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CHEMISTRY

TARGET : JEE Advanced – 2021

CAPS – 7

Ionic Equilibrium

Answer Key

1.	(B)	**2.**	(B)	**3.**	(B)	**4.**	(C)	**5.**	(A)
6.	(C)	**7.**	(B)	**8.**	(D)	**9.**	(AC)	**10.**	(AB)
11.	(AC)	**12.**	(ACD)	**13.**	(CD)	**14.**	(AB)	**15.**	(AC)
16.	(BCD)	**17.**	(A)	**18.**	((A) – S; (B) – S; (C) – Q)				

19. (9.04, 8.78, yes)

20. (a) 8.5×10^{-16}, 5×10^{-12}, 1.7×10^{-9} (b) I^- (c) 1.7×10^{-5}

(d) Br^- = 2.9×10^{-8}, I^- = 5×10^{-8}

21. ($s = 2.236 \times 10^{-5}$ M)

22. ($[H_2CO_3] = 9.85 \times 10^{-6}$ M, $\left[HCO_2^-\right] = 4.9 \times 10^{-4}$M, $\left[CO_3^{-2}\right] = 2.45 \times 10^{-8}$M)

23. (pH = 0.908) **24.** (precipitate will occur)

Solution

1. Say $[H^+]$ contributed from H_2O and HCl be 'x' each

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

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

x x

$[H^+][OH^-] = 10^{-14}$

$(2x)(x) = 10^{-14}$

$$x = \frac{10^{-7}}{\sqrt{2}} = 10^{-8} \times \sqrt{\frac{100}{2}}$$

$$= \sqrt{50} \times 10^{-8}$$

$$\therefore [HCl] = \sqrt{50} \times 10^{-8} M$$

2. buffer capacity $(\beta) = \frac{2.303\ ab}{a+b}$, $a + b = 1$

Max $\beta \Rightarrow$ when a = b = 0.5

$$\beta_{max} = \frac{2.303(0.5)^2}{1} = 0.575$$

$\beta = 2.303\ ab$ ($\because$ a + b =1)

$\beta = 2.303\ (1- b)(b)$

$$\Rightarrow \quad b^2 - b + \frac{\beta}{2.303} = 0 \text{ parabolic equation}$$

$\therefore$ option (B) is answer.

3. Option A: 0.1 M $NaHCO_3$

$$P^H = \frac{1}{2}\left(P_{Ka_1} + P_{Ka_2}\right)$$

Independent of concentration

Option B: 0.2 M NaOH

$P^{OH} = -\log[OH^-]$

P^{OH} will change $\Rightarrow$ P^H will change

Option C: 0.3 M NH_3 + 0.2 M NH_4^+

$$P^{OH} = P^{K_b} + \log\frac{\left[NH_4^+\right]}{\left[NH_3\right]}$$

P^H of buffer does not change from small amount of addition of water

Option D: 0.4 M CH_3COONH_4

(Salt of WA + WB)

$$P^H = 7 + \frac{1}{2}\left(P^{K_a} - P^{K_b}\right)$$

Independent of concentration.

4. $K = 10^{-30}$

$[NH_4^+][NH_2^-] = 10^{-30}$

$[NH_4^+] = 10^{-15}$ ($\because$ $[NH_4^+]$ $[NH_2^-]$)

$\therefore$ 10^{-15} mol NH_4^+ ions is present in 1 lit

Thus, 10^{-16} mol NH_4^+ ions, i.e., 6.022×10^7 $4NH_4^+$ ions are present in 100 cm^3 pure liquid.

5. 10 ml, 0.3 M HCl $\Rightarrow$ 3 mmol HCl

10 ml, 0.1 M NaOH $\Rightarrow$ 1 mmol of NaOH

When HCl, NaOH react, 2 mmol of HCl would be left unreacted

When HA 20ml, 0.1 M HA is added, H^+ of HCl would apply common ion effect on HA.

	HA	$\rightleftharpoons$	H^+	+	A^-
t = 0	2				–
t = t'	2 – x		x + 2 (from HCl)		x

$K_a = 10^{-5}$, total volume = 40 ml

$$K_a = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]}$$

$$10^{-5} = \frac{\left(\frac{x+2}{40}\right)\left(\frac{x}{40}\right)}{\left(\frac{2-x}{40}\right)}$$

$$\Rightarrow \quad 10^{-5}(2-x) = \frac{1}{40}(x^2 + 2x)$$

$$\Rightarrow \quad 2\times10^{-5} - x\times10^{-5} = \frac{1}{40}(2x)$$

$$\Rightarrow \quad 2\times10^{-5} \simeq \frac{1}{20}x$$

$$\Rightarrow \quad x \simeq 40 \times 10^{-5}$$

$$\Rightarrow \quad \frac{\left[A^-\right]}{\left[HA\right]+\left[A^-\right]} = \frac{x}{(2-x)+x} = \frac{x}{2} = 2\times10^{-4}$$

6. $BOH \rightleftharpoons B^+ + OH^-$

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

$K_b = c\alpha^2$

$$\therefore \quad \alpha\% = 100 \times \sqrt{\frac{K_b}{c}}$$

$$\alpha = \frac{\left[B^+\right]}{\left[B^+\right]+\left[BOH\right]}$$

$$\Rightarrow \quad \alpha = \frac{1}{1+\frac{\left[BOH\right]}{\left[B^+\right]}}$$

$$\Rightarrow \quad \alpha = \frac{K_b}{K_b+\left[OH^-\right]}\left(\because K_b = \frac{\left[B^+\right]\left[OH^-\right]}{\left[BOH^-\right]}\right)$$

$$\Rightarrow \quad \alpha = \frac{1}{1+\frac{\left[OH^-\right]}{K_b}}$$

$$\Rightarrow \quad \alpha = \frac{K_b\left[H^+\right]}{K_b\left[H^+\right]+K_w}\left(\because K_w = \left[H^+\right]\left[OH^-\right]\right)$$

7. **(B)**

8. $Al(OH)_3$ exists as Al^{3+} and $[Al(OH)_4]^-$

$\therefore$ solubility (s) = $[Al^{3+}] + [Al(OH)_4]^-$

$K_{sp} = [Al^{3+}][OH^-]^3$

$$K_C = \frac{\left[Al(OH)_4\right]^-}{\left[OH^-\right]^3}$$

$$\therefore \quad s = \frac{K_{SP}}{\left[OH^-\right]^3} + K_C\left[OH^-\right]$$

$$\frac{ds}{d\left[OH^-\right]} = 0 \text{ (for mins)}$$

$$0 = -3K_{sp}\,[OH^-]^{-4} + K_C$$

$$\therefore \quad \left[OH^-\right] = \left(\frac{3K_{SP}}{K_C}\right)^{\frac{1}{4}}$$

9. **(AC)** **10.** **(AB)** **11.** **(AC)** **12.** **(ACD)**

13. From the graph, there are 2 neutralisation points. Thus, the weak electrolyte should be dibasic acid. Thus, the weak electrolyte can $H_2C_2O_4$ or $CH_2(COOH)_2$

14. $ki = 1.8 \times 10^{-16}$ (At T = 25° C)

$kw = 10^{-14}$ (At T = 25° C)

Thus, $k_i < kw$ and $pk_i > pk_w$

15.

H_2A	$\rightleftharpoons$	HA^-	+	H^+
$0.1 - x$		$x - y$		$x + y$

HA^-	$\rightleftharpoons$	A^{2-}	+	H^+
$x - y$		y		$x + y$

Given $y = 10^{-12}$

$\therefore$ $x + y \simeq x$ (y is negligible)

$\therefore$ $[H^+]_{total} = [H^+]$ from first ionization

$P^H = 3$

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

$$K_{a_1} = \frac{[H^+][HA^-]}{[H_2A]}$$

neglecting $y = 10^{-12}$

$$K_{a_1} = \frac{10^{-3} \times 10^{-3}}{0.1}$$

$\therefore$ $K_{a_1} = 10^{-5}$

16. $NH_4Cl \rightarrow NH_4^+$

$\Updownarrow$

$NH_3 + H_3O^+$

$\therefore$ $[Cl^-] = [NH_4Cl] = 10^{-2}M$

- $[NH_4^+] < 10^{-2}$ M due to hydrolysis.
- Salt of SA and WB. Thus $P^H < 7$

$\therefore$ $P^{OH} > 7$

$\therefore$ $[H^+] > 10^{-7}$ M

17. $Al^{3+} + H_2O \rightleftharpoons [Al(OH)]^{2+} + H^+$; $K_h = 1.4 \times 10^{-5}$

$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$; $K = \frac{1}{1.25 \times 10^{-2}}$

11.85 gm of potash alum is added to 1000 cm^3 water

$\therefore$ moles of potash alum $\frac{11.85}{474} = 0.025$

Al^{3+}	+	H_2O	$\rightleftharpoons$	$[Al(OH)]^{2+}$	+	H^+	
$0.025 - x$				x		$x - y$	$K_h = 1.4 \times 10^{-5}$
$\simeq 0.025$							

SO_4^{2-}	+	H^+	$\rightleftharpoons$	HSO_4^-	
$0.05 - y$		$x - y$		y	$K = \frac{1}{1.25 \times 10^{-2}}$
$\simeq 0.05$					

$\Rightarrow$ $\frac{(x-y)x}{0.025} = 1.4 \times 10^{-5}$ .....(1)

$\Rightarrow$ $\frac{y}{(x-y)0.05} = \frac{1}{1.25 \times 10^{-2}}$ .....(2)

Solving (1) and (2)

$(x - y) = 2.9 \times 10^{-5}$

$\therefore$ $[H^+] = \frac{2.9 \times 10^{-5}}{0.1} = 2.9 \times 10^{-4}M$

18. (A) 200 ml, 25% H_2SO_4

$\Rightarrow \quad n_{H_2SO_4} = \frac{200 \times 25 \times 1.225}{100} \times \frac{1}{98} = 0.625\,mol$

$\Rightarrow \quad n_{H^+} = 1.25$ mol

800 ml, 0.525 M $X(OH)_3$

$n_{X(OH)_3} = 0.42$ mol

$n_{OH^-} = 1.26$ mol

After reaction n_{OH} (left) = 0.01 mol

$\therefore \quad P^{OH} = 2$

$P^H = 12$

$\therefore$ Malachite green (11.4 − 13)

(B) $P^H = P^{K_a} + \log\frac{\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]}$

$P^{K_a} = \log(2 \times 10^{-11}) = 10.7$

$P^H = 10.7 + \log\left(\frac{40}{5}\right)$

$P^H \simeq 11.4$

$\therefore$ Malachite green (11.4 − 13)

(C) 50 ml, 0.2 M HA ($K_a = 10^{-15}$)

50 ml, 0.1 M HCl $\Rightarrow n_{HCl} = 5m$ mol

100 ml, 0.13 M NaOH $\Rightarrow n_{NaOH} = 13m$ mol

After HCl and NaOH reacts, n_{NaOH} (left) = 8 mmol

	HA + NaOH →	NaA +	H_2O
t = 0	10 8	–	–
$t = t^1$	2 1	8	–

$\therefore \quad P^H = P^{K_a} + \log\frac{\left[A^-\right]}{[HA]}$

$= -\log\left(10^{-5}\right) + \log 4$

$= 5 + \log 4$

$\simeq 5.6$

$\therefore \quad P^H = 5.6$

$\therefore$ Propyl red (4.6 − 6.4)

19. Initially $[NH_4^+] = 0.1$, $[NH_3] = 0.06$

$$P^{OH} = P^{K_b} + \log\frac{\left[NH_4^+\right]}{\left[NH_3\right]}$$

$$P^{OH} = -\log(1.8\times10^{-5}) + \log\left(\frac{0.1}{0.06}\right) = 4.96$$

$\therefore$ $P^H = 9.04$

$\therefore$ Initial $P^H = 9.04$

Due to CH_3COOH, H^+ is added to system

NH_3	+	$H^+ \rightleftharpoons NH_4^+$
= 0.06 − 0.02	=	0.01 + 0.02
= 0.04	=	0.12

$$P^{OH} = -\log\left(1.8\times10^{-5}\right) + \log\left(\frac{0.12}{0.04}\right) \simeq 5.22$$

$PH \simeq 8.78$

$\therefore$ Final $P^H = 8.78$

Also $\Delta P^H = 0.26$

$\therefore$ The change in P^H is with 0.26 and thus it's a satisfactory buffer.

20. **(a) 8.5×10^{-16}, 5×10^{-12}, 1.7×10^{-9}**

(b) I^-

(c) 1.7×10^{-5}

(d) $Br^- = 2.9 \times 10^{-4}$, $I^- = 5 \times 10^{-8}$

21. $AgCN \rightleftharpoons Ag+ + CN^- \rightarrow K_{SP}$

$$CN^- + H^+ \rightleftharpoons HCN \rightarrow \frac{1}{K_a}$$

$$AgCN + H^+ \rightleftharpoons Ag^+ + HCN \rightarrow K = \frac{K_{SP}}{K_a}$$

$$K = \frac{3.2\times10^{-16}}{6.4\times10^{-10}} = 0.5\times10^{-6}$$

Now, at equilibrium and pH = 3, 'x' moles of Ag^+ & HCN form.

$AgCN + H^+ \rightleftharpoons Ag^+ + HCN$

0.001 x x

$$K = \frac{x^2}{0.001} = 0.5\times10^{-16}$$

$\Rightarrow$ $x = 2.236 \times 10^{-5}$ M

22. PH = 8 $\Rightarrow$ $[H^+] = 10^{-8}$ & $[OH^-]$ would be = 10^{-6}

$NaHCO_3$ added is 0.0005 M.

HCO_3^-	$\rightleftharpoons$	CO_3^{2-}	+	H^+	
0.0005		–		–	$K_2 = 5 \times 10^{-13}$ …(1)
0.0005 – y – z		y		10^{-8}	

HCO_3^-	+	H_2O	$\rightleftharpoons$	H_2CO_3	+	OH^-	
0.0005 – y – z				z		10–6 ; K for this = $\frac{K_W}{K_1} = 2\times10^{-8}$ …(2)	

Comparing K_2 & K it can be said that y << z

$$\therefore \quad K = 2\times10^{-8} = \frac{z(10^{-6})}{0.005 - z} \Rightarrow Z = 9.8\times10^{-6}$$

$\therefore$ $[H_2CO_3] = z = 9.8 \times 10^{-6}$ M

$[HCO_3^-] = 0.0005 - z = 4.9 \times 10^{-4}$ M

$$\text{Also, } K_2 = \frac{y\times10^{-8}}{0.005 - y} = \frac{y.10^{-8}}{4.9\times10^{-4}} = 5\times10^{-13}\text{M}$$

$[HCO_3^-] = 0.005 - y$

$\therefore$ $y = [CO_3^{2-}] = 2.45 \times 10^{-8}$ M

23. $Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+$

0.95x 0.05x 0.05x $K = 6.5 \times 10^{-3}$

$$K = \frac{(0.05x)^2}{0.95x} = 6.5\times10^{-3} \Rightarrow x = 2.47$$

'x' is the dissociation

$\therefore$ $[H^+] = 0.05 \times 2.47 = 0.1235$

$\therefore$ $P^H = -\log[H^+] = -\log(0.1235) = 0.908$

24. (precipitate will occur)

$[Cl^-]$ from NaCl = 0.02 M

$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$

0.05	–	–
0.05 – x	x	2x

$K_{diss} = 4 \times 10^{-19}$ M^2

Since K_{diss} is such a small number $\Rightarrow$ 0.05 – x $\simeq$ 0.05

$$4\times10^{-19} = \frac{x\cdot(2x)^2}{0.05} \Rightarrow x = 1.7\times10^{-7}$$

$[Ag^+]\,[Cl^-] = 0.02 \times 1.7 \times 10^{-7} = 3.4 \times 10^{-9}$

Since $[Ag^+]\,[Cl^-]$ is greater than K_{SP} (AgCl)

$\therefore$ AgCl will be precipitate out!