

# **30th International Chemistry Olympiad**

**Melbourne, Thursday July 9, 1998**

**Theoretical Examination**

**Problems**

**Official Version**

## Attention!

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- Write your name and personal identification code (posted at your workstation) in the upper corner of the first page of each problem's answer sheet. Write your name and code on all remaining answer sheets.
- You have 5 hours to complete all of the tasks, and record your results on the answer sheets. You must stop your work immediately after the STOP command is given. A delay in doing this by 3 minutes will lead to cancellation of the current task and will result in zero points for that task.
- All results must be written in the appropriate areas on the answer sheets. Anything written elsewhere will not be marked. Do not write anything on the back of your answer sheets. If you need more paper for working or a replacement answer sheet, request it from the supervisor.
- When you have finished the examination, you must put all of your papers into the envelope provided, then you must seal the envelope. Only papers in the sealed envelope will be marked.
- Do not leave the examination room until you are directed to do so. A receipt for your sealed envelope will be issued to you as you leave.
- Use only the pen and calculator provided.
- A Periodic Table will be provided for your use.
- This examination has **19** pages and **16** pages of answer sheets.
- Total points for this examination is **131**.
- An official English language version is available if you wish to see it.

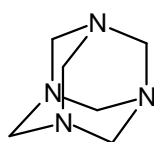
## Problem 1

20 points

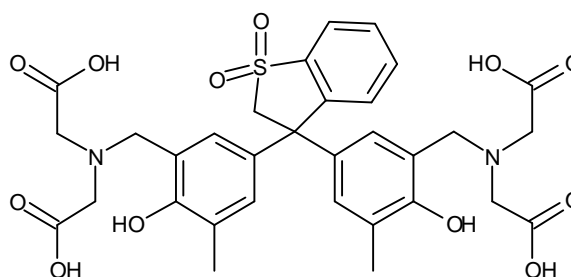
The following 8 steps describe the procedure for analysing a sample of an alloy that contains tin and lead.

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 all the 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. The solution was cooled then a precipitate of some tin compounds and a lead compound appeared.
3. A 25.00 mL aliquot of 0.2000 M Na<sub>2</sub>H<sub>2</sub>EDTA solution was added. The precipitate dissolved and a clear, colourless solution was obtained.
4. This solution was quantitatively transferred to a 250.0 mL volumetric flask and made up to the mark with distilled water.
5. A 25.00 mL aliquot of this solution was treated with 15 mL of a 30 % w/v solution of hexamine (hexamethylenetetramine), 130 mL of water and two drops of Xylenol Orange solution. The pH of the solution 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 mL.
7. 2.0 g of solid NaF was added to the titration flask. The solution immediately 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 mL.

Hexamine and Xylenol Orange have the structures shown below. The pK<sub>b</sub> of hexamine is 9.5. Xylenol Orange is red below pH 4, yellow above pH 5.



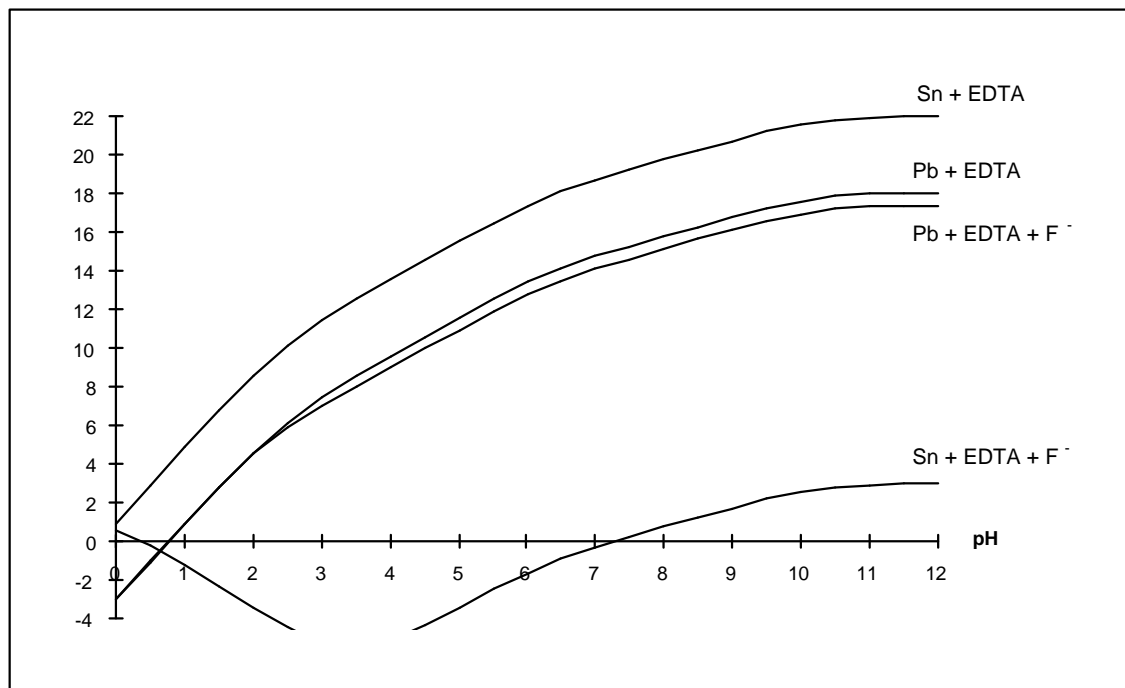
Hexamine



Xylenol Orange (XO)

$K'_{MY}$  is the conditional formation constant =  $\alpha K_{MY}$ .

$K'_{MY}$  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 lead compound that precipitated in Step 3 (at pH 6).
- 1-3. What is the purpose of hexamine in Step 5 of this analysis?
- 1-4. What is the purpose of Xylenol Orange in this analysis?
- 1-5. Write balanced ionic equations for the reactions that occur (i) during the titration and (ii) are 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 this 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 this analysis.
- 1-9. Write a balanced ionic equation that explains why the lines on the graph above of  $\log K'_{MY}$  vs pH for Pb+EDTA and Pb+EDTA+F<sup>-</sup> are coincident below pH 2.
- 1-10. Calculate the percentage by mass of Sn and Pb in the alloy.

**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 planting 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 = 22.3 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. Zinc-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**

<b>Radionuclide</b>	<b>Half-life</b>
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

$$D = \frac{\text{radioactivity per mg of resin}}{\text{radioactivity per mL of eluant.}}$$

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 by writing 1 to 4 (1 is best) the 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 whether each of the following statements is true or false.

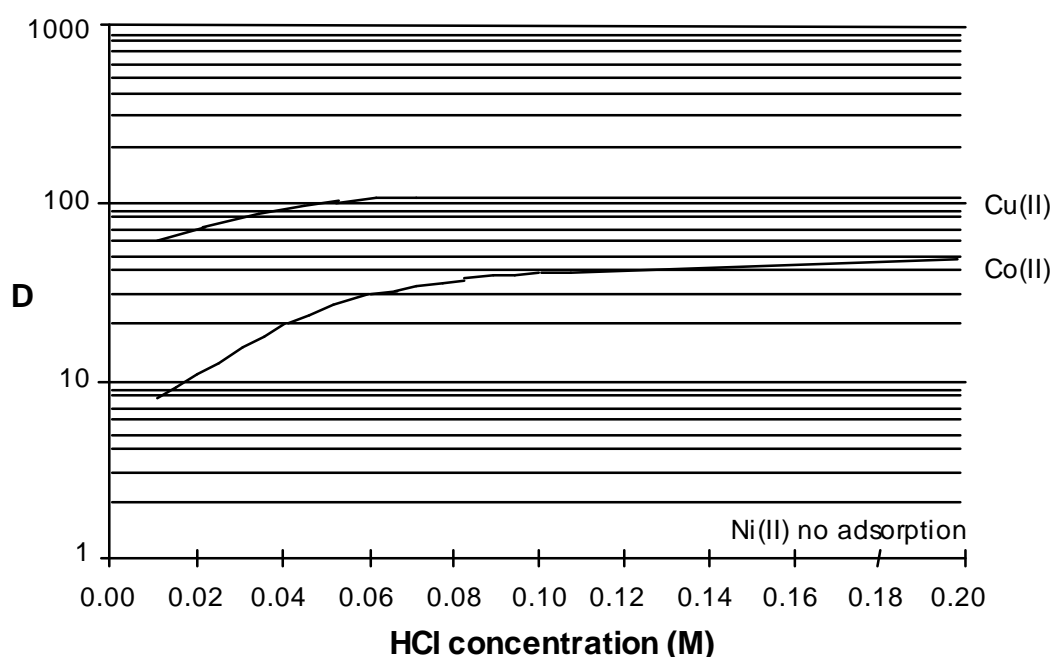
a).	Ni-57 may be present as a contaminant of Co-55.
b).	Co-57 will interfere with the medical use of Co-55.
c).	Cu-67 will interfere with the medical use of Cu-64.
d).	Ga-66 will interfere with the medical use of Ga-67.
e).	Ga-67 will interfere with the medical use of Cu-64.

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 whether each of the following statements is true or false.

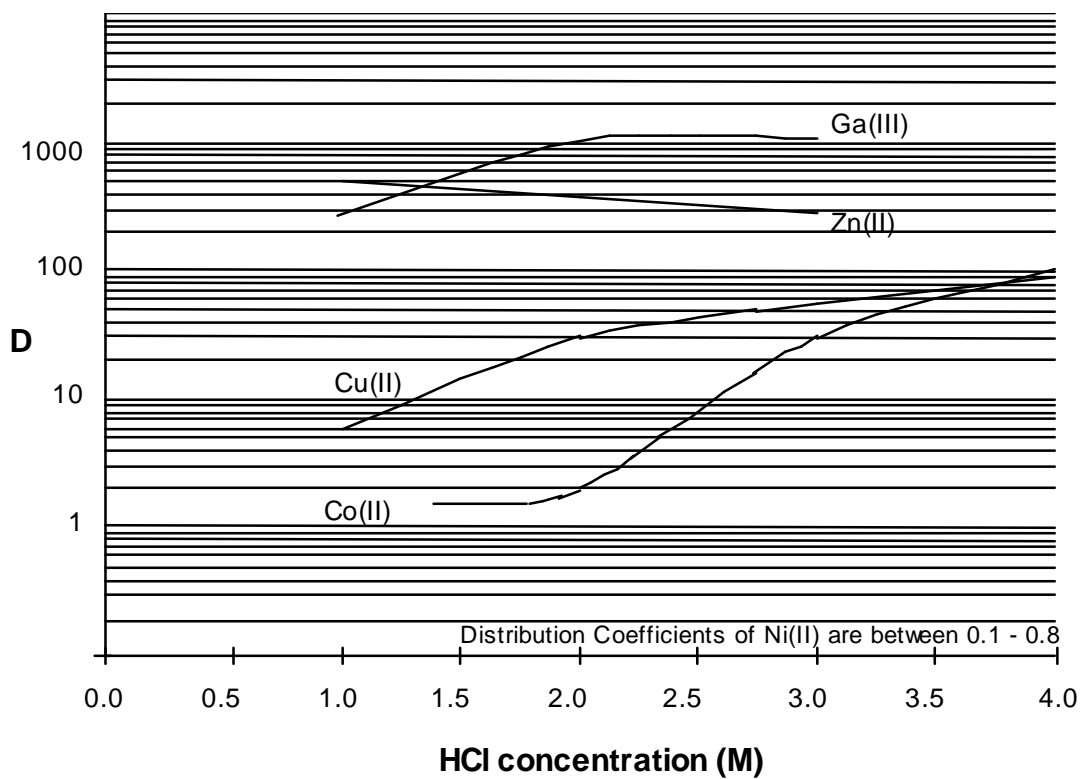
a).	Remove Ni-57 before isolating Co-55.
b).	Separate the Ni-57 from the bombarded target material before isolating the Ga-67.
c).	Separate the radionuclides closer to the end of bombardment.
d).	Allow the Ni-57 to decay before isolation of Co-55.

2-6. If zinc of natural isotopic abundance, instead of enriched Zn-68, was bombarded with high energy protons, indicate whether each of the following statements is true or false.

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 by Cu-64, Co-55, Co-57 and Ni-57 would increase.
d).	Ga-67 would be produced at lower yields and contamination by Cu-64, Co-55, Co-57 and 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)



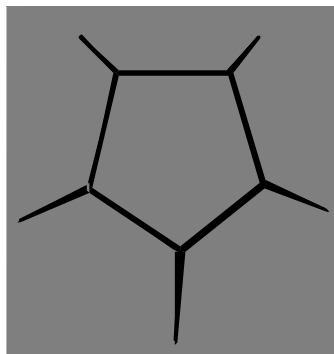
**Figure 2** - Distribution coefficients, D of metal ions between anion exchange resin and 55 % isopropyl alcohol at varying HCl concentrations.

### Problem 3

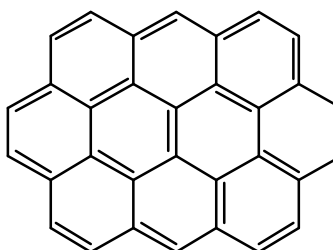
20 points

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

Dodecahedrane,  $C_{20}H_{20}$



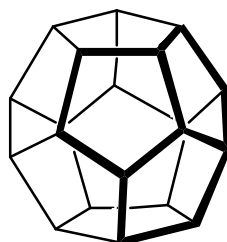
and Ovalene,  $C_{32}H_{14}$ .



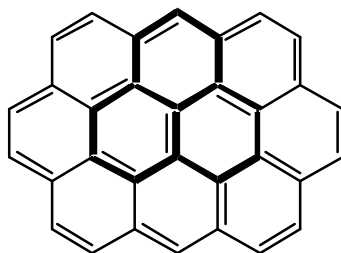
Each  $C_5$  ring of dodecahedrane is a regular pentagon, while each  $C_6$  ring of ovalene can be regarded as a regular hexagon.

- 3-1. What are the  $\angle(\text{CCC})$  angles for each of these rings?
- 3-2. Which configuration (trigonal planar,  $120^\circ$ ; tetrahedral,  $109.5^\circ$ ; or octahedral,  $90^\circ$ ) 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?

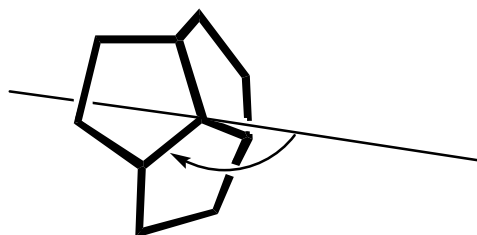
A “junction” is defined here to mean any 3-ring system, sharing a common central carbon atom, within a molecule. Compare the junctions (shown in bold) of three pentagons within dodecahedrane:



and of three hexagons within ovalene:

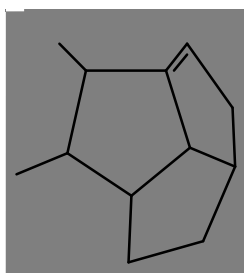


Consider an axis passing through the central carbon atom of each juncture such that the angle the axis forms with all three C-C bonds radiating from this C atom is identical.

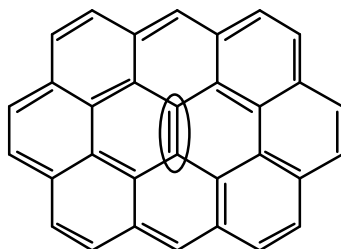


- 3-4. What is the value of this angle for dodecahedrane (make an “educated guess”, to the nearest three degrees), and for ovalene?
- 3-5. Subtracting  $90^\circ$  from each of the above angles describes the deviation from planarity for each juncture. Which juncture is planar ?

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



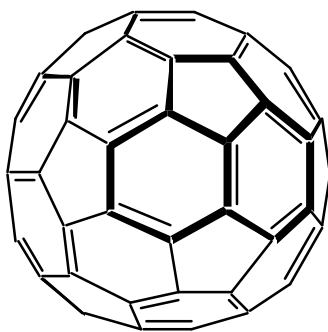
and ovalene:



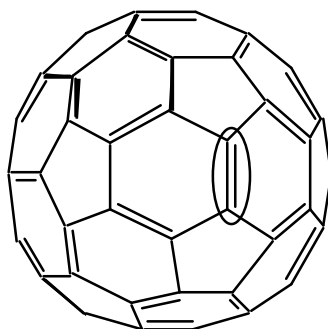
Assume that the molecular framework is rigid and is not significantly distorted by  $H_2$  addition to the (indicated) double bond on each structure. Assume also that all double bonds are localized in assessing these systems.

3-6. Compare the indicated pairs of carbon atoms (encircled above). For which  $C=C$  pair is  $H_2$  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 dodecahedrane.



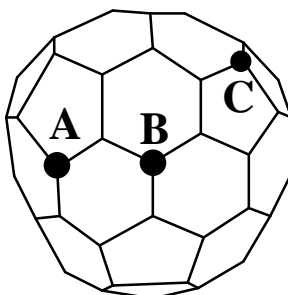
For  $C_{60}$ , all junctures are entirely equivalent. Now consider  $H_2$  addition at a  $C=C$  bond of  $C_{60}$ :



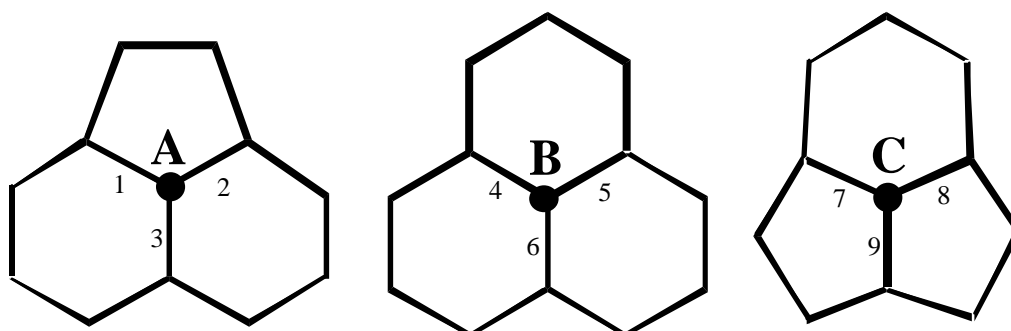
3-7. For which of  $C_{60}$ , dodecahedrene, or ovalene is  $H_2$  addition most exothermic? (Again, assume localization of double bonds)

3-8. For which of  $C_{60}$ , dodecahedrene, or ovalene is  $H_2$  addition least exothermic?

There is evidence for fullerenes smaller than  $C_{60}$ , such as  $C_{58}$ . The  $C_{58}$  structure (ignoring any distinction between 'double' and 'single' bonds) is shown below:

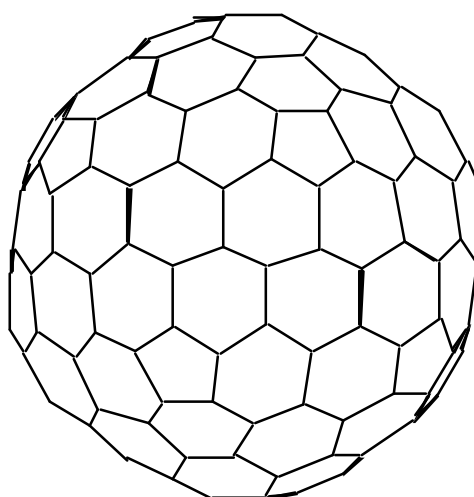


The junctures centred on atoms **A**, **B** and **C** on the above structure can be redrawn for greater clarity:



- 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  $H_2$  addition?

Finally, consider a larger fullerene,  $C_{180}$ :

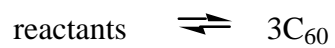


To a first approximation, both  $C_{60}$  and  $C_{180}$  are 'perfect' spheres.

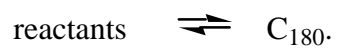
- 3-12. Which has the larger average deviation from planarity at each juncture?  $C_{60}$  or  $C_{180}$ ?
- 3.13 Compare the geometries of  $C_{60}$  and  $C_{180}$ , and graphite. Which of the statements shown on the answer sheet (concerning enthalpies of formation, **in  $kJ\ g^{-1}$  units**) is correct?

Fullerenes are generated on a very rapid timescale, typically milliseconds. In all techniques,  $C_{60}$  is produced in much greater quantities than  $C_{180}$ .

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:



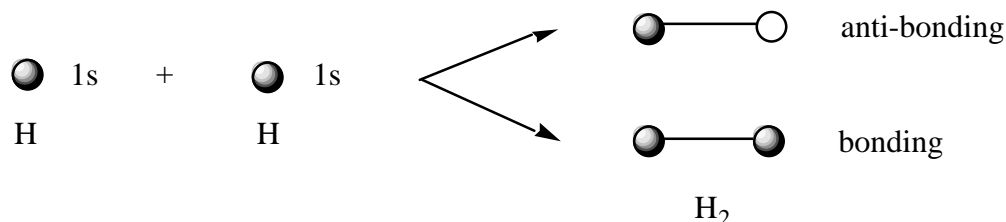
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## Problem 4

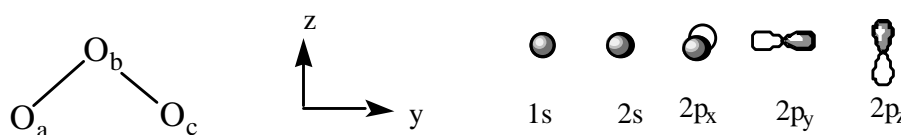
15 points

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.

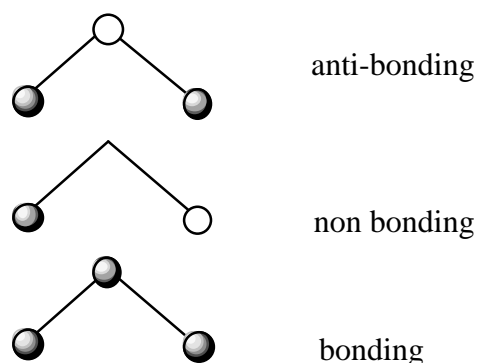
Consider the ozone molecule, O<sub>3</sub>, which is shaped like an Australian boomerang. We can arrange the oxygens as follows (in the *yz* plane) and assume that there are 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub> and 2p<sub>z</sub> orbitals on each atom.



The atoms O<sub>a</sub> and O<sub>c</sub> are "related by symmetry" and the 1s orbitals on these atoms form symmetric and anti-symmetric combinations:



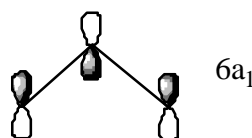
In this molecule the 1s atomic orbital on O<sub>b</sub> is classified as symmetric. It can combine with the symmetric combination of O<sub>a</sub> and O<sub>c</sub> given above (but not with the anti-symmetric combination) to form bonding and anti-bonding molecular orbitals. The anti-symmetric combination 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  $90^\circ$  to  $180^\circ$ ?

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  $135^\circ$  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  $116^\circ$ .

- 4-3. At a bond angle of  $135^\circ$ , 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  $180^\circ$ ,  $180^\circ$  and  $116^\circ$ , respectively. Use the Walsh diagram on the answer sheet to predict whether  $NO_2$  and  $FO_2$  are more or less bent than  $O_3$ .

## Problem 5

15 points

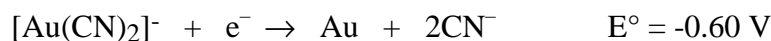
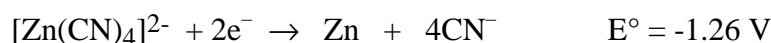
Metallic gold frequently is found in aluminosilicate rocks and it is finely dispersed among other minerals. It may be extracted by treating the crushed rock with aerated sodium cyanide solution. During this process metallic gold is slowly converted to  $[\text{Au}(\text{CN})_2]^-$ , which is soluble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

**Problem 6****20 points**

Unlike carbon, tin can increase its coordination number beyond four. Like carbon, tin forms a chloride,  $\text{SnCl}_4$ .

6-1. Draw two alternative geometries for  $\text{SnCl}_4$ .

Lewis acids such as  $\text{SnCl}_4$  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  $\text{SnCl}_5^-$ .

6-3. Use Valence Shell Electron Pair Repulsion (VSEPR) theory to predict which geometry is likely to be preferred for  $\text{SnCl}_5^-$ .

6-4. Draw three alternative geometries for  $\text{SnCl}_6^{2-}$ .

6-5. Use VSEPR theory to predict which of these geometries is likely to be preferred for  $\text{SnCl}_6^{2-}$ .

A solution containing  $\text{SnCl}_6^{2-}$  (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  $^{120}\text{Sn}$  and  $^{35}\text{Cl}$ .

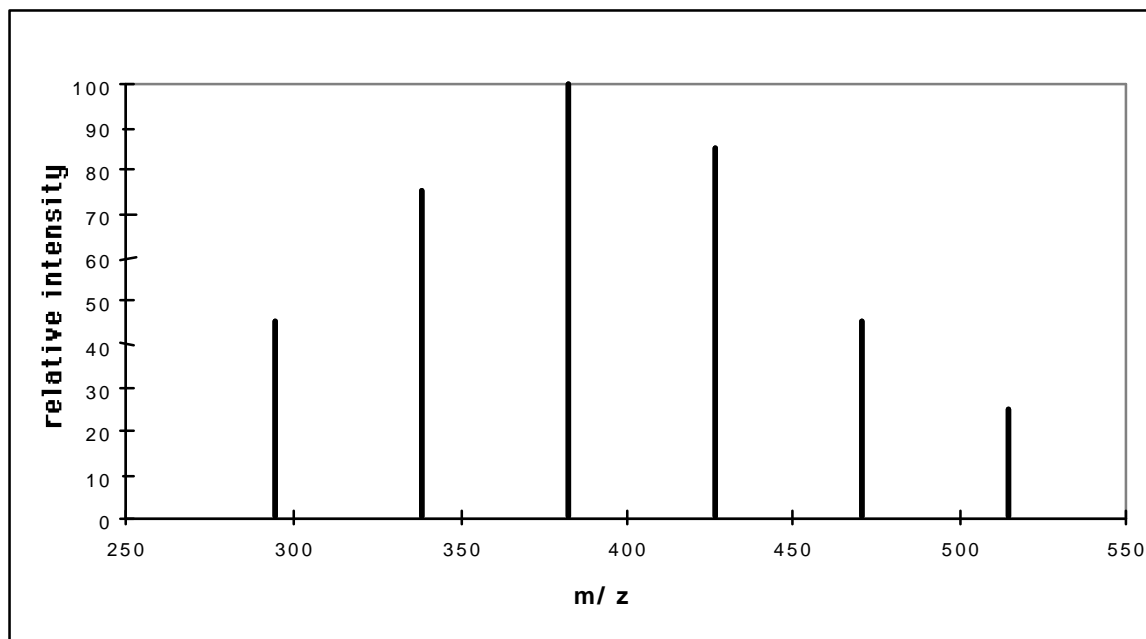
6-6. Write the empirical formula for the tin-containing species detected by this technique.

A solution containing  $\text{SnBr}_6^{2-}$  (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  $^{120}\text{Sn}$  and  $^{79}\text{Br}$ .

6-7. Write the empirical formula for the tin-containing species detected by this technique.

The ESMS spectrum of a solution made by mixing equimolar amounts of  $\text{SnCl}_6^{2-}$  and  $\text{SnBr}_6^{2-}$  (as tetrabutylammonium salts) shows six major species.

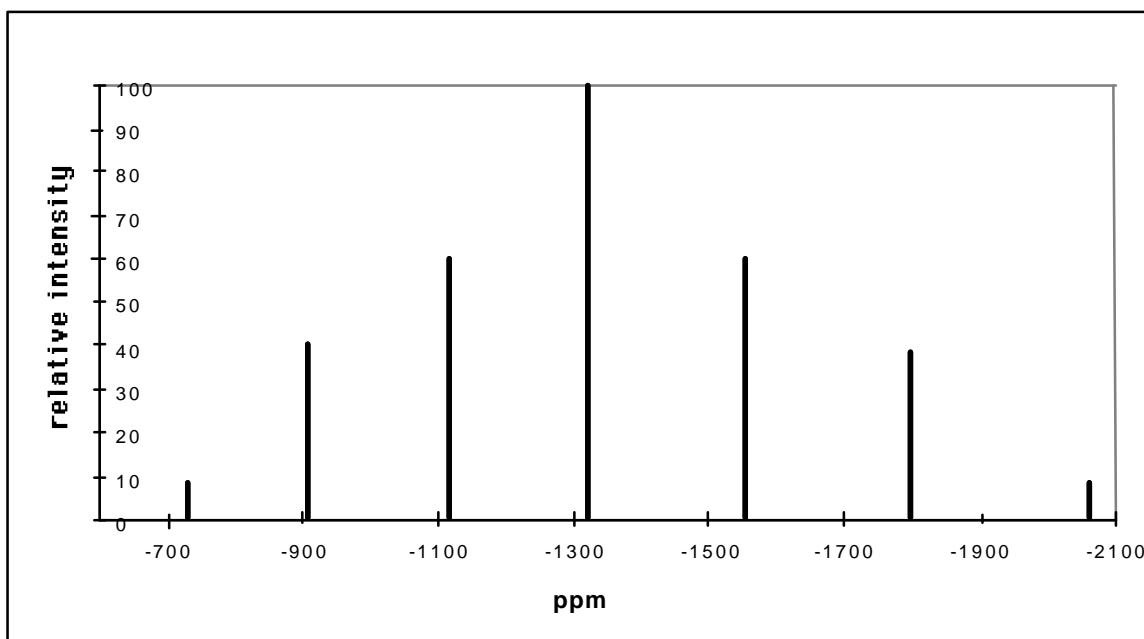


6-8. Write the formula for each of the four new species.

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

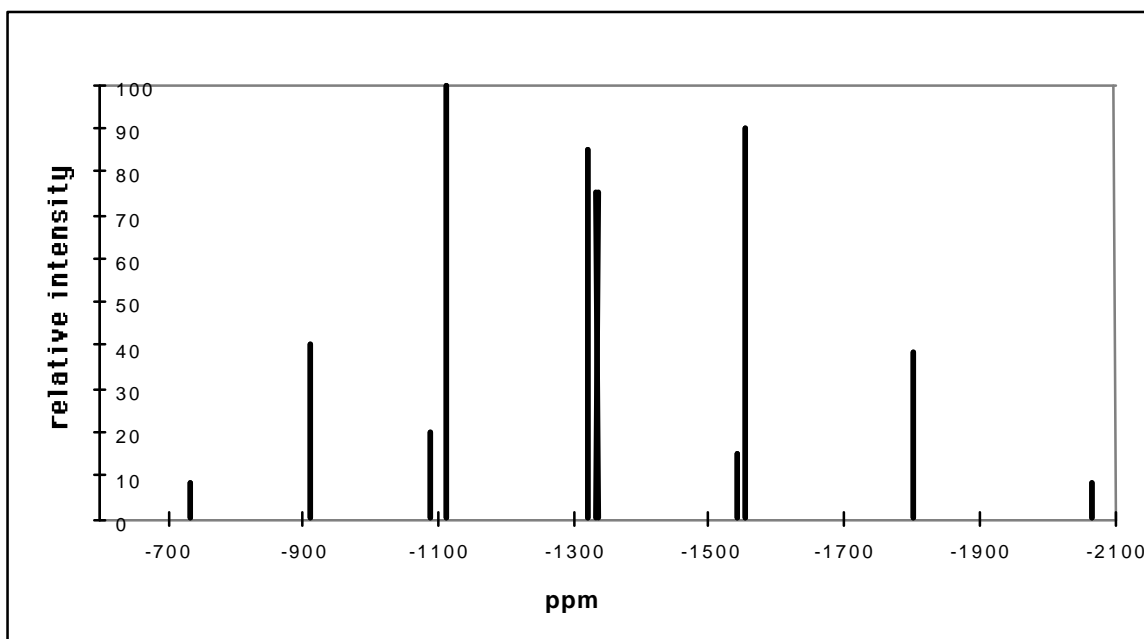
The  $^{119}\text{Sn}$  NMR spectrum of a solution of  $\text{SnCl}_6^{2-}$  (as the tetrabutylammonium salt) contains only one signal which occurs at -732 ppm (relative to tetramethyltin,  $\text{Me}_4\text{Sn}$ ).

The  $^{119}\text{Sn}$  NMR spectrum of a solution of  $\text{SnBr}_6^{2-}$  (as the tetrabutylammonium salt) occurs at -2064 ppm. The  $^{119}\text{Sn}$  NMR spectrum at 60 °C of a solution formed by mixing equimolar amounts of  $\text{SnCl}_6^{2-}$  and  $\text{SnBr}_6^{2-}$  contains seven peaks.



6-9. Write the empirical formula for each of the tin-containing species in this mixture that give rise to the five peaks listed on the answer template.

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

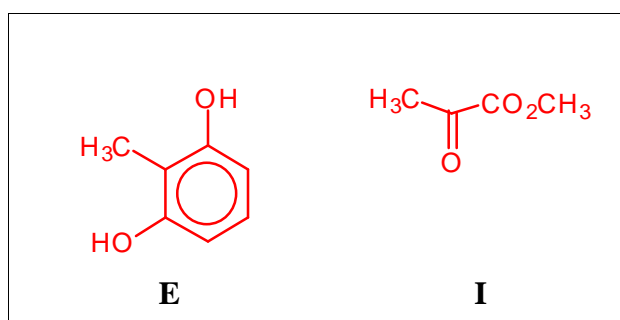


6-10. Draw the geometry for each of the four tin-containing species present in this solution at  $-30\text{ }^\circ\text{C}$  that give rise to the peaks at -1092 and -1115, -1322 and -1336 ppm.

**Problem 7****21 points**

**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  $NaHCO_3$ . Both **A** and **B** gave a violet colour with aqueous  $FeCl_3$ . Reaction of **A** with  $CH_3I$  in the presence of  $K_2CO_3$  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  $BCl_3$  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  $\delta$  11.8 ppm.

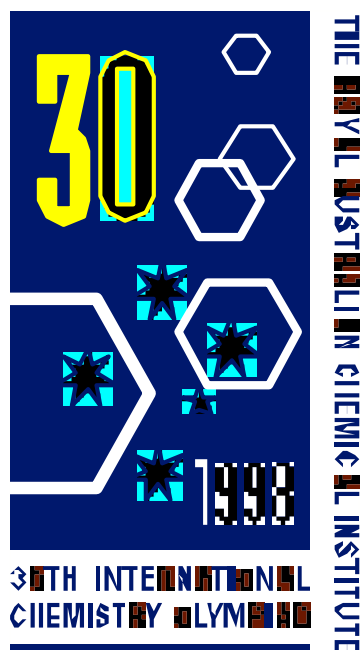


Compound **D** was synthesised as follows: The phenol **E** was methylated ( $MeI/K_2CO_3$ ) to afford **F** ( $C_9H_{12}O_2$ ) which in turn was reduced with lithium metal in liquid ammonia and 2-methyl-propan-2-ol to give the symmetrical unconjugated diene **G**. Conjugation of this diene was achieved by reaction with  $KNH_2$  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  $NaBH_4$  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**.



# **30th International Chemistry Olympiad**

**Melbourne, Thursday July 9, 1998**

## **Theoretical Examination**

**Example Answers and Marking Scheme**

**Official Version**

Name:

Team Code:

## Problem 1

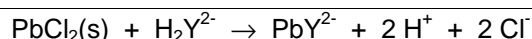
20 points

1-1. What is the lead compound that precipitates in Step 2?

PbCl<sub>2</sub> or any hydroxo species etc.

1 mark

1-2. Write a balanced ionic equation that explains the disappearance of the lead compound that precipitated in Step 3 (at pH 6).



or similar

-1/2 mark for H<sub>4</sub>Y or Y<sup>4-</sup>

1 mark

1-3. What is the purpose of the hexamine in Step 5 of this analysis? Tick one.

<input type="checkbox"/>	It complexes the tin
<input checked="" type="checkbox"/>	It forms a pH buffer
<input type="checkbox"/>	It reacts with oxides of nitrogen and chlorine
<input type="checkbox"/>	It is a pH indicator

1 mark

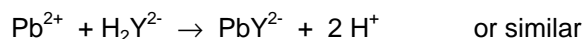
1-4. What is the purpose of the Xylenol Orange in this analysis? Tick one.

<input type="checkbox"/>	It complexes the tin
<input type="checkbox"/>	It acts as a pH buffer
<input checked="" type="checkbox"/>	It is a metallochromic indicator
<input type="checkbox"/>	It is a pH indicator

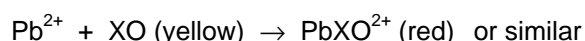
1 mark

1-5. Write balanced ionic equations for the reactions that occur (i) during the titration and (ii) are responsible for the colour change at the endpoint in Step 6 of the analysis.

The standard lead solution is used to complex the excess EDTA from step 5. Some of the EDTA is already tied up as stable SnY and PbY<sup>2-</sup> complexes. These species are not involved in the titration here. EDTA is mainly H<sub>2</sub>Y<sup>2-</sup> at pH 6, so in the following equations, H<sub>2</sub>Y<sup>2-</sup> must be used.



At the endpoint, a slight excess of Pb<sup>2+</sup> forms a red complex with the xylenol orange indicator



The titre here allows the calculation of excess EDTA, and therefore the total amounts of Sn+Pb to be determined.

2 marks

1-6. What is the role of the NaF in Step 7 of the analysis? Tick one.

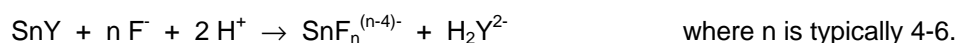
<input checked="" type="checkbox"/>	It complexes the tin
-------------------------------------	----------------------

	It acts as a pH buffer
	It complexes the lead
	It reacts with the Xylenol Orange

**1 mark**

1-7. Write a balanced ionic equation for the reaction that occurs in Step 7.

From the graph of  $\log K_{MY}$  vs pH, it can be seen that the fluoride forms a stable complex with  $\text{Sn}^{4+}$  but not with  $\text{Pb}^{2+}$  at pH 6, displacing EDTA:

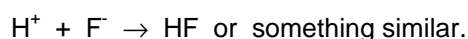
**1 mark**

1-8. Write a balanced ionic equation that explains why the colour changed from red to yellow in Step 7 of this analysis.

The released EDTA destroys the small amount of red  $\text{PbXO}$  complex, producing free (yellow) XO. (Charge on XO ignored)

**1 mark**1-9. Write a balanced ionic equation that explains why the lines on the graph of  $\log K'_{MY}$  vs pH for  $\text{Pb}+\text{EDTA}$  and  $\text{Pb}+\text{EDTA}+\text{F}^-$  are coincident below pH 2.

Below pH 2,  $\text{F}^-$  is protonated and does not compete effectively with Y for  $\text{Pb}^{2+}$

**1 mark**

1-10. Calculate the percentage by mass of Sn and Pb in the alloy.

From step 6, calculate the amount of EDTA in excess from the amount of standard  $\text{Pb}^{2+}$  titrant:  $n(\text{xs EDTA}) = n(\text{std. Pb}^{2+})$

$$= (24.05 \text{ mL})(0.009970 \text{ mol/L}) / (1000 \text{ mL/L}) = 2.398 \times 10^{-4} \text{ mol}$$

Next, calculate the original amount of EDTA present in a 25.00 mL aliquot of the solution of dissolved alloy,  $n(\text{init. EDTA})$

$$= (25.00 \text{ mL} / 250.0 \text{ mL})(25.00 \text{ mL})(0.2000 \text{ mol/L}) / 1000 \text{ mL/L} = 5.000 \times 10^{-4} \text{ mol}$$

Now calculate how much EDTA was consumed by the  $\text{Pb}^{2+}$  and  $\text{Sn}^{4+}$  in a 25 mL aliquot of the solution of dissolved alloy:

$$\begin{aligned} n(\text{EDTA consumed}) &= 5.000 \times 10^{-4} - 2.398 \times 10^{-4} \text{ mol} \\ &= 2.602 \times 10^{-4} \text{ mol} = n(\text{Pb}^{2+} + \text{Sn}^{4+}) \text{ in a 25 mL aliquot} \end{aligned}$$

From the titre in step 7, we calculate the amount of EDTA that is released from  $\text{SnY}$  by reaction with fluoride. (The fluoride is in large excess:  $2.0 \text{ g NaF} = 0.048 \text{ mol F}^-$  or  $0.3 \text{ M}$  in the  $160 \text{ mL}$  solution)

$$\begin{aligned} n(\text{released EDTA}) &= n(\text{std. Pb}^{2+}) \\ &= (15.00 \text{ mL})(0.009970 \text{ mol/L}) / (1000 \text{ mL/L}) = 1.496 \times 10^{-4} \text{ mol} \\ &= n(\text{Sn}^{4+}) \text{ in the 25 mL aliquot, so} \end{aligned}$$

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

So in the original  $0.4062 \text{ g}$  sample of alloy:

$$m(\text{Sn}) = (250 \text{ mL} / 25.00 \text{ mL})(1.496 \times 10^{-4} \text{ mol})(118.69 \text{ g/mol}) = 0.1776 \text{ g and}$$

$$m(\text{Pb}) = (250 \text{ mL} / 25.00 \text{ mL})(1.106 \times 10^{-4} \text{ mol})(207.19 \text{ g/mol}) = 0.2292 \text{ g}$$

-1/2 if sum of these masses used instead of sample mass

The percentages of tin and lead:

$$\text{Sn: } 100 \times (0.1776 / 0.4062) = \mathbf{43.7_2 \%} \text{ and Pb: } 100 \times (0.2292 / 0.4062) = \mathbf{56.4_2 \%}$$

Note the sum comes to 100.14% because of uncertainties in the titres. It is not correct to say %Sn = 100- %Pb or vice versa because there might have been other elements present in the alloy.

-2 marks if only one metal calc and other calc. by difference from 100%

-4 if only 1 calc.

-1 for abuse of sig figs.

**10 marks**

Name:

Team Code:

## Problem 2

20 points

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  
 $= 8 \times 22 \text{ years} = 176 \text{ years}$

2 marks

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

1 mark

**3 marks**

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?

	U-238 – U-234
	U-234 – Th-230
	Th-230 – Ra-226
3	Ra-226 – Rn-222

**1 mark**

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).

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

**3 marks**

A	B	C	D	Marks
4	1	2	3	3
3	1	2	4	2.5

4	2	1	3	2
3	2	1	4	1.5
All other combinations				0

- 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 whether each of the following statements is true or false.

	True	False
Ni-57 may be present as a contaminant of Co-55.		3
Co-57 will interfere with the medical use of Co-55.	3	
Cu-67 will interfere with the medical use of Cu-64.	3	
Ga-66 will interfere with the medical use of Ga-67.		3
Ga-67 will interfere with the medical use of Cu-64.		3

5 marks

- 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 whether each of the following statements is true or false.

	True	False
Remove Ni-57 before isolating Co-55.	3	
Separate the Ni-57 from the bombarded target material before isolating the Ga-67.	3	
Separate the radionuclides closer to the end of bombardment.	3	
Allow the Ni-57 to decay before isolating Co-55.		3

4 marks

- 2-6. If zinc of natural isotopic abundance, instead of enriched Zn-68, was bombarded with high energy protons, indicate whether each of the following statements is true or false.

	True	False
Ga-67 would be produced at five fold higher yields.		3
Ga-67 would be produced at five fold lower yields	3	
Ga-67 would be produced at lower yields and contamination by Cu-64, Co-55, Co-57 and Ni-57 would increase.		3

---

Ga-67 would be produced at lower yields and contamination by Cu-64, Co-55, Co-57 and Ni-57 would remain the same.	3	
---	---	--

**4 marks**

Name:

Team Code:

**Problem 3****20 points**3-1. What are the  $\angle(\text{CCC})$  angles for each of these rings?

	polygon $\angle(\text{CCC})$ angle (degrees)
Dodecahedrane	108
Ovalene	120

**2 marks**3-2. Which configuration do the above  $\angle(\text{CCC})$  angles most closely match?

	Trigonal planar	Tetrahedral	Octahedral
Dodecahedrane	<input type="text"/>	4	<input type="text"/>
Ovalene	4	<input type="text"/>	<input type="text"/>

The  $\angle(\text{CCC})$  angle for dodecahedrane is only slightly lower than the tetrahedral angle, but is much higher than the  $90^\circ$  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.

**2 marks**

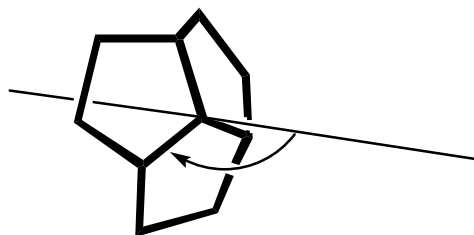
3-3. What is the hybridization which most closely conforms to the geometric structure of these molecules?

	sp	sp <sup>2</sup>	sp <sup>3</sup>
Dodecahedrane	<input type="text"/>	<input type="text"/>	4
Ovalene	<input type="text"/>	4	<input type="text"/>

As above, dodecahedrane conforms quite closely to a tetrahedral arrangement at each C atom, thus sp<sup>3</sup>. Ovalene corresponds exactly to a trigonal planar arrangement, so sp<sup>2</sup>.

**2 marks**

3-4. What is the value of the angle shown below for dodecahedrane (to the nearest 3 degrees), and for ovalene?



dodecahedrane, $C_{20}H_{20}$	109-115	degrees
ovalene, $C_{32}H_{14}$	90	degrees

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  $109.5^\circ$  (more probably  $\sim 112^\circ$ ). For ovalene, all rings are coplanar. The axis angle is clearly  $90^\circ$ .

**2 marks**

3-5. Which juncture is planar?

	dodecahedrane, $C_{20}H_{20}$
3	ovalene, $C_{32}H_{14}$

**1 mark**

3-6. For which  $C=C$  pair is  $H_2$  addition more exothermic ?

dodecahedrene	3
ovalene	

**1 mark**

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. For which of  $C_{60}$ , dodecahedrene, or ovalene is  $H_2$  addition most exothermic?

$C_{60}$	
dodecahedrene	3
ovalene	

**1 mark**

The deviation from planarity, in a  $C_{60}$  juncture, is less than in dodecahedrene (which has very close to tetrahedral, i.e.  $sp^3$ , coordination at each carbon) but is clearly more than in ovalene (which is flat, i.e. ideal for  $sp^2$  hybridization). Thus  $C_{60}$  is intermediate between dodecahedrene and ovalene in its preference for hydrogenated versus dehydrogenated structures. The junctures in dodecahedrene are all pentagons [ $C_5, C_5, C_5$ ]. The junctures in

ovalene are all  $[C_6, C_6, C_6]$ . Those in  $C_{60}$  are  $[C_5, C_6, C_6]$ . 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  $sp^3$  hybridization, rather than  $sp^2$ , at the central carbon atom.]

3-8. For which of  $C_{60}$ , dodecahedrene, or ovalene is  $H_2$  addition least exothermic?

$C_{60}$	
dodecahedrene	
ovalene	3

1 mark

3-9. Which juncture has the least deviation from planarity ?

A?  or B?  or C?

1 mark

3-10. Which juncture has the greatest deviation from planarity ?

A?  or B?  or C?

1 mark

The juncture centred on atom 'A' features two hexagons and a pentagon: this is the same pattern as that seen in the  $C_{60}$  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. Of the above carbon-carbon bonds, numbered from 1 to 9, which represents the most favourable site for  $H_2$  addition?

Bond number:

2 marks

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. Which has the larger average deviation from planarity at each juncture?

$C_{60}$ ?  or  $C_{180}$ ?

1 mark

$C_{180}$  obviously has a larger diameter than  $C_{60}$ , so its average deviation from planarity at a given juncture is less than that found for  $C_{60}$ . [To visualize this, it may help to note that the 'equator' of  $C_{180}$  will be defined by more atoms than are found along  $C_{60}$ 's 'equator'.]

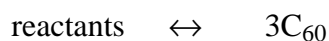
3-13. Which of the following statements is correct, for  $\Delta H^\circ_f$  values in  $\text{kJ g}^{-1}$  units?

	$\Delta H^\circ_f(\text{C}_{60}) < \Delta H^\circ_f(\text{C}_{180}) < \Delta H^\circ_f(\text{graphite})$
3	$\Delta H^\circ_f(\text{C}_{60}) > \Delta H^\circ_f(\text{C}_{180}) > \Delta H^\circ_f(\text{graphite})$
	$\Delta H^\circ_f(\text{C}_{60}) = \Delta H^\circ_f(\text{C}_{180}) < \Delta H^\circ_f(\text{graphite})$
	$\Delta H^\circ_f(\text{C}_{60}) = \Delta H^\circ_f(\text{C}_{180}) = \Delta H^\circ_f(\text{graphite})$
	$\Delta H^\circ_f(\text{C}_{60}) = \Delta H^\circ_f(\text{C}_{180}) > \Delta H^\circ_f(\text{graphite})$
	$\Delta H^\circ_f(\text{C}_{180}) > \Delta H^\circ_f(\text{C}_{60}) > \Delta H^\circ_f(\text{graphite})$

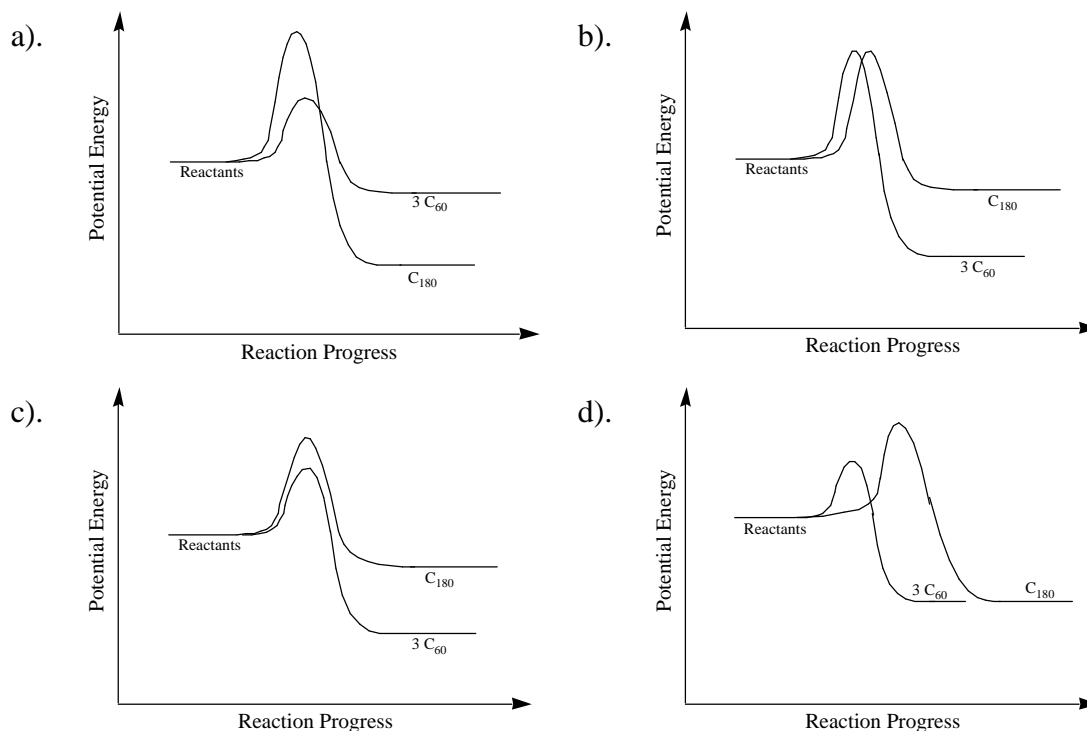
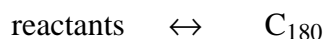
2 marks

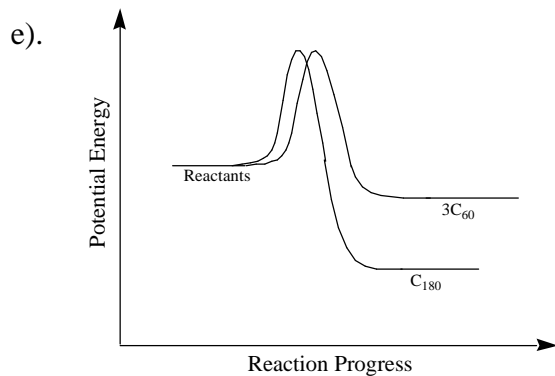
$\text{C}_{60}$  has a larger average deviation from planarity than  $\text{C}_{180}$ , so  $\text{sp}^2$  hybridization is less favourable for the smaller fullerene. However, both fullerenes are non-planar and therefore less amenable to  $\text{sp}^2$  hybridization than graphite (which additionally 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 **a** to **e** best represents the dependence of potential energy upon reaction progress for the two processes:



and

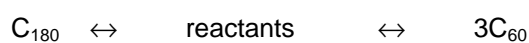




The best graph is:

**a)**

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.

**1 mark**

Name:

Team Code:

**Problem 4****15 points**

- 4-1. On the next page of the answer sheet, construct the molecular orbitals arising from the separate interaction of the 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub> atomic orbitals and fill them in under the column labelled 'Molecular orbitals'. Remember to form the symmetric and anti-symmetric combinations of O<sub>a</sub> and O<sub>c</sub> first.

1 mark for each correct orbital, 0 otherwise.

**9 marks**

- 4-2. Why does the energy of the 6a<sub>1</sub> orbital increase so rapidly as the bond angle changes from 90° to 180°? (Choose one)

- |    |   |  |         |
|----|---|--|---------|
| a) |   | Because the bonding character decreases      | 1 mark  |
| b) |   | Because the anti-bonding character increases | 1 mark  |
| c) | 3 | Both (a) and (b)                             | 2 marks |
| d) |   | Because the overlap decreases                | 0 marks |

The correct answer is c). 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:



linear molecule

**2 marks**

- 4-3. With reference to the Walsh diagram attached, write the symmetry label for the highest occupied orbital for each of the molecules BO<sub>2</sub>, CO<sub>2</sub>, NO<sub>2</sub> and FO<sub>2</sub>, at a bond angle of 135°.

O <sub>3</sub>	BO <sub>2</sub>	CO <sub>2</sub>	NO <sub>2</sub>	FO <sub>2</sub>
6a <sub>1</sub> (24e <sup>-</sup> )	4b <sub>2</sub> (21e <sup>-</sup> )	4b <sub>2</sub> (22e <sup>-</sup> )	6a <sub>1</sub> (23e <sup>-</sup> )	2b <sub>1</sub> (25e <sup>-</sup> )

0.5 marks for each correct label, 0 otherwise.

**2 marks**

- 4-4. Which of the following statements is predicted to be true? (Choose one)

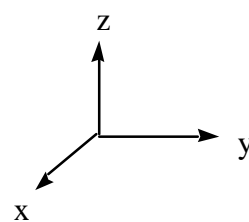
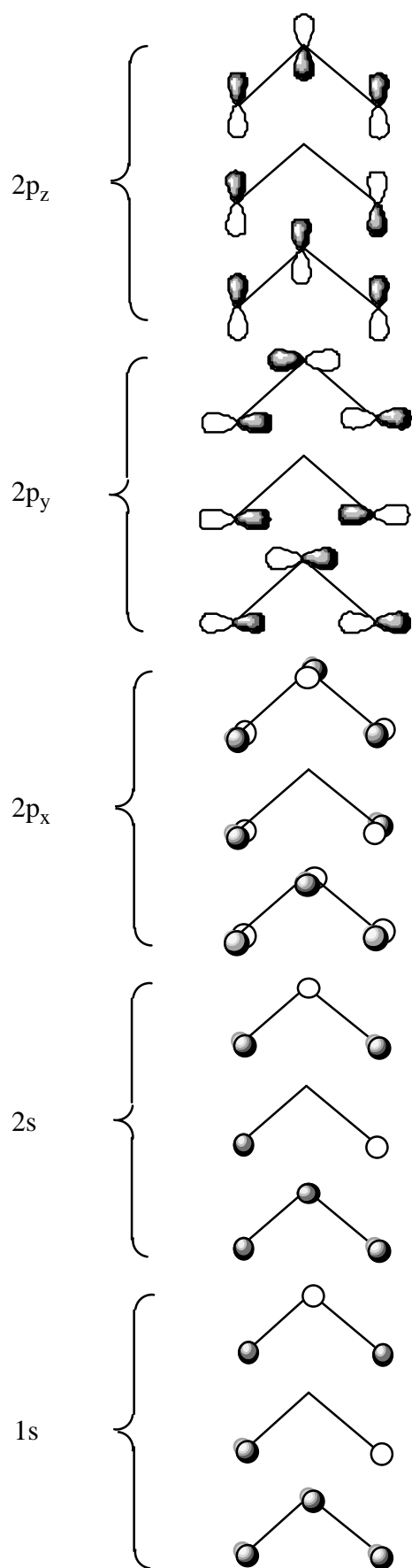
- |    |   |   |         |
|----|---|---|---------|
| a) |   | NO <sub>2</sub> is more bent than O <sub>3</sub> , and FO <sub>2</sub> is more bent than O <sub>3</sub> | 1 mark  |
| b) |   | NO <sub>2</sub> is more bent than O <sub>3</sub> , and FO <sub>2</sub> is less bent than O <sub>3</sub> | 0 marks |
| c) |   | NO <sub>2</sub> is less bent than O <sub>3</sub> , and FO <sub>2</sub> is less bent than O <sub>3</sub> | 1 mark  |
| d) | 3 | NO <sub>2</sub> is less bent than O <sub>3</sub> , and FO <sub>2</sub> is more bent than O <sub>3</sub> | 2 marks |

The correct answer is d). NO<sub>2</sub> is *less* bent than O<sub>3</sub>  
 NO<sub>2</sub> has 23 e<sup>-</sup>, one less than O<sub>3</sub>, (24 e<sup>-</sup>) => 6a<sub>1</sub> is singly occupied  
 => bending is less strong than in O<sub>3</sub> (experimental bond angle is actually 134°)  
 FO<sub>2</sub> is *more* bent than O<sub>3</sub>  
 FO<sub>2</sub> has 25 e<sup>-</sup>, one more than O<sub>3</sub>, => 2b<sub>1</sub> is singly occupied

=> this would favour smaller bond angle, but it is offset by a rise in energy of the  $4b_2$  and  $1a_2$  orbitals => predict slightly smaller bond angle, but not much change from  $O_3$

**2 marks**

Atomic orbitals      Molecular orbitals      Marks



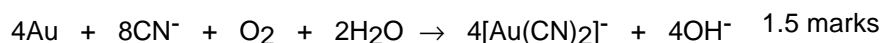
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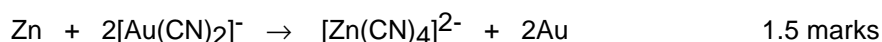
**Problem 5****15 points**

5-1. Write balanced ionic equations for the two reactions.

reaction 1:



reaction 2:

**3 marks**

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 in this case 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.

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

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

$E^\circ_{\text{Ag/Zn}} > E^\circ_{\text{Au/Zn}}$  Therefore the Ag(I) complex will be reduced first.

(i) mol Ag(I) in 500 L =  $500 \times 0.0030 = 1.5 \text{ mol}$

(ii) mol Au(I) in 500 L =  $500 \times 0.010 = 5.0 \text{ mol}$

(iii) mol Zn in 40 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  $[\text{Ag}(\text{CN})_2]^-$

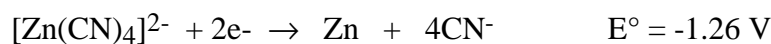
$$[\text{Ag}(\text{CN})_2]^- \text{ remaining} = 1.5 - 1.2 = 0.3 \text{ mol}$$

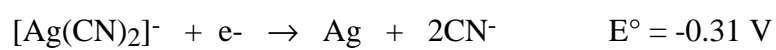
$[\text{Au}(\text{CN})_2]^-$  will not be reduced.

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

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

$$[\text{Au}(\text{CN})_2]^- = \quad \quad \quad \mathbf{0.030 \text{ M}} \quad \quad \quad [\text{Ag}(\text{CN})_2]^- = \quad \quad \quad \mathbf{0.002 \text{ M}}$$

**5 marks**



- 5-3.  $[\text{Au}(\text{CN})_2]^-$  is a very stable complex under certain conditions. What concentration of cyanide ion is required to keep 99 mol% of the gold in solution in the form of the cyanide complex ?  $\{[\text{Au}(\text{CN})_2]^- : K_f = 4 \times 10^{28}\}$



$$99 \text{ mol\% } [\text{Au}(\text{CN})_2]^- \quad K_f = \frac{[\text{Au}(\text{CN})_2^-]}{[\text{Au}^+][\text{CN}^-]^2}$$

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

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

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

Substituting into  $K_f$ :

$$4 \times 10^{28} = 99 / [\text{CN}^-]^2 \quad [\text{CN}^-] = 5 \times 10^{-14} \text{ M}$$

**6 marks**

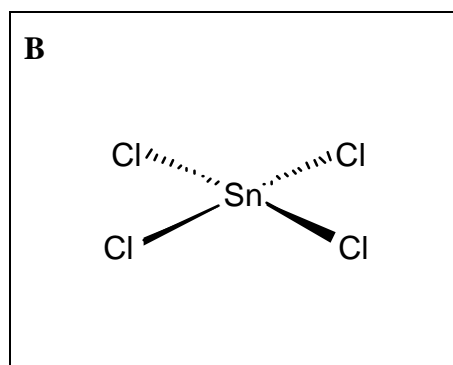
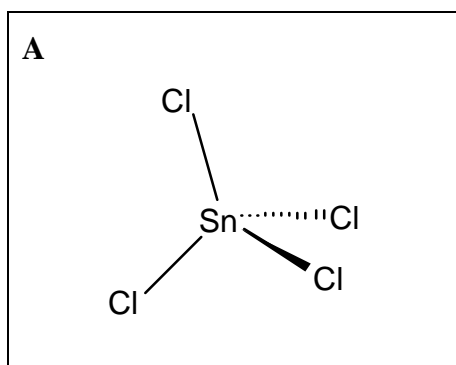
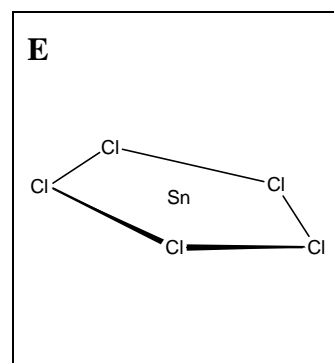
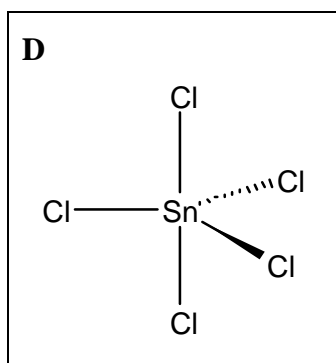
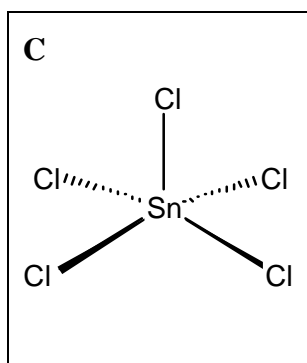
- 5-4. There have been several efforts to develop alternative gold extraction processes which could replace this one. This is because:

	sodium cyanide solutions corrode mining machinery
3	sodium cyanide escapes into ground water and produces hydrogen cyanide which is toxic to many animals.
	gold obtained by this process is not pure.

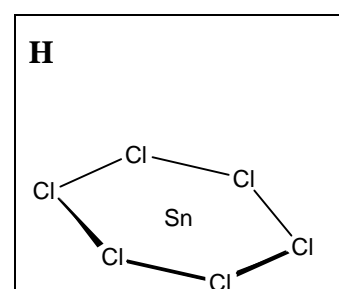
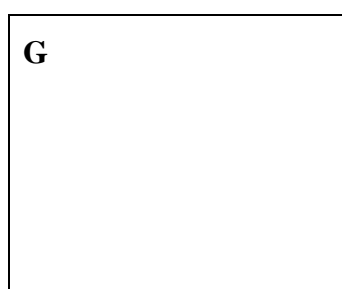
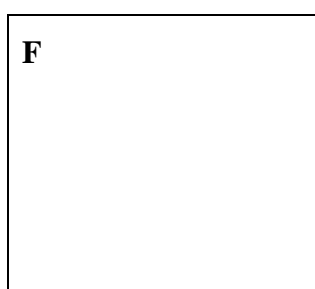
**1 mark**

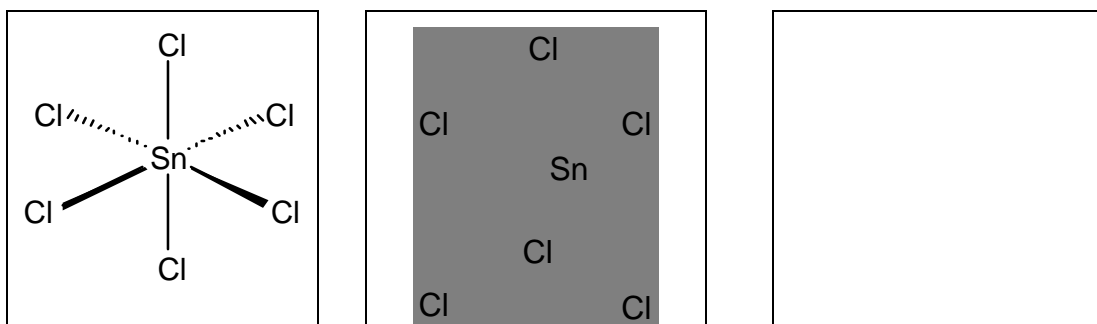
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**Problem 6****20 points**6-1. Draw two alternative structures showing possible geometries for  $\text{SnCl}_4$ **1 mark**6-2. Draw three alternative structures showing possible geometries for  $\text{SnCl}_5^-$ .**1.5 marks**6-3. Use Valence Shell Electron Pair Repulsion (VSEPR) theory to predict which of geometries **C**, **D**, or **E** is likely to be preferred for  $\text{SnCl}_5^-$ .

**C**?  or **D**?  or **E**?

**0.5 marks**6-4. Draw three alternative possible geometries for  $\text{SnCl}_6^{2-}$ .



1.5 marks

6-5. Use Valence Shell Electron Pair Repulsion (VSEPR) theory to predict which geometry of **F**, **G** and **H** is likely to be preferred for  $\text{SnCl}_6^{2-}$

**F**?  or **G**?  or **H**?

0.5 marks

6-6. Write the empirical formula for the tin-containing species in a solution containing  $\text{SnCl}_6^{2-}$  (as the tetrabutylammonium salt) detected by negative ion ESMS.

1 mark

6-7. Write the empirical formula for the tin-containing species in a solution containing  $\text{SnBr}_6^{2-}$  (as the tetrabutylammonium salt) detected by negative ion ESMS.

1 mark

6-8. Write the empirical formula for each of the four new species.





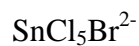




4 marks

- 6-9. Write the empirical formula for the tin-containing species in this mixture that give rise to the peaks listed below:

-912 ppm



-1117 ppm



-1322 ppm



-1554 ppm

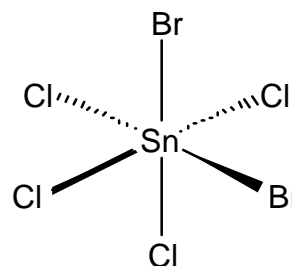
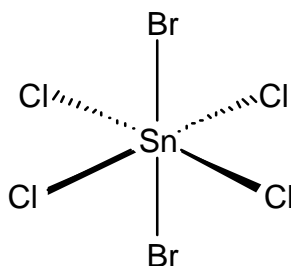


-1800 ppm

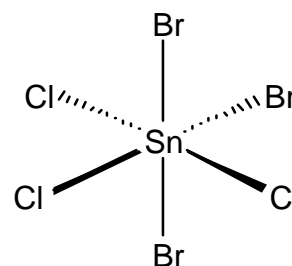
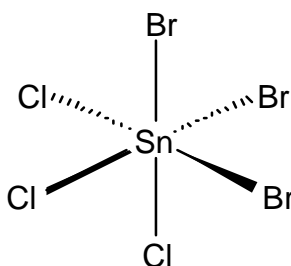

**5 marks**

- 6-10. Draw the geometry for the four tin-containing species present in the solution at  $-30\text{ }^\circ\text{C}$  that give rise to the peaks listed below:

-1092 ppm and -1115 ppm (2 compounds)



-1322 ppm and -1336 ppm (2 compounds)

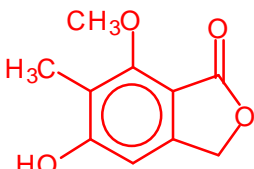
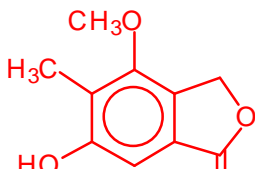
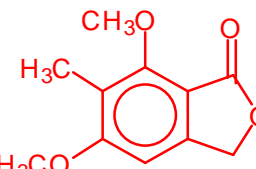
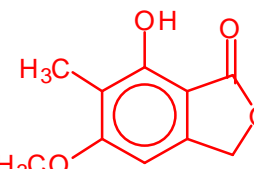
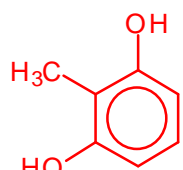
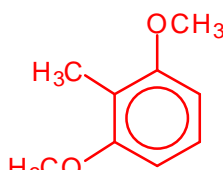
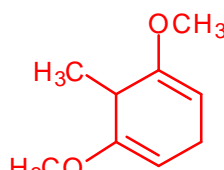
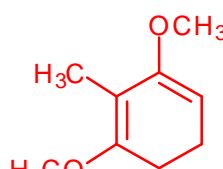
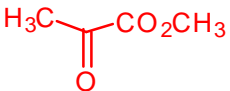

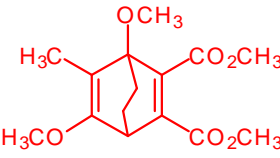
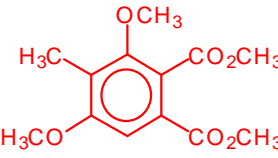
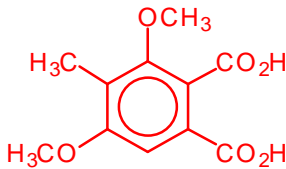
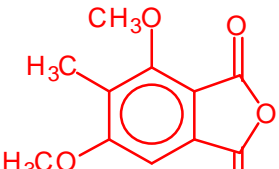
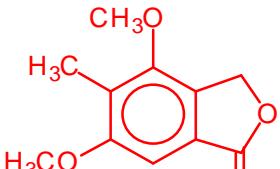

**4 marks**

Note: The structure/ppm assignments for cis/trans and fac/mer can be reversed without any penalty

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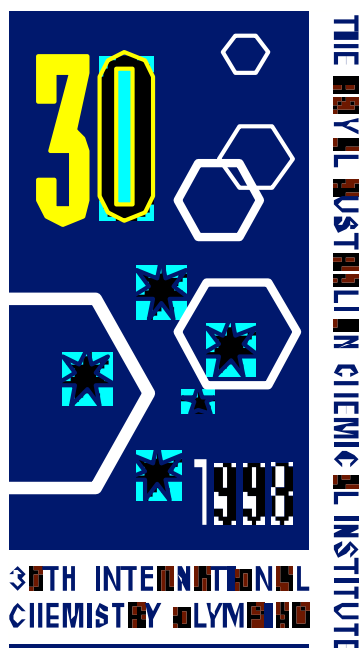
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**Problem 7****21 points**7-1. On the answer template below, fill in the structures of compounds **A** to **O**.

 <p style="text-align: center;"><b>A</b></p>	 <p style="text-align: center;"><b>B</b></p>	 <p style="text-align: center;"><b>C</b></p>	 <p style="text-align: center;"><b>D</b></p>
 <p style="text-align: center;"><b>E</b></p>	 <p style="text-align: center;"><b>F</b></p>	 <p style="text-align: center;"><b>G</b></p>	 <p style="text-align: center;"><b>H</b></p>
 <p style="text-align: center;"><b>I</b></p>	 <p style="text-align: center;"><b>J</b></p>	 <p style="text-align: center;"><b>K</b></p>	 <p style="text-align: center;"><b>L</b></p>
 <p style="text-align: center;"><b>M</b></p>	 <p style="text-align: center;"><b>N</b></p>	 <p style="text-align: center;"><b>O</b></p>	<p style="text-align: center;">Other structure for <b>B</b></p>

1.5 marks for each correct structure





# **30th International Chemistry Olympiad**

**Melbourne, Tuesday July 7, 1998**

**Laboratory Examination**

**Exercises**

**Official Version**

## Attention!

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At all times while you are in the laboratory you must wear safety eye glasses or your own glasses if they have been approved, and use the pipette filler bulb provided. You will receive only ONE WARNING from the laboratory supervisor if you remove your glasses or fill a pipette by mouth.

A second infringement will be considered a major fault incompatible with further experimental work, and you will be dismissed from the laboratory with a resultant zero score for the entire experimental examination.

Do not hesitate to ask a demonstrator if you have any questions concerning safety issues.

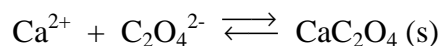
- Please carefully read the text of each experimental task and study the layout of the answer forms before you begin your experimental work.
- Write your name and personal identification code (posted at your workstation) on each answer sheet.
- You have 5 hours to complete all of the experimental tasks, and record your results on the answer sheets. You must stop your work immediately after the STOP command is given. A delay in doing this by 3 minutes will lead to cancellation of the current task and will result in zero points for that task.
- All results must be written in the appropriate areas on the answer sheets. Anything written elsewhere will not be marked. Do not write anything on the back of your answer sheets. If you need more paper for working or a replacement answer sheet, request it from the supervisor.
- When you have finished the examination, you must put all of your papers into the envelope provided, then you must seal the envelope. Only papers in the sealed envelope will be marked.
- Do not leave the examination room until you are directed to do so. A receipt for your sealed envelope will be issued to you as you leave.
- Use only the pen and calculator provided.
- Use only the distilled water, and use the appropriate waste containers for disposal of chemical and other waste materials.
- The number of significant figures in numerical answers must conform to the rules of evaluation of experimental errors. The inability to perform calculations correctly will result in penalty points, even if your experimental technique is flawless.
- This examination has **6** pages and **4** pages of answer sheets.
- Chemicals and/or laboratory ware can be purchased if used up or broken. The cost of each purchase will be the loss of **1** point.
- The official English version of this examination is available if you wish to see it.

# Laboratory Task 1

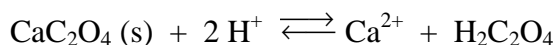
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## Determination of Calcium by precipitation with oxalate followed by titration with permanganate.

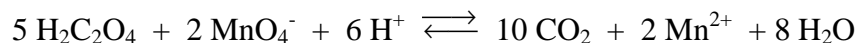
In this exercise, you must determine the amount of calcium ion in a solution that contains both calcium and magnesium, by selectively precipitating only the calcium as calcium oxalate, then quantitatively removing the precipitate from the solution by filtration.



The precipitate must then be re-dissolved in acid:



and the liberated oxalic acid titrated with standard permanganate solution:



### Formation of the calcium oxalate precipitate

1. Use a 25.00 mL pipette and 250.0 mL 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:**

2. Transfer a 25.00 mL aliquot of the dilute calcium/magnesium solution into a 250 mL beaker, add approximately 10 mL of 3 M  $\text{H}_2\text{SO}_4$  and about 50 mL of water.

**CARE!** 3 M  $\text{H}_2\text{SO}_4$  is very corrosive! The following steps involve hot (nearly boiling) solutions. Be careful and beware of steam!



3. Cover the beaker with a watchglass and gently heat on a hotplate until the solution is very hot, but not boiling.
4. Remove the beaker from the heat, then carefully add solid ammonium oxalate (1.5g) 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  $\text{H}_2\text{SO}_4$  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 mL conical flask. Rinse the paper with a few mL 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 washbottle to rinse the watchglass 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 washbottle 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 mL portions of water, collecting the washings in the conical flask.
11. Discard the combined filtrates from the previous steps into the residue bottle labelled “Permanganate/Oxalate residues” then carefully rinse the conical flask with water into the residue bottle.
12. Wash the precipitate one more time with 10 mL 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 mL 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 mL 3 M sulphuric acid, collecting the acid in the conical flask. Finally, rinse the paper with ~ 20 mL water.

**Titration with permanganate**

16. Make the volume up to about 100 mL 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.**

Atomic masses: Ca 40.08, Mg 24.31, Mn 54.94, C 12.01, O 16.00 g/mol

## Laboratory Task 2

---

### 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  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  byproduct.

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 byproduct, 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  $\text{H}^+$  can be exchanged.

When a solution containing 1 mol of  $\text{M}^{\text{n}+}$  is allowed to react with the resin this liberates n mol of  $\text{H}^+$ . 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  $\text{H}^+$  form. Wash the resin using the following procedure to remove all traces of free acid:

1. Transfer your resin to a 250 mL beaker, washing it from the container with about 50 mL 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 mL 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 (pH ~5). You should not need to use more than 200 mL 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 mL 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 mL aliquots of the diluted NaOH solution, using phenolphthalein indicator.

## Analysis Procedure

**You are provided with approximately 40 mL of a 0.005000 M solution of HCl that contains 0.2000 g of a mixture of the cobalt(III) complexes  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  in 40.00 mL.**

6. Use a pipette to transfer a 25.00 mL aliquot of the cobalt complex solution into a 250 mL beaker (beaker #1) and add ~25 mL water.
7. 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  $\text{H}^+$ . You should occasionally gently swirl the mixture to hasten the ion-exchange process.
8. Carefully wash the acidic solution into a second 250 mL beaker (beaker #2) with about 20 mL of distilled water. Try to leave as much as possible of the resin behind.

Notice that the solution is now much lighter in color, 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.

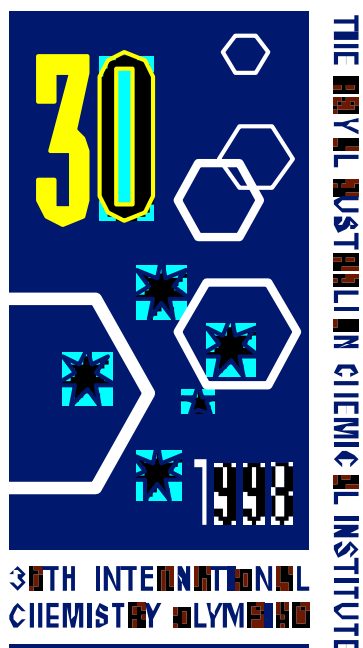
9. Add most of the remainder of your resin (~4g) to the solution in beaker #2 and again allow to stand for at least 5 minutes to allow the cation exchange to take place, liberating more  $\text{H}^+$ .

At the end of this process, the solution should be colorless - 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 (~1g) of your ion-exchange resin.

10. Filter the two resin samples through a carefully washed filter paper, and collect the acidic filtrate in a 100 mL volumetric flask. Carefully wash the resin with small portions of water into the volumetric flask and make up to the mark with water.
11. With this acid solution, titrate 25.00 mL aliquots of your standardised NaOH solution.

**Calculate the number of moles of  $\text{H}^+$  liberated by the 25 mL aliquot of your mixture of cobalt(III) complexes and report the percentage of  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  that is present in your sample.**

Atomic masses: Co 58.93, N 14.01, H 1.01, Cl 35.45, O 16.00 g/mol



# **30th International Chemistry Olympiad**

**Melbourne, Tuesday July 7, 1998**

**Laboratory Examination**

**Example Results and Marking Scheme**

**Official Version**

Name:

Team Code:

## Laboratory Task 1 Results Sheet

### Analysis of calcium/magnesium solution

Ca/Mg solution:            **Blue**   **Red**   **Green**   **Orange**            (circle one)

### Permanganate titration

Concentration of standard  $\text{KMnO}_4$ : .....**0.02039** ..... M

Demonstrators Signature:.....

titration number:	max 2 marks for <u>at least two</u> witnessed precipitates			
	1	2	3	
initial burette reading	0.90	0.80	3.00	mL
final burette reading	28.55	28.45	30.80	mL
volume of standard $\text{KMnO}_4$	27.65	27.65	27.80	mL

average titre = 27.70 mL  $\pm$ 0.07 mL av. dev. ( ie  $\pm$  0.25% relative av. dev.)

In a 25 mL aliquot of dilute Ca/Mg solution:

$n(\text{KMnO}_4)$  required to titrate oxalate from dissolved calcium oxalate precipitate  
 =  $(0.0198 \text{ mol/L})(27.70 \text{ mL})/1000 \text{ mL/L}$  =  $5.485 \times 10^{-4}$  mole

$n(\text{oxalate})$  from dissolved calcium oxalate precipitate  
 =  $5/2 \times 5.485 \times 10^{-4}$  mole =  $1.371 \times 10^{-3}$  mole

**-1 mark for incorrect stoichiometry**

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

[Ca] =  $(1000 \text{ mL/L}) 1.371 \times 10^{-3} \text{ mole}/25.00 \text{ mL}$  = 0.0548 mol/L

In original Ca/Mg solution:

[Ca] =  $0.0548 \text{ mol/L} (1000 \text{ mL}) / 25.00 \text{ mL}$  = 0.548 mol/L

**max 5 marks for correct calculation**

Uncertainty in titre limits the uncertainty in [Ca] to 0.25% at least, or  $\pm$ 0.001 mol/L so 3 sig. figs at most. **-1 mark for less than 3 sig figs, -2 marks for more than 4 sig figs**

**Accuracy (max 13 marks) - recalculated using student's data**

Sliding scale. 13.00 marks for 0 to 1.5% deviation, zero marks for greater than 15% deviation.

**Average concentration of  $\text{Ca}^{2+}$  in Ca/Mg solution: .....**0.548** ..... M**

**20 marks**

Name:

Team Code:

## Laboratory Task 2 Results Sheet

### Standardisation of ~0.0125 M NaOH

Concentration of standard HCl in bottle: ..... **0.01253**..... M

titration number:	1	2	3	
aliquot of NaOH	25	25	25	mL
initial burette reading	13.60	17.40	10.35	mL
final burette reading	37.75	41.50	34.45	mL
volume of standard HCl	24.15	24.10	24.10	mL

average titre = 24.12 mL  $\pm$ 0.03 mL av. dev. ( ie  $\pm$  0.12% relative av. dev.)

$$[\text{NaOH}] = (0.01250 \text{ mol/L})(24.12 \text{ mL})/(25.00 \text{ mL}) = 0.01206 \text{ mol/L}$$

Uncertainty is estimated few ppt so 4 sig. figs are justified.

**-1 mark for less than 4 sig figs, -2 for more than 4 sig figs**

**-2 marks for incorrect calculation**

**Accuracy (max 5 marks) - recalculated using student's data**

Sliding scale. 5.00 marks for 0 to 0.25% deviation, zero marks for greater than 5% deviation.

Average concentration of NaOH: ..... **0.01206**..... M

**5 marks**

Name:

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Cobalt complex solution: **Blue Red Green Orange** (circle one)

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

titration number:	1	2	3	
initial burette reading	26.25	16.10	3.80	mL
final burette reading	48.50	38.40	26.20	mL
volume of ion-exchanged acid solution	22.25	22.30	22.40	mL

**Calculations**average titre of eluted acid = 22.32 mL  $\pm$ 0.06 mL av. dev. ( $\pm$  0.25% rel. av. dev.)

$$[\text{H}^+ \text{ collected in 100 mL vol flask}] = (0.01206 \text{ mol NaOH/L})(25.00 \text{ mL})/(22.32 \text{ mL}) = 0.01351 \text{ mol/L}$$

$$\text{total } n(\text{H}^+) \text{ collected from column} = 0.01351 \text{ mol/L } (100.0 \text{ mL})/(1000 \text{ mL/L}) = 1.351 \times 10^{-3} \text{ mol}$$

$$n(\text{H}^+) \text{ from aliquot put onto column} = 0.00500 \text{ mol/L } (25.00 \text{ mL})/(1000 \text{ mL/L}) = 1.250 \times 10^{-4} \text{ mol}$$

**-1 mark for neglect of HCl**

$$n(\text{H}^+) \text{ ion-exchanged from complexes in aliquot put onto column} = 1.351 \times 10^{-3} \text{ mol} - 1.250 \times 10^{-4} \text{ mol} = 1.226 \times 10^{-3} \text{ mol}$$

let x = mass  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  in 25.00 mL aliquot of mixture added to column

$$\text{mass of mixture added to column} = (25.00 \text{ mL}/40 \text{ mL})(0.2000 \text{ g}) = 0.1250 \text{ g}$$

**-1 mark for use of 0.2g only**

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

$$n(\text{H}^+) \text{ ion-exchanged from } [\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2 = 2(x \text{ g}) / 261.00 \text{ g/mol} = 0.007663 x \text{ mol} \quad \text{-2 for more than 4 sig figs}$$

$$n(\text{H}^+) \text{ ion-exchanged from } [\text{Co}(\text{NH}_3)_6]\text{Cl}_3 = 3(0.1250 - x) \text{ g} / 267.50 \text{ g/mol} = (0.001402 - 0.011214 x) \text{ mol} \quad \text{-1 mark for neglect of cation charges}$$

$$\text{so } 0.007663 x + (0.001402 - 0.011214 x) = 0.001226 \quad \text{or } x = 0.04956 \text{ g}$$

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

**5 marks for correct calculation****Accuracy (max 10 marks)** - recalculated using student's data

Sliding scale. 10.00 marks for 0 to 2.00% deviation, zero marks for greater than 20% deviation.

**Average percentage  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  in sample: ..... 39.6..... % w/w**

Name:

Team Code:

**15 marks**