# NATIONAL JUNIOR COLLEGE 2008 PRELIMINARY EXAMINATIONS

CHEMISTRY Higher 2 9746/03

21 August 2008

## Paper 3 Free Response

2 hours

## **READ THESE INSTRUCTIONS FIRST**

Write your Name, Registration Number and Chemistry group on all the work you hand in. Write in dark blue or black pen. You may use a soft pencil for any diagrams, graphs or rough working. Do not use correction fluid.

## Answer each question on a fresh sheet of paper.

Answer any **four** questions. A Data Booklet is provided. You are reminded of the need for good English and clear presentation in your answers. The number of marks is given in brackets [] at the end of each question or part question.

This question paper consists of **11** printed pages (including this page)

### Answer any four questions.

- 1 (a) (i) What do you understand by the term enthalpy change of atomisation of magnesium?
  - Use the following data together with relevant data from the data booklet, (ii) construct an energy level diagram to calculate the enthalpy change of atomisation of magnesium.

|   | ΔH                     |
|---|------------------------|
|   | / kJ mol <sup>-1</sup> |
| Lattice energy of magnesium chloride                        | -2500                  |
| 1 <sup>st</sup> electron affinity for chlorine              | -349                   |
| Standard enthalpy change of formation of magnesium chloride | -652                   |

- (iii) Suggest, with reason, how the magnitude of the enthalpy change of atomization of magnesium might compare with that of chromium. [7]
- (b) (i) Explain why a solution of chromium(III) chloride is green while aqueous magnesium chloride is colourless. [4]
  - When aqueous sodium carbonate is added to aqueous chromium(III) (ii) chloride, effervescence was observed. Explain the observation with equations where necessary. [2]
- (c) Grignard reagent, RMgCl, is useful in organic synthesis as it enables the combination of two organic molecules into a bigger one by forming a carboncarbon bond. It is prepared by the reaction of magnesium with a halogenoalkane. One of the most important uses of the Grignard reagent is its reaction with carbonyl compounds to form alcohols as shown below.

$$R - MgCI + H = 0 + H_2O + R - C - OH + Mg(OH)CI$$

Given the carbon-magnesium bond in Grignard reagent is highly polar, (i) state the type of reaction between R –MgCl and the aldehyde.

[1]

(ii) R-MgCl reacts with propanal to give compound A. Compound A gives a yellow precipitate with I<sub>2</sub> in aqueous NaOH. When compound A reacts with excess concentrated H<sub>2</sub>SO<sub>4</sub> at 170°C, compounds B and C are formed. Compound B upon reaction with hot acidified potassium manganate(VII), produces compound D and effervescence is observed. Compound C exists as a pair of geometric isomers. Deduce the structure of compounds A - D.

2 Adrenaline is a naturally occurring hormone and stimulant released by the nervous system to prepare the body for immediate physical action during the time of danger or stress. After the discovery of the action of adrenaline, a series of stimulant drugs which are structurally and therapeutically similar to adrenaline were developed by pharmaceutical chemists. One such stimulant is amphetamine as shown below.



- (a) Even though adrenaline and amphetamine are structurally similar, both of them have different solubility in water.
  State which compound is more soluble in water, giving your reasons.
  [2]
- (b) Amphetamine is prepared commercially from compound X via a series of reactions as shown.



### Amphetamine

- (i) What types of reaction are reactions I, II and III?
- (ii) Suggest reagents and conditions for reaction III.
- (iii) Suggest a chemical test to distinguish between compound **X** and amphetamine.

- (c) Amphetamine is able to undergo further reactions to form other compounds. Draw the structural formulae of the organic compounds formed when amphetamine is reacted with
  - (i) excess CH<sub>3</sub>Cl
  - (ii) acid anhydride (an acid derivative),



[4]

- (d) Compound E, an isomer of amphetamine, forms a white precipitate when aqueous bromine is added to it. Suggest a structure for Compound E. [2]
- (e) In order to determine the base strength of amphetamine, 50 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> of hydrochloric acid was added to 55 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> of amphetamine in a polystyrene cup. The changes in temperature were recorded and plotted in Figure 1.



- (i) State one precaution you should observe when carrying out the experiment. [1]
- (ii) By means of appropriate calculations, deduce the base strength of amphetamine.

(You may assume the density of the solution is  $1.00g \text{ cm}^{-3}$  and its specific heat capacity is  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ .) [5]

- 3 Benzene diazonium salts, such as C<sub>6</sub>H<sub>5</sub>N<sub>2</sub><sup>+</sup>Cl<sup>-</sup>, are important intermediates in the synthesis of dyes.
  - (a) An experiment was conducted to study the reaction of 0.00346 mol of benzenediazonium chloride, F, with water at 25° C and 101 kPa.

The progress of the reaction was followed by measuring the volume of nitrogen gas, V<sub>t</sub>, produced at intervals of time after the start of the reaction. The mixture was left until no further reaction appeared to be occurring and the total volume of gas produced, V $_{\infty}$ , was measured.

The table below shows some of the experimental results.

| Time / s                         | 0 | 30   | 60   | 90   | 150  | 210  |
|----------------------------------|---|------|------|------|------|------|
| V <sub>t</sub> / cm <sup>3</sup> | 0 | 15.7 | 27.7 | 37.7 | 52.7 | 63.0 |

- (i) What is the volume of gas,  $V_{\infty}$ , collected when the reaction is complete?
- (ii) By using a graphical method, determine the order of reaction and hence its rate constant.

[6]

- (b) What would be the qualitative effect on the rate constant of changing:
  - (i) the concentration of benzenediazonium chloride
  - (ii) the temperature at which the measurements were made?

[2]

(c) When the rate of this reaction was measured, at 20° C, with a concentration of F (benzenediazonium chloride) of 0.06 mol dm<sup>-3</sup>, in the presence of nitric acid, the results at a series of values for pH were as shown below:

| рН   | Rate x10 <sup>-5</sup> / appropriate units |  |  |
|------|--|--|--|
| 2.15 | 44.6                                       |  |  |
| 2.45 | 22.6                                       |  |  |
| 2.57 | 16.9                                       |  |  |

What can be deduced from these results?

(d) Sunset Yellow, a dye, made from a benzenediazonium salt is used as a food colourant in sweets, orange squash and jams. It may be synthesized by the following reactions:



(ii) Suggest a reaction mechanism for step I. [3]

(i)

- (iii) What type of reaction is step III? [1]
- (iv) The sodium sulphonate groups (SO<sub>3</sub><sup>-</sup> Na<sup>+</sup>) have little effect on the colour of Sunset Yellow. Suggest a reason why those groups are needed in the molecule.

4 Salicylic acid is a colourless crystalline organic acid that is widely used in organic synthesis and functions as a plant hormone. It has the following structure:



salicylic acid

The acid dissociation constants for salicylic acid are:  $K_{a1} = 1.07 \times 10^{-3} \text{ mol } \text{dm}^{-3}$  $K_{a2} = 1.80 \times 10^{-14} \text{ mol } \text{dm}^{-3} \text{ at } 25^{\circ}\text{C}.$ 

- (a) Write an equation to show the first dissociation of salicylic acid. [1]
- (b) Calculate the pH of a 0.100 mol  $dm^{-3}$  solution of salicylic acid at 25°C. [2]
- (c) (i) Using the value obtained in (b) and any other relevant information given, sketch the titration curve showing the changes in pH when 15.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> sodium hydroxide was gradually added to 10.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> salicylic acid.
  - (ii) Suggest a suitable indicator for the above titration?

[5]

(d) Using any relevant information from above, calculate the pH of a 0.200 mol dm  $^{-3}$  solution of  $\ _{\rm H}^{\rm OH}$ 



[2]

- (e) Salicylic acid reacts with ethanol to form compound J and with ethanoyl chloride to form compound K.
  - (i) Draw the structures of J and K. [2]
  - (ii) Suggest **two** chemical tests that can be used to distinguish **J** from **K**. You should state what you would observe for **each** compound in **each** test.

[2]

- (f) Salicylic acid is manufactured from phenol in the industry.
  - (i) Suggest a route for this conversion.
  - (ii) An isomer of salicylic acid is also produced in the conversion from phenol. Draw its structure and state the type of isomerism exhibited. [2]
  - (iii) Predict whether the isomer in (f)(ii) will have a higher or lower boiling point than salicylic acid. Explain your answer. [2]

[Total: 20]

[2]

- 5 (a) When aqueous potassium peoxodisulphate(VI), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> is added to an aqueous solution containing potassium iodide, sodium thiosulphate and starch, a dark blue colour suddenly appears after a short delay. The appearance of this blue colour is accelerated by the presence of small concentration of Fe<sup>2+</sup> (aq)
  - (i) Explain the observations as fully as you can and suggest how iron(II) ions are able to participate in this reaction.
  - (ii) Draw the energy profile diagram for the above reaction in the presence of Fe<sup>2+</sup>(aq).
  - (iii) The deterioration in the air of some organic substances, such as cosmetics, is accelerated by iron(II) ions. Suggest why the deterioration can be slowed down by the addition of a small quantity of EDTA,



[4 + 2 +1]

(b) If a solution of an iron(II) compound is treated with cyanide ions, a white precipitate is first formed which then dissolves in an excess of the reagent to give a yellow solution.

Give the

- (i) formula
- (ii) shape

of the iron-containing species in the yellow solution.

[2]

- (c) Iron(II) ion is an important constituent of haemoglobin, a protein, found in red blood cells.
  - (i) With the aid of a schematic diagram of haem, explain how haemoglobin transports oxygen in the body.
  - (ii) The table below shows the effect of carbon monoxide in air on the human body:

| Concentration of CO in air /ppm | Effects on the human body      |
|---------------------------------|--------------------------------|
| 50                              | Deterioration in motor skills  |
| 100                             | Headache, dizziness and nausea |
| 1000                            | Death within 4 hours           |

Discuss why carbon monoxide is so toxic.

(iii) Suggest an effective way of treating carbon monoxide poisoning.

(d) The building blocks of proteins are the amino acids with the general structure:



(i) Explain why amino acids are crystalline solids with high melting points.

[2]

(ii) Mixtures of amino acids can be separated by ion exchange chromatography. This technique involves pouring the mixture of amino acids dissolved in water at pH 7 down a column containing an ion exchange resin called DEAE-cellulose. The structure of the DEAE-cellulose can be represented as shown in the figure below.



The + signs on the diagram show that the DEAE-cellulose is positively charged at this pH.

An aqueous solution containing 3 amino acids with  $R = (CH_2)_4 NH_2$ ,  $(CH_2)_2 CONH_2$  and  $CH_2 COOH$  was poured down the ion exchange column.

- (I) Predict the order in which the amino acids will be washed off. Explain your answer. [3]
- (II) Explain why DEAE cellulose is not used to separate mixtures of amino acids such as alanine and leucine where the R groups are -CH<sub>3</sub> and -CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>
  [2]

### Answer scheme

1 (a) (i) <u>Energy required</u> when <u>one mole of gaseous magnesium atoms</u> is formed from one mole of <u>magnesium metal</u> (or elemental magnesium) under <u>standard conditions</u> (or 298K, 1atm).



OR: Mg (s)  $\rightarrow$  Mg (g)

By Hess' Law,

 $\Delta H_{f}(MgCl_{2}) = \Delta H_{atm}(Mg) + BE(Cl_{2}) + 1^{st} IE(Mg) + 2^{nd} IE(Mg) + 2[1^{st} EA(Cl)] + \Delta H_{LE}(MgCl_{2})$  $\Delta H_{atm}(Mg) = -652 - 244 - 736 - 1450 + 2(349) + 2500$  $= + 116 \text{ kJ mol}^{-1}$ 

- (iii) Enthalpy of atomization is more endothermic for chromium as the metallic bonds are stronger due to the contribution of more electrons to the sea of delocalized electrons as the 3d and 4s electrons are close in energy.
- (b) (i) Water ligands approach Cr<sup>3+</sup> along axis.
  - Two d-orbitals along axis experience more repulsion thus raised to a higher energy than three d-orbitals in between axis.
  - Originally degenerate d-orbitals undergo d-splitting.
  - Energy gap correspond to  $\lambda$  of visible light ( $\Delta E = \frac{hc}{\lambda}$ )
  - d-subshell of Cr<sup>3+</sup> is partially filled (or 3d<sup>3</sup>)
  - Electron in lower energy d-orbital undergo d-d transition by absorbing energy from the visible light spectrum and is excited to higher energy d-orbital.
  - Complementary green colour observed. Magnesium ion has empty d-subshell, electronic transition from 3p to 4s orbital require energy beyond visible light spectrum.

 $CrCl_3 + 6H_2O \longrightarrow [Cr(H_2O)_6]^{3+} + 3Cl^{-}$ 

(ii)

$$[Cr(H_2O)_6]^{3+} + H_2O \implies [Cr(H_2O)_5OH]^{2+} + H_3O^+$$

Cr<sup>3+</sup> - high charge density

- polarizes the surrounding water molecules
- hydrolysis occurs resulting in acidic solution .

$$2H^+ + CO_3^{2-} \longrightarrow CO_2 + 2H_2O$$

(c) (i) nucleophilic addition





Compound C



Compound D



- 2 (a) Adrenaline more soluble in water. Adrenaline has a more extensive hydrogen bonding as it contains three O-H groups.
  - (b) (i) I: Nucleophilic addition II: Elimination III: Reduction
    - (ii) LiAlH<sub>4</sub>, dry ether OR

H₂, Ni OR NaBH₄

(iii) I<sub>2</sub>, NaOH(aq), Warm Compound X: Yellow precipitate Amphetamine: No yellow precipitate



(d) phenylamine with alkyl side chain H<sub>2</sub>N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

- (e) (i) Use a lid to cover the mixture to minimise heat lost to surroundings OR Ensure constant stirring while monitoring temperature.
  - (ii)  $\Delta H_{neutralisation} = -55.3 \text{ kJ mol}^{-1}$ Hence amphetamine is a weak base.
- 3 (a) (i)

Amt of N<sub>2</sub> formed at 25°C and 101 kPa = 0.00346 mol Using pV = nRT Vol of N<sub>2</sub> formed (V<sub> $\infty$ </sub>) = 84.8 cm<sup>3</sup>

| t/s                     | 0    | 30   | 60   | 90   | 150  | 210  | x    |
|-------------------------|------|------|------|------|------|------|------|
| $V_t$ / cm <sup>3</sup> | 0    | 15.7 | 27.7 | 37.7 | 52.7 | 63.0 | 84.8 |
| $V \infty - V_t$        | 84.8 | 69.1 | 57.1 | 47.1 | 32.1 | 21.9 |      |

Plot a graph of V<sub>t</sub> against t i.e product against time graph OR a graph of  $(V_{\infty} - V_t)$  against t i.e reactant against time graph

From graph of V<sub>t</sub> against t, read off the  $1^{st}$  half-life and the  $2^{nd}$  half-life.

- $1^{st}$  half-life corresponds to time taken for the reaction to be 50% completed i.e.  $V_t =$  $0 \text{ cm}^3 \rightarrow V_t = 84.8/2 \text{ cm}^3$
- $2^{nd}$  half-life corresponds to time taken for the reaction to be 50% completed to 75% completion i.e.  $V_t = 84.8/2 \text{ cm}^3 \rightarrow V_t = 0.75 \times 84.8 \text{ cm}^3$ Since 1<sup>st</sup> half-life  $\approx 2^{nd}$  half-life = 108 s, reaction is a 1<sup>st</sup> order reaction.
- Since it is a 1<sup>st</sup> order reaction, (ii)  $t_{\frac{1}{2}} = \ln 2 / k$  $k = 5.78 \times 10^{-3} s^{-1}$
- Rate constant will not change with a change in conc of benzenediazonium chloride (b) (i) Rate constant will increase with an increase in temp. (ii)

|                     | $[H^+]/mol dm^{-3}$ | рН   | Rate x10 <sup>-5</sup> / approp units |          |       |
|---------------------|---------------------|------|---------------------------------------|----------|-------|
|                     | 0.00708             | 2.15 | 44.6                                  | decrease |       |
| decrease {<br>by 2X | 0.00355             | 2.45 | 22.6                                  | L        | by 2A |
|                     | 0.00269             | 2.57 | 16.9                                  |          |       |

Reaction is  $1^{st}$  order wrt  $[H^+]$ ;  $H^+$  catalyses the rxn.

**Compound G:** 



conc HNO<sub>3</sub>, conc H<sub>2</sub>SO<sub>4</sub>. reflux

**Compound H:** 



tin, conc HCI

Electrophilic substitution (refer to notes) (ii) Give name of mechanism, state the rds and give proper structure of the arenium ion formed.

(ii)

(C)

- (iii) Electrophilic substitution.
- (iv) To make it soluble in water.
- 4 (a) First dissociation of salicylic acid:





 (iii) Isomer will have higher boiling point than salicylic acid. Intra-molecular hydrogen bonding in salicylic acid causes the inter-molecular forces of attraction to be weak van der waals forces. Intermolecular forces of attraction is strong hydrogen bonding in isomer and more energy required to overcome.

5 (a) (i)

$$S_2O_8^{2-}(aq) + 2l^-(aq) \xrightarrow{S_2O_3^{2-}, starch} 2SO_4^{2-}(aq) + l_2(aq)$$

•  $I_2$  once formed rapidly reacts with  $S_2O_3^{2-}$  according to the following eqn:

- When all S<sub>2</sub>O<sub>3</sub><sup>2-</sup> present has reacted, the I<sub>2</sub> liberated will now react with starch to form the dark blue starch-iodine complex.
- Dark blue colour appears after a short delay is because the reaction has high activation energy as it involves the collision between two negatively charged ions,  $S_2O_8^{2-}$  and  $I^-$ .
- Appearance of the blue colour is accelerated in the presence of Fe<sup>2+</sup> as Fe<sup>2+</sup> acts as a homogenous catalyst. Fe<sup>2+</sup> provides an alternative pathway involving lower activation energy for the reaction between S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and I<sup>-</sup>.
- The catalysed pathway involves 2 steps with each step having a low activation energy;

Step 1  $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$   $E^{\circ}_{cell} = +1.24 \text{ V}$ Step 2  $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$   $E^{\circ}_{cell} = +0.23 \text{ V}$ 



(iii) Hexadentate ligand, EDTA, forms a very stable complex with  $Fe^{2+}$ , thereby removing the catalytic effect of  $Fe^{2+}$ .

 $Fe^{2+}$  +  $(EDTA)^{4-} \rightarrow \{Fe(EDTA)\}^{2-}$ 

- **(b) (i)**  $[Fe(CN)_6]^{4-}$ 
  - (ii) Octahedral

(c) (i)



 $O_2$  + Hb  $\leftrightarrow$  Hb $O_2$ 

Oxygen binds to Fe centre weakly and reversibly through dative bonding.

- (ii) CO is a stronger ligand than oxygen. Hence it displaces the oxygen in oxyhaemoglobin readily to form the stable complex, carboxyhaemoglobin (HbCO)
- (iii) Breathe in pure oxygen.
- (d) (i) Amino acids exist as zwitterions due to internal acid-base reaction:



The forces of attraction between these zwitterions (found at fixed sites) are the strong ionic bonds which require much energy to overcome  $\Rightarrow$  high melting point.

(ii) At pH 7,



(ii) R groups in both alanine and leucine are non-polar and not charged  $\Rightarrow$  not attracted to DEAE cellulose  $\Rightarrow$  no separaton by ion exchange chromatography