Catholic Junior College
JC2 Preliminary Examination
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY
Paper 2 Structured Questions

9729/02
26 August 2022
2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculation is expected, where appropriate.

A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Paper 1		**30**
Paper 2	**Q1**	**/13**
	Q2	**/11**
	Q3	**/15**
	Q4	**/12**
	Q5	**/11**
	Q6	**/13**
		75
Paper 3		**80**
Paper 4		**55**
OVERALL (100%)		
GRADE		

1 (a) Fehling's solution is used in Qualitative Analysis of organic compounds.

It is prepared fresh by mixing a solution of $CuSO_4$ (Fehling's A solution) with a mixture of tartrate ions and NaOH (Fehling's B solution). When the two solutions are mixed, the tartrate ions act as ligands to form a complex ion with the Cu^{2+} ions.

(i) Another reagent with similar action to Fehling's solution is Benedict's solution, which is also an alkaline solution of Cu^{2+}, but the ligand forming the complex ion is citrate ion instead of tartrate ion.
Suggest why the presence of the ligand is necessary in Fehling's (and Benedict's) solution.

……

……

……[1]

Fehling's solution was used to distinguish between three unknown compounds, **A**, **B** and **C**:

Compound	Observation with Fehling's solution
A	blue solution
B	red ppt
C	blue solution

It is known that compounds **A**, **B**, and **C** are the following (not necessarily in order):

$C_6H_5COCH_3$ C_6H_5CHO $C_6H_5CH_2CHO$

(ii) Based on the above observations, state the identity of compound **B**.

……[1]

(iii) Give a simple chemical test to distinguish compounds **A** and **C**. In your answer, the observations for each compound must be stated.

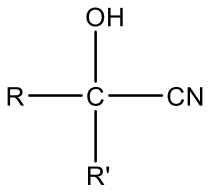
……

……

……

……[2]

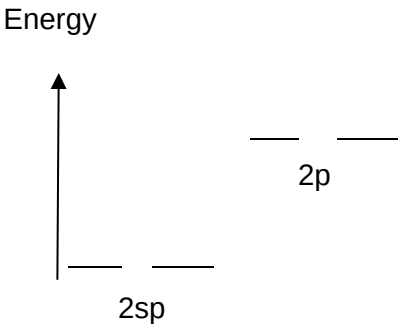
1 **(a)** Compounds **A**, **B** and **C** are all able to form hydroxynitriles when subject to the same reagents and conditions.



(iv) State the reagents and conditions required for the above transformation.

……[1]

(v) The N atom of the nitrile group is sp hybridised. Complete the energy level diagram to show how the electrons are arranged in the second quantum shell of the N atom so that the bonding in the nitrile can occur.



[1]

(vi) Hence, suggest why nitriles are weaker bases than amines, given that N atom in amine is sp^3 hybridised.

……

……..

……

……[1]

(b) Most of the world's copper comes from the mining of copper-containing minerals. Copper ions exist as either one of the two oxidation states, +1 or +2. Two examples of such minerals are bornite and chalcopyrite.

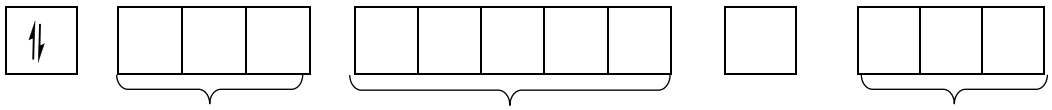
(i) Bornite has the chemical formula Cu_5FeS_4. Given that the oxidation state of S is –2 in bornite, write down the oxidation states of Cu and Fe in bornite.

Oxidation state of Cu: ……

Oxidation state of Fe: …….

[2]

1 (b) (ii) Complete the diagram to show the arrangement of electrons in the third and fourth principal quantum shells of the **ion** of Fe in bornite.



[1]

Chalcopyrite is also composed of the elements Cu, Fe and S. Let the chemical formula of chalcopyrite be Cu_xFeS_y.

Both bornite and chalcopyrite react with HNO_3 to give sulfur precipitate and NO_2 gas.

(iii) The balanced equation for the reaction of bornite and chalcopyrite with HNO_3 are as follows.

$$Cu_5FeS_4 + 26HNO_3 \rightarrow Fe(NO_3)_3 + 5Cu(NO_3)_2 + 4S + 13NO_2 + 13H_2O$$

$$Cu_xFeS_y + (6 + 4x)HNO_3 \rightarrow Fe(NO_3)_3 + xCu(NO_3)_2 + yS + (3 + 2x)NO_2 + (3 + 2x)H_2O$$

When 1 mole each of bornite and chalcopyrite were fully reacted with HNO_3, bornite produced 64.2 g more sulfur precipitate and 1.92×10^5 cm^3 more nitrogen dioxide than chalcopyrite, at room temperature and pressure.

Determine the values of x and y.

[3]

[Total: 13]

2 A sodium-vapor lamp is a gas-discharge lamp that uses sodium in an excited state to produce light at a characteristic wavelength near 5.89 x 10^{-7} m. Low-pressure sodium lamps are highly efficient electrical light sources but due to their yellow light, they are widely used as street lamps. The yellow light is produced by an excited electron in a sodium atom falling from a 3p orbital to the 3s orbital. The wavelength for this transition is 5.898 x 10^{-7} m.

The energy, *E* (in joules), corresponding to the light of wavelength, λ (in metre), is given by the following equation:

$$E = \frac{hc}{\lambda}$$

where *h* is Planck's constant = 6.63 x 10^{-34} J s
c is the speed of light = 3.00 x 10^{8} m s^{-1}

(a) State the electronic configuration of a sodium atom in the ground state.

Na: $1s^2$…… [1]

(b) Draw an energy level diagram to show the electron configuration of a sodium atom in an excited state that produces yellow light.

[1]

(c) Calculate the energy of the yellow light in

(i) J (per atom)
(ii) kJ mol^{-1}

[2]

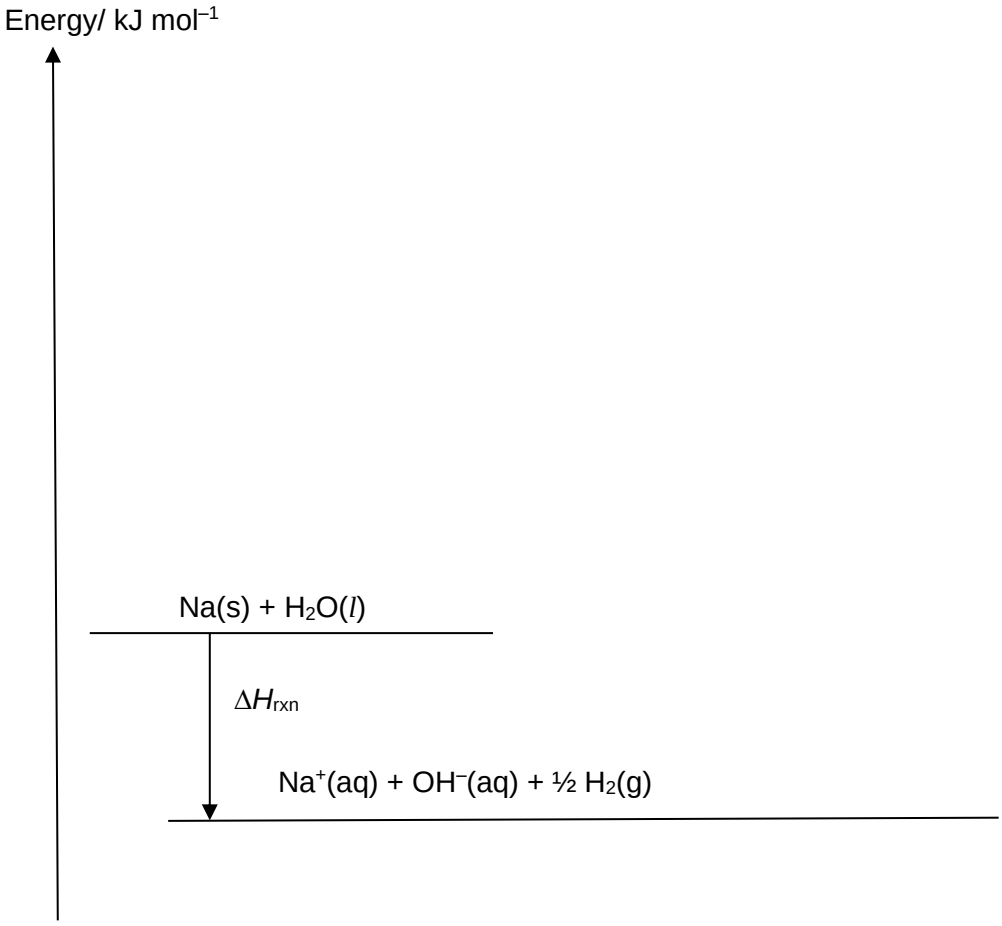
2 (d) Sodium can react with water to form aqueous sodium hydroxide.

$$Na(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \tfrac{1}{2} H_2(g)$$

The following data will be useful in this question.

Enthalpy change of atomisation of Na(s)	= +107 kJ mol^{-1}
Enthalpy change of neutralisation	= –58 kJ mol^{-1}
Enthalpy change of hydration of $Na^+(g)$	= –405 kJ mol^{-1}
Enthalpy change of $2H^+(aq) \rightarrow H_2(g)$	= –796 kJ mol^{-1}

Construct a fully labelled energy level diagram to determine the enthalpy change for the above reaction using relevant data from the above list, together with relevant data from the *Data Booklet*.



[5]

2 **(e)** The melting point of Na is 98 ^{o}C, whereas that of NaOH is 318 ^{o}C. Explain, in terms of structure and bonding, the differences in melting point between them.

……..

……..

……

……..

……

……..

……[2]

[Total: 11]

3 **(a)** Liquid ammonia, like aqueous ammonia is a conductor of electricity, but a very weak one. Liquid ammonia can exhibit this property as it can undergo self-ionisation.

(i) Write an equation between two ammonia molecules to show this property of liquid ammonia.

……..…[1]

(ii) Identify the two different conjugate acid-base pairs in the reaction occurring in **(a)(i)**.

……

…….[1]

(b) Hydrogen sulfide can act as a weak acid.

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq) \qquad pK_a = 7.05 \text{ at } 298 \text{ K}$$

(i) NaHS is a basic salt that undergoes salt hydrolysis. Calculate the pH of 0.100 mol dm^{-3} NaHS(aq).

[2]

(ii) The pK_a for C_6H_5SH is 6.5. Suggest an explanation for the different pK_a values for H_2S and C_6H_5SH.

……

……

……

…….[1]

3 **(c)** A solution containing hydrogensulfite ions, HSO_3^-(aq), and sulfite ions, SO_3^{2-} (aq), can act as a buffer. The K_a of HSO_3^- (aq) is 6.73 x 10^{-8} mol dm^{-3} at 298 K.

A buffer solution is prepared by mixing 50.0 cm^3 of 0.500 mol dm^{-3} $NaHSO_3$ and 25.0 cm^3 of 0.600 mol dm^{-3} NaOH.

By finding $[SO_3^{2-}]$ and $[HSO_3^-]$ after mixing $NaHSO_3$ and NaOH, calculate the pH of the buffer solution formed at 298 K. Show your working clearly.

[2]

(d) Calcium fluoride, CaF_2, occurs naturally in the mineral *fluorspar*. It is the major sources of fluorine for the chemical industry, for making polymers (PTFE), freons and fire retardants. It is also sparingly soluble in water. In its saturated solution, the concentration of CaF_2 is 2.30 x 10^{-4} mol dm^{-3}.

(i) Write an expression for the solubility product, K_{sp}, of calcium fluoride, and calculate its value.

[2]

3 (d) (ii) Use only the relevant data provided below to calculate a value for the enthalpy change of solution of calcium fluoride.

enthalpy change of formation of $CaF_2(s)$	–1220 kJ mol^{-1}
enthalpy change of atomisation of Ca(s)	+178 kJ mol^{-1}
enthalpy change of formation of $Ca^{2+}(aq)$	–543 kJ mol^{-1}
electron affinity of fluorine atoms	–328 kJ mol^{-1}
enthalpy change of formation of $F^-(aq)$	–333 kJ mol^{-1}

[2]

(iii) Hence, predict whether CaF_2 will be more, or less, soluble in hot water than in cold water.

……

……

……[1]

3 (d) (iv) Describe and explain how the solubility of CaF_2, is affected when $CaCl_2$(aq) is added.

……

……

……

……[1]

(v) In non-polar solvents, ethanoic acid, CH_3CO_2H, can form a dimer containing two hydrogen bonds.

$$\underset{\text{monomer}}{2CH_3CO_2H} \rightleftharpoons \underset{\text{dimer}}{(CH_3CO_2H)_2} \qquad K_c = 1.51 \times 10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ at } 298 \text{ K}$$

I A solution of 0.100 mol dm^{-3} CH_3CO_2H is allowed to reach equilibrium in a non-polar solvent at 298 K. The equilibrium concentration of the dimer is 0.0417 mol dm^{-3}. Calculate the $\frac{[(CH_3CO_2H)_2]}{[CH_3CO_2H]}$ ratio at equilibrium. Quote your answer to 3 significant figures.

[1]

II Suggest how the ΔG for this equilibrium in an aqueous solution would differ from the ΔG in a non-polar solvent. Explain your answer.

……

……

……

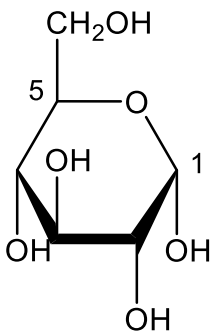
……

……

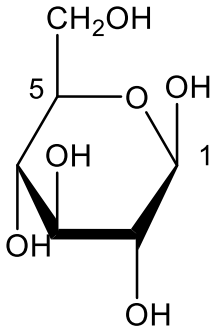
……[1]

[Total: 15]

4 D-glucose can exist in two isomers as α-glucose and β-glucose. In α-glucose, the –OH group attached to carbon 1 and the $–CH_2OH$ group at carbon 5 are in a trans arrangement (opposite of the plane), while in β-glucose, the two groups are in a cis arrangement (same side of the plane).



α-glucose



β-glucose

Each of these isomers can be synthesised and isolated as pure compounds. The α-glucose has an angle of optical rotation of +112° while the β-glucose has an angle of optical rotation of +19°. When either one of the isomers is dissolved in water, the α and β isomers slowly interconvert until equilibrium is established. The optical rotation changes over time and reaches +52.5°.

$$\alpha\text{-glucose(aq)} \rightleftharpoons \beta\text{-glucose(aq)}$$

(a) Given that the optical rotation is directly proportional to the concentration of each isomer of glucose, show that the ratio of the α-glucose to β-glucose in the equilibrium mixture is 36 to 64.

[1]

(b) Write an expression for K_c.

[1]

(c) At higher temperature, the optical rotation is greater than +52.5°. Deduce whether the forward reaction is exothermic or endothermic.

……..

……

……..

……[1]

4 **(d)** *Cis-trans* isomerism also occurs in alkenes where the molecules contain restricted rotation of double bond. *Cis–trans* isomers of alkenes can be synthesised from the elimination reactions of halogenoalkanes.

When a mixture of beryllium hydroxide pellets and ethanol is added to optically active 2–chlorobutane, **P**, **Q**, **R** and **S** are formed. All of them do not react with PCl_5. **P**, **Q** and **R** decolourise potassium manganate(VII), with only **R** producing an effervescence. **S** has the formula of $C_6H_{14}O$ and rotates plane-polarised light.

Give the structures of **P**, **Q**, **R** and **S**.

[4]

(e) The hydroxide ion from beryllium hydroxide undergoes acid-base reaction with ethanol. Write an equation to represent this.

……[1]

(f) Outline the mechanism for the formation of **S** from 2-chlorobutane.

[3]

4 **(g)** How would you expect the rate of the reaction described in **(f)** to change if 2-bromobutane is used?

.....

.....

.....

.....[1]

[Total: 12]

5 This question is regarding the chemistry of chromium and chromium-containing compounds.

(a) A metal ion, $\mathbf{M}^{n+}$, oxidises Cr^{3+} to $Cr_2O_7^{2-}$. In the reaction, the $\mathbf{M}^{n+}$ ion is reduced to $\mathbf{M}^{2+}$. In an experiment, 60.0 cm^3 of 0.040 mol dm^{-3} $\mathbf{M}^{n+}$ was found to react with 10.0 cm^3 of 0.080 mol dm^{-3} Cr^{3+}.

Determine the value of n in $\mathbf{M}^{n+}$.

[3]

(b) **(i)** The variety of colours shown by chromium compounds is typical of transition metals. State **one** other characteristic property of transition metals.

……[1]

(ii) Explain why the transition elements such as chromium have higher melting points as compared to the main group metals in general.

……

……

……

……

……

……

……[3]

5 (b) (iii) Like chromium, iron is a useful *heterogeneous* catalyst. By choosing a suitable example, describe and explain how iron performs this function.

……

……

……

……

……

……

……

……

……

……

……

……[4]

[Total: 11]

6 Biomolecules are substances that are produced by cells and living organisms. They have a wide range of sizes and structures and perform various functions.

(a) Proteins are a type of biomolecule. The chemical used for detecting proteins, biuret reagent, $H_2NCONHCONH_2$, can be formed by heating urea, $(NH_2)_2CO$.

$$2(NH_2)_2CO \rightarrow H_2NCONHCONH_2 + NH_3$$

Step 1: 3.88 g of impure sample of urea $(NH_2)_2CO$ was heated strongly above its melting point. The ammonia liberated was absorbed in 32.0 cm^3 of 2.00 mol dm^{-3} sulfuric acid.

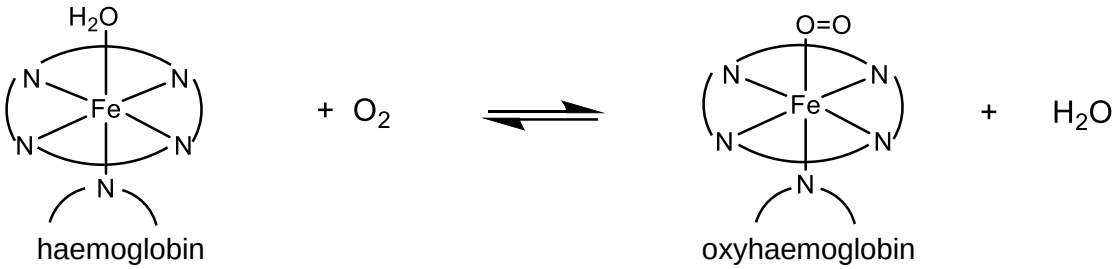
Step 2: The resulting solution was made up to 500 cm^3 with distilled water.

Step 3: 25.0 cm^3 of the solution required 25.50 cm^3 of 0.20 mol dm^{-3} sodium hydroxide solution for neutralisation using methyl orange as an indicator.

Calculate the percentage purity of urea in the sample.

[3]

6 **(b)** Haemoglobin is an example of a protein. The iron in the haemoglobin molecule is surrounded by six ligands. Five of these are nitrogen atoms from the globin protein, and one is from a water molecule. This water molecule is replaced by an oxygen molecule in oxyhaemoglobin. This equilibrium may be expressed as shown:



haemoglobin oxyhaemoglobin

The iron in haemoglobin contains six 3d electrons.

(i) What is oxidation state of the iron in haemoglobin?

……[1]

(ii) Sketch the shape of the $3d_{z^2}$ orbitals of Fe, stating clearly the orientation and axes below.

[1]

(iii) Oxyhaemoglobin is bright red whereas haemoglobin is close to purple.
The colour is due to the absorption of light at specific wavelengths. The colour observed is the complement of the colour absorbed.

Suggest

- the size of d-orbital splitting in the two complexes, oxyhaemoglobin and haemoglobin,
- why oxyhaemoglobin is of a different colour from haemoglobin.

……

……

……

……

……

……

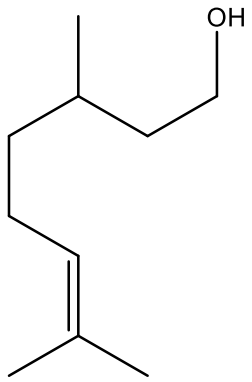
……

……

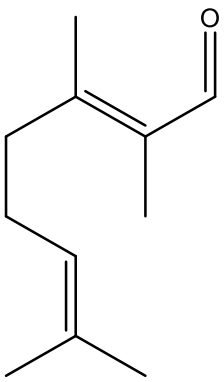
……[4]

6 **(c)** A pheromone is a biomolecule that, when secreted by an individual of a species, can elicit a certain type of behaviour in other members.

The structures of two pheromones secreted by the honeybee to direct others to a food source are shown below.



X



Y

Deduce the type(s) of isomerism (if any) that may be present in each of **X** and **Y** and draw the structural formulae to illustrate various pairs of isomers.

[4]
[Total: 13]

BLANK PAGE