GCE
Edexcel GCE
Chemistry (8080, 9080)
6246/ 02

## Summer 2005

Mark Scheme (Results)

## IGNORE significant figures throughout

## Section A

1. (a) (i) Points plotted correctly

Curve drawn
(1) (2 marks)
(ii) Tangent drawn and at correct place

Calculation of $\Delta y$ and $\Delta x$
$\Delta y \div \Delta x$ to give slope (ignore sign of slope)
Accuracy of answer: accept anything between 0.01 and 0.02
(b) (i) Rate = slope (or more accurately rate =-slope)

OR
$0.060 \div$ their slope ( $=4$ approximately)
so, when the concentration halves, the rate goes down by a factor of 4 ,
so the reaction is second order (standalone mark)
(1) (3 marks)
(ii) Any two of

I Rate $=k\left[\mathrm{~S}_{2} \mathrm{O}_{8}{ }^{2-}\right]\left[\mathrm{H}_{3} \mathrm{ASO}_{3}\right]$
II Rate $=k\left[\mathrm{~S}_{2} \mathrm{O}_{8}{ }^{2-}\right]^{2}$
III Rate $=k\left[\mathrm{H}_{3} \mathrm{AsO}_{3}\right]^{2}$
[Only penalise the omission of $k$ or wrong type of [ ] once. Rate equations must be marked consequentially on their order in (i)]

Repeat experiment using double / different initial $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]$ / initial $\left[\mathrm{H}_{3} \mathrm{AsO}_{3}\right]$,
but keeping the [other] unchanged
E.g. Any one of the following, as applicable to their two chosen rate equations

If initial rate doubles rate equation $\mathbf{I}$ is correct
If initial rate quadruples with doubling $\left[\mathrm{S}_{2} \mathrm{O}_{8}^{2-}\right.$ ], rate equation II is correct
If initial rate does not alter with doubling/ changing $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right.$ ], rate equation III is correct.
If initial rate quadruples with doubling $\left[\mathrm{H}_{3} \mathrm{AsO}_{3}\right]$, rate equation III is correct
If initial rate does not alter with doubling / changing $\left[\mathrm{H}_{3} \mathrm{AsO}_{3}\right]$, rate equation II is correct.

## SECTION B

2. (a) (i) Step 1
hydrogen bromide / HBr / concentrated hydrobromic acid/ $\mathrm{KBr}+$ concentrated $\mathrm{H}_{2} \mathrm{SO}_{4}$

Step 2
sodium/ potassium hydroxide / NaOH / KOH
then any acid OR its formula OR $\mathrm{H}^{+}$

## Step 3

(potassium) (di)chromate((VI)) and sulphuric acid/ acidified
OR their formulae / Tollens' / Fehling's / Benedict's / acidified (potassium) manganate(VII)
(ii)


(1)

Not enough energy/ heat to break (and cause rotation) the ( $\pi$ / double) bond
(1) (2 marks)
(b) (i) $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{CH}(\mathrm{OH}) \mathrm{COO}^{-}$

OR structural formula drawn.
ALLOW acid
(ii) $\mathrm{CH}_{3} \mathrm{C}(\mathrm{OH})(\mathrm{CN}) \mathrm{CH}_{2} \mathrm{COOH}$

OR structural formula drawn
(c) (i)

(ii) The acid is partially ionised

OR equation $\mathrm{HX}\left(\mathrm{H}_{2} \mathrm{O}\right) \quad \mathrm{H}^{+}\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)+\mathrm{X}$
The salt is totally ionised OR equation $\mathrm{NaX} \rightarrow \mathrm{Na}^{+}+\mathrm{X}^{-}$
When $\mathrm{OH}^{-}$ions are added they react with the large reservoir of HX molecules
$\mathrm{OH}^{-}+\mathrm{HX} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{X}^{-}$(or words), thus removing the added $\mathrm{OH}^{-}$ions
Alternative 3rd and $4^{\text {th }}$ marks:
$\mathrm{OH}^{-}$reacts with $\mathrm{H}^{+}$from ionisation of acid
Causing further ionisation of large reservoir of HX
(1)
(1) (4 marks)
(iii) $K_{a}=\left[H^{+}\right] \times[$salt $]$or $\left[H^{+}\right]=\underline{K}_{a} \times[$ weak acid $]$ or $K_{a}=\left[H^{ \pm}\right][\mathrm{X}]$ [weak acid] [salt] [HX]
$\left[\mathrm{H}^{+}\right]=10^{-\mathrm{pH}}=10^{-3.80}=1.58 \times 10^{-4}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)$
(1)
[salt] $=\mathrm{K}_{\mathrm{a}} \times\left[\right.$ weak acid] $\div\left[\mathrm{H}^{+}\right]=2.63 \times 10^{-4} \times 0.500 \div 1.58 \times 10^{-4}$ $=0.832 / 0.830\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)$
(1)
mass of salt in $1000 \mathrm{~cm}^{3}=0.832$ (or 0.830 ) $\mathrm{mol} \mathrm{dm}^{-3} \times 124 \mathrm{~g} \mathrm{~mol}^{-1}$ $=103(\mathrm{~g})$
mass of salt needed to be added to $100 \mathrm{~cm}^{3}=10.3(\mathrm{~g})$

OR
$\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \frac{\text { [salt }]}{\text { [weak acid] }}$ or $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}-\log \frac{\text { [weak acid] }}{\text { [salt] }}$
$\mathrm{pK}_{\mathrm{a}}=-\log 2.63 \times 10^{-4}=3.58$
log [salt]/[weak acid] $=\mathrm{pH}-\mathrm{pK}_{\mathrm{a}}=3.80-3.58=0.22$
[salt]/ [weak acid] $=10^{0.22}=1.66$
[salt] $=1.66 \times 0.500=0.830\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)$
mass of salt in $1 \mathrm{dm}^{3}=0.830 \mathrm{~mol} \mathrm{dm}^{-3} \times 124 \mathrm{~g} \mathrm{~mol}^{-1}=103(\mathrm{~g})$
mass of salt in $100 \mathrm{~cm}^{3}=10.3(\mathrm{~g})$
(1) (5 marks)

Total 18 marks

3 (a) $\mathrm{K}_{\mathrm{C}}=\frac{\left[\text { ester or its formula] } \times\left[\mathrm{H}_{2} \mathrm{O}\right]^{2}\right.}{\left[\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}\right] \times\left[\mathrm{CH}_{3} \mathrm{COOH}\right]^{2}}$
both molar masses
$\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}+2 \mathrm{CH}_{3} \mathrm{COOH} \rightleftharpoons$ Ester $+2 \mathrm{H}_{2} \mathrm{O}$

## Moles at start

$$
24.8 / 62=0.400 \quad 66.0 / 60=1.10
$$

## Moles at equilibrium

$0.400-0.320=0.080$
$1.10-0.640=0.460$
0.320
0.640

Concentration at equilibrium divide above by $\mathbf{0 . 0 9 0 0} \mathbf{~ d m}^{3}$
$0.080 / 0.0900=0.889$
5.11
3.56
7.11

OR explain why volume cancels in this case
$\mathrm{K}_{\mathrm{c}}=\frac{(3.56) \times(7.11)^{2}}{(0.889) \times(5.11)^{2}} \quad=\frac{180}{23.2}$

$$
=7.76 / 7.8 / 7.74 \text { etc. }
$$

There are no units for $K$
(1) (7 marks)
(b) Amount of ethan-1,2-diol $=1054 / 62=17 \mathrm{~mol}$

Amount of ethene $=\frac{560}{28}=20 \mathrm{~mol}$ or $\frac{1054}{1240} \times 100$
Yield $=17 \times 100 \div 20=85 \%$
(1) (2 marks)
(c) (i) Any acid with two COOH groups or its acid dichloride or its dimethyl ester

Accept HOOCCOOH

(Where $R=$ the hydrocarbon part of their diacid).
for correct ester linkage drawn out
for remainder with continuation
(ii) No, because the acid would hydrolyse / is a catalyst for the hydrolysis of the ester.
OR
Yes, not hydrolysed at low temperature / only hydrolysed at high
(1 mark)
temperature
(d) The ester cannot form (intermolecular) hydrogen bonds but the acid can

Q The ester does not have a $\delta$ thydrogen atom
OR
the acid has $\delta$ thydrogen / polar $\mathrm{OH} / \mathrm{O}$ and H have a large difference in electronegativities
thus less energy / heat is required to separate molecules of the ester
but as ethanoic acid has fewer electrons than propanoic acid,
it has weaker intermolecular instantaneous induced dipole/ induced dipole forces / van der Waals / dispersion / London forces

Allow vdW
4. (a) (i)

cycle with state symbols or as energy level diagram.
labels (in symbols, words or numbers)
$\Delta \mathrm{H}_{\text {soln }}=-\Delta \mathrm{H}_{\text {lat }}+\Delta \mathrm{H}_{\text {hyd }} \mathrm{Ca}^{2+}+2 \times \Delta \mathrm{H}_{\text {hyd }} \mathrm{OH}^{-}$OR values
(1) (4 marks)
$\Delta H_{\text {lat }}=-1650+2 \times(-460)-(-16.2)$

$$
=-2553.8
$$

(ii) Solubility increases down the group
(1)
(if this is wrong, no marks available in this part)
$\Delta H_{\text {hyd }}$ of cation decreases / less exothermic
(1)
but $\Delta \mathrm{H}_{\text {latt }}$ decreases more
therefore $\Delta \mathrm{H}_{\text {sol }}$ gets more exothermic / increases
(1) (4 marks)
(b) (i) Calcium hydroxide will be less soluble at the higher temperature,
(1)
(if this is wrong, no marks available in this part)
because the reaction is exothermic (left to right)
(1)
(an increase in temperature will cause a) decrease in the value of $\mathbf{K}$ (and hence drive the equilibrium to the left).
(1)
(ii) The solubility will decrease,
(1)
(if this is wrong, no marks available in this part)
because the addition of $\mathrm{OH}^{-}$ions will increase $\left[\mathrm{OH}^{-}\right]$/ concentration of $\mathrm{OH}^{-}$
(1)
driving the equilibrium to the left.
(1) (3 marks)
(c) The three gases are: hydrogen bromide bromine OR formulae
sulphur dioxide
The hydrogen chloride / $\mathrm{CaCl}_{2}$ / chloride evolved is not a strong enough reducing agent to reduce / cannot reduce the concentrated sulphuric acid (or sulphuric not a strong enough oxidising agent to ...)
(1) (4 marks)

Total 18 marks TOTAL FOR PAPER: 50 MARKS

