Cambridge International Examinations
Cambridge Pre-U Certificate

CHEMISTRY **9791/03**

Paper 3 Part B Written **May/June 2017**

MARK SCHEME

Maximum Mark: 100

Published

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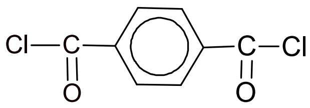
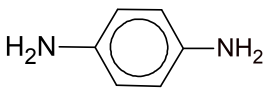
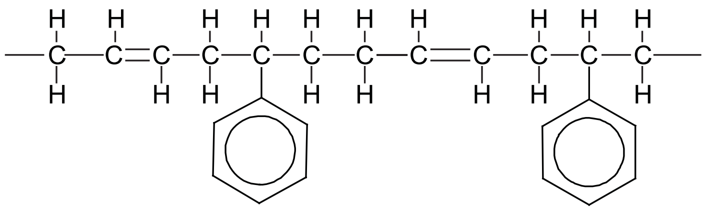
Question	Answer	Marks
1(a)(i)	Minimum of two correct half-life calculations, ca. 1100 s (1) Constant half-life so first order (1)	**2**
1(a)(ii)	Rate = $k[N_2O_5]$	**1**
1(a)(iii)	Values from graph used in $\ln(C_0/C_t) = kt$ e.g. $\ln(2.35/0.5) = k \times 2500$ (1) Rearrange for k e.g. $k = \{\ln(2.35/0.5)\}/2500 = 1.548/2500$ (1) Correct answer with units = $6.190 \times 10^{-4}\ s^{-1}$ (1)	**3**
1(a)(iv)	Slowest step (in the mechanism)	**1**
1(a)(v)	Adds up all 3 steps and show that they cancel to the overall equation	**1**
1(b)(i)	1st order	**1**
1(b)(ii)	2nd order	**1**
1(b)(iii)	Working using any other set of data. e.g. using experiment 3 = $9.22 \times 10^{-7} \times (5/3)^2$ (1) = 2.561×10^{-6} ($mol\ dm^{-3}\ s^{-1}$) (1)	**2**
1(b)(iv)	Rate = $k[H_2][NO]^2$	**1**
1(b)(v)	$k = rate/([H_2][NO]^2)$ e.g. using experiment 3 = $9.22 \times 10^{-7}/(0.1 \times 0.3^2)$ 1.024×10^{-4} (1) $dm^6\ mol^{-2}\ s^{-1}$ (1)	**2**

Question	Answer	Marks
2(a)(i)	Proton / H^+ donor	**1**
2(a)(ii)	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$ (1) acid1 base2 acid2 base1 (1)	**2**
2(b)(i)	50 cm^3 0.002 mol dm^{-3} HCl in total volume of 100 cm^3 = 0.001 mol dm^{-3} (1) pH = $-\log_{10}[H^+]$ so $[H^+] = 10^{-pH} = 10^{-3}$ = 0.001 mol dm^{-3} (1) i.e. HCl fully dissociated so strong (1)	**3**
2(b)(ii)	$(K_a =)\dfrac{[H_3O^+][F^-]}{[HF]}$	**1**
2(b)(iii)	$[HF] = [F^-]$ so pH = pK_a (1) so $\mathbf{K_a} = [H^+] = 10^{-3.2} = 6.31 \times 10^{-4}$ mol dm^{-3} (1) H^+ reacts with F^- / the $HF \rightleftharpoons H^+ + F^-$ equilibrium shifts left (1) (so) approx. constant $[H^+]$ (1)	**4**
2(b)(iv)	$6.31 \times 10^{-4} = [H^+]^2/0.1$ $[H^+] = \sqrt{6.31 \times 10^{-4} \times 0.1} = 7.944 \times 10^{-3}$ (1) pH = $-\log[H^+] = -\log 7.944 \times 10^{-3} = 2.10$ (1)	**2**
2(b)(v)	H–F stronger bond than H–Cl AND HF is a weaker acid than HCl (1) so H–F dissociates less (1)	**2**

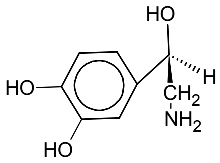
Question	Answer	Marks
2(c)(i)	pH at start = 2.1 (1) Steep up then levelling off (1) pH and volume at half equivalence (3.2 and 15 cm^3) (1) Equivalence point at 30 cm^3 and vertical for at least one square (1) Levelling off at pH 11–13 (1)	**5**
2(c)(ii)	Phenol red (1) pK_a corresponds to pH at equivalence point (1)	**2**

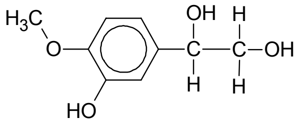
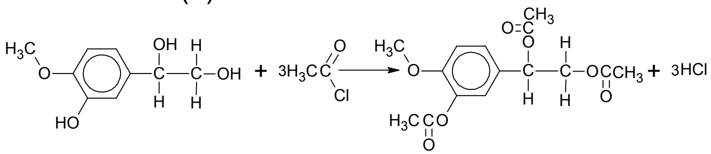
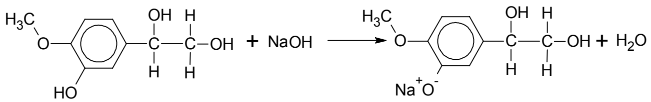
Question	Answer	Marks
3(a)(i)	**A** = condensation (1) **B** = addition (1) **C** = condensation (1)	**3**
3(a)(ii)	**A** = amide (1) **C** = glycosidic (1)	**2**
3(a)(iii)	 (1)  (1)	**2**
3(a)(iv)	 2 benzene rings only attached to the main carbon chain (1) Rest correct (1)	**2**

Question	Answer	Marks
3(b)(i)	No change in functional group level (1) Hydrolysis (1) $H^+(aq)$ / aqueous acid (1) FGL of COO carbon falls / changes from carboxylic to alcohol level / from 3 to 1 (1) Reduction (1) $LiAlH_4$ (1)	**6**
3(b)(ii)	Acidified dichromate / H^+ with $Cr_2O_7^{2-}$	**1**
3(b)(iii)	$C_2H_5OH + 2[O] \rightarrow CH_3CO_2H + H_2O$ Correct species (1) Balancing (1)	**2**
3(b)(iv)	Reaction 3: Reflux (1) Reaction 4: (Immediate **/** continuous) distillation (1) Reflux ensures aldehyde intermediate remains in reaction mixture **or** distillation removes aldehyde to avoid further oxidation (1)	**3**

Question	Answer	Marks
4(a)(i)	Increasing anion size F to I / down the group (1) Cu^{2+} is smaller than Cu^{+} (1) Greater charge of Cu^{2+} than Cu^{+} (1) (so) increased attraction linked to more exothermic lattice energies (1)	**4**
4(a)(ii)	Calculation of predicted value based on ionic model assumes perfect ionic character / spherical ions (1) Bromide more polarisable than fluoride (1) Partial covalency greater in bromide (1)	**3**
4(b)(i)	$E^{\ominus} = +\ 0.51\ \text{V}$ Sign (conditional on answer) (1) Value (1)	**2**
4(b)(ii)	Blue (solution) (of Cu^{2+}) (1) Brown solid (of copper metal) (1)	**2**
4(b)(iii)	$E^{\ominus}_{cell}$ (298 K) = 0.87 – 0.54 = +0.33 V (1) $\Delta G = -nFE^{\ominus}_{cell} = -1 \times 9.65 \times 10^{4} \times 0.33 = -31845$ (1) $-31845 = -(8.31)(298)\ \ln K_c$; $K_c = 3.84 \times 10^{5}$ (1)	**3**
4(b)(iv)	White solid (of CuI) OR brown solution (of I_2)	**1**

Question	Answer	Marks
4(c)	**W** = CuO (1) **X** = Cu_2O (1) **Y** = $Cu(H_2O)_6^{2+}$ (1) **Z** = $CuCl_4^{2-}$ (1) $CuCO_3 \rightarrow CuO + CO_2$ (1) $4CuO \rightarrow 2Cu_2O + O_2$ (1) $CuO + H_2SO_4 + 5H_2O \rightarrow Cu(H_2O)_6^{2+} + SO_4^{2-}$ (1) $2Cu^{2+} + 4I^{-} \rightarrow 2CuI + I_2$ (1) $Cu(H_2O)_6^{2+} + 4Cl^{-} \rightarrow CuCl_4^{2-} + 6H_2O$ (1) **Y** = octahedral AND **Z** = tetrahedral (1)	**10**

Question	Answer	Marks
5(a)(i)	rotates (plane) polarised light anticlockwise	**1**
5(a)(ii)	 (1) Assigns correct priority order OH =1; CH_2NH_2 = 2; ring = 3; H = 4 (1) With lowest priority group facing away / into page remaining groups rank in decreasing order in clockwise direction (1)	**3**
5(b)(i)	(Nucleus has) spin	**1**
5(b)(ii)	Electrons create shielding (1) More shielding = signal shifts upfield / lower values (of delta) / to the right (1)	**2**

Question	Answer	Marks
5(c)	 Fits molecular formula and tri-substituted ring (1) Rest correct (1)  Phenol OH reacts to form correct ester (1) Alcohol OHs react to form correct esters (1)  (1) Signals **A** to **C** singlets due to 3 O–H protons (1) Signal **D** due to CH proton in $CHOHCH_2OH$ group (1) Signal **E** due to CH_2 protons in $CHOHCH_2OH$ group (1) Signal **F** due to CH_3 protons on CH_3 group (1) Signal **D** is a triplet because split by 2 neighbouring protons AND Signal **E** is a doublet because split by one neighbouring proton AND Signal **F** is a singlet because there are no neighbouring protons (1)	**10**