H2 Chemistry TYS 2019 suggested answers

Paper 1 Answer Key

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

2019 A level Paper 1 suggested answers

1)

	Sr^{2+}	W	X^-	Y^{2-}
No of electrons	*36	*36*	*36*	*36*
No of protons	38	36	35	34
No of neutrons	*46	*46	*46	*46
Nucleon Number (no of protons + neutrons)	*84	82	81	80

* told in the question

Ans: **B**

2) Angle of deflection $\propto \frac{Charge}{mass}$

Mass of electron is approximately $\frac{1}{2000}$ the mass of a proton, hence electron has a larger angle of deflection.
The charged particles are attracted to the oppositely charged plate.

Ans: **C**

3) For Group 15 and Group 16 element
Electronic configuration where electrons are lost are as such:

	Group 15 element	**Group 16 element**
1st IE	ns^2 $\underline{np^3}$	ns^2 $\underline{np^4}$
2nd IE	ns^2 $\underline{np^2}$	ns^2 $\underline{np^3}$
3rd IE	ns^2 $\underline{np^1}$	ns^2 $\underline{np^2}$
4th IE	$\underline{ns^2}$	ns^2 $\underline{np^1}$

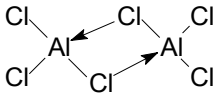
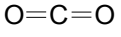
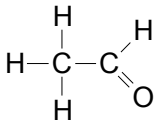
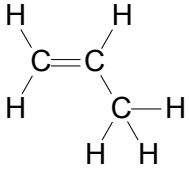
4^{th} IE in group 15 element will experience a slightly large spike as electrons are removed from an inner subshell.
Comparing the values given in the table, 4^{th} IE of option A and C experience a slightly larger spike than that of B and D => A and C belong to Group 15, B and D belong to Group 16.
Between Se and Te, Te is in a period further down the periodic table. This means that it has lower IE (since increase in no. of electron shell and shielding effect outweighs increase in nuclear charge) => Te must be **B**

Ans: **B**

4) BaO_2: ionic compound : Ba^{2+} O_2^{2-} (peroxide ion)
For O_2^{2-} dot and cross: Each O^- is bonded to another O^- by a single covalent bond (told in question).

Ans: **C**

5)

	Molecule	No of bonds
1		6 Sigma bonds
2		2 Sigma bonds 2 Pi bonds
3		6 Sigma bonds 1 Pi bond
4		8 Sigma bonds 1 Pi bond

Ans: **C**

6) Assuming the compounds behave as ideal gases, apply pV = nRT, rearranging, p = $\frac{nRT}{V} = \frac{mRT}{M_r V}$
Since T, V and m is constant, the smaller the M_r, the higher the pressure.

Molecule	CH_4	HCHO	CH_3Cl	HCO_2H
M_r	16	30	50.5	46

Ans: **A**

7) Follow the question closely for the reaction that happens:
NaN_3 (s) $\longrightarrow$ Na (s) + $\frac{3}{2}N_2$ (g)
Amount of NaN_3 = $\frac{5.00}{65.0}$ = 0.07692 mol
Amount of N_2 = 1.5 × 0.07692 = 0.1154 mol

pV = nRT
V = $\frac{nRT}{p} = \frac{0.1154 \times 8.31 \times (30+273)}{9.85 \times 10^4}$ = 0.00295 m^3 = 2.95 dm^3

Ans: **D**

8) Context of question: Period 3 and Period 4 elements behave similarly. As such, Ge behaves similarly to Silicon, which has high melting point due to its giant covalent lattice structure with strong covalent bonds and is also a semiconductor.

Ans: **B**

9) **Clue 1**: X dissolves in HC*l* to give Solution Y, which gives a white ppt insoluble in excess NaOH (aq)

Possible Metal	Solution Y it forms	White ppt it forms	
A*l*	Al^{3+}	$Al(OH)_3$	White ppt dissolves in excess NaOH to give $[Al(OH)_4]^-$
Mg	Mg^{2+}	$Mg(OH)_2$	White ppt insoluble in excess NaOH

Clue 2: Give off gas Z, which reacts with $O_2(g)$ to form H_2O and a white solid oxide that is insoluble in dilute acid or alkali.

Possible Non-Metal	Oxides it forms	Reaction with acid	Reactions with alkali
Si	SiO_2	No rxn	Insoluble in dilute alkali due to strong covalent bonds
P	P_4O_{10}	No rxn	React with bases to give a soluble salt.

Ans: **D**

10)

A	Not relevant, electron affinity is for non-metal forming anion.
B	False, electronegativity decreases down the group
C	True statement, but does not explain why chemical reactivity increases down the group
D	True, easier to lose the valence electrons as a result of increase in electronic shell, M is more easily oxidised to give M^{2+} .

Ans: **D**

11) Assume 100g of solder glass, of which 16g is B_2O_3 and 84g is PbO.

Amount of B_2O_3 = $\frac{16}{10.8 \times 2 + 16.0 \times 3}$ = 0.2298 mol

Amount of B = 0.2298×2 = 0.4596 mol

Amount of PbO = $\frac{84}{207.2 + 16.0}$ = 0.3763 mol

Amount of Pb = 0.3763 mol

$\frac{Amount\ of\ Pb}{Amount\ of\ B}$ = $\frac{0.3763}{0.4596}$ = 0.82

Ans: **A**

12)

A	False, for $\Delta H^{\ominus}_{combustion}$, H_2O should be in liquid state and not gaseous
B	True, $\Delta H^{\ominus}_{formation}$ involves element in the natural state.
C	False, $\Delta H^{\ominus}$atomisation is for per mol of atom formed, and hence, it should be $12 \times \Delta H^{\ominus}$atomisation
D	False, $\Delta H^{\ominus}_{formation}$ involves element in the natural state, hydrogen exist as $H_2(g)$, not H(g) atom.

Ans: **B**

13)

1	False, ΔH = −ve, ΔS = +ve (increase in no. of mol of gas) => $\Delta G < 0$ at all temperature.
2	True, since H_2O_2 can be stored for several week with little decomposition at rtp, suggesting rate is very slow, and hence high E_a.
3	False, ΔS = +ve (increase in no. of mol of gas)

Ans: **D**

14)

1	False. When [substrate]= x, initial rate of reaction remains constant despite any further increase in concentration of substrate.
2	False, since the graph shows that initial rate of reaction remains constant despite any further increase in concentration of substrate. order of reaction = 0 wrt to substrate.
3	True, as enzyme active sites are saturated, increasing substrate conc has no effect on the rate of reaction (as oppose to before [substrate]= x, where increasing conc of substrate increases rate of reaction by allowing more substrate to bind to the active sites of the enzymes).

Ans: **D**

15)

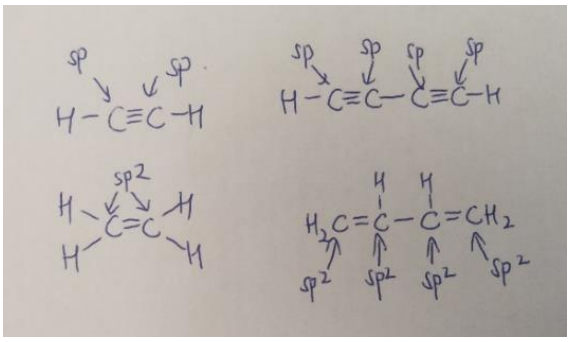
1	False. Increasing concentration may increase rate (if order of reaction wrt reactant is not zero), but only temperature and catalyst increases rate constant. Note : rate = k[reactant]^x
2	False, increasing **Temperature**, not conc, increases the number of particles with energy greater than or equal to activation energy.
3	True. Refer explanation for statement 1.
4	True. Refer explanation for statement 2.

Ans: **D**

16) Recall hybridisation:
Atom in a molecule undergoes hybridization depending on no. of electron regions after bonding.

Type of hybridization:

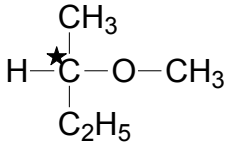
Type of hybridisation	No of eln region around atom (incl. bond pairs and lone pairs)
sp^3	4
sp^2	3
sp	2



Note : H atom does not undergo hybridisation as it has only 1 electron pair region after bonding.

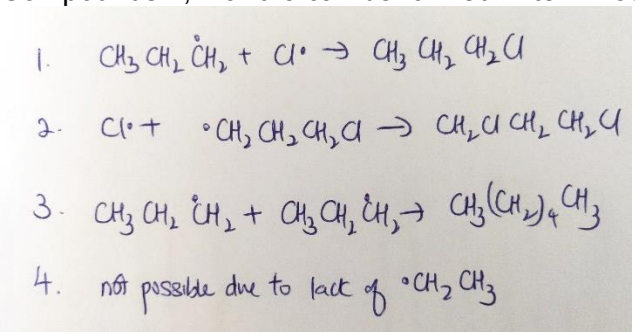
Ans: **A**

17) Chiral C => carbon with 4 different groups attached.



Ans: **B**

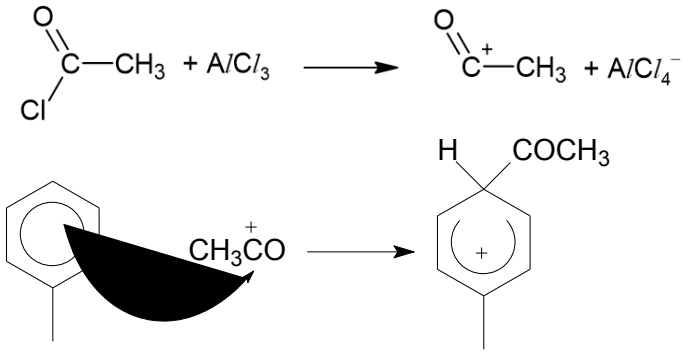
18) Compound 2 is a disubstituted product.
Compounds 1, 2 and 3 can be formed in termination steps of FRS.



Compounds 1 and 2 can also be formed in the propagation steps.

Ans: **A**

19) Reaction is electrophilic substitution.
E^+ must be electron deficient and is generated using a Lewis acid catalyst, $AlCl_3$.



Note : The benzene C that is bonded to 4 groups is sp^3 hybridised and hence it does not take part in the delocalization of pi electron, resulting in the "opening" in the benzene ring.

Ans: **A**

20) In order to for a racemic mixture from nucleophilic substitution/hydrolysis with aq NaOH, heat

1st criteria: must undergo S_N1 mechanism => must be tertiary RX.

2nd criteria: the product must have a chiral C (C atom bonded to 4 different groups).

		1st criteria	2nd criteria
A	$CH_3(CH_2)_6Cl \longrightarrow CH_3(CH_2)_6OH$	☒	☒
B	$(CH_3CH_2)_3Cl \longrightarrow (CH_3CH_2)_3OH$	☑	☒
C	$(CH_3)_2CHCH_2C(CH_3)_2Cl \longrightarrow (CH_3)_2CHCH_2C(CH_3)_2OH$	☑	☒
D	$(CH_3)_2CHC(CH_3)(CH_2CH_3)Cl \longrightarrow (CH_3)_2CHC(CH_3)(CH_2CH_3)OH$	☑	☑

Ans: **D**

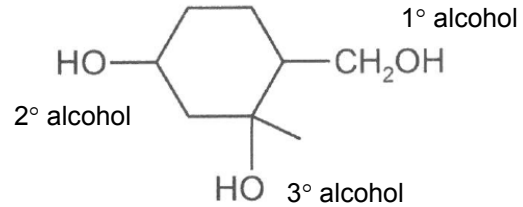
21) Recap reaction with Na, NaOH, Na_2CO_3:

	Na	**NaOH**	**Na_2CO_3 or $NaHCO_3$**
Alcohol	☑	☒	☒
Phenol	☑	☑	☒
Carboxylic acid	☑	☑	☑

- All -OH group react with Na(s).
- Acids (phenol and carboxylic acid) react with strong base like NaOH.
- Phenol (a very weak acid) cannot react with Na_2CO_3 (a very weak base)

Ans: **D**

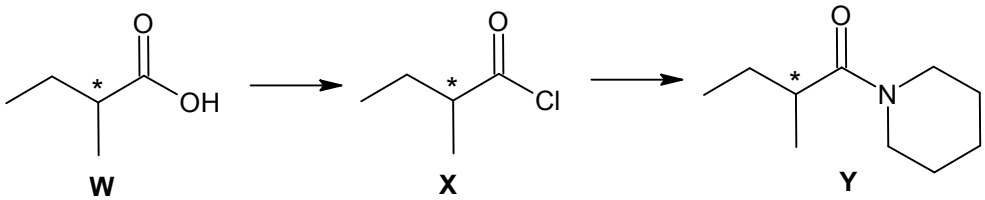
22)



Type of alcohol	**Oxidation product when heated under reflux with <u>excess</u> heat acidified potassium dichromate**
1°	Carboxylic acid (heating with reflux ensures any aldehyde produced is further oxidized to carboxylic acid)
2°	Ketone
3°	Does not oxidise

Ans: **C**

23) Based on the given options, Y is an amide, formed from the reaction between acid chloride (X) and the amine given in the question.
C and D cannot be the answer as the N is not part of the ring, and hence contradict the amine given.
Molecules of W are chiral, and B does not possess any chiral centre.
Hence, ans is A.



W **X** **Y**

Ans: **A**

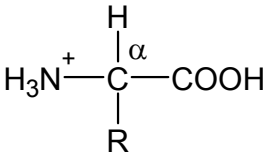
24) P is sparingly soluble in water => bulky structure with strong id-id intermolecular forces of attraction.

P dissolves readily in cold HCl => forms a salt with HCl via acid-base reaction.
The ionic salt product forms ion-dipole interaction with H_2O, hence the salt is more soluble than the molecular form. => P must contain a basic functional group.
Evaporation of the solution reforms the ionic solid.

C is the answer as phenylamine is basic, the ionic salt produced is $C_6H_5NH_3^+Cl^-$

Ans: **C**

25) pK_a values of amino acids are meant for the **<u>protonated form</u>** of the amino acids where the amino groups exist as its conjugate acid $-NH_3^+$.

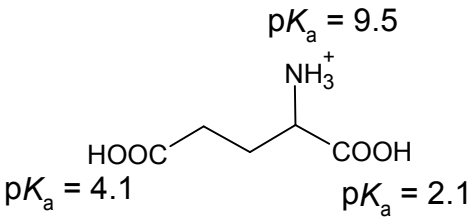


General guideline for relative pK_a values of acidic groups in protonated amino acids.

- $-COOH$ groups have a lower pK_a (more acidic) than $-NH_3^+$ group

For amino acid containing $-COOH$ in the side chain,

- $\alpha-COOH$ has a lower pK_a(more acidic) than side chain $-COOH$



Glutamic acid

<u>Predominant form of amino acids at different pH</u>

Recall that pH affects the ratio of weak acid and its conjugate base in a buffer system

$$pH = pK_a + \lg \frac{[A^-]}{[HA]}$$

When pH = pK_a, it is a maximum buffer capacity where $[A^-] = [HA]$

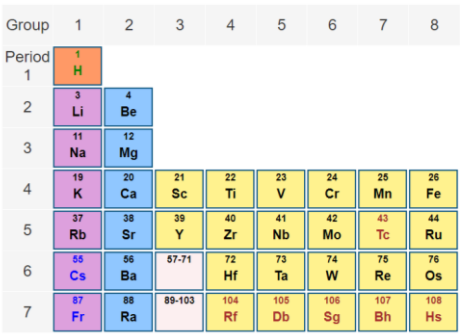
When pH < pK_a (a more acidic environment), [HA] is more than $[A^-]$

When pH > pK_a (a more alkaline environment), $[A^-]$ is more than [HA]

At pH 7, $\alpha-COO^-$, side chain $-COO^-$, $\alpha-NH_3^+$

Ans: **B**

26) Similar to d block element in the previous period, for transition metal cations, *remove electrons from the 5s (outermost shell) first before removal from the 4d.*



Configuration:

Mo: [Kr] $4d^5\ 5s^1$ (similar configuration as Cr)

Mo^{4+} : [Kr] $4d^2$

Ans: **B**

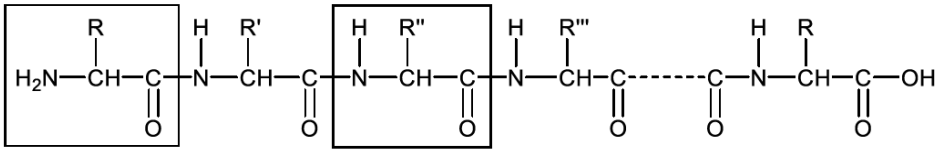
27) From QA notes in the Data Booklet, cations which dissolve in excess sodium hydroxide forming a complex: Al^{3+}, Cr^{3+}, Zn^{2+}
Coordination number for transition metal complex = 6
$Cr(OH)_3\,(s) \rightleftharpoons Cr^{3+}\,(aq) + 3OH^-\,(aq)$
$[Cr(H_2O)_6]^{3+} + 6\,OH^- \rightleftharpoons [Cr(OH)_6]^{3-} + 6H_2O$
Deep green solution

Note $Cr^{3+}(aq)$ can also be represented as $[Cr(H_2O)_6]^{3+}$

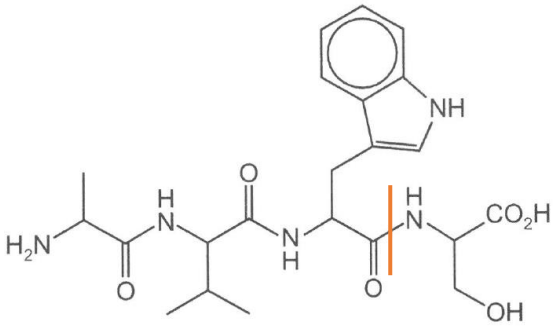
Ans: **C**

28) Chymotrypsin only hydrolyses peptide bond on the carboxyl side of a residue containing an aromatic ring. (as shown by the question)

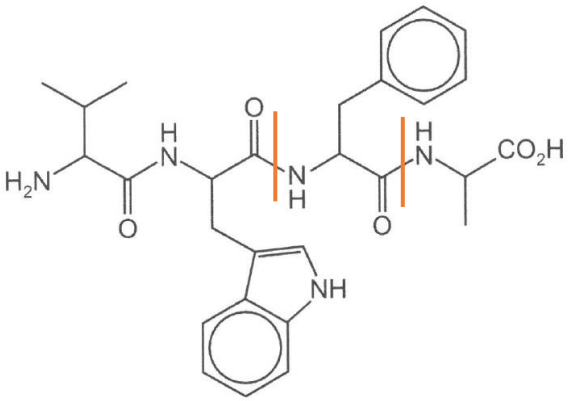
Note the structure of amino acid fragment in a polypeptide chain



A



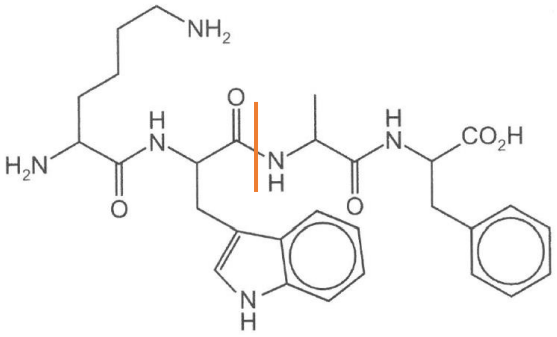
B



Left fragment: tripeptide
Right fragment: monopeptide

Total 3 fragments

C



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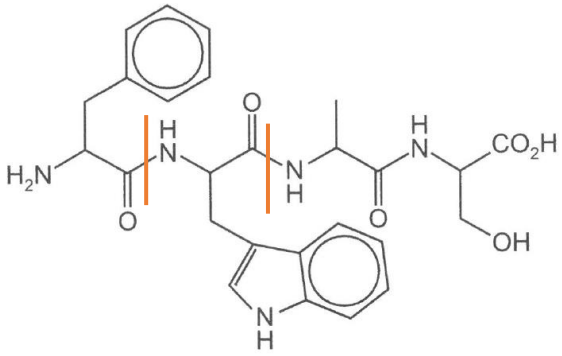


Left fragment: dipeptide
Right fragment: dipeptide

Total 3 fragments

Ans: **C**

29) At standard condition ("~~e~~"), concentration of all species in aq should be 1 mol dm^{-3}.

Ans: **B**

30) Ans: **B/C**
(Examiner Comments mention both answers are acceptable depending on how candidates interpret the qns)

Volume of each Cu atom = $(3 \times 10^{-12})^3 = 2.7 \times 10^{-35}$ m^3
Area of square Cu piece at cathode = $0.1 \times 0.1 = 0.01$ m^2

If interpret qn as total depth of 1000 atoms

Total volume of Cu to be deposited
= $0.01 \times 1000 \times 3 \times 10^{-12} = 3 \times 10^{-11}$ m^3

Total number of Cu atoms required
= $\frac{3 \times 10^{-11}}{2.7 \times 10^{-35}} = 1.111 \times 10^{24}$ atoms

Total mol of Cu atoms required
= $\frac{1.111 \times 10^{24}}{6.02 \times 10^{23}} = 1.846$ mol

$Cu^{2+} + 2e^- \longrightarrow Cu$
$I \times t = n_e \times F$
$4 \times t = 1.846 \times 2 \times 9.65 \times 10^4$
$t = 89070$ s = 24.7 h (**B**)

If interpret qn as total depth of 2000 atoms

Total volume of Cu to be deposited
= $0.01 \times 2000 \times 3 \times 10^{-12} = 6 \times 10^{-11}$ m^3

Total number of Cu atoms required
= $\frac{6 \times 10^{-11}}{2.7 \times 10^{-35}} = 2.222 \times 10^{24}$ atoms

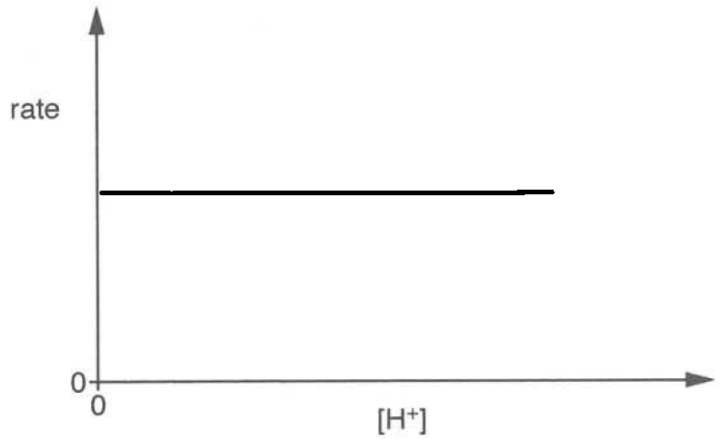
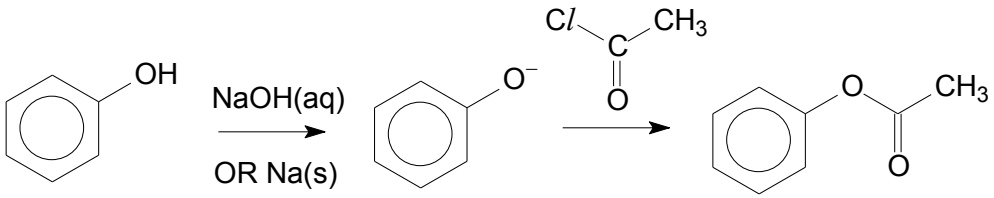
Total mol of Cu atoms required
= $\frac{2.222 \times 10^{24}}{6.02 \times 10^{23}} = 3.691$ mol

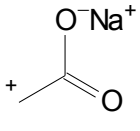
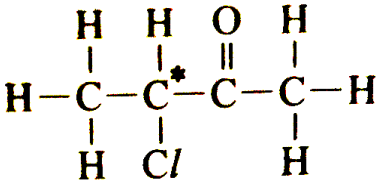
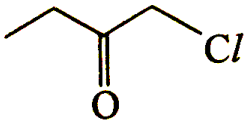
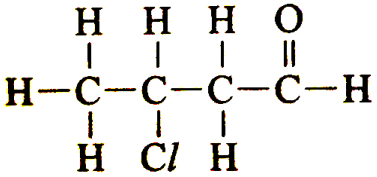
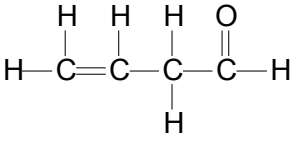
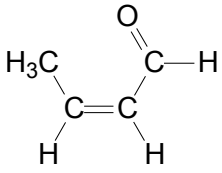
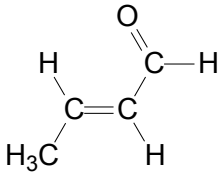
$Cu^{2+} + 2e^- \longrightarrow Cu$
$I \times t = n_e \times F$
$4 \times t = 3.691 \times 2 \times 9.65 \times 10^4$
$t = 178090$ s = 49.5 h (**C**)

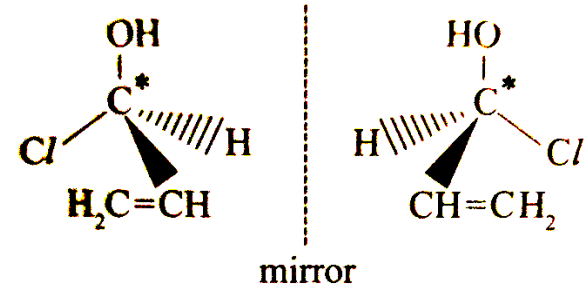
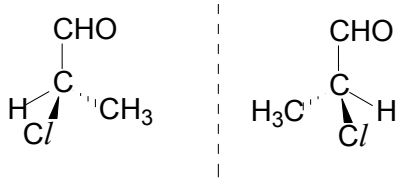
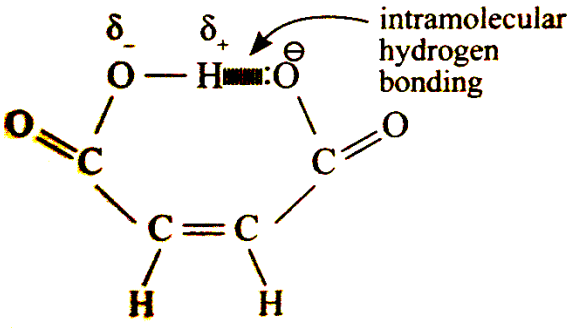
2019 A level Paper 2 suggested answers

1	**(a)**	**(i)**	Ca : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ Ca^{2+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
1	**(a)**	**(ii)**	Ca^{2+} ion has a **smaller** radius than Ca atom. Both Ca and Ca^{2+} experiences the same nuclear charge. The valence electrons of Ca occupy an outer quantum shell compared to Ca^{2+}. See part (i). Valence electrons in Ca atom experience **weaker nuclear attraction** thus it will have a **larger radius** than Ca^{2+} ion.
1	**(a)**	**(iii)**	Down Group 2, the number of filled quantum shells increases. The **valence electrons are further away from the nucleus and experience more shielding from the innershell electron**. Valence electrons thus experience **weaker nuclear attraction despite increase in nuclear charge.** Thus ionic size increases down the group.
1	**(a)**	**(iv)**	A_r of Sr and Ca are 87.6 and 40.1 respectively while their ionic size are 0.113 nm and 0.099 nm respectively. A_r of Sr is more than twice of Ca but ionic radii is not twice. For the same no of ions, **increase in mass is more significant than the increase in volume occupied by Sr** when compared to Ca, hence Sr has a larger density than Ca.
1	**(b)**	**(i)**	$CuCO_3\,(s) \rightarrow CuO(s) + CO_2\,(g)$ Heat
1	**(b)**	**(ii)**	Ionic radius : Mg^{2+} : 0.065 nm, Cu^{2+} : 0.073 nm, Ca^{2+} : 0.099 nm Size The charge/size and hence the polarising power of Cu^{2+} will be higher than that of Ca^{2+} but lower than Mg^{2+}. The electron cloud in carbonate of $CuCO_3$ will be distorted to a larger extent/ the C−O bond will be weakened to a larger extent in $CuCO_3$ compared to that in $CaCO_3$ but a lower extent than that of $MgCO_3$. Thus, the thermal stability of $CuCO_3$ is higher than that of $MgCO_3$ but lower than $CaCO_3$. Hence, the decomposition temperature of copper carbonate could be 450 °C (Any value between 350 °C and 832 °C)
1	**(c)**	**(i)**	1. Cu^{2+} ions can **form complexes** eg. $[Cu(NH_3)_4]^{2+}$ whereas Mg^{2+} ions cannot. 2. Cu^{2+} forms **coloured compounds** whereas Mg^{2+} compounds are white. 3. Cu^{2+} can catalyse reaction while Mg^{2+} cannot. Any 2 of the above

1	**(c)**	**(ii)**	1. Both Mg^{2+} and Cu^{2+} compounds can **react with sodium hydroxide to form ppt that is insoluble in excess** 2. Both Mg^{2+} and Cu^{2+} compounds can **conduct electricity** in the molten state but not in the solid state. 3. Both form precipitates with carbonate. Any 2 of the above
2	**(a)**	**(i)**	H_2O_2 is behaving as a **reducing agent**. When H_2O_2 is reacted with Ag_2O. The oxidation number of **Ag in Ag_2O** is reduced from **+1 to 0** in **Ag**.
2	**(a)**	**(ii)**	Variable 1 : Volume of O_2 gas produced. Variable 2 : length of time for reaction taking place. Instruments used for measurements: Volume of O_2 measured by **frictionless graduated gas syringe**. Duration of reaction measured by stopwatch, **starting stopwatch when reactants are added together is a sealed closed system**.
2	**(b)**	**(i)**	For every 1dm^3 of '20−volume' H_2O_2 solution, Volume of O_2 produced = $20 \times 1 = 20$ dm^3 Amount of $O_2 = \frac{20}{24} = 0.8333$ mol Mol ratio of $H_2O_2 : O_2 = 2 : 1$ Amount of H_2O_2 in 1 dm^3 = $0.8333 \times 2 = 1.667$ mol Concentration H_2O_2 = 1.67 mol dm^{-3}
2	**(b)**	**(ii)**	Mol ratio $Ag_2O : H_2O_2 = 1 : 1$ Amount of $H_2O_2 = \frac{10}{1000} \times 1.667$ $= 1.667 \times 10^{-2}$ mol Amount of $Ag_2O = 1.667 \times 10^{-2}$ mol Mass of $Ag_2O = 1.667 \times 10^{-2} \times (107.9 \times 2 + 16.0)$ $= 3.864 \approx 3.86$ g
2	**(c)**	**(i)**	Draw a tangent at t = 0 and find the gradient of the tangent. This will be the rate of reaction. Initial rate of reaction = $\frac{0.3 - 0}{30 - 0} = 0.01$ absorbance/s
2	**(c)**	**(ii)**	The order of reaction is 1st order with respect to I^-. From the graph, it is observed that the rate of reaction is directly proportional to the increase in the concentration of I^-.
2	**(c)**	**(iii)**	Rate = k $[H_2O_2]$ $[I^-]$
2	**(c)**	**(iv)**	Concentration of $H_2O_2 = \frac{1}{1 + 3 + 5 + 1} \times 0.1$ $= 0.0100$ mol dm^{-3}.

			Rate = k $[H_2O_2]$ $[I^-]$ Y = m X From the graph, Gradient of the graph = k$[H_2O_2]$ $\frac{5.3 \times 10^{-3}}{1.0 \times 10^{-3}} = k \times 0.01$ k = **530 mol^{-1} dm^3 s^{-1}**
2	**(c)**	**(v)**	 Rate is only dependent on $[H_2O_2]$ and $[I^-]$. Changing $[H^+]$ have no effect on the rate of reaction.
3	**(a)**	**(i)**	Phenol is a **weaker nucleophile** as compared to ethanol. The **lone pairs of electrons** on the **O atom on phenol** is **delocalised into the benzene ring**, making it **less available for attack on the electron deficient C** on the carboxylic acid functional group.
3	**(a)**	**(ii)**	Step 1 : NaOH (aq) Step 2 : CH_3COCl  phenyl ethanoate
3	**(b)**	**(i)**	ethanolic KCN, heat

3	**(b)**	**(ii)**	 If S_N1 mechanism, carbocation is formed. The carbocation is not connected to any electron releasing alkyl group, instead it is directly connected to a carboxylate group ($-COO^-$) which is an electron withdrawing group. It would intensify the positive charge on the C in the carbocation making it unstable.
3	**(b)**	**(iii)**	Both the Carbon in the C=O and C–C*l* are electron deficient and maybe attacked by a nucleophile. For substitution to occur, C–C*l* bond and C–O bond has to be cleaved respectively. Bond energy of C–C*l* and C–O bond are 340 and 360 kJ mol^{-1} respectively. It is easier to cleave C–C*l* bond hence more easily substituted. OR $-COO^-$ is stabilized by resonance, there is a partial double bond character in the C−O bond. Hence more energy is required to break the stronger C−O bond, making it unfavorable.
4	**(a)**	**(i)**	$RCOCl + H_2O \rightarrow RCOOH + HCl$ ROCl and ROOH not acceptable.
4	**(a)**	**(ii)**	
4	**(a)**	**(iii)**	
4	**(a)**	**(iv)**	 Note: the 3 alkenes formed are   

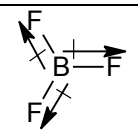
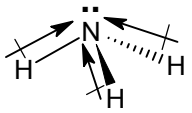
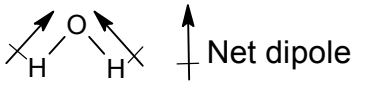
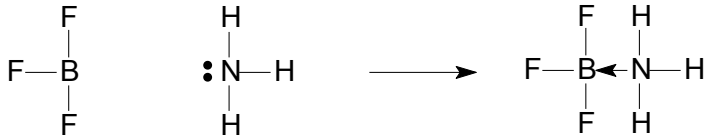
4	**(b)**	**(i)**	State relationship: Isomers G and H are non-superimposable mirror images of each other (Enantiomers / optical isomers). Effect on light: In a racemic mixture containing equal amount of two enantiomers, **net zero rotation of plane polarized light** is observed because **each enantiomer has equal but opposite effect on the plane polarized light**. When pure, each enantiomer rotates the plane polarized light in only either clockwise or anti-clockwise direction, hence exhibits optical activity.
4	**(b)**	**(ii)**	 OR 
4	**(c)**	**(i)**	
4	**(c)**	**(ii)**	**Restricted rotation in C=C** results in **–COOH and −COO⁻ groups on opposite side of C=C**, −COOH and −COO⁻ groups are **too far apart** for intramolecular hydrogen bonding to occur.
4	**(c)**	**(iii)**	Chemistry principle: The strength of an acid increases with the stability of the conjugate base formed upon dissociation, increasing the K_a value. Electronic effect or additional interaction: Intramolecular hydrogen bonding makes conjugate base of cis isomer more stable than the trans isomer, hence cis isomer has greater acid strength and has larger K_{a1} than trans isomer.

5	**(a)**		$[H^+] = 10^{-7} = 1.00 \times 10^{-7}$ mol dm^{-3} $K_c = \frac{[HClO][H^+][Cl^-]}{[Cl_2]}$ $\frac{[HClO]}{[Cl_2]} = \frac{K_c}{[H^+][Cl^-]}$ $= \frac{4.5 \times 10^{-4}}{(1 \times 10^{-7})(1 \times 10^{-3})} = 4.5 \times 10^6$
5	**(b)**		Similarity: Both acids are monobasic acids. Difference: HC*l* is a strong acid that dissociates completely in water while HC*l*O is a weak acid which dissociates partially in water.
5	**(c)**		**<u>Method 1</u>** 1ppm of free chlorine $= \frac{1 \text{ mol of free chlorine}}{1000000 \text{ mol of } H_2O}$ 1 dm^3 solution, mass of H_2O = 1000 g Amount of $H_2O = \frac{1000}{18.0} = 55.56$ mol For 1ppm of chlorine in 1dm^3, amount of free chlorine $= \frac{1}{1000000} \times 55.56 = 5.56 \times 10^{-5}$ mol Concentration of free chlorine = 5.56×10^{-5} mol dm^{-3} **<u>Method 2</u>** 1ppm of free chlorine $= \frac{1 \text{ mol of free chlorine}}{1000000 \text{ mol of } H_2O}$ For every 1 mol of free chlorine, mass of $H_2O = 1000000 \times 18.0 = 18000000$ g Volume of $H_2O = 18000000$ cm^3 = 18000 dm^3 Concentration of 1ppm of free chlorine $= \frac{1 \text{ mol of free chlorine}}{18000 \text{ dm}^3 \text{ of } H_2O} = 5.56 \times 10^{-5}$ mol dm^{-3}
5	**(d)**		$n(S_2O_3^{2-}) = 37.50 \times 10^{-3} \times 4.00 \times 10^{-4}$ $= 1.5 \times 10^{-5}$ mol $n(I_2) = ½ \times n(S_2O_3^{2-})$ $= 7.5 \times 10^{-6}$ mol = n(HC*l*O) Concentration of free chlorine $= \frac{7.5 \times 10^{-6}}{150 \times 10^{-3}}$ $= 5 \times 10^{-5}$ mol dm^{-3} < 5.56×10^{-5} mol dm^{-3} Water quality is not acceptable.

5	**(e)**	**(i)**	$[H^+] = 10^{-8}$ mol dm^{-3}, total free chlorine concentration = 6.0×10^{-5} mol dm^{-3} Let $[C\mathit{l}O^-]$ be x $\quad$ $[HC\mathit{l}O] = 6.0 \times 10^{-5} - x$ $K_a = \frac{[C\mathit{l}O^-][H^+]}{[HC\mathit{l}O]}$ $\frac{x}{6.0 \times 10^{-5} - x} = \frac{3.7 \times 10^{-8}}{10^{-8}}$ $x = 3.7 (6.0 \times 10^{-5} - x)$ $x = 2.22 \times 10^{-4} - 3.7x$ $x = 4.723 \times 10^{-5}$ $[C\mathit{l}O^-] = 4.72 \times 10^{-5}$ mol dm^{-3} $[HC\mathit{l}O] = 1.28 \times 10^{-5}$ mol dm^{-3}
5	**(e)**	**(ii)**	$HC\mathit{l}O\ (aq) \rightleftharpoons H^+\ (aq) + C\mathit{l}O^-\ (aq)$ Higher $[H^+]$ at pH 7 than pH 8. In order to partially offset the increase $[H^+]$, formation of $HC\mathit{l}O$ is favoured. Since $HC\mathit{l}O$ is a more effective disinfectant than $C\mathit{l}O^-$, free chlorine at pH 7 is more effective than pH 8.
5	**(f)**	**(i)**	A free radical is an atom with an unpaired electron.
5	**(f)**	**(ii)**	$H{-}O{-}C\mathit{l} \rightarrow H{-}O\bullet + C\mathit{l}\bullet$ The $O{-}C\mathit{l}$ bond is weaker than the $H{-}O$ bond as can be seen from the bond energy values. Hence, its more likely that the $O{-}C\mathit{l}$ bond undergoes homolytic fission instead.
5	**(f)**	**(iii)**	$\bullet C\mathit{l} + HC\mathit{l}O \longrightarrow C\mathit{l}O\bullet + HC\mathit{l}$ OR $\bullet OH + HClO \longrightarrow C\mathit{l}O\bullet + H_2O$
5	**(f)**	**(iv)**	From Qn : $C\mathit{l}O\bullet + H_2O \rightarrow HC\mathit{l}O_2 + HC\mathit{l}$ (not balanced) [O] $C\mathit{l}O\bullet + H_2O \rightarrow HC\mathit{l}O_2 + H^+ + e^-$ [R] $C\mathit{l}O\bullet + 3\ H^+ + 3\ e^- \rightarrow H_2O + HC\mathit{l}$ ——————————— Overall equation : $4C\mathit{l}O\bullet + 2H_2O \rightarrow 3HC\mathit{l}O_2 + HC\mathit{l}$
5	**(f)**	**(v)**	UV light decomposes $C\mathit{l}O^-$, (refer to part (f)) not the organic species. Position of equilibrium in part (v) will shift right to partially offset decrease in conc of $C\mathit{l}O^-$. maintaining $[C\mathit{l}O^-]$.

5	**(g)**	**(i)**	$CaSO_4$ (s) $\rightleftharpoons$ Ca^{2+} (aq) + SO_4^{2-} (aq) $CaCl_2$ (aq) $\rightarrow$ Ca^{2+} (aq) + $2Cl^-$ (aq) Addition of $CaCl_2$ will increase the concentration of Ca^{2+} ions. Position of equilibrium shift to LHS to favour precipitation of calcium sulfate, preventing the plaster from dissolving.
5	**(g)**	**(ii)**	pOH = 14 – 8.0 = 6.0 $[OH^-] = 10^{-6}$ mol dm^{-3} $K_{sp} = [Ca^{2+}][OH^-]^2$ $5.5 \times 10^{-6} = [Ca^{2+}] (10^{-6})^2$ $[Ca^{2+}] = 5.5 \times 10^6$ mol dm^{-3} A large concentration of calcium ions would be required before calcium hydroxide precipitates at pH 8.0. Hence its highly unlikely that the cloudiness is due to calcium hydroxide formation.

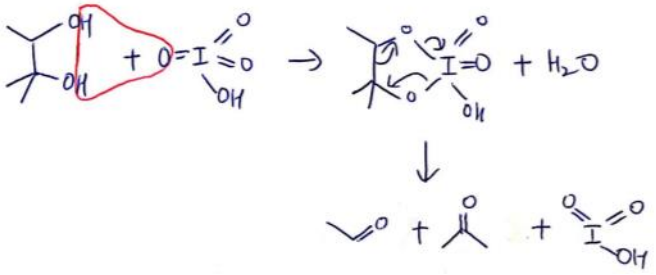
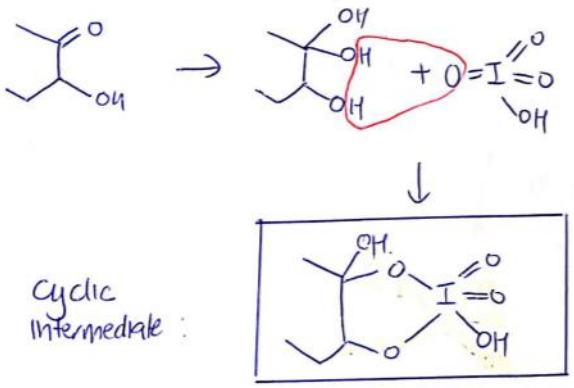
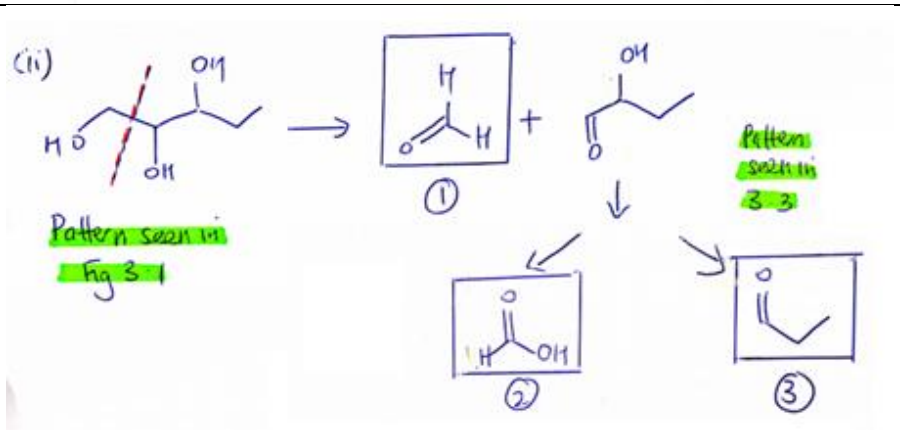
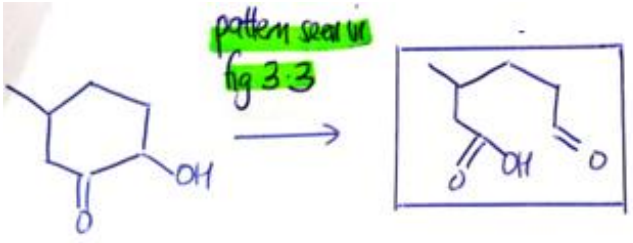
2019 A level Paper 3 suggested answers

1	**(a)**		By VSEPR theory, the electron pairs are arranged as far apart as possible to minimise repulsion. BF_3 has 3 bond pairs and 0 lone pairs, the electron pairs are arranged in trigonal planar geometry and the bond angles is 120 °. Both NH_3 and H_2O have a total of 4 electron pairs and the electron pairs are arranged in tetrahedral geometry. NH_3 has 3 bond pairs and 1 lone pair, H_2O has 2 bond pairs and 2 lone pairs. Since lone pair-lone pair repulsion > lone pair-bond pair repulsion > bond pair-bond pair repulsion, the bond angle in NH_3 is 107 ° and in H_2O is 104.5 ° (or 105 °).
1	**(b)**		 Overall non-polar  Net dipole Overall polar  Net dipole Overall polar
1	**(c)**	**(i)**	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ NH_3 is a Bronsted base (H^+ acceptor) and H_2O is a Bronsted acid (H^+ donor).
1	**(c)**	**(ii)**	 BF_3 is a Lewis acid (electron pair acceptor) and NH_3 is a Lewis base (electron pair donor).
1	**(d)**	**(i)**	In order for a real gas to approach ideal behaviour, the intermolecular forces must be negligible (very weak intermolecular forces) and the volume of the gas **particles** must be negligible compared to the volume of the container (very small gas particles).
1	**(d)**	**(ii)**	BF_3 has instantaneous dipole-induce dipole attractions between molecules which is the weakest intermolecular forces and therefore BF_3 is closest to ideal gas behaviour. Both H_2O and NH_3 has hydrogen bonding between gas molecules. The hydrogen bonding between H_2O molecules is more extensive than the hydrogen bonding between NH_3 molecules and therefore H_2O behaves less ideally than NH_3.
1	**(e)**	**(i)**	Down group 17, the M_r of the halogens increases and the electron cloud size increases which is more easily distorted. Instantaneous dipole-induced dipoles attractions become stronger and requires more energy to overcome. The boiling point increases and hence the volatilities decrease down group 17.

1	**(e)**	**(ii)**	• Cl_2(aq) and KI(aq) $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$ Colourless/pale yellow solution turns brown. • Br_2(aq) and KC*l*(aq) Orange solution remains orange. • I_2(aq) and KBr(aq) Brown solution remains brown.
2	**(a)**	**(i)**	Concentration of saturated solution of CO_2 = 0.040 × 300 = 12.0 mol dm^{-3}
2	**(a)**	**(ii)**	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ ---------(1) $H_2S(aq) \rightleftharpoons HS^-(aq) + H^+(aq)$ ----------(2) $H^+(aq) + CO_3^{2-}(aq) \longrightarrow HCO_3^-(aq)$ ----------(3) $H_2S(aq)$ dissociates partially to give $HS^-(aq)$ and $H^+(aq)$ near deep-sea hydrothermal vent. $H^+(aq)$ react with carbonate ion to give $HCO_3^-(aq)$. As such the concentration of $CO_3^{2-}(aq)$ decreases, and position of equilibrium (1) shift right, resulting in the dissolution of $CaCO_3(s)$, and $Ca(HCO_3)_2(aq)$ is formed.
2	**(b)**		$\Delta H_r^\ominus$ = $\Delta H_f^\ominus$(product) − $\Delta H_f^\ominus$(reactant) = [−1273.3 + 6×(−285.8) + 0] – [6×(−393.5) + 12×(−20.6)] = −379.9 ≈ −380 kJ mol^{-1} Note: $\Delta H_f^\ominus$ S(s) = 0
2	**(c)**	**(i)**	$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ −83 = −379.9 − 298($\Delta S^\ominus$) $\Delta S^\ominus$ = −0.996 kJ mol^{-1} K^{-1}
2	**(c)**	**(ii)**	P = 300 bar and temperature 100 – 400 ^{o}C at deep sea hydrothermal vent, deviates from standard conditions of 1 bar and 298 K. At the higher temperature, H_2O (g) is produced instead of H_2O (l). [glucose and S solid might be of a different state too] Hence ΔS and ΔH may deviate significantly from the $\Delta S^\ominus$ and $\Delta H^\ominus$ causing ΔG to be more negative than $\Delta G^\ominus$.
2	**(d)**	**(i)**	A_r = (32 × 0.935) + (33 × 0.015) + (34 × 0.045) + (36 × 0.005) = 32.125 ≈ 32.13 (4sf)
2	**(d)**	**(ii)**	Half-life is the time taken for the quantity of a species to be reduced to half of it's original quantity.
2	**(d)**	**(iii)**	For radioactivity to fall to 1/8 is 3 half-lives. Time taken = 3 × 87 = 261 days

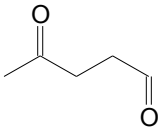
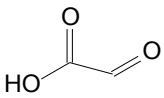
2	**(d)**	**(iv)**	$k = \frac{0.693}{87} = 7.9655 \times 10^{-3}$ $\frac{(^{35}S)_t}{(^{35}S)_0} = 10^{-\frac{7.9655 \times 10^{-3} \times 3}{2.3}} = 0.97646$ (Remaining ^{35}S after 3 days) Percentage decrease = $(1 - 0.97636) \times 100\% = 2.36\%$
2	**(e)**	**(i)**	$pK_b = 14 - 7.05 = 6.95$ $K_b = 10^{-6.95}$ $HS^- + H_2O \rightleftharpoons H_2S + OH^-$ $K_b = \frac{[OH^-]^2}{0.10}$ $[OH^-] = \sqrt{0.10 \times 10^{-6.95}} = 1.06 \times 10^{-4}$ mol dm^{-3} pOH = 3.975 pH = 10.025 = 10.0 (3sf) or 10.03 (2d.p.)
2	**(e)**	**(ii)**	$H_2S \rightleftharpoons HS^- + H^+$ $CH_3CH_2SH \rightleftharpoons CH_3CH_2S^- + H^+$ $C_6H_5SH \rightleftharpoons C_6H_5S^- + H^+$ The conjugate base $CH_3CH_2S^-$ is the most unstable as CH_3CH_2- is an electron donating alkyl group which intensifies the negative charge on $-S^-$, the conjugate base $C_6H_5S^-$ is the most stable as lone pair electron on $-S^-$ can delocalise into the benzene ring and the negative charge on $-S^-$ is dispersed. The more stable the conjugate base, the position of equilibrium shift to the RHS and the stronger the acid. Therefore, C_6H_5SH is the most acidic and has the lowest pK_a followed by H_2S and CH_3CH_2SH.
2	**(e)**	**(iii)**	Bond energy of S−H and O−H bonds are 347 and 460 kJ mol^{-1} respectively. Less energy required to dissociate S−H bond, greater acid dissociation can take place. Hence K_a of R−SH is larger and it's pK_a smaller than R−OH. OR $CH_3CH_2SH \rightleftharpoons CH_3CH_2S^- + H^+$ $CH_3CH_2OH \rightleftharpoons CH_3CH_2O^- + H^+$ O is more electronegative than S, the negative charge on $CH_3CH_2O^-$ is more intensified as compared to $CH_3CH_2S^-$. Hence $CH_3CH_2S^-$ is a more stable conjugate base, the position of equilibrium shift to the RHS and greater acid dissociation can take place. Hence K_a of R−SH is larger and it's pK_a smaller than R−OH.

2	**(f)**	**(i)**	The hydrogen bonding between CH_3CH_2OH is stronger than the permanent dipole-permanent dipole(pd−pd) attractions between CH_3OCH_3 and requires more energy to overcome. Therefore, the boiling point of CH_3CH_2OH is higher than that of CH_3OCH_3. Both CH_3SCH_3 and CH_3OCH_3 are polar molecules with pd−pd and instantaneous dipole−induced dipole(id−id). CH_3SCH_3 has larger M_r and larger electron cloud size which is more easily distorted. The id−id attractions between CH_3SCH_3 is stronger than CH_3OCH_3 and requires more energy to overcome. Therefore, the boiling point of CH_3SCH_3 is higher than that of CH_3OCH_3.
2	**(f)**	**(ii)**	Both compounds are polar molecules with permanent dipole-permanent dipole and instantaneous dipole−induced dipole(id−id). CH_3SCH_3 and CH_3CH_2SH has similar M_r and hence similar electron cloud size. Therefore, the strength of intermolecular forces are similar and requires similar amount of energy to overcome.
3	**(a)**	**(i)**	[R] $ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$ [O] $I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$ Overall equation: $3ClO^- + I^- \longrightarrow 3Cl^- + IO_3^-$
3	**(a)**	**(ii)**	$E^{\ominus}_{cell} = E^{\ominus}_{red} + E^{\ominus}_{ox} = (0.81) + (-0.26) = +0.55$ V
3	**(a)**	**(iii)**	$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$ For 1 mol of IO_3^-, 6 mol of electrons are involved, Hence $\Delta G^{\ominus} = -(6)(96500)(0.55) = -318450$ Jmol^{-1} ≈ -318 kJ mol^{-1} (3sf)
3	**(b)**	**(i)**	Amount of $S_2O_3^{2-} = \frac{36.20}{1000} \times 0.1 = 0.00362$ mol $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$ Amount of $I_2 = 0.00181$ mol (Since O.S. of La is +3) Amount of $La(IO_3)_3 = \frac{1}{138.9 + 3 \times (126.9 + 16.0 \times 3)} = 0.001506$ mol Amount of $IO_3^- = 3 \times 0.001506 = 0.004518$ mol Amount of IO_3^- : Amount of $I_2 = 0.004518 : 0.00181 = 5 : 2$ (shown) **Thinking process:** $5IO_3^- \longrightarrow$ periodate(VII) ion + $2I_2 + O_2$ Based on law of conservation of charges, periodate(VII) ion must have a charge of −5, hence it is IO_6^{5-}. Ionic equation: $5IO_3^- \longrightarrow IO_6^{5-} + 2I_2 + \frac{9}{2}O_2$
3	**(b)**	**(ii)**	$10La(IO_3)_3 \longrightarrow 2La_5(IO_6)_3 + 12I_2 + 27O_2$

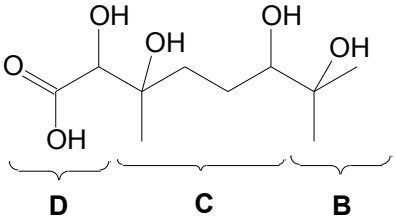
3	(c)	(i)	**Comments:** From Fig 3.2, it can be seen that diol react with HIO_4 via condensation, losing a water. From the next para, it was told that the ketone will undergo hydration to give a gem diol. Hence, the product of this reaction undergone condensation with HIO_4 giving the cyclic intermediate (i) Pattern given in qns.  (2)(i)  Cyclic intermediate :
3	(c)	(ii)	(ii)  Pattern seen in Fig 3.1 Pattern seen in 3.3  pattern seen in fig 3.3

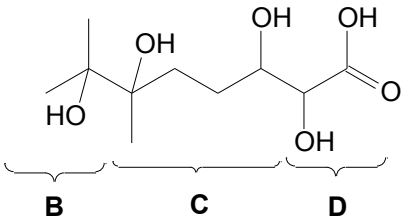
3	(d)	(i)	Note: Concept on degree of unsaturation is not required for H2 Chemistry

Clue	Deduction
Citral: $C_{10}H_{16}O$	3 degree of unsaturation (DOU)=> no benzene ring
Citral: Silver mirror with Tollen's reagent	Oxidation Citral contains aldehyde (1 DOU already)
Citral: Decolouries bromine water	Electrophilic addition Citral contains alkene
Citral: React with cold $KMnO_4$ to form A, $C_{10}H_{20}O_6$	Mild oxidation A has 4 −OH added across, hence Citral should contain 2 C=C, giving 2 pairs of diol.
A: does not react with tollens' reagent, but react with Na_2CO_3.	A no longer contains aldehyde, but carboxylic acid (Acid carbonate rxn) (* note: even though we learn aldehyde oxidises to carboxylic acid with hot $KMnO_4$, here, with clues given, we are expected to know that oxidation occur even with cold $KMnO_4$)
B: C_3H_6O, yellow ppt with alkaline aq I_2	Oxidation B contains methyl carbonyl group
C: $C_5H_8O_2$, give yellow ppt with alkaline aq iodine, give red ppt with Fehling solution	Oxidation C's DOU = 2 Contains aliphatic aldehyde (CHO) Contains methyl carbonyl group for the 2nd degree of unsaturation.
D: $C_2H_2O_3$, give red ppt with Fehling solution	Oxidation D contains aliphatic aldehyde (CHO)

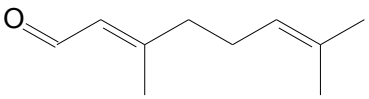
B:  **C:**  **D:** 

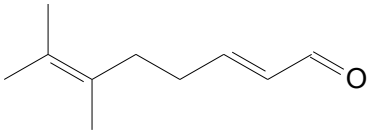
Two possible structures of **A**:

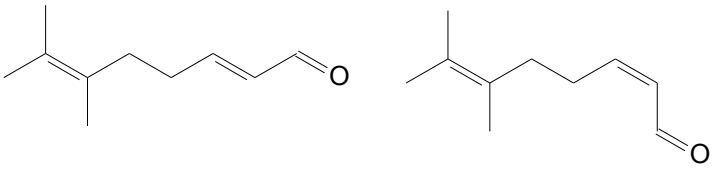


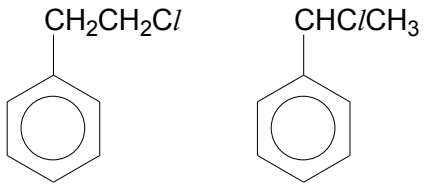


Two possible structures of citral:





3	**(d)**	**(ii)**	cis-trans isomerism  OR 
4	**(a)**		NaC*l*: giant ionic lattice with ionic bonds Dissolves in water but does not hydrolyse in water as Na^+ has low charge/size. pH = 7 NaC*l* + aq $\longrightarrow$ $Na^+ + Cl^-$ A*l*C*l*$_3$: simple covalent molecule. Dissolves in water and Al^{3+}(aq) undergoes partial hydrolysis in water. *Note: Al^{3+} has high charge/size, and hence is able to polarise the O−H bond in its H_2O ligand and donate a H^+ to the neighbouring H_2O molecule as shown below. A*l*C*l*$_3$ + $6H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$ $[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$, pH = 3 (partial dissociation) PC*l*$_5$: simple covalent molecule. PC*l*$_5$ hydrolyses in water to give an acidic solution. *Note: P in PC*l*$_5$ has energetically accessible empty 3d orbitals which can accept a lone pair from water during hydrolysis. PC*l*$_5$ + $4\ H_2O \rightarrow H_3PO_4 + 5HCl$, HC*l* $\rightarrow H^+ + Cl^-$,pH = 1 (complete dissociation)
4	**(b)**	**(i)**	$K_{sp} = [Pb^{2+}][Cl^-]^2\ mol^3\ dm^{-9}$

4	**(b)**	**(ii)**	$K_{sp} = [Pb^{2+}][Cl^-]^2\ mol^3\ dm^{-9}$ Let solubility of $PbCl_2$ be x mol dm^{-3}, $1.7 \times 10^{-5} = (x)(2x)^2$ $x = 1.620 \times 10^{-2}$ Amount of $PbCl_2(s) = \frac{10}{1000} \times 1.620 \times 10^{-2} = 1.620 \times 10^{-4}$ mol Mass of $PbCl_2 = 1.620 \times 10^{-4} \times (207.2 + 2 \times 35.5) = 4.51 \times 10^{-2}$ g $K_{sp} = [Pb^{2+}][I^-]^2\ mol^3\ dm^{-9}$ Let solubility of PbI_2 be y mol dm^{-3}, $9.8 \times 10^{-9} = (y)(2y)^2$ $y = 1.348 \times 10^{-3}$ Amount of $PbI_2 = \frac{10}{1000} \times 1.348 \times 10^{-3} = 1.348 \times 10^{-5}$ mol Mass of $PbI_2 = 1.348 \times 10^{-5} \times (207.2 + 126.9 \times 2) = 6.21 \times 10^{-3}$ g $PbCl_2$ gives a larger mass.
4	**(c)**	**(i)**	
4	**(c)**	**(ii)**	Rate of Nu Sub is independent of $[OH^-]$ => S_N1 mechanism Hence E cannot be 1° RX Hence, E must be 
4	**(c)**	**(iii)**	Reaction to form E: Electrophilic addition. Reaction to form F: Nucleophilic substitution S_N1 Both reactions involve a trigonal planar carbocation intermediate where the nucleophile (Cl^- and OH^-) can attack from both top and bottom of the plane with equal probability, giving rise to 50:50 of both enantiomers, as the product has a chiral carbon.

4 (d) (i) Free Radical Substitution

Initiation

$Cl\!-\!Cl \xrightarrow{uv} 2Cl\bullet$

Propagation

$R\!-\!H + Cl\bullet \longrightarrow R\bullet + HCl$

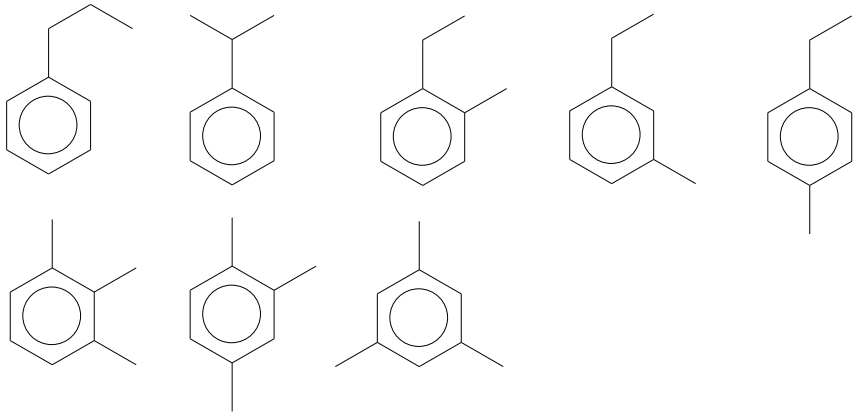
$\bullet R + Cl_2 \longrightarrow R\!-\!Cl + Cl\bullet$

Termination

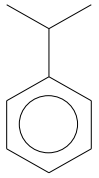
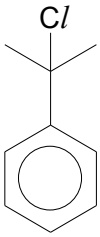
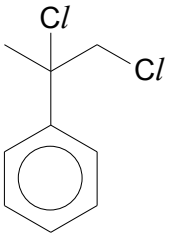
$\bullet Cl + \bullet Cl \longrightarrow Cl_2$

$\bullet R + \bullet R \longrightarrow R\!-\!R$

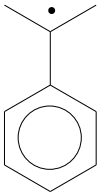
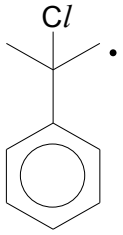
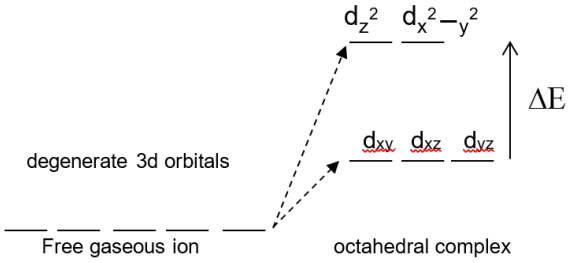
4 (d) (ii)

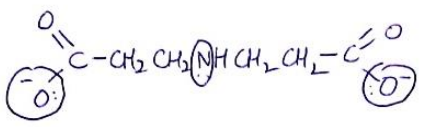
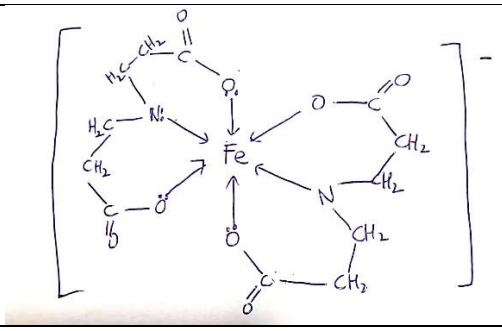


4 (d) (iii)

G	H	J
		

J is disubstituted and contains a chiral centre and H does not.

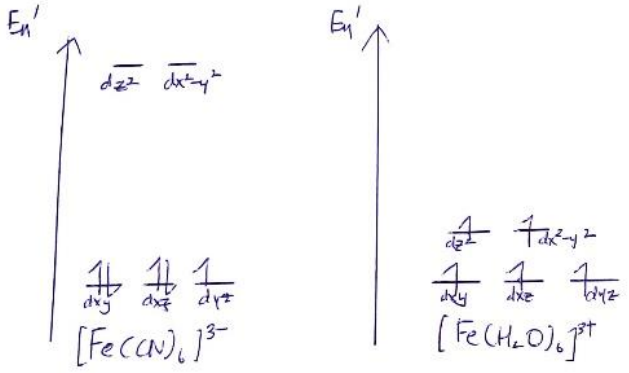
4	**(d)**	**(iv)**	Conversion of G to H involves the radical  , it can be resonance stabilised hence activation energy (E_a) to convert G to H has a much lower E_a than conversion of H to J. (Or the radical is stabilized by greater number of electron donating alkyl group. Conversion of H to J involves the radical  , the radical is attached to 1 electron donating alkyl group only hence very unstable, giving rise to higher E_a, thus slower rate of reaction.
5	**(a)**		Fe^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$
5	**(b)**	**(i)**	Possessing the same energy
5	**(b)**	**(ii)**	 In **octahedral** complexes, the lone pairs electrons of the six ligands approach the central metal ion ***along the x, y and z axes.*** The energy of an electron in any of the d-orbitals will be higher than it is in an isolated atom because of electronic repulsion between the electron pair in ligands and the electrons in the d-orbitals. d_{x2-y2}, d_{z2} orbitals are higher in energy as these orbitals are oriented along the axis and faces direct repulsion from electrons from incoming ligands. d_{xy}, d_{xz} and d_{yz} orbitals are lower in energy as these orbitals are oriented between the axis and faces lesser repulsion from electrons from incoming ligands.

5	**(c)**	**(i)**	L: $BrCH_2CH_2CN$ M: $NC—CH_2CH_2NHCH_2CH_2CN$ Step 1: 1 mole of Ethanolic KCN, Heat Step 2: limited ethanolic NH_3, heat in sealed tube. Step 3: H_2SO_4(aq), heat
5	**(c)**	**(ii)**	Possible side products: Step 1: $NCCH_2CH_2CN$ OR Step 2: $(NCCH_2CH_2)_3N$ or $H_2NCH_2CH_2CN$ or $(NCCH_2CH_2)_4N^+Br^-$ One way to minimise the side product: Step 1: use one mol of KCN to 1 mol $BrCH_2CH_2Br$ Step 2: use ½ mol of NH_3 to 1 mol of $BrCH_2CH_2CN$
5	**(c)**	**(iii)**	
5	**(c)**	**(iv)**	

5 (c) (v)

Since CN^- is a stronger ligand than H_2O and hence the energy gap between the d orbitals are larger, it is energetically more favourable to pair up the electrons in the lower energy d-orbitals compared to promoting the electrons from the lower energy d orbitals to the much higher energy d orbitals. As such, it only has 1 unpaired d electrons (see diagram below).

As the energy gap in $[Fe(H_2O)_6]^{3+}$ is smaller, it is energetically more favourable to promote the electrons to the higher energy level d orbitals than to pair up the electrons in the low energy d orbitals due to interelectronic repulsion.



5 (d) (i)

$K_p = \dfrac{(P_{CO2})^3}{(P_{CO})^3}$ (no units)

5 (d) (ii)

	$Fe_2O_3(s)$	$3CO(g)$	$\rightleftharpoons$	$2Fe(l)$	$3CO_2(g)$
I/bar	-	1		-	
C/bar	-	−x		-	+x
E/bar	-	1−x		-	x

$K_p = 19.9 = \dfrac{(x)^3}{(1-x)^3}$

$\sqrt[3]{19.9} = \dfrac{x}{1-x}$

$x = 0.730$ bar

5 (d) (iii)

No change in number of moles of gas molecules. However, 1 mol of solid react to give 2 mol of liquid, resulting in slightly higher degree of disorderliness, hence $\Delta S^{\ominus}$ is small but positive.