ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examinations

CHEMISTRY
Higher 2 **9746/03**

Paper 3 Free Response **9 September 2008**

2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet, Graph Paper, Answer Paper

READ THESE INSTRUCTIONS FIRST

Write your name and civics group on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

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.

At the end of examination, fasten all your work securely together.

Answer any **four** questions.

1(a) The compound K_3CrO_4 is a green solid. When mixed with dilute H_2SO_4, it disproportionates to yield $Cr^{3+}(aq)$ and $Cr_2O_7^{2-}(aq)$ ions. The mixture produced was mixed with excess KI and the iodine liberated required 32.00 cm^3 of 0.30 mol dm^{-3} $Na_2S_2O_3$ for reaction. Write equations for the following changes:

(i) CrO_4^{3-} to Cr^{3+}

(ii) CrO_4^{3-} to $Cr_2O_7^{2-}$

(iii) the overall equation for the disproportionation of CrO_4^{3-} in acid.

(b) 1 mole of $Cr_2O_7^{2-}$ reacts with excess KI to liberate 3 moles of iodine. Hence, by using the equation in (a)(iii), calculate the mass of K_3CrO_4 used in the disproportionation reaction. [6]

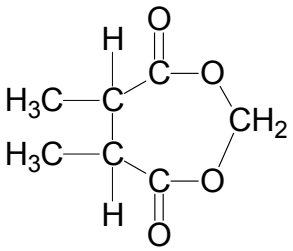
(c) Chromium plating can be carried out on an object in an acidified solution of 2.0 mol dm^{-3} sodium dichromate (VI). The process is carried out on an object of surface area of 0.5 m^2 and the current used is 40 A. Calculate the time needed to plate the object to a thickness of 1.0 x 10^{-5} m.

[Density of chromium is 7.3 g cm^{-3}.] [4]

(d) Explain briefly why it would not be possible to electroplate the object with aluminium from an aqueous solution of aluminium nitrate. [1]

(e) Explain why $Cr^{3+}(aq)$ ion is coloured. [3]

(f) **(i)** A cyclic di-ester can be synthesized from reacting a dicarboxylic acid with a diol. Hence, describe how **2, 3-dichlorobutane** can be converted to compound **A** in ***3 steps***. Include in your answer, the reagents and conditions for each step, including the structures of the intermediate compounds formed.



Compound A

(ii) Name the isomerism exhibited by but-2-ene and draw the isomers.

(iii) A by-product in the reaction between ethylamine, $CH_3CH_2NH_2$ and chloromethane, CH_3Cl, has the formula $C_5H_{14}NCl$ and it gives an immediate precipitate with aqueous silver nitrate. Suggest a structure for this compound and write an equation for its formation.

[6]

[Total : 20]

2(a) Carbon dioxide is often used as a coolant gas in nuclear reactor. It is observed that carbon dioxide shows significant deviations from the ideal behaviour that is predicted by the kinetic theory of gases.

(i) State two assumptions of the kinetic theory of gases. [2]

(ii) From the following sets of conditions, which set of conditions would you expect carbon dioxide to deviate most from ideal gas behaviour? Explain your answer.

Set I	100K and 1 atm
Set II	100K and 5 atm
Set III	300K and 2 atm

[3]

(iii) Carbon dioxide can be liquefied at room temperature just by pressurising them. Why does the application of pressure cause the gas to liquefy? [1]

(b) The solubility product of calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$, at 25^0C is 1.0×10^{-5} mol^3 dm^{-9}.

(i) Calculate the number of moles of $Ca(H_2PO_4)_2$ that can be dissolved in 100 cm^3 of water. [2]

(ii) Will precipitation occur when 30 cm^3 of 3.0×10^{-3} mol dm^{-3} $Ca(NO_3)_2$ is added to 60 cm^3 of 3.0×10^{-2} mol dm^{-3} NaH_2PO_4? [2]

(c) **(i)** Beryllium resembles aluminium in its chemical properties. Both beryllium oxide and aluminium oxide are *amphoteric*. With reference to **either** beryllium oxide or aluminium oxide, explain the term *amphoteric* with appropriate equations. [2]

(ii) Write a balanced equation to show the action of heat on beryllium nitrate. [1]

(iii) Describe and explain how the thermal stability of beryllium nitrate compares with that of strontium nitrate. [3]

(d) State what you would observe in each of the following experiments. Explain the observations by using relevant redox potentials in the *Data Booklet*.

(i) Solid manganese(IV) oxide is added to aqueous iron(II) sulphate solution;

(ii) Chlorine gas is passed through aqueous potassium bromide solution.

[4]

[Total : 20]

[Turn over

3(a) Dinitrogen pentoxide is a colourless gas which decomposes on heating according to the equation:

$N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2} O_2(g)$ $\Delta H > 0$

The data shown in the table below were obtained in an investigation of the rate of decomposition of N_2O_5 at 373K.

Time/ min	**$[N_2O_5]$ / mol dm^{-3}**
0	2.00
20	1.06
40	0.56
60	0.32
80	0.18
100	0.10
120	0.06

(i) State another method by which the rate of decomposition could be followed. [1]

(ii) Use a graphical method to find the order of reaction with respect to N_2O_5 and construct the rate equation for this reaction. [3]

(iii) Determine the rate constant of the reaction, stating the units. [1]

(iv) The following reaction mechanism has been proposed:

Step 1: $N_2O_5 (g) \rightarrow 2NO (g) + \frac{3}{2} O_2 (g)$ slow

Step 2: $2NO (g) + O_2 (g) \rightarrow 2NO_2 (g)$ fast

Sketch a labelled energy profile diagram for the proposed mechanism represented by Step 1 and Step 2. [2]

(b) The N_2O_5 molecule is present in the vapour state, but the structure is ionic in the solid state, existing as $NO_2^+.NO_3^-$.

(i) Draw the dot-and-cross diagrams of NO_2^+ and NO_3^-. [2]

(ii) Draw the displayed formula for the N_2O_5 molecule and suggest the values for the bond angles in this molecule. [2]

3(c) **D**, $C_{12}H_{16}O_3N_2$, is a neutral compound. Upon reaction with hot aqueous sodium hydroxide, **E** and **F** are formed. On acidification, **E** forms $C_2H_4O_2$, which gives effervescence with solid sodium carbonate.

1.52 g of **F**, $C_8H_{12}N_2O$, required 25.0 cm^3 of 0.40 mol dm^{-3} of sulphuric acid for complete reaction at room temperature. 1 mole of **F** is able to decolourise 3 moles of bromine water and give a white suspension **G**.

When acidified orange potassium dichromate (VI) is added to **F**, compound **H** is formed and the solution turned green. A yellow precipitate is also formed when **F** and **H** is reacted with alkaline aqueous iodine respectively.

Suggest the identities of **D**, **E**, **F**, **G** and **H**, explaining your reasoning. [9]

[Total : 20]

[Turn over

4(a) Nitroglycerin, $C_3H_5(NO_3)_3$, is a flammable oil commonly used to manufacture dynamite. The atomisation of nitroglycerin is represented by the equation:

$C_3H_5(NO_3)_3(l) \rightarrow 3C(g) + 5H(g) + 3N(g) + 9O(g)$

Given:

Standard enthalpy change of formation of nitroglycerin(l) / kJ mol^{-1}	-364
Standard enthalpy change of atomisation of carbon (graphite) / kJ mol^{-1}	+715
Standard enthalpy change of formation of $H_2O(g)$ / kJ mol^{-1}	-242
Standard enthalpy change of formation of $CO_2(g)$ / kJ mol^{-1}	-394

(i) Using the data above and relevant values from the *Data Booklet*, draw a labelled energy cycle and use it to calculate the standard enthalpy change of atomisation of nitroglycerin. [4]

Upon ignition, nitroglycerin decomposes to produce nitrogen, oxygen, carbon dioxide and steam.

(ii) Write a balanced equation, with state symbols, for the decomposition of nitroglycerin.

(iii) With reference to above data, calculate the standard enthalpy change of decomposition of nitroglycerin.

(iv) Calculate ΔG^{θ} at 25^0C for this decomposition given that ΔS^{θ} = +208 J $K^{-1}mol^{-1}$. Predict the spontaneity of the reaction at 25^0C.

(v) Is the reaction spontaneous at all temperatures? Explain.

[5]

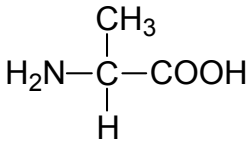
(b) Explain each of the following observations as fully as you can. Write equations where appropriate.

(i) Carbon dioxide gas is produced on adding solid sodium carbonate to aluminium chloride solution, but it is not observed when added to sodium chloride solution. [2]

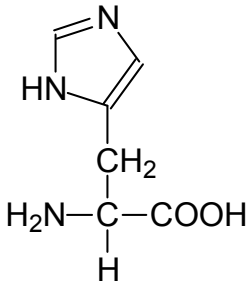
(ii) The atomic radii of the transition elements chromium to copper are similar. [2]

4(c) Vast majority of the amino acids found in nature are mostly α–amino acids, with a $NH_2CH(R)COOH$ structural skeleton, differing only in the side-chain, R.

Carnosine is a dipeptide, composed of the following α–amino acids, alanine and histidine.



alanine



histidine

(i) Draw a possible structure of a molecule of carnosine.

(ii) Draw the structure of an isomer of carnosine, made also from alanine and histidine, which is an amide but ***not*** a peptide. [2]

(d) To reduce pain by stress, animals generate their own opiates. One such opiate is called an enkephalin which is a pentapeptide containing α–amino acids;
alanine (Ala), histidine (His), praline (Pro) and serine (Ser).

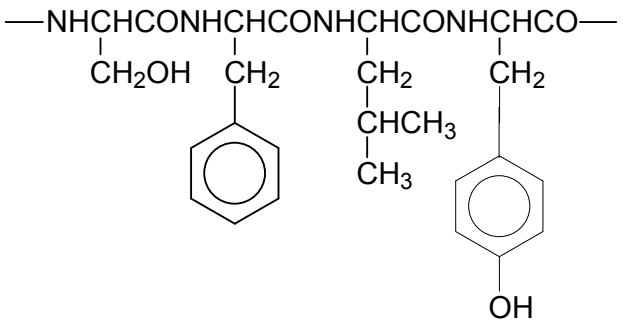
Partial hydrolysis of the enkephalin gave the following dipeptides.

Pro – Ser **His – His** **His – Pro** **Ala – His**

Determine the primary structure of the enkephalin. [1]

[Turn over

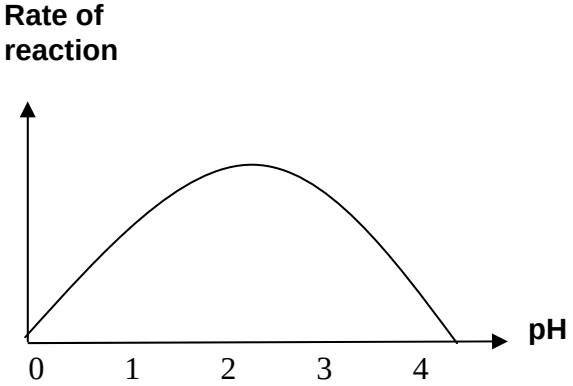
4(e) Pepsin is a digestive enzyme found in gastric juice that contains 327 amino acid resides in a single polypeptide chain. The diagram below shows the structure, at pH 7, of a fragment of pepsin which contains four α–amino acids, serine, phenylalanine, leucine and tyrosine.



(i) Draw a diagram showing how two groups in the pepsin fragment could be involved in maintaining the secondary structure of the polypeptide chain.

[2]

(ii) When food enters our stomach, gastric juice containing pepsin and hydrochloric acid are released to aid in the digestion of proteins. The graph below shows the variation in activity of pepsin with pH.



Explain the shape of the graph as fully as you can. [2]

[Total : 20]

5(a) Maintenance of pH is vital to the cells of all living organisms because enzyme activity is influenced by pH. The phosphate system, $HPO_4^{2-}/H_2PO_4^-$, is one of the important biological buffer systems which provides protection against harmful pH changes in cells.

The following equilibrium exists:

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad Ka_1 = 6.2 \times 10^{-8} \text{ mol dm}^{-3}$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \qquad Ka_2 = 3.6 \times 10^{-13} \text{ mol dm}^{-3}$$

(i) Explain, using equations, why the phosphate system can act as a buffer solution on the addition of a small amount of acid and alkali. [2]

(ii) What is the ratio of HPO_4^{2-} to $H_2PO_4^-$ if the buffer is to control the pH at 7.4? [2]

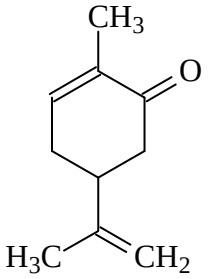
(iii) Given $[HPO_4^{2-}] + [H_2PO_4^-] = 2.0 \times 10^{-2}$ mol dm^{-3}, what is the respective concentrations of HPO_4^{2-} and $H_2PO_4^-$ at pH 7.4? [2]

(iv) Explain the difference between K_{a1} and K_{a2} values. [1]

(b) The boiling point of hydrogen bromide (-87^0C) is higher than the boiling point of hydrogen chloride (-114^0C) but much lower than the boiling point of hydrogen fluoride (20^0C). Explain. [3]

(c) With reference from the *Data Booklet*, suggest how magnesium metal can be recovered from a fused mixture of $MgBr_2$, $CaBr_2$ and NaBr by electrolysis. [2]

(d) **(i)** Carvone is the main flavouring material in spearmint oil.



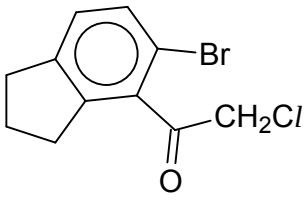
Carvone

A bottle containing carvone was wrongly labelled as 2,4-dimethylcyclohexene. Describe a chemical test used to distinguish between 2,4-dimethylcyclohexene and carvone, clearly stating the observation made. [2]

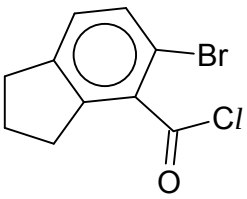
[Turn over

5(d) **(ii)** Give the organic product that would be formed when 2,4-dimethylcyclohexene reacts with iodine monobromide, IBr. Outline the mechanism involved in this reaction. [3]

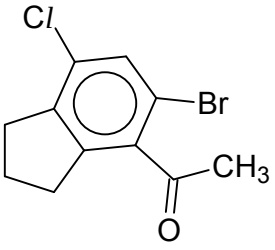
5(e) The structural formulae of three compounds **X**, **Y** and **Z** are given below:



X



Y



Z

How do these compounds differ in their reactions with aqueous silver nitrate solution? Explain your answer. [3]

[Total : 20]

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