## HWA CHONG INSTITUTION
## 2008 C2 H2 CHEMISTRY 9746 PRELIMINARY EXAMINATION
## PAPER 3 FREE RESPONSE (SUGGESTED ANSWERS)

**1** **(a)** **(i)** Dynamic equilibrium refers to a state of balance in a reversible reaction or process in which the rates of the forward and reverse processes are equal.

**(ii)** $K_c = \dfrac{[CH_3CO_2C_2H_5][H_2O]}{[CH_3CO_2H][C_2H_5OH]}$

| | $CH_3CO_2H$ | + $C_2H_5OH$ | $\rightleftharpoons$ | $CH_3CO_2C_2H_5$ | + $H_2O$ |
|---|---|---|---|---|---|
| Initial mol: | 0.5 | 1.0 | | 0 | 0 |
| Eqm mol: | 0.5 – 0.42<br>= 0.08 | 1.0 – 0.42<br>= 0.58 | | 0.42 | 0.42 |

$$K_c = \frac{\frac{0.42}{V}\times\frac{0.42}{V}}{\frac{0.08}{V}\times\frac{0.58}{V}} \quad \text{(where V = total volume of mixture)}$$

$= \underline{\mathbf{3.80}}$

**(iii)** NaOH neutralises the ethanoic acid. $[CH_3CO_2H]$ decreases.
By Le Chatelier's Principle, position of equilibrium shifts to the left.

**(iv)** $CH_3COCl$

**(b)** **(i)** $K_a = \dfrac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]}$

No. of moles of KOH used = $\dfrac{30}{1000}\times 0.6$ = 0.0180

No. of moles of $CH_3CO_2H$ = No. of moles of KOH used = 0.0180

$[CH_3CO_2H]$ in vinegar sample = $\dfrac{0.018}{25/1000}$ = 0.720 mol dm$^{-3}$

pH of vinegar sample = 2.44, $\therefore$ $[H^+] = 10^{-2.44} = 3.63 \times 10^{-3}$ mol dm$^{-3}$

$\therefore K_a = \dfrac{(3.63\times10^{-3})^2}{0.72-3.63\times10^{-3}} = 1.84 \times 10^{-5}$ mol dm$^{-3}$ (shown)

**(ii)** Solution A contains unreacted $CH_3CO_2H$ and its salt, $CH_3CO_2^-K^+$. It is a buffer.

When a small amount of acid is added, $CH_3COO^- + H^+ \rightarrow CH_3CO_2H$.

When a small amount of base is added, $CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$.

The small amount of $H^+$ or $OH^-$ added is removed.
Hence, the solution resists changes in pH.

**(iii)** No. of moles of KOH added = $\frac{10}{1000} \times 0.6 = 6.00 \times 10^{-3}$

No. of moles of $CH_3CO_2H$ remaining = $0.0180 - 6.00 \times 10^{-3} = 0.0120$

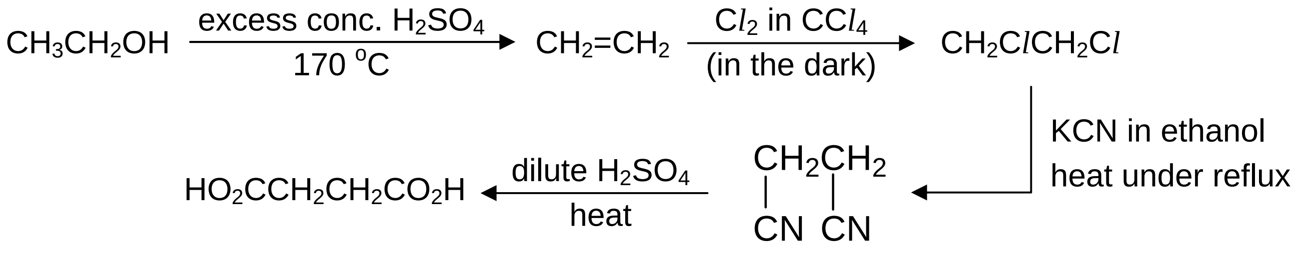
$$K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]} \Rightarrow [H^+] = \frac{K_a\,[CH_3CO_2H]}{[CH_3CO_2^-]} = \frac{1.84 \times 10^{-5} \times \frac{0.012}{V_2}}{\frac{0.006}{V_2}}$$

(where $V_2$ = volume of buffer)

$[H^+] = 3.63 \times 10^{-3}$ mol dm$^{-3}$

pH = $-\lg(3.63 \times 10^{-3})$ = **<u>4.43</u>**

**(c)**



**(d)** Warm each compound with a solution containing $AgNO_3$ in excess $NH_3$(aq) (Tollens' reagent). Only P gives silver mirror.

OR Warm each compound with complex copper(II) ions in alkaline solution (Fehling's solution). Only P gives reddish-brown precipitate.

OR Heat each compound with dilute $H_2SO_4$ and $K_2Cr_2O_7$(aq). Only P turns the orange solution green.

**2** **(a)** **(i)** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

**(ii)** <u>Step 1</u>

Relevant data: $Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$ $E^\ominus = +1.49\ V$

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + H_2O$ $E^\ominus = +1.52\ V$

Overall equation for step 1:

$$MnO_4^- + 8H^+ + 4Mn^{2+} \rightarrow 5Mn^{3+} + 4H_2O$$

$E^\ominus_{cell} = +1.52 - 1.49 = +0.03\ V > 0.\ \therefore$ reaction is feasible

<u>Step 2</u>

Relevant data: $2CO_2 + 2e^- \rightleftharpoons C_2O_4^{2-}$ $E^\ominus = -0.49\ V$

$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$ $E^\ominus = +1.49\ V$

Overall equation for step 2:

$$2Mn^{3+} + C_2O_4^{2-} \rightarrow 2Mn^{2+} + 2CO_2$$

$E^\ominus_{cell} = +1.49 - (-0.49) = +1.98\ V > 0.\ \therefore$ reaction is feasible

**(b)** **(i)** A complex ion is formed by a central metal ion or atom, datively-bonded by surrounding ligands, which can be ions or molecules.

**(ii)** $[Mn(C_2O_4)_3]^{3-}$

**(iii)** In the presence of ligands, d-orbitals (of the transition metal ion) split into 2 energy levels with an energy gap. Electrons are able to be promoted from a lower energy d-orbital to the higher energy one by absorbing energy from the visible spectrum. We observe the complementary colour / the wavelengths that are transmitted.

For Group II metal ions, electronic transition may take place from the ground state to the excited state by absorbing energy outside the visible region, thus compounds are not coloured.

**(c)** **(i)** Solid dissolved in dilute $H_2SO_4$

Withdraw a sample of the solution

Titrate with the $KMnO_4$ solution from a burette until the solution (in conical flask) turns from yellow to orange

Add in a catalyst (eg, $MnSO_4$) or heat the solution, then start the titration

Repeat titration, noting the volume of $KMnO_4$ each time, and stop when values are consistent (to within ±0.10 $cm^3$)

Balanced equation:

$$24H^+ + 3MnO_4^- + 5FeC_2O_4 \rightarrow 3Mn^{2+} + 5Fe^{3+} + 10CO_2 + 12H_2O$$

**(ii)** No. of moles of $KMnO_4$ = $\dfrac{20.50}{1000} \times 0.1 = 2.05 \times 10^{-3}$ mol

No. of moles of $FeC_2O_4$ = $\dfrac{2.05 \times 10^{-3}}{3} \times 5 = 3.42 \times 10^{-3}$ mol

Mass of $FeC_2O_4$ in sample = 0.491 g

∴ percentage purity = **<u>81.8 %</u>**

**3 (a) (i)** Oxidation half-equations to be considered at anode:

| | | | | $E'_{ox}$ / V |
|---|---|---|---|---|
| (1) | $2F^-$ | = | $F_2 + 2e^-$ | –2.87 |
| (2) | $2H_2O$ | = | $O_2 + 4H^+ + 4e^-$ | –1.23 |

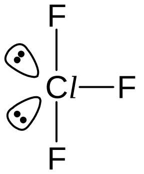
Suppose concentrated NaF is used. Higher concentration of $F^-$ causes position of redox equilibrium (1) to shift to the right, $E_{ox}(F^- / F_2)$ increases.

However, difference between the $E'_{ox}$ values is too large. $E'_{ox}(H_2O / O_2)$ will still be higher than $E'_{ox}(F^- / F_2)$. Hence, $H_2O$ is still oxidised in preference instead of $F^-$. $O_2$ not $F_2$ will be obtained.

**(ii)** Anode : $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
Cathode : $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

**(iii)** No. of moles of $Cl_2$ = $\dfrac{1 \times 10^6}{2 \times 35.5}$ = 14084.5
No. of moles of electrons passed = 14084.5 × 2 = 28169
Q = 96500 × 28169 = $2.718 \times 10^9$ C
$I = \dfrac{2.718 \times 10^9}{24 \times 60 \times 60}$ = **<u>$3.15 \times 10^4$ A</u>**

**(b) (i)** 3 bond pairs, 2 lone pairs around central atom



∴ T-shape molecule

**(ii)** $6H_2O(l) + 4ClF_3(g) \rightarrow 3O_2(g) + 2Cl_2(g) + 12HF(g)$

**(c) (i)** Both HF and HI are simple molecules. HF forms intermolecular hydrogen bonding and that is stronger than the van der Waals' forces (OR dispersion forces) for HI. Therefore, more energy needed for boiling HF.

**(ii)** The reaction between NaCl(s) and concentrated $H_2SO_4$ is:
$NaCl(s) + H_2SO_4(l) \rightarrow HCl(g) + NaHSO_4(s)$

For NaI(s) and conc. $H_2SO_4$:

$NaI(s) + H_2SO_4(l) \rightarrow HI(g) + NaHSO_4(s)$
$2HI(g) + H_2SO_4(l) \rightarrow I_2(g) + SO_2(g) + 2H_2O(l)$
OR $8HI(g) + H_2SO_4(l) \rightarrow 4I_2(g) + H_2S(g) + 4H_2O(l)$

Concentrated $H_2SO_4$ is able to oxidise HI to $I_2$, but not strong enough an oxidising agent to oxidise HC*l*. (OR explain in terms of HI being a better reducing agent than HC*l*.)

HI is so easily oxidised that very little of it remains.

**(iii)** The hot glass rod causes HI to decompose: $2HI(g) \rightarrow H_2(g) + I_2(g)$
The violet vapour is $I_2$.

Reaction involves breaking of H–I bond. H–Br bond is stronger than H–I bond; evidence: bond energy of +366 & +299 kJ mol$^{-1}$ respectively OR justify in terms of size of Br vs I atom.

Heat provided by hot glass rod unable to decompose HBr.

**4 (a)** Boltzmann diagram, correct labels for axes, appropriate shading of areas.

When temperature increases, there is an increase in the fraction of reactant particles with kinetic energy larger than or equal activation energy $E_A$ (refer to shaded areas). Thus, frequency of effective collision increases, reaction rate increases.

**(b) (i)** Order of reaction with respect to a reactant is the power to which its concentration is raised in the rate equation.
The orders of reaction must be found experimentally.

Rate constant (k) is the proportionality constant in the rate equation.
It is a constant at a given temperature.

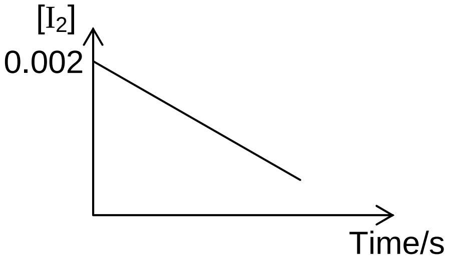
**(ii)** Rate = k $[CH_3COCH_3][H^+]$

**(iii)**

$$k = \frac{\text{Rate}}{[CH_3COCH_3][H^+]} = \frac{1.25\times10^{-6}}{0.05\times0.05} = \underline{\mathbf{5.00\times10^{-4}\ mol^{-1}\ dm^{3}\ s^{-1}}}$$

**(iv)** Catalyst

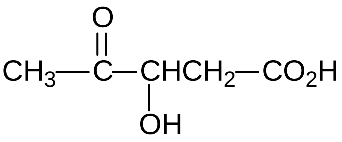
**(v)** linear graph



Logical justification in terms of relative concentrations of reagents & simplification of rate equation

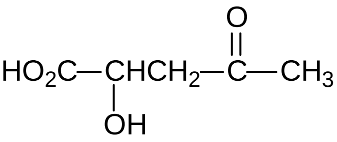
**(c)** **(i)** $I_2$ in NaOH(aq), warm

A:



$$CH_3-\overset{O}{\overset{\|}{C}}-\underset{OH}{\underset{|}{C}}HCH_2-CO_2H$$

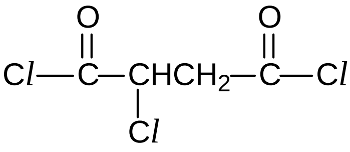
OR



$$HO_2C-\underset{OH}{\underset{|}{C}}HCH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

**(ii)**

D:



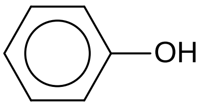
$$Cl-\overset{O}{\overset{\|}{C}}-\underset{Cl}{\underset{|}{C}}HCH_2-\overset{O}{\overset{\|}{C}}-Cl$$

white fumes of HC*l*(g)

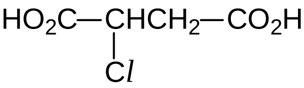
**(iii)** condensation

phenol in NaOH(aq)

**(iv)** F & G:



and



$$HO_2C-\underset{Cl}{\underset{|}{C}}HCH_2-CO_2H$$

**5** **(a)** **(i)** A Bronsted-Lowry base is a proton acceptor

**(ii)**

$$K_b = \frac{[CH_3CH_2CH_2NH_3^+][OH^-]}{[CH_3CH_2CH_2NH_2]}$$

**(iii)**

| | $RNH_2$ | + | $H_2O$ | $\rightleftharpoons$ | $RNH_3^+$ | + | $OH^-$ |
|---|---|---|---|---|---|---|---|
| initial [ ] / mol dm$^{-3}$ | 0.1 | | – | | 0 | | 0 |
| eqm [ ] / mol dm$^{-3}$ | $0.1 - x$ | | – | | $x$ | | $x$ |

$RNH_2$ represents $CH_3CH_2CH_2NH_2$

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

Assume $x << 0.1$; $\therefore\ 4.7 \times 10^{-4} = \frac{x^2}{0.1}$

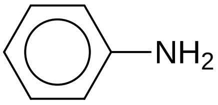
$x = 6.86 \times 10^{-3}$ mol dm$^{-3}$ = $[OH^-]$

$\therefore$ pOH = 2.16, pH = 14 – 2.16 = 11.8

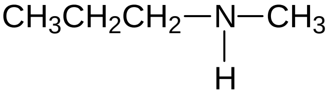
Percentage of $RNH_2$ ionised = $\frac{6.86 \times 10^{-3}}{0.1} \times 100\%$ = **<u>6.86 %</u>**

**(iv)** Indicator: methyl orange
Reason: A weak base-strong acid titration. pH at equivalence point (< 7) is within working pH range of methyl orange OR equivalent

**(b)**



vs $CH_3CH_2CH_2NH_2$



$$CH_3CH_2CH_2-\underset{\displaystyle H}{\underset{|}{N}}-CH_3$$

vs $CH_3CH_2CH_2NH_2$

$RNHR' \quad + \quad H_2O \quad = \quad [RNH_2R']^+ \quad + \quad OH^-$

The strength of the base depends on the availability of the lone pair on the nitrogen atom (the more available the lone pair, the more the above equilibrium lies to the right, the stronger the base)

In phenylamine, the lone pair is delocalised into the benzene ring, making it much less available to accept a proton.
∴ phenylamine is a weaker base than propylamine

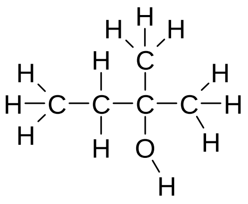
In N-methylpropylamine, there are extra electron-donating alkyl groups on the N-atom, this enhances the availability of the lone pair.
∴ N-methylpropylamine is a stronger base than propylamine

**(c)** **(i)** heat with excess $NH_3$ in a sealed tube

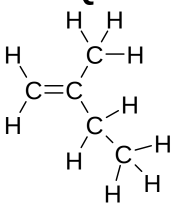
**(ii)** 2 steps:
1. ethanolic (OR alcoholic) KCN, heat under reflux
   product: $CH_3CH_2CN$
2. $LiAlH_4$ in dry ether OR $H_2(g)$, Ni catalyst, heat

**(d)**

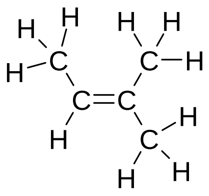
**P**:



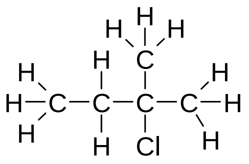
**Q**:



**R**:



**S**:



**Q** and **R** are structural isomers

**Q** or **R** undergoes electrophilic addition with HC*l*(g)

Mechanism: