



# **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.

It complexes the tin

It forms a pH buffer

It reacts with oxides of nitrogen and chlorine

It is a pH indicator

1 mark

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

It complexes the tin

It acts as a pH buffer

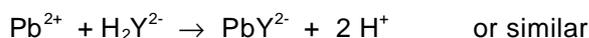
It is a metallochromic indicator

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.

It complexes the tin

It acts as a pH buffer

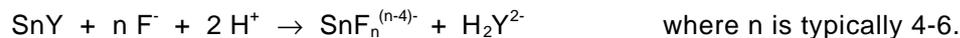
It complexes the lead

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)  $\text{XO}$ . (Charge on  $\text{XO}$  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  $\text{Y}$  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 g  $\text{NaF} = 0.048 \text{ mol F}^-$  or 0.3 M in the 160 mL solution)

$$n(\text{released EDTA}) = n(\text{std. Pb}^{2+})$$

$$= (15.00 \text{ mL})(0.009970 \text{ mol/L}) / (1000 \text{ mL/L}) = 1.496 \times 10^{-4} \text{ mol}$$

$$= n(\text{Sn}^{4+}) \text{ in the 25 mL aliquot, so}$$

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

So in the original 0.4062 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:

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

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:

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**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 x 22 years = 176 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?

- |                                     |                 |
|-------------------------------------|-----------------|
| <input type="checkbox"/>            | U-238 – U-234   |
| <input type="checkbox"/>            | U-234 – Th-230  |
| <input type="checkbox"/>            | Th-230 – Ra-226 |
| <input checked="" type="checkbox"/> | 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).

- |                          |          |  |   |
|--------------------------|----------|--|---|
| <input type="checkbox"/> | <b>A</b> | 0.2 M HCl 96% methanol<br>2.0 M HCl 55% isopropyl alcohol<br>1.0 M HCl 55% isopropyl alcohol | to remove Ni-57 followed by<br>to remove Cu-64 followed by<br>to remove Co-55 |
| <input type="checkbox"/> | <b>B</b> | 0.2 M HCl 96% methanol<br>2.0 M HCl 55% isopropyl alcohol<br>1.0 M HCl 55% isopropyl alcohol | to remove Ni-57 followed by<br>to remove Co-55 followed by<br>to remove Cu-64 |
| <input type="checkbox"/> | <b>C</b> | 2.0 M HCl 55% isopropyl alcohol<br>1.0 M HCl 55% isopropyl alcohol                           | to remove Co-55 followed by<br>to remove Cu-64                                |
| <input type="checkbox"/> | <b>D</b> | 0.2 M HCl 96% methanol<br>3.0 M HCl 55% isopropyl alcohol<br>4.0 M HCl 55% isopropyl alcohol | to remove Ni-57 followed by<br>to remove Co-55 followed by<br>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.		✓
Co-57 will interfere with the medical use of Co-55.	✓	
Cu-67 will interfere with the medical use of Cu-64.	✓	
Ga-66 will interfere with the medical use of Ga-67.		✓
Ga-67 will interfere with the medical use of Cu-64.		✓

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

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

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"/>	<input checked="" type="checkbox"/>	<input type="text"/>
Ovalene	<input checked="" type="checkbox"/>	<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**

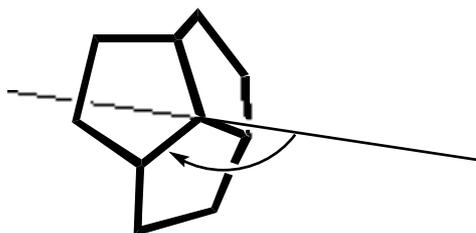
3-3. What is the hybridization which most closely conforms to the geometric structure of these molecules?

	$sp$	$sp^2$	$sp^3$
Dodecahedrane	<input type="text"/>	<input type="text"/>	<input checked="" type="checkbox"/>
Ovalene	<input type="text"/>	<input checked="" type="checkbox"/>	<input type="text"/>

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  $sp^2$ .

**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 <sub>20</sub> H <sub>20</sub>	109-115	degrees
ovalene, C <sub>32</sub> H <sub>14</sub>	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<sub>5</sub> 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°.

**2 marks**

3-5. Which juncture is planar?

<input type="checkbox"/>	dodecahedrane, C <sub>20</sub> H <sub>20</sub>
<input checked="" type="checkbox"/>	ovalene, C <sub>32</sub> H <sub>14</sub>

**1 mark**3-6. For which C=C pair is H<sub>2</sub> addition more exothermic ?

dodecahedrene	<input checked="" type="checkbox"/>
ovalene	<input type="checkbox"/>

**1 mark**

The C=C pair within the dodecahedrene skeleton is more suited to sp<sup>3</sup>-hybridization than sp<sup>2</sup>-hybridization: this favours dihydrogenation to yield dodecahedrane. For ovalene, sp<sup>3</sup>-hybridization is disfavoured relative to sp<sup>2</sup>-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<sub>60</sub>, dodecahedrene, or ovalene is H<sub>2</sub> addition most exothermic?

C <sub>60</sub>	<input type="checkbox"/>
dodecahedrene	<input checked="" type="checkbox"/>
ovalene	<input type="checkbox"/>

**1 mark**

The deviation from planarity, in a C<sub>60</sub> juncture, is less than in dodecahedrene (which has very close to tetrahedral, i.e. sp<sup>3</sup>, coordination at each carbon) but is clearly more than in ovalene (which is flat, i.e. ideal for sp<sup>2</sup> hybridization). Thus C<sub>60</sub> is intermediate between dodecahedrene and ovalene in its preference for hydrogenated versus dehydrogenated structures. The junctures in dodecahedrene are all pentagons [C<sub>5</sub>,C<sub>5</sub>,C<sub>5</sub>]. The junctures in ovalene are all [C<sub>6</sub>,C<sub>6</sub>,C<sub>6</sub>]. Those in C<sub>60</sub> are [C<sub>5</sub>,C<sub>6</sub>,C<sub>6</sub>]. 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<sup>3</sup> hybridization, rather than sp<sup>2</sup>, at the central carbon atom.]

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

$C_{60}$	<input type="checkbox"/>
dodecahedrene	<input type="checkbox"/>
ovalene	<input checked="" type="checkbox"/>

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'.]

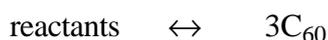
3-13. Which of the following statements is correct, for  $\Delta H_f^\circ$  values in  $\text{kJ g}^{-1}$  units?

<input type="checkbox"/>	$\Delta H_f^\circ(\text{C}_{60}) < \Delta H_f^\circ(\text{C}_{180}) < \Delta H_f^\circ(\text{graphite})$
<input checked="" type="checkbox"/>	$\Delta H_f^\circ(\text{C}_{60}) > \Delta H_f^\circ(\text{C}_{180}) > \Delta H_f^\circ(\text{graphite})$
<input type="checkbox"/>	$\Delta H_f^\circ(\text{C}_{60}) = \Delta H_f^\circ(\text{C}_{180}) < \Delta H_f^\circ(\text{graphite})$
<input type="checkbox"/>	$\Delta H_f^\circ(\text{C}_{60}) = \Delta H_f^\circ(\text{C}_{180}) = \Delta H_f^\circ(\text{graphite})$
<input type="checkbox"/>	$\Delta H_f^\circ(\text{C}_{60}) = \Delta H_f^\circ(\text{C}_{180}) > \Delta H_f^\circ(\text{graphite})$
<input type="checkbox"/>	$\Delta H_f^\circ(\text{C}_{180}) > \Delta H_f^\circ(\text{C}_{60}) > \Delta H_f^\circ(\text{graphite})$

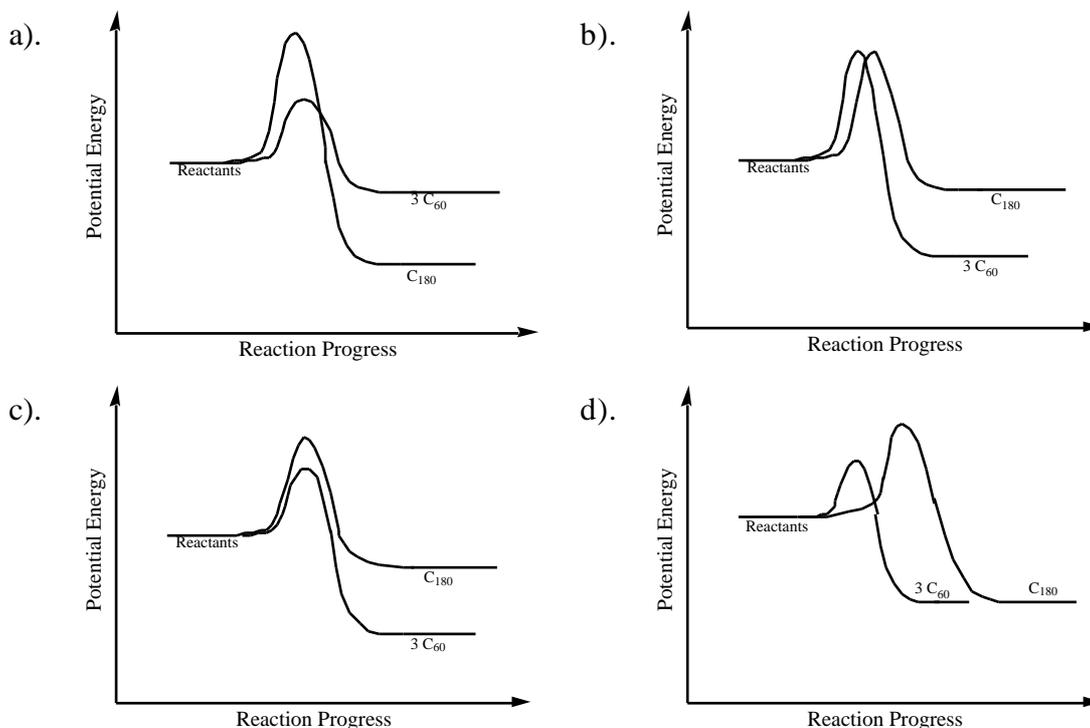
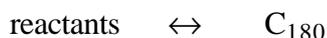
2 marks

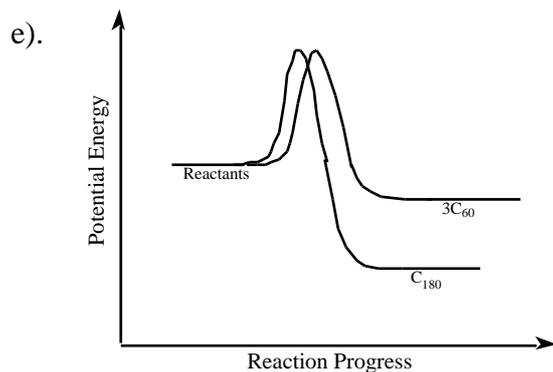
$\text{C}_{60}$  has a larger average deviation from planarity than  $\text{C}_{180}$ , so  $\text{sp}^2$  hybridization is less favourable for the smaller fullerene. However, both fullerenes are non-planar and therefore less amenable to  $\text{sp}^2$  hybridization than graphite (which additionally 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**

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**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
- b)  Because the anti-bonding character increases
- c)  Both (a) and (b)
- d)  Because the overlap decreases

1 mark

1 mark

2 marks

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>
- 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>
- 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>
- d)  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>

1 mark

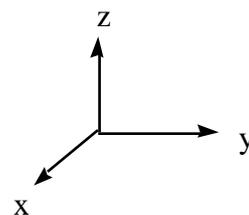
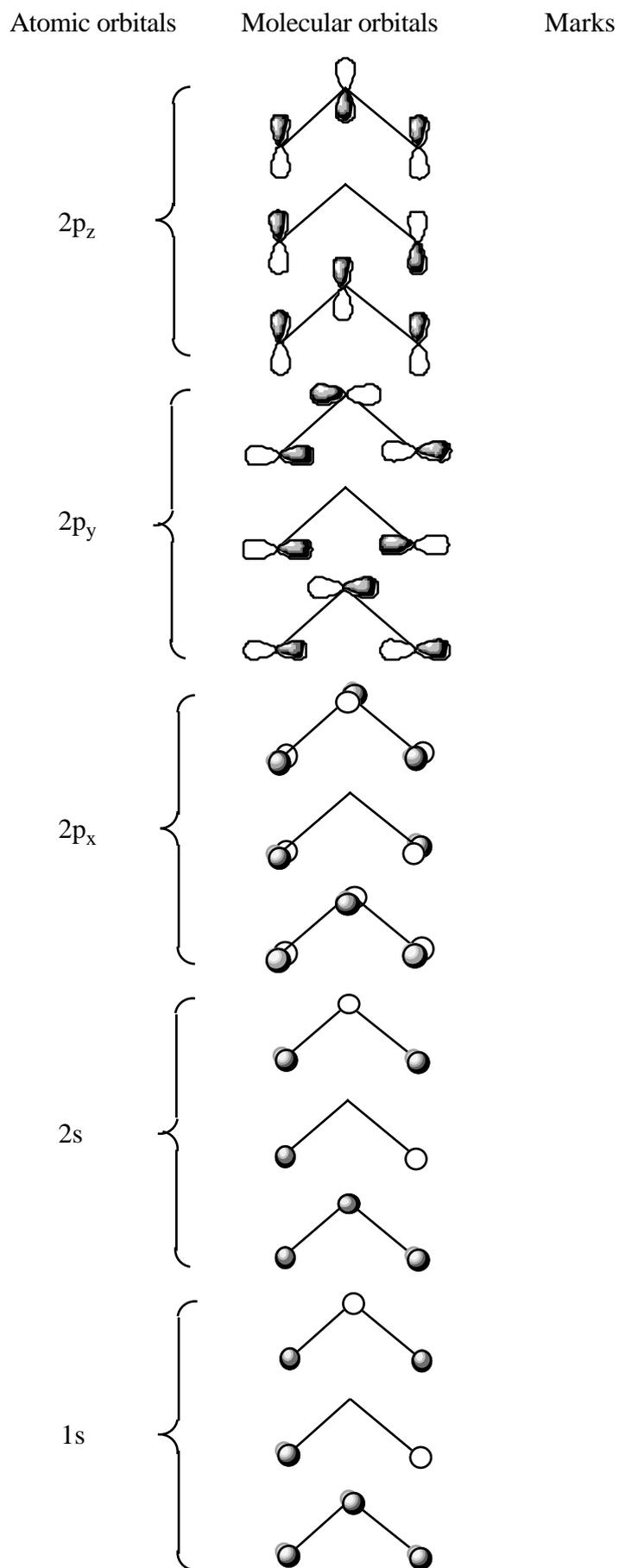
0 marks

1 mark

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<sub>2</sub> and 1a<sub>2</sub> orbitals => predict slightly smaller bond angle, but not much change from O<sub>3</sub>

**2 marks**



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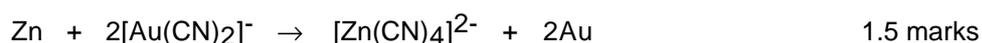
**Problem 5****15 points**

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.

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

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

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

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

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

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

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

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

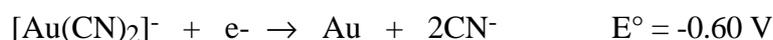
$$[\text{Ag}(\text{CN})_2]^- \text{ remaining} = 1.5 - 1.2 = 0.3 \text{ mol}$$

$[\text{Au}(\text{CN})_2]^-$  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**

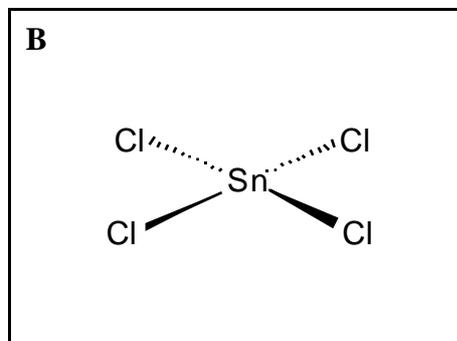
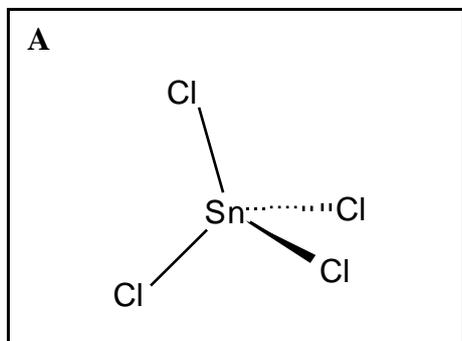
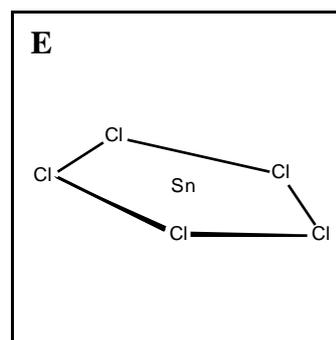
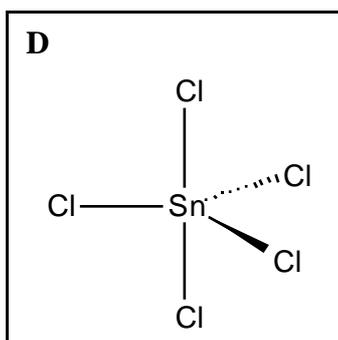
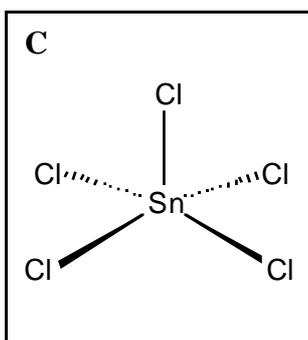
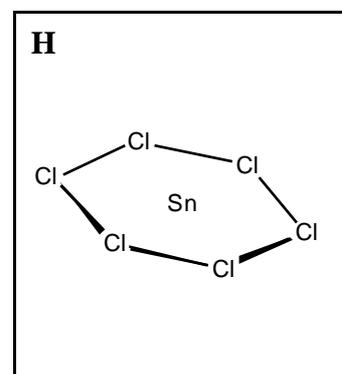
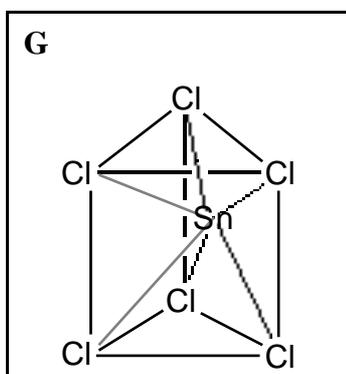
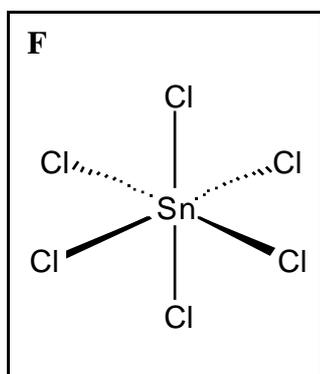
- 5-4. There have been several efforts to develop alternative gold extraction processes which could replace this one. This is because:

<input type="checkbox"/>	sodium cyanide solutions corrode mining machinery
<input checked="" type="checkbox"/>	sodium cyanide escapes into ground water and produces hydrogen cyanide which is toxic to many animals.
<input type="checkbox"/>	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.

$\text{SnCl}_5^-$

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.

$\text{SnBr}_5^-$

1 mark

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

m/z=339  
 $\text{SnCl}_4\text{Br}^-$

m/z=383  
 $\text{SnCl}_3\text{Br}_2^-$

m/z=427  
 $\text{SnCl}_2\text{Br}_3^-$

m/z=471  
 $\text{SnClBr}_4^-$

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  
 $\text{SnCl}_5\text{Br}^{2-}$

-1117 ppm  
 $\text{SnCl}_4\text{Br}_2^{2-}$

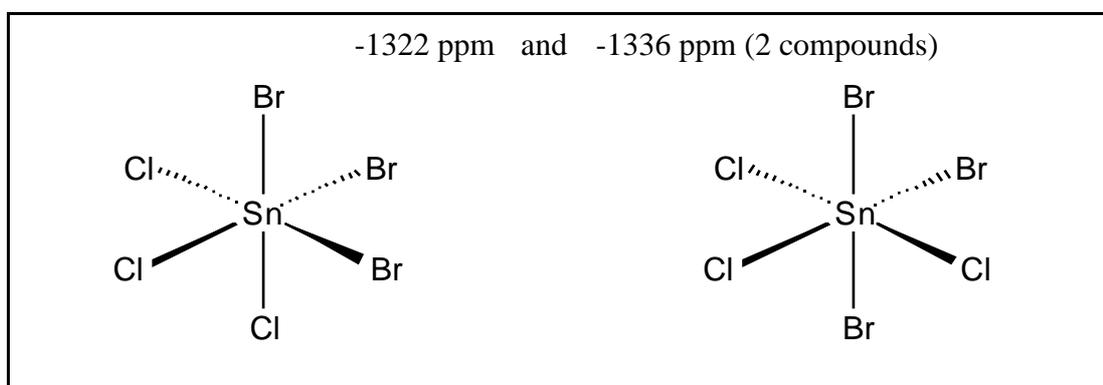
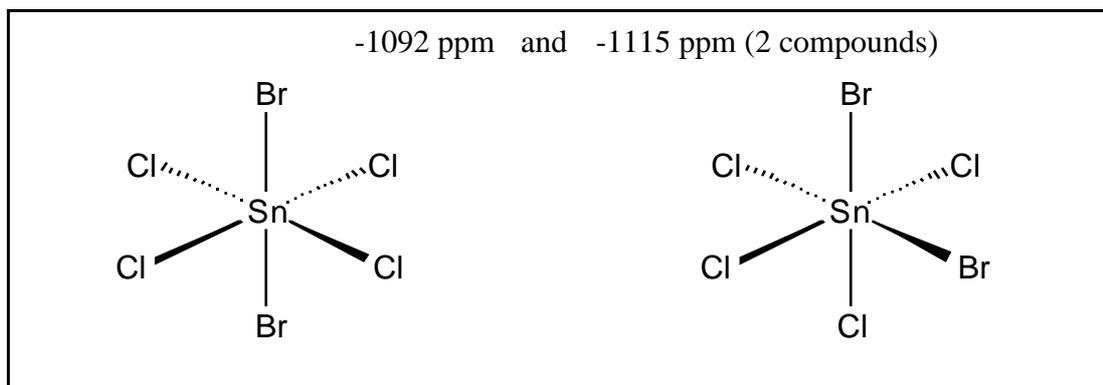
-1322 ppm  
 $\text{SnCl}_3\text{Br}_3^{2-}$

-1554 ppm  
 $\text{SnCl}_2\text{Br}_4^{2-}$

-1800 ppm  
 $\text{SnClBr}_5^{2-}$

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:



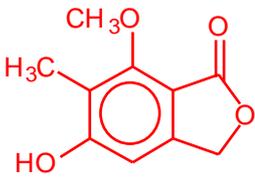
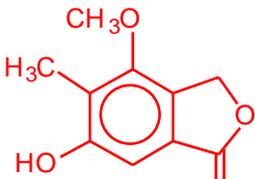
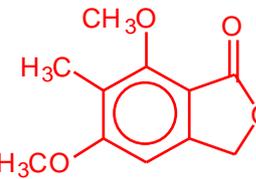
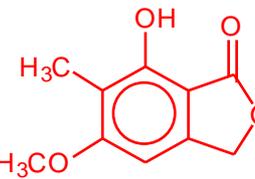
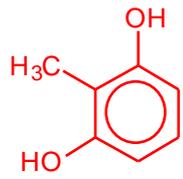
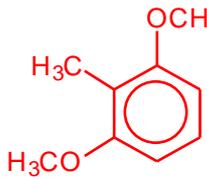
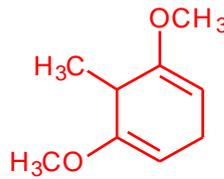
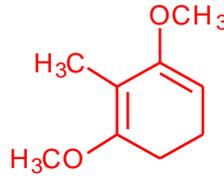
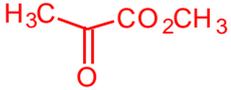
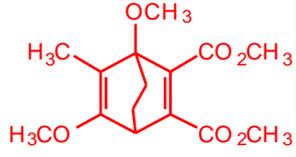
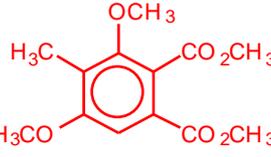
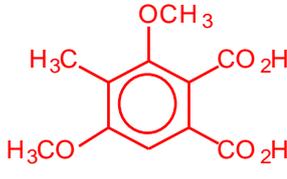
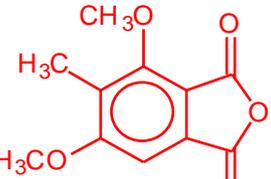
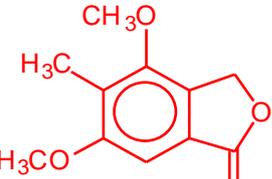
**4 marks**

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

Name:

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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;"><b>Other structure for B</b></p>

1.5 marks for each correct structure