

30th



International Chemistry Olympiad

**7 theoretical problems
2 practical problems**

THE THIRTIETH INTERNATIONAL CHEMISTRY OLYMPIAD 5–14 JULY 1998, MELBOURNE, AUSTRALIA

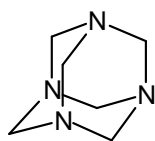
<h2>THEORETICAL PROBLEMS</h2>

PROBLEM 1

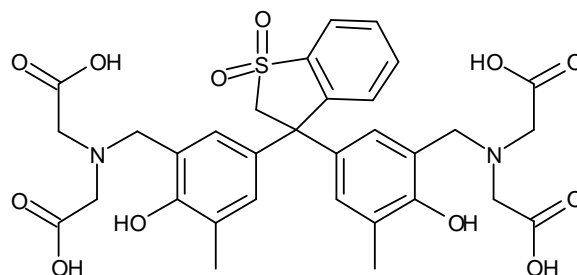
The following 8 steps describe the procedure for analysing a sample of alloy that contains both tin and lead.

1. A 0.4062 g sample of alloy was dissolved by heating it in a small beaker with a mixture of 11 M hydrochloric and 16 M nitric acid. The beaker was heated until the entire alloy dissolved. In this procedure, lead is oxidised to Pb(II) and tin becomes Sn(IV).
2. After 5 minutes of heating to expel oxides of nitrogen and chlorine, some acid remained. When the solution was cooled, a precipitate of some tin compounds and a lead compound appeared.
3. A 25.00 cm³ aliquot of 0.2000 M Na₂H₂EDTA solution was added. The precipitate dissolved and a clear, colourless solution was obtained.
4. This solution was quantitatively transferred to a 250.0 cm³ volumetric flask and made up to the mark with distilled water.
5. A 25.00 cm³ aliquot of this solution was treated with 15 cm³ of a 30 % w/v solution of hexamine (hexamethylenetetramine), some water and two drops of Xylenol Orange solution. The pH of each aliquot was 6.
6. The clear, yellow solution from Step 5 was titrated with standard 0.009970 M lead nitrate solution until the colour just changed from yellow to red. The titre at this endpoint was 24.05 cm³.
7. 2.0 g of solid NaF was added to the titration flask. The solution turned back to yellow.
8. The solution was titrated with more standard 0.009970 M lead nitrate solution until the colour changed to red again. The titre at this endpoint was 15.00 cm³.

Hexamine and Xylenol Orange have the structures shown below. The pK_b of hexamine is 9.5. Xylenol Orange is red below pH 4, yellow above pH 5.



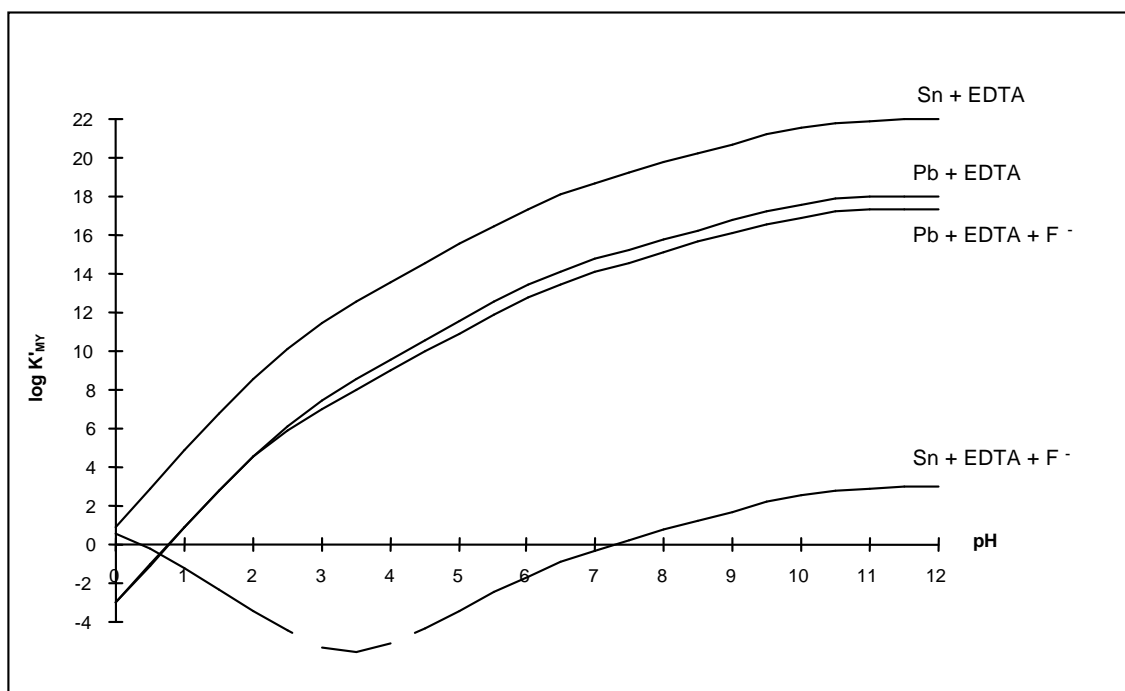
Hexamine



Xylenol Orange (XO)

K_{MY} is the conditional formation constant = αK_{MY} .

K_{MY} for the formation of the EDTA complexes of Pb(II) and Sn(IV), in the presence and absence of fluoride, are shown in the following Figure.



- 1.1 What is the lead compound that precipitates in Step 2?
- 1.2 Write a balanced ionic equation that explains the disappearance of the precipitate in Step 3 (at pH 6).
- 1.3 What is the purpose of hexamine in Step 5 of the analysis?
- 1.4 What is the purpose of Xylenol Orange in the analysis?

- 1.5 Write balanced ionic equations for the reactions occurring during the titration and responsible for the colour change at the endpoint in Step 6 of the analysis
- 1.6 What is the purpose of NaF in Step 7 of the analysis?
- 1.7 Write a balanced ionic equation for the reaction that occurs in Step 7.
- 1.8 Write a balanced ionic equation that explains why the colour changed from red to yellow in Step 7 of the analysis.
- 1.9 Write a balanced ionic equation that explains why the lines on the graph below of $\log K_{MY}$ vs pH for Pb + EDTA and Pb + EDTA + F⁻ are coincident below pH 2.
- 1.10 Calculate the percentage by weight of Sn and Pb in the alloy.

SOLUTION

- 1.1 PbCl₂ or any hydroxo species etc.
- 1.2 $PbCl_2(s) + H_2Y^{2-} \rightarrow PbY^{2-} + 2 H^+ + 2 Cl^-$ or similar
- 1.3 It forms a pH buffer.
- 1.4 It is a metallochromic indicator.
- 1.5 (i) The reaction that occurs during the titration:
 $Pb^{2+} + H_2Y^{2-} \rightarrow PbY^{2-} + 2 H^+$
- (ii) At the endpoint, a slight excess of Pb²⁺ forms a red complex with the xylenol orange indicator:
 $Pb^{2+} + XO \text{ (yellow)} \rightarrow PbXO^{2+} \text{ (red)}$
- 1.6 The role of the NaF: It forms a complex with tin.
- 1.7 From the graph of $\log K_{MY}$ vs pH , it can be seen that the fluoride forms a stable complex with Sn⁴⁺ but not with Pb²⁺ at pH 6, displacing EDTA:
 $SnY + nF^- + 2 H^+ \rightarrow SnF_n^{(n-4)-} + H_2Y^{2-}$ where n is typically 4 - 6.
- 1.8 The released EDTA destroys the small amount of red PbXO complex, producing free (yellow) XO. (Charge on XO ignored)
 $H_2Y^{2-} + PbXO^{2+} \rightarrow PbY^{2-} + XO \text{ (yellow)} + 2 H^+$
- 1.9 Below pH 2, F⁻ is protonated and does not compete effectively with Y for Pb²⁺
 $H^+ + F^- \rightarrow HF$.
- 1.10 The percentage by mass of Sn and Pb in the alloy:
 The amount of EDTA in excess from the amount of standard Pb²⁺ titrant:
 $n(\text{EDTA}) = n(\text{Pb}^{2+}) = 0.02405 \text{ dm}^3 \times 0.009970 \text{ mol dm}^{-3} = 2.398 \times 10^{-4} \text{ mol}$.

The original amount of EDTA:

$$n(\text{EDTA})_{\text{init.}} = 0.1 \times 25.00 \text{ dm}^3 \times 0.2000 \text{ mol dm}^{-3} = 5.000 \times 10^{-4} \text{ mol}$$

EDTA consumed by the Pb^{2+} and Sn^{4+} in a 25 cm^3 aliquot:

$$n(\text{EDTA})_{\text{consumed}} = 5.000 \times 10^{-4} - 2.398 \times 10^{-4} \text{ mol} = 2.602 \times 10^{-4} \text{ mol} = n(\text{Pb}^{2+} + \text{Sn}^{4+}) \text{ in a } 25 \text{ cm}^3 \text{ aliquot.}$$

The amount of EDTA released from SnY by reaction with fluoride:

$$n(\text{EDTA})_{\text{released}} = n(\text{Pb}^{2+})_{\text{stand.}} = 15.00 \text{ cm}^3 \times 0.009970 \text{ mol dm}^{-3} = 1.496 \times 10^{-4} \text{ mol} = n(\text{Sn}^{4+}) \text{ in the } 25 \text{ cm}^3 \text{ aliquot}$$

$$\text{in a } 25 \text{ cm}^3 \text{ aliquot } n(\text{Pb}^{2+}) = (2.602 \times 10^{-4} - 1.496 \times 10^{-4}) \text{ mol} = 1.106 \times 10^{-4} \text{ mol}$$

In the original 0.4062 g sample of alloy:

$$m(\text{Sn}) = 10 \times 1.496 \times 10^{-4} \text{ mol} \times 118.69 \text{ g mol}^{-1} = 0.1776 \text{ g}$$

$$m(\text{Pb}) = 10 \times 1.106 \times 10^{-4} \text{ mol} \times 207.19 \text{ g mol}^{-1} = 0.2292 \text{ g}$$

The percentages of tin and lead:

$$\text{Sn: } 100 \times (0.1776 / 0.4062) = 43.7 \%$$

$$\text{Pb: } 100 \times (0.2292 / 0.4062) = 56.4 \%$$

PROBLEM 2

Part A: Dating Historical Events Using Pb-210

Nathan Thompson, one of the first inhabitants of Lord Howe Island, decided to plant some European deciduous trees in his garden. Unfortunately the exact timing of the planting of the seeds is not known. Over the years, pollen produced by the European oak and elm accumulated at the bottom of the lake near Nathan's house. Very small quantities of radioactive Pb-210 (half-life = 22.0 years) were deposited at the same time. Note that the European oak and elm trees pollinate in their first year of growth.

In 1995, a team of researchers sampled a sediment core from the bottom of the lake. The sediment core was cut into 1 cm slices and examined for pollen and radioactive Pb-210.

The examination of the sediment core found that:

- Pollen of European oak and elm first occur at a depth of 50 cm.
- The activity of Pb-210 at the top of the sediment core is 356 Bq/kg and at 50 cm depth 1.40 Bq/kg.

2.1 In what year did Nathan Thompson plant the seeds?

Radioactive Pb-210 is one of the daughters of U-238. U-238 is present in the earth's crust and for some reason a certain amount of Pb-210 rains out of the atmosphere and attaches itself to sediment particles that accumulate at the bottom of lakes.

- The U-238 decay chain is:
- U-238 – U-234 – Th-230 – Ra-226 – Rn-222 – (Po-218 – Bi-214)* – Pb-210 – Pb-206 (stable)

* Very short half-lives: minutes and days

2.2 Which step in the decay scheme explains how Pb-210 ends up in rainwater while its parent U-238 is only present in the earth's crust?

Part B: Separation of Radionuclides for Nuclear Medicine Applications.

The Ga-67 is used to image lymphoma. It is preferentially produced by bombarding a target enriched in Zn-68 (> 98%) with high energy protons for 11 hrs. Zn-68 has a natural abundance of 18.8%. Due to the target design other radionuclides may be produced (see Table 1). Twelve hours after the end of bombardment, Ga-67 is bound on a cation exchange. Then the other radionuclides and the Zn-68 are eluted in the wash solution leaving Ga-67 bound to the column.

Table 1

Radionuclide	Half-life
Co-55	18.2 hr
Ni-57	36.0 hr
Co-57(daughter of Ni-57)	270 days
Cu-64	12.7 hr
Cu-67	61.7 hr
Zn-65	244 days
Ga-67	78.35 hr
Ga-66	9.4 hr

Cu-64 and Co-55 have ideal half-lives for use in nuclear medicine applications and it would be useful to isolate them from the wash solution.

The distribution coefficient D is a measure of the partition of a metal ion between the ion-exchange resin and the eluant.

For a given ion-exchange resin and eluant, D is given by

$$D = \frac{\text{radioactivity per mg of resin}}{\text{radioactivity per cm}^3 \text{ of eluant}}$$

For a reasonable separation of two metal ions their D values should differ by at least 10 units.

2.3 The wash solution is evaporated to dryness and the residue resuspended in a small amount of 0.2 M HCl 96 % methanol and loaded onto an anion exchange column. Use the distribution coefficients D given in Figures 1 and 2 and rank the best solvent systems (from given alternatives) for eluting Cu-64 and Co-55.

2.4 Having isolated relevant radionuclides, the presence of some long-lived radionuclides could interfere with medical use of Cu-64 or Co-55 or Ga-67. Indicate which of the following statements is either true or false (one or more may be true).

- a) Ni-57 may be present as a contaminant of Co-55.
- b) Co-57 will interfere with the medical use of Co-55.
- c) Cu-67 will interfere with the medical use of Cu-64.
- d) Ga-66 will interfere with the use of Ga-67.
- e) Ga-67 will interfere with the medical use of Cu-64.

2.5 If radionuclide contamination of Cu-64 or Co-55 or Ga-67 occurred, which method would reduce the amount of radionuclide contaminant/s? Indicate which of the following statements is either true or false. (one or more may be true).

- a) Remove Ni-57 before isolating Co-55.
- b) Separate the Ni-57 from the bombarded target material before isolating the Ga-67.
- c) Separate the radionuclides closer to the end of bombardment.
- d) Allow the Ni-57 to decay before isolation of Co-55.

2.6 If zinc of natural isotopic abundance, instead of enriched Zn-68, was bombarded with high energy protons, indicate which of the following statements is either true or false. (one or more may be true).

- a) Ga-67 would be produced at 5 fold higher yields.
- b) Ga-67 would be produced at 5 fold lower yields.
- c) Ga-67 would be produced at lower yields and contamination of Cu-64, Co-55, Co-57, Ni-57 would increase.
- d) Ga-67 would be produced at lower yields and contamination of Cu-64, Co-55, Co-57, Ni-57 would remain the same.

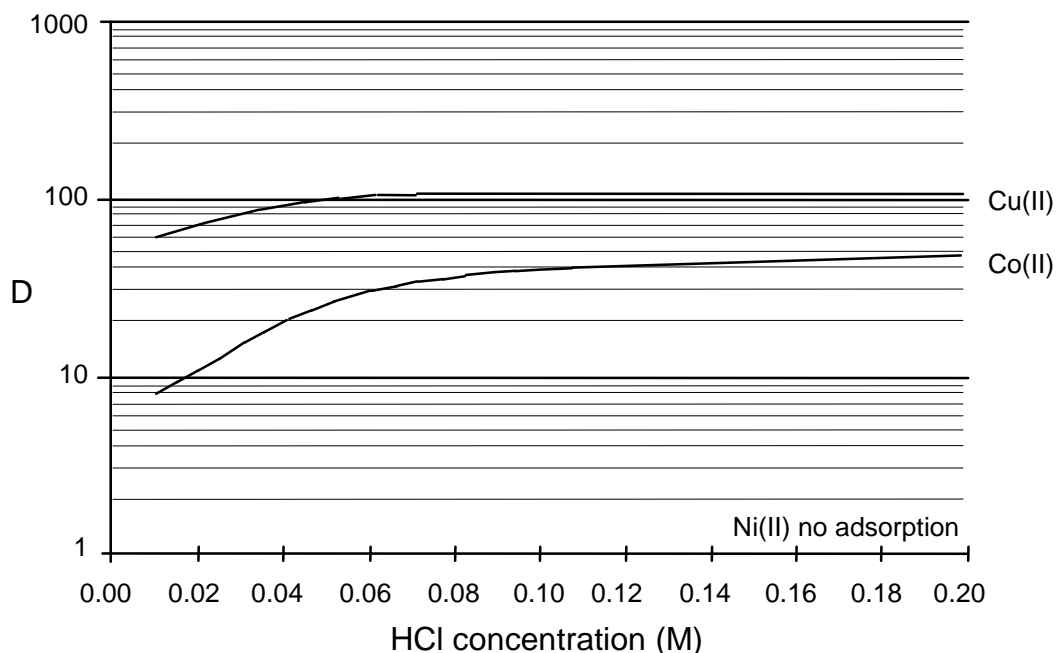


Figure 1. Distribution coefficients, D of metal ions between anion exchange resin and 96 % methanol at varying HCl concentrations. (note D value for Zn > 1000)

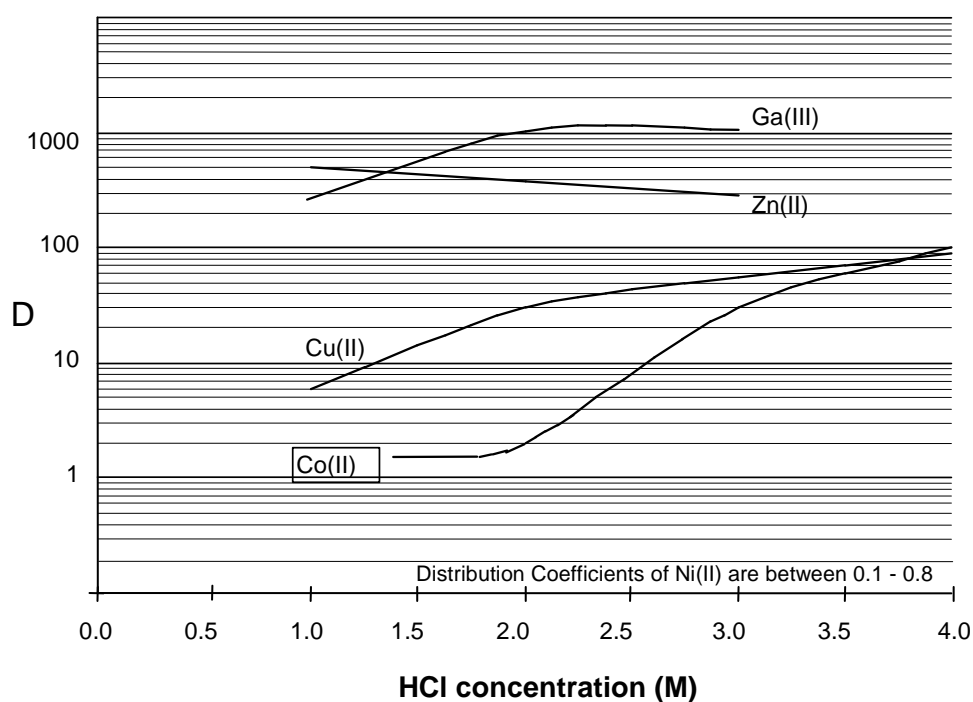


Figure 2. Distribution coefficients, D of metal ions between anion exchange resin and 55 % isopropyl alcohol at varying HCl concentrations.

SOLUTION

2.1 In what year did Nathan Thompson plant the seeds?

Calculations:

Over a depth of 50 cm the apparent decay of Pb-210 was equal to $356 - 178 - 89 - 44.5 - 22.5 - 11.25 - 5.63 - 2.81 - 1.39 = 8$ half-lives = 8×22 years = 176 years

If 1995 was the year of coring then the year of arrival was $1995 - 176 = 1819 (\pm 2)$

2.2 Correct answer: Ra-226 - Rn-222

2.3 Use the distribution coefficients D given in Figures 1 and 2 and rank the following solvent systems for isolating Cu-64 and Co-55 by writing the numbers 1 to 4 in the boxes (1 is best).

- | | | |
|------|---------------------------------|-----------------------------|
| A | 0.2 M HCl 96% methanol | to remove Ni-57 followed by |
| | 2.0 M HCl 55% isopropyl alcohol | to remove Cu-64 followed by |
| | 1.0 M HCl 55% isopropyl alcohol | to remove Co-55 |
|
 | | |
| B | 0.2 M HCl 96% methanol | to remove Ni-57 followed by |
| | 2.0 M HCl 55% isopropyl alcohol | to remove Co-55 followed by |
| | 1.0 M HCl 55% isopropyl alcohol | to remove Cu-64 |
|
 | | |
| C | 2.0 M HCl 55% isopropyl alcohol | to remove Co-55 followed by |
| | 1.0 M HCl 55% isopropyl alcohol | to remove Cu-64 |
|
 | | |
| D | 0.2 M HCl 96% methanol | to remove Ni-57 followed by |
| | 3.0 M HCl 55% isopropyl alcohol | to remove Co-55 followed by |
| | 4.0 M HCl 55% isopropyl alcohol | to remove Cu-64 |

The best sequence: B, C, D, A

The other sequences: B, C, A, D or C, B, D, A or C, B, A, D were also accepted but evaluated by less points.

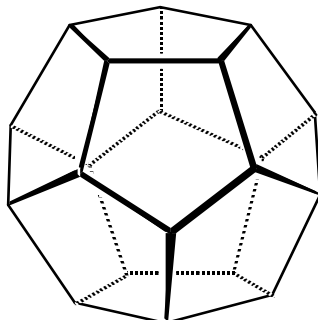
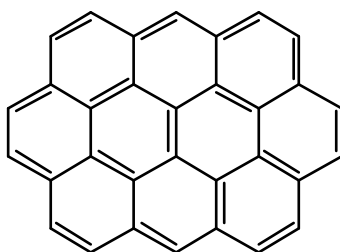
- 2.4 a) False;
 b) True;
 c) True
 d) False
 e) False

- 2.5** a) True
b) True
c) True
d) False

- 2.6** a) False
b) True
c) False
d) True
-
-

PROBLEM 3

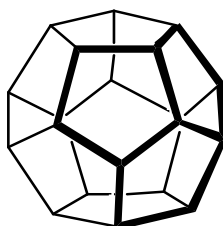
The three-dimensional structures of polycyclic molecules can often be explained in terms of the minimisation of angle strain. Consider the following molecules:

Dodecahedrane, C₂₀H₂₀and Ovalene, C₃₂H₁₄.

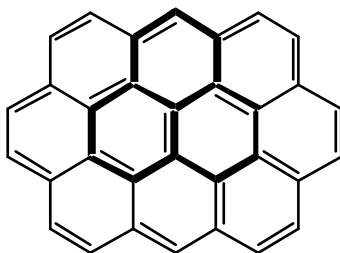
Each C₅ ring of dodecahedrane is a regular pentagon, while each C₆ ring of ovalene can be regarded as a regular hexagon.

- 3.1 What are the $\angle(\text{CCC})$ angles for each of these rings?
- 3.2 Which configuration (trigonal planar, 120°; tetrahedral, 109.5°; or octahedral, 90°) do the above $\angle(\text{CCC})$ angles most closely match?
- 3.3 What is the hybridization (sp , sp^2 , or sp^3) which most closely conforms to the geometric structure of dodecahedrane, and of ovalene?

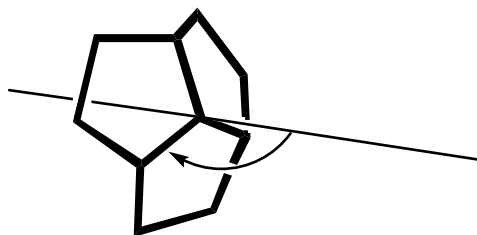
A “junction” is defined here to mean any 3-ring system, sharing a common central carbon atom, within a molecule. Compare the junctions (shown in bold) of three pentagons within dodecahedrane:



and of three hexagons within ovalene:

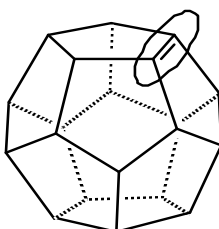


Consider an axis passing through the central carbon atom of each juncture such that the angle the axis forms with all three C-C bonds radiating from this C atom is identical.

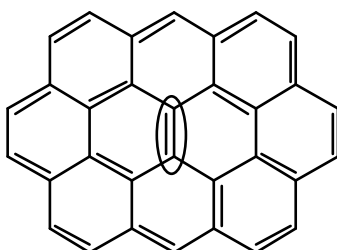


- 3.4** What is the value of this angle for dodecahedrane (make an “educated guess”, to the nearest three degrees), and for ovalene?
- 3.5** Subtracting 90° from each of the above angles describes the deviation from planarity for each juncture. Which juncture is planar ?

Now consider two polycyclic 'alkenes', dodecahedrene ($C_{20}H_{18}$):



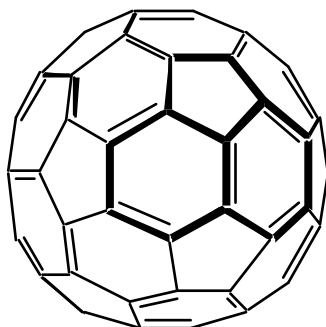
and ovalene:



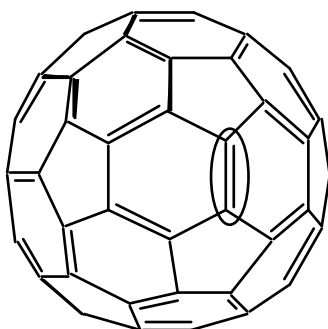
Assume that the molecular framework is rigid and is not significantly distorted by H_2 addition to the (indicated) double bond on each structure. Assume also that all double bonds are localized in assessing these systems.

3.6 Compare the indicated pairs of carbon atoms (encircled above). For which C=C pair is H₂ addition expected to be more exothermic?

And now, on to fullerenes. For all known fullerenes, the deviation from planarity at any juncture is less than is the case for dodecadedrane.



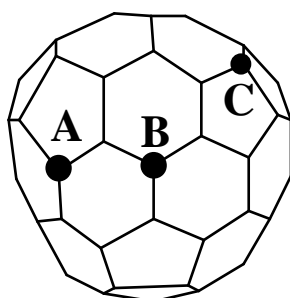
For C₆₀, all junctures are entirely equivalent. Now consider H₂ addition at a C=C bond of C₆₀:



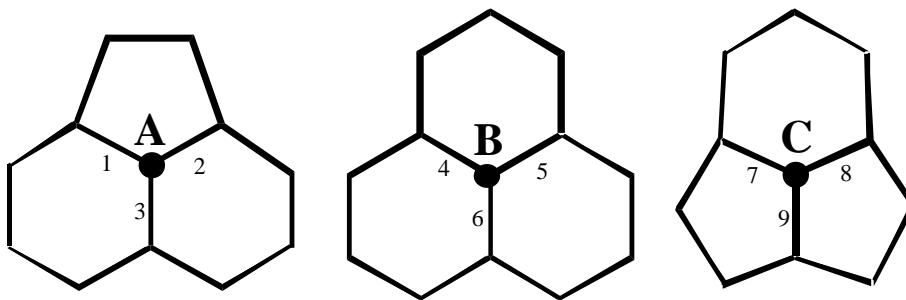
3.7 For which of C₆₀, dodecahedrene, or ovalene is H₂ addition most exothermic? (Again, assume localization of double bonds.)

3.8 For which of C₆₀, dodecahedrene, or ovalene is H₂ addition least exothermic?

There is evidence for fullerenes smaller than C₆₀, such as C₅₈. The C₅₈ structure (ignoring any distinction between 'double' and 'single' bonds) is shown below:

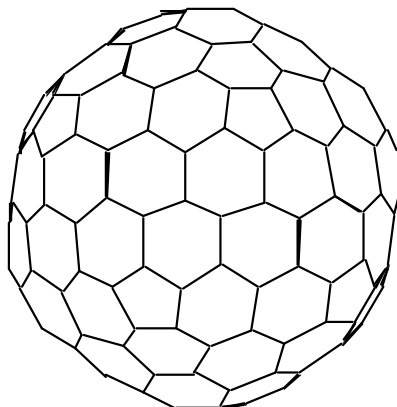


The junctures centred on atoms **A**, **B** and **C** on the above structure can be redrawn for greater clarity:



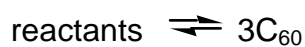
- 3.9 Which juncture has the least deviation from planarity ?
- 3.10 Which juncture has the greatest deviation from planarity ?
- 3.11 Of the above carbon-carbon bonds, numbered from 1 to 9, which represents the most favourable site for H₂ addition?

Finally, consider a larger fullerene, C₁₈₀:

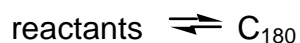


To a first approximation, both C₆₀ and C₁₈₀ are "perfect" spheres.

- 3.12 Which has the larger average deviation from planarity at each juncture? C₆₀ or C₁₈₀?
- 3.13 Compare the geometries of C₆₀ and C₁₈₀, and graphite. Which of the statements shown on the answer sheet (concerning enthalpies of formation, in kJ g⁻¹ units) is correct?
- Fullerenes are generated on a very rapid timescale, typically milliseconds. In all techniques, C₆₀ is produced in much greater quantities than C₁₈₀.
- 3.14 Which of the graphs shown on the answer template best represents the dependence of potential energy upon reaction progress for the two processes:



and



SOLUTION

3.1 Dodecahedrane: 108 °
 Ovalene 120 °

3.2 Dodecahedrane: tetrahedral
 Ovalene: trigonal planar

The $\angle(\text{CCC})$ angle for dodecahedrane is only slightly lower than the tetrahedral angle, but is much higher than the 90° required for octahedral coordination and is obviously too low for a trigonal planar arrangement. The corresponding angle for ovalene is identical to that for trigonal planar.

3.3 Dodecahedrane: sp^3
 Ovalene: sp^2

Reasoning: As above, dodecahedrane conforms quite closely to a tetrahedral arrangement at each C atom, thus sp^3 . Ovalene corresponds exactly to a trigonal planar arrangement, so sp^2 .

3.4 Dodecahedrane, $\text{C}_{20}\text{H}_{20}$ 109 -115 degrees
 ovalene, $\text{C}_{32}\text{H}_{14}$ 90 degrees

Reasoning: For dodecahedrane, the three rings are not coplanar. Determination of the exact axis angle is complicated; but note that the $\angle(\text{CCC})$ angle for a C_5 ring is very close to the tetrahedral angle. Therefore distortion from a tetrahedral configuration at each carbon in dodecahedrane is slight: therefore the axis angle is about 109.5° (more probably –112°). For ovalene, all rings are coplanar. The axis angle is clearly 90°.

3.5 Correct: Ovalene, $\text{C}_{32}\text{H}_{14}$

3.6 H_2 addition is more exothermic dodecahedrene.

Reasoning: The C=C pair within the dodecahedrene skeleton is more suited to sp^3 -hybridization than sp^2 -hybridization: this favours dihydrogenation to yield dodecahedrane. For ovalene, sp^3 -hybridization is disfavoured relative to sp^2 -

hybridization, so dihydrogenation at the indicated site is disfavoured on the grounds of angle strain.

(This is quite apart from any reduction in ovalene's aromaticity, which is also likely to disfavour hydrogenation!)

3.7 H₂ addition from among C₆₀, dodecahedrene, ovalene is most exothermic for dodecahedrene.

Reasoning: The deviation from planarity, in a C₆₀ juncture, is less than in dodecahedrene (which has very close to tetrahedral, i.e. sp³, coordination at each carbon) but is clearly more than in ovalene (which is flat, i.e. ideal for sp² hybridization). Thus C₆₀ is intermediate between dodecahedrene and ovalene in its preference for hydrogenated versus dehydrogenated structures. The junctures in dodecahedrene are all pentagons [C₅,C₅,C₅]. The junctures in ovalene are all [C₆,C₆,C₆]. Those in C₆₀ are [C₅,C₆,C₆]. The implication is that, the more pentagons are found in a juncture, the greater the deviation from planarity and hence the greater the relative stability of sp³ hybridization, rather than sp², at the central carbon atom.

3.8 H₂ addition from among C₆₀, dodecahedrene and ovalene is the least exothermic for ovalene.

3.9 The least deviation from planarity is in **B**.

3.10 The greatest deviation from planarity is in **C**.

Reasoning: The juncture centred on atom 'A' features two hexagons and a pentagon: this is the same pattern as that seen in the Ceo junctures. For 'B', the three surrounding rings are all hexagons, while for 'C', the juncture contains two pentagons and a hexagon. The trend for increasing deviation from planarity with increasing number of pentagons in the juncture indicates that the deviation from planarity will be most severe at 'C', and least severe at 'B'.

3.11 The most favourable site for H₂ addition is at bond number 9.

Reasoning: Bonds 1,2,7, and 8 are each flanked by a pentagon and a hexagon. Bonds 3-6 are each 'sandwiched' between two hexagons. Bond 9 is between two adjacent pentagons. Of these configurations, bond 9 represents the geometry which is most distorted from planarity (preferred by sp^2 hybridization) and is closest to the dodecahedrane skeleton (for which the bond angles are almost ideal for sp^3 hybridization). Thus, bond 9 is the most favourable site for dihydrogenation.

3.12 The larger average deviation from planarity at each juncture is in C₆₀.

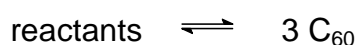
Reasoning: C₁₈₀ obviously has a larger diameter than C₆₀, so its average deviation from planarity at a given juncture is less than that found for C₆₀. [To visualize this, it may help to note that the 'equator' of C₁₈₀ will be defined by more atoms than are found along C₆₀'s 'equator'.]

3.13 The correct statement:

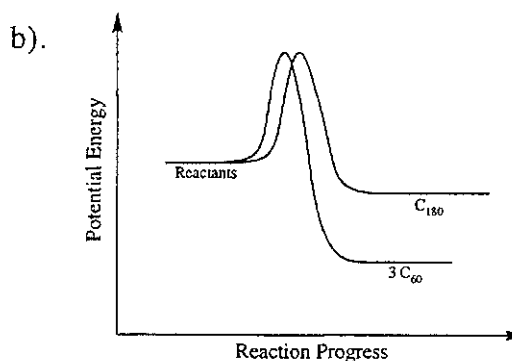
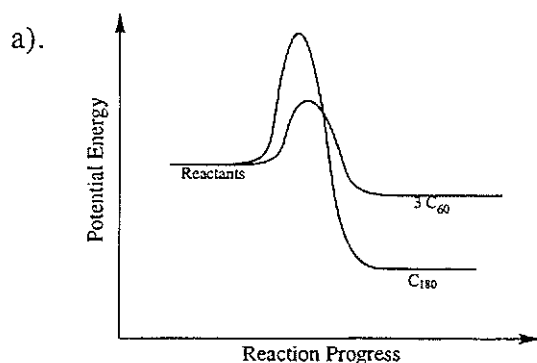
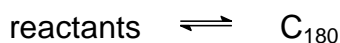
$$\Delta_f H^\circ (\text{C}_{60}) > \Delta_f H^\circ (\text{C}_{180}) > \Delta_f H^\circ (\text{graphite})$$

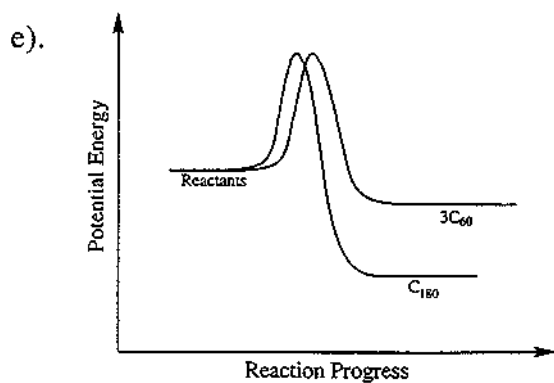
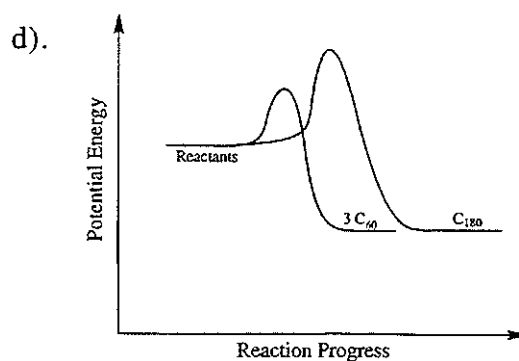
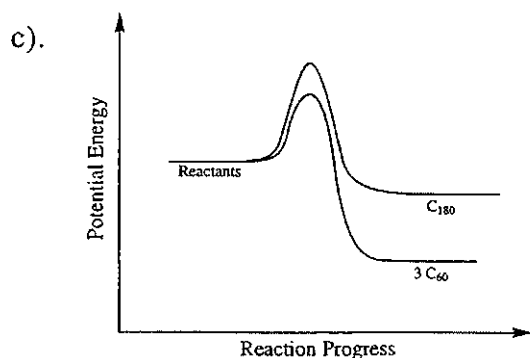
Reasoning: C₆₀ has a larger average deviation from planarity than C₁₈₀, so sp^2 hybridization is less favourable for the smaller fullerene. However, both fullerenes are non-planar and therefore less amenable to sp^2 hybridization than graphite (which additionally gets stabilization from inter-layer electronic effects, although this last point does not have to be considered to attain the correct answer).

3.14 Which of graphs best represents the dependence of potential energy upon reaction progress for the two processes:



and





The best graph is: a)

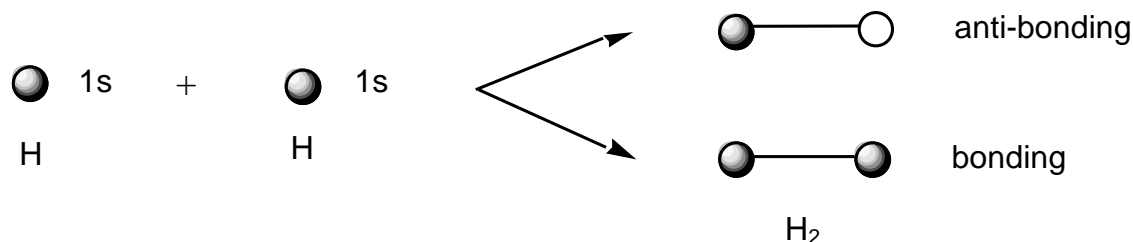
Reasoning: The equilibrium reaction



is characterized by a large positive energy change in going from left to middle, and a negative energy change of smaller magnitude in going from middle to right. Formation of C_{180} is thermodynamically favoured over three C_{60} molecules. However, C_{60} is found to predominate, implying that the reaction is under kinetic control and does not have sufficient time to reach equilibrium.

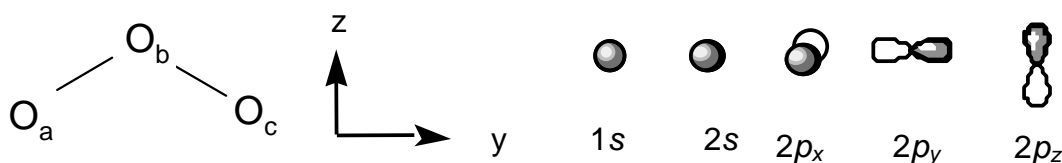
PROBLEM 4

When two hydrogen atoms come together, the 1s atomic orbitals combine to form bonding and anti-bonding molecular orbitals:



In a similar way, we may combine the atomic orbitals of more complicated atoms to form molecular orbitals, taking into account the symmetry of the molecule.

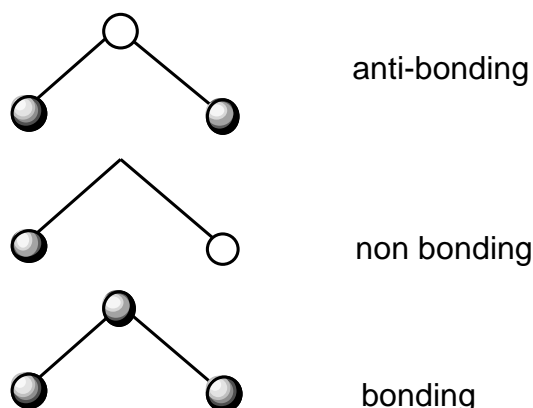
Consider the ozone molecule, O_3 , which is shaped like an Australian boomerang. We can arrange the oxygens as follows (in the yz plane) and assume that there are 1s, 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals on each atom.



The atoms O_a and O_c are "related by symmetry" and the 1s orbitals on these atoms form symmetric and anti-symmetric combinations:



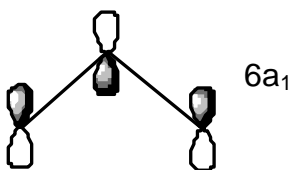
In this molecule the 1s atomic orbital on O_b is classified as symmetric. It can combine with the symmetric combination of O_a and O_c given above (but not with the anti-symmetric combination) to form bonding and anti-bonding molecular orbitals. The anti-symmetric combination is non-bonding. The final three molecular orbitals are:



- 4.1** On the answer sheet, use a similar approach to construct the molecular orbitals arising from the separate interaction of the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. (Remember to form the symmetric and anti-symmetric combinations of O_a and O_c first.)

We may now rearrange these molecular orbitals in order of increasing energy. This can be generalised to other triatomic molecules. The energy of these orbitals is different in a bent triatomic molecule (like ozone) compared to a linear molecule (like carbon dioxide). The variation in orbital energy may be represented in a "Walsh diagram" for XY_2 molecules as shown on the answer sheet. It shows a plot of the energy of each orbital versus the $Y-X-Y$ bond angle. The orbitals have been given labels which we call "symmetry labels".

The $6a_1$ orbital referred to in the Walsh diagram is shown below.



- 4.2** Why does the energy of the $6a_1$ orbital increase so rapidly as the bond angle changes from 90° to 180° ?

Only occupied molecular orbitals affect the geometry, and a doubly occupied orbital has more influence than a singly occupied orbital. For example, O_3 has 24 electrons and so at a bond angle of 135° the orbitals are doubly occupied up to $6a_1$. Thus, the lowest-energy geometry of ozone (taking into account steric repulsion and the contrasting energy

behaviour of the $4b_2$, $1a_2$ and $6a_1$ orbitals) is probably towards the left of the Walsh diagram, which is consistent with the observed bond angle of 116° .

4.3 At a bond angle of 135° , what are the highest occupied orbitals for the molecules BO_2 , CO_2 , NO_2 and FO_2 ?

4.4 The bond angles of BO_2 , CO_2 and O_3 are known experimentally to be 180° , 180° and 116° , respectively. Use the Walsh diagram on the answer sheet to predict whether NO_2 and FO_2 are more or less bent than O_3 .

SOLUTION

4.1 Construction of the molecular orbitals arising from the separate interaction of the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals is shown on the next page.

4.2 Why does the energy of the $6a_1$ orbital increase so rapidly as the bond angle changes from 90° to 180° ? (Choose one)

- Because the bonding character decreases.
- Because the anti-bonding character increases.
- Both (a) and (b).
- Because the overlap decreases.

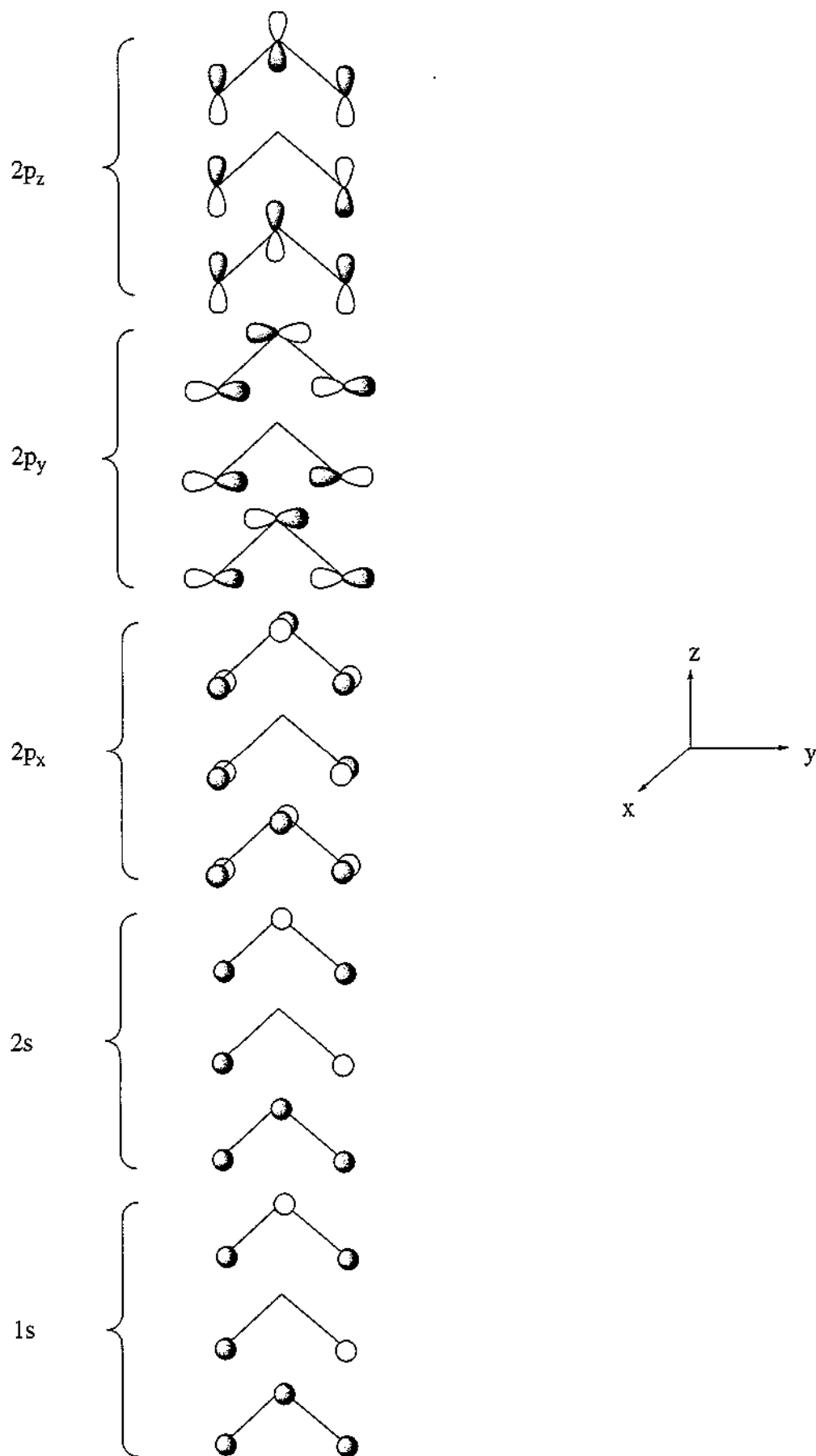
The correct answer is c).

Reasoning: The energy changes so rapidly because the overlap is bonding between all three atoms in the bent molecule, but becomes more and more anti-bonding as the molecule approaches linearity:

4.3	O_3	BO_2	CO_2	NO_2	FO_2
	$6a_x (24e^-)$	$4b_2 (21e^-)$	$4b_2 (22e^-)$	$6a_1 (23e^-)$	$2b_x (25e^-)$

4.4 The correct answer is (d): NO_2 is less bent than O_3 , and FO_2 is more bent than O_3 .

Atomic orbitals Molecular orbitals



PROBLEM 5

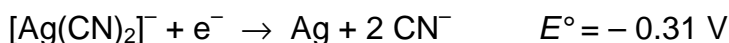
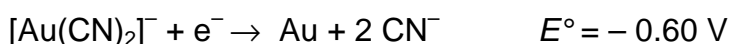
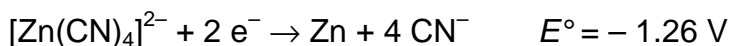
Metallic gold frequently is found in aluminosilicate rocks and it is finely dispersed among other minerals. It may be extracted by treating the crushed rock with aerated sodium cyanide solution. During this process metallic gold is slowly converted to $[\text{Au}(\text{CN})_2]^-$, which is soluble in water (reaction 1).

After equilibrium has been reached, the aqueous phase is pumped off and the metallic gold is recovered from it by reacting the gold complex with zinc, which is converted to $[\text{Zn}(\text{CN})_4]^{2-}$ (reaction 2).

5.1 Write balanced ionic equations for reactions (1) and (2).

Gold in nature is frequently alloyed with silver which is also oxidized by aerated sodium cyanide solution.

5.2 Five hundred litres (500 L) of a solution 0.0100 M in $[\text{Au}(\text{CN})_2]^-$ and 0.0030 M in $[\text{Ag}(\text{CN})_2]^-$ was evaporated to one third of the original volume and was treated with zinc (40 g). Assuming that deviation from standard conditions is unimportant and that all these redox reactions go essentially to completion, calculate the concentrations of $[\text{Au}(\text{CN})_2]^-$ and of $[\text{Ag}(\text{CN})_2]^-$ after reaction has ceased.

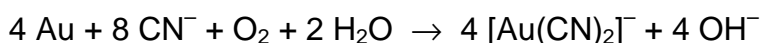


5.3 $[\text{Au}(\text{CN})_2]^-$ is a very stable complex under certain conditions. What concentration of sodium cyanide is required to keep 99 mol% of the gold in solution in the form of the cyanide complex? $\{[\text{Au}(\text{CN})_2]^- : K_f = 4 \times 10^{28}\}$

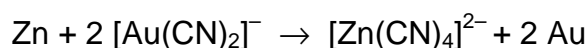
5.4 There have been several efforts to develop alternative gold extraction processes which could replace this one. Why? Choose one of the options on the answer sheet.

SOLUTION

5.1 Reaction 1:



reaction 2:



$$5.2 \quad E^{\circ}(\text{Ag}/\text{Zn}) = -0.31 - (-1.26) = 0.95 \text{ V}$$

$$E^{\circ}(\text{Au}/\text{Zn}) = -0.60 - (-1.26) = 0.66 \text{ V}$$

$$E^{\circ}(\text{Ag}/\text{Zn}) > E^{\circ}(\text{Au}/\text{Zn})$$

Therefore the Ag(I) complex will be reduced first.

$$(i) \quad \text{mol Ag(I) in } 500 \text{ dm}^3 = 500 \times 0.0030 = 1.5 \text{ mol}$$

$$(ii) \quad \text{mol Au(I) in } 500 \text{ dm}^3 = 500 \times 0.010 = 5.0 \text{ mol}$$

$$(iii) \quad \text{mol Zn in } 40 \text{ g} = 40 / 65.38 = 0.61 \text{ mol}$$

1 mol zinc reacts with 2 mol of Ag(I) or Au(I)

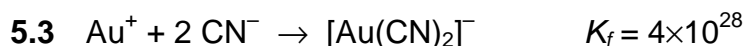
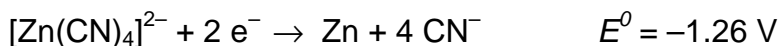
Therefore 0.61 mol Zn will consume 1.2 mol $[\text{Ag}(\text{CN})_2]^-$

$$[\text{Ag}(\text{CN})_2]^- \text{ remaining} = 1.5 - 1.2 = 0.3 \text{ mol}$$

$[\text{Au}(\text{CN})_2]^-$ will not be reduced.

$$\text{Concentration of } [\text{Au}(\text{CN})_2]^- \text{ when reaction has ceased} = 0.010 \times 3 = 0.030 \text{ M}$$

$$\text{Concentration of } [\text{Ag}(\text{CN})_2]^- \text{ when reaction has ceased} = 0.3 \times (3 / 500) = 0.002 \text{ M}$$



99 mol % $[\text{Au}(\text{CN})_2]^-$

$$K_f = \frac{[\text{Au}(\text{CN})_2]^-}{[\text{Au}^+][\text{CN}^-]^2}$$

$$\frac{[\text{Au}(\text{CN})_2]^-}{[\text{Au}^+] + [\text{Au}(\text{CN})_2]^-} = 99 / 100$$

$$\text{Thus: } 100 \times [\text{Au}(\text{CN})_2]^- = 99 \times [\text{Au}^+] + 99 \times [\text{Au}(\text{CN})_2]^-$$

$$\text{Therefore } [\text{Au}^+] = [\text{Au}(\text{CN})_2]^- / 99$$

Substituting into K_f :

$$4 \times 10^{-28} = 99 / [\text{CN}^-]^2$$

$$[\text{CN}^-] = 5 \times 10^{-14}$$

- 5.4** Sodium cyanide escapes into ground water and produces hydrogen cyanide which is toxic to many animals.
-
-

PROBLEM 6

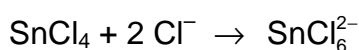
Unlike carbon, tin can increase its coordination number beyond four. Like carbon, tin forms a chloride, SnCl_4 .

6.1 Draw two alternative geometries for SnCl_4 .

Lewis acids such as SnCl_4 react with Lewis bases such as chloride ion or amines. In the case of chloride the following two reactions are observed.



and



6.2 Draw three alternative geometries for SnCl_5^- .

6.3 Use Valence Shell Electron Pair Repulsion (VSEPR) theory to predict which geometry is likely to be preferred for SnCl_5^- .

6.4 Draw three alternative geometries for SnCl_6^{2-} .

6.5 Use VSEPR theory to predict which of these geometries is likely to be preferred for SnCl_6^{2-} .

A solution containing SnCl_6^{2-} (as the tetrabutylammonium salt) was examined by negative ion electrospray mass spectrometry (ESMS). The spectrum contains a single peak at $m/z = 295$.

You may assume that the only isotopes observed in this species are ^{120}Sn and ^{35}Cl .

6.6 Write the empirical formula for the tin-containing species detected by this technique.

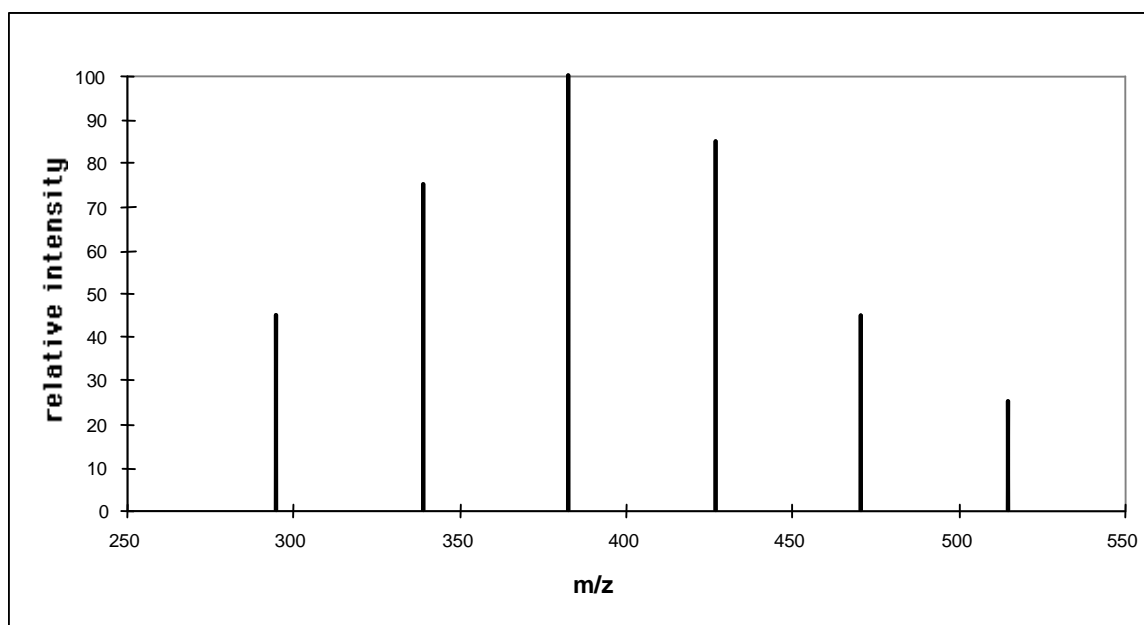
A solution containing SnBr_6^{2-} (as the tetrabutylammonium salt) was examined by negative ion electrospray mass spectrometry (ESMS). The spectrum contains a single peak at $m/z=515$.

You may assume that the only isotopes observed in this species are ^{120}Sn and ^{79}Br .

6.7 Write the formula for the tin-containing species detected by this technique.

The ESMS spectrum of a solution made by mixing equimolar amounts of SnCl_6^{2-} and SnBr_6^{2-} (as tetrabutylammonium salts) shows six major species (Fig. 1).

Fig. 1



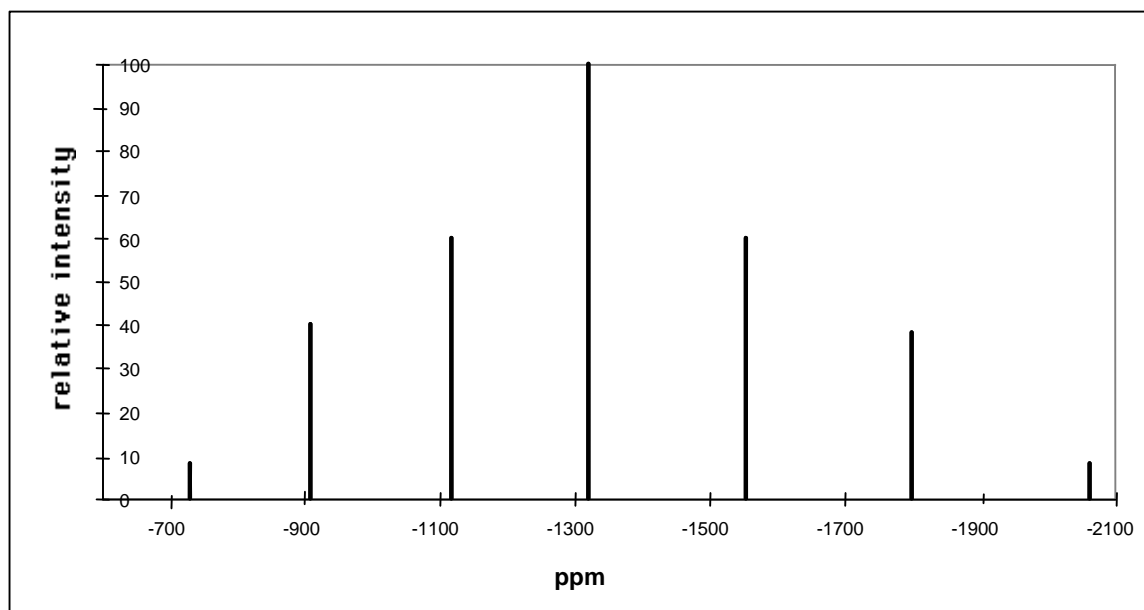
6.8 Write the empirical formula for each of the four new species.

^1H and ^{13}C NMR spectroscopy of molecules enable detection of a separate signal for each proton and ^{13}C nucleus which is in a different environment. These signals are recorded on dimensionless parts per million (ppm) scale relative to some agreed standard reference compound. Similarly, ^{119}Sn NMR gives a signal for each tin atom which is in a different environment.

The ^{119}Sn NMR spectrum of a solution of SnCl_6^{2-} (as the tetrabutylammonium salt) contains only one signal which occurs at -732 ppm (relative to tetramethyltin, Me_4Sn). The ^{119}Sn NMR spectrum of a solution of SnBr_6^{2-} (as the tetrabutylammonium salt) occurs at 2064 ppm. The ^{119}Sn NMR spectrum at 60°C of a solution formed by mixing equimolar amounts of SnCl_6^{2-} and SnBr_6^{2-} contains seven peaks (Fig. 2).

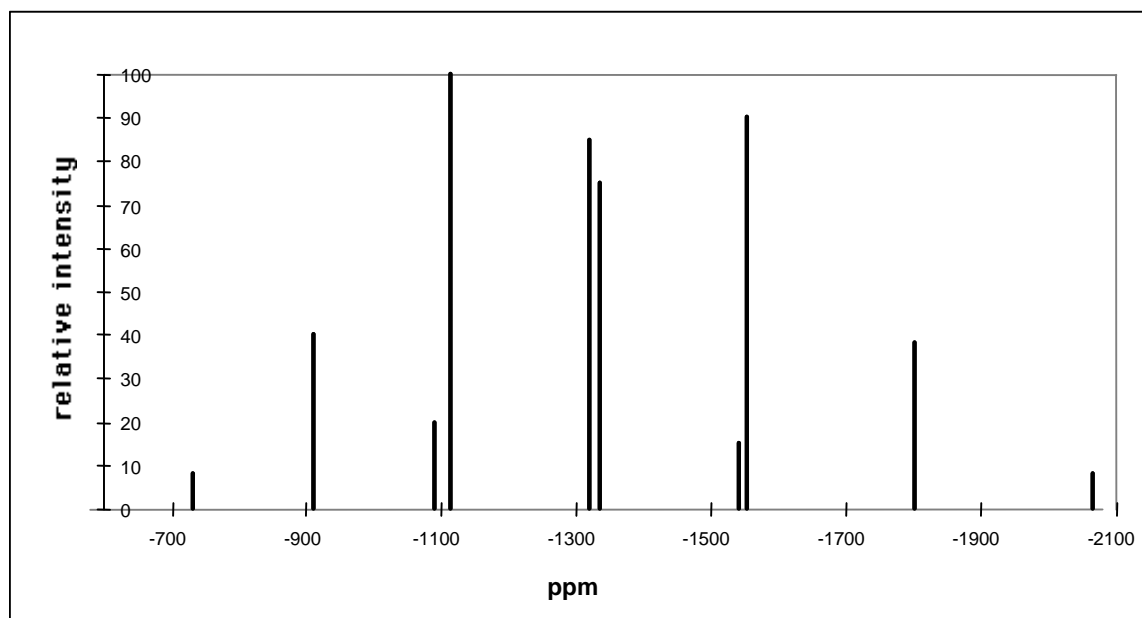
6.9 Write the empirical formula for the tin-containing species in this mixture that give rise to the peaks listed on the answer template.

Fig. 2



Cooling the solution causes a change to this ^{119}Sn NMR spectrum and at $-30\text{ }^\circ\text{C}$ ten peaks are observed (Fig. 3).

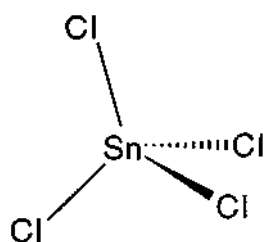
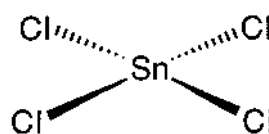
Fig. 3



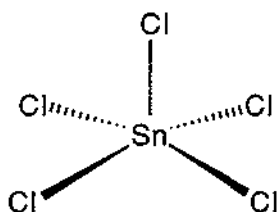
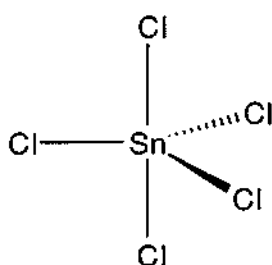
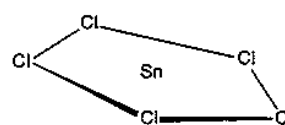
6.10 Draw the geometry for the four tin-containing species present in this solution at $-30\text{ }^\circ\text{C}$ that give rise to the peaks at -1092 and -1115 , -1322 and -1336 ppm.

SOLUTION

6.1

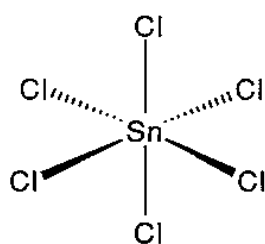
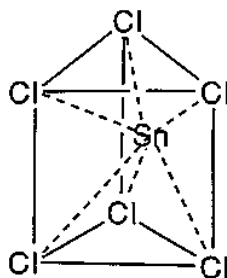
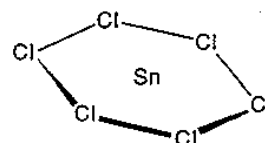
A

B


6.2

C

D

E


6.3 In accordance with VSEPR theory geometry D is likely to be preferred for SnCl_5^- .

6.4

F

G

H


6.5 In accordance with VSEPR theory geometry of F is likely to be preferred for SnCl_5^-

 6.6 SnCl_5^-

 6.7 SnBr_5^-

 6.8 $m/z = 339$: SnCl_4Br^- $m/z = 427$: $\text{SnCl}_2\text{Br}_3^-$
 $m/z = 383$: $\text{SnCl}_3\text{Br}_2^-$ $m/z = 471$: SnClBr_4^-

6.9	- 912 ppm:	$\text{SnCl}_5\text{Br}^{2-}$
	-1117 ppm:	$\text{SnCl}_4\text{Br}_2^{2-}$
	-1322 ppm:	$\text{SnCl}_3\text{Br}_3^{2-}$
	-1554 ppm:	$\text{SnCl}_2\text{Br}_4^{2-}$
	-1800 ppm:	SnClBr_5^{2-}

6.10

-1092 ppm and -1115 ppm (2 compounds)



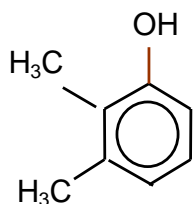
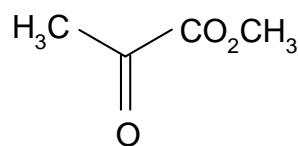
-1322 ppm and -1336 ppm (2 compounds)



PROBLEM 7

The structures needed to read this question are shown in the answer template.

The fungus *Aspergillus nidulans* produces two isomeric aromatic lactones (cyclic esters) **A** and **B** ($C_{10}H_{10}O_4$) each of which dissolved in cold aqueous NaOH but not in aqueous NaHCO₃. Both **A** and **B** gave a violet colour with aqueous FeCl₃. Reaction of **A** with CH₃I in the presence of K₂CO₃ gave **C** ($C_{11}H_{12}O_4$) which was shown by ¹H NMR spectroscopy to contain three non-identical methyl groups one of which was bonded directly to an aromatic ring. Selective demethylation of **C** with BCl₃ followed by aqueous work up gave **D** a new isomer of **A**. The ¹H NMR spectrum of compound **D** clearly showed the presence of an intramolecularly hydrogen bonded hydroxyl group at δ 11.8 ppm.

**E****I**

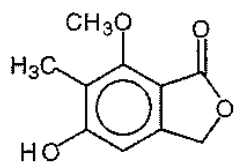
Compound **D** was synthesised as follows: The phenol **E** was methylated (MeI/K₂CO₃) to afford **F** ($C_9H_{12}O_2$) which in turn was reduced with lithium metal in liquid ammonia and 2-methyl-propan-2-ol to give the symmetrical unconjugated diene **G**. Conjugation of this diene was achieved by reaction with KNH₂ in liquid ammonia followed by aqueous work up, a process which afforded only one product **H**. Ozonolysis of **H** followed by non reductive work up afforded amongst other products the ketoester **I**. Compound **H** underwent a Diels-Alder reaction with dimethyl but-2-ynedioate **J** to give the adduct **K** ($C_{15}H_{20}O_6$) which upon heating expelled ethene to afford an aromatic ester **L**. Basic hydrolysis of **L** followed by acidification of the solution gave **M** ($C_{11}H_{12}O_6$) which when heated under vacuum yielded **N** ($C_{11}H_{10}O_5$). Reduction of **N** with NaBH₄ in dimethylformamide gave **C** and an isomeric lactone **O** which could also be obtained by the methylation of **B**.

7.1 Using the answer template provided fill in the structures **A** to **O**.

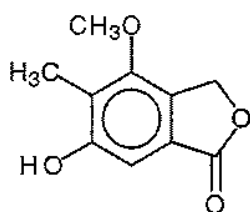
7.2 Using the last space on the answer template provide a second structure for **B**.

SOLUTION

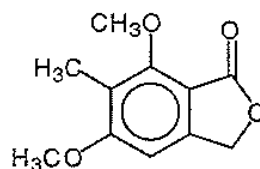
7.1 and 7.2



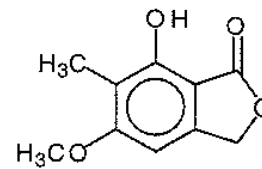
A



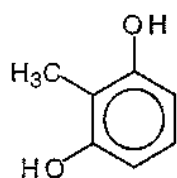
B



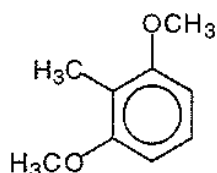
C



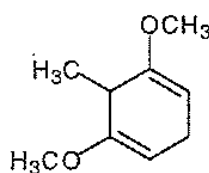
D



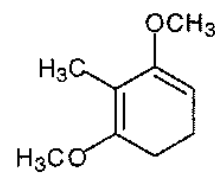
E



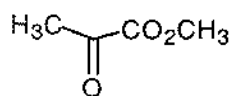
F



G



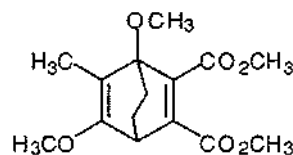
H



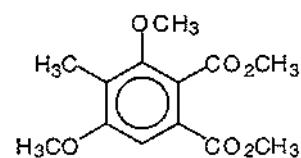
I



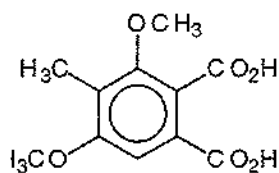
J



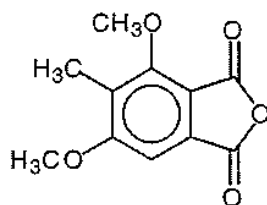
K



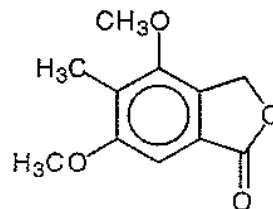
L



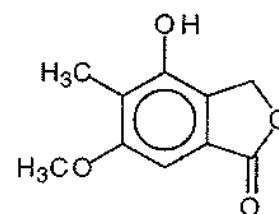
M



N



O



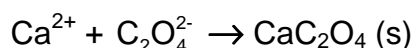
Other structure for **B**

PRACTICAL PROBLEMS

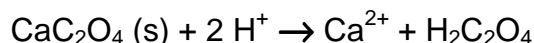
PROBLEM 1 (Practical)

Determination of Calcium by Precipitation with Oxalate Followed by Titration with Permanganate.

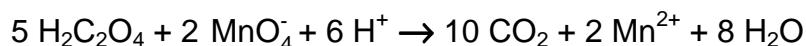
In this exercise, you must determine the amount of calcium ion in a solution that contains both calcium and magnesium, by selectively precipitating only the calcium as calcium oxalate, then quantitatively removing the precipitate from the solution by filtration.



The precipitate must then be re-dissolved in acid:



The liberated oxalic acid is titrated with standard permanganate solution:



Formation of the calcium oxalate precipitate

- Use a 25.00 cm³ pipette and 250.0 cm³ volumetric flask to accurately dilute (by a factor of 10), the calcium/magnesium solution that has been provided for you.

Analyse two samples of the dilute calcium/magnesium solution. You have sufficient reagents for three analyses, but you must plan your time and use of equipment carefully. Take each of your samples through the following procedure:

- Transfer a 25.00 cm³ aliquot of the dilute calcium/magnesium solution into a 250 cm³ beaker, add approximately 10 cm³ of 3 M H₂SO₄ and about 50 cm³ of water.

CARE! 3 M H₂SO₄ is very corrosive! The following steps involve hot (nearly boiling) solutions. Be careful and beware of steam!

- Cover the beaker with a watch glass and gently heat on a hotplate until the solution is very hot, but not boiling.
- Remove the beaker from the heat, then carefully add solid ammonium oxalate (1.5 g) and swirl the beaker until most of the ammonium oxalate dissolves.

CARE! Oxalate solutions are toxic. Do not wash solutions that contain oxalate down the sink. Place them in the "Permanganate/Oxalate residues" bottle at the end of your bench.

5. Add 5 –10 drops of methyl red indicator to the beaker, then while the solution is hot, increase the *pH* of the solution by slowly adding 1 : 1 ammonia solution with constant stirring, until the colour just changes from pink to orange. If you add too much ammonia, the solution will turn yellow. To correct this problem, add 1 drop of 3 M H₂SO₄ to lower the *pH* again, then repeat the *pH* adjustment with ammonia solution.

CARE! 1 : 1 ammonia solution is corrosive and has a very strong smell! Keep the bottle stoppered when not in use.

6. Allow the solution to stand for at least 60 minutes to quantitatively precipitate the calcium oxalate. Do not stir the solution during this time.

You should complete Laboratory Task 2 during this waiting period.

Do not proceed to the next step until you are confident that precipitation is complete.

Filtration of the calcium oxalate precipitate

7. Prepare a filter paper in a filter funnel supported in the neck of a 250 cm³ conical flask. Rinse the paper with a few cm³ of water then decant most of the supernatant solution from step 6. into the filter funnel. Collect the filtrate in the conical flask. Use a wash bottle to rinse the watch glass into the filter funnel.
8. Test the filtrate for the presence of calcium ion by adding a drop of ammonium oxalate test solution to a drop of the filtrate on a black plastic sheet. If a white precipitate (or cloudiness) is formed, the calcium oxalate precipitation in step 6 was unfortunately not complete. Perhaps the *pH* was not adjusted correctly or insufficient time was allowed for precipitation. Depending on the time you have left, you may start the analysis again or you may continue with the present experiment.
9. If there is no detectable calcium ion in the filtrate, use a wash bottle to carefully wash the calcium oxalate precipitate into the filter. Use the rubber “policeman” on the end of a glass rod to remove the last traces of precipitate from the beaker, and rinse these into the filter.
10. Wash the precipitate 4 times with approximately 10 cm³ portions of water, collecting the washings in the conical flask.

11. Discard the combined filtrates from the previous steps into the residue bottle labeled "Permanganate/Oxalate residues" then carefully rinse the conical flask with water into the residue bottle.
12. Wash the precipitate one more time with 10 cm³ of water. Collect this filtrate in the conical flask and test it for the presence of oxalate by adding a drop of saturated calcium nitrate solution to a drop of the filtrate on a black plastic sheet. If a white precipitate (or cloudiness) is formed, continue washing and testing until the washings are free from oxalate.
13. When the precipitate is free of oxalate, discard the washings and rinse and drain the conical flask.

NOTE! Show your demonstrator your precipitates. You must ask your demonstrator to sign your results sheet before proceeding to the next step.

14. Use a glass rod to break a small hole in the bottom of the filter paper and wash the precipitate through the hole into the conical flask with approximately 20 cm³ water. Take care to rinse the rod and the creases of the filter paper.
15. Use a Pasteur pipette to dissolve any traces of calcium oxalate that remain in the paper with 25 cm³ 3 M sulphuric acid, collecting the acid in the conical flask. Finally, rinse the paper with ~ 20 cm³ water.

Titration with permanganate

16. Make the volume up to about 100 cm³ with water, heat the solution to about 60 °C, then when all the calcium oxalate precipitate is dissolved, carefully titrate the hot solution with standard potassium permanganate solution.
CARE! It is not necessary to measure the temperature of the solution with a thermometer. 60 °C is uncomfortably hot to touch.
17. Discard the titrated solution into the residue bottle labelled "**Permanganate/Oxalate residues**".

Calculate the average concentration of calcium ion in the original calcium/magnesium solution that was provided.

Molar masses in g mol^{-1} : Ca 40.08, Mg 24.31, Mn 54.94, C 12.01, O 16.00.

SOLUTION

Model solution

Analysis of calcium/magnesium solution

Permanganate titration

Concentration of standard KMnO_4 solution: $0.02039 \text{ mol dm}^{-3}$

Titration number	1	2	3
initial burette reading (cm^3)	0.90	0.80	3.00
final burette reading (cm^3)	28.55	28.45	30.80
volume of standard KMnO_4 (cm^3)	27.65	27.65	27.80
Average titre (cm^3)	27.70		

In a 25 cm^3 aliquot of dilute Ca/Mg solution:

$n(\text{KMnO}_4)$ required to titrate oxalate from dissolved calcium oxalate precipitate

$$n(\text{KMnO}_4) = 0.0198 \text{ mol dm}^{-3} \times 0.0277 \text{ dm}^3 = 5.485 \times 10^{-4} \text{ mol}$$

$n(\text{oxalate})$ from dissolved calcium oxalate precipitate:

$$n(\text{oxalate}) = 5/2 \times 5.485 \times 10^{-4} \text{ mol} = 1.371 \times 10^{-3} \text{ mol}$$

$n(\text{Ca}^{2+})$ from dissolved calcium oxalate precipitate = $n(\text{oxalate}) = 1.371 \times 10^{-3} \text{ mol}$

$$c(\text{Ca}) = 1.371 \times 10^{-3} \text{ mol} / 0.02500 \text{ dm}^3 = 0.0548 \text{ mol dm}^{-3}$$

In original Ca/Mg solution:

$$c(\text{Ca}) = 0.0548 \text{ mol dm}^{-3}$$

PROBLEM 2 (Practical)**Analysis of a Mixture of Cobalt(III) Complexes**

When the complex $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ is prepared in the laboratory, it often contains a considerable amount of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ by-product.

In this exercise, you must determine the amount of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ in a sample that also contains only $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ as a by-product, using a cation-exchange procedure. The cation exchange resin used in this exercise is a cross-linked polystyrene resin of the strong acid type. It contains $-\text{SO}_3\text{H}$ groups from which the H^+ can be exchanged. When a solution containing 1 mol of M^{n+} is allowed to react with the resin this liberates n mol of H^+ . In this exercise, the solution resulting from ion exchange of the mixture of the two different complex cations is used to titrate a standardised NaOH solution.

Preparation of the cation exchange resin

You are provided with about 10 g of wet resin in the H^+ form. Wash the resin using the following procedure to remove all traces of free acid:

1. Transfer your resin to a 250 cm³ beaker, washing it from the container with about 50 cm³ of water, then let the resin settle. This will take a few minutes.
2. Carefully pour off (decant) as much of the acidic solution as possible into a 'waste' beaker. Try to minimise loss of any of the resin in this process. Wash the resin with ~20 cm³ portions of distilled water and test a drop of washing solution using a glass rod and pH paper until the excess acid is completely removed ($\text{pH} \sim 5$). You should not need to use more than 200 cm³ of water to do this.
3. Drain off all but enough water to leave the resin just covered with water.
Be sure to put all your acidic wash solutions into a waste bottle labelled "acid waste" - not down the sink! Do not allow the resin to dry out.

Preparation and standardisation of approximately 0.0125 M NaOH

4. Prepare 250.0 cm³ of approximately 0.0125 M NaOH by accurately diluting your ~0.125 M NaOH with distilled water in a volumetric flask.
5. With the standard 0.01253 M HCl that is provided, titrate 25.00 cm³ aliquots of the diluted NaOH solution, using phenolphthalein indicator.

Analysis Procedure

You are provided with approximately 40 cm³ of a 0.00500 M solution of HCl that contains 0.2000 g of a mixture of the cobalt(III) complexes [Co(NH₃)₅NO₂]Cl₂ and [Co(NH₃)₆]Cl₃ in 40.00 cm³.

- Use a pipette to transfer a 25.00 cm³ aliquot of the cobalt complex solution into a 250 cm³ beaker (beaker No 1) and add ~25 cm³ water.
 - Use a plastic spoon to add about half (~5 g) of your wet resin to the cobalt(III) solution and allow to stand for at least 5 minutes for ion-exchange to take place, liberating H⁺. You should occasionally gently swirl the mixture to hasten the ion-exchange process.
 - Carefully wash the acidic solution into a second 250 cm³ beaker (beaker No 2) with about 20 cm³ of distilled water. Try to leave as much as possible of the resin behind. Notice that the solution is now much lighter in colour, indicating that most, but not all of the cobalt complex mixture is stuck to the resin. You must now remove the last traces of cobalt(III) from solution (liberating more acid in the process), with a second batch of resin.
 - Add most of the remainder of your resin (~4 g) to the solution in beaker No 2 and again allow to stand for at least 5 minutes to allow the cation exchange to take place, liberating more H⁺.
- At the end of this process, the solution should be colourless - if not, (perhaps you did not wait long enough for ion-exchange to take place) repeat the ion-exchange and washing steps with the last portion (~1 g) of your ion-exchange resin.
- Filter the two resin samples through a carefully washed filter paper, and collect the acidic filtrate in a 100 cm³ volumetric flask. Carefully wash the resin with small portions of water into the volumetric flask and make up to the mark with water.
 - With this acid solution titrate 25.00 cm³ aliquots of your standardized NaOH solution.

Calculate the number of moles of H⁺ liberated by the 25 cm³ aliquot of your mixture of cobalt(III) complexes and report the percentage of [Co(NH₃)₅NO₂]Cl₂ that is present in your sample.

Molar masses in g mol⁻¹: Co 58.93; N 14.01; H 1.01; Cl 35.45; O 16.00.

SOLUTION**Model solution**Standardization of 0.0125 M NaOHConcentration of standard HCl in bottle: 0.01253... mol dm⁻³

Titration number	1	2	3
aliquot of NaOH	25.00	25.00	25.00
initial burette reading (cm ³)	13.60	17.40	10.35
final burette reading (cm ³)	37.75	41.50	34.45
volume of standard KMnO ₄ (cm ³)	24.15	24.10	24.10
Average titre (cm ³)	24.12		

$$c(\text{NaOH}) = 0.01250 \text{ mol dm}^{-3} \times 0.02412 \text{ dm}^3 = 0.01206 \text{ mol dm}^{-3}$$

Aliquot of cobalt complex solution used for ion-exchange: 25 cm³

Titration number	1	2	3
initial burette reading (cm ³)	26.25	16.10	3.80
final burette reading (cm ³)	48.50	38.40	26.20
volume of standard KMnO ₄ (cm ³)	22.25	22.30	22.40
Average titre (cm ³)	22.32		

Calculations $c(\text{H}^+)$ collected in 100 cm³ flask:

$$c(\text{H}^+) = 0.01206 \text{ mol dm}^{-3} \times (25.00 \text{ cm}^3) / (22.32 \text{ cm}^3) = 0.01351 \text{ mol dm}^{-3}$$

total $n(\text{H}^+)$ collected from column:

$$n(\text{H}^+) = 0.01351 \text{ mol dm}^{-3} \times 0.100 \text{ dm}^3 = 1.351 \times 10^{-3} \text{ mol}$$

 $n(\text{H}^+)$ from aliquot put onto column:

$$n(\text{H}^+) = 0.00500 \text{ mol dm}^{-3} \times 0.02500 \text{ dm}^3 = 1.250 \times 10^{-4} \text{ mol}$$

 $n(\text{H}^+)$ ion-exchanged from complexes in aliquot put onto column:

$$n(\text{H}^+) = 1.351 \times 10^{-3} \text{ mol} - 1.250 \times 10^{-4} \text{ mol} = 1.226 \times 10^{-3} \text{ mol}$$

let y = mass $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ in 25.00 cm³ aliquot of mixture added to column mass of mixture added to column = $(25.00 \text{ cm}^3 / 40 \text{ cm}^3) \times 0.2000 \text{ g} = 0.1250 \text{ g}$

then mass $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in aliquot = $(0.1250 - y)$ g

$n(\text{H}^+)$ ion-exchanged from $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$:

$$n(\text{H}^+) = 2 y / 261.00 \text{ g mol}^{-1} = 0.007663x \text{ mol}$$

$n(\text{H}^+)$ ion-exchanged from $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$:

$$n(\text{H}^+) = 3 (0.1250 - y) \text{ g} / 267.50 \text{ g mol}^{-1} = (0.001402 - 0.011214 y) \text{ mol}$$

Thus, $0.007663 y + (0.001402 - 0.011214 y) = 0.001226$ or $y = 0.04956$ g

$$\% [\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2 = 100 (0.04956 \text{ g} / 0.1250 \text{ g}) = 39.6 \%$$