NATIONAL JUNIOR COLLEGE
PRELIMINARY EXAMINATIONS
Higher 2

H

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY
Paper 3 Free response

9647/03
Tues 17 Sep 2013

2 hours

READ THESE INSTRUCTIONS FIRST

Answer any ***four*** questions.

Start your answer to each question on a fresh piece of paper.

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 the examination, fasten all your work securely behind the cover page.

Answer any **four** questions.

1(a) Dinitrogen difluoride is a chemical compound with the formula N_2F_2. It is a gas at room temperature. N_2F_2 was first identified as the thermal decomposition product of fluorine azide, N_3F, in 1952.

(i) Draw a dot-and-cross diagram for N_2F_2. Predict the shape around the central atom using the Valence Shell Electron Pair Repulsion theory.

(ii) N_2F_2 is able to exist as a pair of isomers at low temperature.

State the type of isomerism exhibited by N_2F_2. Hence, draw the structure of the more stable isomer.

[4]

(b) Nitrogen reacts with fluorine to give the compound N_2F_2 in the following equation:

$$N_2(g) + F_2(g) \rightleftharpoons N_2F_2(g)$$

A 1 : 2 mixture of N_2 and F_2 is allowed to reach dynamic equilibrium at 500 K at an equilibrium pressure of 1.12×10^5 Pa in a 500 cm^3 flask. The mass of the equilibrium mixture is found to be 0.578 g.

(i) Explain what is meant by the term *dynamic equilibrium* and write the expression for the equilibrium constant, K_p, for this reaction, stating its units.

(ii) Calculate the average M_r of the gaseous mixture. Hence, calculate the mole fraction of N_2F_2 in the equilibrium mixture.

(iii) Using your answer to **(b)(ii)**, calculate the partial pressure of N_2F_2.

(iv) Predict the sign of ΔS for the reaction, showing your reasoning.

(v) The value of ΔG for the above reaction is negative.

Use this information, together with your answer to **(b)(iv)**, to predict the sign of ΔH for the reaction. Explain your reasoning.

[10]

(c) When phosphorus(III) oxide is heated in air, another oxide **A** which contains 49% of phosphorus by mass is obtained. On hydrolysis, 1 mole of **A** forms a mixture containing 1 mole each of H_3PO_3 and H_3PO_4.

Deduce the identity of **A**.

[2]

(d) Industrially, 1,2–dichloroethane, $CH_2Cl CH_2Cl$ is used to make chloroethene, CH_2=CH*Cl*, the monomer which the polymer PVC is produced from.

When heated with aqueous silver nitrate solution, a white precipitate is observed for 1,2–dichloroethane within 10 minutes but not for chloroethene even after prolonged period.

(i) Why does the reactivity of chloroethene differ from that of 1,2–dichloroethane?

(ii) When aqueous silver nitrate is added to benzoyl chloride, a white precipitate is formed immediately even without heating.

Account for this observation.

[4]

[Total: 20]

2 This question concerns potassium manganate(VII).

(a) Potassium manganate(VII) can be used as a disinfectant. Over time, the concentration of potassium manganate(VII) in aqueous solution decreases due to a redox reaction taking place in the sealed bottles. Oxygen is also formed in this reaction.

Suggest the reducing agent responsible for the decrease in concentration of potassium manganate(VII) solutions on storage in sealed bottles.
Support your answer by quoting relevant data from the *Data Booklet*.

[2]

(b) Compounds containing manganese oxo-anions often disproportionate in aqueous solution. However, it is found that in neutral or alkaline solution, potassium manganate(VII) reacts with sodium sulfite, Na_2SO_3, in a 1:1 mole ratio to give a bright blue solution.

Suggest a formula for the species responsible for the blue colouration and write an ionic equation for the reaction.

[2]

(c) Solutions of potassium manganate(VII) can be standardised against a measured volume of a standard solution of sodium ethanedioate, $Na_2C_2O_4$, under acidic conditions. The contents of the titration flask have to be warmed to 60 °C before commencing the titration.

Explain, as fully as you can, why warming is necessary before commencing the titration.

[2]

(d) A student wanted to investigate the rate of reaction between MnO_4^- and $C_2O_4^{2-}$ ions in an acid medium. The rate of reaction was followed by mixing the following two solutions, and measuring the concentration of remaining MnO_4^- ions at fixed time intervals.

Solution **A**: 100 cm^3 of 0.20 mol dm^{-3} ethanedioic acid, 5 cm^3 of 2 mol dm^{-3} sulfuric acid, 15 cm^3 of 0.20 mol dm^{-3} copper(II) sulfate and 80 cm^3 of water

Solution **B**: 50 cm^3 of 0.020 mol dm^{-3} potassium manganate(VII)

The following results were obtained.

Time/s	$[MnO_4^-]$ / mol dm^{-3}
0	0.0040
10	0.0026
20	0.0016
30	0.00096
50	0.00040
75	0.00016

(i) By means of a graphical method, determine the relevant rate equation under the conditions whereby the reaction was conducted.

(ii) If the rate of consumption of $MnO_4^-(aq)$ at a particular time is 1.2×10^{-4} mol dm^{-3} s^{-1}, what will be the rate of consumption of ethanedioate ions at that time?

(iii) What is the role of copper(II) sulfate in the reaction?

(iv) The experiment is repeated at room conditions in the absence of aqueous copper(II) sulfate. Sketch a graph of the volume of carbon dioxide produced in this reaction against time, and explain the shape of your graph.

[8]

(e) Reagents like potassium manganate(VII) and sodium borohydride, $NaBH_4$, are of great help in elucidating the structure of organic compounds.

Compound **C** of molecular formula, $C_6H_{10}O_2$, produces a yellow precipitate when treated with an alkaline solution of iodine. **C** does not react with an ammoniacal solution of silver nitrate. Treatment of **C** with excess hot acidified concentrated potassium manganate(VII) gives compound **D**, $C_4H_6O_3$, as the only organic product. Compound **C** produces compound **E**, $C_6H_{12}O_2$, when reacted with $NaBH_4$.

Suggest possible structural formulae of **C**, **D** and **E**, explaining your reasoning.

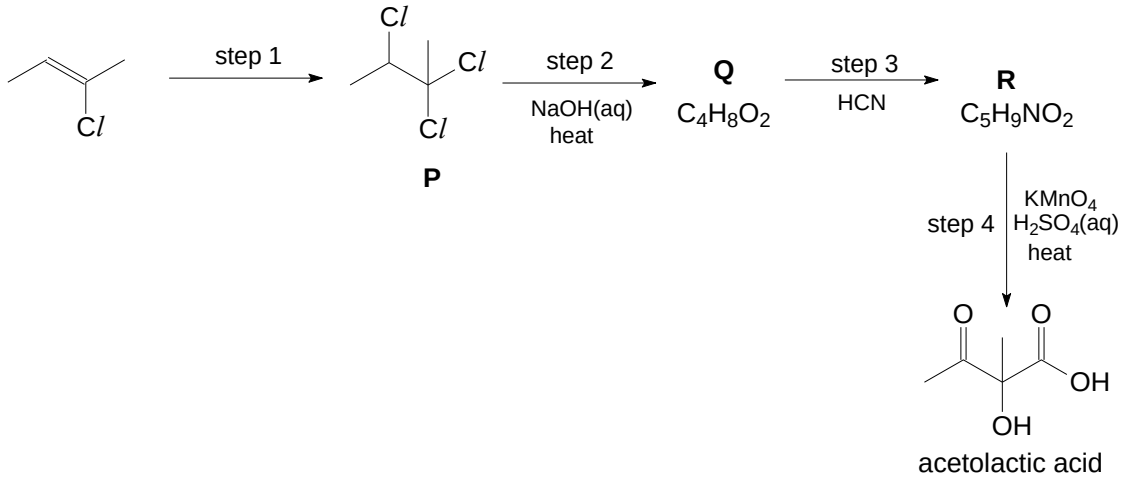
[6]

[Total: 20]

6

3 Acetolactic acid, $C_5H_8O_4$, is a precursor in the biosynthesis of the branched chain amino acids, valine and leucine.

(a) Acetolactic acid can be synthesised from 2-chlorobut-2-ene by the following reactions.



(i) Name the reagent and conditions used in step 1 and describe the mechanism for this reaction. In your answer, you should include curly arrows showing the movement of electrons and any relevant charges and dipoles.

(ii) Compound **P** contains a chiral carbon. Explain why compound **P** obtained from step 1 does not rotate the plane of polarised light.

(iii) Suggest the structures of **Q** and **R**.

(iv) Draw the organic product(s) formed when acetolactic acid is warmed with iodine in the presence of aqueous potassium hydroxide.

[10]

(b) When acetolactic acid is heated with a limited amount of concentrated sulfuric acid under controlled condition, compound **S** with a molar mass of 228 g mol^{-1} is formed. No observable change is seen when **S** is treated with anhydrous $SOCl_2$.

Suggest the structure for **S** and hence, state the role of concentrated sulfuric acid in the reaction with acetolactic acid.

[2]

(c) Acetolactic acid reacts with PCl_5 to produce hydrogen chloride, a hydrogen halide. Hydrogen halides are also formed between hydrogen and halogens.

(i) Define the term *standard enthalpy change of formation of HI (g).*

(ii) The standard enthalpy change of formation, ΔH_f^{θ}, of three hydrogen halides are shown in the table below.

Compound	ΔH_f^{θ} / kJmol^{-1}
HCl (g)	–92
HBr (g)	–36
HI (g)	+26

Comment on these values in the light of the reactivity of chlorine, bromine and iodine with hydrogen.

(iii) How would you expect the volatility of the hydrogen halides to vary from HCl to HI? Explain.

[5]

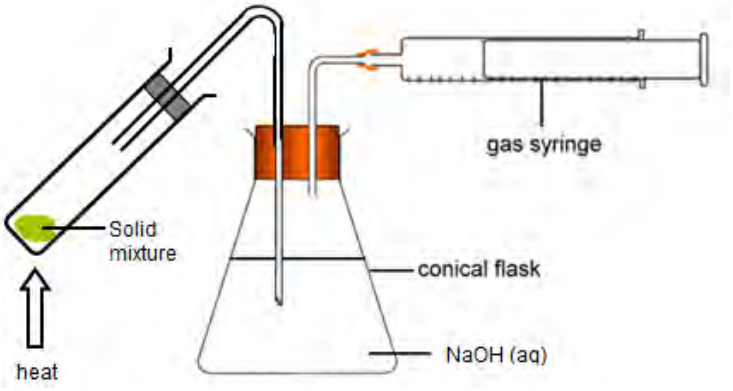
(d) Solid NaBr is added slowly to a 1 dm^3 solution containing 1×10^{-9} mol dm^{-3} $AgNO_3$ and 1×10^{-2} mol dm^{-3} $Pb(NO_3)_2$. The numerical values of the solubility product of AgBr at 25 °C is 5.4×10^{-13} and that of $PbBr_2$ is 6.6×10^{-6}.

Calculate the percentage of Ag^+ that has precipitated at the point when $PbBr_2$ just begins to precipitate.

[3]

[Total: 20]

4(a) A student investigated the thermal decomposition of Group II compounds. He heated a mixture of 2.50 g of magnesium nitrate and magnesium carbonate, as shown in the setup below, till no further change was observed. The volume of gas collected was 78.0 cm^3 at room temperature.



(i) Explain the role of sodium hydroxide in the above setup and identify the gas(es) collected in the gas syringe.

(ii) Calculate the percentage by mass of magnesium nitrate present in the mixture.

[4]

(b) The bond length of various nitrogen-oxygen bonds are as follows.

Bond	N–O	N=O	NO in NO_3^-
Bond Length (pm)	136	115	128

Account for the observed NO bond length in nitrate ion.

[2]

(c) The student carried out another experiment by heating equal amounts of carbonates of magnesium, calcium and barium for two minutes using a Bunsen burner and measured the volume of gas collected. The following table shows the results.

Group II carbonate	$MgCO_3$	$CaCO_3$	$BaCO_3$
Volume of gas collected / cm^3	80	25	5

(i) Using relevant data from the *Data Booklet*, explain the results obtained by the student.

(ii) Hence, estimate the volume of gas collected if the student were to heat an equal amount of strontium carbonate for two minutes.

[4]

(d) The Group II carbonates have little solubility in water and thus limited uses as compared to the Group I carbonates.
The table below shows the solubility of some Group II carbonates.

Group II carbonate	$MgCO_3$	$CaCO_3$	$BaCO_3$
Solubility (mol per 100 g of water)	1.26×10^{-4}	1.30×10^{-5}	1.22×10^{-5}

Suggest an explanation for the trend observed in the solubility of the Group II carbonates.

[2]

(e) Sodium carbonate, a Group I carbonate, can be used to maintain the pH of swimming pool water to the ideal range of 7.0−7.6. If the concentration of sodium carbonate is too high, it will cause skin irritation to swimmers.

The management committee of a public swimming pool hired a chemist to advise them on the need to adjust the pH of pool water. The chemist titrated a 10.0 cm^3 sample of pool water (assume it contains only Na_2CO_3) against a 0.05 mol dm^{-3} of HC*l*.
[The K_{b1} and K_{b2} values of Na_2CO_3 at 25°C are 2.13×10^{-4} and 2.25×10^{-8} respectively.]

(i) The pH at the first equivalence point is found to be greater than 7. Explain this observation with the aid of a relevant equation.

(ii) Given that 20.00 cm^3 of the HC*l* solution was required to turn the phenolphthalein indicator from pink to colourless, calculate the concentration of Na_2CO_3 in the pool water sample.

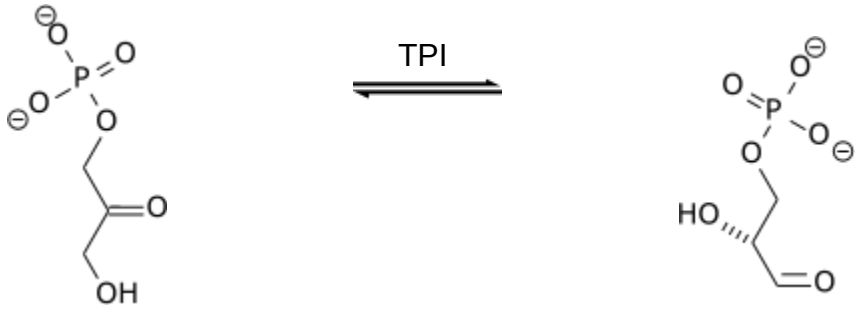
(iii) Calculate the initial pH of the pool water sample.

(iv) Sketch the pH–volume added curve you would expect to obtain when 50.00 cm^3 of the HC*l* solution is added to 10.0 cm^3 of the pool water sample. Label the various key points on the curve.

[8]

[Total: 20]

5(a) Many biological reactions are catalyzed by enzymes. Triose phosphate isomerase, TPI, is the enzyme that catalyses the reversible interconversion of the triose phosphate isomers shown below.



dihydroxyacetone phosphate D–glyceraldehyde 3-phosphate

TPI is a dimer of 2 identical subunits. Each subunit that makes up TPI contains 8 α–helices on the outside and 8 parallel β–strands on the inside of the 3–dimensional structure. The following is a fragment obtained on hydrolysis of the TPI enzyme.

−Ala − Cys − Ile − Gly − Glu –

Amino acid	**Formula of side chain (R in $RCH(NH_2)COOH$)**
Alanine (Ala)	$-CH_3$
Cysteine (Cys)	$-CH_2SH$
Glutamic acid (Glu)	$-CH_2CH_2COOH$
Glycine (Gly)	$-H$
Isoleucine (Ile)	$-CH(CH_3)CH_2CH_3$

(i) Describe what is meant by the *primary structure* of a protein.

(ii) Sketch a suitable diagram to show how the polypeptide chain is held in its secondary structure. You need only describe **<u>one</u>** of the two secondary structures in the 3–dimensional unit.

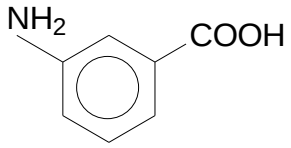
(iii) Proteins can be classified as being globular or fibrous. Deduce the class that TPI belongs to.

(iv) The above fragment can be further hydrolysed to form dipeptides. State the number of possible dipeptides that can be obtained and draw the structural formula of one of the dipeptides.

(v) TPI is an enzyme of kinetic perfection. This means that the rate of enzyme catalysed reaction is limited by the time taken for the reactant to diffuse to the enzyme. To overcome this, the enzyme employs the 'Circe Effect' where it attracts the substrate using electrostatic forces.
State the possible interactions that TPI could effect on dihydroxyacetone phosphate.

[9]

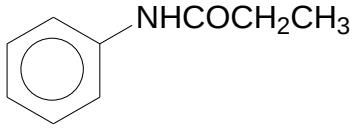
(b) Suggest a synthetic pathway, of not more than 4 steps, to produce compound **V** from benzene.



Compound **V** **[4]**

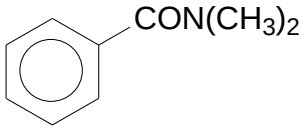
(c) **(i)** Between phenylamine and 4–methylphenylamine, which compound do you expect to have a lower pK_b value? Explain.

(ii) Suggest the reagents and conditions required to convert phenylamine to the following compound **W**.



Compound **W**

(iii) Suggest a suitable chemical test to distinguish the following isomer **X** from compound **W**. State the reagents and conditions and describe your observations for each compound.



Isomer **X**

(iv) Compound **Y** is another structural isomer of compound **W**.
Compound **Y**

- gives an orange precipitate **Z** with 2,4−dinitrophenylhydrazine
- does not gives brick red precipitate with alkaline Cu^{2+} complex

Suggest a possible structure of compound **Y** and hence draw the structure of the orange precipitate **Z**.

[7]
[Total: 20]