H2 CHEMISTRY EXAMINATION YEAR 2022

PAPER 1

1. **C** [3: Chemical Bonding]
   NaF is an ionic compound with giant ionic lattice structure. Thus, it requires the greatest amount of energy to overcome the strong electrostatic forces of attractions between the oppositely charged Na^+ and F^- ions. Hence, it has the highest boiling point.
   $CH_3CH_2NH_2$, CH_3CH_2OH and $CH_3CH_2NH_2$ exist as simple molecular structures, and thus, their boiling points are determined by the weaker intermolecular forces of attractions between the molecules.
   Both CH_3CH_2OH and $CH_3CH_2NH_2$ are able to form the stronger intermolecular hydrogen bonding between their respective molecules whereas $CH_3CH_2CH_3$ forms the weak id-id intermolecular attractions between their molecules. As such, $CH_3CH_2CH_3$ has the lowest boiling point. Oxygen is more electronegative than nitrogen, as such, the hydrogen bonding between CH_3CH_2OH molecules is stronger than those between $CH_3CH_2NH_2$ molecules. As such, CH_3CH_2OH has higher boiling point than $CH_3CH_2NH_2$.

2. **C** [3: Chemical Bonding]
   The Br-Cl covalent bond is polar due to the electronegativity difference between Br and Cl. As we go down the group, electronegativity decreases and thus, Br is less electronegative than Cl. This is because Br has an additional electron shell. Effect of increase in shielding (& increase in radius) outweigh the effect of increase in nuclear charge. Bonding electrons are less attracted to the positive nucleus.

3. **D** [7.2: Acid-Base and Solubility Equilibria]
   pKa is a number that describes the acidity of a particular acid molecule. The lower the value of pKa, the larger the acid dissociation constant, Ka, and thus the stronger the acid, and the greater its ability to donate its protons, H^+.
   Thioacetic acid has a smaller pKa (and thus larger Ka) than ethanoic acid. As such, thioacetic acid is a stronger acid and H^+ is more easily removed. Statement 1 and 2 are incorrect.
   Statement 3 is correct since thioacetic is more acidic, it will have a lower pH value. Sulfur atom is larger than oxygen atom. There will be less effective orbital overlap with the hydrogen atom, and thus S–H bond is weaker than O–H bond, and will be more easily broken.

4. **C** [4: The Gaseous State]
   Let the no. of moles of N_2O be x mol.
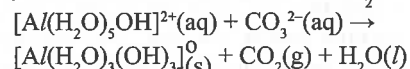   Since equimolar mixture of O_2 and N_2O, ∴ moles of gases, n = $2x$
   pV = nRT
   $$n = 2x = \frac{pV}{RT} = \frac{(3.55 \times 10^7)(5 \times 10^{-3})}{(8.31)(20 + 273)} = 72.9 \text{ mol}$$
   ∴ moles of N_2O, $x = \frac{72.9}{2} = 36.45$ mol
   ∴ Mass of N_2O = 36.45 × [2(14.0) + 16.0]
   = 1603.8 g
   ≈ 1.60 kg (3 s.f.)

5. **A** [9.1: The Periodic Table: Atomic, Physical and Chemical Periodicity]
   1 – $AlCl_3$ dissolves in water with appreciable hydrolysis to give an acidic solution of pH = 3. With Na_2CO_3, a white precipitate of $Al(OH)_3$ is formed with effervescence of CO_2.
   $[Al(H_2O)_5OH]^{2+}(aq) + CO_3^{2-}(aq) \rightarrow$
   $[Al(H_2O)_3(OH)_3]^0_{(s)} + CO_2(g) + H_2O(l)$
   2 – $MgCl_2$ dissolves in water with slight hydrolysis to give a slightly acidic solution of pH = 6.5. It does not react with Na_2CO_3 to give any effervescence.
   3 – $NaCl$ dissolves in water to form a neutral solution with pH = 7. It does not react with Na_2CO_3 to give any effervescence.

6. **B** [9.1: The Periodic Table: Atomic, Physical and Chemical Periodicity]
   Electronegativity increases across the period and decreases down the group. X is phosphorus, $_{15}P$ since it is more electronegative than arsenic, $_{33}As$. Y is sulfur, $_{16}S$ since it is more electronegative than X.

7. **A** [1: The Mole Concept and Stoichiometry]
   Let the mass of 'solder glass' be x g.
   Mass of B_2O_3 = 0.16x g
   Mole of B_2O_3 = $\frac{0.16x}{2(10.8) + 3(16.0)}$ mol
   Mole of B in B_2O_3 = $2\left[\frac{0.16x}{2(10.8) + 3(16.0)}\right]$ mol
   Mass of PbO = 0.84x g
   Mole of PbO = $\frac{0.84x}{207.2 + 16.0}$ mol
   Mole of Pb in PbO = Mole of PbO
   $\frac{\text{Mole of Pb}}{\text{Mole of B}}$
   $= \frac{0.84x}{207.2 + 16.0} \div 2\left[\frac{0.16x}{2(10.8) + 3(16.0)}\right]$
   = 0.81845
   ≈ 0.82

8. **B** [2: Atomic Structure]
Since the sixth ionisation energy values increase from G to H to J to M, the four elements are arranged in the Periodic Table as shown.

	15	16
P3	M	H
	i.e. phosphorus	i.e. sulfur
P4	J	G
	i.e. arsenic	i.e. selenium

Group 15 elements have higher sixth ionisation energy than Group 16 elements since sixth electron is being removed from the next inner principal quantum shell. This requires more energy since the electron is more attracted to the positive nucleus.

Period 4 elements have an additional principal quantum shell than period 3 elements. As such, there will be more shielding effect for period 4 elements and the electron is less attracted to the positive nucleus. As such, sixth ionisation energy of period 4 elements < period 3 elements.

9. **B** [5: Chemical Energetics: Thermochemistry and Thermodynamics]
Cs^+, I^- and Xe have the same number of electrons (isoelectronic configuration) and thus similar shielding effect, but different number of protons in the nucleus. As the nuclear charge increases, the effective nuclear charge increases accordingly, resulting in stronger attraction for the outermost electron and more energy is required to remove the electron i.e. Ionisation energy (enthalpy change, ΔH) increases. Cs^+ has more protons than Xe, which in turn has more protons than I^-. As such, $\Delta H_1 > \Delta H_3 > \Delta H_2$.

10. **D** [3: Chemical Bonding]
L.E. $\alpha \left| \dfrac{q_+ \cdot q_-}{r_+ + r_-} \right|$
All four solids have the same q_+ and q_-. Hence, we need to compare r_+ and r_- only.
From the Data Booklet:
$Pb^{2+}(0.120nm) > Ca^{2+}(0.099nm) > Zn^{2+}(0.074nm) > Ni^{2+}(0.069nm)$
$Br^-(0.195nm) > Cl^-(0.181nm)$
$ZnCl_2$ has the most exothermic lattice energy since the sum of $r_+ + r_-$ is the smallest.

11. **D** [5: Chemical Energetics: Thermochemistry and Thermodynamics]
$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$
From the balanced equation with state symbols, one mole of solid decomposed to form one mole of gas and two moles of liquid. As such, $\Delta S^\theta > 0$.
Since $\Delta H^\theta < 0$; $\Delta G^\theta < 0$ at all temperatures
i.e. the reaction is spontaneous at all temperatures.

12. **C** [8: Reaction Kinetics]
Lead(IV) oxide acts as a heterogenous catalyst in experiment 2, by providing an alternative pathway with lower activation energy. As such, the activation energy is higher in experiment 1. The rate equation for this reaction is rate $= k[H_2O_2]$ where k is the rate constant. Since there is no change in the $[H_2O_2]$ but there's an increase in the rate of reaction, the rate constant, k is higher in experiment 2.

13. **B** [7.1: Chemical Equilibria]

	$2SO_2(g)$	$+ O_2(g)$	$\rightleftharpoons 2SO_3(g)$
Initial amount/mol:	2.00	2.00	–
Change in amount/mol:	-1.80	$-\dfrac{1.80}{2}$	$+1.80$
Equilibrium amount/mol:	0.20	1.10	1.80

$K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

$= \dfrac{\left(\dfrac{1.80}{0.500}\right)^2}{\left(\dfrac{0.20}{0.500}\right)^2\left(\dfrac{1.10}{0.500}\right)}$

$= 36.8$ (3 s.f.)

14. **B** [7.2: Acid-Base and Solubility Equilibria]
$pH = -\lg [H^+]$
$7.4 = -\lg [H^+]$
$\therefore [H^+] = 10^{-7.4}$ mol dm^{-3}
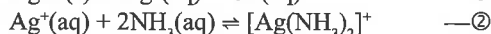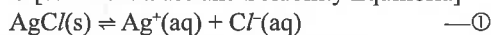$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$ $K_a = 2.5 \times 10^{-4}$
$K_a = \dfrac{[HCO_3^-][H^+]}{[H_2CO_3]}$
$\dfrac{[H_2CO_3]}{[HCO_3^-]} = \dfrac{[H^+]}{K_a}$
$= \dfrac{10^{-7.4}}{2.5 \times 10^{-4}}$
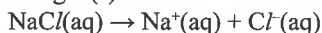$= 1.5924 \times 10^{-4}$
$\approx 1.6 \times 10^{-4}$ mol dm^{-3}
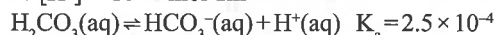
15. **C** [7.2: Acid-Base and Solubility Equilibria]
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ —①
$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+$ —②
When $NH_3(aq)$ is added, Ag^+ will form a soluble complex $[Ag(NH_3)_2]^+$, which will remove Ag^+ ions from the solution, causing IP $< K_{sp}$. Thus, to produce Ag^+, by Le Chatelier's principle, the position of equilibrium in ① shifts to the right so that more $AgCl(s)$ dissolves. Thus, the solubility of $AgCl(s)$ increases.
$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$
Addition of aqueous sodium chloride increases $[Cl^-]$. Presence of this common ion shifts the position of equilibrium in ① to the left. Thus, the solubility of $AgCl(s)$ decreases.

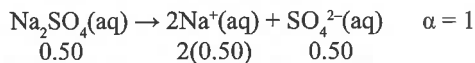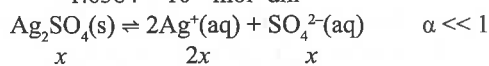16. **C** [7.2: Acid-Base and Solubility Equilibria]

$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$
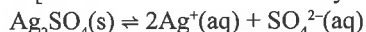
Let the solubility of Ag_2SO_4 be x.

$[Ag^{2+}] = 2x = 0.032$ mol dm^{-3}

$[SO_4^{2-}] = x = \dfrac{0.032}{2} = 0.016$ mol dm^{-3}

$K_{sp} = [Ag^+]^2[SO_4^{2-}]$
$= (0.032)^2(0.016)$
$= 1.6384 \times 10^{-5}$ mol^3 dm^{-9}

$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq) \qquad \alpha \ll 1$
$\quad x \qquad\qquad 2x \qquad\quad x$

$Na_2SO_4(aq) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq) \qquad \alpha = 1$
$\quad 0.50 \qquad\quad 2(0.50) \qquad 0.50$

$\therefore [SO_4^{2-}]_{total} = x + 0.50$ mol dm^{-3}

$K_{sp} = [Ag^+]^2[SO_4^{2-}]$
$1.6384 \times 10^{-5} = [Ag^+]^2(x + 0.50)$

Assume that $x \ll 0.50$;
Thus, $x + 0.50 \approx 0.50$

$\therefore [Ag^+] = \sqrt{\dfrac{1.6384 \times 10^{-5}}{0.50}}$
$= 5.724 \times 10^{-3}$
$\approx 5.7 \times 10^{-3}$ mol dm^{-3}

17. **A** [10.1: Introduction and Isomerism]

1: $(CH_3)_3C \curvearrowright Cl \rightarrow (CH_3)_3C - Cl$

2: $(CH_3)_3C \overset{\frown}{-} Cl \rightarrow (CH_3)_3C^+ + :Cl^-$
    $\qquad\qquad\qquad$ carbocation

3: $(CH_3)_3C \overset{\frown}{-} \overset{+}{O}H_2 \rightarrow (CH_3)_3C^+ + H_2O$
    $\qquad\qquad\qquad$ carbocation

4: $(CH_3)_2C \overset{\frown}{-} Cl \rightarrow (CH_3)_2C + :Cl^-$
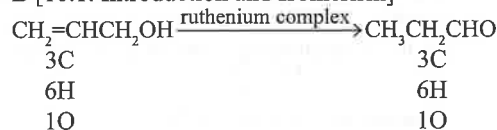 $\quad\;\; ^-\ddot{O}:\qquad\qquad\quad\; \parallel O$
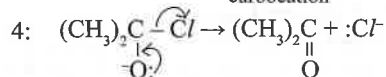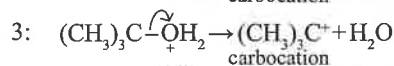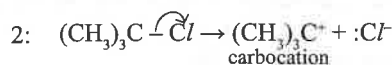
18. **C** [10.1: Introduction and Isomerism]

1 – Correct. Most biological compounds are chiral and act as receptors of small molecule ligands such as chiral drugs.

2 – Incorrect. Enantiomers are stereoisomers, not structural isomers. They also have identical chemical properties except towards optically active reagents.

3 – Incorrect. Enantiomers have identical physical properties except for the direction of plane polarised light.

19. **B** [10.1: Introduction and Isomerism]

$CH_2=CHCH_2OH \xrightarrow{\text{ruthenium complex}} CH_3CH_2CHO$
$\quad 3C \qquad\qquad\qquad\qquad\qquad\quad 3C$
$\quad 6H \qquad\qquad\qquad\qquad\qquad\quad 6H$
$\quad 1O \qquad\qquad\qquad\qquad\qquad\quad 1O$

Since there is no change in the number of carbon, hydrogen and oxygen atoms for the overall process, hydrogenation, oxidation and reduction are not possible. Thus, the reaction is isomerism, whereby the compounds have the same chemical formula (C_3H_6O) but different chemical structures.
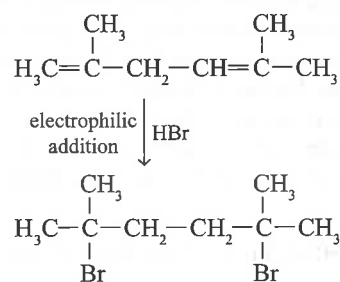
20. **D** [10.2: Hydrocarbons]

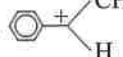Hydrogenation occurs and all the C=C bond is converted to C–C bonds.
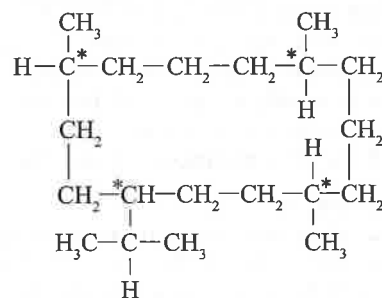
21. **A** [10.2: Hydrocarbons]

When the alkene reacts with two moles of HBr, it follows Markovnikov's rule.

22. **B** [10.3: Halogen Derivatives]

1 – Correct. is the intermediate.

This carbocation intermediate has a flat structure (trigonal planar) and has a plane of symmetry.

2 – Incorrect. In the unimolecular nucleophilic substitution (S_N1) mechanism, the first step involves the formation of a carbocation intermediate (via heterolytic fission of C–X bond).

3 – Incorrect. The racemic mixture formed (equal quantities of both the enantiomers) is a characteristic of S_N1 mechanism, and not S_N2 mechanism, whereby attack by the OH$^-$ ion can take place from both sides of the carbocation.

23. **B** [10.3: Halogen Derivatives]

Alkyl halides (R–X) undergoes alkaline hydrolysis to release the free halide ions. Aryl halides (◯-X) does not undergoes alkaline hydrolysis.
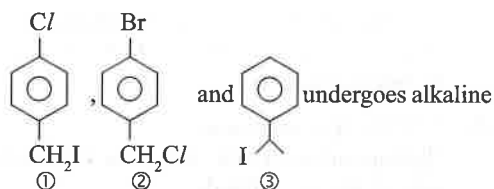
 and undergoes alkaline

hydrolysis to release the free halide ions which combine with Ag^+ ions to form ① AgI(s), ② AgCl(s) and ③ AgI(s) precipitates respectively.

AgCl(s) is soluble in excess NH_3(aq) whereas AgI(s) is insoluble in excess NH_3(aq).

As such, only 2 precipitates (AgI) remains.

24. **B** [10.1: Introduction and Isomerism]
Molecule 1 has only one chiral centre and will not have a plane of symmetry. As such, it is optically active and will rotate plane polarised light.
Molecules 2, 3 and 4 are the same molecular compound with 2 chiral centres.
Molecules 3 and 4 are actually identical and are known as a meso compound. The molecule has a plane of symmetry and they are superimposable on their mirror images even though they contain chiral centres. It is optically inactive and does not rotate plane polarised light.
Molecule 2 does not have a plane of symmetry and is optically active. It will rotate plane polarised light.

25. **D** [10.6: Carboxylic Acids and Derivatives]
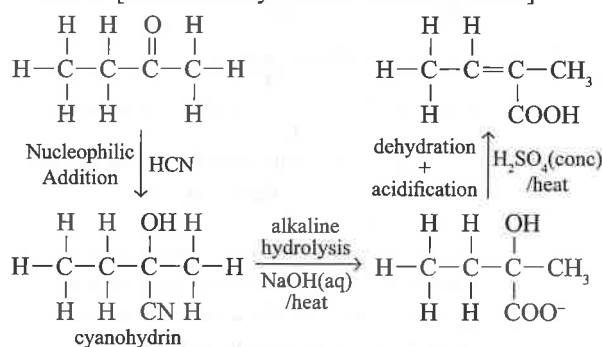
26. **D** [10.6: Carboxylic Acids and Derivatives]
Strength of carboxylic acids (i.e. acidity) depends on the stability of the carboxylate ions.
A – Incorrect. Presence of electron-donating $-CH_3$ group on CH_3CO_2H intensity the electron density of the carboxylate ion, $CH_3CO_2^-$, making it less stable and more likely to grab a proton to form back CH_3CO_2H. As such, CH_3CO_2H is less acidic than HCOOH, and K_a of HCOOH is larger than K_a of CH_3COOH (which is 1.75×10^{-5}).
B – Incorrect. Presence of electron-withdrawing halogen atom on CH_2ClCO_2H will make the carboxylate ion more stable and less likely to grab a proton to form back the acid. As such, CH_2ClCO_2H is more acidic (higher K_a) than CH_3CO_2H.
C – Incorrect. CH_3CO_2H and $C_6H_5CO_2H$ have different K_a values, which means their extent of ionisation is different. As such, in a mixture containing equal concentrations of both acids, concentration of the carboxylate ions (conjugate bases) will not be the same.
D – Correct. $Cl-\langle O \rangle-CO_2H$ is more acidic than $C_6H_5CO_2H$ because the electron-withdrawing Cl atom further stabilises the carboxylate ion and promotes ionisation.
$[H^+]$ in a solution of $Cl-\langle O \rangle-CO_2H$ will be greater than a solution of $C_6H_5CO_2H$, if they are of the same concentration. For the two solutions to have the same pH (i.e. same $[H^+]$), solution of $C_6H_5CO_2H$ must be of higher concentration than $Cl-\langle O \rangle-CO_2H$.

27. **A** [10.7: Nitrogen Compounds]
$CH_3NHCH_2CONH_2$ has both the amine and amide functional groups. Amine is basic and will undergo acid-base reaction with cold HCl(aq) to form a salt. Amide is neutral and do not react with the cold HCl(aq).
$CH_3NHCH_2CONH_2 + HCl \rightarrow$
$[CH_3NH_2CH_2CONH_2]^+Cl^-$

28. **A** [10.5: Carbonyl Compounds]
Both Y and Z turn hot acidified $K_2Cr_2O_7$ from orange to green $\Rightarrow$ presence of 1° alcohol, 2° alcohol or aldehyde.
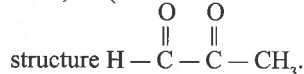Y reacts with alkaline aqueous iodine, but Z does not $\Rightarrow$ Y has $-\overset{O}{\overset{||}{C}}-CH_3$ or $-\overset{OH}{\overset{|}{\underset{H}{\overset{|}{C}}}}-CH_3$ group, but not Z.
Z reacts with sodium metal, but Y does not $\Rightarrow$ Z is an alcohol or carboxylic acid, but Y is not.
$\therefore$ Y has $-\overset{O}{\overset{||}{C}}-CH_3$ group and $-\overset{O}{\overset{||}{C}}-H$ group which can undergo reaction with alkaline aqueous iodine and oxidation by hot acidified $K_2Cr_2O_7$ respectively. Both groups do not react with sodium metal.
Thus, Y (molecular formula $C_3H_4O_2$) has the structure $H-\overset{O}{\overset{||}{C}}-\overset{O}{\overset{||}{C}}-CH_3$.
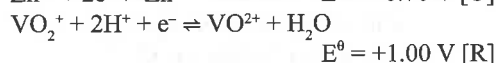Due to the presence of aliphatic aldehyde functional group, Y will react with Fehling's solution.
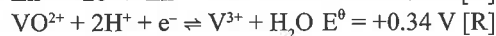Both the aldehyde and ketone functional groups in Y will also react with 2,4-DNPH reagent.

29. **D** [6: Electrochemistry]
<u>With zinc metal:</u>
$Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad\qquad E^\theta = -0.76$ V [O]
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$
$\qquad\qquad\qquad\qquad\qquad E^\theta = +1.00$ V [R]

$E^\theta_{cell} = E^\theta_R - E^\theta_o$
$\qquad = (+1.00) - (-0.76)$
$\qquad = +1.76$ V

Since $E^\theta_{cell} > 0$, reaction is feasible and VO^{2+} is formed.

$Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad\qquad E^\theta = -0.76$ V [O]
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O \; E^\theta = +0.34$ V [R]
$E^\theta_{cell} = E^\theta_R - E^\theta_o$
$\qquad = (+0.34) - (-0.76)$
$\qquad = +1.10$ V

Since $E^\theta_{cell} > 0$, reaction is feasible and V^{3+} is formed.

$Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad\qquad E^\theta = -0.76$ V [O]
$V^{3+} + e^- \rightleftharpoons V^{2+} \qquad\qquad E^\theta = -0.26$ V [R]
$E^\theta_{cell} = E^\theta_R - E^\theta_o$
$\qquad = (-0.26) - (-0.76)$
$\qquad = +0.50$ V

Since $E^\theta_{cell} > 0$, reaction is feasible and V^{2+} is formed.

$Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad\qquad E^\theta = -0.76$ V [O]
$V^{2+} + 2e^- \rightleftharpoons V \qquad\qquad E^\theta = -1.20$ V [R]
$E^\theta_{cell} = E^\theta_R - E^\theta_o$
$\qquad = (-1.20) - (-0.76)$
$\qquad = -0.44$ V

Since $E^\theta_{cell} < 0$, reaction is not feasible.
Thus, the final vanadium specie present is V^{2+}(aq) and resulting solution is violet.
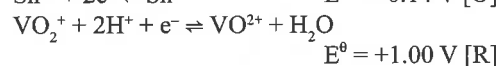
<u>With tin metal:</u>
$Sn^{2+} + 2e^- \rightleftharpoons Sn \qquad\qquad E^\theta = -0.14$ V [O]
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$
$\qquad\qquad\qquad\qquad\qquad E^\theta = +1.00$ V [R]
$E^\theta_{cell} = E^\theta_R - E^\theta_o$
$\qquad = (+1.00) - (-0.14)$
$\qquad = +1.14$ V

Since $E^\theta_{cell} > 0$, reaction is feasible and VO^{2+} is formed.
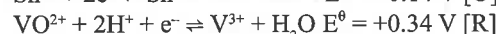
$Sn^{2+} + 2e^- \rightleftharpoons Sn \qquad\qquad E^\theta = -0.14$ V [O]
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O \; E^\theta = +0.34$ V [R]
$E^\theta_{cell} = E^\theta_R - E^\theta_o$
$\qquad = (+0.34) - (-0.14)$
$\qquad = +0.48$ V

Since $E^\theta_{cell} > 0$, reaction is feasible and V^{3+} is formed.

$Sn^{2+} + 2e^- \rightleftharpoons Sn \qquad\qquad E^\theta = -0.14$ V [O]
$V^{3+} + e^- \rightleftharpoons V^{2+} \qquad\qquad E^\theta = -0.26$ V [R]

$E^\theta_{cell} = E^\theta_R - E^\theta_o$
$\qquad = (-0.26) - (-0.14)$
$\qquad = -0.12$ V

Since $E^\theta_{cell} < 0$, reaction is not feasible.
Thus, the final vanadium specie present is V^{3+}(aq) and resulting solution is green.

30. **D** [9.2: An Introduction to the Chemistry of Transition Elements]
Fe atom [Ar] $3d^6 4s^2$
Co atom [Ar] $3d^7 4s^2$
A – Incorrect. 4s electrons do not provide shielding as they are the valence electrons in the outermost shell.
B – Incorrect. Transition metals atomic radii are similar because electrons are added to the inner 3d subshell. Furthermore, Co does not have a 4p electron.
C – Incorrect. 4s electrons are at a higher energy level than 3d, and are removed before the 3d electrons.
D – Correct. The extra 3d electron provide greater shielding effect against the higher nuclear charge in Co, such that the effective nuclear charge is similar for Co and Fe. Hence, first ionisation energy of Co is similar to that of Fe.

PAPER 2
1. [2: Atomic Structure]
   (a) • F & G
       • D
       • A & C

   🔆 **Tip**

particle	identity
A	$^{40}_{18}Ar$
B	$^{40}_{18}Ar^+$
C	$^{40}_{20}Ca$
D	$^{40}_{20}Ca^{2+}$
E	$^{37}_{17}Cl^-$
F	$^{35}_{17}Cl$
G	$^{37}_{17}Cl$

   (b) (i) C is larger since C (Ca atom) has more number of electrons than D (Ca^{2+} ion), while their nuclear charge remains the same. As a result, the attraction of electrons to the nucleus is lesser in C than in D, and the outermost shell is further away from nucleus.

    (ii) E is larger. D (Ca^{2+} ion) and E (Cl^- ion) are isoelectronic (both having 18 electrons). E has fewer protons than D, thus have lower nuclear charge. As a result, the attraction of electrons to the nucleus is lesser in E than in D, and the outermost shell is further away from nucleus.

2.   [2: Atomic Structure/
     1: The Mole Concept and Stoichiometry/
     9.1: The Periodic Table: Atomic, Physical and Chemical Periodicity]

(a) Successive ionisation energies for any atom increases with removal of each electron because the remaining electrons are attracted more strongly by the constant positive charge in the nucleus. As such, more energy is required to overcome the attraction between the nucleus and outermost electron.

(b) 17

(c)

ionisation energy/ kJ mol^{-1}

successive ionisation energies of Se
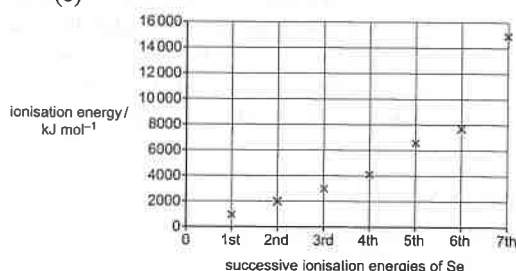
(d) 2.4. Electronegativity refers to the ability of an atom in a covalent bond to attract the bonding electrons. Down the group, electronegativity decreases. This is because the nuclear charge increases but the number of electron shells also increases. Effect of increased shielding effect and distance the outer shell is from the nucleus, outweighs the effect of increased nuclear charge. Outermost shell is less attracted to the positive nucleus.

(e) Mass of Se in 1 brazil nut $= \dfrac{0.57\text{ g}}{6}$
                      $= 0.095$ mg

Mole of Se in 1 brazil nut
$= \dfrac{0.095 \times 10^{-3}}{79.0} = 1.2025 \times 10^{-6}$ mol

Ave. no. of atoms of Se in 1 brazil nut
$= (1.2025 \times 10^{-6})(6.02 \times 10^{23})$
$= 7.239 \times 10^{17}$
$\approx 7.24 \times 10^{17}$ (3 s.f.)

(f) (i) $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$
         $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$
   (ii) $NaOH(aq)$

3.   [10.6: Carboxylic Acids and Derivatives]

(a) Acidic hydrolysis of ester linkage.

(b) (i) Ethanoic acid.
    (ii) $2CH_3COOH + Na_2CO_3 \rightarrow$
        $2CH_3COONa + H_2O + CO_2$
   (iii) Reduction

(c)
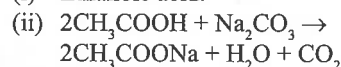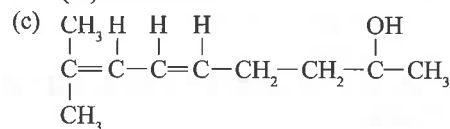
(d) $LiAlH_4$ produces H^-, hydride ions to reduce L (a carboxylic acid). H^- ions cannot attack an electron rich carbon-carbon double bond in alkenes, since they will repel each other away.

(e)

Tip

Structure of M:
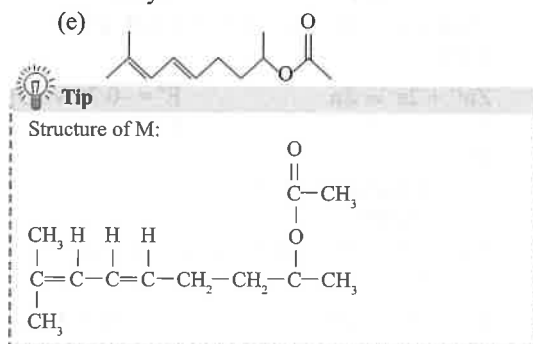
(f) Volume of N $= (6.25 \times 10^{-4})(24)$
              $= 0.015$ $dm^3 = 15$ cm^3
Volume of $CO_2 = 92.5 - 75.5 = 15$ cm^3

$C_xH_yO(g) + (x + \frac{y}{4} - \frac{1}{2})O_2(g) \rightarrow xCO_2(g) + \frac{y}{2}H_2O(l)$
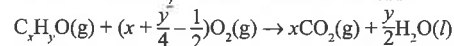
	C_xH_yO	O_2	CO_2	H_2O
Initial vol./cm^3	15	100	0	—
Final vol./cm^3	0	77.5	15	—
Reacted vol./cm^3	15	22.5	15	—
Mole ratio	1	1.5	1	—

$\therefore$ $x = 1$
$\therefore$ $x + \dfrac{y}{4} - \dfrac{1}{2} = 1.5$
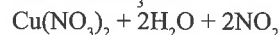 $1 + \dfrac{y}{4} - \dfrac{1}{2} = 1.5$
              $y = 4$

$\therefore$ Formula of N is CH_4O
$\therefore$ N is CH_3OH, methanol.

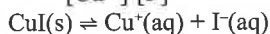4.   [9.2: An Introduction to the Chemistry of Transition Elements]

(a) (i) $Cu + 4HNO_3 \rightarrow$
         $Cu(NO_3)_2 + 2H_2O + 2NO_2$

    (ii) Positive E^{θ}_{cell} value means that ΔG^{θ} is negative and thus the reaction is spontaneous. Concentrated HNO_3 is in excess allowing the reaction to proceed to completion. Concentrated nitric acid is a strong oxidising agent which is capable of oxidising copper to soluble copper(II) ions.
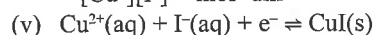
(iii) E^θ_{cell} value would be negative, which means the reaction in equation 1 would be non-spontaneous and would not occur.

(iv) $K_c = \dfrac{[I_2]}{[Cu^{2+}]^2[I^-]^4}$ mol^{-5} dm^{15}

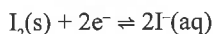$CuI(s) \rightleftharpoons Cu^+(aq) + I^-(aq)$

Units for $K_{sp}(CuI)$
$= [Cu^+][I^-] = $ mol^2 dm^{-6}

(v) $Cu^{2+}(aq) + I^-(aq) + e^- \rightleftharpoons CuI(s)$
$\qquad\qquad\qquad E^\theta = x$ V [R]

$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$
$\qquad\qquad\qquad E^\theta = +0.54$ V [O]

$E^\theta_{cell} = E^\theta_R - E^\theta_o$
$+0.32$ V $= x - (+0.54$ V$)$
$\therefore \qquad x = +0.86$ V
$\qquad\quad = E^\theta \left(Cu^{2+}(aq)/CuI(s)\right)$

(vi) Large K_c value (magnitude of $\times 10^5$) means that the forward reaction would proceed to almost completion forming an accurate amount of I_2 which corresponds to the amount of other reactants.

(vii) Oxidation state: +1
Electronic configuration:
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

(viii) CuI solid is white in colour due to fully-filled 3d orbitals that does not give rise to colour. The 3d sub-shell for Cu$^+$ contains 10 electrons, and thus, no d-d transition is possible.

(b) (i)

	formula of complex ion	number of ligands in complex ion	shape of complex ion
complex ion in **H**	$[Cu(H_2O)_6]^{2+}$	6	**Octahedral**
complex ion in **J**	$[CuCl_4]^{2-}$	4	tetrahedral

(ii) Cl^- ligands have negative charge (as well as being larger in size) and results in greater repulsion between the ligands. H_2O ligands are neutral (as well as being smaller) and results in less repulsion between the ligands.

5. [10.5: Carbonyl Compounds]
   (a) Aldehyde and secondary alcohol.
   (b)

bond type present in **X**	total number of electrons present in each bond type in **X**
σ	12
π	2

(c) (i)

stage	description of stage	equation
1	reaction of ethanal with OH⁻ to make an enolate ion, Y.	
2	addition reaction of Y with ethanal to form Z	
3	protonation of Z to form X	

(ii) *stage 1* Ethanal acts as a Bronsted-Lowry acid as it donates a proton (H$^+$) to the hydroxide ion.
stage 2 Ethanal acts as a Lewis acid as it accepts an electron pair from the enolate ion to form a new bond.

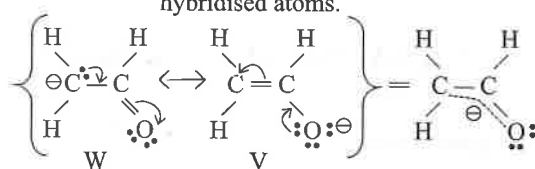(iii) NaOH acts a Bronsted-Lowry base such that it accepts a proton (H$^+$) from ethanal.

(iv)
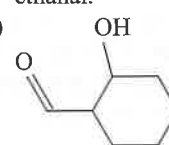
Tip

Reaction mechanism:
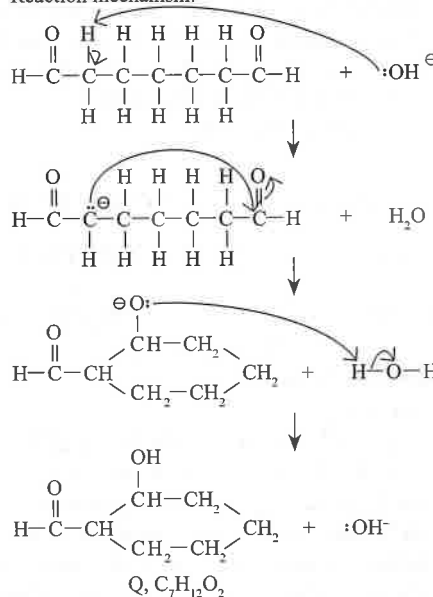
M_r of Q
$= 7(12.0) + 12(1.0) + 2(16.0)$
$= 128.0$ (proven)

(d) (i) Movement of pairs of π electrons from p orbital of an atom to p orbital of another adjacent atom. Negative charge is delocalised between three sp^2 hybridised atoms.

(ii) 4

(iii)

bond type in enolate ion	bond energy/kJ mol⁻¹
carbon-carbon	520
carbon-oxygen	550

Tip

Carbon-carbon & carbon-oxygen bonds in enolate ion has partial double bond character.

(iv) Resonance structure V is preferred because oxygen is highly electronegative (as compared to carbon) and better able to stabilise the negative charge.

6. [6: Electrochemistry]

(a) It refers to the disruption of Earth's climate equilibrium caused by the increased concentrations of greenhouse gases due to human activities, which has led to an increase in the global average temperature.

(b) Formation of acid rain.

(c)
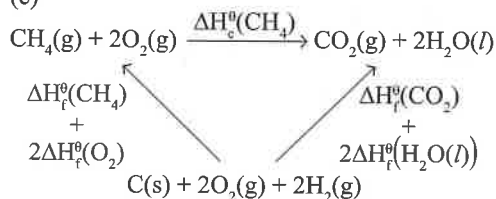
By Hess' Law,
$\Delta H_c^\theta(CH_4)$
$= -[(-74.8) + 2(0)] + [(-393.5) + 2(-285.8)]$
$= -890.3$ kJ mol⁻¹ ≈ -890 kJ mol⁻¹ (3 s.f.)

(d) Higher percentage of $O_2(g)$ is present in the air mixture which increases the percentage combustion efficiency. As such, more heat energy is released during combustion which increases the amount of electricity.

(e) Actual amount of energy produced when 1 mole of $CH_4(g)$ combusts in the plant = 525 + 134 = 659 kJ

From part (c), energy produced when 1 mole of $CH_4(g)$ undergo complete combustion = 890.3 kJ

$\therefore$ Combustion efficiency $= \dfrac{659}{890.3} \times 100 = 74.0\%$ (3 s.f.)

$\therefore$ Approximate percentage of $O_2(g)$ in air mixture = 36%

(f) Melt Li_2CO_3 and maintain it in the molten state so that it can be used as an electrolyte.
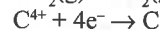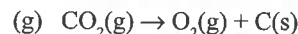
(g) $CO_2(g) \rightarrow O_2(g) + C(s)$
$C^{4+} + 4e^- \rightarrow C$
$Q = It = n_e F$
$n_e = \dfrac{It}{F} = \dfrac{(1.00)(1.00 \times 3600)}{96\,500} = 0.0373$ mol

Mole of C $= \dfrac{1}{4} x\, n_e$

$= \dfrac{1}{4}(0.0373) = 9.326 \times 10^{-3}$

Mass of C $= (9.326 \times 10^{-3})(12.0)$
$= 0.11192$ g

$\therefore$ The electrolysis process is 100%.

(h) (i) Giant molecular structure.

(ii)
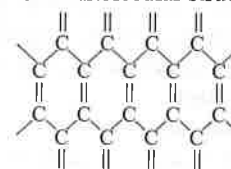
C–C–C bond angle = 120°

PAPER 3
Section A

1. [10.6: Carboxylic Acids and Derivatives/
   10.2: Hydrocarbons/
   5: Chemical Energetics: Thermochemistry and Thermodynamics/6: Electrochemistry]

(a) Order of decreasing relative rate of hydrolysis: C, A, B.

B has the lowest relative rate of hydrolysis. C_6H_5Cl is an aryl halide and C–Cl bond is strengthened by the overlapping of the p-orbitals of Cl atom with the π orbitals of the benzene ring. Delocalisation of lone pair of electrons in p-orbital of Cl atom into the benzene ring results in partial double bond character in the C–Cl bond, so more energy is required to break the stronger C–Cl bond in B as compared to A and C.

C is an acyl halide has the highest relative rate of hydrolysis. The carbonyl carbon in C_6H_5COCl is more electron deficient due to the polarisation by both Cl and O atoms, so the C–Cl bond is very weak and can be more easily hydrolysed, as compared to A which is an alkyl halide where the C–Cl bond is polarised by the Cl atom only.

(b) (i) Chlorination of phenol [Electrophilic substitution]
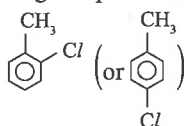Reagent and condition: Cl_2, anhydrous $AlCl_3$
Organic product formed:

OH, Cl (or OH with Cl at para)
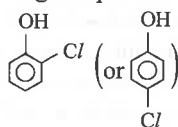
Chlorination of methylbenzene [Electrophilic substitution]
Reagent and condition: Cl_2, anhydrous $AlCl_3$, absence of UV light
Organic product formed:

CH_3, Cl (or CH_3 with Cl at para)

(ii) Both the methyl group (in methylbenzene) and the hydroxy group (in phenol) are activating groups and make the benzene ring more reactive.
Phenol is much more reactive in terms of electrophilic substitution since the hydroxy group is a highly activating group (more activating than methyl group) and makes benzene very electron rich and attractive to electrophiles.

(c) (i) Enthalpy change of hydration is defined as the heat evolved when 1 mole of gaseous ions is dissolved in a large amount of water at 1 bar and 298 K.

(ii)
$$2e^- + Co^{2+}(g) \xrightarrow[+aq]{\Delta H_{hyd}^{\theta}(Co^{2+})} Co^{2+}(aq) + 2e^-$$
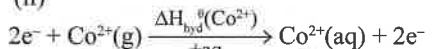
1st + 2nd I.E (Co) = 757 + 1640

$Co(g)$

$\Delta H_{atom}^{\theta}(Co) = +425$ $\Delta H_f^{\theta}(Co^{2+}) = +646$

$Co(s)$

By Hess' Law,
$(+425) + (757 + 1640) + \Delta H_{hyd}^{\theta}(Co^{2+}) = +646$
$\therefore \Delta H_{hyd}^{\theta}(Co^{2+}) = -2176$ kJ mol^{-1}
≈ -2180 kJ mol^{-1} (3 s.f.)

(d) (i) 2,3-dihydroxybutanedioic acid
(ii)

$$3H_2O_2 + {}^-O_2C-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-CO_2^- \rightarrow 2HCO_2^- + 2CO_2 + 4H_2O$$
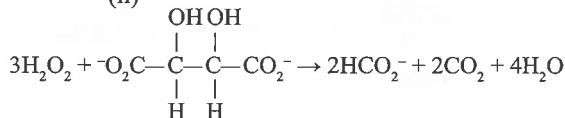
(e) (i) The ability of transition elements to exhibit different oxidation states allow them to act as catalysts.

(ii) Homogenous catalysis since both the catalyst (Co^{2+}) and the reactants (H_2O_2 and dianion D) are in the same phase.

(iii) $H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$
$\qquad E^{\theta} = +1.77$ V [R]—①
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$
$\qquad E^{\theta} = +1.89$ V [O]—②
$E_{cell}^{\theta} = E_R^{\theta} - E_o^{\theta}$
$\qquad = (+1.77) - (+1.89) = -0.12$ V
Since $E_{cell}^{\theta} < 0$; the reaction is not spontaneous.
Increasing the concentration of H_2O_2(aq) will make the reaction spontaneous. An increase in $[H_2O_2]$ will shift the position of equilibrium in ① to the right hand side, based on Le Chatelier's Principle. This results in $E^{\theta}(H_2O_2, H^+/H_2O)$ to become more positive than +1.89V, such that E_{cell}^{θ} will be positive, leading to a spontaneous reaction.

(iv) If the pH is lower than 6.8, the dianion D will be protonated to form a carboxylic acid and so it cannot be oxidised by Co^{3+}.

(v) $\Delta G^{\theta} = -nFE_{cell}^{\theta}$

$Co^{2+}(aq)$ (from Co(s), to Co^{3+}(aq))
$Co(s) \longrightarrow Co^{3+}(aq)$
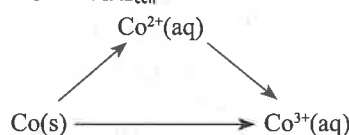
ΔG^{θ} (Co(s) to Co^{2+}(aq))
$= -(2)(96\,500)(-0.28)$
$= +54\,040$ J mol^{-1}
ΔG^{θ} (Co^{2+}(aq) to Co^{3+}(aq))
$= -(1)(96\,500)(+1.89)$
$= -182\,385$ J mol^{-1}
By Hess' Law,
ΔG^{θ} (Co(s) to Co^{3+}(aq))
$= (+54\,040) + (-182\,385)$
$= -128\,345$ J mol^{-1}
$\therefore E^{\theta}$ (Co^{3+}(aq)/Co(s)) $= \dfrac{-128\,345}{(3)(96\,500)}$
$\qquad = +0.443$ V (3 s.f.)

2. [5: Chemical Energetics: Thermochemistry and Thermodynamics/7.1: Chemical Equilibria/ 10.2: Hydrocarbons]

(a) (i) $2NO_2(g) \rightarrow N_2O_4(g)$
After conversion of NO_2(g) to N_2O_4(g), the number of moles of gaseous products is less than gaseous reactants, resulting in less disorderliness, so the entropy of the system decreases.

(ii) When $C_6H_5OH(s)$ solute is dissolved in $C_6H_6(l)$ solvent, a solution (mixture) is formed so the system becomes more disorderly, so the entropy of the system increases.

(b)
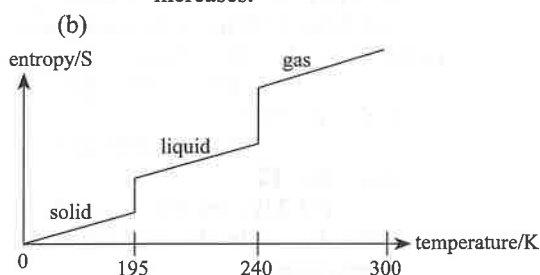
Entropy is zero at 0 K where particles are stationary and in a maximum state of order i.e. no disorder. As temperature increases, solid particles vibrate more, so disorder increases i.e. entropy increases. Melting is associated with an increase in entropy (disorder) since the more ordered solid state is becoming the less ordered liquid state. Greater change in entropy (disorder) at boiling as compared to melting, since gases are considered to have greater random particle movement and disorder.

(c) (i) $K_p = \dfrac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})} \, kPa^{-2}$

Let the initial amount of N_2 added be x mol.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$
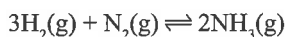
	$3H_2(g)$	$N_2(g)$	$2NH_3(g)$
Initial amount/mol :	$3x$	x	
Change in amount/mol :	$-1.2x$	$-0.4x$	$+0.8x$
Equilibrium amount/mol :	$1.8x$	$0.6x$	$0.8x$

$n_T = n_{H_2} + n_{N_2} + n_{NH_3}$
$= 1.8x + 0.6x + 0.8x = 3.2x$ mol

$P_{NH_3} = \dfrac{0.8x}{3.2x} \times (2.80 \times 10^4) = 7\,000$ kPa

$P_{H_2} = \dfrac{1.8x}{3.2x} \times (2.80 \times 10^4) = 15\,750$ kPa

$P_{N_2} = \dfrac{0.6x}{3.2x} \times (2.80 \times 10^4) = 5\,250$ kPa

$\therefore K_p = \dfrac{(7\,000)^2}{(15\,750)^3(5\,250)}$

$= 2.39 \times 10^{-9}$ kPa^{-2} (3 s.f.)

(ii) Temperature of 450°C and pressure of 200 atm is used to give a higher rate of NH_3 production. Temperature is not too high, so it will give a higher yield of NH_3, according to LCP. Pressure is considered high, so it will give a higher

yield of NH_3, according to LCP, but at the same time, not extremely high such that it is dangerous and involve a higher cost of maintaining equipments. Finely divided iron catalyst is added to increase the rate of production of NH_3 but not the yield. Continuous removal of ammonia by cooling the reaction mixture, will shift the position of equilibrium of the Haber Process to the right, increasing the yield of NH_3.

(d) (i) $CH_2=C=O + 2O_2 \rightarrow 2CO_2 + H_2O$

(ii)

(e)
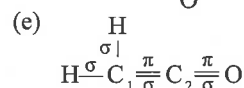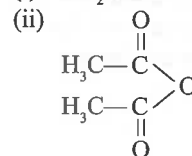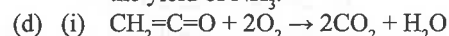
C_1 is sp^2 hybridised while C_2 is sp hybridised. C_1 uses three sp^2 hybridised orbitals to do head-on overlap (3 × σ bonds) with the 1s orbitals of the two hydrogen atoms as well as with one of the sp hybridised orbital of C_2. The other sp hybridised orbital will do a head-on overlap (1 × σ bond) with the p orbital of oxygen. Side-on overlaps (π bonds) occur between the unhybridised p orbitals of C_1 & C_2, as well as between those of C_2 & oxygen.
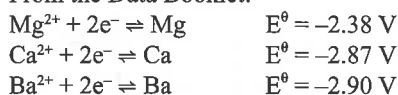
(f)
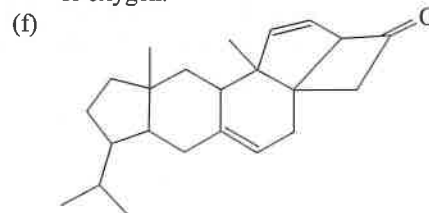
3. [2: Atomic Structure/
9.1: The Periodic Table: Atomic, Physical and Chemical Periodicity/
8: Reaction Kinetics/
10.1: Introduction and Isomerism/
10.2: Hydrocarbons/10.7: Nitrogen Compounds]

(a) $^1H^+$ and $^2H^+$ are deflected towards the negative plate in the electric field whereas electron, e^- is deflected towards the positive plate in the electric field. Since angle of deflection α $\left|\dfrac{charge}{mass}\right|$, $^1H^+$ has a greater angle of deflection than $^2H^+$.

(b) (i)
Relative atomic mass of strontium

$$= \frac{(83.91)(0.56) + 85.91(9.86) + 86.91(7.00) + 87.91(82.58)}{100}$$

$= 87.6204 \approx 87.62$ (2 d.p.)

(ii) From the Data Booklet:

$Mg^{2+} + 2e^- \rightleftharpoons Mg \qquad E^\theta = -2.38$ V
$Ca^{2+} + 2e^- \rightleftharpoons Ca \qquad E^\theta = -2.87$ V
$Ba^{2+} + 2e^- \rightleftharpoons Ba \qquad E^\theta = -2.90$ V

Down Group 2, the E^θ values become more negative. This means that the reduced species (metals) have a higher tendency to get oxidised to the oxidised species (metal ions) i.e. Group 2 elements become more reactive down the group.

(c) Group 2 carbonates are all unstable towards heat, thus Group 2 peroxides will also thermally decompose.

$$MO_2(s) \xrightarrow{\Delta} MO(s) + \frac{1}{2}O_2(g)$$
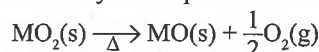
Group 2 peroxides become more thermally stable down the group. Charge density decreases since the cationic radius increases while the charge remains the same. Less polarisation of the O_2^{2-} anions by the larger cations. Since there's less distortion of the electron cloud of O_2^{2-}, the O–O covalent bond is less weakened and the ease of decomposition decreases.

(d)

[benzoyl peroxide]
$\times 10^{-2}$ / mol dm^{-3}
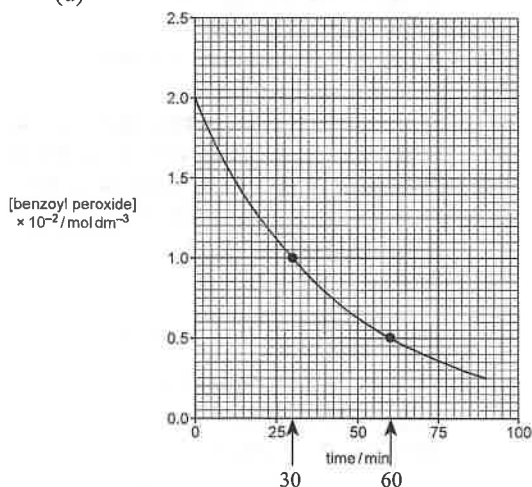
(i) The order of reaction is the power to which the concentration of that reactant is raised to in the experimentally determined rate equation.

(ii) 1st half-life = 30 min – 0 min
= 30 min

2nd half-life = 60 min – 30 min
= 30 min

Since there are two constant half-lifes, the reaction is first order.

$$\frac{[\text{concentration of benzoyl peroxide}]}{[\text{initial concentration}]} = \left(\frac{1}{2}\right)^{\frac{150}{30}}$$

$\therefore$ [concentration of benzoyl peroxide]

$$= \left(\frac{1}{2}\right)^{\frac{150}{30}}(2.0 \times 10^{-2})$$

$$= 6.25 \times 10^{-4} \text{ mol dm}^{-3}$$

(iii) Initial rate of reaction

$$= \frac{2.0 - 0.5 \text{ mol dm}^{-3}}{37.5 \text{ min}}$$

$$= 0.04 \text{ mol dm}^{-3} \text{ min}^{-1}$$

(iv) rate = k[benzoyl chloride]

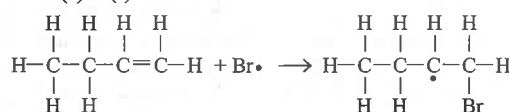$$k = \frac{\text{rate}}{[\text{benzoyl chloride}]}$$

$$= \frac{0.04 \text{ mol dm}^{-3} \text{ min}^{-1}}{2.0 \times 10^{-2} \text{ mol dm}^{-3}}$$
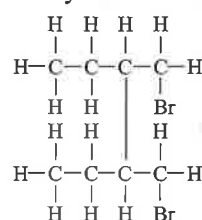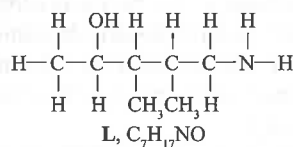
$$= 2 \text{ min}^{-1}$$

(e)

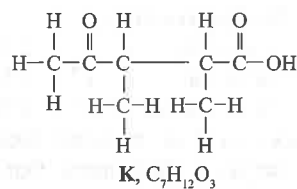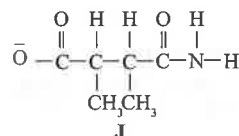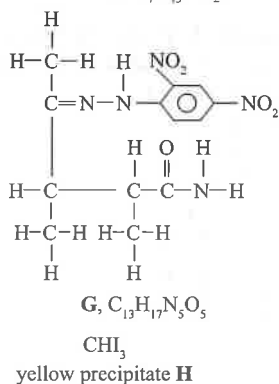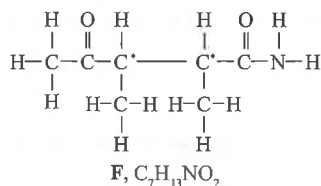
(f) (i)
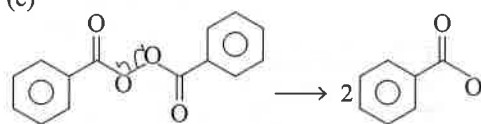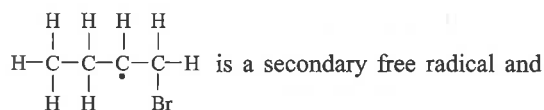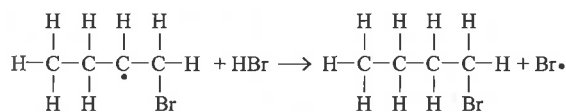
is a secondary free radical and has 2 electron-donating alkyl groups attached to the electron deficient carbon which makes it more stable and thus more likely to be formed.
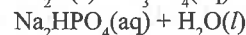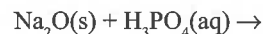
(ii)

(g)

Observations	Deductions
F, $C_7H_{13}NO_2$, has two different functional groups and two chiral carbon atoms	C:H is not ≈1:1 ⇒ **F** does not contain a benzene ring.
F reacts with 2,4-DNPH to form orange precipitate **G**, $C_{13}H_{17}N_5O_5$	Condensation reaction ⇒ **F** contains a carbonyl functional group. ⇒ **G** is a derivative of 2,4-DNPH.
F reacts with alkaline aqueous iodine to form a yellow ppt **H** and organic compound **J**	Tri-iodomethane formation CH_3 $\|$ ⇒ **F** contains $-\underset{\underset{\underset{H}{\|}}{\overset{O}{\overset{\|}{C}}}}{C}-OH$ or $-\overset{O}{\overset{\|}{C}}-CH_3$ group. ⇒ **J** is a carboxylate ion.
F does not react with Fehling's reagent	No oxidation of aliphatic aldehyde ⇒ **F** does not have aliphatic aldehyde. ⇒ **F** has a ketone functional group.
F reacts with aqueous hydrochloric acid in the presence of heat to form organic compound **K**, $C_7H_{12}O_3$	Acidic hydrolysis of amides ⇒ **F** has an amide functional group. ⇒ **K** is a carboxylic acid.
F reacts with excess $LiAlH_4$ to form organic compound **L**, $C_7H_{17}NO$	Reduction of ketone and amide functional group ⇒ **L** contains 2° alcohol and 1° amine functional groups.

$$H-\overset{\overset{H}{\|}}{\underset{\underset{H}{\|}}{C}}-\overset{O}{\overset{\|}{C}}-\overset{\overset{H}{\|}}{\underset{\underset{\underset{\underset{H}{\|}}{H-C-H}}{\|}}{C^*}}\!\!\!-\!\!\!-\overset{\overset{H}{\|}}{\underset{\underset{\underset{H}{\|}}{H-C-H}}{C^*}}-\overset{O}{\overset{\|}{C}}-\overset{\overset{H}{\|}}{\underset{\underset{H}{\|}}{N}}-H$$

F, $C_7H_{13}NO_2$

(structure of **G**, $C_{13}H_{17}N_5O_5$)

CHI_3
yellow precipitate **H**

(structure)

J

(structure)

K, $C_7H_{12}O_3$

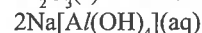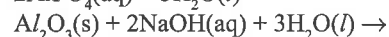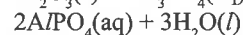(structure)

L, $C_7H_{17}NO$

Section B

4. [9.1: The Periodic Table: Atomic, Physical and Chemical Periodicity/6: Electrochemistry/ 1: The Mole Concept and Stoichiometry/ 7.2: Acid-Base and Solubility Equilibria/ 10.3: Halogen Derivatives]
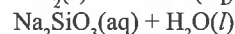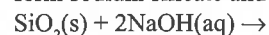
(a) Na_2O does not react with NaOH as both are basic. Na_2O reacts exothermically with acid to form salt and water.
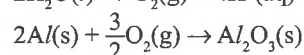$Na_2O(s) + H_3PO_4(aq) \rightarrow$
$Na_2HPO_4(aq) + H_2O(l)$
Al_2O_3 is an amphoteric oxide and thus able to react with both H_3PO_4 and NaOH.
$Al_2O_3(s) + 2H_3PO_4(aq) \rightarrow$
$2AlPO_4(aq) + 3H_2O(l)$
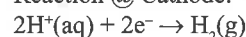$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow$
$2Na[Al(OH)_4](aq)$
SiO_2 is an acidic oxide and thus does not react with H_3PO_4. SiO_2 react with concentrated NaOH(aq) when heated under pressure to form sodium silicate and water.
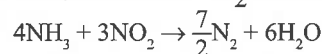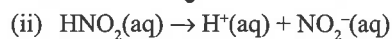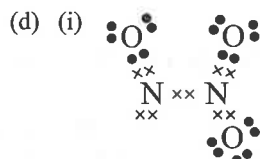$SiO_2(s) + 2NaOH(aq) \rightarrow$
$Na_2SiO_3(aq) + H_2O(l)$

(b) Reactions @ Anode:
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
$2Al(s) + \frac{3}{2}O_2(g) \rightarrow Al_2O_3(s)$
Reaction @ Cathode:
$2H^+(aq) + 2e^- \rightarrow H_2(g)$

(c) $2NH_3 + NO + O_2 \rightarrow \frac{3}{2}N_2 + 3H_2O$
$4NH_3 + 3NO_2 \rightarrow \frac{7}{2}N_2 + 6H_2O$

(d) (i)

(ii) $HNO_2(aq) \rightarrow H^+(aq) + NO_2^-(aq)$
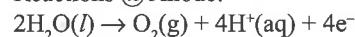
$pK_a = -\lg K_a$

$3.25 = -\lg K_a$

$K_a = 10^{-3.25} = \dfrac{[H^+][NO_2^-]}{[HNO_2]}$

$\dfrac{x^2}{0.25} = 10^{-3.25}$
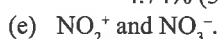
$x = 0.0118569 = [H^+]$

$\therefore$ % of HNO_2 ionised

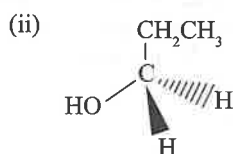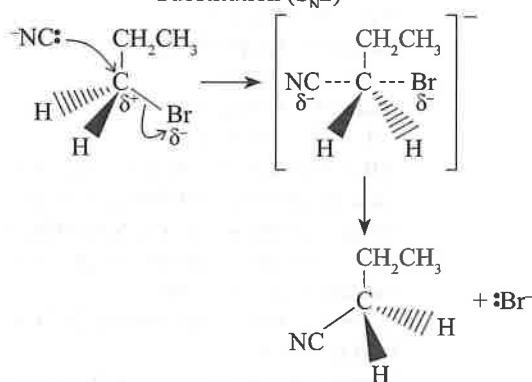$= \dfrac{\text{amount of acid ionised}}{\text{initial amount of acid used}} \times 100$

$= \dfrac{0.0118569}{0.25} \times 100$

$= 4.74276\%$

$\approx 4.74\%$ (3 s.f.)

(e) NO_2^+ and NO_3^-.

(f) (i) Mechanism: Bimolecular Nucleophilic Substitution (S_N2)

(ii)

All 3 halogenoalkanes are 1°RX since there's only one alkyl group attached to the carbon which bonds to the halogen.

(iii) **M** is a straight-chain bromoalkane (RBr) while **N** is a straight-chain iodoalkane (RI). Bromine atom is smaller than iodine atom. Bond energies alone would predict that RI would be the most reactive since the atomic orbitals overlap between C & I in RI would be less effective than the overlap between C & Br in RBr. Electronegativity of halogen alone would predict that RBr would be more reactive since bromine is more electronegative than iodine, and thus C–Br bond will be more polarised than C–I bond. Effect of bond energies due to atomic orbital overlap outweighs the effect of bond polarity when it comes to reaction rate. As such, **N** (RI) is more reactive than **M** (RBr).

O will be the least reactive. 1°RX will undergo S_N2 mechanism predominantly since there will be less steric hindrance and backside attack will be favoured. Comparing **O** to **M** and **N**, the alkyl group in **O** is branched and will be much bulkier. As such, there will be slightly more steric hindrance encountered by the attacking nucleophile. Hence, **O** will be the least reactive among the three halogenoalkanes.

5. [10.7: Nitrogen Compounds/
   7.2: Acid-Base and Solubility Equilibria/
   1: The Mole Concept and Stoichiometry/
   5: Chemical Energetics: Thermochemistry and Thermodynamics/
   10.6: Carboxylic Acids and Derivatives]

(a) Both ethylamine and propane are simple molecular structures with similar M_r (45 and 44 respectively) and thus electron cloud size. As such, they have similar instantaneous dipole-induced dipole attractions (id-id). However, ethylamine is a polar molecule while propane is non-polar. Presence of N–H bond and a lone pair of electrons on N atom in ethylamine provides the additional intermolecular hydrogen bonding between the molecules. Thus, more energy is required to overcome the stronger intermolecular forces of attraction between ethylamine molecules and it will have higher boiling point than propane.

(b) Order in increasing relative basicity in gaseous phase: ethylamine, diethylamine, triethylamine.

From ethylamine to diethylamine to triethylamine, the number of electron-donating ethyl groups on N atom increases, resulting in the increase in availability of lone pair of electrons on the N atom to accept protons.

As such, triethylamine (3° amine) is more basic than diethylamine (2° amine), which is more basic than ethylamine (1° amine).

(c) (i) $CH_3CH_2NH_2(aq)$ and $CH_3CH_2NH_3^+Cl^-$(aq). That region corresponds to an alkaline buffer consisting of the weak base and its conjugate acid.

When a small amount of H^+ ions is added, the additional H^+ ions are removed by the large concentration of $CH_3CH_2NH_2(aq)$ weak base in the buffer, so pH value remains almost unchanged. This is why the slope of the graph only changes gradually in this region of pH 8.0 – 10.0.

(ii) At the equivalence point, the salt $CH_3CH_2NH_3^+Cl^-$ is present.

Hydrolysis of the salt occurs to give $CH_3CH_2NH_3^+$ and Cl^-.

$CH_3CH_2NH_3^+Cl^-(aq) \rightarrow$
$CH_3CH_2NH_3^+(aq) + Cl^-(aq)$
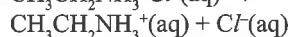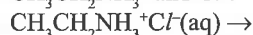
$CH_3CH_2NH_3^+(aq)$ is a conjugate acid and will undergo acid-base reaction with water to produce H_3O^+ ions. As such, the solution is acidic and pH is less than 7.

$CH_3CH_2NH_3^+(aq) + H_2O(l) \rightleftharpoons$
$CH_3CH_2NH_2(aq) + H_3O^+(aq)$
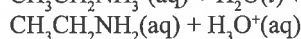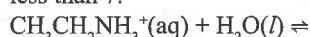
(d) Mole of $S_2O_3^{2-} = \dfrac{15.75}{1000} \times 0.150$

$\qquad = 2.3625 \times 10^{-3}$ mol

Mole of $I_2 = \dfrac{1}{2} \times$ Mole of $S_2O_3^{2-}$

$\qquad = \dfrac{1}{2} \times (2.3625 \times 10^{-3})$

$\qquad = 1.18125 \times 10^{-3}$ mol

$\qquad =$ Mole of ClO^- in 25.0 cm³ soltuion.

Mole of ClO^- in 100 cm³

$= 1.18125 \times 10^{-3} \times \left(\dfrac{100}{25.0}\right)$

$= 4.725 \times 10^{-3}$ mol

$=$ mole of ClO^- in the 5.00 cm³ sample of bleach.

∴ Concentration of ClO^- present in the bleach

$= \dfrac{4.725 \times 10^{-3}\ \text{mol}}{\dfrac{5.00}{1000}\ \text{dm}^3}$

$= 0.945$ mol dm⁻³
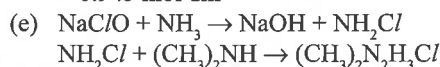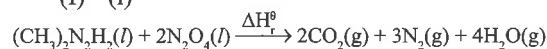
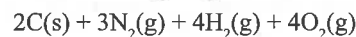(e) $NaClO + NH_3 \rightarrow NaOH + NH_2Cl$
$NH_2Cl + (CH_3)_2NH \rightarrow (CH_3)_2N_2H_3Cl$

(f) (i)

$(CH_3)_2N_2H_2(l) + 2N_2O_4(l) \xrightarrow{\Delta H_r^\theta} 2CO_2(g) + 3N_2(g) + 4H_2O(g)$

(+48.9)
+ 2(–19.6)

2(–393.5) + 3(0)
+ 4(–241.8)

$2C(s) + 3N_2(g) + 4H_2(g) + 4O_2(g)$

By Hess' Law,

$\Delta H_r^\theta = -[(+48.9)+2(-19.6)]+[2(-393.5)$
$\qquad + 3(0) + 4(-241.8)]$
$\qquad = (-9.7) + (-1754.2)$
$\qquad = -1763.9$ kJ mol⁻¹

$\Delta G_r^\theta = \Delta H_r^\theta - T\Delta S_r^\theta$
$\qquad = (-1763.9 \times 10^3) - (298)(+1141.2)$
$\qquad = -2\ 103\ 977.6$ J mol⁻¹
$\qquad = -2\ 100$ kJ mol⁻¹ (3 s.f.)

(ii) $(CH_3)_2N_2H_2(l) + 2N_2O_4(l) \xrightarrow{\text{excess}}$
$2CO_2(g) + 3N_2(g) + 4H_2O(g)$
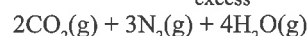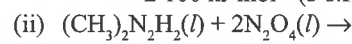
Mole of $(CH_3)_2N_2H_2(l)$ combusted

$= \dfrac{1.5 \times 10^3\ \text{g}}{60} = 25$ mol

∴ Mole of $CO_2(g)$ produced
$= 2 \times 25 = 50$ mol

Mole of $N_2(g)$ produced
$= 3 \times 25 = 75$ mol

Mole of $H_2O(g)$ produced
$= 4 \times 25 = 100$ mol

After passing the product mixture through saturated KOH(aq), $CO_2(g)$, being an acidic oxide will be absorbed and removed. Volume of product mixture will be 175 mol.

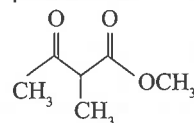At room conditions (1 atm and 293 K), H_2O is a liquid.

Hence, final product is 75 mol of $N_2(g)$.

∴ Final volume of gas,
$Q = 75 \times 24$ dm³ mol⁻¹
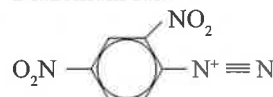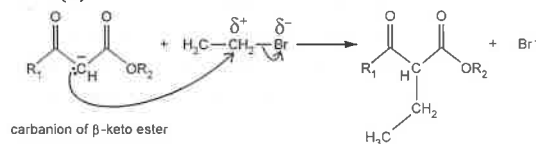$\qquad = 4\ 200$ dm³

(g) β-keto ester:

Diazonium salt:

(h)

carbanion of β-keto ester