EXAMINATIONS BOARD

ADVANCED MATRICULATION LEVEL 2020 FIRST SESSION

| SUBJECT: | Chemistry |
| :--- | :--- |
| PAPER NUMBER: | I |
| DATE: | 29 th September 2020 |
| TIME: | $4: 00$ p.m. to $7: 05 \mathrm{p.m}$. |
|  |  |
| Required Data: | Relative atomic masses: $\mathrm{H}=1 ; \mathrm{C}=12 ; \mathrm{O}=16 ;$ <br>  |
|  | Universal Gas constant $(\mathrm{R})=8.3145 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$. |

## Answer ALL questions

1. This question is about electronic structure and periodicity.
a) Explain what are s-block elements.
$\qquad$
$\qquad$
$\qquad$
b) Give the electronic configuration of the following species in $s, p, d, f$ notation.

Li
$\mathrm{K}^{+}$
$\mathrm{Fe}^{3+}$
c) Describe how atomic size varies down the s block. Explain this trend.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
d) Explain how the first ionisation energy changes down Group 2 of the periodic table.
$\qquad$
$\qquad$
$\qquad$
e) Is the second ionisation energy higher or lower than the first ionisation energy for Group 2 metals? Explain your answer.
$\qquad$
$\qquad$
$\qquad$ (1)
f) Is the first ionisation energy for a Group 1 element higher or lower than the first ionisation energy for a Group 2 element in the same period of the periodic table? Explain your answer.
$\qquad$
$\qquad$
$\qquad$
(Total: 10 marks)
2. This question is about energetics.
a) Define the term standard heat of formation of a compound.
$\qquad$
$\qquad$
$\qquad$
b) Consider the following enthalpies of reaction:
$\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{I})$
$\Delta H^{\circ}=-285.8 \mathrm{~kJ}$
$\mathrm{C}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})$
$\Delta H^{\circ}=-393.5 \mathrm{~kJ}$
$2 \mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 4 \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})$
$\Delta H^{\circ}=-2600 \mathrm{~kJ}$

Hence use Hess's Law to calculate the standard heat of formation of ethyne.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
c) Consider the following reaction:

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

Given that $\Delta \mathrm{H}^{\circ}=-92.38 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and $\Delta \mathrm{S}^{\circ}=-198.3 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$, calculate the Gibbs free energy change at $25^{\circ} \mathrm{C}$ and $500^{\circ} \mathrm{C}$.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
d) At which of the two temperatures is the forward reaction spontaneous? Explain.
$\qquad$
$\qquad$
3. This question is about osmosis.
a) Define osmosis.
$\qquad$
$\qquad$
$\qquad$ (1)
b) Calculate the osmotic pressure when 1.08 g of glucose $\left(\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}\right)$ are dissolved in distilled water to make $60 \mathrm{~cm}^{3}$ of solution at $25^{\circ} \mathrm{C}$.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
c) Explain briefly what is meant by the term reverse osmosis. State the importance of this process in the production of potable water in Malta.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$ (2)
(Total: 7 marks)
4. This question is about radioactivity.
a) Define isotope.
$\qquad$
$\qquad$ (1)
b) Lead-212 is unstable and decays to lead-208. Complete the following decay chain for lead-212.
${ }_{82}^{212} \mathrm{~Pb} \rightarrow{ }_{83}^{212} \mathrm{Bi}+$ $\qquad$ $\rightarrow{ }_{81}^{208} \mathrm{Ti}+$ $\qquad$ $\rightarrow{ }_{82}^{208} \mathrm{~Pb}+$ $\qquad$
c) Carbon-14 is used to estimate the age of carbon-containing artefacts. Explain why this is possible. In your answer include an equation for the decay of Carbon-14.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$ (3)
d) Archaeologists discovered a prehistoric human establishment where they identified ashes from a wood fire. Scientists measured a carbon-14 decay rate of 1.7 counts $\mathrm{min}^{-1} \mathrm{~g}^{-1}$ for these prehistoric ashes. Knowing that the half-life of carbon-14 is 5,730 years and its decay rate in living wood is 13.6 counts $\mathrm{min}^{-1} \mathrm{~g}^{-1}$, estimate the amount of time that passed from the time the wood used in this prehistoric fire was cut.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
5. This question is about the chlorides of Lithium, Beryllium and Nitrogen.
a) Beryllium chloride is an inorganic compound with the formula $\mathrm{BeCl}_{2}$. In the solid form, its crystalline structure can be represented by the diagram in Figure 1.


Figure 1: The crystal structure of Beryllium chloride
i) What do the arrows in this diagram represent?
$\qquad$
ii) Beryllium chloride can be made by reducing Beryllium oxide (BeO) using Carbon in the presence of Chlorine gas at high temperatures. Carbon dioxide is produced as the only side product. Write a balanced chemical equation for this reaction, including state symbols.
b) Nitrogen trichloride $\left(\mathrm{NCl}_{3}\right)$ is an oily substance which is very rarely found in the pure form, since it is very explosive. The structure of $\mathrm{NCl}_{3}$ is given in Figure 2.


Figure 2: The structure of an $\mathrm{NCl}_{3}$ molecule
i) Give the name of the geometrical shape assumed by $\mathrm{NCl}_{3}$ according to the VSEPR theory and state whether the molecule is polar or non-polar.
$\qquad$
$\qquad$
ii) In the space below, draw the Lewis structure (electron dot structure) for $\mathrm{NCl}_{3}$.
$\square$
c) Lithium chloride ( LiCl ) is a solid which has typical properties for a compound of its class. It is extremely soluble in water and is hygroscopic.
i) In the space below, draw the Lewis structure (electron dot structure) for LiCl.

ii) The crystalline lattice structure present in LiCl is identical to that present in solid NaCl . What is the name of this kind of crystalline lattice structure?
iii) Sketch the unit cell of this type of crystalline lattice structure in the space below.
$\square$
iv) What is the main force which keeps the whole solid structure together in LiCl crystals?
$\qquad$
v) What is the main factor which determines which crystalline lattice structure a particular compound attains?
$\qquad$
vi) Is Beryllium more or less electronegative than Lithium?
$\qquad$
vii) Does a diagonal relationship exist between Sodium and Beryllium?
$\qquad$
6. Two students are investigating the reaction between potassium dichromate and propan-2-ol using colorimetry.
a) They first add $5 \mathrm{~cm}^{3}$ of a $0.02 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of potassium dichromate to $45 \mathrm{~cm}^{3}$ of a solution which contains a large excess of acidified propan-2-ol. They notice that the reaction takes exactly 2.50 minutes to complete.
i) Calculate the concentration of potassium dichromate in the reaction mixture at the start of the reaction.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
ii) What colour change should the students observe as the reaction proceeds?
iii) Explain why the acidified propan-2-ol was kept in a large excess.
$\qquad$
$\qquad$
iv) Explain why this experiment cannot be used to determine the order of reaction of potassium dichromate in this reaction.
$\qquad$
$\qquad$
b) The students then repeat the experiment, using a different initial concentration of potassium dichromate. This time they use a computerised colorimetric device to determine the concentration of potassium dichromate at every point in time. The results which they obtained are given in Figure 3.


Figure 3
i) Use the data given in Figure 3 to determine the rate of the reaction at the start of the experiment.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
ii) Define order of reaction.
$\qquad$
$\qquad$
iii) Determine the order of the reaction with respect to potassium dichromate using the data given in Figure 3. Show your working or explain your reasoning.
$\qquad$
$\qquad$
$\qquad$
c) While performing these experiments, the students were careful to keep the temperature of the reaction solution fixed at 298 K . Explain in detail why this is an important precaution. Relate reaction kinetics and the Arrhenius Equation, given below, in your answer.

$$
k=A e^{(-E / R T)}
$$

$\qquad$
$\qquad$
$\qquad$
7. Compound $\mathbf{S}$ is an unsaturated symmetric hydrocarbon. A simplified mass spectrum for compound $\mathbf{S}$ is given in Figure 4 below.


Figure 4: Mass spectrum of hydrocarbon $\mathbf{S}$.
a) Define the underlined terms.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
b) Identify the fragments responsible for the peaks shown in the mass spectrum.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
c) Give the structural formula of compound $\mathbf{S}$.
$\square$
d) Compound $\mathbf{T}$ is a positional isomer of compound $\mathbf{S}$. Give the structure of compound $\mathbf{T}$.
$\square$
e) Compound $\mathbf{T}$ reacts with HBr .
i) Give the product that forms in this reaction.
$\qquad$
ii) Name the rule used to determine the product obtained in part e (i.) above.
$\qquad$
iii) Give the mechanism for this reaction.
$\square$
8. This question is on aliphatic organic substances.
a) For organic compounds $\mathbf{F}$ and $\mathbf{G}$, below:

F:


i) give their systematic name;

F:
G: $\qquad$
ii) write a balanced equation for their reaction with ammonia.

F:
G: $\qquad$
b) Consider the following reaction scheme:

i) Give the structural formulae for organic compounds $\mathbf{A}, \mathbf{B}, \mathbf{C}, \mathbf{D}$.

A:
(1)


C:

D:

Name reagents/conditions r,s,t,u,v,w.
$r:$ $\qquad$ u: $\qquad$

S: $\qquad$ v: $\qquad$ w: $\qquad$
t : $\qquad$
9. Esters may be prepared from the reaction of an alcohol and a carboxylic acid.
a) Name a suitable chemical species that may be used as a catalyst for this reaction.
b) Describe how mechanistic studies for esterification reactions may be carried out using isotopes as tracers.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
c) The ester $\mathrm{CH}_{3} \mathrm{COOCHCH}_{2}$ cannot be produced from the corresponding alcohol because it is very unstable.
i) Draw the structure of this alcohol.
$\square$
ii) Why is the alcohol unstable? Explain.
$\qquad$
$\qquad$
d) On standing in the presence of light, $\mathrm{CH}_{3} \mathrm{COOCHCH}_{2}$ converts slowly into a colourless transparent solid.
i) Account for this change.
$\qquad$
$\qquad$ (2)
ii) Suggest a structure for the solid product.


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## ADVANCED MATRICULATION LEVEL 2020 FIRST SESSION

| SUBJECT: | Chemistry |
| :--- | :--- |
| PAPER NUMBER: | II |
| DATE: | $30^{\text {th }}$ September 2020 |
| TIME: | $4: 00$ p.m. to $7: 05$ p.m. |

A Periodic Table is provided.
Faraday constant $(F)=96500 \mathrm{Cmol}^{-1}$
Universal Gas constant $(R)=8.3145 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$

## Answer TWO questions from each section and ANY other question.

## SECTION A

1. A series of tests are being run in order to determine the properties of a particular chemical which has been extracted from a newly discovered species of plant. The chemical is named $A B$. It is known that the molecular weight of $A B$ is $345 \mathrm{~g} \mathrm{~mol}^{-1}$. $A B$ is of interest to the scientific community since it inhibits the growth of specific types of bacteria.
A back-titration is being performed to determine the number of carboxylic acid functional groups in $A B .0 .500 \mathrm{~g}$ of $A B$ are first dissolved in $50.0 \mathrm{~cm}^{3}$ of water. $25.0 \mathrm{~cm}^{3}$ of $0.300 \mathrm{~mol} \mathrm{dm}^{-3}$ aqueous NaOH are then added to the solution. This represents an excess of NaOH . The solution is stirred well and allowed to rest for a few minutes to ensure that the reaction goes to completion. Assume that the NaOH reacts only with carboxylic acid functional groups in $A B$.
An aliquot of $10.0 \mathrm{~cm}^{3}$ of this solution is then titrated against a solution of $0.0200 \mathrm{~mol} / \mathrm{dm}^{3}$ of $\mathrm{H}_{2} \mathrm{SO}_{4}$, using methyl red as an indicator. A total of $10.5 \mathrm{~cm}^{3}$ of the $\mathrm{H}_{2} \mathrm{SO}_{4}$ solution were required to reach the end-point of the titration. Assume that the $\mathrm{H}_{2} \mathrm{SO}_{4}$ reacts only with the excess NaOH , and not with $A B$ or its salts.
a) Determine the number of carboxylic acid functional groups in AB. Show all your working, include balanced chemical equations where required, and explain your reasoning.
b) Explain the importance of selecting an acid-base indicator correctly. In your answer make sure to:

- explain the function of indicators;
- explain the term pKa, and how this is this linked to the choice of an indicator;
- giving at least TWO named examples of common acid-base indicators and their specific use.
c) The extracted chemical $A B$ is most effective in inhibiting bacteria growth when it is buffered in solution at pH 5. Explain buffer in detail. In you answer make sure to:
- explain what a buffer system is;
- explain what, if any, its effect on the pH of a system is;
- give any example of a buffer system including a balanced chemical equation.
(Total: $\mathbf{2 0}$ marks)

2. This question is about the chemical HI. In the gas-phase at $500 \mathrm{~K}, \mathrm{HI}$ dissociates as follows:

$$
2 \mathrm{HI}_{(\mathrm{g})} \rightleftharpoons \mathrm{H}_{2(\mathrm{~g})}+\mathrm{I}_{2(\mathrm{~g})}
$$

a) Express the partial pressures at equilibrium of each chemical in this reaction only in terms of the following two unknowns: the degree of dissociation of HI, labelling it $\alpha$, and the initial pressure of HI, labelling it i . Assume that all the gases behave ideally.
b) Calculate a value for $K_{p}$ if an initial unknown amount of HI dissociated, forming 0.6 mols of HI and 0.4 mols of $\mathrm{H}_{2}$ at equilibrium. No $\mathrm{H}_{2}$ or $\mathrm{I}_{2}$ was present initially. The pressure present at equilibrium was 1.25 atm .
c) When this mixture of reactants and products is in aqueous solution, another reversible reaction becomes possible in which the triiodide ion is formed. Explain this process, giving balanced chemical equations.
d) HI has a $\mathrm{pK}_{\mathrm{a}}$ of -9.5. Would you expect a solution of HBr to have a higher or lower $\mathrm{pKa}_{\mathrm{a}}$ ? Explain your answer fully and in detail.
e) Give a balanced chemical equation for the reaction of the HI with concentrated sulfuric(VI) acid. Then compare the reducing power of HI to that of other Hydrogen halides by discussing their reaction with concentrated sulfuric(VI) acid.
(Total: $\mathbf{2 0}$ marks)
3. This question is about the transition metals, with particular focus on the metals Chromium and Copper.

Explain each of these statements in detail, giving balanced chemical reactions when relevant.
a) $\mathrm{Cr}(\mathrm{III})$ can be converted to Chromate(VI).
b) The chromate(VI)-dichromate(VI) equilibrium is affected by pH .
c) EDTA can easily displace monodentate ligands in transition metal complexes.
d) Cu reacts with both dilute and concentrated nitric(V) acid.
e) Aqueous $\mathrm{Cu}^{+}$disproportionates, however it can be stabilised in solution or prepared when required.
(Total: $\mathbf{2 0}$ marks)
4. This question is about the chemistry of compounds of oxygen, sulfur and hydrogen.
a) Deuterated compounds are sometimes required for research purposes. Outline reaction schemes and state conditions for the preparation of the following deuterated compounds using $\mathrm{D}_{2} \mathrm{O}$ as deuterium source. More than one step may be required in some cases.
i) $\mathrm{D}_{2} \mathrm{O}_{2}$
ii) $\mathrm{C}_{2} \mathrm{D}_{2}$
iii) $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OD}$
iv) DCl
b) The reaction of hydrogen gas with certain metals produces ionic solids with definite chemical composition while that with other metals forms products with an indefinite composition. Explain this statement.
c) i) Describe the allotropic forms of oxygen and sulfur. Explain why the allotropes of oxygen can be distinguished by chemical means unlike the allotropes of sulfur. Include an equation to represent any reaction in your answer.
ii) The two sulfur atoms in the thiosulfate ion are present in different structural environments. Explain the implication of this on the oxidation state of the ion.
(Total: 20 marks)

## SECTION B

5. Lithium-sulfur batteries, though not yet commercially available, are set to replace lithiumion batteries in the very near future. This change is expected to cause a great improvement in the battery life of many electronic devices such as mobile phones, since lithium-sulfur batteries have a much higher charge density than lithium-ion batteries, and will therefore take a longer time to be depleted of their charge.

The standard electrode potentials of the relevant half-cells at $25^{\circ} \mathrm{C}$ are:

$$
\begin{array}{ll}
\mathrm{S}_{(\mathrm{s})}+2 \mathrm{e}^{-} \rightleftharpoons \mathrm{S}^{2-} & \mathrm{E}^{\circ}=-0.407 \mathrm{~V} \\
\mathrm{Li}^{+}+\mathrm{e}^{-} \rightleftharpoons \mathrm{Li}_{(\mathrm{s})} & \mathrm{E}^{\circ}=-3.040 \mathrm{~V} \\
2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \rightleftharpoons \mathrm{H}_{2(\mathrm{~g})} & \mathrm{E}^{\circ}=0.000 \mathrm{~V}
\end{array}
$$

a) Using the information given above, draw a cell diagram to represent the reaction of the lithium-sulfur battery, calculate its standard electrode potential, and give the full, balanced chemical equation for the reaction.
b) Calculate the standard Gibbs' Free Energy associated with this reaction.
c) Given that Nernst equation is $E=E^{0}-\frac{2.303 R T}{z F} \log _{10} Q$ calculate the potential of the sulfur half-cell at $10{ }^{\circ} \mathrm{C}$ given that the ratio of the concentrations of the oxidised form to the reduced form is 0.15 .
d) Traditional heavy metal batteries pose environmental concerns which are well-known. Li-S batteries are also expected to pose environmental concerns if disposed of incorrectly. Discuss the environmental concerns which the use of sulfur in Li-S batteries might cause if these batteries are disposed of incorrectly.

Another technology which is rapidly being developed as an alternative source of energy is the fuel cell.
e) Explain in sufficient detail the principles of the Hydrogen-Oxygen fuel cell. Include a diagram and balanced chemical equations to aid your explanation.
(Total: $\mathbf{2 0}$ marks)
6. $\mathbf{T}$ is an organic compound having three different elements. It contains $51.9 \%$ by mass of carbon and $9.8 \%$ by mass of hydrogen. The following experiments were performed on compound $\mathbf{T}$.

- Experiment 1: Aqueous sodium hydroxide was added to compound T. The reaction mixture was acidified with dilute nitric acid and silver nitrate was added. This resulted in a white precipitate which dissolved in ammonia solution, giving a colourless solution.
- Experiment 2: Compound $\mathbf{T}$ was mixed with aqueous sodium hydroxide in order to produce compound $\mathbf{S}$. Compound $\mathbf{S}$ reacts with $\mathrm{PCl}_{5}$, producing white fumes that turn damp blue litmus paper red. No change is observed when acidified potassium dichromate(VI) is added to $\mathbf{S}$.
- Experiment 3: 0.302 g of vapourised compound $\mathbf{T}$ occupied a volume of $100 \mathrm{~cm}^{3}$ at a temperature of $100^{\circ} \mathrm{C}$ and a pressure of 1 atm .
a) From the above information, deduce the structural formula of compound $\mathbf{T}$. Explain your reasoning, giving equations where appropriate.
b) Give the mechanism for the reaction of compound $\mathbf{T}$ with aqueous sodium hydroxide. In your answer, name the mechanism that the reaction undergoes and indicate the rate determining step.
c) Compound $\mathbf{T}$ is heated under reflux with $K C N$ in ethanol to produce compound $\mathbf{R}$. Dilute nitric acid is then added to compound $\mathbf{R}$ and heated under reflux to produce compound $\mathbf{U}$. Compound $\mathbf{U}$ is then dissolved in dry ethoxyethane, followed by the addition of $\mathrm{LiAlH}_{4}$, to produce compound $\mathbf{Q}$.
Identify organic compounds $\mathbf{R}, \mathbf{U}$ and $\mathbf{Q}$.
(Total: $\mathbf{2 0}$ marks)

7. This question is on benzene and its derivatives.
a) i) Outline a suitable route for the conversion of benzene to compound $B$ (see below). More than one step may be required. Your answer should include the conditions and the reagents which are used in all the steps.

B:


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ii) How would you modify the scheme given in part a i) in order to produce compound C (see below). Explain your answer, giving canonical forms where possible.

b) Starting from benzene, and any other aliphatic organic substance, show how phenylethanone may be prepared in one step. In your answer you should include the essential experimental conditions and mechanism for the reaction.
c) The following questions are about diazonium salts.
i) Diazonium salt D can be converted into a coloured product on reaction with phenol in the presence of alkali. Write down a possible structural formula for the coloured product.

ii) Although diazonium salts from phenylamine are stable, diazonium salts from ethylamine cannot be isolated. Account for this as fully as you can.
(Total: $\mathbf{2 0}$ marks)
8. Answer the following questions.
a) Outline suitable routes for the following conversions. More than one step may be required for each conversion. Your answers should include reagents and conditions used where appropriate.
i)

ii) bromoethane to butan-2-ol. You may only use bromoethane as an organic reagent, i.e. you have to show how any organic reagent needed in your reaction scheme can be prepared from bromoethane. You may use any inorganic reagent.
b) Define nucleophile and electrophile, giving TWO examples in each case.
c) Discuss why steam distillation is used to separate temperature sensitive compounds. A labelled diagram of a steam distillation setup should be included in your answer.
(Total: $\mathbf{2 0}$ marks)

