AUSTRALIAN
SCIENCE
OLYMPIADS

CHEMISTRY

2004 NATIONAL QUALIFYING EXAMINATION

SOLUTIONS GUIDE

Answers are a guide only and do not represent a preferred method of solving problems.

Section A

1B, 2C, 3A, 4A, 5E, 6D, 7D, 8E, 9B, 10D, 11C, 12E, 13B, 14A, 15C

Section B

Q16

(a) (i) $C_6H_{12}O_6 + 6O_2 \longrightarrow 6H_2O + 6CO_2$ **eqn ①**

Oxidant is oxygen

The reductant is the carbohydrate.

(ii) $C_{16}H_{32}O_2 + 23O_2 \longrightarrow 16CO_2 + 16H_2O$ **eqn ②**

(b)

Oxidation: $Mn^{2+} + 3OH^- \longrightarrow Mn(OH)_3 + e^-$

Reduction: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Balanced: $4Mn^{2+} + O_2 + 8OH^- + 2H_2O \longrightarrow 4Mn(OH)_3$ **eqn ③**

+II 0 -II +I +I -II +III -II +I

(c) (i)

Oxidation: $2I^- \longrightarrow I_2 + 2e^-$

Reduction: $Mn^{3+} + e^- \longrightarrow Mn^{2+}$

Balanced: $2Mn^{3+} + 2I^- \longrightarrow I_2 + 2Mn^{2+}$ **eqn ④**

(ii) Iodine causes the brown colour.

(d)

Oxidation: $I_2 + 6H_2O \longrightarrow 2IO_3^- + 12H^+ + 10e^-$

Reduction: $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$

Balanced: $I_2 + 5H_2O_2 \longrightarrow 2IO_3^- + 2H^+ + 4H_2O$ **eqn ⑤**

0 +I -I +V -II +I +I -II

(e) (i) Disproportionation of hydrogen peroxide:

Oxidation: $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$

Reduction: $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$

Balanced: $2H_2O_2 \longrightarrow 2H_2O + O_2$ **eqn ⑥**

(ii) Coproportionation of iodine;

Oxidation: $2I^- \longrightarrow I_2 + 2e^-$

Reduction: $2IO_3^- + 12H^+ + 10e^- \longrightarrow I_2 + 6H_2O$

Balanced: $5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ **eqn ⑦**

(iii) Amplification factor of 6 for I_2

Looking at the stoichiometry and eqns 4, 5 and 7 we see

$2I^- \underset{④}{\rightarrow} I_2 \underset{⑤}{\rightarrow} 2IO_3^- \underset{⑦}{\rightarrow} 6I_2$

Thus we have six times as much I_2 here than in (c).

(f) (i) Standardisation with dichromate:

Oxidation: $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$

Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

Balanced: $6S_2O_3^{2-} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 3S_4O_6^{2-} + 2Cr^{3+} + 7H_2O$ **eqn ⑧**

(ii)

$$MW(K_2Cr_2O_7) = (2 \times 39.10) + (2 \times 104.00) + (7 \times 112.00) = 294.20$$

$$n_{(K_2Cr_2O_7)} = \tfrac{5}{294.20} \text{ mol} = 0.01699 \text{ mol}$$

$$\text{so } [K_2Cr_2O_7] = \tfrac{5}{294.20} \times \tfrac{1000}{500} \text{ M} = 0.03399 \text{ M}$$

$$n_{(K_2Cr_2O_7)} \text{ in 25 mL aliquot} = \tfrac{5}{294.20} \times \tfrac{1000}{500} \times \tfrac{25}{1000} = 0.0008497\text{mol}$$

$$\text{so } [K_2Cr_2O_7] \text{ (new solution)} = \tfrac{5}{294.20} \times \tfrac{1000}{500} \times \tfrac{25}{1000} \times \tfrac{1000}{250} = 0.003399 \text{ M}$$

$n_{(K_2Cr_2O_7)}$ in 20 mL aliquot $= \frac{5}{294.20} \times \frac{1000}{500} \times \frac{25}{1000} \times \frac{1000}{250} \times \frac{20}{1000}$ $= 0.00006798$ mol

From balanced **eqn** ⑥ mol $S_2O_3^{2-} = 1$ mol $Cr_2O_7^{2-}$

so $n_{(S_2O_3^{2-})}$ in aliquot $= 6 \times \frac{5}{294.20} \times \frac{1000}{500} \times \frac{25}{1000} \times \frac{1000}{250} \times \frac{20}{1000}$ $= 0.0004079$ mol

$$\text{thus } \left[S_2O_3^{2-}\right] = 6 \times \frac{5}{294.20} \times \frac{1000}{500} \times \frac{25}{1000} \times \frac{1000}{250} \times \frac{20}{1000} \times \frac{1000}{16.75}$$

$$= 0.02435 \text{ M}$$

(g) Iodometric titration with thiosulfate

Oxidation: $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$

Reduction: $I_2 + 2e^- \longrightarrow 2I^-$

Balanced: $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$ **eqn ⑨**

(h) $n_{(S_2O_3^{2-})}$ in titre $= 0.02435 \times \frac{23.69}{1000}$

$= 5.769 \times 10^{-4}$ mol

now $Mn(OH)_3 + 3H^+ \longrightarrow Mn^{3+} + 3H_2O$ **eqn ⑩**

Using stoichiometry and eqns 3, 10, 4, 5, 7, and 9 we have

$$O_2 \rightarrow 4Mn(OH)_3 \rightarrow 4Mn^{3+} \rightarrow 2I_2 \rightarrow 4IO_3^- \rightarrow 12I_2 \rightarrow 24S_2O_3^{2-}$$

③ ⑩ ④ ⑤ ⑦ ⑨

which gives us $n_{(O_2)} = 24n_{(S_2O_3^{2-})}$

so $n_{(O_2)}$ inaliquot (250mL) $= \frac{1}{24} \times 0.02435 \times \frac{23.69}{1000}$ mol

so mass of O_2/L $= \frac{1}{24} \times 0.02435 \times \frac{23.69}{1000} \times (2 \times 16.00) \times 4 \times 1000$ mg L^{-1}

= 3.076 ppm

(i) No.

(j) Vaporisation of iodine out of solution, so oxygen content appears to be lower than expected.

Note: dissolution of oxygen from the atmosphere into the titration mixture will give a higher reading than expected. You were specifically asked for the reason of a lower reading.

Q17

(a) $NH_3\,(g) + HNO_3\,(aq) \longrightarrow NH_4NO_3\,(l)$

(b) $2\,NH_4NO_3\,(s) \longrightarrow 2N_2\,(g) + O_2\,(g) + 4H_2O\,(g)$

(c) $NH_4NO_3\,(s) \longrightarrow N_2O\,(g) + 2H_2O\,(g)$

(d) $4NH_3 + 5O_2\,(g) \longrightarrow 4NO\,(g) + 6H_2O\,(g)$

(e) Nitrogen and water. $4NH_3\,(g) + 3O_2\,(g) \longrightarrow 2N_2\,(g) + 6H_2O\,(g)$

(f) $N_2\,(g) + 2O_2\,(g) \longrightarrow 2NO_2\,(g)$

(g) The equilibrium $2\,NO\,(g) \rightleftharpoons N_2O_2\,(g)$ is exothermic, hence increasing the temperature shifts the equilibrium to the left lowering the $[N_2O_2]$ available to react with O_2 to form NO_2.

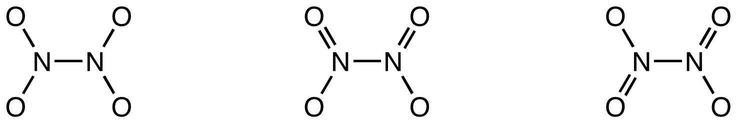
(h) N_2O : $N-N-O$ $N\equiv N-O$ $N=N=O$

Any of these representations but must be linear and the correct order of the atoms.

NO_2 :

N_2O_2 :

N_2O_4 :

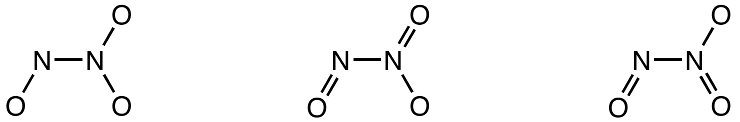


(i) $3\underset{+IV\ -II}{NO_2}\,(g) + \underset{+I\ -II}{H_2O}\,(l) \longrightarrow 2\underset{+I\ +V\ -II}{HNO_3}\,(aq) + \underset{+II\ -II}{NO}\,(g)$

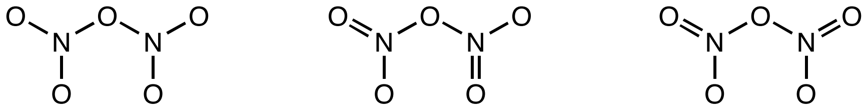
(j) A disproportionation reaction is one in which a species is both oxidised and reduced in the reaction. Here NO_2 is oxidised to HNO_3 and reduced to NO.

(k) $4HNO_3\,(aq) \longrightarrow 4NO_2\,(g) + 2H_2O\,(l) + O_2\,(g)$

(l) N_2O_3 :

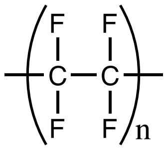


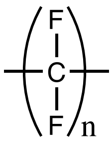
N_2O_5 :



Q18

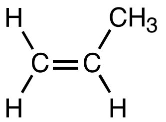
(a)



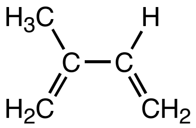


This structure is accepted.

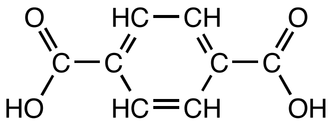
(b)



(c)



(d)



$HO-CH_2\cdot CH_2\cdot OH$

(e) For convenience we will represent the molecules of the two monomers used to make PET as T and E.

Let n = 3

Let us assume that PET is made in two steps

Step 1 $3T + 3E \longrightarrow 3(T{-}E) + 3H_2O$ ie n H_2O

Step 2 $3\,(T{-}E) \longrightarrow (T{-}E)\!\!-\!\!(T{-}E)\!\!-\!\!(T{-}E) + 2H_2O$ ie (n - 1) H_2O

$\therefore$ Total H_2O molecules formed is $2n - 1 = 5$

$\therefore$ for 100 repeating units 199 H_2O molecules are produced

now $100\,T + 100\,E \longrightarrow {-}\!\!\left(T{-}E\right)\!\!{-}_{100} + 199\,H_2O$

$$\text{MW }(T_{C_8H_6O_4}) = (8 \times 12.01) + (6 \times 1.008) + (4 \times 16.00) = 166.128$$

$$\text{MW }(E_{C_2H_6O_2}) = (2 \times 12.01) + (6 \times 1.008) + (2 \times 16.00) = 62.068$$

$$\text{Thus MW (PET)} = 100(166.128 + 62.068) - 199\left((2 \times 1.008) + 16.00\right) = 19234.416$$

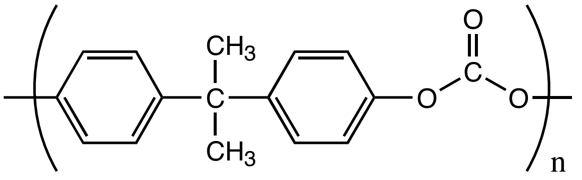
$$\text{Thus } n\text{ (PET)} = \tfrac{1000}{19234.416} = 0.051990$$

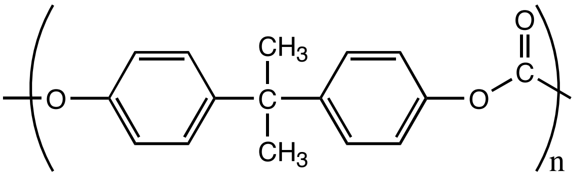
$$\text{and } n\,(H_2O) = 0.051990 \times 199 = 10.346038$$

$$\text{so mass }(H_2O) = 0.051990 \times 199 \times \left((2 \times 1.008) + 16.00\right) = 186.39\text{g}$$

$$= 186\text{g} \quad (\text{to nearest gram})$$

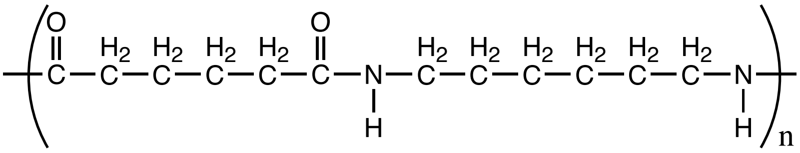
(f)



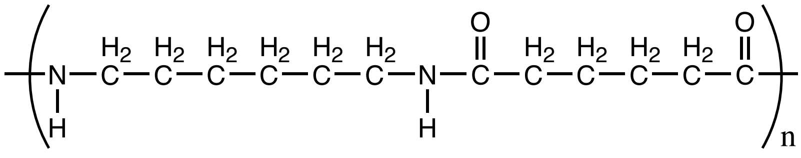


This structure is accepted.

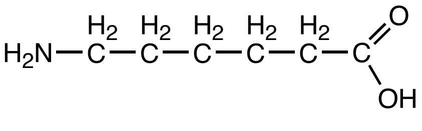
(g)

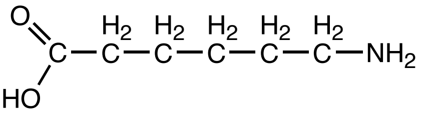


Both structures accepted.

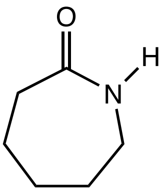


(h)



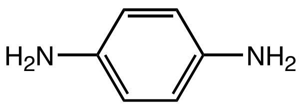


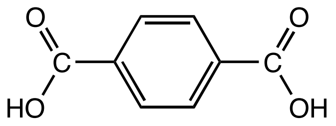
Either accepted



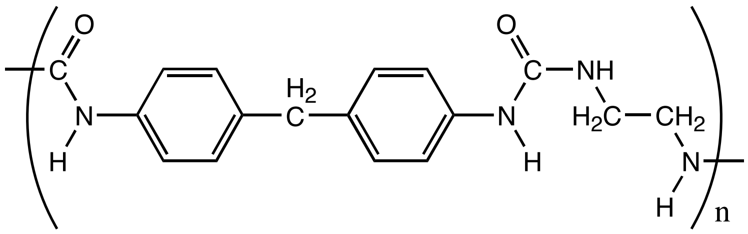
In industry it is actually made from this.

(i)

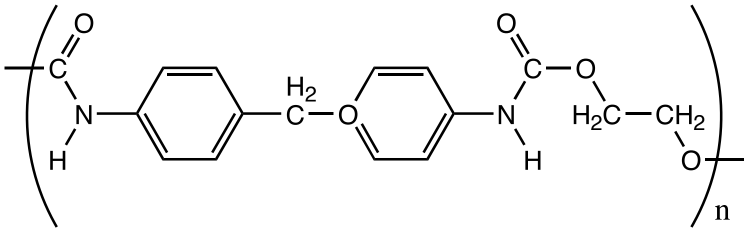




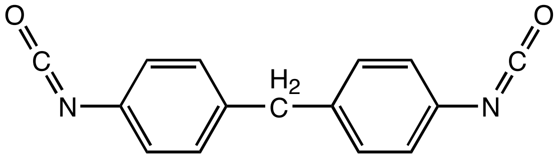
(j)



(k)



(l)



H_2N-NH_2

Q19

(a) 4 α decays
2 β decays

(b)

$$\alpha - \text{particles emitted by} 63\ \mu\text{g in 10 min}\ \&\ \text{hitting screen} = 46$$

$$\text{thus } \alpha - \text{particles emitted by 1 g in 1 min}\ \&\ \text{hitting screen} = \tfrac{46}{10\times 60} \times \tfrac{1}{6.3\times10^{-5}} = 1.2\times10^{3}$$

$$\text{total } \alpha - \text{particles emitted by 1 g in 1 min} = \tfrac{46}{10\times 60} \times \tfrac{1}{6.3\times10^{-5}} \times 4\times\pi\times(1.5\times10^{3})^{2}$$

$$= 3.4\times10^{10}\ \text{g}^{-1}\ \text{s}^{-1}$$

(c) Alpha-particles will quickly rip electrons from air molecules to become ordinary He atoms, which would go undetected.

(d)

$$\text{number of moles of He produced} \quad \text{n} = \tfrac{\text{V}}{\text{V}_\text{n}}$$

$$= \tfrac{6.83\times10^{-6}}{22.4} = 3.05\times10^{-7}\ \text{mol}$$

(e)

From (a) each Ra → Pb decay produces 4 He atoms.

$$\text{and from (b), total number of He atoms} = 4\times\left(3.4\times10^{10}\right)\times\left(0.192\right)\times\left(83\times24\times60\times60\right) = 1.9\times10^{17}$$

(f)

$$N_\text{A} = \tfrac{\left(1.9\times10^{17}\right)}{\left(3.05\times10^{-7}\right)} = 6.2\times10^{23}\ \text{mol}^{-1}$$

(g) body-centred cubic = 2
face-centred cubic = 4

(h)

$$\lambda = \tfrac{2}{\sqrt{3}} d\sin\theta$$

$$d = \tfrac{\sqrt{3}\,\lambda}{2\sin\theta} = \tfrac{\sqrt{3}\times1.54\times10^{-10}}{2\sin 21.68^\circ} = 3.61\times10^{-10}\ \text{m}$$

(i) Density $\rho = \frac{\text{mass}}{\text{volume}} = \frac{\text{m}}{\text{V}} = \frac{7.7522}{6.4 - 5.0} = 7.7 \text{ g cm}^{-3}$

$$\text{mass of unit cell} = \rho d^3 = 7.7 \times \left(\left(3.61 \times 10^{-10}\right) \times 10^{-10} \times 10^{2}\right)^3 = 3.6 \times 10^{-22} \text{ g}$$

(j) mass of 1 Cu atom $= \frac{1}{4} \times 3.6 \times 10^{-22} = 9.0 \times 10^{-23}$ g

$$\text{Thus } N_\text{A} = \frac{63.55 \text{ g mol}^{-1}}{9.0 \times 10^{-23} \text{ g}} = 7.0 \times 10^{23} mol^{-1}$$

(k) The determination of the sample's volume is very imprecise and the main source of error. Could measure it more precisely, e.g., by plunging it into a container filled with water and weighing the overflow; or using a cubic solid and measuring it with callipers, or…