

2016 MJC Prelim P2 Suggested Answers

1 Planning (P)

- (a) Ionic product = $(2.50 \times 10^{-3}) (2.00 \times 10^{-3})^2 = \underline{1.00 \times 10^{-8} \text{ mol}^3 \text{ dm}^{-9}}$. *Show working to consider total volume is different.*

(b) Preparation of $0.01 \text{ mol dm}^{-3} \text{ Pb(NO}_3)_2$ standard solution (100 cm^3)

- 1) Weigh a clean, dry empty weighing bottle using a mass balance.
- 2) Weigh out approximately 0.331 g of solid $\text{Pb(NO}_3)_2$.
- 3) Transfer the solid into a clean 100 cm^3 beaker and reweigh the weighing bottle with the residue to determine the exact mass of $\text{Pb(NO}_3)_2$ used.
- 4) Dissolve the solid carefully with some deionised water and transfer it into a 100 cm^3 volumetric flask.
- 5) Top up the flask to the mark with deionised water, stopper and mix well to obtain a homogeneous solution.

Dilution of KI standard solution (100 cm^3)

- 1) Pipette 25.0 cm^3 of given $0.0400 \text{ mol dm}^{-3} \text{ PbI}_2$ solution into a 100 cm^3 volumetric flask.
- 2) Top of top the mark with deionised water, stopper and mix well.

Possible quantities and concentrations of solutions to be used (4 expt sets)

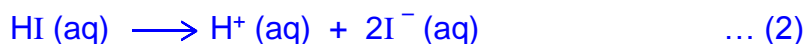
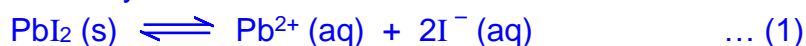
Expt	Vol. of Pb^{2+} / cm^3	Vol of I^- / cm^3	Vol of H_2O / cm^3	$[\text{Pb}^{2+}]_{(\text{mixture})}$ / mol dm^{-3}	$[\text{I}^-]_{(\text{mixture})}$ / mol dm^{-3}	Ionic product of PbI_2
5	2.50	2.00	5.50	0.00250	0.00200	$y_1: 1.00 \times 10^{-8}$
6	1.00	3.00	6.00	0.00100	0.00300	$y_2: 9.00 \times 10^{-9}$
7	2.00	2.00	6.00	0.00200	0.00200	8.00×10^{-9}
8	1.50	2.00	6.50	0.00150	0.00200	6.00×10^{-9}
9	1.00	1.00	8.00	0.00100	0.00100	1.00×10^{-9}

Experimental procedure

- 1) Fill three 50.00 cm^3 burettes with the prepared $0.0100 \text{ mol dm}^{-3} \text{ Pb(NO}_3)_2$ stock solution, $0.0100 \text{ mol dm}^{-3} \text{ KI}$ stock solution and deionised water respectively.
- 2) Run out 1.00 cm^3 of deionised water and 5.00 cm^3 of KI into a 100 cm^3 conical flask / beaker.
- 3) Run out 4.00 cm^3 of $\text{Pb(NO}_3)_2$ into the conical flask / beaker and swirl the flask well / stir with a glass rod.
- 4) Allow the flask / beaker to stand undisturbed for at least 30 min to attain equilibrium.

- 5) Note if any precipitate of yellow PbI_2 is present on standing.
- 6) Repeat the experiment using the various volumes shown in table (*Total volume = 10.00 cm³ / constant*).
- 7) Estimated $K_{\text{sp}} = \frac{y_1 + y_2}{2}$ where y_1 : *minimum ionic product with precipitation* and y_2 : *maximum ionic product without precipitation*.

(c) Solubility would decrease.



Due to presence of common ion (I^{-}), equilibrium position of (1) shifts left.

(d)

Salt	Solubility
PbCO_3	$s^2 = 7.4 \times 10^{-14}$ Solubility = $s = 2.72 \times 10^{-7} \text{ mol dm}^{-3}$
$\text{Pb}(\text{IO}_3)_2$	$4s^3 = 3.7 \times 10^{-13}$ Solubility = $s = 4.52 \times 10^{-5} \text{ mol dm}^{-3}$
$\text{Pb}_3(\text{PO}_4)_2$	$108s^5 = 7.9 \times 10^{-43}$ Solubility = $s = 1.49 \times 10^{-9} \text{ mol dm}^{-3}$

Most effective: PO_4^{3-}

2(ai) $[\text{OH}^{-}] = \sqrt{0.370 \times 5.6 \times 10^{-4}} = 0.01439 \text{ mol dm}^{-3}$
 $\text{pOH} = -\lg 0.01439 = 1.84$ hence $\text{pH} = \underline{12.2}$

(ii) No. of mole of ethylamine = $0.370 \times \frac{60}{1000} = 0.0222$

$$[\text{HC}] = \frac{0.0222}{\frac{20}{1000}} = 1.11 \text{ mol dm}^{-3}$$

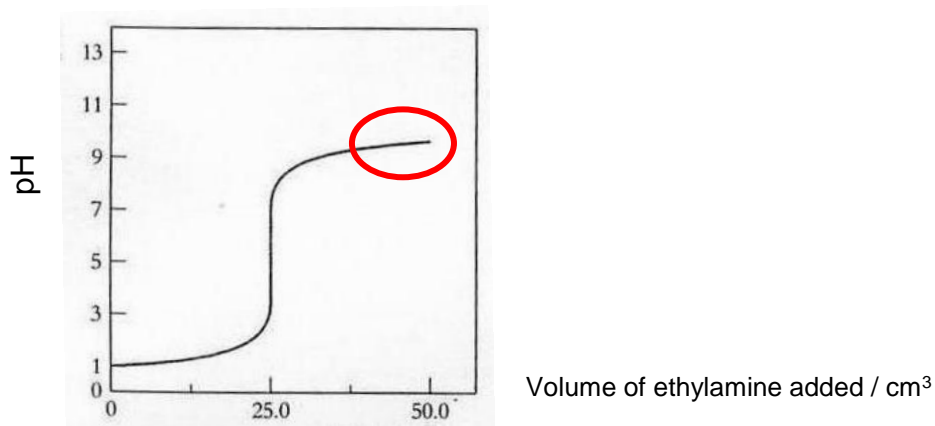
(iii) Heat absorbed by solution = $80 \times 4.18 \times 3.5 = 1170 \text{ J}$

$$\text{No. of moles of H}_2\text{O produced} = 0.370 \times \frac{60}{1000} = 0.0222$$

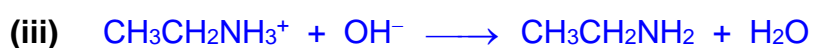
$$\text{Enthalpy change of neutralisation} = -\frac{1170}{0.0222} = \underline{-52.7 \text{ kJ mol}^{-1}}$$

(iv) Some energy evolved from the neutralisation process is used to further dissociate the weak base completely

(bii)



(bi) Methyl orange . Red to orange.

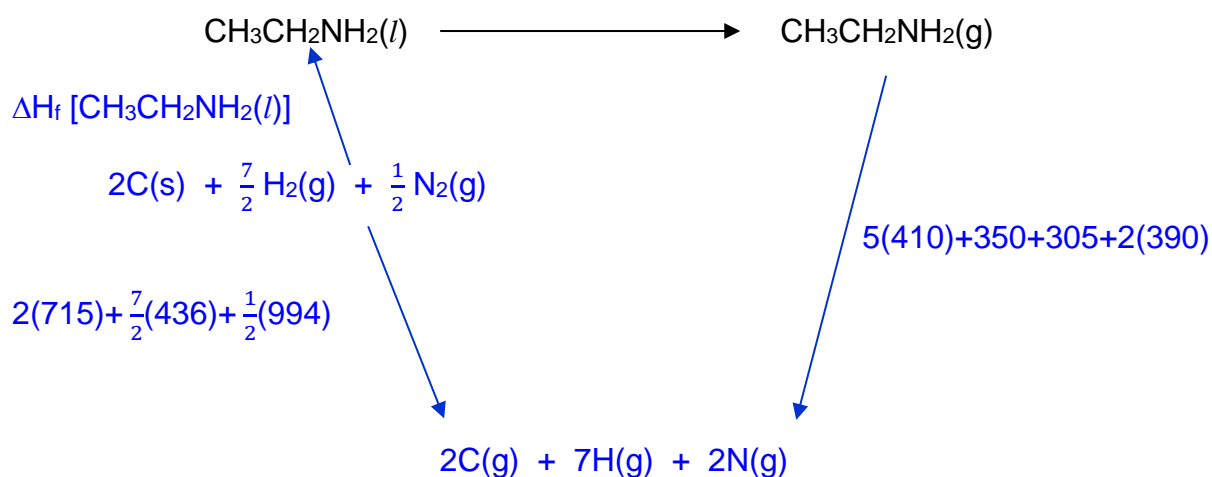


(ci)

Step	Type of reaction	Reagents and conditions
I	condensation	
II	reduction	LiAlH ₄ in dry ether

(ii) Add 2,4-DNPH to sample and heat. Synthesis is complete when no orange ppt is observed. *Accept other possible tests.*

(d)



$$\begin{aligned} \Delta H_f [\text{CH}_3\text{CH}_2\text{NH}_2(l)] + 29 + 3485 &= 3453 \\ \Delta H_f [\text{CH}_3\text{CH}_2\text{NH}_2(l)] &= \underline{-61.0 \text{ kJ mol}^{-1}} \end{aligned}$$

(ei) amide, amine

- (ii) Compound **Q** is more basic than Tamiflu. The electron-donating R group increases the electron density of the lone pair on N atom hence more available to accept a proton. Compound **R** is less basic. The lone pair of electron on N atom is delocalised into the benzene ring hence less available to accept a proton.



- (ii) $E^\ominus = +0.54 \text{ V}$ and $E^\ominus = +1.07 \text{ V}$. As $E^\ominus_{\text{Br}_2/\text{Br}^-}$ is more positive than $E^\ominus_{\text{I}_2/\text{I}^-}$, Br^- is a weaker reducing agent than I^- .

- (iii) Conc. H_3PO_4 is a weaker oxidising agent than conc. H_2SO_4
 $\text{KBr (s)} + \text{H}_3\text{PO}_4 (\text{l}) \longrightarrow \text{HBr (g)} + \text{KH}_2\text{PO}_4 (\text{s})$

- (bi) KCl : ppt dissolves
 KBr : ppt dissolves
 KI : ppt does not dissolve

- (ii) NH_3 ligand combines with $\text{Ag}^+(\text{aq})$ to form diamminesilver(I) complex or $[\text{Ag}(\text{NH}_3)_2]^+$. Ionic product (of $[\text{Ag}^+][\text{I}^-]$ easily) exceed the low K_{sp} value hence thus AgI does not dissolve.

- (c) Number of mole of iodine in 25.0cm^3 aliquot = $\frac{1}{2} \times (0.0400 \times 0.010)$

$$\text{Number of mole of iodine in } 250 \text{ cm}^3 = 2.00 \times 10^{-3}$$

$$\frac{n_{\text{I}_2}}{n_{\text{BrO}_4^{n-}}} = \frac{2 \times 10^{-3}}{5 \times 10^{-4}} = 4$$



$$+7 + 4(-2) = n(-1)$$

$$\underline{n = 1}$$

- (di) $\text{MgCl}_2 (\text{s}) + 6\text{H}_2\text{O} (\text{l}) \longrightarrow [\text{Mg}(\text{H}_2\text{O})_6]^{2+} (\text{aq}) + 2\text{Cl}^- (\text{aq})$
 $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} (\text{aq}) \rightleftharpoons [\text{Mg}(\text{H}_2\text{O})_5(\text{OH})]^+ (\text{aq}) + \text{H}^+ (\text{aq}) \text{ pH} = 6.5$



- (ii) $\text{ZnO} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2\text{O}$
 $\text{ZnO} + 2\text{NaOH} + \text{H}_2\text{O} \longrightarrow \text{Na}_2\text{Zn(OH)}_4$

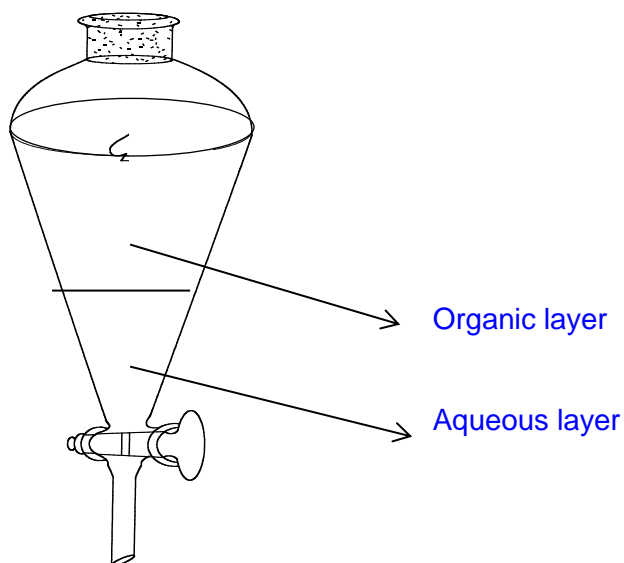
4(ai) Prevent the moisture from reacting with the sodium metal.

(ii) No. of moles of phenol = $(11.8 / 94) = 0.1255$ (same as phenoxide)

No. of moles of 1-bromo-3-methylbutane = $(20.0 \times 1.21) / 151$

Mass of (3-methylbutoxy)benzene = $0.1255 \times 164 = \underline{20.6 \text{ g}}$

(iii)

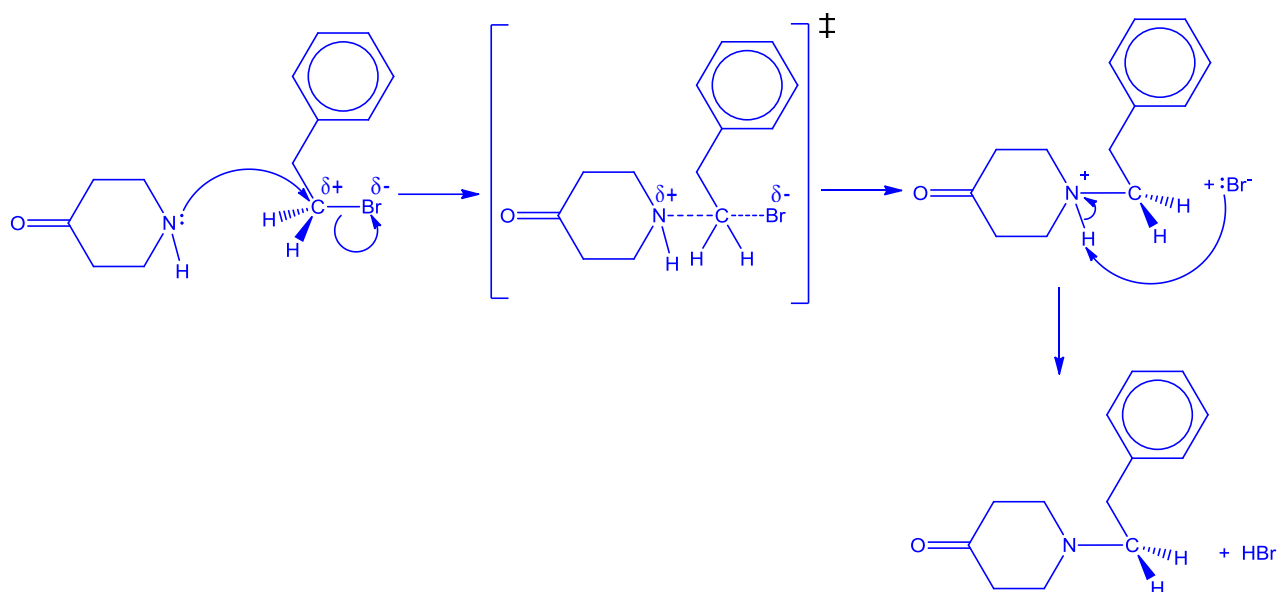


(bi) **1** (unreacted) phenol ; **2** water

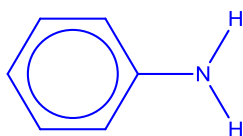
(ii) (3-methylbutoxy)benzene has a higher boiling point. The extensive van der Waals' forces of attraction between (3-methylbutoxy)benzene molecules is stronger than the hydrogen bonding in ethanol.

(iii) Boiling point of the (3-methylbutoxy)benzene is significantly higher than the other impurities. Temperature range is from 214°C - 218°C .

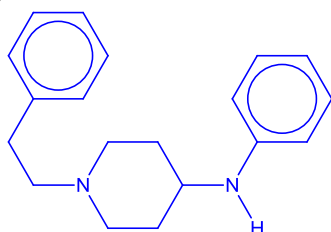
5(a) S_N2



(b)



(c)



(d) Carboxylic acid will undergo acid-base reaction with the amine groups instead.

(e) Add aqueous neutral iron (III) chloride. For morphine, a violet complex observed but not for fentanyl. *Accept other tests.*

6(ai) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

(ii) $E^\ominus_{\text{cell}} = 0.52 - 0.15 = +0.37 > 0$. Hence, Cu^+ disproportionates into pink solid Cu and blue solution of Cu^{2+} .

(iii) The stronger $\text{CH}_3\text{CH}_2\text{NH}_2$ ligands replace H_2O ligands to form a deep blue complex $[\text{Cu}(\text{CH}_3\text{CH}_2\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+}$.



(iv)

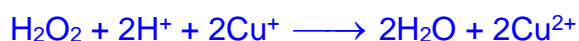
	Cu	C	H	O
% by mass	17.76	26.85	1.68	53.71
No. of moles	$\frac{17.76}{63.5}$	$\frac{26.85}{12.0}$	$\frac{1.68}{1.0}$	$\frac{53.71}{16.0}$
Simplest ratio	1	8	6	12

Chemical formula of anion is $[\text{Cu}(\text{C}_4\text{H}_3\text{O}_6)_2]^{4-}$

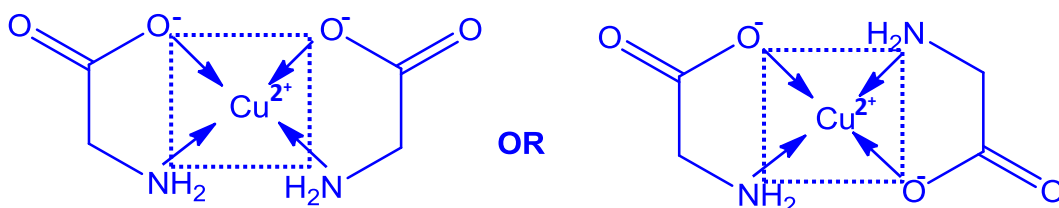
(b) $E^\ominus_{\text{cell}} = 0.15 - (-0.97) = +1.12 \text{ V} > 0$ hence reaction is feasible.



$E^\ominus_{\text{cell}} = 1.77 - 0.15 = +1.62 \text{ V} > 0$ hence reaction is feasible.



(ci)



(ii) Cis-trans isomerism