L-Università ta' Malta

MATRICULATION AND SECONDARY EDUCATION CERTIFICATE
EXAMINATIONS BOARD

**ADVANCED MATRICULATION LEVEL
2022 FIRST SESSION**

SUBJECT: **Chemistry**
PAPER NUMBER: I
DATE: 16th May 2022
TIME: 16:00 to 19:05

Required Data: Universal Gas constant (R) = 8.314 J mol^{-1} K^{-1}.

Answer ALL questions

1. a) Define the term ionisation energy.

    _____

    _____

    _____ (1)

    b) Which of the following pairs of elements has the higher ionisation energy? Briefly explain
    your answers.

       i) Potassium and calcium.

    _____

    _____

    _____

    _____ (2)

       ii) Magnesium and aluminium.

    _____

    _____

    _____

    _____

    _____

    _____

    _____ (3)

c) Define the term first electron affinity.

_____

_____ (1)

d) The first electron affinity of oxygen is -142 kJ mol^{-1}, while the second electron affinity of oxygen is 844 kJ mol^{-1}. Explain why the second electron affinity of oxygen is endothermic.

_____

_____ (2)

(Total: 9 marks)

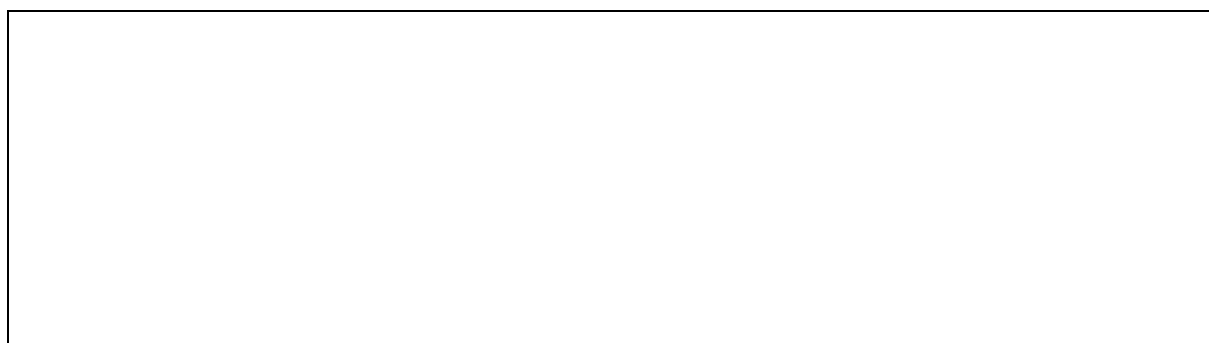2. This question is about bonding.
    a) Use the valence shell electron pair repulsion (VSEPR) theory to draw and name the shapes of the following species. Show your working.

    i) I_3^-

    (3)

    ii) BrF_4^+

    (3)

b) Describe the bonding in metallic elements and account for their electrical conductivity.

_____

_____

_____

_____

_____ (2)

c) Explain why metallic bonding is weaker on going down a group in the periodic table.

_____

_____

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_____

_____

_____ (2)

d) Diamond and graphite are allotropes of carbon. Explain why graphite is soft and slippery while diamond is hard.

_____

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_____

_____ (2)

(Total: 12 marks)

Please turn the page.

_____

3. This question is about periodicity.
   a) The elements across period 3 react with oxygen forming oxides.

   i) State the acid-base character of the oxides of sodium and phosphorus. Write the equations for the reaction of these oxides with water.

   _____

   _____

   _____

   _____

   _____ (4)

   ii) Write equations illustrating the amphoteric nature of the oxide of aluminium.

   _____

   _____ (2)

   b) Consider the chlorides of magnesium, sodium, and nitrogen.
      i) Describe their structure in terms of ionic, covalent or intermediate bonding.

   _____

   _____

   _____ (2)

   ii) Describe with the aid of equations the reaction of these chlorides with water where appropriate.

   _____

   _____

   _____ (3)

   (Total: 11 marks)

_____

4. a) Substance **G** is a solid at room temperature. A sample of substance **G** weighing 6.52 g was heated at a pressure of 101,000 Pa to a temperature of 200 °C. The solid was converted entirely to the gas phase and occupied a volume of 1.00 dm^3. Calculate the relative molecular mass of substance **G**.

    _____

    _____

    _____

    _____

    _____ (3)

    b) Substance **G** dissolves in potassium iodide. The resultant solution gives a blue-black colour in the presence of starch solution. Identify substance **G**. Explain your answer.

    _____

    _____

    _____ (3)

    c) The phase diagram of substance **G** is shown in Figure 1**.**

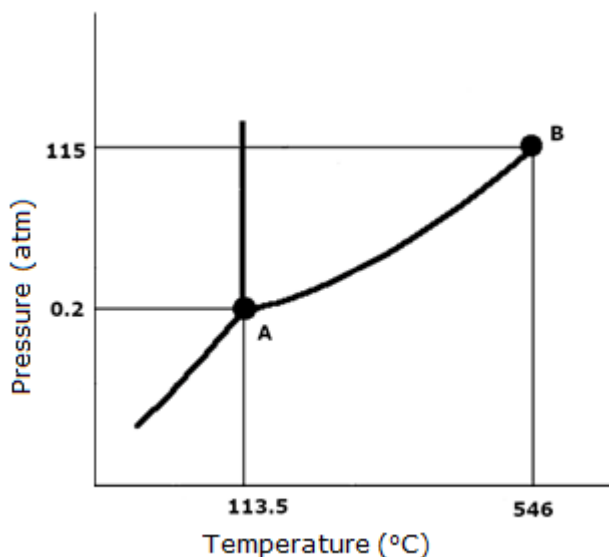Figure 1: Phase diagram of substance **G**

        i) Label points **A** and **B** shown in Figure 1.

        A: _____

        B: _____   (1)

Please turn the page.

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_____

ii) A student gently heated a sample of solid **G** in the fume cupboard and visually observed that solid **G** sublimed at atmospheric pressure. Use the information in Figure 1 to explain whether this observation is correct.

_____

_____

_____

_____

_____

_____

_____ (3)

(Total: 10 marks)

5. Consider the following half equations and their respective $E^{\ominus}$ values.

Zn^{2+} (aq) + 2e$^-$ $\rightleftharpoons$ Zn (s) $E^{\ominus}$ = −0.76 V

Cu^{2+} (aq) + 2e$^-$ $\rightleftharpoons$ Cu (s) $E^{\ominus}$ = +0.34 V

a) Illustrate the cell diagram for a galvanic cell made up of copper and zinc half cells.

_____

_____ (1)

b) Calculate the $E^{\ominus}$ of the galvanic cell given in part (a). In your answer indicate the anode and the cathode and give the overall redox reaction taking place.

_____

_____

_____

_____

_____

_____ (4)

c) When acid is added to Mn_2O_3 a redox reaction takes place, producing MnO_2 and Mn^{2+}.
   i) Write an equation and, by using oxidation numbers, specify what is oxidised and what is reduced.

   _____

   _____

   _____

   _____

   _____

   _____ (3)

   ii) What is this type of redox reaction called?

   _____ (1)

   (Total: 9 marks)

6. a) Define standard enthalpy change of formation.

    _____

    _____

    _____ (2)

    b) Use the following standard enthalpy changes to calculate the standard enthalpy of formation of propene by using a Hess' cycle.

Enthalpy change	Value (kJ mol^{-1})
Standard enthalpy of combustion of carbon (graphite)	−394
Standard enthalpy of combustion of hydrogen	−286
Standard enthalpy change of combustion of propene	−2060

Please turn the page.

_____

_____

_____

_____

_____

_____ (5)

c) The standard enthalpy of formation for cyclopropane is $+53.3$ kJ mol^{-1}. Use your answer to part (b) to calculate the enthalpy of isomerisation of cyclopropane to propene.

_____

_____

_____

_____

_____ (2)

d) The standard entropy, $S^{\ominus}$, in J mol^{-1} K^{-1} for cyclopropane and propene are 237 and 267 respectively. Use these values and your answer to part (c) to explain whether the isomerisation of cyclopropane is feasible at **all** temperatures.

_____

_____

_____

_____

_____ (3)

(Total: 12 marks)

7) When ester **A** was warmed with a dilute solution of NaOH, it gave rise to molecule **B** and a straight-chain carboxylate salt **C**, consisting of five carbon atoms.

The mass spectrum of molecule **B** is shown in Figure 2.
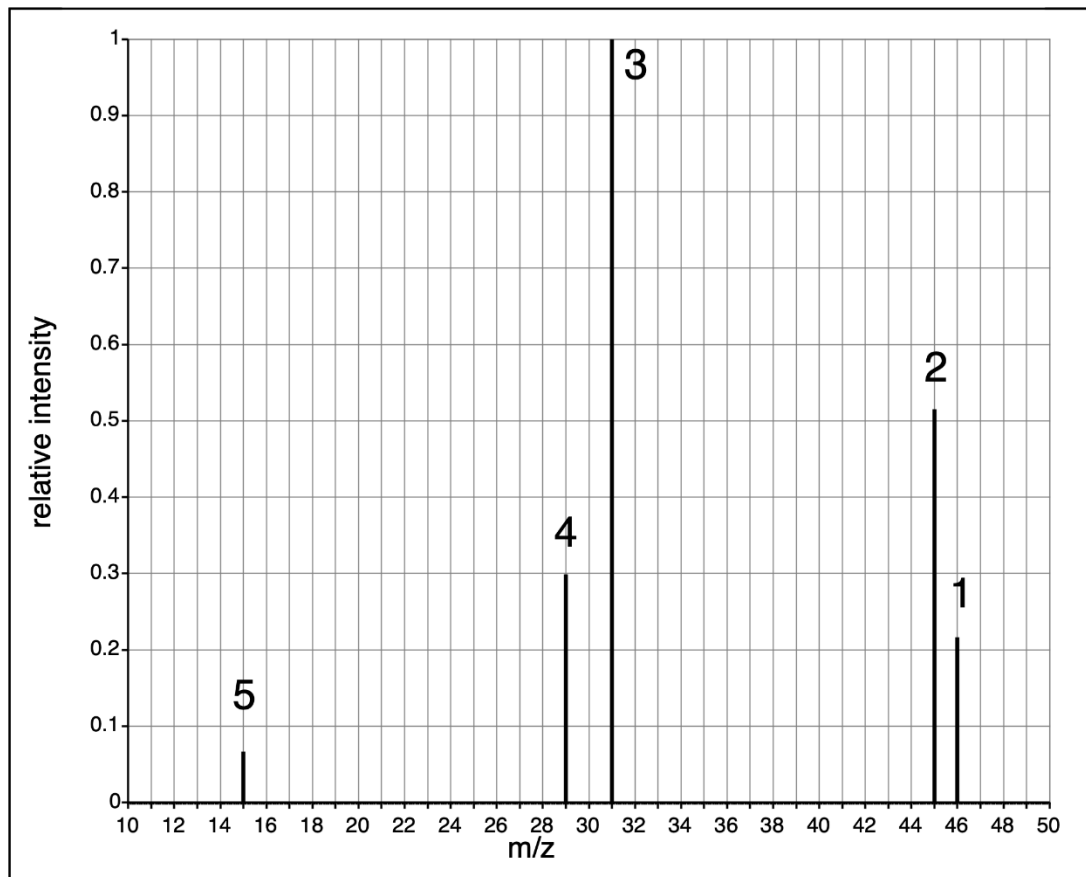
Figure 2: Mass spectrum of molecule **B**

a) Suggest a molecular mass for molecule **B**.

_____ (1)

b) Identify the ions corresponding to the five peaks **1–5** shown in Figure 2.

_____

_____

_____

_____

_____ (4)

c) Give the systematic name of salt **C**.

_____ (1)

d) Deduce the structure of ester **A**.

_____ (1)

e) What advantage is there in using NaOH over sulfuric(VI) acid to hydrolyse the ester?

_____

_____ (1)

f) i) Give the structural formula for a functional isomer of **B.**

_____ (1)

ii) Explain how a mass spectrum could be used to distinguish molecule **B** from its functional isomer.

_____

_____

_____

_____

_____ (2)

(Total: 11 marks)

8) Compound **X** has the following structural formula.
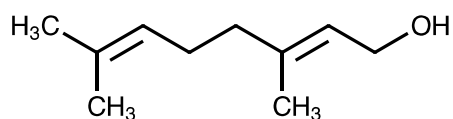
a) Give the molecular formula of **X**.

_____ (1)

_____

b) Give the systematic name of compound **X**.

_____ (1)

c) Underline the statement below that most likely fits the description of compound **X**:
  - It is a a gas at room temperature.
  - It is a volatile liquid at room temperature.
  - It is a liquid at room temperature with a boiling temperature > 100°C.

(1)

d) Compound **X** reacts with 2 moles of H_2 gas over a catalytic surface of Raney Ni to produce compound **Y**. Compound **Y** is then refluxed at 180 °C with an excess of concentrated sulfuric acid to give a hydrocarbon **Z**.

  i) Give the displayed formula of the compound **Y**.

_____ (1)

  ii) Compound **Y** is optically active. Mark the chiral carbon with an asterisk on your answer to part (d) (i).   (1)

  iii) Give the structural formula of the hydrocarbon **Z**.

_____ (1)

  iv) Suggest an alternative reagent/s and reaction conditions for the conversion of compound **Y** into **Z**.

_____

_____ (1)

e) Give the structural formula of the expected major product of the reaction of compound **X** with HBr gas at room temperature and pressure.
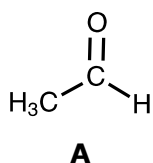

_____ (2)

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f) Give the structural formulae for the products of the reaction of compound **X** with ozone followed by hydrolysis in the presence of zinc and ethanoic acid.

_____

_____

_____ (3)

(Total: 12 marks)

9) Consider the compounds **A** to **D**.

A

B

C

D
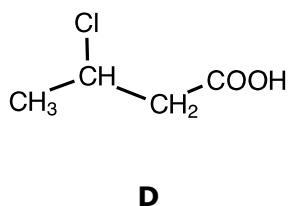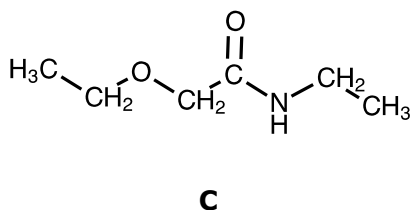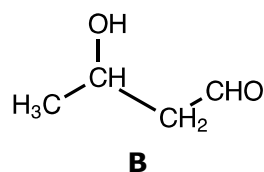
a) Give the systematic names of compounds **B** and **D**.

B: _____

D: _____

(1)

b) Give the reagent/s and reaction conditions for the following conversions. These conversions may require more than one step.
   i) **A** into **B**.

_____

_____ (1)

   ii) **B** into **D**.

_____

_____ (2)

c) An isomer of **D** reacts with an unknown compound **E** to give compound **C**. Give the structural formulae of:

   i) The isomer of **D**.

   _____ (1)

   ii) Unknown compound **E**.

   _____ (1)

d) i) Give a stepwise reaction scheme, including all products formed, to describe what happens when compound **A** is warmed with a solution of I_2 in dilute aqueous NaOH.

   _____

   _____

   _____

   _____ (2)

   ii) Which other compound/s **B, C** and **D** can undergo a similar reaction with I_2/NaOH? Give a reason for your answer.

   _____

   _____

   _____ (2)

e) Describe a chemical test that can be used to distinguish between compounds **B** and **D**. Provide details of the reagents used and the resulting observations.

   _____

   _____

   _____

   _____ (2)

Please turn the page.

_____

f) i) Compound **A** tautomerises to give the enol in the presence of catalytic amounts of acid. Give the structural formula of the enol.

_____ (1)

ii) The equilibrium constant for the tautomerization of compound **A** at room temperature is heavily in favour of the aldehyde. Briefly explain how the technique of infra red spectroscopy can be used to confirm this fact.

_____

_____

_____ (1)

(Total: 14 marks)

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SUBJECT:	**Chemistry**
PAPER NUMBER:	II
DATE:	17th May 2022
TIME:	16:00 to 19:05

A Periodic Table is provided.

Answer TWO questions from each section and ANY other question.

SECTION A

1. This question deals with chemical equilibria.

   a) Gaseous IBr was dissociated into I_2 and Br_2 (in the gaseous state) at a certain temperature until the reaction reached equilibrium. The reaction was carried out in a reaction vessel having a volume of 1.00 dm^3. The value of the equilibrium constant K_c at this temperature is 4.13×10^{-2}.
      i)   Write the chemical equation that represents this equilibrium reaction. (1)

      ii) Write the equation for K_c. (1)

      iii) When starting with pure iodine monobromide (IBr) in the reaction vessel, the equilibrium concentration of gaseous IBr was found to be 0.0124 mol dm^{-3} at the temperature above. Calculate the equilibrium concentrations of iodine and bromine.
      (4)

      iv) Calculate the initial concentration of IBr. (3)

      v)   Give an expression for K_p. (1)

      vi) Calculate K_p. (4)

   b) When ammonia gas is heated, it decomposes, and an equilibrium is established. The decomposition of ammonia is endothermic.
      i)   Write an equation for the decomposition of ammonia. (1)

      ii) In the future, the decomposition of ammonia, made sustainably using solar energy and renewable resources, might be used as an industrial method to manufacture hydrogen. Explain what conditions a chemist might decide to adopt if large quantities of hydrogen were to be produced by this decomposition. (3)

      iii) Suggest a suitable catalyst for this decomposition and discuss its effect on the equilibrium yield and on the amount of hydrogen produced in a given time. (2)

(Total: 20 marks)

2. This question is about the compounds of sulfur.

   a) Explain why sodium thiosulfate cannot be used as a primary standard and how, therefore, you would standardise a thiosulfate solution using potassium iodate(V), given that iodate(V) and iodide ions react under acidic conditions to form iodine. Include balanced redox equations in your answer. (6)

   b) Sodium sulfate(IV) reacts with hydrochloric acid to form a pungent gas.

      i) Write a balanced chemical equation for this reaction and calculate the mass (in g) of gas that can be produced by treatment of 100 g of sodium sulfate(IV) with 175 mL of 5.00 mol dm^{-3} hydrochloric acid. (6)

      ii) The pungent gas reacts with acidified dichromate. Explain how this reaction can be used as a test for the presence of this gas. Illustrate your answer with appropriate chemical equations. (4)

   c) Atmospheric sulfur dioxide is harmful to plants and aquatic environments. Explain the origin of sulfur dioxide in air, how it leads to acid rain formation and why it is harmful to aquatic environments. (4)

   (Total: 20 marks)

3. This question is about transition metals.

   a) Give the name of the complex ion whose formula is $[CrCl_2(H_2O)_4]^+$ and determine the oxidation state and the electronic configuration of the metal ion. (3)

   b) Transition metals form complex ions, with some complexes being more stable than others. $[Cu(EDTA)]^{2-}$ will form in preference of $[Cu(H_2O)_6]^{2+}$. Explain these statements. (6)

   c) i) Draw the shape of the hexaaquairon(III) ion. (1)
      ii) The pH of an aqueous iron(III) chloride solution was measured, and a pH 3 was recorded. Explain this observation. Support your answer with chemical equations. (5)

   d) The dichloridobis(ethylenediamine)cobalt(III) complex ion is an octahedral complex that exhibits geometric isomerism. Draw and identify both isomers. (5)

   (Total: 20 marks)

4. Write short explanatory notes on **each** of the following, illustrating your answer with appropriate chemical structures and equations.

   a) The laboratory preparation of nitrobenzene from benzene, including details of the mechanism of the reaction, the generation of the electrophile, attack of the benzene ring and any intermediates formed. (5)

   b) An azo dye can be obtained from 2-methylphenol and 2-aminobenzoic acid. (5)

   c) The pKa of phenol is 10, while that of phenylmethanol is 15.4. (5)

   d) An aromatic substance with molecular formula C_6H_6O reacts with bromine water to form the derivative $C_6H_3Br_3O$, which, on heating with zinc dust, produces $C_6H_3Br_3$. Two other aromatic compounds have the same molecular formula as the product $C_6H_3Br_3$. (5)
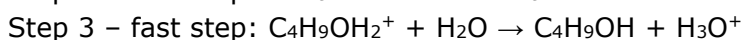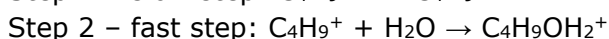
   (Total: 20 marks)

SECTION B

5. This question deals with the chemistry of propanoic acid and its derivatives.

   a) Outline a method of preparation, including reagents and conditions, of propanoic acid, CH_3CH_2COOH, starting from ethanol. (5)

   b) Write chemical equations to represent the synthesis of **each** of the following compounds starting from propanoic acid as the only organic material. State the essential experimental conditions.
      i) propanoic anhydride; (4)

      ii) 1-propyl propanoate; (3)

      iii) propan-1-amine. (4)

   c) Explain why propanoic acid vapour has a relative molecular mass of 148. (2)

   d) i) 2-hydroxypropanoic acid, also known as lactic acid, can undergo poly-condensation to form the polymer poly(lactic acid). Draw the repeat unit for this polymer. (1)

      ii) Suggest a chemical method of regenerating 2-hydroxypropanoic acid from poly(lactic acid). (1)

   (Total: 20 marks)

Please turn the page.

6. This question is about rates of reactions.

    a) A proposed mechanism for a reaction is:
       Step 1 – slow step: $C_4H_9Br \rightarrow C_4H_9^+ + Br^-$
       Step 2 – fast step: $C_4H_9^+ + H_2O \rightarrow C_4H_9OH_2^+$
       Step 3 – fast step: $C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+$

       i)   Deduce the overall balanced equation for the reaction. Show your reasoning.   (2)

       ii) Give the order with respect to each reactant and the overall order of reaction. Show
            your reasoning.   (3)
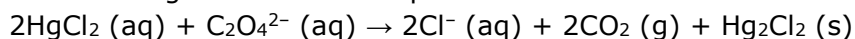
       iii) Write the rate equation for this reaction.   (1)

       iv) Consider the following experimental data:

Time of reaction (s)	$[C_4H_9Br]$ (mol dm^{-3})
0	0.18
40	0.09
80	0.045

            Does this data agree with the rate equation given in part (iii)? Explain your answer. (2)

       v)   Identify the intermediates in the proposed mechanism, give the structural formula of
            the reactant and, in mechanistic terms, suggest why the first step is proposed as a
            slow step while steps 2 and 3 are fast steps.   (5)

    b) The rate of the following reaction in an aqueous solution was monitored.
            $2HgCl_2 (aq) + C_2O_4^{2-} (aq) \rightarrow 2Cl^- (aq) + 2CO_2 (g) + Hg_2Cl_2 (s)$
       The number of moles of Hg_2Cl_2 precipitated over a time period from the start of the reaction
       was measured. Consider the data obtained presented in the table below.

Experiment number	$[HgCl_2]$ mol dm^{-3}	$[C_2O_4^{2-}]$ mol dm^{-3}	Amount of Hg_2Cl_2 precipitated (mol)	Time (s)
1	0.05	0.15	0.032	60
2	0.10	0.15	0.032	30
3	0.10	0.30	0.128	30

       i)   Determine the order of reaction with respect to $HgCl_2$ and $C_2O_4^{2-}$. Hence write the rate
            equation. Show your reasoning.   (5)

       ii) Calculate the value of the rate constant and indicate its units.   (2)

                                                                        (Total: 20 marks)

7. This question is about ionic equilibria.

   a) A volume of 7.2 cm^3 of a 4.50 mol dm^{-3} sodium hydroxide solution was added to 250 cm^3 of a 0.200 mol dm^{-3} ethanoic acid solution. The value of K_a for ethanoic acid is 1.8 x 10^{-5} mol dm^{-3}.
      i)   Calculate the pH of the resulting solution.   (7)

      ii) Explain why the above mixture is a buffer solution.   (1)

   b) i)   A constant blood pH is crucial for the human body's proper functioning. A carbonic acid-hydrogencarbonate ion system achieves this. Describe how this buffer maintains a constant blood pH.   (5)

      ii) Given that K_a for this carbonic acid-hydrogencarbonate ion system is 8.0 x 10^{-7} mol dm^{-3}, explain if this system is at its optimal buffering capacity at the physiological blood pH of 7.4.   (4)

   c) The solubility of barium sulfate at 298 K is 1.05 x 10^{-5} mol dm^{-3}. Find the solubility product of barium sulfate at 298 K, indicating its units.   (3)

(Total: 20 marks)

8. This question is about s-block and group 7 elements. Explain **each** of these statements in detail, giving balanced chemical equations when relevant.

   a) What is meant by the term diagonal relationship? Give **TWO** chemical examples using Li and Mg to illustrate this behaviour.   (5)

   b) The solubilities of group 2 hydroxides (M(OH)$_2$, M = Mg, Ca, Sr), and sulfates(VI) exhibit opposite trends on going down the group in the periodic table.   (5)

   c) Chlorine forms several oxoacids, two of which are chloric(V) acid and chloric(VII) acid. The acidity of these acids increases as the number of oxygen atoms increases. Explain this statement in terms of the structures of their respective anions.   (5)

   d) Show how you can distinguish between the halide ions Cl$^-$, Br$^-$, and I$^-$ by using Ag$^+$ ions and concentrated ammonia solution.   (5)

(Total: 20 marks)

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**ADVANCED MATRICULATION LEVEL
2022 FIRST SESSION**

SUBJECT:	**Chemistry**
PAPER NUMBER:	III – *Practical*
DATE:	3rd June 2022
TIME:	2 hours 5 minutes

1. You are provided with three solutions as follows:

   i) sodium hydroxide, labelled **Sₙ**;
   ii) ethanedioic acid, of concentration 0.0500 mol dm^{-3}, labelled **A**;
   iii) phosphoric(V) acid, of unknown concentration, labelled **P**.

   In this experiment, you are required to:

   i) carry out a titration to determine the molar concentration of solution **Sₙ**;
   ii) use solution **Sₙ** to determine the molar concentration of solution **P**.

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

CANDIDATE LABORATORY NUMBER, n:....................

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_____

Determination of the molar concentration of sodium hydroxide in solution S_n

b) Fill your burette with solution S_n. Pipette a 25 cm^3 aliquot of solution **A** into a conical flask. Using phenolphthalein indicator, titrate to a pink endpoint. Record the results in the table below.

	1st Titration	2nd Titration	3rd Titration
Final burette reading			
Initial burette reading			
Titre (cm^3)			

Mean titre: _____ cm^3 of solution S_n.   (20)

c) Ethanedioic acid and sodium hydroxide react according to the equation:

$$2NaOH \ (aq) + (COOH)_2 \ (aq) \rightarrow (COONa)_2 \ (aq) + 2H_2O \ (l)$$

Calculate the molar concentration of the sodium hydroxide solution S_n to three significant figures.

_____

_____

_____

_____

_____

_____

_____

_____

_____ (3)

_____

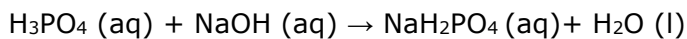**Determination of the molar concentration of the phosphoric(V) acid solution, labelled P.**

d) Pipette a 25.0 cm^3 aliquot of solution **P** into a 250 cm^3 volumetric flask and make up to the mark with distilled water. Label this solution **P$_{DIL}$**.

Fill your burette with solution **S$_n$**. Pipette a 25 cm^3 aliquot of solution **P$_{DIL}$** into a conical flask and, using bromocresol green as an indicator, titrate to a green endpoint. Record your data in the table below.

	1st Titration	2nd Titration	3rd Titration
Final burette reading			
Initial burette reading			
Titre			

Mean titre: _____ cm^3 of solution **S$_n$**.   (22)

e) Phosphoric(V) acid is a triprotic acid. Bromocresol green detects the first equivalence point as follows:

$$H_3PO_4 \text{ (aq)} + NaOH \text{ (aq)} \rightarrow NaH_2PO_4 \text{ (aq)} + H_2O \text{ (l)}$$

Calculate the molar concentration of the undiluted solution **P**.

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_____

_____(5)

(Total: 50 marks)

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**ADVANCED MATRICULATION LEVEL
2022 FIRST SESSION**

SUBJECT:	**Chemistry**
PAPER NUMBER:	III – *Practical*
DATE:	3rd June 2022
TIME:	2 hours 5 minutes

1. You are provided with three solutions as follows:

   i) sodium hydroxide, labelled S_n;
   ii) a solution of hydrochloric acid of concentration 0.150 M, labelled **C**;
   iii) a solution of a crystalline ethanedioic acid, $(COOH)_2.xH_2O$, of concentration 103 g dm^{-3}, labelled **L**.

   In this experiment, you are required to:

   i) carry out a titration to determine the molar concentration of solution S_n;
   ii) use solution S_n to determine the molar concentration of solution **L**.
   iii) find the value of x in $(COOH)_2.xH_2O$.

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

CANDIDATE LABORATORY NUMBER, n:....................

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_____

Determination of the molar concentration of sodium hydroxide in solution S_n

b) Fill your burette with solution **S_n**. Pipette a 25 cm^3 aliquot of solution **C** into a conical flask. Using bromocresol green as an indicator, titrate to a green endpoint. Record the results in the table below.

	1st Titration	2nd Titration	3rd Titration
Final burette reading			
Initial burette reading			
Titre (cm^3)			

Mean titre: _____ cm^3 of solution **S_n**.   (20)

c) Hydrochloric acid and sodium hydroxide react according to the equation:

$$NaOH \text{ (aq)} + HCl \text{ (aq)} \rightarrow NaCl \text{ (aq)} + H_2O \text{ (l)}$$

Calculate the molar concentration of the sodium hydroxide solution **S_n** to three significant figures.

_____

_____

_____

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_____

_____

_____ (2)

_____

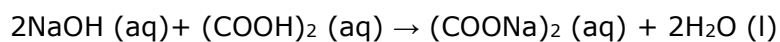**Determination of the molar concentration of solution L**

d) Pipette a 25.0 cm^3 aliquot of solution **L** into a 250 cm^3 volumetric flask and make up to the mark with distilled water. Label this solution **L$_{DIL}$**.

Fill your burette with solution **S$_n$**. Pipette a 25 cm^3 aliquot of solution **L$_{DIL}$** into a conical flask. Using phenolphthalein indicator, titrate to a pink endpoint. Record your data in the table below.

	1st Titration	2nd Titration	3rd Titration
Final burette reading			
Initial burette reading			
Titre			

Mean titre: _____ cm^3 of solution **S$_n$**.   (22)

e) Ethanedioic acid and sodium hydroxide react according to the equation:

$$2NaOH\ (aq) + (COOH)_2\ (aq) \rightarrow (COONa)_2\ (aq) + 2H_2O\ (l)$$

Calculate the molar concentration of the diluted solution **L$_{DIL}$**.

_____

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_____

_____

_____

_____

_____(3)

Please turn the page.

_____

f) Calculate the molar concentration of the undiluted solution **L**.

_____

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_____

_____(1)

g) Given that solution **L** has a concentration of 103 g dm^{-3}, use your answer to part (f) to calculate
   the RMM of $(COOH)_2.xH_2O$ and hence determine the value of x.
   (RAM: C = 12, O = 16 and H = 1)

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_____ (2)

(Total: 50 marks)