

IChO 1997

Theory problems and solutions · Montreal, Canada · 8 theory problems with complete solutions

eulersolve.org/icho/1997/

Problem 1: Structure of a trisaccharide from cottonseed meal

Compound **X** is a trisaccharide which occurs principally in cottonseed meal.

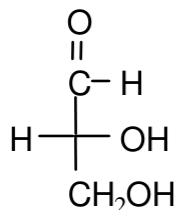
Compound **X** does not react with Benedict's or Fehling's solutions nor does it mutarotate.

Acid-catalyzed hydrolysis gives three different D-hexoses, **A**, **B**, and **C**. Compounds **A** and **B**, as well as compound **1** (see below), all give the same osazone upon reaction with excess acidic phenylhydrazine. Compound **C** reacts with nitric acid to give an optically inactive compound **D**. The Kiliani-Fischer approach is used to establish the configurational relationship between D-glyceraldehyde and **C**. The intermediate aldotetrose which leads to **C** does not give a meso compound when oxidized by nitric acid. When **A** is treated with nitric acid, the dicarboxylic acid (aldaric acid) produced is optically active. Both **A** and **B** react with 5 moles of HIO_4 ; one mole of **A** gives 5 moles of methanoic (formic) acid and one mole of methanal (formaldehyde) while one mole of **B** gives 3 moles of methanoic (formic) acid and 2 moles of methanal (formaldehyde) and one mole of carbon dioxide. Both **A** and **B** are related to the same aldotetrose which is the diastereoisomer of the one to which **C** is related. Methylation of **X** followed by hydrolysis gives a 2,3,4-tri-O-methyl-D-hexose (**E**) (derived from **A**), a 1,3,4,6-tetra-O-methyl-D-hexose (**F**) (derived from **B**), and a 2,3,4,6-tetra-O-methyl-D-hexose (**G**) (derived from **C**).

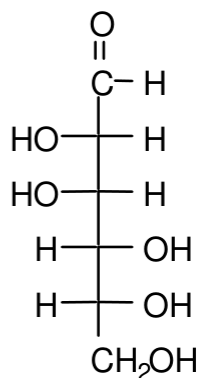
1.1 On the answer sheet, draw Fischer projection formulas of **A**, **B**, **C**, and **D**.

1.2 On the answer sheet, complete the appropriate Haworth projection formulas to clearly show the ring size and absolute stereochemistry of **E**, **F**, and **G**. Either of the anomeric forms are acceptable as an answer.

1.3 On the answer sheet, underline the correct representation of the connectivity sequence of the three monosaccharides present in trisaccharide **X**.



D-Glyceraldehyde



Compound **1**

Answers

- **1.1:** The intended assignments are **A = D-glucose**, **B = D-fructose**, **C = D-galactose**, and **D = meso-galactaric acid (mucic acid)**. Their Fischer projections and stereochemical SMILES are specified below.
- **1.2:** **E = 2,3,4-tri-O-methyl-D-glucopyranose**, **F = 1,3,4,6-tetra-O-methyl-D-fructofuranose**, and **G = 2,3,4,6-tetra-O-methyl-D-galactopyranose**. Explicit β -anomer drawings and SMILES are given below.
- **1.3:** **C – A – B**, equivalently **B – A – C**: **galactose–glucose–fructose**, with glucose in the middle. This is the monosaccharide sequence in raffinose.

Solution

1.1 — Identifying the monosaccharides and drawing their Fischer projections

The supplied compound **1** is **D-mannose**, with its Fischer hydroxyl groups at C2–C5 arranged left–left–right–right:

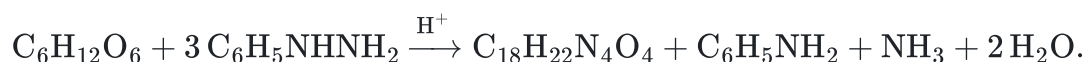


Osazone formation modifies C1 and C2 while retaining the configurations at C3, C4, and C5. Consequently, D-glucose, D-mannose, and D-fructose give the same osazone. Its retained Fischer hydroxyl sequence at C3–C5 is left–right–right.

The common **D-glucosazone**, with hydrazone geometries left unspecified, has SMILES:

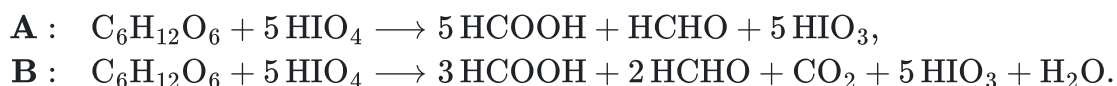


The balanced net reaction is



Here phenylhydrazine is NNc1ccccc1, aniline is Nc1ccccc1, ammonia is N, and water is O.

The periodate results distinguish the aldose **A** from the ketose **B**. The balanced reactions are



Periodic acid is OI(=O)(=O)=O; iodic acid is OI(=O)=O. The carbon-containing products are methanoic acid O=CO, methanal C=O, and carbon dioxide O=C=O.

Exhaustive cleavage breaks all five carbon–carbon bonds:

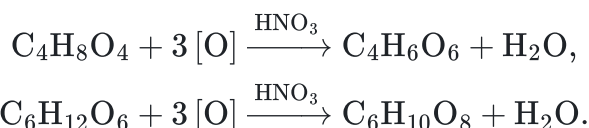
- For **A**, the aldehyde carbon and four secondary alcohol carbons give 5 mol of methanoic acid per mole of sugar. The single terminal primary alcohol gives 1 mol of methanal.
- For **B**, two terminal primary alcohol groups give 2 mol of methanal, three secondary alcohol carbons give 3 mol of methanoic acid, and the ketone carbon gives 1 mol of carbon dioxide.

Thus **B is D-fructose**. Taking the separately labelled compound **1** to be distinct from **A**, the intended assignment is **A = D-glucose**.

To identify **C**, consider chain extension from **D-glyceraldehyde**, $\text{O}=\text{C}[\text{C@H}](\text{O})\text{CO}$. Kiliani–Fischer extension adds a carbon at the aldehyde end while preserving the existing stereocentres. The two possible D-aldotetroses behave differently on oxidation:

Aldotetrose	Fischer OH positions, C2–C3	SMILES	Nitric-acid oxidation product
D-Erythrose	Right, right	$\text{O}=\text{C}[\text{C@H}](\text{O})[\text{C@H}](\text{O})\text{CO}$	meso-Tartaric acid , $\text{O}=\text{C}(\text{O})[\text{C@H}](\text{O})[\text{C@H}](\text{O})\text{C}(=\text{O})\text{O}$
D-Threose	Left, right	$\text{O}=\text{C}[\text{C@@H}](\text{O})[\text{C@H}](\text{O})\text{CO}$	(2S,3S)-Tartaric acid , $\text{O}=\text{C}(\text{O})[\text{C@@H}](\text{O})[\text{C@H}](\text{O})\text{C}(=\text{O})\text{O}$, which is chiral

Nitric acid, $\text{O}=[\text{N}^+](\text{O})\text{O}$, oxidizes both terminal groups to carboxyl groups. The balanced oxidation equations, using $[\text{O}]$ for an oxidizing-oxygen equivalent, are



Because the tetrose leading to **C** gives a non-meso acid, it must be **D-threose**. Its left–right configuration becomes the C4–C5 configuration of **C**.

The aldaric acid **D** must be meso. With identical carboxyl groups at both ends, the required symmetric Fischer hydroxyl sequence is therefore

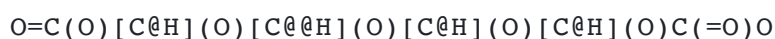
C2–C5: right–left–left–right.

This identifies **C as D-galactose** and **D as galactaric acid**, conventionally called mucic acid.

The requested Fischer projections are specified completely in the following table. Draw the carbon backbone vertically, with C1 at the top. At every stereocentre, place hydrogen opposite the indicated hydroxyl group.

Label and name	Top and bottom groups	Fischer OH positions	Stereochemical SMILES
A: D-Glucose	Top CHO; bottom CH ₂ OH	C2 right; C3 left; C4 right; C5 right	$\text{O}=\text{C}[\text{C@H}](\text{O})[\text{C@@H}](\text{O})[\text{C@H}](\text{O})[\text{C@H}](\text{O})\text{CO}$
B: D-Fructose	Top CH ₂ OH; C2 is C=O; bottom CH ₂ OH	C3 left; C4 right; C5 right	$\text{OCC}(=\text{O})[\text{C@@H}](\text{O})[\text{C@H}](\text{O})[\text{C@H}](\text{O})\text{CO}$
C: D-Galactose	Top CHO; bottom CH ₂ OH	C2 right; C3 left; C4 left; C5 right	$\text{O}=\text{C}[\text{C@H}](\text{O})[\text{C@@H}](\text{O})[\text{C@@H}](\text{O})[\text{C@H}](\text{O})\text{CO}$
D: meso-Galactaric acid (mucic acid)	Both ends COOH	C2 right; C3 left; C4 left; C5 right	$\text{O}=\text{C}(\text{O})[\text{C@H}](\text{O})[\text{C@@H}](\text{O})[\text{C@@H}](\text{O})[\text{C@H}](\text{O})\text{C}(=\text{O})\text{O}$

As a consistency check, oxidation of **A** gives chiral **D-glucaric acid (saccharic acid)**:



Its hydroxyl sequence lacks the symmetry of **D**. The C4–C5 configurations of both **A** and **B** correspond to D-erythrose, the required diastereoisomer of D-threose.

1.2 — Methylation analysis and the Haworth projections

Exhaustive methylation converts the free hydroxyl groups of **X** into methyl ethers. Oxygen atoms already involved in glycosidic bonds or forming the ring oxygen are not methylated. Hydrolysis subsequently restores hydroxyl groups at the glycosidic attachment positions.

Product	Methylated positions	Interpretation in X
E , from A	C2, C3, C4	C5 supplies the pyranose ring oxygen; C1 and C6 participate in glycosidic bonds
F , from B	C1, C3, C4, C6	C5 supplies the furanose ring oxygen; C2 participates in a glycosidic bond
G , from C	C2, C3, C4, C6	C5 supplies the pyranose ring oxygen; C1 participates in a glycosidic bond

Thus **E** and **G** have six-membered pyranose rings, whereas **F** has a five-membered furanose ring.

For the following precise Haworth descriptions:

- Draw each pyranose with O5 at the upper right and C1 at the right, continuing clockwise through C2, C3, C4, and C5.
- Draw the furanose with O5 at the top and C2 at the right, continuing clockwise through C3, C4, and C5.
- "Up" and "down" mean above and below the ring plane. Unlisted hydrogens point opposite the listed substituent.

Choosing the permitted β anomers gives:

Product and name	Substituents up	Substituents down	Stereochemical SMILES
E: 2,3,4-tri-O-methyl-β-D-glucopyranose	C1-OH; C3-OMe; C5-CH ₂ OH	C2-OMe; C4-OMe	<chem>OC[C@H]1O[C@@H](O)[C@H](OC)[C@@H](OC)[C@@H]1OC</chem>
F: 1,3,4,6-tetra-O-methyl-β-D-fructofuranose	C2-OH; C3-OMe; C5-CH ₂ OCH ₃ , containing C6	C2-CH ₂ OCH ₃ , containing C1; C4-OMe	<chem>COC[C@@]1(O)O[C@H](COC)[C@@H](OC)[C@@H]1OC</chem>
G: 2,3,4,6-tetra-O-methyl-β-D-galactopyranose	C1-OH; C3-OMe; C4-OMe; C5-CH ₂ OCH ₃	C2-OMe	<chem>COC[C@H]1O[C@@H](O)[C@H](OC)[C@@H](OC)[C@H]1OC</chem>

Here OMe denotes OCH₃. To draw the corresponding α anomer, reverse the two substituents at the anomeric carbon only. Haworth projections specify relative orientations; they do not imply that the actual rings are planar.

1.3 — Connectivity sequence

The absence of reducing behaviour and mutarotation shows that all three anomeric centres are blocked in glycosidic bonds.

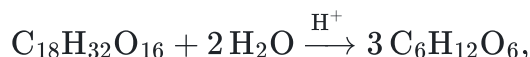
Methylation identifies two attachment positions on **A**, C1 and C6, but only one on each of **B** and **C**, respectively C2 and C1. Therefore **A must be the central residue**, giving



or, in the problem's labels,



Formation of two glycosidic bonds removes two water molecules, so the molecular formula and balanced hydrolysis are



where the three product molecules are **A**, **B**, and **C**.

A compatible connectivity is the **raffinose linkage pattern**, D-galactopyranosyl-(1→6)-D-glucopyranosyl-(1↔2)-D-fructofuranoside. With its three anomeric configurations deliberately unspecified, its SMILES is:

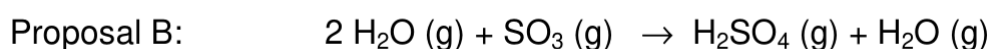
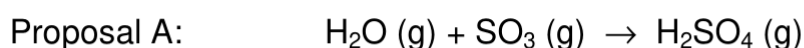
```
OC[C@H]1OC(OC[C@H]2OC(OC3(CO)O[C@H](CO)[C@@H](O)[C@@H]3O)[C@H](O)[C@@H](O)[C@@H]2O)[C@H](O)[C@@H](O)[C@H]1O
```

The requested **sequence** follows directly from the evidence. Assigning this particular pairing of attachment positions requires an additional identification: the alternative pairing C1(**C**)–C1(**A**) and C2(**B**)–C6(**A**) also preserves the same methylation results and nonreducing behaviour.

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.

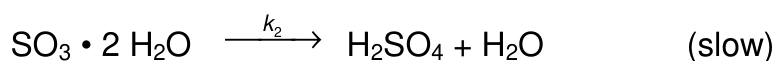
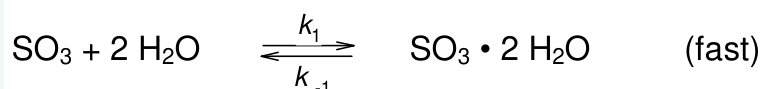
Problem 2: Atmospheric formation of sulfuric acid: kinetics

Professor Molina of the Massachusetts Institute of Technology won the 1995 Nobel Prize in Chemistry for his work on atmospheric chemistry. One reaction that he has studied in detail is the acid rain reaction which produces H_2SO_4 in the atmosphere. He has proposed two possible stoichiometric reactions:



2.1 Using simple collision theory, what reaction orders would be expected for Proposal A and for Proposal B?

Proposal B is thought to proceed by the following two-step process:



($\text{SO}_3 \cdot 2 \text{H}_2\text{O}$ is a complex which is stabilized by hydrogen bonds and $k_2 \ll k_1$ or k_{-1})

2.2 By applying the principle of stationary (steady) states, derive the appropriate rate law and hence the reaction order of the two-step mechanism for Proposal B.

2.3 Recent quantum chemical calculations have shown that the overall reaction activation energies for the two proposals are:

$$E_A = +80 \text{ kJ mol}^{-1} \text{ for Proposal A}$$

$$E_B = -20 \text{ kJ mol}^{-1} \text{ for Proposal B}$$

State the relationship between the rate constant and the temperature (Arrhenius relationship) for each proposal and predict the temperature dependence of the rate constants for each proposal.

2.4 The formation of H_2SO_4 is faster in the upper atmosphere ($T = 175 \text{ K}$) than at the earth's surface ($T = 300 \text{ K}$). Which proposed pathway must dominate in the upper atmosphere given the activation energies in part (iii) and your understanding of the Arrhenius equation?

Official English text of the problem.

Answers

- 2.1:** Proposal A: first order in each reactant, **second order overall**. Proposal B: first order in SO_3 , second order in H_2O , **third order overall**.

- 2.2:**

$$v = \frac{k_1 k_2}{k_{-1} + k_2} [\text{SO}_3] [\text{H}_2\text{O}]^2 \simeq \frac{k_1 k_2}{k_{-1}} [\text{SO}_3] [\text{H}_2\text{O}]^2.$$

The mechanism is **third order overall**.

- 2.3:**

$$k_A = A_A \exp\left(-\frac{80\,000 \text{ J mol}^{-1}}{RT}\right), \quad k_B = A_B \exp\left(+\frac{20\,000 \text{ J mol}^{-1}}{RT}\right).$$

As temperature rises, k_A increases and k_B decreases.

- 2.4: Proposal B** is the dominant pathway indicated by the stated enhancement at lower temperature.

Solution

The chemical species used below are:

Name	Formula	SMILES
Water	H_2O	<chem>o</chem>
Sulfur trioxide	SO_3	<chem>O=S(=O)=O</chem>
Sulfuric acid	H_2SO_4	<chem>OS(=O)(=O)O</chem>
Sulfur trioxide complex with two water molecules	$\text{SO}_3 \cdot 2 \text{H}_2\text{O}$	<chem>O=S(=O)=O.O.O</chem>

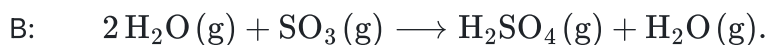
The disconnected SMILES for the complex specifies its molecular components; it does not encode their hydrogen bonds or spatial arrangement.

2.1

The balanced proposed reactions are



and



Under the simple collision model, the frequency of a specified encounter is proportional to the product of the concentrations of all participating molecules.

For A, one water molecule encounters one sulfur trioxide molecule:

$$v_A = k_A[\text{H}_2\text{O}][\text{SO}_3].$$

The reaction is first order in each reactant, giving overall order $1 + 1 = \boxed{2}$.

For B, two water molecules and one sulfur trioxide molecule participate:

$$v_B = k_B[\text{H}_2\text{O}]^2[\text{SO}_3].$$

The reaction is second order in water and first order in sulfur trioxide, giving overall order $2 + 1 = \boxed{3}$.

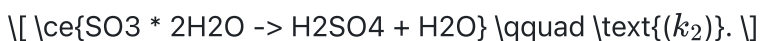
Although one water molecule is regenerated in B, both water molecules participate in the proposed encounter. Cancelling water from the net equation therefore does not remove its kinetic role. These orders follow from the assumed collision model; overall stoichiometry alone does not generally determine reaction order.

2.2

The proposed elementary steps are



and



Let $c = [\text{SO}_3 \cdot 2\text{H}_2\text{O}]$. The complex forms in the forward association step and disappears through both dissociation and product formation:

$$\frac{dc}{dt} = k_1[\text{SO}_3][\text{H}_2\text{O}]^2 - k_{-1}c - k_2c.$$

Applying the steady-state approximation,

$$\frac{dc}{dt} \simeq 0,$$

gives

$$c \simeq \frac{k_1}{k_{-1} + k_2} [\text{SO}_3][\text{H}_2\text{O}]^2.$$

Sulfuric acid forms through the second step, so

$$v = \frac{d[\text{H}_2\text{SO}_4]}{dt} = k_2c.$$

Consequently,

$$v = \frac{k_1 k_2}{k_{-1} + k_2} [\text{SO}_3] [\text{H}_2\text{O}]^2.$$

In the stated slow-conversion limit, $k_2 \ll k_{-1}$, this becomes

$$v \simeq \frac{k_1 k_2}{k_{-1}} [\text{SO}_3] [\text{H}_2\text{O}]^2.$$

Thus the effective rate constant is

$$k_B = \frac{k_1 k_2}{k_{-1} + k_2} \simeq \frac{k_1 k_2}{k_{-1}},$$

and the reaction is **first order in sulfur trioxide, second order in water, and third order overall**.

With concentrations in mol L^{-1} and time in seconds, k_B has units $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$, whereas k_A has units $\text{L mol}^{-1} \text{s}^{-1}$.

2.3

The Arrhenius equation is

$$k = A \exp\left(-\frac{E_a}{RT}\right),$$

where A is the pre-exponential factor and R is the gas constant. Treating A as temperature independent over the interval considered,

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}.$$

For Proposal A,

$$E_A = +80 \text{ kJ mol}^{-1} = +80\,000 \text{ J mol}^{-1},$$

so

$$k_A = A_A \exp\left(-\frac{80\,000 \text{ J mol}^{-1}}{RT}\right).$$

Since $E_A > 0$, $d \ln k_A / dT > 0$: k_A **increases with temperature**.

For Proposal B,

$$E_B = -20 \text{ kJ mol}^{-1} = -20\,000 \text{ J mol}^{-1},$$

so

$$k_B = A_B \exp\left(+\frac{20\,000 \text{ J mol}^{-1}}{RT}\right).$$

Since $E_B < 0$, $d \ln k_B / dT < 0$: k_B **decreases with temperature**, or increases on cooling.

The negative value is an effective activation energy for the overall mechanism. It is consistent with lower temperature favouring formation of the hydrogen-bonded complex strongly enough to outweigh the slowing of its subsequent conversion.

2.4

For either pathway, the Arrhenius equation gives

$$\frac{k(175\text{ K})}{k(300\text{ K})} = \exp\left[-\frac{E_a}{R}\left(\frac{1}{175\text{ K}} - \frac{1}{300\text{ K}}\right)\right].$$

The reciprocal-temperature difference is

$$\frac{1}{175\text{ K}} - \frac{1}{300\text{ K}} = \frac{1}{420}\text{ K}^{-1}.$$

Using $R = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$,

$$\frac{k_A(175\text{ K})}{k_A(300\text{ K})} = \exp\left(-\frac{80\,000}{8.314 \times 420}\right) \approx 1.1 \times 10^{-10},$$

whereas

$$\frac{k_B(175\text{ K})}{k_B(300\text{ K})} = \exp\left(+\frac{20\,000}{8.314 \times 420}\right) \approx 3.1 \times 10^2.$$

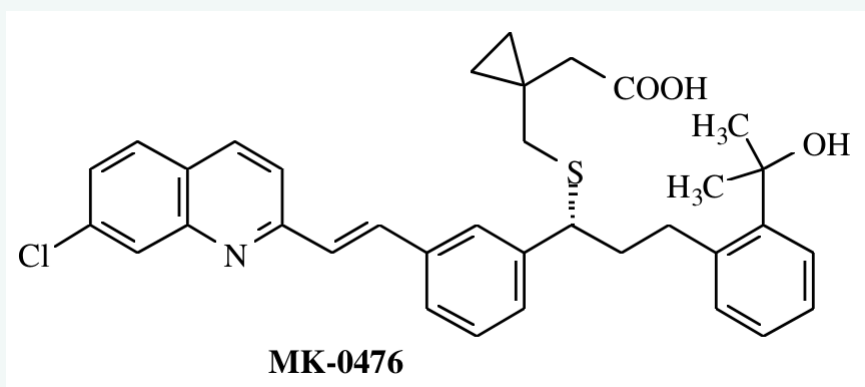
Cooling therefore strongly suppresses pathway A but enhances pathway B. Under the problem's intended comparison, in which the temperature effect is assessed at fixed reactant concentrations, the faster formation at 175 K requires

Proposal B to dominate in the upper atmosphere.

The solution was checked against the official solution.

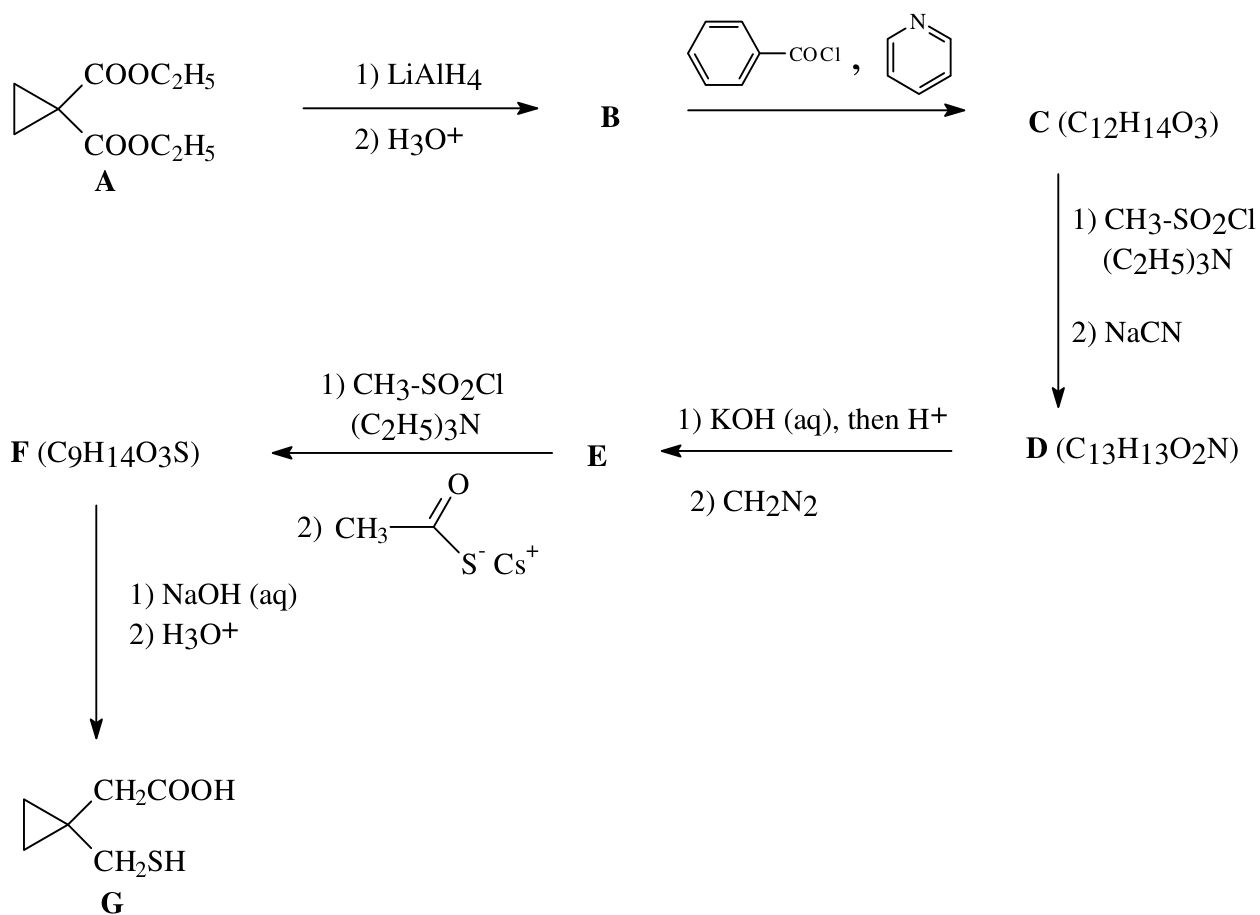
Problem 3: Synthesis of the thiol side chain of the anti-asthma drug MK-0476

Chemists at Merck Frosst Canada in Montréal have developed a promising drug which is useful against asthma. The structure of MK-0476 is shown below.

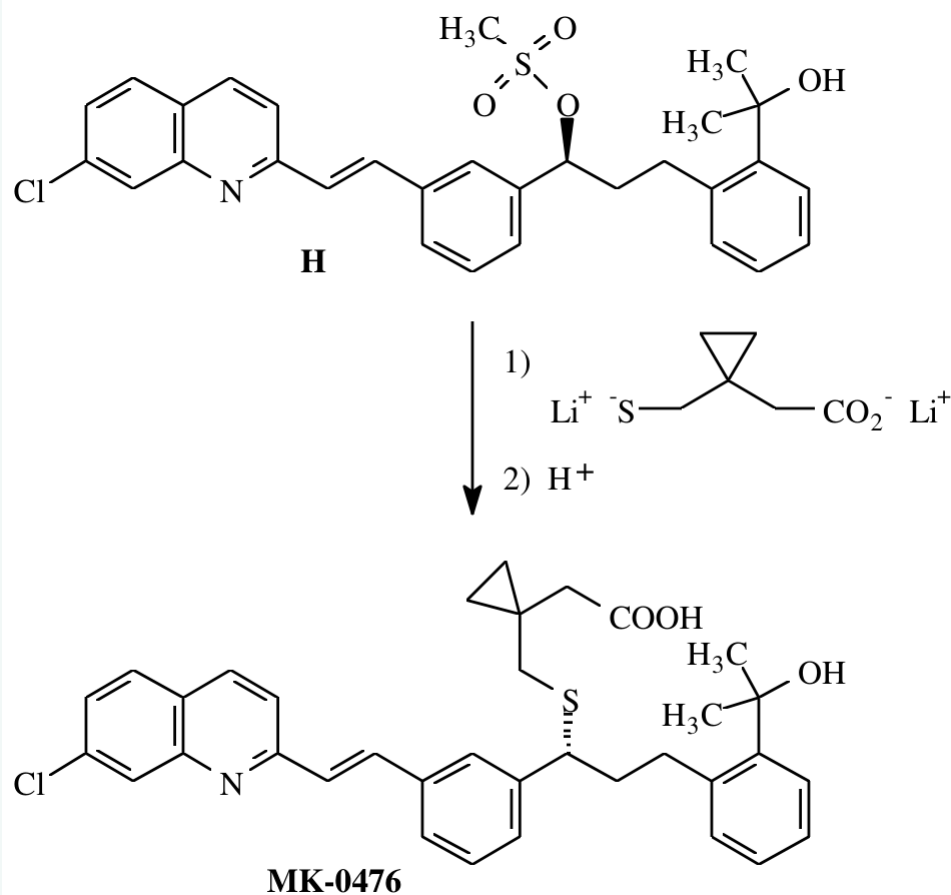


During their investigation, they devised a simple and efficient synthesis, depicted below, for the thiolated portion of MK-0476 starting from diethyl ester **A**.

3.1 Give the structures of the intermediate products **B - F** prepared during this synthesis.



In one of the last steps of the synthesis on MK-0476, the dilithium salt of the above thiol acid (**G**) was coupled with the side chain of the rest of the molecule as shown below.



3.2 Based on the observed stereochemistry of the above reaction, what is the mechanistic designation of this coupling process?

3.3 If the process proceeds by your proposed mechanism, what change would occur to the overall rate of the reaction if the concentration of both the thiolate salt and the substrate **H** were simultaneously tripled?

3.4 For the nucleophilic substitution reaction, model studies were carried out using bromoethane as the substrate to perfect the above coupling. Draw only the structure of the major product of the reaction of one molar equivalent of bromoethane with:

- G** plus two molar equivalents of base
- G** plus one molar equivalent of base

3.5 A side reaction of **G** is its oxidative dimerization.

Draw the structure of the dimeric product, showing all non-bonded electrons.

Official English text of the problem.

Answers

- 3.1.** The cyclopropane ring remains intact in every intermediate.

Product	Name	SMILES
B	1,1-Bis(hydroxymethyl)cyclopropane	<chem>OCC1(CC1)CO</chem>

Product	Name	SMILES
C	[1-(Hydroxymethyl)cyclopropyl]methyl benzoate	<chem>OCC1(CC1)COC(=O)c1ccccc1</chem>
D	[1-(Cyanomethyl)cyclopropyl]methyl benzoate	<chem>N#CCC1(CC1)COC(=O)c1ccccc1</chem>
E	Methyl 2-[1-(hydroxymethyl)cyclopropyl]acetate	<chem>COC(=O)CC1(CC1)CO</chem>
F	Methyl 2-[1-[(acetylsulfanyl)methyl]cyclopropyl]acetate	<chem>COC(=O)CC1(CC1)CSC(=O)C</chem>

- **3.2.** S_N2 , a bimolecular nucleophilic substitution with inversion at the reacting stereocentre: **H** has the *S* configuration and MK-0476 has the *R* configuration.
- **3.3.** The reaction rate becomes **nine times** its original value.
- **3.4(a).** Sulfur is ethylated, giving **2-[1-[(ethylsulfanyl)methyl]cyclopropyl]acetate**, CCSCC1(CC1)CC(=O)[O-]. This is the immediate product under the basic conditions. Acidification gives **2-[1-[(ethylsulfanyl)methyl]cyclopropyl]acetic acid**, CCSCC1(CC1)CC(=O)O.
- **3.4(b).** The carboxylate oxygen is ethylated, giving **ethyl 2-[1-(sulfanylmethyl)cyclopropyl]acetate**, CCOC(=O)CC1(CC1)CS.
- **3.5.** The product is **bis{[1-(carboxymethyl)cyclopropyl]methyl} disulfide**, O=C(O)CC1(CC1)CSSCC2(CC2)CC(=O)O. Draw **two lone pairs on each sulfur and each oxygen atom**: twelve lone pairs, or twenty-four non-bonded electrons, altogether.

Solution

3.1 — Identification of B–F

The starting material **A** is diethyl cyclopropane-1,1-dicarboxylate, CCOC(=O)C1(CC1)C(=O)OCC. Its two ester groups are attached to the same cyclopropane carbon.

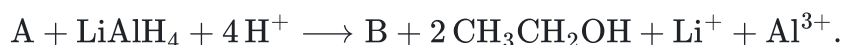
The equations below combine successive operations where appropriate. Compound letters refer to the structures identified above; spectator counterions are omitted where they do not participate.

A → B: reduction of both esters.

Lithium aluminium hydride, $[Li^+].[AlH_4^-]$, reduces each ester group to a primary alcohol:



Thus **B** bears two hydroxymethyl groups on the same ring carbon. The ethoxy groups become ethanol, CCO. An atom- and charge-balanced net equation, including acidic work-up, is



The molecular formula of **B** is C5H10O2.

B → C: protection of one alcohol as a benzoate.

Benzoyl chloride, O=C(C1)C1ccccc1, esterifies one of the two equivalent hydroxyl groups. Pyridine, n1ccccc1, captures the released proton as pyridinium, c1cc[nH+]cc1:



Monobenzoylation adds C7H4O to **B**, giving

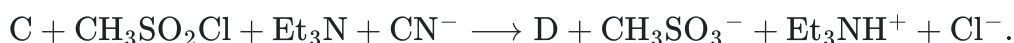


which matches the supplied formula of **C**. Consequently, **C** contains one free $-\text{CH}_2\text{OH}$ group and one protected $-\text{CH}_2\text{OC}(=\text{O})\text{C}_6\text{H}_5$ group.

C → D: conversion of the free alcohol into a nitrile.

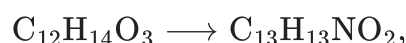
Methanesulfonyl chloride, $\text{CS}(=\text{O})(=\text{O})\text{Cl}$, and triethylamine, $\text{CCN}(\text{CC})\text{CC}$, first convert the free alcohol into a methanesulfonate ester. Cyanide ion, $[\text{C}^-]\text{N}$, then attacks the primary carbon through its carbon end, replacing the leaving group and forming $-\text{CH}_2\text{C}\equiv\text{N}$.

The combined net equation is



Here Et_3NH^+ is triethylammonium, $\text{CC}[\text{NH}^+](\text{CC})\text{CC}$, and CH_3SO_3^- is methanesulfonate, $\text{CS}(=\text{O})(=\text{O})[\text{O}^-]$.

The transformation replaces OH by CN, so



in agreement with the formula supplied for **D**.

D → E: hydrolysis, followed by methyl ester formation.

Aqueous potassium hydroxide hydrolyses both functional groups:

- The nitrile becomes a carboxylate.
- The benzoate protecting group is cleaved, regenerating the primary alcohol.

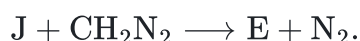
After acidification, the relevant intermediate is **2-[1-(hydroxymethyl)cyclopropyl]acetic acid**, here called **J**, $\text{O}=\text{C}(\text{O})\text{CC1}(\text{CC1})\text{CO}$.

The overall hydrolysis and acidic work-up can be balanced as



The additional products are benzoic acid, $\text{O}=\text{C}(\text{O})\text{c1ccccc1}$, and ammonium ion, $[\text{NH}_4^+]$.

Diazomethane, $\text{C}=[\text{N}^+]=[\text{N}^-]$, then converts the carboxylic acid into its methyl ester:



Nitrogen gas, $\text{N}\equiv\text{N}$, is expelled. The alcohol remains free, so **E** is the hydroxy methyl ester listed above, with formula $\text{C}_7\text{H}_{12}\text{O}_3$.

E → F: installation of the protected thiol.

Mesylation activates the remaining alcohol. The sulfur atom of thioacetate then displaces the leaving group. The reagent is cesium thioacetate, $\text{CC}(=\text{O})[\text{S}^-] \cdot [\text{Cs}^+]$.

The combined net equation is



The side chain changes from $-\text{CH}_2\text{OH}$ to $-\text{CH}_2\text{SC}(=\text{O})\text{CH}_3$. The product therefore contains a methyl ester and an *S*-acetyl-protected thiol. Its formula is



matching the supplied formula of **F**.

F → G: confirmation from the final hydrolysis.

Hydrolysis removes both the methyl ester and the acetyl group on sulfur. Acidification gives **G**, 2-[1-(sulfanylmethyl)cyclopropyl]acetic acid, O=C(O)CC1(CC1)CS.

The balanced net reaction is



The other products are methanol, CO, and acetic acid, CC(=O)O. This produces exactly the two substituents shown for **G**: -CH_2COOH and -CH_2SH on the same cyclopropane carbon.

3.2 — Mechanism and stereochemistry

The organic component of the dilithium salt is the **thiolate–carboxylate dianion of G**, [O-]C(=O)CC1(CC1)C[S-], accompanied by two lithium ions, [Li+].

The thiolate sulfur attacks the stereogenic carbon of **H** from the side opposite the carbon–oxygen bond. Its lone pair forms the new carbon–sulfur bond while the carbon–oxygen bond breaks, with that bonding electron pair passing to the departing methanesulfonate oxygen.

This concerted displacement gives **inversion of configuration**, as expected for an S_N2 mechanism.

For clarity, the complete stereochemical structures are:

- **H**, (1S)-1-{3-[(E)-2-(7-chloroquinolin-2-yl)ethenyl]phenyl}-3-[2-(2-hydroxypropan-2-yl)phenyl]propyl methanesulfonate:
CS(=O)(=O)O[C@@H](CCc1ccccc1C(C)(C)O)c1cccc(/C=C/c2ccc3ccc(Cl)cc3n2)c1
- **MK-0476**, the resulting *R*-configured thioether:
O=C(O)CC1(CC1)CS[C@H](CCc1ccccc1C(C)(C)O)c1cccc(/C=C/c2ccc3ccc(Cl)cc3n2)c1

At the reacting centre, oxygen in **H**, and sulfur in the product, have highest priority. The directly attached aryl group outranks the methylene chain, and hydrogen has lowest priority. Thus the depicted inversion corresponds to $S \rightarrow R$.

Let *M* denote MK-0476. Including the final protonation of its carboxylate, the overall reaction is



SMILES records the configurations, but the **backside attack and simultaneous bond formation and bond cleavage** are mechanistic information conveyed by the explanation above.

3.3 — Effect of tripling both concentrations

For the proposed elementary S_N2 reaction,

$$v = k[H][G^{2-}].$$

After both concentrations are tripled,

$$v' = k(3[H])(3[G^{2-}]) = 9k[H][G^{2-}] = 9v.$$

Therefore, the rate increases **ninefold**. The multiplier is exact. If concentrations are expressed in mol L^{-1} and rate in $\text{mol L}^{-1} \text{s}^{-1}$, *k* has units $\text{L mol}^{-1} \text{s}^{-1}$.

3.4 — Products with bromoethane

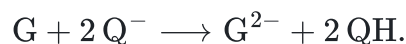
Bromoethane, CCBr, supplies the ethyl group in these substitutions, and bromide ion, [Br-], leaves.

The carboxylic acid group of **G** is more acidic than its thiol group. Accordingly, one equivalent of strong base produces the carboxylate; two equivalents produce the thiolate–carboxylate dianion.

Let Q^- represent the unspecified base and QH its conjugate acid.

(a) Two equivalents of base

Both acidic protons are removed:



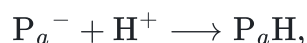
The thiolate sulfur is the more effective nucleophile towards bromoethane and undergoes ethylation:



Here P_a^- is **2-[1-[(ethylsulfanyl)methyl]cyclopropyl]acetate**, CCSCC1(CC1)CC(=O)[O-].

For the requested drawing, retain the cyclopropane ring and place $-CH_2COO-$ and $-CH_2SCH_2CH_3$ on the same ring carbon.

If an acidic work-up is applied,



where P_aH is the corresponding neutral acid, CCSCC1(CC1)CC(=O)O.

(b) One equivalent of base

Only the carboxylic acid is deprotonated:



This **carboxylate monoanion of G** is O=C([O-])CC1(CC1)CS. Its carboxylate oxygen attacks bromoethane:



The product P_b is **ethyl 2-[1-(sulfanylmethyl)cyclopropyl]acetate**, CCOC(=O)CC1(CC1)CS.

For the drawing, place $-CH_2COOCH_2CH_3$ and $-CH_2SH$ on the same cyclopropane carbon.

3.5 — Oxidative dimerization

Oxidation joins the sulfur atoms of two molecules of **G** through an S–S single bond, removing the two thiol hydrogens.

Since no oxidant is specified, the balanced oxidation half-reaction is



The product P_{SS} , **bis{[1-(carboxymethyl)cyclopropyl]methyl} disulfide**, is



and has formula $C_{12}H_{18}O_4S_2$.

To draw it precisely, connect two copies of **G** at sulfur, replacing their two S–H bonds with one S–S bond. Both carboxylic acid groups remain intact.

SMILES does not explicitly display the lone pairs. Add:

- **Two lone pairs to each sulfur atom:** four pairs.
- **Two lone pairs to each of the four oxygen atoms:** eight pairs.

There are therefore **twelve lone pairs**, containing **twenty-four non-bonded electrons**. All atoms in the neutral disulfide have zero formal charge.

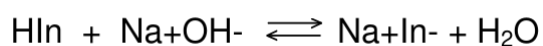
The solution was checked against the official solution.

Problem 4: Spectrophotometry of an acid-base indicator

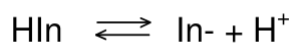
Graph paper is provided for your optional use in this question.

If you choose to use it, print your name and identification code in the upper right corner of the graph paper.

HIn is a weakly acidic indicator.



also written as

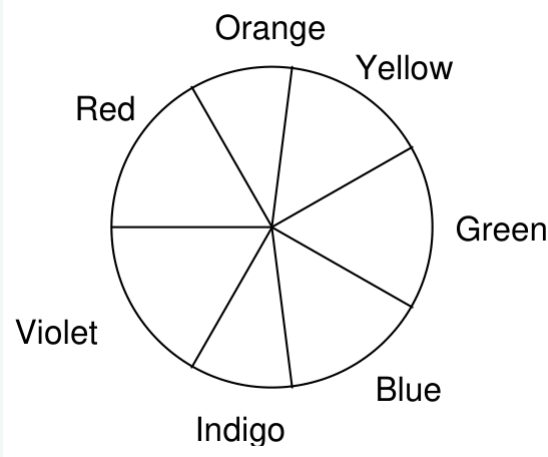


At normal temperatures, the acid dissociation constant for this indicator is $K_a = 2.93 \times 10^{-5}$.

The absorbance data (1.00 cm cells) for $5.00 \times 10^{-4} \text{ M}$ (mol dm^{-3}) solutions of this indicator in strongly acidic and strongly alkaline solutions are given in the following table.

Absorbance Data (A)

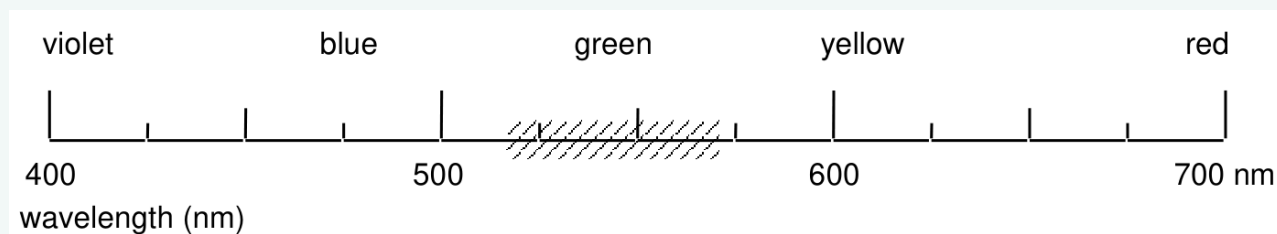
$\lambda, \text{ nm}$	$pH = 1.00$	$pH = 13.00$
400	0.401	0.067
470	0.447	0.050
485	0.453	0.052
490	0.452	0.054
505	0.443	0.073
535	0.390	0.170
555	0.342	0.342
570	0.303	0.515
585	0.263	0.648
615	0.195	0.816
625	0.176	0.823
635	0.170	0.816
650	0.137	0.763
680	0.097	0.588



4.1 Predict the observed colour of the a) acidic and b) basic forms of the indicator.

Using a “50 nm wide bar”, shade the appropriate area of the wavelength scale on the answer sheet which would correspond to the colour of the indicator at the pH values given in the table.

For example, if observed colour is green, your answer would appear as:



4.2 A filter is located between the light source and the sample. What colour filter would be most suitable for the photometric analysis of the indicator in a strongly acidic medium?

4.3 What wavelength range would be most suitable for the photometric analysis of the indicator in a strongly basic medium?

4.4 What would be the absorbance of a $1.00 \times 10^{-4} \text{ M}$ (mol dm^{-3}) solution of the indicator in alkaline form if measured at 545 nm in a 2.50 cm cell?

4.5 Solutions of the indicator were prepared in a strongly acidic solution (HCl , $pH = 1$) and in a strongly basic solution (NaOH , $pH = 13$). Perfectly linear relationships between absorbance and concentration were observed in both media at 490 nm and 625 nm, respectively.

The molar absorptivities at the two wavelengths are:

	$\lambda = 490 \text{ nm}$	$\lambda = 625 \text{ nm}$
$\text{HIn} (\text{HCl})$	$9.04 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$	$3.52 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$
$\text{In}^- (\text{NaOH})$	$1.08 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$	$1.65 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$

($\text{M} = \text{mol dm}^{-3}$)

Calculate the absorbance (1.00 cm cell) at the two wavelengths for an aqueous $1.80 \times 10^{-3} \text{ M}$ (mol dm^{-3}) solution of the indicator HIn .

Official English text of the problem.

Answers

- **4.1** a) Acidic form: **orange**; shade a 50 nm bar approximately over **600–650 nm**. b) Basic form: **blue**; shade approximately **450–500 nm**.
- **4.2** A **blue filter**, transmitting near **485–490 nm**.
- **4.3** The absorption maximum around **625 nm**, preferably approximately **615–635 nm**.
- **4.4** $A_{545} \approx 0.128 \approx 0.13$, using linear interpolation.
- **4.5** $A_{490} = 1.46$, $A_{625} = 0.913$.

Absorbance is dimensionless.

Solution

4.1

The indicator's acidic form, HIn , and conjugate-base anion, In^- , are generic labels: the problem supplies no molecular constitution from which a specific chemical name or structural SMILES could be determined.

Their equilibrium is



where H^+ is the proton, SMILES $[\text{H}^+]$. Thus,

$$K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}, \quad \frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_a}{[\text{H}^+]}.$$

At $pH = 1.00$,

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{2.93 \times 10^{-5}}{10^{-1}} = 2.93 \times 10^{-4},$$

so the spectrum is essentially that of the acidic form. At $pH = 13.00$, the ratio is 2.93×10^8 , so the spectrum is essentially that of the basic form.

The observed colour comes from the transmitted light and is approximately complementary to the principal absorbed colour.

- **a) Acidic form:** The absorption maximum is near 485 nm, in the blue region. Absorption decreases toward the longer wavelengths, giving an **orange** appearance. On the answer sheet, shade a 50 nm interval in the orange region, approximately **600–650 nm**.
- **b) Basic form:** Absorption is strongest around 625 nm, in the orange–red region, while blue light is transmitted strongly. The solution therefore appears **blue**. Shade approximately **450–500 nm**.

4.2

The Beer–Lambert law is

$$A = \epsilon bc,$$

where ϵ is molar absorptivity, b is optical path length, and c is concentration. Sensitivity to concentration is greatest where ϵ is largest.

The acidic form has its largest tabulated absorbance at 485 nm:

$$A_{485} = 0.453.$$

Therefore, use a **blue filter**, transmitting light near **485–490 nm**.

4.3

For the basic form,

$$A_{615} = 0.816, \quad A_{625} = 0.823, \quad A_{635} = 0.816.$$

The region **615–635 nm**, centred on **625 nm**, combines high absorption with a relatively flat maximum. It therefore provides high concentration sensitivity and reduces sensitivity to small wavelength-setting errors.

4.4

First estimate the absorbance at 545 nm for the reference solution, whose concentration and path length are

$$c_{\text{ref}} = 5.00 \times 10^{-4} \text{ mol dm}^{-3}, \quad b_{\text{ref}} = 1.00 \text{ cm}.$$

Linear interpolation between 535 and 555 nm gives

$$A_{545,\text{ref}} \approx 0.170 + \frac{545 - 535}{555 - 535} (0.342 - 0.170) = 0.256.$$

At a fixed wavelength and chemical form, absorbance scales with bc . Hence,

$$\begin{aligned} A_{545} &= A_{545,\text{ref}} \frac{bc}{b_{\text{ref}}c_{\text{ref}}} \\ &\approx 0.256 \left(\frac{2.50 \text{ cm}}{1.00 \text{ cm}} \right) \left(\frac{1.00 \times 10^{-4} \text{ mol dm}^{-3}}{5.00 \times 10^{-4} \text{ mol dm}^{-3}} \right) \\ &= \boxed{0.128 \approx 0.13}. \end{aligned}$$

4.5

The aqueous solution contains both indicator forms because the weak acid partially dissociates. Let

$$C = 1.80 \times 10^{-3} \text{ mol dm}^{-3}$$

be the analytical indicator concentration. Neglecting water's contribution to the proton concentration, set

$$[\text{In}^-] = [\text{H}^+] = x, \quad [\text{HIn}] = C - x.$$

Then

$$K_a = \frac{x^2}{C - x},$$

so

$$x^2 + K_a x - K_a C = 0.$$

The physically meaningful root is

$$\begin{aligned}
 x &= \frac{-K_a + \sqrt{K_a^2 + 4K_a C}}{2} \\
 &= \frac{-2.93 \times 10^{-5} + \sqrt{(2.93 \times 10^{-5})^2 + 4(2.93 \times 10^{-5})(1.80 \times 10^{-3})}}{2} \\
 &= 2.15469 \times 10^{-4} \text{ mol dm}^{-3}.
 \end{aligned}$$

Consequently,

$$\begin{aligned}
 [\text{In}^-] &= 2.15469 \times 10^{-4} \text{ mol dm}^{-3}, \\
 [\text{HIn}] &= 1.80 \times 10^{-3} - 2.15469 \times 10^{-4} = 1.58453 \times 10^{-3} \text{ mol dm}^{-3}.
 \end{aligned}$$

Approximately 12.0% of the indicator is dissociated, so retaining $C - x$ in the equilibrium calculation is appropriate.

The two species' absorbances add:

$$A_\lambda = b (\epsilon_{\text{HIn},\lambda} [\text{HIn}] + \epsilon_{\text{In}^-, \lambda} [\text{In}^-]).$$

Using $b = 1.00 \text{ cm}$, the supplied molar absorptivities in $\text{M}^{-1} \text{ cm}^{-1}$, and concentrations in M :

$$\begin{aligned}
 A_{490} &= (1.00) [(9.04 \times 10^2)(1.58453 \times 10^{-3}) + (1.08 \times 10^2)(2.15469 \times 10^{-4})] \\
 &= 1.45569 \\
 &= \boxed{1.46}.
 \end{aligned}$$

Similarly,

$$\begin{aligned}
 A_{625} &= (1.00) [(3.52 \times 10^2)(1.58453 \times 10^{-3}) + (1.65 \times 10^3)(2.15469 \times 10^{-4})] \\
 &= 0.913278 \\
 &= \boxed{0.913}.
 \end{aligned}$$

The solution was checked against the official solution.

Problem 5: Allotropes of iron and the density of martensite

Iron metal melts at 1811 K. Between room temperature and its melting point, iron metal can exist in different allotropic or crystalline forms. From room temperature to 1185 K, the crystal structure of iron metal exists as a body-centred cubic (bcc) lattice known as α -iron. From 1185 K to 1667 K, the structure becomes face-centred cubic (fcc) and is called γ -iron. Above 1667 K, and up to its melting point, iron reverts to a bcc structure similar to that of α -iron. The latter phase is called δ -iron.

Given that the density of pure iron metal is 7.874 g cm^{-3} at 293 K:

5.1 Calculate the atomic radius of iron (expressed in cm).

5.2 Calculate its density (expressed in g cm^{-3}) at 1250 K.

Notes: Ignore the small effects due to the thermal expansion of the metal.

Clearly define any symbols which you use, e.g. r = atomic radius of Fe.

Steel is an alloy of iron and carbon in which some of the interstitial spaces ("holes") of the crystal lattice (iron) are occupied by small atoms (carbon). Its carbon content typically ranges from 0.1 % to 4.0 %. In a blast-furnace, the melting of iron is facilitated when it contains 4.3 % of carbon by mass. If this mixture is cooled too rapidly the carbon atoms remain dispersed within the α -iron phase. This new solid, called martensite, is extremely hard and brittle. Although it is slightly distorted, the size of the unit cell of this solid (martensite) is the same as that of α -iron (bcc).

Assuming that the carbon atoms are evenly distributed in the iron structure:

5.3 Calculate the average number of carbon atoms per unit cell of α -iron in martensite containing 4.3 % C by mass.

5.4 Calculate the density (expressed in g cm^{-3}) of this material.

Molar masses and constants:

$$M(\text{Fe}) = 55.847 \text{ g mol}^{-1}$$

$$M(\text{C}) = 12.011 \text{ g mol}^{-1}$$

$$N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

Official English text of the problem.

Answers

- **5.1:** $r = 1.241 \times 10^{-8} \text{ cm}$.
- **5.2:** $\rho_\gamma = 8.572 \text{ g cm}^{-3}$ at 1250 K.
- **5.3:** 0.42 carbon atoms per unit cell, on average (calculated value 0.4178).
- **5.4:** $\rho_{\text{martensite}} = 8.23 \text{ g cm}^{-3}$.

Solution

5.1 Atomic radius of iron

Let r be the atomic radius of iron, a_α the edge length of the cubic α -iron unit cell, and ρ_α its density. $M(\text{Fe})$ is the molar mass of iron and N_A is the Avogadro constant.

At 293 K, iron has a bcc structure. Its conventional unit cell contains eight corner atoms, each shared by eight cells, and one atom entirely inside the cell:

$$\text{Number of iron atoms per cell} = 8 \left(\frac{1}{8} \right) + 1 = 2.$$

Consequently,

$$\rho_\alpha = \frac{2M(\text{Fe})}{N_A a_\alpha^3},$$

so

$$a_{\alpha} = \left[\frac{2M(\text{Fe})}{N_A \rho_{\alpha}} \right]^{1/3} = \left[\frac{2(55.847 \text{ g mol}^{-1})}{(6.02214 \times 10^{23} \text{ mol}^{-1})(7.874 \text{ g cm}^{-3})} \right]^{1/3} = 2.866561 \times 10^{-8} \text{ cm}.$$

In a bcc lattice, atoms touch along the body diagonal. This diagonal has length $\sqrt{3} a_{\alpha}$ and spans four atomic radii:

$$\sqrt{3} a_{\alpha} = 4r.$$

Therefore,

$$r = \frac{\sqrt{3}}{4} a_{\alpha} = 1.241 \times 10^{-8} \text{ cm}.$$

5.2 Density at 1250 K

Since $1185 < 1250 < 1667 \text{ K}$, the metal is γ -iron and has an fcc structure. Let a_{γ} be its unit-cell edge length and ρ_{γ} its density.

An fcc unit cell contains eight corner atoms and six face-centred atoms, each face-centred atom shared by two cells:

$$\text{Number of iron atoms per cell} = 8 \left(\frac{1}{8} \right) + 6 \left(\frac{1}{2} \right) = 4.$$

Atoms touch along a face diagonal, giving

$$\sqrt{2} a_{\gamma} = 4r, \quad a_{\gamma} = 2\sqrt{2} r.$$

Using the same atomic radius and neglecting thermal expansion,

$$a_{\gamma} = 3.510806 \times 10^{-8} \text{ cm}.$$

Thus,

$$\rho_{\gamma} = \frac{4M(\text{Fe})}{N_A a_{\gamma}^3} = \frac{4(55.847 \text{ g mol}^{-1})}{(6.02214 \times 10^{23} \text{ mol}^{-1})(3.510806 \times 10^{-8} \text{ cm})^3},$$

$$\boxed{\rho_{\gamma} = 8.572 \text{ g cm}^{-3}}.$$

5.3 Average number of carbon atoms per unit cell

Let x be the average number of carbon atoms per martensite unit cell and $w_C = 0.043$ the carbon mass fraction.

Carbon occupies interstitial sites, so the cell retains its two iron atoms. Its average iron and carbon masses are therefore

$$m_{\text{Fe}} = \frac{2M(\text{Fe})}{N_A}, \quad m_C = \frac{xM(\text{C})}{N_A}.$$

The carbon mass fraction is

$$w_C = \frac{m_C}{m_{\text{Fe}} + m_C} = \frac{xM(\text{C})}{2M(\text{Fe}) + xM(\text{C})}.$$

Solving for x ,

$$x = \frac{2M(\text{Fe})w_C}{M(\text{C})(1 - w_C)} = \frac{2(55.847)(0.043)}{(12.011)(0.957)} = 0.417837.$$

Hence,

$$x \approx 0.42 \text{ carbon atoms per unit cell}.$$

This fractional value is an average over many cells; individual cells contain integer numbers of carbon atoms.

5.4 Density of martensite

The problem specifies that the unit-cell volume remains a_α^3 . The iron mass per cell also remains unchanged, while carbon adds mass.

Because iron accounts for the mass fraction $1 - w_C = 0.957$, the total cell mass is $m_{Fe}/(1 - w_C)$. Therefore,

$$\rho_{\text{martensite}} = \frac{m_{Fe}}{(1 - w_C)a_\alpha^3} = \frac{\rho_\alpha}{1 - w_C} = \frac{7.874}{0.957} \text{ g cm}^{-3} = 8.227795 \text{ g cm}^{-3}.$$

Thus,

$$\rho_{\text{martensite}} = 8.23 \text{ g cm}^{-3}.$$

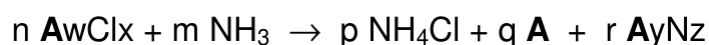
The solution was checked against the official solution.

Problem 6: Refining of platinum metals; a main-group chloride and ammonia

6.1 Much of the world's supply of platinum group metals is derived from the residues recovered from the electrolytic refining of copper and nickel. A flow chart for the recovery of platinum and palladium is shown on the following page.

- Clearly draw the shape (geometry) of both the PtCl_6^{2-} and the PdCl_4^{2-} anions.
- Clearly draw all possible stereoisomeric structures of monomeric $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$. Label the structures that you have drawn with their correct stereochemical descriptors.
- What is the role of the FeSO_4 in the second step of the flow chart? Write a balanced equation for the reaction of FeSO_4 in this step.
- Write a complete balanced equation for the ignition of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ in air to give Pd metal. In this reaction, what is being oxidized and what is being reduced?

6.2 Reaction of a main group chloride (24.71 g) with ammonia (10.90 g) gave a mixture of products consisting of NH_4Cl (25.68 g), a solid element **A** (2.57 g) and a yellow crystalline nitride of this element (7.37 g) according to the equation below.



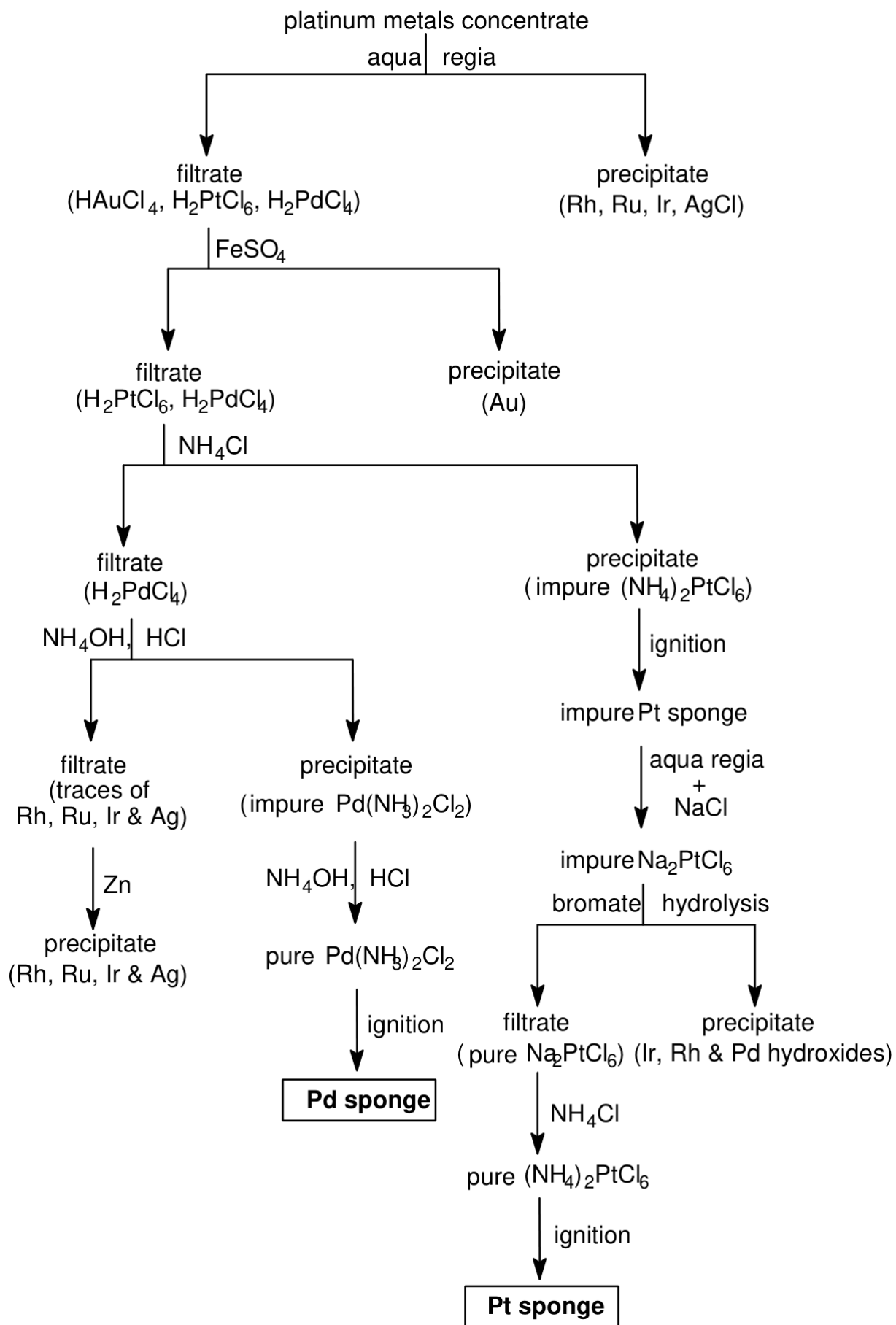
(where n, m, p, q, r, w, x, y and z are coefficients to be determined)

A sample of the nitride exploded violently when struck with a hammer, but it underwent controlled polymerization on heating to give a bronze-coloured, fibrous solid which exhibits metallic conductivity. Element **A** also undergoes polymerization to a high molecular weight linear polymer upon heating.

Molar masses:

$$M(\text{Cl}) = 35.453 \text{ g mol}^{-1} \quad M(\text{N}) = 14.007 \text{ g mol}^{-1} \quad M(\text{H}) = 1.008 \text{ g mol}^{-1}$$

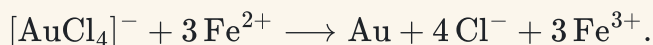
- i) Identify element **A**.
- ii) Write a complete balanced equation for the reaction of the chloride with ammonia.
- iii) Assuming conventional oxidation states, write the balanced redox half-reaction equations involved in this reaction.



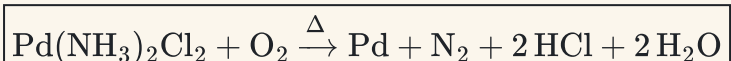
Method of Purification of Platinum and Palladium

Answers

- **6.1(i)** $[\text{PtCl}_6]^{2-}$ is **octahedral**; $[\text{PdCl}_4]^{2-}$ is **square planar**.
- **6.1(ii)** There are **two** stereoisomers: **cis-diamminedichloridopalladium(II)** and **trans-diamminedichloridopalladium(II)**. Identical ligands occupy adjacent positions in the cis isomer and opposite positions in the trans isomer.
- **6.1(iii)** FeSO_4 is a **reducing agent**, precipitating gold:

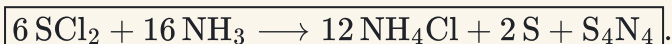


- **6.1(iv)**



Ammonia-ligand nitrogen is oxidized; palladium(II) and oxygen are reduced.

- **6.2(i)** **A is sulfur**.
- **6.2(ii)** The chloride is **sulfur dichloride**, SCl_2 , and the nitride is **tetrasulfur tetranitride**, S_4N_4 :



Thus

$$(n, m, p, q, r) = (6, 16, 12, 2, 1), \quad (w, x, y, z) = (1, 2, 4, 4).$$

- **6.2(iii)** Sulfur disproportionates from +2 to +3 and 0. Balanced half-reactions are



and



Names and SMILES representations are supplied in the corresponding solution parts below.

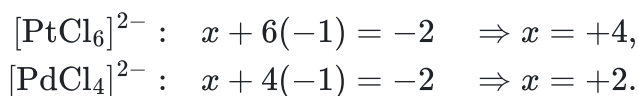
Solution

6.1(i)

The coordination SMILES below use arrows for bonds donated from ligands to the metal. Their spatial geometries are specified explicitly in words.

Ion	Name and SMILES	Geometry and precise drawing description
$[\text{PtCl}_6]^{2-}$	Hexachloridoplatinate(IV), $[\text{Cl}-] \rightarrow [\text{Pt}+4]$ (<-[Cl-])(<-[Cl-])(<-[Cl-])(<-[Cl-])(<-[Cl-])(<-[Cl-])	Octahedral: place platinum at the centre, four chlorido ligands at the corners of an equatorial square, and two axial chlorido ligands directly above and below the centre.
$[\text{PdCl}_4]^{2-}$	Tetrachloridopalladate(II), $[\text{Cl}-] \rightarrow [\text{Pd}+2]$ (<-[Cl-])(<-[Cl-])(<-[Cl-])(<-[Cl-])	Square planar: place palladium at the centre of a square and the four chlorido ligands at its corners, all in one plane.

The metal oxidation states follow from charge balance:



These are the usual six-coordinate, octahedral geometry of platinum(IV), a d^6 ion, and four-coordinate, square-planar geometry of palladium(II), a d^8 ion.

6.1(ii)

The palladium(II) complex is square planar. With two identical ammine ligands and two identical chlorido ligands, only adjacent and opposite arrangements are distinct.

Stereoisomer	SMILES	Precise drawing description
cis-Diamminedichloridopalladium(II)	<chem>[NH3]->[Pd@SP1+2](<-[NH3])(<-[Cl-])<-[Cl-]</chem>	Put palladium at the centre, ammine ligands north and east, and chlorido ligands south and west. Each identical ligand pair subtends 90° .
trans-Diamminedichloridopalladium(II)	<chem>[NH3]->[Pd@SP2+2](<-[NH3])(<-[Cl-])<-[Cl-]</chem>	Put palladium at the centre, ammine ligands north and south, and chlorido ligands east and west. Each identical ligand pair subtends 180° .

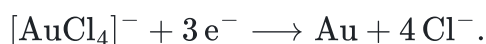
All four donor atoms lie in the same plane. For the atom order written, the extended SMILES descriptors @SP1 and @SP2 distinguish the cis and trans configurations, respectively. Neither isomer is optically active.

6.1(iii)

Iron(II) sulfate, FeSO_4 , SMILES [Fe+2].[O-]S(=O)(=O)[O-], supplies iron(II) ions that reduce dissolved gold(III) to metallic gold. This removes gold from the platinum–palladium solution.

The reacting gold complex is tetrachloridoaurate(III), $[\text{AuCl}_4]^-$, SMILES [Cl-]->[Au+3](<-[Cl-])(<-[Cl-])(<-[Cl-])<-[Cl-].

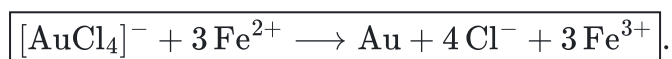
Its reduction half-reaction is



Iron(II) is oxidized:



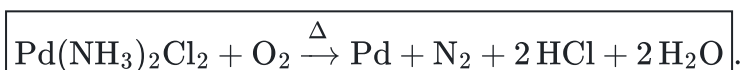
Multiplying the second half-reaction by three and adding gives



Here the iron(II) ion is [Fe+2], the iron(III) ion is [Fe+3], and the chloride ion is [Cl-]. Sulfate is a spectator ion.

6.1(iv)

Complete ignition in air is represented by



The molecular reactant supplied by air is **dioxygen**, $O=O$. The molecular products are **dinitrogen**, $N\equiv N$; **hydrogen chloride**, Cl ; and **water**, O .

The oxidation-state changes are:

Atoms involved	Change	Electron balance per complex
Two ammonia-ligand nitrogen atoms	$-3 \rightarrow 0$	Lose $6e^-$ in total
Palladium	$+2 \rightarrow 0$	Gains $2e^-$
Two oxygen atoms	$0 \rightarrow -2$	Gain $4e^-$ in total

Thus nitrogen is oxidized, while both palladium and oxygen are reduced. Chlorine remains at -1 , and hydrogen remains at $+1$.

6.2(i)

The qualitative observations identify **sulfur**. Elemental sulfur commonly consists of **cyclooctasulfur**, S_8 , SMILES `S1SSSSSSS1`. Its crown-shaped rings open on heating to form long sulfur chains; the SMILES records the ring connectivity, not its crown conformation.

The yellow, impact-sensitive nitride is **tetrasulfur tetranitride**, S_4N_4 , with a localized cage representation `S12=NS3=NS2=NS3=N1`. Its actual structure is a nonplanar cage with delocalized sulfur–nitrogen bonding and weak transannular sulfur–sulfur interactions. Its conversion to a conducting sulfur–nitrogen material matches the remaining observation.

The mass data provide a quantitative check. From the supplied molar masses,

$$M(NH_3) = 14.007 + 3(1.008) = 17.031 \text{ g mol}^{-1},$$

$$M(NH_4Cl) = 14.007 + 4(1.008) + 35.453 = 53.492 \text{ g mol}^{-1}.$$

Hence

$$n(NH_3) = \frac{10.90}{17.031} = 0.6400 \text{ mol},$$

$$n(NH_4Cl) = \frac{25.68}{53.492} = 0.4801 \text{ mol}.$$

The nitrogen atoms not present in ammonium chloride must be in the nitride. Retaining additional digits during calculation,

$$n(\text{N atoms in nitride}) = 0.15994 \text{ mol}.$$

Their mass is

$$m(\text{N in nitride}) = (0.15994)(14.007) = 2.240 \text{ g}.$$

Therefore,

$$m(\text{A in nitride}) = 7.37 - 2.240 = 5.130 \text{ g}.$$

For the general formula in the question,

$$\frac{y}{z}M(\text{A}) = \frac{5.130 \text{ g}}{0.15994 \text{ mol}} = 32.07 \text{ g mol}^{-1}.$$

The 1:1 sulfur-to-nitrogen ratio in the identified nitride gives an inferred sulfur molar mass of approximately 32.1 g mol^{-1} , consistent with sulfur.

The numerical composition constrains the empirical formula; identifying the molecular nitride as S_4N_4 also uses its described chemical properties.

6.2(ii)

All chlorine from the starting chloride appears in ammonium chloride. Thus

$$n(\text{Cl atoms}) = 0.48007 \text{ mol},$$

and

$$m(\text{Cl}) = (0.48007)(35.453) = 17.020 \text{ g}.$$

The sulfur content of the starting chloride is consequently

$$m(\text{S in chloride}) = 24.71 - 17.020 = 7.690 \text{ g}.$$

Using the inferred sulfur molar mass,

$$n(\text{S in chloride}) \simeq \frac{7.690}{32.07} = 0.2398 \text{ mol}.$$

Therefore,

$$\frac{n(\text{Cl atoms})}{n(\text{S atoms})} \simeq \frac{0.4801}{0.2398} = 2.002 \simeq 2.$$

The chloride is **sulfur dichloride**, SCl_2 , SMILES `c1sc1`.

The remaining species are **ammonia**, NH_3 , SMILES `N`, and **ammonium chloride**, NH_4Cl , SMILES `[NH4+] . [Cl-]`.

The product amounts are approximately

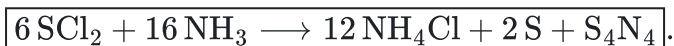
$$n(\text{elemental S atoms}) = \frac{2.57}{32.07} = 0.0801 \text{ mol},$$

$$n(\text{S}_4\text{N}_4) = \frac{0.15994}{4} = 0.03998 \text{ mol}.$$

Dividing all amounts by approximately 0.0400 mol gives

$$\begin{aligned} n(\text{SCl}_2) : n(\text{NH}_3) : n(\text{NH}_4\text{Cl}) : n(\text{elemental S atoms}) : n(\text{S}_4\text{N}_4) \\ \simeq 6 : 16 : 12 : 2 : 1. \end{aligned}$$

Thus the balanced equation in the notation of the question is



The symbol S denotes bulk elemental sulfur. Written explicitly in terms of S_8 , the same balance is



The requested coefficients are

$$\boxed{n = 6, m = 16, p = 12, q = 2, r = 1, w = 1, x = 2, y = 4, z = 4}.$$

The supplied reactant masses total 35.61 g, whereas the product masses total 35.62 g. This 0.01 g difference is consistent with the stated mass precision.

6.2(iii)

In sulfur dichloride, chlorine has oxidation state -1 , so sulfur is $+2$.

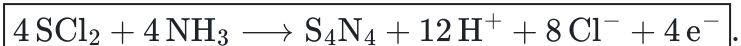
In tetrasulfur tetranitride, conventional assignment of nitrogen as -3 gives

$$4x + 4(-3) = 0 \Rightarrow x = +3$$

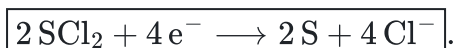
for sulfur. Elemental sulfur has oxidation state 0.

Consequently, four sulfur atoms are oxidized from +2 to +3, releasing four electrons, and two sulfur atoms are reduced from +2 to 0, consuming four electrons. Nitrogen remains at -3.

A balanced oxidation half-reaction is



The corresponding reduction half-reaction is



The hydrogen ion, H^+ , has SMILES `[H+]`. These protons are bookkeeping intermediates: additional ammonia binds them to form the **ammonium ion**, NH_4^+ , SMILES `[NH4+]`:



Adding these equations and combining ammonium and chloride ions into ammonium chloride reproduces



The solution was checked against the official solution.

Problem 7: Thermodynamics of chlorine expansion and of nickel ammine/ethylenediamine complexes

7.1 One mole of Cl_2 (g), which may be assumed to obey the ideal gas law, initially at 300 K and 1.01325×10^7 Pa, is expanded against a constant external pressure of 1.01325×10^5 Pa to a final pressure of 1.01325×10^5 Pa. As a result of the expansion, the gas cooled to a temperature of 239 K (which is the normal boiling point of Cl_2), and 0.100 mol of Cl_2 condensed.

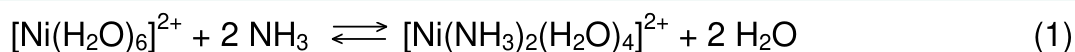
The enthalpy of vaporization of Cl_2 (l) is 20.42 kJ mol⁻¹ at the normal boiling point, the molar heat capacity of Cl_2 (g) at constant volume is $C_v = 28.66$ J K⁻¹ mol⁻¹ and the density of Cl_2 (l) is 1.56 g cm⁻³ (at 239 K). Assume that the molar heat capacity at constant pressure for Cl_2 (g) is $C_p = C_v + R$.

(1 atm = 1.01325×10^5 Pa, $R = 8.314510$ J K⁻¹ mol⁻¹ = 0.0820584 L atm K⁻¹ mol⁻¹)

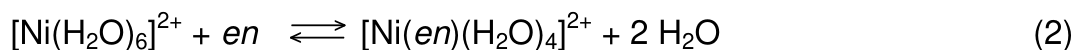
i) Either draw a complete molecular orbital energy diagram or write the complete electronic configuration of Cl_2 . Predict the bond order of Cl_2 and thus whether this molecule will be diamagnetic, ferromagnetic, or paramagnetic.

ii) For the changes described above, calculate the change in the internal energy (ΔE) and the change in the entropy (ΔS_{sys}) of the system.

7.2 For the following reactions occurring in dilute aqueous solution at 298 K:



$\ln K_c = 11.60$ and $\Delta H^0 = -33.5$ kJ mol⁻¹

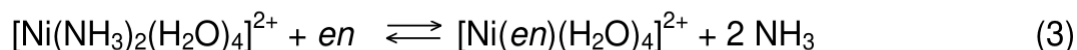


$$\ln K_c = 17.78 \text{ and } \Delta H^0 = -37.2 \text{ kJ mol}^{-1}$$

Note: *en* is ethylenediamine (a neutral bidentate ligand)

$$(R = 8.314510 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0820584 \text{ L atm K}^{-1} \text{ mol}^{-1})$$

Calculate ΔG^0 , ΔS^0 , and K_c at 298 K for reaction [3] occurring in a dilute aqueous solution:



Official English text of the problem.

Answers

- **7.1(i)** Chlorine, Cl_2 , SMILES `ClCl`, has the complete occupied molecular orbital configuration below, taking z along the bond. Each $(\pi n p_{x,y})^4$ denotes two degenerate orbitals containing two electrons each.

$$\begin{aligned} &(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 \\ &(\sigma_g 2p_z)^2 (\pi_u 2p_{x,y})^4 (\pi_g^* 2p_{x,y})^4 (\sigma_u^* 2p_z)^2 \\ &(\sigma_g 3s)^2 (\sigma_u^* 3s)^2 (\sigma_g 3p_z)^2 (\pi_u 3p_{x,y})^4 (\pi_g^* 3p_{x,y})^4. \end{aligned}$$

Its **bond order is 1**, and it is **diamagnetic**.

- **7.1(ii)** For the entire system:

$$\boxed{\Delta E = -3.59 \text{ kJ}}, \quad \boxed{\Delta S_{\text{sys}} = +21.34 \text{ J K}^{-1}}.$$

- **7.2** For reaction (3) at 298 K:

$$\boxed{\Delta G^0 = -15.3 \text{ kJ mol}^{-1}}, \quad \boxed{\Delta S^0 = +39.0 \text{ J K}^{-1} \text{ mol}^{-1}}, \quad \boxed{K_c = 4.83 \times 10^2}.$$

The equilibrium constant uses the usual standard-concentration convention.

Solution

7.1(i): Electronic configuration, bond order, and magnetism

Each chlorine atom supplies 17 electrons, so Cl_2 contains 34 electrons. The complete configuration in the Answers section accounts for all 34; the antibonding $\sigma_u^*(3p_z)$ orbital is empty.

The 20 core electrons occupy equal numbers of bonding and antibonding orbitals, so their contributions to bond order cancel. Of the 14 valence electrons:

- Eight occupy bonding orbitals: two in $\sigma_g(3s)$, two in $\sigma_g(3p_z)$, and four in the two $\pi_u(3p)$ orbitals.
- Six occupy antibonding orbitals: two in $\sigma_u^*(3s)$ and four in the two $\pi_g^*(3p)$ orbitals.

Consequently,

$$\text{bond order} = \frac{N_{\text{bonding}} - N_{\text{antibonding}}}{2} = \frac{8 - 6}{2} = \boxed{1}.$$

All occupied orbitals are doubly occupied. There are no unpaired electrons, so the molecule is **diamagnetic**.

7.1(ii): Internal energy and entropy changes

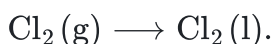
The final system contains

$$n_g = 0.900 \text{ mol}, \quad n_l = 0.100 \text{ mol},$$

at $T_f = 239 \text{ K}$ and $P_f = 1 \text{ atm}$.

Both internal energy and entropy are state functions. We may therefore calculate their changes along the following reversible reference path:

1. Expand the initial 1 mol of gas isothermally at 300 K from 100 atm to 1 atm.
2. Cool that mole of gas at 1 atm from 300 K to 239 K.
3. Condense 0.100 mol reversibly at 239 K and 1 atm:



The required molar heat capacity is

$$C_p = C_v + R = 28.66 + 8.314510 = 36.974510 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Internal energy

For an ideal gas, the isothermal step has $\Delta E_1 = 0$. Cooling contributes

$$\Delta E_2 = nC_v(T_f - T_i) = (1.000)(28.66)(239 - 300) = -1748.26 \text{ J}.$$

To convert the enthalpy of vaporization to an internal-energy change, use

$$\Delta H_{\text{vap}} = \Delta U_{\text{vap}} + P_f(\bar{V}_g - \bar{V}_l).$$

Since $P_f \bar{V}_g = RT_f$,

$$\Delta U_{\text{vap}} = \Delta H_{\text{vap}} - RT_f + P_f \bar{V}_l.$$

Condensation has the opposite sign. Thus

$$\Delta E = nC_v(T_f - T_i) - n_l(\Delta H_{\text{vap}} - RT_f + P_f \bar{V}_l).$$

For the small liquid-volume correction, using the conventional molar mass $M(\text{Cl}_2) \simeq 70.90 \text{ g mol}^{-1}$,

$$\bar{V}_l = \frac{M}{\rho} = \frac{70.90}{1.56} = 45.45 \text{ cm}^3 \text{ mol}^{-1} = 4.545 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}.$$

Hence

$$n_l P_f \bar{V}_l \simeq 0.461 \text{ J}.$$

Combining the contributions,

$$\begin{aligned} \Delta E &= -1748.26 - (0.100)[20420 - (8.314510)(239)] - 0.461 \\ &= -3592.00 \text{ J}. \end{aligned}$$

Therefore,

$$\boxed{\Delta E = -3.59 \text{ kJ}}.$$

Entropy

For the reversible isothermal expansion,

$$\Delta S_1 = nR \ln \frac{P_i}{P_f} = (1.000)(8.314510) \ln 100 = 38.2897 \text{ J K}^{-1}.$$

For cooling at constant pressure,

$$\Delta S_2 = nC_p \ln \frac{T_f}{T_i} = (1.000)(36.974510) \ln \frac{239}{300} = -8.40501 \text{ J K}^{-1}.$$

At the normal boiling point, reversible condensation releases the latent heat at constant temperature:

$$\Delta S_3 = -\frac{n_l \Delta H_{\text{vap}}}{T_f} = -\frac{(0.100)(20420)}{239} = -8.54393 \text{ J K}^{-1}.$$

Thus

$$\begin{aligned}\Delta S_{\text{sys}} &= \Delta S_1 + \Delta S_2 + \Delta S_3 \\ &= 38.2897 - 8.40501 - 8.54393 \\ &= \boxed{+21.34 \text{ J K}^{-1}}.\end{aligned}$$

The entropy increase from expansion exceeds the entropy decreases from cooling and condensation. The reversible reference path gives the entropy difference between the actual initial and final states, even though the actual expansion is irreversible.

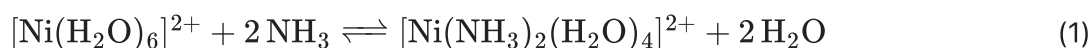
7.2: Nickel complex equilibria

The species used in the reactions are identified below. The coordination SMILES use arrows for donor-to-metal bonds.

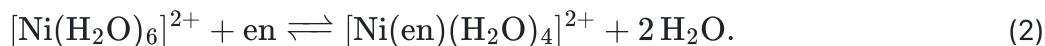
Species and name	SMILES
H ₂ O, water	O
NH ₃ , ammonia	N
H ₂ NCH ₂ CH ₂ NH ₂ , ethylenediamine (ethane-1,2-diamine), abbreviated <i>en</i>	NCCN
[Ni(H ₂ O) ₆] ²⁺ , hexaaquanickel(II) ion	[Ni+2](<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])
[Ni(NH ₃) ₂ (H ₂ O) ₄] ²⁺ , diamminetetraaquanickel(II) ion	[Ni+2](<-[NH3])(<-[NH3])(<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])
[Ni(en)(H ₂ O) ₄] ²⁺ , tetraaqua(ethane-1,2-diamine)nickel(II) ion	[Ni+2]1(<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])<-[NH2]CC[NH2]->1

These complexes have octahedral coordination. Ethylenediamine binds through both nitrogen atoms at adjacent coordination sites, forming a five-membered chelate ring. The SMILES specify connectivity without assigning an octahedral stereoisomer; the problem does not distinguish cis and trans forms of the diammine complex.

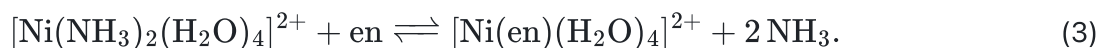
The balanced reactions are



and



Adding reaction (2) to the reverse of reaction (1) cancels the hexaaqua complex and water, giving



Accordingly,

$$\Delta G_3^0 = \Delta G_2^0 - \Delta G_1^0, \quad \Delta H_3^0 = \Delta H_2^0 - \Delta H_1^0, \quad K_{c,3} = \frac{K_{c,2}}{K_{c,1}}.$$

Equilibrium constant

$$\ln K_{c,3} = 17.78 - 11.60 = 6.18,$$

so

$$K_{c,3} = e^{6.18} = 4.83 \times 10^2.$$

Here concentrations are understood relative to the standard concentration, as required for a dimensionless logarithm.

Standard Gibbs energy change

$$\begin{aligned} \Delta G_3^0 &= -RT \ln K_{c,3} \\ &= -(8.314510)(298)(6.18) \\ &= -15312.3 \text{ J mol}^{-1}. \end{aligned}$$

Thus

$$\Delta G_3^0 = -15.3 \text{ kJ mol}^{-1}.$$

Standard entropy change

First,

$$\Delta H_3^0 = (-37.2) - (-33.5) = -3.7 \text{ kJ mol}^{-1}.$$

Using $\Delta G^0 = \Delta H^0 - T\Delta S^0$,

$$\begin{aligned} \Delta S_3^0 &= \frac{\Delta H_3^0 - \Delta G_3^0}{T} \\ &= \frac{-3700 - (-15312.3)}{298} \\ &= 38.9676 \text{ J K}^{-1} \text{ mol}^{-1}. \end{aligned}$$

Therefore,

$$\Delta S_3^0 = +39.0 \text{ J K}^{-1} \text{ mol}^{-1}.$$

The favorable entropy change is consistent with the chelate effect: binding one free ethylenediamine molecule releases two free ammonia molecules. The exchange is also slightly exothermic.

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 8: Electrodeposition of copper monolayers on Pt(100)

An electrolyte is prepared from H_2SO_4 , CuSO_4 and distilled water and its volume is 100.0 cm^3 . The concentrations of H^+ and Cu^{2+} in the electrolyte are $c(\text{H}^+) = 1.000 \text{ M (mol dm}^{-3}\text{)}$ and $c(\text{Cu}^{2+}) = 1.000 \times 10^{-2} \text{ M (mol dm}^{-3}\text{)}$, respectively. Two cubic platinum electrodes are immersed in the electrolyte. Both of the electrodes are single crystals with only one face (100) exposed to the electrolyte (the other five faces are blocked physically by an insulator which is stable in the electrolyte). The exposed surface area of each electrode is equal to 1.000 cm^2 . During an electrolysis a total charge of 2.0000 C is passed between the cathode and the anode. At the cathode, two simultaneous processes are occurring: deposition of an epitaxial (layer-by-layer) Cu layer and H_2 gas generation. At the anode, O_2 gas is generated. The H_2 gas is collected in a flask under the following conditions (assume ideal gas behaviour):

$T = 273.15 \text{ K}$ and $P(\text{H}_2) = 1.01325 \times 10^4 \text{ Pa}$; the volume of H_2 is equal to 2.0000 cm^3

8.1 Write equations of the processes taking place at the electrodes.

8.2 Calculate the number of moles of H_2 gas generated at the cathode and the number of moles of Cu deposited on the electrode.

8.3 Calculate the number of Cu monolayers formed on the Pt (100) cathode.

Note that the lattice constant of Pt is $a(\text{Pt}) = 3.9236 \times 10^{-8} \text{ cm}$.

Both Pt and Cu have the fcc (face centred cubic) crystallographic structure.

Molar masses and constants:

$$M(\text{H}) = 1.00795 \text{ g mol}^{-1}$$

$$M(\text{Cu}) = 63.546 \text{ g mol}^{-1}$$

$$e = 1.60218 \times 10^{-19} \text{ C}$$

$$F = 96485.3 \text{ C mol}^{-1}$$

$$R = 8.314510 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0820584 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$V_m = 22.4141 \text{ dm}^3$$

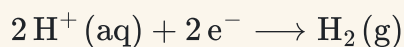
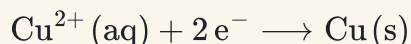
$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

$$N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

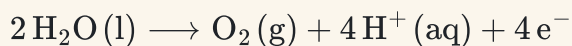
Official English text of the problem.

Answers

- 8.1 Cathode:



Anode:



The molecular and ionic species are copper(II) ion $[\text{Cu}^{2+}]$, hydrogen ion $[\text{H}^{+}]$, molecular hydrogen $[\text{H}_2]$, water H_2O , and molecular oxygen O_2 .

- 8.2

$$n(\text{H}_2) = 8.9230 \times 10^{-6} \text{ mol},$$

$$n(\text{Cu}) = 1.441 \times 10^{-6} \text{ mol}.$$

- 8.3

$$L = 6.681 \times 10^2 \text{ monolayers} \approx 668 \text{ monolayers}.$$

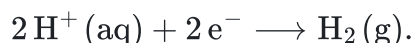
Solution

8.1

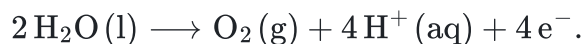
Reduction occurs at the cathode. Copper(II) ions gain two electrons per ion, changing the copper oxidation state from +2 to 0 and depositing copper metal:



Simultaneously, hydrogen ions are reduced to molecular hydrogen. Two hydrogen ions require two electrons to form one molecule:



Oxidation occurs at the anode. Water supplies the oxygen evolved; oxygen changes from oxidation state -2 in water to 0 in molecular oxygen. Balancing atoms and charge in the acidic electrolyte gives:



8.2

The stated hydrogen pressure is $1.01325 \times 10^4 \text{ Pa}$, corresponding to 0.100000 atm . Convert the gas volume to SI units:

$$V = 2.0000 \text{ cm}^3 = 2.0000 \times 10^{-6} \text{ m}^3.$$

Using the ideal-gas equation,

$$\begin{aligned} n(\text{H}_2) &= \frac{PV}{RT} \\ &= \frac{(1.01325 \times 10^4 \text{ Pa})(2.0000 \times 10^{-6} \text{ m}^3)}{(8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})} \\ &= 8.9229558 \times 10^{-6} \text{ mol}. \end{aligned}$$

Here $\text{Pa m}^3 = \text{J}$, so the resulting unit is moles. Therefore,

$$n(\text{H}_2) = 8.9230 \times 10^{-6} \text{ mol}.$$

Each mole of hydrogen and each mole of deposited copper consumes two moles of electrons. Consequently, the cathodic charge balance is

$$Q = 2F n(\text{H}_2) + 2F n(\text{Cu}).$$

The anode carries the same total charge; its charge is not an additional contribution to this cathodic balance. Thus,

$$\begin{aligned} n(\text{Cu}) &= \frac{Q}{2F} - n(\text{H}_2) \\ &= \frac{2.0000 \text{ C}}{2(96485.3 \text{ C mol}^{-1})} - 8.9229558 \times 10^{-6} \text{ mol} \\ &= 1.4413173 \times 10^{-6} \text{ mol}. \end{aligned}$$

Rounding after the subtraction gives

$$n(\text{Cu}) = 1.441 \times 10^{-6} \text{ mol}.$$

As a consistency check, the initial amount of copper(II) ions is

$$(1.000 \times 10^{-2} \text{ mol dm}^{-3})(0.1000 \text{ dm}^3) = 1.000 \times 10^{-3} \text{ mol},$$

which is more than sufficient for this deposit.

8.3

In the epitaxial layer model of the problem, a copper monolayer occupies the surface sites of the Pt (100) lattice.

Consider a square of side a on an fcc (100) face. It contains four corner atoms, each shared among four such squares, and one face-centre atom lying entirely within the square. The number of atoms per square is therefore

$$4 \left(\frac{1}{4} \right) + 1 = 2.$$

Hence the surface atomic density is

$$\sigma_{(100)} = \frac{2}{a^2} = \frac{2}{(3.9236 \times 10^{-8} \text{ cm})^2} = 1.2991537 \times 10^{15} \text{ atoms cm}^{-2}.$$

Only the exposed cathode face receives the copper deposit. For its area $A = 1.000 \text{ cm}^2$, one complete monolayer contains

$$N_1 = \sigma_{(100)} A = 1.2991537 \times 10^{15} \text{ atoms}.$$

The total number of deposited copper atoms, retaining the unrounded mole calculation, is

$$\begin{aligned} N_{\text{dep}} &= n(\text{Cu}) N_A \\ &= (1.4413173 \times 10^{-6} \text{ mol})(6.02214 \times 10^{23} \text{ mol}^{-1}) \\ &= 8.6798144 \times 10^{17} \text{ atoms}. \end{aligned}$$

Thus the deposit expressed in monolayers is

$$L = \frac{N_{\text{dep}}}{N_1} = \frac{n(\text{Cu}) N_A a^2}{2A} = 668.11296.$$

Therefore,

$$L = 6.681 \times 10^2 \text{ monolayers} \approx 668 \text{ monolayers}.$$

The fcc lattice and its (100) orientation describe an extended metallic crystal; molecular SMILES do not encode this surface geometry.

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.