CAMBRIDGE
INTERNATIONAL EXAMINATIONS

JUNE 2002

GCE Advanced Level

MARK SCHEME

MAXIMUM MARK : 60

SYLLABUS/COMPONENT :9701 /4

CHEMISTRY
(STRUCTURED QUESTIONS (A2 CORE))

UNIVERSITY of CAMBRIDGE
Local Examinations Syndicate

1 (a) K_w = $[H^+][OH^-]$ (*or* $[H_3O^+][OH^-]$) [1]

1

(b) $[H^+]$ = $K_w/[OH^-]$ = $1 \times 10^{-14}/0.2$ (= 5×10^{-14} mol dm^{-3}) [1]

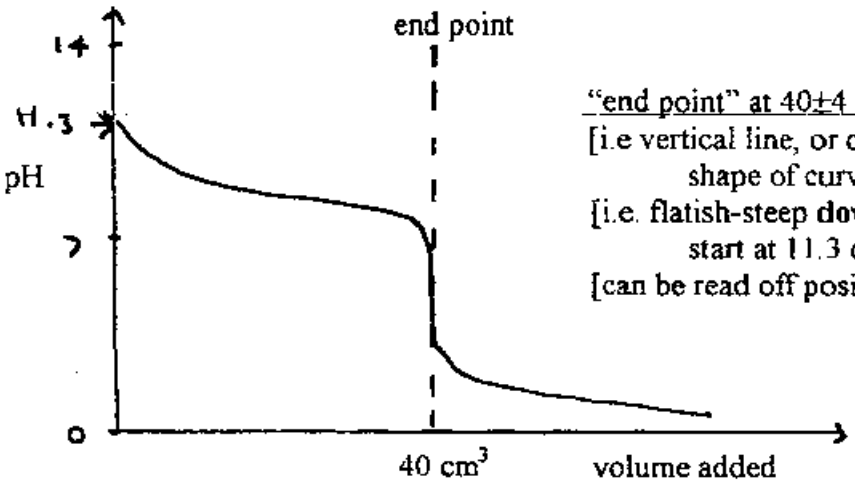
$\therefore$ pH = 13,3 [1]

2

(c) NH_3 is a weak base *or* incompletely ionised [*or* NaOH is strong base] [1]
[*or* an equation showing the equilibrium over to the $NH_3 + H_2O$ side]

1

(d)



"end point" at 40±4 cm^3 [1]
[i.e vertical line, or dotted line]
shape of curve [1]
[i.e. flatish-steep **down**-flatish]
start at 11.3 cm^3 [1]
[can be read off position on axis]

3

(e) methyl orange [1]

1

(f) $NH_3 + H^+ \longrightarrow NH_4^+$ [1]
[*or* NH_3 + HCl *or* H_2SO_4 etc]

$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$ [1]
[*or* NH_4Cl + NaOH etc]

[At least one of the above equations should be shown. Allow a verbal equivalent for the other equation. Correct verbal equivalents for ***both*** *equations are still worth [1] mark only. Any incorrect equation negates the mark for a correct one, but ignore "neutral" equations like* $NH_4Cl \longrightarrow NH_4^+ + Cl^-$*]*

2

total: 10

2 (a)

mix (a solution of) 4-nitrophenyl ethanoate with (a solution of) NaOH
[do NOT allow titration with NaOH] [1]

either [ester] *or* volume of ester solution **is known/fixed/stated** [1]

place in colorimeter (fitted with a suitable filter) (*or* spectrophotometer) [1]

time the reaction / the appearance of yellow colour / the formation of product [1]

measure the **increase in absorbance** over time *or* take time for a **fixed absorbance/colour** to occur [1]

[allow take out samples at known times and titrate with standard acid *for the last two marks]*

5 max 4

(b) (i) from graph (see next page) [N.B. the graph on the question paper has not been reproduced correctly – the shapes of the curves are steeper at the start than the original. Allowance has been made for this in the rate ranges quoted below]

rate (A) = 0.001/18 – 0.001/26 = **3.8 – 5.5 x 10^{-5}** mol dm^{-3} min^{-1}
[*or* **6.3 – 9.0 x 10^{-7}** mol dm^{-3} sec^{-1}] [1]

rate (B) = 0.001/7 – 0.001/12 = **8.3 – 14.3 x 10^{-5}** mol dm^{-3} min^{-1}
[*or* **1.38 – 2.4 x 10^{-7}** mol dm^{-3} sec^{-1}] [1]

correct units for either rate u/c [1]

(ii) order with respect to [OH^-] = 1 u/c [1]

(iii) order with respect to [ester] = 1 u/c [1]

(iv) constant (successive) half lives
(look for evidence of construction lines on graph) [1]

(v) rate = k[OH^-][ester] [allow e.c.f. - expression must fit in with answers for (ii) and (iii)] [1]

(vi) k = rate/([OH^-][ester]) = 4 x 10^{-5}/(0.2 x 1 x 10^{-3})

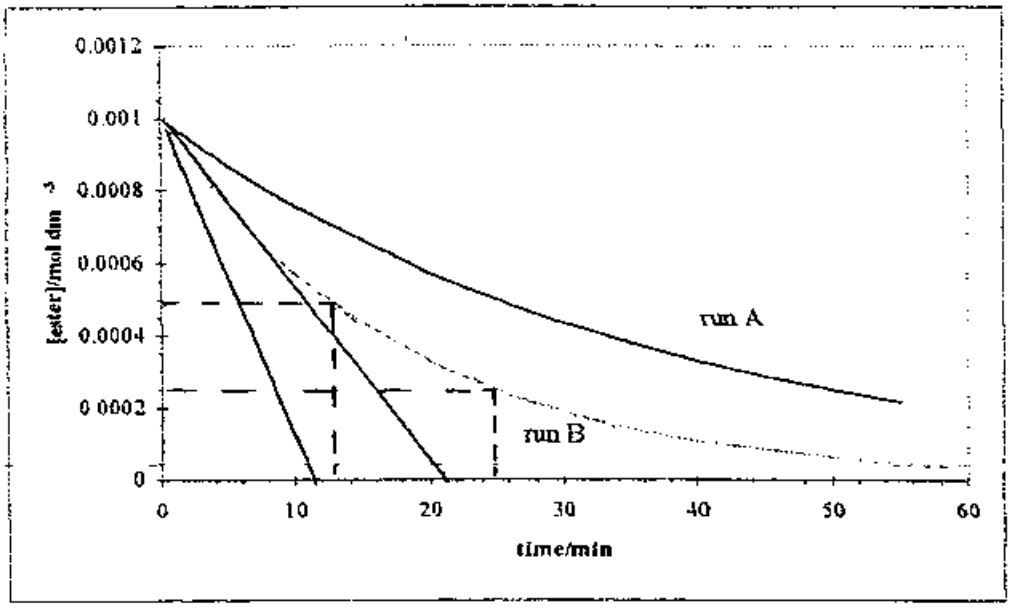
= **0.2 ± 0.05** **mol^{-1} dm^3 min^{-1}** [1] + [1]units
{*or* **0.0033** **mol^{-1} dm^3 sec^{-1}** [1] + [1]}

[allow ecf from part (i) for value of the rate constant and part (v) for rate equation. Units mark is u/c]

9

total: 13

2. Graph for part (b)



3 (a) $Ca(NO_3)_2 \longrightarrow CaO + 2NO_2 + \frac{1}{2}O_2$ [*or* doubled] [1]

1

(b) stabilities **increase** down the group [*or* comparison of two Gp II nitrates] [1]

because as the **ions** [**NOT** atoms]get bigger/have more shells/have smaller charge density u/c [1]

there is **less polarisation** of the nitrate ion/NO_3^-/anion u/c [1]

3

(c) (i) $MNO_3 \longrightarrow MNO_2 + \frac{1}{2}O_2$
[*or* doubled, *or specific Gp* I nitrate] [1]

(ii) 100g loses 10.85g of oxygen this is 10.85/16 = **0.678** moles of O
or 0.339 moles of O_2 per 100g [1]

$\therefore$ 0.678 mol of MNO_3 has a mass of 100g
$\therefore$ 1.0 mol of MNO_3 has a mass of 100/0.678 = 147.5 g

since NO_3 = 62, M = 147.5 – 62 = **85.3** [85 – 85.5] [1]

3

total: 7

4 (a) $[1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6]$ $\mathbf{3d^5}$ [1]

1

(b) (i) *$E^\ominus$ values:* Cl_2/Cl^- **1.36(V)** Br_2/Br^- **1.07(V)** I_2/I^- **0.54(V)** [1]
[$E^\ominus$ values could be read from the answers in (c)]

(Therefore) the halogens are less oxidising from Cl to I u/c [1]

(ii) *$E^\ominus$ values:* Cr^{3+}/Cr^{2+} **-0.41V** Fe^{3+}/Fe^{2+} **0.77V** Co^{3+}/Co^{2+} **1.82V** [1]
[$E^\ominus$ values could be read from the answers in (c). Allow -0.74 for Cr^{3+} and -0.04 for Fe^{3+}]

(Therefore) the 3+ ions become more oxidising from Cr^{3+} to Co^{3+} u/c [1]

4 max 3

(c) (i) no reaction [1]

(ii) $2Co^{3+} + 2Br^- \longrightarrow 2Co^{2+} + Br_2$ [1]
$E^\ominus = 1.82 - 1.07 = \mathbf{0.75V}$ [1]

(iii) $2Cr^{2+} + I_2 \longrightarrow 2Cr^{3+} + 2I^-$ [1]
$E^\ominus = 0.54 - (-0.41) = \mathbf{0.95V}$ [1]

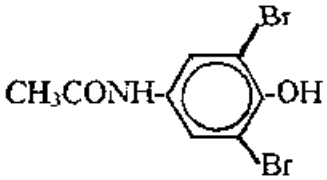
5 max 4

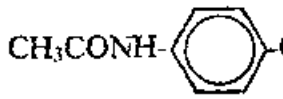
total: 8

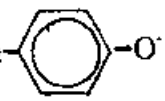
5 (a) amide [NOT peptide] [1]

phenol [NOT hydroxy or alcohol] [1]
[ignore, i.e. do not allow, benzene ring]

2

(b) (i)  (or isomers, ≥ 2 bromines) [1]

(ii)  *[or Na salt – must include charges]* [1]

(iii) $(CH_3CO_2^-)$ +  *[or Na salt – must include charges]* [1]

3

(c) (i) X = CH_3COCl *or* $(CH_3CO)_2O$ [*or* names. NOT ester] [1]

(ii) PCl_5 *or* PCl_3 *or* $SOCl_2$ [*or* names] [1]
[if the anhydride is used, allow P_2O_5, $AlPO_3$, $CH_2{=}C{=}O$, PCl_5 then + CH_3CO_2Na or any other valid method of obtaining anhydrides from acids]
[if X = ester then allow ecf for C_2H_5OH + conc H_2SO_4]

2

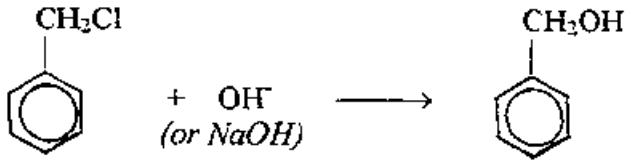
total: 7

6 (a) (i) Al/$AlCl_3$/Fe/$FeCl_3$/I_2 *[(aq), water or light negates this mark]* [1]

(ii) light/hf/uv *or* heat *[(aq) or water negates this mark]* [1]

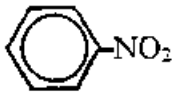
2

(b) (i) A does not react, because the Cl-ring bond is strong/short *or*
Cl is more closely bonded *or* Cl electrons delocalised into the ring [1]

(ii) 

2

total: 4

7 (a) **Y** = 

[1]

reagents for I: conc. HNO_3 + H_2SO_4 [(aq) negates] [1]
[e.c.f.: allow a correct reagent corresponding to the structure of Y.
e.g. if Y = chlorobenzene, allow Cl_2 + Fe etc]

reagents for II: tin/Sn *or* iron/Fe [NOT Zn] + (conc.)HCl
or $LiAlH_4$ [NOT $NaBH_4$] *or* H_2 + Ni [NOT Pt] [1]
[e.c.f.: allow a correct reagent corresponding to the structure of Y.
e.g. if Y = chlorobenzene, allow $NaNH_2$ (NOT NH_3)]

conditions for I: 35°C < T <60°C *[cond. on suitable reagent]* [1]
[e.c.f.: allow the correct conditions corresponding to the structure of Y. e.g. heat]

4

(b) (i) $C_6H_5NH_2 + H^+/HCl/H_2O \longrightarrow C_6H_5NH_3^+$ [+ Cl^-/OH^-] [1]

[product must show ionic N^+]

(ii) **less** basic than NH_3 [1]

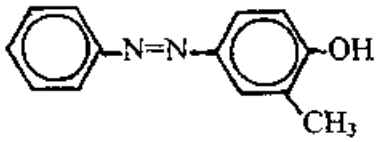
(iii) **lone pair** (on N) is delocalised over the ring [1]
[this mark may be obtained from a diagram - e.g. double dot on N + curly arrow]

3

(c) (i) HNO_2 *or* nitrous (nitric(III)) acid *or* $NaNO_2 + HCl$ [1]

$0°C < T < 10°C$ [1]

(ii) NaOH (aq) *or* dilute *or* in solution (*or* in words) [NOT NH_3(aq)] [1]

(iii)  [1]

4

[CH_3 and OH have to be adjacent, but allow any orientation of N=N w.r.t. OH]

total: 11

No circle in benzene ring: deduct [1] for the whole paper.
Sticks rather than C-H bonds: deduct [1] for the whole paper.