



SUBJECT: **Chemistry**
 PAPER NUMBER: I
 DATE: 23rd May 2018
 TIME: 9:00 a.m. to 12:05 p.m.

Required Data: Relative atomic masses: H = 1; C = 12; N = 14; O = 16; Cl = 35.5,
 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Answer ALL Questions

- 1) a) The group 1 element rubidium has two stable isotopes whose abundances are given in the table below. Calculate the relative atomic mass of rubidium to two decimal places.

Isotope	Abundance (%)
rubidium-85	72.15
rubidium-87	27.85

(2)

- b) Rubidium-87 (atomic number 37) is considered as stable since it has a half-life of billions of years. The age of rubidium bearing rock can be determined by the ratio of rubidium-87 and its decay product strontium-87.

- i) Explain what is meant by the term half-life.

(1)

- ii) Write the nuclear equation for the decay of rubidium-87 to strontium-87.

(2)

Question continues on next page

-
- c) i) Write the equation representing the first ionisation energy of rubidium.

_____ (1)

- ii) State, with reasons, which element of rubidium or strontium would have the higher first ionisation energy.

_____ (2)

- iii) State, with reasons, which element of rubidium or sodium would have the higher first ionisation energy.

_____ (2)

(Total: 10 marks)

- 2) Explain briefly each of the following statements.

- a) The N-H bond angles in ammonia are different to those in the ammonium ion.

_____ (2)

- b) Ammonia in water gives a basic solution whilst ammonium ions in water give an acidic solution.

_____ (2)

-
- c) The electrons in a C=O bond of carbon dioxide are not shared equally between the carbon and oxygen atoms.

(2)

- d) A molecule of carbon dioxide is not polar.

(2)

- e) Sulfur dioxide and carbon dioxide have different shapes.

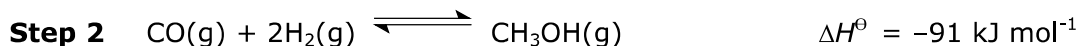
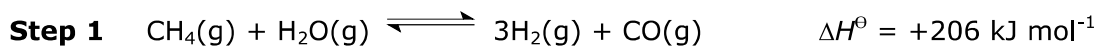
(3)

(Total: 11 marks)

Questions continues on next page

3) This question is about the production of methanol, its combustion and its physical properties when mixed with petrol.

a) Methanol can be synthesised through the gaseous phase reaction between methane and steam in a two-step process:



i) State, with reasoning, what effect, an increase in pressure at constant temperature will have on the equilibrium in Step 1 and that in Step 2.

Effect on Step 1: _____

Effect on Step 2: _____

_____ (2)

ii) State, with reasoning, what effect, an increase in temperature at constant pressure will have on the equilibrium in Step 1 and that in Step 2.

Effect on Step 1: _____

Effect on Step 2: _____

_____ (2)

b) Consider the following thermochemical data:



i) Use these data and any data from part (a) to calculate the standard enthalpy of combustion of gaseous methanol.

_____ (3)

-
- ii) The combustion of one mole of liquid methanol produces 38 kJ mol^{-1} less heat than that of gaseous methanol. Suggest a reason for this difference.

(1)

- c) Methanol is added to petrol to produce a mixture containing 10% methanol. The vapour pressure of methanol above the mixture is significantly higher than that of pure methanol. Suggest reasons for this behaviour.

(3)

(Total: 11 marks)

- 4) Explain the following observations. Support your answers with chemical equations (where relevant).

- a) A compound of lithium reacts vigorously with water to give an alkaline solution and a gas. The compound has a high melting point and on electrolysis the molten compound releases hydrogen at the anode.

(3)

- b) Gas is released when both lithium nitrate(V) and sodium nitrate(V) are heated strongly. However, only one of the nitrates gives off a brown gas whilst the other gives off lower quantities of a colourless gas.

(4)

-
- c) The addition of an acid to a solution of lead nitrate(V) gives a white precipitate which dissolves on heating.

(2)

- d) Hydrogen chloride gas dissolves in a colourless liquid A to give a solution that conducts electricity. However, a solution of the gas in a colourless liquid B, does not conduct electricity.

(2)

(Total: 11 marks)

- 5) Amongst other properties, transition metals have the ability to form complex ions and change oxidation states.

- a) A an aqueous solution of Cr^{3+} contains the hexaaquachromium(III) complex ion, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. Draw the shape of this complex ion.

(1)

- b) Explain the following observations using chemical equations as appropriate:

- i) Aqueous solutions of Cr^{3+} exhibit a pH lower than 7. Explain this observation.

(2)

- ii) Addition of a few drops of ammonia solution to aqueous Cr^{3+} results in a green precipitate which disappears on further addition of ammonia solution.

_____ (2)

- iii) Addition of a few drops of sodium carbonate solution to aqueous Cr^{3+} results in a green precipitate and evolution of a gas.

_____ (2)

- c) Replacement of all the water ligands from the hexaaquachromium(III) by ethandioate ions is said to be favoured due to an increase in entropy.

- i) Write an equation for the replacement of the water ligands by the ethandioate ions.

_____ (1)

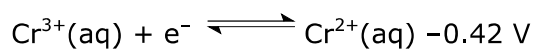
- ii) Explain what is meant by the term entropy.

_____ (1)

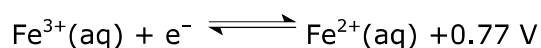
- iii) Explain how entropy increases in the ligand exchange reaction mentioned in this question.

_____ (2)

- d) Using the electrode potentials below, predict whether Cr^{2+} reduces Fe^{3+} or Fe^{2+} reduces Cr^{3+} .



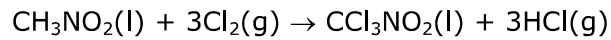
and



_____ (3)

(Total: 14 marks)

-
- 6) Chloropicrin, CCl_3NO_2 , is an insecticide which can be made inexpensively by a process which uses the following reaction:



- a) Calculate the mass (in grams) of nitromethane required to form 300 g of chloropicrin.

_____ (3)

- b) Calculate the volume of chlorine gas at 300 K and $1.01 \times 10^5 \text{ N m}^{-2}$ to form 300 g of chloropicrin.

_____ (3)

- c) There is concern about chloro compounds like chloropicrin depleting the ozone layer.

- i) Explain why the ozone layer is important.

_____ (2)

- ii) Explain how chloropicrin may be harmful to the ozone layer.

_____ (2)

(Total: 10 marks)

7) a) Give the structures of the following compounds:

i) 3-chloro-3-methylhexane

_____ (1)

ii) 1-chloro-4-methylhexane

_____ (1)

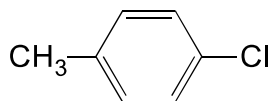
b) 3-chloro-3-methylhexane exists as two optical isomers. Explain what is meant by the term optical isomers.

_____ (2)

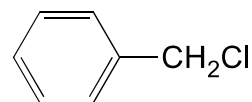
c) One optical isomer of 3-chloro-3-methylhexane reacts with iodide ions to give a mixture of two optical isomers of 3-iodo-3-methylhexane. Suggest why.

_____ (2)

d) Name the structures compounds P and Q.



P



Q

P = _____ (1)

Q = _____ (1)

- e) **Q** can be hydrolysed by OH^- replacing the Cl with a hydroxy group. However, it is not possible to replace the Cl in **P** in the same manner. Suggest a reason for this.

(2)

(Total: 10 marks)

- 8) Compounds **R** and **S** can be prepared from butanal in single step reactions. **S** turns acidified potassium dichromate(VI) solution green. In the presence of a small quantity of concentrated sulfuric(VI) acid, compounds **R** and **S** produce the liquid organic compound **T** with molecular formula $\text{C}_8\text{H}_{16}\text{O}_2$. The infra-red spectrum of **T** indicates an absorption at 1750 cm^{-1} that is typical of $\text{C}=\text{O}$ bonds.

- a) Identify compounds **R**, **S** and **T**.

R = _____ (1)

S = _____ (1)

T = _____ (1)

- b) Give the reagents and conditions that can be used to prepare **R** and **S** from butanal.

(2)

- c) **T** reacts with ammonia to form two organic compounds, one of which is **U**, molecular formula $\text{C}_4\text{H}_9\text{ON}$. **U** undergoes Hoffman degradation to form **V**.

- i) List the reagents used for carrying out Hoffman degradation.

(1)

-
- ii) Write an equation to represent the reaction of **T** with ammonia and include the structural formula of **U**.

(2)

- iii) Give the structural formula and state one chemical property of **V**.

(2)

(Total: 10 marks)

- 9) The aromatic compound **W** has a molecular formula of C_8H_8O . **W** reacts with 2,4-dinitrophenylhydrazine to form a yellow-orange crystalline precipitate. On treatment with iodine in the presence of alkali, **W** generates a pale-yellow precipitate and a solution, which on treatment with hydrochloric acid, deposits a white precipitate.

- a) i) Name and give the structure of **W**.

W = _____

Name	Structure
------	-----------

(2)

- ii) Explain the reactions described. Write chemical equations to show the reactions described in this question.

(3)

b) Write an equation to show how **W** can be synthesised directly from benzene?

(2)

c) Through the use of chemical equations, show how can **W** be converted into phenylethene?

(2)

d) Phenylethene is used to produce an important polymer. From knowledge of the polymerisation of ethene, suggest the structure of the polymer formed by phenylethene and give the steps involved in its production.

(4)

(Total: 13 marks)



SUBJECT:	Chemistry
PAPER NUMBER:	II
DATE:	24 th May 2018
TIME:	9:00 a.m. to 12:05 p.m.

A periodic table is provided.

Answer TWO questions from each section and ANY other question.

SECTION A

- 1) This question concerns acid base equilibria. Answers to all calculations should be to **TWO** decimal places.
- At 298 K, the acid dissociation constant, K_a , for propanoic acid is $1.35 \times 10^{-5} \text{ mol dm}^{-3}$. Calculate the pH of a 0.13 mol dm^{-3} aqueous propanoic acid at 298 K. (4)
 - Calculate the pH of a solution prepared by adding 100 cm^3 of 0.10 mol dm^{-3} aqueous sodium hydroxide to 500 cm^3 of 0.10 mol dm^{-3} propanoic acid. (6)
 - The propanoate ion is known as the conjugate base of propanoic acid. Explain the term conjugate base and calculate the K_b for the propanoate ion. The ionic product of water, K_w is $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K. (4)
 - At 303 K the pH of pure water is found to be 6.92. Explain what this observation implies about the enthalpy change of dissociation of water and explain why pure water is still considered neutral at this temperature. (6)

(Total: 20 marks)

- 2) This question is about phase behaviour and equilibria.
- Sketch a pressure-temperature phase diagram for CO_2 . Indicate on your graph: (i) the regions where different phases exist; (ii) the triple point and (iii) the critical point. (5)
 - Supercritical CO_2 can be used as a green solvent for extraction of organic substances from water. A scientific publication reports the partition constant of an organic substance B between water and supercritical CO_2 as 0.04 and that B is more soluble in supercritical CO_2 than in water. A 20 cm^3 aqueous solution of B contains 40.0 mg of the substance. This is allowed to reach equilibrium with 100 cm^3 of supercritical CO_2 . Calculate the mass of B which remains in the water layer and give your answer to two decimal places. (5)
 - The saturated vapour pressures of benzene and methylbenzene at 303 K are $1.58 \times 10^4 \text{ Pa}$ and $4.92 \times 10^3 \text{ Pa}$ respectively. Calculate the composition of the vapour above a liquid mixture containing twice as many moles of benzene as methylbenzene. (5)
 - When bromobenzene (RMM = 157) is extracted by steam distillation at a pressure of $1.01 \times 10^5 \text{ Pa}$, the mixture boils at $95.5 \text{ }^\circ\text{C}$. At that temperature the vapour pressure of pure water is $8.58 \times 10^4 \text{ Pa}$. Calculate the mass of steam necessary to distil 100 g of bromobenzene. (5)

(Total: 20 marks)

- 3) Unlabelled containers are a headache for any chemical store keeper. Tests can however be carried out to identify the contents of unlabelled containers. Suggest some tests for the following. Your answers should include relevant chemical equations and expected observations.
- Three bottles are known to contain separately aqueous solutions of Na^+ , Mg^{2+} , and Ca^{2+} . Using aqueous reagents only, describe chemical tests that would allow the identification of the cation present in the different sets of containers. (3)
 - Two bottles contain green solutions are believed to contain aqueous solutions of Fe^{2+} and Cr^{3+} . Describe chemical tests to distinguish between the cations. (5)
 - Three white solids are thought to be three different sodium halides, namely, the chloride, the bromide and the iodide. Describe **TWO** different tests that could be used to distinguish between these salts. (7)
 - Three white solids are suspected to be salts of different oxoanions of sulfur. Describe chemical tests that would distinguish between sulfate(IV), sulfate(VI) and thiosulfate. (5)
- (Total: 20 marks)**
- 4) Give a practical laboratory procedure for the following conversions including essential details and balanced chemical equations for the proposed reactions. The methods should only require commonly available materials and may be carried out in more than one step.
- Anhydrous aluminium chloride from aluminium; (4)
 - Sodium thiosulfate-5-water from sodium sulfate(IV); (4)
 - Iron(II) sulfate to $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]\text{SO}_4$; (4)
 - Lithium tetrahydridoaluminate from lithium and aluminium; (4)
 - Potassium manganate(VI) from manganese(IV) oxide. (4)
- (Total: 20 marks)**

SECTION B

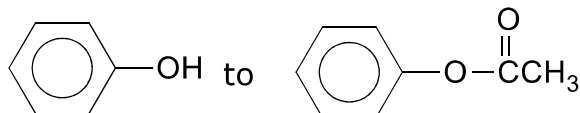
- 5) An isomer of bromooctane undergoes a nucleophilic substitution on reacting with SCN^- . The rate of reaction is directly proportional to the concentration of bromooctane and also directly proportional to the concentration of the anion.
- Given the information above:
 - explain what is meant by the term nucleophilic substitution reaction;
 - deduce the order of the reaction in terms of bromooctane and in terms of SCN^- ;
 - write the rate equation for the reaction. (4)
 - Identify an isomer of bromooctane that could have been used in this reaction and write a mechanism for the reaction. In your answer, you should indicate:
 - molecularity of each step;
 - transition state;
 - rate-determining step. (10)
 - The rate of the reaction increases with temperature but can actually be stopped completely at very low temperatures. Use the collision theory of reaction rates and the distribution of molecular energies to explain these observations. (6)
- (Total: 20 marks)**

- 6) Give full explanations, supported by chemical equations and structures where appropriate, for each of the following observations:
- The reaction of ethene with cold alkaline potassium manganate(VII) produces a liquid which can be converted into two possible products using ethanoyl chloride depending on the amount of this reagent used. The two products have distinctly different solubilities in water. (5)
 - On heating methylbenzene with a mixture of concentrated nitric(V) acid and sulfuric(VI) acid to about 40 °C, the organic layer turns yellow in colour. From this layer, three isomeric compounds in different proportions can be isolated. (5)
 - The two structural isomers of butene can be distinguished on the basis of ozonolysis. (5)
 - On adding ice-cold aqueous sodium nitrate(III) to a cold aqueous of hydrochloric acid followed by phenylamine and 4-methylphenol, an intensely coloured precipitate forms. However, if the mixture obtained after adding phenylamine is heated to near boiling, no coloured precipitate is observed on addition of the 4-methylphenol. (5)

(Total: 20 marks)

- 7) a) Describe how the following conversions may be carried out. In your answer give the reagents, essential reaction conditions, and equations to represent reactions taking place.

i)



(4)

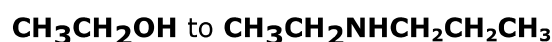
ii) **CH₃COCl** to **CH₃CH₂OH**

(4)

iii) **CH₃CH₂NH₂** to **CH₃CONHCH₂CH₃**

(4)

- b) Describe how the following conversion may be carried out using only inorganic reagents. In your answer give the reagents, essential reaction conditions, and equations to represent reactions taking place.



(8)

(Total: 20 marks)

- 8) An aromatic compound **K** (C₈H₈O₂) reacts with aqueous sodium hydrogencarbonate to give **L** (C₈H₇O₂Na). **L** is converted back into **K** on treatment with aqueous sulfuric(VI) acid. Reaction of **K** with chlorine in the presence of sunlight yields **M** (C₈H₇ClO₂), which on treatment with aqueous alkali followed by acidification produces **N** (C₈H₈O₃). Controlled oxidation of **N** by acidified dichromate yields **O** (C₈H₆O₃). **O** can be further oxidised to **P** (C₈H₆O₄). **K** can be converted into **P** by reaction with alkaline potassium manganate(VII). On suitable treatment, **P** can be dehydrated to compound **Q** (C₈H₄O₃), while **N** can also undergo a dehydration reaction to produce compound **R** (C₈H₆O₂).

- a) Deduce structural formulae for substances **K**, **L**, **M**, **N**, **O**, **P**, **Q** and **R**, giving reasons for your deductions. (16)

- b) State the experimental conditions required for the conversions of:

- P** to **Q**
- N** to **R**.

(4)

(Total: 20 marks)



SUBJECT:	Chemistry
PAPER NUMBER:	III – <i>Practical</i>
DATE:	14 th June 2018
TIME:	3 hours 5 minutes

Answer ALL questions.

- 1) You are provided with the following solutions:
- potassium manganate(VII) of unknown concentration, labelled R_n ;
 - ethanedioic acid of concentration 0.04 mol dm^{-3} , labelled C;
 - a solution prepared by dissolving 30.00 g dm^{-3} of impure ammonium iron(II) sulfate(VI), labelled S;
 - dilute sulfuric(VI) acid

You are required to:

- use solution C to standardize solution R_n
- determine the concentration of iron(II) in solution S and find the percentage purity of the ammonium iron(II) sulfate(VI) solid used to prepare solution S.

Record the value of your laboratory number, n (found on solution R), on your answer book in the following box.

CANDIDATE LABORATORY NUMBER, n: _____

Standardization of solution R_n

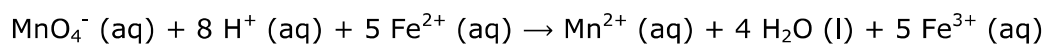
- a) Pipette 25.0 cm^3 of solution C into a conical flask. Using a measuring cylinder, add 20 cm^3 of dilute sulfuric(VI) acid solution and heat the mixture gently to $60 \text{ }^\circ\text{C}$. Titrate with solution R_n to a faint pink endpoint.

Repeat for concordant results. Enter your results in the following table and calculate the mean titre value. (18)

Final burette reading (cm^3)			
Initial burette reading (cm^3)			
Titre (cm^3)			

Mean titre: _____ cm^3 of potassium manganate(VII) solution.

- d) Given that manganate(VII) ions react with iron(II) ions according to the following equation:



calculate the concentration of iron(II) ions in solution S.

(5)

Question continues on next page

- e) Given that the molar mass of ammonium iron(II) sulfate(VI) is $392.13 \text{ g mol}^{-1}$, find the percentage purity of the ammonium iron(II) sulfate(VI) solid used to prepare solution S.

(4)

(Total: 50 marks)

- 2) You are provided with about 10 cm^3 of an aqueous solution, labelled T. This solution is composed of a mixture of **TWO** inorganic salts. Carry out the following chemical tests and suggest two cations and two anions that may be present in the solution.

- a) To 1 cm^3 of T, add aqueous sodium hydroxide solution dropwise until in excess. **Keep the contents of the test tube for the following test.** (5)

<i>Observation</i>	<i>Inference</i>
<hr/>	<hr/>
<hr/>	<hr/>
<hr/>	<hr/>
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-
- b) Heat carefully the contents of the test tube kept from part (a) and test for any vapours evolved using moist litmus paper. (5)

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

- c) To about 1 cm³ of T, add a few drops of aqueous ammonia solution. (5)

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

- d) Acidify about 1 cm³ of T with dilute hydrochloric acid and add drops of barium chloride solution. (5)

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

Question continues on next page

- e) Acidify 1 cm³ of T with a few drops of dilute nitric(V) acid solution. Then add a few drops of silver nitrate(V) solution to the resulting mixture. (5)

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

Hence suggest possible cations and anions that may be present in solution T. (4)

Cations: _____ and _____

Anions: _____ and _____

(Total: 29 marks)

- 3) You are provided with about 1 g of an organic compound labelled B. Perform the following chemical tests and suggest a plausible structure for the organic compound B.
- a) Add about 0.4 g of B to 5 cm³ of water and shake well. **Keep the contents of the test tube for the next test.** (4)

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

- b) Add dilute hydrochloric acid solution dropwise to the contents of the test tube obtained in part (a) until no further change is observed. **Keep the contents of the test tube for the next test.** (4)

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

- c) Add dilute sodium hydroxide solution dropwise until in a large excess to the contents of the test tube from part (b). (4)

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

- d) Place about 0.2 g of B in a dry test tube. Then add 10 drops of propan-1-ol, followed by three drops of concentrated sulfuric(VI) acid. Heat the mixture in a boiling water bath for 1 minute. Neutralize the final reaction mixture with 4 cm³ of aqueous sodium carbonate solution and carefully note the odour. (4)

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

Question continues on next page

- e) Add about 0.1 g of sodium nitrate(III) to 1 cm³ of ice-cold dilute hydrochloric acid solution. Then add about 0.1 g of B and place the mixture in an ice-bath. In a second test tube mix about 0.1 g of 2-naphthol with 3 cm³ of ethanol. Decant the supernatant liquid of the second tube to the cooled reaction mixture of the first test tube. (4)

Observation

Inference

_____	_____
_____	_____
_____	_____
_____	_____

Suggest a possible structure for compound B.

(1)

B is possibly: _____

(Total: 21 marks)