

(ii) Nickel carbonyl has a <u>simple covalent structure</u> with <u>weak</u> <u>intermolecular forces</u> which require little energy to overcome.

(iii)
$$M = \frac{2.00'8.31'(273 + 50)}{1.01'10^5'314'10^{-6}}$$

= 169

(iv) 58.7 + (12.0 + 16.0)x = 169

x = 3.93

= 4 (nearest whole number)

Coordination number is 4

Tetrahedral (accept "square planar")

(b) (i) In transition metal compounds, the presence of ligands causes the 3d orbitals to split into 2 sets of non-degenerate orbitals. The difference in energies (DE) between these 2 sets of 3d orbitals is small and radiation from the visible region of the electromagnetic spectrum is absorbed when an electron moves from a lower energy d-orbital to another unfilled/partially-filled d orbital of

higher energy. The colour observed correspond to the complement of the absorbed colours. Hence, transition metal compounds are often coloured.

(ii) Blue solution $[Cu(H_2O)_6]^{2+}$

Yellow solution CuC/4²⁻

Blue solution was formed from the oxidation of Cu (to Cu²⁺(aq)). Blue solution formed a white solid on heating to due to loss of water <u>ligands</u>. / Splitting of 3d orbitals into 2 sets of different energy no longer occurs.

CuC/42 + 6H2O = [Cu(H2O)6]2 + 4C/

On addition of water, position of equilibrium of $CuCl_4^{2-}$ + $6H_2O$ =

 $[Cu(H_2O)_6]^{2+} + 4Cl^{-} \text{ shifts to the right, forming blue } [Cu(H_2O)_6]^{2+}$ [6]

[3]

(c) Limonene:

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aqueous bromine cold alkaline KMnO4 Menthone: 2,4-DNPH Menthol: PC*l*₅ / SOC*l*₂ Acidified potassium dichromate, heat

Acidified KMnO₄, heat; followed by test with limewater

(i) Oxidation number = 0 - (-2) - 4(+1)(a) = - 2 (ii) Zero 0 OH HO н н OR <u>+2</u> 0 HO Ή OR C%0 (iii) CH₃CH₂CH₂CH₂OH(I) + 6O₂(g) ® 4CO₂(g) + 5H₂O(I) (iv) Temperature increase = 58 - 23 = 35 °C Heat evolved = 35 ' 515 ' 4.18 = 7.53 ´ 10⁴ J Amount of butan-1-ol = 2.30, (4 12.0 + 10 1.0 + 16.0) $= 3.11 \text{ ' } 10^{-2} \text{ mol}$ $DH_{c} = -\frac{27.53 \cdot 10^{4}}{c_{e}^{2}3.11 \cdot 10^{-2}} \frac{\ddot{o}}{\phi}$ $= -2.42 \text{ ' } 10^6 \text{ J mol}^{-1}$

= - 2.42 ´ 10³ kJ mol⁻¹

- (v) The calculated value is <u>less negative (less exothermic)</u> than the true value as there is heat loss to the surroundings and copper can calorimeter.
- (b) (i) Propanedioic acid is a stronger acid than butanedioic acid due to the stabilisation of the anion by hydrogen bonding with the unionised –CO₂H group.



(ii) Removal of H⁺ from an anion (A) that already carries a negative charge is electrostatically unfavourable.

OR

The stabilising hydrogen bonding would be destroyed by the ionisation of the second $-CO_2H$ group.

(iii) Let the acid be HA and the concentration of $H^+(aq)$ be x.

$$K_{a} = \frac{[H^{+}][A^{-}]}{[HA]}$$

$$10^{-4.20} = \frac{x^{2}}{0.25 - x}$$
Since x is small,
$$10^{-4.20} = \frac{x^{2}}{0.25}$$

$$x = 3.97 \text{ ' } 10^{-3} \text{ mol dm}^{-3}$$

$$pH = - \lg (3.97 \text{ ' } 10^{-3})$$

$$= 2.40$$

[7]



(ii) $A/Cl_3(s) + 3H_2O(l) \otimes A/(OH)_3(s) + 3HC/(g)$

OR 2A/Cl₃(s) + 3H₂O(I) ® Al₂O₃(s) + 6HCl(g)

(When a few drops of water is added, A/Cl_3 undergoes hydrolysis to form white fumes of HCl(g) and white insoluble solid of $Al(OH)_3$.)

 $A/C_{l_3}(s) + 6H_2O(I) \otimes [A/(H_2O)_6]^{3+}(aq) + 3Cl^{-}(aq)$

 $[Al(H_2O)_6]^{3+}(aq) + H_2O(I) = [Al(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$

 A/Cl_3 undergoes dissolves readily in water to form hydrated/aqueous $Al^{3+} / Al^{3+}(aq)$ ions which <u>undergoes hydrolysis</u> due to the high charge density of the polarising cation to give a weakly acidic solution.

3 (a) (i) Determine the [I₂] at regular time intervals by guenching the sample of the solution and titrating with aqueous sodium thiosulfate.

> **OR** Measure the electrical conductivity of solution at different time intervals.

> **OR** Measure the pH of the solution at regular time intervals using a pH meter.

(ii) The graph of [I₂] against time is a straight line, indicating that rate is constant despite decreasing [I₂]. Hence, the reaction is zero order with respect to iodine.

From graph 1, when [CH₃COCH₃] is increased from 0.10 mol dm⁻³ to 0.25 mol dm⁻³, gradient/rate of reaction is increased from 1.0 $\acute{}$ 10^{-4} mol dm^{-3} min^{-1} to 2.5 $\acute{}$ 10^{-4} mol dm^{-3} min⁻¹. Gradient/rate is 2.5 times the original gradient/rate when [CH3COCH3] is 2.5 times the original concentration. Hence, the reaction is first order with respect to propanone.

From graph 2, when $[H^+]$ is doubled from 0.20 mol dm⁻³ to 0.40 mol dm⁻³, gradient/rate of reaction is also doubled from 1.67 ' 10^{-4} mol dm⁻³ min⁻¹ to 3.33 ' 10^{-4} mol dm⁻³ min⁻¹. Hence, the reaction is first order with respect to H⁺.

- (iii) Rate = k[CH₃COCH₃][H⁺]
- (iv) Stage 1 is relatively slower than stage 2. / Stage 1 is the slow step. / Stage 1 is the rate determining step.

Rate equation suggests that the slow step/ rate determining step involves only one molecule of propanone and a H⁺ ion.

- (b) (i) NaBH₄ (in aqueous ethanol) OR H₂, Ni, (heat) Reduction
 - (ii) The **electron-withdrawing bromine** atom in 3-bromobutanoate ion disperses the negative charge on the COO⁻ group, making the 3-bromobutanoate ion more stable than the butanoate ion. Hence, 3-bromobutanoic acid is a stronger acid.
 - An increase in concentration of 3-oxobutanoic acid and (iii) 3-hydroxybutanoic acid is buffered by the CO₂/HCO₃⁻ buffer system present in blood. **OR**

Excess ketone bodies are excreted from the human body in urine (since they are water-soluble).

P undergoes oxidation to give Q, which is further oxidised by (C) Fehling's solution/gives positive Fehling's tes to form the salt of R [7]

[8]

[5]

P Q is an <u>aldehyde</u> and **P** is a <u>primary alcohol</u>.

Both ${\bf P}$ and ${\bf R}$ undergoes $\underline{acid-metal\ reaction}$ with sodium to give 1 mole of hydrogen gas

▷ Both **P and R** contain <u>2 O–H groups</u>.

P undergoes (intramolecular) <u>condensation</u> when warmed with concentrated sulfuric acid to produce $S \triangleright S$ is a (cyclic) <u>ester</u>. Structures:



4 (a) (i) Cl₂, AlCl₃ OR Cl₂, FeCl₃ OR Cl₂, Fe

> (ii) Electrophilic substitution $Cl_2 + A/Cl_3 \otimes Cl^+ + A/Cl_4^-$



(iii) Amount of methylbenzene in 118 g
= 118 (7 ´ 12.0 + 8 ´ 1.0)
= 1.28 mol
Amount of 1-chloro-2-methylbenzene produced

= 0.730 mol

Percentage yield = $\frac{0.730}{1.28}$, 100 = 57.0%



(c) Compound A is optically active

Þ compound A contains chiral carbon

C:H ratio in Compound A is close to 1:1

Þ compound A contains benzene ring

Compound A undergoes nucleophilic substitution with NaOH(aq) to form compound ${\bf B}$

- ▷ compound **B** is an alcohol
- Þ compound **A** is an alkyl bromide/alkyl halide

[3]

[10]

Positive iodoform test with Compound B

▷ compound B contains –CH(OH)CH₃

Compound A undergoes elimination to form compound C

- Þ compound A is an alkyl bromide/alkyl halide
- ▷ compound **C** contains C\$C bond / alkene functional group

Compound C undergoes mild oxidation to form compound D

▷ compound **D** is a diol

Compound ${\bf C}$ undergoes vigorous oxidation to form compound ${\bf E}$ and ethanoic acid

Þ compound C is not a terminal alkene



5 (a) (i)



dilute H₂SO₄(aq)

- (ii) Reactions at anode: $2H_2O(I) \otimes O_2(g) + 4H^+(aq) + 4e^ 2Al(s) + 3/2O_2(g) \otimes Al_2O_3(s)$ Reaction at cathode: $2H^+(aq) + 2e^- \otimes H_2(g)$
- (iii) Volume of A/₂O₃ layer = 29.21 $^{\circ}$ 0.02 = 0.584 cm³ Mass of A/₂O₃ = 3.95 $^{\circ}$ 0.584 = 2.31 g Amount of A/₂O₃ = $\frac{2.31}{2^{\circ} 27.0 + 3^{\circ} 16.0}$ = 0.0226 mol Amount of O₂ = 0.0226 $^{\circ}$ 3/2 = 0.0339 mol Amount of electrons passed through the cathode = 0.0339 $^{\circ}$ 4 = 0.136 mol Q = 0.136 $^{\circ}$ 96500 = 13100 C Time needed =13100 $_{\circ}$ 2.0 = 6550 s [10]

(b) (i) $NaCl(s) + H_2SO_4(l) \otimes NaHSO_4(s) + HCl(g)$

(State symbols not required)

(ii)
$$2Cl^{-} + SO_4^{2-} + 4H^+ \otimes Cl_2 + SO_2 + 2H_2O$$

 $E_{cell} = +0.17 - (+1.36)$
 $= -1.19 V$

As $E_{cell} < 0$ V, reaction is energetically non-feasible.



(ii) Heavy metal ions <u>form ionic interactions with - COO</u>, which brings about the formation of insoluble protein salts (i.e. precipitation of protein). This disrupts the <u>ionic interactions</u> in the tertiary structure, and hence leads to denaturation.

Heavy metal ions have a high affinity for sulfur and will <u>bind</u> <u>tightly to the - SH group</u>. This disrupts the <u>disulfide bridges</u> in the tertiary structure, and hence leads to denaturation.

Electrode reaction	<i>E</i> [,] (M ²⁺ /M)/ V
$Mg^{2+} + 2e^{-} = Mg$	-2.38
$Ca^{2+} + 2e^{-} = Ca$	-2.87
$Ba^{2+} + 2e^{-} = Ba$	-2.90

Down the group, $\underline{E}(M^{2+}/M)$ becomes more negative. Therefore, the reducing power increases from Mg to Ba.

Element	1 st IE/ kJ mol ⁻¹	2 nd IE/ kJ mol ⁻¹
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[4]

Mg	736	1450
Са	590	1150
Sr	548	1060
Ва	502	966

OR Quote 1st and 2nd IE values

This is because the <u>atomic radius increases</u> from Mg to Ba and as a result, <u>ionisation energy decreases</u>. Thus, reducing power increases from Mg to Ba.

(ii) Mg reacts with cold water slowly/Mg reacts with steam readily while Ba reacts with cold water vigorously.

[3]