

IChO 1998

Theory problems and solutions · Melbourne, Australia · 7 theory problems with complete solutions

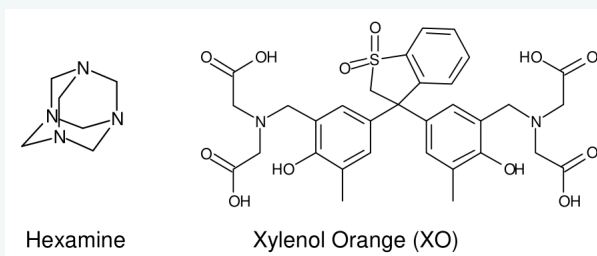
eulersolve.org/icho/1998/

Problem 1: EDTA titration of tin and lead in an alloy

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

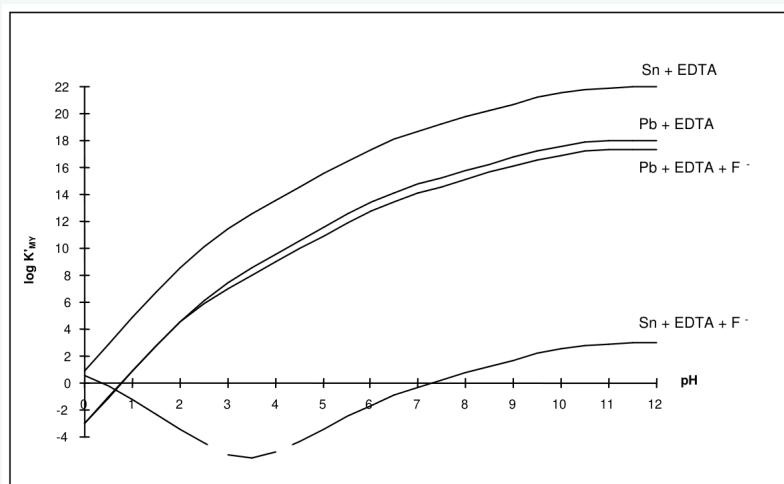
1. A 0.4062 g sample of alloy was dissolved by heating it in a small beaker with a mixture of 11 M hydrochloric and 16 M nitric acid. The beaker was heated until the entire alloy dissolved. In this procedure, lead is oxidised to Pb(II) and tin becomes Sn(IV).
2. After 5 minutes of heating to expel oxides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

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



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

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



1.1 What is the lead compound that precipitates in Step 2?

1.2 Write a balanced ionic equation that explains the disappearance of the precipitate in Step 3 (at pH 6).

1.3 What is the purpose of hexamine in Step 5 of the analysis?

1.4 What is the purpose of Xylenol Orange in the analysis?

1.5 Write balanced ionic equations for the reactions occurring during the titration and responsible for the colour change at the endpoint in Step 6 of the analysis

1.6 What is the purpose of NaF in Step 7 of the analysis?

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

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

1.9 Write a balanced ionic equation that explains why the lines on the graph below of $\log K_{MY}$ vs pH for $Pb + EDTA$ and $Pb + EDTA + F^-$ are coincident below pH 2.

1.10 Calculate the percentage by weight of Sn and Pb in the alloy.

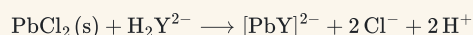
Official English text of the problem.

Answers

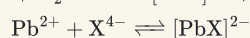
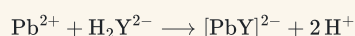
Let Y^{4-} denote fully deprotonated EDTA. For charge-explicit indicator equations, use the formal XO representation X^{4-} and its lead complex $[PbX]^{2-}$. This indicator convention does not identify the unique microscopic protonation state at pH 6; see the discussion and SMILES below.

- 1.1 Lead(II) chloride, $PbCl_2$.

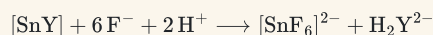
- 1.2



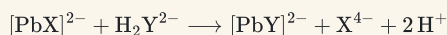
- 1.3 Hexamine neutralizes residual acid and, with its conjugate acid, helps maintain the solution at pH 6.
- 1.4 Xylenol Orange is a metallochromic indicator: free indicator is yellow at pH 6, whereas its lead complex is red.
- 1.5



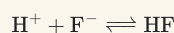
- 1.6 Fluoride selectively masks tin(IV), releasing its bound EDTA for a second titration.
- 1.7



- 1.8



- 1.9



Protonation suppresses fluoride's competition for lead.

- 1.10

$$w(Sn) = 43.70\%, \quad w(Pb) = 56.45\%$$

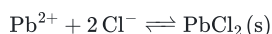
The supplied measurements give a total of 100.15%, a small mass-balance discrepancy.

Solution

1.1

The precipitate is **lead(II) chloride**, $PbCl_2$, SMILES `[Cl-].[Cl-].[Pb+2]`.

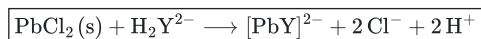
The solution contains lead(II) ions and chloride from hydrochloric acid. Lead(II) chloride is sparingly soluble, and its solubility decreases on cooling:



Lead(II) nitrate would remain soluble. The disconnected SMILES describes the ionic composition of the solid, not its crystal lattice.

1.2

EDTA forms a sufficiently stable, soluble lead complex to drive dissolution of the chloride precipitate. Writing the added ligand as H_2Y^{2-} ,

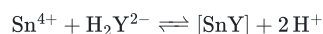


This is the sum of dissolution and complex formation:



Complexation lowers the free lead-ion concentration and therefore draws more solid into solution.

Tin(IV) is also strongly complexed:



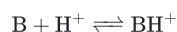
The problem does not identify the tin precipitates individually. If a precipitate is represented as tin(IV) oxide, its corresponding dissolution equation is



This last equation illustrates the principle; it does not establish the identity of every tin solid present.

1.3

Hexamine is a weak base, as indicated by its $pK_b = 9.5$. It accepts protons from the residual acid:



Here **B** is hexamine and BH^+ its conjugate acid. Their mixture provides acid–base buffering and accommodates protons released during complex formation.

Maintaining pH 6 serves two purposes:

- The conditional formation constants of both metal–EDTA complexes are large enough for quantitative complexation.
- Uncomplexed XO is yellow, allowing a distinct red endpoint when lead binds the indicator.

1.4

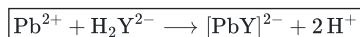
XO acts as a **metallochromic endpoint indicator**.

While unbound EDTA remains, added lead(II) is captured by EDTA. Once that EDTA has been consumed, the first slight excess of lead forms the red lead–XO complex.

Because the pH is maintained at 6, this yellow-to-red endpoint signals **metal binding**, rather than acidification into the indicator's low-pH red range.

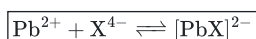
1.5

During the first titration, lead(II) consumes the excess EDTA:



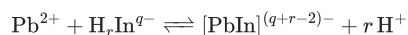
Each mole of added lead consumes one mole of unbound EDTA.

At the endpoint, lead binds XO. In the stated formal indicator convention,



The free-indicator population is yellow; the lead-bound population is red.

The exact microscopic proton balance of XO cannot be determined from the supplied acid–base information. More generally, if binding removes r protons from a free indicator species of charge q^- , the fully balanced form is



The simpler equation above is a formal representation of this indicator chemistry at fixed pH.

1.6

Sodium fluoride, SMILES $[\text{Na}^+] . [\text{F}^-]$, supplies fluoride ions that preferentially complex tin(IV).

The graph shows that, at pH 6:

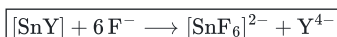
- The tin–EDTA conditional formation constant becomes extremely small in the presence of fluoride.
- The lead–EDTA conditional formation constant remains very large.

Consequently, fluoride displaces EDTA from tin while leaving lead effectively bound to EDTA. The released EDTA can then be measured with additional standard lead nitrate.

This is **selective masking of tin(IV)**.

1.7

Tin(IV) forms **hexafluoridostannate(IV)**, $[\text{SnF}_6]^{2-}$, releasing one EDTA ligand per tin atom:



Including protonation of the released EDTA gives the equivalent equation

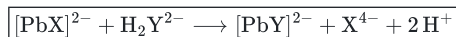


Thus, the second titre measures tin in a **1:1 molar ratio**:

$$n(\text{lead added in second titration}) = n(\text{tin in aliquot})$$

1.8

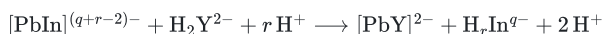
The newly released EDTA removes lead from the red indicator complex, regenerating the yellow free indicator:



Using fully deprotonated EDTA, the equivalent formal equation is



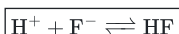
For the general protonation convention introduced in 1.5, the explicitly balanced version is



Further addition of lead nitrate consumes the released EDTA. Once it is exhausted, red lead–XO complex forms again.

1.9

In strongly acidic solution, fluoride is protonated:



Hydrogen fluoride is much less effective than free fluoride ion at competing for lead. Below pH 2, this suppresses the fluoride side reaction sufficiently that the conditional lead–EDTA formation constants with and without added fluoride coincide on the graph.

1.10

Both metals form **1:1 EDTA complexes**. The dilution factor from the aliquot to the original sample is

$$D = \frac{250.0 \text{ cm}^3}{25.00 \text{ cm}^3} = 10.00$$

The 15.00 cm³ second titre is the **additional** volume added after fluoride treatment.

The original EDTA amount is

$$n_{Y,0} = (0.2000 \text{ mol L}^{-1})(25.00 \times 10^{-3} \text{ L}) = 5.000 \times 10^{-3} \text{ mol}$$

Therefore, each aliquot contains

$$n_{Y,\text{aliquot}} = 5.000 \times 10^{-4} \text{ mol}$$

of total EDTA, including bound and unbound ligand.

The first titre measures the EDTA initially left unbound:

$$\begin{aligned} n_{Y,\text{excess}} &= (0.009970 \text{ mol L}^{-1})(24.05 \times 10^{-3} \text{ L}) \\ &= 2.397785 \times 10^{-4} \text{ mol} \end{aligned}$$

Hence, retaining guard digits,

$$\begin{aligned} n_{\text{Sn},a} + n_{\text{Pb},a} &= 5.000 \times 10^{-4} - 2.397785 \times 10^{-4} \\ &= 2.602215 \times 10^{-4} \text{ mol} \end{aligned}$$

The second titre measures EDTA released from tin:

$$\begin{aligned} n_{\text{Sn},a} &= (0.009970 \text{ mol L}^{-1})(15.00 \times 10^{-3} \text{ L}) \\ &= 1.49550 \times 10^{-4} \text{ mol} \end{aligned}$$

Therefore,

$$\begin{aligned} n_{\text{Pb},a} &= 2.602215 \times 10^{-4} - 1.49550 \times 10^{-4} \\ &= 1.106715 \times 10^{-4} \text{ mol} \end{aligned}$$

Scaling to the whole sample,

$$\begin{aligned} n_{\text{Sn}} &= 1.49550 \times 10^{-3} \text{ mol} \\ n_{\text{Pb}} &= 1.106715 \times 10^{-3} \text{ mol} \end{aligned}$$

Using $M_{\text{Sn}} = 118.7 \text{ g mol}^{-1}$ and $M_{\text{Pb}} = 207.2 \text{ g mol}^{-1}$,

$$\begin{aligned} m_{\text{Sn}} &= (1.49550 \times 10^{-3})(118.7) = 0.17751585 \text{ g} \\ m_{\text{Pb}} &= (1.106715 \times 10^{-3})(207.2) = 0.229311348 \text{ g} \end{aligned}$$

Thus,

$$\begin{aligned} w(\text{Sn}) &= \frac{0.17751585}{0.4062} \times 100\% = 43.70\% \\ w(\text{Pb}) &= \frac{0.229311348}{0.4062} \times 100\% = 56.45\% \end{aligned}$$

The reconstructed metal mass is 0.4068272 g, compared with the stated 0.4062 g. The two independently calculated percentages have therefore been reported without forcing their sum to 100%.

Names, SMILES, and structural conventions

The following representations complete the structural identification of species used above. Dative arrows in the complex SMILES represent donor-to-metal bonds; they do not specify three-dimensional geometry.

Species	Name and SMILES
Y^{4-}	Ethylenediaminetetraacetate, EDTA(4-): <chem>[O-]C(=O)CN(CC(=O)[O-])CCN(CC(=O)[O-])CC(=O)[O-]</chem>
H_2Y^{2-}	Dihydrogen ethylenediaminetetraacetate, shown with both amine nitrogens protonated: <chem>[O-]C(=O)C[NH+](CC(=O)[O-])CC[NH+](CC(=O)[O-])CC(=O)[O-]</chem>
$[\text{PbY}]^{2-}$	Lead(II)-EDTA complex: <chem>[Pb+2]12345<-[O-]C(=O)CN->1(CC(=O)[O-]->2)CCN->3(CC(=O)[O-]->4)CC(=O)[O-]->5</chem>
$[\text{SnY}]$	Tin(IV)-EDTA complex: <chem>[Sn+4]12345<-[O-]C(=O)CN->1(CC(=O)[O-]->2)CCN->3(CC(=O)[O-]->4)CC(=O)[O-]->5</chem>
B	Hexamine, or hexamethylenetetramine: <chem>C1N2CN3CN1CN(C2)C3</chem>
BH^+	Monoprotonated hexamine: <chem>C1[NH+]2CN3CN1CN(C2)C3</chem>
$[\text{SnF}_6]^{2-}$	Hexafluoridostannate(IV): <chem>[F-]->[Sn+4](<-[F-])(<-[F-])(<-[F-])(<-[F-])(<-[F-])<-[F-]</chem>
X^{4-}	Xylenol Orange, formal tetracarboxylate representation: <chem>C1(c2cc(CN(CC(=O)[O-])CC(=O)[O-])c(O)c(C)c2)(c2cc(CN(CC(=O)[O-])CC(=O)[O-])c(O)c(C)c2)OS(=O)(=O)c2ccccc21</chem>
$[\text{PbX}]^{2-}$	Lead(II)-XO, schematic 1:1 chelate representation: <chem>[Pb+2]12<-[O-]C(=O)CN->1(CC(=O)[O-]->2)Cc1cc(C2(c3cc(CN(CC(=O)[O-])CC(=O)[O-])c(O)c(C)c3)OS(=O)(=O)c3ccccc32)cc(C)c1O</chem>
SnO_2	Tin(IV) oxide, formula-unit representation: <chem>O=[Sn]=O</chem>
HF	Hydrogen fluoride: <chem>[H]F</chem>
H_2O	Water: <chem>O</chem>

The simple ions are lead(II), [Pb+2]; tin(IV), [Sn+4]; chloride, [Cl-]; fluoride, [F-]; and hydrogen ion, [H+]. Aqueous hydrogen ions are solvated; [H+] is the conventional ionic-equation representation.

The EDTA complex models show coordination through two nitrogen and four oxygen donors. Hexafluoridostannate(IV) has octahedral coordination. The precise lead coordination geometry, additional hydration, and XO donor arrangement are not established by this problem. In particular, the Pb-XO SMILES is a schematic connectivity model, not a determination of its colour-bearing microscopic structure. Solid tin(IV) oxide has an extended lattice rather than discrete molecules of the displayed formula-unit form.

The solution was checked against the official solution.

Problem 2: Dating historical events using Pb-210; separation of radionuclides for nuclear medicine

Part A: Dating Historical Events Using Pb-210

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

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

The examination of the sediment core found that:

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

2.1 In what year did Nathan Thompson plant the seeds?

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

- The U-238 decay chain is:

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

* Very short half-lives: minutes and days

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

Part B: Separation of Radionuclides for Nuclear Medicine Applications.

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

Table 1

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

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

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

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

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

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

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

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

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

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

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

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

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

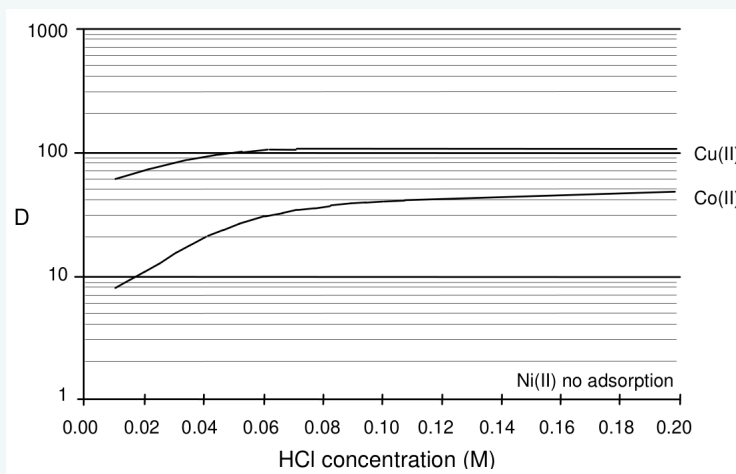


Figure 1. Distribution coefficients, D of metal ions between anion exchange resin and 96 % methanol at varying HCl concentrations. (note D value for Zn > 1000)

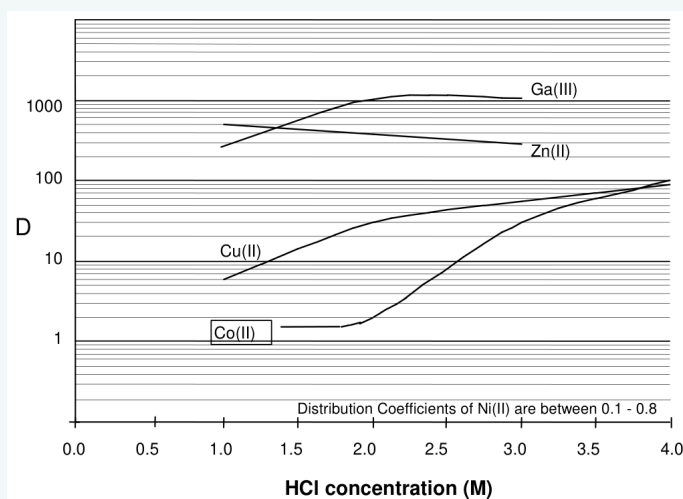


Figure 2. Distribution coefficients, D of metal ions between anion exchange resin and 55 % isopropyl alcohol at varying HCl concentrations.

Official English text of the problem.

Answers

- **2.1:** Approximately **1819**.

- **2.2:** The formation of gaseous radon-222 by alpha decay of radium-226. Radon escapes into the atmosphere, where its decay produces the precursors of Pb-210.
- **2.3:** A suitable elution sequence is: remove Ni-57 using the loading solvent; elute **Co-55 with approximately 2 M HCl in 55% isopropyl alcohol**; then elute **Cu-64 with approximately 1 M HCl in 55% isopropyl alcohol**. Approximately 0.01 M HCl in 96% methanol is another suitable cobalt eluent.
- **2.4:** a) False; b) True; c) True; d) False; e) False. Here d) concerns the stated problem of long-lived contamination.
- **2.5:** a) True; b) True; c) True; d) False.
- **2.6:** a) False; b) True, approximately; c) False; d) True, interpreting contamination as the absolute production of contaminants arising from unchanged target construction.

Solution

2.1 — Dating the first pollen

The dating calculation assumes that the sediment originally had the same Pb-210 activity per unit mass as newly deposited surface sediment, and that subsequent activity loss was caused by radioactive decay.

For activity per unit mass a ,

$$a(t) = a_0 2^{-t/t_{1/2}}.$$

Therefore,

$$\begin{aligned} t &= \frac{t_{1/2}}{\ln 2} \ln \left(\frac{a_0}{a(t)} \right) \\ &= \frac{22.0 \text{ yr}}{\ln 2} \ln \left(\frac{356 \text{ Bq kg}^{-1}}{1.40 \text{ Bq kg}^{-1}} \right) \\ &= 175.8 \text{ yr} \approx 176 \text{ yr}. \end{aligned}$$

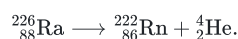
Thus the first pollen was deposited approximately in

$$1995 - 175.8 = 1819.2.$$

Since the trees pollinate during their first year of growth, the planting year was approximately **1819**.

2.2 — Transport from the crust into the atmosphere

The crucial step is



Both mass number and nuclear charge are conserved:

$$226 = 222 + 4, \quad 88 = 86 + 2.$$

Radon-222, atomic SMILES [222Rn], is a noble gas and can escape from rocks and soil into the atmosphere. Its subsequent radioactive descendants ultimately produce Pb-210. These non-gaseous products attach to atmospheric particles and are carried down by rain.

The emitted alpha particle is a helium-4 nucleus, $^4\text{He}^{2+}$, SMILES [4He+2]; the equation above uses conventional nuclear notation.

2.3 — Choosing the eluents

A large D means strong retention on the resin; a small D favours passage into the eluant. A useful eluent therefore gives the desired metal a relatively small D , while maintaining a difference of at least 10 from metals that must remain on the column.

From the stated definition, D has units of $\text{cm}^3 \text{mg}^{-1}$. The following values are approximate graph readings.

Stage	Solvent system	Relevant D values	Result
Load and wash	0.2 M HCl, 96% methanol	Ni: no adsorption; Co: about 50; Cu: about 100; Zn: > 1000	Ni-57 passes through while Co, Cu and Zn remain retained.
Collect cobalt	About 2 M HCl, 55% isopropyl alcohol	Co: about 2; Cu: about 30; Zn: several hundred	Co-55 elutes while Cu and Zn remain more strongly retained.
Collect copper	About 1 M HCl, 55% isopropyl alcohol	Cu: about 6; Zn: about 500	Cu-64 elutes after cobalt has been removed; Zn remains strongly retained.

For the cobalt separation at approximately 2 M acid,

$$D_{\text{Cu}} - D_{\text{Co}} \approx 30 - 2 = 28 > 10.$$

For the subsequent copper–zinc separation,

$$D_{\text{Zn}} - D_{\text{Cu}} \approx 500 - 6 \gg 10.$$

Removing nickel during the initial wash is essential: in the isopropyl alcohol system its D is only 0.1–0.8, so it would accompany a weakly retained cobalt fraction if left on the column.

Figure 1 also supplies a viable cobalt eluent: at approximately **0.01 M HCl in 96% methanol**,

$$D_{\text{Co}} \approx 8, \quad D_{\text{Cu}} \approx 60,$$

giving a difference of approximately 52. Cobalt is more strongly retained under this condition than under the proposed isopropyl alcohol condition, but the separation criterion is satisfied.

The solvent components are:

- Hydrogen chloride, HCl, SMILES c1, used to provide the stated acid concentration.
- Methanol, CH₃OH, SMILES co.

- Propan-2-ol, or isopropyl alcohol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, SMILES CC(O)C.

The relevant metal-ion identities are listed below. These SMILES identify isotope and formal ion charge; the graphs do not specify the actual coordination structures or geometries of the adsorbed species.

Metal-ion names	SMILES
Copper-64(II); copper-67(II)	[64Cu+2]; [67Cu+2]
Cobalt-55(II); cobalt-57(II)	[55Co+2]; [57Co+2]
Nickel-57(II)	[57Ni+2]
Zinc-65(II); zinc-68(II)	[65Zn+2]; [68Zn+2]
Gallium-66(III); gallium-67(III)	[66Ga+3]; [67Ga+3]

2.4 — Identifying the interfering radionuclides

Ordinary ion-exchange chromatography separates different elements through their chemical behaviour. It does not usefully separate isotopes of the same element.

Statement	Answer	Reason
a) Ni-57 may contaminate Co-55.	False	Under the stated separation conditions, nickel is removed during loading and washing because it is not adsorbed in the methanol system.
b) Co-57 interferes with Co-55.	True	Both are cobalt isotopes and accompany one another chemically. Co-57 has a half-life of 270 days, much longer than the 18.2 h half-life of Co-55.
c) Cu-67 interferes with Cu-64.	True	Both are copper isotopes and accompany one another chemically. Cu-67 has a longer half-life: 61.7 h versus 12.7 h.
d) Ga-66 interferes with Ga-67.	False , in the stated long-lived-contaminant sense	Ga-66 has a half-life of only 9.4 h, compared with 78.35 h for Ga-67. Its contribution decreases preferentially during storage.
e) Ga-67 interferes with Cu-64.	False	Gallium has already been retained on the first cation-exchange column, while copper enters the wash solution.

For d), the relative activity follows

$$\frac{a_{66}(t)}{a_{67}(t)} = \frac{a_{66}(0)}{a_{67}(0)} 2^{-t\left(\frac{1}{9.4 \text{ h}} - \frac{1}{78.35 \text{ h}}\right)}.$$

After 12 h this ratio is approximately 0.459 times its initial value. An initially present Ga-66 impurity can still matter before sufficient decay; it is not the persistent, long-lived impurity described in the question.

2.5 — Reducing contamination

Ni-57 produces Co-57 as it decays. Once formed, Co-57 accompanies Co-55 through chemical separation. Removing the nickel parent early prevents further production of this inseparable cobalt impurity.

Statement	Answer	Reason
a) Remove Ni-57 before isolating Co-55.	True	Removing the parent prevents further Co-57 production in material that will supply the cobalt fraction. It cannot remove Co-57 already formed.
b) Remove Ni-57 from the target material before isolating Ga-67.	True	Earlier nickel removal reduces the time available for Co-57 formation before the subsequent cobalt separation.
c) Separate closer to the end of bombardment.	True	Less Co-57 forms before separation, and more of the short-lived desired radionuclides survives.
d) Allow Ni-57 to decay before isolating Co-55.	False	Waiting converts Ni-57 into the problematic Co-57 daughter while Co-55 itself continues to decay.

For example, during the stated 12 h delay, the fraction of Ni-57 that decays is

$$1 - 2^{-12/36.0} = 0.206,$$

or about **20.6%**. Because Co-57 has a 270-day half-life, almost all daughter atoms formed during this short interval remain present.

The benefit of earlier separation in c) concerns daughter formation and preservation of useful activity. It is not a claim that every impurity benefits from earlier use: short-lived Ga-66 is reduced by allowing it to decay.

2.6 — Replacing enriched zinc with natural zinc

The principal intended production reaction is



Mass number and nuclear charge balance:

$$68 + 1 = 67 + 2, \quad 30 + 1 = 31.$$

For the same number of zinc atoms and the same irradiation conditions, the contribution from this reaction is proportional to the Zn-68 abundance. Using 98% as the approximate enriched abundance,

$$\frac{Y_{\text{natural}}}{Y_{\text{enriched}}} \approx \frac{18.8}{98} = 0.192.$$

Thus the natural-zinc yield is approximately one-fifth of the enriched-zinc yield:

$$\frac{Y_{\text{enriched}}}{Y_{\text{natural}}} \approx 5.21.$$

Accordingly:

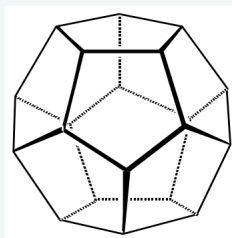
Statement	Answer	Reason
a) Fivefold higher Ga-67 yield.	False	Natural zinc contains substantially less Zn-68.
b) Fivefold lower Ga-67 yield.	True, approximately	The abundance estimate gives a reduction by a factor of about 5.2.
c) Lower Ga-67 yield and increased Cu, Co and Ni contaminant production.	False , under the intended target-construction assumption	Changing zinc enrichment does not increase the amount of the other target materials responsible for these contaminants.
d) Lower Ga-67 yield and unchanged Cu, Co and Ni contaminant production.	True , under the same assumption	Their absolute production remains approximately unchanged when target construction and irradiation are unchanged.

The distinction is between **absolute contaminant production** and **contamination relative to Ga-67**. If contaminant activity remains constant while Ga-67 production falls to about 19%, the contaminant-to-Ga-67 activity ratio increases by about a factor of 5.2.

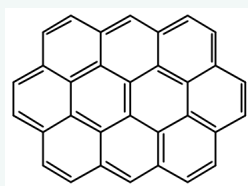
The solution was checked against the official solution.

Problem 3: Angle strain, hybridization and fullerenes

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

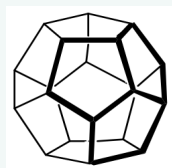
Each C_5 ring of dodecahedrane is a regular pentagon, while each C_6 ring of ovalene can be regarded as a regular hexagon.

3.1 What are the $\angle(CCC)$ angles for each of these rings?

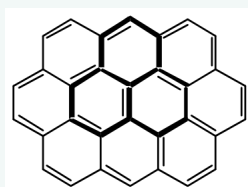
3.2 Which configuration (trigonal planar, 120° ; tetrahedral, 109.5° ; or octahedral, 90°) do the above $\angle(CCC)$ angles most closely match?

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?

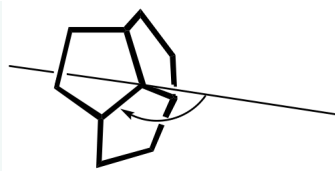
A "juncture" is defined here to mean any 3-ring system, sharing a common central carbon atom, within a molecule. Compare the junctures (shown in bold) of three pentagons within dodecahedrane:



and of three hexagons within ovalene:



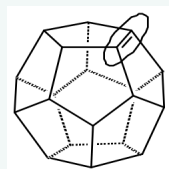
Consider an axis passing through the central carbon atom of each juncture such that the angle the axis forms with all three C—C bonds radiating from this C atom is identical.



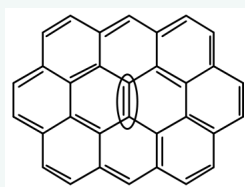
3.4 What is the value of this angle for dodecahedrane (make an “educated guess”, to the nearest three degrees), and for ovalene?

3.5 Subtracting 90° from each of the above angles describes the deviation from planarity for each juncture. Which juncture is planar?

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



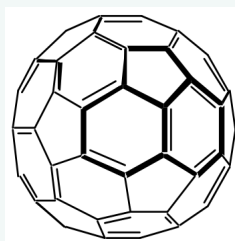
and ovalene:



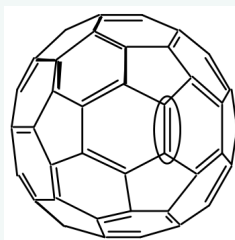
Assume that the molecular framework is rigid and is not significantly distorted by H_2 addition to the (indicated) double bond on each structure. Assume also that all double bonds are localized in assessing these systems.

3.6 Compare the indicated pairs of carbon atoms (encircled above). For which $C=C$ pair is 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.



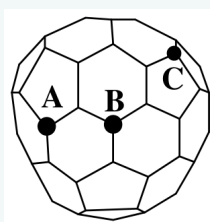
For C_{60} , all junctures are entirely equivalent. Now consider H_2 addition at a $C=C$ bond of C_{60} :



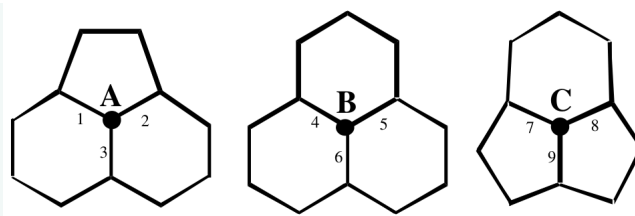
3.7 For which of C_{60} , dodecahedrene, or ovalene is H_2 addition most exothermic? (Again, assume localization of double bonds.)

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:

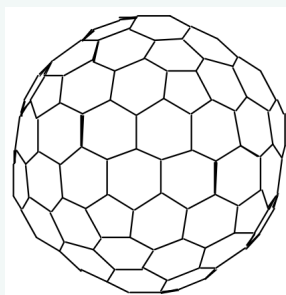


3.9 Which juncture has the least deviation from planarity?

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} :



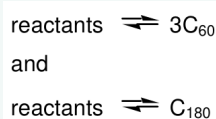
To a first approximation, both C_{60} and C_{180} are "perfect" spheres.

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:



Official English text of the problem.

Answers

SMILES identifiers and their geometric qualifications are given in the solution.

- 3.1: Dodecahedrane: 108° . Ovalene: 120° .
- 3.2: Dodecahedrane: tetrahedral. Ovalene: trigonal planar.
- 3.3: Dodecahedrane: sp^3 . Ovalene: sp^2 .
- 3.4: Dodecahedrane: approximately 111° . Ovalene: 90° .
- 3.5: Ovalene is planar. The deviations are approximately 21° for dodecahedrane and 0° for ovalene.
- 3.6: Addition to the indicated double bond of **dodecahedrene** is more exothermic.
- 3.7: **Dodecahedrene** gives the most exothermic addition.
- 3.8: **Ovalene** gives the least exothermic addition.
- 3.9: **B**.
- 3.10: **C**.
- 3.11: **Bond 9**, shared by two pentagons.
- 3.12: C_{60} .
- 3.13: Per gram,

$$h_f^\circ(\text{C}_{60}) > h_f^\circ(\text{C}_{180}) > h_f^\circ(\text{graphite}) = 0.$$

- 3.14: Choose the graph with a **lower activation barrier leading to 3 C_{60}** , but a **lower final product energy for C_{180}** .

Solution

3.1 — Ring angles

The molecular identifiers are:

- **Dodecahedrane**, $C_{20}H_{20}$: C12C3C4C5C1C1C6C2C2C3C3C4C4C5C1C1C6C2C3C41. Its carbon skeleton is the convex dodecahedral cage shown; SMILES does not specify its regular three-dimensional geometry.
- **Ovalene**, $C_{32}H_{14}$, one Kekulé representation: C1=CC2=CC=C3C=C4C=CC5=CC=C6C=CC7=CC8=CC=C1C1=C2C3=C2C4=C5C6=C7C2=C81. Its fused carbon framework is planar.

The interior angle of a regular n -gon is

$$\alpha_n = \frac{(n-2)180^\circ}{n}.$$

Consequently,

$$\alpha_5 = \frac{3(180^\circ)}{5} = \boxed{108^\circ}, \quad \alpha_6 = \frac{4(180^\circ)}{6} = \boxed{120^\circ}.$$

These are the respective $\angle(\text{CCC})$ angles.

3.2 — Closest configurations

The pentagonal angle 108° differs from the tetrahedral angle 109.5° by only 1.5° . Dodecahedrane therefore most closely matches **tetrahedral geometry**.

The hexagonal angle 120° exactly matches **trigonal planar geometry**, appropriate to ovalene.

3.3 — Hybridization

Tetrahedral geometry corresponds to sp^3 hybridization. Each carbon of dodecahedrane has three carbon neighbours and one hydrogen, making four σ bonds.

Trigonal planar geometry corresponds to sp^2 hybridization. Each carbon of ovalene has three σ -bond directions, with a remaining p orbital contributing to π bonding.

Thus,

$$\boxed{\text{Dodecahedrane: } sp^3; \quad \text{ovalene: } sp^2.}$$

3.4 — Angle between the axis and the bonds

For ovalene, the axis is perpendicular to the molecular plane. Its angle with each of the three carbon–carbon bonds is therefore

$$\boxed{90^\circ}.$$

For dodecahedrane, use the **outward-pointing ray** of the axis, consistent with the obtuse angle indicated in the figure and the subtraction prescribed in 3.5. The geometry is nearly tetrahedral, suggesting an angle near 110° .

The regular-pentagon model also permits an exact check. Let the common axis–bond angle be θ . The three bonds have azimuthal separations of 120° , and the angle between any two bonds is 108° . Hence

$$\cos 108^\circ = \cos^2 \theta + \sin^2 \theta \cos 120^\circ = \frac{3}{2} \cos^2 \theta - \frac{1}{2}.$$

Thus

$$\cos \theta = -\sqrt{\frac{1 + 2 \cos 108^\circ}{3}},$$

where the negative sign selects the outward, obtuse angle. Therefore,

$$\theta = 110.905\dots^\circ.$$

The requested estimate is

$$\boxed{\theta \approx 111^\circ}.$$

3.5 — Deviation from planarity

Using the definition in the question,

$$\delta = \theta - 90^\circ,$$

gives

$$\delta_{\text{dodecahedrane}} = 110.905\dots^\circ - 90^\circ \approx 20.9^\circ,$$

and

$$\delta_{\text{ovalene}} = 90^\circ - 90^\circ = 0^\circ.$$

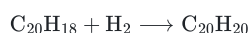
Therefore, **the ovalene juncture is planar**.

3.6 — Hydrogenation of dodecahedrene versus ovalene

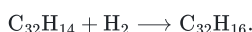
Dodecahedrene, $C_{20}H_{18}$, with the convex cage stereochemistry, is represented by:

C12=C3[C@@H]4[C@@H]5[C@H]1[C@@H]1[C@@H]6[C@H]2[C@@H]2[C@H]3[C@@H]3[C@H]4[C@@H]4[C@H]5[C@H]1[C@@H]1[C@H]6[C@H]2[C@H]3[C@H]4
 Hydrogen is **dihydrogen**, H_2 : [H][H].

The balanced additions are



and



The first product is dodecahedrane. The second is **dihydroovalene hydrogenated at the indicated central bond**, with connectivity SMILES:

C1=C2C=CC3=CC=C4C=CC5=CC6=C7C8=C9C(=C1C=CC9=CC=C8C=C6)C1C2=C3C4=C5C71

The question does not specify the relative stereochemistry of the two new carbon–hydrogen bonds in this latter product.

Hydrogenation changes the two reacting carbon atoms from approximately sp^2 bonding toward sp^3 bonding.

In dodecahedrene, the cage forces these initially unsaturated carbon atoms into strongly pyramidal geometries already close to tetrahedral. The double bond is consequently strained. Hydrogenation makes the preferred bonding geometry much better suited to the existing cage.

In ovalene, the initial planar framework suits sp^2 carbon. Hydrogenation introduces carbon atoms that prefer tetrahedral geometry into a framework assumed to remain approximately planar, increasing their geometric strain.

Thus, even without substantial movement of the framework, hydrogenation gives a greater improvement in geometric compatibility for dodecahedrene:

$$\Delta H_{\text{hyd}}(\text{dodecahedrene}) < \Delta H_{\text{hyd}}(\text{ovalene}).$$

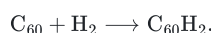
The more negative enthalpy change means **dodecahedrene hydrogenation is more exothermic**. This argument uses the stipulated localized-bond model; aromatic stabilization is not needed.

3.7 — Most exothermic addition among the three compounds

Buckminsterfullerene, C_{60} , has a truncated-icosahedral cage. One explicit-bond SMILES is:

C12=C3C4=C5C6=C7C3=C3C8=C1C1=C9C8=C8C%10=C%11C%12=C%13C%14=C%15C%16=C%17C%18=C%19C%20=C(C4=C2C2=C1C1=C4C9=C9C8=C%11C8=C

Its formal hydrogenation is



For addition of both hydrogens to the exterior at the indicated bond, the product is **1,2-dihydro[60]fullerene**, represented by:

C12=C3C4=C5C6=C1C1=C7C2=C2C8=C3C3=C4C4=C9C%10=C3C3=C8C8=C%11C%12=C%13C%14=C%11C3=C%10C3=C%14[C@H]%10C%11=C3C9=C3C4=C5C4

The carbon junctures of C_{60} are pyramidal, but the question specifies that their deviation from planarity is smaller than in dodecahedrene. Consequently, their geometry is intermediate between the strongly pyramidal dodecahedral cage and planar ovalene.

The strain-based order of hydrogenation enthalpies is therefore

$$\Delta H_{\text{hyd}}(\text{dodecahedrene}) < \Delta H_{\text{hyd}}(C_{60}) < \Delta H_{\text{hyd}}(\text{ovalene}).$$

Thus, **dodecahedrene gives the most exothermic addition**.

3.8 — Least exothermic addition

From the same ordering, **ovalene gives the least exothermic addition**. Its planar carbon framework provides the least favourable fixed geometry for the newly formed sp^3 centres.

3.9 — Juncture with the least deviation from planarity

The three junctures contain:

Juncture	Rings meeting at the carbon	Sum of ideal ring angles	Angular deficit from 360°
A	One pentagon and two hexagons	$108^\circ + 120^\circ + 120^\circ = 348^\circ$	12°
B	Three hexagons	$3(120^\circ) = 360^\circ$	0°
C	Two pentagons and one hexagon	$108^\circ + 108^\circ + 120^\circ = 336^\circ$	24°

Three regular hexagons can meet in a plane without an angular deficit. Therefore,

B has the least deviation from planarity.

These angular deficits compare the local curvature; they are not themselves the axis-based deviation angles defined in 3.5. In an actual curved fullerene, small ring distortions can make a three-hexagon juncture slightly nonplanar.

3.10 — Juncture with the greatest deviation from planarity

Juncture C contains two pentagons and has the largest angular deficit. It requires the strongest local departure from a planar arrangement:

C has the greatest deviation from planarity.

The ordering is

$$B < A < C.$$

3.11 — Most favourable bond for hydrogen addition

Bond 9 is the common edge of two pentagons. Thus, **both ends** of this bond lie at strongly curved junctures involving two pentagons.

Hydrogenation at this bond converts both reacting carbon atoms toward sp^3 bonding where the existing geometry is most favourable to that change. It therefore provides the greatest strain advantage among the indicated sites:

Bond 9.

3.12 — Average deviation in the two spherical fullerenes

For comparable carbon–carbon distances, the larger cage has the larger radius. A sphere's curvature decreases as its radius increases, so neighbouring bond directions change more sharply across the smaller cage.

Therefore,

C_{60} has the larger average deviation from planarity.

For a concrete molecular identifier, an **icosahedral C₁₈₀ fullerene**, constructed as the leapfrog of the C₆₀ cage, has the following SMILES:

C12=C3C4=C5C6=C7C8=C9C%10=C%11C8=C8C%12=C7C7=C5C5=C%13C%14=C7C7=C%15C%14=C%14C%16=C%13C%13=C%17C%18=C%19C%20=C%17C%16=C

This is an explicitly identified structural representative; the radius argument does not require a particular C₁₈₀ isomer. SMILES specifies the cage connectivity, not its spherical conformation.

3.13 — Enthalpies of formation per gram

Graphite, C, consists of extended sheets of carbon atoms in approximately planar *sp*² environments. It is a periodic solid, so it has no finite molecular SMILES; the atomic SMILES [C] would not represent graphite.

Within the problem's geometric model:

- Graphite has essentially no curvature-induced pyramidalization strain.
- C₁₈₀ has some curvature strain.
- C₆₀ has greater curvature strain per carbon atom.

Define the specific standard enthalpy of formation by

$$h_f^\circ = \frac{\Delta_f H^\circ}{M},$$

where $\Delta_f H^\circ$ is in kJ mol⁻¹ and M in g mol⁻¹. Then h_f° is in kJ g⁻¹.

Graphite is the standard reference state of carbon, so its standard enthalpy of formation is zero. The required ordering is

$$h_f^\circ(\text{C}_{60}) > h_f^\circ(\text{C}_{180}) > h_f^\circ(\text{graphite}) = 0 \quad \text{in kJ g}^{-1}.$$

The corresponding formation reactions are



No numerical formation enthalpies are supplied, so only the ordering can be obtained.

3.14 — Potential-energy diagram

The two paths must be compared for the same amount of carbon: one C₁₈₀ cage versus three C₆₀ cages.

Because C₁₈₀ has the lower formation enthalpy per gram,

$$\Delta_f H^\circ(\text{C}_{180}) < 3\Delta_f H^\circ(\text{C}_{60}).$$

Thus, the final energy of C₁₈₀ must be **below** that of 3 C₆₀. Equivalently, the formal atom-balanced conversion



is energetically downhill in this model; this equation does not assert a direct mechanism.

Nevertheless, the rapid formation process produces much more C₆₀. In the intended kinetic interpretation, the route to 3 C₆₀ has the smaller activation barrier.

The required graph should therefore have:

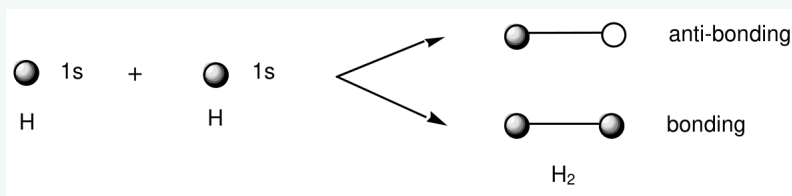
1. **Reaction progress** on the horizontal axis and **potential energy** on the vertical axis.
2. Two curves beginning at the **same reactant energy**.
3. A curve labelled 3 C₆₀ with the **lower peak**, ending at the **higher product energy**.
4. A curve labelled C₁₈₀ with the **higher peak**, ending at the **lower product energy**.

Thus, 3 C₆₀ is favoured kinetically, while C₁₈₀ is favoured thermodynamically within the stated comparison. The information does not fix the absolute product energies relative to the unspecified reactants.

The solution was checked against the official solution.

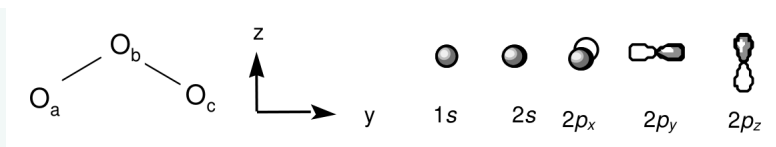
Problem 4: Molecular orbitals of ozone and the Walsh diagram

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.

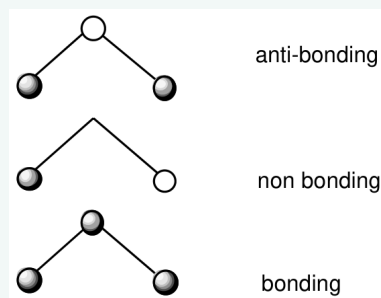
Consider the ozone molecule, O₃, which is shaped like an Australian boomerang. We can arrange the oxygens as follows (in the *yz* plane) and assume that there are 1s, 2s, 2p_x, 2p_y and 2p_z orbitals on each atom.



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



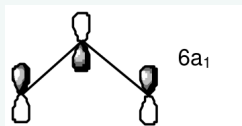
In this molecule the $1s$ atomic orbital on O_b is classified as symmetric. It can combine with the symmetric combination of O_a and O_c given above (but not with the anti-symmetric combination) to form bonding and anti-bonding molecular orbitals. The anti-symmetric combination is non-bonding. The final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

Official English text of the problem.

Answers

- 4.1:** Each atomic-orbital set gives three molecular orbitals, making **12 orbitals**. With coefficient signs listed in the order (a, b, c) , the bonding, non-bonding and anti-bonding patterns in the bent sketch are:
- $2s$ and $2p_x$: $(+, +, +)$, $(+, 0, -)$, $(+, -, +)$.
- $2p_y$ and $2p_z$: $(+, -, +)$, $(+, 0, -)$, $(+, +, +)$.

These describe ozone, O_3 , $[O-][O+]=O$. The $2p_z$ overlap character changes upon straightening.

- 4.2:** The matching, facing lobes in $6a_1$ lose their bonding overlap as the angle opens. At 180° , adjacent $2p_z$ orbitals overlap sideways with opposite phases, producing an anti-bonding interaction and a much higher energy.
- 4.3:** At 135° , the highest occupied orbitals are:
- Boron dioxide, BO_2 , $O=B[O]$: $4b_2$, **singly occupied**.
- Carbon dioxide, CO_2 , $O=C=O$: $4b_2$, **doubly occupied**.
- Nitrogen dioxide, NO_2 , $[O-][N+]=O$: $6a_1$, **singly occupied**.

- Fluorine dioxide in the question's O—F—O model, FO_2 , $[\text{O}-][\text{F}^+][\text{O}]$: $2b_1$, **singly occupied**.
- 4.4:** Nitrogen dioxide is predicted to be **less bent** than ozone, with an angle **greater than 116°** . Fluorine dioxide in the stated model is predicted to be **more bent**, with an angle **less than 116°** .

Solution

The SMILES above specify connectivity and representative localized electronic structures. They do not show molecular-orbital phases, resonance delocalization or bond angles. In particular, the fluorine dioxide representation follows the central-fluorine O—F—O arrangement implicit in the question's XY_2 model.

4.1 — Constructing the molecular orbitals

Let $\phi_{a,q}$, $\phi_{b,q}$ and $\phi_{c,q}$ denote the atomic orbitals of type q on the three atoms. Use the same global axes on every atom: the positive lobe of a p_q orbital points along $+q$.

First form the two terminal-atom combinations, without specifying normalization:

$$T_q^+ = \phi_{a,q} + \phi_{c,q}, \quad T_q^- = \phi_{a,q} - \phi_{c,q}.$$

Consider reflection in the xz plane, which exchanges the terminal atoms.

- For $2s$, $2p_x$ and $2p_z$, this reflection does not reverse the individual orbital's phase. Thus T_q^+ is symmetric and T_q^- is anti-symmetric.
- For $2p_y$, reflection reverses the orbital's phase because y changes sign. Consequently, T_y^+ is anti-symmetric and T_y^- is symmetric.

The central $2p_y$ orbital is also anti-symmetric under this reflection. The other three central orbitals are symmetric. Therefore, **in every set, T_q^+ has the symmetry needed to interact with the corresponding central orbital**.

For completeness, their full symmetry labels in the stated coordinate system are:

Atomic-orbital set	Terminal sum T_q^+	Terminal difference T_q^-	Central orbital
$2s$	a_1	b_2	a_1
$2p_x$	b_1	a_2	b_1
$2p_y$	b_2	a_1	b_2
$2p_z$	a_1	b_2	a_1

Combining T_q^+ with the central orbital in its two possible relative phases produces two molecular orbitals. The terminal difference T_q^- has zero central contribution and is non-bonding in the separate-interaction construction requested.

The required drawings can be specified by the following phase patterns. The signs refer to **whole atomic-orbital coefficients**, in the order (a, b, c) ; they do not prescribe their magnitudes.

Atomic-orbital set	Bonding pattern in the bent sketch	Non-bonding pattern	Anti-bonding pattern in the bent sketch
$2s$	$(+, +, +)$	$(+, 0, -)$	$(+, -, +)$
$2p_x$	$(+, +, +)$	$(+, 0, -)$	$(+, -, +)$
$2p_y$	$(+, -, +)$	$(+, 0, -)$	$(+, +, +)$
$2p_z$	$(+, -, +)$	$(+, 0, -)$	$(+, +, +)$

To draw these precisely:

- $2s$: Use three spheres of the same phase for the bonding orbital. Reverse the central sphere for the anti-bonding orbital.
- $2p_x$: Draw all three orbitals perpendicular to the molecular plane. Corresponding lobes on the same side of the plane have the same phase in the bonding orbital. Reverse the central orbital for the anti-bonding orbital.
- $2p_y$: Draw horizontal p orbitals. Reverse the central orbital relative to the terminal orbitals so that the lobes facing one another along both bonds have matching phases.
- $2p_z$: Draw vertical p orbitals. In the bent bonding arrangement, the central downward lobe and both terminal upward lobes have the same phase. This is the phase arrangement illustrated for $6a_1$.

For every non-bonding drawing, omit the central orbital and give the two terminal orbitals opposite coefficient signs. Reversing every sign in any drawing leaves the physical orbital unchanged.

Thus,

$$4 \text{ atomic-orbital sets} \times 3 \text{ molecular orbitals per set} = \boxed{12 \text{ molecular orbitals}}.$$

The bonding descriptions for $2p_z$ refer to the bent geometry; they do not remain valid unchanged as the molecule becomes linear.

4.2 — Why $6a_1$ rises rapidly in energy

In the illustrated $6a_1$ orbital, the terminal $2p_z$ orbitals have the same coefficient sign, while the central orbital has the opposite sign:

$$\psi_{6a_1} \sim \phi_{a,z} - \lambda \phi_{b,z} + \phi_{c,z}, \quad \lambda > 0.$$

In the bent geometry, the central downward lobe faces the terminal upward lobes, and those facing lobes have matching phases. This gives a bonding contribution.

If the bond angle is θ , the magnitude of the projection of a bond direction onto the z axis is

$$\cos\left(\frac{\theta}{2}\right).$$

As θ increases towards 180° , this projection falls to zero: the favourable end-on component of the overlap disappears.

At 180° , the atoms lie along the y direction. Their $2p_z$ orbitals are then parallel and overlap sideways. Because the central orbital has the opposite coefficient sign from the terminal orbitals, adjacent lobes overlap out of phase. The interaction is now π -anti-bonding.

The combination of **losing bonding overlap and developing anti-bonding overlap** explains the rapid increase in energy.

4.3 — Highest occupied orbitals at 135°

Each neutral molecule contains

$$N_e = Z_X + 2Z_O,$$

where $Z_O = 8$.

In the Walsh diagram of the answer sheet, the frontier orbitals at 135° are ordered

$$1a_2 < 4b_2 < 6a_1 < 2b_1.$$

The problem states that ozone's 24 electrons doubly occupy all orbitals through $6a_1$. Therefore, the successive frontier levels accommodate:

Orbital	Electrons entering this level
$1a_2$	19th and 20th
$4b_2$	21st and 22nd
$6a_1$	23rd and 24th
$2b_1$	25th and 26th

Filling these levels gives:

Molecule	Total electrons	Highest occupied orbital	Occupancy of that orbital
BO_2	$5 + 2(8) = 21$	$4b_2$	1
CO_2	$6 + 2(8) = 22$	$4b_2$	2
NO_2	$7 + 2(8) = 23$	$6a_1$	1
FO_2	$9 + 2(8) = 25$	$2b_1$	1

For the odd-electron species, the highest occupied orbital is also the singly occupied molecular orbital.

4.4 — Comparing the bending with ozone

The Walsh argument compares how the energies of the occupied orbitals change with angle, weighted by their occupancies.

Nitrogen dioxide: Relative to ozone, it has one fewer electron in $6a_1$. Since $6a_1$ is strongly stabilized by bending, single occupation provides a weaker preference for bending than double occupation. The competing preference of other occupied orbitals for a larger angle therefore has greater relative influence.

Hence,

$$\theta(\text{NO}_2) > 116^\circ : \quad \text{nitrogen dioxide is less bent than ozone.}$$

Fluorine dioxide: It retains the doubly occupied $6a_1$ orbital and adds one electron to $2b_1$.

The $2b_1$ orbital is the anti-bonding combination of the out-of-plane $2p_x$ orbitals:

$$\psi_{2b_1} \sim \phi_{a,x} - \mu\phi_{b,x} + \phi_{c,x}, \quad \mu > 0.$$

Although its central-terminal interactions are anti-bonding, its two terminal orbitals have the **same phase**. For fixed central-terminal distance r , the terminal separation is

$$d_{ac} = 2r \sin\left(\frac{\theta}{2}\right).$$

Bending decreases d_{ac} , strengthening the favourable interaction between the same-phase terminal lobes. Thus $2b_1$ gains stabilization on bending. Occupying it adds a further preference for a smaller angle.

The qualitative prediction is therefore

$$\theta(\text{FO}_2) < 116^\circ : \quad \text{fluorine dioxide is more bent than ozone.}$$

The solution was checked against the official solution.

Problem 5: Cyanide extraction of gold

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.

$[\text{Zn}(\text{CN})_4]^{2-} + 2\text{e}^- \longrightarrow \text{Zn} + 4\text{CN}^-$	$E^\circ = -1.26\text{ V}$
$[\text{Au}(\text{CN})_2]^- + \text{e}^- \longrightarrow \text{Au} + 2\text{CN}^-$	$E^\circ = -0.60\text{ V}$
$[\text{Ag}(\text{CN})_2]^- + \text{e}^- \longrightarrow \text{Ag} + 2\text{CN}^-$	$E^\circ = -0.31\text{ V}$

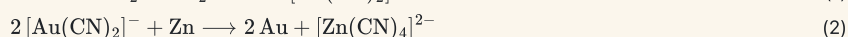
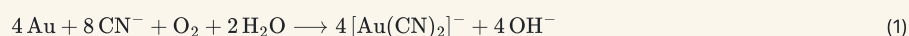
5.3 $[\text{Au}(\text{CN})_2]^-$ is a very stable complex under certain conditions. What concentration of sodium cyanide is required to keep 99 mol% of the gold in solution in the form of the cyanide complex? $\{[\text{Au}(\text{CN})_2]^- : K_f = 4 \times 10^{28}\}$

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

Official English text of the problem.

Answers

• 5.1



• 5.2

$$[[\text{Au}(\text{CN})_2]^-] = 0.0300\text{ mol L}^{-1}$$

$$[[\text{Ag}(\text{CN})_2]^-] \approx 1.7 \times 10^{-3}\text{ mol L}^{-1}$$

Silver consumes the available reducing capacity; gold remains in solution.

• 5.3

$$[\text{CN}^-]_{\text{free}} \approx 5 \times 10^{-14}\text{ mol L}^{-1}$$

This is the equilibrium free cyanide concentration. The total analytical sodium cyanide concentration must also account for bound cyanide.

• 5.4 Choose the option stating that **cyanide is highly toxic and its use creates serious environmental and health hazards**.

Solution

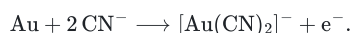
The molecular and ionic species used in the solution have the following names and SMILES. For coordination complexes, the SMILES use dative-bond notation, with cyanide carbon donating to the metal.

Formula	Name	SMILES
NaCN	Sodium cyanide	<chem>[Na+].[C-]#N</chem>
CN^-	Cyanide ion	<chem>[C-]#N</chem>
$[\text{Au}(\text{CN})_2]^-$	Dicyanidoaurate(I) ion	<chem>N#[C-]>[Au+]<[C-]#N</chem>
$[\text{Ag}(\text{CN})_2]^-$	Dicyanidoargentate(I) ion	<chem>N#[C-]>[Ag+]<[C-]#N</chem>
$[\text{Zn}(\text{CN})_4]^{2-}$	Tetracyanidozincate(II) ion	<chem>[Zn+2](<[C-]#N)(<[C-]#N)(<[C-]#N)<[C-]#N</chem>
Au^+	Gold(I) ion	<chem>[Au+]</chem>
O_2	Dioxygen	<chem>O=O</chem>
H_2O	Water	<chem>O</chem>
OH^-	Hydroxide ion	<chem>[OH-]</chem>

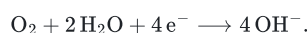
The gold(I) and silver(I) complexes are linear, with carbon-bound cyanide ligands; the zinc(II) complex is tetrahedral. These geometries are not specified by the SMILES. Elemental gold, silver and zinc have atom SMILES [Au], [Ag] and [Zn], respectively; these do not describe their metallic lattices.

5.1 — Balanced ionic equations

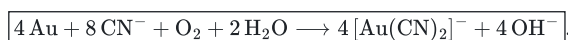
In reaction (1), gold is oxidized from oxidation state 0 to +1:



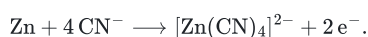
Oxygen from the aerated solution accepts the electrons. In alkaline solution its reduction half-equation is



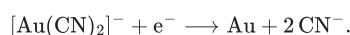
Multiplying the gold half-equation by four and adding gives



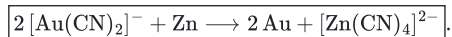
In reaction (2), zinc is oxidized from 0 to +2:



Gold(I) is reduced to metallic gold:



Multiplying the gold reduction by two and adding cancels both the electrons and free cyanide:



5.2 — Concentrations after treatment with zinc

Evaporation changes the volume but preserves the amounts of dissolved metal complexes:

$$n_{\text{Au},0} = (500 \text{ L})(0.0100 \text{ mol L}^{-1}) = 5.00 \text{ mol},$$

$$n_{\text{Ag},0} = (500 \text{ L})(0.0030 \text{ mol L}^{-1}) = 1.50 \text{ mol}.$$

The final solution volume is

$$V_f = \frac{500}{3} \text{ L} = 166.7 \text{ L}.$$

Both complexes can be reduced by zinc:

$$E_{\text{cell,Au}}^\circ = -0.60 - (-1.26) = +0.66 \text{ V},$$

$$E_{\text{cell,Ag}}^\circ = -0.31 - (-1.26) = +0.95 \text{ V}.$$

The silver complex has the higher reduction potential. Furthermore, any deposited gold can reduce silver complex:



with

$$E_{\text{cell}}^\circ = -0.31 - (-0.60) = +0.29 \text{ V}.$$

Thus, under the stipulated completion approximation, metallic gold cannot remain while appreciable silver complex remains: the available reducing capacity is used to deposit silver first.

Using $M(\text{Zn}) = 65.4 \text{ g mol}^{-1}$,

$$n_{\text{Zn}} = \frac{40 \text{ g}}{65.4 \text{ g mol}^{-1}} = 0.6116 \text{ mol}.$$

Each mole of zinc supplies two moles of electrons, whereas each mole of silver complex requires one:



Consequently,

$$n_{\text{Ag deposited}} = 2n_{\text{Zn}} = 1.2232 \text{ mol} < 1.50 \text{ mol}.$$

All zinc is consumed before all the silver can be deposited. The remaining amounts are therefore

$$n_{\text{Ag},f} = 1.50 - 1.2232 = 0.2768 \text{ mol}, \quad n_{\text{Au},f} = 5.00 \text{ mol}.$$

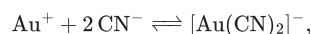
Neglecting any volume change on adding zinc,

$$[[\text{Au}(\text{CN})_2]^-] = \frac{5.00}{500/3} = \boxed{0.0300 \text{ mol L}^{-1}},$$

$$[[\text{Ag}(\text{CN})_2]^-] = \frac{0.2768}{500/3} = 1.66 \times 10^{-3} \text{ mol L}^{-1} \approx \boxed{1.7 \times 10^{-3} \text{ mol L}^{-1}}.$$

5.3 — Cyanide concentration for 99 mol% complexation

The formation equilibrium is



with

$$K_f = \frac{[[\text{Au}(\text{CN})_2]^-]}{[\text{Au}^+][\text{CN}^-]^2} = 4 \times 10^{28}.$$

Assuming dissolved gold occurs only as free gold(I) and its dicyanido complex, a complexed fraction of 0.99 means

$$\frac{[[\text{Au}(\text{CN})_2]^-]}{[\text{Au}^+]} = \frac{0.99}{0.01} = 99.$$

Hence, using concentrations numerically in mol L^{-1} ,

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

and

$$[\text{CN}^-] = 4.97 \times 10^{-14} \text{ mol L}^{-1} \approx \boxed{5 \times 10^{-14} \text{ mol L}^{-1}}.$$

This is the minimum **free cyanide concentration** for at least 99% complexation within this model.

A total sodium cyanide requirement also includes cyanide incorporated into complexes. For example, if gold is the only cyanide-binding species and protonation is neglected,

$$C_{\text{CN,total}} = [\text{CN}^-] + 2[[\text{Au}(\text{CN})_2]^-] = [\text{CN}^-] + 1.98C_{\text{Au,total}}.$$

Thus the very small free cyanide concentration does not by itself specify the total sodium cyanide dose.

5.4 — Reason for seeking alternative processes

Cyanide is highly toxic. Cyanide-bearing solutions and wastes can endanger workers, contaminate water, and harm wildlife, particularly following leaks or accidental releases. These health and environmental hazards motivate alternative extraction processes.

The appropriate answer-sheet option is therefore the one identifying **cyanide toxicity and its environmental consequences**.

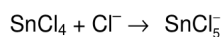
The solution was checked against the official solution.

Problem 6: Tin(IV) halide complexes: geometry, electrospray MS and ^{119}Sn NMR

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

6.1 Draw two alternative geometries for SnCl_4 .

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



and



6.2 Draw three alternative geometries for SnCl_5^- .

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

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

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

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

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

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

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

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

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

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

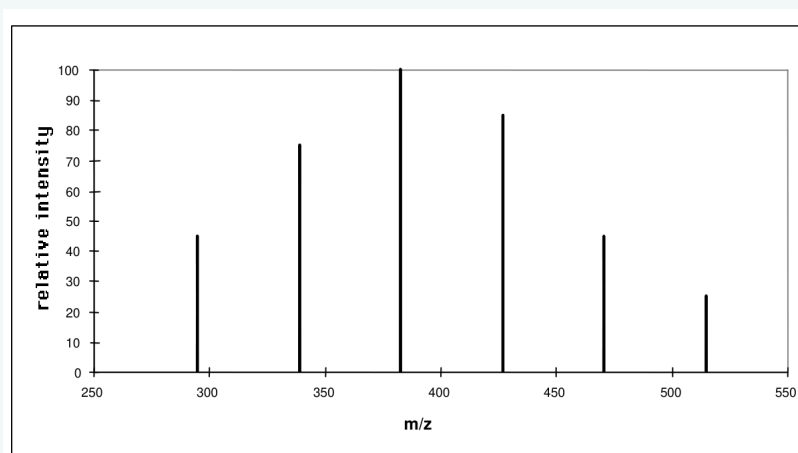


Fig. 1

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

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

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

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

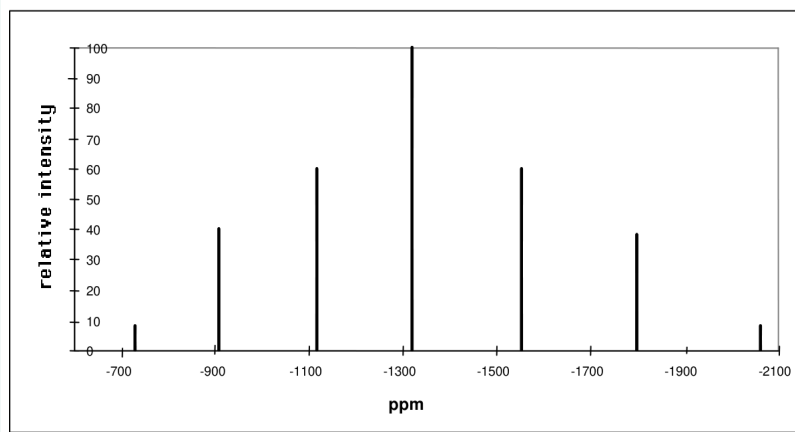


Fig. 2

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

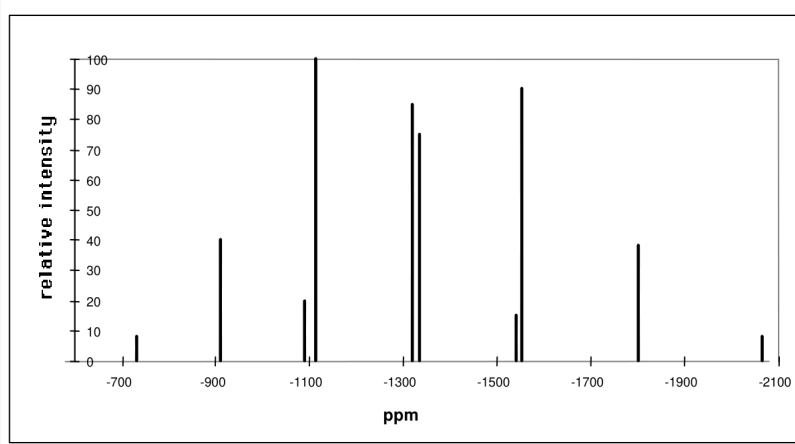


Fig. 3

6.10 Draw the geometry for the four tin-containing species present in this solution at -30°C that give rise to the peaks at -1092 and -1115 , -1322 and -1336 ppm.

Official English text of the problem.

Answers

The SMILES below use single bonds to represent connectivity. Their formal negative charge is placed on Sn; the tin oxidation state remains +4. Coordination geometry is specified separately. The isomer-specific SMILES in **6.10** use extended octahedral stereochemistry notation, @OH1.

- **6.1** Tin(IV) chloride, SnCl_4 , Cl[Sn](Cl)(Cl)Cl: **tetrahedral** and **square planar**.
- **6.2** Pentachloridostannate(IV), $[\text{SnCl}_5]^-$, Cl[Sn-](Cl)(Cl)(Cl)Cl: **trigonal bipyramidal**, **square pyramidal**, and **pentagonal planar**.
- **6.3** **Trigonal bipyramidal**, corresponding to AX_5 .
- **6.4** Hexachloridostannate(IV), $[\text{SnCl}_6]^{2-}$, Cl[Sn-2](Cl)(Cl)(Cl)(Cl)Cl: **octahedral**, **trigonal prismatic**, and **hexagonal planar**.
- **6.5** **Octahedral**, corresponding to AX_6 .
- **6.6** $[\text{SnCl}_5]^-$, pentachloridostannate(IV), Cl[Sn-](Cl)(Cl)(Cl)Cl; nominal $m/z = 295$.
- **6.7** $[\text{SnBr}_5]^-$, pentabromidostannate(IV), Br[Sn-](Br)(Br)(Br)Br; nominal $m/z = 515$.
- **6.8** The four new ions are:

m/z	Formula	Name	SMILES
339	$[\text{SnCl}_4\text{Br}]^-$	Bromidotetrachloridostannate(IV)	<chem>Br[Sn-](Cl)(Cl)(Cl)Cl</chem>
383	$[\text{SnCl}_3\text{Br}_2]^-$	Dibromidotrichloridostannate(IV)	<chem>Br[Sn-](Br)(Cl)(Cl)Cl</chem>
427	$[\text{SnCl}_2\text{Br}_3]^-$	Tribromidodichloridostannate(IV)	<chem>Br[Sn-](Br)(Br)(Cl)Cl</chem>
471	$[\text{SnClBr}_4]^-$	Tetrabromidochloridostannate(IV)	<chem>Br[Sn-](Br)(Br)(Br)Cl</chem>

- 6.9 The seven assignments, from left to right in Fig. 2, are:

Peak	Formula	Name	SMILES
1, -732 ppm	$[\text{SnCl}_6]^{2-}$	Hexachloridostannate(IV)	<chem>Cl[Sn-2](Cl)(Cl)(Cl)(Cl)Cl</chem>
2	$[\text{SnCl}_5\text{Br}]^{2-}$	Bromidopentachloridostannate(IV)	<chem>Br[Sn-2](Cl)(Cl)(Cl)(Cl)Cl</chem>
3	$[\text{SnCl}_4\text{Br}_2]^{2-}$	Dibromidotetrachloridostannate(IV)	<chem>Br[Sn-2](Br)(Cl)(Cl)(Cl)Cl</chem>
4	$[\text{SnCl}_3\text{Br}_3]^{2-}$	Tribromidotrichloridostannate(IV)	<chem>Br[Sn-2](Br)(Br)(Cl)(Cl)Cl</chem>
5	$[\text{SnCl}_2\text{Br}_4]^{2-}$	Tetrabromidodichloridostannate(IV)	<chem>Br[Sn-2](Br)(Br)(Br)(Cl)Cl</chem>
6	$[\text{SnClBr}_5]^{2-}$	Pentabromidochloridostannate(IV)	<chem>Br[Sn-2](Br)(Br)(Br)(Br)Cl</chem>
7, -2064 ppm	$[\text{SnBr}_6]^{2-}$	Hexabromidostannate(IV)	<chem>Br[Sn-2](Br)(Br)(Br)(Br)Br</chem>

- 6.10 All four species are **octahedral**. The assignments are to **pairs of peaks**, without a unique assignment within either pair:

Peak pair / ppm	Isomer	Isomer-specific SMILES
-1092, -1115	cis -Dibromidotetrachloridostannate(IV), $[\text{SnCl}_4\text{Br}_2]^{2-}$	<chem>Br[Sn@OH1-2](Br)(Cl)(Cl)(Cl)Cl</chem>
-1092, -1115	trans -Dibromidotetrachloridostannate(IV), $[\text{SnCl}_4\text{Br}_2]^{2-}$	<chem>Br[Sn@OH1-2](Cl)(Cl)(Cl)(Cl)Br</chem>
-1322, -1336	fac -Tribromidotrichloridostannate(IV), $[\text{SnCl}_3\text{Br}_3]^{2-}$	<chem>Br[Sn@OH1-2](Br)(Br)(Cl)(Cl)Cl</chem>
-1322, -1336	mer -Tribromidotrichloridostannate(IV), $[\text{SnCl}_3\text{Br}_3]^{2-}$	<chem>Br[Sn@OH1-2](Br)(Cl)(Cl)(Cl)Br</chem>

Solution

The auxiliary ions used below are **chloride**, Cl^- , [Cl-], and **bromide**, Br^- , [Br-]. **Tetrabutylammonium**, $[\text{N}(\text{C}_4\text{H}_9)_4]^+$, CCCC[N+](CCCC)(CCCC)CCCC, supplies the counterions. **Tetramethyltin**, $\text{Sn}(\text{CH}_3)_4$, C[Sn](C)(C)C, is the NMR reference.

6.1

The two requested drawings can be described as follows:

- Tetrahedral**: put Sn at the centre of a regular tetrahedron, with one Cl at each vertex. All $\text{Cl}-\text{Sn}-\text{Cl}$ angles are approximately 109.5° .
- Square planar**: put Sn at the centre of a square and the four Cl atoms at its vertices. All five atoms lie in one plane; adjacent bond angles are 90° , and opposite ones are 180° .

These are alternative arrangements for coordination number four. Tetrahedral is the usual geometry of molecular tin(IV) chloride.

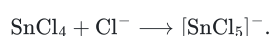
6.2

For five ligands, three alternatives are:

- Trigonal bipyramidal**: three equatorial Cl atoms surround Sn in a plane at 120° intervals. Two axial Cl atoms lie above and below that plane, with an axial-axial angle of 180° and axial-equatorial angles of 90° .
- Square pyramidal**: four Cl atoms form a square around Sn in a basal plane; the fifth lies on the perpendicular axis above Sn.
- Pentagonal planar**: all five Cl atoms and Sn lie in one plane, with Cl at the vertices of a regular pentagon centred on Sn. Adjacent bond directions differ by 72° .

6.3

The Lewis acid-base reaction is



The ion has

$$4 + 5(7) + 1 = 40$$

valence electrons. Giving each terminal chlorine three lone pairs uses 30 electrons, leaving 10 electrons in five $\text{Sn}-\text{Cl}$ bonds. Thus the central atom has **five bonding pairs and no lone pair**, giving the VSEPR designation AX_5 .

The preferred geometry is **trigonal bipyramidal**. It has six ligand-pair angles of 90° , three of 120° , and one of 180° . A square pyramid has eight 90° pairwise angles, while a planar pentagon introduces 72° separations. The trigonal bipyramid therefore gives the preferred distribution of the five bonding domains.

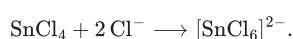
6.4

Three six-coordinate arrangements are:

- Octahedral**: place the ligands along the six directions $+x, -x, +y, -y, +z, -z$, with Sn at the origin.
- Trigonal prismatic**: place three Cl atoms at the vertices of an equilateral triangle above Sn and three at the vertices of an aligned, parallel triangle below it. Corresponding vertices lie directly above one another.
- Hexagonal planar**: place all six Cl atoms at the vertices of a regular hexagon, with Sn at its centre in the same plane.

6.5

The overall addition reaction is



The total number of valence electrons is

$$4 + 6(7) + 2 = 48.$$

The chlorine lone pairs account for 36 electrons, leaving 12 electrons in six bonds. Thus the central atom has six bonding domains and no lone pair: AX_6 . VSEPR predicts an **octahedral** arrangement. Every pair of bond directions is separated by either 90° or 180° . The alternative arrangements introduce smaller separations, including 60° in the planar hexagon.

6.6

Use the given isotope mass numbers as nominal masses in atomic mass units, u. The numerical m/z equals the ion's mass in u divided by the magnitude of its charge in elementary-charge units.

For a mononuclear tin(IV) complex containing n chloride ligands, charge balance gives $z = 4 - n$. For an anion,

$$\frac{120 + 35n}{n - 4} = 295.$$

Therefore,

$$120 + 35n = 295n - 1180 \implies n = 5, \quad z = -1.$$

The detected species is **pentachloridostannate(IV)**:

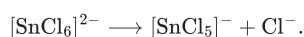
$$[\text{SnCl}_5]^{-}, \quad m = (120 + 5 \times 35) \text{ u} = 295 \text{ u}, \quad m/z = 295.$$

For comparison, the intact six-coordinate dianion would give

$$m/z = \frac{120 + 6(35)}{2} = 165,$$

which does not match the observed peak.

A balanced ion transformation consistent with the observation is



This establishes the appropriate composition and charge without requiring a detailed electrospray mechanism.

6.7

Applying the same charge balance to a bromide complex,

$$\frac{120 + 79n}{n - 4} = 515.$$

Hence,

$$120 + 79n = 515n - 2060 \implies n = 5, \quad z = -1.$$

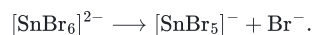
Thus the detected ion is **pentabromidostannate(IV)**:

$$[\text{SnBr}_5]^{-}, \quad m = (120 + 5 \times 79) \text{ u} = 515 \text{ u}, \quad m/z = 515.$$

The intact dianion would instead give

$$m/z = \frac{120 + 6(79)}{2} = 297.$$

The corresponding balanced transformation is



6.8

The mixed five-coordinate ions have compositions

$$[\text{SnCl}_{5-n}\text{Br}_n]^{-}, \quad n = 0, 1, \dots, 5.$$

Replacing one chlorine isotope by one bromine isotope increases the nominal mass by

$$79 \text{ u} - 35 \text{ u} = 44 \text{ u}.$$

Consequently,

$$\frac{m}{u} = 120 + 35(5 - n) + 79n = 295 + 44n.$$

All these ions have charge -1 , giving:

Number of Br ligands, n	m/z	Composition
0	295	$[\text{SnCl}_5]^{-}$
1	339	$[\text{SnCl}_4\text{Br}]^{-}$
2	383	$[\text{SnCl}_3\text{Br}_2]^{-}$
3	427	$[\text{SnCl}_2\text{Br}_3]^{-}$
4	471	$[\text{SnClBr}_4]^{-}$
5	515	$[\text{SnBr}_5]^{-}$

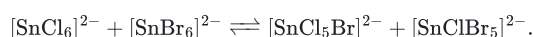
The four interior peaks therefore correspond to the four mixed-halide ions listed in **Answers 6.8**.

6.9

NMR observes the six-coordinate complexes present in solution. Halide redistribution produces the seven possible compositions

$$[\text{SnCl}_{6-n}\text{Br}_n]^{2-}, \quad n = 0, 1, \dots, 6.$$

For example, a balanced redistribution is



The all-chloride endpoint is at -732 ppm. Figure 2 places the all-bromide endpoint at approximately -2064 ppm. The progression of intervening resonances is assigned to successive replacement of Cl by Br, giving the left-to-right assignments in **Answers 6.9**.

At 60°C , geometrical isomers of a given composition interconvert sufficiently rapidly to give an averaged resonance for that composition. Cooling slows their interconversion and resolves additional signals.

The expected number of distinct octahedral geometrical isomers is:

Number of Br ligands	Geometrical possibilities	Number of signals when resolved
0	One arrangement	1
1	One arrangement	1
2	cis, trans	2
3	fac, mer	2
4	cis, trans, classified by the two Cl ligands	2
5	One arrangement	1
6	One arrangement	1
Total		10

Thus the observed change from seven to ten peaks is consistent with resolution of the geometrical isomers of the compositions containing two, three, and four bromide ligands.

6.10

The pair at -1092 and -1115 ppm belongs to the composition $[\text{SnCl}_4\text{Br}_2]^{2-}$, whose two geometrical isomers are **cis** and **trans**.

The pair at -1322 and -1336 ppm belongs to $[\text{SnCl}_3\text{Br}_3]^{2-}$, whose two geometrical isomers are **fac** and **mer**.

For precise drawings, place Sn at the origin and the six ligand sites along $+x, -x, +y, -y, +z, -z$. Occupy the sites as follows; every site not occupied by Br is occupied by Cl.

Isomer	Br positions	Geometrical description
cis - $[\text{SnCl}_4\text{Br}_2]^{2-}$	$+z, +x$	The two Br ligands are adjacent; $\text{Br}-\text{Sn}-\text{Br} = 90^\circ$.
trans - $[\text{SnCl}_4\text{Br}_2]^{2-}$	$+z, -z$	The two Br ligands are opposite; $\text{Br}-\text{Sn}-\text{Br} = 180^\circ$.
fac - $[\text{SnCl}_3\text{Br}_3]^{2-}$	$+z, +x, +y$	The three Br ligands occupy one triangular face. Every $\text{Br}-\text{Sn}-\text{Br}$ angle is 90° .
mer - $[\text{SnCl}_3\text{Br}_3]^{2-}$	$+z, -z, +x$	Two Br ligands are opposite. All three Br ligands lie in a plane through Sn; their pairwise angles are $180^\circ, 90^\circ, 90^\circ$.

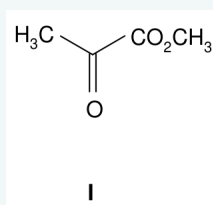
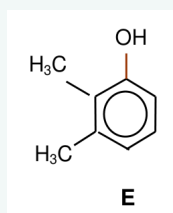
The supplied information identifies these **two isomer pairs**. It does not uniquely determine which individual resonance in each pair belongs to which isomer. Relative peak heights alone cannot establish that assignment without additional assumptions about populations and NMR response.

The solution was checked against the official solution.

Problem 7: Aromatic lactones of *Aspergillus nidulans* and a synthesis of D

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** ($\text{C}_{10}\text{H}_{10}\text{O}_4$) 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** ($\text{C}_{11}\text{H}_{12}\text{O}_4$) 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 ($\text{MeI}/\text{K}_2\text{CO}_3$) to afford **F** ($\text{C}_9\text{H}_{12}\text{O}_2$) 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**.

Official English text of the problem.

Answers

- 7.1. The structures are listed below. The answer requires correcting the lower-left substituent of **E** to methoxy.

Phthalide numbering places the carbonyl at C1, the ring oxygen at position 2 and the methylene at C3. Aromatic positions 4–7 run from the methylene end towards the carbonyl end.

Compound	Name	SMILES
A	5-Hydroxy-7-methoxy-6-methylphthalide	<chem>O=C1OCc2cc(O)c(C)c(OC)c21</chem>
B	4-Hydroxy-6-methoxy-5-methylphthalide; one permissible assignment	<chem>O=C1OCc2c(O)c(C)c(OC)cc21</chem>
C	5,7-Dimethoxy-6-methylphthalide	<chem>O=C1OCc2cc(OC)c(C)c(OC)c21</chem>
D	7-Hydroxy-5-methoxy-6-methylphthalide	<chem>O=C1OCc2cc(OC)c(C)c(O)c21</chem>
E	3-Methoxy-2-methylphenol	<chem>Oc1c(C)c(OC)ccc1</chem>
F	1,3-Dimethoxy-2-methylbenzene	<chem>COc1c(C)c(OC)ccc1</chem>
G	1,5-Dimethoxy-6-methylcyclohexa-1,4-diene	<chem>COC1=CCC=C(OC)C1C</chem>
H	1,3-Dimethoxy-2-methylcyclohexa-1,3-diene	<chem>COC1=C(C)C(OC)=CCC1</chem>
I	Methyl 2-oxopropanoate, or methyl pyruvate	<chem>CC(=O)C(=O)OC</chem>
J	Dimethyl but-2-ynedioate, or dimethyl acetylenedicarboxylate	<chem>COC(=O)C#CC(=O)OC</chem>
K	Dimethyl 1,5-dimethoxy-6-methylbicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate, racemic	<chem>CO[C@]12C(C)=C(OC)[C@H](CC1)C(C(=O)OC)=C2C(=O)OC</chem>
L	Dimethyl 3,5-dimethoxy-4-methylphthalate	<chem>COC(=O)c1c(C(=O)OC)c(OC)c(C)c(OC)c1</chem>
M	3,5-Dimethoxy-4-methylphthalic acid	<chem>O=C(O)c1c(C(=O)O)c(OC)c(C)c(OC)c1</chem>
N	3,5-Dimethoxy-4-methylphthalic anhydride	<chem>O=C1OC(=O)c2c(OC)c(C)c(OC)cc21</chem>
O	4,6-Dimethoxy-5-methylphthalide	<chem>O=C1OCc2c(OC)c(C)c(OC)cc21</chem>

The SMILES for **K** specifies one enantiomer. Its equally formed mirror image is CO[C@@]12C(C)=C(OC)[C@@H](CC1)C(C(=O)OC)=C2C(=O)OC.

- 7.2. The second permissible structure for **B** is **6-hydroxy-4-methoxy-5-methylphthalide**, O=C1OCc2c(OC)c(C)c(O)cc21. The two assignments of **B** may be interchanged between 7.1 and 7.2.

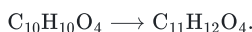
Solution

7.1. Identification of A–O

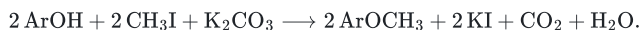
Phenolic groups and methylation.

Solubility in aqueous hydroxide, insolubility in bicarbonate and the violet ferric-chloride reaction indicate phenolic hydroxyl groups in **A** and **B**. The bicarbonate observation also argues against a free carboxylic acid.

Methylation replaces a phenolic hydrogen with methyl, giving the observed formula change:



A balanced general equation for the methylations **A** → **C**, **B** → **O** and **E** → **F** is



Here **Ar** denotes the corresponding substituted aromatic framework.

E → **F** → **G**: methylation and Birch reduction.

The formula-consistent structure of **E** is 3-methoxy-2-methylphenol. Methylating its hydroxyl gives **F**, 1,3-dimethoxy-2-methylbenzene, with the required formula $C_9H_{12}O_2$.

For this paragraph, retain the aromatic numbering of **F**: methoxy groups at C1 and C3, and methyl at C2. Birch reduction adds hydrogen at C2 and C5, leaving double bonds C1=C6 and C3=C4. This gives **G**, whose two halves are equivalent by reflection through the methyl-bearing carbon and the opposite methylene carbon.

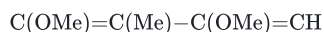
The net reduction is



The proton donor is 2-methylpropan-2-ol, CC(C)(C)O; its conjugate base is lithium tert-butoxide, [Li+].[O-]C(C)(C)C.

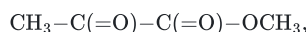
G → **H**, established by ozonolysis.

Base-catalysed double-bond migration gives the conjugated diene **H**, with the sequence



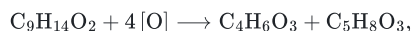
along its four-carbon diene unit. The remaining two ring atoms are methylene groups. No atoms are added or removed, so both **G** and **H** have formula $C_9H_{14}O_2$.

Ozonolysis breaks the two double bonds but preserves the single bond between the two middle diene carbons. One of these bears methyl; the other bears methoxy. Their conversion into carbonyl carbons therefore gives



which is exactly **I**, methyl pyruvate.

The complementary carbonyl fragment is methyl 4-oxobutanoate, $COC(=O)CCC=O$. An atom-balanced representation of the initial cleavage is



where $[O]$ denotes an oxygen-atom oxidizing equivalent. During non-reductive work-up, the aldehyde fragment can undergo further oxidation to methyl hydrogen succinate, $COC(=O)CCC(=O)O$:



The identification of **H** depends on the methyl-pyruvate fragment, regardless of the subsequent fate of the complementary fragment.

H + J → K → L: construction of the aromatic substitution pattern.

The terminal diene carbons of **H** form two new carbon-carbon bonds to the alkyne carbons of **J**. This produces the bicyclo[2.2.2]octadiene **K**:



To draw **K**, connect its two bridgeheads by three two-carbon paths:

- $-CH_2-CH_2^-$;
- $-C(Me)=C(OMe)^-$;
- $-C(CO_2Me)=C(CO_2Me)^-$.

One bridgehead bears methoxy and the other hydrogen. The SMILES in Answers specifies their relative configuration; the reaction gives a racemate.

Heating eliminates the saturated two-carbon bridge as ethene, $C=C$, and produces the aromatic ester **L**:



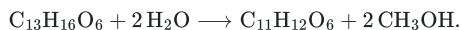
The six substituents around the new benzene ring, in cyclic order, are



Consequently, **L** is dimethyl 3,5-dimethoxy-4-methylphthalate.

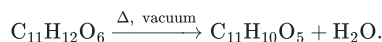
L → M → N: hydrolysis and anhydride formation.

Basic hydrolysis converts both methyl carboxylate groups into carboxylates. Acidification gives the adjacent dicarboxylic acid **M**; the aryl methyl ethers remain intact. The overall equation, including acidification, is



The small-molecule products are methanol, CO , and, in the following dehydration, water, O .

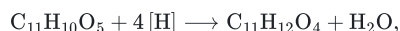
Heating the ortho-dicarboxylic acid under vacuum removes water and closes the five-membered anhydride ring:



Thus **N** is 3,5-dimethoxy-4-methylphthalic anhydride.

N → C and O: the two phthalide orientations.

Reduction can convert either of the two inequivalent anhydride carbonyl groups into the methylene group of a phthalide. The other carbonyl remains as the lactone carbonyl. The balanced net reduction for either product is



where $[H]$ denotes a reducing hydrogen equivalent.

The two possible products are therefore:

- 5,7-dimethoxy-6-methylphthalide;
- 4,6-dimethoxy-5-methylphthalide.

The hydrogen-bond information determines which is **C**.

C → D fixes the lactone orientation and identifies A.

A phenolic hydroxyl at phthalide C7 lies adjacent to the lactone carbonyl and can form a strong intramolecular $O-H \cdots O=C$ hydrogen bond. This produces a six-membered hydrogen-bonded arrangement and explains the strongly downfield signal at $\delta 11.8$ ppm. This hydrogen bond is a spatial interaction and is not encoded in ordinary SMILES.

Accordingly:

- **C** must be 5,7-dimethoxy-6-methylphthalide.
- Selective cleavage of its C7 methyl ether gives **D**, 7-hydroxy-5-methoxy-6-methylphthalide.
- The other reduction product is **O**, 4,6-dimethoxy-5-methylphthalide.

A balanced overall representation of demethylation and aqueous work-up is



Because methylation of **A** gives **C**, **A** has the same framework with one methoxy group replaced by hydroxyl. Since **D** is a different isomer, **A** must have hydroxyl at C5 and methoxy at C7: **5-hydroxy-7-methoxy-6-methylphthalide**.

This assignment also explains the three non-identical methyl groups in **C**: two inequivalent methoxy groups and one aromatic methyl group.

Identification of **B**.

Methylation of **B** gives **O**, so **B** must have the 4,6-dioxygenated-5-methylphthalide framework. One oxygen substituent is hydroxyl and the other methoxy. Either placement satisfies all the observations supplied for **B**.

For 7.1, we choose **4-hydroxy-6-methoxy-5-methylphthalide**.

7.2. The second structure for **B**

Interchanging hydroxyl and methoxy gives **6-hydroxy-4-methoxy-5-methylphthalide**, O=C1OCc2c(OC)c(C)c(O)cc21.

Both candidates have formula $C_{10}H_{10}O_4$, contain a phenolic hydroxyl, and methylate to the same **O**. The supplied observations do not distinguish them.

The solution was checked against the official solution.