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RS•C
ROYAL SOCIETY OF CHEMISTRY

A competition to select the team to represent the

UNITED KINGDOM

at the

XXXVth INTERNATIONAL CHEMISTRY OLYMPIAD

STUDENT QUESTION BOOKLET

Round I - 2003

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- **The time allowed is 2 hours.**
- **Attempt all 8 questions.**
- **Write your answers in the special answer booklet.**
- **In your calculations, please write only the essential steps in the answer booklet.**
- **Always give the appropriate units and number of significant figures.**
- **You are provided with a copy of the Periodic Table.**
- **Do *NOT* write anything in the right hand margin of the answer booklet.**

Some of the questions will contain material you will not be familiar with. However, by logically applying the skills you have learnt as a chemist, you should be able to work through the problems. There are different ways to approach the tasks – even if you cannot complete certain parts of a question, you may still find subsequent parts straightforward.

symbol atomic number mean atomic mass

H 1 1.008																	**He** 2 4.003
Li 3 6.94	**Be** 4 9.01											**B** 5 10.81	**C** 6 12.01	**N** 7 14.01	**O** 8 16.00	**F** 9 19.00	**Ne** 10 20.18
Na 11 22.99	**Mg** 12 24.31											**Al** 13 26.98	**Si** 14 28.09	**P** 15 30.97	**S** 16 32.06	**Cl** 17 35.45	**Ar** 18 39.95
K 19 39.102	**Ca** 20 40.08	**Sc** 21 44.96	**Ti** 22 47.90	**V** 23 50.94	**Cr** 24 52.00	**Mn** 25 54.94	**Fe** 26 55.85	**Co** 27 58.93	**Ni** 28 58.71	**Cu** 29 63.55	**Zn** 30 65.37	**Ga** 31 69.72	**Ge** 32 72.59	**As** 33 74.92	**Se** 34 78.96	**Br** 35 79.904	**Kr** 36 83.80
Rb 37 85.47	**Sr** 38 87.62	**Y** 39 88.91	**Zr** 40 91.22	**Nb** 41 92.91	**Mo** 42 95.94	**Tc** 43	**Ru** 44 101.07	**Rh** 45 102.91	**Pd** 46 106.4	**Ag** 47 107.87	**Cd** 48 112.40	**In** 49 114.82	**Sn** 50 118.69	**Sb** 51 121.75	**Te** 52 127.60	**I** 53 126.90	**Xe** 54 131.30
Cs 55 132.91	**Ba** 56 137.34	**La*** 57 138.91	**Hf** 72 178.49	**Ta** 73 180.95	**W** 74 183.85	**Re** 75 186.2	**Os** 76 190.2	**Ir** 77 192.2	**Pt** 78 195.09	**Au** 79 196.97	**Hg** 80 200.59	**Tl** 81 204.37	**Pb** 82 207.2	**Bi** 83 208.98	**Po** 84	**At** 85	**Rn** 86
Fr 87	**Ra** 88	**Ac+** 89															

***Lanthanides**	**Ce** 58 140.12	**Pr** 59 140.91	**Nd** 60 144.24	**Pm** 61	**Sm** 62 150.4	**Eu** 63 151.96	**Gd** 64 157.25	**Tb** 65 158.93	**Dy** 66 162.50	**Ho** 67 164.93	**Er** 68 167.26	**Tm** 69 168.93	**Yb** 70 173.04	**Lu** 71 174.97
+Actinides	**Th** 90 232.01	**Pa** 91	**U** 92 238.03	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**No** 102	**Lr** 103

1. This question is about heating a cup of coffee

Nescafé have recently launched a self-heating can of coffee. To heat up the coffee, a button is pressed which mixes the heating ingredients – a very dilute solution of sodium / potassium hydroxide and calcium oxide. The can then warms up 210 ml (210 cm^3) of coffee by approximately 40 °C.

(a) Write an equation for the reaction between calcium oxide and water.

(b) The rate of the heating may be controlled by altering the pH of the solution. How would you expect the rate of reaction to vary in acidic, basic and neutral conditions?
[Your answer should simply be the words 'acidic', 'basic' and 'neutral' in the order in which they affect the rate of reaction, fastest first.]

(c) Given the standard enthalpies of formation of calcium hydroxide, calcium oxide and water are –1003, –635 and –286 kJ mol^{-1} respectively, calculate the standard molar enthalpy change for the reaction in **(a)**.

(d) Assuming that the heat capacity for the coffee is the same as that of water, 4.18 J K^{-1} g^{-1}, calculate the energy needed to warm 210 ml of coffee by 40 °C.

(e) Hence calculate the minimum mass of calcium oxide needed in the can to function as specified.

2. This question is about Reinecke's salt

When ammonium dichromate(VI) is added gradually to molten ammonium thiocyanate, Reinecke's salt is formed. It has the formula $NH_4[Cr(SCN)_x(NH_3)_y]$ and the following composition by mass:

Cr	15.5 %
S	38.15 %
N	29.2 %.

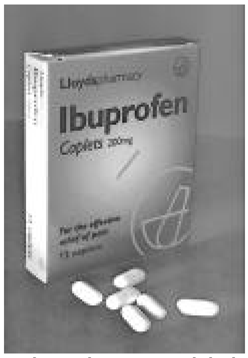
(a) Calculate the values of x and y in the above formula.

(b) Calculate the oxidation number of chromium in the complex.

(c) Suggest a shape for the complex anion.

(d) Draw two possible structures for the anion and state the type of isomerism it exhibits.

3. This question is about Green Chemistry



Increasing concerns over the use and generation of hazardous substances in chemical processes has encouraged some chemists to look for more environmentally friendly ways to make chemical products. To help evaluate a process environmentally, chemists often use the term *'percentage atom economy'*, where

$$\% \text{ Atom Economy} = \frac{\text{RMM of desired product}}{\text{RMM of all products}} \times 100$$

An environmentally friendly chemical process would normally be expected to have a high % atom economy, indicating that a high proportion of the starting materials end up as part of the final product, hence reducing the amount of waste. Efforts are constantly being made to increase the % atom economy of chemical processes. As an example, the manufacture of ethene oxide (C_2H_4O) for many years was via the classical chlorohydrin route:

$$C_2H_4 + Cl_2 + H_2O \longrightarrow ClCH_2CH_2OH + HCl$$

$$ClCH_2CH_2OH + Ca(OH)_2 + HCl \longrightarrow C_2H_4O + CaCl_2 + 2H_2O$$

(a) i) Write a balanced equation for the overall reaction.

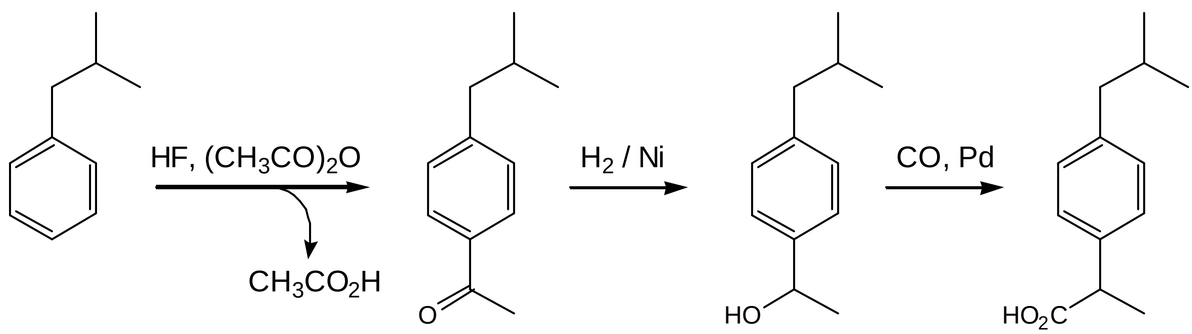
ii) Calculate the % atom economy for this process.

The modern petrochemical route involves the following reaction:

$$C_2H_4 + \tfrac{1}{2}O_2 \xrightarrow{Ag} C_2H_4O$$

(b) Calculate the % atom efficiency of this process.

Ibuprofen, a non-steroidal anti-inflammatory drug, was first synthesised by Boots using a six-step process, with a % atom economy of 40%. When the patent expired in the 1980's, several companies began developing new methods for the preparation of ibuprofen. The BHC Company synthesis, which proved highly successful, is shown below:



Ibuprofen

Step 1 involves the use of ethanoic anhydride, $(CH_3CO)_2O$.

(c) i) Calculate the % atom economy of the BHC Company process.

ii) State the purpose of the HF in step 1.

iii) What happens to the % atom economy if the ethanoic acid is reused?

4. This question is about redox equations

By considering the relevant half equations, write balanced equations for the following chemical reactions:

(a) zinc metal decolourizing copper(II) sulfate solution

(b) chlorine water turning sodium bromide solution orange

(c) magnesium ribbon reacting with dilute hydrochloric acid

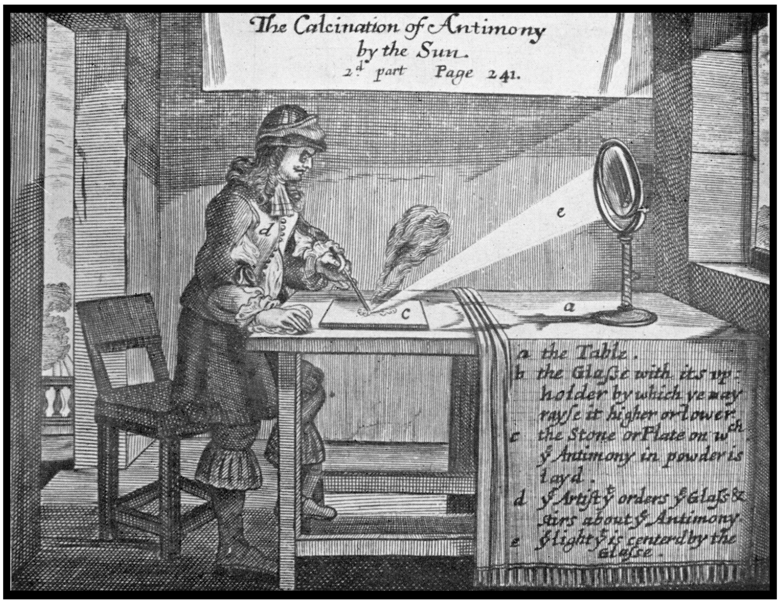
(d) manganese(IV) oxide reacting with concentrated hydrochloric acid to produce a yellow-green gas and a solution of manganese(II) chloride

(e) sodium sulfate(IV) (sulfite) decolourizing an acidified solution of potassium manganate(VII)

(f) tin(II) chloride turning orange acidified potassium dichromate(VI) green

(g) acidified potassium manganate(VII) reacting with a lemon-yellow solution of iron(II) ethanedioate.

5. This question is about the combining proportions of the elements



Understanding the proportions in which the elements combine was a crucial step in developing the atomic theory of matter. The picture above shows an experiment performed in the 1660s in which antimony was heated using the sun's rays to form an oxide.

In the experiment, 'ye Artist' reported that '12 *grains* of antimony increased to 15 *grains* of calx', (a *grain* is an old measure of mass). Given the crudeness of the experiment, this value is remarkably close to the theoretical yield of 14.4 '*grains'*.

(a) Calculate the formula of the oxide formed.

In another experiment published in 1673, Robert Boyle measured the increase in mass when zinc metal is heated in air. He describes the experiment thus:

> *We took a Drachm of filings of Zink and kept it in a Cupelling-fire about three Hours. Then it look'd as if the filings had been calcin'd. This being weigh'd in the same scales gain'd full six grains.*

(b) Given that there are 60 grains in a Drachm, calculate the mass of product (in grains) that would have been produced assuming a yield of 100%.

Assuming that Boyle's measurements are accurate, only a fraction, α, of the zinc must have been converted to the oxide. (α is a fraction between 0 and 1; 0 meaning none of the zinc reacted and 1 meaning all reacted).

(c) Calculate the value of α and hence the masses of zinc oxide and unreacted zinc metal at the end of the experiment.

6. This question is about hydroxylamine and its reaction with iron(III) ions

Hydroxylamine, NH_2OH, is a base and a reducing agent; it reacts with hydrochloric acid to form the salt hydroxylammonium chloride, $NH_3OH^+Cl^-$, and with Fe^{3+} ions to produce Fe^{2+}.

1.00g of hydroxylammonium chloride was dissolved in distilled water and made up to a total volume of 250 cm^3. A 25.0 cm^3 aliquot of this solution was added to a solution containing an excess of both iron(III) ions and sulfuric acid. The mixture was then boiled and allowed to cool. It was then titrated against a solution of 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$, which oxidizes the Fe^{2+} ions back to Fe^{3+} and is itself reduced to Mn^{2+} ions; 28.9 cm^3 of the potassium manganate(VII) solution was required.

(a) Draw the structure for hydroxylammonium chloride, $NH_3OH^+Cl^-$. Include on your diagram the approximate values of the bond angles.

(b) Calculate the ratio of the number of moles of Fe^{3+} ions to the number of moles of hydroxylammonium chloride which have reacted together.

(c) Calculate the oxidation number of the nitrogen in hydroxylammonium chloride and hence in the product.

(d) Suggest which of the following is the nitrogen-containing product formed from the hydroxylammonium chloride:

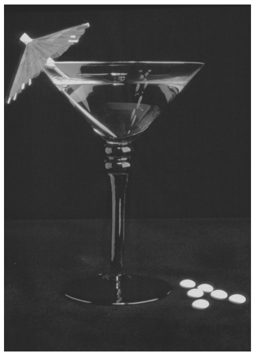
N_2, NO, N_2O, N_2O_4, NH_3.

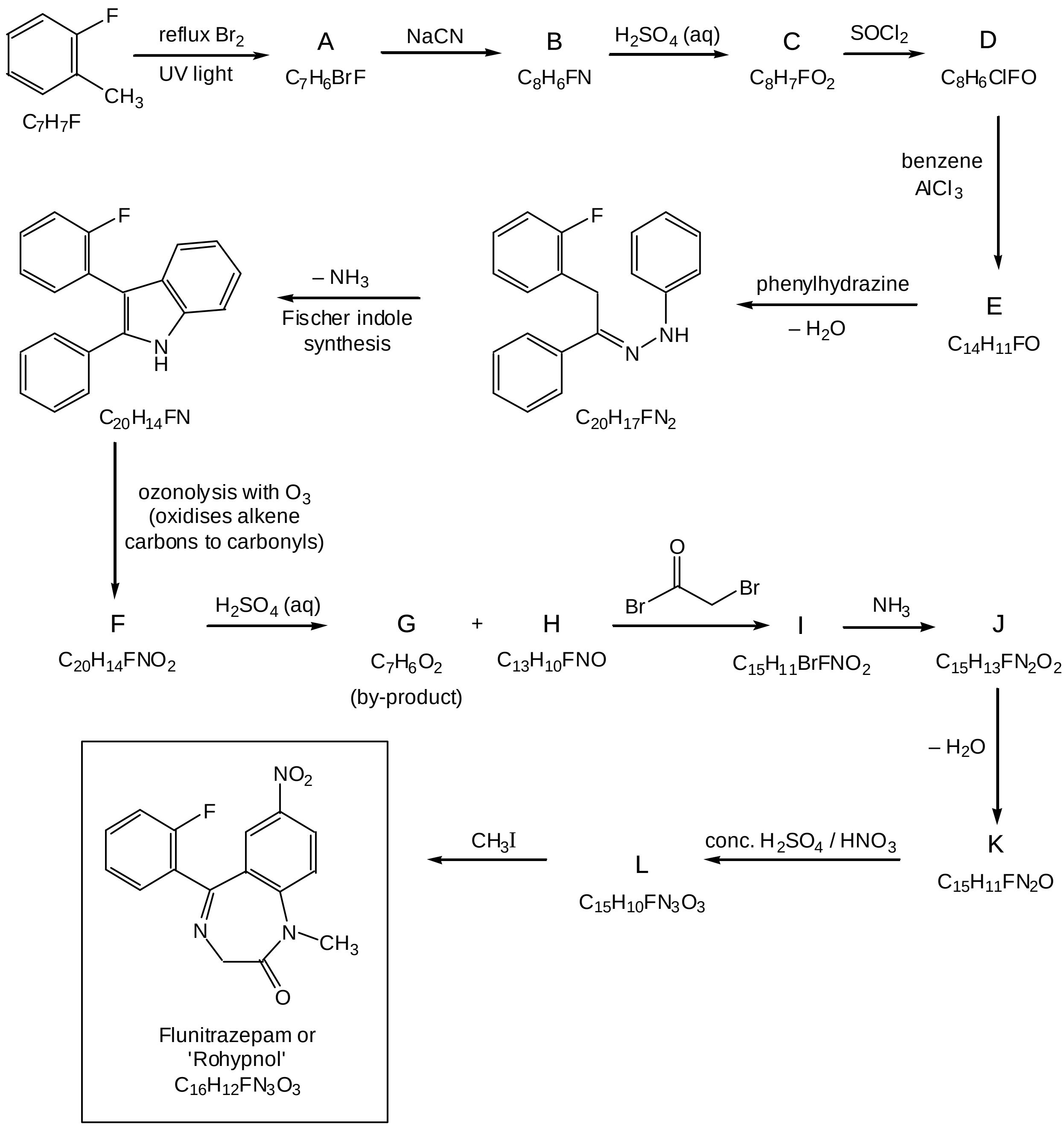
(e) Write a balanced equation for the reaction between hydroxylammonium chloride and iron(III) ions.

7. This question is about the synthesis of Rohypnol

Rohypnol is a trade name for the compound *flunitrazepam* whose structure is shown in the box below. It is a controversial sedative which has been misused to `spike' people's drinks.

Flunitrazepam was first synthesised from (2-fluoro)-methylbenzene as outlined below.





Draw the structures for the reagent phenylhydrazine and compounds **A** to **L**.

8. This question is about polonium

Polonium is a radioactive group VI element, discovered in 1898 by Marie Curie. It occurs naturally in trace amounts in some uranium ores but is now made by neutron irradiation of ^{209}Bi. This produces short-lived ^{210}Bi which decays to polonium by the emission of a beta-particle (an electron):

$^{209}_{83}\mathrm{Bi} + ^{1}_{0}n \rightarrow ^{210}_{83}\mathrm{Bi} + g \qquad ^{210}_{83}\mathrm{Bi} \rightarrow ^{210}_{84}\mathrm{Po} + ^{0}_{-1}b$

Polonium-210 has a half life of 138 days and decays by emitting an alpha particle (a helium nucleus).

(a) What is the electronic configuration of polonium?

(b) What nuclide is formed when polonium-210 decays?

Due to its very short half life and the impedance of the alpha-particles it emits, metallic polonium and its compounds are self heating; 1g of metal produces 141 W. This led to its use in Radioisotope Heater Units (RHUs) to keep satellites warm and functioning in space, and in Radioisotope Thermal Generators (RTGs) to produce electrical power. More recently, plutonium-238 has been used instead of polonium. ^{238}Pu has a much longer half-life but produces less power (0.56 W g^{-1}).

(c) What will be the power output of ^{210}Po after 1 year?

(d) After 5 years, the power output of ^{238}Pu is approximately 96% of its initial value. Estimate the half life of plutonium-238.

Polonium is unique amongst the elements in being the only one to have a simple cubic structure with each atom lying at the corner of a cube.

(e) Given that the density of polonium-210 is 9.142 g cm^{-3}, calculate its atomic radius.

[The Avogadro number, $N_A = 6.022 \times 10^{23}$ mol^{-1}.]

Olympiad Round 1 2003 – Mark Scheme

1. Heating a cup of coffee

(a) $CaO + H_2O \rightarrow Ca(OH)_2$ **(1)**

(b) acidic, neutral, basic **(1)**

(c) $?_rH$ = - 1003 + 635 + 286 = **- 82 kJ mol^{-1}** **(1) fig + sign**

(d) To warm 1g by 1°C requires 4.18 J
210g by 40°C requires 4.18 x 210 x 40 J = **35.1 kJ** **(1)**

(e) 1 mol CaO provides 82 kJ
We need 35.1 kJ = 35.1 / 82 mol = 0.428 mol
Taking RMM for CaO as 56, minimum mass required = 56 x 0.428 = **24.0 g** **(1)**
(Actual mass used in cans = 70g)

Total 5

2. Reinecke's Salt

(a) Cr (Ar = 52.0) is 15.5% of total
Therefore total $= \frac{100}{15.5} \times 52.0 = 335.5$

For 5 $\frac{38.15}{100} \times 335.5 = 128$

$\frac{128}{32} = 4 = x$

Therefore $NH_4[Cr(SCN)_4(NH3)_y] = 335.5$
Therefore 18 + 52 + 4 x 58.1 + 17y = 335.5
Therefore 17y = 33.5
X = 4 **y = 2** **(1, 1)**

(b) +1 + Cr + 4 x -1 + 2 x 0 = 0 **(1)**
Therefore Cr = **+ 3**

(c) Octahedral **(1)**

(d) Two octahedral structures, one with $2NH_3$ groups adjacent, one with them opposite

Geometrical **(1) for 2 shapes**
(1) for geometric or cis/trans

Total 6

3. **Green Chemistry**

(a) (i) $C_2H_4 + Cl_2 + Ca(OH)_2 \rightarrow C_2H_4O + CaCl_2 + H_2O$ extra H_2O ok **(1)**

(ii) % atom economy = $\frac{44}{44 + 111 + 18}$ x 10 (not 23.6)

= 25.4 **(1)**

(b) 100% **(1)**

(c)(i) Mr ibuprofen = 206

% atom economy = $\frac{206}{206 + 60}$ x 100 = 77.4 **(1)**

(ii) Catalyst **(1)**

(iii) goes up to 100% (needed) **(1)**

Total 6

4. **Redox Equations** Any suitable equation

(a) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ **(1)**

(b) $Cl_2(aq) + 2Br^-(aq) \rightarrow 2\,Cl^-(aq) + Br_2(aq)$ **(1)**

(c) $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$ **(1)**

(d) $MnO_2(s) + 4H^+(aq) + 2Cl^- \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Cl_2(g)$ **(1)**

(e) $5SO_3^{2-}(aq) + 6H^+(aq) + 2MnO^-_4(aq) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$ **(1)**

(f) $3Sn^{2+}(aq) + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 3Sn^{4+}(aq) + 7H_2O(l)$ **(1)**

(g) $3MnO^-_4(aq) + 24H^+(aq) + 5Fe^{2+}(aq) + 5C_2O_4^{2-}(aq) \rightarrow 3Mn^{2+}(aq)$
$+ 12H_2O(l) + 5Fe^{3+}(aq) + 10\,CO_2(g)$ **(2)**

Do not penalise
State symbols

Total 8

5. Combining Proportions

(a) 12 grains of Sb give 14.4 grains of oxide
12 grains Sb combine with 2.4 grains of oxygen
suppose conversion factor for grains to grams = k

moles of Sb = 12*k* / 121.8 — if used **(1)**
moles of O = 2.4*k* / 16.0

molar ration Sb : O = (12/121.8) : (2.4/16.0) = 0.9852 : 0.15 = 1:1.5 = 2:3

Formula = **Sb_2O_3** **(2 marks if answer alone given)** **(1)**

(b) 1 mol Zn forms 1 mol ZnO
65.4g Zn forms (65.4 + 16.0) g ZnO = 81.4g
increase in mass by 81.4 / 65.4
so 60 grains should produce (60 x 81.4) / 65.4 grains = **74.5(8) grains** **(2)**

(c) Total mass at end = unreacted Zn + ZnO
60 grains Zn should give 74.58 grains ZnO

If fraction of Zn reacting is a, amount of Zn used is 60 a grains which forms 74.58 a grains of ZnO.
Amount of Zn left = 60 – 60 a
Total mass at end = 60 – 60 a + 74.58 a = 65 grains = 60 + 14.58 a

a = (66 – 60) / 14.58 = **0.41(15)** **(2)**

Mass of unreacted Zn = 60 - 60 a = **35(.31) grains** **(1)**

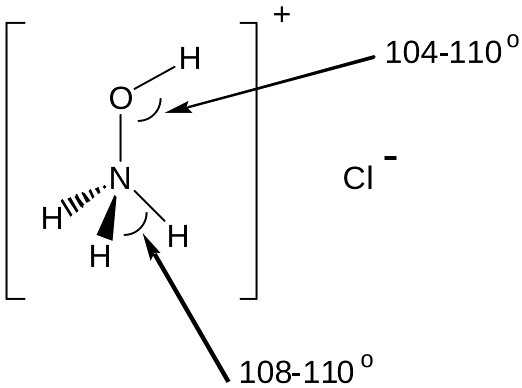
Mass of ZnO = 74.58 a = **30(.69) grains** **(1)**

Total 8

6. Hydroxylamine and its reaction with iron (III) ions

(a)

(1)



no marks for structure except if no angles - then 1 mark.
(1)

(b) Original $NH_3OH^+Cl^-$ solution 1g in 250cm^3 = 4gdm^{-3}

$= \frac{4.00}{69.5} = 0.0576$ mol dm^{-3}

25cm^3 aliquot contains $\frac{25}{1000} \times 0.0576 = 0.00144$ moles

28.9cm^3 of 0.0200 mol dm^{-3} MnO^-_4 contains $\frac{28.9}{1000} \times 0.0200 = 0.000578$ moles **(1)**

1 mole MnO_4^- = 5 moles Fe^{2+}

Therefore No. of moles Fe^{2+} = 5 x 0.000578 = 0.00289 moles

Ratio $NH_3OH^+Cl^-$: Fe^{2+} = **1:2** **(1)**

(c) x + 3 – 2 + 1 = +1 Therefore x = -1

oxidation state of N = -1

As $Fe^{3+} \rightarrow Fe^{2+}$, and ratio is 2:1

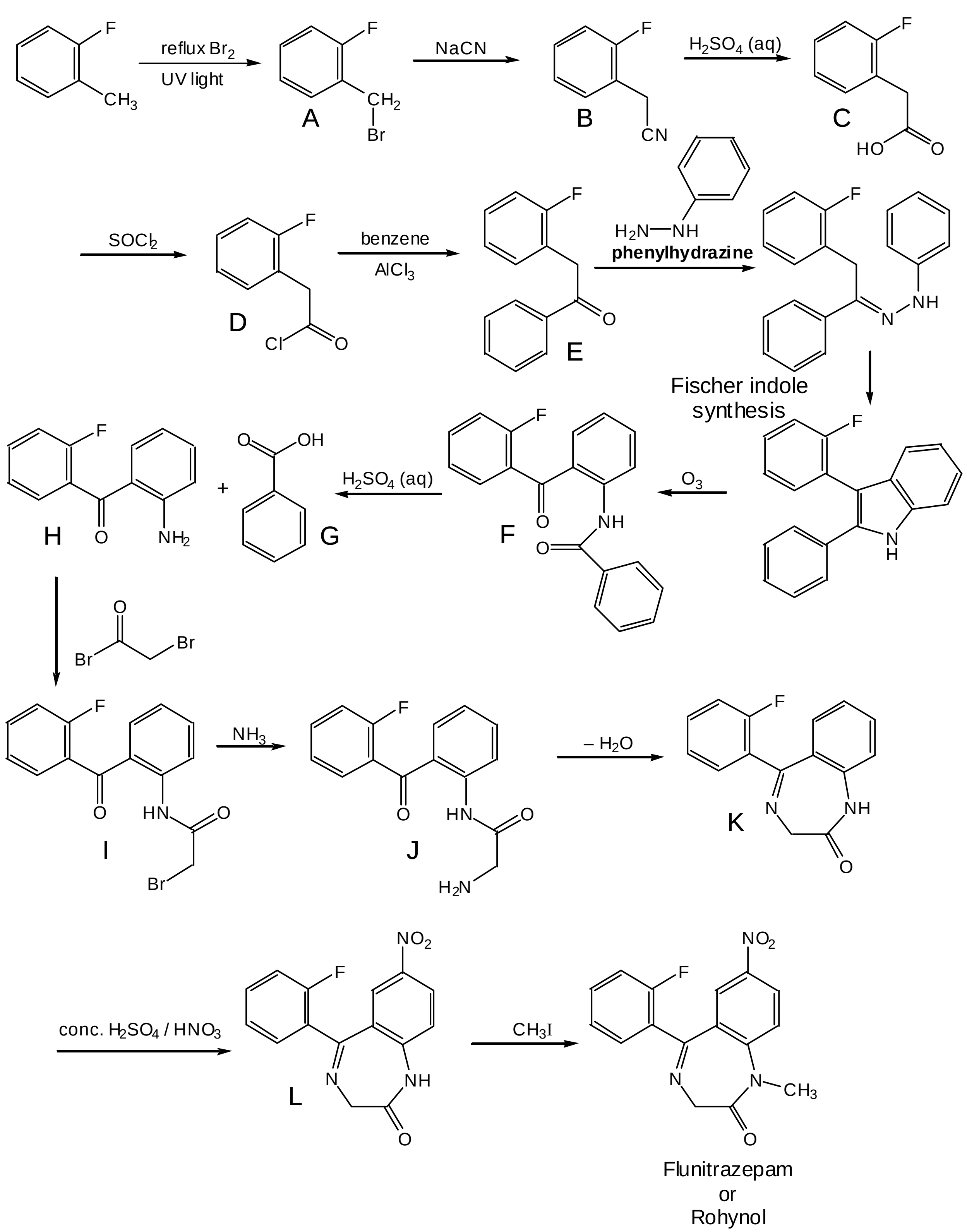
then oxidation state of product goes up by **2 to +1** **(1)**

(d) Product must be N_2O **(1)**

(e) $2NH_3OH^+Cl^- + 4Fe^{3+} \rightarrow N_2O + H_2O + 2Cl^- + 4Fe^{2+} + 6H^+$ **(2)**

Total 8

7. Rohypnol



1 mark for each of A → L + phenylhydrazline **Total 13**

8. Polonium

(a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^4$ **(1)**

exact ordering is irrelevant [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$ is also acceptable

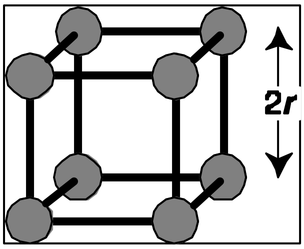
(b) ${}^{206}_{82}Pb$

(1)

(c) half life = 138 days. 1 year = 365 / 138 half lives = 2.645 half lives. Power output after one year = 141 x $(0.5^{2.645})$ = 22.5(4) W g^{-1} **(2)**

(d) after x half lives, power drops to 0.96 of initial, so $[0.5^x] = 0.96$ taking logs: x(ln0.5) = ln(0.96), x = 0.05889 half lives in 5 years so time for one half life = 5 / x = 84.899 years = 85 years **(2)**

(e)



1 unit cell contains 8 x 1/8 atoms = 1 **(1)**
volume of unit cell = $(2r)^3$ where r = radius
9.142 g = 1 cm^3 = 1 x $10^{-6} m^3$ **(1)**
mass of 1 atom = 210 g / 6.022 x 10^{23} = 3.487 x 10^{-22}
volume occupied by 1 atom
= $(2r)^3$ = (1 x 10^{-6} / 9.142) x 3.487 x $10^{-22} m^3$ **(1)**
= 3.814 x $10^{-29} m^3$

so $r = \frac{1}{2}\sqrt[3]{3.8143\times10^{-29}}$ = 1.68(3) x 10^{-10}m = 168pm

(168pm x 2 = 2 unless they can say diameter) **(3 for ans)**
336

Total 9