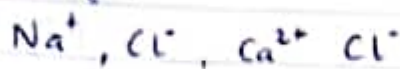


1. 0.01M NaCl and 0.005M  $\text{CaCl}_2$

$$a = \gamma_c$$

$$\log \gamma_i = -A z_i^2 I^{1/2}$$

$$I = \frac{1}{2} \sum c_i z_i^2$$



$$I = \frac{(0.01 \times 1^2) + (0.01 \times 1^2) + (0.005 \times 2^2) + (0.005 \times 1^2 \times 2)}{2}$$

$$I = 0.025$$

$$\log \gamma_{\text{Na}^+} = -A z^2 I^{1/2}$$

$$= -0.51 \times 1^2 \times (0.025)^{1/2}$$

$$= -0.08064$$

$$\gamma_{\text{Na}^+} = 10^{-0.08064}$$

$$\gamma_{\text{Na}^+} = 0.831$$

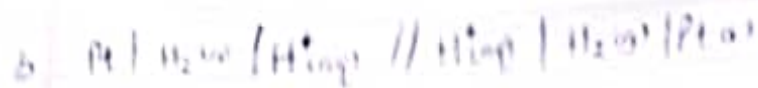
$$a_{\text{Na}^+} = \gamma_{\text{Na}^+} \cdot c$$

$$a_{\text{Na}^+} = 0.831 \times 0.01$$

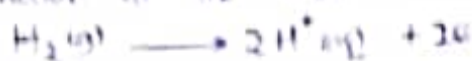
$$a_{\text{Na}^+} = 0.00831$$

(b) (i) Standard electrode potential is the potential difference developed when a metal electrode is placed in 1M solution of its ion at 25°C and pressure of 1 atm

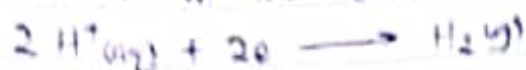
(ii) A concentration cell is an electrochemical cell that generates electric current due to difference in concentration of the same species in two half cells; this current is generated as the cell tries to equalise the concentration across the salt bridge



Reaction at the anode



Reaction at the cathode



$$ii) \Delta G^\circ = -nFE_{\text{cell}}^\circ$$

Using the principle of a concentration cell

$$E_{\text{cell}} = E_{\text{anode}} - E_{\text{cathode}}$$

$$E_{\text{cell}} = E^\circ - \frac{0.0591}{n} \log \left( \frac{a_{\text{ox}}}{a_{\text{red}}} \right)$$

$$= 0 - \frac{0.0591}{2} \log \left( \frac{a_1}{a_2} \right)$$

$$= -\frac{0.0591}{2} \log \left( \frac{0.1}{0.5} \right)$$

$$E_{\text{cell}} = 0.02065 \text{ V}$$

$$2.065 \times 10^{-2} \text{ V}$$

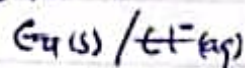
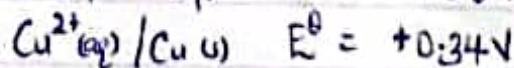
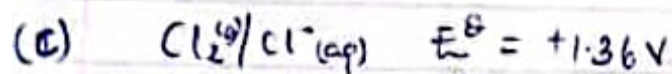
9697

$$\Delta G^\circ = -nFE_{\text{cell}}$$

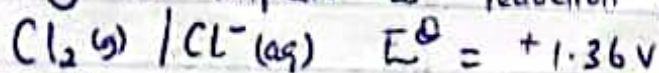
$$= (-2 \times 96500 \times 0.02065)$$

$$= -3985.45$$

$$\Delta G^\circ = -3.98545 \text{ kJ}$$



Re-writing the half cells as reduction potentials



$$E_{\text{cell}} = E_{\text{anode}} - E_{\text{cathode}}$$

$$= +0.34 - +1.36$$

$$E_{\text{cell}} = -1.02 \text{ V}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= +1.36 - 0.34$$

$$E_{\text{cell}} = +1.02 \text{ V}$$



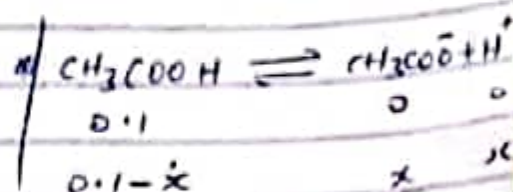
c) dilute buffer of pH 4.70 ;  $\text{NaOOCCH}_3$  and  $\text{CH}_3\text{COOH}$   
 $K_a = 1.75 \times 10^{-5}$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$4.70 = -\log(1.75 \times 10^{-5}) + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$-0.05696 = \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = 0.8771$$



$$[\text{Salt}] = 0.8771 [\text{Acid}]$$

Using 0.1 M of the acid ;

$$\frac{x}{0.1 - x} = 0.8771$$

$$x = \underline{\underline{\quad\quad\quad}}$$

$$[\text{Salt}] = (0.8771 \times 0.1)$$

$$[\text{Salt}] = 0.08771 \text{ M}$$

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

$$[\text{CH}_3\text{COONa}] = 0.08771 \text{ M}$$

$$R_{\text{mm}} \text{ of } \text{CH}_3\text{COOH} = (12 + 3 + 12 + 32 + 1) = 60$$

$$R_{\text{mm}} \text{ of } \text{CH}_3\text{COONa} = (12 + 3 + 12 + 32 + 23) = 82$$

1 mole of  $\text{CH}_3\text{COOH}$  weighs 60g.

0.1 moles of  $\text{CH}_3\text{COOH}$  weighs  $(60 \times 0.1)$

$$= \underline{\underline{6 \text{ g.}}}$$

1 mole of  $\text{CH}_3\text{COONa}$  weighs 82g.

0.08771 moles of  $\text{CH}_3\text{COONa}$  weighs  $82 \times 0.08771$

$$= 7.1922 \text{ g.}$$

Thus to prepare a solution of 0.47 pH ; we need 6g of acid and 7.1922g of the conjugate base.

27  
32  
59  
23  
82

(i)  $1\text{cm}^3$  of  $0.1\text{M HCl}$  +  $1000\text{cm}^3$  of  $0.1\text{M CH}_3\text{COOH} / 0.1\text{M CH}_3\text{COONa}$

$$\text{Initial } \text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{pH} =$$

There was no change in pH because a solution of  $\text{CH}_3\text{COOH} / \text{CH}_3\text{COONa}$  is an acid buffer. ( $\text{H}^+$ )

The small quantities of the acid ( $1\text{ml}$ ) were neutralised by  $\text{CH}_3\text{COO}^-$  from the  $\text{CH}_3\text{COONa}$ , forming the already present  $\text{CH}_3\text{COOH}$  acid which is unionised.

$$\text{CH}_3\text{COO}^- \text{ (aq)} + \text{H}^+ \text{ (aq)} \longrightarrow \text{CH}_3\text{COOH (aq)}$$

(ii)  $3.5\text{g}$  of  $\text{NH}_4\text{OH}$ ,

$$\text{Rmm of } \text{NH}_4\text{OH} = (7+4+16+1) = 28$$

$$\text{No. of moles} = \frac{3.5}{28} = 0.125 \text{ moles in } 2\text{L}$$

$$= 0.0625 \text{ moles per litre}$$

$$\text{Rmm of } \text{NH}_4\text{Cl} = (7+4+35.5) = 46.5$$

$$\text{No. of moles} = \left( \frac{0.535}{46.5} \right) = 0.0115 \text{ moles in } 2\text{L}$$

$$= 0.00575 \text{ moles per litre}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{R } K_a : K_b = 1 : 7.5 \times 10^{-5} \quad K_a = K_b = 1.75 \times 10^{-5}$$

$$K_b = 7.5 \times 10^{-5}$$

$$\text{pOH} = -\log(7.5 \times 10^{-5}) + \log \left( \frac{0.00575}{0.0625} \right)$$

$$\text{pOH} = 3.0887$$

$$\text{pH} = 14 - 3.0887$$

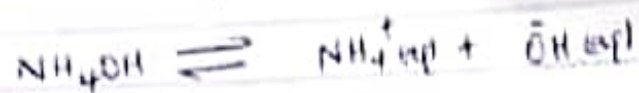
$\text{pH} = 10.911$  ; As initial pH of the solution which remained the same after addition of  $1\text{cm}^3$  of  $0.1\text{M HCl}$  ; since the solution is a buffer.

4.1249



2nd Buffer solution is a solution that resists change in pH when a small amount of base or acid is added.  
 It can be an acidic buffer such as a solution of a weak acid and salt of strong alkali ( $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$ ) or a basic buffer like a solution of a weak base and a salt of a strong acid ( $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$ )

(b) Consider a basic buffer such as  $\text{NH}_4\text{OH} / \text{NH}_4\text{Cl}$



$\text{NH}_4^+$  represents the salt  
 $\text{NH}_4\text{OH}$  represents the base

The base dissociation constant  $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$ .

Making  $[\text{OH}^-]$  the subject,

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

Taking  $\log_{10}$  on both sides,

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

But by defn,  $\text{pOH} = -\log [\text{OH}^-]$  ;  $\log [\text{OH}^-] = -\text{pOH}$ .  
 $\text{pKa} = -\log K_a$  ;  $\log K_a = -\text{pKa}$ .

$$-\text{pOH} ; = -\text{pKa} + \log \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$

$$\text{pOH} = \text{pKa} + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

But  ~~$\text{pOH} + \text{pH} = \text{pKw}$~~  ;  $\text{pH} = \text{pKw} - \text{pOH}$ .  
 $\text{pOH} + \text{pH} = \text{pKw}$ .

$$\text{pKw} - \text{pH} = \text{pKa} + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$-\text{pH} = \text{pKa} - \text{pKw} + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\text{pH} = \text{pKw} - \text{pKa} - \log \frac{[\text{salt}]}{[\text{base}]}$$