**Index No:**_____ **AM 06/I.13m**

**MATRICULATION AND SECONDARY EDUCATION CERTIFICATE EXAMINATIONS BOARD**

**UNIVERSITY OF MALTA, MSIDA**

**MATRICULATION EXAMINATION**
**ADVANCED LEVEL**
**MAY 2013**

| | |
|---|---|
| **SUBJECT:** | CHEMISTRY |
| **PAPER NUMBER:** | I |
| **DATE:** | 3rd May 2013 |
| **TIME:** | 9.00 a.m. to 12.00 noon |

**Required Data:** **Relative atomic masses: H = 1.0**
**The universal gas constant $R$ = 8.314 J $K^{-1}$ $mol^{-1}$**

**Answer all questions.**

1. (a) Define the following terms:

(i) *atomic number;*

_____

_____

(ii) *nucleon number.*

_____

_____

*(2 marks)*

(b) Magnesium has three stable *isotopes* with *mass numbers* 24, 25 and 26.

(i) Define the terms in italics:

*isotope;*

_____

_____

*mass number.*

_____

_____

(ii) The relative atomic mass of magnesium is given as 24.31. Discuss what this implies about the relative abundance of the isotopes.

_____

_____

*(4 marks)*

(c) Using a labelled diagram, describe the main features of a mass spectrometer used to determine the relative atomic mass of an element.

*(4 marks)*
***(Total 10 marks)***

2. At 400 °C, the equilibrium constant, $K_c$ for the following endothermic reaction is 52.2.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(a) Give an expression for $K_c$ for the reaction and state the units of the constant if any.

*(2 marks)*

(b) Predict, stating your reasons, the shift in direction of the reaction as a result of:

(i) an increase in temperature at constant pressure;

(ii) an increase in pressure at constant temperature;

(iii) addition of a catalyst.

_____

_____

*(6 marks)*

(c) One mole each of $H_2(g)$ and $I_2(g)$ are placed in a reaction vessel of 1 $dm^3$ at 400 °C. Calculate the molar concentration of HI(g) at equilibrium.

_____

_____

_____

_____

_____

_____

*(4 marks)*

***(Total = 12 marks)***

3. Consider the hydrogenation of ethene to ethane.

$$CH_2{=}CH_2(g) + H_2(g) \rightarrow CH_3CH_3(g)$$

(a) Given that the standard enthalpy of formation of ethene is +52 kJ $mol^{-1}$ and that of ethane is –85 kJ $mol^{-1}$, calculate the standard enthalpy change of the reaction.

_____

_____

_____

*(2 marks)*

(b) What mass of hydrogen is required to react completely with 5.6 $dm^3$ of ethene at 298 K and 101 325 N $m^{-2}$?

_____

_____

_____

*(3 marks)*

(c) *The bond energy of the* C=C *bond in ethene is not twice that of the* C–C *bond in ethane.* Explain this statement as fully as possible.

_____

_____

_____

*(3 marks)*

(d) The hydrogenation of ethene occurs in the presence of finely divided nickel acting as a *catalyst* in order to increase the rate of reaction.

(i) Explain how catalysts increase the rate of a chemical reaction.

_____

_____

_____

_____

_____

(ii) Explain why finely divided nickel is better for the purpose than a sheet of nickel.

_____

_____

*(3 marks)*

***(Total = 11 marks)***

4. This question is about the elements sodium, magnesium and aluminium.

(a) Using s, p, d, f notation, write the electronic configurations of the atoms Na, Mg, Al and the ions $Na^{+}$, $Mg^{2+}$ and $Al^{3+}$.

_____

_____

_____

_____

_____

*(3 marks)*

(b) Place the ions $Na^+$, $Mg^{2+}$ and $Al^{3+}$ in order of *increasing* ionic radius. Give a reason for this order.

_____

_____

_____

*(3 marks)*

(c) Explain how the first ionisation energy varies from Na to Mg to Al. Give reasons for this observation.

_____

_____

_____

_____

_____

_____

*(4 marks)*

(d) Comment about the ionic/covalent character of the chlorides of sodium, magnesium and aluminium, giving reasons.

_____

_____

_____

_____

*(3 marks)*
***(Total = 13 marks)***

5. Radium is the last member of Group 2 of the Periodic Table. Answer the following questions (a) to (d) using your knowledge of the trends in properties of Group 2 elements.

(a) Explain, giving a reason for your answer, whether radium would be expected to be harder or softer than magnesium.

_____

_____

_____

*(2 marks)*

(b) Explain, giving a reason for your answer, whether radium sulfate would be expected to be more or less soluble than magnesium sulfate.

_____

_____

_____

*(3 marks)*

(c) Explain, giving a reason for your answer, whether radium carbonate would be expected to be more or less thermally stable than calcium carbonate.

_____

_____

_____

_____

*(2 marks)*

(d) Explain how one may attempt to distinguish between a solution containing $Mg^{2+}$ ions and one containing $Ra^{2+}$ ions using only aqueous potassium hydroxide.

_____

_____

_____

_____

*(3 marks)*
***(Total = 10 marks)***

6. (a) Complete the following equations regarding the chemistry of the elements in Group 7 of the periodic table.

$Br_2(aq)$ + ___NaI(aq) → _____

$Cl_2(aq)$ + ___NaBr(aq) → _____

*(2 marks)*

(b) (i) In view of your answer in (a), place the halogens $X_2$ (X= Cl, Br, I) in order of oxidising power, starting with the strongest.

_____

(ii) Relate the oxidising power of halogens to their position in Group 7.

_____

*(3 marks)*

(c) The hypochlorite ion, $OCl^-$, is a thermally unstable species.

(i) Give the systematic name of the hypochlorite ion:

_____

(ii) Write a balanced ionic equation to represent the effect of heat on an aqueous solution containing the hypochlorite ion.

_____

*(3 marks)*

(d) Iodine is only slightly soluble in water. However, iodine is much more soluble in aqueous potassium iodide. Explain this observation and suggest a suitable solvent for iodine.

_____

_____

_____

_____

*(3 marks)*
***(Total = 11 marks)***

7. Lactic acid, $CH_3CH(OH)CO_2H$, is a *chiral molecule* that occurs naturally. The *racemic mixture* is found in sour milk, the (+) *enantiomer* is found in muscle tissue while *(–) lactic acid* does not occur naturally but has to be obtained by resolution of the racemic mixture.

(a) Give the systematic name of lactic acid.

_____

*(1 mark)*

(b) Name the type of isomerism exhibited by lactic acid.

_____

*(1 mark)*

(c) Draw the structure of lactic acid and identify the feature that makes it a chiral molecule.

_____

*(1 marks)*

(d) Explain the three terms written in italics.

*i. chiral* molecule

_____

_____

*ii. racemic* mixture

_____

_____

*iii. enantiomer*

_____

_____

*(3 marks)*

(e) Explain the significance of the symbol '(–)' in the name (–)lactic acid.

_____

*(1 mark)*

(f) Draw the structure of the main organic compound formed when lactic acid reacts with:

(i) phosphorus pentachloride;

(ii) ethanol in the presence of concentrated sulfuric acid.

*(2 marks)*

(g) Lactic acid is formed in muscle tissue during exercise from pyruvic acid $CH_3COCO_2H$.

(i) Name the type of reaction taking place when pyruvic acid is converted to lactic acid.

_____

(ii) Suggest a reagent that may be used to convert pyruvic acid into lactic acid in the laboratory.

_____

(iii) Write chemical equations to describe a laboratory synthesis for pyruvic acid starting from propanoic acid.

_____

_____

_____

*(5 marks)*
***(Total = 14 marks)***

8. An alkene, **A**, of formula $C_8H_{16}$ was treated with ozone followed by hydrolysis and two carbonyl compounds, both of formula $C_4H_8O$ were obtained: **X** which is an aldehyde and **Y** which is a ketone. Both compounds **X** and **Y** can be reduced to the same hydrocarbon.

(a) Describe a test (including results expected) which may be used to show that:

(i) both **X** and **Y** are carbonyl compounds;

_____

_____

(ii) **X** is an aldehyde but **Y** is not.

_____

_____

*(3 marks)*

(b) Deduce the structures of compounds **X** and **Y** from the given information.

_____

_____

_____

*(3 marks)*

(c) Describe and explain the results expected when **X** and **Y** are each treated with iodine solution followed by a few drops of sodium hydroxide solution and warmed gently.

_____

_____

_____

_____

*(4 marks)*

(d) Give the name and structure of the original alkene, A.

_____

*(2 marks)*

(e) The original alkene, **A**, may be converted into a polymer. Draw the structure of a repeating unit of the polymer, write an equation to represent the conversion and name the type of polymerization taking place.

_____

_____

*(3 marks)*

(f) Describe, with the help of a mechanism, the reaction expected to occur when **A** is treated with HBr. Name the main organic product expected and draw its structure.

_____

*(4 marks)*

***(Total = 19 marks)***

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**UNIVERSITY OF MALTA, MSIDA**

**MATRICULATION EXAMINATION**
**ADVANCED LEVEL**
**MAY 2013**

| | |
|---|---|
| **SUBJECT:** | CHEMISTRY |
| **PAPER NUMBER:** | II |
| **DATE:** | 4th May 2013 |
| **TIME:** | 9.00 a.m. to 12.00 noon |

**Required Data:** Relative atomic masses: H = 1; C = 12; O = 16. One mole of any gas or vapour occupies 22.4 $dm^3$ at STP. Self-ionization product for water, $K_w = 1 \times 10^{-14}$ $mol^2$ $dm^{-6}$.

A Periodic Table is provided.

**Answer two questions from each section and any other question.**

## Section A

1. Ethanoic acid has an acid dissociation constant of $1.8 \times 10^{-5}$ mol $dm^{-3}$ at 25 °C.

   (a) Calculate the following properties of a 0.1 mol $dm^{-3}$ aqueous solution of ethanoic acid at 25 °C:

   (i) the percentage of the acid dissociated;
   (ii) the pH of the solution;
   (iii) the concentration of $OH^-$ ions in solution. *(10 marks)*

   (b) Calculate the pH of a solution prepared by adding 100 $cm^3$ of 0.1 mol $dm^{-3}$ aqueous sodium hydroxide to 500 $cm^3$ of 0.1 mol $dm^{-3}$ ethanoic acid. *(6 marks)*

   (c) Explain why the pH of the solution in (b) is resistant to change on addition of small quantities of acid and alkali. *(4 marks)*

   ***(Total = 20 marks)***

2. The hydrolysis of 1-chloroethane by $OH^-$ is found to be first order with respect to each reactant whilst the hydrolysis of 2-chloro-2-methylpropane by $OH^-$ is first order with respect to the chloroalkane.

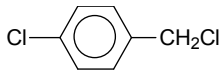
   (a) Write rate equations for the two hydrolysis reactions. *(1 marks)*

   (b) For each reaction give a mechanism that is consistent with the rate law. In each case indicate the rate determining step and identify any transition state or intermediate involved. *(6 marks)*

(c) Explain the different mechanisms in terms of the molecular structure of the two chloroalkanes. *(4 marks)*

(d) Suggest how the progress of the reactions can be followed experimentally. *(4 marks)*

(e) When 0.01 mol of the organic compound **C** reacts with excess aqueous sodium hydroxide and the products of reaction are acidified with dilute nitric acid followed by treatment with excess silver nitrate, 0.01 mol AgCl form as a precipitate.



**(C)**

Account for these observations, giving chemical equations for any reactions mentioned. *(5 marks)*

***(Total = 20 marks)***

3. (a) Explain what is meant by *osmotic pressure* and *reverse osmosis*. Explain the importance of reverse osmosis to Malta. *(6 marks)*

(b) A water-soluble polymer is found to have 54.54% carbon, 9.10% hydrogen and the rest is oxygen. Find the empirical formula of the polymer. (4 marks)

(c) An aqueous solution containing 1 g of the polymer in 100 $cm^3$ water has an osmotic pressure of 1.24 kN $m^{-2}$ at 25 °C. Calculate the molar mass of the polymer and assuming that the empirical formula is the formula of a repeat unit, calculate the number of repeat units in a polymer chain. (R= 8.314 J $K^{-1}$ $mol^{-1}$ and 1 J = 1 Nm.) *(10 marks)*

***(Total = 20 marks)***

4. Explain the following observations.

(a) Carbon dioxide sublimes at –78 °C at 1 atmosphere pressure whilst silicon dioxide melts at 1650 °C. *(4 marks)*

(b) Nitrogen can only form a single chloride, $NCl_3$. However, phosphorus can form both molecular $PCl_3$ and $PCl_5$. *(4 marks)*

(c) The melting point of $H_2O$ is 0 °C whilst $H_2S$ is a gas at this temperature. *(4 marks)*

(d) The acid dissociation constant of HI in water is much higher than that of HF. *(4 marks)*

(e) The species $NH_3$ and $NH_4^+$ have the same number of electron pairs yet the H-N-H bond angle in the two species is not the same. *(4 marks)*

***(Total = 20 marks)***

## Section B

5. Benzene, $C_6H_6$, is an aromatic hydrocarbon. Although its structure can be drawn as  (cyclohexa-1,3,5-triene), it does not undergo addition reactions typical of unsaturated compounds.

   (a) Describe the bonding in benzene and explain why *it does not undergo addition reactions typical of unsaturated compounds*. *(6 marks)*

   (b) Addition of hydrogen to benzene first gives cyclohexadiene, then cyclohexene and finally cyclohexane.

   (i) Explain why the conversion of benzene to cyclohexadiene is the most difficult step.
   (ii) The hydrogenation of benzene may be carried out using the same reagent and catalyst and the same temperature used in the hydrogenation of alkenes but the pressure employed is usually higher. Name the reagents, catalyst and conditions used during the hydrogenation of alkenes.
   (iii) Give the structure of the products obtained, (if any), when benzene, cyclohexadiene, cyclohexene and cyclohexane are treated with excess bromine in tetrachloromethane at room temperature in the dark. *(8 marks)*

   (c) Explain how nitrobenzene and phenylamine can be distinguished on the basis of their interaction with (i) aqueous bromine; (ii) dilute hydrochloric acid and (iii) a mixture of tin and hydrochloric acid. *(6 marks)*

***(Total = 20 marks)***

6. Describe how the following conversions may be carried out. Any inorganic reagents but no organic compounds, other than those given, may be used in conversions (a) to (c). In your answer give the reagents, essential reaction conditions and equations to represent reactions taking place.

   (a) $C_2H_5COOH$ to $C_2H_5NH_2$ *(6 marks)*

   (b) $C_6H_5NH_2$ to $C_6H_5COOH$ *(6 marks)*

   (c) $C_2H_5OH$ to $C_2H_5COOH$ *(6 marks)*

   (d) $C_6H_6$ to $C_6H_5C_2H_5$ (In this conversion you may use an organic reagent.) *(2 marks)*

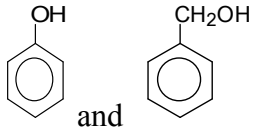
***(Total = 20 marks)***

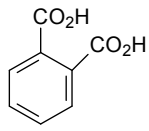
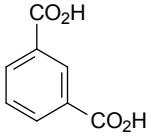
7. Describe chemical tests that may be used to distinguish between the following pairs of compounds. In your answer give the reagent and any necessary conditions, the results expected in each case and a reason for the difference in reaction/observation.

   (a) $ClCH_2COOH$ and $CH_3COCl$ *(4 marks)*

   (b) $(CH_3)_3CCH_2OH$ and $(CH_3)_2C(OH)CH_2CH_3$ *(4 marks)*

   (c) $CH_3CH_2CH(OH)CH_3$ and $CH_3CH_2OCH_2CH_3$ *(4 marks)*

   (d)  and  *(4 marks)*

   (e)  and  *(4 marks)*

**(Total = 20 marks)**

8. This question is about characteristics of the d-block elements. Explain statements (a) to (d), showing how the characteristics arise, and giving specific examples. Where necessary provide balanced chemical equations.

   (a) Several d-block elements and their compounds are used as catalysts. Some are involved in homogeneous catalysis while others are involved in heterogeneous catalysis. *(6 marks)*

   (b) Atoms or ions of d-block elements may interact with ligands to form complexes. A complex may have an overall positive charge, negative charge or no charge. Some ligands are monodentate while others are polydentate. *(6 marks)*

   (c) In their compounds, d-block elements show a variety of oxidation states. An element may have an oxidation state in which it behaves as an oxidizing agent and another in which it acts as a reducing agent. *(4 marks)*

   (d) The $Cu^{2+}$ ion behaves as a typical transition metal but the $Cu^{+}$ ion does not. *(4 marks)*

**(Total = 20 marks)**

**Index No_____** **AM 06/III.13m**

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**UNIVERSITY OF MALTA, MSIDA**

**MATRICULATION EXAMINATION**
**ADVANCED LEVEL**
**MAY 2013**

| | |
|---|---|
| **SUBJECT:** | CHEMISTRY |
| **PAPER NUMBER:** | III – *Practical* |
| **DATE:** | 4th June 2013 |
| **TIME:** | 3 hours |

## Answer all questions.

1. In this experiment you are required to determine:
   i. the molar concentration of the sodium hydroxide in solution $A_n$;
   ii. the molar concentration of a solution of ethanoic acid;
   iii. the dissociation constant of ethanoic acid.

   You are provided with the following solutions:
   i. a solution of sodium hydroxide labelled $\mathbf{A_n}$, where n is the candidate laboratory number;
   ii. a solution of 0.0600 M ethanedioic acid labelled **B**;
   iii. a solution of ethanoic acid **C**.

   *Determination of the molar concentration of sodium hydroxide in solution* $\boldsymbol{A_n}$

   a) Record the value of your laboratory number, n, on your answer book in the following box.

| |
|---|
| CANDIDATE LABORATORY NUMBER, n..... |

   b) Using a pipette, transfer 25.0 mL of solution $\mathbf{A_n}$ into a 250 mL volumetric flask and make up to the mark with distilled water.

   c) Fill the burette with the **diluted** alkali solution. Transfer 25.0 mL of solution **B** into a conical flask and titrate with the **diluted** alkali solution using phenolphthalein as indicator. Report your results in the table below, recording one approximate and two accurate titrations.

| Titration number: | 1. Approximate | 2. Accurate | 3. Accurate |
|---|---|---|---|
| Final burette reading (mL) | | | |
| Initial burette reading (mL) | | | |
| Titre value (mL) | | | |

Mean titre value:.....mL of sodium hydroxide

d) Calculate the molar concentration of the sodium hydroxide solution $\mathbf{A_n}$ to 3 sig. figures.

*Determination of the concentration of ethanoic acid.*

e) By means of a pipette transfer 25.0 mL of solution **C** into a conical flask and titrate with the **diluted** alkali solution, using phenolphthalein as indicator. Report your results in the table below, recording one approximate and two accurate titrations.

| Titration number: | 1. Approximate | 2. Accurate | 3. Accurate |
|---|---|---|---|
| Final burette reading (mL) | | | |
| Initial burette reading (mL) | | | |
| Titre value (mL) | | | |

Mean titre value:.....mL of sodium hydroxide

f) Calculate the molar concentration of ethanoic acid to 3 sig. figures.

g) For ethanoic acid we can write

$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)$$

The acid dissociation constant for this process is given by

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Thus when $[CH_3COOH] = [CH_3COO^-]$, $K_a = [H_3O^+]$ and $pK_a$ = pH of the solution. Therefore, if the solution of ethanoic acid is treated with exactly one half of the amount of strong base, eg. sodium hydroxide, required for complete neutralisation, the pH of the mixture at this point is equal to the $pK_a$ of ethanoic acid.

To 25.0 mL of solution **C** in a conical flask add exactly one half of the amount of **diluted** sodium hydroxide solution as was required in (e) for complete neutralisation. Using the pH indicator paper provided, find the pH of the resultant mixture.

pH of mixture = _____

Hence

$K_a$ of ethanoic acid = _____ mol $dm^{-3}$

*(50 marks)*

2. You are provided with a mixture of two inorganic powders labelled **D**. Carry out the following tests on the mixture and record your observations and inferences in the spaces provided.

(a) Place the entire sample **D** in a small beaker, add about 30 mL water and stir well. Filter and wash the residue with a further 10 mL of water. Collect the filtrate in a small clean beaker. **Retain both the filtrate and the residue** for the following tests.

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

(b) Place the residue in a small test tube dissolve in dilute hydrochloric acid. Test for any gases evolved using lime water. **Keep the contents of the test tube for further tests.**

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

(c) Carry out the following tests on about **1mL portions** of the resulting solution after test (b):
(i) Add sodium hydroxide solution dropwise until in excess.

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

(ii) Add aqueous ammonia dropwise until in excess.

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

(d) Carry out the following tests on about **1mL portions** of the **filtrate**:
(i) Add aqueous sodium hydroxide and heat the mixture.

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

(ii) Add aqueous ammonia dropwise until in excess.

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

(iii)Add aqueous barium chloride, followed by dilute hydrochloric acid solution.

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

*Conclusion*

Powder **D** is probably a mixture of :

_____

_____

*(25 marks)*

3. You are provided with an organic liquid labelled **E**. Carry out the following tests on **E** and record your observations and inferences.

(a) Ignite a few drops of **E** on a crucible lid.

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

(b) Add about 1 mL of **E** to an equal volume of a solution of sodium hydrogencarbonate.

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

(c) Add a few drops of **E** to about 1 mL of 2,4-dinitrophenylhydrazine.

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

(d) Prepare Tollen's reagent as follows: To about 1 mL silver nitrate solution in a clean test tube add one drop of dilute sodium hydroxide and shake the mixture. Then add enough dilute ammonia to just dissolve the precipitate. To this reagent add a few drops of **E** and heat the mixture in a beaker of hot water for a few minutes. On completion of this test, discard the content of the test tube down the drain and dissolve any residue in the tube using warm dilute nitric acid.

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

(e) Add a few drops of **E** to about 1mL of bromine water.

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

(f) Add a few drops of **E** to about 1mL of neutral iron (III) chloride solution**.**

| *Observation* | *Inference* |
|---|---|
| | |
| | |
| | |

*Conclusion*

A possible structure for **E** is:

*(25 marks)*

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