1.1 Rings, polymers and analysis

1 (a) Structure:

Empirical formula: CH

(b) Concentrated nitric acid and concentrated sulfuric acid.

(c) (i) \( \text{NO}_2^+ \)
(ii) \( \text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O} \)
(iii)

2 (a) (i) I: \( \text{Br}_2 \), II: NaOH
(ii) Dye, colouring or indicator.
(iii) Add phenylamine to sodium nitrite and hydrochloric acid below 10 °C. Add this product to an alkaline solution of phenol.

(b)

- The p orbitals overlap above and below the plane of the ring structure.
- The electrons are delocalised and spread across all six carbon atoms.
- In benzene all the bonds are the same length between the lengths of the single and double bonds.

Phenol is more reactive because the ring is activated. The lone pair from the oxygen on the ring is delocalised into the ring so electrophiles are more attracted to the ring than in benzene.

3 (a) (i) \( \text{FeBr}_3 \) or \( \text{AlBr}_3 \)
(ii) Halogen carrier.

4 (a) (i) \( \text{D} = \text{Propanone} \)
(ii) \( \text{E} = \text{Propanal} \)
(b) (i) Reagent(s): 2,4-dinitrophenylhydrazine. Observation: orange precipitate.
(ii) Reagents: Tollens’ reagent. Observation for \( \text{D} \): no change. Observation for \( \text{E} \): Silver mirror formed.
5 (a) \( CH_3CHO + 2[H] \rightarrow CH_3CH_2OH \)

(b) \[
\begin{array}{c}
\text{CH}_3\overset{\delta^+}{C}H_2\overset{\delta^-}{\text{O}} \quad \text{Step 1} \\
\text{CH}_3\overset{\delta^-}{C}H_2\overset{\delta^+}{\text{O}} \quad \text{Intermediate} \\
\text{CH}_3\overset{\delta^-}{C}H_2\overset{\delta^+}{\text{O}} \quad \text{Step 2} \\
\text{Ethyanal} \\
\text{Organic product}
\end{array}
\]

(iii) An electron-pair donor

(iv) The nucleophile is attracted to the positive charge. Lone pair of electrons forms a dative bond. An electron pair from the double bond goes to the oxygen atom. The \( \pi \) bond in the carbonyl bond breaks.

(c) Hydrogen does not have a lone pair of electrons.

6 (a) 

(b) (i) Add Tollens’ reagent. Heat reaction in a water bath. But-2-enal gives a silver precipitate or silver mirror.

(ii) Aldehydes can be oxidised but ketones cannot.

(c) (i) \( CH_3CH=CHCH_2OH \)

(ii) Redox reaction/reduction or addition.

(d) \( C_4H_6O + 5O_2 \rightarrow 4CO_2 + 3H_2O \)


Type of reaction: electrophilic addition.

(b) Recrystallise the product in order to purify the orange precipitate.

Measure the melting points of the crystals.

Compare known melting points with data tables.

8 (a) 

(b) (i) Butan-1-ol can be oxidised to produce butanal and further oxidised to give butanoic acid. This occurs as primary alcohols can be oxidised. Butan-2-ol can be oxidised to produce butanone. No further oxidation occurs as ketones cannot be oxidised. 2-Methylpropan-2-ol cannot be oxidised as it is a tertiary alcohol and is not oxidised.

2-Methylpropan-1-ol can be oxidised to produce 2-methylpropanal and further oxidised to give 2-methylpropanoic acid.

D: 2-methylpropan-1-ol.

E: 2-methylpropanoic acid.

(ii) \[
(\text{CH}_3\text{CH}_2\text{C}_2\text{H}_5\text{COOH} + \text{C}_2\text{H}_6\text{OH} \rightarrow (\text{CH}_3\text{CH}_2\text{C}_2\text{H}_5\text{C}_2\text{H}_5 \text{OH} + \text{H}_2\text{O})
\]

9 (a) (i) Methyl butanoate.

(ii) Heat/boil/warm/reflux with aqueous HCl or aqueous NaOH.
10 (a) (i) Concentrated H₂SO₄.
(ii) This is to prevent the loss of reactants and products by evaporation.
(b) (i)
(ii) Butan-2-ol.
(c) Flavourings or perfumes.
11 (a) A compound containing nitrogen where the nitrogen is attached to one carbon atom only.
(b) C₂H₅NH₂ + H⁺ → C₂H₅N⁺ + H₂O
(c) (i) Stage I: Sn, conc. HCl. Stage II: NaNO₂, HCl.
Stage III: Phenol, NaOH.
(ii) Stage I

12 (a) Stage 1: React phenylamine with sodium nitrite and hydrochloric acid at 10°C or below. This forms a diazonium salt which is unstable and must be kept below 10°C. Stage 2: React the diazonium salt with an alkaline solution of phenol below 10°C.

(b) (i) E₁₁₀

(c) NaOH(aq)
(d) Amine

(iii) Dyes.
13 (a) Diamino – compound contains two amine groups 1,4 – shows the position of the amine groups on the benzene ring.

(b) (i) Reduction/redox reaction.  
(ii) Tin and concentrated HCl. Heat under reflux.  
(iii)  
\[ \begin{array}{c} 
\text{O}_2N \quad \text{NO}_2 + 12[\text{H}] \\
\downarrow \\
\text{H}_2N \quad \text{NH}_2 + 4\text{H}_2\text{O} 
\end{array} \]

(c) (i) The amino group accepts H\(^+\) using its lone pair or electrons on the nitrogen and forming a co-ordinate bond.

(ii)  
\[ \text{Cl}^- \cdot \text{H}_3\text{N}^+ \quad \text{+NH}_3\text{Cl}^- \]

14 (a)  
\[ \text{CH}_3\text{(CH}_2\text{)}_3\text{CH}_2 \quad \text{CH}_2 \quad \text{(CH}_2\text{)}_3\text{COOH} \]

(b) (i) Oleic acid: C\(_{18}\)H\(_{34}\)O\(_2\). Ethanol: C\(_2\)H\(_6\)O.  
Ethyl oleate: C\(_{20}\)H\(_{38}\)O\(_2\)

(ii)  
\[ \text{C}_{18}\text{H}_{34}\text{O}_2 + \text{C}_2\text{H}_6\text{O} \rightarrow \text{C}_{20}\text{H}_{38}\text{O}_2 + \text{H}_2\text{O} \]

(c) Hydrolysis using hot aqueous HCl.

1.2 Polymers and synthesis

1 (a) (i) Hydrochloric acid. Aqueous acid heated under reflux.

(ii) Amino acids.

(iii)  
\[ \begin{array}{c} 
\text{H} \quad \text{N} \quad \text{H} \quad \text{C} \quad \text{O} \\
\text{H} \\
\text{H} 
\end{array} \quad \text{(or equivalent)} \]

(iv) A reaction with water which breaks down a compound into smaller sub-units. In the reaction above the peptide bond is broken.

(b) (i) For stereoisomerism in compound A, there must be a chiral centre, which is a carbon atom with four different groups attached to it. Stereoisomerism occurs when there is a different spatial arrangement of the groups. Two mirror images that are non-superimposable are observed.

(ii) The molecule contains two chiral centres and each chiral centre has two isomers.

2 (a) (i) RCH(NH\(_2\))COOH

(b) (i) An ion which has both a positive and a negative charge. The overall charge is zero.

(ii) A proton is transferred from the acidic COOH group to the basic NH\(_2\) group.

(c) (i) Heat with HCl (aq).

(ii) Hydrolysis.

(d) (i) Ammonia in ethanol.

(ii) Leucine synthesised in the laboratory contains a mixture of two optical isomers. Leucine from meat (a natural source) contains only one of the isomers.

3 (a) For L:  
\[ \begin{array}{c} 
\text{H} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{O} \quad \text{C} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} 
\end{array} \]

For M:

\[ \begin{array}{c} 
\text{H} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{O} \quad \text{C} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} 
\end{array} \]

(b)  
\[ \begin{array}{c} 
\text{O} \quad \text{C} \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{O} \quad \text{C} \quad \text{O} \quad \text{O} \\
\text{O} \quad \text{C} \quad \text{O} \quad \text{O} \\
\text{O} \quad \text{C} \quad \text{O} \quad \text{O} 
\end{array} \]
(c) It is a condensation reaction. When the reaction occurs a small molecule such as water is lost.

(d) Fibres/clothing.

4 (a) (i)

(ii) CH₂
(iii) H

(b) (i) Name of functional group: peptide.

(ii) Condensation.
(iii) Displayed formula of H:

Skeletal formula of H:

(iv) No. of moles of glycine = 1.40/75.0 = 0.0187 moles. Expected no. of moles of dipeptide = 0.0187/2 = 9.33 × 10⁻³ mol.
Expected mass = 9.33 × 10⁻³ × 132 = 1.232 g.
% = (1.10/1.232) × 100. Percentage yield 89.3%

(v)

5 (a) In addition polymerisation, the C=C double bond in an unsaturated molecule (monomer), such as ethene, breaks open and the monomer adds on to a growing polymer chain. The monomers add one at a time to form a long polymer such as poly(ethene), HDPE.

In condensation polymerisation, a polymer such as PET is formed when monomers – in this case ethane-1,2-diol and benzene-1,4-dicarboxylic acid – join together and lose a small molecule for each bond that forms. In the case of this polyester, a water molecule forms for each ester linkage that forms between –OH and HOOC–.

 Addition: Monomer ethene

Condensation

(b) (i)

(ii) Reagents: HCl (aq). Conditions: Heat and reflux
(iii) CH₃COOH

(c)

6 (a) Hexanediol dichloride ↓ 1,6-diaminohexane

Repeat of unit polymer

Other product
(b) (i)

\[
\begin{align*}
\text{HO} & \quad \text{CO} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{H} \\
\text{O} & \quad \text{C} \\
\text{H} & \quad \text{C} \\
\end{align*}
\]

(ii) The intermolecular forces in Nomex® are stronger than in nylon.

7 (a) \(\text{NO}_2\)

(b) \(\text{CH}_3\text{COOH and CH}_3\text{OH}\)

(c)

\[
\begin{align*}
\text{H} & \quad \text{C} & \quad \text{N} \\
\text{H} & \quad \text{C} & \quad \text{N} \\
\text{O} & \quad \text{C} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{N} \\
\text{H} & \quad \text{C} & \quad \text{N} \\
\end{align*}
\]

8 (a) (i) \(\text{NaOH (aq)}\)

(ii) Substitution.

(iii) \(\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{NaCl}\)

(b) (i)

\[
\begin{align*}
\text{H} & \quad \text{C} & \quad \text{O} \\
\text{H} & \quad \text{C} & \quad \text{O} \\
\end{align*}
\]

(ii) \(\text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOCH}_2\text{C}_6\text{H}_5 + \text{H}_2\text{O}\)

(iii) Flavourings.

9 (a) \(\text{C}_{12}\text{H}_{10}\text{O}_5\)

(b) (i) Reagent(s): \(\text{K}_2\text{Cr}_2\text{O}_7 (\text{aq})\).

Conditions: heat with \(\text{H}^+\).

Organic product:

(ii) Reagent(s): \(\text{HCl (aq)}\).

Conditions: aqueous.

Organic products:

(iii) Reagent(s): \(\text{NaOH (aq)}\).

Conditions: none.

Organic product:

10 (a) \(\text{HOOC(CH}_2\text{)}^4\text{COOH and H}_2\text{N(CH}_2\text{)}^6\text{NH}_2\).

(b) condensation polymerisation – small molecule, \(\text{H}_2\text{O}\), is eliminated.

(c) **Structural similarity**

Both have peptide or amide links

Both form H-bonds between molecules.

**Chemical similarity**

Both can be hydrolysed back to monomers by reaction with hot aqueous acid or alkali:

\[
\begin{align*}
\text{e.g.} & \quad -\text{CO}(-\text{CH}_2\text{)}^4\text{CONH}(-\text{CH}_2\text{)}^6\text{NH} & \rightarrow & \text{HOOC}(-\text{CH}_2\text{)}^4\text{COOH} + \text{H}_2\text{N}(-\text{CH}_2\text{)}^6\text{NH}_2
\end{align*}
\]

**Differences**

Protein can be water-soluble, nylon-6,6 not.

Proteins are biodegradable, nylon-6,6 is not.

Nylon-6,6 has a regular chain of alternating monomers. Proteins are made from 20 different amino acids.
11 (a) (i)
\[ \text{CH}_2=\text{CH}_3 \rightarrow [\text{CH}_2=\text{CH}_2]_n \]
(ii) Addition: The monomer has a C=C double bond. The double bond breaks and no substance is lost.
Condensation: A small molecule such as water is lost.

(b)
\[ \text{CH}_3\text{Cl} \]
\[ \text{O} \]
\[ \text{CH}_3 \]
\[ \text{O} \]
\[ \text{OC} \]
\[ \text{H}_2\text{N} \]
\[ \text{H} \]

(c) (i)
\[ \text{CH}_2=\text{CH}_3 \]
\[ \text{Cl} \]
\[ \text{O} \]
\[ \text{OC} \]
\[ \text{H}_2\text{N} \]
\[ \text{H} \]

(ii) H reacts with NaOH, poly(propene) does not. H is an ester and is polar so will be hydrolysed by NaOH. Poly(propene) is non-polar.

12 (a)
\[ \text{O}_2\text{N} \]
\[ \text{N} \]
\[ \text{N} \]
\[ \text{OH} \]
\[ \text{COOH} \]

(b)
\[ \text{O}_2\text{N} \]
\[ \text{NH}_2 \]
\[ \text{NaNO}_2/\text{HCl} \]

Below 10 °C
\[ \text{O}_2\text{N} \]
\[ \text{N} \]
\[ \text{N} \]
\[ \text{Cl}^- \]
\[ \text{Na}^+ \]
\[ \text{OH} \]
\[ \text{COOH} \]

1.3 Analysis
1 (a) (i) Paper, column or thin-layer chromatography.
(ii) The \( R_f \) value.
(iii)

(c) (i) Relative solubility in liquid stationary phase or adsorption to solid stationary phase.
(ii) Each component distributes itself between the mobile phase (carrier gas) and the stationary phase. Different components are held more or less strongly on the stationary phase and this leads to separation. This depends upon molecular size, volatility and extent of bonding to the stationary phase.

(d) Tin and concentrated hydrochloric acid, reflux.
\[ \text{O}_2\text{N} \]
\[ \text{COOH} \]
\[ \text{OH} + 6[\text{H}] \]
\[ \text{OH} + 2 \text{H}_2\text{O} \]
2 (a) Adsorption at 1700 cm⁻¹ shows the presence of C=O. Adsorption at 1200 cm⁻¹ shows the presence of C–O. No broad adsorption at 2500–3500 cm⁻¹ so does not contain O–H.

(b) The mass spectrum shows an M⁺ peak at 116 therefore 116 – 32 (2 oxygen atoms) = 84 therefore 6 carbon atoms maximum. Molecular formula of X = C₆H₁₂O₂. Base peak = 57 CH₃CH₂C=O. NMR. peak areas show 12H atoms and four different proton environments.
δ = 0.9 ppm suggests CH₃ next to CH₂ (triplet)
δ = 1.2 ppm suggests 2 × CH₂ next to CH (as split into a doublet).
δ = 2.3 ppm CH₂ next to CH₃ (quartet)
Other CH₂ next to C=O
δ = 4.1 ppm is CH next to 2 × CH₃.

3 (a) Compound has a molecular mass of 74. Relative empirical formulae mass = 74 (3 × 12 + 6 + 2 × 32) therefore empirical formula = molecular formula = C₃H₆O₂.

4 (a) Low boiling point.

(b) Add 2,4-DNP (2,4-dinitrophenylhydrazine) to the aldehyde or ketone. Purify or recrystallise the orange precipitate. Measure the melting point of the crystals. Compare the results with known values from a data table.

(c) (i) Absorption of energy

(ii) Re-run the spectrum having added D₂O to the sample. The peak due to –O–H will disappear.

(iii) Peak at δ = 1.4 ppm (doublet): (1:1) due to one proton on adjacent carbon atom. peak at δ = 4.3 ppm (quartet): (1:3:3:1) due to three protons on the adjacent carbon atom.

(iv) See graph answer to (c)(i).

(v) The number of protons in the same chemical environment.

5 (a) (i) Compound X is not an aldehyde or a ketone.

(ii) Compound X does not contain C=C and is not a phenol.

(c) Structure 1: ethyl methanoate.
Structure 3: propanoic acid.

(d) Peak at 1750 cm⁻¹ indicates presence of C=O. Peak at 1250 cm⁻¹ indicates presence of C–O. No peak at 2500–3500 cm⁻¹ means it does not contain O–H group. It cannot be structure 3.

(e) Correct structure of compound Y:

![Correct structure of compound Y]

Peaks show no splitting as there are no protons on the neighbouring carbon atoms.
(b) (i) Molecular ion peak would be at 90.

(ii) 4 as OH protons would now be visible.

(c) (i) Absorption of energy

(ii) More fruity because of ester/less sour as acid is used up.

(d) (i) The δ value or chemical shift indicates the type of proton or chemical environment. The number of peaks gives the number of different types of proton or the different numbers of chemical environments. The relative ratio of peak areas shows the number of protons of each type. Splitting patterns give information about the number of neighbouring hydrogen atoms (protons) on the carbon under investigation: the splitting pattern (singlet, doublet, triplet or quartet) is one greater than the number of adjacent protons.

D₂O is used to identify the presence of O–H groups.

(ii) CH₃CH₂COOH + (CH₃)₂CHCH₂OH \[\rightarrow\] CH₃CH₂COOC(CH₃)₂CH(CH₃)₂ + H₂O

7 (a) (i) Find the m/z value of the peak furthest to the right with highest m/z value.

(ii) C₂H₅O₂ has an empirical mass of 59. therefore 118/59 = 2

2 \times \text{empirical formula} = C₄H₆O₄.

(b) (i) OH peak disappears.

(ii) Peak at δ = 3.3 ppm identifies CH group. It shows as a quartet splitting pattern showing presence of three protons on the adjacent carbon atom. There is only one hydrogen in this environment.

Peak at δ = 1.2 ppm identifies CH₃ group. It shows doublet splitting showing the presence of one proton on the adjacent carbon atom. There are three protons in this environment.

Relative peak areas show the number of hydrogens (protons) in the environment.

8 (a) Infrared:

X and Y both have C=O at 1680–1750 cm⁻¹.

X and Y both have C–O at 1000–1300 cm⁻¹.

X and Y both have O–H in range 2500–3300 cm⁻¹.

Only Y has an absorption at 3100–3500 cm⁻¹ for N–H.

Both have different fingerprint regions.

Mass spectrum:

X and Y have different M peaks, X = 88 and Y = 89.

X and Y have some similar fragments, e.g. CH₃CH⁺ at m/z = 28, COOH⁺ at 45, CHCOOH⁺ at 58, CH₃CHCOOH⁺ at 73.

X and Y have some different fragments, e.g. X has CH₃CHCH₃⁺ at m/z = 43 or (CH₃)₂CHCO⁺ at 71; Y has H₂NNCH⁺ at 29, H₂NCHCH₃⁺ at 44, CH₃(NH₂)CHCO⁺ at 72 or NH₂⁺ at 16.
2.1 Rates, equilibrium and pH

1 (a) \( \text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \rightarrow \text{I}_2 + 2\text{H}_2\text{O} \)

(b) (i) Experiment 2 has twice [I\(^-\)] of Experiment 1 and the rate has quadrupled, so order = 2 with respect to I\(^-\).

(ii) \( \text{rate} = k [\text{H}_2\text{O}_2][\text{I}^-]^2 \)

(iii) \( k = \frac{\text{rate}}{[\text{H}_2\text{O}_2][\text{I}^-]^2} \)

Experiment 1: \( k = \frac{1.15 \times 10^{-6}}{(0.01)(0.01)^2} = 1.15 \times 10^{-2} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1} \)

2 From the graph, there is a constant half-life. Therefore, order = 1 with respect to [CH\(_3\)COCH\(_3\)].

From the table, the rate doubles when [H\(^+\)] doubles. Therefore order = 1 with respect to [H\(^+\)].

From the table, the rate stays the same when [I\(_2\)] doubles. Therefore order = 0 with respect to [I\(_2\)].

The rate equation is: \( \text{rate} = k [\text{H}^+][\text{CH}_3\text{COCH}_3] \)

\( k = \frac{2.1 \times 10^{-3}}{0.02 \times 1.5 \times 10^{-3}} = 7.0 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \)

The rate-determining step involves the species in the rate equation: H\(^+\) and CH\(_3\)COCH\(_3\).

A possible two-step mechanism is:
Step 1: CH\(_3\)COCH\(_3\) + H\(^+\) \( \rightarrow \) CH\(_3\)COHCH\(_3\)^+
Step 2: CH\(_3\)COHCH\(_3\)^+ + I\(_2\) \( \rightarrow \) CH\(_3\)COCH\(_3\)I + HI + H\(^+\)

H\(^+\) is used up in the first step and is regenerated in the second step so H\(^+\) is a catalyst.

3 (a) \( K_c = \frac{[\text{I}_2][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} \)

(b) (i) CH\(_3\)COOH, 1.0 mol; C\(_2\)H\(_5\)OH, 7.5 mol

CH\(_3\)COOC\(_2\)H\(_5\), 5.0 mol; H\(_2\)O, 5.0 mol

(ii) \( k_c = \frac{5 \times 5}{1 \times 7.5} = 3.3 \) (no units)

(c) The experiment could be left longer to reach equilibrium.

The compositions of the mixtures could be analysed at time intervals until the compositions do not change any more.

(d) (i) There would be more CH\(_3\)COOC\(_2\)H\(_5\) and H\(_2\)O

There would be less CH\(_3\)COOH

The equilibrium shifts to the right to counteract the effect of increasing the ethanol concentration.

(ii) \( K_c \) stays the same.

(e) The composition stays the same because the catalyst does not shift equilibrium position.

The rates of the forward and reverse reactions are increased by the same amount.

(f) (i) A decrease in \( K_c \) results in more reactants and fewer products. The equilibrium therefore shifts to the left in response to the new value of \( K_c \).

(ii) Increasing the temperature moves the equilibrium to the left to counteract the effect of the increase in energy. The forward reaction is exothermic and the reverse reaction is endothermic.

4 (a) \( K_c = \frac{[\text{HI}^2]}{[\text{H}_2][\text{I}_2]} \)

(b) (i) H\(_2\), 0.14 mol; I\(_2\), 0.04 mol; HI, 0.32 mol

(ii) \( k_c = \frac{0.32^2}{0.14 \times 0.04} = 18.28571429 \)

= 18 (to 2 sig. figs), no units

(c) \( K_c \) is constant because all volumes cancel and the temperature is constant.

The composition is the same as there are the same number of gas moles on either side of the equation.

(d) The forward reaction is exothermic. The equilibrium moves to the left to compensate for the increase in temperature.

(e) (i) I\(_2\)(aq) + H\(_2\)S(g) \( \rightarrow \) 2HI(aq) + S(s)

Amount of I\(_2\) reacted = 1.89 mol,

Therefore amount of HI formed = 3.44 mol

Theoretical amount of HI produced = 3.78 mol

% yield = \( \frac{3.44 \times 100}{3.78} = 91.0\% \)
(iii) $[H]=\frac{3.44 \times 10^{10}}{750} = 4.59 \text{ mol dm}^{-3}$

\[ \text{pH} = -\log 4.59 = -0.66 \]

5 (a) (i) A Brønsted–Lowry acid is a proton donor.

(ii) A weak acid is partially dissociated.

(iii) pH = $-\log[H^+]$

(iv) A buffer solution minimises changes in pH after addition of small amounts of both acids and alkalis.

(b) In the equilibrium $\text{H}_2\text{CO}_3(aq) \rightleftharpoons H^+(aq) + \text{HCO}_3^-(aq)$

Hydrogencarbonate, $\text{HCO}_3^-$, reacts with any added acid:

$\text{HCO}_3^- + H^+ \rightarrow \text{H}_2\text{CO}_3$

The equilibrium moves to the left to counteract increased $[H^+]$. $H^+$ reacts with any added alkali:

$H^+ + \text{OH}^- \rightarrow H_2O$

The equilibrium moves to the right to counteract a decrease in $H^+$.

(c) $K_a = \frac{[H^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$

\[ [H^+] = 10^{-pH} = 10^{-7.4} = 3.98 \times 10^{-8} \text{ mol dm}^{-3} \]

\[ [\text{HCO}_3^-] = \frac{K_a}{[H^+]} = \frac{4.17 \times 10^{-7}}{3.98 \times 10^{-8}} = 10.5 \]

6 (a) A weak acid partially dissociates:

e.g. $\text{HCOOH} \rightleftharpoons H^+ + \text{HCOO}^-$

(b) (i) pH = $-\log(1.55 \times 10^{-3}) = 2.81$

$[H^+]$ deals with negative indices over a very wide range.

(ii) $K_a = \frac{[H^+] [\text{HCOO}^-]}{[\text{HCOOH}]}$

\[ K_a = \frac{(1.55 \times 10^{-3})^2}{0.015} = 1.60 \times 10^{-4} \text{ mol dm}^{-3} \]

\[ pK_a = -\log(1.60 \times 10^{-4}) = 3.80 \]

(iv) Percentage dissociating = $\frac{(1.55 \times 10^{-3}) \times 100}{0.015} = 10.3\%$

(c) (i) $\text{HCOOH} + \text{NaOH} \rightarrow \text{HCOONa} + \text{H}_2\text{O}$

\[ n(\text{HCOOH}) = 0.0150 \times 25.00/1000 = 3.75 \times 10^{-4} \text{ mol} \]

From the graph, the rapid rise in pH takes place after addition of 30 cm$^3$ of NaOH(aq). Therefore 30 cm$^3$ of NaOH(aq) are required for neutralisation. Therefore $[\text{NaOH}] = 3.75 \times 10^{-4} \times 1000/30 = 0.0125$ mol dm$^{-3}$

(iii) $K_w = [H^+][OH^-]$

\[ \text{pH} = -\log(1 \times 10^{-14}/0.0125) = 12.10 \]

(iv) metacresol purple

The indicator’s pH range coincides with the pH change during the sharp increase in pH in the titration curve.

7 (a) The extent of dissociation of the acid

(b) (i) $\text{H}_2\text{SO}_3(aq) + \text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{HSO}_3^-(aq) + \text{CH}_3\text{COOH}_2^+(aq)$

acid 1 base 2 base 1 acid 2

(ii) CH$_3$COOH is a stronger acid than C$_6$H$_5$OH. Therefore, CH$_3$COOH will donate H$^+$ to C$_6$H$_5$OH

CH$_3$COOH(aq) + C$_6$H$_5$OH(aq) $\rightleftharpoons$ CH$_3$COO$^-$ + C$_6$H$_5$OH$^+$

(c) For HCl, pH = $-\log[H^+] = -\log 0.045 = 1.35$

For CH$_3$COOH, $[H^+] = \sqrt{(K_a \times [\text{CH}_3\text{COOH}])}$

$[H^+] = 8.75 \times 10^{-4}$ mol dm$^{-3}$

pH = $-\log 8.75 \times 10^{-4} = 3.058$

(d) 2 mol of each acid produce 1 mol of H$_2$

Mg + 2HCl $\rightarrow$ MgCl$_2$ + $H_2$

Mg + 2CH$_3$COOH $\rightarrow$ (CH$_3$COO)$^-$Mg + $H_2$

HCl is the stronger acid and in solution $[H^+]$ in HCl is greater while CH$_3$COOH will therefore react quicker as its $[H^+]$ is greater.

8 (a) (i) $K_w$ is the ionic product of water

(ii) $K_w = [H^+][OH^-]$

(b) amount of HCl = $\frac{5.00 \times 10^{-3} \times 21.35}{1000} = 1.067 \times 10^{-4}$ mol

amount of Ca(OH)$_2$ = $\frac{1.067 \times 10^{-4}}{2} = 5.34 \times 10^{-5}$ mol

concentration of Ca(OH)$_2$ = $40 \times 5.34 \times 10^{-5} = 2.136 \times 10^{-3}$ mol dm$^{-3}$

(c) $[OH^-] = 2 \times 2.7 \times 10^{-3} = 5.4 \times 10^{-3}$ mol dm$^{-3}$

\[ [H^+(aq)] = \frac{1.0 \times 10^{-14}}{5.4 \times 10^{-3}} = 1.85 \times 10^{-12} \text{ mol dm}^{-3} \]

\[ \text{pH} = -\log(1.85 \times 10^{-12}) = 11.73/11.7 \]

(d) [H$^+$][OH$^-$] = $10^{-14}$ mol$^2$ dm$^{-6}$;

If [OH$^-$] is 100 ($10^2$) × greater than [H$^+$], [OH$^-$] must be $10^{-6}$ and [H$^+$] must be $10^{-8}$

pH = $10^{-14} + 8$.

9 (a) (i) A weak Bronsted–Lowry acid is a proton donor that partially dissociates

(b) $K_a = \frac{[\text{HCOO}^-][H^+]}{[\text{HCOOH}]}$

$[H^+] = \sqrt{(1.58 \times 10^{-4} \times 0.025)} = 1.99 \times 10^{-3}$ mol dm$^{-3}$

\[ \text{pH} = -\log[H^+] = -\log 1.99 \times 10^{-3} = 2.70 \]
(c) (i) A buffer solution minimises pH changes.
(ii) sodium methanoate, HCOONa
HCOONa supplies HCOO\(^-\) as the conjugate base.
(iii) The pH of the buffer solution depends upon the extent of dissociation given by the \(K_a\) value and the relative concentrations of the weak acid and conjugate base.

(d) Mass of HNO\(_3\) = \(\frac{1400 \times 65}{100}\) / 910 g
amount of HNO\(_3\) = \(\frac{910}{63}\) = 14.4 mol
pH = \(-\log[H^+]\) = \(-\log 14.4\) = \(-1.16\)

2.2 Energy
1 (a) (i) Energy is needed to overcome the force of attraction between outer electrons and nucleus
(ii) Electron affinity involves a neutral atom gaining an electron by attraction from the nucleus

(b) (i) \[
\begin{align*}
\Delta H_1 &= +590 \text{ kJ mol}^{-1} \\
\Delta H_2 &= +1150 \text{ kJ mol}^{-1} \\
\Delta H_3 &= +249 \text{ kJ mol}^{-1} \\
\Delta H_4 &= +178 \text{ kJ mol}^{-1} \\
\Delta H_f &= +178 + 249 + 590 + 1150 + (-141) + 798 + (-3459) = -635 \text{ kJ mol}^{-1}
\end{align*}
\]

(ii) Lattice enthalpy of FeO is more negative and more exothermic than lattice enthalpy of CaO.
Ionic radius of Fe\(^{2+}\) must be less than that of a Ca\(^{2+}\) ion. This leads to greater attraction between Fe\(^{2+}\) ions and O\(^{2-}\) ions than between Ca\(^{2+}\) ions and O\(^{2-}\) ions.
2 (a) Lattice enthalpy is the enthalpy change that accompanies the formation of one mole of an ionic compound from its gaseous ions under standard conditions.

\[ \text{Mg}^{2+}(g) + 2 \text{Cl}^-(g) \rightarrow \text{MgCl}_2(s) \]

(b) \[ \Delta H_2 = +1451 \text{ kJ mol}^{-1} \]

\[ \Delta H_1 = +738 \text{ kJ mol}^{-1} \]

\[ 2 \times \Delta H_4 = 2 \times +123 \text{ kJ mol}^{-1} \]

\[ \Delta H_6 = +148 \text{ kJ mol}^{-1} \]

\[ \Delta H = -641 \text{ kJ mol}^{-1} \]

\[ \therefore \Delta H_{LE} = -641 - (+148 + 2 \times 123 + 738 + 1451 + 2 \times (-349)) = -2526 \text{ kJ mol}^{-1} \]

(c) Na\(^+\) has a larger radius than Mg\(^{2+}\) and Br\(^-\) has a larger radius than Cl\(^-\)

Na\(^+\) has a smaller charge than Mg\(^{2+}\)

Br\(^-\) experiences less attraction than Cl\(^-\)

Na\(^+\) experiences less attraction than Mg\(^{2+}\)

Therefore there is much less attraction between Na\(^+\) ions and Br\(^-\) ions than between Mg\(^{2+}\) ions and Cl\(^-\) ions.

One mark for correct spelling, punctuation and grammar in at least two sentences.

3 (a) (i) \( \Delta H_1 \) = Enthalpy change of formation of magnesium oxide

\( \Delta H_2 \) = Enthalpy change of atomisation of magnesium

\( \Delta H_3 \) = First ionisation energy of magnesium

(ii) \( \text{Mg}^{2+}(g) + \text{O}^2-(g) \)

(iii) The electron being gained is repelled by the negative charge of the O\(^2-\) ion.

(b) (i) \[ -602 = 149 + 736 + 1450 + 248 + 650 + \Delta H_{LE} \]

\[ \therefore \Delta H_{LE} = -602 - (149 + 736 + 1450 + 248 + 650) = -3835 \text{ kJ mol}^{-1} \]

(ii) Lattice enthalpy of barium oxide is less exothermic than that of magnesium oxide. This is because Mg\(^{2+}\) has a smaller ionic radius than Ba\(^{2+}\) so there is a stronger attraction between the positive and negative ions.

(c) Magnesium oxide has a high melting point because it has a highly exothermic lattice enthalpy resulting from strong attractive forces between Mg\(^{2+}\) and O\(^{2-}\) ions.

4 (a) \[ \text{NH}_4^+(g) + \text{Cl}^-(g) \]

(b) \[ \Delta H_{hyd}(\text{NH}_4^+) + \Delta H_{hyd}(\text{Cl}^-) = \Delta H_{LE}(\text{NH}_4\text{Cl}) + \Delta H_s(\text{NH}_4\text{Cl}) \]

\[ \Delta H_{hyd}(\text{NH}_4^+) + (-364) = -689 + 15 \]

Rearranging: \( \Delta H_{hyd}(\text{NH}_4^+) = (+364) + (-689 + 15) \)

\[ \therefore \Delta H_{hyd}(\text{NH}_4^+) = -310 \text{ kJ mol}^{-1} \]

(c) There is an increase in disorder on dissolving. Increase in entropy outweighs increase in enthalpy.

5 (a) Energy lost = \( mc \Delta T \) = 108.48 \times 4.18 \times 12.5 = 5668 J = 5.668 kJ

Amount of LiCl dissolved = \( \frac{m}{M} = \frac{8.48}{(6.9 + 35.5)} \)

= 0.200 mol

\[ \therefore \Delta H_{solution} = \frac{1.60}{0.200} = -28.34 \text{ kJ mol}^{-1} \]
There is an increase in disorder on dissolving. Increase in entropy outweighs increase in enthalpy.

(c) (i) X: Lattice enthalpy of LiCl; Y: Enthalpy change of hydration of Li⁺. 
(ii) Li⁺ ions are smaller than Na⁺ ions. Small ions exert more attraction on water molecules and more energy is released.

6 (a) In Equation 1, \( \Delta S \) is +ve because a gas is released. In Equation 2, \( \Delta S \) is –ve because the number of gas molecules decreases.

(b) \( \Delta G = \Delta H - T \Delta S \).

(c) (i) Increase in entropy from formation of a gas outweighs increase in enthalpy. Overall, balance between enthalpy and entropy is such that \( \Delta H - T \Delta S < 0 \).

(ii) At high temperatures, decrease in entropy from decrease in the number of gas molecules outweighs decrease in enthalpy because \( T \Delta S \) becomes more significant. Overall, balance between enthalpy and entropy is such that \( \Delta H - T \Delta S > 0 \).

7 (a) \( \Delta S \) is positive as the forward reaction results in an increase in the moles of gas molecules.

(b) \( \Delta S = \Sigma S^\text{products} - \Sigma S^\text{reactants} \)

\[ = (198 + 3 \times 131) - (186 + 189) = +216 \text{ J K}^{-1} \text{ mol}^{-1} \]

(c) \( \Delta G = \Delta H - T \Delta S \)

At room temperature, \( \Delta G = +210 - 298 \times 0.216 \)
\[ = +145.632 \text{ kJ mol}^{-1} \]

For a reaction to take place, \( \Delta G < 0 \text{ kJ mol}^{-1} \)

(d) When \( \Delta G = 0 \), \( \Delta H = T \Delta S \)
\[ \therefore T = \frac{\Delta H}{\Delta S} = \frac{210}{0.216} = 972 \text{ K} = 699^\circ \text{C} \]

8 (a) The standard electrode potential of a half cell, \( E^\text{\text{\textoe}} \), is the e.m.f. of a half cell compared with a standard hydrogen half cell, measured at 298 K with solution concentrations of 1 mol dm\(^{-3}\) and a gas pressure of 100 kPa (1 atmosphere).

(b) (i) Direction from Cu(s) to Ag(s) shown near to wire

(iii) Standard cell potential = 0.80 – 0.34 = 0.46 V

(iv) \( \text{Cu} + 2\text{Ag}^+ \longrightarrow \text{Cu}^{2+} + 2\text{Ag} \)

(c) \( E^\text{\text{\textoe}} \) for \( \text{Fe}^{2+}/\text{Fe}^{3+} \) is less positive than for \( \text{Cl}^-/\text{Cl}^\text{-} \). Therefore the \( \text{Fe}^{2+} \) has a greater tendency to lose electrons than \( \text{Cl}^- \).

\( E^\text{\text{\textoe}} \) for \( \text{I}^-/\text{I}^\text{-} \) is less positive than for \( \text{Fe}^{2+}/\text{Fe}^{3+} \). Therefore the \( \text{I}^- \) has a greater tendency to lose electrons than \( \text{Fe}^{2+} \).

9 (a) The standard electrode potential of a half cell, \( E^\text{\text{\textoe}} \), is the e.m.f. of a half cell compared with a standard hydrogen half cell, measured at 298 K with solution concentrations of 1 mol dm\(^{-3}\) and a gas pressure of 100 kPa (1 atmosphere).

(b) Standard cell potential = 1.52 – 1.36 = 0.16 V

(c) (i) \( 2\text{MnO}_4^- + 10\text{Cl}^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O} \)

(ii) \( \text{Cl}^- \) from –1 to 0

(iii) \( \text{Mn} \) from +7 to +2

(iii) \( \text{Cl}^- \) has been oxidised

\( \text{Mn} \) in \( \text{MnO}_4^- \) has been reduced

(d) Standard electrode potential applies only to a concentration of 1 mol dm\(^{-3}\), and potentials give no information about rates. When concentration of \( \text{Cl}^- \) decreases, equilibrium moves towards \( \text{Cl}^\text{-} \), and \( \text{Cl}^-/\text{Cl}^\text{-} \) half cell potential becomes less negative. The difference between the electrode potentials becomes smaller and the \( \text{Cl}^-/\text{Cl}^\text{-} \) potential may even become more positive than the \( \text{MnO}_4^-/\text{Mn}^{2+} \) potential. The reaction will then not be feasible.

10 (a) (i)

(ii) Direction from Cr(s) to Cd(s) shown near to wire

(iii) Cr half cell \( E^\text{\text{\textoe}} \) value is more negative.

(b) \( 2\text{Cr(s)} + 3\text{Cd}^{2+}(aq) \longrightarrow 2\text{Cr}^{3+}(aq) + 3\text{Cd(s)} \)

(c) (i) Standard cell potential = –0.40 – (–0.74) = 0.34 V

(ii) Concentration of \( \text{Cr}^{3+} \) decreases so equilibrium moves towards \( \text{Cr}^{3+} \) and Cr half-cell becomes more negative. Therefore there is a bigger difference between the electrode potentials and the cell potential will increase.
11 (a) The standard electrode potential of a half-cell, \( E^\circ \), is the e.m.f. of a half-cell compared with a standard hydrogen half-cell, measured at 298 K with solution concentrations of 1 mol dm\(^{-3}\) and a gas pressure of 100 kPa (1 atmosphere).

(b) (i) solution \( A = 1 \) mol dm\(^{-3}\) HCl(aq) (or 1 mol dm\(^{-3}\) H\(^+\)(aq))

(ii) Direction from hydrogen half-cell along wire to \( S_2O_8^{2-} \) half-cell

(iii) \( S_2O_8^{2-} + H_2 \rightarrow 2SO_4^{2-} + 2H^+ \)

(c) molar mass of \( Na_2S_2O_8 \) = 238.2 g mol\(^{-1}\)

molar mass of \( Na_2SO_4 \) = 142.1 g mol\(^{-1}\)

\[ \therefore \frac{23.82 \text{ g}}{238.2 \text{ g mol}^{-1}} \times \frac{142.1 \text{ g}}{14.21 \text{ g}} = 0.588 \text{ g} \]

\[ \therefore \% \text{ purity} = \frac{0.588}{0.655} \times 100 = 89.8\% \]

2 (a) (i) Blue to green to yellow solution.

(ii) The lone pair on the chloride ion is donated to the copper(II) ion. A co-ordinate (dative covalent) bond is formed.

(b) A light blue precipitate forms, which is soluble in excess ammonia forming a deep blue solution.

(c) Ammonia molecule has one lone pair of electrons and three bonding pairs. The lone pair repels the bonding pairs more than they repel each other, reducing the bond angle. Each ammonia ligand bonded to copper has four bond pairs. So equal repulsion between bonding pairs. Angle larger, at 109.5.

3 Transition elements are d block elements that have an ion with an incomplete d sub-shell. Cu\(^{2+}\) 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\) 3d\(^{3}\)

Note that the d sub-shell is incomplete.

\[ \begin{align*}
\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O} \\
\end{align*} \]

The shape is tetrahedral.

Water molecules are ligands (electron-pair donors) and these form co-ordinate bonds to the central metal. The Cu\(^{2+}\) ion is an electron-pair acceptor.

- Transition metals have variable oxidation states, for example Cu\(^{3+}\) and Cu\(^{+}\).
- Transition metals form coloured compounds: CuCl\(_4^{2-}\) is yellow. [Cu(H\(_2\)O)\(_6\)]\(^{2+}\) is blue.
- Transition metals and their ions act as catalysts. Iron is a catalyst for the Haber process.

4 (a) 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\) 3d\(^{5}\)

Iron has an incomplete d sub-shell in the Fe\(^{3+}\) ion. It is a transition metal.

(b) 1 Variable oxidation state.

2 Forms coloured compounds.

(c) Fe\(^{2+}\) reacts with hydroxide ions to form a green precipitate whereas Fe\(^{3+}\) reacts with hydroxide to form an orange-brown precipitate.

(d) \( 4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \)

(e) (i) Copper may react with MnO\(_4^-\).

Copper reacts with Fe\(^{3+}\) reducing it back to Fe\(^{2+}\).

(ii) Mn in MnO\(_4^-\) changes from oxidation state +7 to +2 in Mn\(^{2+}\) (it is reduced). Fe changes from Fe\(^{2+}\) (+2) to Fe\(^{3+}\) (+3) and is oxidised.
(iii) No. of moles of MnO₄⁻ = \( \frac{(22.5 \times 0.02)}{1000} \) = \( 4.50 \times 10^{-4} \)
Moles of Fe²⁺ = \( 5 \times 4.50 \times 10^{-4} = 2.25 \times 10^{-3} \)
Mass of Fe²⁺ = \( 2.25 \times 10^{-3} \times 55.8 = 0.1256 \) g
Percentage = \( \frac{0.1256}{0.675} \times 100 = 18.6\% \)

5 (a) A pale blue solution forms a light blue precipitate which is soluble in excess ammonia to give a deep blue solution.

(b) ![Diagram of a complex ion](image)

(c) Water has 2 lone pairs and 2 bonding pairs. The two lone pairs repel the bonding pairs more than the bond pairs repel each other. Bond angle is 104.5° but in the ligand a lone pair is used to form a co-ordinate bond to the metal. Water ligand has 3 bond pairs and one lone pair. There is less repulsion. So the bond angle is greater than in a water molecule.

6 (a) Transition elements are catalysts.

(b) (i) ![Diagram of a complex ion](image)

(ii) Cl⁻

(iii) Concentrated hydrochloric acid.

(iv) \( \text{[Cu(H₂O)₆]²⁺ + 4Cl⁻ \rightarrow CuCl₄²⁻ + 6H₂O} \)

This is a reaction where one ligand is replaced by another. Here H₂O is replaced by Cl⁻.

7 (a) Oxygen changes from –1 (H₂O₂) to –2 (in H₂O); it is reduced.

Oxygen changes from –1 (H₂O₂) to 0 (O₂); it is oxidised.

(b) (i) \( 2\text{MnO}_4^- + 6\text{H}^+ + 5\text{H}_2\text{O}_2 \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{O}_2 \)

(ii) No. of moles of MnO₄⁻ = \( (17.5 \times 0.02)/1000 \) = 0.00035

No. of moles of H₂O₂ = \( (0.00035/2) \times 5 \) = 0.000875

0.000875 = (concentration × 25)/1000

Concentration = 0.0350 mol dm⁻³

(c) Name of reagent used: NaOH

Observation: Red-brown precipitate.

8 (a) (i) ![Diagram of a complex ion](image)

(ii) ![Diagram of a complex ion](image)

(iii) Cis–trans.

(b) (i) HCl(conc).

(ii) Ligand substitution.

9 (a) (i) This is the number of co-ordinate bonds formed by ligands to the transition metal ion.

(ii) Square planar.

(b) (i) Ligand substitution.

(ii) \( x = 2, y = 0 \)

(c) (i) ![Diagram of a complex ion](image)

(ii) Cis–trans.

(iii) Cis-platin binds with DNA and prevents cell division, stopping the growth of tumours.

10 (a) (i) \( \text{[Fe(NH₃)₄Cl₂]⁺} \)

(ii) ![Diagram of a complex ion](image)

(iii) 6

(b) Cis-platin is an anti-cancer drug. It binds to DNA and prevents replication, stopping the growth of tumours.

11 (a) +2

(b) No. of moles of \( \text{S}_2\text{O}_3^{2–} = \frac{(0.100 \times 22.0)}{1000} \)

Answer: 0.00220 mol

(c) No. of moles of \( \text{I}_2 = \frac{0.00220}{2} = 0.0011 \)

Answer: 0.00110 mol

(d) No. of moles of Cu²⁺ = \( \frac{0.00110 \times 2}{2} \)

Answer: 0.00220 mol

(e) \( 0.00220 = \frac{(concentration \times 25.0)}{1000} \)

Answer: 0.0880 mol dm⁻³
12 (a) (i) From pink to blue
(ii) Tetrahedral
(iii) Ligand substitution

(c) (i) Optical isomerism
(ii)

13 (a) 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁶; Fe²⁺ has an incompletely filled d subshell.

(b) (i) [Fe(H₂O)₆]²⁺
(ii)

(iii) Each ligand donates an electron pair to the metal ion to form a coordinate (dative covalent) bond.

(c) [Fe(H₂O)₆]³⁺ + 4Cl⁻ ⇄ [FeCl₄]³⁻ + 6H₂O

(d) FeCl₂ gives a green precipitate and FeCl₃ gives a brown-red precipitate.

Fe²⁺(aq) + 2OH⁻(aq) → Fe(OH)₂(s)

(e) Cr changes from +3 to +6, which is oxidation; Fe changes from +6 to +3, which is reduction.

(f) 4FeO₄²⁻ + 20H⁺ → 4Fe³⁺ + 3O₂ + 10H₂O

14 (a) MoO₃ + 2Al → Mo + Al₂O₃
(b) [Kr]4d³, which has an incompletely filled d sub-shell, meaning it is a transition metal ion.
(c) Cr₂O₇²⁻(aq) + 2H⁺(aq) + 3MoO₂(s) → 3MoO₄²⁻(aq) + 2Cr³⁺(aq) + H₂O(l)
(d) (i) K₂FeO₄
(ii) Moles of KOH = 4.00 × 10.0/1000 = 0.0400 mol
Moles of Fe₂O₃ = 1.00/159.6 = 0.00627 mol
From the equation, 1 mol Fe₂O₃ reacts with 10 mol OH⁻ ≡ 10 mol KOH
∴ 0.00400 mol Fe₂O₃ reacts with 0.0400 mole KOH.
∴ Fe₂O₃ is in excess by 0.00227 mol.