## NJC SH2 H2 Chemistry Preliminary Exam Paper 3 Mark Scheme

- **1 (a) (i)**  $4MnO_4^- + 5CH_3CH_2OH + 12H^+ \rightarrow 4Mn^{2+} + 5CH_3COOH + 11H_2O$ 
  - (ii) No. of moles of  $KMnO_4 = 0.20 \times 17.80/1000 = 0.00356 \text{ mol}$ No. of moles of ethanol =  $0.00356 \times 5/4 = 0.00445 \text{ mol}$ Mass of ethanol =  $0.00445 \times 46 = 0.205 \text{ g}$
  - (iii) Volume of ethanol in beer sample =  $0.205/0.789 = 0.259 \text{ cm}^3$ Alcohol content of beer =  $0.259/10 \times 100\% = 2.59\%$
  - (iv) Some ethanol might have evaporated as it is volatile.Or some ethanol might be oxidised by air.
  - (v) End-point is reached when the solution first turn pink.
  - (vi) As the carbon chain length increases, the temporary dipole-induced dipole interactions in alcohol become stronger and the energy released from the formation of hydrogen bonding between alcohol and water is insufficient to overcome the stronger intermolecular forces of attraction between the alcohol molecules.
  - (b) (i)  $C_6H_{12}O_6 \rightarrow 2CO_2 + 2CH_3CH_2OH$ 
    - (ii) Add I<sub>2</sub>(aq) and NaOH(aq) to glucose and ethanol in separate test-tubes, warm the mixture.

Glucose: No yellow precipitate formed. Ethanol: Yellow precipitate is formed.

Equation:  $CH_3CH_2OH + 4I^- + 6OH^- \rightarrow HCO_2^- + CHI_3 + 5I^- + 5H_2O$ 

(c) (i) Nucleophilic substitution





Reagents and conditions of electrophilic addition of water to alkene can be replaced with conc. $H_2SO_4$ , followed by  $H_2O$ ; warm

- 2 (a) (i)  $MgO + SO_2 \rightarrow MgSO_3$ Neutralisation or acid-base reaction
  - (ii) <u>Yes</u>, since <u> $Al_2O_3$  is amphoteric</u> in nature, so can <u>react with an acidic oxide</u> such as  $SO_2$  to remove it.
  - (b) (i) MgO in water: pH 8 9
    - <u>Weakly alkaline</u> solution formed as <u>Mg(OH)<sub>2</sub> is only slightly soluble in water</u> (due to strong ionic bonds between Mg<sup>2+</sup> and OH<sup>-</sup> ions)

Al<sub>2</sub>O<sub>3</sub> in water: pH 7

- Solution is neutral as  $Al_2O_3$  is insoluble in water (due to strong ionic bonds between  $Al^{3+}$  and  $O^{2-}$  ions).

SO<sub>2</sub> in water: pH 2 - 3

Solution is acidic due to the formation of weak acid H<sub>2</sub>SO<sub>3</sub>(aq)

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$
  
 $H_2SO_3 \implies H^+ + HSO_3^-$ 

- (ii)  $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2 Na[Al(OH)_4]$
- (c) (i) Step 1:  $Br_2$  and anhydrous A/Br<sub>3</sub> catalyst Step 2:  $Al_2O_3$ ; heat

(ii) Electrophilic substitution Step 1:  $A/Br_{3+}Br_{2} \rightarrow [A/Br_{4}]^{-} + Br^{+}$ Step 2:



(d) (i) 
$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$$
  
 $K_a = \frac{[Al(H_2O)_5(OH)^{2+}][H_3O^+]}{[Al(H_2O)_6^{3+}]} \text{ or } \frac{[Al(H_2O)_5(OH)^{2+}][H^+]}{[Al(H_2O)_6^{3+}]}$   
 $10^{-5.01} = \frac{(10^{-2.65})^2}{[Al(H_2O)_6^{3+}] - 10^{-2.65}} \qquad \therefore [Al(H_2O)_6^{3+}] = 0.5151 \text{ mol dm}^{-3}$   
[Also accept if  $10^{-5.01} = \frac{(10^{-2.65})^2}{[Al(H_2O)_6^{3+}]} \qquad \therefore [Al(H_2O)_6^{3+}] = 0.5129 \text{ mol dm}^{-3}$   
 $AlCl_3(aq) \rightarrow Al^{3+}(aq) + 3Cl^-(aq)$   
Since  $Al^{3+}(aq) = [Al(H_2O)_6]^{3+}$   
 $\therefore Mass of AlCl_3 = (0.5151) \left(\frac{20}{1000}\right) \times 133.5 \quad [or (0.5129) \left(\frac{20}{1000}\right) \times 133.5 = 1.37 \text{ g}]$   
 $= 1.38 \text{ g}$ 

(ii)  $\underline{Mg^{2+}}$  has a lower charge/size ratio than  $Al^{3+}$ ; so will polarise the O-H bond in water ligand to a lesser extent; thus is a weaker acid and a <u>higher pK<sub>a</sub> value</u> than aq  $Al^{3+}$ 

(iii)  $Mg_3(PO_4)_2$  (s)  $\rightleftharpoons 3Mg^{2+}$  (aq) +  $2PO_4^{3-}$ (aq)  $[Mg^{2+}]^3 [PO_4^{3-}]^2 = (0.10)^3 [PO_4^{3-}]^2 = 1.3 \times 10^{-16}$   $\therefore [PO_4^{3-}]_{min}$  required for  $Mg_3(PO_4)_2$  to be precipitated =  $3.61 \times 10^{-7}$  mol dm<sup>-3</sup> (3 s.f.)  $A/PO_4$ (s)  $\rightleftharpoons Al^{3+}$ (aq) +  $PO_4^{3-}$ (aq)  $[Al^{3+}][PO_4^{3-}] = (0.50) [PO_4^{3-}] = 6.3 \times 10^{-19}$   $\therefore [PO_4^{3-}]_{min}$  required for  $A/PO_4$  to be precipitated =  $1.26 \times 10^{-19}$  mol dm<sup>-3</sup> (4 s.f.) To separate the two ions, add  $PO_4^{3-}$  till  $[PO_4^{3-}] \leq 3.61 \times 10^{-7}$ -mol dm<sup>-3</sup>. <u>Filter the mixture</u>. <u>Mg^{2+} will remain in the filtrate</u>, while the <u>residue is A/PO\_4.</u>

**3 (a)** Mg reacts very slowly with cold water but readily with steam. Ba reacts vigorously with cold water. As E<sup>e</sup>(Ba<sup>2+</sup>/Ba) is more negative, Ba has a higher tendency to be oxidised than Mg. Thus the reaction takes place more readily.

**(b)** (i) 
$$2Sr(NO_3)_2(s) \rightarrow 2SrO(s) + 4NO_2(g) + O_2(g)$$

- (ii) From Mg to Ba, the ionic radius increases from 0.065 nm to 0.135 nm. As the cations have the same charge, the  $\frac{charge}{size}$  decreases, leading to a decreasing polarising power. The large electron cloud of nitrate ion is distorted to a smaller extent down the group and N-O bond is weakened less and less easily broken. Thus thermal stability of nitrates increases from Mg(NO<sub>3</sub>)<sub>2</sub> to Ba(NO<sub>3</sub>)<sub>2</sub>.
- (c) As  $Ca^{2+}$  has a smaller ionic radius than  $Sr^{2+}$ , it has a higher  $\frac{charge}{size}$  and is more extensively hydrated by water molecules. This produces more drag / resistance and hence its ionic speed is lower than expected.
- (d) (i) Elimination.
  - (ii) Base
  - (iii) Comparing experiments 1 and 2, when [NaOCH<sub>3</sub>] increases 1.5 times and [2-bromopropane] is constant, rate increases 1.5 times, showing that it is a 1<sup>st</sup> order reaction with respect to NaOCH<sub>3</sub>.

Comparing experiments 1 and 3, when  $[NaOCH_3]$  doubles and [2-bromopropane] increases 4/3 times, the rate increases 8/3 times, showing that it is a 1<sup>st</sup> order reaction with respect to 2-bromopropane.

(can also be shown via mathematical method)

Let the *n* be the order of reaction with respect to (wrt) 2-bromopropane

 $\frac{0.06}{0.16} = \frac{(0.100)(0.150)^n}{(0.200)(0.200)^n}$  $\frac{3}{8} = \frac{1}{2}(\frac{3}{4})^n$  $\frac{3}{4} = (\frac{3}{4})^n$ n = 1 $rate = k [NaOCH_3] [2-bromopropane]$  $rate constant, k = 4 mol^{-1} dm^3 min^{-1}$ 

- (iv) marking points:
  - lone pair of electrons on O
  - direction of arrows (arrows must start from bond/lone pair of electrons and end on atoms or between two atoms where a pi bond is formed)
  - only one step



- (v) Yes, it is consistent as the mechanism shows 1 molecule of 2-bromopropane reacting with  $1 \text{ CH}_3\text{O}^-$  ion in the rate-determining step.
- (vi) I: C–X bond is broken in the rate-determining step.

C-Cl bond is stronger than C-Br bond as the C-Cl bond length is greater.

When 2-chloropropane is used, the C-Cl bond is less easily broken and the rate is lower.

**II**: The number of electron-donating alkyl group remains the same in both  $CH_3CH_2O^-$  and  $CH_3O^-$ , therefore the electron density of the lone pair remains the same and both bases are equally strong. Hence there is no effect on the rate.

- 4 (a) (i) BaSO<sub>4</sub>  $4Br_2(aq) + S_2O_3^{2^-}(aq) + 5H_2O(l) \rightarrow 8Br^-(aq) + 2SO_4^{2^-}(aq) + 10H^+(aq)$ 
  - (ii)  $Br_2 + e^- \rightleftharpoons 2Br^ E^{\circ} = +1.07 \text{ V}$   $I_2 + e^- \rightleftharpoons 2I^ E^{\circ} = +0.54 \text{ V}$ From  $E^{\circ}$  values,  $Br_2$  is a stronger oxidising agent than  $I_2$  and can oxidise  $S_2O_3^{2^-}$  to  $SO_4^{2^-}$ . The oxidation state of sulfur increases from +2 in  $S_2O_3^{2^-}$  to +6 in  $SO_4^{2^-}$ . Iodine, a weaker O.A, can only oxidise  $S_2O_3^{2^-}$  to  $S_4O_6^{2^-}$ . The oxidation state of sulfur

increases from +2 in  $S_2O_3^{2^-}$  to +2.5 in  $S_4O_6^{2^-}$ .  $I_2(aq) + 2S_2O_3^{2^-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2^-}(aq)$ Hence there is no white precipitate observed.



## (c)

Information	Deduction
B is optically active.	B has a chiral carbon
B does not react with Na <sub>2</sub> CO <sub>3</sub>	B does not have a carboxylic acid.
B dissolves slowly in aq. NaOH	<ul><li>B has phenol.</li><li>B undergoes neutralisation</li></ul>
B reacts with potassium dichromate	<ul><li>B undergoes oxidation.</li><li>B has primary or secondary alcohol</li></ul>

B decolourises aq. Bromine to form white ppt.	<ul> <li>B is a phenol.</li> <li>B undergoes Electrophilic substitution.</li> <li>From molecular formula of C, one of C-2 or C-4 positions is occupied.</li> </ul>
B reacts with concentrated sulfuric acid	<ul> <li>B undergoes elimination of H<sub>2</sub>O.</li> <li>D is an alkene.</li> </ul>
D reacts with acidified KMnO <sub>4</sub>	<ul> <li>D undergoes oxidation cleavage of C=C</li> </ul>

Compound B:

Compound C:





Compound D:



Compound E:



 $\mathsf{CH}_4 \ + \ \mathsf{H}_2\mathsf{O} \implies \mathsf{CO}$ + 3H₂ Initial amount / mol 0 0 х Х Change in amount / -0.9x -0.9x +0.9x +2.7x mol Eqm amount /mol 0.1x 0.1x 0.9x 2.7x Total amount = 0.1x + 0.1x + 0.9x + 2.7x = 3.8x mol

$$K_{p} = \frac{(P_{H_{2}})^{3}(P_{CO})}{(P_{CH_{4}})(P_{H_{2}O})}$$
  
0.033 =  $(\frac{2.7x}{3.8x} \times P_{T})^{3} (\frac{0.9x}{3.8x} \times P_{T}) \div (\frac{0.1x}{3.8x} \times P_{T})^{2}$   
 $P_{T} = 0.0164$  atm

5 (a)

- (b) (i) Le Chatelier's Principle states that when a chemical system in equilibrium is disturbed, the position of equilibrium will shift to partially counteract the disturbance to reestablish a new equilibrium.
  - (ii) Decrease in size of reaction vessel results in an increase in pressure. The position of equilibrium shifts left to produce less gaseous molecules so as to partially offset the increase in pressure. K<sub>p</sub> value does not change as it is only temperaturedependent.

When temperature is decreased, the **position of equilibrium shifts left** to **favour** the **exothermic reaction** (to release heat) so as to partially offset the decrease in temperature.  $K_p$  value decreases since there are lesser amounts of products.

- (c) (i) Reagents: K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, dil H<sub>2</sub>SO<sub>4</sub> Conditions: Heat with distillation
  - (ii) sp<sup>3</sup> C in methanol



sp<sup>3</sup> hybrid orbitals of C

(d) (i) Reagents: limited Cl<sub>2</sub> gasConditions: uv light (or high temperature)

- (ii)  $CH_4 + Cl \rightarrow CH_3 + HCl$  $\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl \rightarrow CH_3CL + C$
- (e) (i) Both are simple covalent molecules.

Electron cloud size: chloropropane < iodopropane (higher M<sub>r</sub>)

Extent of distortion of electron cloud: chloropropane < iodopropane

Strength of td-id: chloropropane < iodopropane

Less energy required to break weaker intermolecular forces of attraction between chloropropane molecules compared to iodopropane molecules, hence lower boiling point.





sp<sup>2</sup> hybrid orbitals of C

(ii) From *Data Booklet*, C–C*l* bond energy is  $340 \text{ kJ mol}^{-1}$ , C–I bond energy is  $240 \text{ kJ mol}^{-1}$ ,

Ease of breaking of C-Cl < C-I

Hence it takes a longer time to form AgCl (white) precipitate.

(iii) No precipitate formed.

The a lone electron pair of Br is delocalised into the  $\pi$ -electron cloud of benzene due to p-orbital overlapping. C-Br bond is thus strong (due to partial double bond character) and does not break to release Br<sup>-</sup> to form AgBr precipitate.

(iv) In propanoyl chloride, carbonyl C has **two** electron-withdrawing groups, O and Cl, bonded to it compared to chloropropane where Cl is the only electron withdrawing group.

Hence, carbonyl C in propanoyl chloride is more electron deficient (has higher partial positive charge) than C in chloropropene. Thus carbonyl C is more susceptible to nucleophilic attack and mild conditions are required.