H2 Chemistry TYS 2021 suggested answers

Paper 1 Answer Key

1	B		**11**	C		**21**	A
2	D		**12**	A		**22**	A
3	C		**13**	B		**23**	A
4	B		**14**	B		**24**	B
5	C		**15**	A		**25**	B
6	D		**16**	A		**26**	D
7	B		**17**	C		**27**	B
8	D		**18**	B		**28**	C
9	D		**19**	D		**29**	C
10	A		**20**	C		**30**	D

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1 Ans: **B**

Statement 1: Correct, as electrons are lighter than protons and angle of deflection $\propto \frac{\text{charge}}{\text{mass}}$

Statement 2: Correct, as electron and proton are attracted towards oppositely charged plate due to electrostatic forces of attraction.

Statement 3: Incorrect, as the beam do not travel in a straight line but curved path.

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2 Ans: **D**

Since the formula of compound is QNO_3, cation is Q^+.
Hence since there is 80 electrons, there should be 81 protons in element Q.
⇨ Element is T*l* in group 13.

As such, nucleon number = 81 + 122= 203.

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3 Ans: **C**

Statement A: Incorrect
F^+: $1s^2\ 2s^2\ 2p^4$ Al^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^1$
Electron is removed from second electronic shell of F which is much closer to the nucleus (vs from 3rd electronic shell for A*l*) hence more energy is required to overcome the stronger attraction between the nucleus and valence electron.

Statement B: Incorrect, 3rd I.E. is removing electron from gaseous X^{2+} to form X^{3+}
F^{2+}: $1s^2\ 2s^2\ 2p^3$
Ne^{2+}: $1s^2\ 2s^2\ 2p^4$
Na^{2+}: $1s^2\ 2s^2\ 2p^5$
Mg^{2+}: $1s^2\ 2s^2\ 2p^6$
Al^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^1$
A*l* 3rd IE involve electron removed from electronic shell 3 while the rest are removed from electronic shell 2.

Statement C: Correct, Na^{3+} and Ne^{2+} are isoelectronic ($1s^2\ 2s^2\ 2p^4$) with same shielding effect. Na^{3+} has a greater proton number, hence a greater nuclear charge and stronger nuclear attraction for the most loosely held electron, resulting in a greater ionisation energy value.

Statement D: Incorrect, successive I.E. involves removal of electrons from the outer filled electronic shell towards the inner filled electronic shell, and hence are **not all** taken from the same shell.

4 Ans: **B**

For element W, there is a big jump in IE between 7th and 8th IE, implying 8th electron is in inner electronic shell and hence 7 valence electrons, thus W is a group 17 element.

Since the elements are consecutive, it means X is in group 18 of the same period, n.

Y and Z are in group 1 and group 2 of the next period (n+1).

As 1st IE generally increases across a period and decreases down the group, X has the highest 1st I.E.
E.g. W is F, X is Ne, Y is Na, Z is Mg, Ne has the highest first I.E.

5 Ans: **C**

From C_2H_6 to C_2H_4 to C_2H_2,
Bond order of the C-C changes from 1 (C−C) to 2 (C=C) to 3 (C≡C).
- ⇨ Bond energy increases
- ⇨ Bond length decreases.

6 Ans: **D**

	molecule	Molecular shape	Polarity
A	BCl_3	**Trigonal planar**	**Non-polar**
B	NCl_3	**Trigonal pyramidal**	**Polar**
C	SO_2	**Bent**	**polar**
D	$CHCl_3$	**tetrahedral**	**polar**

7 Ans: **B**

	Predominant IMF	Average number of H bond per molecule
M	H-bond	2
N	Pd-pd	NA
P	H-bond	1
Q	H-bond	1

Between P and Q, Q has the higher boiling point as carboxylic acid has an additional electronegative C=O which increases the polarity of the O−H bond and strengthen the hydrogen bond, compared to that of P. Furthermore, Q also has stronger id-id due to larger electron cloud.

Hence, order of boiling point, N < P < Q < M

8 Ans: **D**

Dalton's Law of partial pressure:
$P_T = P_A + P_B + P_C + \ldots$

Where P_A, P_B, P_C is the partial pressure of gas A, gas B, gas C etc…

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9 Ans: **D**

SiO_2 is insoluble in water as it has a giant covalent lattice and has strong covalent bond, hence it remains as solid when shaken with water.

SiO_2 is an acidic oxide, hence it does not react with acidic, and remains as solid when shaken with HCl (aq). SiO_2 reacts only with hot concentrated NaOH and thus remains as solid when shaken with NaOH (aq).

10 Ans: **A**

	No. of mol	No of molecules
2.00 g of $HCOOCH_2CH_3$	$\frac{2}{74} = 0.027$	$0.027 \times 6.02 \times 10^{23} = 1.62 \times 10^{22}$
4.00g of $Br_2(l)$	$\frac{4}{158} = 0.0252$	$0.025 \times 6.02 \times 10^{23} = 1.51 \times 10^{22}$
550cm^3 of H_2	$\frac{550}{24000} = 0.0229$	$0.0229 \times 6.02 \times 10^{23} = 1.38 \times 10^{22}$
1.55×10^{22} molecules of water		1.55×10^{22}

11 Ans: **C**

$H_2SO_4 + 2\ NaOH \longrightarrow Na_2SO_4 + 2H_2O$

Amount of $H_2SO_4 = \frac{20}{1000} \times 5 = 0.1$ Amount of $NaOH = \frac{20}{1000} \times 5 = 0.1$

NaOH is limiting reagent.
Amount of NaOH = Amount of water formed

$$\Delta H_n = -\frac{q}{\text{amount of water formed}} = -\frac{(40)(4.18)(50-25)}{0.1} = -41800\ J\ mol^{-1} = -41.8\ kJ\ mol^{-1}$$

12 Ans: **A**

The rate is constant at the start as an equilibrium has been established.

At time t, as the pressure is lowered, there is a reduced frequency of effective collision, hence the rate of forward reaction decreased.

As the pressure slowly returns to atmospheric pressure, the rate of reaction is restored to the original rate of reaction.

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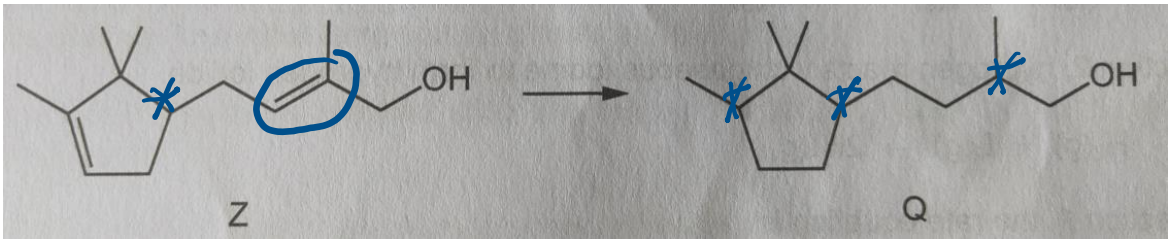
13 Ans: **B**

Statement 1: Correct, looking at the rate equation for reaction 1, as [HBr] is in the denominator of the rate equation, formation of HBr slows down the rate of reaction.

Statement 2: Correct, as the same number of moles of reactants are observed in the rate equation as well as in the overall stoichiometric equation, this implies a single step reaction.

Statement 3: Incorrect, since the order of reaction is NOT 1 wrt Br_2 in reaction 1, doubling its concentration will not double the rate of reaction.

14 Ans: **B**



- * Chiral centre
- Circled in blue: double bond that gives cis trans

Note: double bond in ring does NOT give cis trans isomers.

Total number of stereoisomer = $2^{(\text{no. of chiral C + no. of cis/trans C=C})}$

Z: no of stereoisomer = $2^{(1+1)} = 4$
Q: no of stereoisomer = $2^{(3+0)} = 8$

15 Ans: **A**

A: Correct, propagation step produces $(CH_3)_3C\bullet$ that reacts with X_2 to give $(CH_3)_3CX$.

B: Incorrect, in termination step, two radicals react to form molecule.

C: Incorrect, enthalpy change of reaction also affected by energy released when forming of C−X and H−X bonds.

For reaction with Br_2, $\Delta H = (410 + 193) - (280 + 366) = -43$ kJ mol^{-1}

For reaction with Cl_2, $\Delta H = (410 + 244) - (340 + 431) = -117$ kJ mol^{-1}

D: Incorrect, Initiation produces halogen radical, not halide ion.

16 Ans: **A**

For electrophilic addition of alkene,

pi electrons in the C=C bond of electron rich alkene are donated to the electron-deficient species (electrophile).

Statement D is incorrect, σ bond is strong while π bond is weaker.

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17 Ans: **C**

In absence of sunlight, FRS do not occur,

In presence of iron-containing catalyst (a halogen carrier), an electrophile is generated.

Since C*l* is more electronegative than Br in C*l*−Br, Br^+ electrophile is produced, and it react with benzene via electrophilic substitution.

18 Ans: **B**

Statement 1: incorrect, ionisation energy has to do with gaseous species, so it does not explain the difference in rate of reaction.

Statement 2: correct, the bond pair electron in C−Br bond experiences weaker attraction from the nucleus, leading to smaller BE of C−Br, and rate of reaction is faster.

Statement 3: correct, as the radius of bromine is bigger, the orbital size gets larger and the degree of orbital overlap gets less effective, resulting in a longer and weaker C−Br bond and thus a faster rate of reaction.

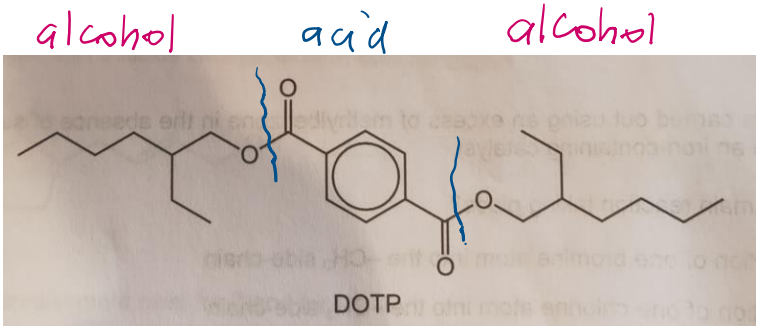
Statement 4: incorrect, proton number does not directly affect the strength of C−X bond. C−Br bond (280 kJ mol^{-1}) is weaker than C−C*l* bond (340 kJ mol^{-1}).

19 Ans: **D**

Student P: incorrect, the negative test only indicates the absence of chloroalkane, bromoalkene and iodoalkane, the compound may not be a halogenoarene. Other organic functional group also has no reaction with warm silver nitrate.

Student Q: incorrect, it may be a fluoroalkane with strong C−F bond, and hence inert towards nucleophilic substitution.

20 Ans: **C**



Ester is present in DOTP, which can be formed from the reaction between an alcohol and a carboxylic acid in the presence of hot concentrated H_2SO_4.

21 Ans: **A**

Strength of base is dependent on the availability of lone pair of electrons for donation to a proton. Since alkyl groups are electron-donating in nature, the more R group present on the amine, the electron density on N increases and the more basic the amine is.

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22 Ans: **A**

Statement 1 is correct. An amide is neutral (and not basic) because the lone pair on N is NOT available for donation to a proton due to delocalisation of the lone pair into the C=O group

Statement 2 is incorrect. Delocalisation of electrons lead to stronger C−N bond (partial double bond) but this does not affect the availability of lone pair on N to accept H^+.

Statement 1 is correct. N-methyethanamide is resonance stabilised, hence it does not gain a proton to form the protonated form (where there is NO delocalisation of electron).

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23 Ans: **A**

X must be able to undergo reduction (reaction with $LiAlH_4$) as well as acidic hydrolysis (reaction with warm HCl).

For the hydrolysis reaction, as the number of carbon remains the same **AND** the N atom is found in the same product, we can imply that the amide is in a cyclic structure.

Acidic hydrolysis of **A** produces the following salt, $HOOC{-}CH_2CH_2CH_2CH_2CH_2{-}NH_3^+Cl^-$

Note: for straight chain amide, hydrolysis of amide bond will result in two products, where the number of carbon would have decreased OR the nitrogen atom will be in another product.

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24 Ans: **B**

The lower the pK_a, the greater the extent of acid dissociation, the stronger the acid.

pK_a(2) is always higher than pK_a(1) of the same acid, as the 2nd proton is removed from a negatively charged species (electrostatic attraction between oppositely charged species), making the 2nd acid dissociation more difficult.

In a very alkaline solution (ie. at a very high pH of 13), the position of eqm for both eqm would shifts to the RHS, and therefore the species that exist at pH 13 is $H_2N{-}CH_2{-}CO_2^-$.

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25 Ans: **B**

Since oxidation of iron is ignored,

Cr in $Cr_2O_4^{2-}$ is oxidised

[O]: $8OH^- + Cr_2O_4^{2-} \longrightarrow 2CrO_4^{2-} + 4H_2O + 6e^-$
(construct half eqn using EOHC method in alkaline medium)

[R]: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Overall equation: $4OH^- + 2Cr_2O_4^{2-} + 3O_2 \longrightarrow 4CrO_4^{2-} + 2H_2O$
So 1 mol of $Cr_2O_4^{2-}$ react with 1.5 mol of O_2

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26 Ans: **D**

$E_{cell} = E(Cu^{2+}/Cu) - E(H^+/H_2)$

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $\quad E^{\ominus}(Cu^{2+}/Cu) = +0.34\ V$

$2H^+ + 2e^- \rightleftharpoons H_2$ $\quad E^{\ominus}(H^+/H_2) = 0.00\ V$

Option A is incorrect. Decreasing pressure of H_2 would cause the POE of H^+/H_2 to shift to RHS, increasing $E(H^+/H_2)$. This will lead to lower cell potential.

Option B is incorrect. Increasing $[H^+]$ would cause the POE of H^+/H_2 to shift to RHS, increasing $E(H^+/H_2)$. This will lead to lower cell potential.

Option C is incorrect. The identify of anion in Cu^{2+}/Cu half cell does not affect the position of eqm.

Option D is correct. When ethanoic acid is used, $[H^+]$ is decreased (as weak acid undergo partial dissociation), POE of H^+/H_2 to shift to LHS, decreasing $E(H^+/H_2)$. This will lead to higher cell potential.

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27 Ans: **B**

[R] $3e^- + Al^{3+} \longrightarrow Al$

Amount of $Al = \dfrac{0.27}{27.0} = 0.01$ mol

Amount of electron transferred = $0.01 \times 3 = 0.03$

$Q = n_e \times F = n_e \times L \times e$

$2904 = 0.03 \times L \times 1.6 \times 10^{-19}$

$L = 6.05 \times 10^{23}$

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28 Ans: **C**

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $\quad E^{\ominus}(Cu^{2+}/Cu) = +0.34V$

$Ni^{2+} + 2e^- \rightleftharpoons Ni$ $\quad E^{\ominus}(Ni^{2+}/Ni) = -0.25V$

At the cathode, Cu^{2+} is reduced in preference to Ni^{2+}. Increase in mass at cathode must be due to increase in mass of copper solid

$I \times t = n_e \times F$ (note : time is in seconds)

$0.50 \times 1.5 \times 60 \times 60 = n_e \times 96500$

$n_e = 0.02798$ mol

Amount of copper solid formed = $½ \times 0.02798 = 0.01399$ mol

Mass of copper solid formed = $0.01399 \times 63.5 = 0.89$g

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29 Ans: **C**

	$E^{\ominus}$
$V^{2+} + 2e \rightleftharpoons V$	–1.20 V
$V^{3+} + e \rightleftharpoons V^{2+}$	–0.26 V
$VO^{2+} + 2H^{+} + e \rightleftharpoons V^{3+} + H_2O$	+0.34 V
$VO_3^{-} + 4H^{+} + e \rightleftharpoons VO^{2+} + 2H_2O$	+1.00 V
$Zn^{2+} + 2e \rightleftharpoons Zn$	–0.76 V

Note: Zn is in excess,

Reaction between Zn and VO_3^{-} to form VO^{2+},

$E^{\ominus}_{cell}$ = +1.00 – (–0.76) = +1.76 V, reaction is feasible

Reaction between Zn and VO^{2+} to form V^{3+},
$E^{\ominus}_{cell}$ = +0.34 – (–0.76) = +1.10 V, reaction is feasible

Reaction between Zn and V^{3+} to form V^{2+},
$E^{\ominus}_{cell}$ = –0.26 – (–0.76) = +0.50 V, reaction is feasible

Reaction between Zn and V^{2+} to form V,
$E^{\ominus}_{cell}$ = –1.20 – (–0.76) = –0.44 V, reaction is NOT feasible

Therefore, zinc can reduce VO_3^{-} to V^{2+}.

30 Ans: **D**

For transition metal, **melting point** will be high due to stronger metallic bond caused by electrostatic forces of attraction between the metal cation and the greater number of delocalised electrons (both 3d and 4s electrons).

Transition elements have high **density**. Transition elements have smaller atomic size (atomic radii in *Data Booklet*) and thus more atoms per unit volume. Furthermore, the transition element atoms are of high atomic mass compared to s-block elements. Hence transition elements have greater mass per unit volume (higher density) as compared to calcium.

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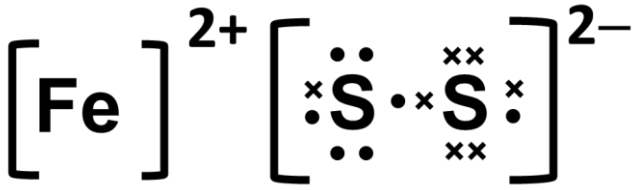
1 (a) (i) Note: A_r of sulfur isotope should be around 32.1, hence atom V and W are sulfur while X and Y are iron.

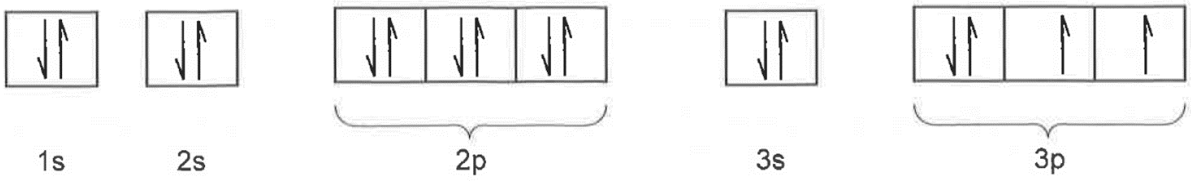
$$A_r \text{ of S} = \frac{31.97 \times 63.8 + 33.97 \times 2.8}{63.8 + 2.8} = \mathbf{32.05} \text{ (4s.f. as required by qn)}$$

1 (a) (ii) The cation is Fe^{2+} ($A_r \approx 54$) and anion is S_2^{2-} ($M_r \approx 64$)



1 (b) Sulfur atom : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

Note: for $3p^4$, electrons will occupy the 3p orbitals singly first before pairing.



1 (c) (i) First ionisation energy of sulfur is the energy required to remove **1 mol of most loosely held electron** from **1 mol of gaseous sulfur atom to form 1 mol of S^+ (g)**.

1 (c) (ii) **First ionisation energy generally increases** across Period 3 due to **increasing nuclear attraction** as a result of **increasing nuclear charge** (due to larger number of protons) and **approximately constant shielding effect** (due to same number of inner principal quantum shell electrons).

First ionisation energy of sulfur is lower than that of phosphorus as the **paired electron in one of the 3p orbital of sulfur experiences inter electronic repulsion**, hence **less energy is required to remove the most loosely held electron of sulfur** than expected.

1 (d) (i) sp hybridisation in C atom of CS_2 involves mixing of **one 2s orbital of C** and **one 2p orbital of C** to produce **two sp hybrid orbitals** arranged in a **linear geometry**. There are **two unhybridised 2p orbitals** for the carbon.

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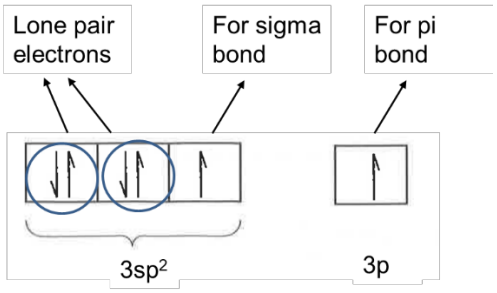
1 (d) (ii) There are **three** sp^2 hybrid orbitals and one unhybridised 3p orbital.

sp^2 hybridised S atom of CS_2 has 2 lone pairs and 2 unpaired electrons.

The two lone pairs and one unpaired electron resides at **each of the three** $3sp^2$ hybrid orbitals. The **sp^2 hybrid orbital with unpaired electron undergoes head on overlap with sp hybrid orbital of C atom** to form a sigma bond.

The **2nd unpaired electron resides at the unhybridised 3p orbital** which **undergoes side way overlap with unhybridised 2p orbital of C atom to form a pi bond.**



2 (a) (i) Down the group, the valence electron is **further away from the nucleus** (due to having more filled principal quantum shell) and **shielding effect increases** (due to greater no. of inner core electrons). These factors **outweigh the increase in nuclear charge.**

Hence, **decreasing nuclear attraction for the valence electrons** and **ionic radius increases**

2 (a) (ii) **Application question based on the context of the question**

Cs^+ has a larger cationic size as compared to Li^+, Na^+ and K^+. This larger cation allows more Cl^- anions to be arranged around it in the crystal structure as shown in the diagram.

2 (b) $$|\text{L.E.}| \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$$

Factor 1: product of the charges of cation and anion

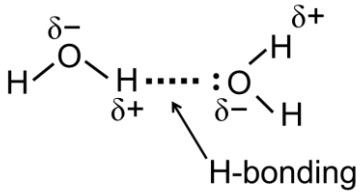
Factor 2: interionic distance

Comparing NaCl and NaF, the product of the charges of the ions are the same, it is observed that when interionic distance decreases from 0.276nm in NaCl to 0.231nm in NaF, the magnitude of lattice energy increases slightly from 771 to 902.

Comparing NaF and MgO, the product of the charges of the ions increases from 1 to 4 while the interionic distance decreases from 0.231nm in NaF to 0.205nm in MgO, it is observed that the magnitude of lattice energy MgO increases significantly from 902 to 3899.

Thus the charge product has a greater effect on the magnitude of lattice energy.

2 (c) (i)



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2 (c) (ii) Energy released when Na^+ and Cl^- ions form ion−dipole interaction with H_2O molecules is sufficient to compensate the energy required to overcome the ionic bond between Na^+ and Cl^- ions and hydrogen bonding between H_2O molecules, hence NaCl is soluble in water.

Na^+ and Cl^- ions **does not** form favourable interaction with hexane molecules, hence NaCl is **insoluble** in hexane.

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2 (d) (i) $NH_4Cl\ (s) + aq \longrightarrow NH_4^+\ (aq) + Cl^-(aq)$
There is an increase in entropy as the solid ionic lattice is dissociated into free moving aqueous ions and therefore there is an increase in the number of ways to arrange the particles and their energies.

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2 (d) (ii) Dissolution of NH_4Cl takes place readily without external input of energy. This change takes place spontaneously, thus ΔG is negative.

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2 (d) (iii) $\Delta G = \Delta H - T\Delta S$
Let $\Delta G = 0$
$\Delta H = T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{15200}{73.5} = \mathbf{207\ K}$$

This value is only theoretical as H_2O exists as solid at this temperature.
Melting point of $H_2O(s)$ is 273K (0 °C)

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3 (a) H−F bond (562 kJ mol^{-1}) is stronger than H−Cl bond (431 kJ mol^{-1}), hence HF is a weaker acid as more energy is required to dissociate HF into H^+ and F^-.

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3 (b)
$$[H^+] = \sqrt{K_a \times [HF]} = \sqrt{(5.62 \times 10^{-4} \times 0.05)} = 0.0053$$

$pH = -\lg[H^+] = \mathbf{2.28}$

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3 (c) (i) When small amount of OH^- is added, $HF + OH^- \longrightarrow F^- + H_2O$

When small amount of H_3O^+ is added, $F^- + H_3O^+ \longrightarrow HF + H_2O$

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3 (c) (ii) HCl is a strong acid while Cl^- is a very weak conjugate base that is neutral.
HCl can remove small amount of OH^- but Cl^- cannot remove small amount of H^+.
Hence it does not behave as a buffer.

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3 (c) (iii) Mixing equal volumes of NaF and HF causes the concentration to be halved.
$$[F^-]_{\text{buffer T}} = (\frac{100}{200}) \times 1.78 = 0.89\ \text{mol dm}^{-3}$$

When H^+ is added to the buffer, it reacts with F^-.

In 75.0 cm^3 of T, Amount of $F^- = \frac{75}{1000} \times 0.89 = 0.06675$ mol

Amount of H^+ added from $H_2SO_4 = 2 \times \frac{50}{1000} \times 0.1 = 0.01$ mol

Resultant amount of F^- after reaction = 0.06675 – 0.01 = 0.05675 mol

$$[F^-]_{\text{final mixture}} = \frac{0.05675}{(125/1000)} = \mathbf{0.454}\ \text{mol dm}^{-3}$$

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3 (d) (i) $pK_a = -\lg K_a$
CCl_3COOH has a smaller pK_a and hence a larger K_a than CH_3COOH.
CCl_3COOH dissociates to a larger extent than CH_3COOH.

3 (d) (ii) pK_a of CF_3COOH = 0.40 (any value smaller than 0.66)

$CCl_3COOH \rightleftharpoons CCl_3COO^- + H^+$
$CF_3COOH \rightleftharpoons CF_3COO^- + H^+$

F is more electronegative than Cl and F exert greater electron withdrawing effect and CF_3COO^- is more stable than CCl_3COO^-.
Acid dissociation of CF_3COOH is more favourable, giving rise to a larger K_a and hence a smaller pK_a value than CCl_3COOH.

3 (e) (i) Let solubility of CaF_2 be s mol dm^{-3}

	$CaF_2(s)$	$\rightleftharpoons$	$Ca^{2+}(aq)$	+	$2\ F^-(aq)$
Initial /mol dm^{-3}			0		0
Change /mol dm^{-3}	$-s$		$+s$		$+2s$
Eqm /mol dm^{-3}			s		$2s$

$K_{sp} = [Ca^{2+}][F^-]^2 = (s)(2s)^2$
$3.90 \times 10^{-11} = 4s^3$
$s = 2.13 \times 10^{-4}$
$[F^-] = 2s =$ **4.26×10^{-4}** mol dm^{-3}

3 (e) (ii) $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$ – eqm 1

In acidic solution, F^- will react with H^+ to form HF (recall 3c(i) answer), causing concentration of F^- to decrease. Based on LCP, position of equilibrium in 1 will shift to the right to partially offset this decrease, resulting in an increase in solubility of $CaF_2(s)$.

4 (a) Presence of strong C−F and C−C bond in PTFE, hence it is generally unreactive.

4 (b) In presence of UV, C−Cl bond would break to produce Cl radicals, and this would result in the depletion of the ozone layer.

4 (c) Decrease in pressure and increase in temperature.

Note: explanation is not required for "state" type of question.

4 (d) (i) it refers to an **even breaking of a covalent bond** where **one electron** from the bond **goes to each of the atom, forming radicals**.

4 (d) (ii)
A: Initiation
B: Propagation or addition
C: Propagation
D: Termination

4 (d) (iii) Free radical addition

Note: The addition reaction (break π bond) involves free radicals instead of the usual electrophile/nucleophile.

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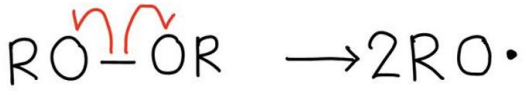
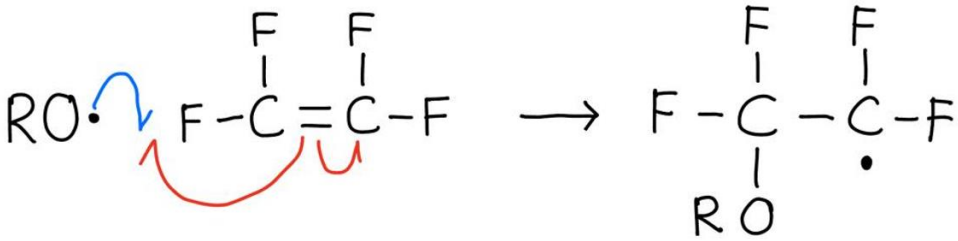
4 (d) (iv) Reaction A:



Reaction B:



Note: 2 half arrows meet to form a new bond

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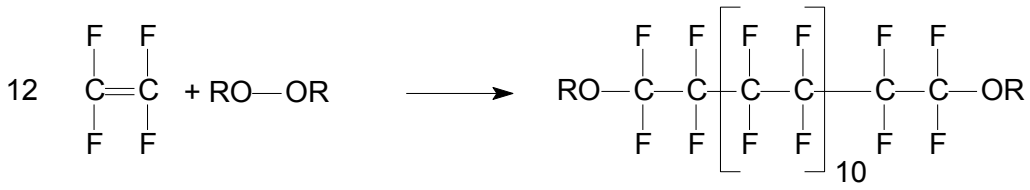
4 (d) (v) Overall equation:



Bonds broken	Bonds formed (−)
1 O−O bond (1 × 150) 12 C=C bonds (12 × 610)	2 C−O bonds between C−OR (2× 360) 23 C−C bonds between 24 CF_2 groups (23 × 350)

ΔH_{rxn} = $\sum$ *BE* of bonds broken in reactants – $\sum$ *BE* of bonds formed in products
= 7470 – 8770
= **−1300 kJ mol^{-1}**

---

4 (d) (vi) For radical **P**, the carbon radical is adjacent to the benzene ring and is resonance stabilised. Radical **P** is more stable than **Q** and **P** is preferentially formed as the major species.

Note: It is incorrect to describe radical P as having two electron donating alkyl group, as benzene is not an alkyl group.

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5 (a) It acts as a reducing agent as it reduces Fe^{3+} to Fe^{2+}.

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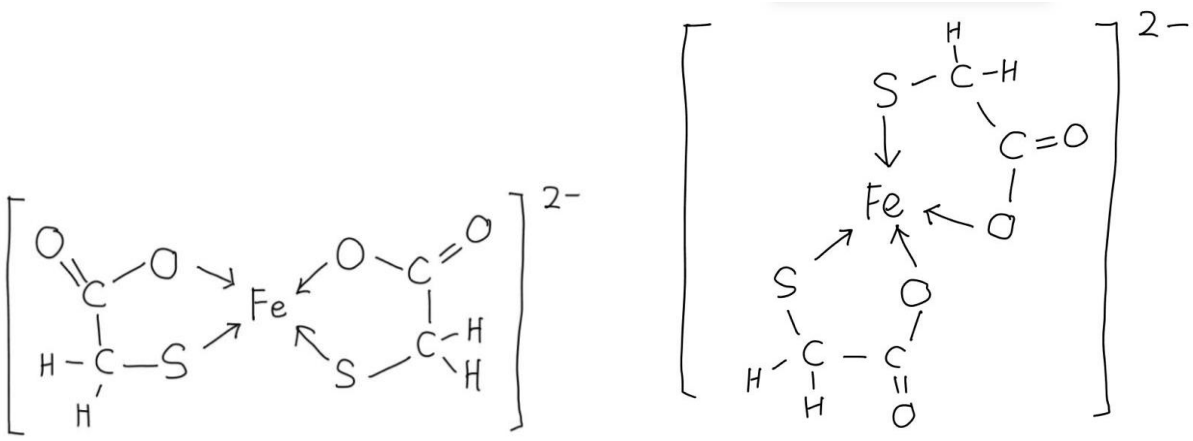
5 (b) Note: Qn state that each ligand forms two bonds with the central Fe^{2+} ion. Two ligands form a total of 4 dative bonds with Fe^{2+}. For coordination number = 4, we can draw either tetrahedral or square planar complex.



5 (c) To provide a basic medium to deprotonate thioglycolic acid and eventually allow the pink coloured complex M to be formed.

5 (d) $Fe(SCH_2CO_2H)_2 + 2NH_3 \longrightarrow [Fe(SCH_2CO_2)_2]^{2-} + 2NH_4^+$

5 (e) (i) $[Fe(H_2O)_6]^{2+} + 2NH_3 \longrightarrow Fe(OH)_2 + 2NH_4^+ + 4H_2O$

Green ppt

5 (e) (ii) Green ppt $Fe(OH)_2$ is oxidised to brown ppt $Fe(OH)_3$ in the presence of oxygen in air.

5 (f) $100cm^3$ of diluted solution contains 10.0ppm of Fe^{2+}
Conc of Fe^{2+} in 100 cm^3 of diluted solution
= 10 mg of Fe^{2+} in 1000 cm^3 solution
= 10×10^{-3} g of Fe^{2+} in 1 dm^3 solution.

$[Fe^{2+}]$ in 100 cm^3 diluted solution = $\frac{10 \times 10^{-3}}{55.8}$ = 0.0001792 mol dm^{-3}

Amount of Fe^{2+} in 100 cm^3 diluted solution = Amount of Fe^{2+} in 10 cm^3 of withdrawn sample.
= $\frac{100}{1000} \times 0.0001792 = 1.792 \times 10^{-5}$ mol

Amount of Fe^{2+} in 250 cm^3 volumetric flask = $\frac{250}{10} \times 1.792 \times 10^{-5} = 4.480 \times 10^{-4}$ mol

Amount of $Fe(NH_4)_2(SO_4).6H_2O$ = Amount of $Fe^{2+} = 4.480 \times 10^{-4}$ mol

Mass of $Fe(NH_4)_2(SO_4).6H_2O = 4.480 \times 10^{-4}$ mol $\times$ 392.0 = **0.176 g**

5 (g) Amount of **Y** = $\frac{1}{139}$ = 7.194×10^{-3} mol

Amount of **Y** : Amount of Fe
= $7.194 \times 10^{-3} : 2.40 \times 10^{-3}$
= 3 : 1

Since it is an octahedral complex, 3 ligands of **Y** forms 6 dative bonds with Fe cation
Each Ligand **Y** forms 2 dative bonds with each central iron.

Amount of **Z** = $\frac{1}{560}$ = 1.786×10^{-3} mol

Amount of **Z** : Amount of Fe
= $1.786 \times 10^{-3} : 1.78 \times 10^{-3}$
= 1 : 1

Since it is an octahedral complex, each ligand of **Z** forms 6 dative bonds with Fe cation

6 (a) (i)

Element	Cr	H	N	S	C*l*	O
Mass in 100g	19.4	5.6	26.1	11.9	13.2	23.8
A_r	52.0	1.0	14.0	32.1	35.5	16.0
No. of mol	0.373	5.6	1.86	0.371	0.372	1.488
Mol ratio	1	15	5	1	1	4

Empirical formula: $CrH_{15}N_5SClO_4$
Since molar mass = 268.6

Molecular formula: n($CrH_{15}N_5SClO_4$) = 268.6
n=1
Molecular formula: $CrH_{15}N_5SClO_4$

6 (a) (ii) Coordination number = 6

Shape: Octahedral bond angle: 90 °

6 (a) (iii) $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$

6 (a) (iv) White ppt is observed upon addition of silver nitrate
=> Free Cl^- (aq) is present. i.e. Cl^- is not dative bonded to cation (not a ligand)

6 ligands in the complex, thus five NH_3 and one SO_4^{2-} as ligands.
Identity of cation: $[Cr(NH_3)_5(SO_4)]^+$

6 (b) (i) Ligand exchange is a reversible reaction. Since position of equilibrium for eqn 6.1 lies on the RHS in the cell, we can conclude that cells in our body has much higher concentration of water than blood, thus ligand exchange between H_2O and Cl^- in Cisplatin takes place to a much greater extent in cells in order to partially offset the high concentration of H_2O.

6 (b) (ii) Presence of a lone pair of electrons to form a dative bond with the metal cation Pt^{2+}.

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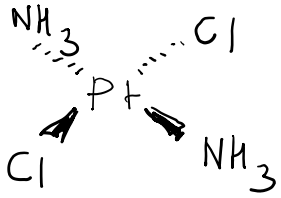
6 (b) (iii)



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6 (b) (iv) Note: Last paragraph in Q6(b) states that two specific ligands found at a specific distance from each other on the DNA molecule substitutes the two H_2O ligands.

The chloride ligands which water molecules exchange with is 180 ° apart in transplatin instead of 90° apart as seen in cisplatin.
The two H_2O ligands cannot be substituted with the two specific ligands found at a specific distance from each other on the DNA molecule due to wrong orientation or different 3−D shape.

Note: This is similar concept as to why one enantiomer may interact with enzyme but its mirror image cannot interact with enzyme due to wrong orientation.

---

6 (c) **D** is symmetrical and has no effect on plane polarised light.
C and **E** and mirror images (enantiomers) rotate plane-polarised light to the same angle but in opposite direction.
(FYI: **D** is trans isomer while **C** and **E** are cis isomer. *based on whether the same groups (Cl^-) ligands) are opposite or adjacent to each other)

Before heating, isomer **D** has an internal plane of symmetry, thus not optically active, no effect on plane polarised light.

After heating, isomers **C** and **E** are without internal plane of symmetry, hence they are optically active. However, they are formed equal amount, this means that the effect on plane polarised light by each isomer is same magnitude but opposite direction. Thus, solution exhibits net zero optical activity.

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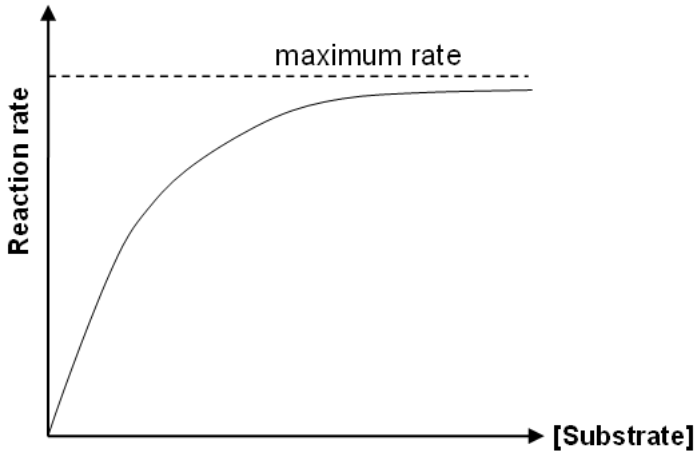
1 (a) (i) $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

$E_{cell} = E(I_2/I^-) - E(S_4O_6^{2-}/S_2O_3^{2-})$
$= +0.54 - (+0.09)$
$=$ **+0.45 V**

1 (a) (ii) [R] $Cl_2 + 2e^- \longrightarrow 2Cl^-$
[O] $5H_2O + S_2O_3^{2-} \longrightarrow 2SO_4^{2-} + 10H^+ + 8e^-$ (construct the half equation using EOHC)

Overall eqn : $4Cl_2 + 5H_2O + S_2O_3^{2-} \longrightarrow 2SO_4^{2-} + 10H^+ + 8Cl^-$

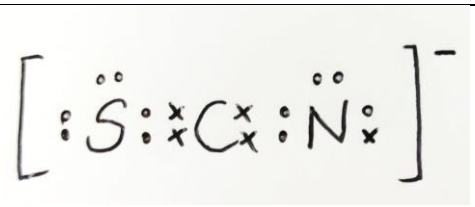
1 (b)



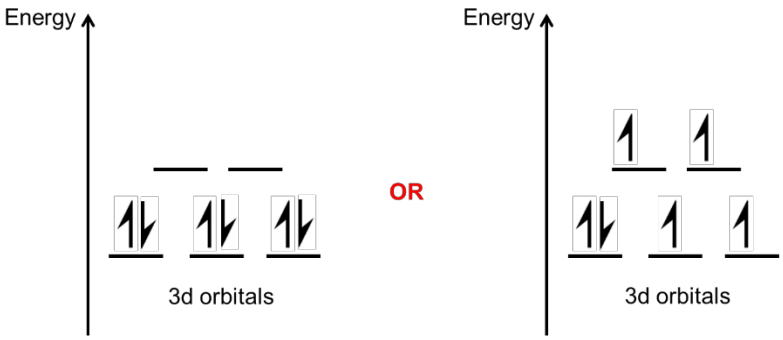
At low [substrate], not all of the active sites are occupied. The rate of reaction increases proportionally with substrate concentration.

At high [substrate], all the active sites of the enzyme are saturated. Any increase in the substrate concentration cannot increase the rate of reaction. The rate of reaction is not affected by the substrate concentration.

1 (c)



1 (d) (i) **Note: Fe^{2+} is [Ar] $3d^6$, either of the following distribution of electrons are acceptable**



1 (d) (ii) Different ligands (H_2O vs O_2) cause different degree of repulsion with the electrons in the 3d orbitals, splitting the 3d orbitals with different energy gaps.

A different wavelength of the visible light is absorbed during d-d transition.

A different complementary colour is observed.

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1 (d) (iii) $Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$

At eqm, [Hb] = $[Hb(O_2)_4]$ due to 50% conversion of Hb

$$K_c = \frac{Hb(O_2)_4}{[Hb][O_2]^4} = \frac{1}{1(7.82 \times 10^{-3})^4}$$

$$= \underline{\mathbf{2.67 \times 10^{8}\ mol^{-4}\ dm^{12}}}$$

---

1 (e) **G**: $CuSO_4$ (aq)
H: Cu
I: $Cu(OH)_2$
J: $[Cu(NH_3)_4]^{2+}$(aq)
K: $Cu(NO_3)_2$

$Cu_2SO_4 + aq \longrightarrow \underset{\mathbf{G}}{CuSO_4} + \underset{\mathbf{H}}{Cu}$ **[disproportionation of Cu^+]**

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons \underset{\mathbf{I}}{Cu(OH)_2}(s)$

$\underset{\mathbf{G}}{[Cu(H_2O)_6]^{2+}}(aq) + 4NH_3(aq) \rightleftharpoons \underset{\mathbf{J}}{[Cu(NH_3)_4]^{2+}}(aq) + 6H_2O(l)$

$\underset{\mathbf{H}}{Cu} + 4HNO_3 \longrightarrow \underset{\mathbf{K}}{Cu(NO_3)_2} + 2NO_2 + 2H_2O$

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2 (a) (i) Volume of the gas particles are negligible compared to the volume of the container.

There are negligible intermolecular forces between the gas particles.

Collisions between gas particles are perfectly elastic.

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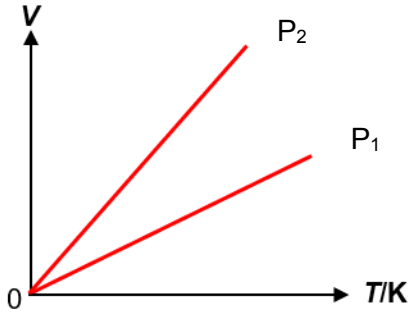
2 (a) (ii)



$pV = nRT$

$V = \frac{nR}{P}(T)$

Gradient = $\frac{nR}{P}$ where $P_1 > P_2$

---

2 (b) $pV = nRT$

$p = \frac{m}{M_r}RT$

$pM_r = \frac{m}{V}RT$

$(700)(44) = \frac{m}{V}(8.31)(-65+273)$

Density = 17.8 g m^{-3}

= $\underline{\mathbf{1.78 \times 10^{-5}\ g\ cm^{-3}}}$

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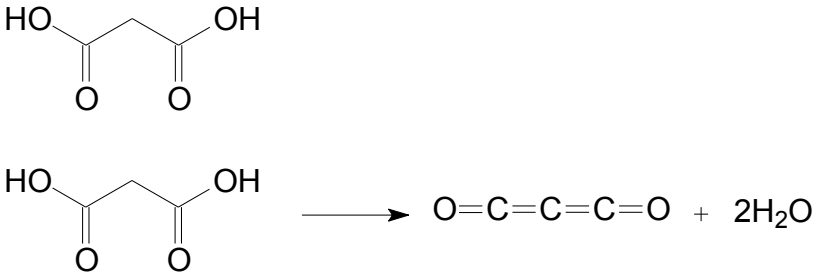
2 (c)



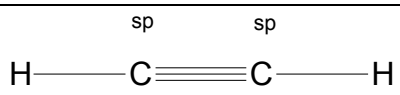
2 (d) $8CO_2 + 46\ H_2O \longrightarrow (CO_2)_8(H_2O)_{46}$

Amount of $(CO_2)_8(H_2O)_{46} = \dfrac{650 \times 1000}{1180} = 550.85$ mol

Amount of $CO_2 = 8 \times 550.85 = 4406.8$ mol

Volume of $CO_2 = 4406.8 \times 24 =$ **1.06×10^5 dm^3**

2 (e) (i)



It is linear w.r.t. to each C atom (2 bond pair regions + 0 lone pair)

- σ bond formed from the head on overlap between sp orbital of C and 1s orbital of H
- σ bond formed from the head on overlap between sp orbital of both carbons
- π bond formed from the side way overlap between p_x orbital of both carbons
- π bond formed from the side way overlap between p_y orbital of both carbons

2 (e) (ii) $K_p = \dfrac{(P_{C2H2})(P_{H2})^3}{(P_{CH4})^2}$

	$2\ CH_4$	$\rightleftharpoons$	C_2H_2	$+\ 3\ H_2$
I /mol	0.800		0	0
C /mol	-0.48 (60% of 0.800)		$+(\frac{1}{2} \times 0.48)$	$+(\frac{3}{2} \times 0.48)$
E /mol	0.32		0.24	0.72

Note: $P_{gas\ A} = \dfrac{n_{gas\ A}}{n_{total\ gas}} \times P_{total}$

Total mol of gas = 0.32 + 0.24 + 0.72 = 1.28 mol

$P_{CH4} = \dfrac{0.32}{1.28} \times 2.50 \times 10^6 = 6.25 \times 10^5$ Pa

$P_{C2H2} = \dfrac{0.24}{1.28} \times 2.50 \times 10^6 = 4.69 \times 10^5$ Pa

$P_{CH4} = \dfrac{0.72}{1.28} \times 2.50 \times 10^6 = 1.406 \times 10^6$ Pa

$K_p = \dfrac{(1.406 \times 10^6)^3\ (4.69 \times 10^5)}{(6.25 \times 10^5)^2}$

= **3.34×10^{12} Pa^2**

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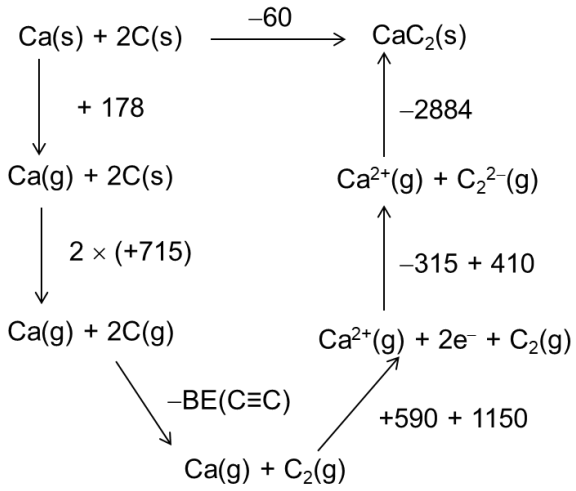
2 (f)



By Hess's law,
−60 = 178 + 2×715 −BE(C≡C) + 590 + 1150 −315 + 410 −2884
BE(C≡C) = **619 kJ mol^{-1}**

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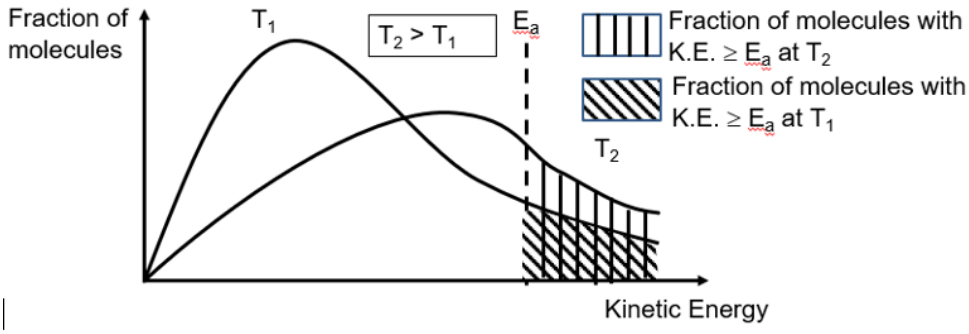
3 (a)



When temperature of the reaction increases, average kinetic energy of the reacting molecules increases.

The fraction of molecules with K.E. ≥ E_a increases as shown in the Boltzmann distribution.

The frequency of effective collisions increases hence rate constant increases.

---

3 (b) **Order of Reaction:** the power to which the concentration of a reactant is raised to in an experimentally determined rate equation.

Rate constant: Proportionality constant relating rate of reaction to concentration of reactant in an experimentally determined rate equation.

Or

Rate = k[A]^x[B]^y
where x is the order of reaction to A and y is the order of reaction to B in an experimentally determined rate equation.
k is the rate constant

---

3 (c) (i) Step 1: Rate = $k_f[O_3]$

Step 2: Rate = $k_2[O_3][O]$

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3 (c) (ii) $(Rate)_{forward} = (Rate)_{backward}$

$k_f[O_3] = k_r[O][O_2]$

$$[O] = \frac{k_f\,[O_3]}{k_r\,[O_2]}$$

3 (c) (iii) For the slow step,

Rate = $k_2[O_3][O]$

$$= k_2[O_3] \times \frac{k_f\,[O_3]}{k_r\,[O_2]}$$

$$= \frac{k_2 \times k_f}{k_r} \times \frac{[O_3]^2}{[O_2]}$$

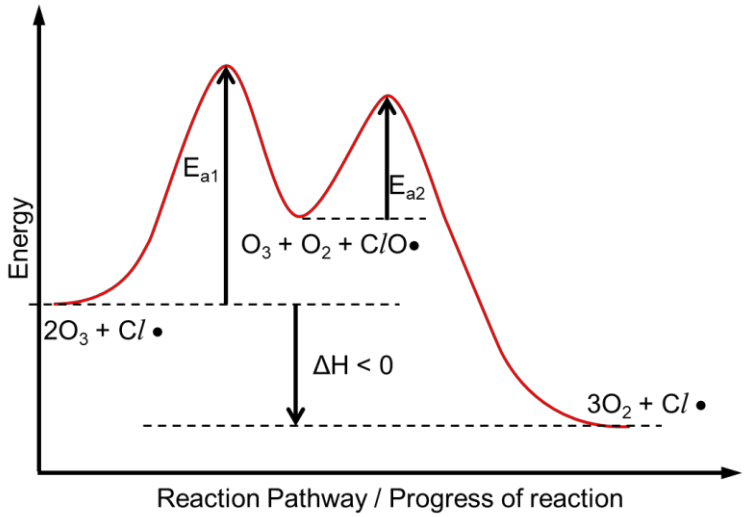
Order of reaction w.r.t. $[O_3]$ = 2

Order of reaction w.r.t. $[O_2]$ = −1

Overall order of reaction = 1

3 (d) (i) C*l*• is a catalyst as it is reacted in step 1 and regenerated in step 2.

3 (d) (ii)



Note: The reactants are $2O_3$ + C*l*•,
in step 1, only 1 mol of O_3 and C*l*• reacted to give the intermediates, another mol of O_3 is unused. (Similar to how we balance the atoms in the energy cycle).

Step 1 OR step 2 could be the slow step, overall reaction is exothermic (as stated in qn)

3 (e) (i) **Adsorption** of H_2 and **A** onto the surface of the Ni catalyst. Weak interactions form between the reactants and catalyst.

Reaction at the surface occurs as reactant molecules are brought closer together and existing interactions (covalent bonds) in the reactant molecules are weakened. (lower E_a)

Desorption of products from the Ni surface to regenerate the catalyst.

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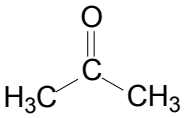
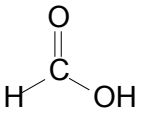
3 (e) (ii)

Information	Deductions
$C_{10}H_{18}O + 2H_2 \longrightarrow C_{10}H_{22}O$ **A** **B**	**A** undergoes **reduction** to give **B**. **A** contains 2 unsaturated functional group (**C=C or C=O**) **B** contains alkane or alcohol
Compound **C** contains one chiral centre.	**C** contains a C atom bonded to 4 different groups
$C_6H_{10}O_5 + \text{conc } H_2SO_4 \longrightarrow C_6H_8O_4$ **C** **F**	**C** undergoes **elimination of H_2O** to give **F** **C** contains alcohol **F** contains C=C
F as a mixture of two stereoisomers but contains no chiral centre	**F** exists as cis-trans isomers, Two different groups attached to each C of the C=C.
C does not react with $K_2Cr_2O_7$	**C** is a tertiary alcohol (since we confirmed C is alcohol from its reaction with conc H_2SO_4)
D reacts with alkaline I_2	**D** undergoes oxidation with I_2 **D** contains methyl carbonyl group (**D** must contain C=O as shown in Fig 3.1)
D does not react with Fehling's reagent	**D** does not contain aldehyde
C, E and F reacts with Na_2CO_3	Acid-carbonate reaction **C**, **E** and **F** contains −COOH
$C_{10}H_{18}O + O_3 \longrightarrow C_6H_{10}O_5 + CH_2O_2 + \mathbf{D}$ **A** **C** **E**	Compound **A** contains 2 C=C Compound **D** contains 3 carbon atoms.

 Compound **D**	 Compound **E** (CH_2O_2)

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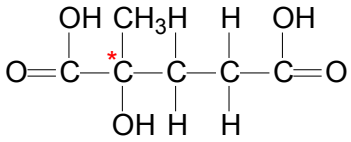
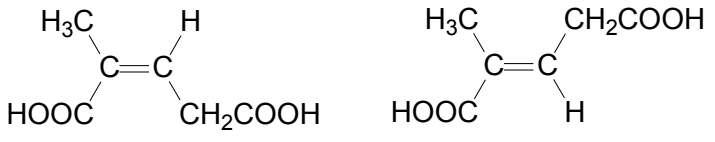
3 (e) (ii) There are a few possible structures of **C** and subsequent structures for **A**, **B** and **F**.

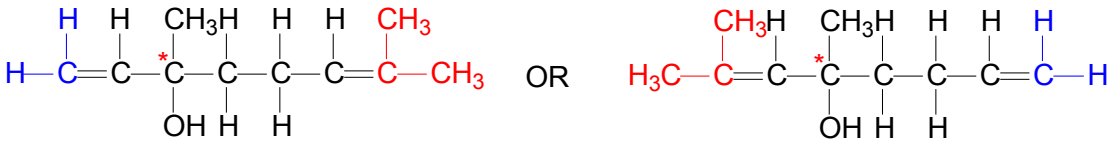
Option 1



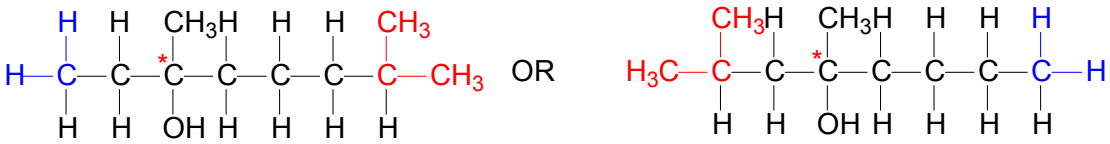
Compound **C** ($C_6H_{10}O_5$)



Compound **F** ($C_6H_8O_4$) **(cis and trans isomers)**

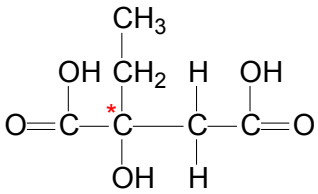


Compound **A** ($C_{10}H_{18}O$)



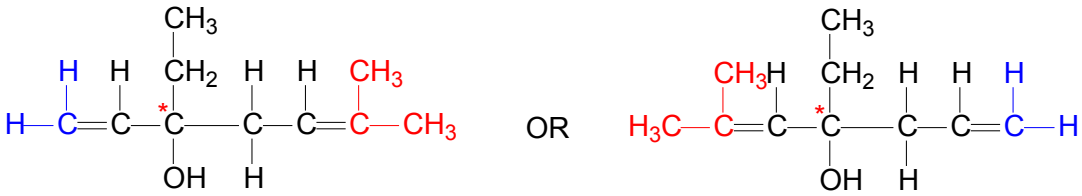
Compound **B** ($C_{10}H_{22}O$)

Option 2

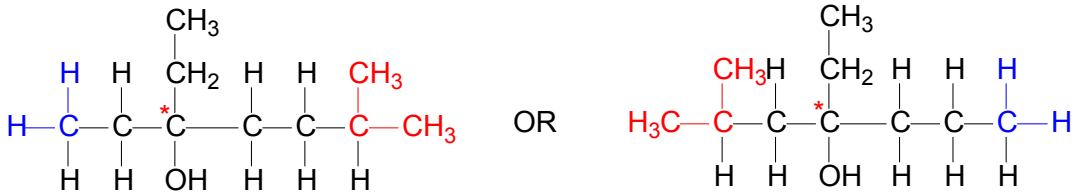


Compound **C** ($C_6H_{10}O_5$)

Compound **F** ($C_6H_8O_4$) **(cis and trans isomers)**



Compound **A** ($C_{10}H_{18}O$)



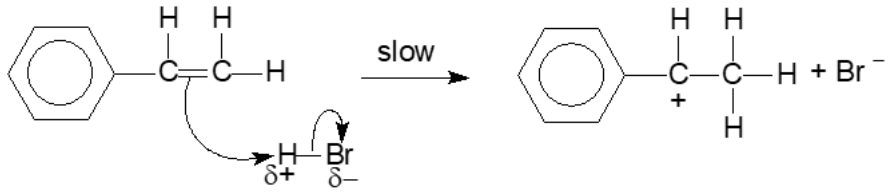
Compound **B** ($C_{10}H_{22}O$)

4 (a) $2\,HX\,(g) \longrightarrow H_2\,(g) + X_2\,(g)$

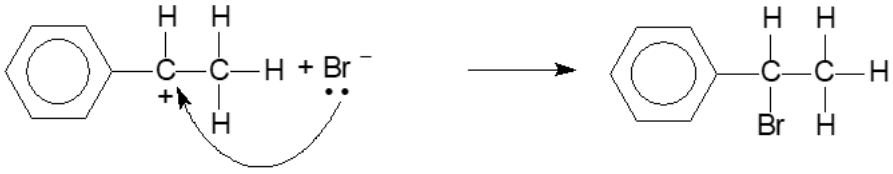
H−X bond is broken during the thermal decomposition of H-X. Down the Group, bond energy of H−X decreases from H−C*l* (431 kJ mol^{-1}) to H−I (299 kJ mol^{-1}), and less energy is needed to overcome the H−X bond.
Thus, the thermal stability of the hydrogen halides decreases down the Group.

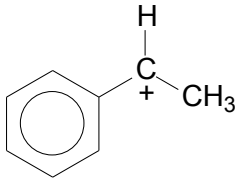
4 (b) Electrophilic Addition

step 1

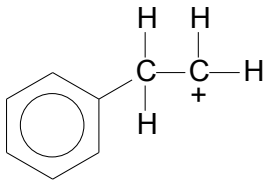


step 2





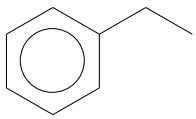
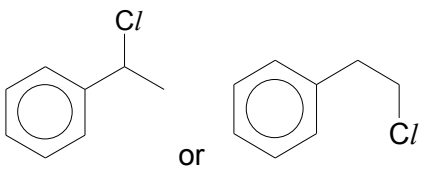
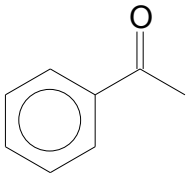
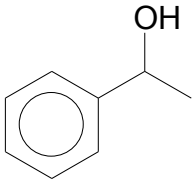
carbocation **A**



carbocation **B**

Carbocation **A** is resonance stabilized while carbocation **B** only has one electron donating alkyl group. Carbocation **A** is formed preferentially in step 1, leading to the formation of the major product.

4 (c) (i)

Q 	**R** 
S 	**T** 

4 (c) (ii)

Step 1:	CH_3CH_2Cl, anhydrous $FeCl_3$,
Step 2:	Limited Cl_2, UV light
Step II:	$LiAlH_4$ in dry ether/ $NaBH_4$ in ethanol/ H_2, Ni, heat / H_2, Pt
Step III:	Excess conc H_2SO_4, heat

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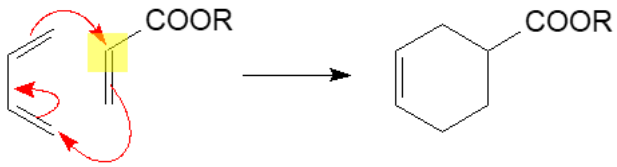
4 (d) **P, $(CH_3)_3C-$** is an electron-donating group. Hence, 2-position and 4-position carbocation will be the more stable as the carbocation is bonded to the electron donating group **P**, which helps to offset its electron deficiency. This is not observed for 3-position carbocation.
Hence isomer 3-position will be formed the least.

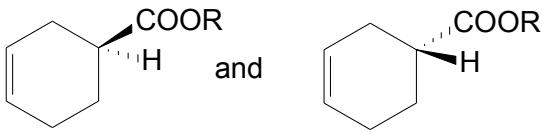
$(CH_3)_3C-$ is a bulky alkyl group, $^+NO_2$ electrophile would experience more steric hindrance when approaching from the 2-position. Comparatively, there will be less steric hindrance when $^+NO_2$ electrophile approach from 4-position.
Isomer 4-position will be formed the most.

4 (e) (i)

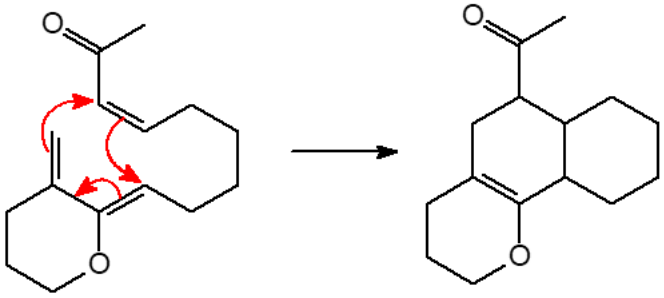


4 (e) (ii) X contains a chiral carbon. A racemic mixture is formed because the reactive carbon centre (highlighted in yellow) is trigonal planar and thus the addition reaction can take place from both top and bottom of the plane with equal probability, forming the two enantiomers in equal amount.

The optical activity of each enantiomer cancels out completely.



4 (e) (iii) Redrawing the structure of W such that it is similar to arrangement in Fig. 4.3



5 (a) $MCO_3(s) \longrightarrow MO(s) + CO_2(g)$

Down the group, cations of Group 2 metals have the same charge but their cation size increases. The $\frac{\text{charge}}{\text{size}}$ ratio of the cation and polarising power decreases down the group.

The electron cloud of CO_3^{2-} anion is being polarised to a smaller extent and the C−O bond is weakened to a smaller extent down the group.

More thermal energy is required to break the C–O bonds in the carbonate anion.

Therefore, thermal stability of the anion increases down the group

5 (b) (i) $2MnO_4^- + 6H^+ + 5H_2C_2O_4 \longrightarrow 10CO_2 + 2Mn^{2+} + 8\ H_2O$

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5 (b) (ii) $Ca^{2+} + C_2O_4^{2-} \longrightarrow CaC_2O_4$

$CaC_2O_4 + 2H^+ \longrightarrow H_2C_2O_4 + Ca^{2+}$

Amount of MnO_4^- used = $\frac{22.40}{1000} \times 0.00100 = 2.24 \times 10^{-5}$ mol

Amount of $H_2C_2O_4 = \frac{5}{2} \times 2.24 \times 10^{-5} = 5.6 \times 10^{-5}$ mol = Amount of CaC_2O_4

Amount of $Ca^{2+} = 5.6 \times 10^{-5}$ mol

Mass of $Ca^{2+} = 5.6 \times 10^{-5} \times 40.1 = 2.25 \times 10^{-3}$ g = **2.25 mg**

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5 (b) (iii) **Note:** R has a unit of J K^{-1} mol^{-1}, hence ΔG needs to be converted to J mol^{-1} when using the formula.

$K_{sp} = 10^{-\left(\frac{49.2 \times 1000}{2.3 \times 8.31 \times 298}\right)} = 2.30 \times 10^{-9}$

---

5 (c) (i) This is a buffer solution

$$pH = pK_a + \lg \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$6.50 = -\lg(1.38 \times 10^{-4}) + \lg \frac{[0.028]}{[HA]}$$

$$2.640 = \lg \frac{[0.028]}{[HA]}$$

[HA] = **6.42×10^{-5} mol dm^{-3}**

---

5 (c) (ii) $$K_c = \frac{[CH_3CH(OH)CO_2^-][H_2NCONH_3^+]}{[CH_3CH(OH)CO_2H][H_2NCONH_2]}$$

$$K_a = \frac{[H^+][CH_3CH(OH)CO_2^-]}{[CH_3CH(OH)CO_2H]}$$

$$K_b = \frac{[H_2NCONH_3^+][OH^-]}{[H_2NCONH_2]}$$

$$K_a \times K_b = \frac{[H^+][CH_3CH(OH)CO_2^-]}{[CH_3CH(OH)CO_2H]} \times \frac{[H_2NCONH_3^+][OH^-]}{[H_2NCONH_2]}$$

$K_a \times K_b = K_c \times [H^+]\,[OH^-]$

$K_a \times K_b = K_c \times K_w$

$$K_b = \frac{K_c \times K_w}{K_a} = \frac{1.74 \times 10^{-4} \times 1 \times 10^{-14}}{1.38 \times 10^{-4}}$$

= **1.26×10^{-14} mol dm^{-3}**

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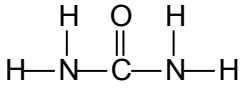
5 (c) (iii)



7 sigma bonds, 1 pi bond

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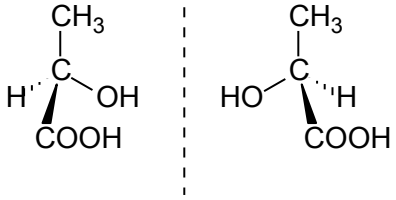
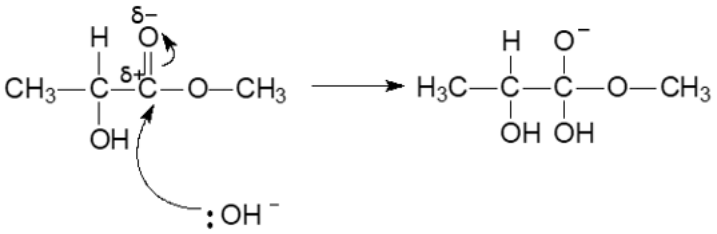
5 (d) (i)



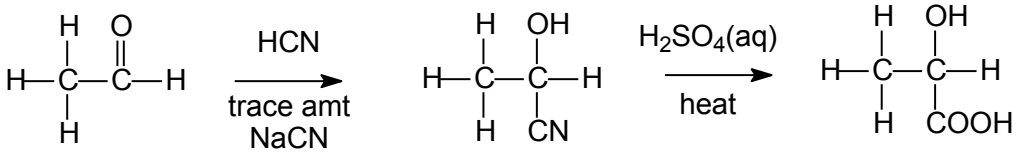
Note : The 4 groups can be assigned in any order, the 2 enantiomers must be mirror images.

5 (d) (ii)

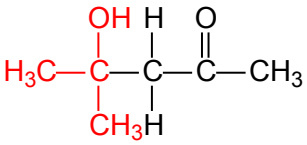


Note : Qn mentioned that OH^- reacts with the C=O group of ester, hence the π bond of C=O is broken.

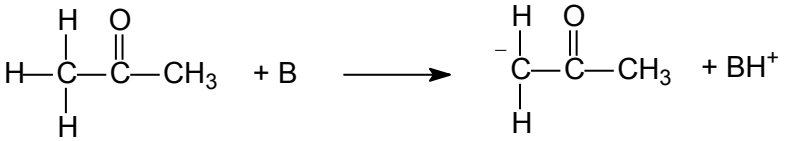
5 (e)

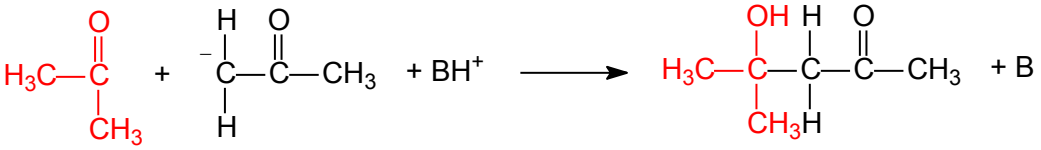


5 (f) (i)

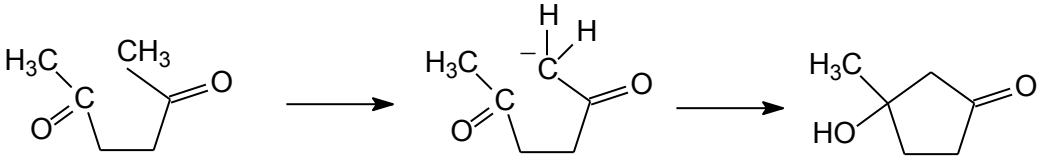


Thinking process:





5 (f) (ii) Note: Cyclic product, it must be an intramolecular reaction.
Thinking process, working backwards



Carbonyl compound **Y** is