AJC H2 Chemistry Prelim 2008 - Paper 3 Suggested Answers

- (a) 3d and 4s electrons are of similar energies
 lose different numbers of these electrons to form ions of similar stability
 - (b) (i) Empirical formula of $Y = MnO_2$
 - (ii) Z = MnO₄⁻ Step II is a disproportionation reaction

 $3 \text{ MnO}_4^{2-} + 2 \text{H}_2 \text{O} \rightarrow 2 \text{ MnO}_4^{-} + \text{MnO}_2 + 4 \text{OH}^{-}$

- (iii) aq CO₂ is acidic / CO₂ dissolves in water to form carbonic acid,
 removes OH⁻ as HCO₃⁻
 Position of equilibrium shifts to the right, hence aids disproportionation
- (c) (i) Anode: Na \rightarrow Na⁺ + e Cathode: MnO₂ + H₂O + e \rightarrow MnO(OH) + OH⁻
 - (ii) $E \bullet (MnO_2/MnO(OH)) = -1.71 V$
- (d) (i) Since $t_{1/2}$ is constant at about 1.5 mins, order of reaction w.r.t. H_2O_2 is 1.
 - (iii) $k = 0.478 \text{ min}^{-1}$

(iv) k increases,

because from the rate equation, if **rate increases even when H_2O_2 concentration remain the same**, then value of k must also increase.

(can explain using Arrhenius equation $k = A e^{(-Ea/RT)}$)

- **2** (a) (i) $\Delta H_{sol} = -157 \text{ kJ mol}^{-1}$
 - (ii) The temperature of the water will *increase*.
 - (iii) $-\Delta H_{hyd}$ of Ca²⁺ will be <u>less exothermic</u> than Cu²⁺.
 - From Data Booklet, ionic radius of Ca^{2+} is 0.099nm while Cu^{2+} is 0.069nm.
 - This is because Ca²⁺ has a larger ionic radius and thus <u>smaller charge density</u> than Cu²⁺.
 - (b) (i) In reaction I and II, <u>2 similar Cu–O bonds are broken</u> and - <u>2 similar Cu–N bonds are formed</u>. Thus, their ΔH_r^{\ominus} values are similar
 - (ii) In reaction I, one ethylenediamine replaces 2 H₂O ligands.
 - There is an increase in the number of particles in aqueous solution and
 thus increase in disorderness or ways of rearrangement.
 - (iii) Reaction I: $\Delta G_r^{\circ} = 60.9 \text{ kJmol}^{-1}$

Reaction II : $\Delta G_r^{\circ} = 43.5 \text{ kJmol}^{-1}$

- ΔG_r^{\ominus} for reaction I is <u>more negative</u> than II.
- Ligand exchange is more spontaneous in reaction I than II.
- Thus, complex product for reaction ${\bf I}$ is $\underline{more\ stable}$ than ${\bf II}.$
- (iv) Ligand exchange with polydentate ligands and its analogous monodentate ligands gives <u>similar ΔH</u>^e values due to formation of similar Cu–N bonds.
 - Polydentate ligands **increases the disorderness** of the system more compared to monodentate ligands.
 - Thus, the <u>positive entropy</u> is the factor which <u>determines a more negative</u> $\Delta \underline{G}_{r}^{\Theta}$ value and formation of more stable polydentate complex.
 - * mathematically, ΔH_r^{\ominus} (reaction I) $\approx \Delta H_r^{\ominus}$ (reaction II); Increase in disorderness $\Rightarrow \Delta S_r^{\ominus}$ (reaction I) > 0 JK⁻¹mol⁻¹ $\therefore \Delta G_r^{\ominus}$ (reaction I) <u>more negative</u> than ΔG_r^{\ominus} (reaction II)
- (c) (i)



(ii) C atoms in C=C : sp^2 hybridisation C atoms in C=N : sp hybridization



- (iv) cis isomer The trans isomer is not possible as the <u>S⁻ are pointing oppositely</u> and anionic X <u>cannot form 2 dative bonds</u> to the central metal ion.
- (v) Dative / coordinate bonds

3 (a)

NaCl and MgCl₂ are both <u>ionic</u>. Hence, they merely <u>dissolve</u> to give <u>ions</u>.

(OR Mg²⁺(aq) undergoes hydrolysis to a very <u>small extent</u>)

AlCl₃ and SiCl₄ are <u>simple covalent</u> and <u>hydrolyze</u> in water to give <u>white fumes of</u> <u>HCl</u> and an <u>acidic solution</u>.

$$AICI_3 + 6H_2O \rightarrow [AI(H_2O)_6]^{3^+} + 3CI^-$$
$$[AI(H_2O)_6]^{3^+} \Leftrightarrow [AI(H_2O)_5(OH)]^{2^+} + H^+$$

or

 $AICI_3 + 6H_2O \Leftrightarrow [AI(H_2O)_5(OH)]^{2+} + H^+ + 3CI^-$

 $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCI$



- (b) (i) $AICI_3 + 3NaOH \rightarrow AI(OH)_3(s) + 3NaCI$ $or <math>AI^{3+}(aq) + 3OH^{-}(aq) \rightarrow AI(OH)_3(s)$
 - (ii) With MgCl₂, a <u>white ppt, insoluble in excess</u> NaOH is observed. Al(OH)₃ is <u>amphoteric</u> while Mg(OH)₂ is <u>basic</u>. Al(OH)₃ <u>reacts with NaOH</u> (to give salt and water), hence dissolves.
- (c) (i) <u>AI-H</u> bond is <u>weaker</u> than the B-H bond.
 - (ii) H⁻ acts as <u>nucleophile</u>. Alkenes are not attacked by nuclephiles as they are <u>electron-rich</u>.



- (iv) reaction II: NaCl, conc. H₂SO₄, reflux / PCl₅, room temp / SOCl₂, room temp. reaction III: KCN in ethanol, reflux reaction IV: dilute H₂SO₄ (or dilute HCl), reflux
- (ii) Test: Add I₂(aq) in NaOH(aq) to each compound and warm. Ethanol gives a <u>yellow ppt of CHI₃</u>. For phenyl methanol, <u>no yellow ppt</u> is observed.
- 4 (a) (i) Step I: free radical substitution Step II: redox Step III: nucleophilic substitution
 - (ii) $\Delta H_{rxn} = -117 \text{ kJ mol}^{-1}$
 - (iii) Butanol and 4-chlorobutanol are assumed to be <u>gaseous molecules</u> when using bond energies in (a)(i). However, both actually exist as <u>liquids</u> under standard conditions.

(iv)

(d) (i)



(v) The yield is likely to be <u>low</u>.

Step 1 produces a **<u>mixture of chlorine substituted products</u>**, not all will undergo nucleophilic substitution to give THF.

<u>OR</u>

The nucleophile $CICH_2CH_2CH_2CH_2O^-$ may react with another of itself to give a **straight chain product** rather than a ring product.





- Shape of α -helix - Show hydrogen bonds between C=O and N-H groups

- (ii) dilute HCl or dil NaOH, reflux
- (b) (i) Denaturation of proteins refer to the <u>disruption of the shape</u> of the protein molecule <u>without altering its primary structure</u> but resulting in the <u>loss of</u> <u>biological activity.</u>
 - (ii) I: Lactic acid dissociates to give H^+ ions, thus lowering the pH. This disrupts the <u>ionic bonds</u> in the protein. -COO⁻ + H⁺ \rightarrow -COOH

II. Ethanol disrupts the intermolecular hydrogen bonds.



- (c) (i) <u>Glycine would be optically inactive</u> but not alanine. Unlike alanine, glycine <u>does</u> <u>not have a chiral carbon</u> as it is bonded to 2 H atoms.
 - (ii) I. Glycine has a much higher melting point than 1-aminobutane because the <u>electrostatic attractions (ionic bond)</u> in the crystal lattice of the zwitterionic form is stronger than the <u>intermolecular hydrogen bonding</u> between 1-aminobutane molecules.

II. Propanoic acid has a higher melting point than 1-aminobutane. Both have hydrogen bonds between their molecules and similar M_r (similar strength of VDW) However, as **oxygen is more electronegative than nitrogen**, the **hydrogen bonds** between propanoic acid is **stronger** than those of 1-aminobutane.

- (d) (i) +2
 - (ii) No change in oxidation number of iron. This is a ligand exchange reaction.
- (e) $Cu^+ 1s^22s^22p^63s^23p^63d^{10} Cu^{2+} 1s^22s^22p^63s^23p^63d^9$

No vacant d orbital for Cu(I), no d-d transition

For Cu(II), d electron to move from lower energy orbital to vacant higher energy orbital, energy is absorbed from the visible light region which is small in magnitude, hence its complementary colour is observed.