TEMASEK JUNIOR COLLEGE

2023 JC2 PRELIMINARY EXAMINATION

Higher 2



CANDIDATE NAME		DNS	
CG	/ 22	SUBJECT TUTOR'S NAME	
CHEMISTRY			9729/03
Paper 3 Free Resp	oonse		14 Sep 2023
			2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, CG and subject tutor's name 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. If additional space is required, you should use the pages at the end of this booklet. The question number must be shown clearly.

Section A Answer all questions.

Section B Answer one question.

A Data Booklet is provided. The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together. The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use				
Section A	Q1		/ 20	
	Q2		/ 22	
	Q3		/ 18	
Section B (Circle one)	Q4	Q5	/ 20	
TOTAL			/ 80	

This document consists of ?? printed pages and ?? blank page.

Section A

Answer all the questions in this section.

- 1 The transition metals such as iron and rhodium are known for their catalytic activity.
 - (a) The reaction between $S_2O_8^{2-}$ ions and I^- ions is very slow. If a small amount of aqueous iron(II) ions is added to the mixture, the rate of reaction increases.
 - (i) Write the electronic configuration for iron(II) ions. [1] $Fe^{2+}: 1s^22s^22p^63s^23p^63d^6$ [1]
 - (ii) Explain why the reaction between $S_2O_8^{2-}$ ions and I^- ions is very slow. [1]

In the uncatalysed reaction, there is a direct reaction between two similarly charged ions. [1] <u>The electrostatic repulsion between the two negatively charged ions partly causes the reaction to have a high activation energy.</u>

- (iii) Explain why the iron(II) ions can be described as a *homogeneous catalyst*. [2]
 <u>Fe²⁺ in the same physical state/same phase as the reactants</u> [1], and it is <u>not</u> <u>consumed/used up OR the Fe²⁺ is regenerated at the end of the reaction</u> [1]
- (iv) State the property, typical of transition metals, which allows iron(II) ions to behave as a catalyst in this reaction.

Include relevant chemical equations to support your answer.

[1] The catalytic activity of transition metals in homogenous catalysis depends on their ability to exist in variable oxidation states.

The catalysed pathway involves the following two steps with lower E_a.

Step 1: $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$ [1]

Step 2: $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$ [1]

(b) Ferrocene is a highly stable compound in which the iron(II) ion is located between two cyclopentadienyl anion rings. Studies have shown that the carbon–iron bonding in ferrocene is capable of free rotation.



[3]

(i) Suggest an alternative structure of ferrocene.



The methylene hydrogen atoms shown in cyclopentadiene below are acidic. Cyclopentadiene can dissociate a proton to form the cyclopentadienyl anion.



cyclopentadiene

 $+ H^{+}$

(ii) Write an expression for the acid dissociation constant, K_{a} , for cyclopentadiene. [1]



Comment:

(iii) Suggest the number of delocalised π electrons in the cyclopentadienyl anion. [1] [1] 6



(iv) Similar to benzene, ferrocene undergoes electrophilic substitution with acetic anhydride and phosphoric acid to form the compound **W**.

[1]

[Turn over



 $\text{compound} \; W$

The steps of the mechanism are as described.

Step 1: Acetic anhydride and phosphoric acid react to form the acylium ion.



Acetic Anhydride

Acylium ion

Step 2: Addition of the acylium ion to one of the carbon atoms on the cyclopentadienyl *anion* ring in ferrocene forms an intermediate.

Step 3: Loss of a proton from the intermediate to form W.

Suggest the mechanism for steps 2 and 3. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]



(c) Hydrogenation of alkenes can be catalysed by the rhodium (Rh)-containing catalyst, Wilkinson's catalyst, RhL₃C*l*, where L is the triphenylphosphine ligand.



triphenylphosphine

(i) Explain using bonding why triphenylphosphine is insoluble in water.

Triphenylphosphine has simple molecular structure.

Energy produced from $[\checkmark]$ instantaneous dipole - induced dipole attraction (idid) between triphenylphosphine and water is $[\checkmark]$ insufficient to overcome the $[\checkmark]$ id-id between triphenylphosphine and $[\checkmark]$ hydrogen bonds between water. $2[\checkmark] = [1]$

The following steps take place when Wilkinson's catalyst is used to carry out the hydrogenation of ethene. Hydrogen is reduced to hydride in step 1.



[2]

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With	consideration of the oxidation state at the Rh metal centre,	
(ii)	identify the step which involves an oxidative addition.	[1]
	[1] Step 1	
(iii)	identify the step which involves a reductive elimination.	[1]
	[1] Step 5	

6

Step 4 of the reaction is the rate-determining step. (iv)

> Suggest why the rate of reaction is slower when 2,3-dimethylbut-2-ene is used in place of ethene. [1]



2,3-dimethylbut-2-ene

The rate of reaction will be slower as there is [1] greater steric hindrance around the metal center for the more highly substituted 2,3-dimethylbut-2-ene.

Triphenylphosphine, PPh₃, is used as nucleophile in the Wittig reaction. (d)

In the Wittig reaction, a carbonyl compound reacts with a halogenoalkane to form an alkene. The conversion is shown in the following unbalanced equation.



Suggest a three-step synthesis involving the Wittig reaction to convert cyclohexene to compound **Q**. [3]

 $_{\sim}$ CH₂CH₃



- 2 This question involves various components found in different types of aerosol propellants and sprays.
 - (a) Dimethylether, CH₃OCH₃, is a colourless gas that is used as an aerosol propellant.

Dimethylether can react with carbon dioxide to form carbon monoxide and hydrogen, as shown by the equation below.

 $CH_3OCH_3(g) + CO_2(g) \Rightarrow 3CO(g) + 3H_2(g) \Delta H = +245 \text{ kJ mol}^{-1}$

(i) Write an expression for the equilibrium constant, K_{p} , for this reaction. Give the units for K_{p} . [2]

 $K_{p} = \frac{(P_{co})^{3} (P_{H_{2}})^{3}}{P_{CH_{3}OCH_{3}} \cdot P_{CO_{2}}}$ [1] atm⁴ or Pa⁴ [1]

In an experiment conducted at 550 K, a mixture of CH_3OCH_3 and CO_2 was introduced into in a 2 m³ sealed vessel. The initial total pressure was 12 atm at this temperature. The reaction was allowed to reach dynamic chemical equilibrium.

- (ii) At equilibrium, the amount of CO was found to be 278.5 mol. Using the *ideal gas equation*, verify that the equilibrium partial pressure of CO in the vessel was 6.3 atm.
 - pV = nRT p = nRT/VPartial pressure of CO at equilibrium = $\frac{278.5 \times 8.31 \times 550}{101325 \times 2.0}$ [1] = <u>6.3 atm (shown)</u> *OR*Partial pressure of CO at equilibrium = $\frac{278.5 \times 8.31 \times 550}{2.0}$ = 636400 Pa atm
 101325 Pa = 1 atm
 636442.125 Pa = $\frac{636400}{101325}$ = <u>6.3 atm (shown)</u> [1]
- (iii) At equilibrium, it was found that 70% of the CH₃OCH₃ had dissociated.

Calculate the equilibrium pressures of CH₃OCH₃ and CO₂ in atm.

	CH ₃ OCH ₃	CO ₂	1	3CO	3H ₂
Initial partial pressure/atm	x	12 - x		0	0
Change in partial pressure/atm	- 0.7 x	- 0.7 x		+ 2.1 x	+2.1 x
Em partial pressure / atm	0.3 x	12 – 1.7 x		2.1 x	2.1 x

[1] for correct equilibrium partial pressures of all gases in the ICE Table in terms of \boldsymbol{x}

Since equilibrium partial pressure of CO in the vessel was 6.3 atm,

[1]

[3]

2.1 x = 6.3 \Rightarrow x = 3 atm

 $P_{CH3OCH3}$ at equilibrium = 0.3 x 3 = <u>0.9 atm [1]</u> P_{CO2} at equilibrium = 12 - 1.7(3) = <u>6.9 atm [1]</u>

(iv) Hence, calculate the value of K_{p} , for this reaction.

 $\begin{aligned} \mathsf{P}_{\mathsf{CH3OCH3}} & \text{at equilibrium} = 0.9 \text{ atm} \\ \mathsf{P}_{\mathsf{co}} &= \mathsf{P}_{\mathsf{H2}} \text{ at equilibrium} = 2.1 \text{ x } 3 = 6.3 \text{ atm} \\ \mathcal{K}_{\mathsf{p}} &= \frac{(\mathsf{P}_{\mathsf{co}})^3 (\mathsf{P}_{\mathsf{H_2}})^3}{\mathsf{P}_{\mathsf{cH_3OCH_3}} \cdot \mathsf{P}_{\mathsf{co_2}}} \\ \mathcal{K}_{\mathsf{p}} &= \frac{(6.3)^3 (6.3)^3}{(0.9)(6.9)} = 62\ 523.5\ /\ 6.21 = \underline{1.01\ x\ 10}^4 \text{ atm}^4 \ \textbf{[1]} \end{aligned}$

(v) Using a value of K_p of 12 Pa, determine the value of ΔG for this reaction and hence, comment on the significance of the sign of ΔG , in relation to the equilibrium composition at 550 K. [2]

 $\Delta \mathbf{G} = -\mathbf{RT} \ln \mathbf{K}_{p} = -(8.31)(550) \ln (12) = -11.4 \text{ kJ mol}^{-1} [1]$

 $\Delta G^{\circ} < 0$, implies that the <u>forward reaction is spontaneous</u> and so there is a <u>higher concentration of products than reactants</u>. [1]

(vi) Explain the effect (if any) on the average M_r of the reactants in the equilibrium mixture value when the experiment was conducted at 300 K instead of 550 K. [2]

When temperature was decreased, the $\sqrt{\text{position of equilibrium shifted left}}$ towards the $\sqrt{\text{exothermic reaction to}}$ release heat.

Hence, the $\sqrt{\text{amount/partial pressure of reactants increases.}}$ Average M_r of the reactants <u>remains the same.</u>

Every 2 $\sqrt{-1}$ mark

- (b) An important property of an aerosol propellant is that it should be a gas at room temperature and pressure.
 - (i) State three assumptions of the kinetic theory as applied to an ideal gas. [3]

<u>Gas particles have negligible volume</u> compared to the volume of the container. [1]

The gas particles exert insignificant intermolecular forces/attractive forces between the particles. [1]

[1] The <u>collisions between gas particles are perfectly elastic</u> and no kinetic energy is lost on collision.

(ii) Fig. 2.1 illustrates the behaviour of 1 mol of ideal gas as well as 1 mol of CH₃OCH₃ at 293 K.





On the **same** axes in Fig. 2.1, sketch and label the graph for 1 mol of CH_3OCH_3 at 550 K. Explain your answer. [2]



[1] for correct graph for both -ve and +ve deviation. BOD labelling

At higher temperature of 550 K, the CH_3OCH gas molecules have <u>higher kinetic</u> energy .Therefore, the intermolecular forces of attraction (or state pd-pd or idid) is LESS significant [1] and the CH_3OCH gas molecules deviate from ideality to a smaller extent.

At higher temperature, total volume of gas increases, hence particle size becomes less significant.

(c) Aerosol sprays containing copper(II) ions were used near a well. Copper(II) hydroxide deposits was observed in the well water.

The value of the solubility product, K_{sp} , of copper(II) hydroxide is 1.80 x 10⁻¹⁹ at 25°C.

The MCL is the maximum concentration of a contaminant in drinking water beyond which the water is not safe for consumption. The MCL for copper(II) ions is 1.3 mg dm⁻³.

Determine if a water sample found in the well whose pH was found to be 7.75, is safe for consumption. [2]

 $[OH^{-}] = 10^{-(14-7.75)} = 5.623 \times 10^{-7} \text{ mol dm}^{-3}$

 $K_{sp} = [Cu^{2+}][OH^{-}]^2$

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 $[Cu^{2+}] = Ksp \div [OH^{-}]^2 = 1.80 \times 10^{-19} / (5.623 \times 10^{-7})^2 [1] = 5.69 \times 10^{-7} \text{ mol dm}^{-3}$

Mass of $Cu^{2+} = 5.69 \times 10^{-7} \times 63.5 = 0.0362 \text{ mg dm}^{-3} + \text{conclusion [1] } 0.0361$

compare amount or mass

Conclusion: [Cu²⁺] lower than MCL hence <u>water is possible for consumption</u>.

(d) Calcium fluoride is a component of aerosol spray and aids in the treatment of muscular tension and torn ligaments.

The data in Table 2.1 will be useful in this question.

Table 2.1

Lattice energy of CaF ₂ (s) / kJ mol ⁻¹	-2640
Standard Gibbs free energy of solution of $CaF_2(s) / kJ mol^{-1}$	+64.4
Standard enthalpy change of hydration of $Ca^{2+}(g) / kJ mol^{-1}$	-1579
Standard enthalpy change of hydration of F ⁻ (g) / kJ mol ⁻¹	-524

- (i) Define the term standard enthalpy change of solution, ΔH^e_{solution}, of CaF₂. [1]
 Energy change when one mole of CaF₂(s) is completely dissolved in a solvent/water to form an infinitely dilute solution at 298 K & 1 bar [1]
- (ii) Construct a labelled energy cycle to calculate the standard enthalpy change of solution of CaF_2 . [2]



[1] for cycle with state symbols. Do not penalise aq $\Delta H^{q}_{soln} (MX) = \Delta H^{q}_{hyd} (M^{+}) + \Delta H^{q}_{hyd} (X^{-}) - \Delta H^{q}_{latt} (MX)$ = [-1579 + 2(-524)] - (-2640)

= <u>+13.0 kJ mol⁻¹</u> [1] with + sign

(iii) Hence, calculate the standard entropy change of solution, $\Delta S^{e}_{solution}$, of CaF₂. [1] $\Delta G^{e}_{sol} = \Delta H^{e}_{sol} - T\Delta S^{e}_{sol}$ +64.4 = +13 - 298(ΔS^{e}_{sol}) $\Delta S^{e}_{sol} = -0.173 \text{ kJ mol}^{-1} \text{ K}^{-1}$ ECF [1] with - sign and correct units

[Total:22]

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- 3 This question is about nitrogen compounds and its reactions.
 - (a) Nitric acid, HNO₃, is used as the main reagent for nitrating aromatic compounds such as benzene, phenylamine and phenol.

The table below shows the different conditions used for the mononitration of benzene, phenylamine and phenol.

	benzene	phenylamine	phenol
Reagents	mixture of concentrated HNO ₃ and concentrated H ₂ SO ₄	dilute HNO₃	dilute HNO ₃
Temperature / °C	60	20	40

(i) Explain the need for concentrated H₂SO₄ in the nitration of benzene, but not for phenylamine and phenol. [2]

Both phenylamine and phenol have [1] <u>electron donating groups / lone pair</u> <u>delocalise into the ring</u>, [1] increase electron density / more electron rich on the benzene ring which <u>activates it towards electrophilic substitution</u>, so no catalyst is needed.

Concentrated H_2SO_4 is used as an acid catalyst to generate the stronger electrophile as the benzene lacks ring activating groups.

(ii) With reference to the data in the table above, comment on the difference in reactivity between phenylamine and phenol towards nitration. [2]

A lower temperature for nitration of phenylamine implies that [1] <u>phenylamine is</u> <u>more reactive than phenol</u>, as [1] <u>N atom is less electron withdrawing /</u> <u>electronegative than O atom</u>, so the <u>electron density on the benzene ring is higher</u> than phenol.

(b) Histidine is a naturally occurring amino acid which is used for repairing damaged tissues and making blood cells.

The structure of the histidine is shown below.



The 2 nitrogen atoms in the ring are sp² hybridised.

(i) Explain why nitrogen atom N_b does not have a p K_b value. [1]

The $[\checkmark]$ lone pair of electrons on N_b are <u>delocalised over the neighbouring C=C</u> bonds, $[\checkmark]$ and <u>not available to accept H⁺</u>

(ii) The pK_b value for nitrogen atom N_a is 8.0.

In terms of hybridisation of nitrogen atom, explain why N_a is more basic than N_b . [1]

The [\checkmark] lone pair electrons on N_a are on the sp² hybrid orbital which lies on the plane / perpendicular to the p-orbitals. Delocalisation cannot occur, [\checkmark] lone pair electrons are available on N_a to accept H⁺

(c) The fully protonated form of histidine, HisH⁺, can be synthesised from the reaction scheme below.



HisH⁺

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(i) Different stereoisomers have different biological properties towards enzymes.

It was found that only 25% of compound **C** could be converted to **D** by the enzyme dehydratase in step 1. Suggest an explanation for this observation. [2]

[1] C has 2 chiral centers, hence there are a total of <u>4 stereoisomers</u>. **[1]** Only <u>one</u> <u>stereoisomer has the correct orientation to bind to the protein receptors in enzyme</u> <u>dehydratase</u>.

(ii) A student attempted to convert compound **D** to enantiomer **E** without the use of enzymes and proposed the following sequence of reactions.

D and **E** are represented by their simplified structures below.



By considering the stereochemical outcome of each step, explain why each of the following steps is **not** suitable to produce a good yield of enantiomer **E**. [2]

- Step 2a
- Step 2c

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[Given that Step 2c follows a second order kinetics reaction]

Step 2a: the [\checkmark] geometry around the carbonyl carbon is trigonal planar, so the [\checkmark] incoming nucleophile H⁻ can approach both top and bottom of the plane with equal probability, producing a racemic mixture, instead of only 1 enantiomer.

Step 2c: reaction is $[\checkmark] S_N 2$, hence the $[\checkmark]$ <u>nucleophile approaches behind the C-Cl</u> <u>bond, which results in an inversion of configuration</u>, instead of the same configuration.

Every 2 [✓] = [1]

- (iii) HPO₄²⁻ is obtained as a side product of step 3.
 Suggest the type of reaction for step 3. [1]
 [1] Hydrolysis
- (iv) State the reagent and condition needed to convert F to HisH⁺ in step 4. [1]
 [1] Acidified K₂Cr₂O₇ or KMnO₄, heat
- (v) The pK_a values for the fully protonated form of histidine, HisH⁺, are shown below.



After step 4, $HisH^+$ is extracted, purified and transferred into a buffer solution at pH 7.55 for storage.

Draw the structure of the predominant species of histidine at this pH. [1]

[1]

(d) The kinetics of the reaction of step 1 was studied using different concentration of **C** with the enzyme dehydratase and the following graph is obtained.



(i) Explain fully the shape of the graph with respect to the order of reaction at low, moderate and high concentration of **C**. [3]

At low [C], [\checkmark] rate of reaction is directly proportional to [C] since active sites are not fully occupied \rightarrow [\checkmark] 1st order reaction

As [C] increases, [\checkmark] the rate increases to a lesser extent and is no longer proportional to [substrate] since more active sites are occupied \rightarrow [\checkmark] mixed order reaction / between 1st and 0th order

At high [C], [\checkmark] rate becomes constant as active sites of enzyme are fully occupied / saturated \rightarrow [\checkmark] 0th order reaction

Every 2 [✓] = [1]

The Michaelis-Menten equation is used to analyse the kinetics of an enzyme-catalysed reaction. At low concentration of C, the equation simplifies to:

Rate =
$$\frac{V_{max}}{K_{M}} \times [C]$$

where K_{M} is the Michaelis constant.

Under certain conditions, the K_M is 2.60 × 10⁻⁵ mol dm⁻³ and V_{max} is 10.4 mol dm⁻³ s⁻¹ for step 1.

(ii) Using your answer in (d)(i) at low concentration of **C**, determine a value for the rate constant, *k* and hence the value of the half-life for step 1. [2]

At low conc of **C**, rate equation follows 1st order kinetics, where

Rate = $\frac{V_{max}}{K_M}$ × [**C**] Since Rate = k [**C**], hence k = $\frac{V_{max}}{K_M}$ = 10.4 / 2.60×10⁻⁵ = 4×10⁵ s⁻¹ [1] Hence half-life = ln 2 / 4×10⁵ = 1.73×10⁻⁶ s [1] bod units

[Total: 18]

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3

Section B

Answer **one** question from this section.

4 Chalcopyrite, CuFeS₂ and similar sulfide ores are the most common ores of copper. The ores typically contain low percentages of copper and have to be concentrated before refining.

In the extraction of copper, the mineral is smelted by heating with air. The equation for this reaction is as follows.

 $8CuFeS_2 + 21O_2 \rightarrow 8Cu + 4FeO + 2Fe_2O_3 + 16SO_2$

(a) A sample of rock contains 1.30 % by mass of chalcopyrite. Assuming this is the only source of copper in the rock, calculate the percentage by mass of copper in the sample. [1]

*M*r CuFeS₂ = 183.5 % Cu = 1.3/100 × 63.5/183.5 × 100 = 0.450 % [1]

(b) The copper obtained during the smelting process may contain impurities such as zinc and silver. It is then refined using electrolysis.

Draw a well-labelled set-up for the electrolysis process and explain, using relevant data from the *Data Booklet*, how each of the two impurity metals is removed from the copper. [4]



At the anode:

[✓] <u>Zn is oxidised</u>. Copper is then oxidized and both <u>zinc and copper dissolves into the</u> <u>electrolyte</u>, because

 $[\checkmark] E^{e}(Zn^{2+}/Zn)$ is more negative than $E^{e}(Cu^{2+}/Cu)$.

 $[\checkmark]$ Ag is not oxidised and collected below the anode / as 'anode mud'/ anode sludge, because

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[\checkmark] <u>E^e(Ag⁺/Ag)</u> is more positive than E^e(Cu²⁺/Cu).

At the cathode:

[\checkmark] <u>Zn²⁺ ions produced from the anode remain in the electrolyte</u> since E^{θ}(Zn²⁺/Zn) is more negative than E^{θ}(Cu²⁺/Cu), and have a lower tendency to be reduced than Cu²⁺ ions at the cathode.

[\checkmark] <u>Cu²⁺ ions would be reduced to Cu(s)</u> and coats the cathode as the E^{θ}(Cu²⁺/Cu) is more positive and have a higher tendency to be reduced.

3[√]: [1]

(i)

(ii)

Copper is a transition element and it can form many complexes.

(c) The reaction scheme shows some reactions of copper and its compounds.



[1]

(d) Copper can form complexes with the ligands ammonia and ethane-1,2-diamine (en), H₂NCH₂CH₂NH₂, as shown below.

equilibrium 1

 \implies $\Sigma u(H_2O)_4(en)]^{2+}(aq) + 2H_2O(I)$ $K_{stab} = 3.98 \times 10^{10}$ $[Cu(H_2O)_6]^{2+}(aq) + en(aq)$ equilibrium 2 $\underset{\leftarrow}{\longrightarrow} u(H_2O)_4(NH_3)_2]^{2+}(aq) + 2H_2O(I) \ K_{stab} = 5.01 \times 10^7$ $[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq)$

> (i) Write an expression for the equilibrium constant, K_{stab} , for equilibrium 2. State its units. [1]

> > $K_{\text{stab}} = \frac{[(Cu(H_2O)_4(NH_3)_2)^{2^+}]}{[(Cu(H_2O)_6)^{2^+}][NH_3]^2} \text{ mol}^{-2} \text{ dm}^6 [1]$

- The standard entropy change, ΔS^{e} , for equilibrium 1 is + 23 J K⁻¹ mol⁻¹ and for (ii) equilibrium 2 is - 8.4 J K⁻¹ mol⁻¹. Suggest an explanation for this difference by reference to both equilibria. [2]
 - [1] Equilibrium 1 has more amount of products than reactants
 - [1] more ways to distribute the particles resulting in greater disorder so ΔS° is positive.
- (iii)

Of the three copper complexes in equilibria 1 and 2, state the formula of the copper complex that is the most stable and explain your choice. [1] [\checkmark] [Cu(H₂O)₄(en)]²⁺ is more stable. [\checkmark] Equilibrium 1 has a higher K_{stab}. Position of equilibrium 1 is more to the right forming a higher concentration of [Cu(H₂O)₄(en)]²⁺. OR

 \checkmark <u>AS°</u> for Equilibrium 1 is more positive, there is greater disorder and system will tend to favour a reaction that leads to greater disorder.

 $2[\checkmark] = [1]$

- (e) Transition element complexes can exhibit stereoisomerism.
 - Name the type of isomerism exhibited by $[Cu(H_2O)_4(NH_3)_2]^{2+}$ and draw the three-(i) dimensional diagrams of the two isomers. [2]

[1] Cis-trans isomerism



[1] accept dotted plane diagram

8

18 DO NOT WRITE IN THIS MARGIN

The diagram below shows the complexes present in human and spider blood.



(ii) Explain, in terms of d-orbital splitting, why the colour of spider blood is blue while human blood is red. [2]

 \checkmark <u>Different metal ion</u> and \checkmark <u>different ligands</u> lead to

[✓] <u>different △E splitting / different d-orbital splitting / larger d-orbital splitting for</u> haemoglobin / smaller d-orbital splitting for oxyhaemocyanin

[✓] <u>Green colour is absorbed for human blood</u>. Hence complementary colour red is observed. <u>Orange colour is absorbed for spider blood</u>. Hence complementary colour blue is observed.

2[√]: [1]

(f) An important compound of copper is copper(I) iodide which is used to prepare the Gilman reagent.

2R'Li + CuI → R'₂CuLi + LiI Gilman reagent This reagent undergoes S_N2 reaction with primary halogenoalkanes to form the intermediate in Step 1. This synthetic method can be used to prepare unsymmetrical alkanes as shown below.



Use of the Data booklet is relevant to this question

- (a) Nickel is a transition element with a variety of uses.
 - (i) Explain what is meant by the term *transition element*. [1]

[1] Transition element is a <u>d-block element that forms one or more stable ions</u> ⁺ in which the <u>d subshell is partially filled</u>.

(ii) Explain why the first ionisation energies of first row transition elements are relatively invariant. [2]

M: [Ar] 3dⁿ 4s²

1st IE from involves the removal of the outermost 4s electrons.

[✓] Across the period, <u>nuclear charge increases</u>

[✓] <u>Screening effect increases as electrons are added to the [√] penultimate 3d</u> <u>subshell</u>, providing a shield between the nucleus and the outer 4s electrons.

[✓] Increase in nuclear charge is only slightly more significant than the increase in screening effect.

Thus, 1st IE remains <u>relatively invariant</u>, as only a small increase in 1^{st} IE is observed. $2[\checkmark] = [1]$

(iii) Suggest why the melting point of nickel is significantly higher than the melting point of calcium. [2]

[✓] Ni contributes both 3d and 4s electrons to the sea of delocalised electrons whereas [✓] Ca only has two 4s electron delocalised.

Thus, $[\checkmark]$ Ni has stronger metallic bonds which require more energy to overcome. $[\checkmark]$

2[√] = [1]

(b) Nickel-Metal hydride (Ni-MH) battery is a rechargeable battery that has a cathode made up of NiO(OH) and an anode made up of hydrogen absorbed within a metal alloy represented as MH.

When the battery discharges, solid metal alloy, M, is formed at the anode and solid nickel (II) hydroxide, $Ni(OH)_2$ is formed at the cathode. The electrolyte is potassium hydroxide. The standard reduction potential of MH/M is -0.83V.

(i) Construct an equation, including state symbols, for the reactions at the cathode and anode. [2]

```
[1] Cathode: NiO(OH)(s) + H<sub>2</sub>O(I) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)
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[1] Anode: MH(s) + OH⁻(aq) \rightarrow M(s) + H₂O(l) + e⁻

(ii) The cell is capable of producing an e.m.f of 1.32 V.

Suggest a value for the standard reduction potential of NiO(OH)/Ni(OH)₂.

 $E^{\circ}_{cell} = E^{\circ}_{red} - E^{\circ}_{oxid}$ 1.32V = $E^{\circ}_{red} - (-0.83)$ [1] $E^{\circ}_{red} = + 0.49V$

- (c) Nickel can form complexes.
 - (i) Suggest a reason for the difference between the following redox potentials. [1]

Ni²⁺ + 2e \rightleftharpoons Ni $E^{\circ} = -0.25$ V [Ni(NH₃)₆]²⁺ + 2e \rightleftharpoons Ni + 6NH₃ $E^{\circ} = -0.51$ V

[1] <u>NH₃ stabilizes Ni(II)</u> making [Ni(NH₃)₆]²⁺ less easily reduced. The E^{Θ} value of Ni(NH₃)₆]²⁺ is thus more negative/less positive.

Nickel forms many complexes in which the central atom is surrounded by four ligands. The complex **X**, $[Ni(R_3P)_2I_2]$, exists as two isomers, one of which has a net dipole moment. The complex **Y**, $[Ni(R_3P)_2Cl_2]$, has only one structure.

 $[R_3P$ is a monodentate ligand where R is CH₃]

(ii) Draw the structure of Y and the two isomers of X. Label your diagrams clearly. [2]

[1]



 R_3P

Y:

'Ni

(d) Nickel is a useful catalyst for many organic reactions. Hydrocyanation synthesizes alkyl nitriles from alkenes using nickel phosphite complexes as catalyst.



(i) Draw the structures of A, B and C and describe the reagent and conditions needed for steps I, II and III. [6]

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[1] each for compounds A, B and C.[1] each for reagent and conditions for step I, II and III

(ii) The equation below shows the combustion of butenone.

$$a \operatorname{CH}_3\operatorname{COCHCH}_2 + b \operatorname{O}_2 \rightarrow c \operatorname{CO}_2 + d \operatorname{H}_2\operatorname{O}_2$$

Suggest values for the coefficients *a*, *b*, *c* and *d*.

[1] a = 1, b = 5, c = 4, d = 3

(iii) Use appropriate data from the *Data Booklet* to calculate the enthalpy change of combustion of butenone. [2]



Butenone (C_4H_6O)

Enthalpy change of combustion

= Energy taken in for bond breaking - Energy given out for bond forming [1] = 6(C - H) + 2(C - C) + 1(C = C) + 1(C = O) + 5(O = O) - 8(C = O) - 6(O - H)= $6(410) + 2(350) + 1(610) + 1(740) + 5(496) - \frac{8(805)}{-6(460)} - 6(460)$ [1] = $-2210 \text{ kJ mol}^{-1}$

ECF was awarded based on the stoichiometry in part (ii)

[Total: 20]