

30th International Chemistry Olympiad

Melbourne, Thursday July 9, 1998

Theoretical Examination

Problems

Official Version

Attention!



- 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.

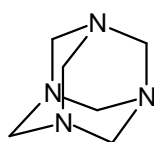
Problem 1

20 points

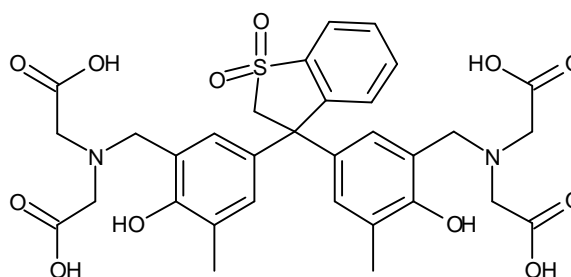
The following 8 steps describe the procedure for analysing a sample of an alloy that contains tin and lead.

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 $\text{Na}_2\text{H}_2\text{EDTA}$ 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_b of hexamine is 9.5. Xylenol Orange is red below pH 4, yellow above pH 5.



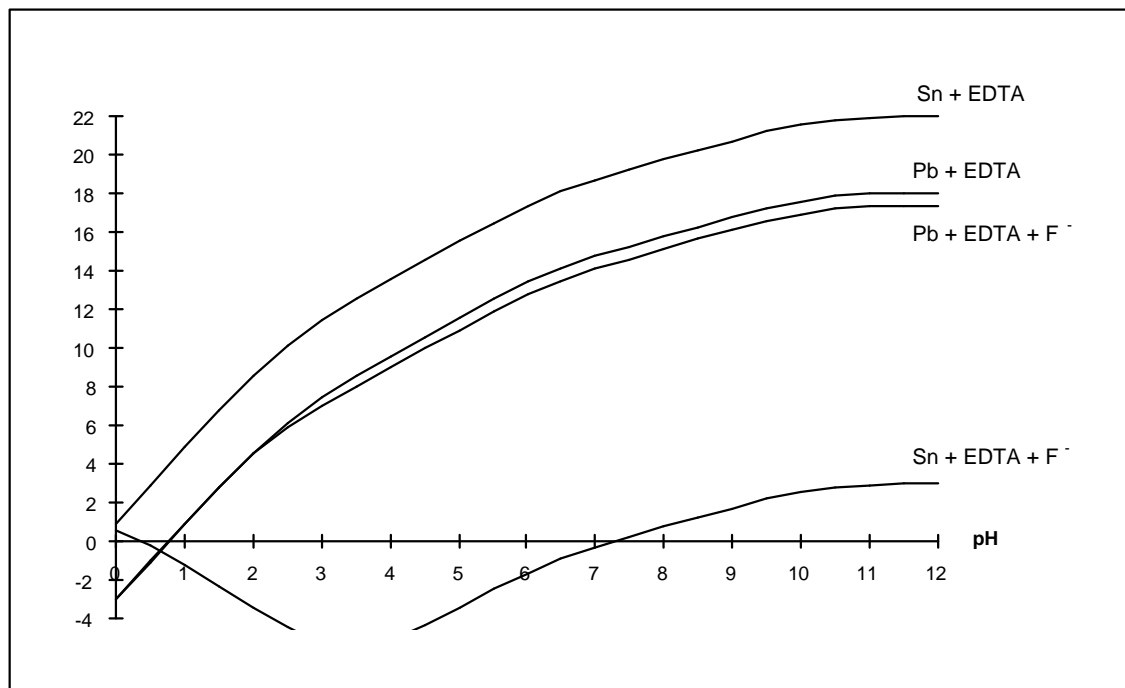
Hexamine



Xylenol Orange (XO)

K'_{MY} is the conditional formation constant = αK_{MY} .

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



- 1-1. What is the lead compound that precipitates in Step 2?
- 1-2. Write a balanced ionic equation that explains the disappearance of the 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⁻ 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

Radionuclide	Half-life
Co-55	18.2 hr
Ni-57	36.0 hr

Co-57(daughter of Ni-57)	270 days
Cu-64	12.7 hr
Cu-67	61.7 hr
Zn-65	244 days
Ga-67	78.35 hr
Ga-66	9.4 hr

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

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

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

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

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.

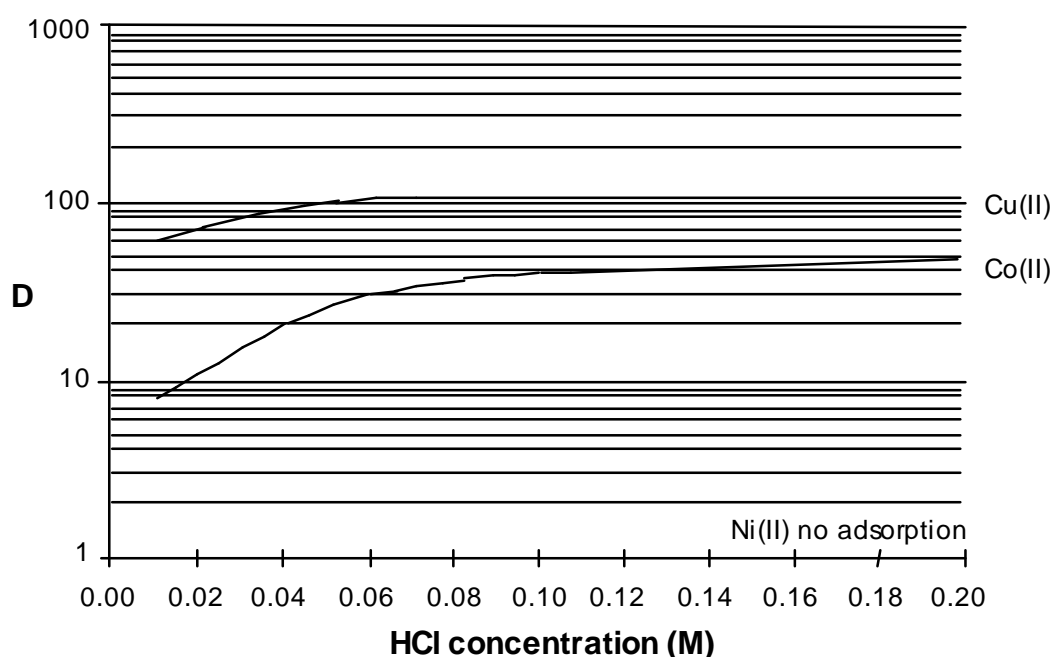


Figure 1 - Distribution coefficients, D of metal ions between anion exchange resin and 96 % methanol at varying HCl concentrations. (note D value for Zn > 1000)

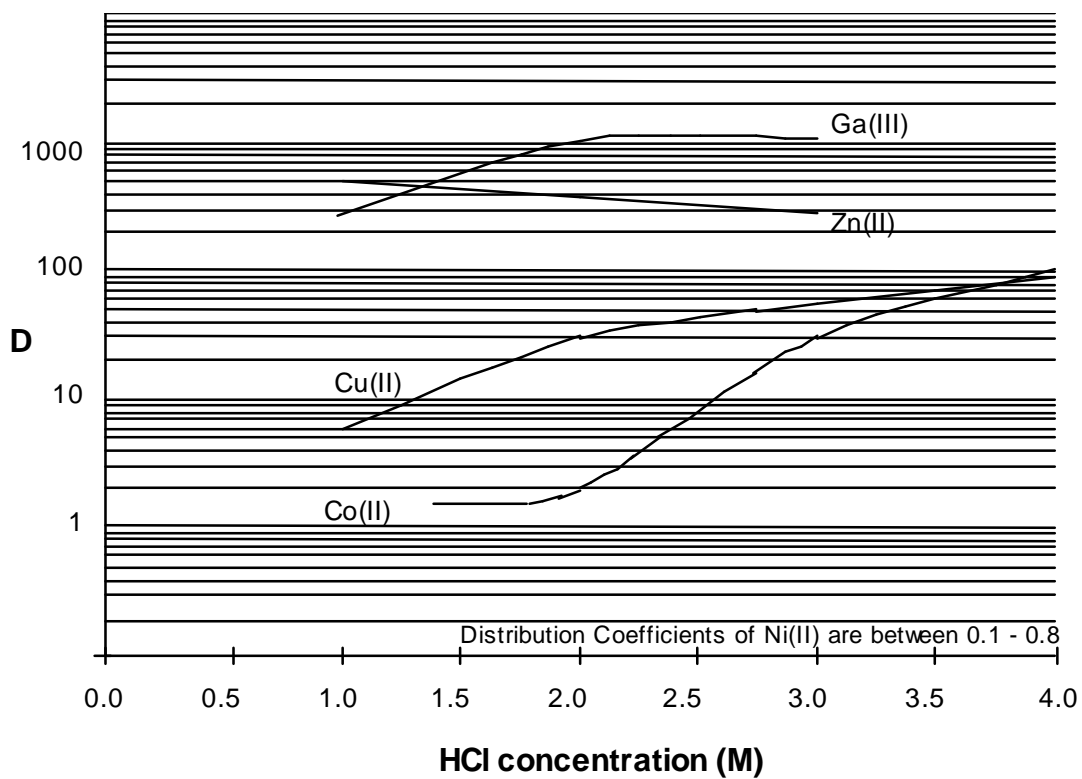


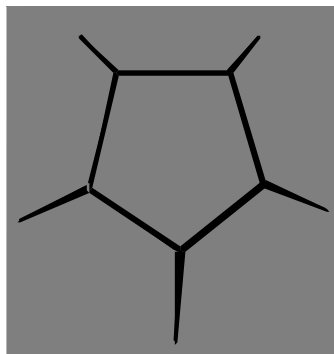
Figure 2 - Distribution coefficients, D of metal ions between anion exchange resin and 55 % isopropyl alcohol at varying HCl concentrations.

Problem 3

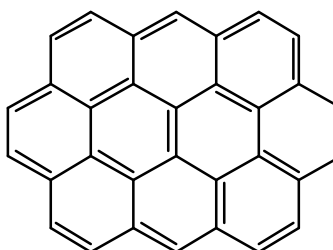
20 points

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

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



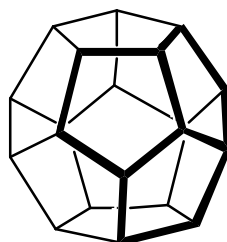
and Ovalene, $C_{32}H_{14}$.



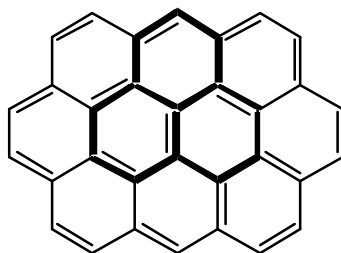
Each C_5 ring of dodecahedrane is a regular pentagon, while each C_6 ring of ovalene can be regarded as a regular hexagon.

- 3-1. What are the $\angle(\text{CCC})$ angles for each of these rings?
- 3-2. Which configuration (trigonal planar, 120° ; tetrahedral, 109.5° ; or octahedral, 90°) do the above $\angle(\text{CCC})$ angles most closely match?
- 3-3. What is the hybridization (sp , sp^2 , or sp^3) which most closely conforms to the geometric structure of dodecahedrane, and of ovalene?

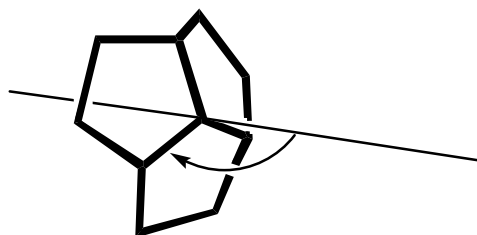
A “junction” is defined here to mean any 3-ring system, sharing a common central carbon atom, within a molecule. Compare the junctions (shown in bold) of three pentagons within dodecahedrane:



and of three hexagons within ovalene:

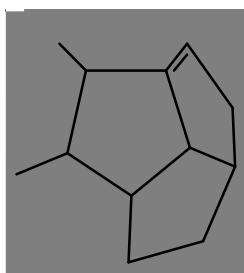


Consider an axis passing through the central carbon atom of each juncture such that the angle the axis forms with all three C-C bonds radiating from this C atom is identical.

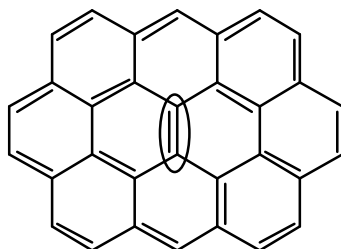


- 3-4. What is the value of this angle for dodecahedrane (make an “educated guess”, to the nearest three degrees), and for ovalene?
- 3-5. Subtracting 90° from each of the above angles describes the deviation from planarity for each juncture. Which juncture is planar ?

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



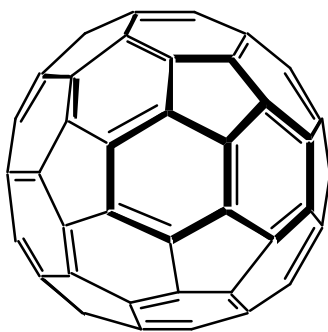
and ovalene:



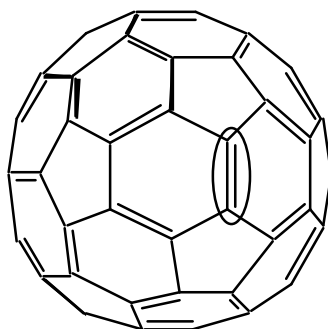
Assume that the molecular framework is rigid and is not significantly distorted by H_2 addition to the (indicated) double bond on each structure. Assume also that all double bonds are localized in assessing these systems.

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.



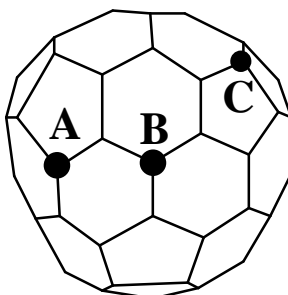
For C_{60} , all junctures are entirely equivalent. Now consider H_2 addition at a $C=C$ bond of C_{60} :



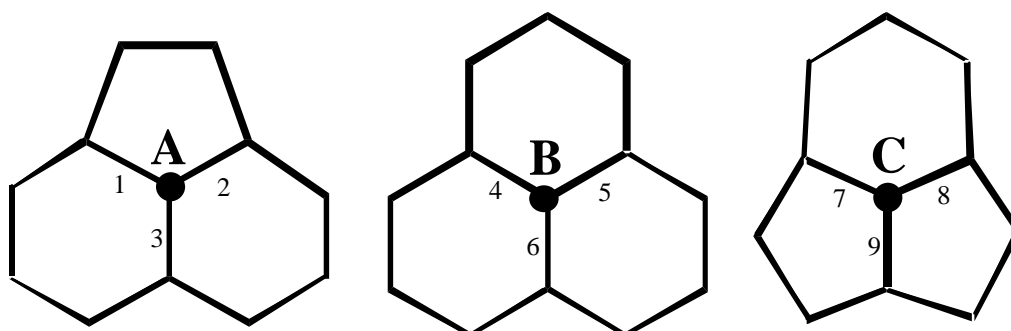
3-7. For which of C_{60} , dodecahedrene, or ovalene is H_2 addition most exothermic? (Again, assume localization of double bonds)

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:

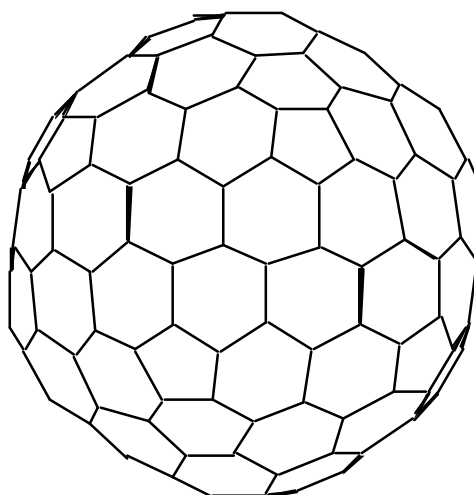


The junctures centred on atoms **A**, **B** and **C** on the above structure can be redrawn for greater clarity:



- 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 H₂ addition?

Finally, consider a larger fullerene, C₁₈₀:

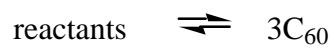


To a first approximation, both C₆₀ and C₁₈₀ are 'perfect' spheres.

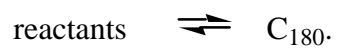
- 3-12. Which has the larger average deviation from planarity at each juncture? C₆₀ or C₁₈₀?
- 3.13 Compare the geometries of C₆₀ and C₁₈₀, and graphite. Which of the statements shown on the answer sheet (concerning enthalpies of formation, **in kJ g⁻¹ units**) is correct?

Fullerenes are generated on a very rapid timescale, typically milliseconds. In all techniques, C₆₀ is produced in much greater quantities than C₁₈₀.

3-14. Which of the graphs shown on the answer template best represents the dependence of potential energy upon reaction progress for the two processes:



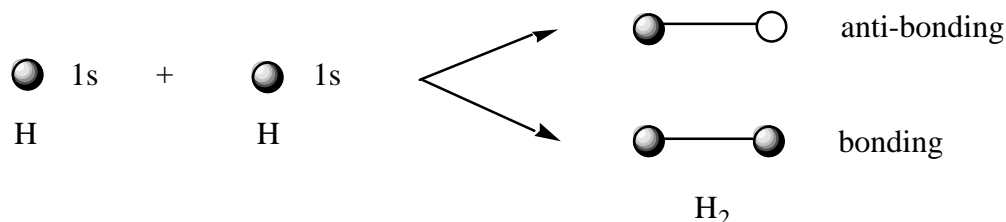
and



Problem 4

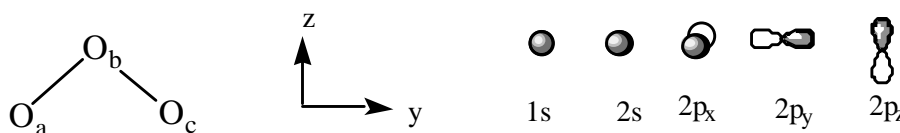
15 points

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.

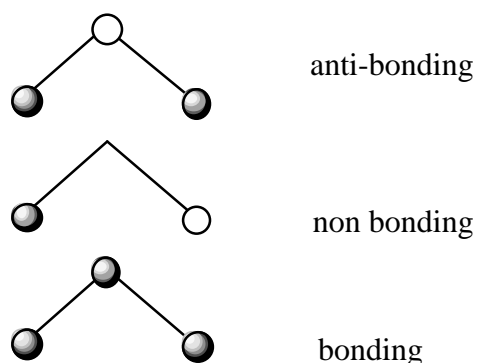
Consider the ozone molecule, O₃, which is shaped like an Australian boomerang. We can arrange the oxygens as follows (in the *yz* plane) and assume that there are 1s, 2s, 2p_x, 2p_y and 2p_z orbitals on each atom.



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



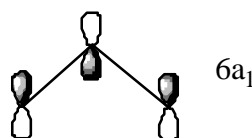
In this molecule the 1s atomic orbital on O_b is classified as symmetric. It can combine with the symmetric combination of O_a and O_c given above (but not with the anti-symmetric combination) to form bonding and anti-bonding molecular orbitals. The anti-symmetric combination is non-bonding. The final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



- 4-1. On the answer sheet, use a similar approach to construct the molecular orbitals arising from the separate interaction of the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. (Remember to form the symmetric and anti-symmetric combinations of O_a and O_c first.)

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

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



- 4-2. Why does the energy of the $6a_1$ orbital increase so rapidly as the bond angle changes from 90° to 180° ?

Only occupied molecular orbitals affect the geometry, and a doubly occupied orbital has more influence than a singly occupied orbital. For example, O_3 has 24 electrons and so at a bond angle of 135° the orbitals are doubly occupied up to $6a_1$. Thus, the lowest-energy geometry of ozone (taking into account steric repulsion and the contrasting energy behaviour of the $4b_2$, $1a_2$ and $6a_1$ orbitals) is probably towards the left of the Walsh diagram, which is consistent with the observed bond angle of 116° .

- 4-3. At a bond angle of 135° , what are the highest occupied orbitals for the molecules BO_2 , CO_2 , NO_2 and FO_2 ?
- 4-4. The bond angles of BO_2 , CO_2 and O_3 are known experimentally to be 180° , 180° and 116° , respectively. Use the Walsh diagram on the answer sheet to predict whether NO_2 and FO_2 are more or less bent than O_3 .

Problem 5

15 points

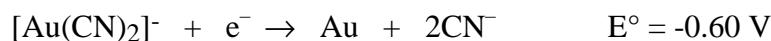
Metallic gold frequently is found in aluminosilicate rocks and it is finely dispersed among other minerals. It may be extracted by treating the crushed rock with aerated sodium cyanide solution. During this process metallic gold is slowly converted to $[\text{Au}(\text{CN})_2]^-$, which is soluble in 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, SnCl_4 .

6-1. Draw two alternative geometries for SnCl_4 .

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



and



6-2. Draw three alternative geometries for SnCl_5^- .

6-3. Use Valence Shell Electron Pair Repulsion (VSEPR) theory to predict which geometry is likely to be preferred for SnCl_5^- .

6-4. Draw three alternative geometries for SnCl_6^{2-} .

6-5. Use VSEPR theory to predict which of these geometries is likely to be preferred for SnCl_6^{2-} .

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

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

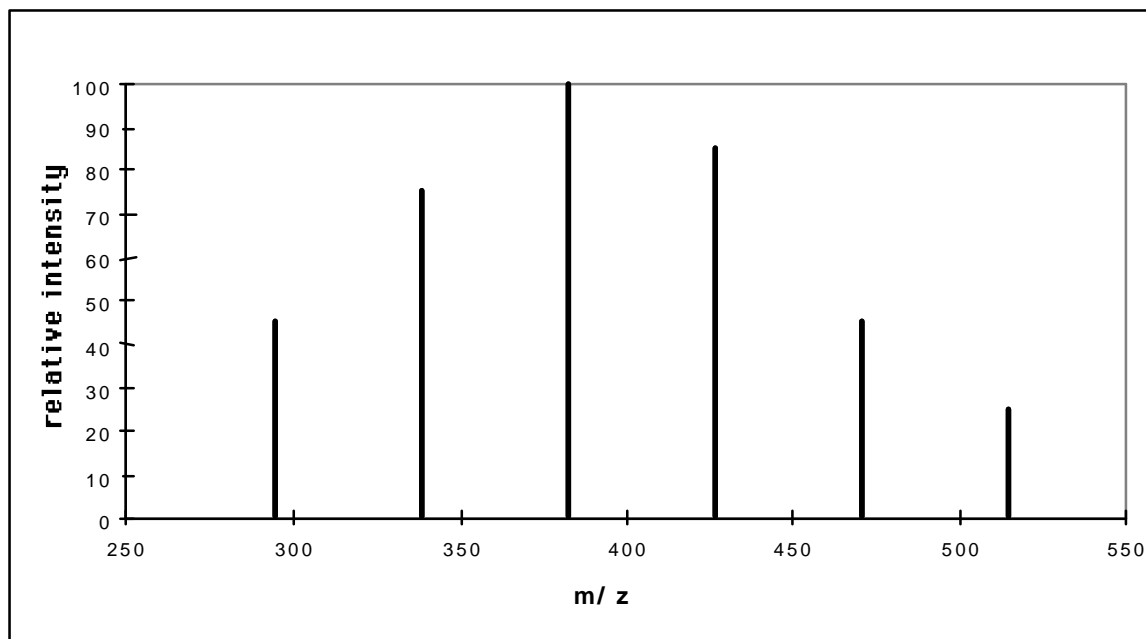
6-6. Write the empirical formula for the tin-containing species detected by this technique.

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

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

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

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

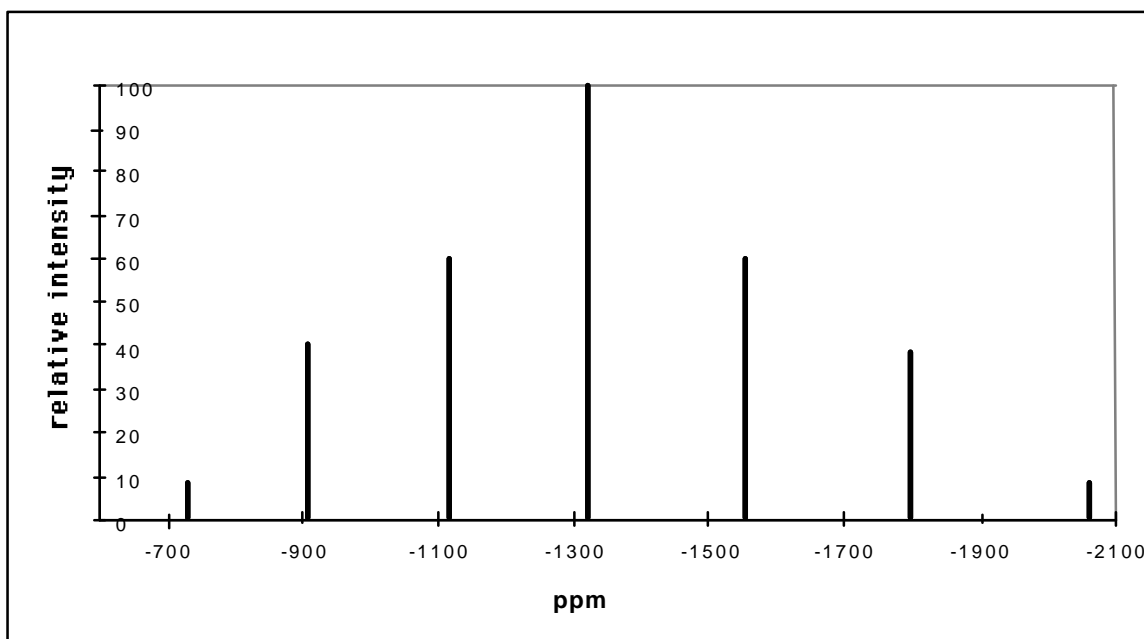


6-8. Write the formula for each of the four new species.

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

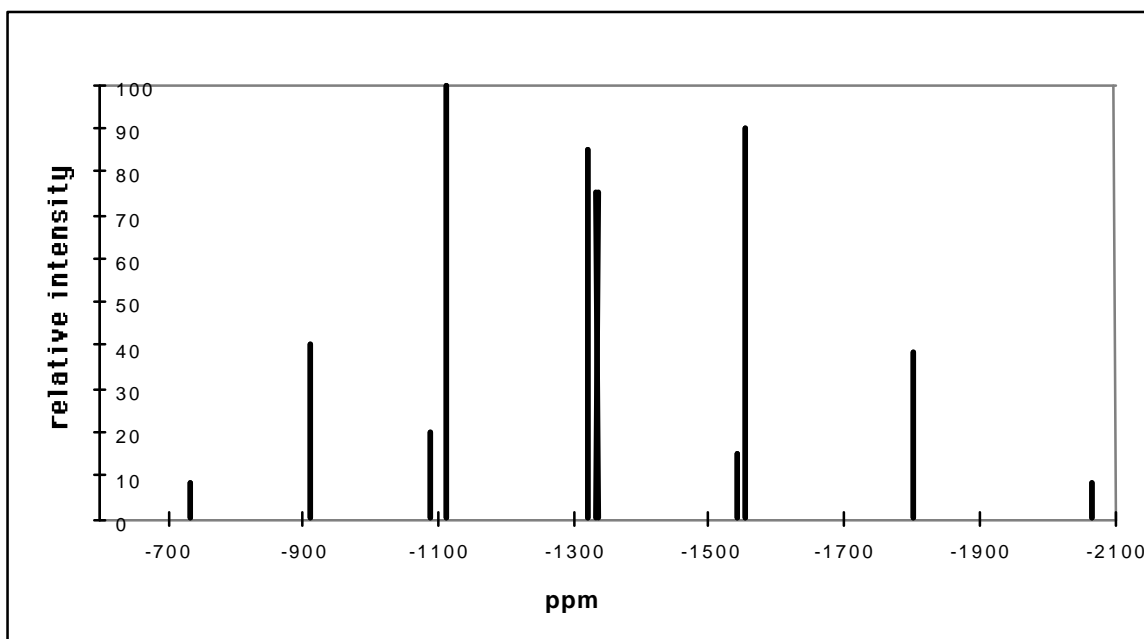
The ^{119}Sn NMR spectrum of a solution of SnCl_6^{2-} (as the tetrabutylammonium salt) contains only one signal which occurs at -732 ppm (relative to tetramethyltin, Me_4Sn).

The ^{119}Sn NMR spectrum of a solution of SnBr_6^{2-} (as the tetrabutylammonium salt) occurs at -2064 ppm. The ^{119}Sn NMR spectrum at 60 °C of a solution formed by mixing equimolar amounts of SnCl_6^{2-} and SnBr_6^{2-} contains seven peaks.



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}Sn NMR spectrum and at $-30\text{ }^\circ\text{C}$ ten peaks are observed.

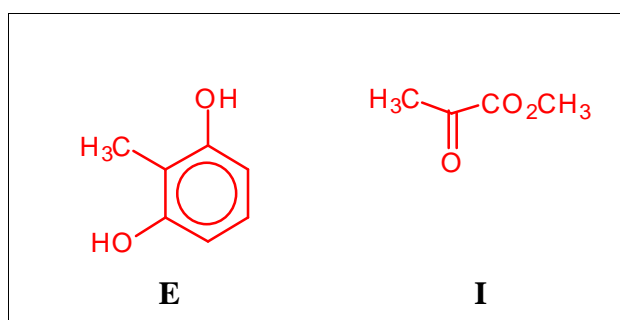


6-10. Draw the geometry for each of the four tin-containing species present in this solution at $-30\text{ }^\circ\text{C}$ that give rise to the peaks at -1092 and -1115 , -1322 and -1336 ppm.

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 δ 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**.