1. 0.01 M NaCl and 0.005M $CaCl_2$

$a = \gamma c$

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

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

~~$I = (N$~~

$Na^+, Cl^-, Ca^{2+}, Cl^-$

$$I = \frac{(0.01 \times 1^2) + (001 \times 1^2) + (0.005 \times 2^2) + (0.005 \times 1^2 \times 2)}{2}$$

$I = 0.025$

$\log \gamma_{Na^+} = -Az^2 I^{1/2}$

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

$= -0.08064$

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

$\gamma_{Na^+} = 0.831$

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

$a_{Na^+} = 0.8 \times 0.01$

$a_{Na^+} = 0.00831$

(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; thus current is generated as the cell tries to equalise the concentration across the salt bridge

(b) $Pt | H_2(g) | H^+(aq) // H^+(aq) | H_2(g) | Pt$

Reaction at the anode

$H_2(g) \longrightarrow 2H^+(aq) + 2e$

Reaction at the cathode

$2H^+(aq) + 2e \longrightarrow H_2(g)$

(i) $\Delta G^\theta = -nFE^\theta_{cell}$

- Using the principle of a concentration cell,

~~$E_{cell} = E_{anode} - E_{cathode}$~~

$$E_{cell} = E^\theta - \frac{0.0591}{n} \log\left(\frac{a_{dil}}{a_{conc}}\right)$$

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

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

$E_{cell} = 0.02065\ V$ $\quad 2.065 \times 10^{-2}\ V$

$\Delta G^\theta = -nFE_{cell}$

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

$= -3985.45$

$\Delta G^\theta = -3.98545\ kJ$

(c) $Cl_2(g) / Cl^-(aq)$ $E^\theta = +1.36\ V$

$Cu^{2+}(aq) / Cu(s)$ $E^\theta = +0.34V$

~~$Cu(s) / Cu^{2+}(aq)$~~

Re-writting the half cells as reduction potentials

$Cl_2(g) / Cl^-(aq)$ $E^\theta = +1.36\ V$

$Cu^{2+}(aq) / Cu(s)$ $E^\theta = +0.34V$

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

$= +0.34 - +1.36$

$E_{cell} = -1.02\ V$

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

$= +1.36 - 0.34$

$E_{cell} = +1.02\ V$

(d) dilute buffer of pH 4.70 ; $NaOOCCH_3$ and CH_3COOH

$K_a = 1.75 \times 10^{-5}$

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

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

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

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

	CH_3COOH	$\rightleftharpoons$	CH_3COO^-	$+ H^+$
#	0.1		0	0
	$0.1 - x$		x	x

$$[Salt] = 0.8771\,[Acid]$$

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

$x =$

∴ Using 0.1 M of the acid ;

$$[Salt] = (0.8771 \times 0.1)$$

$$[Salt] = 0.08771\ M$$

$\Rightarrow [CH_3COOH] = 0.1\ M$;

$[CH_3COONa] = 0.08771\ M$

R_{mm} of $CH_3COOH = (12+3+12+32+1) = 60$.

R_{mm} of $CH_3COONa = (12+3+12+32+23) = 82$.

27
32
59
23
82

1 mole of CH_3COOH weighs 60g.

0.1 moles of CH_3COOH weighs (60×0.1)

$= 6g$.

1 mole of CH_3COONa weight 82 g.

0.08771 moles of CH_3COONa weighs 82×0.08771

$= 7.1922\ g$.

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

(ii) $1cm^3$ of 0.1 M HCl + $1000cm^3$ of 0.1 M CH_3COOH / 0.1 CH_3COONa

Initial $pH = pKa + \log \frac{[Salt]}{[Acid]}$

$pH =$

There was no change in pH because a solution of CH_3COOH/ CH_3COONa is an acid buffer.

The small quantities of the acid (H^+) ($1cm^3$) were neutralised by CH_3COO^- from the CH_3COONa, forming the already present CH_3COOH and is unionised $CH_3COO^-_{(aq)} + H^+_{(aq)} \longrightarrow CH_3COOH_{(aq)}$

(iii) 3.5g of NH_4OH,

R.m.m of $NH_4OH = (7+4+16+1) = 28$.

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

$= 0.0625$ moles per litre

R.m.m of $NH_4Cl = (7+4+35.5) = 46.5$

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

$= 0.00575$ moles per litre

$pOH = pKb + \log \frac{[Salt]}{[base]}$.

R $Ka : Kb = 1 : 7.5 \times 10^{-5}$ $Ka = Kb = 1.75 \times 10^{-5}$

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

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

$pOH = 3.0887$

$pH = 14 - 3.0887$

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

2(a) A buffer solution is a solution that resists change in pH when 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 (CH_3COOH and CH_3COONa) or a base buffer like a solution of a weak base and a salt of a strong acid (NH_4OH and NH_4Cl)

(b) Consider a basic buffer such as $NH_4OH \mid NH_4Cl$

$$NH_4OH \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$$

NH_4^+ represents the salt
$NH_4\bar{O}H$ represents the base

The base dissociation constant $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$.

Making $[\bar{O}H]$ the subject,

$$[\bar{O}H] = \frac{K_b [NH_4OH]}{[NH_4^+]}$$

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

$$\log [\bar{O}H] = \log k_a + \log \frac{[NH_4OH]}{[NH_4^+]}$$

But by defn, $pOH = -\log [OH]$; $\log [OH] = -pOH$.
$pk_a = -\log k_a$. ; $\log k_a = -pk_a$.

$$-pOH ; = -pk_a + \log \frac{[NH_4OH]}{[NH_4^+]}.$$

$$pOH = pk_a + \log \frac{[NH_4^+]}{[NH_4OH]}$$

But ~~$pOH + pH = pK_w$~~ ; $pH = pk_w - pOH$.
$pOH + pH = pk_w$.

$$pk_w - pH = pk_a + \log \frac{[salt]}{[base]}.$$

$$-pH = pk_a - pk_w + \log \frac{[salt]}{[base]}.$$

$$pH = pk_w - pk_a - \log \frac{[salt]}{[base]}$$