

SOLUTIONS

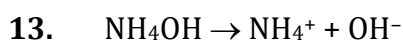
EXERCISE # O-I

1.  $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$   $\Delta H = +ve$   
 $K_w$  if  $T$   $K_{eq} = K_w$
2.  $K_w = [\text{H}^+] \times [\text{OH}^-]$   
 for pure water  $[\text{H}^+] = [\text{OH}^-]$   
 $K_w = 10^{-6.7} \times 10^{-6.7} = 10^{-13.4}$
3.  $\text{pH}_i = 3 \Rightarrow [\text{H}^+]_i = 10^{-3} \text{ M}$   
 $\text{pH}_f = 6 \Rightarrow [\text{H}^+]_f = 10^{-6} \text{ M}$   
 $[\text{H}^+]_i V_i = [\text{H}^+]_f V_f$   
 $10^{-3} \times V_i = 10^{-6} \times V_f$   
 $V_f = 1000 V_i$   
 $C_i = 1000 C_f$
4.  $\text{pH}_i = 2 \Rightarrow [\text{H}^+]_i = 10^{-2} \text{ M}$   
 $\text{pH}_f = 6 \Rightarrow [\text{H}^+]_f = 10^{-6} \text{ M}$   
 $\frac{[\text{H}^+]_i}{[\text{H}^+]_f} = \frac{10^{-2}}{10^{-6}}$   
 $[\text{H}^+]_i = 10^4 [\text{H}^+]_f$
5.  $\text{pH} = 13$ , so  $\text{pOH} = 1 \Rightarrow [\text{OH}^-] = 0.1$   
 $0.1 = \frac{\text{Moles of OH}^-}{0.25}$   
 Moles of  $\text{OH}^- = 0.025$   
 Mass of  $\text{NaOH} = 0.025 \times 40 = 1 \text{ g}$
6.  $\text{pH}$  of acid  $< 7$   
 So  $\text{pH}$  sol should be  $6 - 7$
7.  $[\text{H}^+]_i = 10^{-2}$   $[\text{H}^+]_f = 10^{-3}$   
 initial moles  $= 10^{-2}$  final moles of  $\text{H}^+ = 10^{-3}$   
 Moles of  $\text{H}^+$  should be removed  $= 10^{-2} - 10^{-3} = 0.009$
8.  $[\text{H}^+]_f = \frac{10 \times \frac{1}{200} \times 2 + 40 \times \frac{1}{200} \times 2}{50} = \frac{1}{100} \Rightarrow \text{pH} = 2$
9. **Higher the  $K_a$ , stronger the acid**
10.  $\text{NH}_3$  is base, so  $[\text{OH}^-]$ ,  $[\text{H}^+]$
12.  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$0.1(1 - \alpha) \quad 0.1\alpha \quad 0.1\alpha$$

$$10^{-5} = \frac{0.1\alpha \times 0.1\alpha}{0.1(1 - \alpha)}$$

$$10^{-5} = \frac{0.1\alpha^2}{1 - \alpha} \Rightarrow \frac{\alpha^2}{1 - \alpha} = 10^{-4} \Rightarrow \alpha = 10^{-2}$$



$$c(1 - \alpha) \quad c\alpha \quad c\alpha$$

$$[\text{OH}^-] = c\alpha = 0.02 \times \frac{5}{100} = 10^{-3}$$

$$\text{pOH} = 3 \Rightarrow \text{pH} = 11$$

15.  $[\text{H}^+]_f = \frac{10^{-3} + 10^{-5}}{2} = \frac{101}{2} \times 10^{-5}$

$$\text{pH} = 5 - \log \frac{101}{2} = 3.3$$

16.  $[\text{H}^+] = \sqrt{\text{Ka}_1\text{C}_1 + \text{Ka}_2\text{C}_2} = \sqrt{3 \times 10^{-4} \times 0.03 + 1 \times 10^{-10} \times 0.1} = 3 \times 10^{-3} \text{ M}$

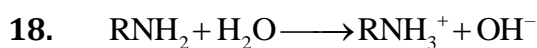
$$[\text{A}^-] = \frac{3 \times 10^{-4} \times 0.03}{3 \times 10^{-3}} = 3 \times 10^{-3} \text{ M}$$

$$[\text{B}^-] = \frac{1 \times 10^{-10}}{3 \times 10^{-3}} = 3.33 \times 10^{-9} \text{ M}$$

17.  $[\text{OH}^-] = \sqrt{\text{Ka}_1\text{C}_1 + \text{Ka}_2\text{C}_2} = \sqrt{6.4 \times 10^{-5} \times \frac{0.1}{2} + 1.8 \times 10^{-5} \times \frac{4}{45} \times \frac{1}{2}} = \sqrt{\frac{8}{2} \times 10^{-6}} = 2 \times 10^{-3} \text{ M}$

$$\text{pOH} = 3 - \log 2$$

$$\text{pH} = 11 + \log 2 = 11.3$$



$$0.01 - x \quad x \quad x$$

$$2 \times 10^{-6} = \frac{x - (x + 10^{-4})}{0.01 - x}$$

$$x^2 + 10^{-4}x - 2 \times 10^{-8} = 0$$

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

$$[\text{OH}^-] = 2 \times 10^{-4}$$

20.  $0.1 \text{ M HCl} + 0.1 \text{ M H}_3\text{PO}_4$  ( $a \ll 1$ )

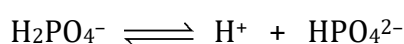


$$0.1(1 - \alpha) \quad 0.1 + 0.1\alpha \quad 0.1\alpha$$

$$\gg 0.1$$

$$[\text{H}^+] = 0.1 \Rightarrow \text{pH} = 1$$

$$K_{a1} = \frac{0.1 \times 0.1\alpha}{0.1} \Rightarrow a = 10 K_{a1}$$



$$0.1\alpha \quad 0.1 \quad \alpha_2$$

$$K_{a2} = \frac{0.1 \times [\text{HPO}_4^{2-}]}{0.1\alpha}$$

$$[\text{HPO}_4^{2-}] = \alpha K_2 = 10 K_{a1} K_{a2}$$

21.  $[\text{HPO}_4^{2-}] = 10 K_{a1} K_{a2}$

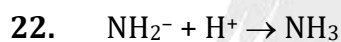


$$10 K_{a1} K_{a2} - x \quad x + 0.1 \quad x$$

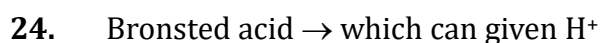
$$\gg 0.1$$

$$K_{a3} = \frac{0.1 \times x}{10 K_{a1} K_{a2} - x} = \frac{0.1 \times x}{10 K_{a1} K_{a2}}$$

$$[\text{PO}_4^{3-}] = x = 100 K_{a1} K_{a2} K_{a3}$$



Base C.A.



Acid Base C.A C.B.



$$K_{eq} = \frac{1}{K_h} = \frac{K_a}{K_w} = \frac{1.8 \times 10^{-5}}{10^{-14}} = 1.8 \times 10^9$$

26.  $K_a \text{ HF} \times K_b \text{ F}^- = K_w$

$$\text{p}K_a = 14 - 10.83 = 3.17$$

$$K_a = 10^{-3.17} = 6.75 \times 10^{-4}$$

28. At 85°C neutral pH < 7

29.  $[\text{H}^+] = \frac{0.01}{100} = 10^{-3} \text{ M} \Rightarrow \text{pH} = 3$

30. (A) 0.1 M NaCl  $\Rightarrow \text{pH} = 7$

(B) 0.1 M  $\text{NH}_4\text{Cl}$   $\Rightarrow \text{pH} < 7$

(C) 0.1 M  $\text{CH}_3\text{COONa}$   $\Rightarrow \text{pH} > 7$

(D) 0.1 M HCl  $\Rightarrow \text{pH} = 1$

31.  $h = \sqrt{\frac{K_w}{K_a} \times C} = \sqrt{\frac{10^{-14} \times 1/80}{1.3 \times 10^{-9}}} = \sqrt{\frac{10^{-6}}{8 \times 1.3}}$

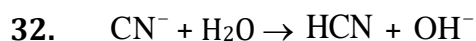


$$\begin{array}{ccc} 1/80(1-h) & h/80 & h/80 \end{array}$$

$$\frac{10^{-14}}{1.3 \times 10^{-9}} = \frac{h^2}{80(1-h)} \quad \text{p} \quad h^2 = \frac{8}{1.3} \times 10^{-4}$$

$$h = 2.48 \times 10^{-2}$$

$$\% h = 2.48$$



$$\begin{array}{ccc} 0.01(1-h) & 0.01h & 0.01h \end{array}$$

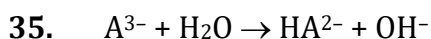
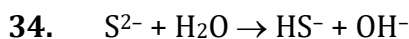
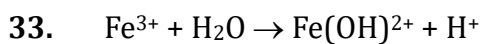
$$\frac{10^{-14}}{1.4 \times 10^{-9}} = \frac{0.01h^2}{1-h}$$

$$h^2 = \frac{10}{1.4} \times 10^{-4}$$

$$h = 2.67 \times 10^{-2}$$

$$\% h = 2.67\%$$

$$K_{b_3} > K_{b_2} > K_{b_1}$$



$$K_{h1} = \frac{K_w}{K_{a3}}$$

$$\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_{a3} + \log C)$$

36.  $\frac{h}{1-h} = \sqrt{K_h}$  (for salt of WA + WB)

h does not depend on conc.

37.  $\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a - \text{p}K_b) = \frac{1}{2} \times (14 + 4.8 - 4.78) = 7.01$

38. Amphiprotic species @ which can given as well as take  $\text{H}^+$  ion.

41. For 1 M NaCl & 1 M HCl solution

$$\Rightarrow \text{pH} < 7$$

42.  $\text{pOH} = \text{p}K_b = 4.74$

$$\text{pH} = 9.26$$

43.  $[\text{OH}^-] = K_b \times \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 1.8 \times 10^{-5} \times \frac{0.05}{0.001} = 9.0 \times 10^{-4}$

44.  $\text{pOH} = 5 - \log 1.85 + \log \frac{500 \times 0.5}{300 \times 0.3}$

$$= 5 + \log \frac{25}{16.2} = 5.188$$

$$\text{pH} = 14 - 5.188 = 8.812$$

$$45. \quad \text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$= 4.82 + \log \frac{3}{2} = 5$$

$$46. \quad \text{pH} = 5 + \log \frac{10 \times 1}{50 \times 2} = 5 - 1 = 4$$

$$47. \quad \text{pH} = 10 - \log 5 + \log \frac{5 \times V_{\text{mL}}}{10 \times 2} = 9$$

$$\log \frac{5V_{\text{mL}}}{20} = \log 0.5$$

$$V_{\text{mL}} = 2 \text{ mL}$$

$$48. \quad 4.74 = 5 - \log 1.34 + \log \frac{x}{0.02}$$

$$x = 1.5 \times 10^{-2} \text{ mol}$$

$$49. \quad 4 = 3.7 + \log \frac{0.1 \times V_{\text{mL}}}{50 \times 0.05}$$

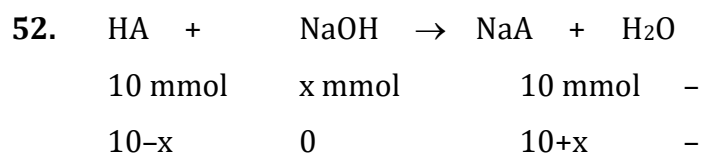
$$2 = \frac{0.01 \times V_{\text{mL}}}{50 \times 0.05} \Rightarrow V_{\text{mL}} = 50 \text{ mL}$$

$$50. \quad \text{If } [\text{NH}_4\text{OH}]^-, [\text{OH}^-], \text{pH}^-$$

$$51. \quad \text{pH} = \text{pK}_a + \log \frac{[\text{C.B.}]}{[\text{Acid}]}$$

$$\text{Ph} - \text{pK}_a = \log \frac{[\text{C.B.}]}{[\text{Acid}]} = 5 = \log 10^5$$

$$[\text{C.B.}] = 10^5 \times [\text{Acid}]$$



$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$5.5 = 5 + \log \frac{10+x}{10-x}$$

$$3.16 = \frac{10+x}{10-x} \Rightarrow x = 5.2$$

$$\text{Mass of NaOH added} = 5.2 \times 40 \times 10^{-3} \text{g} = 2.08 \times 10^{-1} \text{g}$$

53. On moderate dilution pH of buffer solution does not change.

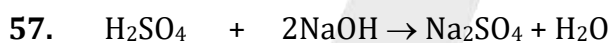
$$54. \text{ Buffer capacity} = \frac{0.02}{0.05} = 0.4$$

$$56. \text{ Moles of OH}^- = \frac{8}{40} = \frac{1}{5}$$

$$\text{Moles of H}^+ = \frac{4.9}{98} \times 2 = \frac{1}{10}$$

$$[\text{OH}^-] = \frac{0.1}{1} = 0.1$$

$$\text{pOH} = 1 \Rightarrow \text{pH} = 13$$



$$0.5 \text{ mmol} \quad 1 \text{ mmol}$$

$$0 \quad 0 \quad 1 \text{ mmol}$$

Solution will be neutral so pH = 7

$$58. \text{ M Moles of H}^+ = 15$$

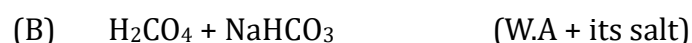
$$\text{M Moles of OH}^- = 5$$

$$[\text{H}^+]_f = \frac{10}{100} = \frac{1}{10} \quad \text{pH}_f = 1$$



$$\text{mmi} \quad 4 \quad 2 \quad 0 \quad 0$$

$$\text{mmf} \quad 2 \quad 0 \quad 2 \quad 2$$



(C)  $\text{NH}_4\text{Cl} + \text{HCl}$  (W.A + its salt)

(A)  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$  (W.A + its salt)



mm : 16 8 0 0

mmf 8 0 8 -

$$\text{pH} = 3.7 + \log \frac{8}{8} = 3.7$$

$$\text{pOH} = 10.3$$

62.  $\text{pH} = 4.74 + \log \frac{0.6}{0.4} = 4.916$

63.  $\text{pH} = \text{pK}_a = 3.7$

64.  $\text{pH} = 5 + \log \frac{25}{75}$  (25% neutralization)

$$= 5 + \log \frac{1}{3}$$

$\text{pH} = 5$  (50% neutralization)

$\text{pH} = 5 + \log \frac{75}{25}$  (75% neutralization)

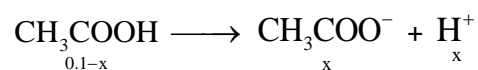
$$= 5 - \log 3$$



mmi 2 2 0 0

mmf 0 0 2 -

$$[\text{CH}_3\text{COOH}] = \frac{2}{20} = 0.1$$



$$1.8 \times 10^{-5} = \frac{x^2}{0.1-x}$$

$$[\text{H}^+] = x = \sqrt{1.8} \times 10^{-3}$$

$$\text{pH} = 2.88$$



66. For 0.1 M NaHA

$$\text{pH} = \frac{7+11}{2} = 9$$

for 0.1 M  $\text{H}_2\text{A}$   $\text{pH} < 7$

for 0.1 M  $\text{Na}_2\text{A}$   $\text{pH} > 7$

for 0.1 M  $\text{NaHA} + 0.1 \text{ M Na}_2\text{A} \Rightarrow \text{pH} = \text{pK}_{a2} = 11$

67.  $\text{N}_3\text{PO}_4 + \text{NaH}_2\text{PO}_4$

$\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$

$\text{Na}_2\text{HPO}_4 + \text{Na}_3\text{PO}_4$

68.  $\text{H}_3\text{PO}_4 + \text{NaOH} \rightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$

mmi 9 5 0 0

mmf 4 0 5 -

$$\text{pH} = 3 + \log \frac{5}{4} = 3.1$$

69.

$$\text{pH} = \text{pK}_{\text{In}} + \log \frac{[\text{In}^-]}{[\text{H In}]}$$

70.  $\text{pH} = \text{pK}_{\text{In}} \pm 1$

71. pH range of methyl red  
 $\Rightarrow 4.2 - 6.3$

72. pH at equivalence point is (5.5 – 11)

73. For HCl Vs  $\text{NH}_4\text{OH} \Rightarrow \text{pH range (3 – 8.5)}$

74. For NaOH Vs  $\text{H}_2\text{C}_2\text{O}_4$  titration  
pH range is (11 – 5.5)

75. Oxalic acid Vs  $\text{KMnO}_4$  titration is a redox titration.

76. For WA Vs SB titration

pH range is 5.5 – 11. So suitable indicator is Hph.

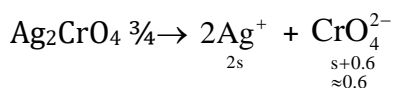
78.  $\text{pH}_i = \text{pK}_a + \log \frac{20}{80}$   
 $\text{pH}_f = \text{pK}_a + \log \frac{80}{20}$   
 $\Delta \text{pH} = 2 \log 4 = 1.2$
79.  $2\text{NaHCO}_3(\text{s}) \xrightarrow{\Delta} \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2\uparrow + \text{H}_2\text{O}\uparrow$       a mol   a/2 mol  
 $\text{Na}_2\text{CO}_3 + \text{HCl} \xrightarrow{\text{HPh}} \text{NaHCO}_3 + \text{NaCl}$   
 $\frac{a}{2} = 0.1 \times 0.5$   
 $a = 0.1 \text{ mol}$   
 $w = 0.1 \times 84 = 8.4 \text{ gm}$   
 $\% \text{ purity} = \frac{8.4}{10} \times 100 = 84\%$
81.  $K_{\text{sp}} = (28)^2 \times (3s)^3 = 108 s^5$
82.  $K_{\text{sp}} = s^2 = 64 \times 10^{-6}$   
 $s = 8 \times 10^{-3} \text{ M}$   
 $= 8 \times 10^{-3} \text{ mol/L}$   
 $= 8 \text{ mol/m}^3$
83.  $s = \frac{14.3 \times 10^{-4}}{143} = 10^{-5} \text{ M}$   
 $K_{\text{sp}} = s^2 = 10^{-10} \text{ M}^2$
84.  $s = \frac{7}{100} = 7 \times 10^{-2} \text{ M}$   
 $K_{\text{sp}} = s^2 = 4.9 \times 10^{-3}$
85. (A)  $K_{\text{sp}} = s^2$   
 $s = \sqrt{80} \times 10^{-19} \text{ M}$   
 (B)  $K_{\text{sp}} = s^2$   
 $s = \sqrt{7} \times 10^{-8} \text{ M}$   
 (C)  $K_{\text{sp}} = 108 s^5 = 1 \times 10^{-72}$   
 $s = \left( \frac{1000}{108} \right)^{1/5} \times 10^{-15} \text{ M}$   
 (D)  $K_{\text{sp}} = 27 s^4$

$$s = \left( \frac{180}{27} \right) \times 10^{-5} \text{ M}$$

86.  $4s^3 = 8.64 \times 10^{-13}$

$$s^3 = 216 \times 10^{-15}$$

$$s = 6 \times 10^{-5} \text{ M (in water)}$$



$$(2s)^2 \times 0.6 = 8.64 \times 10^{-13}$$

$$4s^2 = 14.4 \times 10^{-13}$$

$$s^2 = 3.6 \times 10^{-13}$$

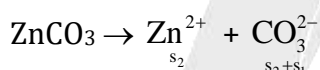
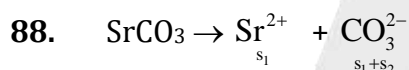
$$s = 6 \times 10^{-7} \text{ M}$$

87.  $0.1 \text{ M CaBr}_2 \Rightarrow [\text{Br}^-] = 0.2 \text{ M}$

$$0.1 \text{ M NaBr} \Rightarrow [\text{Br}^-] = 0.1 \text{ M}$$

$$0.1 \text{ M AgNO}_3 \Rightarrow [\text{Ag}^+] = 0.1 \text{ M}$$

In case of  $0.1 \text{ M CaBr}_2$ , molarity of common ion is maximum so. There maximum common ion effect.



$$\frac{(s_1 + s_2)s_1}{(s_1 + s_2)s_2} = \frac{10^{-10}}{1.5 \times 10^{-11}} = \frac{100}{15}$$

$$\frac{s_1}{s_2} = \frac{20}{3}$$

89.  $[\text{Ba}^{2+}] [\text{CO}_3^{2-}] = K_{sp}$

$$5.1 \times 10^{-9} = [\text{Ba}^{2+}] \times 10^{-4}$$

$$[\text{Ba}^{2+}] = 5.1 \times 10^{-5} \text{ M}$$

90.  $K_{sp} = [\text{Mg}^{2+}] [\text{OH}^-]^2$

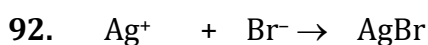
$$1 \times 10^{-11} = 0.1 \times [\text{OH}^-]^2$$

$$[\text{OH}^-] = 10^{-5} \text{ M}$$

$$\text{pOH} = 5 \text{ } \text{pH} = 9$$

91.  $Q_{IP} = 10^{-3} \times 10^{-10} = 10^{-13}$

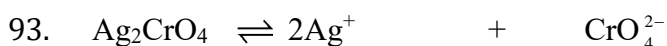
$Q_{IP} < K_{sp}$  (no ppt)



$C_i \quad 10^{-7} M \quad 10^{-7} M \quad 0$

$Q_{ip} = 10^{-7} \times 10^{-7} = 10^{-14}, Q_{ip} < K_{eq}$

So there will be no precipitation



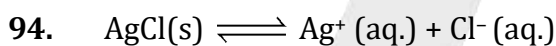
	10mmol	80mmol
5	0	75
	$\frac{x}{500}$	$\frac{75}{500}$

then  $\left(\frac{x}{500}\right)^2 \left(\frac{75}{500}\right) = 15 \times 10^{-12}$

$\frac{x}{500} = 10^{-5}$

$x = 5 \times 10^{-3}$

$[Ag^+] = \frac{5 \times 10^{-3}}{500} = 10^{-5}$



$y \quad x - y \quad 4 \times 10^{-5} - y$

$4 \times 10^{-5} - y = 10^{-5}$

$y = 3 \times 10^{-5}$

$(x - y)(4 \times 10^{-5} - y) = 10^{-10}$

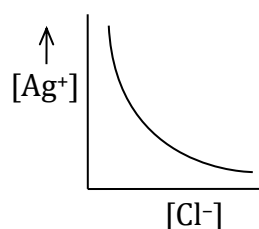
$(x - y)(10^{-5}) = 10^{-10}$

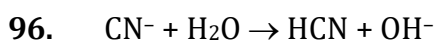
$x - y = 10^{-5}$

$x - 3 \times 10^{-5} = 10^{-5}$

$x = 4 \times 10^{-5}$

95.  $K_{sp} = [Ag^+][Cl^-]$



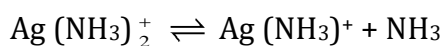


Solubility if  $[\text{OH}^-]$ ,  $[\text{H}^+]$ ,  $\text{pH}$

97. Solubility of  $\text{Ag}_2\text{CO}_3$  will be max. in  $\text{NH}_3$  due to complex formation.



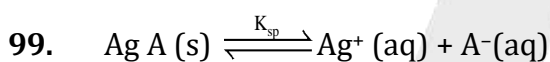
$$\begin{array}{ccc} x & 0.8 & 0.1 \end{array}$$



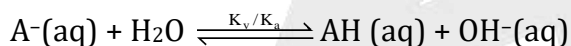
$$\begin{array}{ccc} 0.1 - x & x & 0.8 + x \end{array}$$

$$\begin{array}{ccc} \sim 0.1 & & \sim 0.8 \end{array}$$

$$\frac{1}{K_{f_2}} = \frac{1}{10^4} = \frac{(0.8)x}{0.1} \Rightarrow x = 1.25 \times 10^{-5}$$



$$\begin{array}{ccc} S & & S-x \end{array}$$



$$\begin{array}{ccc} S-x & x & x \end{array}$$

$$10^{-4} = \frac{K_w}{K_a} = \frac{x^2}{S-x} \Rightarrow \frac{10^{-10}}{S-x} \Rightarrow (S-x) = \frac{10^{-10}}{10^{-4}} = 10^{-6}$$

$$\Rightarrow S = x + 10^{-6} \{\text{but } x = 10^{-5}\} \Rightarrow S = (1.1 \times 10^{-5})$$

$$K_{sp} = [\text{Ag}^+(\text{aq})][\text{A}^-(\text{aq})] \Rightarrow 1.1 \times 10^{-5} \times 10^{-6}$$

$$K_{sp} = 1.1 \times 10^{-11}$$

EXERCISE:S-1

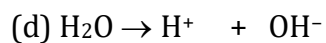
1.  $\text{pH} = 13$   
 $[\text{H}^+] = 10^{-13} \text{ M}$   
 $= 10^{-13} \text{ mol/L}$   
 $= 10^{-13} \times 6 \times 10^{23} \text{ ions/L}$   
 Q 1 L contains  $6 \times 10^{10}$  ions  
 $10^{-3} \text{ L}$  will contain  $= 6 \times 10^{10} \times 10^{-3}$   
 $= 6 \times 10^7 \text{ ions}$
  
2. (i)  $K_w = [\text{H}^+][\text{OH}^-] = 9 \times 10^{-14}$   
 In pure water  
 $[\text{H}^+] = [\text{OH}^-] = 3 \times 10^{-7}$   
 $\text{pH} = 7 - \log 3 = 6.52$   
 (ii) At  $60^\circ\text{C}$  neutral  $\text{pH} = 6.52$   
 If  $\text{pH} < 6.52$  then solution will be acidic and  $\text{pH} > 6.52$ . Then solution will be basic.
  
3.  $2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$   
 $\text{C}(1-\alpha) \quad \text{C}\alpha \quad \text{C}\alpha$   
 $[\text{H}^+] = \frac{1000}{18} \times 3.6 \times 10^{-9} = 2 \times 10^{-7} \text{ M}$   
 $K_w = [\text{H}^+][\text{OH}^-] = 2 \times 10^{-7} \times 2 \times 10^{-7} = 4 \times 10^{-14}$
  
4.  $2\text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NH}_2^-$   
 $[\text{NH}_4^+][\text{NH}_2^-] = 10^{-30}$   
 $[\text{NH}_2^-] = [\text{NH}_4^+] = 10^{-15} \text{ M}$   
 $[\text{NH}_2^-] = 10^{-15} \times 6 \times 10^{23} \text{ ions/L}$   
 1 L contains  $6 \times 10^5 \text{ NH}_2^-$  ions  
 $10^{-6} \text{ L} (1 \text{ mm}^3)$  will contain  $= 6 \times 10^5 \times 10^{-6} = 600 \text{ NH}_2^-$  ions
  
5. (a)  $[\text{H}^+] = 10^{-1} \Rightarrow \text{pH} = 1$   
 (b)  $[\text{OH}^-] = \frac{10^{-3}}{100} = 10^{-5} \text{ M}$

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

$$(c) [OH^-] = \frac{1}{10} \times \frac{2}{10} = 2 \times 10^{-3}$$

$$pOH = 3 - \log 2$$

$$pH = 11 + \log 2 = 11.3$$



$$X + 10^{-8} \quad x$$

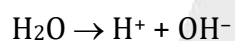
$$K_w = (x + 10^{-8})x = 10^{-14}$$

$$x = 9.5 \times 10^{-8}$$

$$[H^+] = 10.51 \times 10^{-8} M$$

$$pH = 8 - \log 10.51 = 8 - 1.03 = 6.97$$

(e)



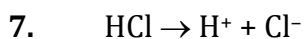
$$x \quad 10^{-10} + x$$

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

$$x \gg 10^{-7}$$

$$pH = 7$$

6. If  $V \rightarrow \text{¥}$ , then solution will almost neutral. So  $pH = 7$



$$x+y \quad x$$



$$x+y \quad y$$

$$x + y = 10^{-6.95}$$

$$(x + y) \times y = 10^{-14}$$

$$y = 10^{-7.05}$$

$$x + y = 11.22 \times 10^{-8}$$

$$y = 8.9 \times 10^{-8}$$

$$x = 2.32 \times 10^{-8} \text{ M}$$



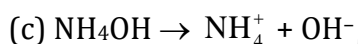
$$\begin{array}{ccc} 0.1-x & x & x \end{array}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.1-x}$$

$$x^2 = 1.8 \times 10^{-6}$$

$$[\text{H}^+] = x = 1.36 \times 10^{-3}$$

$$\text{pH} = 3 - \log 1.3 = 2.87$$

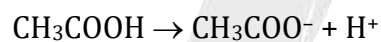


$$\begin{array}{ccc} 0.1-x & x & x \end{array}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.1-x}$$

$$[\text{OH}^-] = x = 1.34 \times 10^{-3}$$

$$\text{pOH} = 2.87 \Rightarrow \text{pH} = 11.13$$



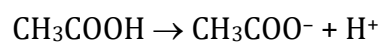
Acid will completely dissociate, so  $a \gg 1$

Taking contribution of water

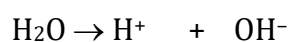
$$[\text{H}^+] = 1.62 \times 10^{-7} \Rightarrow \text{pH} = 6.78$$

$$(g) \frac{K_a}{C} = \frac{1.8 \times 10^{-5}}{10^{-8}} = 1.8 \times 100$$

Acid will completely dissociate, so  $a \gg 1$



$$\begin{array}{ccc} 10^{-8} & 10^{-8} + x & \end{array}$$



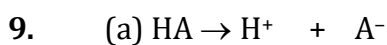
$$\begin{array}{ccc} 10^{-8} + x & x & \end{array}$$

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



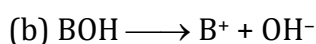
$$x = 9.51 \times 10^{-8}$$

$$[H^+] = 10.51 \times 10^{-8} \Rightarrow \text{pH} = 6.97$$



$$10^{-4.5} \quad 10^{-4.5}$$

$$K_a = \frac{10^{-4.5} \times 10^{-4.5}}{0.1 - 10^{-4.5}} = \frac{10^{-9}}{0.1} = 10^{-8}$$



$$10^{-3.5} \quad 10^{-3.5}$$

$$K_b = \frac{10^{-3.5} \times 10^{-3.5}}{0.1 - 10^{-3.5}} = 10^{-6}$$

10.  $\frac{C_1 \alpha_1^2}{1 - \alpha_1} = \frac{C_2 \alpha_2^2}{1 - \alpha_2}$

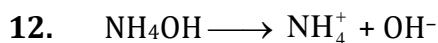
$$\alpha_1^2 = 10^{-2} \alpha_2^2 \Rightarrow \frac{\alpha_2^2}{\alpha_1^2} = 100 \Rightarrow \frac{\alpha_2}{\alpha_1} = 10$$

11.  $1.8 \times 10^{-5} = \frac{1 \times \alpha_1^2}{1 - \alpha_1} = 1 \times \alpha_1^2$

$$6.2 \times 10^{-10} = \frac{1 \times \alpha_1^2}{1 - \alpha_2} = 1 \times \alpha_2^2$$

$$\frac{\alpha_1^2}{\alpha_2^2} = \frac{1.5 \times 10^{-5}}{6.2 \times 10^{-10}} = 2.9 \times 10^{-4}$$

$$\frac{\alpha_1}{\alpha_2} = 1.70 \times 10^2$$

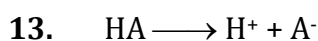


$$10^{-4} \quad 10^{-4}$$

$$10^{-5} = \frac{10^{-8}}{C - 10^{-4}}$$

$$C - 10^{-4} = 10^{-3}$$

$$C = 1.1 \times 10^{-3} \text{ M}$$



$$10^{-3} \quad 10^{-3}$$

$$K_a = \frac{10^{-6}}{10^{-2} - 10^{-3}} = \frac{10^{-6}}{9 \times 10^{-3}} = \frac{1}{9} \times 10^{-3}$$

14.  $5.9 \times 10^{-10} = \frac{x^2}{0.3 - x}$

$$x^2 = 5.9 \times 0.3 \times 10^{-10}$$

$$x = \sqrt{1.77} \times 10^{-5}$$

$$\text{pH} = 5 - \log \sqrt{1.77} = 4.87$$

15.  $[\text{H}^+] = \frac{10^{-4}}{2} + \frac{19}{2} \times 10^{-4} = 10 \times 10^{-4} = 10^{-3}$

$$\Rightarrow \text{pH} = 3$$

16. (a)  $[\text{H}^+] = \frac{10 + 20}{100} = \frac{30}{100}$

$$\text{pH} = 1 - \log 3 = 0.52$$

(b)  $[\text{H}^+] = \sqrt{2 \times 10^{-5} \times 0.1 + 4 \times 10^{-5} \times 0.1} = \sqrt{6} \times 10^{-3}$

$$\text{pH} = 3 - 0.39 = 2.61$$



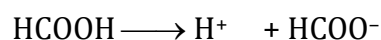
$$0.05 - x \quad x \quad x$$

$$1.8 \times 10^{-4} = \frac{x^2}{0.05 - x}$$

$$x^2 = 1.8 \times 10^{-4} \times 0.05$$

$$x^2 = 9 \times 10^{-6}$$

$$\text{pH}_i = 2.52$$



$$0.05 - x \quad 0.1 + x \quad x$$

$$1.8 \times 10^{-4} = \frac{(0.1 + x)x}{0.05 - x}$$

$$x^2 + 0.1x - 9 \times 10^{-6} = 0$$

$$x = 0.9 \times 10^{-4}$$

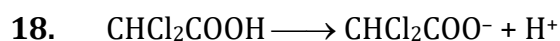
$$[H^+] = 0.1$$

$$pH_f = 1$$

$$\Delta pH = 1 - 2.52 = -1.52$$

$$1.8 \times 10^{-4} = \frac{0.1 \times [HCOO^-]}{0.05}$$

$$[HCOO^-] = 0.9 \times 10^{-4} = 9 \times 10^{-5} \text{ M}$$



$$\begin{array}{ccc} 0.01-x & x & x+0.01 \end{array}$$

$$3 \times 10^{-2} = \frac{x(x+0.01)}{0.01-x}$$

$$x^2 + 4 \times 10^{-2}x - 3 \times 10^{-4} = 0$$

$$x = 0.64 \times 10^{-2}$$

$$[H^+] = 1.64 \times 10^{-2} \text{ M}$$

$$[CHCl_2COO^-] = x = 0.64 \times 10^{-2} \text{ M}$$

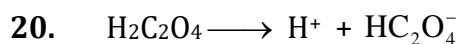
19.  $[H^+] = \sqrt{1.8 \times 10^{-5} \times 0.02 + 6.4 \times 10^{-5} \times 0.01} = 10^{-3} \text{ M}$

$$1.8 \times 10^{-5} = \frac{[CH_3COO^-] \times 10^{-3}}{0.02 - 10^{-3}}$$

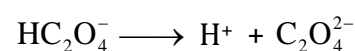
$$[CH_3COO^-] = 1.8 \times 10^{-2} \times 19 \times 10^{-3} = 3.42 \times 10^{-4} \text{ M}$$

$$6.4 \times 10^{-5} = \frac{[C_7H_5O_2^-] \times 10^{-3}}{0.01 - 10^{-3}}$$

$$[C_7H_5O_2^-] = 6.4 \times 10^{-2} \times 9 \times 10^{-3} = 5.76 \times 10^{-4} \text{ M}$$



$$\begin{array}{ccc} 0.1-x & x+y & x-y \end{array}$$



$$\begin{array}{ccc} x-y & x+y & y \end{array}$$

$$10^{-2} = \frac{(x+y)(x-y)}{0.1-x}$$

$$10^{-5} = \frac{(x+y)y}{x-y}$$

$$10^{-5} = \frac{x \times y}{x}$$

$$K_{a1} \gg K_{a2}, \text{ so } x \gg y$$

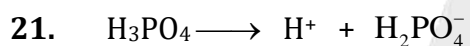
$$10^{-2} = \frac{x^2}{0.1-x}$$

$$x^2 + 10^{-2}x - 10^{-3} = 0 \text{ P } x = 2.7 \times 10^{-2}$$

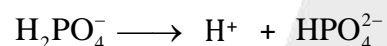
$$[H^+] = [HC_2O_4^-] = 2.7 \times 10^{-2} \text{ M}$$

$$[C_2O_4^{2-}] = 10^{-5} \text{ M}$$

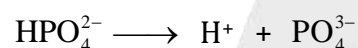
$$[H_2C_2O_4] = 7.3 \times 10^{-2} \text{ M}$$



$$10^{-2}-x \quad x+y+z \quad x-y$$



$$x-y \quad x+y+z \quad y-z$$



$$y-z \quad x+y+z \quad z$$

$$K_{a1} \gg K_{a2} \gg K_{a3}, \text{ so } x \gg y \gg z$$

$$10^{-3} = \frac{(x+y+z)(x-y)}{10^{-2}-x}$$

$$10^{-3} = \frac{x^2}{10^{-2}-x}$$

$$x^2 + 10^{-3}x - 10^{-5} = 0 \text{ P } x = 2.7 \times 10^{-3}$$

$$10^{-8} = \frac{(x+y+z)(y-z)}{x-y}$$

$$10^{-8} = \frac{x \times y}{x} \text{ P } y = 10^{-8}$$

$$10^{-13} = \frac{(x+y+z) \times z}{y-z}$$

$$10^{-13} = \frac{x \times z}{y} = \frac{2.7 \times 10^{-3} \times 2}{10^{-8}}$$

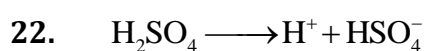
$$z = \frac{1}{2.7} \times 10^{-18} = 3.7 \times 10^{-19}$$

$$[H^+] = [H_2PO_4^-] = 2.7 \times 10^{-3} \text{ M}$$

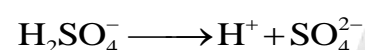
$$[HPO_4^-] = 10^{-8} \text{ M}$$

$$[PO_4^{3-}] = 3.7 \times 10^{-19}$$

$$H_3PO_4 = 7.3 \times 10^{-3} \text{ M}$$



$$0.2 \quad 0.2 \quad 0.2$$



$$0.2-x \quad 0.2+x \quad 0.2$$

$$10^{-2} = \frac{(0.2+x)}{0.2-x}$$

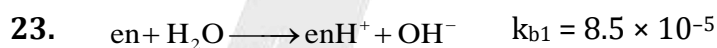
$$x^2 + 21 \times 10^{-2}x - 2 \times 10^{-3} = 0$$

$$x = 0.9127 \times 10^{-2}$$

$$[H^+] = 0.209127 \text{ M}$$

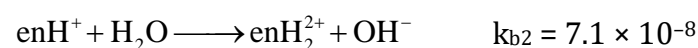
$$[SO_4^{2-}] = 0.009127 \text{ M}$$

$$[HSO_4^-] = 0.190873 \text{ M}$$



$$0.1-x \quad x-y \quad x+y$$

$$\approx x \quad \approx x$$



$$x-y \quad y \quad x+y$$

$$\approx x \quad \approx x$$

$$k_{b1} \gg k_{b2} \quad \text{so} \quad x \gg y$$

$$8.5 \times 10^{-5} = \frac{x^2}{0.1-x} \Rightarrow x^2 = 8.5 \times 10^{-6} \Rightarrow x = 2.91 \times 10^{-3}$$

$$[OH^-] = 2.91 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = 11.46$$

$$7.1 \times 10^{-8} = \frac{x \times y}{x} \Rightarrow y = 7.1 \times 10^{-8}$$

$$[\text{enH}_2^{2+}] = 7.1 \times 10^{-8} \text{ M}$$

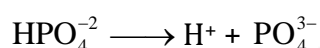
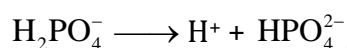
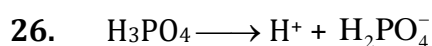
24. All cations ( $\text{Cu}^{2+}$ ,  $\text{NH}_4^+$ ) are acid and all anions ( $\text{C}_2\text{H}_5\text{O}^-$ ,  $\text{F}^-$ ,  $\text{SO}_3^{2-}$ ) are base

Solution of salt of SA + SB  $\longrightarrow$  Neutral ( $\text{KNO}_3$ )

Solution of salt of SA + WB  $\longrightarrow$  Acidic ( $\text{ZnCl}_2$ )

Solution of salt of WA + SB  $\longrightarrow$  Basic ( $\text{NaOCl}$ ,  $\text{CH}_3\text{COONa}$ ,  $\text{Na}_2\text{CO}_3$ )

25.  $K_a(\text{HOCl}) = \frac{10^{-14}}{4 \times 10^{-10}} = 3.5 \times 10^{-5}$



(i) Dissociation constant of  $\text{HPO}_4^{2-} = K_{a_3} = 10^{-12}$

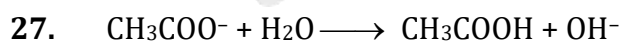
(ii)  $K_a \text{H}_2\text{PO}_4^- \times K_b \text{HPO}_4^{2-} = K_w$

$$K_b \text{HPO}_4^{2-} = \frac{10^{-14}}{10^{-8}} = 10^{-6}$$

(iii)  $K_a \text{H}_3\text{PO}_4 \times K_b \text{H}_2\text{PO}_4^- = K_w$

$$K_b \text{H}_2\text{PO}_4^- = \frac{10^{-14}}{10^{-3}} = 10^{-11}$$

(iv)  $K_b \text{PO}_4^{3-} = \frac{K_w}{K_{a_3}} = \frac{10^{-14}}{10^{-12}} = 10^{-2}$



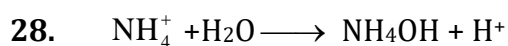
$$\begin{array}{ccc} 0.08 - x & & x \quad x \end{array}$$

$$\frac{10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.08 - x}$$

$$\frac{10^{-9}}{1.8} = \frac{x^2}{0.08}$$

$$x^2 = \frac{0.08}{1.8} \times 10^{-9} = 0.44 \times 10^{-10}$$

$$x = [\text{OH}^-] = 0.66 \times 10^{-5} \text{ M}$$

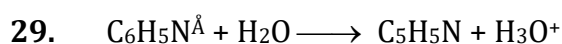


$$2-x \qquad \qquad \qquad x \qquad x$$

$$\frac{10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{2-x}$$

$$x^2 = \frac{2 \times 10^{-9}}{1.8}$$

$$x = [\text{H}^+] = \frac{10}{3} \times 10^{-5} \Rightarrow \text{pH} = 4.48$$

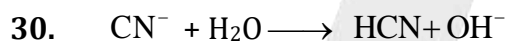


$$0.25-x \qquad \qquad \qquad x \qquad x$$

$$\frac{10^{-14}}{K_b} = \frac{4 \times 10^{-6}}{0.25 - 2 \times 10^{-3}}$$

$$\frac{10^{-14}}{K_b} = \frac{4 \times 10^{-6}}{0.25}$$

$$K_b = \frac{0.25 \times 10^{-14}}{4 \times 10^{-6}} = \frac{1}{16} \times 10^{-8} = 6.25 \times 10^{-10}$$



$$0.06(1-h) \qquad \qquad 0.06h \quad 0.06h$$

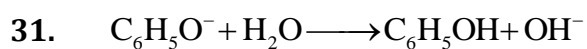
$$\frac{10^{-14}}{6 \times 10^{-10}} = \frac{0.06h^2}{1-h}$$

$$\frac{1}{6} \times 10^{-14} = \frac{0.06h^2}{1-h}$$

$$0.06h^2 = \frac{1}{6} \times 10^{-4}$$

$$h^2 = \frac{1}{36} \times 10^{-2}$$

$$h = \frac{1}{60} = 0.0166 = 1.66 \%$$



$$10^{-3}-x \qquad \qquad \qquad x \qquad x$$

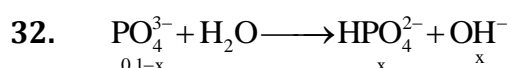
$$\frac{10^{-14}}{1.05 \times 10^{-10}} = \frac{x^2}{10^{-3} - x}$$

$$10^{-4} = \frac{x^2}{10^{-3} - x}$$

$$x^2 + 10^{-4}x - 10^{-7} = 0$$

$$[\text{OH}^-] = x = \frac{\sqrt{41} - 1}{2} \times 10^{-4} = 2.7 \times 10^{-4}$$

$$\text{pH} = 10 + \log 2.7 = 10.3$$



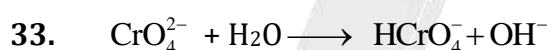
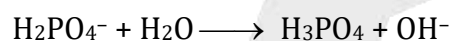
$$\frac{10^{-14}}{4.5 \times 10^{-13}} = \frac{x^2}{0.1 - x}$$

$$\frac{x^2}{0.1 - x} = \frac{1}{45}$$

$$45x^2 + x - 0.1 = 0$$

$$[\text{OH}^-] = x = 4.911 \times 10^{-1}$$

$$[\text{H}_2\text{PO}_4^-] = 6.2 \times 10^{-8} \text{ M}$$

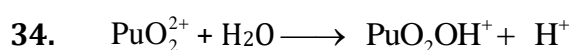


$$K_{h1} = \frac{K_w}{K_{a2}} \frac{10^{-14}}{3.1 \times 10^{-7}} = \frac{x^2}{0.005 - x}$$

$$\frac{10^{-7}}{3.1} = \frac{x^2}{5 \times 10^{-3}} \Rightarrow x^2 = \frac{5 \times 10^{-10}}{3.1}$$

$$x = h = 1.26 \times 10^{-5}$$

$$h = \frac{1.26 \times 10^{-5}}{5 \times 10^{-3}} = 2.52 \times 10^{-3}$$





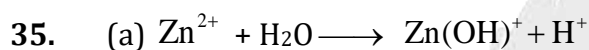
$$\begin{array}{ccc} 0.01-x & x & x \\ = 10^{-4} & = 10^{-4} & \end{array}$$

$$K_b = \frac{10^{-8}}{0.01-10^{-4}} = \frac{10^{-8}}{0.01} = 10^{-6}$$

$$K_a(\text{PuO}_2^{2+}) \times K_b(\text{PuO}_2\text{OH}^+) = K_w$$

$$K_a \text{PuO}_2^{2+} = 10^{-6}$$

$$K_b \text{PuO}_2\text{OH}^+ = \frac{10^{-14}}{10^{-6}} = 10^{-8}$$



$$\begin{array}{ccc} 0.001-x & x & x \\ 10^{-9} = \frac{x^2}{10^{-3}-x} \end{array}$$

$$x^2 = 10^{-12}$$

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

(b)  $K_a \text{Zn}^{2+} \times K_b \text{Zn}(\text{OH})^+ = K_w$

$$10^{-9} \times K_b \text{Zn}(\text{OH})^+ = 10^{-14}$$

$$K_b \text{Zn}(\text{OH})^+ = 10^{-5}$$

36.  $\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a - \text{p}K_b)$

$$\text{pH} = 7$$

37.  $\text{pH} = \frac{\text{p}K_2 + \text{p}K_1}{2} = \frac{10.34 + 6.34}{2} = 8.34$

38.  $\text{pH} = \frac{\text{p}K_2 + \text{p}K_1}{2} = \frac{5.44 + 2.94}{2} = 4.19$

39.  $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$

$$1.8 \times 10^{-5} = \frac{0.1 \times [\text{OH}^-]}{5 \times 10^{-2}}$$

$$[\text{OH}^-] = 1.8 \times 5 \times 10^{-6} = 9 \times 10^{-6} \text{ M}$$

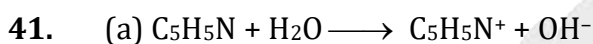
40. Moles of  $(\text{NH}_4)_2\text{SO}_4 = x$

Moles of  $\text{NH}_3 = 1$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$4.74 = 4.74 + \log \frac{2x}{0.1}$$

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



$$0.2 - x \qquad \qquad x \qquad \qquad x$$

$$1.5 \times 10^{-9} = \frac{x^2}{0.2 - x}$$

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

$$[\text{OH}^-] = x = \sqrt{3} \times 10^{-5} \text{ M}$$

$$\text{pOH} = 5 - \frac{1}{2} \log 3 \Rightarrow \text{pH} = 9 + \frac{1}{2} \log 3 = 9.15$$

(b) Equilibrium will shift to backward reaction so  $[\text{OH}^-]$ , pOH, pH

(c)  $\text{pOH} = \text{pK}_b + \log \frac{[\text{C}_5\text{H}_5\text{NH}^+]}{[\text{C}_5\text{H}_5\text{N}]}$

$$= 9 - \log 1.5 + \log \frac{0.3}{0.1} = 9 - \log 1.5 + \log 3 = 9.3$$

$$\text{pH} = 4.7$$



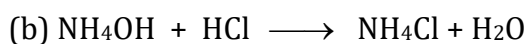
$$0.1 \quad 0.05 \quad 0.1 \quad - \quad \text{(initial moles)}$$

$$0.05 \quad 0 \quad 0.15 \quad - \quad \text{(moles at equilibrium)}$$

$$\text{pOH}_i = 4.74 \Rightarrow \text{pH}_i = 9.26$$

$$\text{pOH}_f = 4.74 + \log \frac{0.05}{0.15} = 4.74 - \log 3$$

$$\text{pH}_f = 9.26 + \log 3 = 9.74$$



$$0.1 \quad 0.05 \quad 0.1 \quad \text{(initial moles)}$$

$$0.05 \quad 0 \quad 0.05 \quad \text{(moles at equilibrium)}$$

$$pOH_i = 4.74 \Rightarrow pH_i = 9.26$$

$$pOH_f = 4.74 + \log \frac{0.05}{0.15} = 4.74 + \log 3$$

$$pH_f = 9.26 - \log 3 = 8.78$$

43. (a) millimoles of  $OH^- = 8$

$$\text{millimoles of } H^+ = 3$$

$$[OH^-] = \frac{5}{50} = 0.1$$

$$pOH = 1 \Rightarrow pH = 13$$

(b) millimoles of  $H^+ = 0.2$

$$\text{millimoles } OH^- = 0.2$$

Hence solution will be neutral, so  $pH = 7$

(d) millimoles of  $H^+ = 1 \times 2$

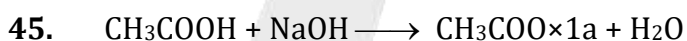
$$\text{millimoles of } OH^- = 1$$

$$[H^+] = \frac{1}{20}$$

$$pH = \log 20 = 1.3$$

44. In case of (iii) buffer can be prepared

In case of (iv) and (v) buffer can be prepared if moles of weak acid or weak base is more



$$10\text{m mol} \quad 5\text{m mol} \quad - \quad -$$

$$5\text{m mol} \quad 0 \quad 5\text{m mol} \quad -$$

$$pH = pK_a = 4.74$$

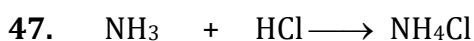


$$7.5\text{m mol} \quad 5\text{m mol} \quad - \quad -$$

$$2.5\text{m mol} \quad 0 \quad 5\text{m mol} \quad -$$

$$pOH = 4.74 + \log \frac{2.5}{5} = 4.74 - \log 2$$

$$pH = 9.26 + \log 2 = 9.56$$



20m mol    15m mol    -

5m mol        0            15m mol

$$\text{pOH} = 4.74 + \log \frac{15}{5} = 4.74 + \log 3$$

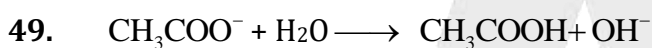
$$\text{pH} = 9.26 - \log 3 = 8.78$$



10m mol    7.5m mol        -        -

2.5m mol    0                    5m mol    -

$$\text{pOH} = 4.74 + \log \frac{2.5}{5} = 4.74 + \log \frac{1}{2}$$



0.1-x                    x                    x

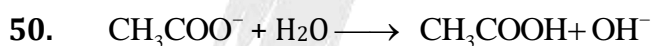
$$\frac{10^{-14}}{10^{-5}} = \frac{x^2}{0.1-x}$$

$$10^{-9} = \frac{x^2}{0.1}$$

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

$$x = [\text{OH}^-] = 10^{-5}$$

$$\text{pOH} = 5 \Rightarrow \text{pH} = 9$$



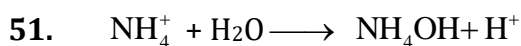
0.05-x                    x                    x

$$\frac{10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.05-x}$$

$$x^2 = 0.05 \times 10^{-14} = 1.8 \times 10^{-5}$$

$$[\text{OH}^-] = x = 0.52 \times 10^{-5}$$

$$[\text{H}^+] = 1.92 \times 10^{-9} \text{ M} \Rightarrow \text{pH} = 8.71$$

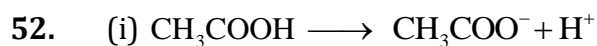


0.2-x                    x                    x

$$\frac{10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.2 - x}$$

$$x^2 = \frac{1}{9} \times 10^{-9}$$

$$[H^+] = x = 1.05 \times 10^{-5} \Rightarrow \text{pH} = 4.98$$



$$0.1 - x \qquad \qquad x \qquad \qquad x$$

$$2 \times 10^{-5} = \frac{x^2}{0.1 - x}$$

$$x^2 = 2 \times 10^{-6}$$

$$[H^+] = x = \sqrt{2} \times 10^{-3}$$

$$\text{pH} = 3 - 0.15 = 2.85$$



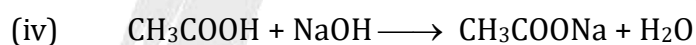
$$\begin{array}{ccc} 5\text{mmol} & 1\text{mmol} & - \\ 4\text{mmol} & 0 & 1\text{mmol} \end{array}$$

$$\text{pH} = 4.7 + \log \frac{1}{4} = 4.7 - 0.6 = 4.1$$



$$\begin{array}{ccc} 5\text{mmol} & 2\text{mmol} & - \\ 3\text{mmol} & 0 & 2\text{mmol} \end{array}$$

$$\text{pH} = 4.7 + \log \frac{2}{3} = 4.52$$



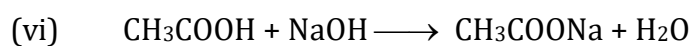
$$\begin{array}{ccc} 5\text{mmol} & 2.5\text{mmol} & - \\ 2.5\text{mmol} & 0 & 2.5\text{mmol} \end{array}$$

$$\text{pH} = \text{pK}_a = 4.7$$

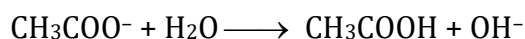


$$\begin{array}{ccc} 5\text{mmol} & 4\text{mmol} & - \\ 1\text{mmol} & 0 & 4\text{mmol} \end{array}$$

$$\text{pH} = 4.7 + \log 4 = 5.3$$



5mmol	5mmol	–
0	0	5mmol



$$0.05 - x \qquad \qquad x \qquad \qquad x$$

$$\frac{10^{-14}}{2 \times 10^{-15}} = \frac{x^2}{0.05 - x}$$

$$x^2 = \frac{1}{2} \times 10^{-9} \times 0.05 = \frac{1}{4} \times 10^{-10}$$

$$[\text{OH}^-] = x = \frac{1}{2} \times 10^{-5}$$

$$\text{pOH} = 5 + \log 2$$

$$\text{pH} = 9 - \log 2 = 8.7$$

53.  $\text{pK}_{\text{In}} = 2$

$$\text{K}_{\text{In}} = 10^{-2}$$

$$\text{K}_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \Rightarrow 10^{-2} = \frac{4 \times 10^{-3} [\text{In}^-]}{[\text{HIn}]}$$

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{10}{4} = 2.5$$

$$\% \text{ of } [\text{HIn}] = \frac{1}{3.5} \times 100 = 28.57 \%$$

54.  $\text{pH}_i = \text{pK}_a + \log \frac{25}{75} = \text{pK}_a + \log \frac{1}{3}$

$$\text{pH}_f = \text{pK}_a + \log \frac{75}{25} = \text{pK}_a + \log 3$$

$$\Delta \text{pH} = 2 \log 3 = 0.96$$

55.  $\text{K}_{\text{In}} = \frac{[\text{H}^+] \times [\text{Basic}]}{[\text{Acidic}]}$

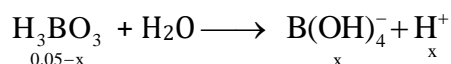
$$6 \times 10^{-5} = \frac{10^{-5} \times [\text{Basic}]}{[\text{Acidic}]}$$

$$\% \text{ of } [\text{Basic}] = \frac{6}{7} \times 100 = 85.71 \%$$

56.  $\text{pH} = \text{pK}_{\text{In}} \pm 1$

$\text{pH range of indicator} = 2.4 - 4.4$

57. At equivalence point  $\text{H}_3\text{BO}_3$  will present in solution.



$$7.2 \times 10^{-10} = \frac{x^2}{0.05 - x}$$

$$x^2 = \frac{7.2}{20} \times 10^{-10}$$

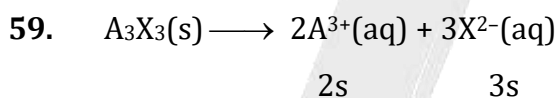
$$[\text{H}^+] = x = \sqrt{\frac{7.2}{20}} \times 10^{-5} \text{ M}$$

$$\text{pH} = 5 - \frac{1}{2} \log \frac{7.2}{20} = 5.44$$

$\text{pH range of titration} = 4.44 - 6.44$

So suitable indicator methyl red (4.2 - 6.3)

58. (018)

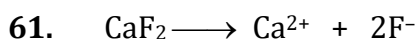


$$K_{\text{sp}} = (2s)^2 \times (3s)^3 = 108s^5 = 1.08 \times 10^{-23}$$

$$s = 10^{-5} \text{ M}$$

60.  $s = \frac{0.038}{3.04} = 1.25 \times 10^{-3} \text{ M}$

$$K_{\text{sp}} = s^2 = (1.25)^2 \times 10^{-8} = 1.56 \times 10^{-8} \text{ M}$$



$$4.1 \times \frac{10^{-4}}{2} \quad 4.1 \times 10^{-4}$$

$$K_{\text{sp}} = \frac{4.1 \times 10^{-4}}{2} \times (4.1 \times 10^{-4})^2 = 3.44 \times 10^{-11}$$

$$62. \quad s = \frac{2.4 \times 10^{-5}}{60} \times 10 = 4 \times 10^{-6} \text{ M}$$

$$K_{sp} = 4s^3 = 4 \times (4 \times 10^{-6})^3 \\ = 2.56 \times 10^{-16}$$

63. For MX

$$s^2 = K_{sp} = 4 \times 10^{-18}$$

$$s = 2 \times 10^{-9} \text{ M}$$

For QX<sub>2</sub>

$$4s^2 = K_{sp} = 4 \times 10^{-18}$$

$$s = 10^{-6} \text{ M}$$

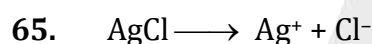
Solubility of QX<sub>2</sub> is more



$$s \quad s+0.1 \gg 0.1$$

$$s \times 0.1 = 5 \times 10^{-12}$$

$$[\text{Cu}^+] = s = 5 \times 10^{-11} \text{ M}$$



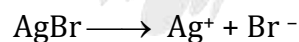
$$s \quad s+0.2$$

$$s \times 0.2 = 1 \times 10^{-10}$$

$$s = 5 \times 10^{-10} \text{ M}$$



$$s_1+s_2 \quad s_1$$



$$s_1+s_2 \quad s_2$$

$$(s_1 + s_2)s_1 = 1.1 \times 10^{-12}$$

$$(s_1 + s_2)s_2 = 5 \times 10^{-13}$$

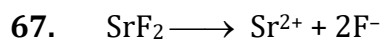
$$(s_1 + s_2)^2 = 1.6 \times 10^{-12}$$

$$s_1 + s_2 = \sqrt{1.6} \times 10^{-6}$$

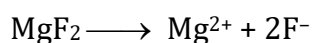
$$s_1 = \frac{1.1 \times 10^{-12}}{\sqrt{1.6} \times 10^{-6}} = 9 \times 10^{-7} \text{ M}$$

$$s_2 = \frac{5 \times 10^{-13}}{\sqrt{1.6} \times 10^{-6}} = 4 \times 10^{-7} \text{ M}$$





$$s_1 \quad 2(s_1 + s_2)$$



$$s_2 \quad 2(s_1 + s_2)$$

$$s_1 \times 2(s_1 + s_2) = 4 \times 10^{-9}$$

$$s_2 \times 2(s_1 + s_2) = 9.5 \times 10^{-9}$$

$$3(s_1 + s_2)^2 = 13.5 \times 10^{-9}$$

$$(s_1 + s_2)^2 = \frac{13.5}{3} \times 10^{-10} = 4.5 \times 10^{-10}$$

$$s_1 + s_2 = \sqrt{4.5} \times 10^{-5}$$

$$[\text{F}^-] = 2(s_1 + s_2) = 2 \times \sqrt{4.5} \times 10^{-5} \text{ M} = 1.34 \times 10^{-4} \text{ M}$$



$$(a) Q_{IP} = 10^{-3} \times (10^{-5})^2 = 10^{-13}$$

$$\text{So } Q_{IP} < K_{sp} \quad \text{No ppt}^n$$

$$(b) Q_{IP} = 10^{-3} \times 10^{-6} = 10^{-9}$$

$$Q_{IP} > K_{sp} \quad \text{ppt}^n \text{ will occur}$$

69.  $\frac{8 \times 10^{-6} \times v}{v+1} \times \frac{10^{-4}}{v+1} = 2 \times 10^{-10}$

$$(v-1)^2 = 0 \text{ } \therefore v = 1 \text{ L}$$

70.  $K_{sp} = 4s^3 = 4 \times (10^{-3})^3 = 4 \times 10^{-9}$

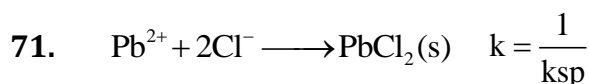
$$4 \times 10^{-9} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$= [\text{Ag}^+]^2 [10^{-1}]$$

$$[\text{Ag}^+] = 2 \times 10^{-4} \text{ M}$$

$$[\text{Ag}^+] \text{ moles precipitated} = 2 \times 10^{-3} - 2 \times 10^{-4} = 1.8 \times 10^{-4}$$

$$\text{moles of Ag}_2\text{CrO}_4 \text{ precipitated} = 9 \times 10^{-4}$$



$$0.1x \quad 0.75 \text{ M} \quad 0$$

$$x \quad 0.55 \text{ M} \quad 0.1 \text{ M}$$

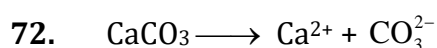
$$\frac{1}{1.7 \times 10^{-4}} = \frac{1}{x \times (0.55)^2}$$

$$x = \frac{1.7}{(0.55)^2} \times 10^{-4} = 5.6 \times 10^{-4}$$

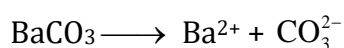
$$[\text{Pb}^{2+}] = 5.6 \times 10^{-4}$$

$$\text{Moles of Pb}^{2+} = 5.6 \times 10^{-5}$$

$$\text{Mass of Pb}^{2+} = 5.6 \times 208 \times 10^{-5} = 1.2 \times 10^{-3} \times 10^{-2} \text{ mg} = 12 \text{ mg}$$



$$7 \times 10^{-5}$$



$$7 \times 10^{-5}$$

$$\frac{7 \times 10^{-5} \times [\text{CO}_3^{2-}]}{7 \times 10^{-5} \times 0.1 \times [\text{CO}_3^{2-}]} = \frac{45 \times 10^{-10}}{K_{\text{sp}}(\text{BaCO}_3)}$$

$$K_{\text{sp}}(\text{BaCO}_3) = 4.9 \times 10^{-10}$$

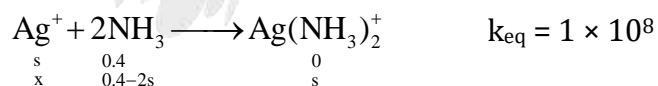


$$K_f = K_1 \times K_2 \times K_3 = 130 \times 16 \times 1 = 2080$$

$$K_d = \frac{1}{K_f} = 4.8 \times 10^{-4}$$



$$x \quad s$$



$$\begin{matrix} s & 0.4 & 0 \\ x & 0.4-2s & s \end{matrix}$$

$$\frac{s}{x(0.4-2s)} = 1 \times 10^8$$

$$\left( \frac{s}{0.4-2s} \right)^2 = 10^8 \times 5 \times 10^{-13}$$

$$\frac{s}{0.4-2s} = \sqrt{50} \times 10^{-3}$$

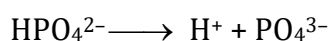
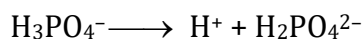
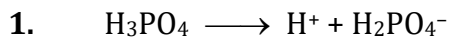
$$s = \sqrt{50} \times 10^{-3} \times 0.4 = 2.82 \times 10^{-3} \text{ M}$$

75. (a)  $[Ag^+] = 10^{-2}$  (b)  $[CO_3^{2-}] = 4 \times 10^{-2}$  (d)  $CO_3^{2-} + H^+ \longrightarrow HCO_3^-$

As  $[H^+]$  increases, solubility of  $Ag_2CO_3$  increases.

$$d > c > a > b$$

EXERCISE # O-II



if  $K_1 \gg K_2$

$$[H^+] = [H_2PO_4^-] \quad [HPO_4^{2-}] = K_2$$

$$[H^+] = \sqrt{K_1(H_3PO_4)} \quad [H^+] \gg [PO_4^{3-}]$$

2. (A) **TRUE**  $K_b A^- = \frac{K_w}{K_a HA} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$

(B) **TRUE** If  $T \uparrow$ ,  $K_w \uparrow$

(C) **TRUE** Acidic strength  $\propto K_a \propto \frac{1}{pK_a}$

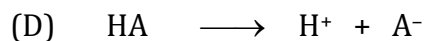
(D) **TRUE** Salt of SA + WB ( $NH_4Cl$ ) undergoes cationic hydrolysis.

3. (A) If  $T$  increases, then  $[H^+]$  increases,  $pH^-$

(B) If  $T$  increases, then  $[OH^-]$  increases,  $pOH^-$

(C) For  $10^{-4} M HCl$ ,  $pH = 4$

$$10^{-5} = \frac{0.01x^2}{1-x} \Rightarrow x^2 = 10^{-4} \Rightarrow x = 10^{-2} \Rightarrow pH = 2$$



$$C(1-\alpha) \quad c\alpha \quad c\alpha$$

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow \alpha \propto \frac{1}{\sqrt{C}}$$

4. (A) **FALSE** At half equivalence point  $pH = pK_a$

(B) **TRUE**  $pH = 4.74 + \log \frac{0.1}{0.01} = 5.74$

(C) **TRUE**  $\text{pH} = \text{pK}_a + \log \frac{[\text{C.B.}]}{[\text{Acid}]}$

(D) **FALSE** Buffer capacity is max when  $\frac{S}{a} = 1$

5. (A) As, T increases,  $K_w$  increases and  $[\text{H}^+]$   $[\text{OH}^-]$  also increase, so neutral  $\text{pH} < 7$   
If  $\text{pOH} = 7$ , then  $\text{pH} < 7$  solution will be acidic.

(B)  $\text{pH} = -\log [\text{H}^+]$

(C) For  $\text{CH}_3\text{COONa}(\text{aq})$

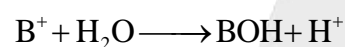
$$[\text{OH}^-] = \sqrt{\frac{K_w}{K_a} \times C} \quad \text{P} \quad [\text{OH}^-] \propto \sqrt{C}$$

On dilution  $[\text{OH}^-]^-$ ,  $\text{pOH}$ ,  $\text{pH}^-$

(D) Buffer capacity =  $2.303 \frac{s \cdot a}{s + a}$

6. 0.1 M BOH ( $K_b = 10^{-5}$ ), it is weak base.

For salt BCl



$$0.1 - x \quad \quad x \quad \quad x$$

$$10^{-9} = \frac{x^2}{0.1x} \Rightarrow x^2 = 10^{-10} \Rightarrow x = 10^{-5} \Rightarrow \text{pH} = 5$$

7. For ppt  $Q_{ip} > K_{sp}$

$$K_{sp} \text{ of AgCl} = 1.8 \times 10^{-10}$$

(A)  $Q_{ip} = \frac{10^{-4}}{2} \times \frac{10^{-4}}{2} = \frac{1}{4} \times 10^{-8}$

$Q_{ip} > K_{sp}$  (ppt will take place)

(B)  $Q_{ip} = \frac{10^{-5}}{2} \times \frac{10^{-5}}{2} = \frac{1}{4} \times 10^{-10}$

$Q_{ip} < K_{sp}$  (ppt does not take place)

(C)  $Q_{ip} = \frac{10^{-6}}{2} \times \frac{10^{-6}}{2} = \frac{1}{4} \times 10^{-12}$

$Q_{ip} < K_{sp}$  (ppt does not take place)

$$(D) \quad Q_{ip} = \frac{10^{-10}}{2} \times \frac{10^{-10}}{2} = \frac{1}{4} \times 10^{-20}$$

$Q_{ip} < K_{sp}$  (ppt does not take place)

8. (A) **TRUE**  $K_{sp} \text{ AgCl} > K_{sp} \text{ AgBr}$

So AgBr will ppt first

(B) **TRUE** For  $M_2X \quad K_{sp} = 4s^3$

For  $Q_{y2} \quad K_{sp} = 4s^3$

For  $Pz3 \quad K_{sp} = 27s^3$

(C) **FALSE**  $Li_3Na_3 (AlF_6)_2 \longrightarrow 3Li^+ + 3Na^+ + 2AlF_6^{3-}$

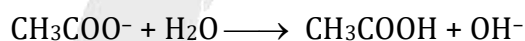
3s      3s      2s

$$K_{sp} = 2916 \times s^8$$

9. (A) **TRUE** due to common – ion effect of  $Cl^-$ .

(B) **TRUE**

(C) **TRUE** Due hydrolysis of  $CH_3COOH$  solubility increases.

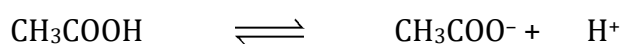


(D) **TRUE**

10. In original solution

$$[H^+] = \sqrt{K_a \times C} = \sqrt{10^{-6} \times 1} = 10^{-3}M$$

11. Let resulting solution (After dilution) have concentration Co



Co                                      0                      0

Co-X                                      X                      X

$$pH = 2 \times 3 = 6 \qquad [H^+] = x = 10^{-6}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{x \cdot x}{(C_0 - x)}$$

$$10^{-6} = \frac{(10^{-6})^2}{C_0 - 10^{-6}}$$

$$C_0 = 2 \times 10^{-6} \text{ M}$$

Now, for  $\text{CH}_3\text{COOH}$

$$1 \text{ M} \times 1 \text{ litre} = 2 \times 10^{-6} \text{ M} \times V$$

$$V = 5 \times 10^5 \text{ litre.}$$



$$2 \times 10^{-6}, V \quad 0.5 \times 10^{-6}, V$$

$$\frac{1.5 \times 10^{-6} \times V}{2V} \quad 0 \quad \frac{0.5 \times 10^{-6} \times V}{2V}$$

$$\text{pH} = \text{pK}_a + \log_{10} \left( \frac{\text{anion}}{\text{acid}} \right)$$

$$= 6 - \log_{10} 3 = 5.523$$

13. pH at I half equivalence point =  $\text{p}^{K_{a_3}} = 12$

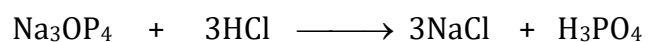
$$\text{pH at I equivalence point} = \frac{\text{p}^{K_{a_2}} + \text{p}^{K_{a_3}}}{2} = 10$$

$$\Rightarrow \text{p}^{K_{a_2}} = 8$$

$$\text{pH at II equivalence point} = \frac{\text{p}^{K_{a_1}} + \text{p}^{K_{a_2}}}{2} = 6$$

$$\Rightarrow \text{p}^{K_{a_1}} = 4$$

At III equivalence point



$$\begin{array}{ccccccc} 100 & 300 & & - & & - & \\ \times & \times & & 100 & & 100 & \end{array}$$

$$C = \frac{100}{400} = \frac{1}{4} \text{ M}$$

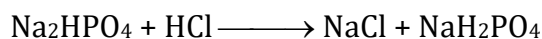
$$K_{a_1} = 10^{-4} = \frac{(\text{H}^+)^2}{C} \Rightarrow (\text{H}^+) = \sqrt{K_{a_1} C}$$

$$= \frac{10^{-2}}{2}$$

$$= 5 \times 10^{-3}$$

$$\text{pH} = 3 - \log 5$$

14. at II half equivalence point



$$\begin{array}{cccc} 100 & 50 & - & - \\ 50 & \times & 50 & 50 \end{array}$$

$$\text{pH} = \text{p}^{K_{a_2}} + \log \frac{50}{50} = \text{p}^{K_{a_2}} = 8$$

15. Equilibrium constant =  $K_w / K_{a_3}$

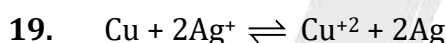
16. Let moles of HA is x and moles of HB is (1-x) which reacts with NaOH

$$x \times 11.8 + (1-x) \times 12.4 = 12.25$$

$$17. [\text{H}^+] = \sqrt{K_{a_1} C_1 + K_{a_2} C_2} = \sqrt{1 \times 10^{-5} + 9 \times 10^{-5}} = 10 \times 10^{-3} = 10^{-2}$$

$$\text{pH} = 2$$

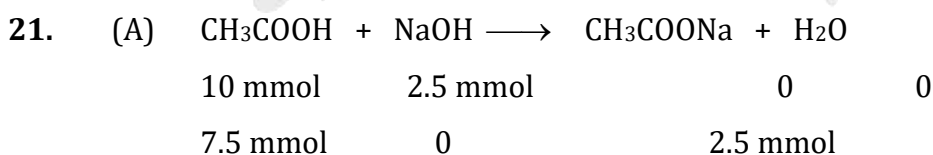
$$18. \text{Number of moles Cu oxidised} = \frac{7.04}{64} \times 10^{-3} \\ = 1.1 \times 10^{-4}$$



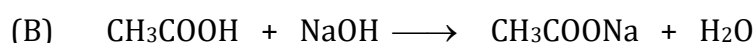
Since equilibrium constant is very large

$$[\text{Ag}^+] = 2.2 \times 10^{-4}$$

$$20. K_{sp} = [\text{Ag}^+]^2 [\text{BrO}_3] \\ = 4.84 \times 10^{-8}$$

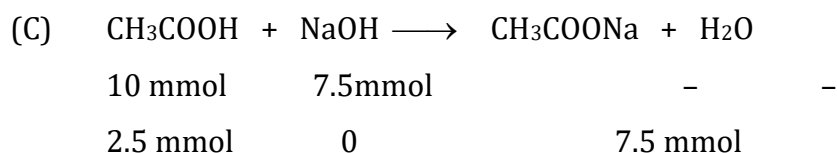


$$\text{pH} = \text{p}K_a + \log \frac{2.5}{7.5} = \text{p}K_a - \log 3$$



$$\begin{array}{ccccccc} 10 \text{ mmol} & & 5 \text{ mmol} & & & & \\ 5 \text{ mmol} & & 0 & & 5 \text{ mmol} & & \end{array}$$

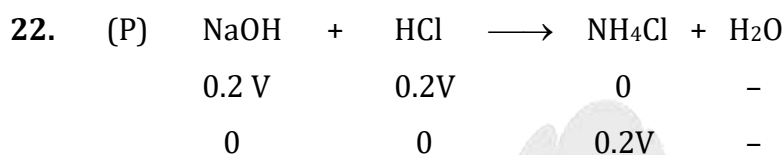
at half equivalence point  $\text{pH} = \text{p}K_a$



$$\text{pH} = \text{pK}_a + \log 3$$

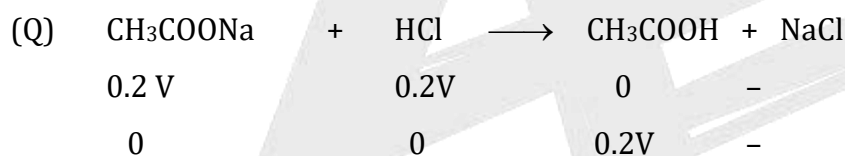
(D) It volume of final solution is doubled then conc. will be half.

$$\text{pH} = \frac{1}{2} (\text{pK}_w + \text{pK}_a + \log \frac{1}{2}) = \frac{1}{2} (\text{pK}_w + \text{pK}_a - 2)$$



$$[\text{NH}_4\text{Cl}] = 0.1 \text{ M}$$

$$\text{pH} = \frac{1}{2} (\text{pK}_w - \text{pK}_b - \log C) = \frac{1}{2} (14 - 5 - \log 0.1) = 5$$



$$[\text{CH}_3\text{COOH}] = 0.1 \text{ M}$$



$0.1 - x$	$x$	$x$
-----------	-----	-----

$$10^{-5} = \frac{x_2}{0.1 - x}$$

$$x = 10^{-3} \Rightarrow \text{pH} = 2$$

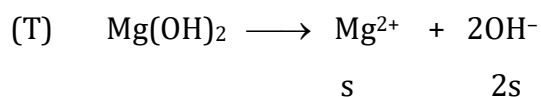


$$\text{pH} = \frac{\text{pK}_{a_3} + \text{pK}_{a_2}}{2} = \frac{10 + 6}{2} = 5$$

(S)  $\text{pH} = \text{pK}_{a1} + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$

at half equivalence point

$$[\text{HCO}_3^-] = [\text{H}_2\text{CO}_3] \Rightarrow \text{pH} = 5$$





$$4s^3 = 5 \times 10^{-16}$$

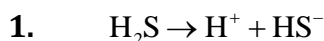
$$s^3 = \frac{1}{8} \times 10^{-15} \text{ } \therefore s = \frac{1}{2} \times 10^{-5}$$

$$[\text{OH}^-] = 10^{-5}$$

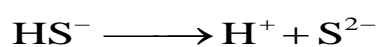
$$\Rightarrow \text{pOH} = 5$$

$$\Rightarrow \text{pH} = 10$$

### Exercise: S-II



$$\begin{array}{ccc} 0.1-x & x+2 \times 10^{-4} & x-y \\ & \approx 2 \times 10^{-4} & \approx x \end{array}$$



$$\begin{array}{ccc} x-y & 2 \times 10^{-4} & y \\ & \approx x & \end{array}$$

$$10^{-7} = \frac{2 \times 10^{-4} \times x}{0.1-x} = \frac{2 \times 10^{-4} \times x}{0.1}$$

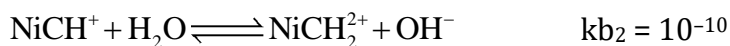
$$x = [\text{HS}^-] = 5 \times 10^{-5} \text{ M}$$

$$10^{-14} = \frac{2 \times 10^{-4} \times y}{5 \times 10^{-5}}$$

$$y = [\text{S}^{2-}] = 2.5 \times 10^{-15} \text{ M}$$



$$\begin{array}{ccc} 0.02-x & x-y & x+y \\ & \approx x & \approx x \end{array}$$



$$\begin{array}{ccc} x-y & y & x+y \\ & \approx x & \approx x \end{array}$$

$$k_{b1} \gg k_{b2} \quad , \quad x \gg y$$

$$7 \times 10^{-7} = \frac{x^2}{0.02-x} \Rightarrow x^2 = 1.4 \times 10^{-8} \Rightarrow x = [\text{OH}^-] = \sqrt{1.4} \times 10^{-4}$$

$$[\text{OH}^-] = 7 \times 10^{-6} \Rightarrow \text{pH} = 10.073$$

3. For  $\text{NaHCO}_3$

$$\text{pH} = \frac{\text{p}K_{a_2} + \text{p}K_{a_1}}{2} = \frac{6.38 + 10.32}{2}$$

For  $\text{Na}_2\text{HPO}_4$

$$\text{pH} = \frac{\text{p}K_{a_3} + \text{p}K_{a_2}}{2} = \frac{12 + 7.2}{2} = 9.6$$

For  $\text{NaH}_2\text{PO}_4$

$$\text{pH} = \frac{\text{p}K_{a_2} + \text{p}K_{a_1}}{2} = \frac{7.2 + 2.12}{2} = 4.66$$

4. (a)  $\text{H}_3\text{PO}_4 + \text{NaOH} \longrightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$

6            3            0            (initial mmoles)

3            0            3            (equilibrium mmoles)

$$\text{pH} = \text{p}K_{a_1} = 3 - \log 7.5 = 2.12$$

(b)  $\text{H}_3\text{PO}_4 + \text{NaOH} \longrightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$

6            6            0            (initial mmoles)

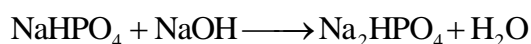
0            0            6            (equilibrium mmoles)

$$\text{pH} = \frac{\text{p}K_{a_2} + \text{p}K_{a_1}}{2} = \frac{7.2 + 2.12}{2} = 4.66$$

(c)  $\text{H}_3\text{PO}_4 + \text{NaOH} \longrightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$

4.8    7.2            0            (initial mmoles)

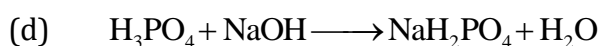
0       2.4            4.8            (equilibrium mmoles)



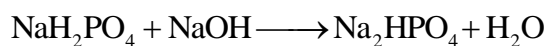
4.8    2.4            0            (initial mmoles)

2.4    0            2.4            (equilibrium mmoles)

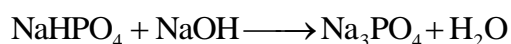
$$\text{pH} = \text{p}K_{a_2} = 7.2$$



4	10	0	(initial mmoles)
0	6	4	(equilibrium mmoles)



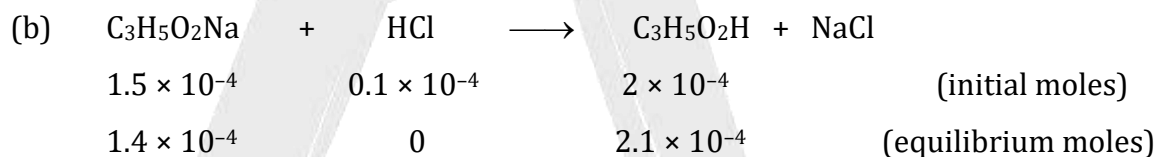
4	6	0	(initial mmoles)
0	2	4	(equilibrium mmoles)



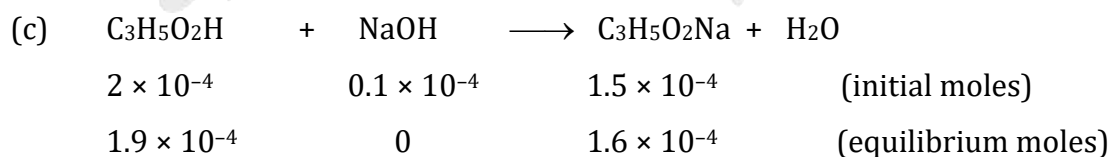
4	2	0	(initial mmoles)
2	0	2	(equilibrium mmoles)

$\text{pH} = \text{pka}_3 = 12$

5. (a)  $\text{pH} = 5 - \log 1.34 + \log \frac{0.015}{0.02} = 5 - \log 1.34 + \log 0.75 = 4.75$



$\text{pH} = 4.87 + \log \frac{1.4 \times 10^{-4}}{2.1 \times 10^{-4}} = 4.693$



$\text{pH} = 4.87 + \log \frac{1.6 \times 10^{-4}}{1.9 \times 10^{-4}} = 4.795$

(d) % change in case of b

$\Delta\text{pH} = \frac{4.75 - 4.693}{4.75} \times 100 = 1.2\%$

% change in case of c

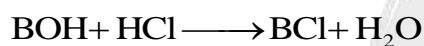
$$\Delta \text{pH} = \frac{4.75 \times 4.75}{4.75} \times 100 = 0.94\%$$



$$50C \quad 1 \quad 0 \quad 0 \quad (\text{initial moles})$$

$$50C-1 \quad 0 \quad 1 \quad - \quad (\text{equilibrium moles})$$

$$14 - 9.84 = \text{p}K_b + \log \frac{1}{50C-1} \quad (\text{i})$$



$$50C \quad 2.5 \quad 0 \quad 0 \quad (\text{initial moles})$$

$$50C-2.5 \quad 0 \quad 2.5 \quad - \quad (\text{equilibrium moles})$$

$$14 - 9.24 = \text{p}K_b + \log \frac{2.5}{50C-2.5} \quad (\text{ii})$$

$$(\text{i}) - (\text{ii})$$

$$0.6 = \log \frac{2.5(50C-1)}{50C-2.5} = \log 4 \Rightarrow C = 0.1$$

$$\text{p}K_b = 4.75, \quad K_a = 1.8 \times 10^{-5}$$

at equivalence point

$$\text{pH} = \frac{1}{2} (\text{p}K_w - \text{p}K_b - \log C) = \frac{1}{2} (14 - 4.76 - \log 0.05) = 5.27$$

7.  $\text{pH} = \text{p}K_{\text{In}} = 7.2$

$$\text{pH} = 7.2 + \log \frac{5}{1} = 7.2 + 0.7 = 7.9$$

for new indicator

$$7.9 = \text{p}K_{\text{In}} + \log 21 \Rightarrow \text{p}K_{\text{In}} = 7.3$$

$$\text{pH} = \text{p}K_{\text{In}} = 7.3 \quad (\text{when 50\% is ionized})$$

9. When MnS start to ppt, FeS has already ppted for ppt<sup>n</sup> of MnS

$$0.01 \times [S^{2-}] = 2.5 \times 10^{-13}$$

$$[S^{2-}] = 2.5 \times 10^{-11} = 25 \times 10^{-12}$$

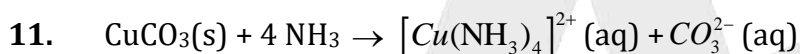
$$9.6 \times 10^{-21} = \frac{[H^+]^2 \times 25 \times 10^{-12}}{0.1}$$

$$[H^+]^2 = \frac{9.6}{25} \times 10^{-10} \text{ } \therefore [H^+] = \sqrt{\frac{9.6}{25}} \times 10^{-5}$$

$$\text{pH} = 5.21$$

10. 
$$\frac{[Ca^{2+}][CO_3^{2-}]}{[Ca^{2+}][F^-]^2} = \frac{x}{4y^3}$$

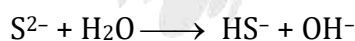
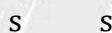
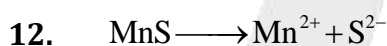
$$\frac{2}{[F^-]^2} = \frac{x}{4y^3} \Rightarrow [F^-] = \sqrt{\frac{8y^3}{x}}$$



$$\begin{array}{ccccccc} 0.1 & & x & & 0 & & 0 \\ & \approx 0 & & x-0.4 & & 0.1 & 0.1 \end{array}$$

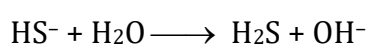
$$\frac{[Cu(NH_3)_4]^{2+} [CO_3^{2-}]}{[NH_3]^4} = k_{sp} \times k_f = 2.8 \times 10^3$$

$$\frac{0.1 \times 0.1}{(x-0.4)^4} = 2.8 \times 10^3 \Rightarrow x = 0.444 \text{ M}$$



$$\frac{k_w}{k_2} = \frac{[HS^-][OH^-]}{[S^{2-}]}$$

$$[HS^-] = \frac{k_w}{k_2} \times \frac{[S^{2-}]}{[OH^-]} = [S^{2-}] \times \frac{[H^+]}{k_2}$$



$$\frac{k_w}{k_1} = \frac{[H_2S][OH^-]}{[HS^-]}$$

$$[H_2S] = \frac{k_w}{k_1} \times \frac{[HS^-]}{[OH^-]} = \frac{[H^+]}{k_1} [HS^-]$$

$$[H_2S] = \frac{[H^+]^2}{k_1 k_2} [S^{2-}]$$

$$s = [S^{2-}]_f + [HS^-]_f + [H_2S]_f$$

$$s = [S^{2-}]_f \left[ 1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1 k_2} \right]$$

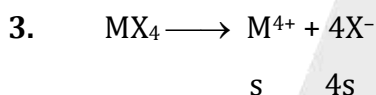
$$K_{sp} = \frac{s \cdot s}{1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1 k_2}}$$

$$s = \sqrt{K_{sp} \left( 1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1 k_2} \right)}$$

### EXERCISE # JEE-MAINS

1.  $K_{sp} = 4s^3 = 4 \times (1.0 \times 10^{-5})^3 = 4 \times 10^{-15}$

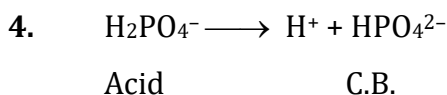
2.  $K_{sp} = 4s^3$   
 $= 4x^3$



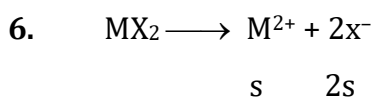
$$K_{sp} = s \times (4s)^4$$

$$= 256 s^5$$

$$s = \left( \frac{K_{sp}}{256} \right)^{1/5}$$



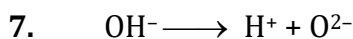
5.  $pH = 5.4$   
 $[H^+] = 10^{-5.4} = 10^{0.6} \times 10^{-6} = 4 \times 10^{-6}$



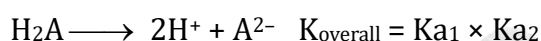
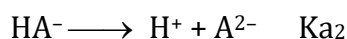
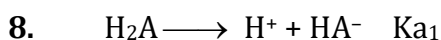
$$K_{sp} = 4s^3 = 4 \times 10^{-12}$$

$$s = 10^{-3} \text{ M}$$

$$[M^{2+}] = 10^{-3} \text{ M}$$



Acid C.B.



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

$pH = pK_a = 4.5$  (if acid is half ionize)

$pOH = 9.5$

10.  $K_{sp} = s^2 = 1.0 \times 10^{-8}$

$s = 10^{-4} \text{ M}$

$= 10^{-6} \times 283 \text{ g/L}$

$= 283 \times 10^{-5} \text{ g/100 mL}$

$= 2.83 \times 10^{-3} \text{ g/100 mL}$

11.  $pH = \frac{1}{2} (pK_w + pK_a - pK_b) = \frac{1}{2} (14 + 4.8 - 4.78)$   
 $= \frac{1}{2} \times 14.02 = 7.01$

12. For ppt<sup>n</sup> to start

$K_{sp} = Q_{ip}$

$[Ba^{2+}] \times 10^{-4} = 5.1 \times 10^{-9}$

$[Ba^{2+}] = 5.1 \times 10^{-5} \text{ M}$

13. For ppt<sup>n</sup> to start

$K_{sp} = Q_{ip}$

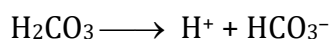
$$0.05 \times [\text{Br}] = 5 \times 10^{-13}$$

$$[\text{Br}^-] = 10^{-11} \text{ M}$$

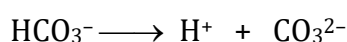
$$\text{moles of Br}^- = 1 \times 10^{-11}$$

$$\text{mass of KBr} = 1 \times 10^{-11} \times 120 = 1.2 \times 10^{-9} \text{ g}$$

14.  $K_1 \gg K_2$



$$\begin{array}{ccc} c - x & x & x - y \\ & & \gg x \end{array}$$



$$\begin{array}{ccc} x - y & x + y & y \\ \gg x & \gg x & \end{array}$$

$$[\text{H}^+] \gg [\text{HCO}_3^-] = 1.2 \times 10^{-6} \text{ M}$$

$$[\text{CO}_3^{2-}] = K_{a2} = 4.8 \times 10^{-11} \text{ M}$$

15.  $K_{sp} = Q_{ip}$

$$10^{-3} \times [\text{OH}^-]^2 = 1.1 \times 10^{-11}$$

$$[\text{OH}^-]_{\min} = 10^{-4}$$

$$\text{pOH} = 4 \Rightarrow \text{pH} = 10$$

16. In reaction (ii)  $\text{H}_2\text{PO}_4^{2-}$  given  $\text{H}^+$  ion.

17.  $K_{sp} = 27s^3$

$$27s^3 = 1.6 \times 10^{-30}$$

$$s = \left( \frac{1.6 \times 10^{-30}}{27} \right)^{1/3}$$

18.  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \quad \text{pH} = 5$

$$\begin{array}{ccc} 1 - x & x & x \end{array} \quad [\text{H}^+] = 10^{-5}$$

$$K_a = \frac{10^{-5} \times 10^{-5}}{1} = 10^{-10}$$

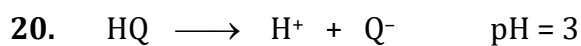
19. If  $K_{sp} < Q_{ip}$

$$K_{sp} = 1.7 \times 10^{-10}$$

For option (4)

$$Q_{ip} = 1 \times 10^{-2} \times (1 \times 10^{-3})^2 = 10^{-8}$$





$$0.1 - x \quad x \quad x \quad [\text{H}^+] = 10^{-3}$$

$$K_a = \frac{10^{-3} \times 10^{-3}}{0.1} = 10^{-5}$$

21. For ppt<sup>n</sup> to start

$$K_{sp} = Q_{ip}$$

$$5.1 \times 10^{-9} = [\text{Ba}^{2+}] \times [\text{CO}_3^{2-}]$$

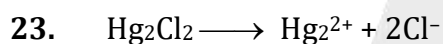
$$[\text{Ba}^{2+}] \times 10^{-4} = 5.1 \times 10^{-9}$$

$$[\text{Ba}^{2+}] = 5.1 \times 10^{-5} \text{ M}$$

22.  $[\text{OH}^-] = 5 \times 10^{-2}$

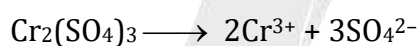
$$\text{pOH} = 2 - \log 5$$

$$\text{pH} = 12 + \log 5 = 12.7$$



$$s \quad 2s$$

$$K_{sp} = 4s^3 \quad \text{p} \quad s = \left( \frac{K_{sp}}{4} \right)^{1/3}$$



$$2s \quad 3s$$

$$K_{sp} = 108s^5 \quad \text{p} \quad s = \left( \frac{K_{sp}}{108} \right)^{1/5}$$

$$\text{For } \text{BaSO}_4 \quad K_{sp} = s^2 \quad \text{p} \quad s = (K_{sp})^{1/2}$$

$$\text{For } \text{CrCl}_3 \quad K_{sp} = 27s^4 \quad \text{p} \quad s = \left( \frac{K_{sp}}{27} \right)^{1/4}$$

24. Moles of  $\text{CH}_3\text{COOH} = \frac{5}{60} = 0.083$

$$\text{Moles of } \text{CH}_3\text{COONa} = \frac{7.5}{62} = 0.091$$

$$\text{pH} = 4.76 + \log \frac{0.091}{0.083}$$

$$\text{pH} > 4.76$$

$$\text{Range of pH } \approx \text{pK}_a \pm 1$$

$$25. \quad \text{pH}_i = 1 \quad [\text{H}^+]_i = 0.1$$

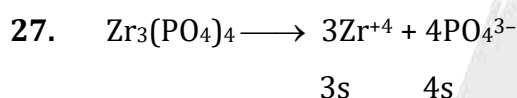
$$\text{pH}_f = 2 \quad [\text{H}^+]_f = 0.01$$

$$M_i V_i = M_f V_f$$

$$0.1 \times 1 = 0.01 \times V_f \Rightarrow V_f = 10 \text{ L}$$

water should be added = 9L

26. Refer notes.



$$3s \quad 4s$$

$$K_{sp} = (3s)^3 \times (4s)^4 = 6912 s^7$$

$$s = \left( \frac{K_{sp}}{6912} \right)^{1/7}$$

$$28. \quad \text{pH} = \frac{1}{2} (\text{pK}_w + \text{pK}_a - \text{pK}_b)$$

$$= \frac{1}{2} (14 + 3.2 - 3.4)$$

$$= \frac{1}{2} \times 13.8 = 6.9$$

29. pH range of methy orange = 3.1 – 4.4

in titration of W.A. Vs SA at end point pH should be less than 7.

30. ppt<sup>n</sup> to start

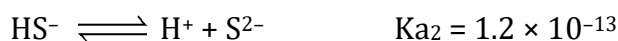
$$K_{sp} = Q_{ip}$$

$$[\text{Ba}^{2+}]_f [\text{SO}_4^{2-}]_f = K_{sp} \text{ BaSO}_4$$

$$\frac{50 \times 1}{500} \times \frac{M_i \times 450}{500} = 1 \times 10^{-10}$$

$$M_i = 1.1 \times 10^{-9} \text{ M}$$





$$1.2 \times 10^{-20} = \frac{[\text{H}^+]^2 \times [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$1.2 \times 10^{-20} = \frac{(0.2)^2 \times [\text{S}^{2-}]}{0.1}$$

$$[\text{S}^{2-}] = 3 \times 10^{-20} \text{ M}$$

32.  $\text{CH}_3\text{COOK}$  is salt of WA + S.B.

So  $\text{pH} > 7$

33.  $K_{sp} \text{ PbCl}_2 = 3.2 \times 10^{-8} = 4s^3$

$$s = 2 \times 10^{-3} \text{ M} = 0.414 \text{ g/L}$$

$$\text{Vol. of water require to dissolve 1g of PbCl}_2 = \frac{0.1}{0.414} = 0.241 \text{ L}$$

34. (i) M Mol of  $\text{H}^+$  = 15

M Mol of  $\text{OH}^-$  = 5

$$[\text{H}^+]_f = \frac{10}{100} = 0.1 \Rightarrow \text{pH} = 1$$

35.  $2\text{NH}_4\text{OH} + \text{H}_2\text{SO}_4 \longrightarrow (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$

6                      2                      0                      -

2                      0                      2                      -

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} = 4.7 + \log \frac{4}{2} = 4.7 + \log 2$$

$$\text{pH} = 9.3 - \log 2 = 9$$

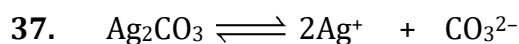
36.  $\text{Ca}(\text{OH})_2 + \text{Na}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + 2\text{NaOH}$

0.1 m mole                      0.014 m mole                      0                      0

0.086 m mole                      0                      0.014 m mol                      0.014 m mole

$$\text{Mass of CaSO}_4 = 0.014 \times 136 = 1.90 \text{ g}$$

$$[\text{OH}^-] = \frac{0.014}{0.2} = 0.28 \text{ M}$$

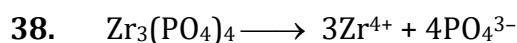


$$s_1 \quad 2s_1 + 0.1 \quad s_1$$

$$\gg 0.1$$

$$8 \times 10^{-12} = (0.1)^2 \times s_1$$

$$s_1 = 8 \times 10^{-10} \text{ M}$$



$$s \quad 3s \quad 4s$$

$$K_{sp} = 6912 s^7$$

$$s = \left( \frac{K_{sp}}{6912} \right)^{1/7}$$

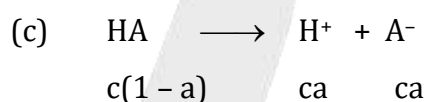
39. Initial pH > 7, at equivalence point pH = 7

40. (a)  $[\text{H}^+] = \frac{400 \times 0.1 \times 2 - 400 \times 0.1}{800} = 0.05 \text{ M}$

$$\text{pH} = 1.3$$

(b)  $K_w = [\text{H}^+][\text{OH}^-]$

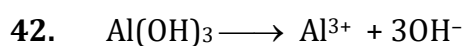
$$T, \quad K_w$$



$$K_a = \frac{c\alpha^2}{1 - \alpha} \quad \text{p} \quad 10^{-5} = 10^{-5} \times \frac{\alpha^2}{1 - \alpha} \quad \text{p} \alpha = \frac{1}{2}$$

(d) Le-Chatelier principle is applicable to common ion effect.

41.  $\text{pH} = \frac{1}{2} (\text{p}K_w - \text{p}K_b - \log c) = \frac{1}{2} (14 - 5 - \log 2 \times 10^{-2}) = 5.35$

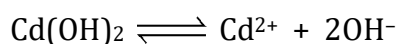


$$s \quad 3s + 0.2$$

$$\gg 0.2$$

$$(0.2)^3 \times s = 2.4 \times 10^{-24} \Rightarrow s = 3 \times 10^{-22} \text{ M}$$

43.  $K_{sp} = 4s^3 = 4 \times (1.84 \times 10^{-5})^3$



$$s \quad 2s + 0.01$$

$$\gg 0.01$$

$$s \times (0.01)^2 = 4 \times (1.84 \times 10^{-5})^3$$

$$s = 2.49 \times 10^{-10} \text{ M}$$

44. pH of 0.01 M HCl = 2

pH of 0.01 M NaOH = 12

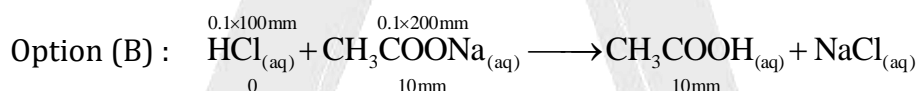
pH of 0.01 M  $\text{CH}_3\text{COONa} > 7$

pH of 0.01 M NaCl = 7

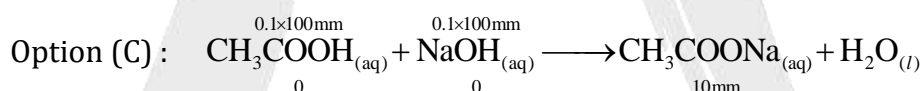
order of pOH : A > D > C > B

45. Acidic buffer solution contains weak acid and its salt with strong base.

Option (A) : Solution is containing strong acid and its salt with strong base.

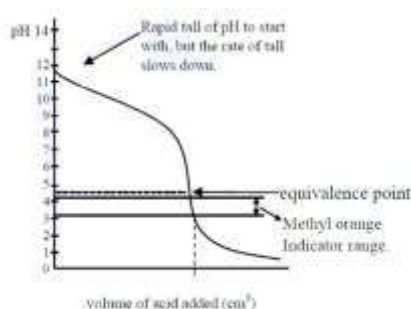


Resulting solution contains weak acid and its salt with strong base.



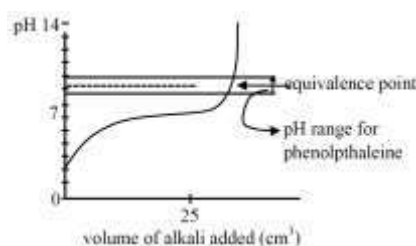
Resulting solution contains only salt of weak acid and strong base.

46. Titration curve for strong acid and weak base initially a buffer of weak base and conjugate acid is:



Formed, thus pH falls slowly and after equivalence point, so the pH falls sharply so methyl orange,

having pH range of 3.2 to 4.4 will work as indicator. So statement-I is correct.

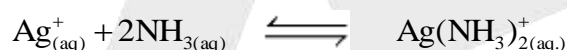


Titration curve for weak acid and strong base (NaOH) Initially weak acid will form a buffer so pH

increases slowly but after equivalence point. It rises sharply covering range of phenolphthalein so it will

be suitable indicator so statement-II is false.

50. Let moles added = a



$$t = 0 \quad 0.8 \quad \left(\frac{a}{2}\right)$$

$$t = \infty \quad 5 \times 10^{-8} \left(\frac{a}{2} - 1.6\right) \quad 0.8$$

$$\frac{0.8}{(5 \times 10^{-8}) \left(\frac{a}{2} - 1.6\right)^2} = 10^8$$

$$\Rightarrow \frac{a}{2} - 1.6 = 0.4 \Rightarrow a = 4$$

51.  $K_a$  of Butyric acid  $\Rightarrow 2 \times 10^{-5}$   $pK_a = 4.7$

pH of 0.2 M solution

$$\text{pH} = \frac{1}{2} pK_a - \frac{1}{2} \log C$$

$$= \frac{1}{2} (4.7) - \frac{1}{2} \log(0.2)$$

$$= 2.35 + 0.35 = 2.7$$

$$\text{pH} = 2.7 \times 10^{-1}$$

52.  $\text{HCl} + \text{H}_2\text{SO}_4$

$$[\text{H}^+] = \frac{(0.01 \times 200) + (0.01 \times 2 \times 400)}{600}$$

$$= \frac{2+8}{600} = \frac{10}{600} = \frac{1}{60}$$

$$\text{pH} = -\log \left[ \frac{1}{60} \right]$$

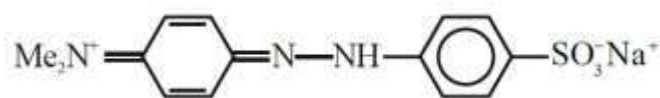
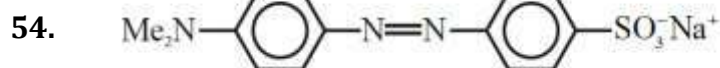
$$= 1.78$$

53.  $\text{pOH} = 14 - 8.26$

$$= \text{pK}_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$= 5.74 = 4.74 + \log \frac{[\text{NH}_4^+]}{0.2} \Rightarrow [\text{NH}_4^+] = 2$$

$$\text{Hence, } \text{NH}_4\text{Cl} = 2 \times 53.5 = 107 \text{ g}$$



(QUINONOID FORM)

55. In deionized water no common ion effect will take place so maximum solubility



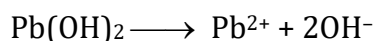
$$\begin{array}{ccccccc} 2\text{m mol} & 3\text{mmol} & 10 & & - & & \\ 0 & 1\text{mmol} & 2\text{m mol} & & - & & \end{array}$$

$$[\text{OH}^-] = \frac{1}{500} = 2 \times 10^{-3}$$

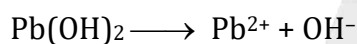
$$\text{pH} = 11 + \log 2 = 11.3$$

2.  $\text{pH} = 8 \Rightarrow \text{pOH} = 6$

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



$$K_{\text{sp}} = 4s^2 = 4 \times (6.7)^3 \times 10^{-18} = 1.2 \times 10^{-15}$$



$$\begin{array}{ccc} s & & 2s + 10^{-6} \end{array}$$

$$s(2s + 10^{-6}) = 1.2 \times 10^{-15}$$

$$s \times 10^{-2} = 1.2 \times 10^{-15}$$

$$s = 1.2 \times 10^{-3} \text{ M}$$

4.  $\text{HCl} \Rightarrow \text{pH} < 7$

$$\text{NaCl} \Rightarrow \text{pH} = 7$$

$$\text{NaCN} \Rightarrow \text{pH} > 7$$

$$\text{NH}_4\text{Cl} \Rightarrow \text{pH} < 7$$

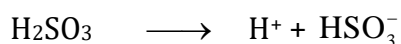
$$\text{NaCN} < \text{NaCl} > \text{NH}_4\text{Cl} > \text{HCl}$$

5. Amount of  $\text{SO}_2$  in atmosphere =  $\frac{10}{10^6} = 10 \times 10^{-6}$

$$\text{Molar conc. of } \text{SO}_2 \text{ in water} = \text{Amount of } \text{SO}_2 \times \text{Solubility of } \text{SO}_2$$

$$= 10 \times 10^{-6} \times 1.3653$$

$$= 1.3653 \times 10^{-5} \text{ M}$$



$$\begin{array}{ccc} 1.3653 \times 10^{-5} - x & x & x \end{array}$$

$$K_a = \frac{x^2}{1.3653 \times 10^{-5} - x} = 10^{-1.92}$$

$$x = 1.364 \times 10^{-5} \quad \text{pH} = 4.865$$



6. Equation of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  = Equation of  $\text{NaOH}$

$$\frac{10}{250} \times \frac{63}{126} \times 2 = 0.1 \times V(\text{L})$$

$$V(\text{L}) = \frac{1}{25}$$

$$V(\text{mL}) = 40$$

7.  $\text{A}_p\text{B}_q(\text{s}) \longrightarrow p\text{A}^{q+}(\text{aq}) + q\text{B}^{p-}(\text{aq})$

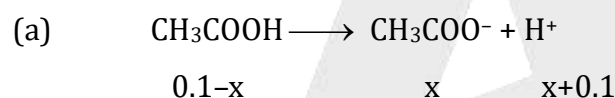
s                      ps                      qs

$$K_{sp} = (\text{ps})^p(\text{qs})^q$$

$$= p^p q^q (\text{s})^{p+q}$$

8.  $[\text{CH}_3\text{COOH}]_f = 0.1 \text{ M}$

$[\text{HCl}]_f = 0.1 \text{ M}$



$$1.75 \times 10^{-5} = \frac{x(x+0.1)}{0.1-x}$$

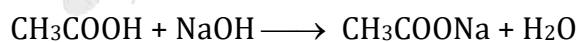
$$x = 1.75 \times 10^{-5}$$

$$0.1 \times \alpha = 1.75 \times 10^{-5}$$

$$\alpha = 1.75 \times 10^{-4}$$

$$[\text{H}^+] = 0.1 \Rightarrow \text{pH} = 1$$

(b) Moles of  $\text{NaOH} = \frac{6}{40} = 0.15 \text{ mol}$



$n_i$             0.1            0.05            0            -

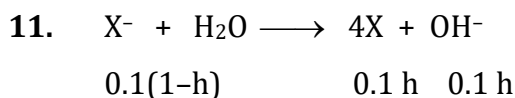
$n_f$             0.05            0            0.05            -

0.1 moles  $\text{NaOH}$  will be consumed by 0.1 mol of  $\text{HCl}$

$$\text{pH} = \text{pK}_a = 4.75$$

9.  $T$  increases,  $K_w$  increases,  $\text{H}^+$ ,  $\text{pH}^-$

10. Which has minimum value of  $K_{sp}$  i.e.  $\text{HgS}$



$$K_h = \frac{K_w}{K_a(HX)} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$$

$$K_h = \frac{Ch^2}{1-h} = \frac{0.1h^2}{1-h} = 10^{-9}$$

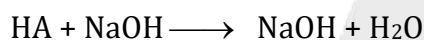
$$0.1h^2 = 10^{-9}$$

$$h^2 = 10^{-8}$$

$$h = 10^{-4}$$

$$\% h = 0.01 \%$$

12. At end point HA will completely reacts with NaOH



$$[A^-] = 0.05 \text{ M}$$

$$pH = \frac{1}{2} (pK_w + pK_a + \log C)$$

$$= \frac{1}{2} (14 + 6 - \log 5 + \log 0.05)$$

$$= \frac{1}{2} (20 - \log 5 - \log 20)$$

$$\Rightarrow pH = 9$$



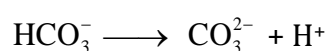
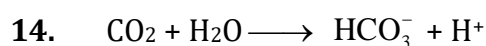
$$0.1 \text{ mol} \quad 0.08 \text{ mol} \quad 0$$

$$0.02 \text{ mol} \quad 0 \quad 0.05 \text{ mol}$$

$$[OH^-] = K_b \times \frac{[CH_3NH_2]}{[CH_3NH_3^+]}$$

$$= 5 \times 10^{-4} \times \frac{0.02}{0.08} = \frac{5}{4} \times 10^{-4}$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{4}{5} \times 10^{-10} = 8 \times 10^{-11} \text{ M}$$



15. For MX

$$K_{\text{sp}} = s^2 = 4 \times 10^{-8}$$

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

For  $\text{MX}_2$

$$K_{\text{sp}} = 4s^3 = 32 \times 10^{-14}$$

$$s^3 = 8 \times 10^{-15}$$

$$s = 2 \times 10^{-5} \text{ M}$$

For  $\text{M}_3\text{X}$

$$K_{\text{sp}} = 27s^4 = 2.7 \times 10^{-15}$$

$$s = 10^{-14} \text{ M}$$

$$\text{MX} > \text{M}_3\text{X} > \text{MX}_2$$



It equivalence point

Moles of BOH = moles of HCl

$$2.5 \times \frac{2}{5} = \frac{2}{15} \times V(\text{mL})$$

$$V(\text{mL}) = 7.5 \text{ mL}$$

$$V_f = 10 \text{ mL}$$

$$[\text{BCl}] = \frac{1}{10} = 0.1 \text{ M}$$



$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$

$$10^{-2} = \frac{0.1-h^2}{1-h}$$

$$h = 0.27$$

$$p[\text{H}^+] = 0.1 \times h = 0.027 \text{ M}$$

17.  $\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a + \log C)$

$$= \frac{1}{2} (14 + 4 + \log 0.01) = \frac{1}{2} \times 16 = 8$$

18. (A)  $\text{HNO}_3 + \text{CH}_3\text{COOH}$  (S.A. + W.A.)

It can't be a buffer

- (B)  $\text{KOH} + \text{CH}_3\text{COONa}$  (S.B. + Salt)

It can't be a buffer

- (C)  $\text{CH}_3\text{COONa} + \text{HNO}_3 \longrightarrow \text{CH}_3\text{COOH} + \text{NaNO}_3$

It can form buffer if volume of  $\text{CH}_3\text{COONa}$  and  $\text{HNO}_3$  is different.

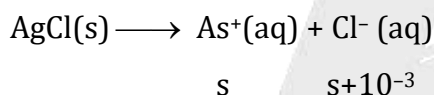
- (D)  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$

It is a buffer

19. For  $\text{CuCl}$

$$K_{\text{sp}} = s^2 = 10^{-6}$$

$$s = 10^{-3}$$

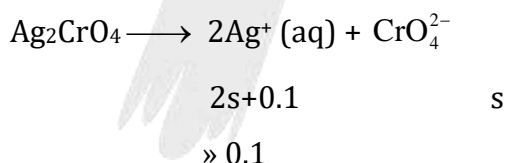


$$s(s + 10^{-3}) = 1.6 \times 10^{-10}$$

$$s \times 10^{-3} = 1.6 \times 10^{-10}$$

$$s = 1.6 \times 10^{-7}$$

20. For  $\text{Ag}_2\text{CrO}_4$   $K_{\text{sp}} = 1.1 \times 10^{-12}$



$$(0.1)^2 \times s = 1.1 \times 10^{-12}$$

$$s = 1.1 \times 10^{-10} \text{ M}$$

21.  $r \propto [\text{H}^+]^1$

$$\frac{\sqrt{K_a \times C}}{1} = \frac{1}{100}$$

$$\sqrt{K_a \times C} = 10^{-2}$$

$$K_a = 10^{-4}$$

22. From exp.-1

$$5.7 \times 1000 = C \times 5.7$$

From exp-2

$$q = C \times 5.6$$

$$q = 5.65 \text{ kJ}$$

$$\Delta H = -\frac{5.6}{0.1} = -56 \text{ kJ. / mol}$$

$$\Delta H_{\text{ion}} = -56 + 57 = 1 \text{ kJ/ mol}$$

23.  $\text{CH}_3\text{COOH} + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

$$0.2 \text{ mol} \quad 0.1 \text{ mol} \quad 0 \quad 0$$

$$0.1 \text{ mol} \quad 0 \quad 0.1 \text{ mol} \quad 0$$

$$\text{pH} - \text{pK}_a = 4.7$$

24. 
$$s = \sqrt{K_{\text{sp}} \left( \frac{[\text{H}^+]}{K_a} + 1 \right)}$$

$$= \sqrt{20 \times 10^{-10} \left( \frac{10^{-3}}{10^{-8}} + 1 \right)}$$

$$= \sqrt{2 \times 10^{-5}} = 4.47 \times 10^{-3} \text{ M}$$

25. (P)  $\text{CH}_3\text{COOH} + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

$$2\text{m mol} \quad 1\text{m mol} \quad 0 \quad -$$

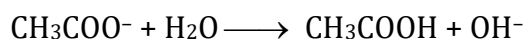
$$1\text{m mol} \quad 0 \quad 1\text{m mol} \quad -$$

If forms a buffer and pH does not change with dilution.

(Q)  $\text{CH}_3\text{COOH} + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

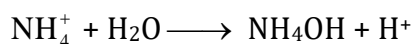
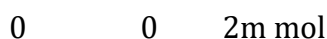
$$2\text{m mol} \quad 2\text{m mol} \quad 0 \quad -$$

$$0 \quad 0 \quad 2\text{m mol} \quad -$$

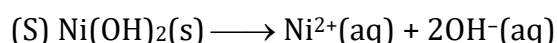


$$[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{C}}$$

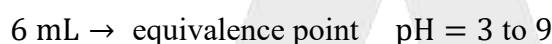
$$[\text{H}^+] \propto \frac{1}{\sqrt{C}}$$



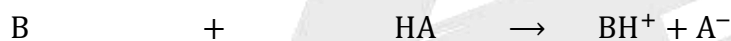
$$[\text{H}^+] = \sqrt{\frac{K_w}{K_b}} \times C \quad \text{p} [\text{H}^+] \propto \sqrt{C}$$



On dilution  $[\text{OH}^-]$  remains same in saturated solution of  $\text{Ni}(\text{OH})_2$



Equivalence point



Total volume = 12ml

$$\text{Concentration of Salt} = \frac{0.6}{12}$$

$$\text{pH} = 6 = \sqrt{\frac{K_w}{K_b}} \times c = \sqrt{\frac{10^{-14} \times 0.6}{K_b \times 12}} \quad \{\text{pH} = 0.6, [\text{H}^+] = 10^{-6}\}.$$

$$\Rightarrow [\text{H}^+] = 10^{-6} = \sqrt{\frac{K_w}{K_b} \times \frac{0.1 \times 6}{12}}$$

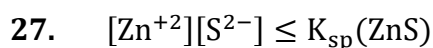
$$10^{-12} = \frac{10^{-14} \times 10^{-1}}{K_b} \times \frac{1}{2}$$

$$K_b = 5 \times 10^{-4}$$

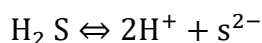
$$\text{p}K_b = -\log K_b = -\log (5 \times 10^{-4}) = -\log 5 + 4\log 10$$

$$\text{p}K_b = 4 - 0.7$$

$$\text{p}K_b = 3.3$$



$$[\text{S}^{2-}] \leq \frac{5}{4} \times \frac{10^{-22}}{0.05}$$



$$[\text{S}^{2-}] = \frac{K_{\text{net}} \times [\text{H}_2\text{S}]}{[\text{H}^+]^2}$$

$$\frac{K_{\text{net}} \times [\text{H}_2\text{S}]}{[\text{H}^+]^2} \leq \frac{5}{4} \times \frac{10^{-22}}{10^{-2} \times 5}$$

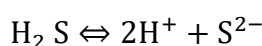
$$[\text{H}^+]^2 \geq \frac{10^{-21} \times 10^{-1} \times 4}{10^{-20}}$$

$$[\text{H}^+] \geq 2 \times 10^{-1} = 0.2$$

Alternate:

$$[\text{Zn}^{+2}][\text{S}^{2-}] \leq K_{\text{sp}}$$

$$[\text{S}^{2-}] \leq \frac{5}{4} \times \frac{10^{-22}}{0.05} = \frac{1}{4} \times 10^{-20}$$



$$[\text{H}^+]^2 = \frac{K_1 K_2 \times [\text{H}_2\text{S}]}{[\text{S}^{2-}]} = \frac{10^{-21} \times 0.1}{[\text{S}^{2-}]}$$

$$[\text{S}^{2-}] = \frac{10^{-22}}{[\text{H}^+]^2} \leq \frac{1}{4} \times 10^{-20}$$

$$[\text{H}^+] \geq 0.2$$

28. First acid base reaction between  $\text{H}_2\text{CO}_3$  and  $\text{NaOH}$  takes place. In the final solution, we have 0.01 mole  $\text{Na}_2\text{CO}_3$  and 0.02 moles of  $\text{NaHCO}_3$ . Here, we have a buffer of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ .

$$\therefore \text{pH} = \text{pK}_{\text{a}_2} + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 10.32 + \log \frac{\left(\frac{0.01}{0.1}\right)}{\left(\frac{0.02}{0.1}\right)}$$

$$= 10.32 + \log \frac{1}{2}$$

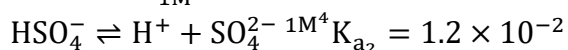
$$= 10.32 - \log 2$$

$$= 10.32 - 0.3$$

$$= 10.02$$

$$\therefore \text{pH} = 10.02$$

29.  $\text{H}_2\text{SO}_4 \rightarrow \underset{1\text{M}}{\text{H}}^+ + \text{HSO}_4^{2-}$  ( $K_{\text{a}_1}$  is very large)



$$[\text{SO}_4^{2-}] \text{ coming from } \text{Na}_2\text{SO}_4 = 1.8 \times 10^{-2}$$

$$\frac{[\text{SO}_4^{2-}][\text{H}^+]}{[\text{HSO}_4^-]} = \frac{1.8 \times 10^{-2} \times 1}{1} > K_{\text{a}_2}$$

∴ Rather than dissociation of  $\text{HSO}_4^-$  into  $\text{H}^+$  and  $\text{SO}_4^{2-}$  ions, association between already present  $\text{H}^+$  and  $\text{SO}_4^{2-}$  will take place.

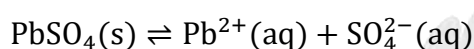
$$\therefore [\text{SO}_4^{2-}] = 1.8 \times 10^{-2} - x$$

$$\left. \begin{aligned} [\text{H}^+] &= 1 - x \approx 1 \\ [\text{HSO}_4^-] &= 1 + x \approx 1 \end{aligned} \right\} \text{ (assuming } x \ll 1)$$

$$\frac{(1.8 \times 10^{-2} - x)1}{1} = 1.2 \times 10^{-2}$$

$$\Rightarrow x = 0.6 \times 10^{-2}$$

$$[\text{SO}_4^{2-}] = 1.2 \times 10^{-2} \text{ M}$$



If solubility of  $\text{PbSO}_4 = s \text{ M}$

$$\therefore [\text{Pb}^{2+}] = s$$

$$[\text{SO}_4^{2-}] = s + 1.2 \times 10^{-2} \approx 1.2 \times 10^{-2}$$

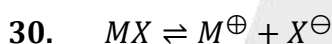
(assuming  $s \ll 1.2 \times 10^{-2}$ )

$$\therefore s \times 1.2 \times 10^{-2} = 1.6 \times 10^{-8}$$

$$s = \frac{1.6}{1.2} \times 10^{-6} = 1.33 \times 10^{-6}$$

On comparing with  $X \times 10^{-Y}$

$$Y = 6$$



$$S = \sqrt{K_{\text{sp}} \left( 1 + \frac{[\text{H}^{\oplus}]}{K_a} \right)}$$

$$10^{-4} = \sqrt{K_{\text{sp}} \left( 1 + \frac{10^{-7}}{K_a} \right)}$$

$$10^{-3} = \sqrt{K_{\text{sp}} \left( 1 + \frac{10^{-2}}{K_a} \right)}$$

Squaring Equation [(1)/(2)] gives

$$10^{-2} = \frac{\left( 1 + \frac{10^{-7}}{K_a} \right)}{\left( 1 + \frac{10^{-2}}{K_a} \right)}$$



$$10^{-2} + \frac{10^{-4}}{K_a} = 1 + \frac{10^{-7}}{K_a}$$

$$\frac{10^{-4} - 10^{-7}}{K_a} = 0.99$$

$$\frac{10^{-4}}{K_a} = 0.99$$

$$K_a = \frac{10^{-4}}{0.99} = \frac{1}{99} \times 10^{-2}$$

$$K_a = 2 + \log 99 = 4$$

A