H2 Chemistry TYS 2015 suggested answers

Questions that are no longer in syllabus

Paper 1	
Paper 2	3(d)
Paper 3	2(b), 3(a), 3(c)(i)&(ii)

Paper 1 Answer Key

1	B		**11**	D		**21**	B		**31**	D
2	B		**12**	C		**22**	D		**32**	A
3	C		**13**	D		**23**	B		**33**	C
4	C		**14**	B		**24**	A		**34**	A
5	B		**15**	D		**25**	D		**35**	B
6	D		**16**	D		**26**	D		**36**	A
7	B		**17**	A		**27**	D		**37**	C
8	C		**18**	C		**28**	C		**38**	C
9	A		**19**	B		**29**	B		**39**	A
10	B		**20**	A		**30**	A		**40**	B

2015 A level Paper 1 suggested answers

1 order of filling atomic orbitals: 1s, 2s, 2p, 2p, 3s, 3p, 4s, 3d

Ground state valence shell e configuration of Group 14 element: $ns^2\ np^2$; larger n value, higher the energy level.

B is the ans.

2 **In hydrocarbons:**

- σ bonds in C-C and C-H bonds can be formed from the overlap of either s and/or p orbitals

Note: C atoms should be forming σ bonds using **sp / sp^2 / sp^3 hybrid orbitals.**

- π bonds in C=C bonds can only be formed from the side-on overlap of p orbitals, **not** s orbitals

B is the best ans

3 no. of protons in OH^- = atomic no. of O + atomic no. of H
= 8 + 1 = 9

No. of electrons in OH^- = no. of protons in OH^- + net -ve charge on OH^-
= 9 + 1 = **10**

No. of neutrons in OH^- = (mass no. – atomic no.) of O + (mass no. – atomic no.) of H
= (16 – 8) + (1 – 1) = **8**

C is the ans

4 Both Ca and Na are metallic elements with strong metallic bonding (electrostatic forces of attraction) between delocalized sea of electrons and the cations.

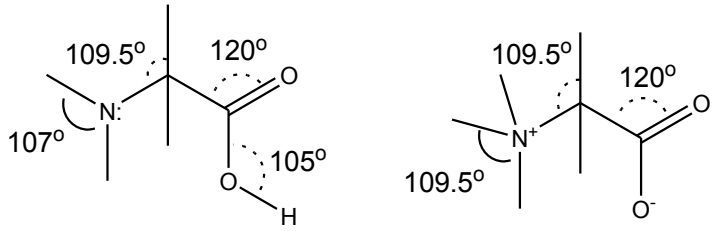
Melting point depends on metallic bond strength.

Ca (in Group 2) can lose **2** e's per atom to form Ca^{2+}, Na (in Group 1) can only lose **1** e per atom to form Na^{+}.

C is the ans.

Note: Option D is wrong as the strength of metallic bond depends on number of delocalized electrons, NOT the total number of electrons.

5



B is the ans

6 LE: energy released when 1 mol of an **ionic solid** is formed from its constituent **gaseous ions**

D is the ans

7

	NaOH	+ HC*l*	→	NaC*l*	+ H_2O (*l*)
Initial / mol	0.000625 (L.R.)	0.0025		0	-
Change / mol	−0.000625	−0.000625		+0.000625	-
Final / mol	0	0.001875		−0.000625	-

$$[HCl] = \frac{\frac{0.001875}{12.5+25.0}}{1000} = 0.0500 \text{ mol dm}^{-3}$$

B is the ans

8 **Based on the production of CO_2 and CO in 9:1 ratio**

$10CH_4 + 19½\ O_2 \rightarrow 9CO_2 + CO + 20\ H_2O$

For gases under the same conditions, vol ratio = mol ratio
$\therefore$ Vol of O_2 needed to burn 1 dm^3 CH_4 = 1 × 19.5/10 = 1.95 dm^3
C is the ans

9 $CO_2(g) + nH_2O(l) \rightleftharpoons CO_2.nH_2O(aq)$

H bonds are formed $\Rightarrow \Delta H < 0$

Gas turns aq $\Rightarrow \Delta S < 0$ (less disordered arrangement)

A is the ans

10 $E^{\ominus}$: standard electron potential at 25 ^{o}C, 1 atm pressure, 1 mol dm^{-3} of the ions/substance involved

B is the ans

11

	$CH_3CO_2H(g)$	$\rightleftharpoons$ $CH_3CO_2^-$ +	H^+
$[\ ]_{eqm}$ / mol dm^{-3}	$(1 - \alpha)C$	αC	αC

$$K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3COH]} = \frac{(\alpha C)^2}{(1-\alpha)C} = \frac{\alpha^2 C}{1-\alpha}$$

D is the ans

12 $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) + \text{heat}$ $\Delta H < 0$

Increase P, eqm shift right to favour side with less moles of gas to partially offset the increase in P.
Decrease T, eqm shift right to favour forward exothermic reaction to partially offset decrease in T by producing heat.
C is the ans

13

	$H_2O(g)$ +	$CO(g)$	$\rightleftharpoons$ $H_2(g)$	+ $CO_2(g)$
Eqm amount / mol	1 – y	1 – y	y	y

At eqm, total amt = 2(1 – y) + 2y = 2 mol

proportion of $H_2(g)$ in eqm mixture = $\frac{y}{2}$ x 100 = 33.3% $\quad \therefore y = \frac{2}{3}$

$$K_c = \frac{[H_2][CO_2]}{[H_2O][O_2]} = \frac{(0.666)^2}{(0.334)^2} = 3.997 \approx 4.0$$

D is the ans

14

Given:	rate	$= k[H_2]\,[NO]^2$	
also	6.0	$= k\,(0.5)(2.0)^2$	
	$\Rightarrow k$	$= 3$	
Thus,	x	$= 3\,(0.5)\,(1.0)^2$	$= 1.5$
	y	$= 3\,(1.0)\,(1.0)^2$	$= 3$
and	0.75	$= 3\,(1.0)\,(z)^2$	$\Rightarrow z = 0.5$

B is the ans

15 Elements in the same group have the same valence shell e configuration. Ionic radius increases down a group.

Down Group 2, charge-density of M^{2+} and hence its polarizing power decreases, there is less distortion of electron cloud of NO_3^- anion; less weakening of N-O bond in NO_3^- anion.

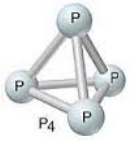
Hence the nitrates become more difficult to decompose.

D is the ans

16 **A** is **not** the ans: S forms SO_2, SO_3

B is **not** the ans: Ar, has the highest 1st IE (Refer to Data Booklet values)

C is **not** the ans: $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

D is the ans P_4, 

17) Option A is correct, $[Cu(NH_3)_4(H_2O)_2]^{2+}$ can also be represented as $[Cu(NH_3)_4]^{2+}$, a dark blue solution.
Option B is wrong, NH_3 complex of Cu^{2+} is $[Cu(NH_3)_4]^{2+}$, a dark blue solution.
Option C is wrong, $Cu(OH)_2$ is a pale blue precipitate.
Option D is wrong, $[Cu(H_2O)_6]^+Cl^-$ is $CuCl$, a white precipitate as Cu^+ has an electronic configuration of $3d^{10}$.

Ans: **A**

18 atomic radius decreases across the period: Mg > Al > Si > P (Refer to Data Booklet)

P is a simple covalent substance → lowest mp

Mg and Al have metallic lattice with strong metallic bonds between cations and sea of delocalised electrons, Al has higher mp than Mg

Si has a covalent lattice with strong covalent bonds between Si atoms and has the highest mp in Period 3

mp: P < Mg < Al < Si

C is the ans

19 Given: $Cr_2O_7^{2-}$ is reduced to $[Cr(H_2O)_6]^{3+} \Rightarrow Cr_2O_7^{2-}$ is oxidising only in acidic medium

$\Rightarrow$ **Y** is either 1° alcohol or 2° alcohol or aldehyde

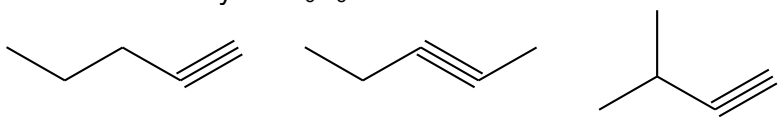
B is the ans (**X** is sulfuric acid & **Y** is ethanol)

20 PCl_5 can react with –OH group in both alcohol and carboxylic acid.

M is $CH_3CHBrCHClCOCl$

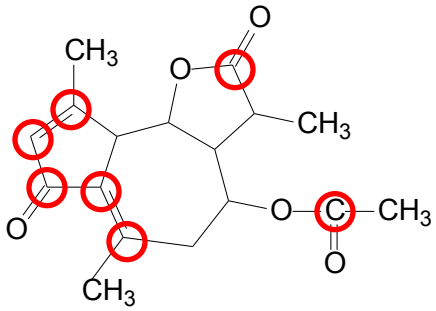
A is the ans

21 isomers of non-cyclic C_5H_8 with 1 C≡C bond:



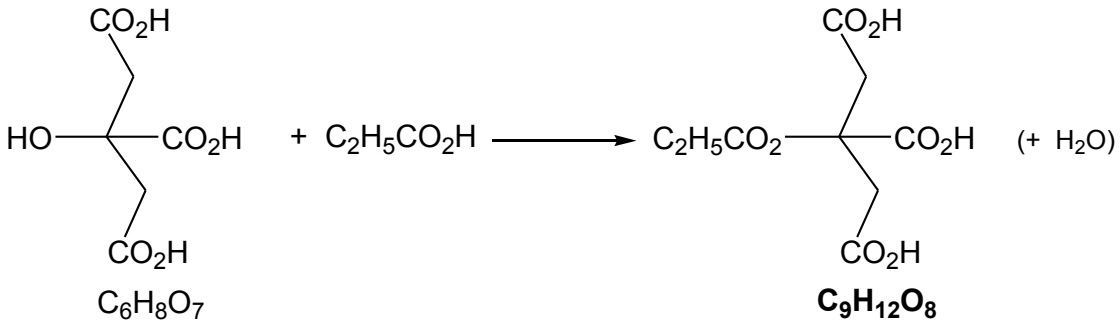
B is the ans

22 **D** is the ans; all **7** sp^2 hybridised C are circled

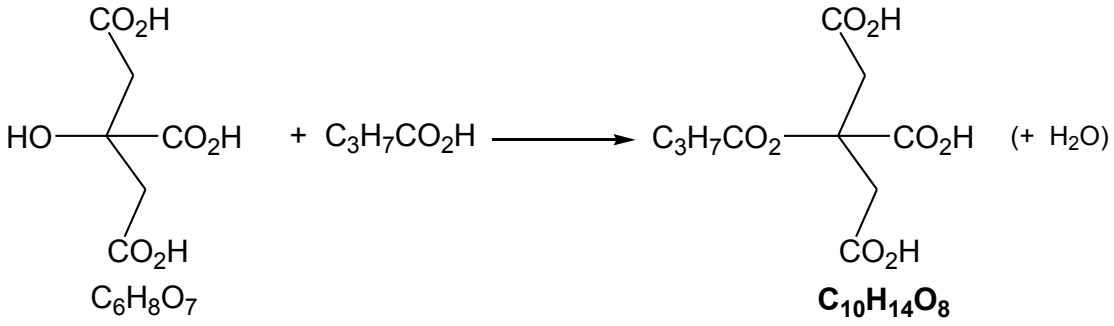


23 $NaBH_4$ can reduce aldehydes to 1° alcohols, but not alkenes (C=C).
CH_2=$CHCH_2CHO$ is reduced to CH_2=$CHCH_2CH_2OH$
B is the ans

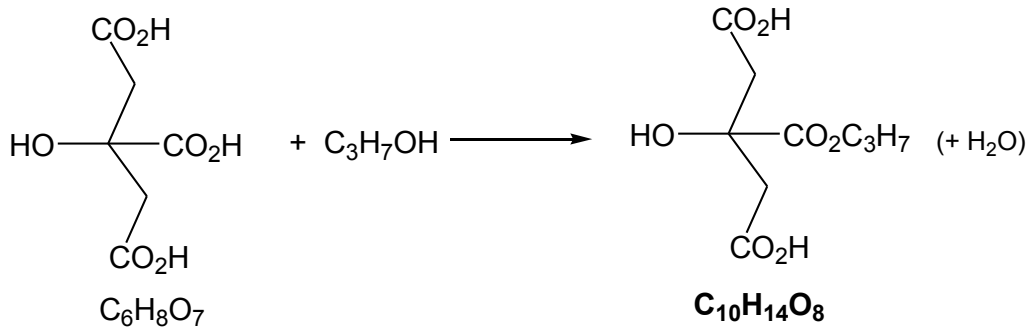
24 **A** is the ans



B is **not** the ans:

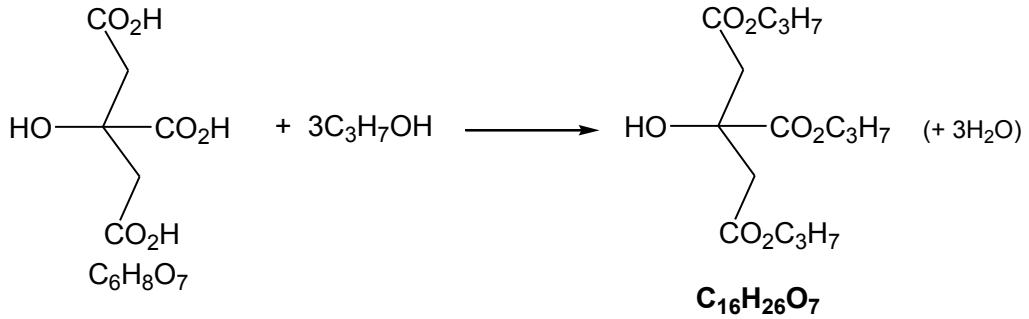


C is **not** the ans: (only 1 ROH to react with a –CO_2H group)



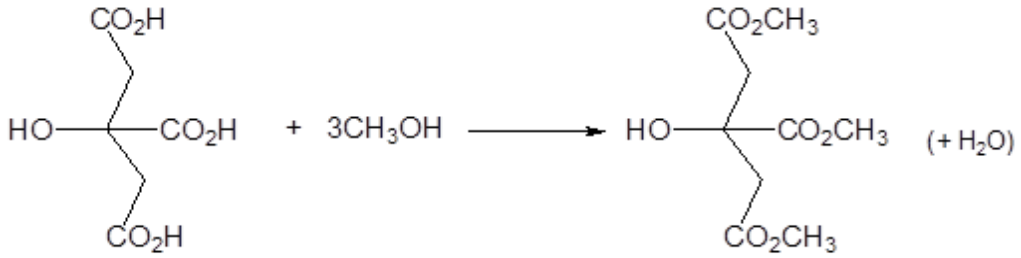
$C_6H_8O_7$ **$C_{10}H_{14}O_8$**

Or (3 ROH's should have reacted with all 3 $-CO_2H$ groups)



$C_6H_8O_7$ **$C_{16}H_{26}O_7$**

D is **not** the ans:



$C_6H_8O_7$ **$C_9H_{14}O_7$**

25 Both CCl_4 and C_6H_5Cl are inert towards hydrolysis; no ppt will form when each is shaken with $AgNO_3$(aq).

Carbon in CCl_4 does not have energetically accessible orbitals to accept a lone pair from water.

C-C*l* bond in C_6H_5Cl cannot be broken due to partially double bond character. p-orbital of C*l* can overlap with the unhybridised p orbitals of carbon atoms in the benzene ring, hence lone pair in C*l* can delocalised into the benzene ring pi electron cloud, strengthening the C-C*l* bond.

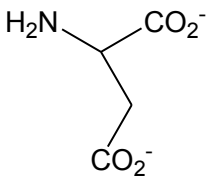
D is the ans

CH_3COCl undergoes hydrolysis much more readily than $CH_3CH_2CHClCH_3$ due to the presence of more highly e-deficient carbon centre (C with electronegative O and C*l* attached); thus prone to attack by water (nucleophile). Acyl chlorides can react with water readily at room temperature.

$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$

26 In solution at pH 11, deprotonation of acidic protons occurs readily.

Predominant structure of aspartic acid is:



D is the ans

27 Upon oxidation, there is an increase of 14 units in $M_r \Rightarrow$ 1 O is added & 2 H removed.

A: aldehyde, RCHO $\rightarrow$ carboxylic acid, RCOOH change in mass = +16 $\therefore$ **A** is **not** the ans

B: aldehyde cannot be oxidized to ketone $\therefore$ **B** is **not** the ans

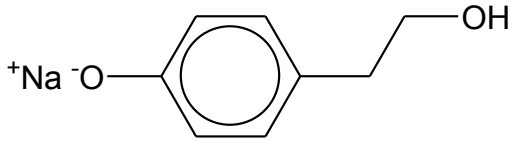
C: 1° alcohol, $RCH_2OH \rightarrow$ aldehyde, RCHO change in mass = -2 $\therefore$ **C** is **not** the ans

D: 1° alcohol, $RCH_2OH \rightarrow$ carboxylic acid, RCOOH change in mass = +16 – 2 = 14

$\therefore$ **D** is the ans.

28 **C** is the ans

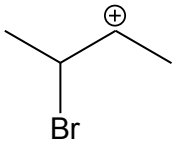
Phenol is acidic, can be neutralised by cold NaOH(aq); alcohol is neutral and does not react with cold NaOH(aq).



29 Electrophilic substitution of phenol using Br_2(aq)

B is the ans

30 Reaction involved is electrophilic addition of alkene. Br^+ from Br_2 acts as the electrophile.

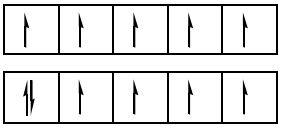


A is the ans

31 valence shell e configuration of Mn^{2+}: $3d^5$; **no** paired 3d e's

valence shell e configuration of Fe^{2+}: $3d^6$; **2** paired 3d e's

valence shell e configuration of Co^{3+}: $3d^6$; **2** paired 3d e's



D is the ans.

32 Si and Ge are Group 14 elements (metalloids). They form simple covalent compounds with C*l* and CH_3 group, options **1** and **2** are true.

A*l*$^{3+}$ has high charge-density and would polarise Br^- anion readily, thus A*l*Br_3 is an essentially covalent compound.

or A*l*C*l*$_3$ is an essentially covalent compound; Br^- is larger than C*l*$^-$, thus A*l*Br_3 should be an essentially covalent compound. **3** is also true.

Note: If A*l*Br_3 is an ionic compound, we would expect its melting point to be much higher than the given value of 265 °C due to the high lattice energy contributed by A*l*$^{3+}$

A is the ans.

33 **1** is false: Matter has mass and occupies space.

C is the ans.

34 For a cell to function as a battery (to supply electrical energy), $E^{\ominus}_{cell} > 0$

$\therefore$ $E^{\ominus}_{cell}$ = +0.74 – (–0.76) = +1.50 V

Overall reaction: $2NH_4^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2NH_3(g) + H_2(g)$

Zn dissolves into solution as $Zn^{2+}(aq)$ ion, thus Zn casing becomes thinner.

A is the ans as all 3 statements are true.

35 **1** is true: presence of a catalyst increases both k_f and k_b in a reversible reaction as it lowers E_a's for both forward and backward reactions.

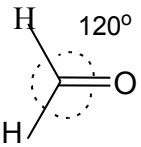
2 is true: heating (increasing T) increases both k_f and k_b. (The shift in position of equilibrium to the left only implies the increase in rate of backward reaction in more than the increase in rate of forward reaction.

3 is false: increasing concentrations of reactants increases only rate of forward reaction, note affecting the rate constants.

B is the ans.

Note: rate constant, k, is affected by temperature and catalyst (The two factors in the Boltzmann's distribution)

36 **1** is true:



$H_2\ C\ O$

2 is true: ON +1 0 -2

3 is true: $HCHO + O_2 \rightarrow H_2O + CO_2$

A is the ans

37 free radical – species with a single or an unpaired electron or odd number of electrons

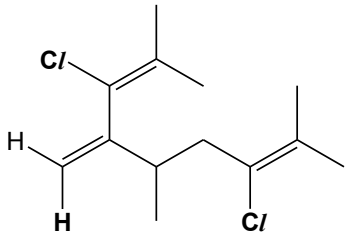
1 is **false**

2 is true

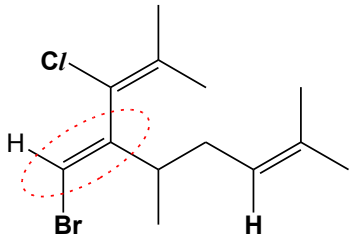
3 is true: homolytic fission results in each constituent atom of a covalent bond, X-Y, taking its original share of electrons in the bond

C is the ans

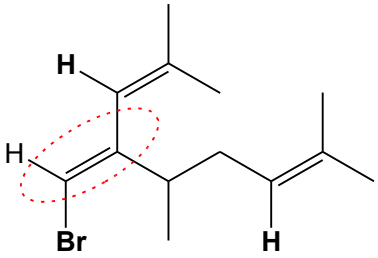
38

1 is false: 

, no geometrical isomerism

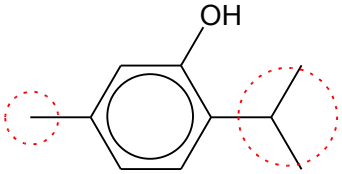
2 is true: 

, shows geometrical isomerism at the highlighted C=C bond

3 is true: 

, shows geometrical isomerism at the highlighted C=C bond

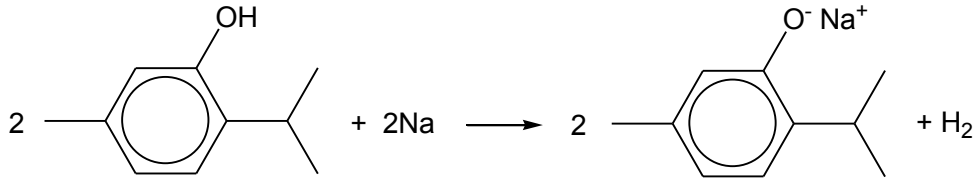
C is the ans.

39 **1** is true: both $-CH_3$ and $-CH(CH_3)_2$ in thymol can undergo side-chian oxidation with $KMnO_4$/ OH^- when heated; 

2 is true: CH_3COCl reacts with –OH group of thymol in NaOH(aq) to form ester.

Note: Converting phenol to phenoxide prior to the reaction will increase the yield of the ester.

3 is true: −OH group reacts with Na to give H_2,



A is the ans.

40

1 is true: 2 Chiral C with no plane of symmetry

2 is true: 2 Chiral C with no plane of symmetry

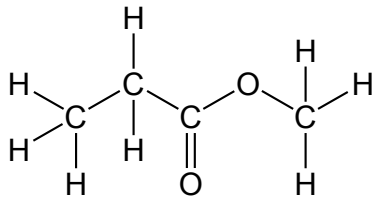
3 is **false**: it is a meso compound with an internal mirror plane where the optical activity of each C atom cancels out completely.

B is the ans.

2015 A level Paper 2 suggested answers

1 Planning (P)

(a) $CH_3CH_2CO_2H(l) + CH_3OH(l) \rightleftharpoons CH_3CH_2CO_2CH_3(l) + H_2O(l)$



methylpropanoate

(b) To determine accurate concentration of 3 mol dm^{-3} HC*l*(aq)

(I) without dilution

Procedure

1 Pipette **10.0** cm^3 of **3** mol dm^{-3} HC*l*(aq) into a clean 250 cm^3 conical flask and add 2 - 3 drops of phenolphthalein indicator. (or methyl orange)

2 Fill a burette with 1.00 mol dm^{-3} NaOH(aq). Record initial burette reading. Titrate the acid with NaOH(aq) till colour changes from colourless to first trace of permanent pink. Record the final burette reading. Calculate the volume of NaOH(aq) used.

(colour change will be red to yellow if using methyl orange)

3 Repeat steps 1 - 2 for consistent results (within ±0.10 cm^3).

(Wear gloves and goggles when performing the experiment as the concentrated acid is corrosive.)

Calculations:

Assume average volume of NaOH (aq) used is V_0 cm^3

$\therefore$ accurate conc of HC*l*(aq) = $\frac{V_0}{10.0} \times 1.00 = \frac{V_0}{10}$ mol dm^{-3}

Comments :

*10.0 cm^3 of 3 mol dm^{-3} HC*l*(aq) would require around 30 cm^3 of 1.00 mol dm^{-3} NaOH(aq). Volumes of titre and aliquot are within acceptable values.*

(II) Determination of K_c for the ester formation

Procedure

Points to note:

- vol of the HC*l*(aq) added must be small and measured accurately. (amount of HC*l*(aq) in the reaction mixture remains unchanged throughout the experiment as it acts as a catalyst).

- perform the experiment in a fume cupboard as methanol is volatile and toxic.

- no naked flame should be around as methanol is flammable.

- gloves and googles must be worn at all times.

(Any masses of acid and methanol can be used in the 2 experiments as long as the total mass of each **does not exceed 10 g**, the given amount)

1 Using an electronic balance, measure **accurately about** 3.0 g of propanoic acid liquid using a dry and clean weighting bottle. Transfer the acid into a clean and dry 250 cm^3 conical flask. Then weigh the residual acid liquid and the weighing bottle. Determine the exact mass of propanoic acid transferred into the conical flask.

2 Using another clean and dry weighing bottle, repeat step 1 to measure **accurately about** 6.0 g of methanol into the same conical flask.

3 Add 1.00 cm^3 of **3** mol dm^{-3} HCl(aq) from a burette into the flask. Swirl the flask to ensure thorough mixing of chemicals. Stopper the flask.

4 Repeat Steps 1 – 3 to add 6.0 g of propanoic acid, 3.0 g of methanol and 1.00 cm^3 of **3** mol dm^{-3} HCl(aq) in another clean and dry conical flask.

5 Place both the conical flasks in a thermostatically-controlled water bath set at, say 30 ^oC, **and seal the opening of the flask** to prevent evaporation of the volatile compounds. Allow the mixture to equilibrate **for a week. (Read Qn)**

6 Fill another burette with 1.00 mol dm^{-3} NaOH(aq). Record initial burette reading. Titrate the acid with NaOH(aq) till colour changes from colourless to first trace of permanent pink. Record the final burette reading. Calculate the volume of NaOH(aq) used.
(colour change will be red to yellow if using methyl orange)

Data and Calculations

Let mass of propanoic acid used = 3.0 g, mass of methanol used = 6.0 g, vol of HC*l*(aq) used = 1.00 cm^3, Vol of NaoH = V_2 cm^3, Total vol of reaction mixture at eqm = V_{total} cm^3

Initial $\eta_{propanoic\ acid}$ = $\frac{3.0}{74.0}$ = **0.04054** mol initial $\eta_{methanol}$ = $\frac{6.0}{32.0}$ = **0.1875** mol

η_{HCl} added = $\frac{1.00}{1000} \times \frac{V_0}{10}$ = $\frac{V_0}{10000}$ mol (from **(II)**)

Amt of water from 1.00 cm^3 of HC*l*(aq) = $\frac{1}{18}$ mol

	propanoic acid +	methanol ⇌	ester +	water
initial amt / mol	0.04054	0.1875	0	$\frac{1}{18}$
eqm amt / mol	**a**	**0.1875** – **b**	**b**	**b** + $\frac{1}{18}$

$\eta_{propanoic\ acid}$ at equilibrium = $\frac{V_2}{10^3}$ x 1.00 – $\frac{V_0}{10000}$ = **a** mol

[propanoic acid]$_{eqm}$ = $\frac{a}{\frac{V_{total}}{10^3}}$ mol dm^{-3}

$\eta_{propanoic\ acid}$ reacted = $\eta_{methanol}$ reacted
= 0.04054 – **a**
= **b** mol
= η_{ester} formed = η_{water} formed

$\eta_{methanol}$ at equilibrium = **(**0.1875 – **b**) mol

$[methanol]_{eqm} = \frac{0.1875 - b}{\frac{V_{total}}{10^3}}$ mol dm

$[ester]_{eqm} = \frac{b}{\frac{V_{total}}{10^3}}$ mol dm^{-3}

$\therefore [water]_{eqm} = \frac{b + \frac{1}{18}}{\frac{V_{total}}{10^3}}$ mol dm^{-3}

Substituting the terms into $K_c = \frac{[ester][water]}{[propanoic\,acid][methanol]}$ to determine its value.

2(a)(i) The amount of energy **evolved** when one mole of a substance undergoes complete combustion in **excess oxygen** at 298 K and 1 bar.

(ii) Petrol consists of a mixture of hydrocarbons of different carbon numbers and thus does not have a fixed $\Delta H_c^{\ominus}$ value.

(b)(i) **Considering pV = nRT, with V and T kept constant, a larger P will imply greater amount of methane gas, and hence greater amount of energy produced for each dm^3 of methane.**

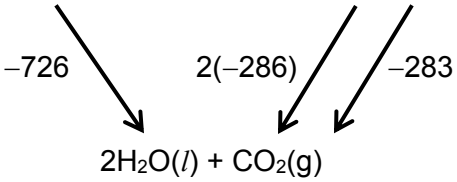
Energy released per dm^3 of methane = $0.0358 \times \frac{24.8 \times 10^6}{101 \times 10^3}$ = 8.79 MJ

(ii) When hydrogen is burnt, it released energy and water. The produce is clean (H_2O only) and not a pollutant.

(c) Methanol has **stronger hydrogen bonds due to presence of OH group** and stronger **temporary dipole–induced dipole interactions as its larger electron cloud** is more easily distorted. Thus significantly more energy is needed to overcome the stronger interactions between methanol molecules than the weaker **temporary dipole–induced dipole interactions** between methane molecules.

Thus methanol has a significantly higher b.p.

d(i) $3/2O_2(g) + CH_3OH(l) \xrightarrow{\Delta H} 2H_2(g) + CO(g) + 3/2O_2(g)$



$\Delta H^{\ominus}$ = (–726) –[2(–286) + (–283)] = **+129** kJ mol^{-3}

(ii) For reaction to be spontaneous, $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} \leq 0$

$\therefore T\Delta S^{\ominus} \geq \Delta H^{\ominus}$

T (+332) ≥ +129000

$$T \geq \frac{+129000}{+332} = \mathbf{389}\ \text{K}$$

(e) Carbon monoxide and oxygen act as a ligand and can bind to Fe^{2+} ion in the haemoglobin molecule through dative covalent bond. However, CO binds more strongly to the Fe^{2+} ion and this deprives O_2 to be transported around the body.

3(a)(i) $H_2(g) + Cl_2(g) \xrightarrow{\Delta H_r} 2HCl(g)$

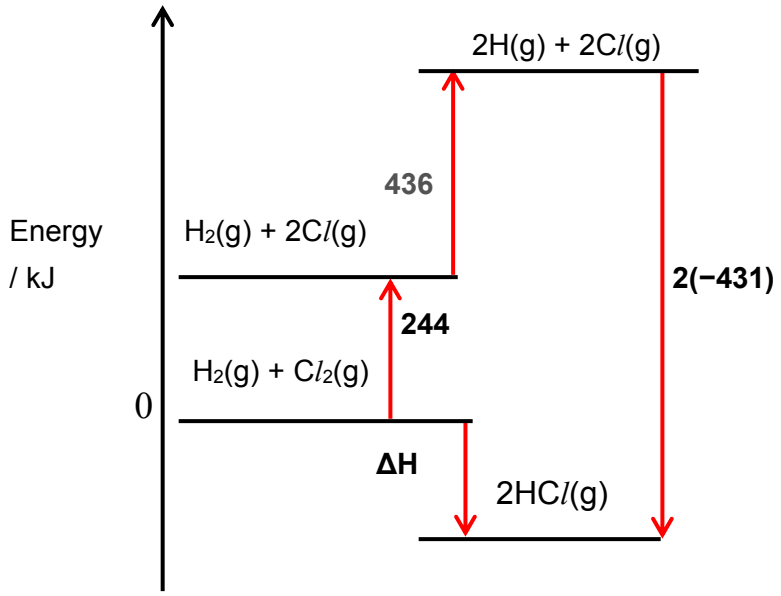
ΔH_r = ΣBE(bonds broken) – ΣBE(bonds formed)

= BE(H–H) + BE(C*l*–C*l*) – 2BE(H–C*l*)

= 436 + 244 – 2(431)

= **–182** kJ mol^{-1}

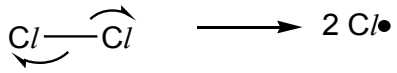
(ii)



Note the relative magnitude of the energy gap, bond breaking of C*l*–C*l* **occurs first.**

(b)(i) Light provides sufficient energy to break C*l*–C*l* bonds (homolytic fission).

(ii) Free radical substitution



(iii) each •C*l* formed can result in thousands of chain reactions subsequently, hence reaction continues. **In addition, the reaction is exothermic and thus further increases** the rate of reaction.

(c) **Comparing the BE of Br-Br (193 kJ mol^{-1}) vs** C*l*–C*l* **(244 kJ mol^{-1}). The reaction for Br_2 should occur more readily. However, the statement mention that Br_2 is less reactive. Hence we should be comparing the** ΔH_r for the 2 reactions.

For reaction of Br_2 (g) and H_2(g):

ΔH_r = 436 + 193 – 2(366)

= **–103** kJ mol^{-1}

ΔH_r for the reaction involving bromine is less exothermic, this shows that the product is less stable as compared to the product for the reaction between H_2 and Cl_2.

(d)(i) Not in syllabus

(ii) Not in syllabus

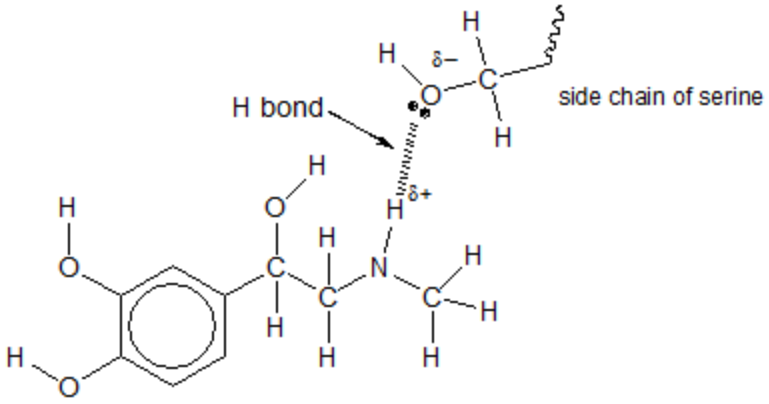
(e) Add aqueous Cl_2 into the two unknown aqueous solutions of these 2 gases:

Solution containing HBr will turn orange due to the formation of Br_2 (aq).

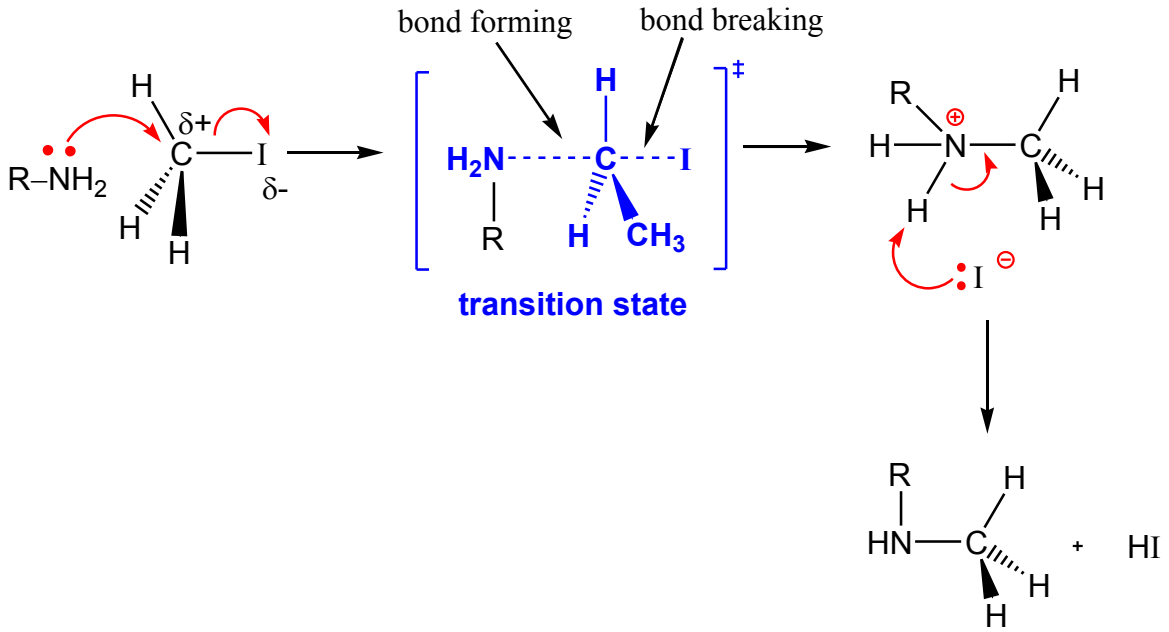
Cl_2 + 2Br$^-$ → 2 Cl^- + Br_2

Solution containing HC*l* will remain colourless/pale yellow (due to Cl_2 (aq))

4(a) Comment: displayed formula with any hydrogen bond can be acceptable if formed between δ+ hydrogen atom and lone pair on the N or O atom of the 2 molecules, with all partial charges responsible for the formation of the hydrogen bond shown.



(b)(i) S_N2 mechanism:



Comment: [4] marks for this question. After transtion state, must include positively charged intermediate along with relevant bond breaking to give products.

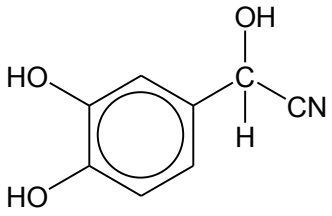
(ii) CH_3I is a primary alky halide with little steric hindrance for S_N2 mechanism due the small size of the H atoms attached to the central carbon.

OR

CH_3I cannot undergo S_N1 as the carbocation formed will be unstable as H atoms are not electron-donating and cannot stabilize the positive charge on the central carbon.

(c)(i) step 1: HCN, trace amount of NaCN(aq) / NaOH(aq)

step 2: $LiAlH_4$ in dry ether OR H_2 (g), Pt(s)



intermediate compound

(ii) In formation of the intermediate compound, the $^{-}$:CN nucleophile attacks the trigonal planar electron deficient carbonyl C with equal chances from either side of the plane to form the enantiomers in equal amounts.

Only one of the enantiomers is active in the human body. Thus the other 50% of the drug synthesised is inactive.

(d)(i) [R] $Ag_2O + 2e^- + 2H^+ \rightarrow 2Ag + H_2O$

(ii) $C_9H_{13}NO_3 + 2Ag_2O \rightarrow C_9H_9NO_3 + 4Ag + 2H_2O$

Amt of Ag_2O = 2 × (**Amt of** $C_9H_{13}NO_3$)

$$= 2 \times \frac{50.0}{1000} \times 3.0 \times 10^{-3} = 3.00 \times 10^{-4} \text{ mol}$$

Mass of Ag_2O used = (3.00×10^{-4}) × (2 × 107.9 + 16) = **0.0695** g

5(a) **X** and **Y** are chlorobenzenes.

Due to the delocalisation of lone electron pair on C*l* into the pi electron cloud of benzene ring, C—C*l* bond has partial double bond character and cannot be broken easily to undergo nucloephilic substitution with NaOH(aq) even with heating under reflux.

(b)(i)

	C	H	C*l*
% by mass	49.0	2.7	48.3
Relative amount	$\frac{49.0}{12.0}$ = 4.08	$\frac{27.0}{1.0}$ = 2.7	$\frac{48.3}{35.5}$ = 1.36
Simplest ratio	3	2	1

Empirical formula of **X** = $C_3H_2C\mathit{l}$

(ii) $pV = nRT = \frac{mRT}{M_r}$

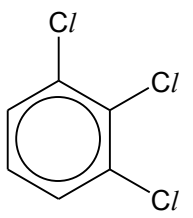
$M_r = \frac{(0.344)(8.31)(273+181)}{(101\times10^3)(87.4\times10^{-6})} = 147.0 \text{ g mol}^{-1}$

Let molecular formula of **X** be $(C_3H_2Cl)_n$

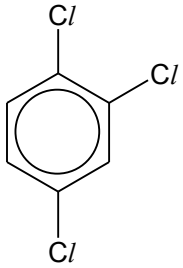
$\therefore (36 + 2 + 35.5)n = 147.0 \quad \Rightarrow n = 2$

Molecular formula of **X** is $C_6H_4Cl_2$

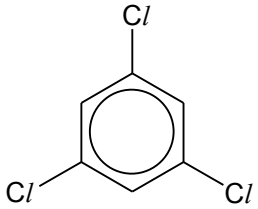
(c) Structures for **Y**:



1,2,3-trichlorobenzene



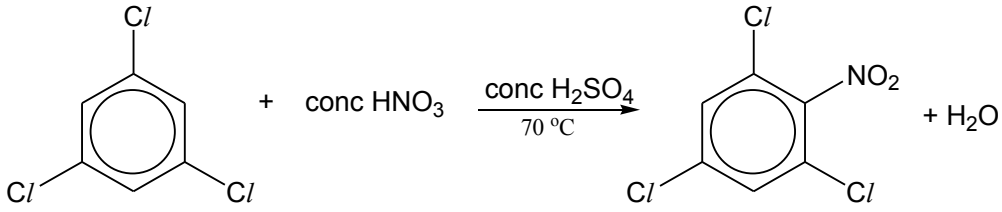
1,2,4-trichlorobenzene



1,3,5-trichlorobenzene

(d) Mono-nitration of **Y** gives only 1 compound $\Rightarrow$ **Y** must be 1,3,5-trichlorobenzene

(Note: C*l* is 2-, 4-directing)



1,3,5-trichlorobenzene

2015 A level Paper 3 suggested answers

1(a)(i) Only menthol react with Na to give H_2 gas.

$2\ ROH + 2\ Na \rightarrow 2\ RO^-Na^+ + H_2$

$2 menthol \equiv H_2$

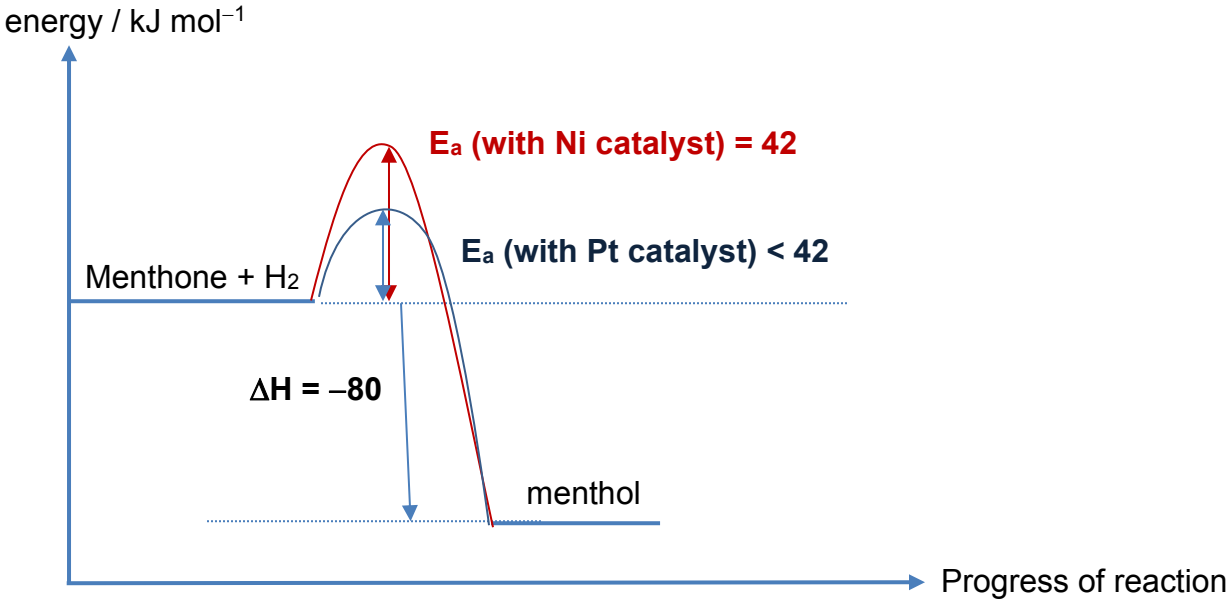
$\therefore$ amt of methol = 2 (amt of H_2) = $2 \times 1.32 \times 10^{-2} = 2.64 \times 10^{-2}$ mol

Mass of menthol in the sample = $(2.64 \times 10^{-2})(10 \times 12.0 + 20.0 + 16.0) = 4.118 = 4.12$ g

$\therefore$ Percentage by mass of menthol in peppermint oil = $\frac{4.118}{10.0} \times 100\%$ **= 41.2%**

(ii) 3 chiral C; $2^3 = 8$ optical isomers

(b)(i) & (ii)



(iii) **Heterogeneous catalysis** is involved in the reaction:

Reactants are **adsorbed** on the surface of the catalyst; the reactant molecules are **brought closer together with correct orientation** and the **bonds to be broken are weakened, thus E_a for the reaction is lowered**.

The products formed **desorb** and leave the surface of the catalyst.

(iv) Palladium. Pd is in the same group as Ni and Pt, thus it is expected to display similar properties, including the catalytic activity.

(c) **A**, **B** , **C** are isomers with molecular formula $C_{10}H_{16}O$
- molecular formula suggests no benzene ring

- A, **B** , **C** are reduced by H_2/Pt to menthol, $C_{10}H_{20}O$
$\Rightarrow$ **A**, **B** , **C** have 2 double bonds per molecule

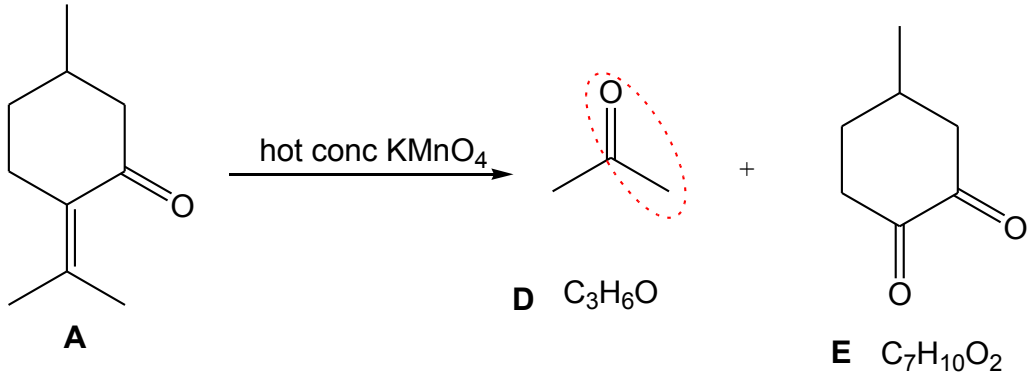
- **A**, **B** , **C** decolourise aq Br_2 through electrophilic addition
$\Rightarrow$ **A**, **B** , **C** have C=C bond.

- **A**, **B** , **C** undergo condensation with 2,4-DNPH to give orange ppt; but **not** oxidised by Fehling solution

⇒ **A**, **B** , **C** are not aliphatic aldehydes, **A**, **B** , **C** are ketones

A, **B** , **C** undergoes **oxidative cleavage** of C=C bond with hot conc $KMnO_4$

A gives **D**, C_3H_6O, and **E**, $C_7H_{10}O_2$:



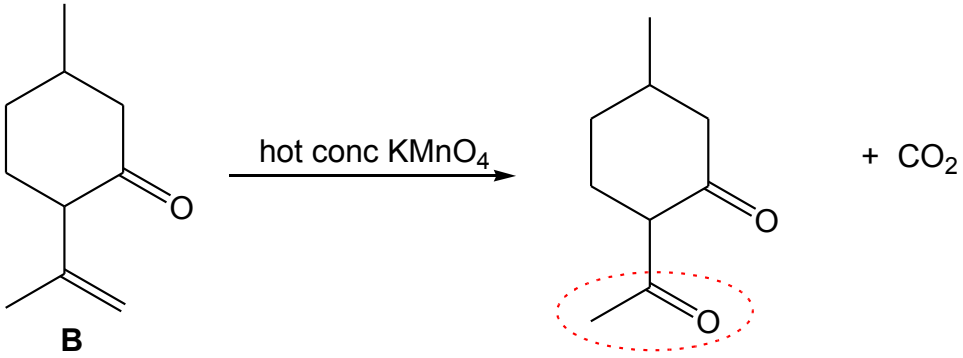
A

D C_3H_6O

E $C_7H_{10}O_2$

B gives CO_2 and **F**, $C_9H_{14}O_2$

⇒ **B** has terminal C=C bond/ **B** contains terminal alkene.

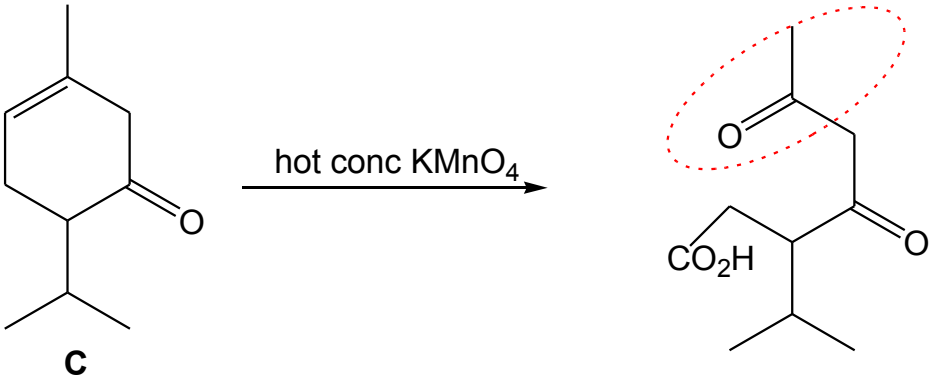


B

F $C_9H_{14}O_2$

C gives **G**, $C_{10}H_{16}O_4$

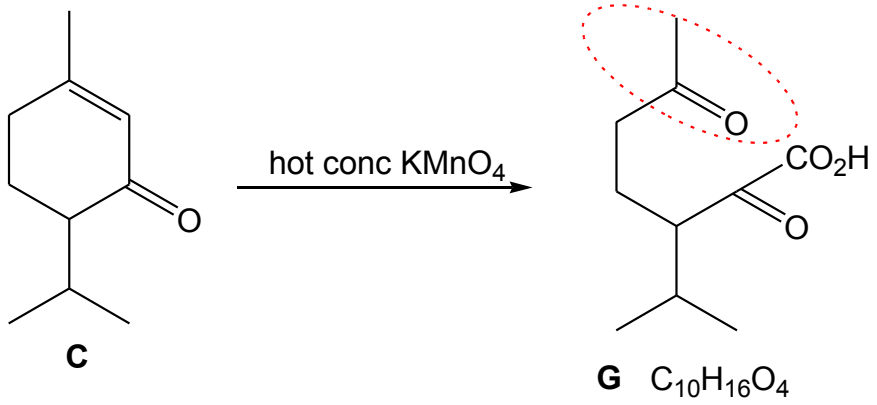
⇒ **C** has C=C in the ring:



C

G $C_{10}H_{16}O_4$

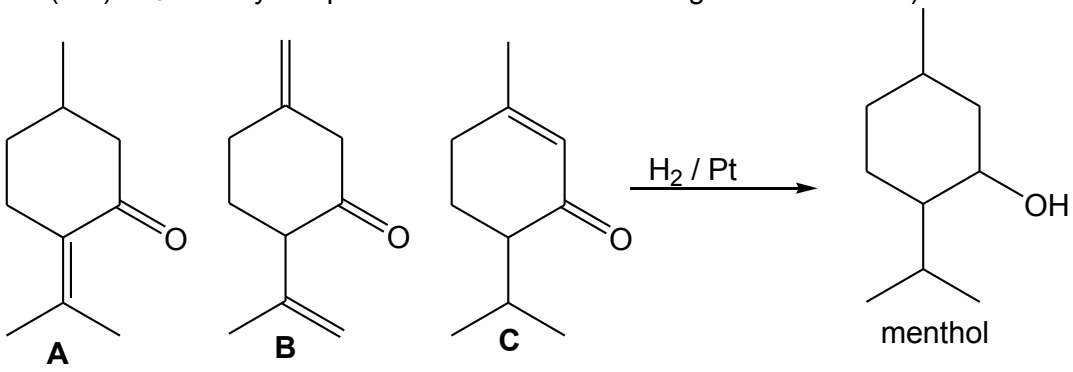
OR



D, **F** , **G** give yellow ppt with aq alkaline I_2

$\Rightarrow$ **D**, **F** , **G** have $-COCH_3$ group as **circled**

(**not** $-CH(OH)CH_3$ as they are products of oxidative cleavage of C=C bonds)



- **A**, **B** , **C** are reduced by H_2/Pt to menthol.

2(a) Volatilities of non-polar halogen **decrease** from Cl_2 to I_2 due to their **increasing electron cloud size**; strength of the intermolecular temporary dipole-induced dipole interactions increases, more energy is required to vapourise the halogens from Cl_2 to I_2.

(b) Not in syllabus

(c)(i) BE(H–F) = +562 kJ mol^{-1}

BE(H–Cl) = +431 kJ mol^{-1}

BE(H–Br) = +366 kJ mol^{-1}

BE(H–I) = +299 kJ mol^{-1}

H–F bond is the strongest and the most difficult to be broken; does not dissociate completely in aq solution; hence HF(aq) is a weaker acid.

(ii) HCl(aq) is a strong acid and dissociates completely

$[H^+] = [HCl] = 0.50$ mol dm^{-3}

$\therefore$ pH = –lg [0.50] = **0.301**

HF(aq) is a weak acid and does not dissociate completely

$$K_a = \frac{[H^+][F^-]}{[HF]} = \frac{x^2}{0.50 - x} = 5.6 \times 10^{-4}$$

Assume x is small, hence 0.50–x ≈ x

$[H^+] = x = 0.0167$ mol dm^{-3}

$\therefore$ pH = **1.78**

(d) Reaction between aq silver nitrate and chloride ions:

Formation of white ppt of AgC*l* which dissolves in excess aq NH_3 due to formation of $[Ag(NH_3)_2]^+$ complex

$$Cl^-(aq) + Ag^+(aq) \rightleftharpoons AgCl(s)$$

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq) \text{ or } [Ag(NH_3)_2]^+ Cl^-(aq)$$

Reaction between aq silver nitrate and iodide ions:

Formation of yellow ppt of AgI which remain insoluble in excess aq NH_3 despite formation of $[Ag(NH_3)_2]^+$ complex as AgI has a much lower K_{sp} value than AgC*l*

$$I^-(aq) + Ag^+(aq) \rightleftharpoons AgI(s)$$

(e)(i) At constant T, value of pV remain constant with changing pressure for an ideal gas.

(ii) pV = nRT

$$\therefore V = \frac{0.40 \times 8.31 \times 300}{12.0 \times 10^5} = \mathbf{8.31 \times 10^{-4}}\ m^3 = 0.831\ dm^3$$

(iii)

Pressure, *p* / Pa	Volume, *V* / dm^3	Pressure x Volume, *pV* / Pa dm^3
5.0×10^5	1.924	9.62×10^5
10.0×10^5	0.926	9.26×10^5
15.0×10^5	0.592	8.88×10^5

At p = 12.0×10^5 Pa,

estimated value of pV = $9.26 \times 10^5 - \left(\frac{2}{5}\right)(9.26 - 8.88)(10^5)$ = **9.108×10^5** Pa dm^3

= **9.11×10^5** Pa dm^3

$$\therefore V = \frac{9.108 \times 10^5}{12.0 \times 10^5} = \mathbf{0.759\ dm^3}$$

(iv) Calculated volume of HC*l*(g) is less than that of ideal HC*l*(g) molecules as there are significant intermolecular forces of attraction (permanent dipole-permanent dipole interaction) between HC*l* molecules. Hence the gas particles are close together and occupy a smaller volume as compared to ideal gas.

(f)(i) Given $\Delta G = \Delta H - T\Delta S = 0$

$$\therefore \Delta S = \frac{\Delta H}{T} = \frac{+16.8 \times 1000}{188} = \mathbf{+89.36} = \mathbf{+89.4}\ \text{J mol}^{-1}\ \text{K}^{-1}$$

Entropy of the system increases / ΔS has a positive sign.

On vapourisation, there are more gaseous particles and hence disorder. There are more ways in which the gas particles and their energies can be distributed.

(ii) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$= +16.8 - (298)(+89.36 \times 10^{-3}) = -9.83\ \text{kJ mol}^{-1}$

$\Delta G^{\ominus}$ is negative, hence vapourisation of HC*l* is spontaneous.

3(a)(i) Not in syllabus

(ii) Not in syllabus

(b)(i) any value between solubility of $Ca(OH)_2$ and $Ba(OH)_2$. [Between 0.025 and 0.41 mol dm^{-3}]

(ii) Solubility of $Ca(OH)_2$ $= 2.5 \times 10^{-2}$ mol dm^{-3}

$[OH^-] = 5.0 \times 10^{-2}$ mol dm^{-3}

pH $= 14 - (- \lg (5.0 \times 10^{-2}) =$ **12.7**

(iii) $K_{sp}(Mg(OH)_2) = [Mg^{2+}]\,[OH^-]^2$ mol^3 dm^{-9}

$= (1.6 \times 10^{-4})\,(2 \times 1.6 \times 10^{-4})^2$

$= \mathbf{1.64 \times 10^{-11}}$ mol^3 dm^{-9}

(iv)

	$[OH^-]$ / mol dm^{-3}	$[Mg^{2+}]$/ mol dm^{-3}	$[Ba^{2+}]$ / mol dm^{-3}
original saturated $Mg(OH)_2$	3.2×10^{-4}	1.6×10^{-4}	-
original saturated $Ba(OH)_2$	8.2×10^{-1}	-	4.1×10^{-4}
solution mixture	½ $(3.2 \times 10^{-4} + 8.2 \times 10^{-1})$ $= 4.101 \times 10^{-1}$	½ (1.6×10^{-4}) $= 8.0 \times 10^{-5}$	½ (4.1×10^{-4}) $= 2.05 \times 10^{-1}$

Ionic product of $Mg(OH)_2 = (8.0 \times 10^{-5})(4.101 \times 10^{-1})^2 =$ **$1.35 \times 10^{-5} > K_{sp}(Mg(OH)_2)$**

Ionic product of $Ba(OH)_2 = (2.05 \times 10^{-1})(4.10 \times 10^{-1})^2 =$ **$3.45 \times 10^{-2} <$** $K_{sp}(Ba(OH)_2)$

$\therefore$ Only $Mg(OH)_2$ will precipitate out as a white ppt; **not** $Ba(OH)_2$.

(c)(i) Not in syllabus

(ii) Not in syllabus

(iii) NaOH(aq)/KOH(aq) or HCl(aq)/H_2SO_4 (aq) /HNO_3 (aq) ; prolonged heating

Comment: indicate either dilute or aqueous or in solution

(iv) gly-asp

asp-gly

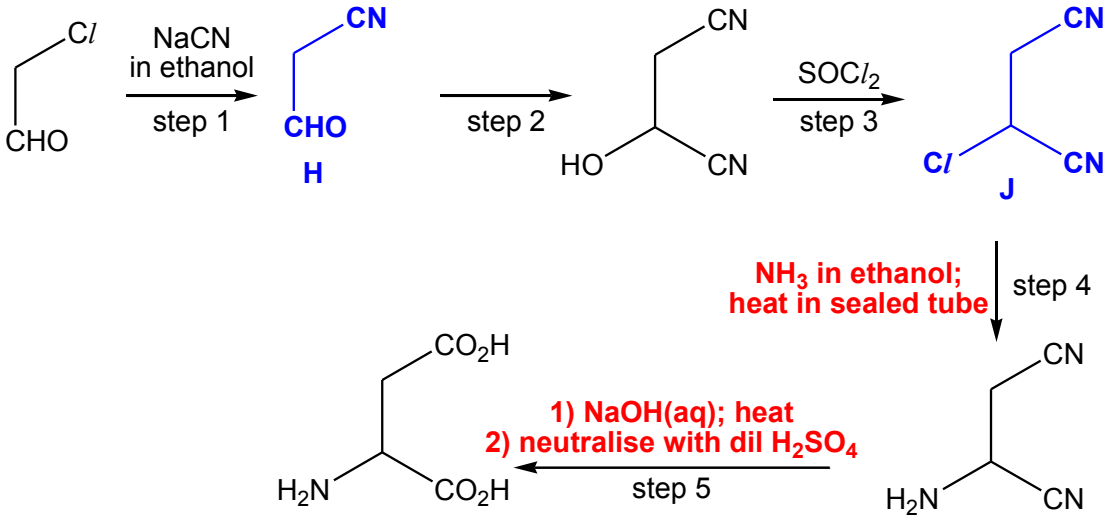
gly-tyr

tyr-ile

ile-ser

∴ hexa-peptide is **gly-asp-gly-tyr-ile-ser**

(d)(i) & (ii) **H** & **J**; reagents and conditions for steps 4 & 5 as shown:



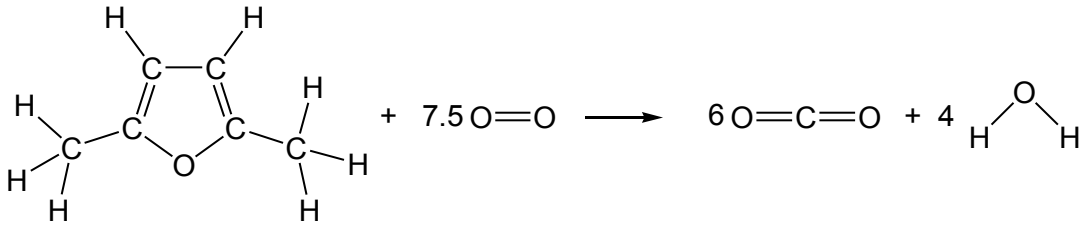
For step 5, also accept HCl(aq)/H_2SO_4 (aq) /HNO_3 (aq), heat

4(a)

step	1	2	3
Type of reaction	hydrolysis	Elimination of water (dehydration)	reduction

(b) DMF, $C_6H_8O + \frac{15}{2} O_2 \rightarrow 6CO_2 + 4H_2O$

or



ΔH_c(DMF, calculated)

= ΣBE(bonds broken) – ΣBE(bonds formed)

= [8BE(C-H) + 3BE(C-C) + 2BE(C=C) + 2BE(C-O) + $\frac{15}{2}$ BE(O=O)] – [12BE(C=O) + 8BE(O-H)]

= [8(410) + 3(350) + 2(610) + 2(360) + $\frac{15}{2}$ (496)] – [12 (805) + 8(460)]

= **–3350** kJ mol^{-1}

(c) heat gained by 200 g water = (200)(4.18)(32) = 26752 J

heat released from burning DMF = 26752 $\times \frac{100}{80}$ = 33440 J

ΔH_c (DMF) = –33440 ÷ $\frac{1.00}{96.0}$ = **–3210** kJ mol^{-1}

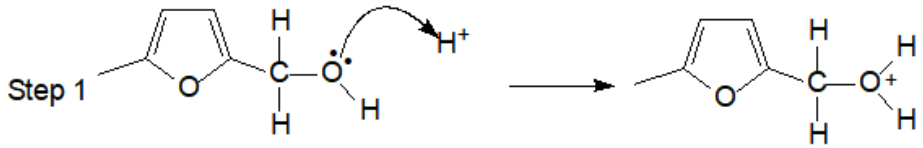
ΔH_c(DMF, expt) is **less exothermic** than ΔH_c(DMF, calculated)

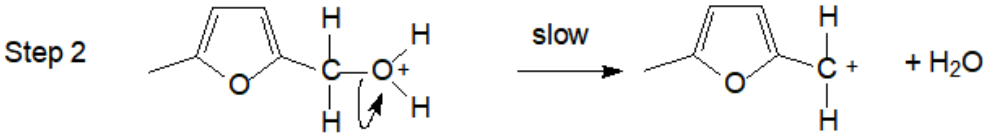
Reasons:

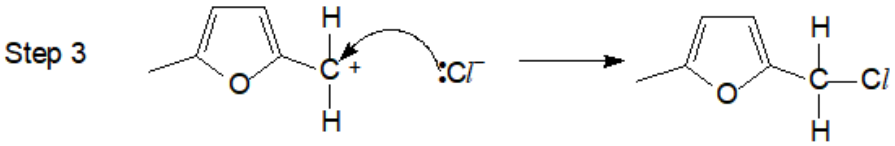
- DMF is a liquid at room temperature and BE values in *Data Booklet* are for gaseous molecules, the energy involved in the conversion of liquid DMF to gaseous state is not accounted for.
- bond energy values in *Data Booklet* are average values and may not be the same as those in substances given in the question.

Note: Do not accept heat lost to surrounding as the question already stated only 80% of heat is transferred.

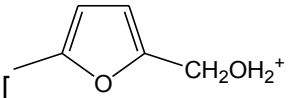
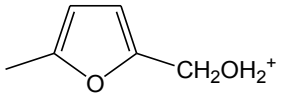
(d)(i) From given data, rate for reaction 4 = k[H$^+$] [HMF]







Step 2 is rate-determining (involving bond breaking).

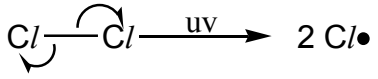
Comment : rate = k [], since formation of one  involves one H$^+$ and HMF each, rate = k [H$^+$] [HMF]

(ii) $K_2Cr_2O_7$ in H_2SO_4 (aq), heat under reflux (**NOT $KMnO_4$**, otherwise C=C bond will be cleaved)

(e)(i) ester **(ii)** $HOCH_2CH_2OH$ **(iii)** trace conc H_2SO_4; heat under reflux

Comment: conc H_2SO_4 (aq) is wrong

(f) Free radical substitution

Initiation: 

Propagation: $R—CH_3 + Cl\bullet \rightarrow R—\dot{C}H_2 + HCl$

$R—\dot{C}H_2 + Cl_2 \rightarrow R—CH_2Cl + Cl\bullet$

Termination: $2\ R—\dot{C}H_2 \rightarrow R—CH_2CH_2—\ R$

$R—\underset{\bullet}{C}H_2 + Cl\bullet \rightarrow R—CH_2Cl$

5(a)(i) proton number: number of protons **in the nucleus** of an atom

nucleon number: total number of protons and neutrons **in the nucleus** of an atom

(ii) let relative percentage abundance of ^{7}Li = a

$$\frac{7.016 \times a + 6.015 \times (100-a)}{100} = 6.942$$

$$a = 92.61$$

$\therefore$ relative percentage abundance of ^{7}Li = **92.61%**, relative percentage abundance of ^{6}Li = **7.39%** (2 dp)

(iii) $^{6}_{3}Li + {}^{2}_{1}H \rightarrow 2\,{}^{4}_{2}He$

$^{6}_{3}Li + {}^{2}_{1}H \rightarrow {}^{4}_{2}He + {}^{3}_{2}He + {}^{1}_{0}n$

$^{6}_{3}Li + {}^{2}_{1}H \rightarrow {}^{7}_{3}Li^{-} + {}^{1}_{1}p^{+}$

X: $^{3}_{2}He$ **Y**: $^{7}_{3}Li^{-}$

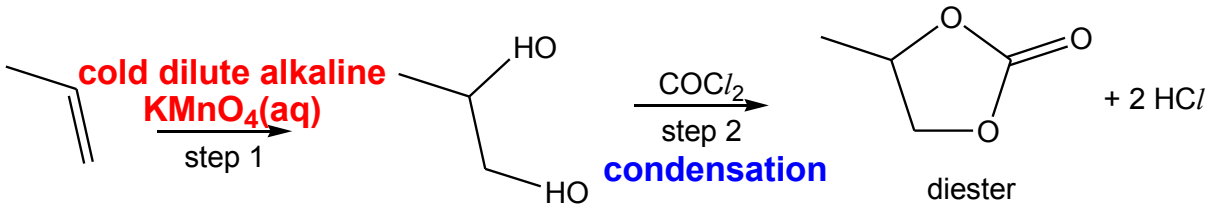
(b)(i) Metallic bonding. Li atoms lose the valence electrons into the sea of delocalized electrons of graphite. The resultant Li^+ ions can formed metallic bonding with the sea of delocalized electrons in graphite.

(ii) • empirical formula of Co compound in the cathode before discharge is CoO_2; thus oxidation number of Co is **+4**

• based on the structure provided for the cathode after the cell is totally discharged, we can see that the Co is only bonded to 3 neighboring oxygen through 3 single bonds; thus oxidation number of Co is **+3**

(iii) shape of BF_4^-: tetrahedral (**4** bond pairs of electrons and no lone pairs around B)

(iv) cold $KMnO_4$ in H_2SO_4 (aq)/ cold $KMnO_4$ in NaOH (aq)



(v) condensation

(c)(i) $2Li_2O_2 + 2CO_2 \rightarrow 2Li_2CO_3 + O_2$

(CO_2 is removed and O_2 is produced)

(ii) Li^+ ion has high charge-density (+1 charge over an extremely small size) and polarises CO_3^{2-} ion, distorting the large electron cloud and weakening C-O bonds in CO_3^{2-}. Thus Li_2CO_3 decomposes easily upon heating, similar to $MgCO_3$.

(d)(i) $CH_3CH_2CH_2Br$ and CH_3CH_2CHO or $CH_3CH_2CH_2CHO$ and CH_3CH_2Br

(ii) CH_3Br and $(CH_3CH_2)_2CO$ or $CH_3CH_2COCH_3$ and CH_3CH_2Br

(e) **P**: $CH_3CH_2CH_2CH_2CH_2CH_2OH$ (1^o alcohol)

Q: $CH_3CH_2CH_2CH(OH)CH_2CH_3$ (2^o alcohol)

R: $(CH_3CH_2)_2C(OH)CH_3$ (3^o alcohol)

Step 1: add acidified $K_2Cr_2O_7$(aq) separately to each sample and heat under reflux:

- Samples that change orange $K_2Cr_2O_7$(aq) to green is either **P** or **Q**
- Sample that $K_2Cr_2O_7$(aq) remain orange is **R**

Step 2: Isolate the oxidized product from the reaction mixtures that showed colour change.

Step 3: To each isolated product, add **2,4-dinitrophenylhydrazine** and shake:

- Sample with orange precipitate produced is **Q** (**Q** is oxidised to a ketone)
- Sample with no ppt is **P** (**P** oxidised to carboxylic acid)

OR

Step 3: To each isolated product, add Na_2CO_3(aq) and shake:

- Sample with no effervescence produced is **Q** (**Q** is oxidised to a ketone)
- Sample with effervescence, and gas produced formed white ppt in limewater is **P** (**P** oxidised to carboxylic acid)

Comment: If the oxidized product is not isolated before adding Na_2CO_3(aq), presence of H_2SO_4(aq) used to acidify $K_2Cr_2O_7$(aq) will also cause CO_2(g) to be liberated.