

**Topic 7.2 : Ionic Equilibrium**1 **ACJC/2009/P3/Q4(a)**

$$(i) K_{sp} = [Mg^{2+}][OH^-]^2$$

$$(ii) \text{Solubility of } Mg(OH)_2 = \frac{9.08 \times 10^{-3} \text{ g dm}^{-3}}{58.3}$$

$$= 1.557 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\therefore \text{In a saturated solution, } [Mg^{2+}] = 1.557 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[OH^-] = 2 \times 1.557 \times 10^{-4}$$

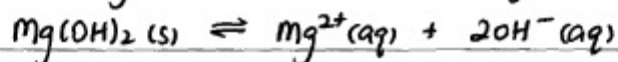
$$= 3.114 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{Hence, } K_{sp}(Mg(OH)_2) = (1.557 \times 10^{-4})(3.114 \times 10^{-4})^2$$

$$= 1.510 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$$

$$= 1.5 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9} \text{ (2 sf)}$$

(iii) The solubility of  $Mg(OH)_2$  is lower in  $Mg(NO_3)_2(aq)$ .



In  $Mg(NO_3)_2(aq)$ ,  $[Mg^{2+}]$  is higher. The equilibrium above thus shifts to the left to use up some of the excess  $Mg^{2+}$ .

$$(iv) [Mg^{2+}] = \frac{50 \times 3.2 \times 10^{-4}}{80}$$

$$= 2.0 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[OH^-] = \frac{30 \times 5.0 \times 10^{-4}}{80}$$

$$= 1.875 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{Now, } [Mg^{2+}][OH^-]^2 = (2.0 \times 10^{-4})(1.875 \times 10^{-4})^2$$

$$= 7.03 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$$

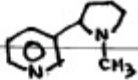
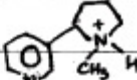
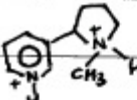
$$< K_{sp}(Mg(OH)_2)$$

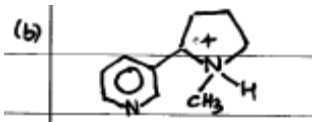
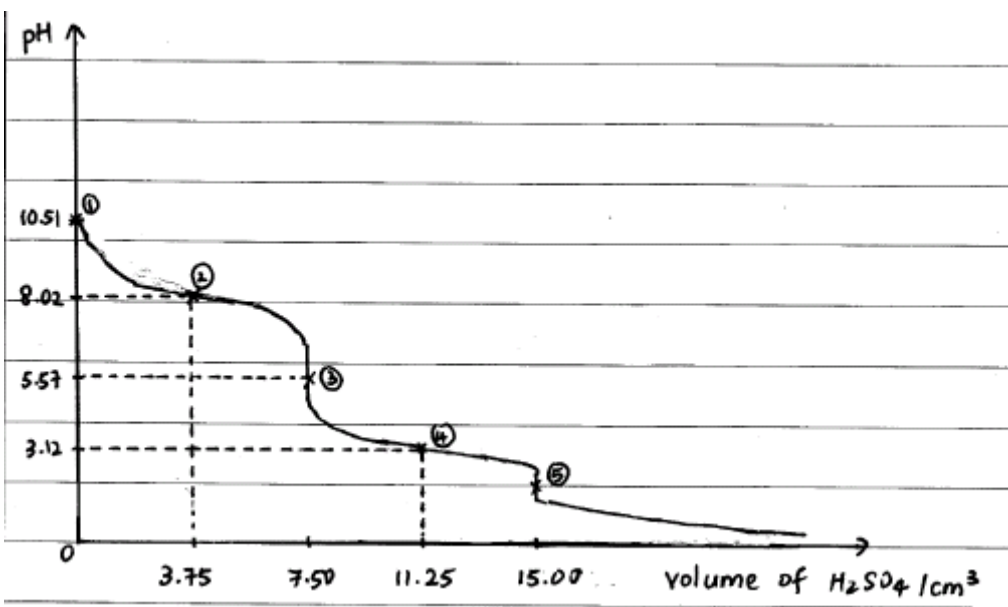
$\therefore$  No precipitation occurs.

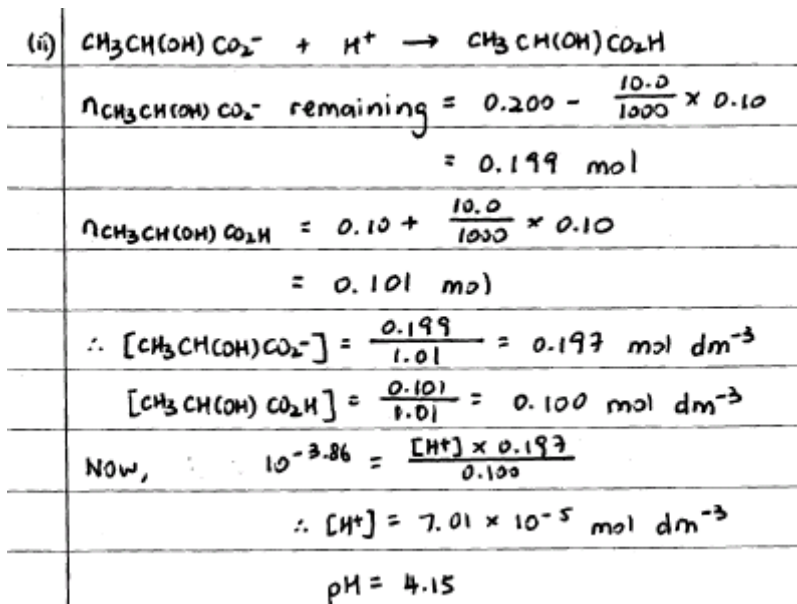
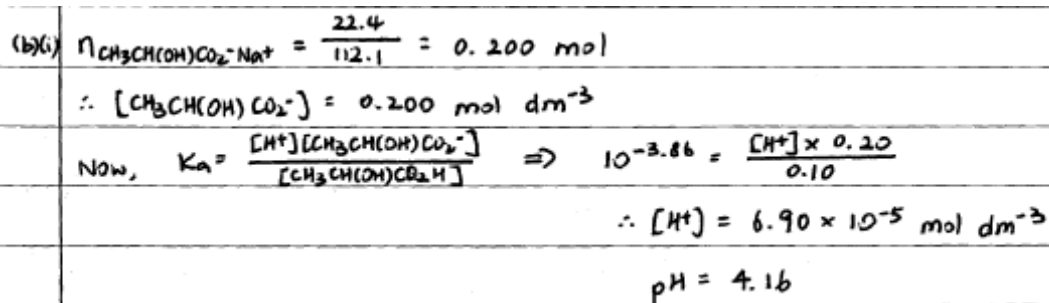
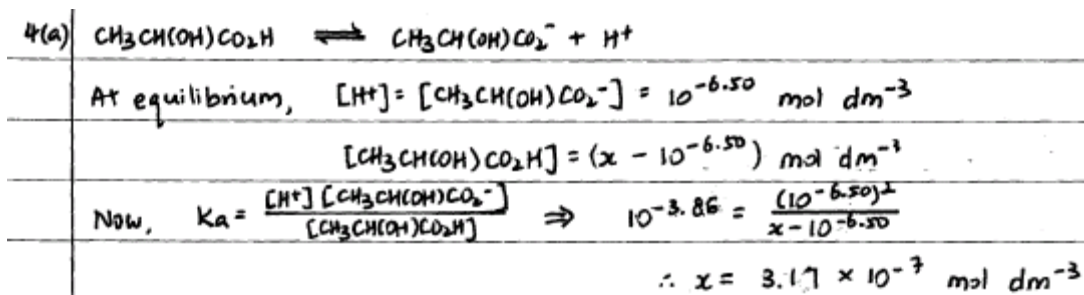
2 AJC/2009/P2/Q4(a)-(b)

4(a) (Not required by syllabus — specially written for enrichment purposes only)

Point	$V_{H_2SO_4}/cm^3$	Significance	Calculation of pH
①	0.00	Initial pH	$[OH^-] = \sqrt{cK_b} = 3.236 \times 10^{-4} \text{ mol dm}^{-3}$ $pOH = 3.49 \Rightarrow pH = 10.51$
②	3.75	max. buffer capacity ( $B_2/B_2H^+$ )	$pOH = pK_{b1} = 5.98 \Rightarrow pH = 8.02$
③	7.50	$B_2$ completely neutralised to $B_2H^+$	$pOH = \frac{pK_{b1} + pK_{b2}}{2} = 8.43 \Rightarrow pH = 5.57$
④	11.25	max. buffer capacity ( $B_2H^+/B_2H_2^{2+}$ )	$pOH = pK_{b2} = 10.88 \Rightarrow pH = 3.12$
⑤	15.00	$B_2H^+$ completely neutralised to $B_2H_2^{2+}$	$pH \approx 2$ (very hard to calculate exactly)

$B_2 =$  
 $B_2H^+ =$  
 $B_2H_2^{2+} =$  



3 AJC/2009/P3/Q4(a)-(b), (e)


(e) (i)	$K_{sp}(\text{Fe}(\text{OH})_2) = [\text{Fe}^{2+}][\text{OH}^-]^2$
	For precipitation to occur, $[\text{Fe}^{2+}][\text{OH}^-]^2 > K_{sp}$
	$(0.010) \times [\text{OH}^-]^2 > 1.6 \times 10^{-14}$
	$[\text{OH}^-] > 1.265 \times 10^{-6} \text{ mol dm}^{-3}$
	$\therefore \text{pOH} = -\lg(1.265 \times 10^{-6}) = 5.90$
	$\text{pH required} = 14 - 5.90 = 8.10$

**4 CJC/2009/P3/Q3(c)**

- (c)
- (i) Since  $K_{\text{stab}}$  of  $[\text{Fe}(\text{CN})_6]^{3-}$  is larger than  $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$  is the more stable complex. Ligand exchange will occur.  
**Deep red solution turns orange yellow.**
- (ii)  $\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+} \quad +0.77 \text{ V}$   
 $[\text{Fe}(\text{CN})_6]^{3-} + e \rightarrow [\text{Fe}(\text{CN})_6]^{4-} \quad +0.36 \text{ V}$

From  $K_{\text{stab}}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$  is more stable than  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$  is **less likely to be reduced** than  $\text{Fe}^{3+}(\text{aq})$  or  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .  
 $[\text{Fe}(\text{CN})_6]^{3-}$  is **stabilized by CN<sup>-</sup> ligands**, resulting in a lower  $E^\circ$  value.

**5 CJC/2009/P3/Q4(a)-(b)**
**4(a)**

- (i)  $[\text{H}^+] = \sqrt{2.9 \times 10^{-14}} = 1.70 \times 10^{-7} \text{ mol dm}^{-3}$   
 $\therefore \text{pH} = -\log(1.70 \times 10^{-7}) = 6.77$
- (ii) Neutral, as  $[\text{H}^+] = [\text{OH}^-]$
- (iii)  $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$

As temperature increases,  $K_w$  increases; so the equilibrium position shifts to the right. Therefore, the forward reaction (dissociation of water) is **endothermic**.



$$\text{p}K_b = 3.25$$

$$-\log K_b = 3.25$$

$$\therefore K_b = 5.62 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\therefore K_a = \frac{K_w}{K_b} = \frac{2.9 \times 10^{-14}}{5.62 \times 10^{-4}} = 5.16 \times 10^{-11} \text{ mol dm}^{-3}$$

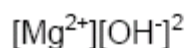
$$[\text{H}^+] = \sqrt{K_a \times c} = \sqrt{5.16 \times 10^{-11} \times 0.0200}$$

$$= 1.02 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(1.02 \times 10^{-6}) = 5.99$$

**6 DHS/2009/P2/Q4**

- (a) Write an expression for the solubility product,  $K_{sp}$  of magnesium hydroxide.



- (b) Calculate the solubility of magnesium hydroxide in  $\text{g dm}^{-3}$  for a saturated solution of magnesium hydroxide at  $25^\circ\text{C}$ .

Let the solubility be  $x$ .

$$[\text{Mg}^{2+}][\text{OH}^-]^2 = 5.61 \times 10^{-12}$$

$$x(2x)^2 = 5.61 \times 10^{-12}$$

$$x = 1.119 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{Solubility} = 6.53 \times 10^{-3} \text{ g}$$

- (c) Calculate the solubility of  $\text{Mg}(\text{OH})_2$  in  $5.00 \times 10^{-2} \text{ mol dm}^{-3}$  aqueous sodium hydroxide.

Let the solubility of  $\text{Mg}(\text{OH})_2$  be  $x \text{ mol dm}^{-3}$ .

$$[\text{Mg}^{2+}][\text{OH}^-]^2 = 5.61 \times 10^{-12}$$

$$x(2x + 0.05)^2 = 5.61 \times 10^{-12}$$

Assuming that  $x$  is so small such that  $2x + 0.05 \sim 0.05$ ,

$$x(0.05)^2 = 5.61 \times 10^{-12}$$

$$x = 2.24 \times 10^{-9} \text{ mol dm}^{-3}$$

- (d) Equal volumes of solutions containing  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$  magnesium nitrate and  $6.0 \times 10^{-3} \text{ mol dm}^{-3}$  of sodium hydroxide are mixed. Predict if a precipitate will be formed. Explain your answer with the aid of relevant calculations.

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 5.61 \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$$

On mixing aq  $\text{Mg}(\text{NO}_3)_2$  and  $\text{NaOH}$ :

## Ionic Equilibrium – Suggested Solutions

$$\begin{aligned}\text{New } [\text{Mg}^{2+}] &= V \times 5.0 \times 10^{-3} / 2V = 2.5 \times 10^{-3} \text{ mol dm}^{-3} \\ \text{New } [\text{OH}^-] &= V \times 6.0 \times 10^{-3} / 2V = 3 \times 10^{-3} \text{ mol dm}^{-3}\end{aligned}$$

At saturation point,  $K_{sp}$  = Ionic product

$$\begin{aligned}\text{Ionic product} &= [\text{Mg}^{2+}][\text{OH}^-]^2 \\ &= 9 \times 10^{-8} [1] > 5.61 \times 10^{-12} [1]\end{aligned}$$

Yes there will be a ppt.

### 7 **DHS/2009/P3/1(a)**

- (i) Suggest a suitable indicator, if the titration were to be repeated without the use of a data logger. Explain your reasoning.

Phenolphthalein. The pH transition range of the indicator **lies within** the sharp pH change over its **equivalence point**.

- (ii) Calculate the value of  $K_a$  for pyruvic acid.

$$\begin{aligned}\text{No. of mol of NaOH} &= \frac{30}{1000} \times 0.01 \\ &= 3 \times 10^{-4}\end{aligned}$$

$$\text{No. of mol of pyruvic acid} = 3 \times 10^{-4}$$

$$[\text{pyruvic acid}] = \frac{3 \times 10^{-4}}{\frac{10}{1000}} = 0.03 \text{ mol dm}^{-3}$$

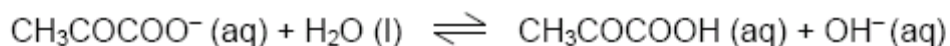
From graph, pH = 2.5

$$\text{Hence } [\text{H}^+] = 10^{-2.5} = 3.162 \times 10^{-3}$$

$$K_a = \frac{[\text{H}^+]^2}{[\text{pyruvic\_acid}]} = \frac{(3.162 \times 10^{-3})^2}{0.03 - 3.162 \times 10^{-3}} = 3.73 \times 10^{-4} \text{ mol dm}^{-3}$$

- (iii) Explain, with the aid of an appropriate equation, why the pH at equivalence point is greater than 7.

[7]



$\text{CH}_3\text{COCOO}^-$  undergoes **salt hydrolysis**.

**$[\text{OH}^-] > [\text{H}^+]$** .

**8 HCl/2009/P2/Q1(b)**

- (b) (i)  $[\text{Ba}^{2+}][\text{F}^-]^2 = 1.84 \times 10^{-7}$  where  $[\text{Ba}^{2+}] = 0.05 \text{ mol dm}^{-3}$   
 $\therefore [\text{F}^-] = \sqrt{(1.84 \times 10^{-7} / 0.05)}$   
 $= 1.92 \times 10^{-3} \text{ mol dm}^{-3}$
- (ii)  $[\text{Ca}^{2+}]_{\text{remaining}} = 3.45 \times 10^{-11} / (1.92 \times 10^{-3})^2$   
 $= 9.38 \times 10^{-6} \text{ mol dm}^{-3}$

**9 HCl/2009/P2/Q2(a)**

- (a) (i) no. of moles of glycolic acid =  $0.20/76.0 = 2.63 \times 10^{-3} \text{ mol}$   
 volume of NaOH required =  $2.63 \times 10^{-3} / 0.10 \times 1000 = 26.3 \text{ cm}^3$
- (ii) no. of moles of  $\text{CH}_2\text{OHCOO}^-$  salt formed at equivalence =  $2.63 \times 10^{-3} \text{ mol}$   
 conc. of  $\text{CH}_2\text{OHCOO}^- = 2.63 \times 10^{-3} / (26.3 + 20.0) = 0.0568 \text{ mol dm}^{-3}$

	$\text{CH}_2\text{OHCOO}^-$	+	$\text{H}_2\text{O}$	=	$\text{CH}_2\text{OHCOOH}$	+	$\text{OH}^-$
Initial conc. / $\text{mol dm}^{-3}$	0.0568				–		–
Eqm conc./ $\text{mol dm}^{-3}$	$0.0568 - x$				$x$		$x$

$$K_b \text{ of glycolate} = K_w/K_a \text{ of glycolic acid} = 1 \times 10^{-14} / 1.48 \times 10^{-4}$$

$$= 6.76 \times 10^{-11} \text{ mol dm}^{-3}$$

$$K_b = x^2 / (0.0568 - x) \approx x^2 / 0.0568 \text{ (assume } x \ll 0.0568 \text{ mol dm}^{-3}\text{)}$$

$$x = 1.959 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pOH} = 5.708$$

$$\text{pH} = 14 - 5.708 = 8.29$$

- (iii) Metacresol purple because its working range coincides with the sharp jump of the titration curve which lies in the alkaline pH region (equivalence pH = 8.29).

**10 HCl/2009/P3/Q5(a)**

- 5 (a) (i) A solution that is able to resist pH changes when small quantities of acid or base are added.
- (ii) When a small amount of  $\text{OH}^-$  is added,  $\text{OH}^-$  ions can be removed from the system by the reaction:  $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$   
 {or  $\text{H}_2\text{CO}_3 + \text{OH}^- \rightarrow \text{HCO}_3^- + \text{H}_2\text{O}$ }  
 Hence pH remains almost constant.

## Ionic Equilibrium – Suggested Solutions

(iii)  $7.90 \times 10^{-7} = 10^{-7.4} [\text{HCO}_3^-] / [\text{CO}_2]$   
 $[\text{HCO}_3^-] / [\text{CO}_2]$  is 20:1

Blood has greater capacity for absorbing  $\text{H}^+$  since there is a much higher concentration of the base component  $\text{HCO}_3^-$ .

(iv)  $\text{CO}_2$  exhaled is recycled. Blood  $\text{CO}_2$  level is raised and the buffer equilibrium shifts to the right thus increasing  $[\text{H}^+]$ . Hence blood pH will drop.

### 11 IJC/2009/P2/Q4(a)

(i) Explain what is meant by the term base dissociation constant,  $K_b$  of morphine.



$$K_b = \frac{[\text{MorH}^+][\text{OH}^-]}{[\text{Mor}]}$$

(ii) Calculate the pH of 0.20 mol dm<sup>-3</sup> morphine solution.

At equilibrium,  $[\text{OH}^-] = [\text{MorH}^+] = x \text{ mol dm}^{-3}$

$[\text{Mor}] = 0.20 \text{ mol dm}^{-3}$  (assume  $x \ll 0.20$ )

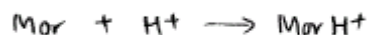
Now,  $7.40 \times 10^{-7} = \frac{x^2}{0.20}$

$$x = 3.85 \times 10^{-4} \text{ mol dm}^{-3}$$

i.e.  $\text{pOH} = -\lg(3.85 \times 10^{-4}) = 3.41$

$$\text{pH} = 14 - 3.41 = \underline{\underline{10.6}}$$

(iii) Calculate the amount of salt formed in the buffer solution.



$$n_{\text{MorH}^+} = n_{\text{HCl}} = \underline{\underline{0.01 \text{ mol}}}$$

(iv) Calculate the pH of the buffer solution.

$$n_{\text{Mor}} = \frac{100}{1000} \times 0.2 = 0.01 = 0.01 \text{ mol}$$

$$\therefore [\text{Mor}] = [\text{MorH}^+] \Rightarrow \text{pOH} = \text{p}K_b = 6.13$$

$$\therefore \text{pH} = 14 - 6.13 = \underline{\underline{7.87}}$$



**12 JJC/2009/P3/Q2(a)-(b)**

2. (a) (i) A weak acid is a proton donor that dissociates partially.

$$(ii) [H^+] = \underline{5.66 \times 10^{-3}} \text{ mol dm}^{-3} \quad [1]$$

$$\text{pH} = \underline{2.25} \quad [1]$$

(iii) Amount of acid used =  $5 \times 10^{-3}$  mol

Amount of NaOH required =  $5 \times 10^{-3}$  mol

Volume of NaOH required =  $0.0500 \text{ dm}^3 = 50 \text{ cm}^3$

$$[OH^-] = \sqrt{K_b \text{ of acetylsalicylic acid} \times \text{conc of salt solution}}$$

$$= \sqrt{\frac{1.00 \times 10^{-14}}{3.2 \times 10^{-4}} \times \frac{5 \times 10^{-3}}{0.05 + 0.05}} \quad [1]$$

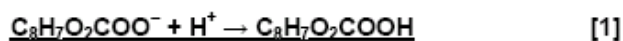
$$= 1.25 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pOH} = 5.90$$

$$\text{pH} = \underline{8.10} \quad [1]$$

$$(b) (i) \text{pH} = \text{p}K_a = -\lg(3.2 \times 10^{-4}) = \underline{3.49} \quad [1]$$

(ii) When  $H^+$  is added:



When  $OH^-$  is added:



(iii) Amount of HC/ added =  $2.00 \times 10^{-4}$  mol

In the resultant solution:

$$\text{Amount of } C_8H_7O_2COO^- \text{ left} = \underline{2.5 \times 10^{-3} - 2 \times 10^{-4}} = 2.30 \times 10^{-3} \text{ mol}$$

$$\begin{aligned} \text{Concentration of } C_8H_7O_2COO^- &= \frac{2.30 \times 10^{-3}}{50 + 25 + \frac{2}{1000}} \\ &= 0.0299 \text{ mol dm}^{-3} \end{aligned}$$

## Ionic Equilibrium – Suggested Solutions

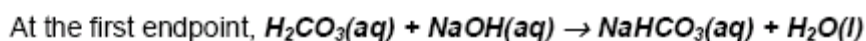
2. (b) (iii) Amount of  $C_8H_7O_2COOH = \underline{2.5 \times 10^{-3} + 2 \times 10^{-4}} = 2.70 \times 10^{-3}$  mol

$$\begin{aligned} \text{Concentration of } C_8H_7O_2COOH &= \frac{2.70 \times 10^{-3}}{50 + 25 + \frac{2}{1000}} \\ &= 0.0351 \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \text{pH of the resulting solution} &= -\lg(3.2 \times 10^{-4}) + \lg \frac{0.0299}{0.0351} \\ &= \underline{\underline{3.43}} \end{aligned}$$

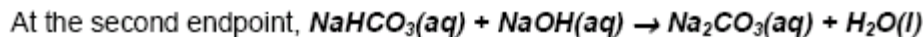
### 13 MI/2009/P2/Q2(b)

(i) Calculate the amount of  $H_2CO_3$  present in the sample of blood plasma.



$$\begin{aligned} \text{Amount of } H_2CO_3 \text{ present} &= \text{Amount of NaOH used for the 1st endpoint} \\ &= \frac{1.30}{1000} \times 7.50 \times 10^{-3} \\ &= 9.75 \times 10^{-6} \text{ mol} \end{aligned}$$

(ii) Calculate the amount of  $HCO_3^-$  present in the sample of blood plasma. [2]



**Note:** Amount of  $HCO_3^-$  present for step 2 of the titration

$$\begin{aligned} &= \text{Amount of } HCO_3^- \text{ present originally} + \text{Amount of } HCO_3^- \text{ produced} \\ &\quad \text{from step 1 of the titration} \\ &= \text{Amount of } HCO_3^- \text{ present originally} + 9.75 \times 10^{-6} \end{aligned}$$

$$\begin{aligned} \text{Amount of } HCO_3^- \text{ present altogether} \\ &= \text{Amount of NaOH used for the 2nd endpoint only} \\ &= \frac{14.60}{1000} \times 7.50 \times 10^{-3} \quad ; \\ &= 1.095 \times 10^{-4} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Amount of } HCO_3^- \text{ present originally} &= 1.095 \times 10^{-4} - 9.75 \times 10^{-6} \quad ; \\ &= 9.98 \times 10^{-5} \text{ mol} \end{aligned}$$

(iii) Hence determine the  $K_a$  of carbonic acid.

$$\begin{aligned} \text{pH of buffer} &= \text{p}K_a + \lg \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \\ 7.4 &= \text{p}K_a + \lg \left( \frac{9.975 \times 10^{-5} / 10.0}{9.75 \times 10^{-6} / 10.0} \right) \\ \text{p}K_a &= 7.4 - \lg \left( \frac{9.975 \times 10^{-5}}{9.75 \times 10^{-6}} \right) \\ \text{p}K_a &= 6.39 \\ K_a &= 4.07 \times 10^{-7} \text{ mol dm}^{-3} \end{aligned}$$

(iv) The theoretical value for the  $K_a$  of carbonic acid is  $4.47 \times 10^{-7} \text{ mol dm}^{-3}$ . Suggest an error or limitation of this experiment which would have resulted in the difference in the value calculated in (b)(iii). [1]

***There is a large percentage error in the titration values recorded as the volume of NaOH used for the first endpoint is very small.*** ;

OR 
$$\begin{aligned} \% \text{ error} &= 2 \times \frac{\frac{1}{2} \times 0.10}{1.30} \times 100\% \\ &= 7.69\% \end{aligned}$$

(v) Using the theoretical value for the  $K_a$  of carbonic acid, calculate the pH of the first endpoint. [4]



$$K_w = K_a \times K_b$$

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{4.47 \times 10^{-7}}$$

$$= 2.237 \times 10^{-8} \text{ mol dm}^{-3}$$

$$K_b = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]}$$

$$= \frac{[\text{OH}^-]^2}{[\text{HCO}_3^-]}$$

$$[\text{OH}^-] = \sqrt{2.237 \times 10^{-8} \times 0.01095}$$

$$= 1.565 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\begin{aligned} [\text{HCO}_3^-] &= \frac{1.095 \times 10^{-4}}{10.0} \times 1000 \\ &= 0.01095 \text{ mol dm}^{-3} \end{aligned} \quad ;;$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14 - [-\lg(1.565 \times 10^{-5})] \quad ;;$$

$$= 9.19$$

14 **MJC/2009/P2/Q2**

- (a) Determine whether a precipitate is formed when the common washing-up liquid was accidentally mixed with 0.200 dm<sup>3</sup> of 'hard' water.

$$\begin{aligned} \text{Ionic product of } (C_{18}H_{19}SO_3)_2Ca &= (7.143 \times 10^{-5}) (3.643 \times 10^{-5})^2 \\ &= \underline{9.48 \times 10^{-14} \text{ mol}^3 \text{ dm}^{-9}} \end{aligned}$$

Ionic product > K<sub>sp</sub> ⇒ precipitate of (C<sub>18</sub>H<sub>19</sub>SO<sub>3</sub>)<sub>2</sub>Ca is formed. ---

- (i) Write the K<sub>c</sub> expression for the reaction.

$$K_c = \frac{[CaP_3O_{10}^{3-}]}{[Ca^{2+}][P_3O_{10}^{3-}]}$$

- (ii) Hence, calculate the concentration of tripolyphosphate ions required to reduce the calcium ion concentration in a typical sample of "hard water" to 1.0 × 10<sup>-6</sup> mol dm<sup>-3</sup>.

*Let x be the initial concentration of P<sub>3</sub>O<sub>10</sub><sup>5-</sup> required*

At equilibrium,

$$7.7 \times 10^8 = \frac{2.49 \times 10^{-4}}{(1.0 \times 10^{-6})(x - 2.49 \times 10^{-4})}$$

$$\underline{x = 2.493 \times 10^{-4} \text{ mol dm}^{-3}}$$

15 **MJC/2009/P3/Q4(a)**

- 4(ai) K<sub>a1</sub> and K<sub>a2</sub> are the acid dissociation constant of the carboxylic acid group and phenolic group respectively. K<sub>a1</sub> is smaller K<sub>a2</sub> because carboxylic acid group is more acidic than the phenolic group.
- (ii) H<sup>+</sup> from the 2<sup>nd</sup> dissociation is negligible and can be ignored and all the H<sup>+</sup> comes from the 1<sup>st</sup> dissociation.

$$\begin{aligned}
 [\text{H}^+] &= \sqrt{cK_a} \\
 &= \sqrt{0.05 \times 6.31 \times 10^{-5}} \\
 &= 1.78 \times 10^{-3} \text{ mol dm}^{-3}
 \end{aligned}$$

Hence, pH = **2.75**

(iii) For acidic buffer

$$\begin{aligned}
 \text{pH} &= \text{p}K_a + \lg \frac{[\text{salt}]}{[\text{acid}]} \\
 &= -\lg 6.31 \times 10^{-5} + \lg \frac{[6.25 \times 10^{-4} / 0.03125]}{[6.25 \times 10^{-4} / 0.03125]} \\
 &= **4.20**
\end{aligned}$$

Salt hydrolysis



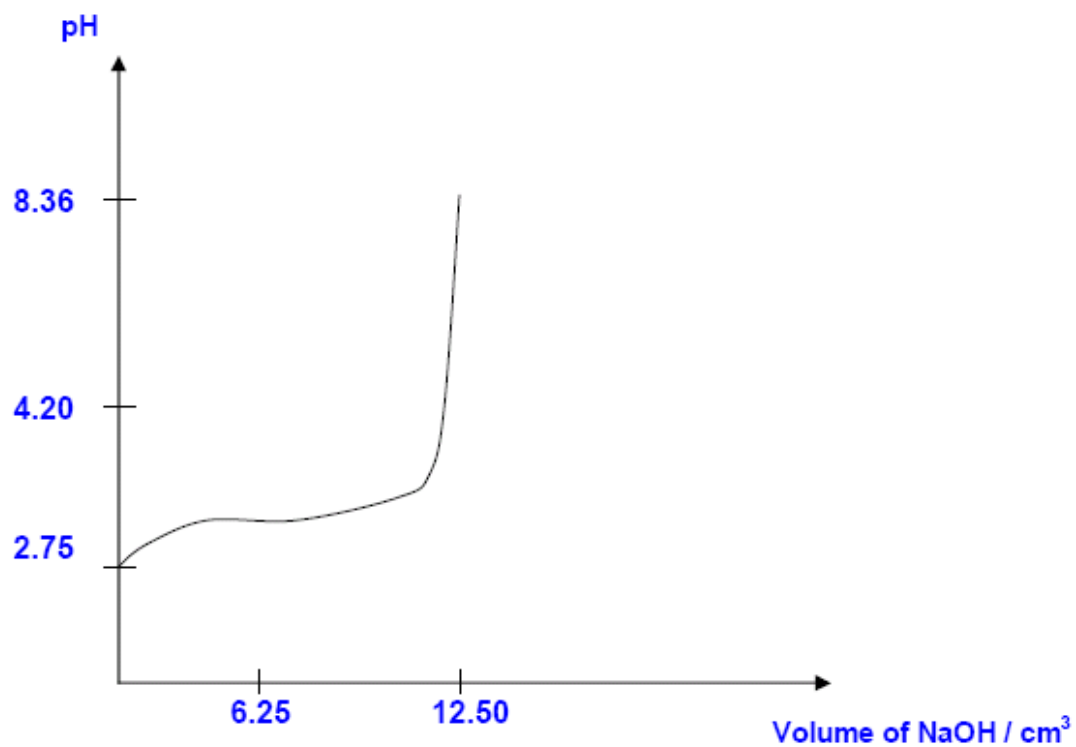
$$K_{b1} = \frac{K_w}{K_{a1}} = \frac{1 \times 10^{-14}}{6.31 \times 10^{-5}} = 1.58 \times 10^{-10} \text{ mol dm}^{-3}$$

$$\begin{aligned}
 [\text{OH}^-] &= \sqrt{cK_b} \\
 &= \sqrt{3.33 \times 10^{-2} \times 1.58 \times 10^{-10}} \\
 &= 2.29 \times 10^{-6} \text{ mol dm}^{-3}
 \end{aligned}$$

$$\text{pOH} = -\lg 2.29 \times 10^{-6} = 5.63$$

$$\text{pH} = 14 - 5.63 = **8.36**$$

(iv)

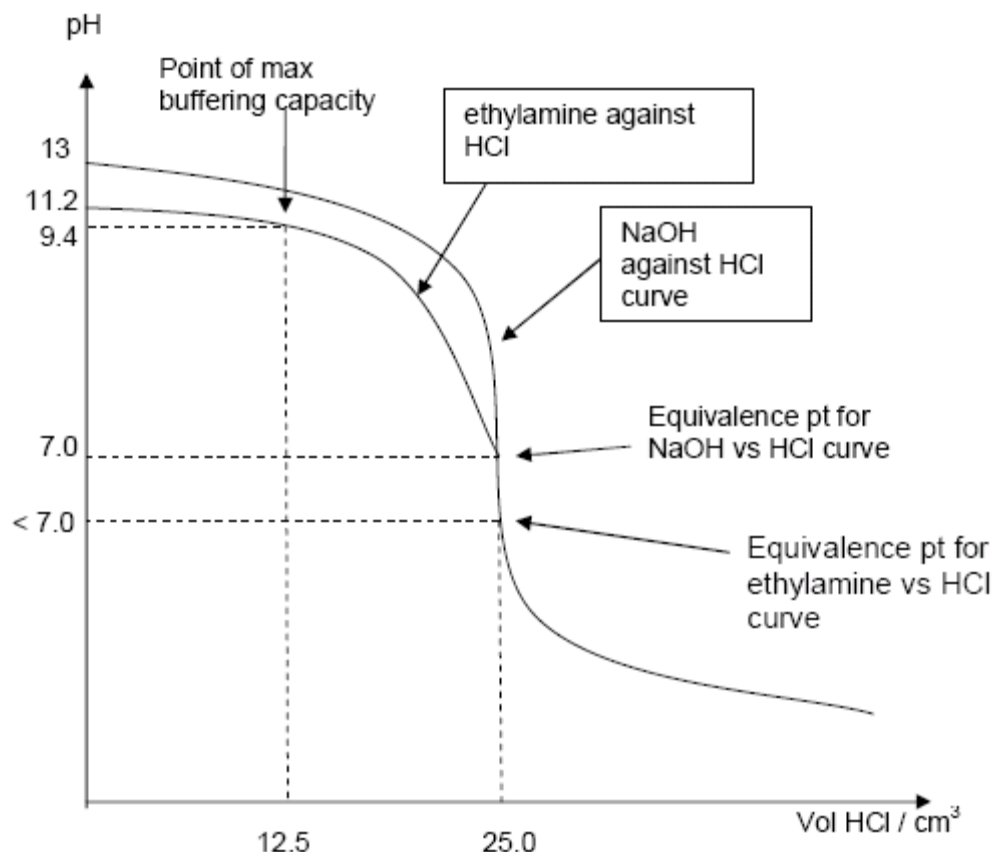


16 **NJC/2009/P3/Q2(a)**

2 (i)(I) Minimum  $[Ag^+] = 8.52 \times 10^{-14} \text{ moldm}^{-3}$

(II) Minimum  $[Ag^+] = 3.17 \times 10^{-5} \text{ moldm}^{-3}$

(ii)  $[I^-] = 2.69 \times 10^{-12} \text{ moldm}^{-3}$

17 NJC/2009/P3/Q5(e)(ii)

 18 NYJC/2009/P3/Q4(a)-(b)

4(a) (i)  $[\text{OH}^-] = \sqrt{5.6 \times 10^{-4} (0.200)} = 1.058 \times 10^{-2} \text{ mol dm}^{-3}$

$\text{pOH} = -\lg 1.058 \times 10^{-2} = 1.98 \quad \text{pH} = 12.02$

(ii) Using  $\frac{0.200 \times V_{\text{CH}_3\text{CH}_2\text{NH}_2}}{0.120 \times 40.0} = \frac{1}{1} \Rightarrow V_{\text{CH}_3\text{CH}_2\text{NH}_2} = 24.0 \text{ cm}^3$

(iii) When vol = 48.0 cm<sup>3</sup>, solution reached max buffering capacity



Let  $x$  be  $[\text{I}^-]$

$$9.8 \times 10^{-9} = \frac{1}{2}x(x)^2$$

$$x = \sqrt[3]{2(9.8 \times 10^{-9})} = 2.696 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Solubility of PbI}_2 = \frac{2.696 \times 10^{-3}}{2} \text{ mol dm}^{-3}$$

(ii) Let C be  $[\text{Pb}^{2+}]$  before mixing

$$[\text{Pb}^{2+}] \text{ after mixing} = \frac{C}{2} \quad [\text{I}^-] \text{ after mixing} = \frac{0.500}{2} \quad [1\text{m}]$$

for ppt to appear, IP of  $\text{PbI}_2 > K_{\text{sp}}$  of  $\text{PbI}_2$

$$\left(\frac{C}{2}\right) \left(\frac{0.500}{2}\right)^2 > 9.8 \times 10^{-9} \quad [1\text{m}]$$

$$\Rightarrow C > 3.136 \times 10^{-7} \text{ mol dm}^{-3}$$

**19 PJC/2009/P2/Q3(b)**


$$[\text{Fe}^{3+}] = 3.6/(580.8) = 6.20 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{IO}_3^-] = 3 \times 6.20 \times 10^{-3} = 0.0186 \text{ mol dm}^{-3}$$

$$K_{\text{sp}} \text{ of } \text{Fe}(\text{IO}_3)_3 = [\text{Fe}^{3+}]_{\text{eqm}} \times [\text{IO}_3^-]_{\text{eqm}}^3$$

$$= 3.99 \times 10^{-8} \text{ mol}^4 \text{ dm}^{-12} \text{ at } 298 \text{ K}$$

(ii) Due to the Common Ion Effect, the solubility decreases.

Let the solubility be  $x \text{ mol dm}^{-3}$

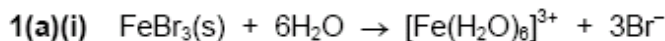
$$[\text{IO}_3^-]_{\text{total}} = 0.105 + 3x \approx 0.105 \text{ mol dm}^{-3}; \text{ since } 3x \text{ is small compared to } 0.105$$

$$K_{\text{sp}} \text{ of } \text{Ce}(\text{IO}_3)_3 = [\text{Ce}^{3+}]_{\text{eqm}} \times [\text{IO}_3^-]_{\text{eqm}}^3$$

$$3.99 \times 10^{-8} \text{ mol}^4 \text{ dm}^{-12} = x(0.105)^3 \text{ mol}^4 \text{ dm}^{-12}$$

$$x = 3.44 \times 10^{-5} \text{ (check: } 3x = 1.03 \times 10^{-4} \ll 0.105)$$

$$\text{Solubility of } \text{Fe}(\text{IO}_3)_3 \text{ in } 0.100 \text{ mol dm}^{-3} \text{ KIO}_3 = \underline{3.44 \times 10^{-5} \text{ mol dm}^{-3}}.$$

**20 PJC/2009/P3/Q1(a)**


Due to high charge density of  $\text{Fe}^{3+}$  ion, it is able to polarize the water molecule weakening the O—H bond, releasing  $\text{H}^+$  ion. Hence a solution of  $\text{FeBr}_3$  has pH less than 7 at 298 K.

(ii)  $K_{\text{a}}(\text{Fe}^{3+}(\text{aq})) = 6.34 \times 10^{-6} \text{ mol dm}^{-3}$



**21 PJC/2009/P3/Q3(a)**

$$3(a) \text{ (i) } K_a = 10^{-pK_a} = 10^{-6.80} = 1.58 \times 10^{-7} \text{ mol dm}^{-3}$$

$$K_a = [\text{C}_{10}\text{H}_{14}\text{N}] [\text{H}_3\text{O}^+] / [\text{C}_{10}\text{H}_{14}\text{NH}^+]$$

$$K_a = [\text{H}_3\text{O}^+]^2 / [\text{C}_{10}\text{H}_{14}\text{NH}^+]$$

$$[\text{H}_3\text{O}^+] = [(1.58 \times 10^{-7})(0.100)]^{1/2} = 1.26 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = 3.90$$

(ii) When pH is decreased,  $[\text{H}_3\text{O}^+]$  increases and position of equilibrium shift to the left, concentration of conjugate of nicotine increases.

$$(iii) \text{ pH} = \text{p}K_a(\text{C}_{10}\text{H}_{14}\text{NH}^+) + \log_{10} [\text{C}_{10}\text{H}_{14}\text{N}] / [\text{C}_{10}\text{H}_{14}\text{NH}^+] = 6.50$$

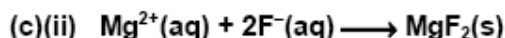
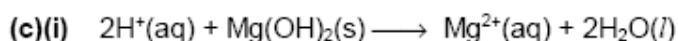
$$(iv) [\text{C}_{10}\text{H}_{14}\text{N}]_{\text{new}} = (5 \times 0.100 - 0.200v) / (5.00 + v)$$

$$[\text{C}_{10}\text{H}_{14}\text{NH}^+]_{\text{new}} = (5 \times 0.200 + 0.200v) / (5.00 + v)$$

$$\text{pH} = \text{p}K_a(\text{C}_{10}\text{H}_{14}\text{NH}^+) + \log_{10} [\text{C}_{10}\text{H}_{14}\text{N}] / [\text{C}_{10}\text{H}_{14}\text{NH}^+]$$

$$6.40 = 6.80 + \log_{10} \frac{(5 \times 0.100 - 0.200v)/(5.00 + v)}{(5 \times 0.200 + 0.200v)/(5.00 + v)}$$

$$\text{solving, } v = 0.364 \text{ dm}^3$$

**22 RI/2009/P2/Q1(c)**


The  $\text{Mg}^{2+}$  released from the acid–base reaction in the stomach reacts with the  $\text{F}^-$  present to form a precipitate of  $\text{MgF}_2$  which is **insoluble** and is thus **not easily absorbed** by the body.

(c)(iii) Precipitation occurs when

$$[\text{Mg}^{2+}][\text{F}^-]^2 > K_{\text{sp}}$$

$$[\text{Mg}^{2+}] \left[ \left( \frac{1 \times 10^{-3}}{19.0} \right) / 1.0 \right]^2 > 5.16 \times 10^{-11}$$

$$[\text{Mg}^{2+}] > 0.0186 \text{ mol dm}^{-3}$$

$$(\text{vol. of milk of magnesia needed})(1.40) = (0.0186)(\text{vol. of liquid in stomach})$$

$$\text{i.e. vol. of milk of magnesia needed} = 0.0133 \text{ dm}^3$$

(i.e. 13.3 cm<sup>3</sup>)

**23 RI/2009/P3/Q1(a)**

(a)(i) Amount of lactic acid = Amount of NaOH needed for neutralisation  

$$= \frac{20.00}{1000} \times 0.120 = 0.0024 \text{ mol}$$

Concentration of lactic acid =  $0.0024 \div \frac{25.0}{1000} = 0.0960 \text{ mol dm}^{-3}$

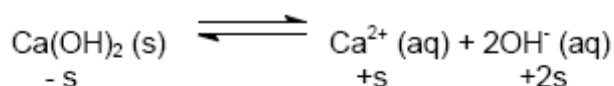
(ii)  $\text{p}K_a = \text{pH}$  at half-neutralisation = 3.85 (when  $V_{\text{NaOH}} = 10 \text{ cm}^3$ )  
 $K_a = 10^{-3.85} = 1.41 \times 10^{-4} \text{ mol dm}^{-3}$

Alternatively,  $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$

Initially,  $[\text{H}^+] = [\text{A}^-] = 10^{-2.45} = 3.548 \times 10^{-3} \text{ mol dm}^{-3}$

$K_a = \frac{3.548 \times 10^{-3} \times 3.548 \times 10^{-3}}{0.0960 - 3.548 \times 10^{-3}} = 1.36 \times 10^{-4} \text{ mol dm}^{-3}$  where HA = lactic acid

- (iii) At equivalence point, the resultant mixture is a solution of sodium lactate,  $\text{H}_3\text{CH}(\text{OH})\text{COO}^-\text{Na}^+$ .  
 Being the conjugate base of a weak acid, lactate ion hydrolyses in water to give  $\text{OH}^-$ :  
 $\text{CH}_3\text{CH}(\text{OH})\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{CH}(\text{OH})\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$   
 The formation of  $\text{OH}^-$  causes the pH at equivalence point to be greater than 7.

**24 SAJC/2009/P2/Q6**


(a)  $K_{\text{sp}} = s(2s)^2 = 4s^3 = 1.0 \times 10^{-12}$   
 $s = 6.30 \times 10^{-5}$ , solubility in water is  $6.30 \times 10^{-5} \text{ mol dm}^{-3}$ .

(b)  $[\text{Ca}^{2+}] = (0.10 + s)$   
 $[\text{OH}^-] = 2s$   
 $K_{\text{sp}} = (0.10 + s)(2s)^2$   
 $1.1 \times 10^{-12} = (0.10 + s)(2s)^2$   
 $s = 1.58 \times 10^{-6} \text{ mol dm}^{-3}$

(c)  $[\text{Ca}^{2+}] = 1 \times 10^{-3} / 2 = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$   
 $[\text{OH}^-] = 2 \times 2 \times 10^{-3} / 2 = 2 \times 10^{-3} \text{ mol dm}^{-3}$   
 Ionic product =  $0.5 \times 10^{-3} \times (2 \times 10^{-3})^2 = 2 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9} > K_{\text{sp}}$   
 Hence, precipitation takes place.

## 25 SAJC/2009/P3/Q4

4. (a) (i) pH of lactic acid = 2.5

$$[H^+] = 10^{-2.5}$$

Since lactic acid is a weak monobasic acid,

$$K_a = [H^+]^2 / [CH_3CHOH(COOH)] \quad \text{OR} \quad [H^+] = \sqrt{K_a [HA]}$$

$$= (10^{-2.5})^2 / 0.080$$

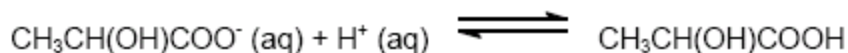
$$= 1.28 \times 10^{-4} \text{ mol dm}^{-3}$$

(ii) Maximum buffer capacity occurs when [salt]=[acid]

$$\text{pH} = \text{p}K_a$$

$$= -\log 1.25 \times 10^{-4}$$

$$= 3.90$$

(iii) When a small amount of  $H^+$  is added,

The additional acid,  $H^+$ , is removed by large concentration of  $CH_3CH(OH)COO^-$  from the salt.

Thus,  $H^+$  changes very slightly and the pH remains almost constant.

(iv) At the equivalence point, only basic salt is present.

$$\text{No. of moles of salt formed} = 0.08 \times 10 / 1000 = 8 \times 10^{-4} \text{ mol}$$

$$[\text{salt}] = 8 \times 10^{-4} / 26 \times 1000 = 0.031 \text{ mol dm}^{-3}$$

$$[OH^-] = \sqrt{[(1 \times 10^{-14} / 1.25 \times 10^{-4}) \times 0.031]} = 1.55 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pOH} = 5.8$$

$$\text{pH} = 8.2$$

A suitable indicator is phenolphthalein.

## 26 SRJC/2009/P2/Q4

(a) Explain the term acid dissociation constant,  $K_a$ , as applied to ethanoic acid. [1]

Acid dissociation constant,  $K_a$  is a measure of the **strength of a weak acid**

OR



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad [1\text{M}]$$

(b) Calculate the initial pH of the 20.0 cm<sup>3</sup> sample of ethanoic acid. [2]



Let the  $[\text{H}^+]$  be  $x \text{ mol dm}^{-3}$

$$\frac{(x)(x)}{0.01 - x} = K_a$$

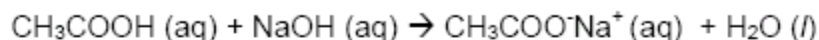
Since  $K_a < 10^{-4} \text{ mol dm}^{-3}$ ; assume that  $x$  is so small that  $0.01 - x \approx 0.01$

$$\frac{(x)(x)}{0.01} = 1.8 \times 10^{-5} \quad [1 \text{ M}]$$

$$[\text{H}^+] = \underline{4.242 \times 10^{-4} \text{ mol dm}^{-3}} \quad [1/2 \text{ M}]$$

$$\begin{aligned} \text{pH} &= -\lg [4.24 \times 10^{-4}] \\ &= \underline{3.37} \quad [1/2 \text{ M}] \end{aligned}$$

(c) Calculate the equivalence volume of NaOH and hence, the end point pH. [4]



$$\begin{aligned} \text{Amount of CH}_3\text{COOH} &= \frac{20}{1000} \times 0.01 \\ &= 2.000 \times 10^{-4} \text{ mol} \end{aligned}$$

Since  $n_{\text{CH}_3\text{COOH}} : n_{\text{NaOH}} = 1:1$

$$\text{Amount of NaOH} = \underline{2.000 \times 10^{-4} \text{ mol}} \quad [1/2 \text{ M}]$$

$$\begin{aligned} \text{Equivalence volume of NaOH} &= \frac{2 \times 10^{-4}}{0.02} \\ &= \underline{0.0100 \text{ dm}^3} = \underline{10.0 \text{ cm}^3} \quad [1\text{M}] \end{aligned}$$

At equivalence point,

$$\begin{aligned} [\text{CH}_3\text{COO}^-] &= \frac{2 \times 10^{-4}}{\frac{30}{1000}} \\ &= 6.667 \times 10^{-3} \text{ mol dm}^{-3} \quad [1/2 \text{ M}] \end{aligned}$$

Ionic Equilibrium – Suggested Solutions

Let the  $[\text{OH}^-]$  at equivalence point be  $y \text{ mol dm}^{-3}$

	$\text{CH}_3\text{COO}^- (\text{aq})$	$+$	$\text{H}_2\text{O}(\text{l})$	$\rightleftharpoons$	$\text{CH}_3\text{COOH} (\text{aq})$	$+$	$\text{OH}^- (\text{aq})$
Initial [ ]:	$6.667 \times 10^{-3}$		-		0		0
$\Delta$ in [ ]:	-y		-		+y		+y
Eqm [ ]:	$6.667 \times 10^{-3} - y$		-		y		y

$$K_a \times K_b = K_w$$

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

$$= 5.556 \times 10^{-10} \text{ mol dm}^{-3} \quad [1/2 \text{ M}]$$

$$\frac{(y)(y)}{(6.667 \times 10^{-3}) - y} = K_b$$

Since  $K_b < 10^{-4} \text{ mol dm}^{-3}$ ; assume that  $x$  is so small that  $6.667 \times 10^{-3} - x \approx 6.667 \times 10^{-3}$

$$\frac{(y)(y)}{6.667 \times 10^{-3}} = 5.556 \times 10^{-10} \quad [1/2 \text{ M}]$$

$$[\text{OH}^-] = 1.924 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\lg (1.924 \times 10^{-6}) = 5.716 \quad [1/2 \text{ M}]$$

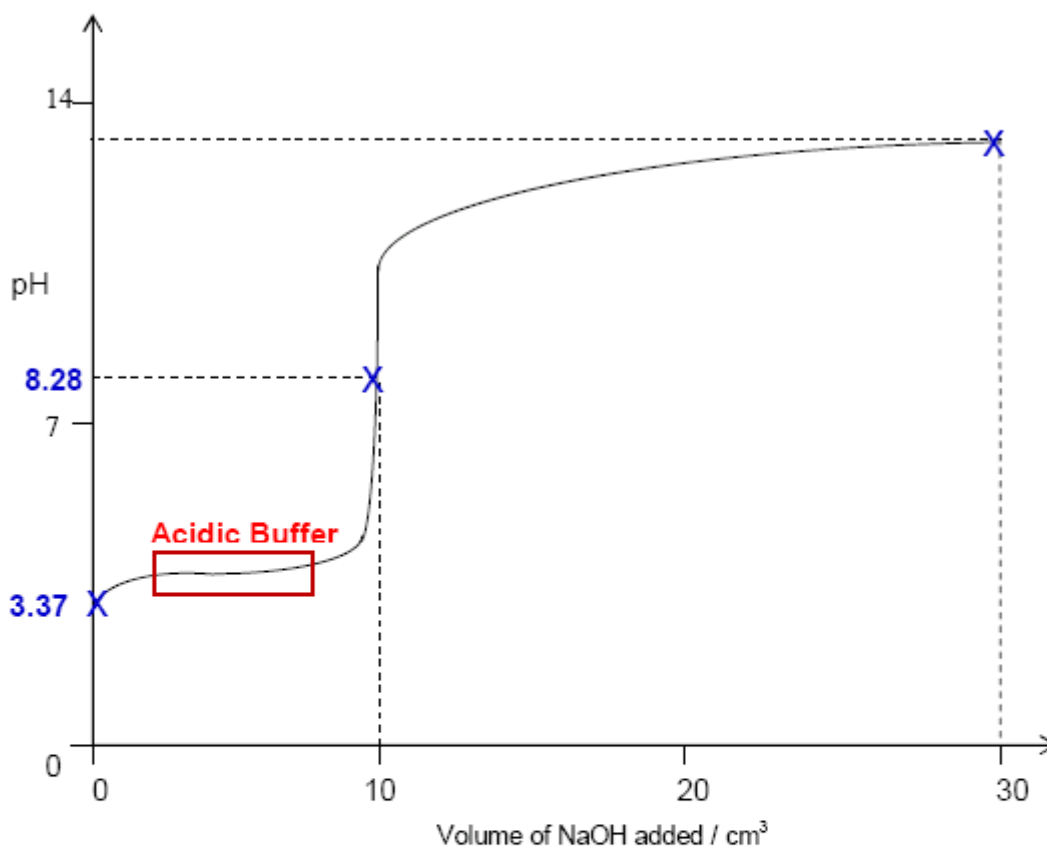
$$\text{pH} = 14 - 5.716$$

$$= \underline{\underline{8.28}} \quad [1/2 \text{ M}]$$

[4]

Ionic Equilibrium – Suggested Solutions

(d) The reaction is continued until 30 cm<sup>3</sup> of sodium hydroxide has been added. On the given grid, using the pH values you have determined from (b) and (c), sketch how the pH changes and indicate clearly the buffer region. [3]



Mark all 3 points (initial, endpoint and final pH) correctly – [1M]

Correct shape of the graph – [1M]

Correct indication of buffer region – 1M]

(e) State and explain the choice of a suitable indicator for this reaction. [2]

Phenolphthalein. [1M]

Its pH transition range ( $\approx 8 - 9.8$ ) lies within the sharp pH change over the equivalence point. [1M]

**27 SRJC/2009/P3/Q3(c)**

(i) A sample of sodium hypochlorite, NaOCl, was dissolved in 100 cm<sup>3</sup> of 0.123 mol dm<sup>-3</sup> HOCl solution forming a buffer of pH 6.20. Determine the ratio of the concentration of OCl<sup>-</sup> to HOCl in the solution. [1]

$$\text{pH} = \text{pK}_a + \lg \frac{[\text{OCl}^-]}{[\text{HOCl}]}$$

$$6.20 = 7.50 + \lg \frac{[\text{OCl}^-]}{[\text{HOCl}]}$$

$$\lg \frac{[\text{OCl}^-]}{[\text{HOCl}]} = -1.30$$

$$\frac{[\text{OCl}^-]}{[\text{HOCl}]} = 0.0501$$

(ii) The buffer is then used to absorb HCl gas. By using the above ratio or otherwise, calculate the amount of gaseous HCl (in mol) that is required to be added to the buffer solution until it reaches pH 6. [4]

$$\frac{[\text{OCl}^-]}{[\text{HOCl}]} = 0.0501$$

$$\begin{aligned} [\text{OCl}^-] &= 0.0501[\text{HOCl}] \\ &= 0.0501 \times 0.123 \\ &= 0.006162 \text{ mol dm}^{-3} \end{aligned}$$

On addition of HCl, let x be the concentration of H<sup>+</sup>

$$\begin{aligned} [\text{HOCl}]_{\text{new}} &= 0.123 + x \\ [\text{OCl}^-]_{\text{new}} &= 0.006162 - x \end{aligned}$$

$$\begin{aligned} 6.00 &= 7.50 + \lg \frac{[\text{OCl}^-]}{[\text{HOCl}]} \\ 6.00 &= 7.50 + \lg \frac{0.006162 - x}{0.123 + x} \end{aligned}$$

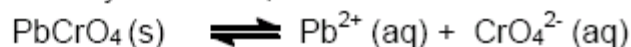
$$\begin{aligned} -1.50 &= \lg \frac{0.006162 - x}{0.123 + x} \\ 0.03162 &= \frac{0.006162 - x}{0.123 + x} \\ 0.03162(0.123) + 0.03162x &= 0.006162 - x \\ 1.03162x &= 0.00227 \\ x &= 0.00220 \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \text{amount of HCl} &= 0.00220 \times \frac{100}{1000} \\ &= 0.000220 \text{ mol} \end{aligned}$$

**28 TJC/2009/P3/Q1(d)**

(d) (i) •  $K_{sp} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}]$

Let the solubility of  $\text{PbCrO}_4$  be  $x \text{ mol dm}^{-3}$



•  $K_{sp} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}]$   
 $1.69 \times 10^{-14} = x^2$   
 $x = \sqrt{K_{sp}}$

•  $= 1.30 \times 10^{-7} \text{ mol dm}^{-3}$

The solubility of  $\text{PbCrO}_4$  is  $1.30 \times 10^{-7} \text{ mol dm}^{-3}$ .

(ii)

•  $[\text{Pb}^{2+}] = \frac{K_{sp}}{[\text{CrO}_4^{2-}]} = \frac{1.69 \times 10^{-14}}{0.010}$

•  $= 1.69 \times 10^{-12} \text{ mol dm}^{-3}$

**29 TJC/2009/P3/Q3**

- (a) (i) •  $\left\{ \begin{array}{l} \text{At the surface of the sea, pressure of } \text{CO}_2 \text{ is } 1 \text{ atm (normal atmospheric pressure)} \\ \text{At } 300 \text{ m below sea level, the pressure of } \text{CO}_2 = \frac{300}{10} + 1 \\ \hspace{10em} = 31 \text{ atm} \end{array} \right.$

• Solubility of  $\text{CO}_2$  300 m below sea level  
 $= \frac{31}{1} \times 3.29 \times 10^{-2}$   
 $= 1.02 \text{ mol dm}^{-3}$

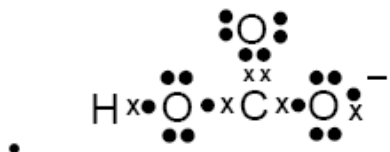
(ii) (i) •  $[\text{H}^+] = \sqrt{K_a \times C}$   
 $= \sqrt{4.5 \times 10^{-7} \times 1.02}$   
 $= 6.77 \times 10^{-4} \text{ mol dm}^{-3}$

•  $\text{pH} = -\lg(6.77 \times 10^{-4})$   
 $= 3.17$



Ionic Equilibrium – Suggested Solutions

(II)



(III) • Trigonal planar

(iii)  
(I) •  $K_{a2} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$

(II) 
$$K_{a1} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]}$$

$$= 4.5 \times 10^{-7} \text{ mol dm}^{-3}$$

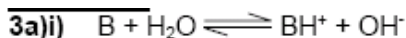
$$K_{a2} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$$

•  $= \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]} \times \frac{[\text{CO}_2]}{[\text{H}_2\text{CO}_3]}$

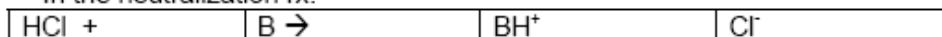
$= 4.5 \times 10^{-7} \times 400$

•  $= 1.80 \times 10^{-4} \text{ mol dm}^{-3}$

**30 TPJC/2009/P3/Q3(a)-(b)**



ii) In the neutralization rx:



At the end of rx: there is salt, BH<sup>+</sup>Cl<sup>-</sup>, water and excess B to make a buffer soln.

Let the vol HCl = x dm<sup>3</sup>

Vol of B used = (1-x) dm<sup>3</sup>

	HCl +	B →	BH <sup>+</sup>	Cl <sup>-</sup>
Initial /mol	0.05x	0.05(1-x)	-	-
Change	-0.05x	-0.05x	+0.05x	+0.05x
Final/ mol	-	0.05(1-x) - 0.05x = 0.05-0.1x	0.05x	0.05x

## Ionic Equilibrium – Suggested Solutions

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

$$[\text{OH}^-] = 10^{-14}/10^{-9.2} = 10^{-4.8}$$

$$K_b = 3.17 \times 10^{-5} = \frac{[\text{BH}^+]}{[\text{B}]} \times 10^{-4.8}$$

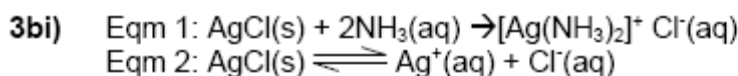
$$2.00 = 0.05x/0.05-0.1x$$

$$0.1 - 0.2x = 0.05x$$

$$x = 0.400 \text{ dm}^3, \text{ vol HCl};$$

$$\text{vol B} = 0.600 \text{ dm}^3$$

- iii) Dilution has no effect on the ratio of  $\frac{[\text{BH}^+]}{[\text{B}]}$  and  $K_b$ , hence pH remains the same at 9.2.



refer eqm1: Addition of ammonia soln form the complex,  $[\text{Ag}(\text{NH}_3)_2]^+$ , hence reducing the  $[\text{Ag}^+(\text{aq})]$ , this affect the eqm 2, by LCP, system tries to replenish the  $\text{Ag}^+(\text{aq})$  by causing eqm 2 to shift to the right, resulting in more AgCl to dissolve.

- ii) In  $2 \text{ dm}^3$  soln,  
 Amt of AgCl dissolved  
 $= 5.00 \times 10^{-5} - 1.88 \times 10^{-5} = 3.12 \times 10^{-5} \text{ mol}$   
 Let amt of complex  $\text{Ag}^+$  be  $y \text{ mol}$ .

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

$$1.8 \times 10^{-10} = \frac{(3.12 \times 10^{-5} - y)}{2.00} \times \frac{(3.12 \times 10^{-5})}{2.00}$$

$$y = 0.810 \times 10^{-5} \text{ mol in } 2.00 \text{ dm}^3$$

$$\text{hence, } [\text{complexed Ag}^+] = 0.810 \times 10^{-5} / 2.00$$

$$= 4.05 \times 10^{-6} \text{ mol dm}^{-3}$$

### 31 VJC/2009/P2/Q2(b)

- (i) Calculate the concentration of hydrogen ions in the solution after barium hydroxide is added.

$$[\text{H}^+] = 10^{-2.88} = 1.32 \times 10^{-3} \text{ mol dm}^{-3}$$

- (ii) Using your answer to (i) and the given information, calculate the value of the acid dissociation constant,  $K_a$ , of HF.

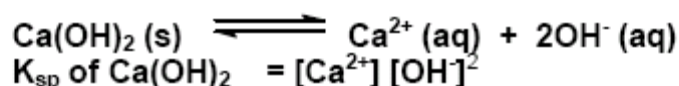
$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

$$= 1.32 \times 10^{-3} \times (1/2)$$

$$= 6.60 \times 10^{-4} \text{ mol dm}^{-3}$$

32 VJC/2009/P3/Q2(a)

- (i) Write an expression for the solubility product of  $\text{Ca(OH)}_2$ .



- (ii) Calculate the pH of a saturated solution of  $\text{Ca(OH)}_2$  at  $25^{\circ}\text{C}$  given that its solubility is  $0.830 \text{ g dm}^{-3}$ .

$$M_r \text{ of } \text{Ca(OH)}_2 = 74.1$$

$$\text{Solubility of } \text{Ca(OH)}_2 = \frac{0.830}{74.1} = 1.12 \times 10^{-2} \text{ mol dm}^{-3}$$

$$[\text{OH}^{-}] = 2 \times 1.12 \times 10^{-2} = 2.24 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{pH} = 14 - \lg(2.24 \times 10^{-2}) = 12.35$$

- (ii) Determine the solubility product of  $\text{Ca(OH)}_2$  at  $25^{\circ}\text{C}$ , stating its units.

$$\begin{aligned} K_{\text{sp}} \text{ of } \text{Ca(OH)}_2 &= [\text{Ca}^{2+}][\text{OH}^{-}]^2 \\ &= (1.12 \times 10^{-2})(2.24 \times 10^{-2})^2 \\ &= 5.62 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9} \end{aligned}$$

- (iii) Explain and predict qualitatively the effect(if any) on the solubility and solubility product of  $\text{Ca(OH)}_2$  when  $25.0 \text{ cm}^3$  of  $0.050 \text{ mol dm}^{-3}$  solution of potassium hydroxide is added to the solution in (ii)

The common ion,  $\text{OH}^{-}$ , from the very soluble KOH would cause eqm in (i) to shift left, hence lowering the solubility of  $\text{Ca(OH)}_2$ .

$K_{\text{sp}}$  of  $\text{Ca(OH)}_2$  would not be affected as temperature is constant.

- (iv) Write a balanced equation to show the reaction between carbon dioxide and baryta water.



- (v) Which solution, lime or baryta water, is more sensitive to the detection of carbon dioxide gas at  $25^{\circ}\text{C}$ ? Explain your answer with reference to the data given in table in (a).

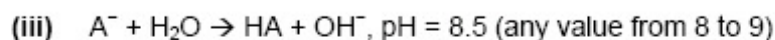
As the  $K_{\text{sp}}$  of  $\text{CaCO}_3$  is lower, the ionic product of  $[\text{Ca}^{2+}][\text{CO}_3^{2-}]$  would exceed the  $K_{\text{sp}}$  of  $\text{CaCO}_3$  more readily hence lime water would be more sensitive.

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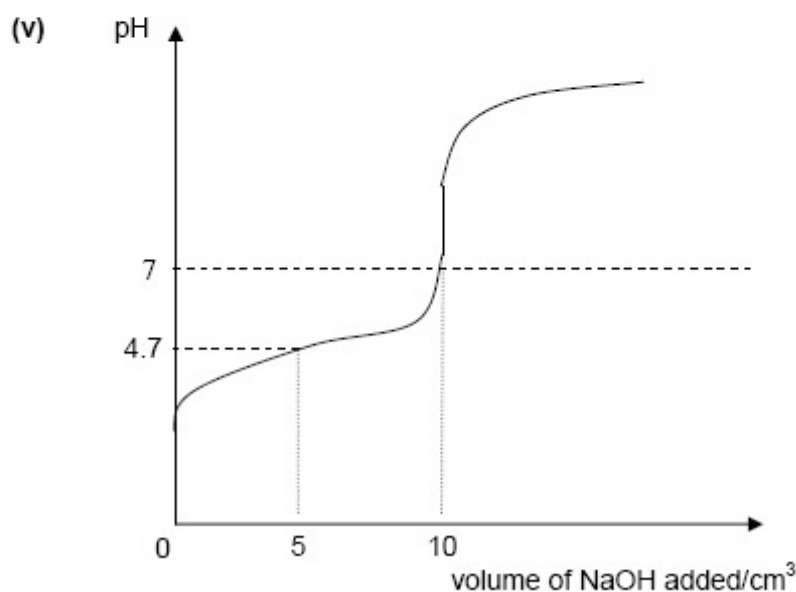
**33 YJC/2009/P2/Q3(c)**

(c) (i)  $[H^+] = \sqrt{K_a \times c} = \sqrt{2.05 \times 10^{-5} \times 0.100} = 1.43 \times 10^{-3} \text{ mol dm}^{-3}$   
 $pH = -\log(1.43 \times 10^{-3}) = 2.84$

(ii)  $\frac{n_{NaOH}}{n_{HA}} = 1 = \frac{c_{NaOH} \times V_{NaOH}}{c_{HA} \times V_{HA}}$   
 $\Rightarrow V_{NaOH} = \frac{c_{HA} \times V_{HA}}{c_{NaOH}} = \frac{0.100 \times 20.0 \times 10^{-3}}{0.200} = 0.0100 \text{ dm}^3 = 10.0 \text{ cm}^3$



(iv)  $pH = pK_a = -\log(2.05 \times 10^{-5}) = 4.7$



(vi) Phenolphthalein. End point pH lies within the pH range of the indicator

**34 YJC/2009/P3/Q1(e)**

(e) (i)  $K_{sp} = [Mg^{2+}(aq)] [OH^-(aq)]^2$  : units:  $\text{mol}^3 \text{ dm}^{-9}$

(ii)  $[Mg^{2+}(aq)]$  in the saturated solution  
 $= \sqrt[3]{\frac{2.00 \times 10^{-11}}{4}} = 1.71 \times 10^{-4} \text{ mol dm}^{-3}$

(iii)  $[Mg^{2+}(aq)]$  extracted =  $0.0540 - 1.71 \times 10^{-4} = 0.0538 \text{ mol dm}^{-3}$   
 Maximum % of Mg extracted =  $\frac{0.0538}{0.0540} \times 100 = 99.6\%$