

HWA CHONG INSTITUTION 2018 C1 H2 CHEMISTRY PROMOTIONAL EXAMINATIONS SUGGESTED SOLUTIONS

Paper 1

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

Comments

The large dip between D and E shows that the electron to be removed from E is in the next quantum shell. Hence D has the electronic configuration of a noble gas ns² np⁶ and belongs to Group 18.

To do this question quickly, you should check the group number of the given 2 в elements and recall the group's valence electronic configuration.

Ga – Group 13 (ns² np¹) Se - Group 16 (ns² np⁴) Cs – Group 1 (ns¹)

Hence only Ga and Se fulfil both criteria stated. Cs does not fulfil the 1st criterion.

For this question, you will have to work out the structures for all the given species 3 D and their number of bond pairs (bp) vs number of lone pairs (lp) to deduce their shapes and bond angles.

	I		II	
А	NO ₃ -	3 bp (120º)	NO ₂ -	2 bp, 1 lp (<120°)
в	C/F₄ [−]	4 bp, 2 lp (90°)	SF ₆	6 bp (90°)
С	XeF ₄	4 bp, 2 lp (90°)	BrF ₅	5 bp, 1 lp (<90°)
D	BrO₃ [−]	3 bp, 1 lp (104°)	CIO3-	3 bp, 1 lp (106°)

For option **D**, although both have the same shape and number of bp and lp, Br is less electronegative than C/. Hence its bonding electrons are further from the central atom. Hence the bond angle is smaller as repulsion between the bond pairs is smaller.

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H has a dipole moment and hence is polar Option A: H dipole-permanent dipole interactions between the mole

dispersion forces. There is only dispersion forces between r as the molecule has no dipole moment and is non-polar. He higher boiling point (bp) than the trans isomer.

Option B: Hydrogen bonding (CH₃CH₂OH) is stronger th

H) interactions. Hence CH₃CH₂(permanent dipole point.

 CH_3C

Option C: Both molecules have hydrogen bonds present ethanoic acid has higher boiling point is because molecules dimers and this also leads to stronger dispersion forces b (refer to Chapter 2, page 95 of Foundation Topic booklet)

has intramolecular hydrogen bondin Option D: groups, hence it will have less extensive intermolecular hydr bp.

For CO₂, since both C=O bonds have dipoles of equal mag 5 в directions, they cancel each other off and resulted in overal

> For COS, the overall polarity is lower than that of COSe. That is more polar (larger dipole moment) than C=Se as it is able C=O dipole moment. This leads to a lower overall polarity of

> This also follows the trend of electronegativity decreasing and Se are all Group 16 elements), hence leading to de electronegativity values between C and the Group 16 elen less polar down the group).

r. There are permane ecules in addition ^{C/}	ent to H	
molecules of H ence the <i>cis</i> isomer h	C/	
an permanent dipo		
OH has higher boili	ing	
. One reason for w s of ethanoic acid fo between its molecule	rm es.	
ng between the two C rogen bonds and low	OH ver	
nitude and in oppos I 0 polarity.	ite	
t means that C=S bo e to cancel out more f 0.71.	of	
down the group (O, ecreasing difference ments (C=X bonds a	, S in are	
1		

To predict the graphical relationship between two variables, you can rearrange the ideal gas equation pV=nRT in the form y = mx + c, according to what is given in the x and y axis.

	Α	$p = nRT\frac{1}{v}$. Hence this is a y=kx graph where k=nRT. At
-		temperature T2, the gradient of the line should be steeper. (wrong g
2	В	pV = nRT. Since pV is always a constant and not affected by value
		this is a y=k graph where k=nRT. At T2, the line should be at a
n,		value. (wrong graph)
	С	pV = nRT. There is an inverse relationship between p and V. For a
-		volume, the pressure should be higher at T2. Hence the graph should
_		outwards. (correct graph)
	D	$V = \frac{nRT}{p}$. Hence this is a y=kx graph where k= $\frac{RT}{p}$. At T ₂ , the gradient
		line should be steeper. (wrong graph)
_		

n(NH2CONH2) = 0.150 ÷ 60 = 0.00250 mol

The volumes of gases was measured at room temperature and pressure, thus H₂O exists as a liquid.

- CO2 is an acidic gas, and will be removed by the alkaline NaOH.
- Therefore, the remaining volume consists only of N₂ gas.

 $n(N_2) = 0.00250 \times 2 = 0.00500 \text{ mol}$

Vol of gas after passing through NaOH = 0.00500 × 24 = 0.12 dm³

- = 120 cm³
- The molar mass of the sample of palladium is higher than the molar mass of 8 isotopically pure ¹⁰⁶Pd. This outcome can only occur when a heavier isotope of Pd is present in the sample. Since ¹⁰⁸Pd is the only option which fits this criteria, ¹⁰⁸Pd must be the source of the discrepancy.

Note that no calculation is required, nor should it be attempted, in this question.

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higher graph)

e of p, higher

given ld shift

of the

10

12

С

Given that ΔH^{e_r} is negative and ΔS^{e_r} is negative (because of the decrease in number of moles of gas), this reaction is feasible at low T. The -TAS* term is positive, and at high T may become larger than the negative ΔH°_{T} . 2 Students may use this formula to calculate the enthalpy change of reaction: $\Delta H_{r}^{e} = \sum \Delta H_{c}^{e}$ (reactants) $- \sum \Delta H_{c}^{e}$ (products). 3 Nickel and the reactants exist in different phases. Ni is a solid while ethanal and hydrogen are both gases in this reaction. Both the alkene and aldehyde functional groups will be reduced by

Option A: Thermal decomposition of solid CaCO3 will form CO2(g) and increase the С number of gaseous particles. Hence ΔS is positive as there are more ways that particles and the energy can be distributed in gases as compared to solids.

Option B: Sublimation causes solid CO2 to become gaseous CO2. Hence ΔS is positive.

Option C: In the process of rusting, O2 (g) reacts with solid iron to form solid iron oxide. Hence there is a decrease in the number of gaseous particles and ΔS is negative.

Option D: The reaction between NaOH and ammonium chloride produces NH₃ (g Hence ΔS is positive.

11	D	1	H ⁺ does not fulfill the criteria of a catalyst as it is con
			regenerated.
		2	Both are formed from reactants and consumed
			subsequent steps. Yes, they are intermediates of the
		3	Step 1 is the slow step, therefore it must have the
			therefore must have a lower Ea than step 1.
		4	Based on the mechanism, the slow step (step 1) indic
			is first order with respect to H2O2 and first order with

You should work out the initial pressure of O2 for each of the experiments by subtracting initial pressure of NO from total initial pressure.

Experiment	1	Ш	
Total initial pressure / atm	1.00	1.60	2
Initial pressure of NO / atm	0.40	0.40	C
Initial pressure of O ₂ / atm	0.60	1.20	1
Initial rate of reaction / atm s ⁻¹	1.08	2.16	8

hydrogen under the given conditions. The correct product should be

sumed without being

to form products in reaction. e highest Ea. Step 2

cates that the reaction respect to I⁻.

IV 2.00 \mathcal{X} 0.20 0.80 1.20 x - 0.20 8.64 1.08

From experiment I and II, the pressure of NO remained unchanged while pressure of O2 is doubled. Rate is doubled and this indicates that reaction is first order with respect to O₂.

From experiment II and III, the pressure of O2 remained unchanged while pressure of NO is doubled. Rate is quadrupled and this indicates that reaction is second order with respect to NO.

Α	Reaction is second order with respect to NO.
в	The rate equation should be rate = $kP_{NO^2}P_{O2}$.
С	To find units of k, take the units of rate divided by the units of the pre-
	terms in the rate equation: $\frac{atm s^{-1}}{atm(atm^2)} = atm^{-2} s^{-1}$.
D	Comparing experiments I and IV, when pressure of NO is halved, the remains the same. Since the order with respect to NO is 2 (this should caused the rate to decrease four times) then the pressure of O ₂ must quadrupled in order for the rate to remain the same. Hence partial pressure of O ₂ must be $0.60 \times 4 = 2.40 = x - 0.20$. Therefore $x = 2.60$.

- Since the forward reaction is exothermic, an increase in temperature will 13 A result in a lower yield as the position of equilibrium will shift towards the left to absorb the additional heat.
 - 2 The reaction has an equal amount of gas on both sides of the equation, thus a change in pressure will have no effect on the position of equilibrium.
 - $K_{\rm P}$ is temperature dependent (except when the enthalpy change of the 3 reaction is zero).
- From the information provided and graph, the following ICE table can be obtained: 14 в $P(g) + 3Q(g) \rightleftharpoons PQ_3(g)$

	Р	Q	PQ
Initial amount/ mol	0.2	0.5	0.4
Change in amount/ mol	-0.1	-0.3	+0.
Equilibrium amount/ mol	0.1	0.2	0.5

Hence,

$$\kappa_{c} = \frac{\frac{0.5}{5}}{\frac{0.1}{5} \times (\frac{0.2}{5})^{3}} = \frac{0.5 \times 5^{3}}{0.1 \times (0.2)^{3}}$$

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15 D

В

В

С

D

16



The C=O bond in the ester functional group should not be mistaken as a ketone.



Chlorogenic acid has 4 chiral centres, and 1 C=C bond which exhibits cistrans isomerism. Thus, it has 2⁵, i.e. 32, stereoisomers.



Each sp² hybridized carbon is labelled('*'), and there are 10 in total. Chlorogenic acid and cryptochlorogenic acid share the same molecular formula, and functional groups, thus they are constitutional isomers. More specifically, they are positional isomers as they differ only in the position of the ester group on the cyclohexane ring.





Cis-trans isomerism is possible at the C=C bondd marked '*'.



Carboxylic acid



- 17 Α
- A This molecule is not a possible product because it has an extra carbon atom which cannot be accounted using the mechanism of free radical

substitution. (2 / • radicals reacting in the termination step should give a molecule with 8 carbon atoms, see option B)

- This compound can be formed from the termination step involving the 2 B alkyl radicals shown below.
- This compound can be formed from the termination step shown below.
- This molecule is a typical monosubstituted product of the free radical D substitution.

18

D



Of the 3 C=C bonds, only 2 C=C bonds will yield products which are tertiary bromoalkanes. To determine the number of products which are tertiary bromoalkanes, a table may be helpful.



Addition across C=C1 gives rise to combinations 'a' and 'b', where neither are tertiary bromoalkanes.

Addition across C=C2 gives rise to combinations 'c' and 'd', where only 'c' is a tertiary bromoalkane.

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Addition across C=C3 gives rise to combinations 'e' and 'f', where only 'e' is a tertiary bromoalkane.

**all labels are arbitrary, they just help with the thought process.

Thus, the various permutations and combinations are listed below, and any product that features 'c' or 'e' is a tertiary bromoalkane.



Thus, only 6 out of the 8 possible products are tertiary bromoalkanes.

Note that you have to consider all products, major or minor. If only major products are considered, there will be no answer.

C When excess KMnO₄(aq) is used together with NaOH(aq) at low temperature, mild 19 oxidation occurs, and two -OH groups are added across each C=C bond.

> When excess KMnO4(aq) is used together with dilute sulfuric acid at high temperature, strong oxidation (or oxidative cleavage) occurs, and the C=C bond is broken.

One of the fragments created during oxidative cleavage is ethanedioic acid, which would be oxidised further in the reaction to form carbon dioxide, which is not considered an organic compound.

+ CO2

D

 NO_2 The nitration step will not produce the desired product as the major product since chlorine is 2,4-directing yet we need -NO2 to be directed to the 3-position relative to Cl.



The nitro substituent is 3-directing and the chloro substituent is 2,4directing and hence in the alkylation step, they direct the methyl group to different positions (i.e. the directing effects do not mutually reinforce one another). Thus, a mixture of products will be formed resulting in very low yield of the desired product.



The methyl and chloro substituents are 2,4-directing and hence in the nitration step, they direct the nitro group to different positions (i.e. the directing effects do not mutually reinforce one another). Thus, a mixture of products will be formed resulting in very low yield of the desired product.





In the nitration step, -CH₃ directs -NO₂ to the 4-position since -CH₃ is 2,4directing. In the chlorination step, both methyl and nitro substituents direct the chloro group to the desired position.

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Paper 2

Mrs Tay SA: S60 - S72 Mr Lim JY: S73 – S7K

1	(a)	(i)	$K_{p} = \frac{P_{C_{6}H_{12}}}{P_{C_{6}H_{6}} \cdot (P_{H_{2}})^{3}} [1]$			
			You should know how to write the	e K _p expres	sion ç	given
		(ii)	$0.0305 = \frac{0.61}{2.70 \cdot (P_{H_2})^3}$			
			$P_{\rm H_2}$ = 1.949 atm = 1.95 atm (3 s.f.) [1]		
			Substitute the value of K_p and benzene into the expression to obtain the expression the expression to obtain the expression to obtain the expression the expressio	the partial otain P _{H2} .	pres	sures
		(iii)	Initial pressure/ atm Change in pressure/ atm Equilibrium pressure/ atm	C ₆ H ₆ (g) <i>m</i> -0.61 2.70	-	3H ₂ (<i>n</i> -0.61 1.94
			From the table above, $n = 1.949 + 5.67 \times V_B = 3.779 \times 6.0$ Hence $V_B = 4.0 \text{ dm}^3$ [1]	+ 0.61 × 3 =	= 3.77	79 atm
			Accept if student works backward	ls to get da	ta tha	at fits

From the table, m = 3.31 atm and since total volume = 6.0 dm³, V_A = 2.0 dm³ $P_{C_6H_6} \times 2.0 = 3.31 \times 6.0$

 $x = P_{C_6H_6} = 9.93 \text{ atm } [1]$

The initial partial pressures of benzene, *m*, and hydrogen, *n*, used in the ICE table are the partial pressures AFTER connecting and mixing the gases but BEFORE the reaction has started. Since we have the equilibrium partial pressure of the product, C6H12(g), we know that the change in pressure of C₆H₁₂(g) is +0.61 atm. Therefore, we can find the change in pressures of C₆H₆(g) and H₂(g) using the stoichiometric ratio, and hence work backwards to find *m* and *n*. Once we are able to calculate *m* and *n*, this becomes a standard question that you are used to. Since the temperature is kept constant throughout, we can use P1V1 = P2V2 to find volume of B and subsequently the partial pressure of benzene gas before connecting the vessels.

(b) $3H_{2}(g)$

> = $6 \times BE(C=C (benzene)) + 3 \times BE(H-H) - 6 \times BE(C-C) - 6 \times BE(C-H)$ [1] $= 6 \times 520 + 3 \times 436 - 6 \times 350 - 6 \times 410$



= -132 kJ mol⁻¹ [1]

[1] for identifying correct bonds (and number) broken and bonds formed [1] for correct answer

Take note that in your Data Booklet, there are a few values given for the bond energy between 2 C atoms. In benzene, we should use the value of 520 kJ mol⁻¹ for the bond energies of the 6 C to C bonds, and not use the value of 3 C=C double bonds (610 kJ mol⁻¹) and 3 C-C single bonds (350 kJ mol⁻¹). You should draw out all the structures (and all bonds) if you cannot visualise the number of bonds broken and number of bonds formed.

(c) I K_p will not change. [1/2] The removal of the catalyst will not affect the position of the equilibrium/ catalyst only affects how fast the equilibrium is reached/ catalyst only affects the rate of the reaction/ catalyst does not affect the equilibrium composition/ Kp is only affected by temperature. [1]

II Kp will decrease. [1/2] When the temperature was increased, the backward reaction, which is endothermic, was favoured to absorb heat, therefore Kp must have decreased. [1] (ecf based on (b))

Referring to your Physical Chemistry notes (Chapter 7, page 137), you should know that the only factor that affects the value of Kp is temperature. A catalyst only increases the rate at which equilibrium is reached, but will NOT change the final equilibrium concentrations or partial pressures. Since the forward reaction is exothermic, increasing the temperature will cause backward endothermic reaction to be favoured. Kp must have decreased.

Dr Ella Sze: S60 – S6K Ms Wong HM: S70 – S72, S76 – S7K Ms Grace Chua: S73 – S75

2 (a) UV light OR heat [1]

Recall the conditions for free radical substitution.

(b) More than one bromine may be incorporated onto the alkyl substituent if excess liquid bromine is used. [1]

Vague answers like "multi-substituted / multi-brominated products may be formed" are not accepted as substitution may refer to free radical substitution or electrophilic substitution but reaction 1 refers strictly to free radical substitution.

Recall that it is difficult to control the extent of free radical substitution, multisubstituted products may be formed such as (dibromomethyl)benzene and (tribromomethyl)benzene) in this case. For free radical substitution, the use of limited liquid bromine (in other words, excess methylbenzene) can only maximise the yield of monobrominated product, it cannot prevent but can minimise multisubstitution.

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For free radical substitution, a H atom attached to an sp³-h can be substituted by Br but a H atom attached to an sp²-h will not be substituted as a H-C(sp²) bond is stronger than sp² orbital has more s character than an sp³ orbital.

Under the reagents and conditions of liquid bromine in the presence of UV light or heat, electrophilic substitution should not occur due to the absence of a strong electrophile. Br2 is a weaker electrophile compared to Br+.

(i) Name of mechanism: Electrophilic substitution [1]

 $FeBr_3 + Br_2 \rightarrow Br^+ + [FeBr_4]^-$



Mechanism [2]

Minus 0.5 mark for each of the following possible type max. of 2 marks

- Missing/incorrect equation for the generation of
- Missing/incorrect label of slow step
- Missing FeBr₃ and/or HBr
- Incorrect structure(s)
- Missing/incorrect arrows
- Missing lone pair on Br of FeBr₄⁻

In the slow step, two π electrons from the delocalised π electron cloud of methylbenzene (represented by a full arrow) is used in the formation of C-Br bond in the carbocation intermediate. This leaves four π electrons delocalised over the five overlapping p orbitals on the five sp²-hybridised carbon atoms in the ring of the carbocation intermediate.

In the fast step, the proton on the sp³-hybridised carbon in the ring is removed by the Brønsted base FeBr₄⁻. The C-H bond in the carbocation intermediate breaks in the process, providing the two electrons (represented by a full arrow) to restore the stable delocalised π electron cloud.

The stable delocalised π electron cloud is disrupted / loss of aromatic stability in the formation of the carbocation intermediate. [1]

In the slow step, two π electrons from the delocalised π electron cloud of methylbenzene (represented by a full arrow) are used in the formation of the C-Br bond in the carbocation intermediate. This means that the stability

nybridised	carbon at	om
hybridised	carbon at	om
a H-C(sp ³	³) bond as	an

5		Z
) +	FeBr ₃ +	HBr
H ₃		
of mista	akes up to	<u>a</u>
felectrop	phile Br⁺	

conferred by the six delocalised π electrons of the ring is disrupted, so the process has high activation energy and is thus the slow step.

Note that the benzene ring of methylbenzene is not made up of alternating three C=C and three C-C bond. The π electron cloud is made up of 6 delocalised π electrons due to the overlapping of six p orbitals on the 6 sp²hybridised carbon atoms in the benzene ring of methylbenzene.



Methyl substituent (-CH3) is 2,4-directing, hence 2-bromomethylbenzene bromomethylbenzene will be the major products. 3-bromomethylben: formed, will be the minor product.

(e) The methyl substituent donates electron density into the ring via inductive effect, making the ring in methylbenzene more electron rich [1] and hence methylbenzene is more prone to electrophilic attack than benzene.

Students are expected to state and explain the relative ease of methylbenzene undergoing electrophilic substitution as compared to benzene. You should approach the question by looking at the difference between the structure of methylbenzene and benzene. Merely stating that it is easier for methylbenzene to undergo reaction 2 than benzene because methyl group is activating will not earn you full credit.

Sodium benzoate is soluble in the aqueous layer due to favourable ion-dipole (f) (i) interactions formed between its ions and water molecules. [1]

> Sodium benzoate is an ionic compound with electrostatic forces of attractions between oppositely charged sodium cations and benzoate anions. In aqueous solution, ion-dipole interactions can form between sodium cations and polar water molecules, and between benzoate anions and polar water molecules.



 \oplus `О-----_I---Na` ion-dipole interaction

benzoate ion

Unreacted methylbenzene is soluble in the hexane layer due to favourable dispersion forces / instantaneous dipole-induced dipole interactions formed between non-polar methylbenzene molecules and non-polar hexane molecules.

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izei	ne,	if

Excess dilute H₂SO₄ / dilute HC/ / dilute HNO₃ [1] (ii)

Note: The word "excess" is not required. ACCEPT any mineral acid but name/formula must be specified. REJECT "dilute acid".

Sodium benzoate reacts with dilute mineral acid to gi acid-base reaction. Sodium benzoate is the proton a mineral acid is the proton donor.



- 1. Add diethyl ether to the resultant mixture and shake (iii) 2. Separate into the aqueous layer and diethyl ether la
 - a separatory funnel
 - 3. Benzoic acid will be in the diethyl ether layer
 - 4. Evaporate the solvent diethyl ether to obtain pure acid

OR

- Filter to obtain white precipitate/solid of benzoic acid [1]
- 2. Wash the white solid with small volume of cold water, and dry the white solid.

You are expected to recall that benzoic acid will form as a white precipitate from side-chain oxidation of methylbenzene under acidic conditions, hence benzoic acid is insoluble in aqueous solution. In this case, you can filter the mixture to obtain the white precipitate of benzoic acid, and the unreacted dilute mineral acid will be found in the filtrate. It is necessary to wash the white precipitate of benzoic acid with some small volume of cold water in order to wash away any dilute mineral acid. The white precipitate of benzoic acid is dried to remove water.

You can also solve this question by using the information provided that benzoic acid is soluble in diethyl ether and diethyl ether is immiscible with water. Add diethyl ether to the resultant mixture and shake to ensure the benzoic acid dissolves in diethyl ether. Since diethyl ether is immiscible with water, two layers will be formed: the organic layer with benzoic acid dissolved in diethyl ether and the aqueous layer containing the unreacted dilute mineral acid. You may find it helpful to refer to Introduction to Organic Chemistry (I) Page 31 under extraction to separate two immiscible liquids using a separating funnel.

ve benzoic a acceptor and	acid via a the dilu	an te
D ₂ H		00
) +	NaC/	T
c acid		-
e <u>aver</u> using	[1]	
white solid	of benzo	ic



OR

A tertiary radical intermediate formed from X is more stable than a primary radical intermediate formed from methylbenzene. [1]

because

stability of

The radical intermediate formed from X has inductively electron-donating methyl groups which stabilises the electron-deficient radical intermediate. [1]

You are told that X was more reactive towards side-chain oxidation than methylbenzene. You can thus infer that X can form a more stable radical intermediate than methylbenzene.

Ms Tan CS: S60 – S6C Mr Sim WH: S6D – S6G, S78 – S7K Ms Grace Chua: S6H – S77

3 (a) $\Delta G^{\oplus} = \Delta H^{\oplus} - T \Delta S^{\oplus}$ $= 2(286) - 298 (2 \times 0.163)$

= +475 kJ mol⁻¹ [1]

Since $\Delta G^{\oplus} > 0$, the **reaction is not spontaneous** and energy from the sunlight is needed to drive the reaction. [1]

Enthalpy change of formation of H₂O(l) is for the formation of 1 mole of H₂O(l) from its constituent elements as represented by $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$. The given reaction is the reverse reaction and involves 2 moles of H₂O. Hence ΔH^{\oplus} for reaction (1) = $-(-286) \times 2 = 572 \text{ kJ mol}^{-1}$ Similarly, ΔS^{\ominus} for reaction (1) = $-(-163) \times 2 = 326 \text{ J K}^{-1} \text{ mol}^{-1}$ Use the equation $\Delta G^{\oplus} = \Delta H^{\oplus} - T\Delta S^{\oplus}$ to find ΔG^{\oplus} . Remember to convert ΔS^{\oplus} to kJ K-1 mol-1.

Based on the sign of ΔG^{\ominus} , we know that the reaction is not spontaneous and hence energy must be supplied to drive the reaction. Do note that a positive ΔG^{\ominus} means the reaction is not spontaneous and vice versa. If you calculated a negative ΔG^{\ominus} but you know the reaction is not spontaneous, you should check through your calculations.

To flush out dissolved oxygen in the original CAN solution [1] (b)

Since the experiment involves measuring the amount of oxygen produced in the reaction, any dissolved oxygen in the original CAN solution must be removed to obtain an accurate value of oxygen produced. This can be done by bubbling nitrogen gas through the solution.

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To maintain a closed system or reaction vessel / to avoid oxygen from entering the system / to prevent loss of oxygen. [1]

Since the oxygen gas produced may escape, the catalyst must be added without the loss of gas in a closed system. Also, oxygen from the atmosphere must not enter the system which can affect the measurement of the concentration of dissolved oxygen produced.

Total $\eta(O_2)$ produced = $\frac{26.00}{1000} \times \frac{0.169}{32.0} = 1.373 \times 10^{-4} \text{ mol } [1/_2]$ $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

 $\eta(e^{-})$ lost by H₂O = $1.373 \times 10^{-4} \times 4 = 5.49 \times 10^{-4}$ mol = $\eta(e^{-})$ gained by Ce in CAN [1/2]

Original oxidation state of Ce = +4 [1/2]

$$\eta(\text{Ce}^{4+}) = \frac{25.0}{1000} \times 0.0220 = 5.50 \times 10^{-4} \text{ mol } [1/2]$$

Mole ratio of Ce4+ : e- gained = 1 : 1 [1/2] (or words to that effect)

Final oxidation state of Ce = +4 - 1 = +3 [1/2]

It was mentioned in the question that water was oxidized to O2 using CAN. Hence Ce in CAN was reduced. To find the final oxidation state of Ce, we need to know the number of moles of electrons transferred. This can be found by determining the number of moles of O2 produced. Do note that the total volume of the reaction mixture is 26.00 cm³ on addition of the catalyst. Based on the mole ratio of Ce⁴⁺ to e⁻, we can find the final oxidation state of Ce.

Do take note that proper statements and presentation of answer are required. Intermediate steps should be given to an appropriate number of significant figures and units should be given.

(i) Gradient = $\frac{-6.88 - (-6.22)}{-4.88 - (-4.16)}$ = 0.917 \approx 1 \Rightarrow order of reaction = 1 [1]

You need to read the context given to answer this question.

From the rate equation expressed in logarithmic form: lg(rate) = lg k' + n lg[catalyst]

n is the gradient of the straight line. n is the order of reaction with respect to the catalyst.

Do take note that the graph of lg(rate) against lg[catalyst] will be a straight line regardless of the order of reaction and the gradient gives the order of reaction. You should NOT be using the shape of the graph nor half-life (there is no time axis!) to find the order of reaction.

(c)

TOF = k'(ii) $-6.88 = \log k' + 0.917 (-4.88) \Rightarrow k' = 3.94 \times 10^{-3} s^{-1}$

```
Accept answer where students use n = 1.
Rate = k'[catalyst]
10^{-6.88} = k'(10^{-4.88})
k = 0.0100 s<sup>-1</sup>
```

rate of change of [O2] Since rate = k'[catalyst] and TOF = [catalyst] TOF = k'

Find k' by substituting the values of Ig (rate) and the corresponding value of Ig [catalyst] into the rate equation in logarithmic form.



At higher temperatures, the proportion of molecules with kinetic energy greater than or equal to activation energy increases [1].

Thus, frequency of effective collision increases and reaction rate increases. [1]

You are expected to know how to explain how a change in temperature affects the rate of reaction using a Boltzmann distribution. Pay attention to the drawing of the Boltzmann distribution and the marking points required. Refer to Section 7.3 of Reaction Kinetics lecture notes.

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(i) sp² hybridised. [1] (e)

Since the shape about the carbon atom is trigonal planar, it is sp² hybridised. Label the diagram clearly since two types of orbitals are present. Also, you are only required to draw the orbitals around carbon a.

Sp2 hybrid orbitals

Accept "sp2" and "p" as label

Side-on overlap of the unhybridised p orbital on each carbon results in (ii) partial double bond character in this carbon-carbon bond. [1]

unhybridised 2p orbital

Each ring structure is resonance stabilised (similar to benzene). When the unhybridised p orbital on carbon labelled a overlap with the carbon labelled b, an extended delocalized π electron is formed. The carbon-carbon bond between carbon labelled a and carbon labelled b will have bond strength that is intermediate between a double bond and single bond (partial double bond character).

(iii)

The difference in the cis and trans isomers is due to the position of the N.



[1]



Paper 3

Mrs J Tano: S60 – S66 Mrs Violet Teo: S67 – S6K Mr Teo ME: S70 – S79 Mrs Crystal Cheong: S7A – S7K

Le Chatelier's Principle states that when a system in equilibrium is 1 (a) subjected to a change in conditions which disturbs the equilibri position of equilibrium will shift in a way so as to reduce that cha

There are 4 points to note when writing this definition:

- 1) System must be already at equilibrium before a change is im
- 2) It is the position of the equilibrium that shifts, not the 'equ which doesn't make sense
- 3) Note that the word 'reduce' is used, which does not indicate a complete reversal of the change imposed. Any words that indicate a complete reversal will not be accepted. Some accepted synonyms are: 'counter', 'counteract', 'oppose' & 'minimise'.
- 4) Advice here is to memorise the definition and not write it in your own words as it is inevitable that you miss out the nuances in meaning of the definition.

(ii) $\Delta G_r^{\ominus} = \Delta H_r^{\ominus} - T \Delta S_r^{\ominus}$

$$\Delta G_{\rm r}^{\oplus} = -92 - (723 \text{ x} - \frac{199}{1000}) = +51.9 \text{ kJ mol}^{-1}$$

Some common mistakes:

- Failing to divide ∆S by 1000 so that the units of ∆S (given mol⁻¹) and that of ΔH (given in kJ mol⁻¹) are the same.
- Forgetting to include the negative sign for ∆S in the calculation
- Wrong units

(iii) $\Delta G_r^{\ominus} = - RT ln K$

+51900 = - 8.31 x 723 x lnK

K = 1.77 x 10⁻⁴

K very small, hence the vield of ammonia is low.

*Do not accept K < 1. Ignore units given.

Some common mistakes:
1) Failing to multiply ΔG by 1000 so that the units of ΔG is in J
required by the equation.

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2) Failing to convert the temperature to K from °C.

Inability to evaluate K (i.e. don't know how to get K from lnK)

For those students who failed to multiply ΔG by 1000, the K value obtained is 0.991 which is almost 1. This means that the ratio of reactants to products are almost the same.

(iv) Pressure between 200 - 300 atm [1]

High pressure causes the equilibrium position to move to right and increase the yield of ammonia. [1]

The most common mistake was to discuss the economic considerations for using 250 atm. While most discussions were correct, they were not awarded any marks because the question asked for the impact of the condition (i.e. pressure) on the yield. The question was not asking for why the pressure was not as high as possible.

(b)

The chlorine atom. Since the product obtained is 1-chlorobutan-2-ol, the (i)

carbocation intermediate must be either However, a secondary carbocation is more stable. Hence, the chlorine must have been added first and it must therefore be the electrophilic site OR chlorine is less electronegative than O, hence it will be electrondeficient/possess a partial positive charge. [1]

There were only 3 possible answers to this question: H, O or C/ atom.

While the H atom was the least electronegative, and hence a possible electrophilic site, it is quite clear from the product that the HOC/ molecule added across the double bond as OH fragment and C/ atom. Hence this option should be ruled out based on the product given. Otherwise if H was added to the C=C bond, then the nucleophile that attacks the carbocation should be OC/ and the product obtained will be different from what is given (CH₃CH(OC/)CH₃).

The O atom should not be chosen as it is more electronegative than the C/ atom. This can be easily deduced from its position in the periodic table relative to that of CI. This would mean that the O should carry a δ - charge while the Cl carry the δ + charge due to their difference in electronegativity.

The question asked the student to 'deduce' so a reason must be given for your choice. Many students failed to provide a reason despite selecting the correct electrophilic site.

Electrophilic addition (ii)

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on.		

[1]

[1]

mol-1 as



*Any errors, deduct 1/2 : e.g. missing/wrong δ+/ δ-, slow/fast, a wrong carbocation etc.

There were 4 possible reaction mechanisms that could be drawn:

- The attacking electrophile was the H atom on the HOC/ molecular students who chose this route, usually a dead end is reached the O-H bond should be broken and not the O-C/ bond. No were awarded for this case as the wrong carbocation was gene Marks were deducted if the O-C/ bond was broken instead of H bond.
- The attacking electrophile was the O atom on the HOC/ mo Error carry forward was allowed if the O atom was identified electrophilic site in (b)(i). The less stable carbocation was ger before the CF nucleophile attacked the carbocation to for required product.
- The attacking electrophile was the CI atom on the HOCI mo This was the correct answer.
- 4) The attacking electrophile was CI⁺. Half a mark was deducte using the wrong electrophile since there was no need to first the HOC/ molecule. Based on the comparison of electronic sectors and the sectors and the sectors and the sectors and the sectors are set of the sectors and the sectors are set of the sectors and the sectors are set of the sectors reactions of Br2 with an alkene versus Br2 with benzene, it i clear that the alkene functional group is sufficiently reactive to I to react with a molecular electrophile (HO⁵⁻⁻⁻Cl⁶⁺) which wa partially electron deficient (as signified by the δ + charge) rather the more powerful C/+ electrophile (due to stronger el deficiency as signified by the full + charge).

Some common mistakes:

- The curly arrows do not start from the lone pairs, and the arrow do not point to the atoms (but the '+' or ' δ +' charges).
- Missing dipoles on the HOC/ molecule, or on the wrong atoms
- 3) Missing product in the first step: OH⁻ was missing
- 4) Missing 'slow' in the first step

Enantiomerism. [1] (iii)

*Optical isomerism not accepted

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Geometry about central carbon atom of the carbocation is planar, allowing equal probability for OH⁻ to attack the top and bottom face. [1] This results in formation of equal amounts of both enantiomers / racemic mixture. [1]

The explanation for this part was quite poorly done due to misreading of the question. The question asked for 'how' the stereoisomers were formed. The question did not ask for why enantiomerism was possible (which was what many students explained). No credit was given for explaining how enantiomerism arose due to the four different groups attached to a carbon atom in the final product.

Some points to note:

- 1) It is the geometry about the central carbon of the carbocation that is planar. The carbocation is not necessarily always planar.
- 2) Please reference the carbocation in your answer and not some vague reference like 'molecule' or 'carbon' or for some, there was a complete lack of reference to the carbocation and the attendant geometry around the central carbon atom.
- 3) It is necessary to indicate that the attacks from the top & bottom face have equal probability. Without this statement, there is no reason why the enantiomers formed are in equal proportions.

Some common mistakes:

- 1) The question asked for type of stereoisomerism, 'enantiomerism' should be written rather than 'enantiomers'.
- Do not use 'optical isomerism'. It is not accepted.



This part was really quite incredibly poorly done. Some useful tips when attempting to join back molecular fragments after an oxidative cleavage:

1) Always count the number of carbon atoms of the original compound and compare with the number of carbon atoms of all the fragments. This will easily reveal if there were any terminal C=C bonds which then indicate that the terminal C atoms were lost as CO₂ gas in the cleavage process. For example, for compound A (with 8 C atoms), the product had only 3 carbons. This indicated that compound A should comprise 2 halves of the product to make 6 carbon atoms, while there should be another 2 C atoms missing (to make a total of 8 C atoms), meaning that there should be 2 terminal C=C bonds in the molecule. Since the two terminal C=O groups in the product should be used to join together two product molecules to form the 6membered ring (given in question), it leaves the centre C=O group to carry the terminal C=C bond.

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 CH_2CH_3

hence

[1] x 3 structures

11



Once a compound has been pieced together, always check that you 3) can get the cleavage products by breaking the C=C bonds and comparing with the given cleavage products in the question. This will enable you to check that you have not placed the C=C bonds in the wrong place on the molecule you have pieced together.



Correct ionic radii trend [1] Incorrect axes & labels -1/2 *Ignore units on axes

(c)

(i)

*Ionic radii trend can be discontinuous / Si need not be included

These were the points that the markers looked for when marking these trends:

- Both series should have downward trends. This is part of the content that needs to be remembered by students. It could also be easily ascertained by checking the data booklet. Some students were obviously confused the radii trends with the IE trends.
- The cations should be smaller than all the atoms. Hence Na⁺ ion (the largest cation) should be found below C/ (the smallest atom). It was quite common to find that C/ was even smaller than A/3+ (or Si4+) which didn't make any sense since the cations have one less quantum shell than the atoms.
- The anions should be larger than their respective atoms, with P³⁻ larger than Na. If Si was taken to form Si4-, then it should also be larger than Na.
- The horizontal axis did not need to be labelled should all the points 4) be labelled individually as some students did. Otherwise, writing 'elements', 'Period 3 elements', or 'proton/atomic number' were accepted. 'Protons' was not acceptable.

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(ii)

Across the series, atomic radii decreases as *nuclear charge increases while shielding effect remains almost the same, hence *effective nuclear charge increases and draw the valence electrons closer to the nucleus. [1]

Across both the cation and anion series, ionic radii decreases as *nuclear charge increases while shielding effect remains the same, hence *effective nuclear charge increases and draw the valence electrons closer to the nucleus. [1]

Cations are smaller than anions as they have one less quantum shell. [1]

*Required to be mentioned only once, or can be lumped together.

The part was quite well done and quite clearly many students understood the reasoning behind the trends. Those who confused the IE trends with radii trends should spend some time comparing the two explanations as they look similar.

It is necessary to discuss both the nuclear charge and shielding effect before making the conclusion that the effective nuclear charge increased. While 'number of protons' was accepted in this case, 'nuclear charge' is the correct term and should be used as such.

Marks were deducted if reference to ions were unclear (i.e. markers were unsure if the reference was to the atom or the ion. For example, the ionic radii decreased from Na to A/). Please be more specific in referencing the ions, Na⁺ to Al³⁺ would be unambiguous.

The terms 'one more valence shell', 'one more subshell' are not the same as 'one more quantum/electron shell' when explaining why the anions are larger than the cations.

Ms Sophie Bobillier: S60 – S71 Mr Sam Lee: S72 – S7K

Overall, it is clear that this question was demanding in terms of time, and despite many sections being well attempted by students, many did not manage to complete it.

It is the average energy required to break one mole of a covalent bond in 2 (a) (i) the gaseous state. [1]

> Many students understood this definition qualitatively but forgot about the quantitative aspect, that is, that one mole of a covalent bond is broken in order to get the bond energy values given. Other common omissions included the reference to the bond energy being an 'average' value, and the fact that the bond should be in the gaseous state.

B.E.(C=O) = 740 kJ mol-1 B.E.(C-N) = 305 kJ mol-1

12

B.E.(N-H) = 390 kJ mol-1 B.E.(C-C) = 350 kJ mol⁻¹ B.E.(C-H) = 410 kJ mol⁻¹ [1]

Since the C–N bond has the lowest bond energy, the C–N bond will be the bond broken by the protease. [1]

This question requires students to interpret the skeletal structure given, and to assess all the covalent bonds present, quoting the BE value for each. As such, full credit was given only when all five types of bonds were considered. The C-H bond was commonly forgotten.

Interestingly, many thought (incorrectly) that the presence of the protease enzyme meant that the strongest C=O bond would be the one that is broken. This concept is not chemically sound because, while the enzyme does facilitate bond-breaking by providing a pathway of lower activation energy, it does not mean that the enzyme is able to 'choose' to break the strongest bond.

Role of P: (Bronsted-Lowry) acid, because it donates/loses a proton (to become Q) Role of Q: (Bronsted-Lowry) base, because it accepts/gains a proton (to become P) [2]

This question was generally well answered. Students who referred to the proton (H⁺) as "an H atom" were penalised.

Adds Folin's reagent to the reaction mixture, and measure the absorbance or (C) transmittance or colour intensity over time, using a colorimeter or spectrophotometer [1].

*Reject clock method as it does not involve continuous monitoring over time.

Because the question asked how you would monitor the rate of reaction over time, only answers that suggest continuous monitoring were accepted, while clock methods that required timing the appearance of a blue colour were rejected.

Students needed to specify the variable to be measured (absorbance, transmittance or colour intensity), and, for a more complete answer, should mention the instrument that could carry out such a measurement (colorimeter or spectrophotometer). Non-technical terms such as "degree of blue colour" or "concentration of blue" were not accepted.

Careful! Colorimeter ≠ calorimeter. "color" means colour, while "calor" is a reference to heat!

Graph plotting (ii)

- Axes labels, chosen scales, axes the correct way around [1]
- Correct points and best fit curve (mark lost for straight line, or misplotted points) [1]

Manipulation of data [2]

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From graph (dotted construction lines must be shown, and values read correctly)

- time taken for the concentration of casein to fall from 0.1000 mol dm⁻ ³ to 0.0500 mol dm⁻³, t₁, is 6.4 min. (can be shown on graph)
- time taken for the concentration of casein to fall from 0.0500 mol dm-³ to 0.0250 mol dm⁻³, t₂, is 12.8 - 6.4 = 6.4 min. (can be shown on graph)

Since t₁ = t₂, t₃ is constant, therefore, reaction is first order with respect to [casein].

(the reason for concluding that it is a first order reaction must be given)

0.005-0.100

8-0 Gradient of tangent = = - 0.011875 mol dm⁻³ min⁻¹ ∴ initial rate of reaction = 1.19 × 10⁻² mol dm⁻³ min⁻¹ (to 3 s.f.)

(Tangent at t = 0 min must be drawn correctly, coordinates must be read correctly, and range accepted for initial rate was: 0.00900 - 0.0150 mol dm-³ min⁻¹)

Students are reminded to show their construction lines clearly on the graph, and to use a ruler. Unfortunately many errors were made because of misreading of students' own scales.

Values of two half-lives have to be shown, and it is recommended that students show these clearly on the graph. Simply stating that 'half-life is constant' without supporting this with values is not sufficient to earn full credit. Similarly, concluding that the reaction is first order without stating the supporting evidence is also incomplete.

The coordinates used to calculate the gradient of the tangent line should also be shown clearly on the graph, so that the examiner does not have to decipher students' working. Students who misread their own coordinates were penalised.



 $-642 = +120 + 244 + 736 + 1450 + 2(-349) + L.E.(MgCl_2)$: L.E.(MgCl₂) = -2494 kJ mol⁻¹ (exact value) or -2490 kJ mol⁻¹ (to 3 s.f.)

Cycle (must show all processes separately) [3] [1]

Correct calculation of L.E. based on labelled cycle

Since the question asked that all individual processes be shown, there were penalties for combining steps instead of keeping them separate (e.g. EA and IE should be separate).

A number of students did not know that the formula of magnesium chloride was MgC/2, opting instead for the (incorrect) MgC/. Many students also did not realise that they had to refer to the data booklet for further values, that is, the bond energy of C/-C/ and the first and second I.E. of Magnesium. Each step should result in conservation of charge, and students should therefore remember to include electrons in order to keep it balanced!

As for any energetics question, state symbols are crucial to the enthalpy data used, and hence should be included in the diagram.

Students are reminded to include units on the axis, making it easier to write values in the diagram (without units).

 $\eta CO_2 = 2.573 \div 44.0 = 0.05848 \text{ mol}$ (e) (i) \therefore mass of C in 1.176 g of **T** = 0.05848 \times 12.0 = 0.7017 g (to 4 s.f.)

= 0.702 g (to 3 s.f.) [1] η H₂O = 0.643 ÷ 18.0 = 0.03572 mol mole ratio of H atoms to water molecules = 2 : 1

∴ mass of H in 1.176 g of T = 0.03572 × 2 × 1.0 = 0.07144 g (to 4 s.f.) = 0.0714 g (to 3 s.f.) [1]

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This question part proved more difficult to students than (e)(ii). Many students were unable to even interpret what the question wanted, attempting (incorrectly) to draw ICE tables or to solve for the empirical formula directly.

What was important to realise here was that, upon burning T in excess oxygen, all of the carbon in T was converted to carbon dioxide, and all of the hydrogen in T was converted into water.

Also, note that in this context, 'mass of hydrogen' referred to the mass of the element H in T, not to the diatomic molecule hydrogen (H₂), though the same mass would be calculated even with the latter misinterpretation.

nNaOH = (22.10/1000) × 0.0700 = 1.547 × 10⁻³ mol = nHC/ remaining

 η HC/ reacted with ammonia = (80.0/1000 × 0.100) – 1.547 × 10⁻³ $= 6.453 \times 10^{-3} \text{ mol}$ [1] $= \eta NH_3$

- = ηN in 1.176 g of **T**
- $NH_3 + HC \rightarrow NH_4C/$
- ∴ mass of N in 1.176 g of T
- $= 6.453 \times 10^{-3} \times 14.0$ = 0.09034 g (to 4 s.f.) = 0.0903 g (to 3 s.f.) [1]

This part was generally well done for students who managed to reach this far.

However, there were some unreasonable equations given to account for the absorption of ammonia by HC/, though these were ignored.

Again, in this context, note that 'mass of nitrogen' referred to the mass of the element N in T, not to the diatomic molecule of nitrogen (N2), though just like in (ii) the correct mass would be calculated even with this misinterpretation.

Mass of O in 1.176 g = 1.176 - 0.7017 - 0.07144 - 0.09034 (iii) = 0.3123 g nO in 1.176 g = 0.01953 mol [1]

	С	Н	N	0
Mass in 1.176 g of T / g	0.7017	0.07144	0.09034	0.3123
No. of moles / mol	0.0584 8	0.07144	6.453 × 10 ⁻³	0.01953
Mole ratio	9	11	1	3

∴ empirical formula of T is C₉H₁₁NO₃ [1] Few students were able to reach this question part

who did forgot about the oxygen present in T.

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			1	4 🤍	

There were also many careless errors, including omission or addition of zeros after the decimal point, which affected the entire calculation of mole ratios.

Several students also found a mass ratio instead of a mole ratio, which is a big conceptual error.

Mrs Cheng ML: S60 – S70 Ms Soh SK: S71 – S7K

3	(a)	(i)	A dynamic equilibrium refers to a state where the forward and bar reactions are both taking place but at the same rate such that there is change to the concentrations of the reactants and products. [1]
			The idea that <u>both forward and backward reactions are taking</u> necessary to address the term " <i>dynamic</i> ", as opposed to a static equilibrium address the term " <i>equilibrium</i> ", the last two underlined points necessary.
			Note that because the forward and backward reactions have the sar the <u>net</u> <u>concentrations</u> of reactants and products remain unch However, the concentrations of the reactants and the products a necessarily equal!
		(ii)	Using the definition of a Dobson unit given in the question, 300 DU = 300 x 0.01 mm = 3.0 mm layer of ozone
			Since we are finding the no. of ozone molecules over an "area of 1.0 volume of column = 3.0×10^{-3} (in m) x 1.0 (in m ²) = 3.0×10^{-3} m ³
			Since we are to "assume ozone behaves ideally", we can use the idequation: PV = nRT at s.t.p., $P = 10^5 Pa (1 bar) and T = 273 K (0 °C)$ $\Rightarrow 10^5 x 3.0 x 10^{-3} = n x 8.31 x 273$ $\Rightarrow n = 0.1322 mol$ OR at s.t.p., molar volume = 22.7 dm ³ n = 0.003 x 1000 / 22.7 = 0.1322 mol
			no. of O ₃ molecules = 0.1322 x 6.02 x 10 ²³ = <u>7.96 x 10²²</u>
			Many students lost marks here due to not reading the question of enough. For example, the question asks to find "number of molecul states "standard temperature and pressure". Yet many students sto finding the number of moles of ozone and/or used the r.t.p. co instead.
			Many students also incorrectly converted lengths, area and volume. note the conversions as follows: Since 1 m = 10 dm = 100 cm = 1000 mm, $\Rightarrow 1 \text{ m}^2 = 10^2 \text{ dm}^2 = 100^2 \text{ cm}^2 = 1000^2 \text{ mm}^2$
20	18 HC	C1 H	H2 Chemistry Promotional Exam

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 $\Rightarrow 1 \text{ m}^3 = 10^3 \text{ dm}^3 = 100^3 \text{ cm}^3 = 1000^3 \text{ mm}^3$

A significant number of students failed to use the 300 DU data in their calculations.

 $O_3 + O \rightarrow 2O_2$ [1] (i) (b)

> To find the overall equation of a reaction from its mechanism, add up all the individual elementary steps in the given mechanism. Please simplify by cancelling the common species on both sides i.e. C/.

To derive the rate equation, look for the rate-determining (slow) step in the mechanism. The rate will depend on the concentrations of the reacting species in this slow step, and their orders will depend on the molecularity in this step.

For this mechanism, the first step is the slow step. Since one C/• reacts with one O3 molecule in this step, we can deduce that the rate is first order wrt C/• and first order wrt O3. Since O3 is an actual reactant in the overall reaction (i.e. not an intermediate), and C/• is a catalyst (and catalysts can appear in the rate equation!), the rate equation will be written as above.

(iii)



[1] correct shape of curve and correct axes (i.e. "energy" vs "progress of reaction")

 2 peaks, E_{a1} > E_{a2}, products energy lower than reactants [1] correct labels

- · correct species indicated as the reactants, intermediates and products
- correct indication of E_{a1}, E_{a2}, ΔH with correct arrows

Since the mechanism shows two elementary steps, there must be two peaks in the reaction pathway diagram. Since the first step is a slow step, the Ea for the first step must be larger than that of the second step. Since the question says the given reaction is exothermic, the energy level of the starting reactants must be higher than that of the final products. Next, label the axes, E_a and ΔH on the diagram.

Cl++202

progress of reaction

15

The energy levels must be clearly labelled with the correct species. The energy level of the reactants must include all reactants in the reaction (i.e. Cl., O3 and O.) and not just the reacting species in the first step. The energy level of the intermediate step must contain the products of the first step (C/O. and O₂), as well as the remaining unreacted O_•. The energy level of the products includes all products of the steps, minus the intermediates.

Please note that a "reaction pathway diagram" (see Topic 6 Kinetic p.100, Topic 5 Energetics p.4) is a different diagram from an "ener diagram" (see Topic 5 Energetics p.9).



Observe that Cl₂O₂ is "twice" that of C/O. so it is likely that the combined to form one Cl₂O₂ molecule. Hence we can deduce a sing is formed between the two O atoms in a "C/-O-O-C/" fashion.

Many students lost marks due to missing or incorrect number of electrons on O or CI. Note that each O should either have 6 dots or 6 crosses and each C/ should either have 7 dots or 7 crosses. Each O can form 2 bonds and each CI can form 1 bond and achieve octet without the need for any dative bond or double bond.

Note that it is unlikely for C/ atom to form 2 bonds and be the central atoms instead of O.

Cl. is the more effective catalyst since it results in a lower activation energy (v) for the reaction compared to •NO. [1]

Recall that the role of a catalyst is to speed up a reaction by providing an alternative reaction pathway of lower Ea (compared to without catalyst). Between two catalysts therefore, the one that provides a pathway of lower Ea would be considered more effective in its role.

Note that this question is about kinetics, and not thermodynamics. Hence be careful with your terms used: the reaction with lower activation energy is not necessarily "more energetically favorable".

- (c) The <u>boiling point of HCFCs will be lower</u> than that of CFCs since the replacement of C/ with H means fewer number of electrons and a smaller electron cloud size of the HCFC molecules, resulting in weaker intermolecular dispersion forces and less energy required to overcome these forces.
- HCFC would have a lower density than CFC since its molecular mass is smaller, assuming the number of particles occupying per unit volume is the same.

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[1/2] correct physical property [1½] correct explanation with correct conclusion (higher/lower)

From the information given, we know each CFC molecule contains one more C/ atom than a HCFC molecule (which has instead one more H atom). Notice the difference in size and no. of electrons in these two atoms (C/vs H). This will have impact on the electron cloud size of the molecule, and hence dispersion forces and boiling point.

The difficulty lies in the fact that no actual molecules are given. Hence it is uncertain whether replacing a polar C-C/ bond with a non-polar C-H bond would truly make the overall molecule more or less polar. Note that having more polar bonds does not always lead to a more polar molecule, since the net dipole moment (and polarity) of a molecule depends on its shape and the orientation of the individual dipole moments (the polar bonds).

On the other hand, having fewer polar bonds also does not always give a more polar molecule since it depends on the whether the existing dipole moments are cancelled or not. Hence arguments either way about the polarity of molecules and stronger/weaker pd-pd interactions are not given credit.

As we cannot tell for sure whether HCFC molecules are more or less polar than CFC molecules, answers about solubility are also not given credit.

Two serious misconceptions were revealed from many students' answers, so make sure you sort them out with the explanations below (if still unclear, please check with your tutors!):

- 1. Having a C-H bond does NOT mean the molecule can form hydrogen bonding with itself or water! Remember that to be able to form hydrogen bonding, the molecule must have a H attached to O, N or F (not C or other elements!).
- When discussing boiling points of simple molecular compounds, the strength of the covalent bonds within the molecule is irrelevant. To boil such compounds, we break the intermolecular forces, and NOT the covalent C-H or C–Cl bonds!
- HFC-134: (d) (i)

 $134 + 90 = 224 \Rightarrow$ molecular formula is C₂H₂F₄ [1]

This answer is easily obtained by following the instructions on how to use the code number in the question.

Note that when the question asks for molecular formula, you must write the molecular formula and not just draw the structure.

(ii)

H-C-C-F F-C-C-F

[1] correct drawing of the two isomers [1] constitutional OR positional isomerism

From the molecular formula C₂H₂F₄, we can only draw two possible constitutional isomers (same molecular formulae but different structural formulae): one with 3 F atoms on one C atom and 1 F atom on the other AND both C atoms having 2 F atoms each. Since the only difference is the positions of the F atoms, they are also called positional isomers.

Note that your structures drawn must fit the molecular formula from (d)(i). Notice that the molecular formula C2H2F4 shows the compound is saturated and hence there is no C=C bond present.

(e)

(i) 2,3,3,3-tetrafluoropropene [1]

The parent chain contains three C atoms (so stem is "prop") and the principal functional group is a C=C double bond (so suffix is "ene"), hence the name ends with "propene" (no need to indicate position of double bond since there is only one way of placing it).

There are four fluoro substituents (so "tetrafluoro"), three attached to the third carbon (carbon-1 is the one at the end with the double bond), and one attached to the second carbon (so "2,3,3,3" to indicate their positions).

This question was very poorly done. Please review the basics of IUPAC nomenclature in your organic chemistry notes.

(ii) Br₂ (aq)

HFO-1234yf: yellow-orange aqueous bromine turns colorless (or decolorises)

HFC-134a: aqueous bromine remains yellow-orange (or does not decolorise)

or

Br2 (1) or Br2/CC14

HFO-1234yf: reddish-brown Br2 turns colorless (or decolorises) HFC-134a: Br2 remains reddish-brown (or does not decolorise) or

KMnO4, dil H2SO4

HFO-1234yf: purple KMnO₄ turns colorless (or decolorises) and effervescence of colorless odorless CO2 gas

HFC-134a: KMnO4 remains purple (or does not decolorise) and no effervescence

KMnO₄, dil NaOH

HFO-1234yf: purple KMnO4 turns colorless (or decolorises) and brown ppt of MnO₂

HFC-134a: KMnO₄ remains purple (or does not decolorise) and no brown ppt

[1] correct reagent

[1/2] correct observations for HFO-1234yf

[1/2] correct observations for HFC-134a

2018 HCI C1 H2 Chemistry Promotional Exam

HFO-1234yf has a C=C double bond (alkene functional group) but HFC does not. Therefore, use distinguishing tests that react with the C=C double bond and result in observable changes i.e.

- Br₂(aq), r.t.
- Br₂(/), r.t.
- Br2/CC/4, r.t.
- KMnO₄(aq), dilute H₂SO₄, heat (*will produce CO₂ so will have effervescence of CO₂ besides decolorisation) KMnO₄(aq), dilute NaOH, heat (*will produce CO₂ but no
- effervescence since CO2 will be absorbed by NaOH (aq) and will have brown ppt of MnO₂ since in NaOH, besides decolorisation)
- KMnO₄(aq), dilute H₂SO₄, cold (*will not produce CO₂)
- KMnO₄(aq), dilute NaOH, cold (*will not produce CO₂ but will have brown ppt of MnO₂ since in NaOH besides decolorisation) are all applicable.

Experimental details like 1 cm³, test-tubes, add dropwise etc. are more for planning question in practical rather than for this question - note this question asks to "state" the reagent only. However, incorrect conditions e.g. using uv light/heat is penalized since both compounds will give the same observations (as free radical substitution would be possible with uv/heat).

Note that your answer must include the observations for BOTH compounds, not just for the one that gives the positive test. Color changes must include the original color and final color e.g. "yellow-orange bromine turns colorless", "purple KMnO4 decolorises" etc. For correct color of bromine in various states and solvents, refer to the Data Booklet p.57.

Step 1: oxidation or oxidative cleavage [1] Step 2: hydrolysis or substitution [1]

In step 1, notice that the C=C double bond is cleaved to form C=O which should remind us of the oxidative cleavage of C=C bond using KMnO₄.

In step 2, notice that H₂O is used and the -COF group became -CO₂H, producing a HF at the same time. Hence H₂O is used here to split up the original molecule like a "hydrolysis" would. Alternatively, we can see the reaction as a substitution of F in the -COF group with OH. It is in fact a nucleophilic acyl substitution. Hence answers with "electrophilic/free radical" substitution are incorrect.