

JUNE 2002

GCE Advanced Level

MARK SCHEME

MAXIMUM MARK : 60

SYLLABUS/COMPONENT :9701 /4
CHEMISTRY
(STRUCTURED QUESTIONS (A2 CORE))



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

1

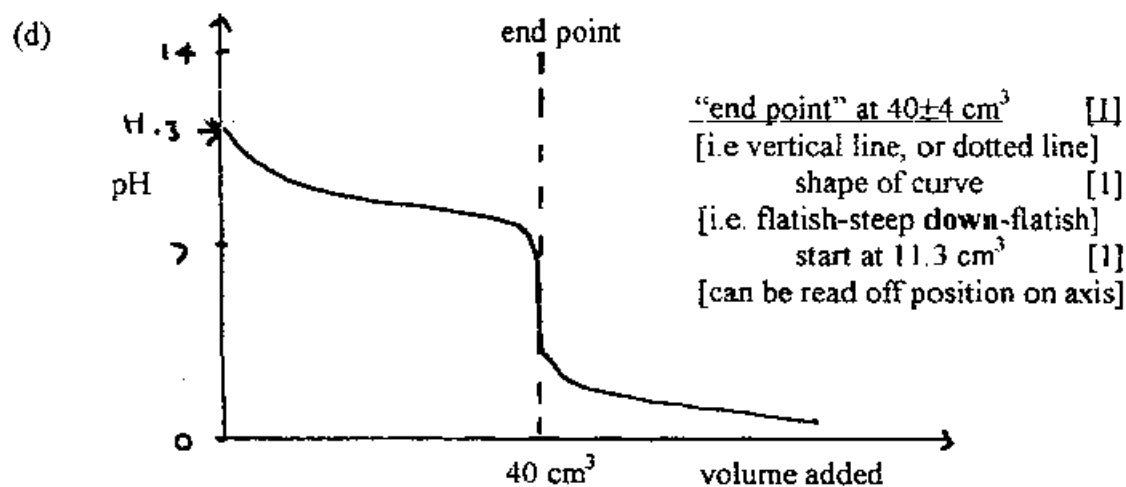
(b) $[H^+] = K_w/[OH^-] = 1 \times 10^{-14}/0.2 (= 5 \times 10^{-14} \text{ mol dm}^{-3})$ [1]

$\therefore \text{pH} = 13.3$ [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 $\text{NH}_3 + \text{H}_2\text{O}$ side]

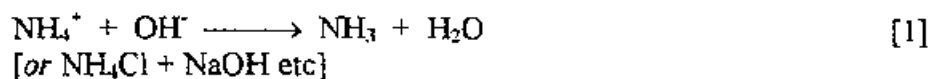
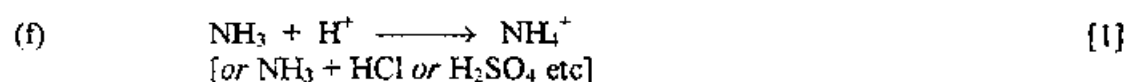
1



3

(e) methyl orange [1]

1



[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 $\text{NH}_4\text{Cl} \longrightarrow \text{NH}_4^+ + \text{Cl}^-$]

2

total: 10

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- 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) = $0.001/18 - 0.001/26 = 3.8 - 5.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}$
[or $6.3 - 9.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ sec}^{-1}$] [1]
- rate (B) = $0.001/7 - 0.001/12 = 8.3 - 14.3 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}$
[or $1.38 - 2.4 \times 10^{-7} \text{ mol dm}^{-3} \text{ sec}^{-1}$] [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 = $k[\text{OH}][\text{ester}]$ [allow e.c.f. - expression must fit in with answers for (ii) and (iii)] [1]

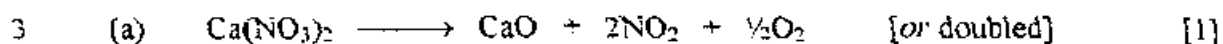
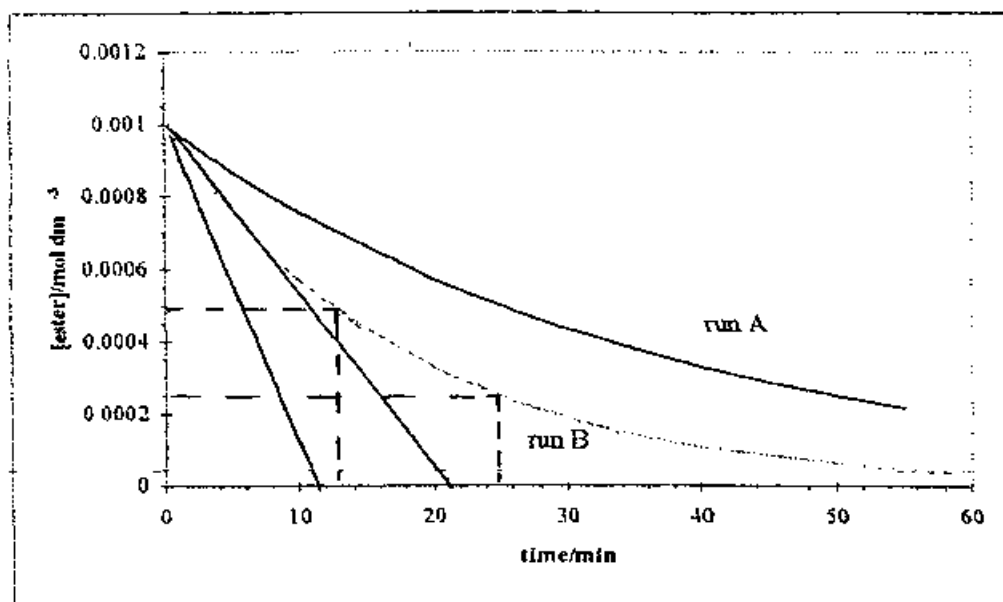
$$\begin{aligned} \text{(vi)} \quad k &= \text{rate}/([\text{OH}][\text{ester}]) = 4 \times 10^{-5}/(0.2 \times 1 \times 10^{-3}) \\ &= 0.2 \pm 0.05 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1} \quad [1] + [1]_{\text{units}} \\ &\quad \text{[or } 0.0033 \text{ mol}^{-1} \text{ dm}^3 \text{ sec}^{-1} \quad [1] + [1]] \end{aligned}$$

[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

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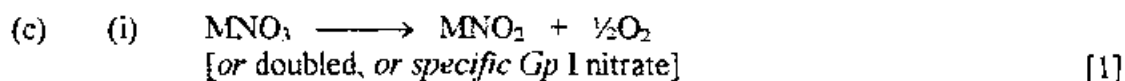
2. Graph for part (b)



(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]



(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]

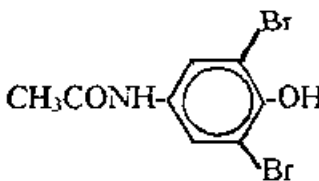
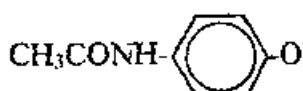
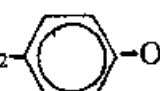
$\therefore$ 0.678 mol of MNO_3 has a mass of 100g

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

since $\text{NO}_3 = 62$, $M = 147.5 - 62 = 85.3$ [85 – 85.5] [1]

3
total: 7

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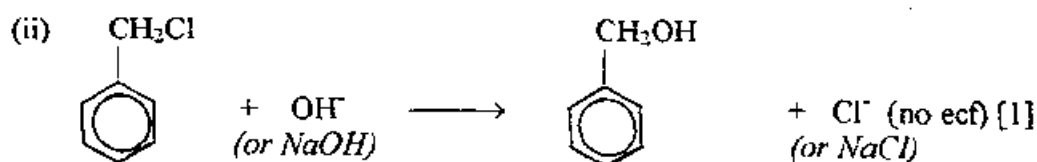
- 4 (a) $[1s^2 2s^2 2p^6 3s^2 3p^6] 3d^5$ [1]
- (b) (i) E° values: Cl_2/Cl^- 1.36(V) Br_2/Br^- 1.07(V) I_2/I^- 0.54(V) [1]
[E° values could be read from the answers in (c)]
- (Therefore) the halogens are less oxidising from Cl to I u/c [1]
- (ii) E° values: Cr^{3+}/Cr^{2+} -0.41V Fe^{3+}/Fe^{2+} 0.77V Co^{3+}/Co^{2+} 1.82V [1]
[E° 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]
 $E^\circ = 1.82 - 1.07 = 0.75V$ [1]
- (iii) $2Cr^{2+} + I_2 \longrightarrow 2Cr^{3+} + 2I^-$ [1]
 $E^\circ = 0.54 - (-0.41) = 0.95V$ [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) $(CH_3CO_2^-) + NH_2-$  [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

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- 6 (a) (i) $\text{Al}/\text{AlCl}_3/\text{Fe}/\text{FeCl}_3/\text{I}_2$ [(aq), water or light negates this mark] [1]
(ii) light/hf/uv or heat [(aq) or water negates this mark] [1]

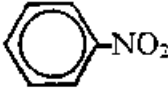
2

- (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]



2

total: 4

- 7 (a) $\text{Y} =$  [1]

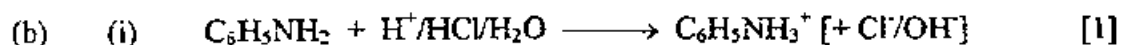
reagents for I: $\text{conc. HNO}_3 + \text{H}_2\text{SO}_4$ [(aq) negates] [1]
[e.c.f.: allow a correct reagent corresponding to the structure of Y.
e.g. if Y = chlorobenzene, allow $\text{Cl}_2 + \text{Fe}$ etc]

reagents for II: $\text{tin/Sn or iron/Fe [NOT Zn] + (conc.)HCl}$
or LiAlH_4 [NOT NaBH_4] or $\text{H}_2 + \text{Ni}$ [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: $35^\circ\text{C} < \text{T} < 60^\circ\text{C}$ [cond. on suitable reagent] [1]
[e.c.f.: allow the correct conditions corresponding to the structure of Y. e.g. heat]

4

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[product must show ionic N^+]

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

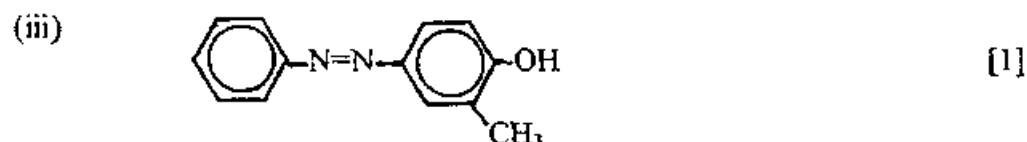
(iii) **lone pair** (on N) is delocalised over the ring [1]
[this mark may be obtained from a diagram – e.g. double dot on N + curly arrow]

3

(c) (i) HNO_2 or nitrous (nitric(III)) acid or $\text{NaNO}_2 + \text{HCl}$ [1]

$0^\circ\text{C} < T < 10^\circ\text{C}$ [1]

(ii) NaOH (aq) or dilute or in solution (or in words) [NOT $\text{NH}_3(\text{aq})$] [1]



4

[CH₃ and OH have to be adjacent, but allow any orientation of $\text{N}=\text{N}$ 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.