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<td>CHEMISTRY (STRUCTURED QUESTIONS (A2 CORE))</td>
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1. (a) \[ K_w = [H^+][OH^-] \quad \text{or} \quad [H_3O^+][OH^-] \] \[ \quad \text{[1]} \]

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

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

(c) \( \text{NH}_3 \) is a weak base \ or \ incompletely ionised \( \text{or} \) \( \text{NaOH} \) is strong base \ [or an equation showing the equilibrium over to the \( \text{NH}_3 + \text{H}_2\text{O} \) side] \[ \quad \text{[1]} \]

(d) \[ \text{end point} \quad \text{at} \ 40\pm4 \ 	ext{cm}^3 \] \[ \text{[i.e. vertical line, or dotted line]} \]

\[ \text{shape of curve} \] \[ \text{[i.e. flatish-steep down-flatish]} \]

\[ \text{start at} \ 1\ 1.3 \ 	ext{cm}^3 \] \[ \text{[can be read off position on axis]} \]

2. (e) \text{methyl orange} \[ \quad \text{[1]} \]

(f) \[ \text{NH}_3 + H^+ \quad \rightarrow \quad \text{NH}_4^+ \] \[ \text{[or NH}_3 + \text{HCl or H}_2\text{SO}_4 \text{ etc]}} \[ \quad \text{[1]} \]

\[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} \] \[ \text{[or NH}_3\text{Cl + NaOH etc]} \[ \quad \text{[1]} \]

\[ \text{At least one of the above equations should be shown. Allow a verbal equivalent for the other equation. Correct verbal equivalents for both equations are still worth [1] mark only. Any incorrect equation negates the mark for a correct one, but ignore "neutral" equations like NH}_3\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^- \]

3. total: 10
2. (a) mix (a solution of) 4-nitrophenyl ethanolate 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 coloorimeter (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 10⁻³ 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 w/c [1]

(ii) order with respect to [OH⁻] = 1 w/c [1]

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

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

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

(vi) \[
k = \frac{\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] \quad \text{[or 0.0033 \text{ mol}^{-1} \text{ dm}^3 \text{ sec}^{-1} \quad [1] \quad \text{units}]

\]

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

total: 13
2. Graph for part (b)

3  (a)  \( \text{Ca(NO}_3\text{)}_2 \rightarrow \text{CaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \) \([\text{or doubled}]\)  [1]

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

because as the ions \([\text{NOT atoms}]\) get bigger/have more shells/have smaller charge density \(\text{u/c} \) [1]

there is **less polarisation** of the nitrate ion/\(\text{NO}_3^-\)/anion \(\text{u/c} \) [1]

3  (c)  (i)  \( \text{MNO}_1 \rightarrow \text{MNO}_2 + \frac{1}{2}\text{O}_2 \) \([\text{or doubled, or specific Gp I nitrate}]\)  [1]

(ii) 100g loses 10.85g of oxygen, this is \(10.85/16 = 0.678\) moles of \(\text{O}_2\) or \(0.339\) moles of \(\text{O}_2\) per 100g \(\text{[1]}\)

\[ \therefore 0.678 \text{ mol of MNO}_1 \text{ has a mass of 100g} \]

\[ \therefore 1.0 \text{ mol of MNO}_3 \text{ has a mass of } 100/0.678 = 147.5 \text{ g} \]

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

**total: 7**
4 (a) \[ \text{[}3s^2 3p^6 \text{]} 3d^5 \] [1]

(b) (i) \( E^0 \) values: Cl\(_2\)/Cl\(^-\) 1.36(V) \( \text{Br}_2/\text{Br}^- \) 1.07(V) \( \text{I}_2/\text{I}^- \) 0.54(V) [1]

(\( E^0 \) values could be read from the answers in (c)]

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

(ii) \( E^0 \) values: \( \text{Cr}^{3+}/\text{Cr}^{2+} \) -0.41V \( \text{Fe}^{3+}/\text{Fe}^{2+} \) 0.77V \( \text{Co}^{3+}/\text{Co}^{2+} \) 1.82V [1]

(\( E^0 \) values could be read from the answers in (c). Allow -0.74 for \( \text{Cr}^{3+} \) and -0.04 for \( \text{Fe}^{3+} \))

(Therefore) the 3+ ions become more oxidising from \( \text{Cr}^{3+} \) to \( \text{Co}^{3+} \) u/c [1] 4 max 3

(c) (i) no reaction [1]

(ii) \[ 2\text{Co}^{3+} + 2\text{Br}^- \rightarrow 2\text{Co}^{2+} + \text{Br}_2 \] \( E^0 = 1.82 - 1.07 = 0.75 \text{V} \) [1]

(iii) \[ 2\text{Cr}^{2+} + \text{I}_2 \rightarrow 2\text{Cr}^{3+} + 2\text{I}^- \] \( E^0 = 0.54 - (-0.41) = 0.95 \text{V} \) [1] 5 max 4 total: 8

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

phenol [NOT hydroxy or alcohol]
[ignore, i.e. do not allow, benzene ring] [1] 2

(b) (i) \[
\begin{array}{c}
\text{Br} \\
\text{CH}_3\text{CONH-}\\
\text{Br} \\
\text{OH}
\end{array}
\] (or isomers, ≥ 2 bromines) [1]

(ii) \[
\begin{array}{c}
\text{CH}_3\text{CONH} \\
\text{Br}
\end{array}
\] [or Na salt - must include charges] [1]

(iii) \[
\begin{array}{c}
\text{CH}_3\text{CO}_2^- \\
\text{OH}
\end{array}
\] [or Na salt - must include charges] [1] 3

(c) (i) \( X = \text{CH}_3\text{COCl} \) or \( \text{(CH}_3\text{CO})_2\text{O} \) [or names, NOT ester] [1]

(ii) \( \text{PCl}_3 \) or \( \text{PCl}_2 \) or \( \text{SOCl}_2 \) [or names] [1]

[if the anhydride is used, allow \( \text{P}_2\text{O}_5, \text{AlPO}_4, \text{CH}_2=\text{C}=\text{O}, \text{PCl}_3 \) then plus \( \text{CH}_3\text{CO}_2\text{Na} \) or any other valid method of obtaining anhydrides from acids]

[if \( X = \text{ester} \) then allow ecf for \( \text{CH}_3\text{OH} + \text{conc H}_2\text{SO}_4 \)]

2 total: 7
6 (a) (i) Al/AlCl₃/Fe/FeCl₃/H₂

\[ (aq) \text{ or light negates this mark} \] [1]

(ii) light/ultraviolet light or heat

\[ (aq) \text{ or water negates this mark} \] [1]

(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) \[ \text{CH₃Cl} \quad \text{CH₃OH} \]

\[
\text{+ OH}^- \text{ (or NaOH)} \quad \text{+ Cl}^- \text{ (no cef)} [1]
\]

\[
\text{or NaCl}
\]

total: 4

7 (a) \[ \text{Y = } \text{NO}_2 \] [1]

reagents for I: conc. HNO₃ + H₂SO₄

\[ (aq) \text{ negates} \] [1]

[e.g. if Y = chlorobenzene, allow Cl₂ + Fe etc]

reagents for II: tin/Sn or iron/Fe [NOT Zn] + (conc.)HCl

or LiAlH₄ [NOT NaBH₄] or H₂ + Ni [NOT Pt] [1]

[e.g. if Y = chlorobenzene, allow NaBH₄ [NOT NH₄]]

conditions for I: \[ 35°C < T < 60°C \]

\[ \text{cond. on suitable reagent} \] [1]

[e.g. if Y = chlorobenzene, allow NaBH₄]
(b) (i) \( \text{C}_6\text{H}_5\text{NH}_2 + \text{H}^+ / \text{HCl} / \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{NH}_3^+ [\text{+ Cl}^- / \text{OH}^-] \) [1]

\( \text{product must show ionic } \text{N}^- \)

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

(iii) lone pair (on N) is delocalised over the ring [1]

\( \text{this mark may be obtained from a diagram - e.g. double dot on N + curly arrow} \)

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

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

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

(iii) \[ \text{[CH}_3\text{ and OH have to be adjacent, but allow any orientation of N=N w.r.t. OH]} \] [1]

\( \text{total: 11} \)

No circle in benzene ring: deduct [1] for the whole paper.