MJC Preliminary Exam 2011 H2 Chemistry Paper 3 – Mark Scheme

1(a) Lattice energies are often used as a measure of the energetic stability of ionic compounds. Usually ionic compounds with the same crystal structure can be compared based on the lattice energy value.

Lattice energies need to be determined experimentally using thermochemical data. However based on electrostatic considerations (i.e. attraction and repulsion of ions), theoretical values of the lattice energies can be calculated using equations such as the Kapustinskii equation:

$$\Delta H_{latt} = -107.1 \times \frac{\upsilon \times z_+ \times z_-}{r_+ + r_-} \text{ kJ mol}^{-1}$$

where v is the number of ions in the empirical formula z_+, z_- is the charge of the cation and anion respectively r_+, r_- is the ionic radius (in nm) of the cation and anion respectively

The table below shows the numerical values of lattice energies for a series of magnesium and other related compounds.

Compound	LiCl	MgCl ₂	MgBr ₂	MgI ₂	MgO
Experimental	- 853	- 2526	- 2440	- 2327	- 3933
value / kJ mol ⁻¹					

(i) Define, with the aid of an equation, the lattice energy of magnesium oxide.

Lattice energy of magnesium oxide is the *energy released* when one mole of magnesium oxide is formed from its constituent gaseous ions at *298K and 1 atm*.

 $Mg^{2+}(g) + O^{2-}(g) \rightarrow MgO(s)$

(ii) By quoting appropriate data from the *Data Booklet*, explain why the lattice energies of the magnesium halides decrease from $MgCl_2$ to MgI_2 .

From the *Data Booklet*, ionic radii in nm of Cl: 0.181, Br⁻: 0.195, I⁻: 0.216

Since $|\Delta H_{\text{latt}}| \propto \frac{q_+q_-}{r_++r_-}$, but the cation and charges of the ions are the

same, lattice energy would decrease as ionic radii of the halide increases down the group.

(iii) By using appropriate data from the *Data Booklet*, calculate the theoretical lattice energy of magnesium chloride.

$$\Delta H_{latt} = -107.1 \times \frac{\upsilon \times z_{+} \times z_{-}}{r_{+} + r_{-}}$$
$$\Delta H_{latt} = -2612 \text{ kJ mol}^{-1}$$

(iv) The lithium and magnesium ion have similar ionic radii. Based on this assumption, use the value calculated in (a)(iii) to estimate the theoretical lattice energy of lithium chloride.

$$\Delta H_{latt}$$
 for LiCl = $\frac{1}{3} \times \Delta H_{latt}$ for MgCl₂
 ΔH_{latt} for LiCl = -871 kJ mol⁻¹

(v) Explain the differences between the theoretical and experimental values for lithium chloride and magnesium chloride respectively, and comment whether the assumption made in (a)(iv) is a valid one.

[10]

Compound	LiC <i>l</i>	MgCl ₂
Theoretical	- 871	- 2612
value / kJ mol ⁻¹		
Experimental	- 853	- 2526
value / kJ mol ⁻¹		

There is a discrepancy between the experimental and theoretical lattice energies for ionic compounds with partial covalent character.

Hence for LiC*I*, there is very little covalent character as there is a much smaller difference between the theoretical and experimental values. Hence, the ionic radius of Li^+ is likely to be as that predicted by the assumption.

Conversely the charge density of Mg^{2+} is relatively high, resulting in greater polarization of the Cl⁻ electron cloud, hence the larger degree of covalent character in $MgCl_{2.}$

(b) Describe, and suggest an explanation for, the trend observed in the thermal decomposition of nitrates of the Group II elements from magnesium to barium. Write a general equation for the reaction that occurs on heating.

[3]

Down the group,

- radius of cations increases
- charge density of cations decreases
- polarising power of cations decreases
- cation is less able to distort electron cloud of NO₃²⁻ anion
- Thermal decomposition of nitrates decreases
- Thermal stability of nitrates increases and higher temperature required to bring about decomposition.

 $M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

(c) In an experiment, water is added to a test tube containing the solid remaining after magnesium carbonate has been heated. Dilute sulfuric acid is then added to the test tube. The procedure is repeated to the solid remaining after barium carbonate has been heated.

Describe and explain what you would see in both experiments.

[3]

MgO solid did not dissolve in water. MgO solid dissolves in dilute sulfuric acid to form colourless solution of MgSO₄.

BaO solid dissolves in water to form an alkaline solution of $Ba(OH)_2$. When dilute sulfuric acid is added, white ppt of $BaSO_4$ is seen.

MgO is a basic ionic oxide and reacts with dilute sulfuric acid. MgSO₄ is soluble in water whereas BaSO₄ is insoluble in water.

(d) The hexadentate ligand EDTA⁴⁻ forms a complex both with magnesium ions and calcium ions. With a suitable indicator, this can be used to determine the total concentration of magnesium ions and calcium ions in a mixture.

A sample of a mixture of anhydrous magnesium chloride and anhydrous calcium chloride had a mass of 0.344 g and was dissolved in water to make 100 cm³ of solution. A 10 cm³ portion of this solution required 33.3 cm³ of 0.010 mol dm⁻³ EDTA⁴⁻ for complete reaction.

(i) Suggest the formulae of both complexes formed.

[Mg(EDTA)]²⁻ and [Ca(EDTA)]²⁻

(ii) Calculate the mass of the anhydrous magnesium chloride in the mixture.

[4] [Total: 20]

Let the mass of the anhydrous magnesium chloride in the mixture = x g Hence total no. of moles of Mg²⁺ and Ca²⁺ = $\frac{x}{95.3} + \frac{0.344-x}{111.1}$

No. of mole of $EDTA^{4-} = 0.000333$

total no. of moles of Mg²⁺ and Ca²⁺ in 100 cm³ = 0.00333

Hence 0.00333 = $\frac{x}{95.3} + \frac{0.344 - x}{111.1}$

x = 0.157 g

2(a) A mixture was prepared using 1.00 mol of ethanedioic acid and 2.00 mol of ethanol. At a given temperature, the mixture was left to reach *dynamic equilibrium* according to the following equation.

 $(COOH)_2 + 2C_2H_5OH \implies (COOC_2H_5)_2 + 2H_2O \qquad \Delta H < 0$

The equilibrium mixture contained 36.8 g of ethanol.

(i) What do you understand by the term *dynamic equilibrium*?

At dynamic chemical equilibrium in a reversible reaction, rate of forward reaction is equal to rate of backward reaction and the substances are still reacting together although the concentration of the reactants and products remain constant.

(ii) Write an expression for K_c for this reaction.

$$K_{\rm C} = \frac{[(COOC_2H_5)_2][H_2O]^2}{[(COOH)_2][C_2H_5OH]^2}$$

(iii) Use your expression in (a)(ii) to calculate the value of K_c .

Eqm. mol $(COOH)_2 + 2C_2H_5OH \iff (COOC_2H_5)_2 + 2H_2O$ $0.4 \qquad 0.8 \qquad +0.6 \qquad +1.2$

Let volume of mixture be V dm³

$$K_{\rm C} = \frac{\left(\frac{0.6}{V}\right)\left(\frac{1.2}{V}\right)^2}{\left(\frac{0.4}{V}\right)\left(\frac{0.8}{V}\right)^2}$$

= 3.38

(iv) For this equilibrium, predict the effect of an increase in temperature on the value of K_c .

[6]

When the temperature is increased, equilibrium position shifts to the left towards endothermic reaction to absorb heat by Le Chatelier's principle.

The no. of mole of ester and water decreases and no. of mole of ethanedioic acid and ethanol increases, and hence the value of K_c decreases.

- (b) A buffer solution is prepared by adding 10.00 cm³ of 0.100 mol dm⁻³ potassium hydroxide to 25.00 cm³ of 0.400 mol dm⁻³ ethanoic acid. (p*K*a of ethanoic acid is 4.75)
 - (i) What is meant by the term *buffer*?

A buffer solution is one which is capable of maintaining a fairly constant pH (by resisting pH change) when small amounts of acid or base are added to it.

(ii) Explain how the solution above acts as a buffer when H⁺ ions are added.

When a small amount of H⁺ is added

 $CH_{3}COO^{-} + H^{+} \rightarrow CH_{3}COOH$

The H^+ is removed as CH_3COOH by CH_3COO^- .

[H⁺] is slightly changed and pH of buffer solution remains fairly constant.

(iii) Calculate the pH of the buffer solution formed.

No. of mole of KOH = 0.00100

In the buffer solution, No. of mole of $CH_3COOK = 0.00100$

No. of mole of CH₃COOH = $\left(0.400 \times \frac{25}{1000}\right) - 0.00100$ = 0.00900

pH= pK_a + lg $\frac{[salt]}{[acid]}$ pH = 4.75 + $lg\left(\frac{\frac{0.001}{V}}{\frac{0.00900}{V}}\right)$ where V is volume of buffer = 3.80

(iv) Suggest why the concentration of potassium hydroxide in a solution slowly decreases when left open to air.

[6]

Potassium hydroxide reacts with carbon dioxide in the air.

(c) A solution was prepared by reacting 1 mol of lysine with 2 mol of hydrochloric acid. This solution was titrated with aqueous sodium hydroxide. The titration curve obtained is shown below.



(i) Draw the structure of the species present at point **W**, **X**, **Y** and **Z** on the curve.

СООН	ÇOO -	Ç00 [−]	COO -
H ₃ N ⁺ - СН	H ₃ N*- СН	H ₂ N-ÇH	H2N-CH
СН2	학원일	©H2	CH
СН2	학원일	©H2	CH2
СН2	CH2	CH2	CH2
NH3 ⁺	NH ₃ *	NH3 ⁺	NH2
W	x	Y	Z

(ii) Define *isoelectric point*.

The pH at which a particular amino acid exists as a zwitterion is called the isoelectric point of that amino acid.

(iii) Use the titration curve to suggest the *isoelectric point*, and the pK_a values of the alpha-carboxyl group, the alpha-amino group and the amino group of the side chain of lysine.

isoelectric point of lysine = 10 pK_a of the alpha-carboxyl group = 2 pK_a of the alpha-amino group = 9.5 pK_a of the amino group of the side chain = 10.5

(iv) State the number of different compounds (exclude stereoisomers) that could be formed when one molecule of lysine reacts with one molecule of proline.

proline : HO NH

4

[8] [Total: 20]

[Turn over

- **3(a)** At standard temperature and pressure, oxygen is an odourless gas with the molecular formula O_2 . Oxygen may also be found in the form of oxide, O^{2-} or ozone, O_3 .
 - (i) Sketch a graph of the pH of the solution when the highest oxide of the elements from sodium to sulfur are added separately to water.



(ii) With the aid of equations, state and explain the resulting pH of the solution for these pair of compounds when they are added separately to water.

1 SiO₂ and SiC l_4

 SiO_2 does not react with water because there is no solute-solvent forces are strong enough to break down the network of extensive covalent bonding within the 3-dimensional structure. Hence pH of solution = 7

SiCI₄ undergo complete hydrolysis to form strongly acidic solution with pH=2

 $SiCl_4$ (I) + 2H₂O (I) \rightarrow SiO_2 (s) + 4HCl (g)

2 Al₂O₃ and AlC l_3

 Al_2O_3 does not dissolve in water because the ion-dipole interaction is not strong enough to overcome the lattice energy. Hence pH of solution = 7

 $AICl_3$ undergoes both hydration and hydrolysis to form an acidic solution with pH=3

 $\begin{array}{l} \mathsf{A}/\mathsf{C}l_3 \ (\mathsf{s}) \xrightarrow{H_2O} \mathsf{A}|^{3_+} (\mathsf{aq}) + 3\mathsf{C}l^{-} (\mathsf{aq}) \\ [\mathsf{A}/(\mathsf{H}_2\mathsf{O})_6]^{3_+} (\mathsf{aq}) \end{array} \rightleftharpoons \begin{array}{l} [\mathsf{A}/(\mathsf{H}_2\mathsf{O})_5(\mathsf{OH})]^{2_+} (\mathsf{aq}) + \mathsf{H}^+(\mathsf{aq}) \end{array}$

- (iii) Explain the following observations as fully as you can.
 - **1** The first electron affinity of oxygen is exothermic while the second electron affinity of oxygen is endothermic.

1st EA is exothermic because the attraction between the nucleus of O atom and the added electron is greater than the repulsion between the electrons.

 2^{nd} EA is endothermic because energy is required to overcome the repulsion when electron are added to negatively charged O⁻ ion.

2 The first ionisation of oxygen is less endothermic than that of the preceding element in the Periodic Table.

1st IE of O is less endothermic than that of N due to interelectron repulsion between the paired electrons in the 2p orbital.

3 The boiling point of oxygen is lower than that of ozone.

Number of electrons of O_3 is greater than that of O_2 .

[10]

Boiling point of ozone is higher because more energy is required to overcome the stronger van der Waals' forces of attraction between ozone molecules than van der Waals' forces of attraction between oxygen molecules.

(b) The diagram below shows the structure of O_3 .



(i) The O-O bond length is 148 pm while the O=O bond length is 121 pm.

Suggest a reason why the bond length between the oxygen atoms in ozone is actually 128 pm. (1 pm = 10^{-12} m)

The pi electrons are delocalised over the 3 oxygen atoms.

Both manganate(VII) ion and ozone and can cause oxidative cleavage of alkenes.



compound A

(ii) Draw the structural formulae of the products formed when compound **A** reacts with hot acidified aqueous potassium manganate(VII).



CO₂ H₂O

(iii) When ozone reacts with compound **A**, one of the products gives a positive result with ammonical silver nitrate solution. Suggest the structural formulae of the products formed.



When ozone reacts with nitrogen dioxide, gaseous N_2O_5 and oxygen gas is produced. N_2O_5 is a rare example of a compound that adopts two structures depending on the conditions: as an ionic salt when in the solid state, but a molecule when in the gaseous state.

(iv) Gaseous N₂O₅ is a symmetrical molecule with the two nitrogen atoms bonded to one central oxygen atom.

Draw a dot-and-cross diagram to show the bonding in N_2O_5 molecule. Use your diagram to suggest the shape and the bond angle with respect to nitrogen. Determine whether the molecule is polar or non-polar.



trigonal planar 120° polar

(v) Solid N_2O_5 contains a cation that can react with benzene via a substitution reaction.

Suggest the identity of the cation and anion present in the solid N₂O₅.

NO_2^+ and NO_3^-

(vi) N_2O_5 decomposes completely to give nitrogen dioxide and oxygen.

Write an equation for this reaction.

[10] [Total: 20]

$2 \text{ N}_2\text{O}_5 \rightarrow 4 \text{ NO}_2 + \text{O}_2$

- 4 Nitric oxide is a chemical compound with chemical formula NO. It is an extremely important intermediate in the chemical industry. Nitric oxide is an air pollutant and it reacts with water to form nitrous acid, HNO₂, and nitric acid, HNO₃.
- (a) In the laboratory, nitric oxide is conveniently generated by reduction of nitric acid with copper and has the overall E^{e}_{cell} value of + 0.62 V.
 - (i) Write the half-equation for the reduction of nitric acid to nitric oxide and determine its standard electrode potential.

 $NO_3^- + 4H^+ + 3e \rightarrow NO + 2H_2O$ $E^{e}_{red} = + 0.96 V$

(ii) Explain the effect of using copper powder of the same mass on the rate and feasibility of the reaction.

[4]

Copper powder will increase the rate of reaction as the surface area is increased.

As copper is a solid, E_{oxid}^{e} is not affected, and hence the E_{cell}^{e} and feasibility of the reaction will not be affected.

(b) The non-elementary reaction between NO and O_2 is a third order reaction and N_2O_4 is formed as the product. The first step involves the formation of the unstable dimer, N_2O_2 .

$$2NO \implies N_2O_2$$
 $\Delta H = -16 \text{ kJ mol}^{-1}$

This is followed by the rate-determining step.

$$N_2O_2 + O_2 \rightarrow N_2O_4$$

(i) Draw a diagram to show the shape and bonding in N_2O_2 and hence suggest a reason why N_2O_2 is unstable.



 N_2O_2 unstable as the nitrogen atoms have partial positive charge, δ^+ (or electron deficient) since they are attached to electronegative O atoms and they are adjacent to each other.

(ii) Using data from *Data Booklet* and relevant information given, calculate the bond energy of nitrogen-oxygen bond in NO.

Bond energy of nitrogen-oxygen bond in N_2O_2 is 607 kJ mol⁻¹.

 $2NO \implies N_2O_2 \qquad \Delta H = -16 \text{ kJ mol}^{-1}$ - 16 = 2×BE (NO _{nitric oxide}) - [BE (N-N) + 2×BE (N=O)] BE (NO _{nitric oxide}) = <u>679 kJ mol}^{-1}</u>

(iii) Determine the rate equation for the reaction between NO and O₂.

rate = $k [NO]^2 [O_2]$

(iv) Suggest why is there an unusual observation that the reaction between NO and O₂ becomes slower as the temperature is increased?

[6]

$$2NO \implies N_2O_2$$
 $\Delta H = -16 \text{ kJ mol}^{-1}$

According to Le Chatelier's Principle, when the temperature increased, the equilibrium position will shift left towards the endothermic reaction to absorb the heat.

When this takes place, there will be less N_2O_2 created to react with the O_2 in the rate determining step. Thus the rate will slow down.

- (c) Nitric oxide reacts with potassium hydroxide to produce potassium nitrite, KNO_2 , dinitrogen oxide, N_2O , and water.
 - (i) Write a balanced equation for this reaction.

 $4NO + 2KOH \rightarrow 2KNO_2 + H_2O + N_2O$

(ii) State the type of reaction in (c)(i).

[2]

Disproportionation

(d) Nitrous acid is involved in the synthesis of azo dyes such as methyl orange. The first step involves the reaction of nitrous acid with phenylamine to form aryl diazonium cation. The second step involves the reaction between the cation and another arene compound to form the azo dye.



(i) Name the type of the reaction for step **2**.

Electrophilic substitution

(ii) It is possible to form another isomer of the azo dye in step 2.

Draw the structure of this isomer and suggest why this isomer is less likely to be formed.

Since R/alkyl group is 2,4 -directing,



It is less likely to be formed due to <u>steric hindrance</u> between the bulky aryl diazonium and R groups.

When nitrous acid reacts with propylamine, an alcohol and a neutral diatomic gas is obtained instead of the corresponding alkyl diazonium cation.

(iii) Write a balanced equation for this reaction.

 $CH_3CH_2CH_2NH_2 + HNO_2 \rightarrow CH_3CH_2CH_2OH + N_2 + H_2O$

(iv) Suggest why the alkyl diazonium cation is not obtained.

Alkyl diazonium cation is highly unstable. It decomposes to give carbocation and N_2 . The driving force for this reaction is the formation of N_2 , an exceptionally stable molecule.

В

ННН

·H

H-Ċ

(v) Optically active compound A, C₃H₈NOC*l*, contains three different functional groups. One of the functional groups is amine. A reacts with nitrous acid to form compound B, C₃H₇O₂C*l* which is optically inactive.

Draw the structures of **A** and **B**.

[8] [Total: 20]



5 The compound *chloroxylenol* and *Triclosan* are two chlorinated phenol compounds which has been featured for its anti-microbial action, and used in soaps and detergents. While these compounds are relatively safe for humans to handle, they may have a tendency to persist in the environment for a long period of time, where in turn, they can be converted to other more toxic compounds, causing environmental problems.



(a) By considering their solubility and reaction with water, suggest two reasons why such compounds are likely to persist in the environment.

[2]

- 1. Due to the large hydrophobic benzene ring, even though there is the presence of hydrogen bonding with –OH groups, the compounds are likely to be insoluble in water.
- 2. As halogenoarenes, the C-C*l* bond is not susceptible to nucleophilic substitutions, and the compounds cannot be hydrolysed in water.

As such they are difficult to remove by natural processes in the environment.

(b) (i) Suggest suitable reagents and conditions which would convert 3,5-dimethylphenol to *chloroxylenol*.

Reagent: Chlorine in organic solvent Conditions: r.t.p (ii) State and outline the mechanism by which the reaction in (b)(i) is likely to occur.

Electrophilic substitution

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Step 1: Formation of positively-charged carbocation intermediate



Step 2: Loss of proton, H^{+} to form a stable benzene ring.



(c) *Triclosan* can be synthesised from 2,4-dichlorophenol.



Compare the acidity of 2,4-dichlorophenol with *chloroxylenol*.

[2]

[3]

2,4-dichlorophenol is a stronger acid than *chloroxylenol* as there is the presence of more electron-withdrawing -Cl groups attached to the benzene ring.

This decreases the intensity of the negative charge on the O atom in the phenoxide ion from 2,4-dichlorophenol more than that in *chloroxylenol*, hence the phenoxide ion from 2,4-dichlorophenol is more stable.

A compound related to 2,4-dichlorophenol and *chloroxylenol* known as catechol, can be found in small quantities in fruits and vegetables. When mixed with an enzyme and with exposure to oxygen, catechol is converted to brown melanoid pigments, which accounts for why these fruits would turn brown when cut and left exposed to air. In the laboratory, this oxidation can be studied through the use of suitable metal complexes (e.g. Zn^{2+} , Ni^{2+}) in the presence of azacrown ethers, such as **A** and **B** shown below.



(d) Using your knowledge of the rate of enzymatic activity, sketch a graph to illustrate how the rate of 'browning' of fruits change with increasing concentration of catechol.



(e) (i) Draw the structure of complex formed from the reaction between compound **A** with Ni^{2+} respectively, indicating clearly its shape.



(ii) Suggest the likely shape of the complex formed between Ni²⁺ and compound **B**.

Trigonal bipyramidal

[1]

[2]

Compounds **C** and **D** are isomers of catechol, and they have a formula of $C_6H_6O_2$. These compounds are insoluble in water and sodium carbonate, but soluble in sodium hydroxide.

Upon careful warming with potassium manganate(VII), catechol and compounds C and D produce 3 compounds labelled E, F and G respectively. Compounds E, F and G all give an orange precipitate upon warming with 2,4-dinitrophenylhydrazine. In addition, 1 mole of each compound decolourises 2 moles of bromine dissolved in tetrachloromethane.

However combustion of molar quantities of **G** requires half a molar equivalent of oxygen gas lesser compared to combustion of **E** and **F**. Also upon further vigorous heating which breaks down their ring structure, compounds of **F** and **G** give rise to two molecules of $C_3O_5H_2$, whereas **E** produces $C_4O_6H_2$.

(f) Suggest the structures of catechol and compounds **C** to **G**, explaining clearly the chemistry involved and your reasoning.

[10] [Total: 20]

Since catechol and compounds **C** and **D** are insoluble in water

⇒ They are likely to be hydrophobic (i.e. presence of large alkyl groups/benzene rings).

Since catechol and compounds ${\bf C}$ and ${\bf D}$ are soluble in sodium hydroxide but not sodium carbonate

- \Rightarrow They are acidic in nature
- ⇒ But do not contain –COOH groups, i.e. likely to be phenols

Catechol and compounds **C** and **D** undergo oxidation with $KMnO_4 / H^+$.

The products **E** to **G** undergo condensation reaction with 2,4-DNPH \Rightarrow Presence of carbonyl compound in these products.

The products E to G undergo electrophilic addition reactions with $Br_2\,/\,CCl_4$

 \Rightarrow Presence of C=C double bond

Since each mole of **E** to **G** react with 2 moles of bromine \Rightarrow Presence of two C=C double bonds

The combustion of ${\bf G}$ takes up half a molar quantity of oxygen gas lesser than ${\bf E}$ and ${\bf F}$

⇒ Presence of one more oxygen in the formula when compared with E and F

Based on their formulae





The loss of 2 C in the oxidation products of ${\ensuremath{\text{E}}}$ is likely due to the production of CO_2

⇒ Presence of ethanedioic acid formed upon ring cleavage

Based on the structure of ${\bf F}$ and ${\bf G},$ and that they all are oxidation products of isomers of catechol



Based on the formula of $C_6H_6O_2$ and the products upon oxidation, catechol and compounds **C** and **D** are likely to be



