

HWA CHONG INSTITUTION 2021 C1 H2 CHEMISTRY PROMOTIONAL EXAM SUGGESTED SOLUTIONS

General comments:

Give answers that are clear, concise, coherent and in legible handwriting.

Do not cram your answers or write into the edges of the page. If more space is required, use the additional page at the end of Paper 3, or request for writing paper for Paper 2.

Attempt all calculation questions, so that you would be able to move on to subsequent parts. Follow through marks may be awarded (error carried forward) for correct working steps.

For Paper 3, answers should always be written on the lines, except when the question specifies answers to be written in the table/figure itself.

Avoid the use of ambiguous terms like "it" or "they", when there are multiple species, groups, and/or interactions in a question. Use terms like C=C carbon / C=O double bond to refer to specific atoms or bonds, especially if there are a few different kinds of carbons / more than one double bond in the molecule.

Be careful with the terms atoms, molecules, ions, carbocation, radical, elements, compounds – these differ in meaning and are not interchangeable.

For Paper 1, plan your time well so you do not leave any answer unshaded on the OMS.

Pa	per	17
_		

	7								
1	2	3	4	5	6	7	8	9	10
С	С	В	В	D	Α	С	Α	D	В
11	12	13	14	15	16	17	18	19	20
D	Α	В	С	В	С	В	С	D	Α

Comments

1 C Since the s and p subshells in inner quantum shells are completely filled, the s and p electrons from the inner quantum shells are all paired. Hence, we only need to consider the valence shell electronic configuration of the particles.

Option	Explanation						
<u> </u>	Cr: 3d ⁵ 4s ¹ . It contains an unpaired s electron.						
2	Ge: 4s ² 4p ² . It contains an unpaired p electron.						
3	S: 3s ² 3p ⁴ . Hence, valence shell electronic configuration of S ^{2–} is 3s ² 3p ⁶ .						
	It does not contain an unpaired s electron or an unpaired p electron.						
4 /	Sc: 3d ¹ 4s ² . It does not contain an unpaired s electron or an unpaired p						
5 6	electron.						

C Balancing the mass number and proton number on both sides of the equation,

 $_{0}^{1}n + _{7}^{16}X \rightarrow _{6}^{14}C + _{1}^{3}H$

Total no. of protons present in products = 6 + 1 = 7= No. protons present in reactants

Since a neutron has proton number of zero, X has 7 protons \Rightarrow X is N (identity of an element is based on the no. of protons it possesses)

 \therefore X contains 16 – 7 = 9 neutrons

3 B Given that Y has at least 19 electrons, the Period number of Y must be 4 or higher. From Period 4 onwards, the d subshell needs to be considered when deducing the electronic configuration of the element from successive ionisation energy data.

Options **C** and **D** are incorrect. The graph shows a sharp increase from the 15^{th} to 16^{th} ionisation energy, which indicates that the 16^{th} electron is in an inner quantum shell. If Y is a Period 4 Group 17 element ([Ne] $3s^23p^63d^{10}4s^24p^5$), after removal of the first seven electrons, there should be a gradual increase in energy for the removal of the ten 3d electrons. A similar reasoning applies for why Y cannot be a Group 14 element.

A possible electronic configuration for Y may be $1s^22s^22p^63s^23p^63d^54s^2$, which is that of manganese. After removal of two electrons, a small jump is expected since the third electron is in an inner 3d subshell. After removal of another five electrons, a slightly greater increase occurs from the 7th to 8th ionisation energies, as the 8th electron is in an inner 3p subshell.



 C_x is bonded to a H atom besides two other C and one C_l , hence C_x is tetrahedral with a bond angle of 109.5°. C_y is also bonded to four groups, so it has a bond angle of 109.5°. C_z has 3 groups of bonding electrons in total, so its bond angle is 120°.

D BaO₂ contains Ba²⁺ and O₂²⁻. Each O atom gains one electron from Ba, as denoted by the open circle in the dot-and-cross diagram. The dot-and-cross diagram for options A, B and C shows O²⁻, O₂ and O₂⁻ respectively.

6 A The Lewis structures of the molecules provided by the question are drawn in the table below, together with an indication of whether a net dipole exists.

т HWA	First molecule	Net dipole?	Second molecule	Net dipole?
г 8 и 1	o ^{\$} ≈0		0=C=0	E 1 1 🗙 1 0
2	F`AF		F B F	×
3	F F// F ₩ ₩ ₹ F		F I F`-Si F	X

From the above, it is clear that all options are correct. Therefore **A** is the option which we will pick.

- 7 **C** After combining flasks A, B and C, total volume = 7 dm³ At 40°C, water vapour condenses to water and is no longer a gas. Using pFVF/TF = $p_1V_1/T_1 + p_2V_2/T_2$ we will find the new final pressure (pF) after mixing. (pF)(7)/(313) = (2)(1)/(383) + (4)(2)/(383) PF = 1.2 kPa
- **8** A Since we know that H_2S is being oxidised to form elemental sulfur, we would be able to balance the oxidation half equation: $H_2S \rightarrow S + 2H^+ + 2e$

The question mentioned that H_2S reacted with BrO_3^- in a 5:2 ratio. When 5 moles of H_2S get oxidised, 10 moles of electrons would be given out and transferred to 2 moles of BrO_3^- . This implies that every mole of BrO_3^- would take in 5 moles of electrons as they get reduced.

Oxidation state of Br in $BrO_{3^{-}} = +5$ After taking in 5 moles of electrons, the new oxidation state = +5 - 5 = 0

9 D C_xH_y $(x + y/4) O_2$ x CO₂ y/2 H₂O Initial 10cm³ 100 cm³ Change -65 +40-10 Final 35 cm³ 40 cm³

> Volume of $CO_2 = 40 \text{ cm}^3$ (CO_2 is an acidic gas and reacted with KOH) Volume of unreacted $O_2 = 75 - 40 = 35 \text{ cm}^3$ Volume of O_2 reacted = $100 - 35 = 65 \text{ cm}^3$

 $\frac{n_{CO2}}{n_{CxHy}} = \frac{40}{10} = \frac{x}{1}$ Hence, x = 4 $\frac{n_{O2}}{n_{CxHy}} = \frac{65}{10} = \frac{4+y/4}{1}$ Hence, y = 10

$\Delta G = \Delta H - T \Lambda S$ 10 B

Forward osmosis is spontaneous as the separation of water is done via a natural osmotic pressure gradient, without an external pressure. $\Rightarrow \Delta G$ is negative

 ΔH is negligible $\Rightarrow \Delta S$ must be positive.

Although there are fewer ways to rearrange the energy of the water and solute molecules in the fruit juice after being concentrated, the ways to rearrange the energy of the water molecules after passing through the membrane in the diluted saline water and the ions in the diluted saline water more than compensate so there is a net positive change in entropy.

11 D $\Delta H_{sol} = -mc\Delta T \div n_{MgCl2}$

The surrounding which absorbed the heat released from dissolution of the solid is the 100 cm³ of deionised water. Hence, m should be the mass of water alone.

The change in temperature, ΔT , is the same value whether in °C or K.

H⁺(aq) is a catalyst and hence its concentration is expected to remain constant 12 during the reaction. It is thus not possible to monitor the rate of reaction by following [H⁺(aq)].

The reaction produces a gaseous product, hence the rate of reaction may be followed by measuring the changes in total mass of the reaction mixture in an open flask (option **B**), volume of gas produced (option **C**), or gas pressure (option **D**).

В Total volume of the reaction mixture for expt 2 is half that of expt 1. Multiplying the 13 volume of each reactant and deionized water by 2 for easy comparison with expt 1, the initial concentration of RBr is the same for both expts, while the initial concentration of NaOH is decreased two times for expt 2. Since rate is halved for expt 2, the reaction is 1st order for NaOH. Option A is incorrect.

> In all expts, NaOH was in excess. The rate equation may hence be simplified to an overall pseudo first order reaction, where rate = k'[RBr] with k' = k[NaOH].

In expt 1, $t_{1/2} = \ln 2 \div k = \ln 2 \div k [\text{NaOH}] = \ln 2 \div k (0.40) = t \min$

In expt 3, $t_{1/2} = \ln 2 \div k = \ln 2 \div k [\text{NaOH}] = \ln 2 \div k (0.04) = 10t \text{ min Option } \mathbf{B}$ is correct. Alternatively, comparing expts 1 and 3, when [RBr] is doubled, half-life should remain at t min since reaction is 1st order for RBr. However, as [NaOH] is 10 times lower in expt 3, half-life should be larger at 10t min.

To determine the rate constant, the actual initial concentrations of RBr and NaOH in the reaction mixture needs to be calculated. It is wrong to substitute the given concentrations of RBr and NaOH (0.010 and 0.50 mol dm⁻³) because these are their concentrations before mixing. Using expt 1,

 $k = (3.0 \times 10^{-5}) \div \{(10 \times 0.010 \div 50)(40 \times 0.50 \div 50)\} = 0.0375 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$

For expt 3, total volume is identical to that in expt 1. With twice the concentration of RBr and one-tenth the concentration of NaOH, the rate of reaction, *x*, should be 6.0 \times 10⁻⁶. Option **D** is incorrect.

14	С	Option	Explanation					
		1	Correct. Only the rate equation of the hydrogen/iodine reaction corresponds to the overall equation of the reaction.					
	1.1	2	Wrong. No conclusion can be drawn over whether free radicals are involved in the mechanism.					
	Н	W ³ A	Correct. Two molecules of HI are formed for every one molecule of I_2 consumed.					
	Ι	4	Correct. As [HBr] increases, the value of the denominator in the rate equation increases so the rate of reaction decreases.					

15 B Both equilibrium yield and rate of reaction need to be considered when choosing the optimal conditions for industrial processes.

Option	Explanation
AA	Wrong. A catalyst only increases the rate of reaction; it does not affect equilibrium yield.
В	Correct. High pressures favour the forward reaction as it produces fewer
	moles of gases. Equilibrium yield of methanol product becomes higher.
С	Wrong. At lower pressures, the reactant molecules are further apart and
	are hence expected to collide less frequently. The rate of formation of
2 13	methanol should be lower as a result.
D	Wrong. Although equilibrium yield of methanol is higher at lower
N.N.7.A.	temperatures (since forward reaction produces heat), lower temperatures
WA	would cause the rate of formation of methanol to decrease.

16	С	Option	Explanation
		1	Both the carbon atoms in C=C of propene are sp ² hybridised (trigonal
			planar about each C). However, the carbon in the methyl group is sp ³ hybridised and has a tetrahedral shape about this carbon. Hence,
		r C	propene is not a planar molecule. Option 1 is incorrect.
		2	All the six carbons on the benzene ring are sp ² hybridised (trigonal planar
		WA	about each C). Hence, benzene is a planar molecule and all C and H
		NST	atoms lie on the same plane. Option 2 is correct.
		3	Ethyne has the structure $H-C=C-H$. Both carbon atoms are sp hybridized
			with linear geometry. Hence, all four atoms lie on the same plane. Option
		13	3 is correct.

17 B There are 2 alkene groups in Lanosterol but there is no cis-trans isomerism about the two C=C groups. One of them is in a cyclohexene ring and the other has two identical groups bonded to the same carbon atom.



Total number of enantiomers = 2^n where n is the number of chiral carbons

There are 7 chiral carbons in Lanosterol as indicated by the *. Hence, there are 2⁷ stereoisomers in total.

18 C The 9 hydrogen atoms circled below are equivalent and will result in the formation of the same radical.



Hence, three different radicals (shown below) can be formed by 2,2dimethylbutane and the answer is **C**.

19 D When ethene undergoes an electrophilic addition with aqueous bromine, the Br₂ electrophile attacks the electron rich C=C to form the carbocation, ⁺CH₂CH₂Br. The carbocation then undergoes an attack by Br⁻, H₂O (aqueous solvent) or NH₃, leading to the products shown in options A, B and C respectively. Option D would not be formed in this reaction.

20 A	Option	Explanation
	1	The alkenes can undergo a reaction with H ₂ but the type of reaction is reduction or addition, not an <u>electrophilic</u> addition. Hence, Option 1 is incorrect.
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Up, down trend from P₄, S₈ to Cl₂; P₄, S₈, Cl₂ and Ar must all be below Mg, and Cl₂ and Ar below P₄ [1/2]

This is a standard recall question. Students should be able to deduce the melting points across the period from the structure and bonding of the various elements. Sulfur has a slightly higher melting point than phosphorus and chlorine as it exists as S_8 molecule while the latter two exist as P_4 and Cl_2 . Most students simply drew a decreasing trend instead.

- Aluminium has a <u>giant metallic lattice/ structure</u> [1/2] with strong <u>metallic</u> <u>bonding</u> [1/2] between positive AI ions and the sea of delocalized valence electrons, so the melting points for AI is relatively high.
 - Silicon has the highest melting points due to its <u>giant molecular</u> <u>structure/giant covalent structure</u> [1/2] with strong <u>covalent bonds</u> [1/2] between silicon atoms. A lot of energy is needed to overcome the strong covalent bonds during melting.
 - Argon exists as <u>monoatomic gas/ individual, discrete atoms [1/2]</u>, <u>weak</u> <u>dispersion forces</u> [1/2] between the atoms. Thus less energy required to overcome the weak dispersion forces between the argon atoms, argon has the lowest melting point.

Common mistakes include describing argon as a molecule or having a simple molecular structure when it actually exists as discrete atoms. Students need to be able to distinguish between atoms and molecules. The link between the amount of energy required to break the bonds and how high the melting point is has to be clearly made.

(b) (i) Aluminium has one more quantum shell than beryllium, hence shielding effect is greater [0.5]. However, aluminium has a larger nuclear charge than beryllium [0.5] which nullifies the larger shielding effect.

Thus effective nuclear charge is relatively the same for both metals, [0.5] the attraction for electrons of another nucleus is relatively the same [0.5] which results in them having similar electronegativity.

Δ

Many students could explain the difference in nuclear charge and shielding effect between aluminium and beryllium, leading to the relatively similar effective nuclear charge. However, many failed to make the link between effective nuclear charge and electronegativity. It is not sufficient to simply state that the attraction for valence electrons is similar, explicit reference to bonding electrons or electrons of another nucleus has to be made.



Be in BeCl₂ is <u>electron deficient</u> with only 4 valence electrons hence it can accept 2 lone pairs from the 2 neighbouring chlorine atoms, forming 2 dative bonds per repeating unit. As it is a section of a polymer, the Be atoms at the two ends will not have full octet structure as the other BeCl₂ repeating units are not drawn. Students have to make the link from the dimer of aluminium chloride and understand that two dative bonds from two different chlorine atoms are formed with the electron deficient Be atom. Common mistakes include drawing of dot-cross diagram instead of Lewis structures, drawing of the dative bond in the wrong direction from the metal to chlorine.

2 (a)

Constitutional isomers have the <u>same molecular formula but different structural</u> <u>formula</u> i.e. different arrangement of atoms.

This is a standard recall question. Many students were confused and gave the definition of stereoisomerism instead.







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(b) (i) Electrophilic addition [1]









Br

1 mark for each step, -0.5 for every small mistake. [2] (dipole moment, 'slow' step, lone pairs on Br⁻, arrows, charges must be present)

Many students forgot to name the mechanism at the start of their answers. Common **mistakes** include pointing the curly arrows to the charge instead of the atom, starting curly arrows from mid-air. Students should be able to deduce the dipole moment in iodobromide from the respective electronegativities. The electron deficient iodine will first add across the double bond at the terminal C atom, thereby forming the more stable tertiary carbocation, which leads to the major product X.

(ii)

Br

This is the minor product which results when the iodine adds across the double bond at the second C atom to form the primary carbocation which is less stable. Some students fail to recognize that two different carbocation intermediates can be formed and thought that there was some form of rearrangement of the methyl groups instead.

(iii) Both major and minor products are formed from a different carbocation

intermediate. The <u>tertiary carbocation intermediate is more stable than the</u> <u>primary carbocation</u> intermediate OR there are <u>more electron donating alkyl</u> groups attached to disperse the positive charge on the carbon atom. The tertiary

carbocation intermediate will be formed preferentially, which leads to the

[1]

formation of the major product. [1]

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Some form of comparison is needed to explain the difference in proportions. It is not sufficient to simply say "the carbocation intermediate formed is more stable, therefore it is the major product." Many students explained about tertiary carbocation having electron donating alkyl groups but made no comparison to the minor product. A handful had problems identifying the type of carbocation formed and said it was secondary instead of tertiary.

(iv) It will be optically inactive. [0.5] Even though there is a chiral carbon present in X, the **positively charged** carbon in the carbocation intermediate has a trigonal planar structure.[0.5] Hence there is <u>equal probability</u> [0.5] for the Br[□] ion to attack from top and bottom of the plane, forming the two enantiomers in the <u>equimolar ratio</u>, 50:50, <u>racemic mixture</u>. [0.5]

This question was badly answered. Many students said that it was optically active and went on to explain how there are 4 different substituents on the chiral carbon atom. The question asked about a sample of X formed in the reaction above, hence one must look at the mechanism of the reaction and see if both enantiomers will be formed in the mechanism steps. The product might be chiral when present in isolation, but the resultant sample will not be optically active if present as a racemic mixture, as in this mechanism.

 $k(0.25)^{x}(0.25)^{y}$

rate1

x = 1

(c) (i) Working mathematically or qualitatively

 $\frac{rate3}{rate2} = \frac{k(1.00)^{1}(0.50)^{y}}{k(0.50)^{1}(0.25)^{y}}$ $\frac{1.12 \times 10^{-3}}{2.80 \times 10^{-4}} = 2(2)^{y}$ y = 1

 $\overline{rate2} = \frac{1}{k(0.50)^x(0.25)^y}$

 $\frac{1.40 \times 10^{-4}}{2.80 \times 10^{-4}} =$

By comparing experiment 1 and 2, when [2-methylbut-1-ene] was doubled, the rate was also doubled. Hence the order of reaction with respect to [2-methylbut-1-ene] is 1. [1]

By comparing experiment 2 and 3, when [2-methylbut-1-ene] was doubled and [IBr] was also doubled, the rate increased by 4 times. Hence the order of reaction with respect to [IBr] is 1. [1]

This was generally well done. Common mistakes include forgetting to label /state which experiments were being compared. A handful did all the working correctly but failed to conclude what order was the reaction and with respect to which reactant.

(ii) Yes it is. Both reactants are involved in the <u>slow</u> step /rate determining step [0.5] in the mechanism where <u>one molecule of iodobromide reacts with one molecule</u> <u>of 2-methylbut-1-ene.</u> [0.5]

It is essential to state that the molecularity of each reactant in the slow step is one. Merely saying that both reactants are present in the slow step does not necessary conclude that both of them are first order. Students need to understand the link between the mechanism and rate equation.

Br₂ is non-polar while there is a permanent dipole moment in the IBr molecule [0.5] since Br and I have different electronegativity. Hence Br₂ is a weaker electrophile, reaction will be slower. [0.5]

OR

Bond energy of Br-Br is stronger than that of I-Br,[0.5] more energy required to break the bond during the slow step. [0.5]

It is insufficient to simply say that there is a difference in electronegativity. Elaboration on how this difference affects the strength of the electrophile and hence the rate of the reaction is necessary. Many students could only get the part about polarity.

a) (i) Le Chatelier's Principle states that if the conditions of a system at equilibrium are changed, the position of equilibrium shifts so as to reduce that change. [1]

Students should appreciate that the LCP refers to systems at equilibrium. It is the position of equilibrium that shifts to reduce (not completely remove) any changes made to the conditions of the system.

(ii) According to Le Chatelier's Principle, for an endothermic dissolution process, the position of the equilibrium would shift to favour dissolution (shifts to the right) when temperature increases so as to offset the increase in temperature. [1]

This corresponds to a solubility curve with a positive gradient, which indicates increasing solubility with increasing temperature. [1]

Many students made generic statements or vague statements that did not answer the question directly, resulting in partial or no marks even though they may understand the underlying ideas. Students need to address the context of the question and answer the question directly.

The first mark requires the use of the LCP to explain why an increase in temperature would favour an endothermic dissolution process. The second mark requires students to link to the positive gradient of the solubility curve, which shows increasing solubility with temperature.

Many students refer to the dissolution process as a reaction, and refer to the dissolved state as products. This is incorrect, as dissolution is a physical process, NOT a chemical reaction. Students should take note to answer to the context of the question.

For data-based questions, students should make reference to the given data in their responses where possible.



(d)



(iii) $\Delta H^{e}_{solution}$ is defined for a solute being completely dissolved in an infinite volume of solvent. However, the solubility of a compound is the maximum mass of solute that can dissolve to form a saturated solution. Hence, a relationship between these two quantities may not necessarily exist. OR

The relationship between solubility of compounds and temperature should be predicted from ΔG° (which includes the effect of entropy change). [1]

This question tests students' ability to identify erroneous assumptions or flaws in argument, by clearly understanding the definitions of enthalpy terms and how they may or may not apply to a given situation.

(iv) There are 3 pairs of possible answers for this part. [1] KClO₃ / KNO₃ NH₄Cl / KCl NH₃ / KNO₃

The magnitude of $\Delta H^{e}_{solution}$ for KClO₃ (41.4) is larger than that for KNO₃ (34.9) but the curve for KNO₃ shows a greater increase in solubility with temperature increase compared to KClO₃. [1] *(replace compounds accordingly with suitable pair)*

Students should look through the enthalpy change values and compare the values with the solubility curve of the respective compound. The objective is to find a pair of compounds where the magnitude of enthalpy change value is larger for one but the change in solubility with respect to temperature ("average gradient") shown by the solubility curve is smaller than the other compound.

A number of students misinterpreted or did not follow the requirement of the question, which is to state one pair of compounds, resulting in penalty.

 $[KCl] = 8.5 \times (39.1 + 35.5) = 634 \text{ g dm}^{-3} [1] = 63.4 \text{ g per } 100 \text{ cm}^{-3}$ OR

From Fig 3.1, maximum [KC*l*] at 100° C = ~55 g per 100 cm³ = ~7.37 mol dm⁻³ [1]

From the graph, the maximum solubility of in liquid water at 100 °C is ~55 g per 100 cm³, which is below that needed. OR

A solution of 8.5 mol dm⁻³ concentration is only possible if the temperature of water is raised above 100°C [1]

Students first should realise that the units of the concentration in the graph are not the same as that stated in the question. Therefore, some sort of units conversion is required to be done for a comparison.

Once the units conversion is done, students should realise that the required concentration lies outside the bounds of the solubility curve, which ends at 100°C, above which water is no longer liquid.

(b)

Some students managed to calculate the correct concentration but then performed a wrong units conversion for the volume term, resulting in a penalty. Students should understand that 634 g dm⁻³ means there are 634 grams of solute dissolved in 1000 cm³ of water. Hence if there was 100 cm³ of this solution, there should be 63.4 grams of solute dissolved. Calculations should be performed with understanding, not simply attempting to apply formulas.

For data-based questions, students should make reference to the given data in their responses where possible. In this question, data should be quoted from Figure 3.1, not Table 3.1.

lonic bonds between K⁺ and C*l*⁻ are broken during dissolution [1] and the ions become free to move about in the solvent, resulting in more ways to distribute energy and an increase in entropy. Hence, the sign of Δ S is positive. [1]

During dissolution, some water molecules form ion-dipole interaction with the K⁺ and Cl^{-} ions [1].

These water molecules become restricted to positions around the ions, no longer able to freely move/exchange neighbours, resulting in less ways to distribute energy and a decrease in entropy. Hence, the sign of ΔS is negative for this bond formation. [1]

[1] Describe the breaking of ionic bonds between K⁺ and Cl⁻

(c)

[1] idea that ions have increased mobility, leading to positive sign for ΔS

[1] Describe water molecules forming ion-dipole interaction with K⁺ and Cl⁻ ions

[1] decrease in mobility / less degrees of freedom of movement for the <u>water</u> molecules leading to negative sign for ΔS

[-1] overall if more/less ways to distribute energy not mentioned

[-1] overall if sign (positive or negative) of ΔS was not given

This question exposed serious misconceptions and confusion by students with respect to type of compounds and the chemical bond present. Many students talk about KC*l* being molecules when it is an ionic compound, yet is able to later mention that it becomes ions. Potassium is a Group 1 metal which

almost always forms ionic compounds. These students should revise their Chemical Bonding and see their tutors if they are unable to understand this part.

Some students gave conflicting answers where the ions gain mobility in the first part and then lost mobility in the second part. The entire process occurs as a whole. The same particles cannot be gaining and losing mobility at the same time. The particles that lost mobility during the dissolution process are the water molecules that are now bonded to the ions and unable to move freely as compared to when they were not bonded to ions in liquid water.

Some students did not address the requirements of the question, which is to state and explain the sign of Δ S, resulting in penalty.

Students should refrain from spamming terms they do not fully understand. In this case "more ways to 'distribute' energy" is not the same as 'disperse energy'. Students should use explicit terms to describe the K⁺ and Cl^- ions and water

7



(d)



molecules instead of generic vague terms like "particles". Other generic terms like "increased disorder" does not explain anything. Students should explicitly explain

what type of change occurred for the ions and water molecules.

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cycle.

(iv) $Cl_2(g) + \frac{3}{2}O_2(g)$ ClO_3 $\Delta H^{\Theta}_{f} ClO_{3}(g)$ $\Delta H^{\Theta}_{hydration} ClO_3^{-1}$ $\Delta H^{\Theta}_{f} ClO_{3}(aq)$ $= -359.6 \ kJ \ mol^{-1}$ $= -98.8 \ kJ \ mol^{-1}$ $ClO_3^{-}(aq)$

[1] for correct energy cycle, with penalties for minor mistakes $\Delta H^{e_{f}} C/O_{3}^{-}(g) = \Delta H^{e_{f}} C/O_{3}^{-}(aq) - \Delta H^{e_{hydration}} C/O_{3}^{-} = -98.8 + 359.6 = +260.8 \text{ kJ}$ mol⁻¹ ecf from parts (ii) and (iii). [1]

Many students did not attempt this part as they could not obtain an answer for (d)(iii). Students should always attempt all calculation parts so they can move on to subsequent parts.

Students can also label the energy cycle using enthalpy terms instead of the numerical values for partial credit, rather than not attempting at all.

This question was not meant to be particularly challenging as the question and (d)(iii) are both asking for enthalpy changes of formation, which makes the use of elements in their standard states the obvious choice as a starting point.













Paper 3 HWA CHONG HWA CHONG
1 (a) (i) [¹/₂] 2250 and 2190
[1/2] estimated $pV = \frac{2250 + 2190}{2} = 2220$ (only 2220 accepted)
[1] $V = \frac{2220}{1250} = 1.776 \text{ or } 1.78 \text{ (allow ecf from } pV \text{ value)}$
The question says 'Use your values of pV (i.e. 2250 and 2190) to estimate the pV when $p = 1250$ '. Since 1250 kPa is the average of 1000 kPa and 1500 kPa, it is logical to simply take the average of 2250 and 2190.
(ii) [1] $V = \frac{nRT}{p} = \frac{1 \times 8.31 \times (12+273)}{1250 \times 1000} = 0.00189 \text{ m}^3 = 1.89 \text{ dm}^3 (4 \text{ sf answer is } 1.895 \text{ dm}^3)$
The question says 'if it were to behave ideally', hence use the ideal gas equation. Remember to convert p and T to SI units (Pa and K respectively). The calculated V (0.00189) would be in SI units as well i.e. m ³ .
(iii) [¹ / ₂] There are significant dispersion forces between CO ₂ molecules.
(reject 'intermolecular attractions'). [½] So the gas molecules attract more closely together.
[1] Hence the actual gas volume is smaller than that predicted by the ideal gas equation.
The estimated <i>actual</i> volume of CO ₂ (1.78 dm ³) is smaller than the predicted <i>ideal</i> volume (1.89 dm ³). The question wants you to explain 'in terms of the properties of CO ₂ molecules' – this would refer to the intermolecular attractions i.e. dispersion forces between CO ₂ molecules. Explain clearly how dispersion forces lead to V_{actual} (1.78 dm ³) < V _{ideal} (1.89 dm ³). Some students wrote that the volume of CO ₂ <i>molecules</i> is significant. This is incorrect because that would instead make $V_{actual} > V_{ideal}$. Also, the volume of CO ₂ <i>molecules</i> becoming significant will only be a concern at very high pressures; the pressure here is only about 12 atm.
(b) [1] role of Pt: heterogeneous catalyst
[$\frac{1}{2}$] The reactant molecules (alkene and H ₂) adsorb onto the active sites on the catalyst surface.
 [1] + [1] for any two effects of adsorption The adsorption process brings the reactant molecules closer together,
 weakens the covalent bonds within the reactant molecules thus lowering the activation energy for reaction, and orientates the reactant molecules correctly for reaction.
[¹ / ₂] The product molecules (alkane) then desorbs from the catalyst surface.
This is a gas phase reaction, alkene + $H_2 \xrightarrow{Pt}$ alkane. The question wants students to <i>state</i> the 'role of platinum': Pt is a heterogeneous catalyst (the spelling is <i>heterogeneous</i> not heterogenous which many students incorrectly wrote).
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Describing the 'mode of action' of Pt means to describe *how Pt works*. The key points are

- adsorption or adsorb this is an important concept for heterogeneous catalysis
- effects of adsorption
- desorption or desorb

(c)

Many students gave a general discussion about catalyst/catalysis (e.g. alternative pathway / higher percentage of reactant molecules with energy greater than or equal activation energy) which apply to homogeneous catalysts as well and does not address the 'mode of action' of Pt as a heterogeneous catalyst.

(i) [1] The C=C double bond is electron-rich and would attract electrophiles.

[1] Nucleophiles are also electron-rich and would be repelled by the C=C double bond (*or* would not be attracted to *or* cannot react with).

or Nucleophiles are attracted to a positively charged carbon / partially positively charged carbon / electron deficient carbon, but the C=C double bond does not contain such a carbon.

You just need two short sentences to address the *two* things required by the question:

- why alkenes react with electrophiles
- why alkenes don't usually react with nucleophiles

You should consider the *nature* of the C=C double bond in relation to the *nature* of electrophiles vs. nucleophiles.

(ii) [1] The electronegative O atom causes an electron-withdrawing effect on the C=C.

[1] The π electrons in the C=C delocalise to the C=O. / The π electrons delocalise across C=C–C=O. (Students must state clearly delocalise 'from where to where' to score this mark.)

[1] This causes the C=C carbon to gain a δ + charge such that it could react with the nucleophile. / This makes the C=C carbon electron deficient enough such that it could react with the nucleophile.

In the previous part, we looked at why alkenes don't usually react with nucleophiles – because nucleophiles are attracted to a δ + carbon / electron deficient carbon, but the alkene group does not contain such a carbon. So when this part shows that the alkene-carbon (in propenal) reacts with a nucleophile (^{-}CN), you should consider how the O atom and the C=O group could cause the alkene-carbon to gain a δ + charge or become electron deficient.

Some students wrote that N is more electronegative than C, so the C in \neg CN would gain a δ + charge. This is incorrect. The C in \neg CN is already printed with a – charge, you should not consider it developing a δ + charge at the same time!

Study the question's opening statement and instructions carefully. You should explain how electronegativity, electron-withdrawing effect and delocalisation 'modified the reactivity of <u>the alkene group</u>' in propenal not the reactivity of <u>-CN</u>.

The delocalisation of π electrons across C=C–C=O of propenal is illustrated by the diagram below.



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(ii) The lone electron-bond pair repulsion in NO₂ is weaker than bond pair-bond pair repulsion. [1] (or words with clear and correct explanation)

 NO_2 has a total of 3 electron groups around N (one lone electron and 2 bond pairs). The basic shape is trigonal planar with 120° bond angle. Since NO_2 has one lone electron, the repulsion of this lone electron with its bond pair is weaker than a typical bond pair-bond pair repulsion. Thus, its bond pairs experiences less electronic repulsion from one another, and the bond pairs are pushed further, increasing the bond angle to 134°.

(iii) Delocalisation of lone pair of electrons from datively bonded O atom to the double bonded O / over the O=N \rightarrow O group / over the N and O atoms / over the π system. [1]

This results in both the nitrogen-oxygen bonds in NO_2 having a bond length inbetween a single N–O and double N=O bond length / or have partial double bond character. [1]

N in NO₂ is sp² hybridised and thus there is a continuous overlap of p orbitals of the N and 2 oxygen atoms. Delocalisation of electrons result when p orbitals on 3 or more adjacent atoms overlap, forming a continuous π electron cloud. As a result, the two nitrogen-oxygen bonds have partial double bond character, and we expect its bond length to be somewhere in-between that of N–O and N=O bonds. Students are discouraged from using the term "resonance" without further elaboration on the delocalisation of electrons over the π system.

Cl

(iv) Step 1:

Step 2:



 NO_2

step 1: correct half arrows $[\frac{1}{2}]$ and correct NO_2 and Cl^{\bullet} radicals $[\frac{1}{2}]$ step 2: correct half arrows for N–Cl $[\frac{1}{2}]$ and correct Cl^{\bullet} radical + its half arrow $[\frac{1}{2}]$

By looking at the products formed in step 1, we know that N–C*l* bond will be broken. Inferring from the previous NO₂ Lewis structure drawn above, where the N atom in NO₂ has a lone electron (unpaired), we can conclude that it is a homolytic fission of N–C*l* bond to generate ${}^{\circ}NO_{2}$ and C*l* ${}^{\circ}$ radicals. For step 2, looking at the products ${}^{\circ}NO_{2}$ and C*l*₂, we will know that ${}^{\circ}NO_{2}$ is a radical. Thus homolytic fission of N–C*l* bond occur again, and the 2 C*l* ${}^{\circ}$ radicals combined to form a C*l*₂ molecule. Many students forgot to include unpaired electrons for ${}^{\circ}NO_{2}$ and C*l* ${}^{\circ}$ radicals in both steps.



(ii)

$A_p = (P_{NO})^2 (P_{O_2})$						
Usage of square brackets subrackets usually represents of $K_{\rm P}$ should be MPa ⁻¹ .)	ich as [P ₀₂] c concentratior	or [P _{NO₂} n, rathe] ² will not be er than partia	acce al pre	epted as ssure. (L	square Jnits for
	2NO	<-	O2	≓ (î	2NO2	
Initial amount / mol	146		62.8		0	
Change / mol	- 26.2		- 26.2/2		+ 26.2	

49.7

26.2

Total number of moles of gas at equilibrium = 119.8 + 49.7 + 26.2 = 195.7 [1]

119.8

$$K_{p} = \frac{(P_{NO_{2}})^{2}}{(P_{NO})^{2}(P_{O_{2}})} = \frac{\left(\frac{26.2}{195.7} \times P_{T}\right)^{2}}{\left(\frac{119.8}{195.7} \times P_{T}\right)^{2} \left(\frac{49.7}{195.7} \times P_{T}\right)} = 0.0198$$
 [1]
$$P_{T} = \frac{(26.2)^{2}}{(119.8)^{2} \left(\frac{49.7}{195.7} \times 0.0198\right)} = 9.51 \text{ MPa} \text{ [1]}$$

ecf based on wrong Kp expression in (c)(i) but with correct substitution of values

ecf for correct computation, no marks if expression is totally wrong in the various partial pressure terms

ICE table with initial, change and equilibrium amounts is highly recommended to compute the values prior to substitution in the K_p expression. Note that partial pressure of a gas is equal to mol fraction \times total pressure. We recommend students to simplify your calculations before expanding it to solve for K_{p} . As the question demands for final equilibrium pressure in MPa, you can use the value of $K_{\rm p}$ directly as it is already given in MPa⁻¹.

(i)

$$K_{\rm c} = \frac{[{\rm CH}_3 {\rm CO}_2 {\rm C}_2 {\rm H}_5][{\rm H}_2 {\rm O}]}{[{\rm CH}_3 {\rm CO}_2 {\rm H}][{\rm C}_2 {\rm H}_5 {\rm O}{\rm H}]} \quad (no \ units)$$

Equilibrium amount / mol

Unlike other aqueous systems, the Kc expression of this esterification equilibrium must include the concentration of H₂O. This is because all the four components are given as liquids, and the change in the concentration of any one component will affect the concentration of H₂O, and vice versa.

[1]

This is different from other equilibria in aqueous solutions, in which H₂O is a solvent, for example,

 $CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^{-}(aq) + H^{+}(aq)$ In these aqueous systems, the change in the concentration of the components do not change the concentration of H₂O. Also, if more H₂O is added to an aqueous

	system (during concentration aqueous syste	g dilution), the of H ₂ O remains ms, the concent	concentration unchanged be ration of H ₂ O is	of all solutes w cause H ₂ O is the not included in th	ill drop, but the solvent. In these e K_c expression.
	Please refer to	page 103 to 104	4 of Chemical E	quilibria lecture n	otes.
(ii)	Initial n(HC <i>l</i>) =	$\frac{15.00}{1000} \times 1.00 =$	0.015 mol [1]	
	no of moles, n where c = cond	= c × V centration in mol	dm^{-3} , and V =	volume of the solu	ution in dm ³ .
(iii)	Mass of HC <i>l</i> so Mass of HC <i>l</i> =	blution = 15.00 = 0.015 × 36.5 =	× 1.05 = 15.75 = 0.548 g	5g inst	
	∴ mass of H₂C ∴ initial n(H₂O	0 in HC <i>l</i> solution) = $\frac{15.202}{18}$ = 0.8	= 15.75 – 0.5 345 mol [½]	48 = 15.202 g [¹ /2]
	The mass of th The mass of th The mass of H Therefore, the total mass of s Attempts to ca because inform	The HC <i>l</i> solution is the HC <i>l</i> solution is Cl itself is calcu- mass of H ₂ O is olution. Iculate in terms of nation like the de	s the <u>sum of the</u> is calculated fro lated from its no obtained by su of the volumes v ensity of pure H	e mass of HC <i>I</i> and om the volume an o of moles (a(i) ar btracting the mas will not lead to the C <i>I</i> is not given.	$\frac{1 \text{ that of } H_2O}{d \text{ density of } HCl.}$ d density of HCl. nswer) and its M_r . s of HCl from the e required answer
(iv)	$n(NaOH) = \frac{95}{1.0}$ At equilibrium,	$\frac{.0}{.0} \times \frac{11.30}{1000} \times 0.2$ n(CH ₃ CO ₂ H) =	50 = 0.2684 m 0.2684 - 0.01	nol 5 = 0.2534 mol	高中學
	Since the NaO from the total a You also need obtain the amo	H reacted with b mount of acids. I to scale up the punt of CH ₃ CO ₂ H	oth acids, you i amounts from present in the	need to subtract th 1.00 cm ³ of mixi 'entire mixture'.	ne amount of HC <i>l</i> ture to 95 cm ³ to
(v)		CH ₃ CO ₂ H +	C₂H₅OH ≓	$CH_3CO_2C_2H_5$	+ H ₂ O
	initial amt /mol	0.438	0.601	0.205	0.845
	change /mol	-0.1846	-0.1846	+0.1846	+0.1846
	equilibrium amt /mol	0.2534	0.4164	0.3896	1.0296
	$K_{\rm c} = \frac{\frac{0.3896}{\rm V} \times}{\frac{0.2534}{\rm V} \times}$	$\frac{1.0296}{V}{\frac{V}{0.4164}}$ = 3.80	(total volume	e V = 95.0 cm³)	
	Correct change All three correct	e in moles (0.253 ct equilibrium am	34 – 0.438 = – 0 iounts <mark>[1]</mark> ecf b	0.1846) <mark>[1]</mark> ecf bas ased on 'change i	sed on biv –0.438 n mol' row

Correct value of Kc [1] ecf based on eqm amts and Kc expression

The use of an ICE table is recommended for equilibria calculations like this. Since the volume term (V) cancels out in the numerator and denominator of the K_c expression, there is no need to convert all the terms into concentration in mol dm⁻³.

(i) Mechanism:

(b)

Initiation

 $Br \xrightarrow{\bigcap} Br \xrightarrow{uv} 2Br \cdot$

Propagation

 $\begin{array}{rcl} \mathsf{Br}\bullet \ + \ \mathsf{CH}_3\mathsf{CH}_3 \ \rightarrow \ \mathsf{HBr} \ + \ \bullet\mathsf{CH}_2\mathsf{CH}_3 \\ \bullet\mathsf{CH}_2\mathsf{CH}_3 \ + \ \mathsf{Br}_2 \ \rightarrow \ \mathsf{CH}_3\mathsf{CH}_2\mathsf{Br} \ + \ \mathsf{Br}\bullet \end{array}$

Termination

- $Br \bullet + Br \bullet \rightarrow Br_2$
- $Br \bullet + \bullet CH_2CH_3 \rightarrow CH_3CH_2Br$
- •CH₂CH₃ + •CH₂CH₃ \rightarrow CH₃(CH₂)₂CH₃

All points correct [3]

For each mistake, deduct 1/2 mark.



For organic chemistry questions that ask for 'describe the mechanism', it is important to <u>write equations</u>, rather than use words, to describe each step of the mechanism.

For free radical substitution mechanism, it is also important to <u>name the initiation</u>, <u>propagation</u>, <u>and termination stages</u>, and <u>show the movement of electrons</u> by using curly arrows (at least in the initiation step).

Note that the intermediates for this mechanism are called '<u>free radicals</u>' (not carbon radicals), which are <u>neutral species</u> containing unpaired electrons. The <u>unpaired electron</u> must be indicated clearly on the <u>correct atom</u> of the radical.

The propagation stage must contain two steps, because the Br• radical consumed in the first propagation step must be regenerated in the second step. No hydrogen radical H• is produced because it is energetically less favourable to replace the broken C–H bond by a weaker C–Br bond.

The termination stage should show all three likely recombinations of radicals.

(ii) Ratio of products A : B : C : D = 6 : 1 : 2 : 3 [1]

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∴assuming all H have the same relative reactivity, percentages of products are 50.0%, 8.33%, 16.67% and 25.0% respectively [1] ecf this based on ratio obtained It is helpful to classify the hydrogen atoms in methylbutane that are replaced (substituted) to form the various bromoalkane products.

Product	Α	B	С	D
Type of H atom substituted	primary	tertiary	secondary	primary
No of equivalent H atoms	6	1	2	3

(iii) Relative reactivity of H atoms to form **B** : **C** = $\frac{93.5}{8.33}$: $\frac{6.2}{16.67}$ = 11.22 : 0.372 = 30.2 : 1

As stated in the question, the relative reactivity is the ratio of the percentage of product to the predicted percentage.

[1]

(iv) B is formed by substituting a tertiary H atom in methylbutane, i.e. B is formed via a tertiary free radical, which is a more stable intermediate than secondary and primary radicals. [1]

Answers which mention 'carbocations' are not given credit because free radical substitution does not involve any ions.

The reason why tertiary radicals are more stable than primary or secondary radicals is because the electron deficient tertiary carbon atom is stabilised by the electron donation by three alkyl groups.

So the product **B** is formed with the highest proportion among the bromoalkane products (i.e. the major product) despite the tertiary H atom being outnumbered by the primary and secondary H atoms.



3 isomers [1] 1 or 2 isomers [½]

There are only three unique constitutional isomers. A common mistake is to draw additional isomers which are the same as the others.









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