$$

37 a) at 0 ml NaOH
for CH_3COOH, $[H^+] = \sqrt{K_a \cdot C} = \sqrt{2} \times 10^{-3}$

$$pH = 3 - \frac{1}{2}\log 2 = 2.85$$

b) at 20 ml NaOH

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

CH_3COOH	$NaOH$	CH_3COONa
5	$20 \times 0.1 = 2$	—
3	×	2

Acidic buffer

$$pH = pK_a + \log(S/a) = (5 - \log 2) + \log(2/3)$$

c) at 25 ml NaOH

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

CH_3COOH	$NaOH$	CH_3COONa
5	$25 \times 0.1 = 2.5$	—
2.5	×	2.5

$$pH = pK_a + \log(S/a) = 5 - \log 2 + \log\left(\frac{2.5}{2.5}\right)$$
$$= 4.699$$

d) at 40 ml NaOH

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

CH_3COOH	$NaOH$	CH_3COONa
5	4	—
1	×	4

$$pH = pK_a + \log(S/a) = 5 - \log 2 + \log(4/1)$$
$$= 5.0310$$

(e) at 50 ml NaOH :- CH_3COONa, $c = \frac{0.1}{2}$ M

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log c = 8.699$$

(38)

$$pH = pK_{In} + \log\frac{[In^-]}{[HIn]}$$

when $[In^-] = [HIn] = 50\% \Rightarrow pH = pK_{In} = 3$

but

$$\underset{10^{-3}}{K_{In}} = \frac{[H^+][In^-]}{[HIn]} = 4\times10^{-3} \times \frac{(100-x)}{x}$$

$\Rightarrow x = \%$ of $HIn = 80\%$

(39)

$$Ka = 6\times10^{-5} = \frac{[H^+][In^-]}{[HIn]} = 10^{-5} \times \left(\frac{x}{100-x}\right)$$

$\Rightarrow x = \%$ of basic form $(In^-) = 85.71\%$

(40) theoritically indicator changes the colour when

$pH = pK_{In} = 4 - \log 4 = 3.4$

i.e pH range $= 2.4$ to 4.4

So suitable for titrations involving strong acids only like option (b) & (c)

(41)

$$pH = pK_{In} + \log\left(\frac{In^-}{HIn}\right)$$

$pH_1 = pK_{In} + \log(25/75)$

$pH_2 = pK_{In} + \log(75/25)$

$\Delta pH = pH_2 - pH_1 = 2\log 3 = 0.954$

	HIn (Red)	In^- (blue)
Case-1	75%	25%
Case-2	25%	75%

(42) $\underline{MX}$:- $K_{sp} = s^2 \Rightarrow s_1 = \sqrt{K_{sp}} = 2\times10^{-9}$ M

$\underline{aX_2}$:- $K_{sp} = 4s^3 \Rightarrow s_2 = \left(\frac{K_{sp}}{4}\right)^{1/3} = 10^{-6}$ M

$s_2 > s_1$

(43) $S = \frac{0.0608}{304} = 2\times10^{-4}$ M

$K_{sp} = s^2 = (2\times10^{-4})^2 = 4\times10^{-8}$

(44) $CuI(s) \rightleftharpoons Cu^{+}(aq) + I^{-}(aq)$; K_{sp}

x mol/L $\quad x \quad (x+0.1)$ ← from NaCl

$\simeq 0.1$

$K_{sp} = [Cu^{+}][I^{-}] = x \times 0.1$

$x = \frac{K_{sp}}{0.1} = 5\times10^{-11}$ M

(45) $CaF_2(s) \rightleftharpoons Ca^{+2}(aq.) + 2F^{-}(aq.)$; K_{sp}

$x \quad 2x = 4\times10^{-4}$

$K_{sp} = x(2x)^2 = 2\times10^{-4} \times (4\times10^{-4})^2 = 3.2\times10^{-11}$

(46) $K_{sp} = 4s^3$

$= 4(4\times10^{-6})^3$

$= 2.56\times10^{-16}$

$S = \frac{2.4\times10^{-5}\times1000}{60\times100}$

$= 4\times10^{-6}$ mol/L

(47) $K_{sp} = (2)^2 (3)^3 s^5 = 108\, s^5$

$$s = \left(\frac{K_{sp}}{108}\right)^{1/5} = \left(\frac{1.08\times10^{-23}}{108}\right)^{1/5} = 10^{-5}\, M$$

(48)

$$AgCl\,(s) \rightleftharpoons Ag^+(aq.) + Cl^-(aq.) : K_{sp}$$

'x' mol/L x $(x + 2\times0.1)$ ← from $BaCl_2$

$\simeq 0.2$

$K_{sp} = x \times 0.2$

$$x = \frac{K_{sp}}{0.2} = 5\times10^{-10}$$

(49)

$$Ca_3(PO_4)_2\,(s) \rightleftharpoons 3\,Ca^{+2}(aq.) + 2\,PO_4^{3-}(aq.) : K_{sp}$$

'x' $(3x + 0.1)$ $2x$

$\simeq 0.1$ ← from $CaCl_2$

$$K_{sp} = [Ca^{+2}]^3 [PO_4^{3-}]^2 = (0.1)^3 (2x)^2$$

$$x = \left(\frac{10^{-15}}{(0.1)^3 \times 4}\right)^{1/2} = 5\times10^{-7}\, M$$

(50)

$$AgSCN\,(s) \rightleftharpoons Ag^+(aq.) + SCN^-(aq.) : K_{sp_1}$$

x $(x+y)$ x

$$AgBr(s) \rightleftharpoons Ag^+(aq.) + Br^-(aq.) : K_{sp_2}$$

y $(x+y)$ y

$K_{sp_1} = (x+y)x$ --- (1) ; $K_{sp_2} = (x+y)y$ --- (2)

(1) + (2) ⇒ $(x+y) = \sqrt{K_{sp_1} + K_{sp_2}} = 2\times10^{-6}$

⇒ $x = 1.6\times10^{-4}\, M$; $y = 4\times10^{-7}\, M$

(51)

$$K_{sp} \times K_f = \left(\frac{x}{c-2x}\right)^2 \Rightarrow \frac{x}{c-2x} = \sqrt{K_{sp} \times K_f}$$

here $c = 0.2M$ & x is solubility

$$\frac{x}{0.2-2x} = 4 \times 10^{-4} \Rightarrow$$

$$\Rightarrow x = 8 \times 10^{-3} M$$

(52)

$$\frac{K_{sp}}{K_a} = \frac{x^2}{[H^+]} \quad ; \quad x = \text{solubility}$$

$$x = \sqrt{\frac{K_{sp}}{K_a} \times [H^+]} = \sqrt{\frac{8 \times 10^{-10}}{5 \times 10^{-10}} \times 10^{-3}} = 4 \times 10^{-2} M$$

(53)

(a) $Q_{sp} = [Mg^{+2}][OH^-]^2 = 10^{-3} \times (10^{-5})^2 = 10^{-13}$

$Q_{sp} < K_{sp} \Rightarrow$ no ppt.

(b) $Q_{sp} = (10^{-3})(10^{-3})^2 = 10^{-9}$

$Q_{sp} > K_{sp} \Rightarrow$ ppt.

(54) After mixing of solns.

$$[Ag^+] = \frac{C_1V_1}{V_1+V_2} = 2 \times 10^{-4} \times \frac{200}{600} = \frac{2}{3} \times 10^{-4} M$$

$$[Cl^-] = \frac{C_2V_2}{V_1+V_2} = 1.2 \times 10^{-6} \times \frac{400}{600} = 8 \times 10^{-7} M$$

$$Q_{sp} = [Ag^+][Cl^-] = \frac{16}{3} \times 10^{-11} < K_{sp} \Rightarrow \underline{\text{No ppt}}$$

(55)

$$K_{sp} = 8 \times 10^{-8} = \underbrace{[Ba^{+2}]}_{2 \times 10^{-5}} [SO_4^{2-}]$$

$$[SO_4^{2-}] = 4 \times 10^{-3} \text{ mol/L}$$

mass of Na_2SO_4 in 500 ml $= \dfrac{4 \times 10^{-3}}{2} \times 142$ ← Mw. of Na_2SO_4

$= 0.284$ gm