Suggested Solutions for H2 Chemistry Prelim Paper 3

1 **(a)** **(i)** $S(g) \rightarrow S^{+}(g) + e^{-}$ [1]

(ii) Less energy is required to remove the higher energy 3p electron from A*l* compared to the 3s electron from Mg. [1]

(b) **(i)** $CuCO_3 \rightarrow CuO + CO_2$ [1]

(ii) Ionic radius of Ca^{2+} = 0.099 nm

Ionic radius of Cu^{2+} = 0.073 nm

Decomposition temperature of $CuCO_3$ is expected to be lower.

Charge density of Cu^{2+} is greater than Ca^{2+} due to the smaller ionic radius of Cu^{2+}. Cu^{2+} ion is able to polarise (the electron cloud of) CO_3^{2-} ion to a larger extent, hence weakening the C`O bond to a larger extent. [2]

(c) **(i)** $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

pH = 13 [1]

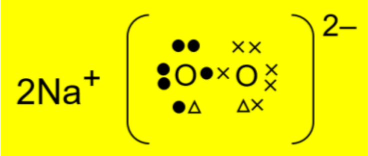
(ii) $SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$

pH = 2 [1]

(d) **(i)** Na(s) is an electrical conductor due to the presence of delocalised valence electrons which can migrate freely through the metallic structure when a potential difference is applied.

$Na_2O(s)$ does not conduct electricity because its ions are held in fixed positions in a giant lattice structure / it has no mobile ions. [2]

(ii)



[1]

(iii) Na_2O_2 has a giant ionic lattice structure while H_2O_2 has a simple molecular/ covalent structure.

More energy is needed to overcome the stronger electrostatic forces of attraction between Na^{+} and O_2^{2-} compared to the hydrogen bonds between H_2O_2 molecules.

Hence, Na_2O_2 has a higher melting point than H_2O_2 and is a solid at room temperature. [2]

(e) **(i)** $$K_c = \frac{[Pb^{2+}][Cr^{2+}]^2}{[Cr^{3+}]^2}$$ [1]

(ii) Equilibrium $[Pb^{2+}(aq)]$ = ½(2.96 × 10^{-4}) [2]

$$= 1.48 \times 10^{-4} \text{ mol dm}^{-3}$$

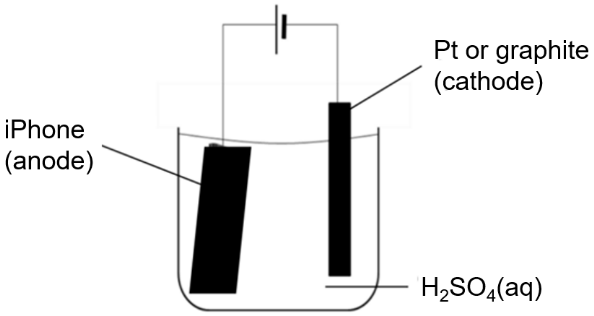
$$K_c = \frac{(1.48 \times 10^{-4})(2.96 \times 10^{-4})^2}{(0.200)^2}$$

$$= 3.24 \times 10^{-10} \text{ mol dm}^{-3}$$

(iii) The <u>concentration of all aqueous species/ ions will be lowered</u>. Since there are <u>more aqueous species/ ions on the right</u> of the equation, the <u>position of equilibrium shifts right</u>. [2]

[Total: 17]

2 **(a)** **(i)**



[2]

(ii) $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

$2Al(s) + 3/2O_2(g) \rightarrow Al_2O_3(s)$ [2]

(iii) Volume of Al_2O_3 = 96.2 × 0.03

= 2.886 cm^3

Mass of Al_2O_3 = 3.95 × 2.886

= 11.40 g

Amount of $Al_2O_3 = \frac{11.40}{2(27.0)+3(16.0)}$

= 0.1118 mol

Amount of $O_2 = 0.1118 \times \frac{3}{2}$

= 0.1677 mol

Amount of electrons passed = 0.1677 × 4

= 0.6708 mol

Q = nF = It

0.6708 × 96500 = 2.0 × t

t = 3.24×10^4 s [3]

(b) Step 1: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$ [2]

Step 2: $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$

(c) **(i)** $BaSO_4$ [1]

(ii) Upon reaction with Br_2, the oxidation state of sulfur increases from +2 in $S_2O_3^{2-}$ to +6 in SO_4^{2-}.

Upon reaction with I_2, the oxidation state of sulfur increases from +2 in $S_2O_3^{2-}$ to +2.5 in $S_4O_6^{2-}$.

Therefore, Br_2 is a stronger oxidising agent than I_2. [2]

(d) **P** does not rotate plane-polarised light.

⇒ **P** does not contain a chiral carbon.

P is insoluble in both HC*l*(aq) and NaOH(aq)/ **P** does not undergo acid-base reaction.

⇒ **P** is neutral.

P undergoes alkaline hydrolysis with hot NaOH(aq).

⇒ **P** contains ester and nitrile groups.

1 mole of **R** undergoes acid-base reaction with 1 mole of Na_2CO_3(aq).

⇒ **R** contains 2 –COOH groups.

Q undergoes oxidation to give HCOOH and a pale yellow precipitate, CHI_3.

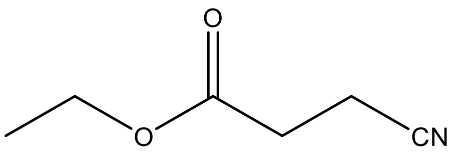
⇒ **Q** contains a $–CH(OH)CH_3$ or $–COCH_3$ group.

P undergoes reduction with LiA*l*H_4 to form **Q** and **S**.

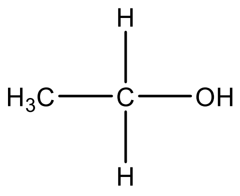
⇒ Both **Q** and **S** contain a primary –OH group.

⇒ **S** contains a $–CH_2NH_2$/ primary amine group.

P

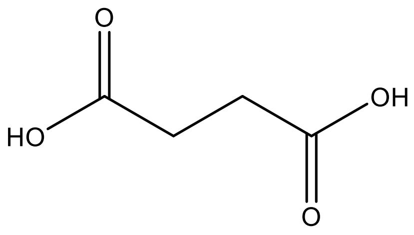


Q

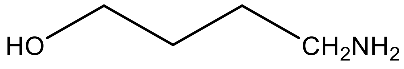


$H_3C-\underset{H}{\overset{H}{C}}-OH$

R



S



[8]

[Total: 20]

3 **(a)** **(i)** Primary amine, primary alcohol [1]

(ii) To act as a Lewis base, the <u>lone pair of electrons on N</u> of TRIS is <u>donated into the vacant orbital</u> of <u>H^+/ proton</u> from hydrochloric acid, resulting in the formation of a <u>dative bond</u> between N of TRIS and H^+. [2]

(b) **(i)** Initial [TRIS] = $\frac{121.14}{12.0\times4+14.0+(16.0\times3)+11.0}$ = 1.001 mol dm^{-3}

$K_b = \frac{10^{-14}}{8.32\times10^{-9}} = 1.202\times10^{-6}$ mol dm^{-3}

$$= \frac{[TRISH^+][OH^-]}{[TRIS]} = \frac{x^2}{1.001-x}$$

Assuming x is very small,

$[OH^-] = x = \sqrt{(1.202\times10^{-6})(1.001)} = 1.097\times10^{-3}$ mol dm^{-3}

pOH = $-\lg(1.097\times10^{-3}) = 2.96$

pH = 14 – pOH = 11.0 [3]

(ii) $7.5 = -\lg(8.32\times10^{-9}) + \lg(\frac{[TRIS]}{[TRISH^+]})$

$\lg(\frac{[TRIS]}{[TRISH^+]}) = -0.580$

$\frac{[TRIS]}{[TRISH^+]} = 10^{-0.580} = 0.263$

Or

$K_a = 8.32\times10^{-9} = \frac{[TRIS](10^{-7.5})}{[TRISH^+]}$

Or

$K_b = 1.202\times10^{-6} = \frac{[TRISH^+](10^{6.5})}{[TRIS]}$ [1]

(iii) $\frac{[TRIS]}{[TRISH^+]} = 0.263 = \frac{1.001-x}{x}$

$[TRISH^+] = x = 0.7926$ mol dm^{-3}

Amount of HC*l* required = amount of $TRISH^+$ in 1 dm^3

Volume of HC*l* required = 0.7926/11.0 = 0.0721 dm^3

[2]

Or

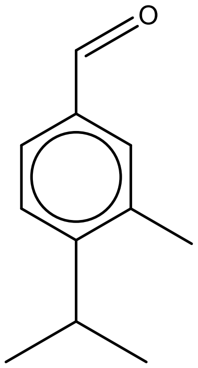
Alternative for finding [TRISH$^+$]:

$$\frac{[\text{TRIS}]}{[\text{TRISH}^+]} = \frac{0.263}{1}$$

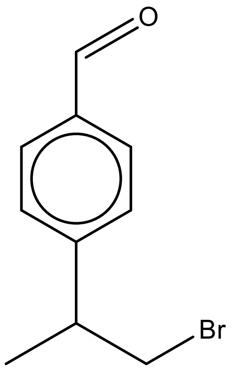
$$\begin{array}{lccccc} & \text{TRIS} & + & \text{H}^+ & \rightarrow & \text{TRISH}^+ \\ \text{Eqm [ ]} & \frac{0.263}{1.263}\times 1.001 & & & & \frac{1}{1.263}\times 1.001 \end{array}$$

$$[\text{TRISH}^+] = \frac{1}{1.263}\times 1.001 = 0.7926 \text{ mol dm}^{-3}$$

(c) **(i)**



A



B

[2]

(ii) Formation of cream ppt of AgBr shows that compound **B** undergoes nucleophilic substitution with NaOH(aq) to release bromide ion for precipitation by $AgNO_3$.

Compound **B** is an alkyl bromide/ halide. [2]

(iii) Step 1: $CH_3CHClCH_3$, anhydrous $AlCl_3$

Step 2: acidified $K_2Cr_2O_7$, heat with immediate distillation [2]

(iv) Warm with Tollens' reagent.

Silver mirror/ black/ grey ppt formed with cuminaldehyde but no silver mirror/ black/ grey ppt formed with compound **D**.

Or

I_2 in NaOH(aq), warm.

Pale yellow ppt formed with compound **D** but no ppt formed with cuminaldehyde.

Or

acidified/H_2SO_4(aq), $K_2Cr_2O_7$(aq), heat

Orange acidified $K_2Cr_2O_7$(aq) turned green with cuminaldehyde, but remained orange with **D**.

[2]

(d) **(i)** Transition metals have partially filled 3d orbitals.

In the presence of ligand field, the 3d orbitals are split into 2 sets of non-degenerate orbitals with small difference in energies.

Visible light of the electromagnetic spectrum is absorbed for the transfer of an electron from a lower energy d-orbital to an unfilled/ partially filled d orbital of higher energy.

The colour of complex observed corresponds to the complement of the absorbed colours. [3]

(ii) Complex is violet-red. Since yellow-green light is absorbed for d-d transition, the complementary colour violet-red will be observed. [1]

(iii) (**M^{4+}** $1s^2 2s^2 2p^6 3s^2 3p^6$)

M $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ [1]

(iv) Either of the following:

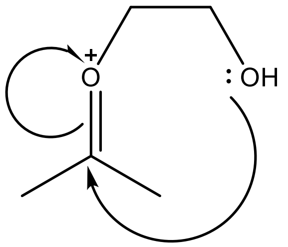
- In an octahedral ligand field of F^-, the energy gap between the non-degenerate 3d orbitals becomes very large.
- Radiation/ light absorbed for d-d transition is not from visible light range. [1]

[Total: 23]

4 **(a)** **(i)** The C`C bond in propanone is formed from the overlap between $sp^2$ and $sp^3$ hybridised carbons while the C`C bond in propane is formed from the overlap between sp^3 hybridised carbons.

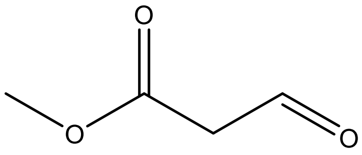
sp^2 hybridised orbitals have greater s character/ lower p character, are shorter/ smaller and closer to the nucleus, making the C`C bond shorter than expected. [2]

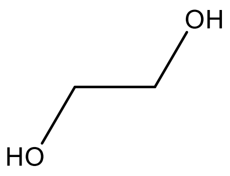
(ii)



[2]

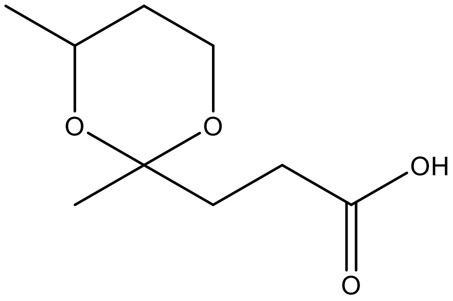
(iii)

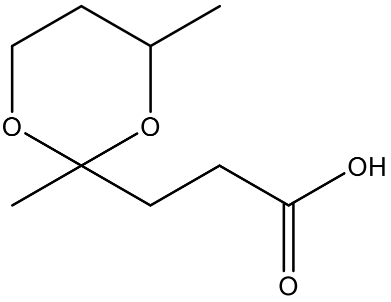




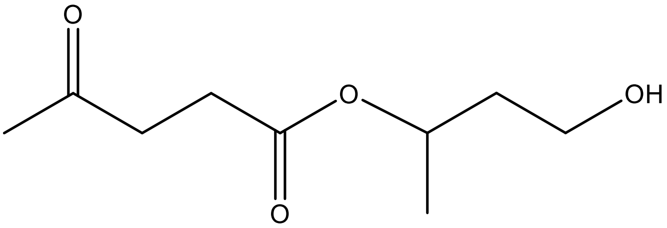
[2]

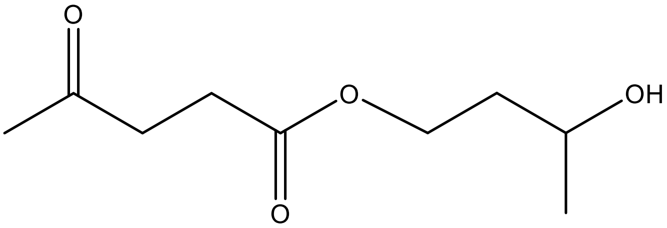
(iv) **S (one of the 2)**



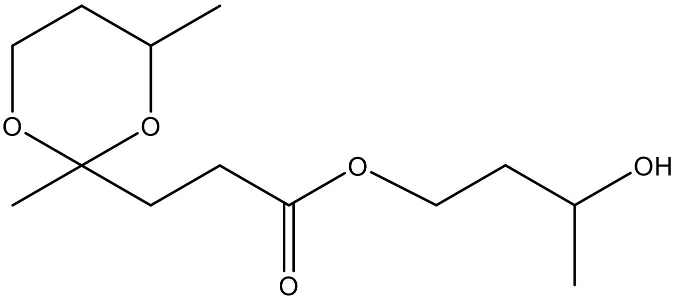


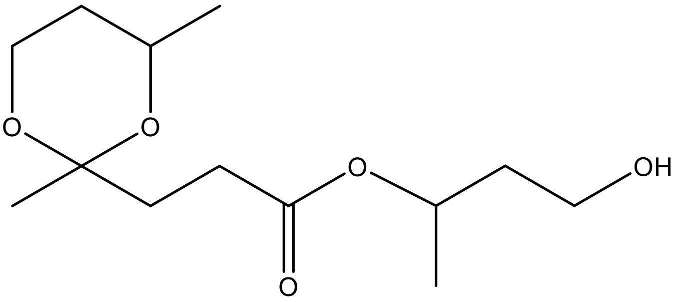
T (one of the 2)



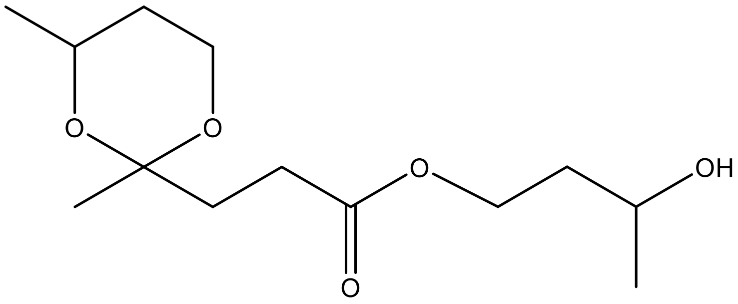


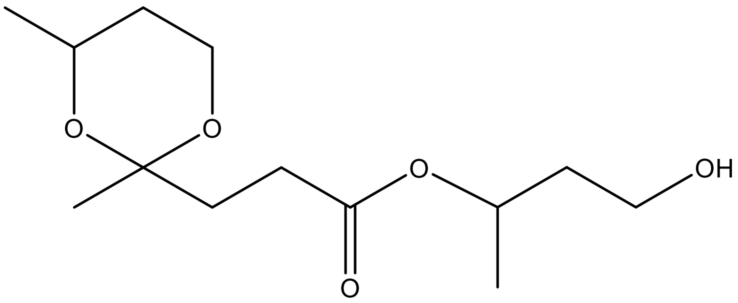
U (one of the 4)





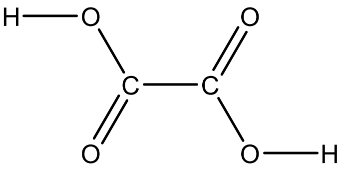
[3]



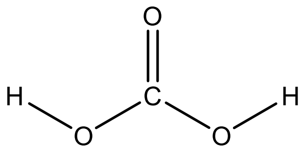


(b) **(i)** Cold alkaline $KMnO_4$ [1]

(ii)



or



[1]

(c) **(i)** $[CH_3COCH_3(aq)]$ <u>remains approximately constant throughout the experiment so rate of reaction is independent of $[CH_3COCH_3(aq)]$.</u>

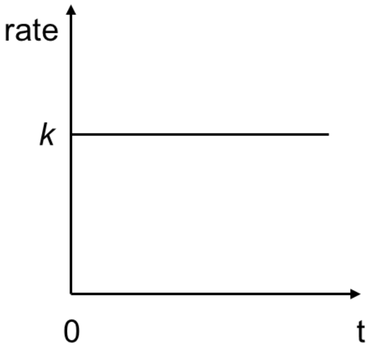
Thus experimental results can be used to determine the order of reaction with respect to I_2(aq) and H^+(aq). [1]

(ii) A <u>straight line/ linear</u> plot is obtained/ graph has a <u>constant (negative) gradient</u>.

Rate of reaction is constant regardless of the concentration of I_2.

Reaction is independent of $[I_2]$ and reaction is <u>zero order</u> with respect to I_2. [1]

(iii)



[1]

(iv) Rate of expt 1 = –gradient of expt 1 = $-\left(\frac{0.6-0.35}{0-300}\right)$ = 0.000833 s^{-1}

Rate of expt 2 = –gradient of expt 2 = $-\left(\frac{0.6-0.1}{0-300}\right)$ = 0.00166 s^{-1}

Since rate of reaction doubled when $[H^+]$ is doubled, reaction is first order with respect to H^+. [2]

(v) Let the rate equation be rate = $k[H^+][CH_3COCH_3]^n$

$$\frac{(\text{Rate})_3}{(\text{Rate})_4} = \frac{k[H^+]_3[CH_3COCH_3]_3^n}{k[H^+]_4[CH_3COCH_3]_4^n}$$

$$\frac{(2.45)}{(3.68)} = \frac{k(0.002)(0.001)^n}{k(0.001)(0.003)^n}$$

n = 1

Reaction is first order with respect to CH_3COCH_3. [1]

(vi)
1. Start the stopwatch when propanone solution, iodine solution and dilute sulfuric acid of known concentrations are mixed.
2. Monitor the change in absorbance/ concentration of the unreacted iodine throughout the reaction

   OR

   At regular time intervals, a known volume of the reaction mixture is pipetted out and quench before analysis.
3. Plot a graph of iodine concentration against time.
4. The initial rate of reaction can be determined by drawing a tangent to the curve at *t* = 0s, and subsequently calculating the gradient.
5. Substitute the initial concentrations of reactants and initial rate into rate = $k[H^+][CH_3COCH_3]$ and calculate *k*.

Alternative for steps 3-5:

Plot $[I_2]$ vs time graph while making sure CH_3COCH_3 is in large excess and overall order of reaction is 1. Find half life from graph plotted and calculate *k*.

rate = $k'[H^+]$, where $k' = k[CH_3COCH_3]$

$k' = \ln 2 / t_{1/2}$

$k[CH_3COCH_3] = \ln 2 / t_{1/2}$ [3]

[Total: 20]

5 **(a)** **(i)** Bond energy is the average enthalpy change when one mole of covalent bonds between atoms in gaseous molecules is broken. [1]

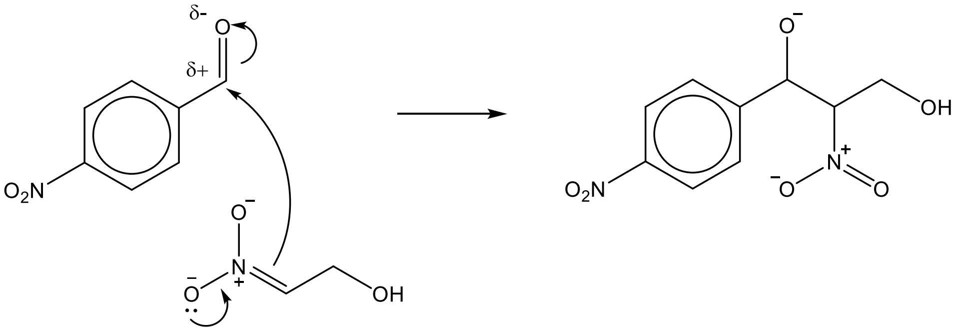
(ii) ΔH_r = ΣE(bonds broken) – ΣE(bonds formed)

= [E(C^O) + E(C\`H)] – [$E$(C\`C) + E(C\`O) + $E$(O\`H)]

= [(+740) + (+410)] – [(+350) + (+360) + (+460)]

= -20 kJ mol^{-1} [2]

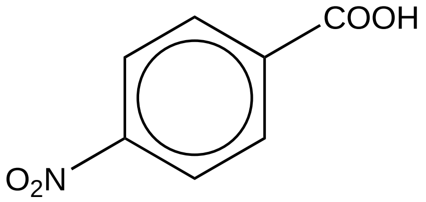
(b) **(i)**



[2]

(ii) Reduction [1]

(c) **(i)**



[1]

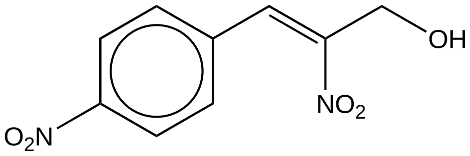
(ii) Step 1: conc. HNO_3, conc. H_2SO_4, maintained at 30 °C

Step 3: $SOCl_2$/ PCl_5/ PCl_3, (room temperature) [2]

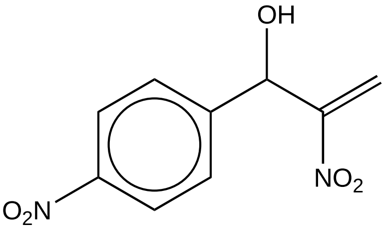
(d) **(i)** Excess concentrated H_2SO_4, heat

Or Al_2O_3, heat [1]

(ii)



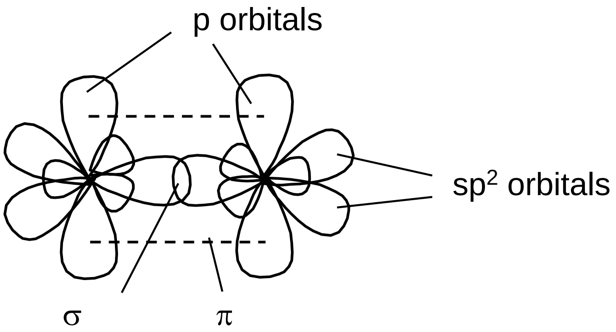
major



minor

The major product is more stable because it is the more substituted alkene (Saytzeff rule). [3]

(iii) The C atoms in alkenes are sp^2 hybridised. [2]



(e) **(i)** $K_{sp} = [Ag^+][NO_2^-]$ [1]

(ii) $$[AgNO_2] = \frac{0.155/153.9}{100/1000}$$
$$= 0.01007\ mol\ dm^{-3}$$

$K_{sp} = (0.01007)^2 = 1.01 \times 10^{-4}$ mol^2 dm^{-6} [2]

(f) **(i)** $E^\ominus_{cell} = +1.52 - (+0.42) = +1.10$ V [1]

(ii) $\Delta G^\ominus = -nFE^\ominus_{cell}$

$= -(10)(96500)(+1.10)$

$= -1.06 \times 10^6$ J mol^{-1} [1]

[Total: 20]