CJC CJC
RIALE ST CE

Catholic Junior College JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME		
CLASS	2Т	

CHEMISTRY

Paper 3 Free Response

13 September 2022 2 hours

9729/03

Candidates answer on the Question Paper. Additional Materials: Data Booklet

MARK SCHEME & EXAMINER'S COMMENTS

This document consists of 28 printed pages

Section A

Answer **all** the questions in this section.

- 1 Chromium is a hard, steel-grey metal with a lustrous appearance. It is valued for its high corrosion resistance and hardness and is commonly used to manufacture alloys such as steel. Chromium plating is sometimes used to give a polished mirror finish to steel. Chromium compounds are also often used as pigments, known as chrome yellow.
 - (a) The following sequence of reactions involving chromium illustrates many of the characteristics properties of transition metals.



(i) Solutions of transition metals are frequently coloured. With reference to $[Cr(H_2O)_6]^{2+}$, explain fully why it forms a blue solution. [2]

In the presence of H₂O ligands, the partially filled degenerate d-orbitals

of Cr²⁺ ion are split into 2 groups of non-degenerate d orbitals with a

small energy gap. In the presence of visible light, d electron in a d

orbital of lower energy <u>absorbs orange light</u> and <u>is promoted to the</u>

higher energy d* orbital (d-d* electronic transition).

.....

The complementary colour (blue) which is not absorbed appears as the

<u>colour of [Cr(H₂O)₆]²⁺ observed</u>.

EXAMINER'S COMMENTS

Most students were only able to get the second mark for stating the correct colour absorbed.

Common mistakes made are as follows:

- Missing keywords, eg 'partially filled' in the answer note that if the d orbitals are empty (eg Sc³⁺ ion) or fully filled (eg Cu⁺ ion), there is no d-d* electronic transition (no colour observed) even if splitting of the d orbitals takes place.
- Stating that the a *d* orbital of lower energy state is promoted instead of a *d* electron in the orbital of lower energy.

(ii) Suggest the identity of the grey-green precipitate formed in the reaction between $[Cr(H_2O)_6]^{3+}$ and aqueous sodium hydroxide. With the aid of an equation, explain fully how it is formed. [2]

The grey-green precipitate is <u>Cr(OH)₃</u> .
$[Cr(H_2O)_6]^{3+} + 3OH^- \rightarrow Cr(OH)_3 + 6 H_2O$
When OH^- ions are added to $[Cr(H_2O)_6]^{3+}$ solution, an
precipitation/acid-base reaction occurs to form Cr(OH) ₃ .
OR
The grey-green precipitate is <u>Cr(OH)₃(H₂O)</u> ₃ .

 $[Cr(H_2O)_6]^{3+} + 3OH^- \rightarrow Cr(OH)_3(H_2O)_3 + 3 H_2O$

When OH^- ions are added to $[Cr(H_2O)_6]^{3+}$ solution, a <u>ligand</u> <u>displacement reaction</u> occurs to form $Cr(OH)_3(H_2O)_3$.

EXAMINER'S COMMENTS

Most students were able to state the correct identity of the precipitate.

Common mistakes made in the second mark are either giving an unbalanced equation or stating Na as the final product (which is not possible), for example: $[Cr(H_2O)_6]^{3+} + 3NaOH \rightarrow Cr(OH)_3 + 3Na + 6H_2O$

1 (a) (iii) Chromium(III) ions can also react with iminodiacetate ions (tridentate ligand) to form a chelating complex ion. Draw the structure of the complex ion, showing the shape clearly.

[1]



 Legend can also be accepted to represent ligand used.



(iv) Identify the species present in the yellow and orange solutions.
 Hence write an equation to show the formation of the species in the orange solution from that in the yellow solution.

Species present in yellow solution: <u>CrO4</u>²

Species present in orange solution: $\underline{Cr_2O_7}^{2-}$

 $2 \text{ CrO}_4^{2-} + 2 \text{ H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$

EXAMINER'S COMMENTS

This question was very badly done. Many students just guessed and gave random identities of the two solutions, which shows they do not understand the chromium-containing species responsible for the two colours. (b) Draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential of the Cr³⁺(aq)/Cr(s) half-cell, indicating the direction of electron flow. [3]



Students were unable to identify cathode and the anode, and thus drew the wrong direction of electron flow. In addition, there were many missing details in the answers i.e. stating of standard conditions, labelling the electrodes wrongly. Some students even drew an electrolytic cell diagram and showed poor understanding of how standard electrode potentials are obtained.

(c) Chromium is electrolytically deposited on the cathode from a solution containing Cr³⁺(aq) using inert electrodes.

Calculate the volume of oxygen, at room temperature and pressure, produced at the anode when 1.00 kg of chromium is deposited on the cathode. [2]

 $\begin{array}{ll} [O]: \ \ H_2O(l) \to 2H^+(aq) + \frac{1}{2} \ O_2(g) + 2e^{-.} \ (x3) \\ [R]: \ \ \ Cr^{3+}(aq) + 3e^{-} \to Cr(s) \ \ (x2) \\ \\ Overall equation: \ 3H_2O + 2Cr^{3+} \to 6H^+ + \frac{3}{2} \ O_2 + 2Cr \\ \\ Amount of chromium in \ 1.00 \ kg = \frac{1000}{52.0} = 19.2 \ mol \\ \\ Amount of \ O_2 \ produced = \frac{19.2}{2} \ \times \frac{3}{2} \\ = 14.4 \ mol \\ \\ Volume \ of \ O_2 \ produced = 14.4 \ x \ 24 \\ = 346 \ dm^3 \ (to \ 3 \ s.f.) \end{array}$

EXAMINER'S COMMENTS

Most students were able obtain the correct overall equation and find the volume of O_2 produced. Common mistakes included forgetting to convert kg into g when finding number of moles of Cr, using the ideal gas equation to solve this question.

5

- (d) Chrome yellow containing Na₂CrO₄, has been used for a long time as a yellow pigment in oil paintings.
 - (i) Use the standard redox potentials below to explain why the yellow colour changes when the painting is exposed to an atmosphere containing sulfur dioxide.

$$SO_4^{2-} + 4H^+ + 2e^- \Longrightarrow 2H_2O + SO_2 \qquad E^{\circ} = +0.17 \vee CrO_4^{2-} + 8H^+ + 3e^- \Longrightarrow Cr^{3+} + 4H_2O \qquad E^{\circ} = +1.33 \vee [2]$$

$$E_{cell}^{\circ} = E_{red}^{\circ} - E_{oxid}^{\circ} = +1.33 - (+0.17) = +1.16 \vee E_{cell}^{\circ} > 0 \text{ (reaction is energetically favourable) and hence yellow colour changes}$$

EXAMINER'S COMMENTS

Most students did not find the overall E_{cell}° to determine if the reaction is feasible. Common mistakes included explaining how the presence of SO₂ changes the position of the equilibrium according to LCP.

1 (d) (ii) Suggest why this colour change takes a long time.

[1]

 E_{cell}° tells us whether a reaction is spontaneous (thermodynamically feasible) but does not predict the rate of a chemical reaction. (kinetically feasible); Reaction has a high activation energy; low concentrations of SO₂ in atmosphere

[Total: 15]

EXAMINER'S COMMENTS

This question was poorly done. A variety of answers were given, but students failed to note that the presence of SO₂ in the atmosphere is actually very low, thus this reaction does not take place under standard conditions. In addition, reactions which are energetically feasible, i.e. $E_{cell}^{\circ} > 0$ does not mean it may proceed, as the activation energy of the reaction may be very high.

2 (a) Tartaric acid is a white crystalline diprotic organic acid. It can be synthesised from ethene in four steps.





Draw the structures of the intermediates, **A**, **B** and **C**, and give the required reagents and conditions for each step of the conversion. [7]



Step 1: cold, NaOH(aq), KMnO₄

Step 2. K₂Cr₂O₇ in dilute H₂SO₄, heat with (immediate) distillation

HCN(aq), trace amount of NaCN(aq)/NaOH(aq), cold Step 3:

dilute H₂SO₄, heat

Step 4:....

EXAMINERS' COMMENTS

With the molecular formula of compound B provided, it is pleasing to see that most students can deduce this. However, a fair number used $KMnO_4$ in Step 2 which is not accepted as it will oxidise the resultant molecule, ethanedioic acid to carbon dioxide. In addition, it is important to state the acidifying agent (H₂SO₄) or alkaline agent (NaOH) to remove ambiguity as other agents such as hydrochloric acid would result in the latter being oxidised to chlorine gas.

2 (b) Salts of tartaric acid are known as tartrates or hydrogen tartrates. One of these salts, potassium hydrogen tartrate, KC₄H₅O₆, is a weak monobasic acid and is sparingly soluble in water.

An experiment was conducted to determine the K_{sp} of the salt, KC₄H₅O₆. 1.00 g of the salt, KC₄H₅O₆ was dissolved in a beaker containing 100 cm³ of water and was stirred constantly for 15 minutes at constant temperature until a saturated solution was produced.

20.0 cm³ of the filtered solution was titrated against 0.035 mol dm⁻³ NaOH, using phenolphthalein as an indicator. The volume of NaOH needed for the indicator to change colour is 12.50 cm³.

(i) Calculate the initial concentration of potassium hydrogen tartrate used in the titration. [1]

Amt. of KC₄H₅O₆ = 0.035 x $\frac{12.50}{1000}$ = 4.375 x 10⁻⁴ mol

 $[KC_4H_5O_6] = 4.375 \times 10^{-4} \div \frac{20.0}{1000} = 0.0219 \text{ mol dm}^{-3} (3 \text{ sf})$

(ii) Hence, calculate the K_{sp} value of potassium hydrogen tartrate. [1]

 $K_{\rm sp} = [K^+][C_4H_5O_6^-] = (0.0219)^2 = 4.79 \times 10^{-4} \, \text{mol}^2 \, \text{dm}^{-6}$

EXAMINER'S COMMENTS

Poorly answered question. It is worrying that most students that obtained an incorrect answer is due to the assumption that all the 1.00 g of potassium salt dissolved in water when is clearly stated it is sparingly soluble in the first paragraph. Hence, back titration with NaOH was required.

(c) The van 't Hoff equation relates equilibrium constants to enthalpy (ΔH) and entropy changes (ΔS) as follows:

$$\ln K_{\rm sp} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where R is the molar gas constant and T is measured is in Kelvin. The titration in **(b)** was repeated at different temperatures and the following results were obtained.



2

(c) (i) Using the information provided, calculate ΔH and ΔS for the dissolution of potassium hydrogen tartrate in water. [2]

Gradient value = $\frac{\Delta H}{R} = |\frac{12+10}{0.0038-0}|$ = 5789

 $\Delta H = 5789 \text{ x } 8.31 = +48110 \text{ J mol}^{-1}$ = +48.1 kJ mol⁻¹

y-intercept value = $\frac{\Delta S}{R}$ = 12

 $\Delta S = 12 \times 8.31 = +99.7 \text{ J K}^{-1} \text{ mol}^{-1}$

(ii) Hence, predict the temperature at which potassium hydrogen tartrate becomes soluble in water. [1]

 $\Delta G = \Delta H - T \Delta S = 0$

 $T = \Delta H / \Delta S = 48110 / 99.7 = 483 K$

EXAMINER'S COMMENTS

This question demonstrates the poor mathematical interpretation of the expression provided. To solve both thermodynamic constants, some students were busy solving simultaneous questions when a simple conversion using linear law was sufficient to obtain it.

(d) At 800 K, nitrogen monoxide reacts with hydrogen as shown below in an enclosed gas tank.

 $2H_2(g) + 2NO(g) \longrightarrow 2H_2O(g) + N_2(g)$ rate = $k(P_{H_2})(P_{NO})^2$

[1]

On the same axes, sketch suitable graphs on the same axes below to illustrate clearly how the rate of reaction would vary when partial pressures of

(i) H₂

(ii) and NO

is increased respectively.



EXAMINER'S COMMENTS

This question is poorly attempted due to overthinking on the students' part. Some left the axis blank while others were drawing equilibrium graphs of concentration against time. It is important that candidates realise what is asked in the question before presenting their answers.

- **2** (e) Nitrogen dioxide, NO₂, is an air pollutant produced from volcanic eruptions and combustion of fossil fuels in automobile engines.
 - (i) Draw the dot-and-cross diagram for nitrogen dioxide, NO₂, molecule stating its shape and bond angle.
 [2]

Species	Dot-and-cross diagram	Shape and bond angle
NO ₂	$\overset{x}{\overset{x}}\overset{x}{\overset{x}}\overset{o}{\overset{o}}\overset{o}{\overset{N}}\overset{v}{\overset{v}}\overset{v}{\overset{v}}\overset{v}{\overset{o}}\overset{v}{\overset{v}}{\overset{v}}\overset{v}{\overset{v}}\overset{v}{\overset{v}}\overset{v}{\overset{v}}\overset{v}{\overset{v}}{\overset{v}}\overset{v}{\overset{v}}\overset{v}{\overset{v}}\overset{v}{\overset{v}}\overset{v}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}{\overset{v}}\overset{v}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}{\overset{v}}{\overset{v}}\overset{v}{\overset{v}}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}{\overset{v}}\overset{v}{\overset{v}}\overset{v}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}{\overset{v}}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}{\overset{v}}\overset{v}{\overset{v}}\overset{v}}\overset{v}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}{\overset{v}}{\overset{v}}\overset{v}{\overset{v}}\overset{v}}\overset{v}{\overset{v}}\overset{v}{\overset{v}}}\overset{v}{\overset{v}}\overset{v}}{\overset{v}}\overset{v}{\overset{v}}v$	Shape:bent Bond angle: x>120° range of values (121 ° –

EXAMINER'S COMMENTS

Most candidates were able to draw a structure of NO₂, albeit the central nitrogen atoms has 9 electrons around it. It is important for candidates to check upon drawing, especially for Period 2 elements, that it does not exceed 8 electrons which on this occasion requires the formation of a dative covalent bond from N to O.

(ii) A 1.00 dm³ gas cylinder is used to store 35.0 g of NO₂ at 25° C. The gas cylinder is fitted with a safety valve that will rupture when there is a great difference between the internal pressure and the atmospheric pressure. The gas cylinder fitted with a burst disc can withstand a pressure difference of 2500 kPa.

Calculate the pressure exerted by NO_2 at 25° C in kPa. [1]

$$PV = \frac{m}{M_r}RT$$
$$P = \frac{nRT}{V}$$

$$=\frac{\frac{35.0}{46.0}\times8.31\times298}{1.00\times10^{-3}}$$

= 1 884 kPa

(iii) Assuming the atmospheric pressure is 101 kPa, calculate the maximum internal pressure of the gas cylinder. [1]

Maximum pressure difference = Internal pressure – Atmospheric pressure

2500 = Internal pressure – 101

Internal pressure = 2500 + 101

2 (e) (iv) Hence, determine the maximum temperature that this gas cylinder can be exposed to before the burst disc ruptures. [1]

PV = nRT
T =
$$\frac{PV}{nR}$$

= $\frac{2601 \times 10^3 \times 1.00 \times 10^{-3}}{8.31 \times \frac{35.0}{46.0}}$
= 411 K

- (f) A gas tank contains a mixture of NO₂ and monoatomic gas **A** in the ratio of 4:1. At 300 K, the total pressure of the gas mixture is 100 kPa.
 - Given that the density of the gas mixture is 1638 g m⁻³, calculate the average relative molecular mass of the mixture to 1 decimal place. [1]

 $M_r = \frac{\rho RT}{P} = \frac{1638 \times 8.31 \times 300}{100\ 000} = 40.8$

(ii) Hence, calculate the A_r of monoatomic gas **A** and suggest its identity. [2]

Given that the mixture of NO_2 and monoatomic gas A is in the ratio of 4:1,

 $(0.8 \times 46.0) + (0.2 \times A_r \text{ of monoatomic gas A}) = 40.8$

 $A_{\rm r}$ of A = <u>20.0</u>

A is <u>neon</u>

EXAMINER'S COMMENTS

Other than the handful of careless mistakes involving the conversion of units, most students are able to solve these questions pretty well.

[Total: 21]

- 3 This question is about nitrogen containing compounds.
 - (a) Nitrogen monoxide reacts with chlorine to form nitrosyl chloride, according to the equation:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

In an experiment, student **A** kept the amount of $Cl_2(g)$ in large excess while the initial partial pressure of NO(g) was varied at constant temperature of 550 K.

time / s	P _{NO} / atm	(Rate / P _{NO}) / s ⁻¹	(Rate / (P _{NO}) ²) / (atm ⁻¹ s ⁻¹)
0	0.917	1.033 × 10 ⁻⁴	1.126 × 10 ⁻⁴
1000	0.827	9.312 × 10⁻⁵	1.126 × 10⁻⁴
2000	0.753	8.486 × 10⁻⁵	1.127 × 10⁻⁴
3000	0.691	7.788 × 10⁻⁵	1.127 × 10⁻⁴
4000	0.638	7.190 × 10⁻⁵	1.127 × 10⁻⁴

The table below shows the experimental results obtained.

(i) Suggest why the amount of $Cl_2(g)$ was kept in large excess.

[1]

Since the amount of $Cl_2(g)$ was kept in *large excess*, <u>the partial</u> <u>pressure of $Cl_2(g)$ remains relatively constant</u> so that <u>any change in rate</u> is due to the changes in the partial pressure of NO(g) only.

.....

EXAMINER'S COMMENTS

This question requires students to see the reason behind keeping the amount of $Cl_2(g)$ in large excess and hence link to how it affect the determination of the rate of reaction. Many students were not able to be awarded full credit.

(ii) Define the term order of reaction.[1]The order of reaction with respect to a reactant is defined as the power

to which the <u>concentration of a reactant</u> is raised to in the

experimentally - determined rate equation.

.....

EXAMINER'S COMMENTS

This is a recall question that was not well attempted. Students were not able to give all the keywords required.

(iii) Using the data from the table above, deduce the order of reaction with respect to NO(g). [1]

Since Rate = $k(P_{NO})^2$

<u>Rate/(P_{NO})² = k is constant throughout the reaction</u> (and thus rate of reaction is directly proportional to (P_{NO})²), the reaction is <u>second order with respect to NO</u>.

<u>EXAMINER'S COMMENTS</u> This question required students to see that Rate/ $(P_{NO})^2 = k$ is constant throughout the reaction and hence determine the order of reaction. Students were not able to get full credit.

3 (a) (iv) In another experiment, the initial partial pressure of NO(g) was 4.2 atm and it was reacted with $Cl_2(g)$ at a constant temperature of 550 K. The partial pressure of $Cl_2(g)$ was recorded at time intervals of 30 seconds.

time / s	partial pressure of Cl ₂ (g)/ atm
0	0.78
30	0.76
60	0.72
90	0.70
120	0.66
150	0.63
180	0.59
210	0.57
240	0.54
270	0.52

The data obtained are tabulated below.

time / s	partial pressure of Cl ₂ (g)/ atm
300	0.49
330	0.46
360	0.44
390	0.42
420	0.39
450	0.38
480	0.36
510	0.34
540	0.33
570	0.32

Using the data but without plotting of any graph, deduce the order of reaction with respect to $Cl_2(g)$. [1]

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1<sup>st</sup> t<sub>1/2</sub>
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- = time taken for $P_{C/2}$ to decrease from 0.78 atm to 0.39 atm
- = 420 s

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2<sup>nd</sup> t<sub>1/2</sub>
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= time taken for $P_{C/2}$ to decrease from 0.76 atm to 0.38 atm (or $0.66 \rightarrow 0.33$) = 480 - 60

= 420 s

Since $t_{1/2}$ is constant at 420s, the reaction is first order with respect to Cl_2 .

EXAMINER'S COMMENTS This question required students find the half life which was not well attempted.

(v) Write the rate equation for the overall reaction. Hence, calculate the rate constant, stating its units.
 [3]

Rate = k (P_{NO})²(P_{Cl2}) Rate = k' (P_{Cl2}) where k' = k (P_{NO})² $t_{1/2} = 420 \text{ s} = \frac{\ln 2}{k(P_{NO})^2} = \frac{\ln 2}{k(4.2)^2}$ k = 9.36 × 10⁻⁵ atm⁻² s⁻¹

EXAMINER'S COMMENTS

This question required students to determine the rate equation from the above parts. And hence calculate with the units stated. Common mistakes includes leaving the rate equation in terms of concentration instead of partial pressures and some thought that the rate is s^{-1} but it should be atm s^{-1}

3 (b) In another reaction, $2NO_2(g) + 4CO(g) \longrightarrow N_2(g) + 4CO_2(g)$, it was found that the rate equation is rate = $k[NO_2]^2$.

A proposed mechanism for this reaction is shown.

Step 1	$NO_2(g) + NO_2(g) \longrightarrow 2NO(g) + O_2(g)$	slow
Step 2	$2NO(g) + O_2(g) + 4CO(g) \longrightarrow N_2(g) + 4CO_2(g)$	fast

Explain whether it is consistent with the established rate equation. [1]

The .mechanism . is .consistent .with .the .established .rate .equation. .<u>One</u> molecule of NO₂ reacts with one molecule of NO₂ in the slow rate determining step whereas rate equation shows 2 moles of NO₂ reacting in the slow rate determining step.

EXAMINER'S COMMENTS

This question required students to state the correlation of the number of reactants in the slow step with the rate equation. This question is fairly well attempted.

- (c) Tryptophan metabolism plays an important role in the mechanisms associated with the gut-brain axis. At least 90% of human intake of tryptophan is converted to kynurenine for further metabolism via a catalyst.
 - (i) Explain how the activation energy of a reaction is affected by the presence of a catalyst, and with an appropriate sketch of a Maxwell–Boltzmann distribution curve, explain how a catalyst increases the rate of reaction. [3]



The catalyst lowers the activation energy of the reaction by providing an <u>alternative pathway</u> for the reaction to occur.

With a lower activation energy, according to the Maxwell-Boltzmann distribution, there will be a higher proportion of reactants with energy greater or equal to this lower activation energy, *E*_a'. Thus, there is higher frequency of effective collisions between reactants since they possess sufficient energy for reaction. Therefore, the rate of reaction increases.

EXAMINER'S COMMENTS

This is recall question on the Maxwell-Boltzmann distribution curve. However, this was not well attempted with many keywords or marking points missed hence not given full credit.

Common mistakes includes the wrong Maxwell-Boltzmann curve, the lack of keywords like "frequency of effective collisions".

3 (c) (ii) Kynurenine has the molecular formula C₁₀H₁₂N₂O₃. When dissolved, an aqueous solution of kynurenine is almost neutral and maintains its pH upon addition of small amounts of aqueous sodium hydroxide or hydrochloric acid. Addition of this solution to aqueous 2,4-dinitrophenylhydrazine causes an orange precipitate to form.

Kynurenine reacts with NaBH₄ to form compound L, $C_{10}H_{14}N_2O_3$. Heating L with concentrated H_2SO_4 produces only M, $C_{10}H_{12}N_2O_2$. Heating M with acidified KMnO₄ under reflux results in the formation of compound N, $C_3H_5NO_4$ and anthranilic acid.

The molecular structure of anthranilic acid is as shown below.



anthranilic acid

Reaction of **N** with LiAlH₄ in dry ether produces compound **O**, C₃H₉NO₂. A solution of **O** turns litmus paper blue.

Suggest possible structures for L, M, N, O and kynurenine. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. [13]

INFORMATION	DEDUCTION
Kynurenine has the molecular formula	C:H is approximately 1:1. It contains a
$C_{10}H_{12}N_2O_3$	benzene ring
When dissolved, an aqueous solution of kynurenine is almost neutral	
Kynurenine maintained its pH upon addition of small amounts of aqueous sodium hydroxide or hydrochloric acid	It functions as a <u>buffer</u> .
Addition of the kynurenine to aqueous	Presence of carbonyl group
2,4-DNPH caused an orange precipitate to	Condensation reaction.
form.	
Kynurenine reacts with NaBH ₄ to form compound L, C ₁₀ H ₁₄ N ₂ O ₃	Reduction of ketone group in kynurenine.
Heating L with concentrated H ₂ SO ₄	Elimination of H and OH groups from L to
produces only \mathbf{M} , $C_{10}H_{12}N_2O_2$.	form alkene in M . Indicate the presence of –OH group on L .
Heating M with acidified KMnO ₄ under reflux	Oxidative cleavage of C=C bond occurred
results in the formation of compound N,	as 2 molecules were obtained
C ₃ H ₅ NO ₄ and anthranilic acid	
Reaction of N with LiA/H ₄ in dry ether	Reduction of carboxylic acid group in N.
produces compound O , C ₃ H ₉ NO ₂ . A solution	
of O turns litmus blue.	



[Total: 24]

EXAMINER'S COMMENTS

This is an elucidation question that requires students to use the information to explain the type of reaction and functional group present. And hence deduce the structures.

Many students were only able to achieve partial credits.

Some of the common mistakes includes:

- deduction of amide groups in kynurenine,

- identification of type of reaction when L is reacted with concentrated $H_2SO_4\,as$ hydrolysis

Section B

Answer one question from this section.

- 4 An anaesthetic is a drug used to induce a temporary loss of sensation or awareness. They may be classified as general anaesthetics that result in a reversible loss of consciousness, or local anaesthetics which cause a reversible loss of sensation for a limited region of the body without necessarily affecting consciousness.
 - (a) Procaine, one of the first injectable local anaesthetic used during surgery has the following structure:



Procaine

(i) State the oxidation state of C_1 in Procaine. [1]

0

EXAMINER'S COMMENTS This question was badly done. Many different values were given.

(ii) Procaine can be made by the following reaction scheme:



State the reagents and conditions used for steps 1, 2, 3 and 4. Draw the structure of intermediate X. [5]

Step 1: anhydrous PCI₅ / SOCI₂, r.t.p. OR anhydrous PCI₃, heat

 Step 2:
 HOCH2CH2CI, r.t.p.

 Step 3:
 1) Sn, conc. HCI, heat under reflux; 2) NaOH(aq)

 Step 4:
 NH(CH2CH3)2, heat under reflux

NOTE: Step 3 and 4 are interchangeable

Structure of intermediate X:



EXAMINER'S COMMENTS This question was badly done.

Common mistakes made are as follows:

- Step 1: stating Cl_2 with anhydrous $FeCl_3$ (this is used for electrophilic substitution of Cl^+ onto the benzene ring) or Cl_2 with uv light (this is for free radical substitution of an alkane/alkyl group which is not present in the starting compound).
- Step 2: stating HOCH₂CH₂Cl with conc H₂SO₄ and heat, which will lead to the dehydration of the alcohol (to form an alkene). Note that acyl chloride will react readily with an alcohol to form an ester, no catalyst is needed.
- Step 3: using *LiAlH*₄ and dry ether to reduce nitrobenzene to phenylamine which is not possible as an azo compound is formed instead (refer to Nitrogen Compounds lecture notes Pg 17-11).
- Step 4: giving *conc NH*₃ as the reactant will not lead to the structure of Procaine.
- 4 (a) (iii) One molecule of Procaine contains two nitrogen atoms, both of which can act as a base by accepting a proton. On the diagram below, circle the nitrogen atom which will be a stronger base. Explain your reasoning. [2]



The <u>alkyl groups</u> attached to the N atom are <u>electron-donating groups</u>, hence making the <u>lone pair of electrons on the N atom more available to</u> <u>accept a proton</u>. OR

The lone pair of electrons on the N atom of phenylamine can be delocalised into the π electron system of benzene ring, thus making the lone pair of electrons less available to accept a proton

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EXAMINER'S COMMENTS

This question was well done. Many students were able to identify the correct nitrogen atom and give the correct explanation.

21

A small minority of student mentioned 'negative charge on nitrogen atom' or 'stabilising the negative ion' and was penalised, because the nitrogen atom will only carry a positive charge (conjugate acid) after accepting a proton.

4 (a) (iv) Procaine undergoes hydrolysis rapidly in the small intestines where the pH is about 9. Give the structural formulae of the products obtained from the hydrolysis under such conditions. [2]







(b) Prilocaine, an amide-based local anaesthetic, is commonly used in dentistry. Prilocaine is synthesised when the following substituted acyl chloride undergoes a condensation (addition-elimination) reaction with 2-methylphenylamine.

22



Prilocaine The reaction above takes place in three steps.

The first step involves the nucleophilic addition of 2-methylphenylamine to the substituted acyl chloride to form the following dipolar ion as an intermediate.



In the second step, the nitrogen atom on another molecule of 2-methylphenylamine acts as a base and accepts a proton from the dipolar ion intermediate.

In the final step, the C=O bond of the amide bond is restored when the chlorine atom leaves as a chloride ion.

With reference to the information provided above, suggest a three-step mechanism for the formation of Prilocaine.

You may wish to represent the substituted acyl chloride as R Show all partial charges and curly arrows clearly in your answer.

Cl











EXAMINERS' COMMENTS This question was mostly left blank.

For the few students who attempted, the curly arrows were randomly positioned. Students are reminded of the need to read the information given in the question carefully which will help them to structure their answers. **4 (c)** Limiting the intake of certain essential nutrients, either proteins or amino acids for several days before surgery may reduce the risk of serious surgical complications such as heart attack or stroke.

Histidine is an essential amino acid utilised by the body to develop and maintain healthy tissues. The structure of the fully protonated form of histidine is given below.



Histidine

The pK_a values of the respective functional groups attached to the α -carbon in histidine are given in the following table.

functional group	p <i>K</i> a value
о сон	1.82
HN HN NH ⁺	6.00
NH ₃ +	9.17

- 4 (c) (i) With reference to the given pK_a values, suggest the major species present in solutions of histidine with the following pH values:
 - pH 4
 - pH 8
 - pH 12

[3]



EXAMINERS' COMMENTS This question was badly done. Only a very small minority of students scored the full three marks.

4

(c) (ii) Histidine is also important for digestion in human body as it helps to produce gastric juices in the stomach.

A stomach juice sample is extracted from a patient to determine the concentration of histidine by titrating it with aqueous sodium hydroxide.

Draw a labelled titration curve of pH against amount of NaOH(aq) added when one mole of fully protonated histidine is titrated with NaOH(aq)

You should clearly label the following points in your titration curve.

amounts of NaOH required at each equivalence point



EXAMINERS' COMMENTS

This question was mostly left blank.

For the few students who attempted to sketch a graph, the common mistakes observed were:

- showing only one or two equivalence points
- labelling the y-axis as volume of NaOH and hence the wrong values were stated
- the pH values of at the three maximum buffer capacities were pH 4, 8 and 12, which were the values in the question in (c)(i) and is totally irrelevant

- 4 (c) (iii) Histidine can be converted to histamine by an enzyme called histidine decarboxylase. The enzyme undergoes partial hydrolysis to produce the following fragments:
 - ala-cys-phe
 - lys-asp-asp-gly
 - phe-arg-lys
 - ala-cys-phe-phe-arg-lys
 - asp-asp-gly

Give the sequence of the nine amino acid residues of the enzyme. [1]

Reasoning:

ala-cys-phe

lys-asp-asp-gly ala-cys-phe-phe-arg-lys phe-arg-lys asp-asp-gly

The sequence of the enzyme is ala-cys-phe-phe-arg-lys-asp-asp-gly

[Total: 20]

EXAMINERS' COMMENTS This question was well-done. Many students scored the full credit here. **5** Wittig reaction is a very important tool in organic chemistry and is particularly useful for the synthesis of alkenes, as the double bond forms specifically at the location of the original aldehyde or ketone. The Wittig reagent used is triphenyl phosphonium ylide, Ph₃P=CR"R", where the phenyl group is abbreviated as 'Ph'.



phosphonium ylide

where R,R',R",R" = H or alkyl

(a) Draw the structures of the carbonyl compound and the specific phosphonium ylide that can be used to produce the following organic compound.



EXAMINER'S COMMENTS

This question was done quite well. Most students were able to recognise the pattern and deduce the carbonyl compound and the phosphonium ylide to form the organic compound. Some even gave both the alternative answers.

5 (b) The synthesis of methylpropene via the Wittig reaction is shown below.



EXAMINER'S COMMENTS

Most students were able to get (i) correct, but did not manage to identify that butyl lithium functioned as a Bronsted-Lowry base as it has removed a proton from Ph_3PCH_3 in order to form the phosphonium ylide in (ii). Some students showed electrophilic addition mechanism of propene with HBr, instead of methylpropene with HBr. Most students managed to get the mechanism correct.

(iv) Describe and explain the trend in the thermal stability of the hydrogen halides HCl, HBr and HI. Include an equation for the thermal decomposition reaction in your answer.
 [3]

Hydrogen halides decompose on heating to give hydrogen gas and halogens.

 $2HX \rightarrow H_2 + X_2$ where X is a halogen. [1]

The thermal stability decreases down from UCI UDs and UI [4]

The thermal stability decreases down from HCI, HBr and HI. [1]

Down the group, as the size of the halogen atom increases.

The **H–X** bond length increases and is weaker.

Hence, the bond energy of H-X decreases, and thermal stability decreases

down the group. [1]

EXAMINER'S COMMENTS

This question was poorly done. Common mistakes included stating that HX is an ionic compound, and explaining that the size of the halide ion increases down the group. Many students also failed to explain that as the size of the halogen atoms increased, the effectiveness of orbital overlap decreases/ bond length increases and thus bond strength weakens down the group. Many students also gave the wrong equation for the thermal decomposition of the hydrogen halides; $H-X \rightarrow H^+ + X^-$

(b) (v) Hence, by stating relevant information from the *Data Booklet*, suggest how the rate of the reaction will change in (b)(iii) when hydrogen chloride is used instead of hydrogen bromide.

Bond energy H–Cl : 431 kJ mol⁻¹ Bond energy H–Br: 366 kJmol⁻¹

When hydrogen halides react with alkenes, the H-X bond has to be broken. Since the <u>breaking of H-X bond takes place in the slow, rate-</u> <u>determining step</u>, the stronger H-X bond, the slower the reaction will be. Thus <u>rate of reaction will be slower</u> when hydrogen chloride is used instead of hydrogen bromide.

EXAMINER'S COMMENTS

This question was done well. Many students were able to score the full marks for this section.

5 (c) Wittig reaction is also used in the industry to synthesise β-carotene. β-carotene is a food colouring that can be extracted from the pigmentation found in red-orange plants and fruits such as carrots. It can be synthesised using excess of an aldehyde and 2 molecules of phosphonium ylide.



 β -carotene

(i) The phosphonium ylide used to synthesise β -carotene is given below, where Ph represents a phenyl group,



Suggest the structure of the aldehyde that can be used to produce β -carotene. [1]



Structure of the aldehyde is:



EXAMINER'S COMMENTS

5

This question was poorly done. Many students did not pick out information from the question, that 2 molecules of phosphonium ylide was used, and thus drew the wrong structure of the aldehyde.

(d) The long conjugated hydrocarbon chain in β -carotene leads to its intense orange colour.

A conjugated system contains a series of alternating single and double bonds, in which there is a p orbital on each atom and electrons are delocalised in the molecule. This generally lowers the overall energy of the molecule and increases its stability.

The table below contains information about cyclohexene and naphthalene. Cyclohexene contains one carbon-carbon double bond and shows chemical properties common to other alkenes. Napthalene, $C_{10}H_8$, shows chemical properties common to aromatic compounds.

alkene	conditions for reaction with hydrogen	product	calculated enthalpy change of hydrogenation/ kJmol ⁻¹
cyclohexene	room temperature, nickel catalyst	cyclohexane	-118
naphthalene	_	decalin	?

- (i) Calculate the enthalpy change of hydrogenation of naphthalene. [1] $\Delta H = 5 \times (-118) = -590 \text{ kJmol}^{-1}$
- (ii) The actual value for the enthalpy change of complete hydrogenation of naphthalene is -335 kJ mol⁻¹. Explain why this is so, in terms of hybridisation and interactions of the orbitals in the carbon atoms within a naphthalene molecule. [2]

Each carbon atom is $\underline{sp^2}$ hybridised and there is an unhybridised <u>p</u> orbital on each carbon atom which overlaps sideways to form a

orbitation each carbon atom which overlaps sideways to form a

resonance structure, giving the molecule extra stability.

EXAMINER'S COMMENTS

This question was poorly done. Many students did not identify the type of hybridisation that C in naphthalene had, and the reason why it is more stable, when the question specifically asked for it. Moreover, the clue, "A conjugated system contains a series of alternating single and double bonds, in which there is a p orbital on each atom and electrons are delocalised in the molecule." has been also given in the question, which students could have included in their answer.

 5 (e) Dyes possess colour as they have an extended conjugated system. Compound F is used in the manufacture of dyes and paints. It can be synthesised from methylbenzene in three steps as shown.



(i) Suggest structures for the organic compounds D and E.

[2]

F



33

[Total: 20]

EXAMINER'S COMMENTS

This question was mostly well attempted. Most students were able to identify the organic compounds D and E, and state the correct reagents and conditions required.