

**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

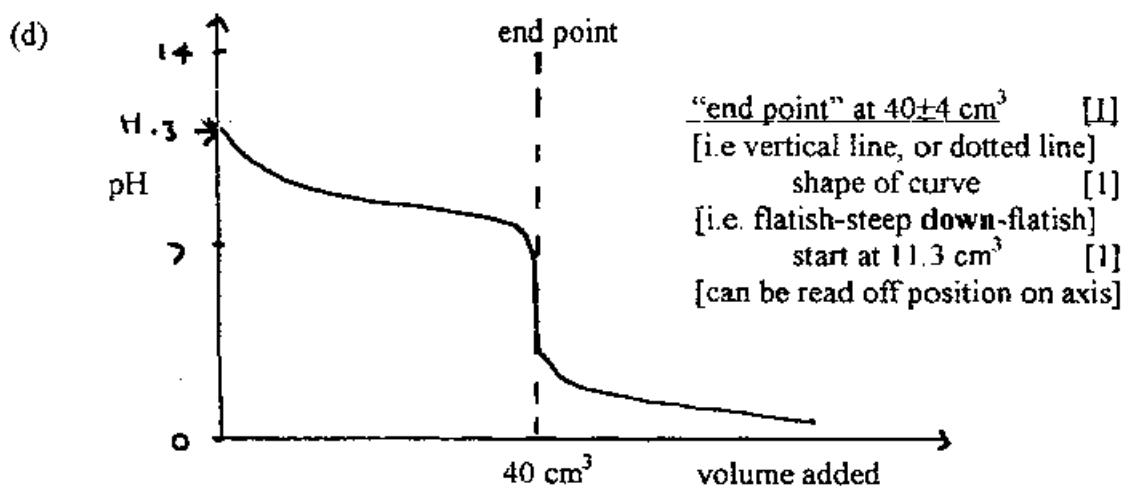
(b)  $[H^+] = K_w/[OH^-] = 1 \times 10^{-14}/0.2 (= 5 \times 10^{-14} \text{ mol dm}^{-3})$  [1]

$\therefore \text{pH} = 13.3$  [1]

2

(c)  $\text{NH}_3$  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]

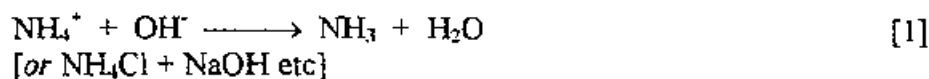
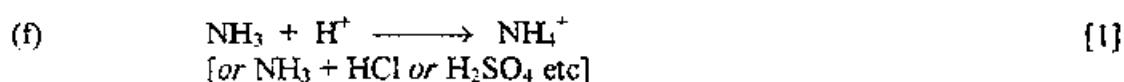
1



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]*

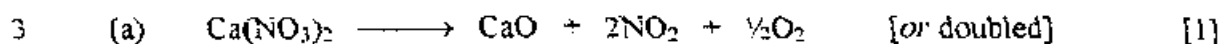
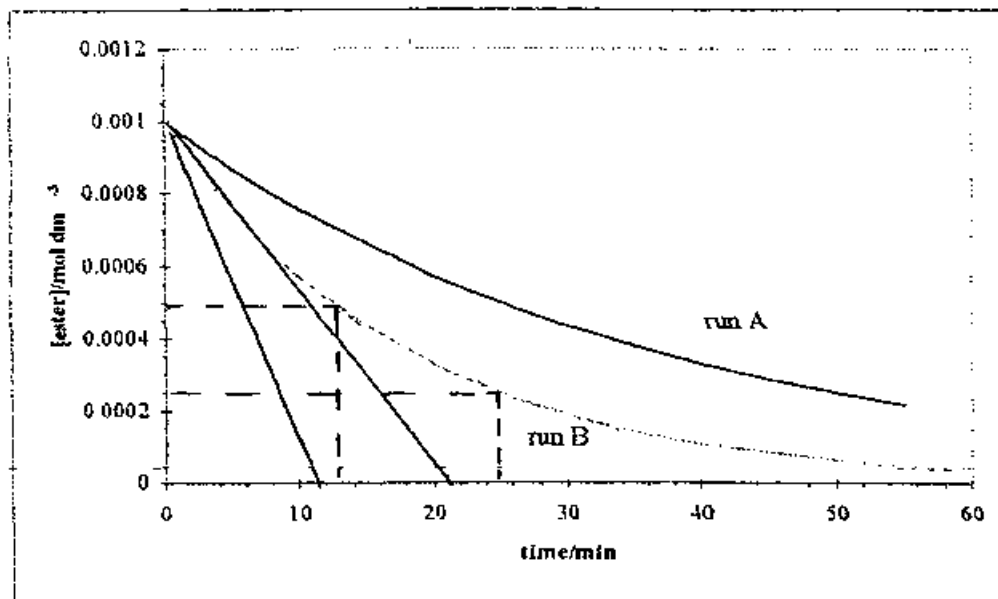
**5 max 4**

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

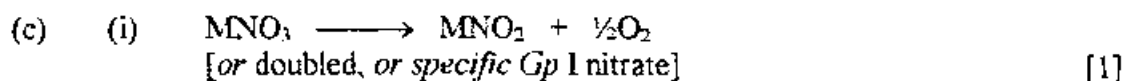
2. Graph for part (b)



(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/ $\text{NO}_3^-$ /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  $\text{O}_2$  per 100g [1]

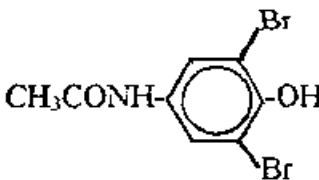
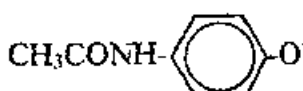
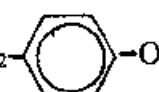
$\therefore$  0.678 mol of  $\text{MNO}_3$  has a mass of 100g

$\therefore$  1.0 mol of  $\text{MNO}_3$  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]

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- 4 (a)  $[1s^2 2s^2 2p^6 3s^2 3p^6] 3d^5$  [1]
- (b) (i)  $E^\circ$  values:  $Cl_2/Cl^-$  1.36(V)  $Br_2/Br^-$  1.07(V)  $I_2/I^-$  0.54(V) [1]  
*[ $E^\circ$  values could be read from the answers in (c)]*  
 (Therefore) the halogens are less oxidising from Cl to I u/c [1]
- (ii)  $E^\circ$  values:  $Cr^{3+}/Cr^{2+}$  -0.41V  $Fe^{3+}/Fe^{2+}$  0.77V  $Co^{3+}/Co^{2+}$  1.82V [1]  
*[ $E^\circ$  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]*
- (b) (i)  (or isomers,  $\geq 2$  bromines) [1]
- (ii)  [or Na salt - must include charges] [1]
- (iii)  $(CH_3CO_2^-) + NH_2-$   [or Na salt - must include charges] [1]
- (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  $C_2H_5OH + conc H_2SO_4$ ]*

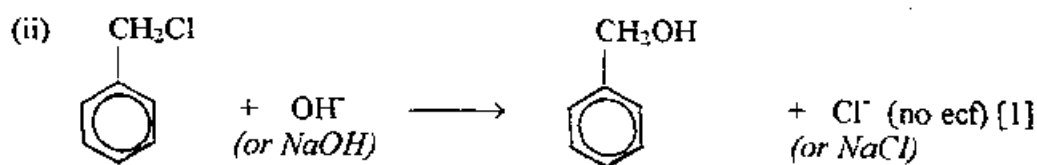
**2**  
**total: 7**

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- 6 (a) (i) Al/AlCl<sub>3</sub>/Fe/FeCl<sub>3</sub>/I<sub>2</sub> [(aq), water or light negates this mark] [1]  
(ii) light/hf/uv or heat [(aq) or water negates this mark] [1]

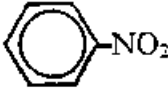
2

- (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) Y =  [1]

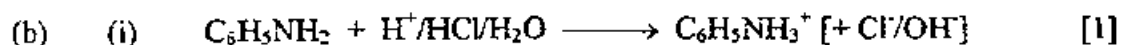
reagents for I: conc. HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> [(aq) negates] [1]  
[e.c.f.: allow a correct reagent corresponding to the structure of Y.  
e.g. if Y = chlorobenzene, allow Cl<sub>2</sub> + Fe etc]

reagents for II: tin/Sn or iron/Fe [NOT Zn] + (conc.)HCl [1]  
or LiAlH<sub>4</sub> [NOT NaBH<sub>4</sub>] or H<sub>2</sub> + Ni [NOT Pt]  
[e.c.f.: allow a correct reagent corresponding to the structure of Y.  
e.g. if Y = chlorobenzene, allow NaNH<sub>2</sub> (NOT NH<sub>3</sub>)]

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

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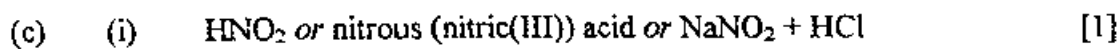


*[product must show ionic  $\text{N}^+$ ]*

(ii) **less basic than  $\text{NH}_3$**  [1]

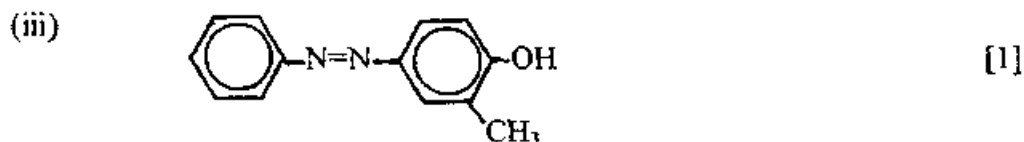
(iii) **lone pair (on N) is delocalised over the ring** [1]  
*[this mark may be obtained from a diagram - e.g. double dot on N + curly arrow]*

3



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

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



4

*[ $\text{CH}_3$  and  $\text{OH}$  have to be adjacent, but allow any orientation of  $\text{N}=\text{N}$  w.r.t.  $\text{OH}$ ]*

**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.*