

(d) Number of moles of OH^- :

$$12.5 \times 10^{-3} \times 0.08 \text{ [1]}$$

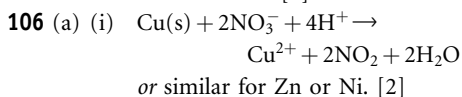
Number of moles of H^+ :

$$12.5 \times 10^{-3} \times 0.08 \text{ [1]}$$

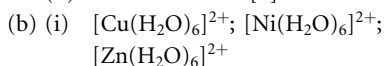
Concentration of

$$\text{H}^+ = \frac{12.5 \times 10^{-3} \times 0.08}{10 \times 10^{-3}} \text{ [1]}$$

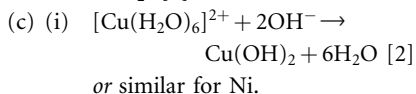
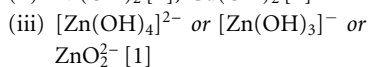
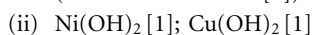
$$= 0.1 \text{ mol dm}^{-3} \text{ [1]}$$



(ii) Redox reaction. [1]

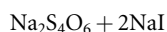
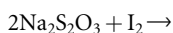
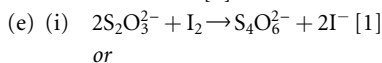


(all three correct for [2])



(ii) Acid–base reaction. [1]

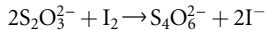
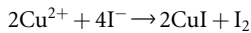
(d) Sodium hydroxide is added to remove the nitric acid. [1] Nitric acid is an oxidising agent and would interfere with the titration (oxidises I^- to I_2). [1] Finally sulphuric acid is added to make sure the solution is acidic before titration. [1]



The indicator would be starch. It should be added when the solution is pale yellow. [1] If it is added too soon it gives an insoluble complex. [1]

(ii) Number of moles of

$$\text{S}_2\text{O}_3^{2-} = 18.7 \times 10^{-3} \times 0.1 \text{ [1]}$$



so 1 mole of thiosulphate

corresponds to 1 mole of Cu^{2+} .

Number of moles of Cu^{2+} in $25 \text{ cm}^3 = 18.7 \times 10^{-3} \times 0.1$ [1]

Number of moles of Cu^{2+} in 500 cm^3

$$= \frac{500}{25} \times 18.7 \times 10^{-3} \times 0.1$$

$$= 0.0374 \text{ [1]}$$

Mass Cu^{2+} in

$$500 \text{ cm}^3 = 0.0374 \times 63.5$$

$$= 2.375 \text{ g [1]}$$

$$\% \text{Cu} = \frac{2.375}{9.5} \times 100 = 25\% \text{ [1]}$$

(iii) For the reaction between

copper(II) and iodide ions:

$$E_{\text{cell}}^\ominus = +0.15 - 0.54 = -0.39 \text{ V}$$

This is negative, and so the

reaction would not be expected

to take place. [1] However, the

CuI formed is insoluble. [1] This

means that Cu^+ is removed by

precipitation, so $[\text{Cu}^+]$ is less

than 1 mol dm^{-3} , which means

E_{cell} is different from E^\ominus . [1]

107 (a) (i) $k = \frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]}$

$$\text{Units: } \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})^3}$$

$$= (\text{mol dm}^{-3})^{-2} \text{ s}^{-1}$$

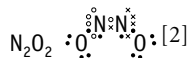
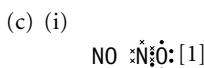
$$= \text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1} \text{ [1]}$$

(ii) The rate would double [1] since the rate is directly proportional to the oxygen concentration [1].

(iii) If the concentration of NO was halved, the rate would decrease by a factor of $(\frac{1}{2})^2$, since the reaction is second order, i.e. $\frac{1}{4}$. [2]

(b) (i) Overall order is 3. [1]

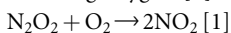
(ii) It is very unlikely that three particles will collide simultaneously [1], in the correct orientation [1].



NO has an unpaired electron which pairs up with a similar one on another NO molecule. [1]

(ii) Bond energy is usually defined in terms of bonds being broken. In this case an N–N bond is made. [2]

(iii) The rate depends on the concentration of oxygen as well, so there must be a slow step involving oxygen. [1]



(d) (i) Increasing the temperature causes the equilibrium to move in the endothermic direction [1] so the reaction would move to the left [1] since this reaction is exothermic.

(ii) Increasing the temperature would increase the rate of production of NO_2 . [1] However, high temperatures are expensive to maintain and may therefore be

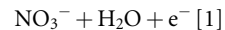
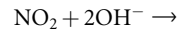
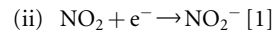
uneconomic. [1] Also, increasing the temperature reduces of yield of NO_2 so a compromise must be reached. [1]

(e) (i) Disproportionation reaction or redox reaction. [1]

Oxidation number of N in NO_2 is +4; in NO_2^- it is +3; in NO_3^- it is +5.

\therefore N is simultaneously oxidised and reduced:

disproportionation. [1]



108 (a) (i) Choice of axes [1]; points plotted correctly [1]; smooth curve drawn accurately [1]; end-point $16.0 (\pm 0.3) \text{ cm}^3$ [1].

Number of moles of

$$\text{NaOH} = 16 \times 10^{-3} \times 0.05$$

$$= 8 \times 10^{-4} \text{ [1]}$$

Number of moles of A in 10 cm^3

$$= 8 \times 10^{-4} \text{ [1]}$$

Number of moles of

A in 1000 cm^3

$$= 8 \times 10^{-4} \times \frac{1000}{10} = 0.08 \text{ [1]}$$

$$M_r \text{ of A} = \frac{7.2}{0.08} = 90 \text{ g mol}^{-1} \text{ [1]}$$

(ii) Method 1

pH of solution of A = 2.5 [1]

Therefore, concentration of H^+ = $3.16 \times 10^{-3} \text{ mol dm}^{-3}$ [1]

$$K_a = \frac{[\text{H}^+]^2}{\text{HA}}$$

$$= \frac{(3.16 \times 10^{-3})^2}{0.08}$$

$$= 1.25 \times 10^{-4} \text{ [1] mol dm}^{-3} \text{ [1]}$$

Method 2

$\text{pH} = \text{p}K_a$ at half the equivalence

point. [1]

pH value at 8.0 cm^3 NaOH (read from graph) = 3.9 [1]

$$K_a = -\text{antilog } 3.9$$

$$= 1.25 \times 10^{-4} \text{ [1] mol dm}^{-3} \text{ [1]}$$

(b) Number of moles of C = $\frac{40}{12} = 3.33$

$$\text{Number of moles of H} = \frac{6.67}{1} = 6.67$$

$$\text{Number of moles of O} = \frac{53.33}{16} = 3.33$$

Ratio C : H : O = 1 : 2 : 1

Empirical formula = CH_2O [1]

Empirical formula mass = 30, but $M_r = 90$

so molecular formula = $C_3H_6O_3$ [1]
 $CH_3C^*H(OH)COOH$ [1]

* = asymmetric carbon atom [1]

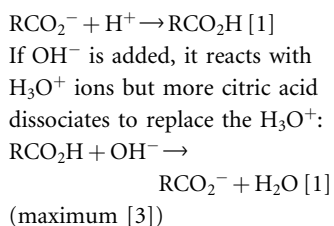
- (c) $15:CH_3$; $30:CH_3OH$;
 $45:COOH$ / CH_3CHOH ;
 $75:CH(OH)COOH$ ([1] for each peak)
- (d) First, add NaOH to neutralise the acid group. [1] Add PCl_5 [1] and steamy fumes of HCl confirms the presence of $-OH$. [1] Add $I_2/NaOH$. [1] The formation of a yellow precipitate of iodoform confirms the OH is on the second carbon atom, next to a CH_3 group.

109 (a) (i)
$$K_a = \frac{[H_3O^+][RCO_2^-]}{[RCO_2H]} [1]$$

(ii) Assume that $[H_3O^+] = [RCO_2^-]$
then $7.4 \times 10^{-4} = \frac{[H_3O^+]^2}{0.2} [1]$
 $[H_3O^+] = \sqrt{(7.4 \times 10^{-4} \times 0.2)}$
 $= 0.01216 [1]$
 $pH = -\lg(0.01216)$
 $= 1.91 [1]$

- (b) (i) A buffer is used when it is necessary that a solution should resist changes in pH [1] when small amounts of acid or alkali are added [1].

- (ii) The citrate ions from the salt suppress the ionisation of the acid. [1] As a result there is an excess of undissociated acid, and an excess of citrate ions. [1] If H^+ is added, it reacts with citrate ions:



- (iii) Assume concentration of citric acid = 0.2 mol dm^{-3}
Assume concentration of citrate ions = 0.4 mol dm^{-3}

$$K_a = \frac{[RCO_2^-][H_3O^+]}{[RCO_2H]}$$

$$7.4 \times 10^{-4} = 0.4 \times \frac{[H_3O^+]}{0.2} [1]$$

$$[H_3O^+] = 7.4 \times 10^{-4} \times \frac{0.2}{0.4}$$

$$= 3.7 \times 10^{-4} \text{ mol dm}^{-3}$$

$$pH = -\lg(3.7 \times 10^{-4})$$

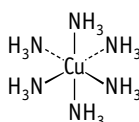
$$= 3.43 [1]$$

- (c) (i) To test for $-OH$: add PCl_5 or $SOCl_2$ [1]; steamy/white fumes of $HCl(g)$ [1] or add sodium metal [1] and test for hydrogen (squeaky pop with a lighted splint) [1].
- (ii) Aqueous sodium hydroxide/ aqueous potassium hydroxide or dilute hydrochloric acid. [1]
- (iii) Add sodium carbonate solution (or any soluble carbonate) [1]; carbon dioxide is evolved, which forms a white precipitate with limewater [1] or add magnesium ribbon and water; hydrogen is evolved [1] which makes a squeaky pop with a lighted splint [1].
- 110 (a) (i) $Cu = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ or $[Ar] 3d^{10} 4s^1$
 $Cu^+ = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ or $[Ar] 3d^{10} [1]$
- (ii) If it followed the sequence, copper would be $[Ar] 3d^9 4s^2 [1]$
- (iii) 3d shell is full so no electronic transitions are possible [1]; colours arise as a result of electronic transitions in 3d shell [1].

- (b) In aqueous solution:
 $2Cu^+ \rightarrow Cu^{2+} + Cu [1]$
 $E^\ominus = -0.15 + (+0.52) [1]$
 $= +0.37 \text{ V} [1]$
 Cu^+ disproportionates [1]; i.e. it is simultaneously oxidised to Cu^{2+} and reduced to $Cu(s)$ [1]. A blue solution of $CuSO_4$ [1] and a brown precipitate of Cu [1] would be observed.

- (c) A blue precipitate of $Cu(OH)_2$ would be first observed. [1] This is precipitation reaction. [1]
 $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow [Cu(OH)_2(H_2O)_4] + 2H_2O [1]$
As excess ammonia is added, the precipitate dissolves to form a deep blue solution. [1] This contains $[Cu(H_2O)_2(NH_3)_4]^{2+}$. [1] This is a ligand-exchange or substitution reaction. [1]

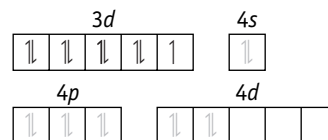
- (d) (i)



Octahedral – must be drawn in 3D [1]. Copper has six pairs of

bonding electrons, which position themselves as far apart as possible [1] giving an octahedron.

- (ii)



- (e) Transition metals have successive ionisation energies quite close in value, so several oxidation states are stable. However, copper(III) is unlikely to form as the ionisation energy would be too large [1] to be offset by an increase in hydration or lattice energy [1].

Copper(III) compounds would be:

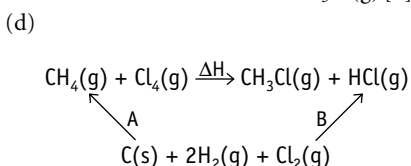
- strong oxidising agents (reduced to copper(II))
- coloured in solution
- acidic in solution owing to the polarising power of the small, highly charged ion.

(any 2 for [2])

- 111 (a) (i) Step I
Bonds broken: $+435 \text{ kJ mol}^{-1}$ (C—H)
Bonds made: -432 kJ mol^{-1} (H—Cl)
 $\Delta H = +3 \text{ kJ mol}^{-1} [1]$
- Step II
Bonds broken: $+435 \text{ kJ mol}^{-1}$ (C—H)
Bonds made: -346 kJ mol^{-1} (C—Cl)
 $\Delta H = +89 \text{ kJ mol}^{-1} [1]$
Step I is more likely [1] as it is less endothermic [1].
- (ii) Step I: C_2H_6 (from $\dot{C}H_3 + \dot{C}H_3$) [1]
Step II: H_2 [1]
- (b) (i) A Bronsted-Lowry acid is a proton donor. [1]
- (ii) HF is the weakest acid because the H—F bond is stronger than H—Cl, H—Br, H—I [1]; hydrogen bonding occurs between H—F molecules [1].
- (c) (i) $BCl_3 + 3H_2O \rightarrow B(OH)_3 + 3HCl [2]$
- (ii) Boron only has six valence electrons. [1] It can easily accept lone pairs from the water

molecules [1] as it is electrophilic [1].

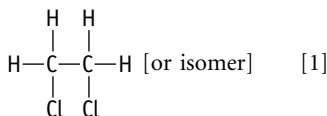
- 112 (a) A reaction, initiated by light or UV radiation [1], in which one atom or group is replaced by another [1].
- (b) (i) $\text{Cl}_2 \rightarrow \text{Cl}^\cdot + \text{Cl}^\cdot$ [1]
 (ii) $\text{CH}_4 + \text{Cl}^\cdot \rightarrow \text{CH}_3^\cdot + \text{HCl}$ [1]
 $\text{CH}_3^\cdot + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}^\cdot$ [1]
 (iii) $\text{Cl}^\cdot + \text{Cl}^\cdot \rightarrow \text{Cl}_2$
 $\text{CH}_3^\cdot + \text{Cl}^\cdot \rightarrow \text{CH}_3\text{Cl}$
 $\text{CH}_3^\cdot + \text{CH}_3^\cdot \rightarrow \text{C}_2\text{H}_6$
 (any 1 for [1])
- (c) $\Delta H_f^\ominus(\text{CH}_3\text{Cl})$ is the enthalpy change when 1 mole of CH_3Cl [1] is formed from its elements [1] in their standard states [1].
 $\text{C(s)} + 1\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl(g)}$ [1]



$$\begin{aligned} \Delta\text{H} &= \text{B} - \text{A} \\ &= \Delta H_f^\ominus(\text{CH}_3\text{Cl}) + \Delta H_f^\ominus(\text{HCl}) \\ &\quad - \Delta H_f^\ominus(\text{CH}_4) \\ &= -82 - 72 - (-75) \\ &= -79 \text{ kJ mol}^{-1} [3] \end{aligned}$$

(minus [1] for each error)

- (e) (i) C : H : Cl
 Mass ratio = 24.2 : 4.1 : 71.7
 Mol ratio = $\frac{24.2}{12} : \frac{4.1}{1} : \frac{71.7}{35.5}$
 $= 2.02 : 4.1 : 2.02$
 $= 1 : 2 : 1$
 Empirical formula = CH_2Cl
 ([3], minus [1] for each error)
- (ii) Empirical formula mass = 49.5;
 $M_r = 98$
 So molecular formula = $\text{C}_2\text{H}_4\text{Cl}_2$
 Structural formula:

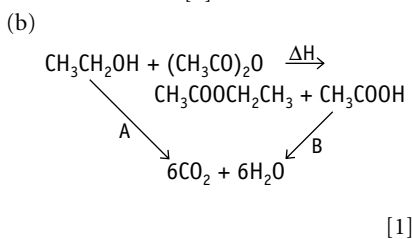


- (iii) Higher peaks are due to isotopes. [1]
 100 could be due to presence of one ^{37}Cl atom instead of one ^{35}Cl , 102 could be due to presence of two ^{37}Cl atoms [1]. (other isotopes, ^{13}C and ^2H , are also possible)

Peaks will be smaller because the isotopes are less abundant.

113 (a) (i)
$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{OH}][\text{CH}_3\text{COOH}]} \quad [1]$$

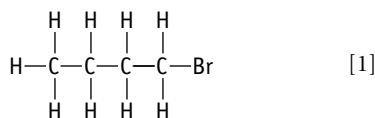
- (ii) If there are x moles of ethanoic acid at equilibrium, we can say
 $[\text{CH}_3\text{COOH}] = x/V$
 (V = total volume)
 $[\text{CH}_3\text{CH}_2\text{OH}] = x/V$
 $[\text{CH}_3\text{COOCH}_2\text{CH}_3] = 2x/V$
 $[\text{H}_2\text{O}] = 2x/V [1]$
 So $K_c = \frac{2x \times 2x}{x \times x}$ (V cancels out)
 $= 4 [1]$



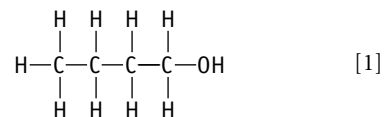
$$\begin{aligned} \Delta\text{H} &= \text{A} - \text{B} \\ &= \Delta H_c(\text{CH}_3\text{CH}_2\text{OH}) \\ &\quad + \Delta H_c(\text{CH}_3\text{CO})_2\text{O} \\ &\quad - \Delta H_c(\text{CH}_3\text{COOCH}_2\text{CH}_3) \\ &\quad - \Delta H_c(\text{CH}_3\text{COOH}) [1] \\ &= -1367 - 1794 - (-2238) \\ &\quad - (-874.1) \\ &= -48.9 \text{ kJ mol}^{-1} [1] \end{aligned}$$

- (c) (i) Renewable energy source; production of ethanol consumes same amount of CO_2 as its combustion produces, so no net CO_2 release; saves Brazil importing oil; creates agricultural employment (any 1 for [1])
- (ii) Energy produced by 1 g
 $= \Delta H_c^\ominus / M_r$
 Octane: $\frac{-5470}{114.23}$
 $= -47.89 \text{ kJ g}^{-1} [1]$
 Ethanol:
 $\frac{-1367}{46.07} = -29.67 \text{ kJ g}^{-1} [1]$
- (iii) By the catalytic hydration of ethene. [1]

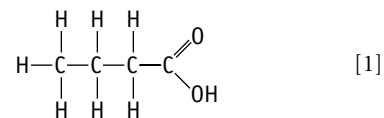
114 (a) A:



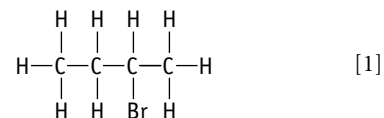
B:



C:

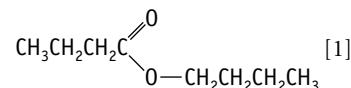


D:



- (b) Add bromine water. [1] If $\text{C}=\text{C}$ is present, it loses its colour. [1] (or alkaline manganate(VII) goes green)
- (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{NaHCO}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COONa} + \text{H}_2\text{O} + \text{CO}_2$ [1]

(d)



- (e) Potassium dichromate with dilute sulphuric acid [1] (or potassium manganate(VII) with dilute sulphuric acid.) Heat under reflux. [1]
- (f) (i) $\text{H}_2\text{O} + \text{HA} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$

$$\begin{aligned} K_a &= \frac{[\text{H}_3\text{O}^+] \times [\text{A}^-]}{[\text{HA}]} \\ &= [\text{H}_3\text{O}^+]^2 / [\text{HA}] [1] \\ [\text{H}_3\text{O}^+] &= \sqrt{(K_a \times [\text{HA}])} \\ &= \sqrt{(1.51 \times 10^{-5} \times 0.1)} \\ &= 1.23 \times 10^{-3} \text{ mol dm}^{-3} [1] \\ \text{pH} &= -\lg(1.23 \times 10^{-3}) [1] \\ &= 2.91 [1] \end{aligned}$$

(ii) Buffer solution. [1]

(iii)
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Number of moles of salt
 $= \frac{5.5}{110}$
 $= 0.05 [1]$
 Concentration of the salt
 $= \frac{0.05}{0.5}$
 $= 0.1 \text{ mol dm}^{-3} [1]$

$$[\text{H}_3\text{O}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]}$$

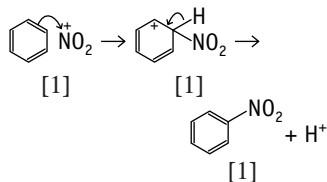
$$= \frac{1.51 \times 10^{-5} \times 0.1}{0.1} [1]$$

$$\text{pH} = -\lg(1.51 \times 10^{-5})$$

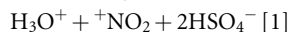
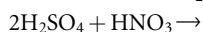
$$= 4.82 [1]$$

- 115 (a) (i) Concentrated sulphuric acid, concentrated nitric acid [1]; heat (70 °C) [1]

(ii)



Formation of $^+\text{NO}_2$:



- (iii) Concentrated hydrochloric acid and tin [1] followed by sodium hydroxide to release the amine [1]; heat [1].

(b) (i) A:



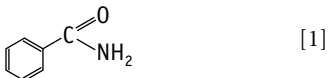
B:



C:



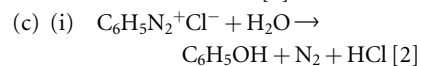
D:



- (ii) Step 3 is a Hoffmann degradation. Bromine and dilute potassium hydroxide [1] followed by concentrated

potassium or sodium hydroxide [1]; warm [1].

- (iii) There are fewer steps, so the yield would be better. [1]



- (ii) From the graph it can be shown that the reaction has a constant half-life. [1]

e.g. $V_\infty - V_t$ halves from 200 cm^3 to 100 cm^3 in 300 s [1]; from 150 cm^3 to 75 cm^3 in 300 s [1].

Therefore, reaction must be first order with respect to benzenediazonium chloride. [1]

- (iii) Not necessarily.

The other reagent is water [1] which may or may not contribute to the overall order of reaction. [1]