Name

Anglo-Chineze School (Independent)



YEAR 6 PRELIMINARY EXAMINATION 2023 INTERNATIONAL BACCALAUREATE DIPLOMA PROGRAMME CHEMISTRY HIGHER LEVEL

PAPER 2

Wednesday

13th September 2023

2 hours 15 minutes

INSTRUCTIONS TO CANDIDATES

- Do not open this examination paper until instructed to do so.
- Write your candidate session number in the box above.
- A calculator is required for this paper.
- A copy of the Chemistry Data Booklet is required for this paper.
- Write your answers in the boxes provided.
- If you use additional sheets of paper for your answer, attach them to the booklet. Indicate the question number clearly on these sheets.
- All drawings must be in ink.

For exami	ner's use
Qn 1	/6
Qn 2	/22
Qn 3	/8
Qn 4	/10
Qn 5	/13
Qn 6	/9
Qn 7	/15
Qn 8	/7
Wrong s.f.	
/units	
Total	/90



This question paper consists of <u>31</u> printed pages including this cover page.

Answer **all** questions. Write your answers in the boxes provided.

1.	Carb	on consists	of 4 a	allotrop	es in th	ne fo	orm of	diar	nond,	graph	ite,	fullerene	and	
	grap	hene.												
	(a)	State and	explain	the o	differenc	e in	electr	ical	condu	ictivity	of	diamond	and	[2]
	. ,	graphite.	·							,				

Diamond is a non-conductor Graphite is a good conductor Diamond uses all the valence electrons in bonding/ no free electrons Graphite has delocalized electrons to conduct electricity

Marker comments

Most students can answer the question. Some students misused words like "lone pairs" or lone electrons

(b)	Explain why the carbon-carbon bonds in graphite are stronger than the carbon-	[2]
	carbon bonds found in diamond.	

Resonance or delocalization of pi electrons in graphite/ overlap of pi electrons or overlap sp²-sp² and sp³-sp³ C

Resulting in shorter bonds/ partial double bond character in C-C bonds/ 1.333 Bond order

Marker comments

A few students related this to Diamond having a weaker London Dispersion Force compared to the dipole-dipole forces in graphite, this is a conceptual misunderstanding. Students are to note that the bond resulting from delocalised electrons is not 1.5 bond order and it is not a double bond in graphite but rather a partial double bond.

(C)	State th	ne type	of	hybridization	around	the	carbon	atoms	in	diamond	and	[2]
	graphite.			-								

Diamond: sp³ Graphite: sp²

Marker comments

Generally well done

The energy cycle shown can be used to calculate the enthalpy change of formation of KCl (s). Each arrow indicates a transformation, W, X, and Y. Each transformation consists of one or more steps.



(a) (i) Calculate the value of the following transformations using section 8 of the [4] data booklet and the following information.

Enthalpy change of atomisation of K (s)	+89 kJ mol ⁻¹
Enthalpy change of atomisation of $Cl_2(g)$	+121 kJ mol ⁻¹
Enthalpy change of solution of KCl (s)	–17 kJ mol ^{–1}
Enthalpy change of hydration of Cl ⁻ (g)	–365 kJ mol ^{–1}
Enthalpy change of hydration of K⁺(g)	–340 kJ mol ^{–1}

Transformation **W**: K (s) + $\frac{1}{2}$ Cl₂ (g) \rightarrow K⁺ (g) + Cl⁻ (g) K(s) \rightarrow K⁺ (g) $\Delta H = +89 + 419 = +508 \text{ kJ mol}^{-1}$ $\frac{1}{2}$ Cl₂ (g) \rightarrow Cl⁻ (g) $\Delta H = +121 + (-349) = -228 \text{ kJ mol}^{-1}$ $\Delta H = 508 - 228 = +280 \text{ kJ mol}^{-1}$ Transformation **Y**: K⁺ (g) + Cl⁻ (g) \rightarrow KCl (aq)

 $\Delta H = -365 - 340 = -705 \text{ kJ mol}^{-1}$

Marker comments

For W, many students divided 121 by 2 as they mistook it as bond energy. Some students used the BE in the data booklet but this is not allowed as Q did not require them to refer to section 11 of the data booklet. For Y, some students mistook and included -17 in their calculation

	(ii)	Using your answer to (a)(i) and the given data to calculate the enthalpy	[2]
		change of formation of KCl (s).	
		If you did not get answers to (a)(i) , use +200 kJ mol ⁻¹ and —650 kJ mol ⁻¹ for	
		W and Y respectively, but these are not the correct answers.	

for substituting enthalpy change of solution $\Delta H = +280 + (-705) + (17) = -408 \text{ kJ mol}^{-1} \text{ Or}$ $\Delta H = +200 + (-650) + (17) = -433 \text{ kJ mol}^{-1}$

Marker comments

Most students are awarded full ECF.

	(iii)	State	and	explain	the	sign	for	the	entropy	change	for the	formation	of	[1]
		KCl (s).											

The sign will be <u>negative</u> as the <u>number of moles of gases decreases</u> from 0.5 mol to 0 mol. Accept change in phase from gas to solid

Marker comments:

Many students did not make clear reference to gas but just stated fewer ways to distribute energy or less disorder. Quite a few misread the Q as enthalpy and explain using bond formation and bond breaking.

	(iv)	Deduce, giving reasons, whether altering the temperature would change	[2]
		the spontaneity for the formation of KCl (s).	

As temperature <u>increases</u>, <u> $-T\Delta S$ </u> becomes <u>more positive</u>,hence <u> ΔG </u> becomes <u>more positive</u> and reaction becomes <u>non-spontaneous</u>.

Marker comments:

Most students were able to get this Q correct.

(b)	Explain why the enthalpy change of hydration of $K^{+}(g)$ is less exothermic than	[1]
	that of Ca ²⁺ (g).	

<u>**Ca**²⁺</u> has a <u>higher charge density</u> than <u>**K**⁺</u>, hence it forms stronger ion-dipole interaction with water molecules and releases more hydration energy.

Accept explanation using charge and ionic size.

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Marker comments

Most students were able to get this Q correct.

	(c)	(i)	Explain why the ionic radius of K^+ is smaller than that of Cl^- .	[2]	
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<u>K</u>⁺ and <u>Cl</u>⁻ are isoelectronic OR same <u>number of electrons</u>. However, <u>K</u>⁺ has <u>a bigger</u> <u>nuclear charge than Cl</u>⁻, hence the electrostatic attraction between valence electrons and nucleus is stronger resulting in a smaller radius.

Marker comments

Many students mentioned the same number of quantum shells. Some incorrect answers include, K lost an electron and 1 quantum shell but not for Cl, or greater interelectronic repulsion in Cl⁻.

	(ii)	Explain the decreasing trend in the first ionization energies of group 1 and	[1]
		group 17 elements down the group.	

Down the group, there is **increasing shells of electrons and the electron to be removed is further away from the nuclear**.

Marker comments

Most students were able to get this Q correct.

	(iii)	The Periodic Table groups together elements with similar properties. In most Periodic Tables, hydrogen is placed at the top of Group 1, but in	[2]
		some it is placed at the top of Group 17.	
		Using your knowledge of chemistry, state one reason for hydrogen being	
		placed above either Group 1 or Group 17.	

Reason why hydrogen is placed above Group 1:

Group 1 elements and hydrogen has 1 valence electrons (same valence electronic configuration)

Group 1 elements and hydrogen form cation with charge of 1+

Reason why hydrogen is placed above Group 17:

Group 17 elements and hydrogen both needs to gain 1 electron to have a stable electronic configuration.

Group 17 elements and hydrogen forms anions with charge of 1-

Group 17 elements and hydrogen forms a diatomic molecule with a single bond.

Marker comments

Students kept referring to sharing 1 electron in forming an ionic bond. No mark is given for stating, shares 1 electron in covalent bond forming as it is typical for atoms to share 1 e too.

	(iv)	The hydrogen spectral data can give information on the frequency for its	[2]
		convergence limit. Using sections 1, 2 and 8 of the data booklet, calculate	
		the frequency of the photon to remove electron from gaseous hydrogen	
		atoms.	

E of one photon = $\frac{1312 \times 1000}{6.02 \times 10^{23}}$ = 2.18 x 10⁻¹⁸ J E= *hv* $v = \frac{2.18 \times 10^{-18}}{6.63 \times 10^{-34}}$ = 3.28 x 10¹⁵ s⁻¹

Marker comments

Many students calculated wavelength instead of frequency and they also did not divide by L.

(d)	Chloride ions can act as ligands. When concentrated hydrochloric acid is added					
	to a solution containing pink $[Co(H_2O)_6]^{2+}$, a blue solution of $[CoCl_4]^{2-}$ is formed					
	and the following equilibrium is established.					
	$[\operatorname{Co}(\operatorname{H}_2\operatorname{O})_6]^{2+} + 4\operatorname{Cl}^- \rightleftharpoons [\operatorname{Co}\operatorname{Cl}_4]^{2-} + 6\operatorname{H}_2\operatorname{O}$					
	(i) Complete the electronic configuration of Co ion in $[CoCl_4]^{2-}$.	[1				

1s²2s²2p⁶3s²3p⁶3d⁷

Marker comments

Some students forgot to remove 4s electrons first

	(ii)	Use Le Chatelier's principle to suggest the expected observations when	[2]	
		silver nitrate solution is added dropwise to the blue solution of $[CoCl_4]^{2-}$.		
		Explain your answer.		

When silver nitrate is added, <u>AgCI</u> ppt is produced which <u>decreases the [CI-]</u>. By LCP, <u>position of equilibrium shifts left</u> to produce some Cl⁻. Hence, a <u>pink solution</u> will be observed. Accept violet/purple solution

Marker comments

Some students mistook that $AgNO_3$ will cause ligand exchange and hence the colour will change. Some students mistook that adding $AgNO_3$ adds water and hence POE will shift left because to reduce water added.

	(iii)	Bubbling air through different aqueous mixtures of CoCl ₂ , NH ₄ Cl and NH ₃ ,	[2]
		produces various complex ions with general formula $[Co(NH_3)_{6-n}Cl_n]^{3-n}$.	
		Determine the oxidation state of the cobalt and the type of bond formed in	
		these complex ions.	

Oxidation state: <u>+3</u> Type of bond formed: <u>Dative covalent bond</u>

Marker comments Most students can answer the questions.

3. (a) Hydrogen iodide can be made by heating hydrogen gas and iodine vapour in a reversible reaction.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(i) Determine the standard enthalpy change, ΔH , for the reaction, using [2] section 11 of the data booklet.

```
Bonds broken:
+436 + 151 = +587 kJ mol<sup>-1</sup>
Bonds formed:
2(298) = +596 \text{ kJ mol}^{-1}
\Delta H = 587 - 596 = -9 \text{ kJ mol}^{-1}
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for correct bonds broken and bonds formed for correct calculation of enthalpy change (BE_{reactant} - BE_{product})

Marker comments

A significant number of candidates were unfamiliar with the formula involved. A few of them ignored the coefficient in the equation and calculated the incorrect value.

(ii) Enthalpy change of reaction calculated using bond enthalpy values [1] usually deviate from the literature value. However, the enthalpy change calculated in (a)(i) coincides with the literature value. Explain why this is so.

Since <u>all</u> the reactants and products are <u>diatomic molecules</u>, the bond enthalpies value from the data booklet is the <u>actual value</u>.

Marker comments

Many assumed that there is no deviation as the reaction was already in gaseous state; or indicated the lack of partial ionic character or minimal intermolecular forces of attraction which is irrelevant. Many did not realise that the bond-breaking and bond-formation in the reaction involved only one type of each bond in the molecules and thus no average BE is involved.

(b) At 400 K, the rate constant for the forward reaction is approximately 1000 [2 times greater than the rate constant for the backward reaction. The overall orders of the forward and backward reactions are the same.

Forward reaction: $H_2(g) + I_2(g) \rightarrow 2HI(g)$

Backward reaction: $2HI(g) \rightarrow H_2(g) + I_2(g)$

Use this information to explain what will happen if equal concentrations of HI (g), H₂ (g) and I₂ (g) are mixed at 400 K.

You should comment on:

- The relative initial rates of the forward and backward reactions
- The position of the equilibrium reached.

Since the overall orders of the forward and backward reactions are the same and rate constant for the forward reaction is approximately 1000 times greater than rate constant for the backward reaction, the **forward reaction is greater than backward reaction**.

Hence, equilibrium will be established <u>on the right/product side</u> Can also explain by using calculations.

Marker comments

A number of candidates did not understand that the given information refers to the amount of reactants and product at the initial state. The rate constant reflected the relative rate of forward

and reverse reaction. Many of them also misinterpreted the question and predicted the shift in POE using Le Chatelier's principle to counteract the change.

(c) (i) At exactly 700 K, the value of the equilibrium constant is 56. [1] Calculate the ΔG , Gibbs free energy change for the reaction, in kJ per mole, using sections 1 and 2 of the data booklet.

 $\Delta G = -RTInK_{c}$ = -8.31 x 700 x In56 = -23415 J mol⁻¹ = -23 kJ mol⁻¹ Do not penalise dp/sf)

Marker comments

Errors were made due to careless mistakes, including missing out the negative sign, not knowing the calculation yielded the answer in J mol⁻¹ which needs to be converted, performing the calculation without In56 or incorporating 700K.

(ii) When 0.218 mol sample of hydrogen iodide was heated in a flask of [2]

2 dm³, the equilibrium was established at 700 K.

Calculate the equilibrium concentrations of hydrogen and iodine.

	H_2	2	2HI
Initial mol	0	0	0.218
Change mol	+χ	+χ	—2x
Equilibrium mol	x	х	0.218–2x

 $K_c = \frac{\frac{(0.218-2x)^2}{2^2}}{\frac{x^2}{2}} = 56$ – no ecf awarded if ICE is not done/done incorrectly

 $\frac{(0.218 - 2x)}{x} = \sqrt{56}$

0.218 — 2x = 7.483x x= 0.0230 mol

 $[H_2] = [I_2] = 0.0230/2 = 0.0115 \text{ mol dm}^{-3}$

Marker comments

Many candidates did not perform the ICE table calculation. A significant number of them did not incorporate the change in ICE according to stoichiometry coefficients. Some constructed the calculation using reversible reaction and used 56 instead of $\frac{1}{56}$ while others did not include the square operation to [HI].

4.	(a)	The	diagram	below	shows	two	electrolytic	cells	connected	in	series.	
		Conc	centrated (CuCl₂ (a	q) is use	ed as	the electroly	te and	graphite ele	ctro	des are	
		used										



	(i)	Cell 2 is intended for copper-plating a coin. Write the half-equations of the	[2]
		reactions occurring at electrodes X and Y .	

Reaction at electrode X: 2Cl⁻ (aq) \rightarrow Cl₂ (g) + 2e

Reaction at electrode Y: Cu^{2+} (aq) + 2e \rightarrow Cu (s)

Marker comments

Candidates either wrote the equations oppositely or overlooked that concentrated $CuCl_2$ (aq) was used and gave a half equation producing O_2 (g). Some gave half equation at electrode X having Cu oxidised or electrode Y involving $Cu^+(aq)$, which Cu and Cu^+ were not present.

	(ii)	As the copper plating process was occurring in Cell 2, 4.52 g of Cu was	[2]
		plated on the coin after 10 minutes. Identify the product formed at	
		electrode ${\bf B}$ and calculate the mass of the product formed at electrode ${\bf B}$	
		after 10 minutes.	

The product at B is Mg

Amount of Cu = $\frac{4.52}{63.55}$ = 0.071125 mol Amount of Mg = 0.071125 mol

Mass of Mg = 0.071125 x 24.31 = 1.729 = 1.73 g – ecf awarded if the mole ratio used is correct

Marker comments

Many did not pay attention to the given electrolyte being molten MgCl₂ and stated other products formed. While ecf was given for the correct calculation with respect to Cu, careless mistakes were made as candidates were either unable to present the correct mole ratio or calculated using incorrect Mr.

	E⇔/V
$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$	– 0.76 V
$V^{3+}(aq) + e^{-} \rightleftharpoons V^{2+}(aq)$	-0.26 V
$VO^{2+}(aq) + 2H^{+}(aq) + e^{-} \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34 V
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00 V

(b) The standard electrode potentials of four half-cells are given below.

	(i)	Deduce the balanced equation, including state symbols, for the overall	[2]
		reaction with the greatest standard cell potential, $E^{\ominus}_{\text{cell}}$ and calculate the	
		standard cell potential, $E^{\ominus}_{\text{cell}}$.	

 $2VO_2^+(aq) + 4H^+(aq) + Zn(s) \rightarrow 2VO^{2+}(aq) + 2H_2O(l) + Zn^{2+}(aq)$ – no mark awarded for incorrect coefficients or no state symbols $E^{\ominus}_{cell} = 1.00 - (-0.76) = 1.76 \text{ V}$

Marker comments

A number of candidates gave the incorrect equation due to the use of wrong half equation. Careless mistakes were made as there was no state symbols. Some candidates also wrote the balanced equation in an opposite manner where it would give a negative E^{\ominus}_{cell} .

	(ii)	Calculate the value of ΔG^{\ominus} using your answer in (b)(i) in kJ mol ⁻¹ .	[2]
		(If you did not obtain an answer to (b)(i) , use 1.55 V, but this is not the	
		correct value.)	

n = 2 for the above overall eqn [1m] – ecf awarded based on the e⁻ obtained from (i) $\Delta G^{\ominus} = -(2 \times 96500 \times 1.76) = -339680 \text{ J mol}^{-1} = -340 \text{ kJ mol}^{-1}$

Marker comments

Many candidates forgot to place a negative sign to the final answer or leave the answer as kJ mol⁻¹ when the calculated value was in J mol⁻¹ and needs to be converted.

(c)	Electrochemical or voltaic cells were introduced as a tool for studying the	[2]
	thermodynamic properties of fused salts more than a century ago. A voltaic cell	
	that converts chemical energy into electrical energy. Corrosion of iron is like the	
	processes that occur in a voltaic cell. The initial steps involve the following half-	
	equations:	
	Fe ²⁺ (aq) + 2e [−] ≓ Fe (s)	
	$\frac{1}{2} O_2(g) + H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq)$	
	An iron half-cell, Fe (s) /Fe ²⁺ (aq), can be connected to a hydroxide half-cell, O ₂ (g)/OH ⁻ (aq).	
	Draw a diagram of the voltaic cell under standard conditions. Label the polarity	
	of the electrodes, voltmeter, electron movement, and information on the	

	electrodes and electrolytes used.



Accept cor

1. chemicals and conditions: $OH^{-}(aq)$ at cathode and Fe^{2+} (aq) at anode; 1M each) 2. set-up: cathode: O_2 (g) gas electrode with Pt, 100 kPa & 298K, anode: Fe anode, salt bridge, voltmeter and terminals: +, - or anode cathode for polarity

Marker comments

Candidates are reminded to read the information provided carefully to identify the correct chemicals to be used in the set up. The details of the set up should be clearly illustrated especially the crucial parts, eg salt bridge, gas electrode, materials used as the electrodes, without which, the voltaic cell will not operate.

5.	A 0.25 mol dm ^{-3} ethylamine solution is prepared and it has a pH of 12.0.		`
	(a)	Suggest, with suitable calculations, if ethylamine is a strong or weak base.	[2]

If ethylamine is a strong base, pH = 14 - [-lg(0.25)] = 13.4Since pH 12.0 < pH 13.4, so it is a weak base OR If pH is 12.0, [OH⁻] = 10^{-(14-12.0)} = 0.0100 mol dm⁻³

Since [OH⁻] present < [ethylamine], ethylamine dissociates partially and thus it is a weak base.

Do not accept if a base is proven weak due to low pKb or low Kb.

Marker comments

Generally well done.

(b) A 20 cm³ of 0.25 mol dm⁻³ ethylamine solution was titrated against a 0.30 mol dm⁻³ aqueous hydrochloric acid. The pH curve for the reaction is as shown.



Volume of HCl / cm³

(b)	(i)	Formulate an equation for the reaction between ethylamine and	[1]
		hydrochloric acid.	

$CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3Cl$

Marker comments

Some candidates used a reversible arrow sign which is incorrect for a neutralization reaction while others were unable to produce the correct formula of salt and identified molecules, eg H_2 or H_2O as products in the equation.

	(ii)	Identify the major species at these points.	[2]

P: $CH_3CH_2NH_3^+$, Cl^- , $CH_3CH_2NH_2$ - must include base and conjugate acid

 \mathbf{Q} : CH₃CH₂NH₃⁺, Cl⁻

Marker comments

Many candidates did not include the conjugate acid in **P** though it is buffer region.

	(iii)	Determine the pH at the equivalence point, to two decimal places	[4]
		using section 1 and 21 of the data booklet.	

CH₃CH₂NH₂ + HCl → CH₃CH₂NH₃Cl mol ratio 1:1 Volume of HCl added = $20 \times \frac{0.25}{0.30}$ = 16.667 cm³ (5sf) c(CH₃CH₂NH₃⁺) = $\frac{\frac{20}{1000}(0.25)}{\frac{20+16.667}{1000}}$ = 0.13635 mol dm⁻³ (5sf) CH₃CH₂NH₃⁺ \rightleftharpoons CH₃CH₂NH₂ + H⁺ pK_a = 14 - pK_b = 14 - 3.35 = 10.65 [H⁺] = $\sqrt{(10^{-10.65})(0.13635)}$ = 1.74714 x 10⁻⁶ mol dm⁻³ pH = - log₁₀[H⁺] = 5.7567 ≈ 5.76 (2dp)

Marker comments

Many candidates adopted the incorrect workflow in calculation and led to incorrect pH value. The concentration of conjugate acid was incorrectly determined as the total volume of the mixture was not considered.

	(iv)	The buffer solution is formed when hydrochloric acid is added to	[2]
		ethylamine solution at the appropriate volumes. Determine the	
		volume where the maximum buffer capacity occurs.	

Volume of HCl added to reach an endpoint = 16.67 cm^3 Since buffer region occurs before the endpoint MBC occurs at $\frac{1}{2}$ volume of endpoint = 8.335 cm^3 = 8.35 cm^3

Marker comments

Many candidates calculated the MBC using total volume of resulting solution instead of volume of HCl used to reach endpoint. There were also a number of candidates that stated MBC to be after the equivalence point.

(c)A student repeated the experiment in (b) using phenolphthalein instead of
a pH probe.[2]A pH probe.Predict, giving a reason, if the volume of endpoint obtained from the
titration would be different from that obtained using a pH probe.[2]

The volume of endpoint obtained is <u>lower than expected</u> as the <u>colour change</u> <u>occurs before the equivalence point</u>.

Marker comments

Some candidates were unable to distinguish that endpoint refers to volume while equivalence point refers to pH value in a pH curve and used the expression inaccurately. A number of candidates also stated that the added indicator would affect the amount of H⁺ ions present in solution and affected the volume of HCl used, which is not true.

6. The rate equation for the hydrolysis of esters was determined by a series of experiments. The hydrolysis of 0.015 mol dm⁻³ ethyl 2–methyl butanoate was carried out at 355K, using 0.75 mol dm⁻³ hydrochloric acid. The experiment was repeated using 0.75 mol dm⁻³ sulfuric acid at 355K. The following graphs were obtained.



(a) Using the graphs above, deduce the order of reaction with respect to H⁺ [3] and ethyl 2-methyl butanoate. Hence, write the rate equation of the hydrolysis of the ester, ethyl 2-methyl butanoate.

The half-life for 0.75 mol dm⁻³ HCl is constant at around 26.5 min, The order wrt to ester is 1. The half-life for 0.75 mol dm⁻³ H₂SO₄ is constant at around 13.5 min, The order wrt to ester is 1. When the concentration of H⁺ doubles the half-life is approximately halved/ the initial rate doubles. The initial rate of 0.75 mol dm⁻³ H⁺ /HCl is 3.63×10^{-4} mol dm⁻³ min⁻¹ Accept range from 3.0 to 4.25×10^{-4} The initial rate of 1.50 mol dm⁻³ H⁺ /H₂SO₄ is 7.80 x 10⁻⁴ mol dm⁻³ min⁻¹ Accept range from 6.9 to 8.84×10^{-4} **To confirm the initial rate again** The order wrt to H⁺ is 1.

Rate = k [ester] [H⁺]

Marker comments

Students did not show working on how the order was obtained. A handful of scripts do not have markings on the graph, and it was not clear how they came to the conclusion of first order for both. In addition, since this involves a continuous method, it would be more accurate to use the initial rate by drawing the tangent at t=0 rather than to use average rate. For students who did initial rate, one must be mindful to draw a tangent such that it touches only one point on the curve. Some students compare half life to see how the rate is affected when concentration of H⁺ ions were changed which was acceptable. However, some students mistook a doubling of half lives to be doubling of rate which is incorrect.

(b) The hydrolysis of 0.015 mol dm⁻³ of ethyl 2–methyl butanoate was [2] repeated at 500K, using 0.75 mol dm⁻³ hydrochloric acid. Given that the initial rate of the hydrolysis at 500K was 4.67 x 10⁻³ mol dm⁻³ min⁻¹, calculate the rate constant for the hydrolysis of ethyl 2-methyl butanoate at 500K and state its units.

Rate = k [ester] [H⁺] Using 0.75 mol dm⁻³ hydrochloric acid 4.67 x 10⁻³ = k (0.75) (0.015) k = 0.415 mol⁻¹ dm³ min⁻¹

Accept ECF from (a) if wrong rate equation is given.

Marker comments

Most of the students were able to get this part correct, however there is a need to be mindful about the units given for rate which is in min⁻¹ instead of s⁻¹.

(c) In the absence of a catalyst, the hydrolysis of ethyl 2-methyl butanoate is [2] very slow. Sketch and label a suitable Maxwell Boltzmann distribution curve to show how the rate will change if the catalyst is removed.



(d)	Using the data and section 2 of the data booklet, calculate the activation	[2]
	energy in kJ mol ⁻¹ , for the hydrolysis of ethyl 2-methyl butanoate at 400K	
	and 300K without a catalyst.	

Temperature	Rate Constant, <i>k</i>
300K	0.12
400K	0.20

 $\ln \left(\frac{0.12}{0.20}\right) = \frac{Ea}{8.31} \times \left(\frac{1}{400} - \frac{1}{300}\right)$ E_a = 5093.95 = 5.09 = 5.1 kJ mol⁻¹

Accept 2 or 3 sf

Marker comments

A couple of students calculated two activation energies at the two temperatures using k= $Ae^{(Ea/RT)}$ but the Arrhenius constant was not given so this method should not be used, unless they express A in terms of other variables and equate them to be the same to find Ea. Some students forgot the units of R and leave the final calculated answer to be kJ mol⁻¹ instead of J mol⁻¹.

7. (a) 1-phenylethyl benzoate is an ester that is used in numerous cosmetic products and can be made from ethylbenzene by the following reaction scheme.



(i) Compound **A** shows optical activity. Draw the three-dimensional [1] representations of the two enantiomers.



(ii) Ethylbenzene undergoes oxidation in step I to form benzoic acid [1]
 and carbon dioxide as the only carbon-containing products.

Formulate a balanced equation for the oxidation of ethylbenzene using [O].

$C_6H_5CH_2CH_3 + 6 \text{ [O]} \rightarrow C_6H_5CO_2H + CO_2 + 2H_2O$

Marker comments:

Question was quite badly done as students seem unfamiliar to balance in terms of [o]. Some even tried to balance in terms of electrons (only for half equations) when it is not necessary when balancing with [O]. Some students balance H with H_2 and some students failed to give CO_2 as a product when the question specifically said CO_2 is produced.

(iii) An optically pure sample of A is reacted in step II and the organic [2] product is found to be optically inactive.

State the mechanism that occurs, and the reagents and conditions required.

Type of reaction: Unimolecular nucleophilic substitution / SN1 Reagents and conditions: NaOH(aq), heat with reflux **Marker comments:** Generally well done

(iv) Explain the mechanism of the reaction in step II using curly arrows [3] to represent the movement of electron pairs.



- (v) Explain why the organic product in step II is optically inactive.
- The positively charged carbon in the carbocation intermediate is **trigonal planar**, there is **equal probability of OH**⁻ **attacking from either side of the plane to form equimolar ratio of both enantiomers / a racemic mixture**

Marker comments: Most students were able to get this right if they were able to identify it's an unimolecular mechanism instead of the bimolecular one.

(vi) Identify the inorganic by-product in step III.

[1]

[2]

Inorganic by-product: hydrogen chloride / HCl **Marker comments:** Generally well done.

(b) Halogenoalkanes, such as bromomethane, tends to attract nucleophiles due to its electron deficient carbon. When bromomethane is reacted with magnesium in ether, it forms an organomagnesium compound, as shown.

 CH_3 -Br + Mg \rightarrow CH_3 -MgBr

The organomagnesium compound instead undergoes reaction with electrophiles. One such reaction is with carbonyl compound:



Explain why the organomagnesium compound undergoes reaction [1]
 with electrophile instead of nucleophile.

Carbon is more electronegative than magnesium / is partially negative / has higher electron density / negative charge (if student assume ionic bond)

Marker comments

Most students did not identify which part of the organomagnesium compound is the electron rich site.

(ii) Compound C can be synthesised in two steps from compound B [3] with the use of an organomagnesium compound in one of the steps.





compound B

compound \boldsymbol{C}

Suggest the synthetic route including all the necessary reactants and steps.



(iii) State the name of compound C, applying International Union of [1]
 Pure and Applied Chemistry (IUPAC) rules.



Some students identified the incorrect carbon chain while some students gave 4 methyl instead of 2-methyl.

- 8. A student performed a reaction to synthesize 3-chloropropanoic acid.
 - (a) After the isolation of the organic products from the reaction, the student analyzed a sample of 3-chloropropanoic acid using mass spectroscopy and obtained the following mass spectrum.



Suggest the formula of the species for the peaks at the following m/z values. [2]

73: CH₂CH₂COOH⁺

108: CH235ClCH2COOH+

Marker comments

Most candidates were able to get the structure for m/z = 73 but the majority did not indicate the isotope of chlorine for the molecular ion with m/z = 108. A small handful of candidates still forgot to include the positive charge or included the negative charge for the species.

(Question 8 continued)

(b) Upon the separation and isolation of the two isomers of 3-chloropropanoic [1 acid, the student used Infrared red (IR) spectroscopy to analyze the samples. Explain why the molecule absorbs infrared red radiation whereas some molecules do not.

Molecules absorb IR when the vibration results in a change in the net dipole moment. Molecules will not absorb IR when the vibration does not result in a change in the net dipole moment.

Marker comments

Very poorly done.

Common misconceptions:

- The molecule does not have vibrating bonds, or the frequency of the vibrating bonds is out of IR range.

- The molecule is polar or has polar bonds for it to be IR active.

However, candidates are to take note that a molecule in the ground state is not stationary but constantly moving through space. The energy needed to excite the bonds in a molecule occurs in the IR region. When the molecule absorbs a photon, the bonds vibrate more vigorously. In order for a vibrational mode to absorb infrared light, it must result in a periodic change in the dipole moment of the molecule.

Hence, in a polyatomic molecule, it is more correct to consider the molecule stretching and bending as a whole, rather than considering the individual bonds. Non-polar molecules like CO_2 and P_4 also have vibrational modes that are IR active.

(c)	The low-resolution ¹ H NMR spectra were obtained for 2-chloropropanoic acid,	
	CH ₃ CHClCOOH, and 3-chloropropanoic acid, CH ₂ ClCH ₂ COOH:	



2-chloropropanoic: ¹H NMR spectrum Y 3-chloropropanoic: ¹H NMR spectrum X

Integration ratio 2:2:1 matches the ratio of H in each environment for 3-chloropropanoic acid. 3:1:1 matches the ratio of H in each environment for 2-chloropropanoic acid.

Marker comments

Generally well done. A small handful of candidates measured the height of the peaks rather than that of the integral lines and got the wrong integration ratio.

(ii) Deduce the splitting pattern of the peaks in another isomer, [2] propanoyl chloride, CH₃CH₂COCl in high-resolution ¹H NMR spectrum.



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