#### IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2013, for Internal Students of the Imperial College of Science, Technology and Medicine

This paper is also taken for the relevant examination for the Associateship

## CHEMISTRY FOUNDATION PAPER ONE

Tuesday 08<sup>th</sup> January 2013, 14:00-16:15

# USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

Found/0113 Turn Over

#### 1F2 – Atomic Structure

#### NB. This question is worth 25 marks.

Answer parts a) and b) and EITHER part c) OR part d) of this question.

- a) Answer **ALL** parts of this question.
  - i) Write down the sets of quantum numbers that define the 1s, 4s and 5s atomic orbitals.

(3 marks)

ii) For n = 4 and l = 1, draw all the orbitals associated with the different values of  $m_l$ 

(3 marks)

iii) The electron affinity of lithium is a negative value, whereas the electron affinity of beryllium is a positive value. Use electron configurations to explain this observation.

(4 marks)

iv) The first four ionization energies of an element X are 403, 2633, 3900 and 5080 kJ mol<sup>-1</sup>. Suggest to which periodic group X belongs and give reasons for your choice.

(4 marks)

- b) Using the Rydberg Equation, calculate (i) the *frequency* (in Hz) and (ii) the *energy* (in kJ mol<sup>-1</sup>) of the energy level transition from 6 → 3 in the atomic spectrum of hydrogen.

  (6 marks)
- c) Using Slater's Rules, calculate  $Z_{eff}$  for a 4s and a 3d electron in zinc, and thereby predict

(5 marks)

d) Order the following in terms of the strength of hydrogen bonding:

which electron will be preferentially removed when zinc is ionised.

HF, H<sub>2</sub>S, NH<sub>3</sub>, OH<sub>2</sub>, SiH<sub>4</sub>.

Discuss the electronic factors responsible for the order.

(5 marks)

## 1F3 – Aromatic Chemistry

#### NB. 'Half a question' (out of 12.5 marks).

Answer part a) and EITHER part b) OR part c) of this question.

CI
$$HNO_3$$

$$H_2SO_4$$

$$O_2N$$

$$O_2N$$

$$O_3$$

$$H_2SO_4$$

$$O_3$$

$$O_3$$

$$O_2$$

$$O_3$$

$$O_4$$

$$O_3$$

$$O_3$$

$$O_4$$

$$O_3$$

$$O_4$$

$$O_3$$

$$O_4$$

$$O_3$$

$$O_4$$

$$O_5$$

$$O_4$$

$$O_5$$

$$O_4$$

$$O_5$$

$$O_5$$

$$O_5$$

$$O_7$$

$$O_8$$

$$O_9$$

$$O_8$$

$$O$$

- a) Answer **BOTH** parts of this question
  - i) Draw the mechanism for the transformation of starting material 1 to product 2 including formation of the active electrophile.

(4 marks)

ii) Heating of compound 2 with sulfur trioxide in sulfuric acid gives a major isomer product 3. Draw product 3, rationalising the regiochemistry obtained through the use of resonance diagrams.

(4.5 marks)

b) Intermediate 2 can be prepared regioisomerically pure in two steps from compound 4. Identify the reaction conditions required for both steps.

(4 marks)

c) What product would be obtained when treating compound 1 with KNH<sub>2</sub> in NH<sub>3</sub> and comment on the mechanism?

(4 marks)

## 1F4 - Chemical Equilibria

#### NB. This question is worth 25 marks.

Answer part a) and **EITHER** part b) **OR** part c) of this question.

- a) Answer **ALL** parts of this question
  - i) Describe what is meant by a *state function* and a *path function* and give **ONE** example of each.

(2 marks)

ii) Describe what is meant by chemical potential and activity coefficient.

(2 marks)

iii) Calculate the work is done if an ideal gas is compressed from  $1000 \text{ cm}^3$  to  $500 \text{ cm}^3$  by a constant external pressure of  $2 \times 10^5 \text{ Pa}$ ? Comment on the sign of your result.

(3 marks)

iv) When sodium nitrate (NaNO<sub>3</sub>) dissolves in water at room temperature, the solution cools down. What sign (positive or negative) would you expect the enthalpy change, entropy change and Gibbs free energy change to have for this dissolution? Explain your choice of sign for each parameter and state what you might expect to happen if you cooled the solution further.

(3 marks)

v) Lemon juice is  $0.3 \text{ mol dm}^{-3}$  citric acid. Assuming the relevant pK<sub>a</sub> of citric acid is 3.09, calculate the pH of lemon juice.

(3 marks)

QUESTION CONTINUED OVERLEAF

- b) Answer **ALL** parts of this question.
  - i) Describe what is meant by a *closed isobaric system*.

(2 marks)

ii) 1 gram of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) is fully combusted in an isobaric calorimeter containing 200 grams of water. Use the information below to calculate the temperature increase of the water in the calorimeter, assuming that all the heat given out during the combustion is transferred to the water and there is no heat loss.

Combustion of glucose: 
$$C_6H_{12}O_6 + 6 O_2 \rightarrow 6 CO_2 + 6 H_2O$$
  
 $\Delta_f H^{\theta} [C_6H_{12}O_6] = -1271 \text{ kJ mol}^{-1}$   
 $\Delta_f H^{\theta} [CO_2] = -394 \text{ kJ mol}^{-1}$   
 $\Delta_f H^{\theta} [H_2O] = -286 \text{ kJ mol}^{-1}$   
 $C_{P,m} [H_2O] = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ 

(10 marks)

- c) Answer **ALL** parts of this question.
  - i) Describe what is meant by an *electrolytic cell* and a *galvanic cell*.

(2 marks)

ii) Describe the characteristics of an ideal rechargeable battery.

(3 marks)

iii) A Nickel – Cadmium rechargeable battery is made by coupling the following two electrochemical half cell reactions (both shown as reductions):

$$NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + 2OH^ E^0 = 0.49 \text{ V}$$
  
 $Cd(OH)_2 + 2e^- \rightleftharpoons Cd + 2OH^ E^0 = -0.81 \text{ V}$ 

Write down the full cell reaction for a Nickel – Cadmium battery (with the spontaneous cell reaction in the forward direction) and calculate the standard cell potential.

(4 marks)

iv) Calculate the equilibrium constant  $(K_{eq})$  for the Nickel – Cadmium cell reaction under standard conditions.

(3 marks)

# 1F5 – Stereochemistry

### NB. 'Half a question' (out of 12.5 marks).

This is a multiple choice question. A correct answer will be given full marks. An incorrect answer will be given zero. Please only mark *one* answer per question.

Answer ALL of the following:

1) Based on diagram **X**, which is the correct Newman diagram below?

(2 marks)

$$B)$$
 OHC CONH<sub>2</sub>

2) For which one of the molecules below has the correct order of priority been assigned?

(2 marks)

QUESTION CONTINUED OVERLEAF

3) What is the correct stereochemical assignment of the chiral molecule below? (3.5 marks)

- A) R
- B) *S*
- C) achiral
- D) meso
- 4) Which of the following molecules is chiral and dissymmetric? (2.5 marks)

5) Which of the following molecules is *meso*?

(2.5 marks)

$$\begin{array}{c} & \text{NH}_2 \\ \text{HO}_2\text{C} & \text{NH}_2 \\ \text{CO}_2\text{H} \end{array}$$

$$\begin{array}{c} & \text{NH}_2 \\ \text{HO}_2\text{C} & & \text{NH}_2 \\ & \text{CO}_2\text{H} \end{array}$$

$$\begin{array}{c} \text{NH}_2\\ \text{HO}_2\text{C} & \text{NH}_2\\ \text{CO}_2\text{H} \end{array}$$

$$HO_2C$$
 $NH_2$ 
 $CO_2F$ 
 $NH_2$