

IChO 1996

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Problem 1: Tellurium chloroaluminates from the Te - TeCl₄/AlCl₃ system

The stereoregular polymerization of unsaturated hydrocarbons is usually considered as one of the most important for the industrial organic chemistry. The salts of big nonlinear cations carrying a sufficiently high charge to attack the electron density distributed along the π -bonds of the olefin molecules are usually used as the catalysts in these processes. Chloroaluminate anions (like AlCl_4^-) possessing a highly delocalized negative charge are used usually as the anions. The necessity to develop new catalysts of this kind urged the chemists to study the interaction in the system A - B, where A = Te(cryst ·) and B = (TeCl₄ + 4 AlCl₃). The second component B was considered as an analog of Te(IV) chloroaluminate $\text{Te}[\text{AlCl}_4]_4$ which, however, cannot be isolated as an individual compound. It was found out that the interaction of the components A and B can lead to the formation of three new compounds (**I**, **II** and **III**) in the systems containing initially 77.8, 87.5 and 91.7 mol. % of the component A, respectively. It was also noticed that while in the case of compounds **II** and **III** no side products were formed, the formation of **I** was accompanied by the evolution of 1 mole of volatile TeCl₄ per two moles of **I**.

The compounds **I** and **II** attracted a particular interest of investigators. They both have pinkish-purple color and both dissociate into three ions as the conductivity studies in melted NaAlCl_4 showed. The cryoscopic measurements in NaAlCl_4 melt enabled to determine the molecular weights of these compounds being equal to $1126 \pm 43 \text{ g mol}^{-1}$ and $867 \pm 48 \text{ g mol}^{-1}$ for **I** and **II**, respectively. In the IR spectra of both compounds there is only one band observed which can be attributed to a vibration mode of a bond formed by Te atom. This band lies at 133 cm^{-1} and is therefore so low in energy that this bond undoubtedly is a kind of Te - Te interaction. The ^{27}Al NMR data for the complexes **I** and **II** show that in each compound there is only one type of tetrahedrally coordinated aluminum. However, the observed chemical shifts of aluminium for the compounds **I** and **II** are different, thus manifesting that Al atoms are different in them.

1.1 Determine Te : Al : Cl minimal atomic ratio for the complexes **I**, **II** and **III**.

1.2 Write the molecular-formulae of the compounds **I** and **II**.

1.3 Write the formulae of the anions and cations in compounds **I** and **II**.

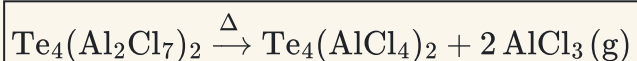
1.4 Draw stereochemical formulae of cations and anions in the structures of **I** and **II** assuming that the cations in **I** and **II** are examples of inorganic aromatic systems.

1.5 Which compound has a higher thermal stability, **I** or **II**, taking into account that AlCl₃ is extremely volatile compound.

1.6 If one of the compounds **I** or **II** can be transformed into the other by heating, write the corresponding reaction equation.

Answers

- **1.1** The minimal Te : Al : Cl ratios are **I**: 2 : 2 : 7; **II**: 2 : 1 : 4; **III**: 3 : 1 : 4.
- **1.2 I**: $\text{Te}_4\text{Al}_4\text{Cl}_{14}$, equivalently $\text{Te}_4(\text{Al}_2\text{Cl}_7)_2$. **II**: $\text{Te}_4\text{Al}_2\text{Cl}_8$, equivalently $\text{Te}_4(\text{AlCl}_4)_2$.
- **1.3** Both contain the **cyclotetratellurium dication**, Te_4^{2+} , SMILES $[\text{Te}^+]1=[\text{Te}^+][\text{Te}][\text{Te}]1$. The anions are:
 - **I**: **heptachlorodialuminate(1-)**, Al_2Cl_7^- , SMILES $\text{Cl}[\text{Al}-](\text{Cl})(\text{Cl})[\text{Cl}+][\text{Al}-](\text{Cl})(\text{Cl})\text{Cl}$.
 - **II**: **tetrachloroaluminate(1-)**, AlCl_4^- , SMILES $[\text{Al}-](\text{Cl})(\text{Cl})(\text{Cl})\text{Cl}$.
- **1.4** The common cation is a **square planar, six- π -electron aromatic ring**. The anion of **II** is tetrahedral; the anion of **I** consists of **two tetrahedra sharing one chloride vertex**.
- **1.5** **II** has the higher thermal stability under the stated volatility criterion.
- **1.6**



The SMILES represent connectivity and localized formal charges. The actual cation has delocalized bonding; its geometry and the anion coordination geometries are described in 1.4 below.

Solution

1.1 — Minimal atomic ratios

The component ratios follow from

$$n_A : n_B = x_A : (1 - x_A).$$

Allowing for the reported rounding,

$$\begin{aligned} \text{I} : 77.8 : 22.2 &\simeq 7 : 2, \\ \text{II} : 87.5 : 12.5 &= 7 : 1, \\ \text{III} : 91.7 : 8.3 &\simeq 11 : 1. \end{aligned}$$

One mole of component B, $\text{TeCl}_4 + 4 \text{AlCl}_3$, supplies 1 mol Te atoms, 4 mol Al atoms and 16 mol Cl atoms.

The molecular reagents are **tellurium tetrachloride**, TeCl_4 , SMILES $\text{Cl}[\text{Te}](\text{Cl})(\text{Cl})\text{Cl}$, and **aluminium trichloride**, AlCl_3 , monomer SMILES $\text{Cl}[\text{Al}](\text{Cl})\text{Cl}$.

For **I**, the volatile by-product must be included. Let its formula contain t Te atoms, a Al atoms and c Cl atoms. Per mole of **I**:

- The aluminium balance requires $a/4$ mol B.
- The feed ratio requires $7a/8$ mol A.
- The stated by-product is $1/2$ mol TeCl_4 .

Consequently,

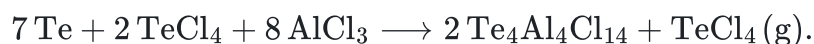
$$t = \frac{7a}{8} + \frac{a}{4} - \frac{1}{2} = \frac{9a-4}{8}, \quad c = 16\frac{a}{4} - 4\frac{1}{2} = 4a - 2.$$

Integral atom counts require $a = 4, 12, 20, \dots$. The smallest possibility is

$$(t, a, c) = (4, 4, 14),$$

whose molar mass agrees with experiment, as checked in 1.2. The next possibility, $\text{Te}_{13}\text{Al}_{12}\text{Cl}_{46}$, would have a molar mass exceeding 3600 g mol^{-1} , so it is excluded.

The corresponding balanced formation equation is



It reproduces both the 7 : 2 component ratio and the evolution of one mole of TeCl_4 per two moles of I. Thus

$$\boxed{\text{I : Te : Al : Cl} = 2 : 2 : 7.}$$

For II and III, all feed atoms enter the products:

Compound	Feed	Te atoms	Al atoms	Cl atoms	Minimal ratio
II	$7A + B$	$7 + 1 = 8$	4	16	2 : 1 : 4
III	$11A + B$	$11 + 1 = 12$	4	16	3 : 1 : 4

Therefore,

$$\boxed{\text{II : 2 : 1 : 4,} \quad \text{III : 3 : 1 : 4.}}$$

1.2 — Molecular formulae

Using standard atomic molar masses

$$M_{\text{Te}} = 127.60, \quad M_{\text{Al}} = 26.98, \quad M_{\text{Cl}} = 35.45 \quad (\text{g mol}^{-1}),$$

the empirical-formula masses are

$$\begin{aligned} M_{\text{emp},I} &= 2(127.60) + 2(26.98) + 7(35.45) \\ &= 557.31 \text{ g mol}^{-1}, \end{aligned}$$

$$\begin{aligned} M_{\text{emp},II} &= 2(127.60) + 26.98 + 4(35.45) \\ &= 423.98 \text{ g mol}^{-1}. \end{aligned}$$

The measured-to-empirical mass ratios are

$$\frac{1126 \pm 43}{557.31} = 2.02 \pm 0.08, \quad \frac{867 \pm 48}{423.98} = 2.04 \pm 0.11.$$

Both select an integer multiplier of 2. Hence

$$\boxed{\text{I} = \text{Te}_4\text{Al}_4\text{Cl}_{14}, \quad \text{II} = \text{Te}_4\text{Al}_2\text{Cl}_8.}$$

Their calculated molar masses are

$$M_I = 1114.62 \text{ g mol}^{-1}, \quad M_{II} = 847.96 \text{ g mol}^{-1},$$

both within the respective experimental intervals.

1.3 — Identification of the ions

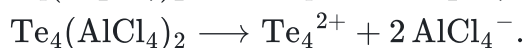
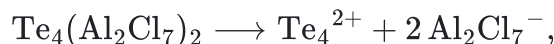
With aluminium in oxidation state +3 and chlorine in oxidation state −1, the total charge required on the tellurium unit is

$$\text{I} : 14 - 4(3) = +2,$$

$$\text{II} : 8 - 2(3) = +2.$$

The low-frequency IR band supports a bonded tellurium cluster. Both compounds therefore contain the Te_4^{2+} cation identified above.

Each formula unit produces three ions. One Te_4^{2+} cation must therefore accompany two singly charged chloroaluminate anions:



The anion charges also follow directly:

$$2(+3) + 7(-1) = -1, \quad (+3) + 4(-1) = -1.$$

Thus the complete salts, with disconnected ionic SMILES, are:

- **I — tetratellurium(2+) bis(heptachlorodialuminate), $\text{Te}_4(\text{Al}_2\text{Cl}_7)_2$:**
[Te+]1=[Te+][Te][Te]1.Cl[Al-](Cl)(Cl)[Cl+][Al-](Cl)(Cl)Cl.Cl[Al-](Cl)(Cl)[Cl+][Al-](Cl)(Cl)Cl
- **II — tetratellurium(2+) bis(tetrachloroaluminate), $\text{Te}_4(\text{AlCl}_4)_2$:**
[Te+]1=[Te+][Te][Te]1.[Al-](Cl)(Cl)(Cl)Cl.[Al-](Cl)(Cl)(Cl)Cl

1.4 — Stereochemical structures and aromaticity

For the common **cyclotetratellurium dication**, draw four Te atoms at the corners of a square, connect successive corners, and place a circle inside the ring to indicate delocalization. Enclose the ring in brackets with an overall 2+ charge. The four atoms are coplanar, and the four ring bonds are equivalent.

The valence-electron count is

$$4(6) - 2 = 22.$$

Four ring σ bonds account for 8 electrons, and one lone pair in the ring plane on each Te accounts for another 8. The remaining

$$22 - 8 - 8 = 6$$

electrons occupy the conjugated system of four perpendicular p orbitals. This satisfies Hückel's aromaticity condition:

$$6 = 4n + 2, \quad n = 1.$$

The high symmetry is consistent with the single observed Te–Te stretching band. The localized double bond in the SMILES represents one resonance contributor.

For **II**, draw the **tetrachloroaluminate anion**, AlCl_4^- , as a tetrahedron: Al at its center and four Cl atoms at its vertices. A wedge-and-dash drawing has two bonds in the page, one solid wedge and one dashed wedge. Enclose it in brackets with charge -1 .

For **I**, draw the **heptachlorodialuminate anion**, Al_2Cl_7^- , as two tetrahedra sharing one vertex:

- A single chloride bridges the two Al atoms.
- Each Al also has three terminal chlorides.
- Each Al therefore has four chloride neighbours in tetrahedral coordination.

This gives $3 + 1 + 3 = 7$ chlorides in total. The two Al centers are equivalent, explaining the single aluminium environment in I. Their environment contains a bridging chloride, whereas II has four terminal chlorides around Al; this accounts for the different ^{27}Al chemical shifts.

1.5 — Relative thermal stability

The heptachlorodialuminate anion can release volatile aluminium trichloride:

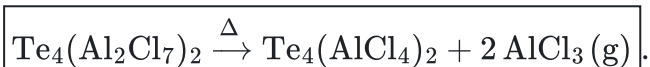


Relative to II, I contains two additional AlCl_3 units per tellurium cation. Heating allows these units to escape, leaving II. Therefore, under the stated volatility criterion,

II has the higher thermal stability.

1.6 — Thermal conversion

Applying the anion conversion twice per formula unit gives



The equation conserves four Te atoms, four Al atoms and fourteen Cl atoms. Thus **I transforms into II upon loss of aluminium trichloride.**

The solution was checked against the official solution.

Problem 2: Detection limit for bismuth: gravimetric and multiplicative methods

The detection limit is one of the basic parameters in quantitative analysis of trace amounts of elements. The detection limit is expressed as the least mass of an element which can be determined by a given method with a given accuracy.

As an example we shall consider the method used for the determination of microscopic amounts of bismuth. In 1927 German chemist Berg suggested to precipitate bismuth as a practically insoluble salt: 8-hydroxyquinolinium tetraiodobismuthate $[\text{C}_9\text{H}_6(\text{OH})\text{NH}][\text{BiI}_4]$ ($M_r = 862.7$).

2.1 a) Draw the structural formulae of the cation and anion of this salt.

b) What is the oxidation state of Bi atom in this compound?

2.2 Evaluate the smallest mass of bismuth (in mg), which can be determined reliably by Berg method, if the smallest mass of precipitate which can be reliably measured is 50.0 mg.

For the determination of trace amounts of bismuth R. Belcher and co-workers from Birmingham developed a multiplicative method. According to this method a chain of reactions followed by a titration of the final product is carried out. A detailed description follows.

Step 1: To a given small amount ($\approx 2 \text{ cm}^3$) of cold acidified solution containing trace amounts of Bi^{3+} 50 mg of potassium hexathiocyanatochromate(III) ($\text{K}_3[\text{Cr}(\text{SCN})_6]$) is added in the cold, that leads to practically quantitative precipitation of bismuth.

2.3 Write a balanced net ionic equation of this reaction.

Step 2: The precipitate is filtered off, washed by cold water, and treated with 5 cm³ of 10 % solution of sodium hydrogen carbonate. Upon this treatment the initial precipitate transforms into the precipitate of oxobismuth(III) carbonate (BiO)₂CO₃ with liberation of hexathiocyanatochromate(III) ions into solution.

2.4 Write a balanced net ionic equation of this reaction.

Step 3: To the slightly acidified filtrate transferred to a separatory funnel 0.5 cm³ of saturated iodine solution in chloroform are added, and the mixture is vigorously shaken. Iodine oxidizes the ligand of the complex ion to ICN and sulphate ion.

2.5 Write a balanced net ionic equation of this reaction.

Step 4: Upon 5 minutes 4 cm³ of 2 M H₂SO₄ solution are added to the mixture. The acidification leads to the reaction of coproportionation with the evolution of molecular iodine.

2.6 Write a balanced net ionic equation of the reaction occurred on acidification.

Step 5: Iodine is quantitatively extracted by 4 portions of chloroform. Aqueous layer is transferred to a flask, to which 1 cm³ of bromine water is added, and the mixture is mixed for 5 minutes.

2.7 Write the balanced net ionic equations of the reactions occurred upon the addition of bromine water. Note that an excess of bromine can react with hydrogen cyanide to give BrCN, and iodide is oxidized into IO₃⁻.

Step 6: To eliminate an excess of molecular bromine 3 cm³ of 90 % methanoic (formic) acid is added to the mixture.

2.8 Write a balanced net ionic equation of this reaction.

Step 7: To the slightly acidic solution an excess (1.5 g) of potassium iodide is added.

2.9 Write the balanced net ionic equations of the reactions occurred upon the addition of KI, taking into consideration that iodide reacts with BrCN in a similar manner as with ICN to form molecular iodine.

Step 8: The resulting solution is titrated by a standard 0.00200 M Na₂S₂O₃ solution. The results thus obtained are used to calculate the content of bismuth in the sample taken for analysis.

2.10 a) How many moles of thiosulphate are equivalent to 1 mol of bismuth in the initial sample?

b) What is the least mass of bismuth which can be determined by this method (assume that reliable determination requires no less than 1 cm³ of standard 0.00200 M Na₂S₂O₃ solution)?

2.11 By how many times the multiplicative method just described is more sensitive than Berg's gravimetric method?

Official English text of the problem.

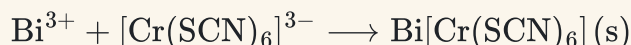
Answers

- **2.1(a)** Cation: **8-hydroxyquinolinium**, C9H8NO+, Oc1cccc2ccc[nH+]c12: quinoline protonated at its ring nitrogen, with an OH group at position 8. Anion: **tetraiodobismuthate(III)**, $[\text{BiI}_4]^-$, [Bi-](I)(I)(I)I: central Bi bonded to four iodine atoms, with overall charge -1 .

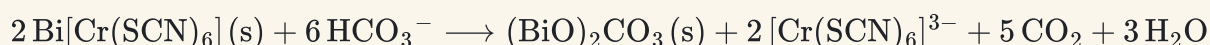
- **2.1(b)** The oxidation state of Bi is $+3$.

- **2.2** 12.1 mg Bi .

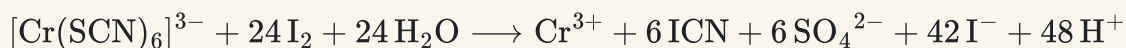
- **2.3**



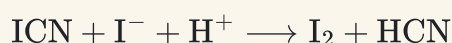
- **2.4**



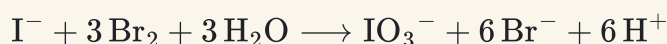
- **2.5**



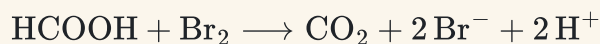
- **2.6**



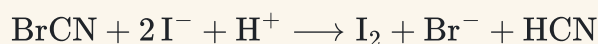
- **2.7**



- **2.8**



- **2.9**



- **2.10(a)** $228 \text{ mol thiosulphate per mol Bi}$.

- **2.10(b)** $1.83 \times 10^{-3} \text{ mg Bi} = 1.83 \mu\text{g Bi}$.

- **2.11** $6.61 \times 10^3 \text{ times}$.

Names and SMILES for the species in these equations are collected at the end of the solution.

Solution

The calculations use $M(\text{Bi}) = 209.0 \text{ g mol}^{-1}$. The given relative formula mass corresponds to a precipitate molar mass of 862.7 g mol^{-1} .

2.1(a) Structures of the ions

The cation is **8-hydroxyquinolinium**, Oc1cccc2ccc[nH+]c12.

To draw it, draw the two fused aromatic six-membered rings of quinoline. The nitrogen occupies position 1 in the pyridine ring; attach a hydrogen to this nitrogen and give it a positive charge. Attach a neutral hydroxyl group to carbon 8 on the benzene ring. The fused aromatic skeleton is planar.

Protonation occurs at nitrogen; the phenolic oxygen retains its hydrogen.

The anion is **tetraiodobismuthate(III)**, $[\text{Bi}-](\text{I})(\text{I})(\text{I})\text{I}$.

Its Lewis connectivity is a central Bi atom with four single Bi–I bonds, one lone pair on Bi, and an overall charge of -1 . Each iodine has three lone pairs. Enclose the ion in brackets and place the negative charge outside. This describes connectivity and electron bookkeeping; the empirical formula does not establish the salt's detailed solid-state coordination geometry.

The negative formal charge assigned to Bi in this covalent SMILES representation is **not** its oxidation state.

2.1(b) Oxidation state of bismuth

Each iodide ligand has oxidation state -1 . If the oxidation state of Bi is x ,

$$x + 4(-1) = -1,$$

hence

$$\boxed{x = +3}.$$

2.2 Gravimetric detection limit

There is one Bi atom per formula unit of precipitate. Its bismuth mass fraction is therefore

$$w_{\text{Bi}} = \frac{209.0}{862.7} = 0.2423.$$

Thus a minimum measurable precipitate mass of 50.0 mg contains

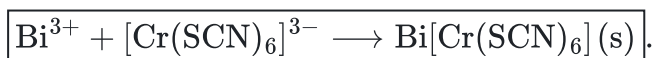
$$m_{\text{Bi},\text{min}} = (50.0 \text{ mg}) \frac{209.0}{862.7} = \boxed{12.1 \text{ mg}}.$$

2.3 Precipitation with hexathiocyanatochromate(III)

Chromium is in oxidation state $+3$, and each of the six thiocyanate ligands has charge -1 . The complex therefore has charge

$$+3 + 6(-1) = -3.$$

It combines with Bi^{3+} in a 1 : 1 ratio to form the neutral, insoluble salt:

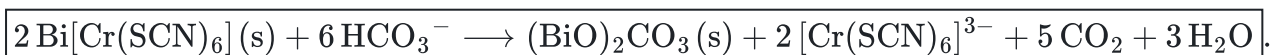


Consequently, each mole of precipitated bismuth carries **six moles of thiocyanate ligands** into the subsequent reactions. Washing removes the excess soluble precipitating reagent.

2.4 Conversion into oxobismuth(III) carbonate

Hydrogen carbonate converts the bismuth-containing solid into $(\text{BiO})_2\text{CO}_3$, while the chromium complex passes into solution unchanged. Excess hydrogen carbonate also neutralizes the acidity associated with forming the oxobismuth units.

Balancing bismuth, the complex ions, hydrogen, oxygen, carbon and charge gives



Both sides have total charge -6 . Two moles of the original precipitate release two moles of complex anion, preserving the 1 : 1 relation between initial Bi and recovered chromium complex.

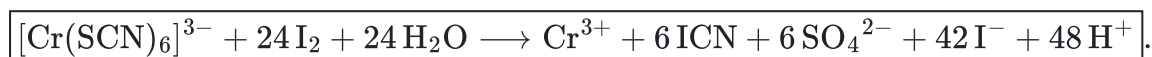
2.5 Oxidation of the thiocyanate ligands by iodine

For each thiocyanate ligand, its sulfur becomes sulphate, while its carbon and nitrogen form cyanogen iodide.

First balance the reaction for one ligand. Four water molecules provide the four oxygen atoms of sulphate, and eight protons balance hydrogen. Charge balance then requires seven iodide ions. Together with the iodine atom in cyanogen iodide, these require four iodine molecules:



There are six ligands per complex, and chromium remains in oxidation state +3. Thus

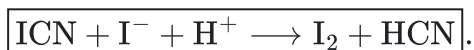


Per mole of initial bismuth, this produces

6 mol ICN and 42 mol iodide.

2.6 Reaction on acidification

Cyanogen iodide reacts with iodide to release molecular iodine. Acid converts the cyanide fragment into hydrogen cyanide:



The six moles of cyanogen iodide therefore consume six of the 42 moles of iodide. Per mole of initial Bi, the aqueous solution now contains

$$42 - 6 = 36 \text{ mol iodide}$$

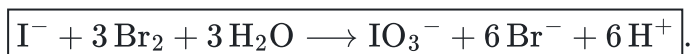
and

$$6 \text{ mol HCN}.$$

The molecular iodine formed here, together with any excess iodine from Step 3, is subsequently extracted into chloroform. It is therefore **not included in the final titration**.

2.7 Reactions with bromine water

Iodide is oxidized from oxidation state -1 to $+5$ in iodate, losing six electrons. Three bromine molecules accept these six electrons:



Hydrogen cyanide also reacts with bromine, forming cyanogen bromide:

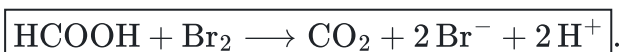


Accordingly, per mole of initial bismuth the analytical products are now

36 mol iodate and 6 mol cyanogen bromide.

2.8 Removal of excess bromine

Formic acid is oxidized to carbon dioxide. Its carbon changes oxidation state from $+2$ to $+4$, supplying the two electrons needed to reduce one bromine molecule:



Removing excess bromine prevents it from liberating additional iodine when potassium iodide is added.

2.9 Liberation of iodine by added iodide

Iodate reacts with iodide in acidic solution:



Thus each mole of iodate produces three moles of molecular iodine.

Cyanogen bromide also oxidizes iodide. Its bromine becomes bromide, and its cyanide fragment becomes hydrogen cyanide:



Each mole of cyanogen bromide therefore produces one mole of molecular iodine.

2.10(a) Thiosulphate equivalent of bismuth

The complete accounting per mole of initial bismuth is:

Stage	Amounts derived from 1 mol initial Bi
Recovery of the chromium complex	1 mol $[\text{Cr}(\text{SCN})_6]^{3-}$, containing six thiocyanate ligands
Oxidation by iodine	6 mol $\text{ICN} + 42\text{ mol I}^-$
Acidification and extraction of iodine	6 mol $\text{HCN} + 36\text{ mol I}^-$ remain
Treatment with bromine	6 mol $\text{BrCN} + 36\text{ mol IO}_3^-$
Addition of excess iodide	$6 + 3(36) = 114\text{ mol I}_2$

The iodine–thiosulphate titration reaction is



Each mole of iodine consumes two moles of thiosulphate. Hence

$$\frac{n(\text{S}_2\text{O}_3^{2-})}{n(\text{Bi})} = 2[6 + 3(36)] = \boxed{228}.$$

Equivalently, each thiocyanate ligand ultimately gives 19 iodine molecules and consumes 38 thiosulphate ions; six ligands give $6(38) = 228$.

2.10(b) Detection limit of the multiplicative method

The minimum titrant volume is

$$1\text{ cm}^3 = 1 \times 10^{-3}\text{ L}.$$

The corresponding amount of thiosulphate is

$$n_{\min}(\text{S}_2\text{O}_3^{2-}) = (0.00200\text{ mol L}^{-1})(1 \times 10^{-3}\text{ L}) = 2.00 \times 10^{-6}\text{ mol}.$$

Therefore,

$$n_{\min}(\text{Bi}) = \frac{2.00 \times 10^{-6}}{228} = 8.77 \times 10^{-9}\text{ mol}.$$

The minimum bismuth mass is

$$\begin{aligned} m_{\min}(\text{Bi}) &= (8.77 \times 10^{-9}\text{ mol})(209.0\text{ g mol}^{-1}) \\ &= 1.83 \times 10^{-6}\text{ g} \\ &= \boxed{1.83 \times 10^{-3}\text{ mg} = 1.83\text{ }\mu\text{g}}. \end{aligned}$$

2.11 Relative sensitivity

Sensitivity here is compared through the reciprocal detection limits. The improvement factor is

$$F = \frac{m_{\min, \text{Berg}}}{m_{\min, \text{multiplicative}}}.$$

Using the unrounded calculated masses,

$$F = \frac{12.1131 \text{ mg}}{0.00183333 \text{ mg}} = 6607.16.$$

Thus the multiplicative method is

$$6.61 \times 10^3 \text{ times more sensitive}.$$

Names and SMILES for the reaction species

The chromium coordination SMILES below use the conventional N-bound, octahedral representation: six thiocyanate nitrogen donors surround chromium. The arrows encode donor-to-metal bonds, but not octahedral geometry. Dot-separated SMILES for ionic solids describe formula-unit composition rather than their crystal lattices.

Species	Name	SMILES
$[\text{C}_9\text{H}_6(\text{OH})\text{NH}][\text{BiI}_4]$	8-Hydroxyquinolinium tetraiodobismuthate(III)	<chem>Oc1cccc2ccc[nH+]c12.[Bi-](I)(I)(I)I</chem>
Bi^{3+}	Bismuth(III) ion	<chem>[Bi+3]</chem>
Cr^{3+}	Chromium(III) ion	<chem>[Cr+3]</chem>
SCN^-	Thiocyanate ion	<chem>N#[S-]</chem>
$[\text{Cr}(\text{SCN})_6]^{3-}$	Hexathiocyanatochromate(III) ion	<chem>[Cr+3](<-N#[S-])(<-N#[S-])(<-N#[S-])(<-N#[S-])(<-N#[S-])(<-N#[S-])</chem>
$\text{Bi}[\text{Cr}(\text{SCN})_6]$	Bismuth(III) hexathiocyanatochromate(III)	<chem>[Bi+3].[Cr+3](<-N#[S-])(<-N#[S-])(<-N#[S-])(<-N#[S-])(<-N#[S-])(<-N#[S-])</chem>
HCO_3^-	Hydrogen carbonate ion	<chem>O=C(O)[O-]</chem>
$(\text{BiO})_2\text{CO}_3$	Oxobismuth(III) carbonate	<chem>[Bi+3].[Bi+3].[O-2].[O-2].[O-]C(=O)[O-]</chem>
CO_2	Carbon dioxide	<chem>O=C=O</chem>
H_2O	Water	<chem>O</chem>
I_2	Molecular iodine	<chem>II</chem>
I^-	Iodide ion	<chem>[I-]</chem>
H^+	Hydrogen ion	<chem>[H+]</chem>
SO_4^{2-}	Sulphate ion	<chem>[O-]S(=O)(=O)[O-]</chem>
ICN	Cyanogen iodide	<chem>IC#N</chem>
HCN	Hydrogen cyanide	<chem>C#N</chem>
Br_2	Molecular bromine	<chem>BrBr</chem>
Br^-	Bromide ion	<chem>[Br-]</chem>

Species	Name	SMILES
BrCN	Cyanogen bromide	BrC#N
IO ₃ ⁻	Iodate ion	[O-]I(=O)=O
HCOOH	Methanoic (formic) acid	C(=O)O
S ₂ O ₃ ²⁻	Thiosulphate ion	[O-]S(=O)(=O)[S-]
S ₄ O ₆ ²⁻	Tetrathionate ion	[O-]S(=O)(=O)SSS(=O)(=O)[O-]
CHCl ₃	Chloroform	ClC(Cl)Cl
H ₂ SO ₄	Sulphuric acid	OS(=O)(=O)O
K ⁺	Potassium ion, a spectator counterion	[K+]
Na ⁺	Sodium ion, a spectator counterion	[Na+]

The cyanogen halides and hydrogen cyanide have linear heavy-atom arrangements. No stereochemical specification is needed for the species used here.

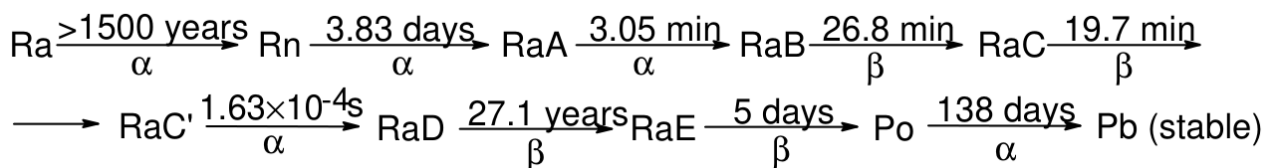
The solution was checked against the official solution.

Problem 3: Avogadro's number from the decay of radium

In 1908 Rutherford together with H.Geiger measured the rate of emission of α -particles (x) by radium (in the nature this element is represented by a single nuclide $^{226}_{88}\text{Ra}$) and found that 1.00 g of radium emits $x = 3.42 \times 10^{10}$ α - particles per second.

In 1911 Rutherford and American physical chemist B.Boltwood measured the rate of formation of helium from radium. This experiment permits to obtain the most accurate value of Avogadro's number available at that time, given that the value of molar volume of ideal gas was well established. To achieve this goal a sample of radium salt purified from decay products and containing $m = 192$ mg of Ra was put into a device and the volume of the evolved helium was measured. After 83 days ($t = 83.0$ days) of the experiment 6.58 mm^3 of He was collected ($V_{\text{He}} = 6.58 \text{ mm}^3$ corrected to 0°C and 1 atm).

To understand the results of this experiment we shall need the kinetic scheme of radioactive decay of Ra which is given below (half-lives are over the arrows, the type of decay is below the arrows).



(RaA - RaE are intermediate products of radon decay).

3.1 Write the first six radioactive decays using a modern notation showing atomic and mass numbers of all nuclei involved.

As a rough first approximation half-lives of all radium decay products, except those of RaD and Po, may be assumed to be negligible compared to the time of measurement t . Using this approximation perform the following calculations.

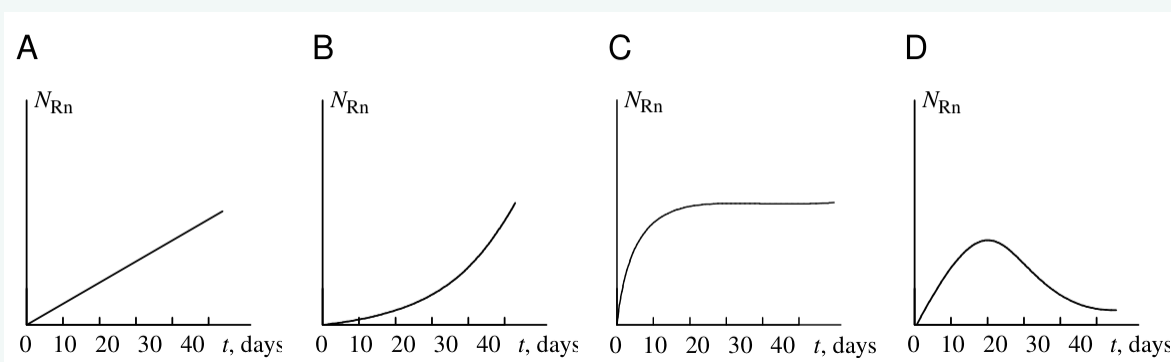
3.2 a) How many helium atoms were formed from each decayed radium atom after 83 days?

b) How many helium atoms were formed in total during the experiment?

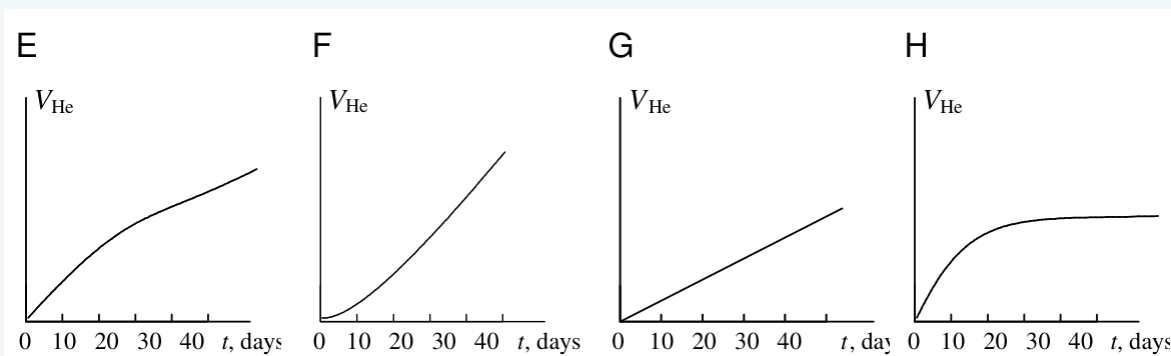
3.3 Calculate an approximate value of Avogadro's number from the above data.

For a more accurate computation of Avogadro's number the half-life of radon $T_{1/2}(\text{Rn}) = 3.83$ days cannot be neglected as it is comparable with the duration of experiment t and not all of radon atoms decayed to the end of experiment.

3.4 Choose which of the plots given below displays the time dependence of the number N_{Rn} of radon atoms in the course of the experiment.



3.5 Choose which of the plots given below shows the time dependence of the volume of helium in the course of the experiment.



3.6 Choose the relation between the decay rate k of any given nuclide and its half-life $T_{1/2}$.

3.7 a) Using a short kinetic scheme



(where k_1 and k_2 are the rate constants of the corresponding reactions) and the plot which you have selected in question 4, write a relation between the number of radon atoms at the end of experiment N'_{Rn} and the number of radium atoms N_{Ra} .

b) Calculate N'_{Rn} using the rate of radium decay given above ($x = 3.42 \times 10^{10}$ α -particles per gram of radium per second).

3.8 How many helium atoms could be formed from radon atoms remaining at the end of experiment N'_{Rn} , if all these atoms had decayed to RaD?

3.9 Using the solutions of the above questions calculate a better approximation to:

- the number of helium atoms formed;
- the Avogadro's number.

Official English text of the problem.

Answers

- 3.1:** The first six decays are $\alpha, \alpha, \alpha, \beta^-, \beta^-, \alpha$, producing successively $^{222}_{86}\text{Rn}$, $^{218}_{84}\text{Po}$, $^{214}_{82}\text{Pb}$, $^{214}_{83}\text{Bi}$, $^{214}_{84}\text{Po}$, and $^{210}_{82}\text{Pb}$. The balanced equations are given below.
- 3.2(a):** 4 helium atoms per decayed radium atom.
- 3.2(b):** 1.88×10^{17} helium atoms.
- 3.3:** $N_A \approx 6.41 \times 10^{23} \text{ mol}^{-1}$.
- 3.4:** Plot **C**.
- 3.5:** Plot **F**.
- 3.6:** $k = \ln 2 / T_{1/2}$.
- 3.7(a):** $k_1 N_{\text{Ra}} \approx k_2 N'_{\text{Rn}}$, hence $N'_{\text{Rn}} \approx (k_1 / k_2) N_{\text{Ra}}$.
- 3.7(b):** $N'_{\text{Rn}} = 3.13 \times 10^{15}$ radon atoms.
- 3.8:** $3N'_{\text{Rn}} = 9.40 \times 10^{15}$ additional helium atoms.
- 3.9(a):** 1.79×10^{17} helium atoms.
- 3.9(b):** $N_A \approx 6.09 \times 10^{23} \text{ mol}^{-1}$.

The numerical Avogadro constants use $V_m = 22.4 \text{ L mol}^{-1}$ at 0°C and 1 atm.

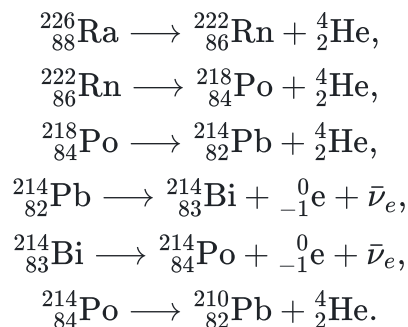
Solution

3.1 — The first six radioactive decays

In an α -decay, the mass number decreases by four and the atomic number decreases by two. In a β^- -decay, the mass number remains unchanged and the atomic number increases by one. Applying these rules successively gives:

Historical designation	Modern nuclide	Name
Ra	$^{226}_{88}\text{Ra}$	Radium-226
Rn	$^{222}_{86}\text{Rn}$	Radon-222
RaA	$^{218}_{84}\text{Po}$	Polonium-218
RaB	$^{214}_{82}\text{Pb}$	Lead-214
RaC	$^{214}_{83}\text{Bi}$	Bismuth-214
RaC'	$^{214}_{84}\text{Po}$	Polonium-214
RaD	$^{210}_{82}\text{Pb}$	Lead-210

The balanced nuclear equations are



Here $\bar{\nu}_e$ is an electron antineutrino. Each equation conserves mass number and electric charge.

An α -particle is a helium-4 nucleus, ${}^4\text{He}^{2+}$, SMILES [4He+2]. After acquiring two electrons, it becomes a neutral helium-4 atom, ${}^4\text{He}$, SMILES [4He]. Thus each emitted α -particle contributes one collected helium atom.

3.2(a) — Helium atoms per decayed radium atom

Under the first approximation, the transformations from radium to RaD occur effectively immediately. There are four α -decays along this part of the chain:

- Radium-226 to radon-222.
- Radon-222 to polonium-218.
- Polonium-218 to lead-214.
- Polonium-214 to lead-210.

RaD has a half-life of 27.1 years, much longer than 83 days, so further decay is neglected at this accuracy. Consequently,

4 helium atoms per decayed radium atom.

3.2(b) — Total helium atoms in the first approximation

The radium half-life exceeds 1500 years, so its activity is effectively constant during 83 days. The sample's radium decay rate is

$$R = mx = (0.192 \text{ g})(3.42 \times 10^{10} \text{ g}^{-1}\text{s}^{-1}) = 6.5664 \times 10^9 \text{ s}^{-1}.$$

The duration is

$$t = 83.0 \times 24 \times 3600 = 7.1712 \times 10^6 \text{ s}.$$

The number of radium atoms that decay is therefore

$$D = Rt = (6.5664 \times 10^9)(7.1712 \times 10^6) = 4.708896768 \times 10^{16}.$$

Multiplying by four,

$$N_{\text{He}}^{(0)} = 4D = 1.8835587072 \times 10^{17},$$

or, to three significant figures,

$$N_{\text{He}}^{(0)} = 1.88 \times 10^{17} \text{ atoms}.$$

3.3 — First approximation to Avogadro's number

Using the standard ideal-gas molar volume at the stated conditions,

$$V_m = 22.4 \text{ L mol}^{-1}, \quad V_{\text{He}} = 6.58 \text{ mm}^3 = 6.58 \times 10^{-6} \text{ L}.$$

The collected amount of helium is

$$n_{\text{He}} = \frac{V_{\text{He}}}{V_m} = \frac{6.58 \times 10^{-6}}{22.4} = 2.9375 \times 10^{-7} \text{ mol.}$$

Hence

$$N_{\text{A}}^{(0)} = \frac{N_{\text{He}}^{(0)}}{n_{\text{He}}} = \frac{1.8835587072 \times 10^{17}}{2.9375 \times 10^{-7}} = \boxed{6.41 \times 10^{23} \text{ mol}^{-1}}.$$

3.4 — Time dependence of the radon inventory

Initially, the purified sample contains no radon. Radium supplies radon at the approximately constant rate R , while radon decays at rate $k_2 N_{\text{Rn}}$. Therefore,

$$\frac{dN_{\text{Rn}}}{dt} = R - k_2 N_{\text{Rn}}, \quad N_{\text{Rn}}(0) = 0.$$

The solution is

$$N_{\text{Rn}}(t) = \frac{R}{k_2} (1 - e^{-k_2 t}).$$

The radon inventory starts at zero, increases with a progressively decreasing slope, and approaches the plateau R/k_2 . Thus the correct plot is

[C].

3.5 — Time dependence of the helium volume

Each radium decay immediately supplies one helium atom. Each radon decay, followed by the short-lived intermediates down to RaD, supplies three more. Thus

$$\frac{dN_{\text{He}}}{dt} = R + 3k_2 N_{\text{Rn}} = R (4 - 3e^{-k_2 t}).$$

The helium production rate increases from R initially to $4R$ once the radon inventory reaches equilibrium. In particular,

$$\frac{d^2 N_{\text{He}}}{dt^2} = 3Rk_2 e^{-k_2 t} > 0.$$

The helium volume is proportional to N_{He} , so it increases with upward curvature and eventually becomes nearly linear. The matching plot is

[F].

The idealized curve has a nonzero initial slope because radium itself emits α -particles from the start.

3.6 — Decay constant and half-life

Radioactive decay follows

$$N(t) = N(0)e^{-kt}.$$

At one half-life,

$$\frac{N(T_{1/2})}{N(0)} = \frac{1}{2} = e^{-kT_{1/2}}.$$

Taking logarithms gives

$$k = \frac{\ln 2}{T_{1/2}}.$$

3.7(a) — Relation between radon and radium inventories

The radon production rate is

$$R = k_1 N_{\text{Ra}}.$$

Under the constant-parent approximation, the finite-time relation is

$$N'_{\text{Rn}} = \frac{k_1 N_{\text{Ra}}}{k_2} (1 - e^{-k_2 t}).$$

At 83.0 days,

$$e^{-k_2 t} = 2^{-83.0/3.83} = 2.99 \times 10^{-7},$$

so radon is effectively at its equilibrium plateau. Production and decay rates are consequently equal:

$$k_1 N_{\text{Ra}} \approx k_2 N'_{\text{Rn}},$$

or

$$N'_{\text{Rn}} \approx \frac{k_1}{k_2} N_{\text{Ra}}.$$

3.7(b) — Number of radon atoms remaining

The radon decay constant is

$$k_2 = \frac{\ln 2}{3.83 \times 86400 \text{ s}} = 2.09466 \times 10^{-6} \text{ s}^{-1}.$$

Therefore,

$$N'_{\text{Rn}} \approx \frac{R}{k_2} = \frac{6.5664 \times 10^9 \text{ s}^{-1}}{2.09466 \times 10^{-6} \text{ s}^{-1}} = \boxed{3.13 \times 10^{15} \text{ atoms}}.$$

Including the finite-time factor leaves this rounded result unchanged.

3.8 — Helium still obtainable from the remaining radon

Between radon-222 and RaD, three α -decays occur. Therefore each remaining radon atom would produce three additional helium atoms upon reaching RaD.

Using the unrounded radon inventory,

$$N_{\text{He,additional}} = 3N'_{\text{Rn}} = 3(3.13483 \times 10^{15}) = \boxed{9.40 \times 10^{15} \text{ atoms}}.$$

The initial radium-to-radon α -particle has already been emitted, so it is not included in this additional yield.

3.9(a) — Improved number of helium atoms formed

The first approximation counted four helium atoms for every radium decay. It therefore included three helium atoms not yet produced for every radon atom still present at the end.

Subtracting this missing production,

$$N_{\text{He}} = 4Rt - 3N'_{\text{Rn}}.$$

Numerically,

$$N_{\text{He}} = 1.8835587072 \times 10^{17} - 9.4044986 \times 10^{15} = 1.7895137 \times 10^{17}.$$

Thus

$$N_{\text{He}} = 1.79 \times 10^{17} \text{ atoms.}$$

3.9(b) — Improved Avogadro constant

The measured amount of helium remains 2.9375×10^{-7} mol. Hence

$$N_A = \frac{N_{\text{He}}}{n_{\text{He}}} = \frac{1.7895137 \times 10^{17}}{2.9375 \times 10^{-7}} = \boxed{6.09 \times 10^{23} \text{ mol}^{-1}}.$$

This incorporates the finite radon lifetime while retaining the problem's approximations for the other decay products.

The solution was checked against the official solution.

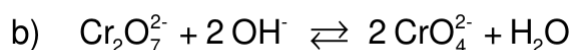
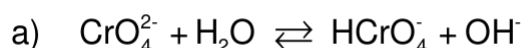
Problem 4: Chromate-dichromate equilibria and precipitation

The precipitation is widely used in classical methods of the quantitative and qualitative analysis for the separation of ions. The possibility of separation is determined by the equilibrium concentrations of all species in a solution to be analyzed.

Potassium dichromate is one of the most widely used precipitating reagents. The following equilibria are established in aqueous solutions of Cr(VI).



4.1 Calculate the equilibrium constants



The ionic product of water $K_W = 1.0 \times 10^{-14}$.

4.2 In what direction shall the equilibrium state 1b shift upon the addition of the following reagents to the aqueous solution of potassium dichromate?

- a) KOH
- b) HCl
- c) BaCl₂
- d) H₂O

The solubility product of BaCrO₄ is 1.2×10^{-10} . BaCr₂O₇ is well soluble in water.

4.3 Calculate the pH value of the following solutions

- a) 0.010 M K_2CrO_4
 b) 0.010 M $\text{K}_2\text{Cr}_2\text{O}_7$
 c) 0.010 M $\text{K}_2\text{Cr}_2\text{O}_7 + 0.100 \text{ M CH}_3\text{COOH}$

Dissociation constant of acetic acid $K_a = 1.8 \times 10^{-5}$.

4.4 Calculate the equilibrium concentrations of the following ions in the solution of 0.010 M $\text{K}_2\text{Cr}_2\text{O}_7 + 0.100 \text{ M CH}_3\text{COOH}$

- a) CrO_4^{2-}
 b) $\text{Cr}_2\text{O}_7^{2-}$

Pb^{2+} and Ag^+ form poorly soluble compounds with chromate and dichromate ions.

The solubility products of these compounds are indicated below.

PbCrO_4	$K_{s1} = 1.2 \times 10^{-14}$
Ag_2CrO_4	$K_{s2} = 1.3 \times 10^{-12}$
$\text{Ag}_2\text{Cr}_2\text{O}_7$	$K_{s3} = 1.1 \times 10^{-10}$

To the aqueous solution of the mixture of $1.0 \times 10^{-3} \text{ M Pb(NO}_3)_2$ and $2.0 \times 10^{-4} \text{ M AgNO}_3$ an equal volume of 0.020 M solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.200 M CH_3COOH was added.

- 4.5** a) Shall Pb^{2+} be precipitated?
 b) Shall Ag^+ be precipitated?
 c) Shall a quantitative separation of Pb^{2+} and Ag^+ ions be thus achieved?

The quantitative precipitation is achieved if the residual concentration of the ion being precipitated is not higher than $1 \times 10^{-6} \text{ M}$.

Official English text of the problem.

Answers

- **4.1(a):** $K = 3.2 \times 10^{-8}$.
- **4.1(b):** $K = 4.4 \times 10^{13}$.
- **4.2(a):** Right, toward chromate.
- **4.2(b):** Left, toward dichromate.
- **4.2(c):** Right, as barium chromate precipitates.
- **4.2(d):** Right; dilution raises the pH and increases the fraction of chromium present as chromate.
- **4.3(a):** pH = 9.25.
- **4.3(b):** pH = 4.20.
- **4.3(c):** pH = 2.87.
- **4.4(a):** $[\text{CrO}_4^{2-}] = 3.0 \times 10^{-6} \text{ M}$.
- **4.4(b):** $[\text{Cr}_2\text{O}_7^{2-}] = 3.7 \times 10^{-3} \text{ M}$.
- **4.5(a):** Yes, as lead(II) chromate, PbCrO_4 .
- **4.5(b):** No; neither silver chromate nor silver dichromate precipitates.

- **4.5(c):** Yes. The residual $[\text{Pb}^{2+}] \approx 4.9 \times 10^{-9} \text{ M}$, including precipitation's effect on the solution equilibria; silver remains dissolved.

Solution

Concentrations are treated as ideal, with water activity equal to unity. All logarithms are decimal.

The molecular and ionic identities used below are:

Species	Name	SMILES
CrO_4^{2-}	Chromate ion	<chem>[O-][Cr](=O)(=O)[O-]</chem>
HCrO_4^-	Hydrogen chromate ion	<chem>O[Cr](=O)(=O)[O-]</chem>
$\text{Cr}_2\text{O}_7^{2-}$	Dichromate ion	<chem>[O-][Cr](=O)(=O)O[Cr](=O)(=O)[O-]</chem>
H^+	Hydrogen ion, representing the aqueous proton	<chem>[H+]</chem>
OH^-	Hydroxide ion	<chem>[OH-]</chem>
H_2O	Water	<chem>O</chem>
CH_3COOH	Acetic acid	<chem>CC(=O)O</chem>
CH_3COO^-	Acetate ion	<chem>CC(=O)[O-]</chem>
K^+	Potassium ion	<chem>[K+]</chem>
Ba^{2+}	Barium(II) ion	<chem>[Ba+2]</chem>
Pb^{2+}	Lead(II) ion	<chem>[Pb+2]</chem>
Ag^+	Silver(I) ion	<chem>[Ag+]</chem>
Cl^-	Chloride ion	<chem>[Cl-]</chem>
NO_3^-	Nitrate ion	<chem>[O-][N+](=O)[O-]</chem>

The chromium oxyanion SMILES specify connectivity and one localized representation of bonding. Each chromium atom has tetrahedral oxygen coordination; dichromate consists of two tetrahedra sharing an oxygen. SMILES do not specify these geometries or aqueous proton solvation. Dot-separated salt SMILES below specify formula-unit composition, not crystal structure.

Write

$$h = [\text{H}^+], \quad x = [\text{HCrO}_4^-], \quad y = [\text{CrO}_4^{2-}], \quad z = [\text{Cr}_2\text{O}_7^{2-}].$$

The supplied equilibria are

$$\text{HCrO}_4^- \rightleftharpoons \text{H}^+ + \text{CrO}_4^{2-}, \quad K_1 = \frac{hy}{x} = 10^{-6.50} = 3.1623 \times 10^{-7},$$

and

$$2 \text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}, \quad K_2 = \frac{z}{x^2} = 10^{1.36} = 22.9087.$$

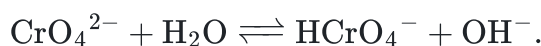
The chromium balance is

$$C_{\text{Cr}} = x + y + 2z,$$

where C_{Cr} counts moles of chromium atoms per litre.

4.1(a)

The requested reaction is



Adding the reverse of the first supplied equilibrium to



gives

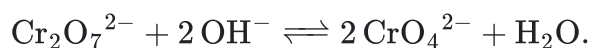
$$K_b = \frac{K_W}{K_1} = \frac{1.0 \times 10^{-14}}{10^{-6.50}} = 10^{-7.50}.$$

Thus

$$\boxed{K_b = 3.2 \times 10^{-8}}.$$

4.1(b)

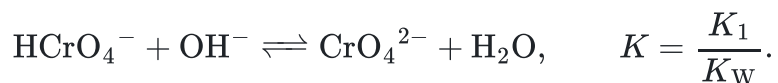
The requested reaction is



Combine



with twice



Therefore

$$K = \frac{1}{K_2} \left(\frac{K_1}{K_W} \right)^2,$$

so

$$\log K = -1.36 + 2(-6.50 + 14.00) = 13.64,$$

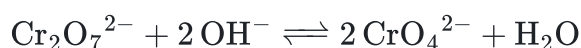
and

$$\boxed{K = 4.4 \times 10^{13}}.$$

4.2(a)

Directions refer to the reaction as written in **4.1(b)**.

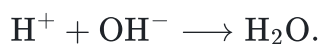
Adding potassium hydroxide increases $[\text{OH}^-]$, driving



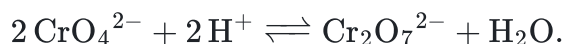
to the right.

4.2(b)

Hydrochloric acid supplies hydrogen ions, which consume hydroxide:

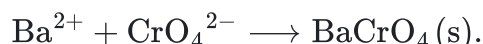


The equilibrium shifts **to the left**. Its acid-driven form is



4.2(c)

Barium ions remove chromate by precipitation:



The solid is **barium chromate**, $[\text{Ba}+2] \cdot [\text{O}-][\text{Cr}](=\text{O})(=\text{O})[\text{O}-]$.

Removal of chromate drives the equilibrium **to the right**. The stated solubility of barium dichromate excludes a competing dichromate precipitation in this treatment.

4.2(d)

Dilution shifts the equilibrium **to the right**.

The potassium dichromate solution is acidic. Dilution lowers h , raises the pH, and therefore increases

$$[\text{OH}^-] = \frac{K_{\text{W}}}{h}.$$

This conclusion can also be checked directly from the coupled balances. For potassium dichromate alone,

$$[\text{K}^+] = C_{\text{Cr}} = x + y + 2z.$$

Electroneutrality gives

$$[\text{K}^+] + h = x + 2y + 2z + [\text{OH}^-],$$

hence

$$h = y + \frac{K_{\text{W}}}{h}.$$

Thus $y = h - K_{\text{W}}/h$. Together with

$$x = \frac{hy}{K_1}, \quad z = K_2 x^2,$$

the chromium balance shows that decreasing C_{Cr} decreases h and y . However,

$$\frac{y}{z} = \frac{K_1^2}{K_2 h^2 y}$$

increases. The chromate-to-dichromate ratio therefore rises. Dilution decreases the absolute chromate concentration while increasing its fraction of total chromium.

4.3(a)

For 0.010 M potassium chromate, hydrolysis produces approximately equal concentrations of hydrogen chromate and hydroxide:



Let $t = [\text{OH}^-]$. Neglecting the small hydrolysis depletion initially,

$$K_{\text{b}} \simeq \frac{t^2}{0.010}.$$

Therefore

$$t \simeq \sqrt{(3.1623 \times 10^{-8})(0.010)} = 1.78 \times 10^{-5} \text{ M}.$$

Consequently,

$$\text{pOH} = 4.75, \quad \boxed{\text{pH} = 9.25}.$$

The hydrolysis fraction is only about 0.18%. Also,

$$z \simeq K_2 t^2 \approx 7.2 \times 10^{-9} \text{ M},$$

so dichromate formation is negligible here. Solving the full balances gives $\text{pH} = 9.2498$.

4.3(b)

For 0.010 M potassium dichromate,

$$C_{\text{Cr}} = 0.020 \text{ M}.$$

As shown in 4.2(d),

$$h = y + [\text{OH}^-] \simeq y.$$

The acid equilibrium therefore gives

$$h^2 \simeq K_1 x.$$

Since y is small relative to the total chromium concentration, first solve

$$x + 2K_2 x^2 \simeq 0.020.$$

The positive root is

$$x \simeq \frac{\sqrt{1 + 8K_2(0.020)} - 1}{4K_2} = 1.2658 \times 10^{-2} \text{ M}.$$

Hence

$$h \simeq \sqrt{(3.1623 \times 10^{-7})(1.2658 \times 10^{-2})} = 6.33 \times 10^{-5} \text{ M},$$

and

$$\boxed{\text{pH} = 4.20}.$$

Retaining all species in the balances gives $h = 6.3196 \times 10^{-5} \text{ M}$ and $\text{pH} = 4.1993$.

4.3(c)

Acetic acid dissociates according to



Its total concentration is $C_A = 0.100 \text{ M}$, so

$$[\text{CH}_3\text{COO}^-] = \frac{K_a C_A}{K_a + h}.$$

Chromium and potassium concentrations remain

$$C_{\text{Cr}} = [\text{K}^+] = 0.020 \text{ M}.$$

Combining their mass and charge balances gives

$$h = y + [\text{CH}_3\text{COO}^-] + \frac{K_W}{h}.$$

The usual weak-acid estimate is

$$h \simeq \sqrt{K_a C_A} = \sqrt{(1.8 \times 10^{-5})(0.100)} = 1.34 \times 10^{-3} \text{ M}.$$

For a check including chromium speciation, solve

$$x + \frac{K_1 x}{h} + 2K_2 x^2 = 0.020,$$

$$h = \frac{K_1 x}{h} + \frac{K_a(0.100)}{K_a + h} + \frac{K_w}{h}.$$

These yield

$$h = 1.33418 \times 10^{-3} \text{ M}, \quad x = 1.26570 \times 10^{-2} \text{ M},$$

and therefore

$$\boxed{\text{pH} = 2.87}.$$

4.4(a)

Using the equilibrium values from 4.3(c),

$$[\text{CrO}_4^{2-}] = \frac{K_1 x}{h} = \frac{(3.1623 \times 10^{-7})(1.26570 \times 10^{-2})}{1.33418 \times 10^{-3}}.$$

Thus

$$\boxed{[\text{CrO}_4^{2-}] = 3.0 \times 10^{-6} \text{ M}}.$$

4.4(b)

Similarly,

$$[\text{Cr}_2\text{O}_7^{2-}] = K_2 x^2 = 22.9087(1.26570 \times 10^{-2})^2 = 3.66998 \times 10^{-3} \text{ M}.$$

Thus

$$\boxed{[\text{Cr}_2\text{O}_7^{2-}] = 3.7 \times 10^{-3} \text{ M}}.$$

4.5(a)

Mixing equal volumes halves every analytical concentration. Before precipitation,

$$[\text{Pb}^{2+}]_0 = 5.0 \times 10^{-4} \text{ M}, \quad [\text{Ag}^+]_0 = 1.0 \times 10^{-4} \text{ M}.$$

The formal dichromate and acetic acid concentrations become 0.010 M and 0.100 M, respectively, matching 4.4.

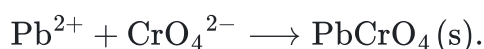
For lead chromate, the initial ion product is

$$Q_{\text{Pb}} = [\text{Pb}^{2+}]_0 [\text{CrO}_4^{2-}] = (5.0 \times 10^{-4})(3.0 \times 10^{-6}) = 1.5 \times 10^{-9}.$$

Since

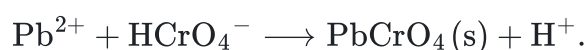
$$Q_{\text{Pb}} \gg K_{s1} = 1.2 \times 10^{-14},$$

lead precipitates:



The solid is **lead(II) chromate**, $[\text{Pb}^{2+}] \cdot [\text{O}^-] [\text{Cr}] (=0) (=0) [\text{O}^-]$.

The chromium equilibria replenish chromate as it is consumed. For example, the net reaction using hydrogen chromate is

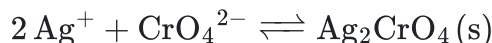


4.5(b)

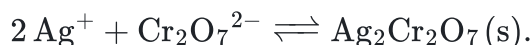
The two possible silver precipitates are:

- **Silver(I) chromate**, $[Ag^+] \cdot [Ag^+] \cdot [O^-][Cr](=O)(=O)[O^-]$.
- **Silver(I) dichromate**, $[Ag^+] \cdot [Ag^+] \cdot [O^-][Cr](=O)(=O)O[Cr](=O)(=O)[O^-]$.

Their precipitation equilibria are



and



For silver chromate,

$$Q_{Ag,Cr} = [Ag^+]_0^2[CrO_4^{2-}] = (1.0 \times 10^{-4})^2(3.0 \times 10^{-6}) = 3.0 \times 10^{-14} < 1.3 \times 10^{-12}.$$

For silver dichromate,

$$Q_{Ag,Di} = [Ag^+]_0^2[Cr_2O_7^{2-}] = (1.0 \times 10^{-4})^2(3.670 \times 10^{-3}) = 3.67 \times 10^{-11} < 1.1 \times 10^{-10}.$$

Thus **neither silver salt precipitates**. The final-equilibrium check below confirms this after lead precipitation.

4.5(c)

Using the excess-reagent approximation, the residual lead concentration is

$$[Pb^{2+}] \simeq \frac{K_{s1}}{[CrO_4^{2-}]} = \frac{1.2 \times 10^{-14}}{3.0 \times 10^{-6}} = 4.0 \times 10^{-9} \text{ M}.$$

This is already far below the required $1.0 \times 10^{-6} \text{ M}$.

For a more complete check, allow for both chromium removal and the acidity released during precipitation. Let

$$p = [Pb^{2+}], \quad s = 5.0 \times 10^{-4} - p,$$

where s is the amount of lead chromate precipitated per litre.

The final chromium balance and lead solubility condition are

$$x + y + 2z = 0.020 - s, \quad py = K_{s1}.$$

Electroneutrality, including the spectator ions, gives

$$h = s + y + \frac{K_a(0.100)}{K_a + h} + \frac{K_W}{h}.$$

Together with $y = K_1x/h$ and $z = K_2x^2$, these equations give

$$h = 1.609 \times 10^{-3} \text{ M},$$

$$y = 2.442 \times 10^{-6} \text{ M}, \quad z = 3.536 \times 10^{-3} \text{ M},$$

and

$$\boxed{p = 4.9 \times 10^{-9} \text{ M} < 1.0 \times 10^{-6} \text{ M}}.$$

With silver remaining at $1.0 \times 10^{-4} \text{ M}$, its final ion products are

$$Q_{Ag,Cr} = 2.44 \times 10^{-14} < K_{s2}, \quad Q_{Ag,Di} = 3.54 \times 10^{-11} < K_{s3}.$$

Therefore **lead is precipitated quantitatively while silver remains dissolved**, achieving the specified separation.

The solution was checked against the official solution.

Problem 5: Potentiometry and spectrophotometry of iron and its cyanide complexes

Potentiometric and spectrophotometric methods are widely used for the determination of equilibrium concentrations and equilibrium constants in solution. Both methods are frequently used in combination to achieve simultaneous determination of several species.

Solution **I** contains a mixture of FeCl_2 (aq) and FeCl_3 (aq), and solution **II** contains a mixture of $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$. The concentrations of iron-containing species satisfy the relations $[\text{Fe}^{2+}]_{\text{I}} = [\text{Fe}(\text{CN})_6^{4-}]_{\text{II}}$ and $[\text{Fe}^{3+}]_{\text{I}} = [\text{Fe}(\text{CN})_6^{3-}]_{\text{II}}$. The potential of platinum electrode immersed into the solution **I** is 0.652 V, while the potential of platinum electrode immersed into solution **II** is 0.242 V. The transmittance of the solution **II** measured relative to the solution **I** at 420 nm is 10.7 % (optical pathlength $l = 5.02$ mm). The complexes $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, and $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ do not absorb light at 420 nm.

Molar absorption at this wavelength $\varepsilon([\text{Fe}(\text{CN})_6^{3-}]) = 1100 \text{ M}^{-1} \text{ cm}^{-1}$.

Standard redox potential for $\text{Fe}(\text{H}_2\text{O})_6^{3+}/\text{Fe}(\text{H}_2\text{O})_6^{2+}$ is 0.771 V.

The factor before the logarithm in the Nernst equation is 0.0590.

5.1 Write Nernst equations for redox systems of

- a) solution **I**,
- b) solution **II**.

5.2 What are the units of the pre-logarithm factor 0.0590 in the Nernst equation?

5.3 Calculate the ratio of the stability constants $\beta[\text{Fe}(\text{CN})_6^{3-}]/\beta[\text{Fe}(\text{CN})_6^{4-}]$.

5.4 What is the absolute range of variation for the following physical values

- a) transmittance T ;
- b) absorbance A .

5.5 Sketch the graphs of concentration dependences satisfying the Lambert-Beer law for

- a) absorbance A ;
- b) transmittance T ;
- c) molar absorption ε .

5.6 Calculate the concentrations of

- a) Fe^{2+} in solution **I**;
- b) Fe^{3+} in solution **II**.

5.7 Mixing solutions **I** and **II** gives intense blue colour. What species is characterized by this colour? Write the reaction equation.

Official English text of the problem.

Answers

- 5.1(a)

$$E_I = 0.771 \text{ V} + (0.0590 \text{ V}) \log_{10} \frac{[\text{Fe}^{3+}]_I}{[\text{Fe}^{2+}]_I}.$$

- 5.1(b)

$$E_{II} = E_{\text{CN}}^{\circ} + (0.0590 \text{ V}) \log_{10} \frac{[\text{Fe}(\text{CN})_6]^{3-}_{II}}{[\text{Fe}(\text{CN})_6]^{4-}_{II}}, \quad E_{\text{CN}}^{\circ} = 0.361 \text{ V}.$$

- 5.2 Volts, V.

- 5.3

$$\frac{\beta[\text{Fe}(\text{CN})_6]^{3-}}{\beta[\text{Fe}(\text{CN})_6]^{4-}} = 8.90 \times 10^6.$$

- 5.4(a) $0 \leq T \leq 1$, or 0% to 100%.
- 5.4(b) $0 \leq A < \infty$; $A \rightarrow +\infty$ as $T \rightarrow 0^+$.
- 5.5(a) $A = \varepsilon l c$: a straight line through the origin, with slope εl .
- 5.5(b) $T = 10^{-\varepsilon l c}$: a decreasing, upward-convex exponential curve, starting at $T = 1$ and approaching zero.
- 5.5(c) ε is independent of concentration: a horizontal line.
- 5.6(a)

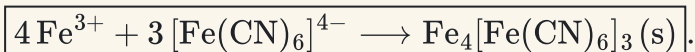
$$[\text{Fe}^{2+}]_I = 0.183 \text{ M}.$$

- 5.6(b) The determined ferricyanide concentration is

$$[\text{Fe}(\text{CN})_6]^{3-}_{II} = 1.76 \times 10^{-3} \text{ M}.$$

This is the concentration of iron(III) **bound in ferricyanide**. The literal free $[\text{Fe}^{3+}]_{II}$ cannot be determined from the supplied data.

- 5.7 Prussian blue, iron(III) hexacyanidoferrate(II), conventionally represented as $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$:



Solution

Use base-10 logarithms and the concentration form of the Nernst equation intended by the problem. In aqueous solution, the shorthand Fe^{2+} and Fe^{3+} denotes hydrated ions.

The names and SMILES of the species used below are:

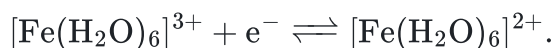
Species	Name	SMILES
Fe^{2+}	Iron(II) ion	[Fe+2]

Species	Name	SMILES
Fe^{3+}	Iron(III) ion	[Fe+3]
H_2O	Water	O
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	Hexaaquairon(II) ion	[Fe+2](<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	Hexaaquairon(III) ion	[Fe+3](<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])
CN^-	Cyanide ion	[C-]#N
$[\text{Fe}(\text{CN})_6]^{4-}$	Hexacyanidoferrate(II), ferrocyanide	[Fe+2](<-[C-]#N)(<-[C-]#N)(<-[C-]#N)(<-[C-]#N)(<-[C-]#N)(<-[C-]#N)
$[\text{Fe}(\text{CN})_6]^{3-}$	Hexacyanidoferrate(III), ferricyanide	[Fe+3](<-[C-]#N)(<-[C-]#N)(<-[C-]#N)(<-[C-]#N)(<-[C-]#N)(<-[C-]#N)

These coordination SMILES use dative-bond arrows. The six-coordinate complexes are octahedral; the cyanide ligands bind to the central iron through carbon. The SMILES shown do not specify the octahedral geometry.

5.1 — Nernst equations

(a) Solution I. The reduction half-reaction is

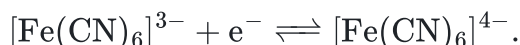


One electron is transferred, so

$$E_{\text{I}} = E_{\text{aq}}^{\circ} + (0.0590 \text{ V}) \log_{10} \frac{[\text{Fe}^{3+}]_{\text{I}}}{[\text{Fe}^{2+}]_{\text{I}}},$$

where $E_{\text{aq}}^{\circ} = 0.771 \text{ V}$.

(b) Solution II. The corresponding half-reaction is



Therefore,

$$E_{\text{II}} = E_{\text{CN}}^{\circ} + (0.0590 \text{ V}) \log_{10} \frac{[[\text{Fe}(\text{CN})_6]^{3-}]_{\text{II}}}{[[\text{Fe}(\text{CN})_6]^{4-}]_{\text{II}}}.$$

The given concentration equalities make the two oxidized-to-reduced concentration ratios equal. Subtracting the two Nernst equations gives

$$E_{\text{I}} - E_{\text{II}} = E_{\text{aq}}^{\circ} - E_{\text{CN}}^{\circ},$$

hence

$$E_{\text{CN}}^{\circ} = 0.771 - (0.652 - 0.242) = \boxed{0.361 \text{ V}}.$$

5.2 — Units of the pre-logarithm factor

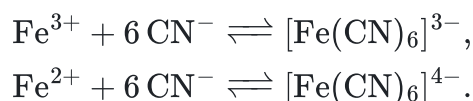
The logarithm is dimensionless, so its coefficient must have the same units as the electrode potential: **volts**.

Equivalently, for a one-electron reaction the coefficient is $2.303RT/F$, with units

$$\frac{\text{J mol}^{-1}}{\text{C mol}^{-1}} = \text{J C}^{-1} = \text{V}.$$

5.3 — Ratio of stability constants

Using aqueous-ion shorthand, the complex-formation equilibria are



Define their overall formation constants by

$$\beta_{\text{III}} = \frac{[\text{Fe}(\text{CN})_6]^{3-}}{[\text{Fe}^{3+}][\text{CN}^{-}]^6}, \quad \beta_{\text{II}} = \frac{[\text{Fe}(\text{CN})_6]^{4-}}{[\text{Fe}^{2+}][\text{CN}^{-}]^6}.$$

Dividing and rearranging gives

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = \frac{[\text{Fe}(\text{CN})_6]^{3-}}{[\text{Fe}(\text{CN})_6]^{4-}} \frac{\beta_{\text{II}}}{\beta_{\text{III}}}.$$

Substitution into the aquo-ion Nernst equation shows that

$$E_{\text{CN}}^{\circ} = E_{\text{aq}}^{\circ} - (0.0590 \text{ V}) \log_{10} \frac{\beta_{\text{III}}}{\beta_{\text{II}}}.$$

Consequently,

$$\log_{10} \frac{\beta_{\text{III}}}{\beta_{\text{II}}} = \frac{0.771 - 0.361}{0.0590} = 6.94915,$$

and

$$\boxed{\frac{\beta_{\text{III}}}{\beta_{\text{II}}} = 8.90 \times 10^6}.$$

Thus cyanide stabilizes iron(III) relative to its free aqueous ion much more strongly than it stabilizes iron(II), lowering the reduction potential of the complexed couple.

5.4 — Ranges of transmittance and absorbance

(a) Transmittance is the ratio of transmitted to incident light intensity:

$$T = \frac{I}{I_0}.$$

For an absorbing sample,

$$\boxed{0 \leq T \leq 1}.$$

The endpoints correspond to complete attenuation and complete transmission.

(b) Absorbance is

$$A = -\log_{10} T.$$

Thus $T = 1$ gives $A = 0$, and A increases without bound as T approaches zero:

$$\boxed{0 \leq A < \infty}.$$

At exactly zero transmission, absorbance is infinite in the limiting sense.

5.5 — Concentration-dependence graphs

At fixed wavelength and optical pathlength, the Lambert-Beer law is

$$A = \epsilon l c, \quad T = 10^{-A} = 10^{-\epsilon l c}.$$

For each graph, place concentration c on the horizontal axis.

(a) Absorbance. The vertical axis is dimensionless A . Draw a straight line through $(0, 0)$, increasing with slope ϵl .

(b) Transmittance. The vertical axis is T , either as a fraction or a percentage. Draw a smooth decreasing curve beginning at $(0, 1)$, or $(0, 100\%)$. It is convex upward and approaches $T = 0$ asymptotically, without reaching zero at a finite concentration.

(c) Molar absorption. The vertical axis is ϵ , in $\text{M}^{-1} \text{cm}^{-1}$. Draw a horizontal line because ϵ is independent of concentration within the Lambert-Beer regime. For ferricyanide at 420 nm, this line is at

$$\epsilon = 1100 \text{ M}^{-1} \text{cm}^{-1}.$$

5.6 — Concentrations

Only ferricyanide absorbs at the stated wavelength. Solution I therefore provides a nonabsorbing reference under the stated assumptions.

Convert the experimental quantities:

$$T = \frac{10.7}{100} = 0.107, \quad l = 5.02 \text{ mm} = 0.502 \text{ cm}.$$

The absorbance is

$$A = -\log_{10}(0.107) = 0.970616.$$

Hence the ferricyanide concentration is

$$[\text{Fe}(\text{CN})_6]^{3-}]_{\text{II}} = \frac{A}{\epsilon l} = \frac{0.970616}{(1100 \text{ M}^{-1} \text{cm}^{-1})(0.502 \text{ cm})} = 1.75773 \times 10^{-3} \text{ M}.$$

By the given equality,

$$[\text{Fe}^{3+}]_{\text{I}} = 1.75773 \times 10^{-3} \text{ M}.$$

(a) Iron(II) in solution I. Its Nernst equation gives

$$\log_{10} \frac{[\text{Fe}^{3+}]_{\text{I}}}{[\text{Fe}^{2+}]_{\text{I}}} = \frac{0.652 - 0.771}{0.0590} = -2.01695,$$

so

$$\frac{[\text{Fe}^{3+}]_{\text{I}}}{[\text{Fe}^{2+}]_{\text{I}}} = 9.61725 \times 10^{-3}.$$

Therefore,

$$[\text{Fe}^{2+}]_{\text{I}} = \frac{1.75773 \times 10^{-3} \text{ M}}{9.61725 \times 10^{-3}} = 0.182768 \text{ M},$$

or

$$\boxed{[\text{Fe}^{2+}]_{\text{I}} = 0.183 \text{ M}}.$$

carboxylic acid D. According to spectral data all hydrogen atoms in this acid except the one in carboxylic group are contained in methyl groups. The density of vapours of D corrected to normal conditions (0 °C, 1 atm) is 9.1 g dm^{-3} .

Compound A is more reactive than compound B in the reaction with cold neutral potassium permanganate. A single compound F is formed from A, and a 1 : 1 mixture of isomers G1 and G2 is formed from B.

6.2 Draw the structural formulae of the compound D both in aqueous solution and in vapour phase.

6.3 Write the formula of compound C.

6.4 Draw the structures of isomers A and B.

6.5 a) Write the reactions of the transformation of A or B into C and D.

b) Write the reactions of the transformation of A and B into F, G1 and G2.

6.6 Compounds G1 and G2 readily react with acetone in the presence of acids and form compounds H1 and H2. Draw the structures of H1 and H2.

6.7 Compounds A and B react with bromine. One of the products of these reactions is non-polar (dipole moment of this molecule is practically equal to zero) and optically inactive. Draw the stereochemical formula of this product, and write the reaction of its formation. Determine the absolute configuration of chiral atoms in this molecule (if any) and mark them according to *R*, *S* nomenclature by *R* or *S* letters.

Alkenes react with peroxyacids with the addition of oxygen to double bond to form a three-member oxygen-containing ring. This epoxidation reaction is highly stereospecific to retain the relative positions of substituents at the bond to which the oxygen atom is attached.

The epoxidation of compound A by peroxyacetic acid yields a single compound K. Under the same conditions B gives a mixture of isomers L1 and L2 (the ratio is 1:1).

6.8 Is the compound K optically active? Draw the stereochemical formula of K. Are the individual compounds L1 and L2 optically active? Draw the stereochemical formulae of L1 and L2.

Official English text of the problem.

Answers

- 6.1:** $\boxed{\text{C}_n\text{H}_{2n}}$. For A and B, $n = 10$.
- 6.2:** D is **2,2-dimethylpropanoic acid (pivalic acid)**, $(\text{CH}_3)_3\text{CCOOH}$. In aqueous solution its neutral molecular form is $\text{CC}(\text{C})(\text{C})\text{C}(=\text{O})\text{O}$. In the vapour it forms a **cyclic hydrogen-bonded dimer**, $\text{CC}(\text{C})(\text{C})\text{C}(=\text{O})\text{O} \cdot \text{CC}(\text{C})(\text{C})\text{C}(=\text{O})\text{O}$, with two reciprocal $\text{O}-\text{H} \cdots \text{O}=\text{C}$ hydrogen bonds. These hydrogen bonds are not encoded by the dot-separated SMILES.
- 6.3:** C is **2,2-dimethylpropanal (pivaldehyde)**, $(\text{CH}_3)_3\text{CCHO}$, molecular formula $\text{C}_5\text{H}_{10}\text{O}$, $\text{CC}(\text{C})(\text{C})\text{C}=\text{O}$.

- **6.4:**

A: (3Z)-2,2,5,5-tetramethylhex-3-ene, CC(C)(C)/C=C\C(C)(C)C; the two tert-butyl groups are on the same side of the double bond.

B: (3E)-2,2,5,5-tetramethylhex-3-ene, CC(C)(C)/C=C/C(C)(C)C; the two tert-butyl groups are on opposite sides.

- **6.5(a):** Reductive ozonolysis of either A or B gives **two molecules of C per alkene molecule**. Oxidation of C gives D. Balanced equations are given below.
- **6.5(b):** Syn dihydroxylation gives:

F: meso-(3R,4S)-2,2,5,5-tetramethylhexane-3,4-diol, CC(C)(C)[C@H](O)[C@H](O)C(C)(C)C, from A.

G1: (3R,4R)-2,2,5,5-tetramethylhexane-3,4-diol, CC(C)(C)[C@H](O)[C@H](O)C(C)(C)C.

G2: (3S,4S)-2,2,5,5-tetramethylhexane-3,4-diol, CC(C)(C)[C@H](O)[C@H](O)C(C)(C)C.

B gives G1 and G2 in a **1:1 racemic mixture**.

- **6.6:**

H1: (4R,5R)-4,5-di-tert-butyl-2,2-dimethyl-1,3-dioxolane, CC1(C)O[C@H](C(C)(C)C)[C@H](C(C)(C)C)O1.

H2: (4S,5S)-4,5-di-tert-butyl-2,2-dimethyl-1,3-dioxolane, CC1(C)O[C@@H](C(C)(C)C)[C@H](C(C)(C)C)O1.

These are enantiomeric cyclic acetals, with the two tert-butyl groups **trans**.

- **6.7:** Anti bromination of **B** gives **meso-(3R,4S)-3,4-dibromo-2,2,5,5-tetramethylhexane**, CC(C)(C)[C@H](Br)[C@H](Br)C(C)(C)C. It is optically inactive. Its staggered conformation with each pair of identical groups anti has a centre of inversion and zero dipole moment by symmetry.

- **6.8:**

K: meso-(2R,3S)-2,3-di-tert-butyloxirane, CC(C)(C)[C@H]1O[C@H]1C(C)(C)C. Its tert-butyl groups are **cis**; it is **optically inactive**.

L1: (2R,3R)-2,3-di-tert-butyloxirane, CC(C)(C)[C@H]1O[C@H]1C(C)(C)C.

L2: (2S,3S)-2,3-di-tert-butyloxirane, CC(C)(C)[C@@H]1O[C@H]1C(C)(C)C.

L1 and L2 have **trans** tert-butyl groups. Each pure enantiomer is optically active; their 1:1 mixture is optically inactive.

Solution

The labels G1/G2 and L1/L2 are assigned here to the indicated enantiomers. Interchanging the labels within either pair is equally valid, provided H1 and H2 remain paired with their respective diols.

6.1 — General formula

For a hydrocarbon C_xH_y , using the conventional atomic masses 12 and 1,

$$\frac{12x}{12x + y} = 0.857, \quad \frac{y}{x} = 12 \left(\frac{1}{0.857} - 1 \right) \simeq 2.00.$$

Thus the empirical formula is CH_2 , and the general molecular formula is

$$\boxed{\text{C}_n\text{H}_{2n}}.$$

Its degree of unsaturation is

$$\text{DBE} = \frac{2n + 2 - 2n}{2} = 1.$$

The ozonolysis establishes that this unsaturation is a carbon–carbon double bond.

6.2 — Identification and structures of D

At normal conditions, the ideal-gas molar volume is approximately $22.4 \text{ dm}^3 \text{ mol}^{-1}$. The apparent molar mass of the vapour particles is therefore

$$\begin{aligned} M_{\text{vapour}} &= \rho V_m \\ &= (9.1 \text{ g dm}^{-3})(22.4 \text{ dm}^3 \text{ mol}^{-1}) \\ &= 203.84 \text{ g mol}^{-1} \simeq 2.0 \times 10^2 \text{ g mol}^{-1}. \end{aligned}$$

Carboxylic acids associate in the vapour through two hydrogen bonds to form cyclic dimers. Taking the vapour species to be this dimer gives a monomer molar mass near 102 g mol^{-1} .

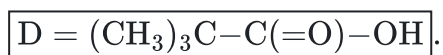
Since the starting hydrocarbons are acyclic monoalkenes, the acid formed from an aldehyde ozonolysis product is a saturated monocarboxylic acid, with general formula $\text{C}_m\text{H}_{2m}\text{O}_2$. Consequently,

$$M_D = (14m + 32) \text{ g mol}^{-1},$$

and

$$14m + 32 \simeq \frac{204}{2} = 102, \quad m = 5.$$

Thus D has molecular formula $\text{C}_5\text{H}_{10}\text{O}_2$. Nine of its ten hydrogen atoms must belong to methyl groups. Those nine hydrogens form three methyl groups, all attached to the remaining non-carboxyl carbon:



This is **2,2-dimethylpropanoic acid**, $\text{CC}(\text{C})(\text{C})\text{C}(=\text{O})\text{O}$.

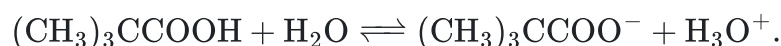
The proposed dimer has molar mass 204 g mol^{-1} , giving

$$\rho_{\text{calculated}} = \frac{204 \text{ g mol}^{-1}}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 9.11 \text{ g dm}^{-3} \simeq 9.1 \text{ g dm}^{-3},$$

in agreement with the given density.

For the requested drawings:

- **Aqueous solution:** draw one solvated $(\text{CH}_3)_3\text{C}-\text{C}(=\text{O})-\text{OH}$ unit. Ordinary weak-acid ionization also occurs:



The ions are **2,2-dimethylpropanoate (pivalate)**, $\text{CC}(\text{C})(\text{C})\text{C}(=\text{O})[\text{O}^-]$, and **hydronium**, $[\text{OH}_3^+]$; water is O .

- **Vapour:** draw two acid molecules with their carboxyl groups facing one another. Each hydroxyl hydrogen points towards the other molecule's carbonyl oxygen. The two reciprocal hydrogen bonds form an eight-membered hydrogen-bonded ring, counting the two hydrogen atoms; the

tert-butyl groups point outward. The dimer SMILES is CC(C)(C)C(=O)O.CC(C)(C)C(=O)O. It represents the two molecular components but does not encode their hydrogen bonds or conformation.

6.3 — Identification of C

Oxidation of an aldehyde replaces its aldehydic hydrogen by a hydroxyl group while retaining the carbon skeleton:

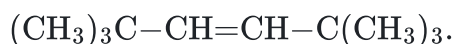


Therefore C is **2,2-dimethylpropanal**, CC(C)(C)C=O:



6.4 — Identification of A and B

Reductive ozonolysis converts each alkene carbon into a carbonyl carbon. Because the only organic product is (CH3)3CCHO, each original alkene carbon must have carried one hydrogen and one tert-butyl group:



The molecular formula is C10H20, consistent with

$$100 \frac{10(12)}{10(12) + 20(1)} = 85.7\%.$$

Cold, neutral permanganate adds two hydroxyl groups **syn**, meaning from the same face of the double bond.

For this symmetrical alkene:

- The **cis**, or *Z*, isomer gives the single meso diol.
- The **trans**, or *E*, isomer gives the *R,R* and *S,S* diols in equal amounts.

Hence

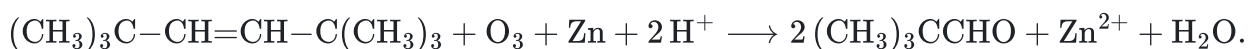


A is **(3Z)-2,2,5,5-tetramethylhex-3-ene**, CC(C)(C)/C=C\C(C)(C)C; B is **(3E)-2,2,5,5-tetramethylhex-3-ene**, CC(C)(C)/C=C/C(C)(C)C.

To draw A, place the tert-butyl groups on the same side of the double bond and the hydrogens on the other side. For B, place the tert-butyl groups on opposite sides. The greater reactivity of A is consistent with the steric strain caused by its two bulky groups occupying the same side of the double bond.

6.5(a) — Conversion into C and D

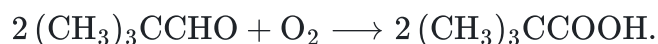
The balanced net ionic equation for reductive ozonolysis, including the zinc/acid work-up, is



This applies to both A and B. Each alkene molecule gives **two identical molecules of C**.

The small species in this equation are **ozone**, O=[O+][O-]; **zinc**, [Zn]; the **hydrogen ion**, [H+]; the **zinc(II) ion**, [Zn+2]; and **water**, O.

The oxidant used to convert C into D is not specified. Using **dioxygen**, $\text{O}=\text{O}$, to express the overall oxidation stoichiometry gives

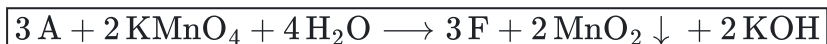


Thus aldehyde C is oxidized to pivalic acid D without changing the carbon skeleton.

6.5(b) — Formation of F, G1 and G2

Cold, neutral permanganate produces a vicinal diol by syn addition, through a cyclic manganese-containing intermediate followed by hydrolysis.

Here A and B have formula $\text{C}_{10}\text{H}_{20}$, and F, G1 and G2 each have formula $\text{C}_{10}\text{H}_{22}\text{O}_2$. The balanced equations, with these compound labels, are

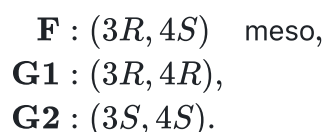


and



The inorganic species are **potassium permanganate**, $[\text{K}^+] \cdot [\text{O}^-] [\text{Mn}] (= \text{O}) (= \text{O}) = \text{O}$; **manganese(IV) oxide**, $[\text{Mn}^{+4}] \cdot [\text{O}^{2-}] \cdot [\text{O}^{2-}]$; and **potassium hydroxide**, $[\text{K}^+] \cdot [\text{OH}^-]$. These ionic SMILES give formula-unit representations rather than crystal structures.

The configurations are



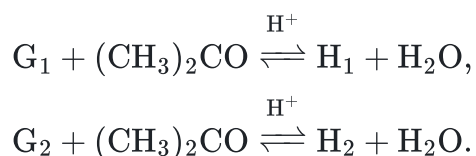
For precise Fischer projections, put the sequence tert-butyl–C3–C4–tert-butyl vertically, with vertical bonds directed away from the observer:

- **F**: both hydroxyl groups on the left and both hydrogens on the right.
- **G1**: the C3 hydroxyl group on the left and the C4 hydroxyl group on the right.
- **G2**: the C3 hydroxyl group on the right and the C4 hydroxyl group on the left.

Addition to either face of A gives the same meso molecule F. Addition to the two faces of B gives the two enantiomers G1 and G2; achiral reaction conditions give them in equal amounts.

6.6 — Structures of H1 and H2

A vicinal diol reacts with **acetone**, $\text{CC}(=\text{O})\text{C}$, under acid catalysis to form a five-membered cyclic ketal, commonly called an **acetoneide**:



Both equations have the molecular-formula balance



The two diol oxygen atoms bond to the former acetone carbonyl carbon. The bonds at the original stereogenic carbons retain their configurations.

For the drawings, construct the five-membered ring in the order O1–C2–O3–C4–C5–O1. Put two methyl groups on C2, and one tert-butyl group and one hydrogen on each of C4 and C5. The tert-butyl groups are **trans**, one above and one below the ring.

- **H1:** (4*R*, 5*R*), CC1(C)O[C@H](C(C)(C)C)[C@H](C(C)(C)C)O1.
- **H2:** (4*S*, 5*S*), CC1(C)O[C@@H](C(C)(C)C)[C@H](C(C)(C)C)O1.

These are the enantiomers of **4,5-di-tert-butyl-2,2-dimethyl-1,3-dioxolane**.

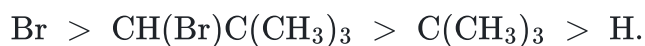
6.7 — Non-polar, optically inactive bromination product

Bromination proceeds by **anti addition**: formation of a bromonium intermediate is followed by attack from the opposite face. Anti addition to the *E* alkene **B** gives the meso dibromide:



Here the reactant is **B**, bromine is BrBr, and the product is **meso-(3*R*,4*S*)-3,4-dibromo-2,2,5,5-tetramethylhexane**, CC(C)(C)[C@H](Br)[C@@H](Br)C(C)(C)C.

At each stereocentre, the CIP priority order is



The adjacent stereogenic carbon outranks the tert-butyl carbon because their next attached-atom lists are respectively (Br, C, H) and (C, C, C).

A precise Fischer projection has tert-butyl–C3–C4–tert-butyl vertically, with **Br on the left and H on the right at both centres**. This assigns

$$\boxed{C3 = R, \quad C4 = S}.$$

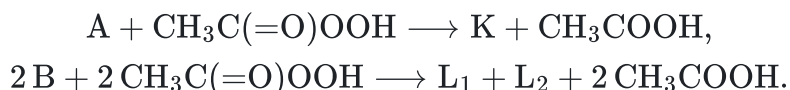
The molecule is meso and therefore optically inactive despite containing two stereogenic carbons.

To represent its non-polar conformation, draw a staggered Newman projection along C3–C4 with the two tert-butyl groups anti, the two bromine atoms anti, and the two hydrogen atoms anti. This conformation has a centre of inversion at the midpoint of C3–C4, so its bond-dipole contributions cancel. The stereochemical SMILES specifies the configuration but does not impose this conformation.

6.8 — Epoxides K, L1 and L2

Epoxidation transfers oxygen to the double bond stereospecifically, retaining the relative positions of the substituents. The reagents and accompanying product are **peroxoacetic acid (peracetic acid)**, CC(=O)OO, and **acetic acid**, CC(=O)O.

With K, L1 and L2 each having formula C₁₀H₂₀O, the balanced reactions are



For precise stereochemical drawings, place the oxirane triangle in the plane of the page with O at the top, C2 at the lower left and C3 at the lower right. A solid wedge points towards the observer; a dashed wedge points away.

Compound	Tert-butyl group at C2	Tert-butyl group at C3	Configuration	Optical activity
K	Solid wedge	Solid wedge	(2 <i>R</i> , 3 <i>S</i>), cis, meso	Inactive
L1	Solid wedge	Dashed wedge	(2 <i>R</i> , 3 <i>R</i>), trans	Active as a pure enantiomer
L2	Dashed wedge	Solid wedge	(2 <i>S</i> , 3 <i>S</i>), trans	Active as a pure enantiomer

At each carbon, the hydrogen points in the opposite direction to its tert-butyl group.

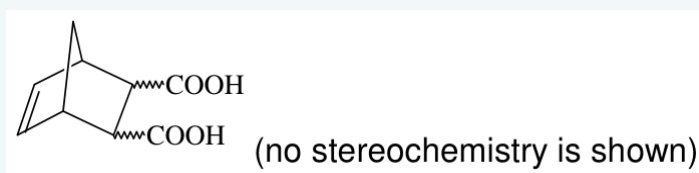
K is **meso-(2*R*,3*S*)-2,3-di-tert-butyloxirane**, CC(C)(C)[C@H]1O[C@H]1C(C)(C)C. Its mirror plane passes through oxygen and the midpoint of the carbon–carbon bond, perpendicular to the ring plane. Therefore K is achiral and optically inactive.

L1 and L2 are respectively **(2*R*,3*R*)-** and **(2*S*,3*S*)-2,3-di-tert-butyloxirane**, CC(C)(C)[C@H]1O[C@@H]1C(C)(C)C and CC(C)(C)[C@@H]1O[C@H]1C(C)(C)C. They are non-superimposable mirror images. Each enantiomer is optically active individually, while the 1:1 mixture formed from B has zero net optical rotation.

The solution was checked against the official solution.

Problem 7: Stereochemistry of 5-norbornene-2,3-dicarboxylic acids

Stereochemistry of organic compounds can sometimes be determined by studying their chemical behaviour. The stereochemical configuration of one of the isomers of 5-norbornene-2,3-dicarboxylic acids (compound **X**)



was established by the following experiments.

On heating this substance decomposes producing water and a new compound **Y**. Compound **Y** slowly dissolves in excess of aqueous NaOH with the formation of product X_1 same to that is formed in the reaction of **X** with NaOH. The resulting solution of X_1 is treated by I_2 to give compounds containing iodine. Acidification of the solution leads to a mixture of two isomeric compounds, **A** and **B** in the 3 : 1 ratio. The titration of 0.3913 g of compound **A** by 0.1000 M aqueous solution of NaOH in the presence of phenolphthalein takes 12.70 cm³ of alkali. The same amount of 0.1000 M solution of NaOH is required for the titration of 0.3913 g of compound **B**. On heating compound **A** slowly transforms into compound **C**, which contains no iodine and is able to react with water. Under the same conditions compound **B** does not undergo this transformation, but on heating with hydrochloric acid slowly transforms into **A**.

All reactions must be written as balance equations. No mechanisms are required.

7.1 Mark by asterisks (*) the asymmetric carbon atoms in the structure of 5-norbornene-2,3-dicarboxylic acids.

7.2 Draw the stereochemical formulas of all stereoisomers of compound **X**, and the structures of products of their dehydration in those cases when it is possible.

7.3 Write the reactions of NaOH with a stereoisomer of **X** and a stereoisomer of **Y**.

7.4 Calculate the molar mass of compound **A**. Write the reactions leading from X_1 to **A**.

7.5 Write the reaction of the formation of **C** from **A** and the reaction of **C** with water.

7.6 Draw the stereochemical formula of compound **X** which satisfies all of the data given in the problem.

7.7 Write the reactions leading from **B** to **A**.

7.8 Are the compounds **A** and **B** diastereomers?

Official English text of the problem.

Answers

- **7.1:** Mark **C1, C2, C3 and C4**, including both bridgehead carbon atoms.
- **7.2:** There are **four stereoisomers**: the meso cis-endo,endo and cis-exo,exo forms, and a pair of trans enantiomers. Each cis form gives its corresponding five-membered cyclic anhydride; neither trans form can do so without changing configuration. Their stereochemical SMILES are given below.
- **7.3:** Both the diacid and its anhydride consume two equivalents of sodium hydroxide to give the same disodium dicarboxylate, X_1 .
- **7.4:** $M(A) = 308.1 \text{ g mol}^{-1}$. **A** is a five-membered iodolactone with one remaining carboxylic acid group.
- **7.5:** **A** loses hydrogen iodide to form the **2,6:3,5-dilactone C**. Complete hydrolysis of **C** consumes two water molecules and gives the corresponding endo,endo-dihydroxy diacid.
- **7.6:** **X** is **cis-endo,endo-5-norbornene-2,3-dicarboxylic acid**, O=C(O)[C@@H]1[C@H](C(=O)O)[C@@H]2C=C[C@H]1C2.
- **7.7:** Acid-catalysed hydrolysis opens the six-membered lactone of **B**; subsequent esterification using the other carboxyl group produces the five-membered lactone **A**.
- **7.8:** **No**. **A** and **B** are constitutional isomers, differing in which carboxyl group forms the lactone.

Solution

Throughout, use the original norbornene numbering: the bridgeheads are **C1 and C4**, and the three bridges are



The carboxyl groups are attached to C2 and C3. An **endo** carboxyl group points toward the other two-carbon bridge of the cage; an **exo** group points away from it.

A **2,6-lactone**, for example, means that the carboxyl group attached to C2 forms an ester linkage to an oxygen attached to C6. The carboxyl carbon is an additional atom, not C2 itself.

For A, B, their sodium salts and the iodohydroxy intermediate below, each SMILES specifies one enantiomer. The reactions starting from achiral X give the corresponding racemic products.

The small molecules and salts used in the equations are: water O; sodium hydroxide [Na+].[OH-]; iodine I₂; sodium iodide [Na+].[I-]; hydrochloric acid, represented in aqueous ionic form, [H+].[Cl-]; sodium chloride [Na+].[Cl-]; and hydrogen iodide I.

7.1 — Asymmetric carbon atoms

The parent compound is **5-norbornene-2,3-dicarboxylic acid**, with unspecified stereochemistry:

O=C(O)C1C(C(=O)O)C2C=CC1C2

Place asterisks on

C1*, C2*, C3*, C4*.

C2 and C3 each carry hydrogen, a carboxyl group and two different paths through the cage. Each bridgehead, C1 and C4, carries hydrogen and three distinguishable carbon paths.

C5 and C6 are trigonal alkene carbons; C7 bears two hydrogen atoms.

7.2 — All stereoisomers and their dehydration products

The rigid bridge system constrains the bridgehead configurations; the four asymmetric carbons do not give 2⁴ independently accessible configurations.

Stereoisomer of 5-norbornene-2,3-dicarboxylic acid	Stereochemical description	SMILES
cis-endo,endo	Both carboxyl groups endo; meso	<chem>O=C(O)[C@@H]1[C@H](C(=O)O)[C@@H]2C=C[C@H]1C2</chem>
cis-exo,exo	Both carboxyl groups exo; meso	<chem>O=C(O)[C@@H]1[C@H](C(=O)O)[C@H]2C=C[C@@H]1C2</chem>
trans-endo,exo	C2 carboxyl endo and C3 carboxyl exo in the fixed numbered cage	<chem>O=C(O)[C@H]1[C@H](C(=O)O)[C@H]2C=C[C@@H]1C2</chem>
trans-exo,endo	Mirror image of the preceding trans isomer	<chem>O=C(O)[C@@H]1[C@@H](C(=O)O)[C@H]2C=C[C@@H]1C2</chem>

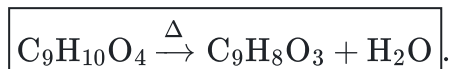
Thus there are **two achiral cis isomers and two enantiomeric trans isomers**.

In either cis isomer, the neighbouring carboxyl groups can form a five-membered cyclic anhydride. The original configurations at C2 and C3 are retained.

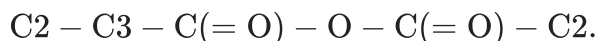
Starting acid	Dehydration product	SMILES
cis-endo,endo	cis-endo,endo-5-norbornene-2,3-dicarboxylic anhydride , Y _{endo}	<chem>O=C1OC(=O)[C@H]2[C@@H]1[C@H]2C1</chem>

Starting acid	Dehydration product	SMILES
cis-exo,exo	cis-exo,exo-5-norbornene-2,3-dicarboxylic anhydride, Y_{exo}	<chem>O=C1OC(=O)[C@H]2[C@@H]1[C@@H]2C=C[C@H]2C1</chem>

For each cis isomer, the balanced dehydration equation is



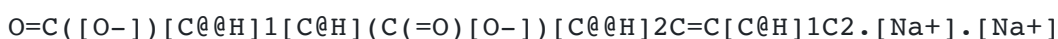
To sketch either product, connect the two carboxyl carbonyl carbons through a single anhydride oxygen, giving the ring sequence



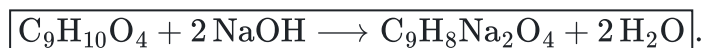
The trans carboxyl groups lie on opposite faces and cannot form this small anhydride ring without a configurational change.

7.3 — Reactions with sodium hydroxide

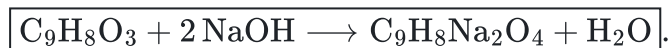
Choose the cis-endo,endo acid and its anhydride. Both produce **disodium cis-endo,endo-5-norbornene-2,3-dicarboxylate**, X_1 :



Neutralization of the diacid gives



Hydrolysis and neutralization of the anhydride give



The corresponding exo acid and exo anhydride likewise give the same exo dicarboxylate as one another.

7.4 — Molar mass of A and its formation from X_1

Iodination permits intramolecular lactone formation: one carboxyl group becomes an ester, while the other remains available for acid–base titration. Thus A and B are monobasic iodolactones.

The amount of sodium hydroxide used is

$$n(\text{NaOH}) = (0.1000 \text{ mol L}^{-1})(12.70 \times 10^{-3} \text{ L}) = 1.270 \times 10^{-3} \text{ mol} .$$

Since one mole of A consumes one mole of sodium hydroxide at the acid–base endpoint,

$$M(A) = \frac{0.3913 \text{ g}}{1.270 \times 10^{-3} \text{ mol}} = \boxed{308.1 \text{ g mol}^{-1}} .$$

Strictly, the titration first gives the acid equivalent mass; its equality to the molar mass follows from the presence of **one free carboxyl group**.

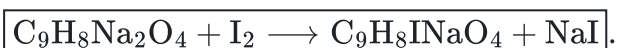
The formula is $\text{C}_9\text{H}_9\text{IO}_4$, consistent with the original diacid incorporating one iodine atom and losing one carboxyl hydrogen during iodolactonization.

The structures established by the subsequent heating and hydrolysis tests are:

Compound	Name and precise connectivity	SMILES
A	2,6-lactone of exo-5-iodo-endo-6-hydroxynorbornane-endo-2,endo-3-dicarboxylic acid. A five-membered γ -lactone; the C3 carboxyl group remains free.	<chem>O=C1O[C@@H]2[C@@H](I)[C@H]3C[C@@H]2[C@@H]1[C@H]3C(=O)O</chem>
B	3,6-lactone of exo-5-iodo-endo-6-hydroxynorbornane-endo-2,endo-3-dicarboxylic acid. A six-membered δ -lactone; the C2 carboxyl group remains free.	<chem>O=C(O)[C@@H]1[C@H]2C[C@@H]3[C@H](I)[C@H]2OC(=O)[C@@H]31</chem>
A_{Na}	Sodium carboxylate of A	<chem>O=C1O[C@@H]2[C@@H](I)[C@H]3C[C@@H]2[C@@H]1[C@H]3C(=O)[O-].[Na+]</chem>
B_{Na}	Sodium carboxylate of B	<chem>O=C([O-])[C@@H]1[C@H]2C[C@@H]3[C@H](I)[C@H]2OC(=O)[C@@H]31.[Na+]</chem>

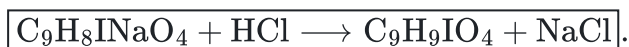
For A, the lactone ring contains C2, C1, C6, the ester oxygen and the C2 carboxyl carbon: **five atoms**.
For B, the corresponding ring through C3, C2, C1 and C6 contains **six atoms**.

Formation of the sodium iodolactone from X_1 is balanced as



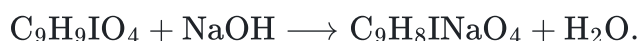
The organic product on the right is A_{Na} or B_{Na} , according to which carboxyl group closes the ring.

Using hydrochloric acid to express the acidification explicitly,



The resulting A:B ratio is the stated **3:1**.

For either isolated iodolactone, the acid–base titration is



Both therefore have the same molar mass and consume the same amount of alkali for equal masses.

7.5 — Formation of C and its reaction with water

In A, the remaining endo carboxyl group at C3 is suitably placed to form a second five-membered lactone involving C5. The exo iodine at C5 is replaced by an endo ester oxygen, with loss of hydrogen iodide.

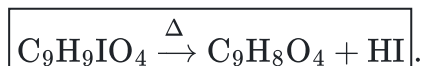
The product **C** is the **2,6:3,5-dilactone of endo-5,endo-6-dihydroxynorbornane-endo-2,endo-3-dicarboxylic acid**:



It has formula $\text{C}_9\text{H}_8\text{O}_4$. Its two lactone connections are:

- the C2 carboxyl group to the endo oxygen at C6;
- the C3 carboxyl group to the endo oxygen at C5.

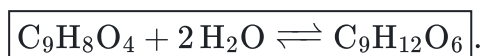
The balanced thermal reaction is



Complete hydrolysis opens both ester rings, producing **endo-5,endo-6-dihydroxynorbornane-endo-2,endo-3-dicarboxylic acid**, designated **E**:

O=C(O)[C@@H]1[C@H]2C[C@H]([C@@H](O)[C@H]2O)[C@@H]1C(=O)O

The balanced hydrolysis equation is



In a drawing of E, both hydroxyl groups and both carboxyl substituents are endo.

7.6 — Identification of X

Anhydride formation establishes that the two carboxyl groups are **cis**, leaving the endo,endo and exo,exo possibilities.

Formation of the lactone connections to C5 and C6 requires the carboxyl groups to face inward toward that bridge. The formation of the second lactone in C establishes the necessary orientation of the remaining carboxyl group as well.

Consequently,



Its stereochemical SMILES is

O=C(O)[C@@H]1[C@H](C(=O)O)[C@@H]2C=C[C@H]1C2

To draw X, retain the original norbornene skeleton and its C5=C6 double bond, place **both carboxyl groups endo**, and place the hydrogens on C2 and C3 exo. Its dehydration product is Y_{endo} from part 7.2.

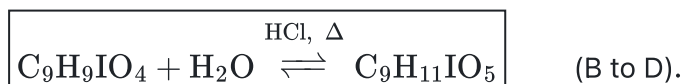
7.7 — Conversion of B into A

B already contains the **3,6-lactone** connection. Its free C2 carboxyl group is not positioned to give the second five-membered lactone formed from A, explaining the different thermal behaviour.

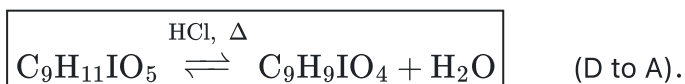
In hot aqueous hydrochloric acid, B can first undergo lactone hydrolysis. This gives **exo-5-iodo-endo-6-hydroxynorbornane-endo-2,endo-3-dicarboxylic acid**, designated **D**:

O=C(O)[C@@H]1[C@H]2C[C@H]([C@H](I)[C@H]2O)[C@@H]1C(=O)O

The balanced opening of B is



The C2 carboxyl group of D can then esterify the endo hydroxyl group at C6, forming the five-membered 2,6-lactone A:



Water cancels from the overall conversion, and hydrochloric acid acts catalytically. The iodine position and the configurations of the cage carbon atoms are retained; the carboxyl group participating in the ester linkage changes.

7.8 — Are A and B diastereomers?

No. Diastereomers must have the same atom connectivity.

In A, the carboxyl group at **C2** forms the ester bond to the oxygen at C6. In B, the carboxyl group at **C3** forms that bond. Their lactone rings consequently contain five and six atoms, respectively.

Thus A and B are **constitutional isomers**, specifically regioisomeric iodolactones.

The solution was checked against the official solution.