## Hwa Chong Institution 2012 C2 H2 Chemistry Prelim Paper 3 Answers

1(a)(i)



- (ii)  $P_4$  is highly reactive due to strong repulsion between bond pairs of electrons / highly strained bond angle of  $60^{\circ}$
- (iii) P<sub>4</sub> is a simple non-polar covalent molecule and is unable to form favorable interactions with polar water molecules but able to form favorable interactions with non-polar carbon disulfide through dispersion forces.
- (iv) White phosphorus burns with a bright white flame / light.
- $\begin{array}{lll} \text{(v)} & P_4(s) + 3O_2(g) \to P_4O_6(s) & \text{or} & P_4(s) + 5O_2(g) \to P_4O_{10}(s) \\ & P_4O_6(s) + 6H_2O(g) \to 4H_3PO_3(s) & \text{or} & P_4O_{10}(s) + 6H_2O(g) \to 4H_3PO_4(s) \end{array}$
- (b)(i) negligible intermolecular forces of attraction or negligible forces of attraction between the gas particles
  - volume of gas particle/molecules is negligible compared to the volume of its container
- (ii) Each gaseous P<sub>4</sub> molecule must have dissociated / decomposed / disintegrated into two gaseous molecules
- (c)(i) They consist of metal atoms with few valence electrons which can be readily lost to form the <u>delocalised sea of electrons</u> to act as mobile charges (resulting in metallic bonding) & have high electrical conductivity.
- (ii) s-block elements can only lose 1-2 e's per atom while TM can lose more e's from both <u>3d</u> and 4s <u>subshells</u> per atom to form metallic bonding due to close proximity of the 3d and 4s subshells. Thus TM's have stronger metallic bonding and <u>more energy</u> is needed to melt the metal and thus they have higher mp.
- (iii) electronic configurations of Fe: [Ar] 3d<sup>6</sup> 4s<sup>2</sup>; of Mn: [Ar] 3d<sup>5</sup> 4s<sup>2</sup> or electronic configurations of Fe<sup>2+</sup>: [Ar] 3d<sup>6</sup>; of Mn<sup>2+</sup>: [Ar] 3d<sup>5</sup>

Due to <u>inter-electronic repulsion in 3d subshell of  $Fe^{2+}$ </u>, 3d electrons are higher in energy, thus the 3<sup>rd</sup> e's are easier to be removed

(d)(i)  $\frac{\text{No of mol of KMnO}_4 \text{ formed}}{\text{No of mol of MnO}_2 \text{ formed}} = \frac{\frac{1}{5} \times \frac{20.0}{1000} \times 1.00}{\frac{0.174}{54.9 + 2 \times 16.0}} = \frac{2}{1}$ 

Let O.N of Mn in A be n+

[R] 
$$Mn^{n^+} + 2H_2O + (n-4)e^- \rightarrow MnO_2 + 4H^+$$
 (i)

[O]  $Mn^{n+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + (7 - n)e^-$  (ii)

From equations (i) & (ii):  $\frac{no \text{ of mol of } MnO_4^-}{no \text{ of mol of } MnO_2^-} = \frac{n-4}{7-n} = \frac{2}{1} \qquad \Rightarrow n = 6$ 

 $\therefore$  Oxidation number of Mn = <u>+6</u>

A is K<sub>2</sub>MnO<sub>4</sub>

(ii) Equation:  $3MnO_4^{2-} + 4H^+ \rightarrow MnO_2 + 2MnO_4^- + 2H_2O$ or  $3K_2MnO_4 + 2H_2SO_4 \rightarrow MnO_2 + 2KMnO_4 + 2K_2SO_4 + 2H_2O$ or  $3MnO_3 + H_2O \rightarrow MnO_2 + 2MnO_4^- + 2H^+$ 

<u>Disproportionation</u> ( $MnO_4^{2-}$  is simultaneously reduced to  $MnO_2$  and oxidised to  $MnO_4^{-}$ )

(iii) Mn is a TM and can form compounds of variable oxidation numbers due to close proximity of energy levels of 4s and 3d subshells and electrons can be easily lost or gained.

K and Ca can only form compounds of +1 and +2 respectively as <u>a lot more energy is</u> required to remove more electrons from an inner quantum (3p) shell, and thus they do not form compounds with more than 1 oxidation state.

- 2 (a) (i) Nucleophilic addition
  - (ii) The negatively charged hydroxide ion is a **stronger nucleophile** than a neutral water molecule.
  - (iii) **steric** reason (propanone is sterically more hindered as it has two methyl groups attached to the carbonyl carbon)

**electronic** reason (propanone has two electron donating methyl groups lowering the partial positive charge on the carbonyl carbon, making the carbonyl carbon less susceptible to nucleophilic attack)



- (b) (i) The protonation of the carbonyl group makes the **carbonyl carbon more** electron deficient (greater partial positive charge on carbonyl carbon) and thus more susceptible for the alcohol to attack, speeding up the rate of reaction.
  - (ii) In step IV, there is an elimination of water (dehydration). With the removal of water, the forward reaction is favoured and thus drives the equilibrium to the right to produce more acetal.

## OR

Water can be a competing nucleophile in step **II** and step **V**, forming other side products. Hence, with the removal of water, the formation of acetal would be favoured over the formation of the diol.



- 1. acetal formation (e.g. ethane-1,2-diol / any alcohol and acid catalyst)
- 2. reduction of carboxylic acid to alcohol (LiA/H<sub>4</sub> in dry ether)
- 3. acid hydrolysis of acetal back to ketone (any dilute mineral acids, heat)

(c) (i) Anode: 
$$2C\Gamma$$
 (aq)  $\rightarrow CI_2(g) + 2e^-$   
Cathode:  $2H_2O(I) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ 

- \*(ii) O<sub>2</sub> + 4H<sup>+</sup> +4e<sup>-</sup> ⇒ 2H<sub>2</sub>O +1.23V Cl<sub>2</sub> + 2e<sup>-</sup> ⇒ 2CΓ +1.36V Since E<sup>⊕</sup>(O<sub>2</sub>/H<sub>2</sub>O) is less positive than E<sup>⊕</sup>(Cl<sub>2</sub>/CΓ), water is expected to be discharged.
  High concentration of chloride ion in solution causes drop in E<sup>⊕</sup>(Cl<sub>2</sub>/CΓ) to be lower than +1.23V, hence it is preferentially discharged.
- (iii) Cold:  $Cl_2(g) + 2OH^-(aq) \rightarrow C\Gamma(aq) + ClO^-(aq) + H_2O(l)$ Hot:  $3Cl_2(g) + 6OH^-(aq) \rightarrow 5C\Gamma(aq) + ClO_3^-(aq) + 3H_2O(l)$

## 3(a)(i)

Exhibits optical isomerism	Structure must contain a chiral carbon
Reacts with sodium carbonate to	Structure must contain carboxylic acid functional
give CO <sub>2</sub>	group (accept –CO <sub>2</sub> H, reject –COOH)
Reacts with potassium	Oxidative cleavage has occurred on a terminal
manganate to give CO <sub>2</sub>	alkene.



## (ii)

B gives a much acidic solution than A	Structure must contain acid chloride functional group
<b>C</b> is neutral	Alcohol, aldehyde or ketone functional groups could be present
<b>B</b> and <b>C</b> gives organic ppt with 2,4-DNPH <b>C</b> gives brick red ppt with Fehling's	Aldehyde functional group present in C
solution	Ketone functional group present in B



Possible Cs (not exhaustive):



(must have aldehyde functional group. Alkene, aldehyde, ketone, ether accepted for rest of the structure)

(iii) B: The acid chloride functional group <u>hydrolyses/dissolves/reacts</u> completely in water to give <u>HCl(aq)</u> a <u>strong acid/dissociates completely</u> in water. Hence the solution is highly acidic.

**A**: The carboxylic acid functional group is only <u>weakly acidic</u> and only <u>partially</u> <u>dissociates</u> in water, giving a low concentration of  $H^+$ 

(b) The **p** orbitals (reject pi-orbitals) of <u>all the carbon atoms/ of every benzene ring</u> in the structure now overlap and allow the electrons to **delocalize** over the entire structure/chain/polymer.

Benzene exists as discrete **non polar covalent molecules**. They are **not charge carriers** and hence do not conduct electricity.

- (c)(i) AgC/(s) +  $e \rightarrow Ag(s) + C\Gamma(aq)$ Na<sub>2</sub>Mn<sub>5</sub>O<sub>10</sub>(s) + 2AgC/(s)  $\rightarrow$  2NaC/(aq) + 5MnO<sub>2</sub>(s) + 2Ag(s)
- (ii) no. of moles of Na<sup>+</sup> lost = 5.0 / 23 = 0.2174 mol no. of moles of electrons used = 0.2174 mol

Q = 0.2174 x 96500 = 20978 C

- (iii) Correct electrodes  $(Na_2Mn_5O_{10}/MnO_2(s) \text{ and } Ag/AgC/(s))$  and seawater (accept 0.600 mold dm<sup>-3</sup> NaCl) as the electrolyte.
- (iv) At the sodium manganese manganate electrode  $2Na^{+}(aq) + 5MnO_{2}(s) + 2e \rightleftharpoons Na_{2}Mn_{5}O_{10}(s)$

When the fresh water is replaced with sea water, the [Na<sup>+</sup>] increases, hence by LCP, the equilibrium is shifted to the right. Hence the electrode potential becomes more positive.

At the silver/silver chloride electrode

 $AgC/(s) + e \rightleftharpoons Ag(s) + C\Gamma(aq)$ 

When the fresh water is replaced with sea water, the [Cl<sup>-</sup>] increases, hence by LCP, the equilibrium is shifted to the left. Hence the electrode potential becomes more negative.

(v)  $E_{cell}$  at end of charing phase = 0.56 - 0.34 = +0.22V  $E_{cell}$  at start of discharge phase = 0.65 - 0.29 = +0.36V Potential gained by system = +0.14V 4 (a) (i) Step 1 : C/• + H-CH<sub>3</sub>  $\rightarrow$  H-C/ + •CH<sub>3</sub>  $\Delta H = -431 + 434 = +3 \text{ kJ mol}^{-1}$ 

Step 2 : •CH<sub>3</sub> + C/-C/  $\rightarrow$  CH<sub>3</sub>-Cl + C/•  $\Delta$ H = -340 + 244 = -96 kJ mol<sup>-1</sup>

(ii) Enthalpy/kJ mol<sup>-1</sup>



(iii The main contributing energetic factors are the decrease in the C-X and H-X bond strengths, which results in the reaction becoming decreasingly ) exothermic / increasingly endothermic, and hence reactivity decreases.

**(b (i)** 
$$(V_n - V_t) \alpha$$
 [C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>C/] (remaining)







Solving,  $E_a = 97.5 \text{ kJ mol}^{-1}$ 

Since rate has units of mol  $dm^{-3} s^{-1}$ , and k has the units of  $s^{-1}$ , the order of (ii) reaction must be 1.

Therefore, rate equation is given by : Rate =  $k [C_6H_5N_2CI]$ .

(iii Mechanism : S<sub>N</sub>1 or unimolecular nucleophilic substitution

(iv



(d (i) The  $Cu^+$  catalyst converts to a  $Cu^{2+}$  intermediate before reverting back to its original +1 oxidation state.



- 1. Diazotisation : HNO<sub>2</sub>, HC*I*, 10 °C
- 2. Sandmeyer reaction : CuBr, heat
- 3. Alkylation : CH<sub>3</sub>C*I*, A*I*C*I*<sub>3</sub>, heat
- 4. Oxidation : KMnO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, heat

Alternative scheme :



- 1. Bromination :  $Br_2(I)$
- 2. Diazotisation : HNO<sub>2</sub>, HC*I*, 10 °C
- 3. Sandmeyer reaction : CuCN, heat
- 4. Hydrolysis : dilute H<sub>2</sub>SO<sub>4</sub>, heat

5(a)(i)

 $\Delta H_{sol} = -LE + \Delta H_{hyd}$ = -(-2833) + (-1891) + (-1004) = -62 kJ mol<sup>-1</sup>

(ii) No. of moles of MgSO<sub>4</sub> = 2/ 120.4 =  $1.661 \times 10^{-2}$  mol Heat released by solution of MgSO<sub>4</sub> =  $62 \times 1.661 \times 10^{-2}$  = <u>1029.9 J</u>

Heat gained by water =  $15(4.18)(\Delta T)$  15(4.18)(T) = 1029.0  $\Delta T = 16.4 \text{ K}$ Final temp = 25 + 16.4 = 41.4 °C

(b)(i) A: BaCO<sub>3</sub> and B: MgCO<sub>3</sub>

 $MCO_3$  (s)  $\rightarrow$  MgO (s) + CO<sub>2</sub> (g)

Mg<sup>2+</sup> has greater charge density, hence polarizing the anion to a greater extent. This causes magnesium carbonate to be less stable to heat.

BaO (s) + H<sub>2</sub>O (I)  $\rightarrow$  Ba(OH)<sub>2</sub> (aq)

(c)(i) Ba<sup>2+</sup> is precipitated first

When BaCO<sub>3</sub> precipitates;  $[CO_3^{2^-}]_{min} = 5.1 \times 10^{-8} \text{ mol } \text{dm}^{-3}$ 

(ii) As Mg(OH)<sub>2</sub> starts to precipitate,  $[CO_3^{2-}] = 3.5 \times 10^{-7} \text{ mol dm}^{-3}$   $\therefore [Ba^{2+}]$  remaining in solution  $= \frac{5.1 \times 10^{-9}}{3.5 \times 10^{-7}} = 0.0146 \text{ mol dm}^{-3}$ (iii) % of Ba<sup>2+</sup> remained in solution  $= \frac{0.0145}{0.10} \times 100 = 14.6 \% >> 1\%$ 

 $\Rightarrow$  separation is not effective

(d)(i) hydrogen bond: between –CH<sub>2</sub>OH, –CO<sub>2</sub>H of lysozyme and –CH<sub>2</sub>OH, –CO<sub>2</sub>H of the polysaccharide

or ionic interaction: between  $-(CH_2)_4 NH_3^+$  of lysozyme and  $-CO_2^-$  of the polysaccharide

- (ii) Correct drawing of a tripeptide (correct peptide bond) Correct choice of amino acids (with at least one of the amino acids being able to form hydrogen bond or ionic interactions
- (iii) water / H<sub>2</sub>O
- (e)(i) 1. Acid group will react with ammonia hence excess ammonia is needed. <u>OR</u>
   2. To lower the chances of the amine product undergoing multiple substitutions
  - (ii) HO<sub>2</sub>CCH(CH<sub>3</sub>)NHCH(CH<sub>3</sub>)CO<sub>2</sub>H
- (f)(i) HO<sub>2</sub>CCH<sub>2</sub>CHO
  - (ii) Elimintation