

IChO 1991

Theory problems and solutions · Lodz, Poland · 6 theory problems with complete solutions

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Problem 1: Dissolution of Tl_2S and CuS in acids

1.1 Show that 0.1 mol of Tl_2S dissolves in a 1 M solution of any strong monoprotic non-coordinating acid.

1.2 Show that 0.1 CuS dissolves in a 1 M HNO_3 but not in a 1 M HCl solution.

Information:

Assume that Cu^{2+} ions do not form stable complexes with chloride ions in aqueous solutions.

$$E^0(\text{S}/\text{S}^{2-}) = -0.48 \text{ V} \quad E^0(\text{NO}_3^-/\text{NO}(\text{aq})) = 0.96 \text{ V}$$

$$pK_a(\text{H}_2\text{S}) = 7$$

$$pK_a(\text{HS}^-) = 13$$

$$K_{sp}(\text{Tl}_2\text{S}) = 1 \times 10^{-20}$$

$$K_{sp}(\text{CuS}) = 1 \times 10^{-35}$$

Solubility of NO in water (298 K): $2.53 \times 10^{-2} \text{ mol dm}^{-3}$

Solubility of H_2S in water (298 K): 0.1 mol dm^{-3}

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad F = 96487 \text{ C mol}^{-1}$$

Official English text of the problem.

Answers

The numerical demonstrations use 1.00 dm^3 of each initially 1 M acid, since the printed problem omits the volume.

- 1.1:** All 0.1 mol of Tl_2S dissolves. After complete dissolution, its ion product is 6.3×10^{-23} , below $K_{sp} = 10^{-20}$.
- 1.2:** All 0.1 mol of CuS dissolves in nitric acid through oxidation of sulfide to sulfur and reduction of nitrate to nitrogen monoxide. The overall equilibrium constant is approximately 1.4×10^{41} . In hydrochloric acid, its equilibrium solubility is only $3.2 \times 10^{-8} \text{ mol dm}^{-3}$.

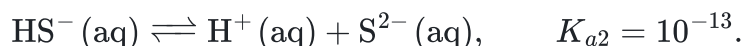
Solution

Use $T = 298 \text{ K}$, approximate activities by concentrations divided by the standard concentration 1 mol dm^{-3} , and assign unit activity to pure solids and water. Concentrations inserted into equilibrium quotients below are numerical values in mol dm^{-3} . Neglect solution-volume changes.

1.1 — Dissolution of thallium(I) sulfide

The acid dissociation equilibria are



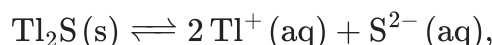


Consequently,

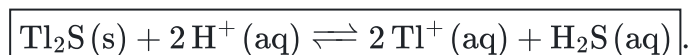
$$[\text{S}^{2-}] = \frac{K_{a1}K_{a2}[\text{H}_2\text{S}]}{[\text{H}^{+}]^2} = \frac{10^{-20}[\text{H}_2\text{S}]}{[\text{H}^{+}]^2}.$$

Thus, strong acid greatly suppresses the free sulfide-ion concentration.

Combining dissolution,



with sulfide protonation gives



Its equilibrium constant is

$$K_{\text{Tl}} = \frac{K_{sp}(\text{Tl}_2\text{S})}{K_{a1}K_{a2}} = \frac{10^{-20}}{10^{-20}} = 1.$$

Test complete dissolution of 0.1 mol in 1.00 dm³ of initially 1 M acid. The resulting concentrations would be approximately

$$\begin{aligned} [\text{Tl}^{+}] &= 0.20 \text{ mol dm}^{-3}, \\ [\text{H}_2\text{S}] &= 0.10 \text{ mol dm}^{-3}, \\ [\text{H}^{+}] &= 1.00 - 2(0.10) = 0.80 \text{ mol dm}^{-3}. \end{aligned}$$

The hydrogen sulfide concentration reaches the quoted solubility; any escape of this gas would further favor dissolution.

The corresponding sulfide concentration is

$$[\text{S}^{2-}] = \frac{10^{-20}(0.10)}{(0.80)^2} = 1.56 \times 10^{-21} \text{ mol dm}^{-3}.$$

Therefore,

$$Q_{sp} = [\text{Tl}^{+}]^2[\text{S}^{2-}] = (0.20)^2(1.56 \times 10^{-21}) = 6.25 \times 10^{-23} < 10^{-20}.$$

Even after all the solid has dissolved, the solution remains undersaturated with respect to Tl₂S.

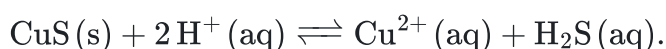
Complete dissolution is therefore thermodynamically favored.

Within the stated model, a strong monoprotic non-coordinating acid supplies the required hydrogen ions, while its anion does not enter this equilibrium. The conclusion therefore does not depend on the identity of that anion.

1.2 — Dissolution of copper(II) sulfide

In hydrochloric acid

The corresponding acid-driven reaction is



Its equilibrium constant is

$$K_{\text{Cu,acid}} = \frac{K_{sp}(\text{CuS})}{K_{a1}K_{a2}} = \frac{10^{-35}}{10^{-20}} = 10^{-15}.$$

Let s be the molar solubility in initially 1 M hydrochloric acid. Almost all dissolved sulfide is present as hydrogen sulfide, so

$$[\text{Cu}^{2+}] \simeq [\text{H}_2\text{S}] \simeq s, \quad [\text{H}^+] \simeq 1.$$

Hence,

$$K_{\text{Cu,acid}} = \frac{[\text{Cu}^{2+}][\text{H}_2\text{S}]}{[\text{H}^+]^2} \simeq s^2,$$

giving

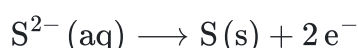
$$s \simeq \sqrt{10^{-15}} = 3.2 \times 10^{-8} \text{ mol dm}^{-3}.$$

Proton consumption at this concentration is negligible, confirming the approximation. The hydrogen sulfide concentration is also far below its quoted solubility.

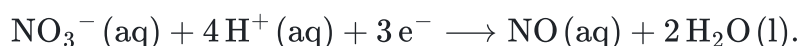
Thus, only about $3.2 \times 10^{-8} \text{ mol}$ dissolves in 1.00 dm^3 . By the stipulated absence of stable copper-chloride complexes, complex formation provides no additional driving force. **The requested 0.1 mol does not dissolve in this volume of hydrochloric acid.**

In nitric acid

Nitrate provides an additional dissolution pathway by oxidizing sulfide to elemental sulfur. The relevant half-reactions are



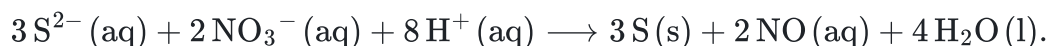
and



The standard cell potential is

$$E_{\text{cell}}^0 = 0.96 - (-0.48) = 1.44 \text{ V}.$$

Balancing the electron transfer gives



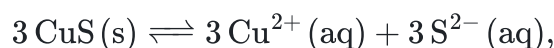
Six electrons are transferred, so

$$\ln K_{\text{redox}} = \frac{6FE_{\text{cell}}^0}{RT},$$

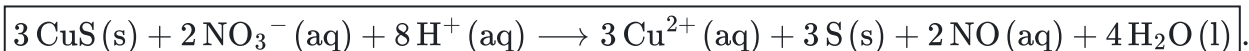
or

$$\log_{10} K_{\text{redox}} = \frac{6(96487)(1.44)}{(8.314)(298) \ln 10} = 146.13.$$

This oxidation must also overcome the low solubility of the solid. Adding three dissolution reactions,



produces the overall reaction



Equilibrium constants multiply when reactions are added:

$$K_{\text{overall}} = K_{\text{sp}}(\text{CuS})^3 K_{\text{redox}} = (10^{-35})^3 10^{146.13}.$$

Therefore,

$$K_{\text{overall}} \simeq 1.4 \times 10^{41}.$$

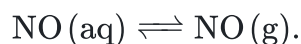
To check complete dissolution explicitly, 0.1 mol of CuS consumes

$$n(\text{H}^+) = \frac{8}{3}(0.1) = 0.267 \text{ mol}, \quad n(\text{NO}_3^-) = \frac{2}{3}(0.1) = 0.0667 \text{ mol}.$$

In the chosen 1.00 dm^3 volume, the final concentrations would consequently be

$$[\text{Cu}^{2+}] = 0.100, \quad [\text{H}^+] = 0.733, \quad [\text{NO}_3^-] = 0.933 \text{ mol dm}^{-3}.$$

The reaction generates 0.0667 mol of nitrogen monoxide. At the quoted gas-solubility condition, only 0.0253 mol can remain dissolved in this volume; excess gas can escape:



Using the quoted dissolved concentration as an upper bound,

$$Q_{\text{overall}} = \frac{[\text{Cu}^{2+}]^3 [\text{NO}]^2}{[\text{NO}_3^-]^2 [\text{H}^+]^8} \leq \frac{(0.100)^3 (0.0253)^2}{(0.933)^2 (0.733)^8} \simeq 8.8 \times 10^{-6}.$$

Since

$$Q_{\text{overall}} \ll K_{\text{overall}},$$

all 0.1 mol of copper(II) sulfide dissolves in the nitric acid, with ample acid remaining.

Species names and SMILES

Formula	Name	SMILES
Tl ₂ S	Thallium(I) sulfide	[Tl+] . [Tl+] . [S-2]
CuS	Copper(II) sulfide	[Cu+2] . [S-2]
Tl ⁺	Thallium(I) ion	[Tl+]
Cu ²⁺	Copper(II) ion	[Cu+2]
H ⁺	Hydrogen ion, proton	[H+]
S ²⁻	Sulfide ion	[S-2]
HS ⁻	Hydrosulfide ion	[SH-]
H ₂ S	Hydrogen sulfide	S
HNO ₃	Nitric acid	O=[N+]([O-])O
HCl	Hydrogen chloride; hydrochloric acid in water	Cl
NO ₃ ⁻	Nitrate ion	[O-][N+](=O)[O-]
Cl ⁻	Chloride ion	[Cl-]
NO	Nitrogen monoxide, nitric oxide	[N]=O
H ₂ O	Water	O
S ₈	Cyclooctasulfur, the molecular form of ordinary solid sulfur	S1SSSSSSS1

The sulfide-solid SMILES record the formal ionic compositions used in the equilibrium model; they do not describe crystal bonding or geometry. The acid SMILES show neutral molecules, while the strong acids are dissociated in the calculations. Proton hydration is implicit. Reaction equations write elemental sulfur as S(s) per sulfur atom; the S₈ SMILES specifies ring connectivity without specifying its crown conformation.

The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 2: Structure of a hydrocarbon polymer and its degradation products

A polymer **X** contains 88.25 % C and 11.75 % H. In dilute solutions it reacts with bromine and ozone. The thermal degradation of **X** produces a volatile liquid **Y** in 58 % yield. **Y** starts boiling at 34 °C and contains 88.25 % C and 11.72 % H. Some higher boiling products are formed both from the cracking of **X** and from Diels-Alder type cyclization of **Y**. The vapour of **Y** was 34 times as dense as hydrogen.

The product of bromination of **Y** yields a compound containing 82.5 % bromine by mass. Ozonolysis of **Y** followed by mild reduction gave **A** and **B** in a molar ratio **A** : **B** = 2 : 1. Only compound **B** gave a positive result for the iodoform reaction.

2.1 Determine the molecular formula and the molar mass of **Y**.

2.2 Show the structures of compounds **Y**, **A**, and **B**.

2.3 Give an equation for the reaction of **Y** with bromine.

In the catalytic hydrogenation of 13.6 g of **X**, 0.2 mole of hydrogen was absorbed. Ozonolysis of **X** followed by mild reduction yielded compound **Z** (60.0 % C, 8.0 % H).

2.4 Give the molecular formula of **Z** and the degree of unsaturation of **X**.

Compound **Z** gave a positive reaction with Fehling's solution. Mild oxidation of **Z** gave an acid **C**. A solution of acid **C** was titrated with aqueous KOH solution (phenolphthalein as indicator). 0.001 mol KOH was necessary for neutralization of 0.116 g of **C**.

In the iodoform reaction a probe 2.90 g of **C** yielded 9.85 g of iodoform. In addition, the alkaline filtrate yielded compound **D** upon acidification.

2.5 What is the molar mass of **C** and what functional groups are present in **Z**?

When heated, **D** loses water to form **E**. Both **D** and **E** react with an excess of acidified ethanol to **F** (C₈H₁₄O₄).

2.6 Sketch the structures of **C**, **D**, **E**, **F** and **Z**.

2.7 **X** exists in isomeric forms which are stereoregular. Show the structure (containing at least 3 monomer units) for two possible stereoisomers of **X**.

Official English text of the problem.

Answers

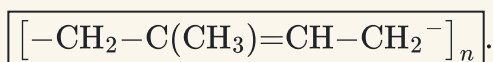
- **2.1 Y:** C_5H_8 , with $M = 68 \text{ g mol}^{-1}$.
- **2.2 Y** is **isoprene (2-methylbuta-1,3-diene)**, $\text{C}=\text{C}(\text{C})\text{C}=\text{C}$. **A** is **methanal (formaldehyde)**, $\text{C}=\text{O}$. **B** is **2-oxopropanal (methylglyoxal)**, $\text{CC}(=\text{O})\text{C}=\text{O}$.
- **2.3**

$$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2 + 2 \text{ Br}_2 \longrightarrow \text{BrCH}_2-\text{C}(\text{Br})(\text{CH}_3)-\text{CHBr}-\text{CH}_2\text{Br}$$

The product is **1,2,3,4-tetrabromo-2-methylbutane**, $\text{BrCC}(\text{Br})(\text{C})\text{C}(\text{Br})\text{CBr}$; its stereochemistry is not specified by the data.
- **2.4 Z:** $\text{C}_5\text{H}_8\text{O}_2$. **X** contains one $\text{C}=\text{C}$ bond per C_5H_8 repeat unit.
- **2.5** $M(\text{C}) = 116 \text{ g mol}^{-1}$. **Z** contains **one aldehyde group** and **one methyl ketone group**.
- **2.6**

Compound	Name	SMILES
C	4-Oxopentanoic acid, or levulinic acid	<chem>CC(=O)CCC(=O)O</chem>
D	Butanedioic acid, or succinic acid	<chem>O=C(O)CCC(=O)O</chem>
E	Succinic anhydride	<chem>O=C1CCC(=O)O1</chem>
F	Diethyl butanedioate, or diethyl succinate	<chem>CCOC(=O)CCC(=O)OCC</chem>
Z	4-Oxopentanal	<chem>CC(=O)CCC=O</chem>

- **2.7 X** is **1,4-polyisoprene**, with repeat unit



Three-repeat fragments of the two stereoregular forms are:

cis-1,4-Polyisoprene: $\text{*C/C(C)=C\CC/C(C)=C\CC/C(C)=C\C*}$

trans-1,4-Polyisoprene: $\text{*C/C(C)=C/CC/C(C)=C/CC/C(C)=C/C*}$

Here * denotes continuation of the polymer chain. The backbone substituents are on the same side of every double bond in the cis form and on opposite sides in the trans form.

Solution

Calculations use the conventional rounded atomic masses 12, 1, 16, 80, 127 for carbon, hydrogen, oxygen, bromine and iodine, respectively.

2.1 — Molecular formula and molar mass of Y

At equal temperature and pressure, gas densities are proportional to molar masses. The reference is molecular hydrogen, H_2 , $[\text{H}][\text{H}]$, so

$$M(\text{Y}) = 34M(\text{H}_2) = 34(2) = 68 \text{ g mol}^{-1}.$$

The elemental analysis gives

$$n(\text{C}) : n(\text{H}) = \frac{88.25}{12} : \frac{11.72}{1} = 7.354 : 11.72 \simeq 5 : 8.$$

Thus the empirical formula is C_5H_8 , whose formula mass is

$$5(12) + 8(1) = 68.$$

It is therefore also the molecular formula:

$$\boxed{\text{Y} = \text{C}_5\text{H}_8, \quad M(\text{Y}) = 68 \text{ g mol}^{-1}}.$$

The quoted percentages total 99.97%; this small discrepancy does not change the formula.

2.2 — Identification of Y, A and B

The degree of unsaturation of **Y** is

$$\text{DBE} = \frac{2(5) + 2 - 8}{2} = 2.$$

Let x be the number of moles of bromine added per mole of **Y**. The bromine mass fraction of the addition product gives

$$\frac{160x}{68 + 160x} = 0.825,$$

hence $x \simeq 2$. Together with the Diels–Alder behavior and ozonolysis, this identifies **Y** as a diene.

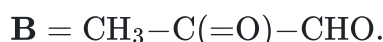
Ozonolysis produces two molecules of **A** and one of **B**, containing five carbon atoms altogether.

Because an iodoform-positive carbonyl compound needs at least two carbon atoms, **A** must contain one carbon and **B** three carbons.

The one-carbon carbonyl product is therefore **methanal**, $\text{C}=\text{O}$:



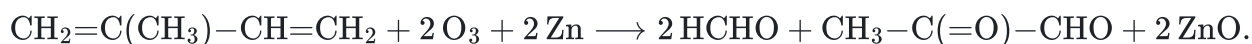
Cleavage of two double bonds produces four carbonyl oxygen atoms in total. After accounting for two molecules of methanal, the remaining product has formula $\text{C}_3\text{H}_4\text{O}_2$. Its positive iodoform reaction identifies a methyl ketone group. Consequently, **B** is **2-oxopropanal**, $\text{CC}(=\text{O})\text{C}=\text{O}$:



Reconnecting each of its carbonyl carbons to a terminal methylene group reconstructs **isoprene**, $\text{C}=\text{C}(\text{C})\text{C}=\text{C}$:



A balanced overall ozonolysis equation, choosing zinc as the mild reducing reagent, is



This gives precisely the observed ratio **A** : **B** = 2 : 1.

2.3 — Bromination of Y

Excess bromine, Br_2 , adds across both double bonds:



The product is **1,2,3,4-tetrabromo-2-methylbutane**, $\text{BrCC}(\text{Br})(\text{C})\text{C}(\text{Br})\text{CBr}$, with formula $\text{C}_5\text{H}_8\text{Br}_4$. Its bromine content is

$$w(\text{Br}) = \frac{4(80)}{68 + 4(80)} \times 100\% = 82.47\% \simeq 82.5\%.$$

The reported product therefore corresponds to complete addition of two equivalents of bromine.

2.4 — Formula of Z and unsaturation of X

The composition of **X** corresponds to C_5H_8 repeat units, each of molar mass 68 g mol^{-1} . Thus 13.6 g contains

$$n(\text{repeat units}) = \frac{13.6 \text{ g}}{68 \text{ g mol}^{-1}} = 0.200 \text{ mol}.$$

This absorbs 0.2 mol of hydrogen. Since each carbon–carbon double bond consumes one molecule of hydrogen,

$$\boxed{\text{X contains one C=C bond per C}_5\text{H}_8 \text{ repeat unit}}.$$

For **Z**, the oxygen percentage is

$$100.0 - 60.0 - 8.0 = 32.0\%.$$

Its atomic ratio is

$$\frac{60.0}{12} : \frac{8.0}{1} : \frac{32.0}{16} = 5 : 8 : 2,$$

giving empirical formula $\text{C}_5\text{H}_8\text{O}_2$.

Cleavage of successive backbone double bonds produces fragments with two carbonyl ends. There is one such double bond per five-carbon repeat interval, so the fragment contains one empirical formula unit:

$$\boxed{\text{Z} = \text{C}_5\text{H}_8\text{O}_2}, \quad M(\text{Z}) = 100 \text{ g mol}^{-1}.$$

These polymer calculations neglect end groups. The measured unsaturation is a per-repeat quantity; the total whole-chain DBE requires the chain length and end-group structures.

2.5 — Molar mass of C and functional groups in Z

Reductive ozonolysis gives carbonyl groups. The positive Fehling reaction shows that at least one of the two carbonyl groups in **Z** is an aldehyde.

Let q be the number of aldehyde groups oxidized to carboxyl groups. Each oxidation adds one oxygen atom without changing the carbon or hydrogen count, so

$$M(\text{C}) = 100 + 16q.$$

The titration gives the acid's equivalent mass:

$$\frac{M(\text{C})}{q} = \frac{0.116 \text{ g}}{0.001 \text{ mol}} = 116 \text{ g mol}^{-1}$$

per mole of neutralized carboxyl groups. Therefore,

$$100 + 16q = 116q, \quad q = 1.$$

Hence **Z** contains one aldehyde group and one ketone group, and

$$\boxed{M(\text{C}) = 116 \text{ g mol}^{-1}}, \quad \text{C} = \text{C}_5\text{H}_8\text{O}_3.$$

Iodoform, or **triiodomethane**, $\text{IC}(\text{I})\text{I}$, has molar mass

$$M(\text{CHI}_3) = 12 + 1 + 3(127) = 394 \text{ g mol}^{-1}.$$

The experimental amounts are

$$n(\text{C}) = \frac{2.90}{116} = 0.0250 \text{ mol},$$

$$n(\text{CHI}_3) = \frac{9.85}{394} = 0.0250 \text{ mol}.$$

Thus each molecule of **C** produces one molecule of iodoform, establishing one methyl ketone group. Mild oxidation preserves this ketone group, so **Z** contains

one $-\text{CHO}$ group and one $-\text{C}(=\text{O})\text{CH}_3$ group.

2.6 — Structures of C, D, E, F and Z

The haloform reaction converts the methyl ketone group of **C** into a carboxyl group while removing its methyl carbon as iodoform. After acidification, **D** is therefore a four-carbon dicarboxylic acid.

Formation of the diethyl ester **F**, $\text{C}_8\text{H}_{14}\text{O}_4$, is consistent with



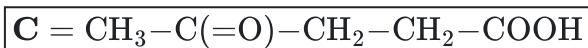
because replacing the two acidic hydrogens by ethyl groups adds C_4H_8 overall.

The loss of water on heating identifies **D** as **succinic acid**, $\text{O}=\text{C}(\text{O})\text{CCC}(=\text{O})\text{O}$:

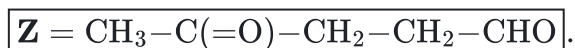


Its two carboxyl groups form a stable five-membered cyclic anhydride. The alternative four-carbon diacid, **methyldimaleic acid**, $\text{CC}(\text{C}(=\text{O})\text{O})\text{C}(=\text{O})\text{O}$, characteristically decarboxylates on heating instead.

Working backward from succinic acid gives:

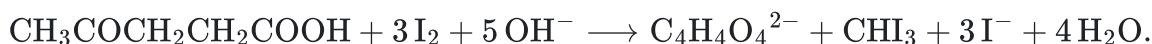


and



Thus **C** is **levulinic acid**, $\text{CC}(=\text{O})\text{CCC}(=\text{O})\text{O}$, and **Z** is **4-oxopentanal**, $\text{CC}(=\text{O})\text{CCC}=\text{O}$.

The balanced haloform reaction in alkaline solution is



The product $\text{C}_4\text{H}_4\text{O}_4^{2-}$ is the **succinate ion**, $\text{O}=\text{C}([\text{O}^-])\text{CCC}(=\text{O})[\text{O}^-]$. Acidification gives **D**:

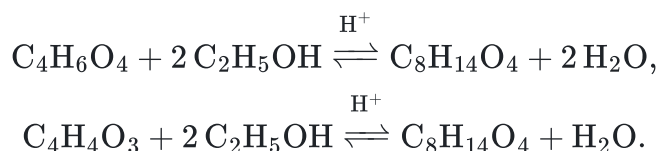


Heating gives **succinic anhydride E**, $\text{O}=\text{C}1\text{CCC}(=\text{O})\text{O}1$:

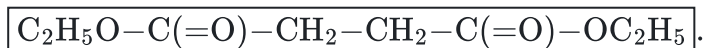


To sketch **E**, draw a five-membered ring containing, consecutively, one oxygen atom, a carbonyl carbon, two methylene carbons and a second carbonyl carbon, closing back to the ring oxygen.

Both **D** and **E** give **diethyl succinate F**, $\text{CCOC}(=\text{O})\text{CCC}(=\text{O})\text{OCC}$, with excess acidified **ethanol**, CCO :



The structure of **F** is



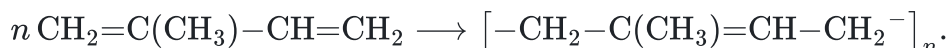
2.7 — Two stereoregular structures of **X**

The ozonolysis product



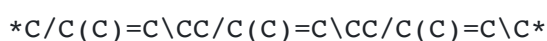
shows that successive double bonds in **X** are separated by two methylene groups. One alkene carbon bears hydrogen, and the other bears methyl. Reconnecting successive carbonyl ends therefore gives

1,4-polyisoprene:



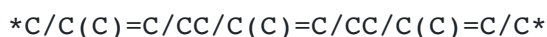
Its two stereoregular forms are:

- **cis-1,4-Polyisoprene**, the principal polymer of natural rubber:



At every double bond, draw the two backbone methylene substituents on the **same side**. These double bonds have *Z* configuration in the continuing polymer chain.

- **trans-1,4-Polyisoprene**, the principal polymer of gutta-percha:



At every double bond, draw the two backbone methylene substituents on **opposite sides**. These double bonds have *E* configuration.

Each SMILES contains three complete five-carbon repeat units. The asterisks denote chain continuation; the SMILES specify double-bond configuration, without imposing a particular three-dimensional chain conformation.

The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 3: Silver/silver chloride and calomel electrodes

Type II electrodes that are made of a metal covered with a sparingly soluble salt of the metal are dipped into a soluble salt solution containing an anion of the sparingly soluble salt. The silver/silver chloride (Ag , AgCl/Cl^-) and the calomel electrode (Hg , $\text{Hg}_2\text{Cl}_2/\text{Cl}^-$) are examples of such electrodes. The standard emf of a cell built of those electrodes

$(-)\text{Ag}, \text{AgCl}/\text{Cl}^- \parallel \text{Hg}_2\text{Cl}_2/\text{Hg} (+)$ is $E^0 = 0.0455 \text{ V}$ at $T = 298 \text{ K}$. The temperature coefficient for this cell is $dE^0/dT = 3.38 \times 10^{-4} \text{ V K}^{-1}$.

3.1 Give the equations of the reactions taking place at both the cell electrodes and the overall cell reaction.

3.2 Calculate the Gibbs free energy change (ΔG^0) for the process taking place in the cell at 298 K. What does its sign imply?

3.3 Calculate the enthalpy change for the process taking place at 298 K.

$$\Delta S = n F \Delta E / \Delta T.$$

3.4 Knowing the standard potential of Ag/Ag^+ electrode is $E^0 = 0.799 \text{ V}$ and the solubility product of AgCl $K_{sp} = 1.73 \times 10^{-10}$, calculate the standard electrode potential value of the silver/silver chloride electrode. Derive an expression showing the dependence between $E^0(\text{Ag}/\text{Ag}^+)$ and $E^0(\text{Ag}, \text{AgCl}/\text{Cl}^-)$.

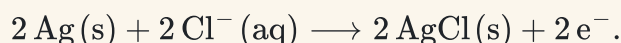
3.5 Calculate the solubility product of Hg_2Cl_2 knowing that the standard potential of the calomel electrode is $E^0 = 0.798 \text{ V}$.

$$F = 96487 \text{ C mol}^{-1}, \quad R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, \quad T = 298 \text{ K}$$

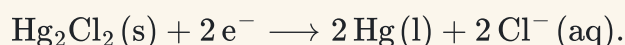
Official English text of the problem.

Answers

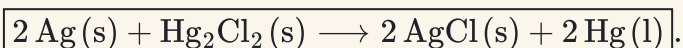
- **3.1** Negative electrode, oxidation:



Positive electrode, reduction:



Overall:



- **3.2** $\Delta G^\circ = -8.78 \text{ kJ mol}^{-1}$. The forward reaction is thermodynamically spontaneous under standard conditions at 298 K.
- **3.3** $\Delta H^\circ = +10.7 \text{ kJ mol}^{-1}$. The reaction is endothermic.
- **3.4**

$$E_{\text{AgCl}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{RT}{F} \ln K_{sp}(\text{AgCl}) = 0.222 \text{ V}.$$

- **3.5** The printed potential is inconsistent with the preceding data. If 0.798 V denotes $E_{\text{Hg}_2^{2+}/\text{Hg}}^\circ$, the result is

$$K_{sp}(\text{Hg}_2\text{Cl}_2) = 1.12 \times 10^{-18}.$$

Solution

All electrode potentials below use the reduction convention. Thermodynamic changes are per mole of the overall reaction written in **3.1**. Solubility products are expressed using dimensionless activities.

The species and their SMILES representations are:

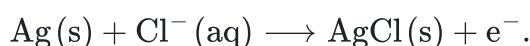
Species	SMILES
Silver, Ag	[Ag]
Mercury, Hg	[Hg]
Chloride ion, Cl^-	[Cl-]

Species	SMILES
Silver(I) ion, Ag^+	[Ag+]
Mercury(II) dimer ion, Hg_2^{2+}	[Hg+][Hg+]
Silver(I) chloride, AgCl	[Ag+]·[Cl-]
Mercury(II) chloride (calomel), Hg_2Cl_2	Cl[Hg][Hg]Cl

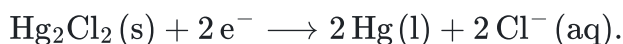
These SMILES represent atoms, ions, or formula-unit connectivity, not bulk metallic or crystal structures. The calomel representation does not encode the linear geometry of its $\text{Cl}-\text{Hg}-\text{Hg}-\text{Cl}$ unit.

3.1 Electrode reactions and overall reaction

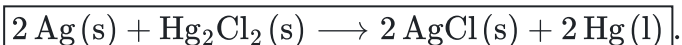
The negative electrode of this galvanic cell is the anode, where oxidation occurs. Silver changes from oxidation state 0 to +1, forming insoluble silver(I) chloride:



At the positive electrode, the cathode, mercury(II) in calomel is reduced to elemental mercury. Each formula unit contains two mercury atoms, each requiring one electron:



Multiplying the silver half-reaction by two and adding cancels both electrons and chloride ions:



Thus the electron-transfer number for this reaction is $n = 2$.

3.2 Gibbs free energy change

For a reversible electrochemical cell,

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ.$$

Therefore,

$$\begin{aligned}\Delta G^\circ &= -2(96487 \text{ C mol}^{-1})(0.0455 \text{ V}) \\ &= -8780.317 \text{ J mol}^{-1} \\ &= \boxed{-8.78 \text{ kJ mol}^{-1}}.\end{aligned}$$

The negative sign means that the reaction as written proceeds spontaneously in the thermodynamic sense under standard conditions at 298 K, and can supply electrical work.

3.3 Enthalpy change

Using the given temperature coefficient,

$$\Delta S^\circ = nF \frac{dE_{\text{cell}}^\circ}{dT}.$$

Hence,

$$\begin{aligned}\Delta S^\circ &= 2(96487)(3.38 \times 10^{-4}) \\ &= 65.2252 \text{ J mol}^{-1} \text{ K}^{-1}.\end{aligned}$$

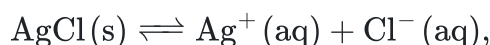
Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$,

$$\begin{aligned}
\Delta H^\circ &= \Delta G^\circ + T\Delta S^\circ \\
&= -8780.317 + (298)(65.2252) \\
&= 10656.8 \text{ J mol}^{-1} \\
&= \boxed{+10.7 \text{ kJ mol}^{-1}}.
\end{aligned}$$

The reaction is endothermic. Its positive entropy change makes $T\Delta S^\circ$ sufficiently large to give a negative ΔG° .

3.4 Standard silver/silver chloride electrode potential

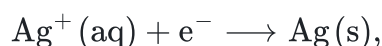
The dissolution equilibrium is



with

$$K_{sp}(\text{AgCl}) = a_{\text{Ag}^+}a_{\text{Cl}^-}.$$

For the reduction



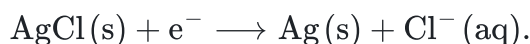
the Nernst equation is

$$E = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{RT}{F} \ln a_{\text{Ag}^+}.$$

Substituting $a_{\text{Ag}^+} = K_{sp}/a_{\text{Cl}^-}$ gives

$$E = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{RT}{F} \ln K_{sp} - \frac{RT}{F} \ln a_{\text{Cl}^-}.$$

The silver/silver chloride reduction is



Its standard potential is obtained at $a_{\text{Cl}^-} = 1$. Thus, in the notation of the question,

$$\boxed{E^0(\text{Ag, AgCl/Cl}^-) = E^0(\text{Ag/Ag}^+) + \frac{RT}{F} \ln K_{sp}(\text{AgCl})}.$$

Numerically,

$$\begin{aligned}
E_{\text{AgCl}}^\circ &= 0.799 + \frac{(8.314)(298)}{96487} \ln(1.73 \times 10^{-10}) \\
&= 0.2218218 \text{ V} \\
&= \boxed{0.222 \text{ V}}.
\end{aligned}$$

3.5 Solubility product of calomel

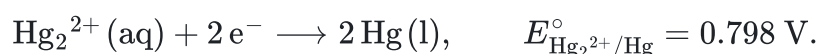
First, the given cell emf fixes the calomel electrode potential:

$$E_{\text{cell}}^\circ = E_{\text{calomel}}^\circ - E_{\text{AgCl}}^\circ.$$

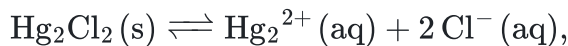
Therefore,

$$E_{\text{calomel}}^\circ = 0.0455 + 0.2218218 = 0.2673218 \text{ V}.$$

This conflicts with the 0.798 V explicitly called the calomel potential in part 3.5. A consistent calculation is possible if that value instead refers to



Under this interpretation, calomel dissolves according to



so

$$K_{sp}(\text{Hg}_2\text{Cl}_2) = a_{\text{Hg}_2^{2+}} a_{\text{Cl}^-}^2.$$

Adding this dissolution reaction to the mercury(I) reduction gives the calomel electrode reaction. The corresponding standard Gibbs energies therefore satisfy

$$-2FE_{\text{calomel}}^\circ = -RT \ln K_{sp} - 2FE_{\text{Hg}_2^{2+}/\text{Hg}}^\circ.$$

Rearranging,

$$K_{sp} = \exp \left[\frac{2F}{RT} (E_{\text{calomel}}^\circ - E_{\text{Hg}_2^{2+}/\text{Hg}}^\circ) \right].$$

Using the unrounded intermediate potential,

$$\begin{aligned} K_{sp} &= \exp \left[\frac{2(96487)}{(8.314)(298)} (0.2673218 - 0.798) \right] \\ &= \boxed{1.12 \times 10^{-18}}. \end{aligned}$$

The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 4: Hydrogen atom energy levels, Lyman series and the photoelectric effect

The energy of stable states of the hydrogen atom is given by: $E_n = -2.18 \times 10^{-18} / n^2$ [J]

where n denotes the principal quantum number.

4.1 Calculate the energy differences between $n = 2$ (first excited state) and $n = 1$ (ground state) and between $n = 7$ and $n = 1$.

4.2 In what spectral range is the Lyman series lying?

4.3 Can a single photon, emitted in the first and/or sixth line of the Lyman series, ionize:

a) another hydrogen atom in its ground state?

b) a copper atom in the Cu crystal?

The electron work function of Cu is $\Phi_{\text{Cu}} = 7.44 \times 10^{-19}$ J.

4.4 Calculate the de Broglie wavelength of the electrons emitted from a copper crystal when irradiated by photons from the first line and the sixth line of the Lyman series.

$$h = 6.6256 \times 10^{-34} \text{ J s}; \quad m_e = 9.1091 \times 10^{-31} \text{ kg}; \quad c = 2.99792 \times 10^8 \text{ m s}^{-1}$$

Official English text of the problem.

Answers

- **4.1** $E_2 - E_1 = \boxed{1.64 \times 10^{-18} \text{ J}}$; $E_7 - E_1 = \boxed{2.14 \times 10^{-18} \text{ J}}$.
- **4.2** The **ultraviolet**, specifically vacuum ultraviolet: approximately 91.1–121 nm, with 91.1 nm the series limit.
- **4.3(a)** **Neither** photon can ionize a ground-state hydrogen atom.
- **4.3(b)** **Both** photons can eject an electron from the copper crystal.
- **4.4** First line: $\boxed{\lambda_e = 5.20 \times 10^{-10} \text{ m} = 0.520 \text{ nm}}$. Sixth line: $\boxed{\lambda_e = 4.16 \times 10^{-10} \text{ m} = 0.416 \text{ nm}}$. These correspond to the maximum-energy photoelectrons.

Solution

4.1 — Energy differences

For an excited level n , its energy above the ground state is

$$\Delta E_{n,1} = E_n - E_1 = 2.18 \times 10^{-18} \left(1 - \frac{1}{n^2}\right) \text{ J}.$$

Thus,

$$\Delta E_{2,1} = 2.18 \times 10^{-18} \left(1 - \frac{1}{4}\right) = 1.635 \times 10^{-18} \text{ J} \approx \boxed{1.64 \times 10^{-18} \text{ J}},$$

and

$$\Delta E_{7,1} = 2.18 \times 10^{-18} \left(1 - \frac{1}{49}\right) = 2.135510 \dots \times 10^{-18} \text{ J} \approx \boxed{2.14 \times 10^{-18} \text{ J}}.$$

These positive energy differences equal the photon energies emitted in the downward transitions. The atom's energy changes during emission have the opposite sign.

4.2 — Spectral range of the Lyman series

The Lyman series consists of transitions from $n = 2, 3, \dots$ to $n = 1$. Its first line is therefore $2 \rightarrow 1$, and its sixth line is $7 \rightarrow 1$.

Using $E_\gamma = hc/\lambda_\gamma$, the longest wavelength is that of the first line:

$$\lambda_{\gamma,1} = \frac{(6.6256 \times 10^{-34})(2.99792 \times 10^8)}{1.635 \times 10^{-18}} = 1.21486 \dots \times 10^{-7} \text{ m} \approx 121 \text{ nm}.$$

As $n \rightarrow \infty$, the photon energy approaches $2.18 \times 10^{-18} \text{ J}$, giving the short-wavelength limit:

$$\lambda_{\text{limit}} = \frac{hc}{2.18 \times 10^{-18}} = 9.11148 \dots \times 10^{-8} \text{ m} \approx 91.1 \text{ nm}.$$

Thus, the entire series lies in the **ultraviolet**, specifically the vacuum-ultraviolet region.

4.3 — Can the photons cause ionization?

(a) Ground-state hydrogen

Ionization requires raising the electron from $E_1 = -2.18 \times 10^{-18} \text{ J}$ to the continuum at zero energy. The required energy is therefore

$$E_{\text{ion}} = 0 - E_1 = 2.18 \times 10^{-18} \text{ J}.$$

Both photon energies are smaller:

$$\begin{aligned} E_{\gamma,1} &= 1.635 \times 10^{-18} \text{ J} < E_{\text{ion}}, \\ E_{\gamma,6} &= 2.135510 \dots \times 10^{-18} \text{ J} < E_{\text{ion}}. \end{aligned}$$

Consequently, **neither photon can ionize a ground-state hydrogen atom**. They can excite it to the corresponding bound level.

(b) Copper crystal

For electron emission from the copper crystal, the relevant threshold is the work function:

$$\Phi_{\text{Cu}} = 7.44 \times 10^{-19} \text{ J}.$$

Since

$$E_{\gamma,1} > \Phi_{\text{Cu}} \quad \text{and} \quad E_{\gamma,6} > \Phi_{\text{Cu}},$$

both photons can eject an electron by the photoelectric effect. The supplied work function describes electron removal from the solid.

4.4 — De Broglie wavelengths of the emitted electrons

The photoelectric equation gives the maximum kinetic energy:

$$K_{\text{max}} = E_{\gamma} - \Phi_{\text{Cu}}.$$

For a nonrelativistic electron,

$$K = \frac{p^2}{2m_e}, \quad \lambda_e = \frac{h}{p} = \frac{h}{\sqrt{2m_e K}}.$$

For irradiation by the **first Lyman line**,

$$K_{\text{max},1} = 1.635 \times 10^{-18} - 7.44 \times 10^{-19} = 8.91 \times 10^{-19} \text{ J},$$

so

$$\lambda_{e,1} = \frac{6.6256 \times 10^{-34}}{\sqrt{2(9.1091 \times 10^{-31})(8.91 \times 10^{-19})}} = \boxed{5.20 \times 10^{-10} \text{ m}}.$$

For irradiation by the **sixth Lyman line**, retaining unrounded intermediate values,

$$K_{\text{max},6} = 2.135510 \dots \times 10^{-18} - 7.44 \times 10^{-19} = 1.391510 \dots \times 10^{-18} \text{ J},$$

and

$$\lambda_{e,6} = \frac{6.6256 \times 10^{-34}}{\sqrt{2(9.1091 \times 10^{-31})(1.391510 \dots \times 10^{-18})}} = \boxed{4.16 \times 10^{-10} \text{ m}}.$$

These are the minimum de Broglie wavelengths, corresponding to the maximum kinetic energies. Photoelectrons emitted with less kinetic energy have longer wavelengths.

The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 5: Halogen derivatives of hydrocarbons

After passing 0.25 mol of hydrocarbon **A** over heated pumice (950 K) in an iron pipe, compound **B** in yield of 80 % (i. e. 15.4 g) and 2.4 dm³ of hydrogen, (295 K, 102 kPa) were obtained.

B and hydrogen are the only products. A mixture of halogen derivatives **C**, **D**, **E**, **F** and **G** is produced from **B** by reaction with a halogen in presence of a Lewis acid. Compounds **C** to **G** contain each one halogen atom more than the preceding compound. For the compounds **C** to **F** only one of the possible isomers is formed. In compound **G** there is no such preference and its three isomers **G**₁, **G**₂ and **G**₃ are found in the mixture. Compounds **C** to **F** racemize easily so that no optical isomerism occurs. However racemization is difficult for **G**₁, **G**₂, and especially for **G**₃. In the mass spectrum of **E** only three isotopic peaks were observed. Their relative intensities are 1: 1: 0.3.

Information:

- $k_{\text{ortho}} > k_{\text{para}}$ in compound **B**.
- The effect of the first halogen in the ring: $k_{\text{para}} > k_{\text{ortho}}$.
- Compounds **D** and **F** in one of their conformations have a center of symmetry.
- The contribution of carbon and hydrogen isotopes in the mass spectrum of **E** are negligible.
- Natural abundance of halogen isotopes:

$$^{19}\text{F} = 100 \text{ \%};$$

$$^{35}\text{Cl} = 75.53 \text{ \%}; \ ^{37}\text{Cl} = 24.47 \text{ \%};$$

$$^{79}\text{Br} = 50.54 \text{ \%}; \ ^{81}\text{Br} = 49.46 \text{ \%};$$

$$^{127}\text{I} = 100 \text{ \%}.$$

5.1 Give the structures of **A**, **B**, **C**, **D**, **E**, **F**, **G**₁, **G**₂ and **G**₃.

5.2 Explain your choice for the halogen.

5.3 Draw and label stereo-formulas of the rotational isomers of **D** for $\Phi = 0, \pi/2, \pi$, and $3\pi/2$, where Φ denotes the dihedral or torsional angle in radians and $\vartheta = 0$ describes the configuration with maximal energy.

5.4 Draw profiles of the energy changes as a function of the angle of rotation around the C—C bond for compounds **C** and **D**.

5.5 Give a sequence of **G**₁, **G**₂, **G**₃ according to their increasing difficulty of racemization. Explain your answer.

5.6 Draw stereo-formulas of the enantiomers of **G**₃.

5.7 Suggest a chemical reaction or a biological method by which compounds like these can be destroyed.

Answers

- **5.1** The structures are given below. Number the two rings of biphenyl from the atoms forming the connecting bond, 1 and 1'. Define **G₁**, **G₂**, **G₃** by adding the fifth chlorine to **F** at positions 3, 4, 6, respectively.

Compound	Name	SMILES
A	Benzene	<chem>c1ccccc1</chem>
B	Biphenyl	<chem>c1(-c2ccccc2)ccccc1</chem>
C	2-Chlorobiphenyl	<chem>c1(-c2ccccc2)c(Cl)cccc1</chem>
D	2,2'-Dichlorobiphenyl	<chem>c1(-c2c(Cl)cccc2)c(Cl)cccc1</chem>
E	2,2',5-Trichlorobiphenyl	<chem>c1(-c2c(Cl)cccc2)c(Cl)ccc(Cl)c1</chem>
F	2,2',5,5'-Tetrachlorobiphenyl	<chem>c1(-c2c(Cl)ccc(Cl)c2)c(Cl)ccc(Cl)c1</chem>
G₁	2,2',3,5,5'-Pentachlorobiphenyl	<chem>c1(-c2c(Cl)ccc(Cl)c2)c(Cl)c(Cl)cc(Cl)c1</chem>
G₂	2,2',4,5,5'-Pentachlorobiphenyl	<chem>c1(-c2c(Cl)ccc(Cl)c2)c(Cl)cc(Cl)c(Cl)c1</chem>
G₃	2,2',5,5',6-Pentachlorobiphenyl, equivalently 2,2',3,5',6- pentachlorobiphenyl	<chem>c1(-c2c(Cl)ccc(Cl)c2)c(Cl)ccc(Cl)c1Cl</chem>

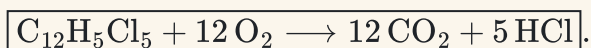
- **5.2** The halogen is **chlorine**. Three chlorine atoms give the isotope-peak ratio
1 : 0.972 : 0.315 : 0.0340.

The first three peaks match the stated 1 : 1 : 0.3; a weak fourth peak is predicted.

- **5.3** For **D**: 0, coplanar with the two ortho chlorines on the same side, highest energy; $\pi/2$, one twisted enantiomer; π , coplanar with the chlorines on opposite sides, possessing an inversion center; $3\pi/2$, the mirror-image twisted enantiomer.
- **5.4** **C** has equivalent coplanar barriers at 0, π , 2π . **D** has higher barriers at 0, 2π and a lower coplanar barrier at π . Both have intervening regions of lower energy with noncoplanar rings.
- **5.5** With the labels defined above, increasing difficulty of racemization is

$$\boxed{G_2 < G_1 < G_3}.$$

- **5.6** **G₃** has two axial enantiomers. Fixing the front ring, perpendicular rear-ring orientations at $+\pi/2$ and $-\pi/2$ give an explicit mirror-image pair, described below. Their ordinary connectivity SMILES is the same as that listed for **G₃**.
- **5.7** Controlled complete incineration destroys these compounds. For a pentachlorobiphenyl:



Solution

5.1 — Identification of the hydrocarbons and substitution patterns

The amount of hydrogen, hydrogen gas $[H][H]$, is

$$n(H_2) = \frac{pV}{RT} = \frac{(102 \text{ kPa})(2.4 \text{ dm}^3)}{(8.314 \text{ kPa dm}^3 \text{ mol}^{-1} \text{ K}^{-1})(295 \text{ K})} = 0.0998 \text{ mol} \approx 0.10 \text{ mol}.$$

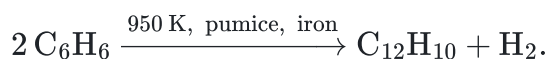
At 80 % yield, the amount of **A** converted into the stated products is

$$n_{\text{converted}}(\mathbf{A}) = 0.80(0.25 \text{ mol}) = 0.20 \text{ mol}.$$

The hydrogen has mass approximately 0.20 g. Since **B** and hydrogen are the only products, mass balance gives

$$M(\mathbf{A}) = \frac{15.4 \text{ g} + 0.20 \text{ g}}{0.20 \text{ mol}} \approx 78 \text{ g mol}^{-1}.$$

This is consistent with benzene, C_6H_6 . The aromatic substitution and rotation about a bond joining two rings identify **B** as biphenyl, formed by dehydrogenative coupling:



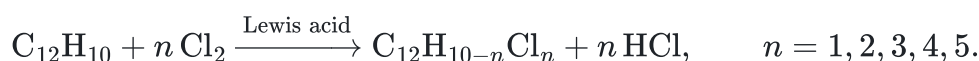
The predicted biphenyl amount and mass are

$$n(\mathbf{B}) = \frac{0.80(0.25)}{2} = 0.10 \text{ mol},$$

$$m(\mathbf{B}) = (0.10 \text{ mol})(154 \text{ g mol}^{-1}) = 15.4 \text{ g}.$$

Thus both the mass of **B** and the hydrogen volume agree with the proposed reaction.

As established in 5.2, the substituent is chlorine. Chlorine, $ClCl$, undergoes successive electrophilic aromatic substitutions in the presence of a Lewis acid, producing hydrogen chloride, HCl . The balanced overall equation for each degree of substitution is



The substitution sequence follows from the directing and symmetry information:

1. **C**: In biphenyl, the stated $k_{\text{ortho}} > k_{\text{para}}$ selects position 2. Hence **C** is **2-chlorobiphenyl**.
2. **D**: An inversion center at the midpoint of the inter-ring bond must interchange identically substituted rings. The second chlorine therefore occupies the equivalent ortho position on the other ring, giving **2,2'-dichlorobiphenyl**. Its coplanar, opposite-side conformation has the required inversion center.
3. **E**: Each ring now carries one chlorine. The next chlorine enters para to an existing chlorine: position 5, which is para to position 2. The two rings are equivalent before this substitution, so **E** is **2,2',5-trichlorobiphenyl**.
4. **F**: The inversion-center condition requires matching substitution patterns on the two rings. The fourth chlorine therefore enters position 5', giving **2,2',5,5'-tetrachlorobiphenyl**.
5. **G**: In **F**, the remaining positions on either ring are 3, 4, 6. Interchanging the rings does not generate additional constitutional isomers. Thus there are exactly three possibilities:

$$\begin{aligned} \mathbf{G}_1 &: 2, 2', 3, 5, 5', \\ \mathbf{G}_2 &: 2, 2', 4, 5, 5', \\ \mathbf{G}_3 &: 2, 2', 5, 5', 6. \end{aligned}$$

These are the structures and SMILES listed in **Answers**.

5.2 — Identification of the halogen from the isotope pattern

E contains three halogen atoms. Fluorine and iodine each have only one isotope in the supplied abundance data, so neither can produce the observed halogen-derived isotope cluster.

For chlorine, put

$$p = 0.7553, \quad q = 0.2447.$$

The probabilities of incorporating zero, one, two, or three ^{37}Cl atoms are the terms of

$$(p + q)^3 = p^3 + 3p^2q + 3pq^2 + q^3.$$

Consequently,

$$I_M : I_{M+2} : I_{M+4} : I_{M+6} = p^3 : 3p^2q : 3pq^2 : q^3.$$

Normalizing to the first peak gives

$$1 : 3\frac{q}{p} : 3\left(\frac{q}{p}\right)^2 : \left(\frac{q}{p}\right)^3 = \boxed{1 : 0.9719 : 0.3149 : 0.03401}.$$

For **E**, $\text{C}_{12}\text{H}_7\text{Cl}_3$, these correspond to nominal molecular-ion masses 256, 258, 260, 262.

The first three intensities round to the reported 1 : 1 : 0.3. The fourth is much smaller, although it is not mathematically zero.

By contrast, three bromine atoms, using the supplied abundances, would give approximately

$$1 : 2.936 : 2.873 : 0.937,$$

which does not match. Thus **chlorine is the intended identification**.

5.3 — Rotational isomers of D

Use the following precise end-on convention:

- Look along the inter-ring bond from unprimed $C1$ toward primed $C1'$.
- Keep the front ring fixed, with its $C2$ chlorine at **12 o'clock** and its $C6$ hydrogen at **6 o'clock**.
- Define $\Phi = 0$ when the rear $C2'$ chlorine is also at 12 o'clock.
- Increase Φ by rotating the rear ring clockwise in this view.

The requested drawings then have these features:

Φ	Rear $C2'$ chlorine	Rear $C6'$ hydrogen	Conformation and stereochemical label
0	12 o'clock	6 o'clock	Coplanar; chlorines on the same side of the axis; achiral; greatest steric crowding and maximal energy
$\pi/2$	3 o'clock	9 o'clock	Perpendicular ring planes; chiral conformer I
π	6 o'clock	12 o'clock	Coplanar; chlorines on opposite sides; achiral; inversion center at the inter-ring bond midpoint
$3\pi/2$	9 o'clock	3 o'clock	Perpendicular ring planes; chiral conformer II, the mirror image of I

At $\Phi = 0$, the ortho chlorine atoms approach one another directly. At $\Phi = \pi$, each ortho chlorine instead encounters an ortho hydrogen. The latter coplanar passage therefore has the lower steric barrier.

The SMILES for **D** specifies connectivity; these angular descriptions specify its conformations.

5.4 — Torsional-energy profiles of **C** and **D**

Plot energy vertically and Φ , from 0 to 2π , horizontally, using the convention in **5.3**.

For **C**, the unsubstituted ring has equivalent ortho positions. Rotating it by π produces an equivalent arrangement, so

$$E_C(\Phi + \pi) = E_C(\Phi).$$

The coplanar arrangements at 0, π , 2π have identical steric interactions and therefore equal barrier heights. Draw equivalent lower-energy, noncoplanar regions between successive coplanar barriers.

For **D**, the two coplanar arrangements differ:

- At 0 and 2π , an ortho chlorine faces an ortho chlorine: the higher barrier.
- At π , the two close contacts are chlorine–hydrogen contacts: the lower barrier.
- Between these coplanar arrangements lie two mirror-related, noncoplanar energy wells.

Thus a qualitative steric sketch follows this pattern:

Angle	0	Near $\pi/2$	π	Near $3\pi/2$	2π
C	High	Low	Equally high	Equally low	High
D	Highest	Low	Lower local maximum	Equally low	Highest

For **D**, reflection requires

$$E_D(\Phi) = E_D(2\pi - \Phi).$$

These are qualitative profiles. Conjugation favors coplanarity whereas steric repulsion favors twisting, so the exact minimum angles need not be precisely $\pi/2$ and $3\pi/2$; the supplied information does not determine numerical energies or fine details of the curves.

5.5 — Increasing difficulty of racemization

For these axially chiral biphenyls, interconversion of the enantiomers requires rotation through a coplanar arrangement. The relevant comparison is therefore the steric cost of the easiest coplanar passage.

- **G₂**, with the additional chlorine at 4, retains only two chlorines ortho to the inter-ring bond. The added chlorine is relatively remote from that bond.
- **G₁**, with the additional chlorine at 3, also has two ortho chlorines, but the 3-chlorine crowds the adjacent 2-chlorine. This **buttressing effect** increases the steric obstruction to rotation.
- **G₃**, with the additional chlorine at 6, has three ortho chlorines. One ring now carries chlorine on both sides of the inter-ring bond. Either coplanar passage therefore brings an ortho chlorine on one ring against an ortho chlorine on the other.

The expected steric order is consequently



5.6 — Enantiomers of G_3

Retain the common numbering used above: the unprimed ring has chlorines at 2, 5, 6, and the primed ring at 2', 5'.

The two axial enantiomers of **2,2',5,5',6-pentachlorobiphenyl**—equivalently **2,2',3,5',6-pentachlorobiphenyl**—have connectivity SMILES

c1(-c2c(Cl)ccc(Cl)c2)c(Cl)ccc(Cl)c1Cl.

Ordinary SMILES does not distinguish the frozen axial configurations here. The following end-on descriptions specify an explicit enantiomeric pair.

Look from unprimed $C1$ toward primed $C1'$. Fix the front ring vertically, with $C2$ at 12 o'clock and $C6$ at 6 o'clock. Its chlorine at $C5$ lies on the $C6$ side.

Feature	Enantiomer I	Enantiomer II
Front ring	Fixed as described	Identical fixed orientation
Rear $C2'$, bearing chlorine	3 o'clock	9 o'clock
Rear $C6'$, bearing hydrogen	9 o'clock	3 o'clock
Rear $C5'$, bearing chlorine	On the $C6'$ side, to the left	On the $C6'$ side, to the right
Ring-plane torsion	$+\pi/2$	$-\pi/2$

Reflection in the plane of the front ring converts I into II. They are nonsuperimposable mirror images: the axial R_a/S_a pair.

Although both ortho positions of the front ring bear chlorine, its two paths around the ring are different: the path through $C6$ encounters chlorine at $C5$, whereas the path through $C2$ encounters hydrogen at $C3$. The primed ring likewise has inequivalent paths through $C2'$ and $C6'$. Thus the substitution pattern supports axial chirality.

5.7 — Destruction

A suitable chemical method is **controlled high-temperature incineration in excess oxygen**, with sufficient residence time for complete oxidation and capture of the hydrogen chloride produced.

For any of the pentachlorobiphenyl isomers:



The reactant is a pentachlorobiphenyl listed above; the other molecular species are oxygen $\text{O}=\text{O}$, carbon dioxide $\text{O}=\text{C}=\text{O}$, and hydrogen chloride ClH .

The equation balances all atoms: twelve carbons form twelve carbon dioxide molecules, while the five hydrogens and five chlorines form five hydrogen chloride molecules.

The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 6: Production of sulphuric acid and oleum

Sulphuric acid is produced by catalytic oxidation of SO_2 to SO_3 , absorption of SO_3 in concentrated sulphuric acid forming oleum (containing 20 % SO_3 by mass) and appropriate dilution hereafter. The gas leaving the catalyst chamber contains nitrogen, oxygen, a trace of SO_2 and 10 % (by volume) of SO_3 . Sulphur trioxide, SO_3 , is converted into sulphuric acid (98 % by mass) and/or oleum.

6.1 Assuming that oleum is the only product formed, calculate the mass of water which is required for 1000 m^3 of gas leaving the catalyst chamber (273 K, 101.3 kPa).

6.2 Assuming that only 98 % sulphuric acid is produced, calculate the necessary mass of water and the mass of product produced thereby.

6.3 In the industry both oleum and 98 % sulphuric acid are produced in a mass ratio of $x = m_1/m_2$, where m_1 denotes the mass of oleum, m_2 the mass of 98 % sulphuric acid. Find an expression $y = f(x)$ to describe the relation between the mass of water consumed for 1000 m^3 gas (denoted y) and the value of x . Show that the results of 6.1) and 6.2) are in good agreement with your mathematical expression.

Official English text of the problem.

Answers

- **6.1:** Water required: $\boxed{61.5 \text{ kg}}$.
- **6.2:** Water required: $\boxed{89.3 \text{ kg}}$; mass of 98 % sulphuric acid produced: $\boxed{446 \text{ kg}}$.
- **6.3:** For $x = m_1/m_2 \geq 0$,

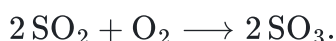
$$y \approx (357 \text{ kg}) \frac{36x + 49}{209x + 196}.$$

Only 98 % acid corresponds to $x = 0$, giving $y = 89.3 \text{ kg}$. Only oleum corresponds to $x \rightarrow \infty$, giving $y \rightarrow 61.5 \text{ kg}$.

Solution

The reaction species are sulphur dioxide ($\text{O}=\text{S}=\text{O}$), oxygen ($\text{O}=\text{O}$), sulphur trioxide ($\text{O}=\text{S}(\text{=O})=\text{O}$), sulphuric acid ($\text{OS}(\text{=O})(\text{=O})\text{O}$), and water (O).

Catalytic oxidation produces sulphur trioxide:



The net reaction consuming water during acid production is



Use the molar masses

$$M(\text{SO}_3) = 80.0, \quad M(\text{H}_2\text{O}) = 18.0, \quad M(\text{H}_2\text{SO}_4) = 98.0 \quad \text{kg kmol}^{-1}.$$

We balance the overall process, so circulating sulphuric acid cancels from the input and output streams. The stated oleum composition means 20 % excess SO_3 and 80 % H_2SO_4 on an analytical mass basis. Oleum and aqueous sulphuric acid are mixtures and therefore have no single molecular SMILES.

6.1

Treating the gas as ideal, the volume fraction of SO_3 equals its mole fraction. Using

$$R = 8.314 \text{ kPa m}^3 \text{ kmol}^{-1} \text{ K}^{-1},$$

the amount of sulphur trioxide available is

$$n(\text{SO}_3) = \frac{0.10 pV}{RT} = \frac{0.10(101.3)(1000)}{8.314(273)} = 4.4631 \text{ kmol}.$$

Thus, its mass, denoted S , is

$$S = 4.4631(80.0) = 357.048 \text{ kg}.$$

Let y_1 be the water required and m_1 the oleum produced. All added water reacts, producing $(98/18)y_1$ kilograms of sulphuric acid. Since the oleum contains 80 % sulphuric acid,

$$\frac{98}{18}y_1 = 0.80m_1.$$

The total mass balance is

$$m_1 = S + y_1.$$

Combining these equations,

$$98y_1 = 14.4(S + y_1),$$

so

$$y_1 = \frac{14.4}{83.6}S = \frac{36}{209}(357.048) = 61.501 \text{ kg}.$$

Therefore,

$$\boxed{m_{\text{water}} = 61.5 \text{ kg}}.$$

6.2

All sulphur trioxide now reacts to form sulphuric acid. The mass of pure acid formed is

$$m(\text{H}_2\text{SO}_4) = 4.4631(98.0) = 437.384 \text{ kg}.$$

Since this constitutes 98 % of the product,

$$m_2 = \frac{437.384}{0.98} = 446.310 \text{ kg}.$$

The required water has two contributions: water incorporated into sulphuric acid and water remaining in the 98 % solution:

$$\begin{aligned} y_2 &= n(\text{SO}_3)M(\text{H}_2\text{O}) + 0.02m_2 \\ &= 4.4631(18.0) + 0.02(446.310) \\ &= 80.336 + 8.926 \\ &= 89.262 \text{ kg}. \end{aligned}$$

Hence,

$$\boxed{m_{\text{water}} = 89.3 \text{ kg}}, \quad \boxed{m_{98\% \text{ acid}} = 446 \text{ kg}}.$$

6.3

For an oleum mass m_1 , the incoming sulphur trioxide supplies both the excess SO_3 , of mass $0.20m_1$, and the SO_3 incorporated into $0.80m_1$ of sulphuric acid. Thus its total contribution is

$$\left(0.20 + 0.80 \frac{80}{98}\right)m_1 = \frac{209}{245}m_1.$$

For a mass m_2 of 98 % sulphuric acid, the required sulphur trioxide mass is

$$0.98 \frac{80}{98}m_2 = \frac{4}{5}m_2.$$

The sulphur trioxide balance is therefore

$$S = \frac{209}{245}m_1 + \frac{4}{5}m_2.$$

The overall mass balance gives the water input:

$$y = m_1 + m_2 - S = \frac{36}{245}m_1 + \frac{1}{5}m_2.$$

Substituting $m_1 = xm_2$,

$$S = \left(\frac{209}{245}x + \frac{4}{5}\right)m_2, \quad y = \left(\frac{36}{245}x + \frac{1}{5}\right)m_2.$$

Eliminating m_2 yields

$$y = S \frac{36x + 49}{209x + 196} \approx (357 \text{ kg}) \frac{36x + 49}{209x + 196}.$$

The limiting cases reproduce the earlier answers:

- **Only 98 % sulphuric acid:** $m_1 = 0$, so $x = 0$:

$$y(0) = S \frac{49}{196} = \frac{S}{4} = 89.3 \text{ kg}.$$

The product mass is $m_2 = S + y = 446 \text{ kg}$, agreeing with **6.2**.

- **Only oleum:** $m_2 \rightarrow 0$, so $x \rightarrow \infty$:

$$\lim_{x \rightarrow \infty} y = S \frac{36}{209} = 61.5 \text{ kg},$$

agreeing with **6.1**.

The solution was checked against the official solution.