

IChO 1988

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Problem 1: Flatlandia: the periodic system of a two-dimensional world

The periodic system of the elements in our three-dimensional world is based on the four electron quantum numbers $n = 1, 2, 3, \dots$; $l = 0, 1, \dots, n - 1$, $m = 0, \pm 1, \pm 2, \dots, \pm l$; and $s = \pm 1/2$. In Flatlandia, a two-dimensional world, the periodic system is thus based on three electron quantum numbers: $n = 1, 2, 3, \dots$; $m_l = 0, \pm 1, \pm 2, \dots, \pm(n - 1)$; and $s = \pm 1/2$ where m_l plays the combined role of l and m_l of the three dimensional world. The following tasks relate to this two-dimensional world, where the chemical and physical experience obtained from our world is supposed to be still applicable.

1.1 Draw the first four periods of the Flatlandian periodic table of the elements. Number them according to their nuclear charge. Use the atomic numbers (Z) as symbols of the specific element. Write the electron configuration for each element.

1.2 Draw the hybrid orbitals of the elements with $n = 2$. Which element is the basis for the "organic" chemistry in Flatlandia? Find the Flatlandian analogous for ethane, ethene and cyclohexane. What kind of aromatic ring compounds are possible?

1.3 Which rules in Flatlandia correspond to the octet and the 18-electron rules in the three dimensional world?

1.4 Predict graphically the trends in the first ionization energies of the Flatlandian elements with $n = 2$. Show graphically how the electronegativities of the elements increase in the Flatlandian periodic table.

1.5 Draw the molecular orbital energy diagrams of the neutral homonuclear diatomic molecules of the elements with $n = 2$. Which of these molecules are stable in Flatlandia?

1.6 Consider simple binary compounds of the elements ($n = 2$) with $Z = 1$. Draw their Lewis structure, predict their geometries and propose analogues for them in the three-dimensional world.

1.7 Consider elements with $n \leq 3$. Propose an analogue and write the chemical symbol from our world for each of these Flatlandian elements. On the basis of this chemical and physical analogue predict which two-dimensional elements are solid, liquid or gaseous at normal pressure and temperature.

Official English text of the problem.

Answers

- **1.1** Using the usual Aufbau analogy, the first four periods contain **2, 6, 6 and 10 elements**, respectively: $Z = 1-2, 3-8, 9-14, 15-24$. The complete table and configurations appear below.
- **1.2** The available hybrids are sp , **linear at 180°** , and sp^2 , **trigonal at 120°** . Element **5** is the carbon analogue. Writing **X** for element 5 and **H** for element 1, the ethane, ethene and cyclohexane analogues are X_2H_4 , X_2H_2 **and** X_6H_6 . Conventional benzene-type aromatic rings are unavailable in the ideal hybridization model; the limitation of this conclusion is discussed below.
- **1.3** The corresponding rules are the **six-electron rule** and the **ten-electron rule**.
- **1.4** First ionization energy generally increases from $Z = 3$ to 8, with expected dips at **5** and **7**. Electronegativity increases broadly **to the right and upwards**; element **7** is the most electronegative of these main-group elements.
- **1.5** The predicted bond orders for the dimers of $Z = 3, 4, 5, 6, 7, 8$ are 1, 0, 1, 2, 1, 0. Thus the elementary MO model predicts bound dimers for **3, 5, 6 and 7**.
- **1.6** The simplest hydrides are: element 3, EH , predominantly ionic; element 4, EH_2 , linear as an isolated molecule; element 5, EH_3 , trigonal planar; element 6, EH_2 , bent; element 7, EH , diatomic. Element 8 has no ordinary stable hydride.
- **1.7** The proposed analogues, in order $Z = 1$ through 14, are **H, He, Li, Be, C, O, F, Ne, Na, Mg, Si, S, Cl, Ar**. Predicted solids are **3, 4, 5, 9, 10, 11, 12**; gases are **1, 2, 6, 7, 8, 13, 14**; **none is predicted to be liquid**.

Solution

The quantum numbers determine orbital capacities exactly. To construct a chemical periodic table, an additional analogy is necessary: I use the ordinary Aufbau ordering with $|m_l|$ replacing l , together with Pauli exclusion and Hund's rule.

Notation for structures. Ordinary SMILES cannot encode a different periodic system. Accordingly, `[*:5]` below means a wildcard atom labelled as **Flatlandian element 5**, not ordinary boron. The number after the colon is a label under this convention. `[H]` denotes element 1. These SMILES describe connectivity and formal bond orders; the accompanying text specifies Flatlandian electron counts and geometry.

1.1 — Periodic table and electron configurations

For a given n , the permitted orbital quantum numbers are

$$m_l = -(n-1), \dots, -1, 0, 1, \dots, n-1.$$

There are $2n-1$ spatial orbitals, each accommodating two electrons. Thus

$$N_n = 2(2n-1) = 4n-2.$$

The first four **shell capacities** are consequently 2, 6, 10, 14.

We can name the subshells by analogy:

Subshell	Values of m_l	Spatial orbitals	Electron capacity
s	0	1	2
p	$-1, +1$	2	4
d	$-2, +2$	2	4
f	$-3, +3$	2	4

The analogue of the $n + l$ ordering uses $n + |m_l|$, with smaller n filled first when sums are equal. Through the fourth period, this gives

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p.$$

In particular, $3d$ fills in the fourth period. Shell capacities therefore differ from period lengths.

The requested periodic-table sketch is:

Period	s^1	s^2	d -block 1	d -block 2	d -block 3	d -block 4	p^1	p^2	p^3	p^4 , closed shell
1	1									2
2	3	4					5	6	7	8
3	9	10					11	12	13	14
4	15	16	17	18	19	20	21	22	23	24

Element 2 is placed with the other closed-shell elements despite having configuration $1s^2$.

Define the closed cores

$$[2] = 1s^2, \quad [8] = 1s^2 2s^2 2p^4, \quad [14] = 1s^2 2s^2 2p^4 3s^2 3p^4.$$

The unrearranged Aufbau configurations are:

Z	Electron configuration	Z	Electron configuration
1	$1s^1$	13	$[8] 3s^2 3p^3$
2	$1s^2$	14	$[8] 3s^2 3p^4$
3	$[2] 2s^1$	15	$[14] 4s^1$
4	$[2] 2s^2$	16	$[14] 4s^2$
5	$[2] 2s^2 2p^1$	17	$[14] 3d^1 4s^2$
6	$[2] 2s^2 2p^2$	18	$[14] 3d^2 4s^2$
7	$[2] 2s^2 2p^3$	19	$[14] 3d^3 4s^2$
8	$[2] 2s^2 2p^4$	20	$[14] 3d^4 4s^2$
9	$[8] 3s^1$	21	$[14] 3d^4 4s^2 4p^1$
10	$[8] 3s^2$	22	$[14] 3d^4 4s^2 4p^2$
11	$[8] 3s^2 3p^1$	23	$[14] 3d^4 4s^2 4p^3$
12	$[8] 3s^2 3p^2$	24	$[14] 3d^4 4s^2 4p^4$

There is a qualification concerning transition-metal exceptions. Transplanting the empirical preference for half-filled and filled d subshells suggests the alternative configurations

$$Z = 17 : [14] 3d^2 4s^1, \quad Z = 19 : [14] 3d^4 4s^1.$$

These are the possible analogues of chromium- and copper-type rearrangements. Whether they actually occur requires relative orbital and interaction energies, which are not supplied.

1.2 — Hybrid orbitals and organic analogues

The $n = 2$ shell contains one s orbital and two real p orbitals, which we may call p_x and p_y . Both lie in Flatlandia's plane.

Two hybridization patterns are available:

1. sp hybridization

$$h_{\pm} = \frac{s \pm p_x}{\sqrt{2}}.$$

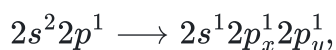
Draw two large hybrid lobes pointing in opposite directions along a straight line, at 180° . The unused p_y orbital has two opposite-sign lobes perpendicular to that line, but still within the plane. It can form a π bond.

2. sp^2 hybridization

$$h_k = \frac{s}{\sqrt{3}} + \sqrt{\frac{2}{3}} (\cos \theta_k p_x + \sin \theta_k p_y), \quad \theta_k = 0^\circ, 120^\circ, 240^\circ.$$

Draw three large hybrid lobes along three rays separated by 120° , with a smaller back lobe opposite each large lobe. No unused p orbital remains.

Element 5 has three valence electrons. Promotion permits



so it can form three covalent bonds and attain a six-electron valence shell. It occupies the role of carbon as a versatile, catenating framework element.

For this part, let **X** denote element 5 and **H** element 1.

Requested analogue	Flatlandian formula and name	Flatlandian connectivity SMILES	Geometry
Ethane, CC	X_2H_4 , Flatlandian ethane analogue	<code>[*:5]([H])([H])[*:5]([H])[H]</code>	One single bond between two sp^2 centres; each centre also bonds to two hydrogen atoms. The three bond directions at either centre are approximately 120° .
Ethene, C=C	X_2H_2 , Flatlandian ethene analogue	<code>[H][*:5]=[*:5][H]</code>	Each centre is sp -hybridized. All four nuclei lie on a straight line. The double bond consists of one σ bond and one in-plane π bond.
Cyclohexane, C1CCCCC1	X_6H_6 , Flatlandian cyclohexane analogue	<code>[*:5]1([H])[*:5]([H])[*:5]([H])[*:5]([H])[*:5]1[H]</code>	A planar regular hexagon with single ring bonds, approximately 120° internal angles, and one outward-pointing hydrogen at each vertex.

The cyclic analogue has twelve σ bonds: six around the ring and six to hydrogen. It is fully saturated. Three-dimensional chair and boat conformations are unavailable.

For **ordinary benzene-type aromaticity**, each ring atom needs orbitals for its σ framework plus a separate orbital supporting continuous cyclic π overlap. An sp^2 centre in Flatlandia has used all three available valence orbitals. An sp centre retains a p orbital, but its ideal σ -bond directions are collinear and cannot close an unstrained ring.

Thus the elementary hybridization construction gives **no conventional benzene-type aromatic organic rings**. This argument does not prove that every conceivable bent-bond or σ -aromatic cluster is impossible.

1.3 — Analogues of the octet and 18-electron rules

For main-group bonding, the available valence orbitals are one s and two p orbitals:

$$2(1 + 2) = 6 \text{ electrons.}$$

Therefore,

octet rule $\longrightarrow$ six-electron rule.

The first shell retains its two-electron closure.

For transition-metal bonding, the corresponding s , p and d set contains

$$1 + 2 + 2 = 5$$

spatial orbitals. Hence

$$2(1 + 2 + 2) = 10 \text{ electrons,}$$

and

18-electron rule $\longrightarrow$ ten-electron rule.

As in our world, these are useful closed-shell counting rules, not guarantees that every stable compound satisfies them.

1.4 — Ionization energies and electronegativities

Across the second period, increasing nuclear charge generally binds the valence electrons more strongly. Two familiar electronic effects interrupt that trend.

Element	Valence configuration	Expected feature of first ionization energy
3	$2s^1$	Low: removal gives the closed first shell.
4	$2s^2$	Higher: the $2s$ subshell is filled.
5	$2s^2 2p^1$	A dip relative to 4: the electron removed is in the less penetrating $2p$ subshell.
6	$2s^2 2p^2$	Rises: the two p orbitals are singly occupied with parallel spins.
7	$2s^2 2p^3$	An expected dip relative to 6: one p orbital now contains a pair; ionization relieves pairing repulsion and leaves the half-filled p subshell.
8	$2s^2 2p^4$	Highest in the period: increased nuclear attraction and a complete valence shell.

For the requested graph, place $Z = 3, 4, 5, 6, 7, 8$ along the horizontal axis and first ionization energy on the vertical axis. Draw an overall rising sequence with local downward steps at 5 and 7:

$$I_1(3) \nearrow I_1(4) \searrow I_1(5) \nearrow I_1(6) \searrow I_1(7) \nearrow I_1(8).$$

This specifies a qualitative curve; the problem supplies no numerical ionization energies.

For electronegativity, draw arrows on the periodic table:

increasing across a main-group period: $\longrightarrow$

increasing up a group: $\uparrow$

Thus the broad direction of increase is towards the upper right, excluding the closed-shell column in the usual elementary treatment. Element 7, one electron short of a sextet, occupies the fluorine-like position.

1.5 — Molecular orbital diagrams and stable dimers

Choose the internuclear axis as x .

- The two $2s$ orbitals produce σ_s and σ_s^* .
- The two $2p_x$ orbitals produce σ_p and σ_p^* .
- The two $2p_y$ orbitals produce π_p and π_p^* .

There is **only one bonding π orbital and one antibonding π orbital**. The twofold π degeneracy familiar in three dimensions is absent.

A conventional ordering with relatively weak s - p mixing is

$$\sigma_s < \sigma_s^* < \sigma_p < \pi_p < \pi_p^* < \sigma_p^*.$$

To sketch each diagram, draw these six horizontal levels in increasing energy. Fill each occupied level with a paired up and down arrow according to the following table. The occupied core levels $\sigma_{1s}^2 \sigma_{1s}^{*2}$ are common to every molecule and cancel in the bond-order calculation.

Each atom contributes $Z - 2$ valence electrons, so the dimer contains $2(Z - 2)$.

$$\text{Bond order} = \frac{N_{\text{bonding}} - N_{\text{antibonding}}}{2}.$$

Dimer	Valence electrons	Valence MO configuration	Bond order	Elementary prediction
Element-3 dimer	2	σ_s^2	1	Bound
Element-4 dimer	4	$\sigma_s^2 (\sigma_s^*)^2$	0	No net covalent bond
Element-5 dimer	6	$\sigma_s^2 (\sigma_s^*)^2 \sigma_p^2$	1	Bound
Element-6 dimer	8	$\sigma_s^2 (\sigma_s^*)^2 \sigma_p^2 \pi_p^2$	2	Bound
Element-7 dimer	10	$\sigma_s^2 (\sigma_s^*)^2 \sigma_p^2 \pi_p^2 (\pi_p^*)^2$	1	Bound
Element-8 dimer	12	$\sigma_s^2 (\sigma_s^*)^2 \sigma_p^2 \pi_p^2 (\pi_p^*)^2 (\sigma_p^*)^2$	0	No net covalent bond

Corresponding connectivity representations are:

Species or predicted dissociation limit	SMILES
Element-3 dimer	[*:3][*:3]
Two separated element-4 atoms	[*:4].[*:4]

Species or predicted dissociation limit	SMILES
Element-5 dimer	[*:5][*:5]
Element-6 dimer	[*:6]=[*:6]
Element-7 dimer	[*:7][*:7]
Two separated element-8 atoms	[*:8].[*:8]

Stronger s - p mixing can reverse the order of the two bonding p -derived levels:

$$\sigma_s < \sigma_s^* < \pi_p < \sigma_p < \pi_p^* < \sigma_p^*.$$

For this alternative, put the last pair of the element-5 dimer into π_p instead of σ_p . All the listed bond orders and stability conclusions remain unchanged.

All occupied levels in these elementary diagrams contain paired electrons. In particular, the element-6 dimer is predicted to be diamagnetic.

Here “unbound” means **no net covalent stabilization in this elementary MO model**; a zero formal bond order does not by itself exclude weak interactions or correlation-induced binding.

1.6 — Hydrides, Lewis structures and geometries

In the following table, Z denotes the element specified by the Z column. Every ordinary covalent bond contains two electrons, and hydrogen requires a duet.

Z	Flatlandian hydride and SMILES	Lewis structure and geometry	Proposed three-dimensional analogue
3	Element-3 hydride, EH , $[*+ : 3] \cdot [\text{H}-]$	Predominantly an element-3 cation and a hydride anion. Put one electron pair on the hydride ion. The condensed material is ionic; an isolated two-nucleus species is linear.	Lithium hydride, LiH , $[\text{Li}+] \cdot [\text{H}-]$
4	Element-4 dihydride, EH_2 , $[\text{H}][*:4][\text{H}]$	Two single bonds, no lone pair on the central atom. The isolated molecule is linear, 180° , using sp hybrids. It has only four electrons around the central atom and is electron deficient.	Beryllium hydride, BeH_2 , $[\text{H}][\text{Be}][\text{H}]$
5	Element-5 trihydride, EH_3 , $[*:5]([\text{H}])([\text{H}])[\text{H}]$	Three single bonds and no lone pair on the central atom. Trigonal planar, approximately 120° , with a complete sextet.	Methane, CH_4 , c
6	Element-6 dihydride, EH_2 , $[\text{H}][*:6][\text{H}]$	Two single bonds and one lone pair on the central atom. Three electron-pair domains give a bent molecule: idealized angle 120° , reduced by stronger lone-pair repulsion.	Water, H_2O , o
7	Element-7 hydride, EH , $[\text{H}][*:7]$	One single bond and two lone pairs on element 7. A complete sextet surrounds it. The molecule is diatomic and therefore linear.	Hydrogen fluoride, HF , $[\text{H}]\text{F}$
8	No ordinary stable simple hydride	The valence shell is already closed.	Neon has no ordinary stable hydride.

The central-atom electron counts in the three sextet-satisfying covalent hydrides are

$$\begin{aligned}
 Z = 5 : & \quad 3 \text{ bond pairs} = 6 \text{ electrons,} \\
 Z = 6 : & \quad 2 \text{ bond pairs} + 1 \text{ lone pair} = 6 \text{ electrons,} \\
 Z = 7 : & \quad 1 \text{ bond pair} + 2 \text{ lone pairs} = 6 \text{ electrons.}
 \end{aligned}$$

The element-4 hydride is the electron-deficient exception. As with ordinary beryllium hydride, bridging or polymerization could increase coordination in the condensed phase; the linear prediction concerns its isolated monomer.

These analogies concern chemical role and bonding tendency. They do not imply identical coordination numbers or lone-pair counts in the two worlds.

1.7 — Analogous elements and physical states

For the first three periods, choose analogues using the following criteria:

- The first closed shell and the *s*-block positions correspond directly.
- Element 5 occupies the half-filled-valence-shell, framework-forming role of carbon.
- Elements 6 and 7 need two and one additional electrons, respectively, to complete their valence shells, giving oxygen-like and fluorine-like roles.
- The next period repeats those relationships.

Flatlandian <i>Z</i>	Proposed analogue	Reason for the analogy	Predicted state
1	H	One electron; duet-forming first-shell chemistry	Gas
2	He	Closed first shell	Gas
3	Li	Second-period s^1 metal	Solid
4	Be	Second-period s^2 metal	Solid
5	C	Catenating covalent framework element	Solid
6	O	Two electrons short of a closed shell; divalent covalent chemistry	Gas
7	F	One electron short of a closed shell; halogen-like chemistry	Gas
8	Ne	Closed second valence shell	Gas
9	Na	Third-period s^1 metal	Solid
10	Mg	Third-period s^2 metal	Solid
11	Si	Heavier homologue of the framework-forming element 5	Solid
12	S	Heavier, divalent homologue of element 6	Solid
13	Cl	Heavier halogen-like homologue of element 7	Gas
14	Ar	Closed third-period valence shell	Gas

Thus

Solids: 3, 4, 5, 9, 10, 11, 12

Gases: 1, 2, 6, 7, 8, 13, 14

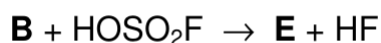
Liquids: none among these elements.

These phase assignments are the requested predictions from chemical analogy, rather than deductions from the quantum-number count alone.

The solution was checked against the official solution.

Problem 2: Fluorides of an element A and the electron-density maps of compound E

Upon heating of a mixture of **A** and fluorine (molar ratio 1 : 9, pressure approximately 1 MPa) to 900 °C three compounds (**B**, **C** and **D**) are formed. All three products are crystalline solids at ambient temperature with melting points below 150 °C. The fluorine content of **C** is found to be 36.7 % and that of **D** 46.5 % (by weight). When **B** is treated with anhydrous HOSO_2F at $-75\text{ }^\circ\text{C}$ a compound **E** is formed:



E is a solid which is stable for weeks at 0 °C, but decomposes in days at room temperature. The electron density distribution of **E** obtained through X-ray diffraction studies is shown on two intersecting, mutually perpendicular planes (see Fig. 1).

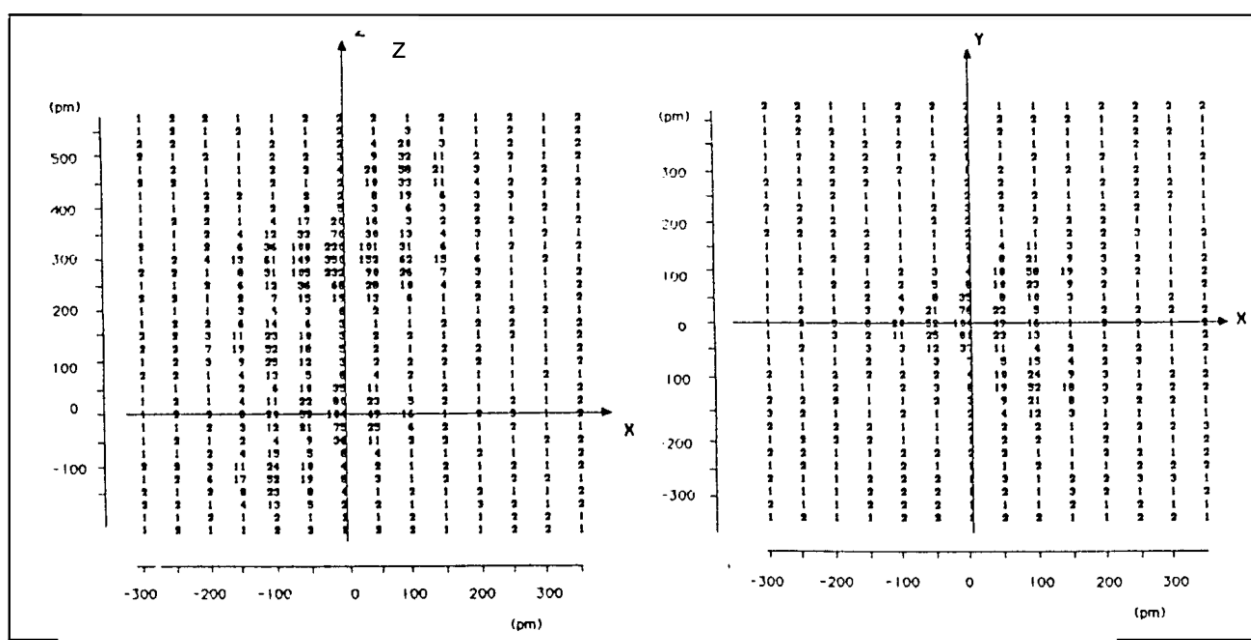


Fig. 1

The numbers indicated on the maps relate to the electron density in the neighbourhood of the atoms of **E** as a function of the spatial coordinates. The maxima found in these maps coincide with the locations of the atoms and the values are approximately proportional to the number of electrons in the atom in question.

2.1 Show where the maxima lie by drawing the contour curves around the maxima, connecting points of equal electron densities. Label each maximum to show the identities of the atoms in **E**.

2.2 When 450.0 mg of **C** was treated with an excess of mercury, 53.25 ml of **A** was liberated at a pressure of 101.0 kPa and a temperature of 25 °C. Calculate the relative atomic mass of **A**.

2.3 Identify **A**, **B**, **C**, **D** and **E**.

2.4 Use the valence-shell electron-pair repulsion theory (VSEPR) to propose electron-pair geometries for **B** and **C**. Using the two electron density maps, sketch the molecular geometry of **E**.

The original mixture was hydrolysed in water. **B** reacts to **A** while liberating oxygen and producing aqueous hydrogen fluoride. Hydrolysis of **C** leads to **A** and oxygen (in molar ratio of 4 : 3) and yields an aqueous solution of AO_3 and hydrogen fluoride. **D** hydrolyses to an aqueous solution of AO_3 and hydrogen fluoride.

2.5 Write the equations for the three hydrolysis reactions.

2.6 Quantitative hydrolysis of a mixture of **B**, **C** and **D** gives 60.2 ml of gas (measured at 290 K and 100 kPa). The oxygen content of this gas is 40.0% (by volume). The amount of AO_3 dissolved in water is titrated with an aqueous 0.1 molar FeSO_4 solution and 36.0 ml used thereby. During the titration Fe^{2+} is oxidized to Fe^{3+} and AO_3 is reduced to **A**. Calculate the composition (% by moles) of the original mixture of **B**, **C** and **D**.

Official English text of the problem.

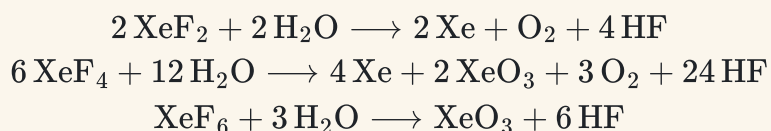
Answers

- 2.1:** In the xz map, label the maxima from highest to lowest z : **F**, **Xe**, **O**, **S**, **O**. In the xy map, label the common central maximum **S**, the positive- y maximum **F**, and the negative- y maximum **O**. Specifically, the maximum of **52** at $(-100, -125)$ in the xz map is **O**, and the maximum of **58** at $(+100, +100)$ in the xy map is **F**.
- 2.2:** $A_r(\text{A}) \approx 131.3$, dimensionless.
- 2.3:**

Label	Identity	SMILES
A	Xenon, Xe	[Xe]
B	Xenon difluoride, XeF_2	F[Xe]F
C	Xenon tetrafluoride, XeF_4	F[Xe](F)(F)F
D	Xenon hexafluoride, XeF_6	F[Xe](F)(F)(F)(F)F
E	Xenon(II) fluoride fluorosulfate, FXeOSO_2F	F[Xe]OS(=O)(=O)F

- 2.4:** **B** has trigonal-bipyramidal electron-pair geometry and a linear molecular geometry. **C** has octahedral electron-pair geometry and a square-planar molecular geometry. **E** has approximately linear $\text{F}-\text{Xe}-\text{O}$, a bent $\text{Xe}-\text{O}-\text{S}$ linkage, and approximately tetrahedral coordination around sulfur. Its sulfur-bound fluorine lies at positive y in the xy map.

• 2.5:



• 2.6: The original mixture contains, by moles,

$\text{XeF}_2 : 23.8\%$,	$\text{XeF}_4 : 71.4\%$,	$\text{XeF}_6 : 4.8\%$.
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Solution

2.1 — Electron-density maxima

The maxima locate atomic centres. Their heights distinguish the heavy xenon atom from sulfur and from the lighter oxygen and fluorine atoms. The relevant electron counts are

$$Z(\text{Xe}) = 54, \quad Z(\text{S}) = 16, \quad Z(\text{F}) = 9, \quad Z(\text{O}) = 8.$$

The xenon identification is independently confirmed by the atomic-mass calculation in 2.2.

The contour drawing should contain nested closed inner curves around the following centres. Coordinates are in pm; apart from the two labelled peak maxima (52 and 58), they are approximate readings of the map.

Map	Position	Atom and structural role
$xz, y = 0$	Uppermost small peak, approximately (+100, +475)	F , bonded to Xe
$xz, y = 0$	Very large peak near (0, +300)	Xe
$xz, y = 0$	Peak near (−100, +125), between Xe and S	O , bridging Xe and S
$xz, y = 0$	Central peak near (0, 0)	S
$xz, y = 0$	(−100, −125), maximum 52	O , terminal oxygen on S
$xy, z = 0$	Central peak near (0, 0)	S , the same atom as in the other map
$xy, z = 0$	(+100, +100), maximum 58	F , bonded to S
$xy, z = 0$	Lower-right peak, approximately (+100, −125)	O , the other terminal oxygen on S

Contours connect equal-density points, with higher values toward each centre; interpolation is appropriate between printed grid points. For example, a contour at density 55 can enclose the fluorine maximum of 58, whereas it cannot enclose the oxygen maximum of 52.

The distinction between these two peaks is consistent with

$$\frac{58}{52} = 1.115 \approx \frac{9}{8},$$

the fluorine-to-oxygen electron-count ratio.

Counting the shared sulfur only once gives one Xe, one S, three O and two F atoms.

2.2 — Relative atomic mass of A

Mercury removes the fluorine from **C**, liberating elemental **A**. The non-fluorine mass in the sample is

$$m(\text{A}) = (450.0 \text{ mg})(1 - 0.367) = 284.85 \text{ mg} = 0.28485 \text{ g}.$$

Using $T = 298.15 \text{ K}$ and $R = 8.314 \text{ kPa L mol}^{-1} \text{ K}^{-1}$,

$$n(\text{A}) = \frac{pV}{RT} = \frac{(101.0 \text{ kPa})(0.05325 \text{ L})}{(8.314 \text{ kPa L mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = 2.16968 \times 10^{-3} \text{ mol}.$$

The gaseous element is monatomic xenon, consistent with the large electron-density maximum. Therefore,

$$M(\text{A}) = \frac{0.28485 \text{ g}}{2.16968 \times 10^{-3} \text{ mol}} = 131.2865 \text{ g mol}^{-1}.$$

Thus

$$A_r(\text{A}) \approx 131.3.$$

2.3 — Identification of A–E

The atomic mass and electron-density map identify **A** as xenon.

For a fluoride XeF_n , the fluorine mass fraction w_{F} satisfies

$$w_{\text{F}} = \frac{nM(\text{F})}{M(\text{Xe}) + nM(\text{F})}.$$

Hence, using $M(\text{F}) = 19.00 \text{ g mol}^{-1}$,

$$n = \frac{w_{\text{F}}}{1 - w_{\text{F}}} \frac{M(\text{Xe})}{M(\text{F})}.$$

For **C**,

$$n = \frac{0.367}{0.633} \frac{131.2865}{19.00} = 4.006 \approx 4,$$

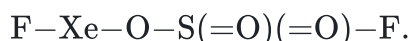
so **C** is xenon tetrafluoride, XeF_4 .

For **D**,

$$n = \frac{0.465}{0.535} \frac{131.2865}{19.00} = 6.006 \approx 6,$$

so **D** is xenon hexafluoride, XeF_6 .

The maps establish the connectivity of **E** as



Thus **E** is xenon(II) fluoride fluorosulfate. The conventional double bonds represent the two terminal sulfur–oxygen bonds.

Fluorosulfuric acid, HOSO_2F , has SMILES `OS(=O)(=O)F`; hydrogen fluoride, HF , has SMILES `[H]F`.

The reaction is



It replaces one xenon-bound fluorine with an oxygen-bound fluorosulfate group. Therefore **B** is xenon difluoride, XeF_2 .

2.4 — Electron-pair and molecular geometries

For **B**, XeF_2 , xenon has two bonding pairs and three lone pairs: AX_2E_3 . Five electron domains give a **trigonal-bipyramidal electron-pair arrangement**. The three lone pairs occupy equatorial positions, leaving the fluorine atoms in the two axial positions. Consequently, the molecule is **linear**, with a 180° bond angle.

For **C**, XeF_4 , xenon has four bonding pairs and two lone pairs: AX_4E_2 . Six electron domains give an **octahedral electron-pair arrangement**. The lone pairs occupy opposite positions, leaving four fluorines in a plane. Consequently, the molecule is **square planar**, with adjacent bond angles of 90° .

For **E**, the requested sketch can be described as follows:

1. Place sulfur at the common central maximum of the two maps.
2. In the xz plane, draw the bridging oxygen above and to the left of S. Continue from this oxygen upward and to the right to Xe, and then farther upward and to the right to the terminal Xe-bound F. The O—Xe—F unit is approximately straight.
3. Draw one terminal sulfur–oxygen bond downward and to the left in the xz plane, toward the oxygen maximum of 52.
4. Draw the remaining two sulfur bonds in the xy plane: the sulfur-bound **F** is at positive x , positive y , and the other terminal **O** is at positive x , negative y .

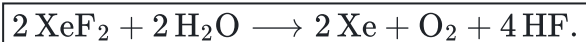
Sulfur therefore has approximately **tetrahedral coordination** by three oxygen atoms and one fluorine atom. The bridging S—O—Xe unit is **bent**, while F—Xe—O is approximately **linear**.

The SMILES given in 2.3 specify connectivity; they do not encode these xenon coordination geometries or the molecule's orientation in the plotted planes.

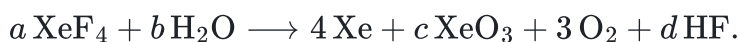
2.5 — Hydrolysis reactions

The additional molecular species are water, H_2O , O ; oxygen, O_2 , $\text{O}=\text{O}$; and xenon trioxide, XeO_3 , $\text{O}=[\text{Xe}](=\text{O})=\text{O}$. Hydrogen fluoride was specified in 2.3.

For **B**, balancing fluorine and hydrogen first and then oxygen gives



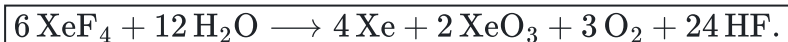
For **C**, use the specified xenon-to-oxygen ratio of 4 : 3. Write



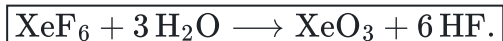
Element balances give

$$a = 4 + c, \quad d = 4a, \quad b = 2a, \quad b = 3c + 6.$$

Therefore $a = 6$, $b = 12$, $c = 2$ and $d = 24$:



For **D**, all xenon forms xenon trioxide:



2.6 — Composition of the fluoride mixture

Let the initial amounts of XeF_2 , XeF_4 and XeF_6 be x , y and z mol, respectively.

The total amount of gas collected during hydrolysis is

$$N = \frac{pV}{RT} = \frac{(100 \text{ kPa})(0.0602 \text{ L})}{(8.314 \text{ kPa L mol}^{-1} \text{ K}^{-1})(290 \text{ K})} = 2.496827 \times 10^{-3} \text{ mol}.$$

Volume fractions equal mole fractions under these conditions, so

$$n(\text{O}_2) = 0.400N, \quad n(\text{Xe}) = 0.600N.$$

The hydrolysis equations give

$$x + \frac{2}{3}y = 0.600N$$

and

$$\frac{1}{2}x + \frac{1}{2}y = 0.400N.$$

Thus

$$x + y = 0.800N,$$

and subtraction yields

$$\frac{1}{3}y = 0.200N.$$

Consequently,

$$\begin{aligned} y &= 0.600N = 1.498096 \times 10^{-3} \text{ mol}, \\ x &= 0.200N = 4.993654 \times 10^{-4} \text{ mol}. \end{aligned}$$

To find z , use the titration. Iron(II) sulfate, FeSO_4 , has ionic SMILES $[\text{Fe}+2] \cdot [\text{O}-]\text{S}(=\text{O})(=\text{O})[\text{O}-]$. Its iron(II) ions, Fe^{2+} , $[\text{Fe}+2]$, are oxidized to iron(III) ions, Fe^{3+} , $[\text{Fe}+3]$.

Xenon in XeO_3 has oxidation state $+6$, so reduction to xenon requires six electrons per xenon atom. The balanced titration equation in acidic solution is



where the hydrogen ion, H^+ , has SMILES $[\text{H}+]$.

Therefore,

$$n(\text{Fe}^{2+}) = (0.1 \text{ mol L}^{-1})(0.0360 \text{ L}) = 3.60 \times 10^{-3} \text{ mol},$$

and

$$n(\text{XeO}_3) = \frac{3.60 \times 10^{-3}}{6} = 6.00 \times 10^{-4} \text{ mol}.$$

Hydrolysis produces $y/3$ mol of xenon trioxide from **C** and z mol from **D**:

$$\frac{y}{3} + z = 6.00 \times 10^{-4}.$$

Hence

$$z = 6.00 \times 10^{-4} - \frac{1.498096 \times 10^{-3}}{3} = 1.006346 \times 10^{-4} \text{ mol}.$$

The total initial amount is

$$x + y + z = 2.098096 \times 10^{-3} \text{ mol}.$$

Compound	Initial amount / mmol	Mole percentage
B , XeF_2	0.4994	23.8%
C , XeF_4	1.4981	71.4%

Compound	Initial amount / mmol	Mole percentage
D, XeF ₆	0.1006	4.8%

The solution was checked against the official solution.

Problem 3: Combustion in a car engine and catalytic oxidation of CO

A typical family car has four cylinders with a total cylinder volume of 1600 cm³ and a fuel consumption of 7.0 l per 100 km when driving at a speed of 90 km/h. During one second each cylinder goes through 25 burn cycles and consumes 0.4 g of fuel. Assume that fuel consists of 2,2,4-trimethylpentane, C₈H₁₈. The compression ratio of the cylinder is 1:8.

3.1 Calculate the air intake of the engine (m³/s). The gasified fuel and air are introduced into the cylinder when its volume is largest until the pressure is 101.0 kPa. Temperature of both incoming air and fuel are 100 °C. Air contains 21.0 % (by volume) of O₂ and 79.0 % of N₂. It is assumed that 10.0 % of the carbon forms CO upon combustion and that nitrogen remains inert.

3.2 The gasified fuel and the air are compressed until the volume in the cylinder is at its smallest and then ignited. Calculate the composition (% by volume) and the temperature of the exhaust gases immediately after the combustion (exhaust gases have not yet started to expand). The following data is given:

Compound	ΔH_f (kJ/mol)	C_p (J/mol K)
O ₂ (g)	0.0	29.36
N ₂ (g)	0.0	29.13
CO (g)	-110.53	29.14
CO ₂ (g)	-395.51	37.11
H ₂ O (g)	-241.82	33.58
2,2,4-trimethylpentane	-187.82	

3.3 Calculate the final temperature of the leaving gases assuming that the piston has moved to expand the gases to the maximum volume of the cylinder and that the final gas pressure in the cylinder is 200 kPa.

3.4 To convert CO (g) into CO₂ (g) the exhaust gases are led through a bed of catalysts with the following work function:

$$\frac{n(\text{CO})}{n(\text{CO}_2)} = \frac{1}{4}k \left[\frac{n(\text{CO})}{n(\text{CO}_2)} \right]_1 v e^{-T/T_0}$$

where $[n(\text{CO})/n(\text{CO}_2)]_1$ is the molar ratio before the catalyst, v is the flow rate in mol/s and T the temperature of the gases entering the catalyst (the same as the temperature of the leaving exhaust gases). T_0 is a reference temperature (373 K) and k is equal to 3.141 s/mol. Calculate the composition (% by volume) of the exhaust gases leaving the catalyst.

Official English text of the problem.

Answers

- **3.1:** Air intake = $3.96 \times 10^{-2} \text{ m}^3 \text{ s}^{-1}$, at 101.0 kPa and 100 °C.
- **3.2:** Composition is given below. The constant-pressure heat balance gives $T \approx 2.06 \times 10^3 \text{ K}$, **assuming a 373 K starting temperature** and the enthalpy convention explained below.
- **3.3:** $T_{\text{exit}} \approx 709 \text{ K} \approx 436 \text{ °C}$.
- **3.4:** Composition is given below; approximately 82.6% of the entering carbon monoxide is oxidized.

Both compositions include water vapour.

Gas: name, formula, and SMILES	3.2: After combustion, vol.%	3.4: After catalyst, vol.%
Nitrogen, N ₂ , N#N	75.00	75.25
Oxygen, O ₂ , O=O	7.43	7.11
Carbon monoxide, CO, [C-]#[O+]	0.83	0.14
Carbon dioxide, CO ₂ , O=C=O	7.44	8.16
Water, H ₂ O, O	9.31	9.34

Small deviations from 100% arise from rounding.

Solution

We treat the gases as ideal and use

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, \quad T_{\text{in}} \approx 373 \text{ K}.$$

The fuel is **2,2,4-trimethylpentane (isooctane)**, CC(C)(C)CC(C)C, with molar mass

$$M(\text{C}_8\text{H}_{18}) \approx 114.0 \text{ g mol}^{-1}.$$

3.1 — Air intake

Interpreting 1600 cm³ as the sum of the maximum cylinder volumes, each cylinder has

$$V_{\text{max}} = \frac{1600}{4} = 400 \text{ cm}^3.$$

The engine performs $4(25) = 100$ burn cycles per second. Thus the total volume of incoming **fuel vapour plus air** is

$$\dot{V}_{\text{mix}} = 100(400 \times 10^{-6}) = 0.0400 \text{ m}^3 \text{ s}^{-1}.$$

The corresponding molar flow is

$$\dot{n}_{\text{mix}} = \frac{P\dot{V}_{\text{mix}}}{RT_{\text{in}}} = \frac{101000(0.0400)}{8.314(373)} = 1.30275 \text{ mol s}^{-1}.$$

The stated fuel consumption is 0.4 g **per second per cylinder**, so

$$\begin{aligned} \dot{m}_f &= 4(0.4) = 1.6 \text{ g s}^{-1}, \\ \dot{n}_f &= \frac{1.6}{114.0} = 0.0140351 \text{ mol s}^{-1}. \end{aligned}$$

Subtracting the fuel vapour gives

$$\dot{n}_{\text{air}} = 1.30275 - 0.0140351 = 1.28872 \text{ mol s}^{-1}.$$

Therefore,

$$\dot{V}_{\text{air}} = \frac{\dot{n}_{\text{air}} R T_{\text{in}}}{P} = 0.0395691 \approx 3.96 \times 10^{-2} \text{ m}^3 \text{ s}^{-1}.$$

3.2 — Combustion products and temperature

One mole of fuel contains eight moles of carbon atoms. Since 10.0% form carbon monoxide, the products contain

$$n(\text{CO}) = 0.800 \text{ mol}, \quad n(\text{CO}_2) = 7.200 \text{ mol}$$

per mole of fuel. The eighteen hydrogen atoms give nine water molecules.

The oxygen requirement is consequently

$$\frac{0.8 + 2(7.2) + 9}{2} = 12.1$$

moles of oxygen per mole of fuel. The balanced reaction is



The incoming oxygen and nitrogen flows are

$$\dot{n}(\text{O}_2)_{\text{in}} = 0.210(1.28872) = 0.270631 \text{ mol s}^{-1},$$

$$\dot{n}(\text{N}_2)_{\text{in}} = 0.790(1.28872) = 1.01809 \text{ mol s}^{-1}.$$

The combustion consumes

$$12.1\dot{n}_f = 0.169825 \text{ mol s}^{-1}$$

of oxygen, leaving an excess.

Product	Molar-flow calculation	Molar flow, mol s ⁻¹
CO ₂	7.2 $\dot{n}_f$	0.101053
CO	0.8 $\dot{n}_f$	0.0112281
H ₂ O	9 $\dot{n}_f$	0.126316
O ₂	0.210 $\dot{n}_{\text{air}}$ - 12.1 $\dot{n}_f$	0.100806
N ₂	0.790 $\dot{n}_{\text{air}}$	1.01809
Total		1.35749

For ideal gases, volume fractions equal mole fractions:

$$\text{vol.\% of species } i = 100 \frac{\dot{n}_i}{1.35749}.$$

This gives the composition in the Answers table.

For the temperature, we treat the combustion as taking place at **constant pressure**, as the given C_p data and reaction enthalpy imply, and use C_p . We assume no heat loss and constant heat capacities. To obtain a numerical temperature, we additionally take 373 K as the precombustion temperature and treat the supplied reaction enthalpy as applicable at that reference temperature.

Using the tabulated formation enthalpies exactly as printed, the reaction enthalpy per mole of fuel is

$$\begin{aligned}\Delta_r H &= 7.2(-395.51) + 0.8(-110.53) + 9(-241.82) - (-187.82) \\ &= -4924.656 \text{ kJ mol}^{-1}.\end{aligned}$$

Thus the rate of heat release is

$$-\dot{n}_f \Delta_r H = (0.0140351)(4924.656) = 69.118 \text{ kJ s}^{-1}.$$

The heat-capacity flow of all products, including excess oxygen and inert nitrogen, is

$$\begin{aligned}\dot{C}_{p,\text{products}} &= 0.101053(37.11) + 0.0112281(29.14) \\ &\quad + 0.126316(33.58) + 0.100806(29.36) \\ &\quad + 1.01809(29.13) \\ &= 40.9355 \text{ J s}^{-1} \text{ K}^{-1}.\end{aligned}$$

The enthalpy balance is

$$\dot{C}_{p,\text{products}}(T_{\text{comb}} - 373) = -\dot{n}_f \Delta_r H.$$

Therefore,

$$T_{\text{comb}} = 373 + \frac{69118}{40.9355} = 2061.5 \text{ K} \approx 2.06 \times 10^3 \text{ K}.$$

This value assumes that the compressed mixture is at 373 K before ignition and neglects the temperature dependence of the reaction enthalpy; the problem does not specify these further.

3.3 — Temperature after expansion

There are 100 burn cycles per second across the engine, so the quantity of exhaust gas in one cylinder after one burn is

$$n_{\text{cycle}} = \frac{1.35749}{100} = 0.0135749 \text{ mol}.$$

At the end of expansion, the cylinder volume is 400 cm^3 and its pressure is 200 kPa. Hence

$$\begin{aligned}T_{\text{exit}} &= \frac{P_{\text{exit}} V_{\text{max}}}{n_{\text{cycle}} R} \\ &= \frac{200000(400 \times 10^{-6})}{0.0135749(8.314)} \\ &= 708.83 \text{ K}.\end{aligned}$$

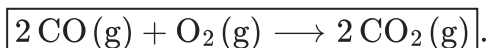
Thus

$$T_{\text{exit}} \approx 709 \text{ K} \approx 436^\circ \text{C}.$$

The compression ratio gives $V_{\text{min}} = 400/8 = 50 \text{ cm}^3$, but this intermediate volume is unnecessary here: the specified final pressure, maximum volume, and amount of gas determine the final temperature directly.

3.4 — Composition after catalytic oxidation

The catalyst promotes



Before the catalyst,

$$r_1 = \frac{n(\text{CO})}{n(\text{CO}_2)} = \frac{0.8}{7.2} = \frac{1}{9}.$$

The total incoming molar flow and temperature are

$$v = 1.35749 \text{ mol s}^{-1}, \quad T = 708.83 \text{ K}.$$

The prescribed work function gives the outlet ratio

$$\begin{aligned} r_2 &= \frac{1}{4}(3.141) \left(\frac{1}{9} \right) (1.35749) e^{-708.83/373} \\ &= 0.0177088. \end{aligned}$$

Let x be the molar flow of carbon monoxide oxidized, in mol s^{-1} . Then

$$\frac{0.0112281 - x}{0.101053 + x} = r_2,$$

so

$$x = \frac{0.0112281 - r_2(0.101053)}{1 + r_2} = 0.00927431 \text{ mol s}^{-1}.$$

This corresponds to

$$\frac{x}{0.0112281} \times 100 = 82.6\%$$

conversion of carbon monoxide.

The oxygen consumption is $x/2$. The outgoing flows are therefore:

Gas	Outlet molar flow, mol s^{-1}
CO	$0.0112281 - x = 0.00195376$
CO ₂	$0.101053 + x = 0.110327$
O ₂	$0.100806 - x/2 = 0.0961693$
H ₂ O	0.126316
N ₂	1.01809

Oxidation decreases the total gas amount, because three reactant molecules become two product molecules. Consequently,

$$\dot{n}_{\text{out}} = 1.35749 - \frac{x}{2} = 1.35285 \text{ mol s}^{-1}.$$

Normalizing by this **new total** gives

N ₂ : 75.25%,	O ₂ : 7.11%,
CO ₂ : 8.16%,	CO : 0.14%,
H ₂ O : 9.34%.	

The solution was checked against the official solution.

Problem 4: Photodecomposition of AgCl in chloride determination, pH

of a weak-acid mixture and conditional constants

Chloride ions are analytically determined by precipitating them with silver nitrate. The precipitate is undergoing decomposition in presence of light and forms elemental silver and chlorine. In aqueous solution the latter disproportionates to chlorate(V) and chloride. With excess of silver ions, the chloride ions formed are precipitated whereas chlorate(V) ions are not.

4.1 Write the balanced equations of the reactions mentioned above.

4.2 The gravimetric determination yielded a precipitate of which 12 % by mass was decomposed by light. Determine the size and direction of the error caused by this decomposition.

4.3 Consider a solution containing two weak acids HA and HL, 0.020 molar and 0.010 molar solutions, respectively. The acid constants are 1×10^{-4} for HA and 1×10^{-7} for HL. Calculate the pH of the solution.

4.4 M forms a complex ML with the acid H_2L with the formation constant K_1 . The solution contains another metal ion N that forms a complex NHL with the acid H_2L . Determine the conditional equilibrium constant, K'_1 for the complex ML in terms of $[H^+]$ and K values.

$$K_1 = \frac{[ML]}{[M][L]}$$
$$K'_1 = \frac{[ML]}{[M'][L']}$$

$[M']$ = total concentration of M not bound in ML

$[L']$ = the sum of the concentrations of all species containing L except ML

In addition to K_1 , the acid constants K_{a1} and K_{a2} of H_2L as well as the formation constant K_{NHL} of NHL are known.

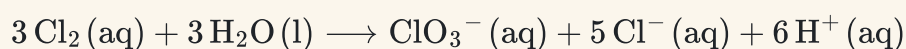
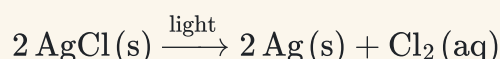
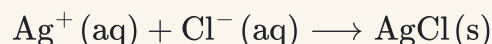
$$K_{NHL} = \frac{[NHL]}{[N][L][H^+]}$$

You may assume that the equilibrium concentration $[H^+]$ and $[N]$ are known, too.

Official English text of the problem.

Answers

• **4.1**



The chloride formed undergoes the first reaction again.

• **4.2** The chloride determination has a **positive relative error of approximately 7.0%**.

- 4.3

$$\text{pH} \approx 2.86$$

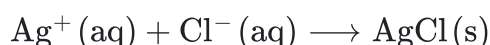
- 4.4

$$K'_1 = \frac{K_1}{1 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2}{K_{a1}K_{a2}} + K_{\text{NHL}}[\text{N}][\text{H}^+]}$$

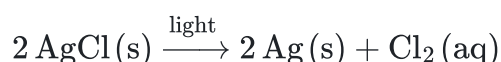
Solution

4.1 — Precipitation, photodecomposition and disproportionation

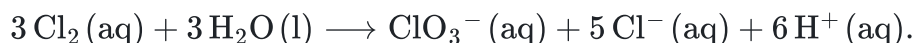
Silver nitrate supplies silver(I) ions, which precipitate chloride as silver chloride:



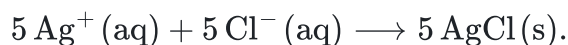
Nitrate is a spectator ion. Light causes reduction of silver(I) to silver metal and oxidation of chloride to chlorine:



In the stipulated disproportionation, chlorine changes from oxidation state 0 to +5 in chlorate(V) and to −1 in chloride. One chlorine atom undergoing oxidation therefore supplies the electrons needed to reduce five chlorine atoms. Balancing oxygen, hydrogen and charge gives



The five chloride ions are then reprecipitated:



Thus, every **six moles of silver chloride photodecomposed** produce six moles of silver metal and, subsequently, five moles of newly precipitated silver chloride.

The names and SMILES of the specified substances are:

Species	SMILES
Silver(I) ion, Ag^+	[Ag+]
Chloride ion, Cl^-	[Cl-]
Silver nitrate, AgNO_3	[Ag+] . [O-] [N+] (=O) [O-]
Nitrate ion, NO_3^-	[O-] [N+] (=O) [O-]
Silver chloride, AgCl	[Ag+] . [Cl-]
Elemental silver, Ag	[Ag]
Chlorine, Cl_2	ClCl
Water, H_2O	O
Chlorate(V) ion, ClO_3^-	[O-] [Cl] (=O)=O
Hydrogen ion, H^+	[H+]

The salt SMILES represent ionic composition, not crystal lattices; [Ag] represents a silver atom, not the metallic lattice. Aqueous solvation and resonance averaging are also not shown.

4.2 — Gravimetric error

Take 100 g of the original silver chloride precipitate. Photodecomposition consumes 12 g, leaving 88 g unchanged.

Using the standard molar masses

$$M(\text{Ag}) = 107.87 \text{ g mol}^{-1}, \quad M(\text{AgCl}) = 143.32 \text{ g mol}^{-1},$$

the silver metal produced has mass

$$m(\text{Ag}) = 12 \text{ g} \times \frac{107.87}{143.32} = 9.032 \text{ g}.$$

From 4.1, five-sixths of the chloride released by photodecomposition returns as silver chloride. Consequently,

$$m(\text{new AgCl}) = \frac{5}{6}(12 \text{ g}) = 10 \text{ g}.$$

The final solid therefore weighs

$$m_{\text{final}} = 88 + 9.032 + 10 = 107.032 \text{ g}.$$

In the gravimetric calculation, this entire mass is treated as silver chloride. Since the same gravimetric conversion factor is applied to the original and final masses,

$$\begin{aligned} \text{relative error} &= \frac{m_{\text{Cl,found}} - m_{\text{Cl,true}}}{m_{\text{Cl,true}}} \times 100\% \\ &= \frac{107.032 - 100}{100} \times 100\% \\ &= +7.032\%. \end{aligned}$$

Thus,

The chloride content is overestimated by approximately 7.0%.

The mass increases because reprecipitation incorporates additional silver ions from the solution into the solid.

4.3 — pH of the weak-acid mixture

The equilibria are



Let $h = [\text{H}^+]$. Combining each acid's dissociation equilibrium with its material balance gives

$$[\text{A}^-] = \frac{0.020K_{a,\text{HA}}}{h + K_{a,\text{HA}}}, \quad [\text{L}^-] = \frac{0.010K_{a,\text{HL}}}{h + K_{a,\text{HL}}}.$$

Neglecting water autoionization, electroneutrality requires

$$h = [\text{A}^-] + [\text{L}^-].$$

Using concentrations in mol L^{-1} , the equation to solve is therefore

$$h = \frac{0.020(10^{-4})}{h + 10^{-4}} + \frac{0.010(10^{-7})}{h + 10^{-7}}.$$

The stronger acid dominates. Ignoring the weaker acid initially gives the quadratic

$$h^2 + 10^{-4}h - 0.020(10^{-4}) = 0,$$

whose positive root is

$$h_0 = \frac{-10^{-4} + \sqrt{(10^{-4})^2 + 4(0.020)(10^{-4})}}{2} = 1.36510 \times 10^{-3} \text{ mol L}^{-1}.$$

Solving the equation including both acids gives

$$h = 1.36548 \times 10^{-3} \text{ mol L}^{-1}.$$

At this concentration,

$$[A^-] = 1.36474 \times 10^{-3} \text{ mol L}^{-1}, \quad [L^-] = 7.32 \times 10^{-7} \text{ mol L}^{-1},$$

confirming that the weaker acid contributes very little additional hydrogen ion.

Hence, using the usual dilute-solution concentration approximation,

$$\boxed{\text{pH} = -\log_{10}(1.36548 \times 10^{-3}) = 2.8647 \approx 2.86.}$$

4.4 — Conditional formation constant

Use the charge-suppressed ligand notation of the question and write $h = [H^+]$. The two acid dissociation constants are

$$K_{a1} = \frac{h[HL]}{[H_2L]}, \quad K_{a2} = \frac{h[L]}{[HL]}.$$

Thus,

$$[HL] = \frac{h}{K_{a2}}[L], \quad [H_2L] = \frac{h^2}{K_{a1}K_{a2}}[L].$$

The given competing-complex formation constant yields

$$[NHL] = K_{NHL}[N]h[L].$$

All ligand-containing species except ML must be included in $[L']$:

$$\begin{aligned} &= [L] + [HL] + [H_2L] + [NHL] \\ &= [L] \left(1 + \frac{h}{K_{a2}} + \frac{h^2}{K_{a1}K_{a2}} + K_{NHL}[N]h \right). \end{aligned}$$

No other species containing M are specified, so

$$[M'] = [M].$$

Substitution into the definition of the conditional constant gives

$$\begin{aligned} K'_1 &= \frac{[ML]}{[M'][L']} \\ &= \frac{[ML]}{[M][L]} \frac{[L]}{[L']}. \end{aligned}$$

Therefore,

$$\boxed{K'_1 = \frac{K_1}{1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1}K_{a2}} + K_{NHL}[N][H^+]}}.$$

Protonation and formation of NHL both reduce the fraction of the available ligand present as free L .

The acids, conjugate bases, metals and complexes in 4.3–4.4 are generic symbols rather than specified chemical identities. Unique chemical names and SMILES cannot be assigned to them from the supplied information; the coordination geometries of ML and NHL are likewise unspecified.

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: Synthesis of a secondary alcohol G from phenol and the mass spectrum of D

A common compound **A** is prepared from phenol and oxidized to compound **B**. Dehydration of **A** with H_2SO_4 leads to compound **C** and treatment of **A** with PBr_3 gives **D**. In the mass spectrum of **D** there is a very strong peak at $m/e = 83$ (base peak) and two molecular ion peaks at m/e 162 and 164. The ratio of intensities of the peaks 162 and 164 is 1.02. Compound **D** can be converted to an organomagnesium compound **E** that reacts with a carbonyl compound **F** in dry ether to give **G** after hydrolysis. **G** is a secondary alcohol with the molecular formula $\text{C}_8\text{H}_{16}\text{O}$.

5.1 Outline all steps in the synthesis of **G** and draw the structural formulae of the compounds **A** – **G**.

5.2 Which of the products **A** – **G** consist of configurational stereoisomeric pairs?

5.3 Identify the three ions in the mass spectrum considering isotopic abundances given in the text.

Official English text of the problem.

Answers

- 5.1** The compounds are:

Compound	Name	SMILES
A	Cyclohexanol	<chem>OC1CCCCC1</chem>
B	Cyclohexanone	<chem>O=C1CCCCC1</chem>
C	Cyclohexene	<chem>C1=CCCCC1</chem>
D	Bromocyclohexane	<chem>BrC1CCCCC1</chem>
E	Cyclohexylmagnesium bromide	<chem>Br[Mg]C1CCCCC1</chem>
F	Ethanal (acetaldehyde)	<chem>CC=O</chem>
G	1-Cyclohexylethan-1-ol	<chem>CC(O)C1CCCCC1</chem>

The synthesis proceeds through phenol $\rightarrow$ **A** $\rightarrow$ **D** $\rightarrow$ **E**, followed by addition to **F** and hydrolysis to **G**. Oxidation and dehydration of **A** give **B** and **C**, respectively.

- 5.2** Only **G** forms a configurational stereoisomeric pair. It is obtained as a racemic mixture of:

(*R*)-1-cyclohexylethan-1-ol, C[C@H](O)C1CCCCC1, and
 (*S*)-1-cyclohexylethan-1-ol, C[C@@H](O)C1CCCCC1.

- **5.3** The three ions are:

<i>m/e</i>	Ion and name	SMILES
83	$\text{C}_6\text{H}_{11}^+$, cyclohexyl cation	<chem>[CH+]1CCCCC1</chem>
162	$[\text{C}_6\text{H}_{11}^{79}\text{Br}]^{+\bullet}$, bromine-79-containing bromocyclohexane molecular radical cation	<chem>[79Br+]C1CCCCC1</chem>
164	$[\text{C}_6\text{H}_{11}^{81}\text{Br}]^{+\bullet}$, bromine-81-containing bromocyclohexane molecular radical cation	<chem>[81Br+]C1CCCCC1</chem>

The molecular-ion SMILES place the formal positive charge and radical on bromine; each molecular ion is an odd-electron species.

Solution

5.1

The molecular-ion peaks separated by two mass units, with almost equal intensities, indicate one bromine atom: the two isotopologues contain ^{79}Br and ^{81}Br . Subtracting their nominal isotope masses gives the same remaining mass:

$$162 - 79 = 164 - 81 = 83.$$

A cyclohexyl group, C_6H_{11} , has nominal mass

$$6(12 \text{ u}) + 11(1 \text{ u}) = 83 \text{ u}.$$

This assignment also explains the base peak through loss of a bromine atom. Together with preparation from phenol and conversion of an alcohol using PBr_3 , it identifies **D** as bromocyclohexane and **A** as cyclohexanol.

Oxidation of this secondary alcohol gives cyclohexanone **B**, while dehydration gives cyclohexene **C**. Magnesium insertion into the carbon–bromine bond gives cyclohexylmagnesium bromide **E**.

A Grignard reagent gives a secondary alcohol when it adds to an aldehyde other than methanal. Since **E** supplies six carbon atoms and **G** contains eight, **F** must be the two-carbon aldehyde ethanal. The product therefore has the connectivity



which gives the required molecular formula $\text{C}_8\text{H}_{16}\text{O}$.

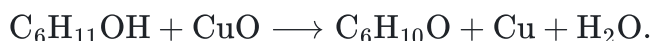
The requested structural drawings can be described precisely as follows: **A–E** each contain a six-membered carbon ring. **A** has a hydroxyl substituent; **B** has an oxygen double-bonded to one ring carbon; **C** has one double bond within the ring; **D** has a bromine substituent; and **E** has a ring carbon directly bonded to magnesium, which is also bonded to bromine. **F** is CH_3-CHO . **G** has a cyclohexane ring bonded to the hydroxyl-bearing carbon of a $-\text{CH}(\text{OH})-\text{CH}_3$ side chain.

The balanced reactions are:

1. **Hydrogenation of phenol to A.** Phenol Oc1ccccc1 is hydrogenated with hydrogen [H][H] over nickel [Ni], with heat and pressure:

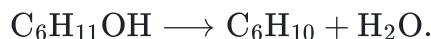


2. **Oxidation of A to B.** One suitable oxidant is heated copper(II) oxide $[\text{Cu}^{+2}] \cdot [\text{O}^{-2}]$:

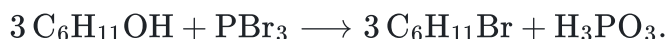


The other products are copper $[\text{Cu}]$ and water O .

3. **Dehydration of A to C.** Heating with concentrated sulfuric acid $\text{O}=\text{S}(=\text{O})(\text{O})\text{O}$ eliminates water:

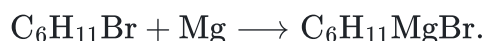


4. **Conversion of A to D.** Phosphorus tribromide $\text{BrP}(\text{Br})\text{Br}$ replaces the hydroxyl group by bromine:



The phosphorus-containing product is phosphorous acid $\text{O}=[\text{PH}](\text{O})\text{O}$.

5. **Formation of E.** Treat **D** with magnesium $[\text{Mg}]$ in dry diethyl ether CCOCC :



The SMILES for **E** represents its formal carbon–magnesium–bromine connectivity. Ether coordination and aggregation of the Grignard reagent are not specified by that representation.

6. **Addition of E to F.** In dry ether, the cyclohexyl group bonds to the carbonyl carbon of ethanal, and the carbonyl oxygen becomes an alkoxide:



The intermediate is 1-cyclohexylethoxymagnesium bromide, $\text{CC}(\text{O}[\text{Mg}]\text{Br})\text{C1CCCCC1}$.

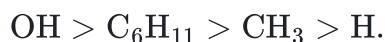
7. **Hydrolysis to G.** An aqueous acidic work-up protonates the alkoxide. A balanced net ionic equation is:



Here hydronium is $[\text{OH}_3^+]$, the magnesium(II) ion is $[\text{Mg}^{+2}]$, and bromide is $[\text{Br}^-]$.

5.2

Only **G** has a stereogenic carbon atom. Its hydroxyl-bearing carbon is attached to four different substituents: hydroxyl, cyclohexyl, methyl, and hydrogen. Their CIP priority order is



Consequently, **G** has the two enantiomers specified in the Answers section. The planar carbonyl group of **F** can be attacked from either face. With achiral reagents and conditions, the two enantiomers form in equal amounts.

The substituted ring carbons of **A**, **D**, and **E** are not stereogenic because the two directions around each ring are equivalent. Axial and equatorial forms are interconverting conformations, not configurational stereoisomers. **B** and **F** have no stereogenic elements, and ordinary cyclohexene **C** does not furnish a configurational pair under these conditions.

5.3

All three assigned ions are singly charged. Their nominal masses are

$$\begin{aligned}
 m_{\text{nom}}(\text{C}_6\text{H}_{11}^+) &= 6(12 \text{ u}) + 11(1 \text{ u}) = 83 \text{ u}, \\
 m_{\text{nom}}([\text{C}_6\text{H}_{11}^{79}\text{Br}]^{+\bullet}) &= 83 \text{ u} + 79 \text{ u} = 162 \text{ u}, \\
 m_{\text{nom}}([\text{C}_6\text{H}_{11}^{81}\text{Br}]^{+\bullet}) &= 83 \text{ u} + 81 \text{ u} = 164 \text{ u}.
 \end{aligned}$$

The base peak is assigned to the cyclohexyl cation produced by carbon–bromine bond cleavage:



The expelled neutral radicals are bromine-79 atoms [^{79}Br] or bromine-81 atoms [^{81}Br]. Both molecular isotopologues therefore produce the same fragment at $m/e = 83$.

Using the stated intensity ratio as the bromine isotope-abundance ratio,

$$\frac{x_{79}}{x_{81}} = 1.02, \quad x_{79} + x_{81} = 1,$$

gives

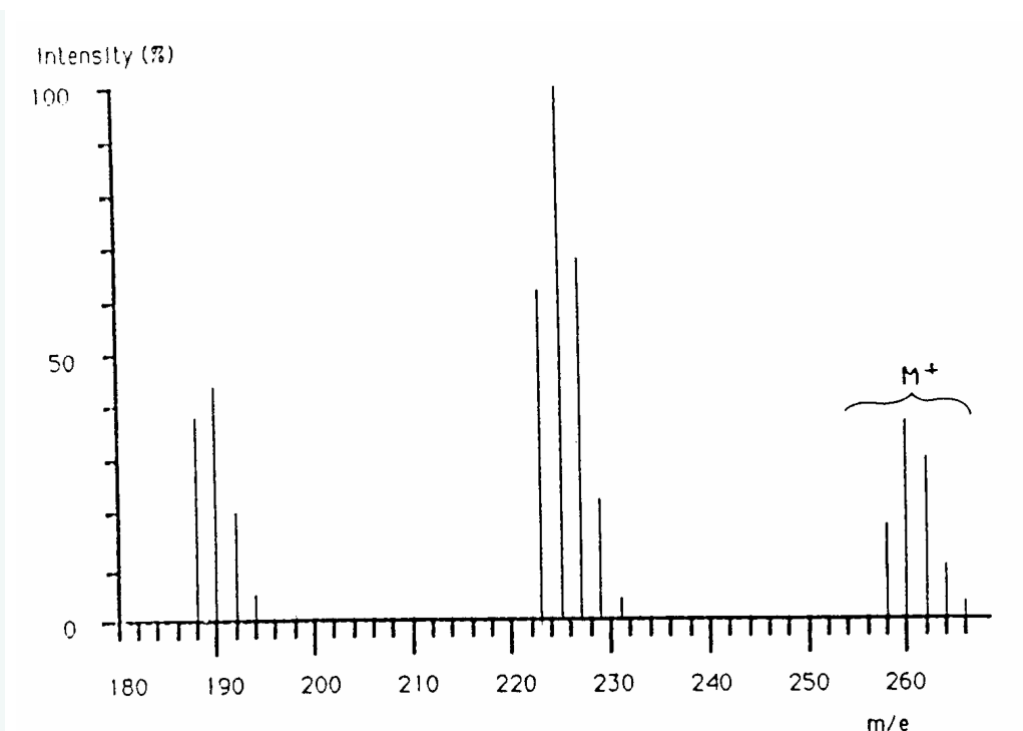
$$x_{79} = \frac{1.02}{2.02} \approx 50.5\%, \quad x_{81} = \frac{1}{2.02} \approx 49.5\%.$$

Thus the slightly stronger molecular-ion peak at 162 contains ^{79}Br , and the peak at 164 contains ^{81}Br .

The solution was checked against the official solution.

Problem 6: Identification of a bio-accumulated pollutant X from its mass spectrum

Upon analyzing sea mussels a new bio-accumulated pollutant **X** was found as determined by mass spectroscopy coupled to a gas chromatograph. The mass spectrum is illustrated in figure. Determine the structural formula of **X** assuming that it is produced out of synthetic rubber used as insulation in electrolysis cells that are used for the production of chlorine. Give the name of the compound **X**. The isotopic abundances of the pertinent elements are shown in the figure and table below. Intensities of the ions $m/e = 196, 233, 268$ and 270 are very low and thus omitted. Peaks of the ^{13}C containing ions are omitted for simplicity.

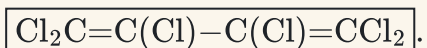


Element	Mas	Norm.abundanc	Mass	Norm.abundanc	Mas	Norm.abundanc
H	1	100.0	2	0.015		
C	12	100.0	13	1.1		
N	14	100.0	15	0.37		
O	16	100.0	17	0.04	18	0.20
P	31	100.0				
S	32	100.0	33	0.80	34	4.4
Cl	35	100.0			37	32.5
Br	79	100.0			81	98.0

Official English text of the problem.

Answers

- **Problem 6: X is hexachlorobutadiene**, systematically **1,1,2,3,4,4-hexachlorobuta-1,3-diene**, with molecular formula C_4Cl_6 and structural formula



SMILES: ClC(Cl)=C(Cl)C(Cl)=C(Cl)Cl.

Solution

Problem 6

The molecular-ion cluster begins at $m/e = 258$, with successive peaks separated by 2. This is characteristic of substitution of ^{35}Cl by ^{37}Cl . The supplied relative abundances give

$$r = \frac{\text{abundance of } ^{37}\text{Cl}}{\text{abundance of } ^{35}\text{Cl}} = \frac{32.5}{100.0} = 0.325.$$

For a species containing n chlorine atoms, the intensity of the peak containing k heavy chlorine atoms, relative to the peak containing only light chlorine atoms, is

$$\frac{I_{M+2k}}{I_M} = \binom{n}{k} r^k.$$

In particular,

$$\frac{I_{M+2}}{I_M} = nr.$$

The first two molecular-ion peaks have an intensity ratio of approximately 1 : 2. Six chlorine atoms predict $I_{260}/I_{258} = 6(0.325) = 1.95$, consistent with the figure. The complete predicted envelope is:

m/e	Intensity relative to $I_{258} = 100$
258	100
260	195
262	158.4
264	68.7
266	16.7
268	2.18
270	0.118

This also explains why the peaks at 268 and 270 are very weak. Thus, **X contains six chlorine atoms.**

Using the integer isotope masses supplied, the mass remaining after accounting for six light chlorine atoms is

$$258 \text{ u} - 6(35 \text{ u}) = 48 \text{ u}.$$

For the carbon framework derived from the rubber,

$$N_C = \frac{48 \text{ u}}{12 \text{ u}} = 4.$$

There is no remaining mass for hydrogen, giving the molecular formula



The fragment clusters provide an independent consistency check. Their lowest-mass peaks are

$$223 = 258 - 35, \quad 188 = 258 - 2(35),$$

consistent with loss of one chlorine atom and net loss of two chlorine atoms, respectively. The corresponding isotope patterns fit five and four remaining chlorine atoms:

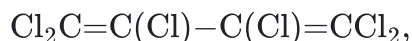
Cluster begins at m/e	Chlorine atoms	Predicted first-to-second peak ratio	Highest-mass member
223	5	1 : 1.625	$48 + 5(37) = 233$
188	4	1 : 1.300	$48 + 4(37) = 196$

The highest-mass members require every remaining chlorine atom to be ^{37}Cl , explaining the other two weak, omitted peaks.

Counting each halogen atom as a hydrogen atom, the degree of unsaturation is

$$\text{DBE} = \frac{2(4) + 2 - 6}{2} = 2.$$

The synthetic-rubber origin points to a four-carbon diene framework. Buta-1,3-diene, also called 1,3-butadiene, has SMILES C=CC=C. Replacing all six hydrogen atoms of this framework by chlorine gives



which has exactly two double bonds and the required formula and mass spectrum.

Therefore, **X is hexachlorobutadiene**, or **1,1,2,3,4,4-hexachlorobuta-1,3-diene**, SMILES ClC(Cl)=C(Cl)C(Cl)=C(Cl)Cl. Neither double bond has *E/Z* stereochemistry because each terminal carbon bears two identical chlorine atoms.

The answers were checked against the official answers published by the organisers.