

IChO 2008

Theory problems and solutions · Budapest, Hungary · 9 theory problems with complete solutions

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Problem 1: An acid solution with a damaged label

The label on a bottle containing a dilute aqueous solution of an acid became damaged. Only its concentration was readable. A pH meter was nearby, and a quick measurement showed that the hydrogen ion concentration is equal to the value on the label.

1.1 Give the formulae of four acids that could have been in the solution if the pH changed one unit after a tenfold dilution.

1.2 Could it be possible that the dilute solution contained sulfuric acid?

Sulfuric acid: $pK_{a2} = 1.99$

☐ Yes ☐ No

If yes, calculate the pH (or at least try to estimate it) and show your work.

1.3 Could it be possible that the solution contained acetic acid?

Acetic acid: $pK_a = 4.76$

☐ Yes ☐ No

If yes, calculate the pH (or at least try to estimate it) and show your work.

1.4 Could it be possible that the solution contained EDTA (ethylene diamino tetraacetic acid)? You may use reasonable approximations.

EDTA: $pK_{a1} = 1.70$, $pK_{a2} = 2.60$, $pK_{a3} = 6.30$, $pK_{a4} = 10.60$

☐ Yes ☐ No

If yes, calculate the concentration.

Official English text of the problem.

Answers

- 1.1** Four suitable examples are hydrochloric acid, HCl , Cl ; hydrobromic acid, HBr , Br ; hydroiodic acid, HI , I ; and nitric acid, HNO_3 , $O=[N^+]([O^-])O$. The pH **increases by one unit**.
- 1.2** **No**, for dilute sulfuric acid.
- 1.3** **Yes**. At $25^\circ C$, $pH \approx 6.25$.

- **1.4 Yes.** $c(\text{EDTA}) \approx 7.1 \times 10^{-3} \text{ mol dm}^{-3}$, corresponding to $pH \approx 2.15$.

Solution

Let C denote the analytical concentration of the acid and $h = [\text{H}^+]$. The label and measurement give

$$h = C.$$

The additional dilution condition belongs to **1.1**. Parts **1.2–1.4** test the original equality.

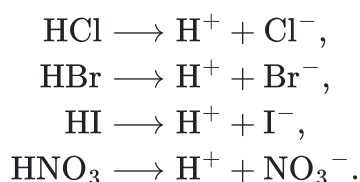
Use ideal dilute-solution equilibria and, for numerical calculations involving water, the standard value at 25°C ,

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}.$$

Here hydrogen ion, H^+ , has SMILES `[H+]`; hydroxide ion, OH^- , `[OH-]`; and water, H_2O , `O`. The notation H^+ represents the aqueous proton; these SMILES do not depict its hydration.

1.1 — Four suitable acids

A strong monoprotic acid dissociates essentially completely. The four examples in the answer undergo



The conjugate bases are chloride, `[Cl-]`; bromide, `[Br-]`; iodide, `[I-]`; and nitrate, `[O-][N+](=O)[O-]`.

Provided water's contribution is negligible both before and after dilution,

$$[\text{H}^+] \approx C, \quad [\text{H}^+]_{\text{diluted}} \approx \frac{C}{10}.$$

Consequently,

$$\Delta pH = -\log_{10} \left(\frac{[\text{H}^+]_{\text{diluted}}}{[\text{H}^+]_{\text{initial}}} \right) = -\log_{10} \frac{1}{10} = \boxed{+1}.$$

Thus all four acids satisfy the observations to the usual strong-acid approximation.

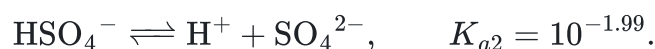
1.2 — Sulfuric acid

Sulfuric acid, H_2SO_4 , has SMILES `OS(=O)(=O)O`. Its ions are hydrogen sulfate, HSO_4^- , `OS(=O)(=O)[O-]`, and sulfate, SO_4^{2-} , `[O-]S(=O)(=O)[O-]`.

In a dilute solution, the first dissociation is effectively complete:



The second dissociation also produces hydrogen ions:



Neglecting undissociated sulfuric acid, the mass balance is

$$C = [\text{HSO}_4^-] + [\text{SO}_4^{2-}],$$

whereas electroneutrality requires

$$h = [\text{HSO}_4^-] + 2[\text{SO}_4^{2-}] + [\text{OH}^-].$$

Subtracting gives

$$h - C = [\text{SO}_4^{2-}] + [\text{OH}^-] > 0.$$

In particular, the finite second dissociation produces sulfate and additional hydrogen ions. Therefore $h = C$ cannot hold in this dilute-solution model.

No

1.3 — Acetic acid

Acetic acid, CH_3COOH , has SMILES `CC(=O)O`; acetate, CH_3COO^- , has SMILES `CC(=O)[O-]`.

The relevant equilibria are



and



It is essential to retain water autoionization here. The mass and charge balances are

$$C = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]$$

and

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

Imposing $C = h$ gives

$$[\text{CH}_3\text{COOH}] = [\text{OH}^-] = \frac{K_w}{h},$$

and hence

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

Substituting into the acid-dissociation expression,

$$K_a = \frac{h[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{h(h - K_w/h)}{K_w/h},$$

we obtain

$h^3 - K_w h - K_a K_w = 0.$

With $K_a = 10^{-4.76}$, the positive physical root is

$$h = C \approx 5.64 \times 10^{-7} \text{ mol dm}^{-3},$$

so

$pH \approx 6.25.$

A useful estimate follows by neglecting $K_w h$ in the cubic:

$$h \approx (K_a K_w)^{1/3},$$

giving

$$pH \approx \frac{pK_a + pK_w}{3} = \frac{4.76 + 14.00}{3} = 6.253.$$

The numerical root also gives

$$[\text{CH}_3\text{COOH}] = [\text{OH}^-] \approx 1.77 \times 10^{-8} \text{ mol dm}^{-3},$$

$$[\text{CH}_3\text{COO}^-] \approx 5.46 \times 10^{-7} \text{ mol dm}^{-3}.$$

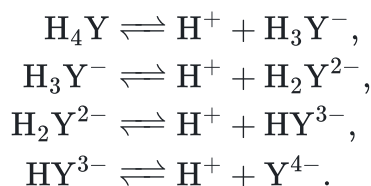
Thus the undissociated acid concentration exactly matches the hydroxide concentration, allowing the total hydrogen ion concentration to equal the analytical acid concentration.

Yes

1.4 — EDTA

Write ethylenediaminetetraacetic acid as H_4Y . Its conventional neutral structural SMILES is O=C(O)CN(CC(=O)O)CCN(CC(=O)O)CC(=O)O.

The successive equilibria are



Names and representative SMILES for the ions are:

Ion	Name	Representative SMILES
H_3Y^-	Trihydrogen edetate	<chem>O=C(O)C[NH+](CC(=O)[O-])CC[NH+](CC(=O)[O-])CC(=O)[O-]</chem>
H_2Y^{2-}	Dihydrogen edetate	<chem>[O-]C(=O)C[NH+](CC(=O)[O-])CC[NH+](CC(=O)[O-])CC(=O)[O-]</chem>
HY^{3-}	Hydrogen edetate	<chem>[O-]C(=O)CN(CC(=O)[O-])CC[NH+](CC(=O)[O-])CC(=O)[O-]</chem>
Y^{4-}	Edetate	<chem>[O-]C(=O)CN(CC(=O)[O-])CCN(CC(=O)[O-])CC(=O)[O-]</chem>

EDTA has zwitterionic protonation microstates. The equilibrium symbols denote the total concentration at each protonation level; the given macroscopic pK_a values do not specify a unique proton arrangement.

Initially neglect the third and fourth dissociations and water autoionization; these approximations will be checked below. The mass balance becomes

$$C = [\text{H}_4\text{Y}] + [\text{H}_3\text{Y}^-] + [\text{H}_2\text{Y}^{2-}],$$

and the charge balance is

$$h = [\text{H}_3\text{Y}^-] + 2[\text{H}_2\text{Y}^{2-}].$$

Since $h = C$, subtraction gives

$$[\text{H}_4\text{Y}] = [\text{H}_2\text{Y}^{2-}].$$

The first two dissociation constants satisfy

$$K_{a1} = \frac{h[\text{H}_3\text{Y}^-]}{[\text{H}_4\text{Y}]}, \quad K_{a2} = \frac{h[\text{H}_2\text{Y}^{2-}]}{[\text{H}_3\text{Y}^-]}.$$

Multiplying and using the equality above,

$$K_{a1}K_{a2} = h^2 \frac{[\text{H}_2\text{Y}^{2-}]}{[\text{H}_4\text{Y}]} = h^2.$$

Therefore

$$pH = \frac{pK_{a1} + pK_{a2}}{2} = \frac{1.70 + 2.60}{2} = 2.15.$$

As $C = h$,

$$C = 10^{-2.15} \text{ mol dm}^{-3} \approx \boxed{7.1 \times 10^{-3} \text{ mol dm}^{-3}}.$$

The neglected dissociations are indeed small:

$$\frac{[HY^{3-}]}{[H_2Y^{2-}]} = \frac{K_{a3}}{h} = 10^{-6.30+2.15} \approx 7.1 \times 10^{-5},$$

$$\frac{[Y^{4-}]}{[HY^{3-}]} = \frac{K_{a4}}{h} = 10^{-10.60+2.15} \approx 3.5 \times 10^{-9}.$$

Also,

$$[OH^-] = \frac{K_w}{h} \approx 1.4 \times 10^{-12} \text{ mol dm}^{-3},$$

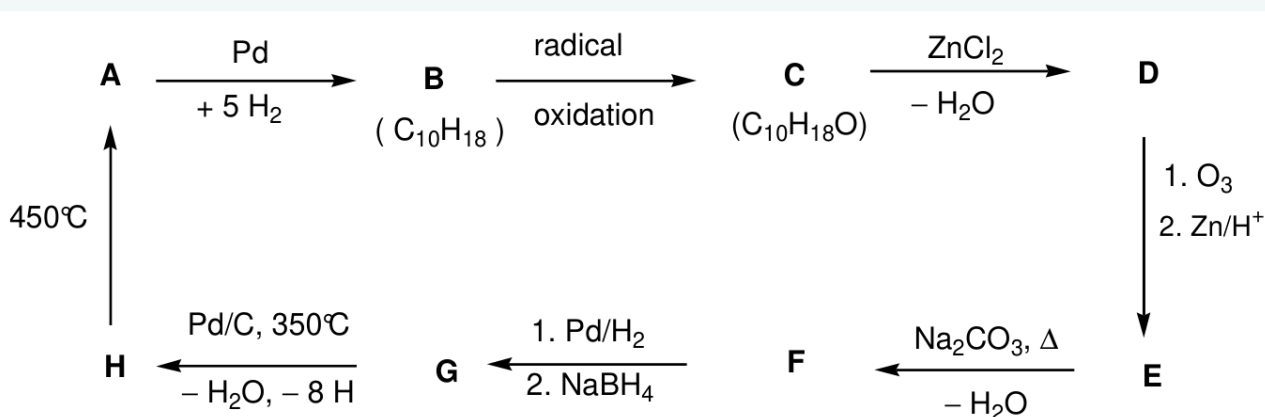
which is negligible. The approximation is therefore fully adequate.

Yes

The solution was checked against the official solution.

Problem 2: From an aromatic hydrocarbon to compounds A-H

Determine the structure of the compounds **A - H** (stereochemistry is not expected), based on the information given in the following reaction scheme:



Hints:

- A** is a well-known aromatic hydrocarbon.
- A hexane solution of **C** reacts with sodium (gas evolution can be observed), but **C** does not react with chromic acid.
- ^{13}C NMR spectroscopy shows that **D** and **E** contain only two kinds of CH_2 groups.
- When a solution of **E** is heated with sodium carbonate an unstable intermediate forms at first, which gives **F** on dehydration.

Answers

Problem 2 — structures A–H:

- **A:** Naphthalene — c1ccc2ccccc2c1
- **B:** Decalin (bicyclo[4.4.0]decane) — C1CCC2CCCCC2C1
- **C:** Bicyclo[4.4.0]decan-1-ol — OC12CCCCC1CCCC2
- **D:** Bicyclo[4.4.0]dec-1(6)-ene — C1CCCC2=C1CCCC2
- **E:** Cyclodecane-1,6-dione — O=C1CCCCC(=O)CCCC1
- **F:** Bicyclo[5.3.0]dec-1(7)-en-2-one — O=C1CCCCC2=C1CCC2
- **G:** Bicyclo[5.3.0]decan-2-ol — OC1CCCCC2C1CCC2
- **H:** Azulene — C1=CC=C2C=CC=C2C=C1

Stereochemistry is omitted as requested. The SMILES for **H** gives a Kekulé representation of its aromatic structure.

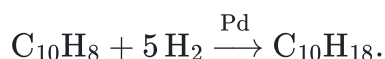
Solution

A and B — aromatic hydrocarbon and complete hydrogenation

Addition of five equivalents of hydrogen gives $C_{10}H_{18}$, so **A** has molecular formula $C_{10}H_8$. Its degree of unsaturation is

$$DBE = \frac{2(10) + 2 - 8}{2} = 7.$$

Naphthalene accounts for these seven units through two rings and five double bonds. Complete hydrogenation gives **B**, decalin, retaining the two fused six-membered rings:



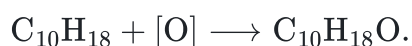
The NMR and ozonolysis clues below confirm this choice of carbon skeleton; the molecular formula alone would not uniquely identify naphthalene.

C — oxidation at a bridgehead

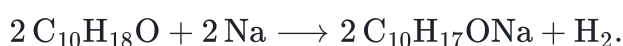
Reaction with sodium, with hydrogen evolution, indicates an alcohol. Resistance to chromic acid identifies it as a **tertiary alcohol**, whose hydroxyl-bearing carbon has no hydrogen available for ordinary alcohol oxidation.

The only tertiary carbon atoms in decalin are its two equivalent bridgeheads. Consequently, **C** is bicyclo[4.4.0]decan-1-ol, with the hydroxyl group on a bridgehead.

Using [O] for one oxygen-atom equivalent supplied by the unspecified radical oxidant, the transformation is



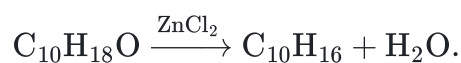
Its reaction with sodium is



The organic product is sodium bicyclo[4.4.0]decan-1-olate, $[\text{Na}^+] \cdot [\text{O}^-]\text{C12CCCCC1CCCC2}$; the gas is hydrogen, $[\text{H}][\text{H}]$.

D — dehydration and the symmetry clue

Zinc chloride promotes dehydration:



Loss of the hydroxyl group from one bridgehead and hydrogen from the other forms a double bond **along the bond shared by the two six-membered rings**. Thus **D** is bicyclo[4.4.0]dec-1(6)-ene.

This placement explains the NMR observation. Its eight methylene carbons fall into exactly two equivalent sets:

- Four methylene carbons directly adjacent to an alkene carbon.
- Four remaining methylene carbons, one position farther away.

A double bond between a bridgehead and a neighboring non-bridgehead carbon would destroy this symmetry.

E — reductive ozonolysis

Ozonolysis cleaves the shared double bond of **D**. Neither alkene carbon carries a hydrogen, so both become ketone carbonyls.

Removing the shared bond leaves the ten-carbon outer perimeter as one ring. The carbonyl groups occupy positions 1 and 6, identifying **E** as cyclodecane-1,6-dione.

Including the acidic zinc workup, a balanced net equation is



The NMR clue is again satisfied: the four methylene groups adjacent to carbonyl groups are equivalent, and the other four form a second equivalent set.

F — intramolecular aldol condensation

Number the ring of **E** so that its carbonyl carbons are C1 and C6. Under the basic conditions, enolate formation at C2 allows this carbon to attack the carbonyl carbon C6. The carbonyl π electrons move onto oxygen, and protonation produces a hydroxyl group.

The new C2–C6 bond creates:

- A five-membered ring: C2–C3–C4–C5–C6.
- A seven-membered ring: C2–C1–C10–C9–C8–C7–C6.

The unstable aldol intermediate is therefore **7-hydroxybicyclo[5.3.0]decan-2-one**, $\text{O}=\text{C1CCCC2}(\text{O})\text{C1CCC2}$.

Dehydration removes the hydroxyl group at C6 and a hydrogen at C2, using the original numbering of **E**. This forms C2=C6, conjugated with the remaining carbonyl group. The resulting enone is **F**, bicyclo[5.3.0]dec-1(7)-en-2-one.

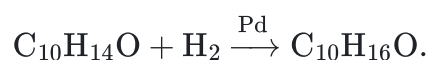
The overall condensation balance is



Thus the double bond of **F** lies along the shared edge of its five- and seven-membered rings, and the carbonyl group lies in the seven-membered ring next to that edge.

G — hydrogenation followed by carbonyl reduction

Palladium-catalysed hydrogenation reduces the alkene of **F**:



The intermediate is **bicyclo[5.3.0]decan-2-one**, O=C1CCCCC2C1CCC2.

Sodium borohydride then reduces the ketone to a secondary alcohol, giving **G**, bicyclo[5.3.0]decan-2-ol. Using $[\text{H}]$ to denote a formal hydrogen-atom reducing equivalent,



The fused five- and seven-membered carbon skeleton remains intact through both steps.

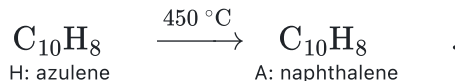
H — aromatization and return to A

Heating **G** over palladium on carbon removes water and eight hydrogen atoms, equivalent to four molecules of hydrogen:



The product retains the fused five- and seven-membered rings and contains five double bonds. It is therefore **H**, azulene, a nonbenzenoid aromatic hydrocarbon with a delocalized ten- π -electron system.

Finally, heating azulene to 450 °C rearranges its carbon skeleton to the two fused six-membered rings of naphthalene:

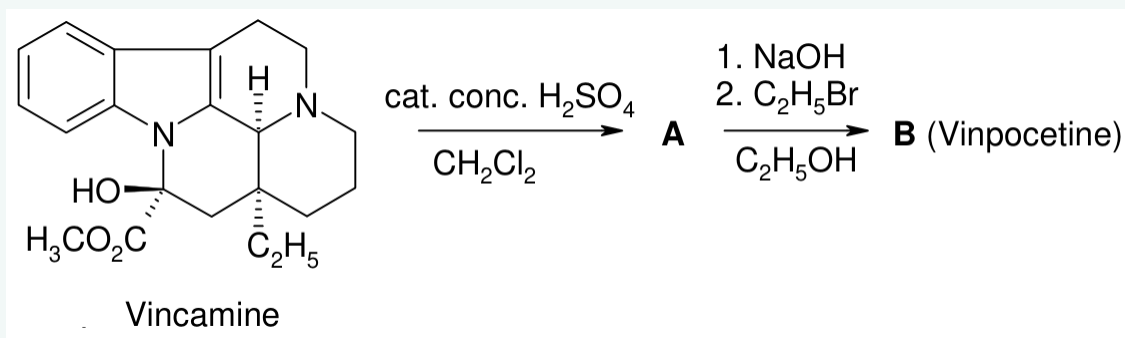


This closes the reaction sequence and confirms the assignments.

The solution was checked against the official solution.

Problem 3: Vinpocetine and its metabolites

Vinpocetine (Cavinton®, Calan®) is one of the best selling original drugs developed in Hungary. Its preparation relies on a natural precursor, (+)-vincamine (C_{21}H_{26}N_2O_3), which is isolated from the vine plant, *vinca minor*. The transformation of (+)-vincamine to vinpocetine is achieved in two steps depicted below.



All compounds (**A** to **F**) are enantiomerically pure compounds.

- The elementary composition of **A** is: C 74.97%, H 7.19%, N 8.33%, O 9.55%.
- **B** has 3 other stereoisomers.

3.1 Propose structures for the intermediate **A** and vinpocetine (**B**).

A study of the metabolism of any drug forms a substantial part of its documentation. There are four major metabolites each formed from vinpocetine (**B**): **C** and **D** are formed in hydrolysis or hydration reactions, while **E** and **F** are oxidation products.

Hints:

- The acidity of the metabolites decreases in the order **C** >> **E** >> **D**. **F** does not contain an acidic hydrogen.
- **C** and **E** each have 3 other stereoisomers, while **D** and **F** each have 7 other stereoisomers.
- **F** is a pentacyclic zwitterion and it has the same elementary analysis as **E**:
C 72.11 %, H 7.15 %, N 7.64 %, O 13.10 %.
- The formation of **E** from **B** follows an electrophilic pattern.
- The formation of **D** from **B** is both regio- and stereoselective.

3.2 Propose one possible structure for each of the metabolites **C**, **D**, **E** and **F**!

3.3 Draw a resonance structure for **B** that explains the regioselective formation of **D** and the absence of the alternate regioisomer in particular.

Official English text of the problem.

Answers

The following SMILES preserve the two surviving carbon stereocenters of the supplied vincamine structure.

- **3.1**

A — Methyl apovincamate (apovincamine), $C_{21}H_{24}N_2O_2$:

COC(=O)C1=C[C@]2(CC)CCCN3CCc4c([C@@H]32)n1c1cccc41

B — Vinpocetine (ethyl apovincamate), $C_{22}H_{26}N_2O_2$:

CCOC(=O)C1=C[C@]2(CC)CCCN3CCc4c([C@@H]32)n1c1cccc41

- **3.2**

C — Apovincaminic acid, $C_{20}H_{22}N_2O_2$:

O=C(O)C1=C[C@]2(CC)CCCN3CCc4c([C@@H]32)n1c1cccc41

D — Ethyl vincamate, $C_{22}H_{28}N_2O_3$, choosing the alcohol configuration shown for the starting vincamine:

CCOC(=O)[C@@]1(O)C[C@]2(CC)CCCN3CCc4c([C@@H]32)n1c1cccc41

E — 10-Hydroxyvinpocetine, $C_{22}H_{26}N_2O_3$, one possible phenolic oxidation product:

CCOC(=O)C1=C[C@]2(CC)CCCN3CCc4c([C@@H]32)n1c1ccc(O)cc41

F — Vinpocetine N-oxide, $C_{22}H_{26}N_2O_3$, choosing one configuration at the oxidized tertiary-amine nitrogen:

CCOC(=O)C1=C[C@]2(CC)CCC[N+](=O)3([O-])CCc4c([C@@H]32)n1c1ccccc41

- **3.3**

Charge-separated enamine resonance contributor of vinpocetine:

CCOC(=O)C1[CH-][C@]2(CC)CCCN3CCC4=C([C@@H]32)[N+]=1c1ccccc14

In the drawing, make the bond between the indole nitrogen and the ester-bearing alkene carbon double, make the original alkene bond single, and place positive charge on that nitrogen and negative charge on the other alkene carbon. Preserve the remaining framework and carbon stereochemistry.

Solution

3.1 — Identification of A and B

Using standard atomic molar masses 12.011 , 1.008 , 14.007 , $15.999 \text{ g mol}^{-1}$ for carbon, hydrogen, nitrogen and oxygen, respectively, a 100.00 g sample of **A** gives the atomic ratio

$$\begin{aligned} n_C : n_H : n_N : n_O &= \frac{74.97}{12.011} : \frac{7.19}{1.008} : \frac{8.33}{14.007} : \frac{9.55}{15.999} \\ &= 6.242 : 7.133 : 0.5947 : 0.5969 \approx 21 : 24 : 2 : 2. \end{aligned}$$

Thus **A** has molecular formula $C_{21}H_{24}N_2O_2$, with molar mass approximately $336.44 \text{ g mol}^{-1}$. Compared with vincamine, it has lost one molecule of water:



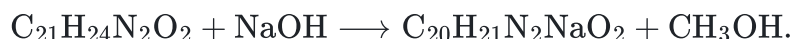
The starting (+)-vincamine is represented by

COC(=O)[C@@]1(O)C[C@]2(CC)CCCN3CCc4c([C@@H]32)n1c1ccccc41.

Acid-catalysed dehydration removes the hydroxyl group from the carbon bearing the methyl ester and a hydrogen from the adjacent methylene carbon. The resulting double bond lies between those two carbons. This gives **A**, methyl apovincamate.

The hydroxyl-bearing stereocenter disappears upon formation of the alkene. The two other carbon stereocenters retain their configurations.

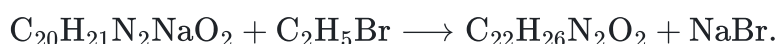
Sodium hydroxide then hydrolyses the methyl ester:



The intermediate is **sodium apovincamate**:

[Na+].O=C([O-])C1=C[C@]2(CC)CCCN3CCc4c([C@@H]32)n1c1ccccc41.

Its carboxylate oxygen alkylates bromoethane, producing the ethyl ester **B**:



Consequently, **B is vinpocetine, ethyl apovincamate**. Its two carbon stereocenters give

$$2^2 = 4$$

stereoisomers, hence three others besides the specified enantiomer. The endocyclic double bond in the six-membered ring does not introduce an independent pair of geometrical isomers.

For a drawing, retain the original dashed bonds to the bridgehead hydrogen and ethyl group, replace the alcohol-containing segment by the alkene, and change the ester methyl group to ethyl for **B**.

The small species used here are water O, sodium hydroxide [Na+].[OH-], methanol CO, bromoethane CCB_r, and sodium bromide [Na+].[Br-]. The stated catalyst and solvents are sulfuric acid OS(=O)(=O), dichloromethane ClCCl, and ethanol CCO.

3.2 — Identification of C, D, E and F

The common analysis of **E** and **F** gives

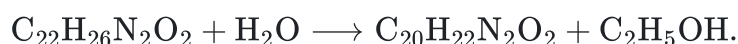
$$\frac{72.11}{12.011} : \frac{7.15}{1.008} : \frac{7.64}{14.007} : \frac{13.10}{15.999} \approx 22 : 26 : 2 : 3.$$

Therefore,

$$\boxed{\mathbf{E, F : C_{22}H_{26}N_2O_3}}, \quad M \approx 366.46 \text{ g mol}^{-1}.$$

Each is formed by adding one oxygen atom to **B**, without changing its total hydrogen count.

C: ester hydrolysis. Hydrolysis of the ethyl ester gives apovincaminic acid:



The carboxylic acid group explains why **C** is the most acidic metabolite. Hydrolysis leaves the two carbon stereocenters unchanged, giving four stereoisomers in total.

D: hydration of the alkene. Addition of water gives



The hydroxyl group must attach to the alkene carbon already bonded to the indole nitrogen and ester group. The adjacent alkene carbon becomes a methylene group. This creates **one** new carbon stereocenter, giving three in total and therefore eight stereoisomers.

The selected **D** is ethyl vincamate. Draw it like the original vincamine, with an ethyl ester replacing the methyl ester: the hydroxyl bond projects toward the viewer, and the ester bond projects behind the plane.

Putting hydroxyl on the other alkene carbon would make **both** former alkene carbons stereogenic. That alternative would have four carbon stereocenters, inconsistent with the stated eight stereoisomers.

E: aromatic hydroxylation. Its intermediate acidity suggests a phenol. Electrophilic aromatic hydroxylation introduces one oxygen atom while replacing an aromatic hydrogen by hydroxyl; the total hydrogen count is unchanged.

One possible structure is **10-hydroxyvinpocetine**. In the supplied drawing, put hydroxyl on the upper-left benzene carbon, para to the benzene fusion carbon bonded directly to the indole nitrogen. This introduces no new stereocenter, so **E** has four stereoisomers.

F: tertiary-amine oxidation. Oxidation of the saturated tertiary-amine nitrogen gives the amine oxide, containing the formally charged linkage N⁺—O[−].

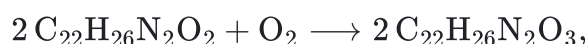
This assignment explains all its properties:

- It adds one oxygen atom without changing the hydrogen count.

- It retains all five rings.
- It is a zwitterion, with net charge zero.
- It introduces no hydroxyl or nitrogen-bound hydrogen.
- The tetrahedral amine-oxide nitrogen has four distinguishable substituents and becomes a configurationally stable stereocenter.

Thus **F** has two carbon stereocenters and one nitrogen stereocenter, giving eight stereoisomers. The SMILES supplied above chooses the *S* configuration at this nitrogen.

For either oxidation, an atom-balanced formal equation is



with the product being **E** or **F**, respectively. This expresses the net elemental change; the problem does not specify the biological oxidant. Dioxygen is $\text{O}=\text{O}$.

The assignments satisfy the stereochemical counts:

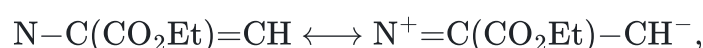
Compound	Characteristic group	Configurationally stable stereocenters	Total stereoisomers
C	Carboxylic acid	2 carbon	4
D	Tertiary alcohol	3 carbon	8
E	Phenol	2 carbon	4
F	Tertiary-amine N-oxide	2 carbon + 1 nitrogen	8

The acidity order follows from stabilization of the conjugate bases: carboxylate is strongly stabilized by delocalization over two oxygens, phenoxide is stabilized by aromatic delocalization, and the alcohol's alkoxide lacks comparable resonance stabilization. Hence



3.3 — Resonance and hydration regioselectivity

Call the ester-bearing alkene carbon C_α , and the adjacent alkene carbon C_β . The relevant local resonance relationship is



where the remaining ring bonds are understood.

Starting from a Kekulé representation, move the indole nitrogen's lone pair into the bond to C_α , and move the alkene π -electron pair onto C_β . The full charge-separated contributor is the structure given in **Answers 3.3**.

This contributor identifies C_β as the electron-rich end of the alkene. Protonation there gives an iminium ion whose positive charge is stabilized by nitrogen donation. This **vinpocetine-derived iminium ion** is CCOC(=O)C1C[C@]2(CC)CCCN3CCC4=C([C@@H]32)[N+]=1c1cccc14.

Water attacks its electrophilic C_α ; subsequent deprotonation produces **D**, with hydroxyl on the ester-bearing carbon.

The opposite protonation would place positive charge at C_β , while the newly saturated C_α would interrupt conjugation with nitrogen. That pathway lacks the iminium stabilization, explaining the observed hydration regioselectivity and the absence of the alternate regioisomer.

The solution was checked against the official solution.

Problem 4: Ring opening of oxiranes

A major transformation route for oxiranes (epoxides) is ring opening. This may be accomplished in various ways.

On acid catalysis the reactions proceed through cation-like (carbenium ion-like) species. For substituted oxiranes the direction of ring opening (which C–O bond is cleaved) depends on the stability of the intermediate carbenium ion. The more stable the intermediate carbenium ion the more probable its formation. However, an open carbenium ion (with a planar structure) only forms if it is tertiary, benzylic or allylic.

On base catalysis the sterically less hindered C–O bond is cleaved predominantly.

Keep stereochemistry in mind throughout the whole problem. To depict stereochemistry use only the

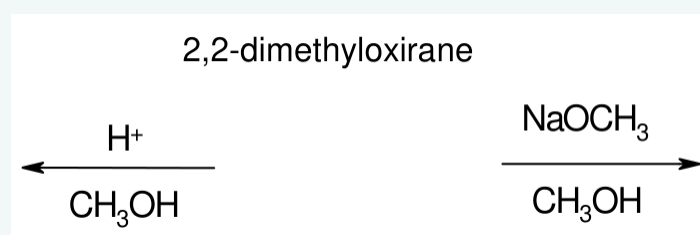


bond symbols and nothing else where necessary.

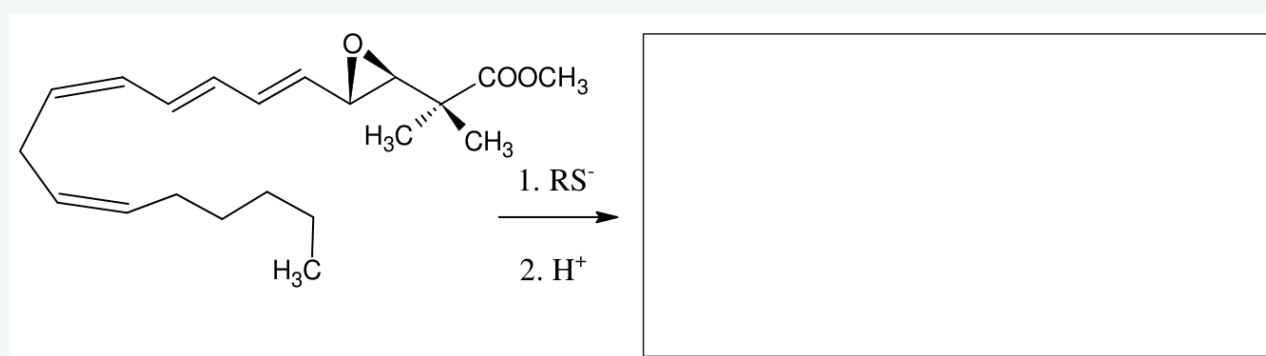
4.1 Draw the structure of the reactant and the predominant products when 2,2-dimethyl-oxirane (1,2-epoxy-2-methylpropane) reacts with methanol at low temperatures, catalysed by

(i) sulphuric acid

(ii) NaOCH_3 .



4.2 Draw the structure of the predominant product when the epoxide ring of the following leukotriene derivative is opened with a thiolate (RS^-).



Different porous acidic aluminosilicates can also be used to catalyse the transformation of alkyl oxiranes. In addition to ring opening, cyclic dimerisation is found to be the main reaction pathway producing mainly 1,4-dioxane derivatives (six-membered saturated rings with two oxygen atoms in positions 1,4).

4.3 Draw the structure(s) of the most probable 1,4-dioxane derivative(s) when the starting compound is (S)-2-methyloxirane ((S)-1,2-epoxypropane). Give the structure of the reactant as well.

4.4 Draw the structure(s) of the substituted 1,4-dioxane(s) when the epoxide reacting is (R)-1,2-epoxy-2-methylbutane ((R)-2-ethyl-2-methyloxirane). Give the structure of the reactant as well.

4.5 Give the structure(s) of the substituted 1,4-dioxane(s) when this reaction is carried out with racemic 1,2-epoxy-2-methylbutane (2-ethyl-2-methyloxirane).

Official English text of the problem.

Answers

- **4.1** Reactant: **2,2-dimethyloxirane**, CC1(C)CO1.
- **(i)** Acid catalysis: **2-methoxy-2-methylpropan-1-ol**, COC(C)(C)CO, with structure $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{OCH}_3$.
- **(ii)** Base catalysis: **1-methoxy-2-methylpropan-2-ol**, COCC(C)(C)O, with structure $\text{CH}_3\text{OCH}_2\text{C}(\text{CH}_3)_2\text{OH}$.
- **4.2** The product has **hydroxy at C3 and SR at C4**, with configuration **(3S,4R)**. Its name is **methyl (3S,4R,5E,7E,9Z,12Z)-3-hydroxy-2,2-dimethyl-4-(organosulfanyl)octadeca-5,7,9,12-tetraenoate**.
SMILES: COC(=O)C(C)(C)[C@H](O)[C@H](S*)/C=C/C=C/C=C\C/C=C\CCCC
Here * represents the unspecified organic group R.
- **4.3** Reactant: **(S)-2-methyloxirane**, C[C@H]1CO1.
Product: **cis-(2R,5R)-2,5-dimethyl-1,4-dioxane**, O1[C@H](C)CO[C@H](C)C1.
- **4.4** Reactant: **(R)-2-ethyl-2-methyloxirane**, CC[C@]1(C)CO1. The products are three stereoisomers of **2,5-diethyl-2,5-dimethyl-1,4-dioxane**:

Product	SMILES
cis-(2R,5R)	<chem>O1[C@](C)(CC)CO[C@](C)(CC)C1</chem>
cis-(2S,5S)	<chem>O1[C@@](C)(CC)CO[C@@](C)(CC)C1</chem>
trans, meso-(2R,5S), identical to (2S,5R)	<chem>O1[C@](C)(CC)CO[C@@](C)(CC)C1</chem>

Here **cis/trans** describes the relationship between the two methyl groups; the two ethyl groups have the same cis/trans relationship.

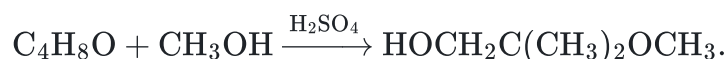
- **4.5** The products are **the same three stereoisomers listed in 4.4**: the (2R,5R)/(2S,5S) enantiomeric pair and the meso-(2R,5S) compound.

Solution

4.1

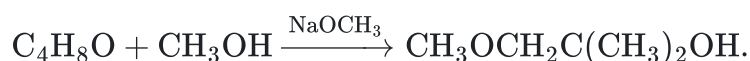
The reactant is a three-membered ring containing oxygen, a methylene carbon and a carbon bearing two methyl groups. The reagents are methanol, CO; sulphuric acid, OS(=O)(=O)O; and sodium methoxide, [Na+].[O-].

(i) Acid catalysis. Protonation activates the epoxide. Cleavage at the carbon bearing two methyl groups is favoured because it produces a tertiary carbenium centre. The original epoxide oxygen remains attached to the methylene carbon. Methanol attacks the tertiary centre through its oxygen, and deprotonation gives the product:



Thus, the methoxy group is attached to the more substituted carbon, while the hydroxy group is attached to the methylene carbon.

(ii) Base catalysis. Methoxide attacks the less hindered methylene carbon by an S_N2 mechanism. The electrons of its breaking bond to the epoxide oxygen move onto oxygen. Proton transfer from methanol then produces the alcohol and regenerates methoxide:



Neither product has a stereogenic centre, because the substituted carbon bears two identical methyl groups.

4.2

Number the chain from the ester carbonyl carbon, C1. The geminal methyl groups are at C2, and the epoxide occupies C3 and C4.

The supplied trans-(3S,4S) reactant is **methyl (3S,4S,5E,7E,9Z,12Z)-3,4-epoxy-2,2-dimethyloctadeca-5,7,9,12-tetraenoate**:



The organothiolate ion, $[\text{S}^-]$, attacks **C4**. C3 is more hindered because it lies next to the carbon bearing two methyl groups and the ester substituent.

Attack occurs opposite the breaking C4–oxygen bond, giving inversion at C4. The C3–oxygen bond remains intact, so C3 retains its configuration. Acid work-up supplies a proton, $[\text{H}^+]$, to the oxygen.

Consequently:



The balanced overall reaction, with R unchanged, is



To draw the product, replace the epoxide bridge with a hydroxy group at C3 and an SR group at C4, using wedges and hashed wedges consistent with **(3S,4R)**. Preserve the four alkene configurations: **5E, 7E, 9Z and 12Z**. The specified anti relationship concerns the direction of attack relative to the breaking bond; the resulting open chain can rotate about its single bonds.

4.3

The oxygen of one epoxide attacks the more substituted carbon of an acid-activated second epoxide. Subsequent intramolecular attack closes the six-membered ring, again opening an epoxide at its more substituted carbon.

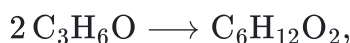
The resulting ring contains two consecutive units of the form



so the methyl groups occupy **positions 2 and 5** of the 1,4-dioxane ring.

Each attacked carbon is secondary. Under the rules given in the problem, an open planar carbenium ion does not form, and each opening proceeds with inversion. Both original stereogenic centres therefore invert. Their relevant priority order remains oxygen, ring methylene carbon, methyl, hydrogen, so both **S** centres become **R** centres.

The balanced dimerisation is



catalysed by the acidic aluminosilicate.

The product is **cis-(2R,5R)-2,5-dimethyl-1,4-dioxane**. Draw a six-membered ring with oxygen atoms at positions 1 and 4 and methyl groups at positions 2 and 5 on the **same face**, with absolute configurations (2R,5R). In either chair conformation, one methyl group is axial and the other is equatorial.

4.4

The favoured opening again occurs at the more substituted epoxide carbon, producing the **2,5-substituted dioxane skeleton**.

Here, however, that carbon is bonded to three carbon groups: methyl, ethyl and the ring methylene group. Ring opening can therefore produce a **planar tertiary carbenium centre**. Formation of the new carbon–oxygen bond can occur from either face, so the starting **R** configuration is lost.

This happens at both substituted centres. The possible configuration combinations are

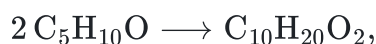


The last two represent the same compound because positions 2 and 5 are symmetry-related. Thus there are **three distinct stereoisomers**:

- **(2R,5R)** and **(2S,5S)** are an enantiomeric pair. In each, the methyl groups lie on the same face of the ring, and the ethyl groups lie on the opposite face.
- **(2R,5S)** is **meso**. Its methyl groups lie on opposite faces, as do its ethyl groups.

For a wedge-and-dash drawing, the two cis structures are mirror images. For the meso structure, put one methyl group on a solid wedge and the other on a hashed wedge, with each ethyl group opposite the methyl group on the same carbon.

The balanced reaction is



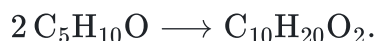
with the acidic aluminosilicate as catalyst. The problem does not specify the relative amounts of the three stereoisomers.

4.5

The racemic starting material contains equal amounts of **(R)-2-ethyl-2-methyloxirane**, CC[C@]1(C)CO1, and **(S)-2-ethyl-2-methyloxirane**, CC[C@@]1(C)CO1.

As in 4.4, the favoured ring openings pass through planar tertiary carbenium centres, erasing the original configurations. Therefore, the racemic reactant gives the **same three products**: (2R,5R), (2S,5S), and meso-(2R,5S).

The balanced overall dimerisation remains



The solution was checked against the official solution.

Problem 5: Two white crystalline substances

A and **B** are white crystalline substances. Both are highly soluble in water and can be moderately heated (up to 200 °C) without change but both decompose at higher temperatures. If an aqueous solution of 20.00 g **A** (which is slightly basic, $pH \approx 8.5$ -9) is added to an aqueous solution of 11.52 g **B** (which is slightly acidic, $pH \approx 4.5$ -5) a white precipitate **C** forms that weighs 20.35 g after filtering, washing and drying. The filtrate is essentially neutral and gives a brown colour reaction with an acidified **KI** solution. When boiled, the filtrate evaporates without the appearance of any residue.

The white solid **D** can be prepared by the heating of **A** in the absence of air. The exothermic reaction of **D** with water gives a colourless solution. This solution, if kept in an open container, slowly precipitates a white solid **E** and leaves water. Upon prolonged exposure to air at room temperature, solid **D** is transformed into **E** as well. However, heating **D** in air at 500 °C produces a different white substance **F**, which is barely soluble in water and has a mass of only 85.8% of the **E** formed from the same amount of **D**. **F** gives a brown colour reaction with an acidified solution of **KI**.

E can be converted back into **D** but ignition above 1400 °C is required for this purpose. The reaction of **B** and **D** in water forms the precipitate **C** and is accompanied by a characteristic odour.

5.1 Give the formulae of the substances **A** - **F**

5.2 Write balanced equations for all the reactions mentioned. (The equation for the thermal decomposition of **B** is not required.)

Official English text of the problem.

Answers

• 5.1

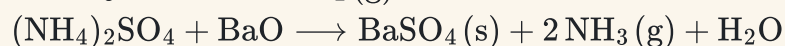
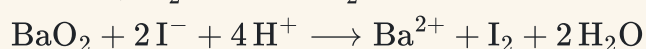
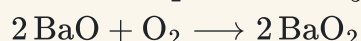
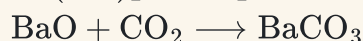
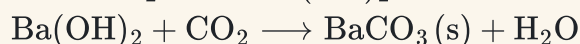
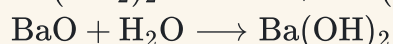
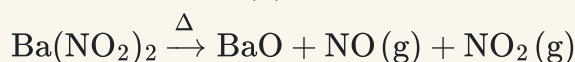
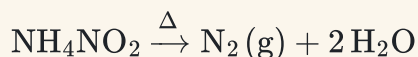
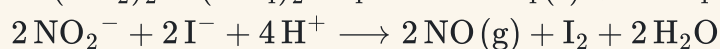
Substance	Formula	Name	SMILES
A	<chem>Ba(NO2)2</chem>	Barium nitrite	<chem>[Ba+2].[O-]N=O.[O-]N=O</chem>

Substance	Formula	Name	SMILES
B	$(\text{NH}_4)_2\text{SO}_4$	Ammonium sulfate	<chem>[NH4+] . [NH4+] . [O-]S(=O)(=O)[O-]</chem>
C	BaSO_4	Barium sulfate	<chem>[Ba+2] . [O-]S(=O)(=O)[O-]</chem>
D	BaO	Barium oxide	<chem>[Ba+2] . [O-2]</chem>
E	BaCO_3	Barium carbonate	<chem>[Ba+2] . [O-]C(=O)[O-]</chem>
F	BaO_2	Barium peroxide	<chem>[Ba+2] . [O-][O-]</chem>

The ionic SMILES describe formula units; they do not show the extended crystal lattices. Polyatomic anions are represented by one resonance form.

• 5.2

The required balanced equations are:



Here, **A** is heated without air; peroxide formation occurs in air at 500 °C; carbonate decomposition requires heating above 1400 °C. An alternative overall representation of **A**'s thermolysis is discussed below.

Solution

5.1 — Identification of A–F

Identifying the metal from D, E and F.

The exothermic reaction of **D** with water, followed by precipitation upon exposure to air, suggests a basic metal oxide that forms a soluble hydroxide. Atmospheric carbon dioxide then produces an insoluble carbonate. Thus, for a divalent metal, the likely formulae are



Heating the oxide in air produces an oxidizing compound **F**. A peroxide, MO_2 , explains its ability to oxidize acidified iodide.

For equal initial quantities of **D**, the carbonate and peroxide contain equal amounts of metal. If x is the metal's molar mass,

$$\frac{m(F)}{m(E)} = \frac{x + 32.00 \text{ g mol}^{-1}}{x + 60.01 \text{ g mol}^{-1}} = 0.858.$$

Therefore,

$$x \approx 137 \text{ g mol}^{-1},$$

which identifies **barium**.

Using ordinary atomic masses gives

$$\frac{M(\text{BaO}_2)}{M(\text{BaCO}_3)} \approx \frac{169.33}{197.33} = 0.8581,$$

in agreement with the stated 85.8%. Hence

$$\boxed{D = \text{BaO}, \quad E = \text{BaCO}_3, \quad F = \text{BaO}_2}.$$

The high temperature required to regenerate **D** is also consistent with the thermal stability of barium carbonate.

Identifying B and C.

The characteristic odour when **B** reacts with the basic oxide **D** indicates ammonia. Therefore, **B** contains ammonium ions. This also explains its slightly acidic aqueous solution.

The quantities of **A** and **B** must be essentially stoichiometric: an appreciable excess of either original salt would leave a residue on boiling. In forming **C**, one barium ion replaces two ammonium ions while retaining the precipitating anion. Thus,

$$n(\text{Ba}) = \frac{m(C) - m(B)}{M(\text{Ba}) - 2M(\text{NH}_4^+)}.$$

Using $M(\text{Ba}) = 137.327 \text{ g mol}^{-1}$ and $M(\text{NH}_4^+) = 18.039 \text{ g mol}^{-1}$,

$$n(\text{Ba}) = \frac{20.35 - 11.52 \text{ g}}{137.327 - 2(18.039) \text{ g mol}^{-1}} \approx 0.08721 \text{ mol}.$$

The anionic contribution to **C**, per mole of barium, is therefore

$$\frac{20.35 \text{ g}}{0.08721 \text{ mol}} - 137.327 \text{ g mol}^{-1} \approx 96.02 \text{ g mol}^{-1}.$$

This agrees with sulfate, whose molar mass is approximately 96.06 g mol^{-1} . Consequently,

$$\boxed{B = (\text{NH}_4)_2\text{SO}_4, \quad C = \text{BaSO}_4}.$$

Identifying A and the filtrate.

There is one barium atom per formula unit of **A**, so

$$M(A) \approx \frac{20.00 \text{ g}}{0.08721 \text{ mol}} = 229.3 \text{ g mol}^{-1}.$$

Subtracting the barium contribution leaves approximately

$$229.3 - 137.3 = 92.0 \text{ g mol}^{-1}.$$

This corresponds to two nitrite ions, each approximately 46.0 g mol^{-1} . Thus,

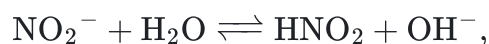
$$\boxed{A = \text{Ba}(\text{NO}_2)_2}.$$

The filtrate is consequently ammonium nitrite. It accounts for both remaining observations:

- Nitrite oxidizes iodide to brown iodine in acidic solution.

- Ammonium nitrite decomposes on heating into nitrogen and water, leaving no solid residue.

The acid–base behaviour also agrees with the identification:



which explains the slightly basic solution of **A**, and



which explains the slightly acidic solution of **B**. The filtrate contains no excess strong acid or strong base; “essentially neutral” need not mean exactly $\text{pH} = 7$.

Numerical check of the precipitation.

Substance	Molar mass / g mol^{-1}	Amount calculated from the stated mass / mol
$\text{Ba}(\text{NO}_2)_2$	229.337	0.0872079
$(\text{NH}_4)_2\text{SO}_4$	132.139	0.0871812
BaSO_4	233.388	0.0871939

These amounts agree within the rounding of the supplied masses. Taking the displayed reactant masses literally, the calculated precipitate mass is

$$m(\text{BaSO}_4) = 0.0871812 \text{ mol} \times 233.388 \text{ g mol}^{-1} = 20.3471 \text{ g} \approx \boxed{20.35 \text{ g}}.$$

5.2 — Explanation of the reactions

Precipitation and behaviour of the filtrate.

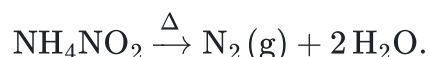
Mixing **A** and **B** precipitates barium sulfate and leaves ammonium nitrite in solution:



In the acidified iodide test, nitrogen in nitrite is reduced from oxidation state +3 to +2, while iodide is oxidized to iodine:



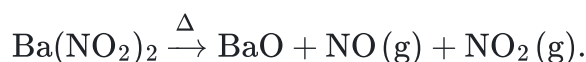
On boiling, the ammonium nitrite undergoes internal oxidation–reduction:



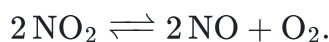
Its two nitrogen atoms, initially at oxidation states -3 and $+3$, both end at 0 .

Preparation and hydration of **D**.

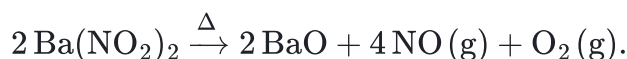
A balanced overall representation of barium nitrite thermolysis is



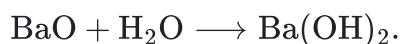
At high temperature, nitrogen dioxide can dissociate:



Including this dissociation gives the alternative overall form

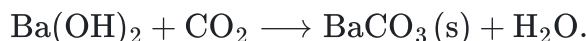


The resulting barium oxide reacts exothermically with water:

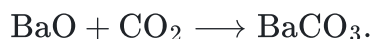


Formation of E from solution or directly from D.

Atmospheric carbon dioxide precipitates barium carbonate from the hydroxide solution:



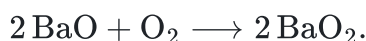
The overall conversion of the solid oxide during prolonged exposure to air is



Moisture can facilitate this conversion through hydration followed by carbonation.

Formation and iodide test of F.

At 500 °C, oxygen converts barium oxide into barium peroxide:



In acidic solution, the peroxide oxygens are reduced from oxidation state -1 to -2 , oxidizing iodide:



Regeneration of D and reaction of B with D.

Above 1400 °C,



Finally, barium oxide neutralizes ammonium ions while barium sulfate precipitates:



The characteristic odour is that of **ammonia**.

For completeness, the additional molecular and ionic species used in the solution have the following names and SMILES:

Species	Name	SMILES
NH_4NO_2	Ammonium nitrite	[NH4+] . [O-]N=O
$\text{Ba}(\text{OH})_2$	Barium hydroxide	[Ba+2] . [OH-] . [OH-]
Ba^{2+}	Barium(II) ion	[Ba+2]
NH_4^+	Ammonium ion	[NH4+]
NO_2^-	Nitrite ion	[O-]N=O
SO_4^{2-}	Sulfate ion	[O-]S(=O)(=O)[O-]
HNO_2	Nitrous acid	O=NO
OH^-	Hydroxide ion	[OH-]
H_3O^+	Hydronium ion	[OH3+]
H^+	Hydrogen ion, represented formally as a proton	[H+]
I^-	Iodide ion	[I-]
I_2	Iodine	II
H_2O	Water	O
CO_2	Carbon dioxide	O=C=O
O_2	Dioxygen	O=O
N_2	Dinitrogen	N#N
NH_3	Ammonia	N

Species	Name	SMILES
NO	Nitrogen monoxide, nitric oxide	[N]=O
NO ₂	Nitrogen dioxide	[O-][N+]=O

The proton notation represents solvated acidity in the aqueous equations. The dioxygen SMILES gives connectivity but does not encode its triplet ground state.

The solution was checked against the official solution.

Problem 6: Clathrate hydrates of chlorine and methane

A feathery, greenish solid precipitate can be observed if chlorine gas is bubbled into water close to its freezing point. Similar precipitates form with other gases such as methane and noble gases. These materials are interesting because vast quantities of the so-called methane-hydrates are supposed to exist in nature (comparable in quantity with other natural gas deposits).

These precipitates all have related structures. The molecules of water just above its freezing point form a hydrogen-bonded structure. The gas molecules stabilize this framework by filling in the rather large cavities in the water structure forming clathrates. The crystals of chlorine and methane clathrates have the same structure. Their main characteristics are dodecahedra formed from 20 water molecules. The unit cell of the crystal can be thought as a body-centered cubic arrangement built from these dodecahedra which are almost spherical objects. The dodecahedra are connected via additional water molecules located on the faces of the unit cell. Two water molecules can be found on each face of the unit cell. The unit cell has an edge dimension of 1.182 nm.

There are two types of cavities in this structure. One is the internal space in the dodecahedra (**A**). These are somewhat smaller than the other type of voids (**B**), of which there are 6 for each unit cell.

6.1 How many type **A** cavities can be found in a unit cell?

6.2 How many water molecules are there in a unit cell?

6.3 If all cavities contain a guest molecule, what is the ratio of the number of water to the number of guest molecules?

6.4 Methane hydrate is formed with the structure in **c**) at temperatures between 0-10 °C. What is the density of the clathrate?

6.5 The density of chlorine hydrate is 1.26 g/cm³. What is the ratio of the number of water and guest molecules in the crystal?

Which cavities are likely to be filled in a perfect chlorine hydrate crystal? Mark one or more.

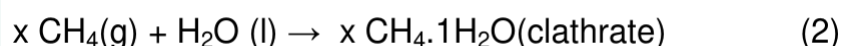
☐ Some **A** ☐ Some **B** ☐ All **A** ☐ All **B**

Covalent radii reflect atomic distances when the atoms are covalently bonded. Non-bonded or van der Waals radii give a measure of the atomic size when they are not bonded covalently (modelled as hard spheres).

Atom	Covalent radius (pm)	Nonbonded radius (pm)
H	37	120
C	77	185
O	73	140
Cl	99	180

6.6 Based on the covalent and non-bonded radii of these atoms estimate lower and upper bounds for the average radii of the cavities where possible. Show your reasoning.

Let us consider the following processes



6.7 What are the signs of the following molar quantities referring to these reactions in the given direction at 4 °C? Mark with a –, 0 or +.

	sign
$\Delta G_{\text{m}}(1)$	
$\Delta G_{\text{m}}(2)$	
$\Delta H_{\text{m}}(1)$	
$\Delta H_{\text{m}}(2)$	
$\Delta S_{\text{m}}(1)$	
$\Delta S_{\text{m}}(2)$	
$\Delta S_{\text{m}}(2) - \Delta S_{\text{m}}(1)$	
$\Delta H_{\text{m}}(2) - \Delta H_{\text{m}}(1)$	

Official English text of the problem.

Answers

- **6.1:** 2 type **A** cavities per unit cell.
- **6.2:** 46 water molecules per unit cell.
- **6.3:** Water : guest = 46 : 8 = 23 : 4 = 5.75 : 1.
- **6.4:** $\rho = 0.962 \text{ g cm}^{-3}$.
- **6.5:** Water : chlorine = 46 : 6 = 23 : 3 $\approx$ 7.67 : 1. Select **All B** only; the **A** cavities are empty in the intended ideal structure.
- **6.6:** In the spherical fitting approximation, the free-cavity radii satisfy

$$234 \text{ pm} \leq r_A < 279 \text{ pm}, \quad r_B \geq 279 \text{ pm}.$$

Guest sizes provide no upper bound for r_B .

- **6.7:** In the order listed in the question:

+, −, −, −, −, −, −, −.

These signs assume the hydrate-forming conditions described in the problem.

Solution

The molecular species are water, H_2O , SMILES o; methane, CH_4 , SMILES c; and chlorine, Cl_2 , SMILES ClCl. Methane is tetrahedral, and chlorine is a linear diatomic molecule. Ice consists of water molecules. SMILES does not specify these substances' physical phases or the extended hydrogen-bonded cage structure of a clathrate.

6.1

A body-centered cubic arrangement has eight corner positions, each shared by eight unit cells, and one position wholly inside the cell. Each dodecahedron contains one **A** cavity. Therefore,

$$N_A = 8 \left(\frac{1}{8} \right) + 1 = \boxed{2}.$$

Here N_A denotes the number of **A** cavities, not Avogadro's constant.

6.2

The two dodecahedra contribute

$$2(20) = 40$$

water molecules per unit cell.

There are also two additional water molecules on each of the six faces. Each face is shared by two neighboring cells, so these contribute

$$6(2) \left(\frac{1}{2} \right) = 6.$$

Consequently,

$$N_{\text{water}} = 40 + 6 = \boxed{46}.$$

6.3

There are two **A** cavities and six **B** cavities:

$$N_{\text{guest}} = 2 + 6 = 8.$$

With one guest molecule in every cavity,

$$\boxed{N_{\text{water}} : N_{\text{guest}} = 46 : 8 = 23 : 4 = 5.75 : 1}.$$

6.4

For full methane occupancy, one unit cell contains 46 water molecules and eight methane molecules.

Use the standard constants

$$N_{\text{Av}} = 6.02214 \times 10^{23} \text{ mol}^{-1},$$

$$M(\text{H}_2\text{O}) = 18.015 \text{ g mol}^{-1}, \quad M(\text{CH}_4) = 16.043 \text{ g mol}^{-1}.$$

The edge length and unit-cell volume are

$$a = 1.182 \text{ nm} = 1.182 \times 10^{-7} \text{ cm},$$
$$V_{\text{cell}} = a^3 = 1.651400568 \times 10^{-21} \text{ cm}^3.$$

The mass per cell is

$$m_{\text{cell}} = \frac{46M(\text{H}_2\text{O}) + 8M(\text{CH}_4)}{N_{\text{Av}}} = \frac{957.034 \text{ g mol}^{-1}}{6.02214 \times 10^{23} \text{ mol}^{-1}} = 1.5892 \times 10^{-21} \text{ g}.$$

Thus,

$$\rho = \frac{m_{\text{cell}}}{V_{\text{cell}}} = 0.96233 \text{ g cm}^{-3} \approx \boxed{0.962 \text{ g cm}^{-3}}.$$

6.5

Let n be the number of chlorine molecules per unit cell. The water framework still contains 46 water molecules. With

$$M(\text{Cl}_2) = 70.90 \text{ g mol}^{-1},$$

the density satisfies

$$\rho = \frac{46M(\text{H}_2\text{O}) + nM(\text{Cl}_2)}{N_{\text{Av}}a^3}.$$

Therefore,

$$n = \frac{\rho N_{\text{Av}}a^3 - 46M(\text{H}_2\text{O})}{M(\text{Cl}_2)} = 5.986 \approx 6.$$

The small departure from six is consistent with the stated density's precision: exactly six chlorine molecules would give 1.261 g cm^{-3} , which rounds to 1.26 g cm^{-3} .

The ideal composition therefore has

$$\boxed{N_{\text{water}} : N_{\text{Cl}_2} = 46 : 6 = 23 : 3 \approx 7.67 : 1}.$$

There are exactly six larger **B** cavities. The intended size-selective interpretation is that chlorine occupies these larger cavities, leaving the smaller **A** cavities empty. Thus the answer-sheet selection is:

☐ Some **A** ☐ Some **B** ☐ All **A** ☒ All **B**

The density determines the guest count; identifying the occupied cavities additionally uses this size-based interpretation.

6.6

Approximate a cavity by a sphere capable of enclosing its guest molecule.

For methane, the carbon–hydrogen bond length is estimated from the covalent radii:

$$d_{\text{C-H}} = 77 + 37 = 114 \text{ pm}.$$

A hydrogen atom's outer nonbonded surface extends a further 120 pm. Hence a sphere centered on the carbon atom and enclosing methane has radius

$$r_{\text{methane}} = \max(185, 114 + 120) \text{ pm} = \boxed{234 \text{ pm}}.$$

For chlorine, the estimated bond length is

$$d_{\text{Cl-Cl}} = 2(99) = 198 \text{ pm}.$$

Measured from the bond midpoint, the outermost surface is one half-bond length plus one chlorine nonbonded radius away:

$$r_{\text{chlorine}} = \frac{198}{2} + 180 = \boxed{279 \text{ pm}}.$$

Methane fits into both cavity types. Under the size-exclusion interpretation of **6.5**, chlorine fits into **B** but is too large for **A**. Therefore the effective free-space radii satisfy

$$\boxed{234 \text{ pm} \leq r_A < 279 \text{ pm}},$$

$$\boxed{r_B \geq 279 \text{ pm}}.$$

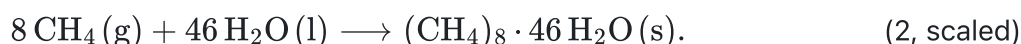
No larger guest that fails to enter **B** is specified, so this comparison supplies no upper bound for r_B . These are approximate spherical fitting bounds, since the molecules and cages are not perfect spheres.

6.7

Process (1) is freezing:



Process (2), written with integer coefficients, is methane clathrate formation:



The solid product denotes the clathrate's composition. Dividing this equation by 46 gives the normalization used in the question, with

$$x = \frac{8}{46} = \frac{4}{23}.$$

Thus both processes are compared per mole of water.

At 4 °C, liquid water is stable relative to ordinary ice, so freezing is unfavorable:

$$\Delta G_m(1) > 0.$$

Freezing releases heat and produces a more ordered phase:

$$\Delta H_m(1) < 0, \quad \Delta S_m(1) < 0.$$

Under the hydrate-forming conditions assumed in the question, process (2) is favorable:

$$\Delta G_m(2) < 0.$$

It orders the water framework and confines methane that was initially gaseous. The intended qualitative entropy comparison is therefore

$$\Delta S_m(2) < \Delta S_m(1) < 0.$$

Using

$$\Delta H_m = \Delta G_m + T\Delta S_m,$$

both terms on the right are negative for process (2), so

$$\Delta H_m(2) < 0.$$

Furthermore,

$$\Delta H_m(2) - \Delta H_m(1) = [\Delta G_m(2) - \Delta G_m(1)] + T[\Delta S_m(2) - \Delta S_m(1)] < 0,$$

because both bracketed differences are negative.

The completed table is:

Quantity	Sign
$\Delta G_m(1)$	+
$\Delta G_m(2)$	—
$\Delta H_m(1)$	—
$\Delta H_m(2)$	—
$\Delta S_m(1)$	—
$\Delta S_m(2)$	—
$\Delta S_m(2) - \Delta S_m(1)$	—
$\Delta H_m(2) - \Delta H_m(1)$	—

The solution was checked against the official solution.

Problem 7: The dithionate ion

The dithionate ion ($S_2O_6^{2-}$) is a rather inert inorganic ion. It can be prepared by bubbling sulphur-dioxide continuously into ice-cooled water to which manganese dioxide is added in small increments. Dithionate and sulphate ions are formed under these circumstances.

7.1 Write the balanced chemical equations for the two reactions.

After the reaction is complete, $Ba(OH)_2$ is added to the mixture until the sulphate ions are fully precipitated. This is followed by the addition of Na_2CO_3 .

7.2 Write the balanced equation for the reaction that takes place upon addition of Na_2CO_3 .

Sodium dithionate is then crystallized by evaporating some of the solvent. The prepared crystals dissolve readily in water and do not give a precipitate with $BaCl_2$ solution. When the solid is heated and maintained at $130^\circ C$, 14.88 % weight loss is observed. The resulting white powder dissolves in water and does not give a precipitate with $BaCl_2$ solution. When another sample of the original crystals is kept at $300^\circ C$ for a few hours, 41.34 % weight loss occurs. The resulting white powder dissolves in water and gives a white precipitate with $BaCl_2$ solution.

7.3 Give the composition of the prepared crystals and write balanced equations for the two processes that occur during heating.

Although dithionate ion is a fairly good reducing agent thermodynamically, it does not react with oxidants in solution at room temperature. At $75^\circ C$, however, it can be oxidized in acidic solutions. A series of kinetic experiments were carried out with bromine as an oxidant.

7.4 Write the balanced chemical equation for the reaction between bromine and dithionate ion.

The initial rates (v_0) of the reaction were determined in a number of experiments at $75^\circ C$.

$[\text{Br}_2]_0 \text{ (mmol dm}^{-3}\text{)}$	$[\text{Na}_2\text{S}_2\text{O}_6]_0 \text{ (mol dm}^{-3}\text{)}$	$[\text{H}^+]_0 \text{ (mol dm}^{-3}\text{)}$	$v_0 \text{ (nmol dm}^{-3} \text{ s}^{-1}\text{)}$
0.500	0.0500	0.500	640
0.500	0.0400	0.500	511
0.500	0.0300	0.500	387
0.500	0.0200	0.500	252
0.500	0.0100	0.500	129
0.400	0.0500	0.500	642
0.300	0.0500	0.500	635
0.200	0.0500	0.500	639
0.100	0.0500	0.500	641
0.500	0.0500	0.400	511
0.500	0.0500	0.300	383
0.500	0.0500	0.200	257
0.500	0.0500	0.100	128

7.5 Determine the order of the reaction with respect to Br_2 , H^+ and $\text{S}_2\text{O}_6^{2-}$, the experimental rate equation, and the value and unit of the rate constant.

In similar experiments, chlorine, bromate ion, hydrogen peroxide and chromate ion have all been used as oxidizing agents at 75°C . The rate equations for these processes are analogous to the one observed with bromine, the units of all rate constants are the same, the values are 2.53×10^{-5} (Cl_2), 2.60×10^{-5} (BrO_3^-), 2.56×10^{-5} (H_2O_2), and 2.54×10^{-5} ($\text{Cr}_2\text{O}_7^{2-}$).

Experiments were also carried out in acidic sodium dithionate solution without any oxidizing agent. When following the processes by UV spectrophotometry, the slow appearance of a new absorption band around 275 nm was observed. Although hydrogen sulphate ion is a detectable product of the reaction, it does not absorb any light above 200 nm.

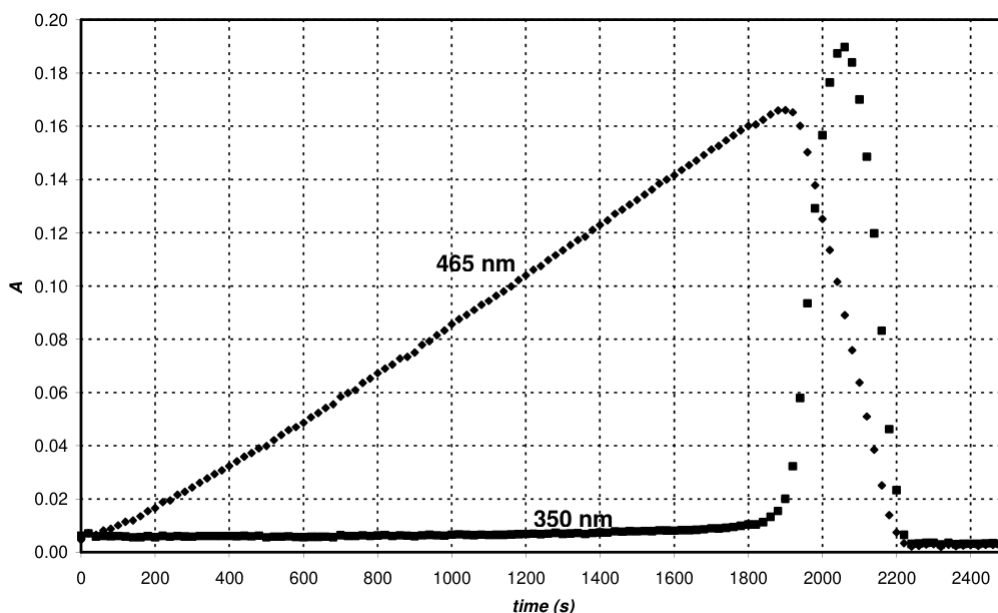
7.6 Give the formula of the major species causing the new absorption band and write the balanced equation of the chemical reaction occurring in the absence of oxidants.

An experiment was carried out to follow the absorbance at 275 nm with initial concentrations: $[\text{Na}_2\text{S}_2\text{O}_6] = 0.0022 \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.70 \text{ mol dm}^{-3}$, and the temperature was 75°C . A pseudo first-order kinetic curve was found with a half-life of 10 hours and 45 minutes.

7.7 Calculate the rate constant of the reaction.

Suggest a balanced chemical equation for the rate determining step of the reactions that used an oxidizing agent.

When periodate ion (which is present as H_4IO_6^- in aqueous solution) was used as an oxidant for dithionate ion, the two kinetic curves depicted in the graph were detected at 75°C in the same experiment at two different wavelengths. The initial concentrations were $[\text{H}_4\text{IO}_6^-] = 5.3 \cdot 10^{-4} \text{ mol dm}^{-3}$, $[\text{Na}_2\text{S}_2\text{O}_6] = 0.0519 \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.728 \text{ mol dm}^{-3}$. At 465 nm, only I_2 absorbs and its molar absorption coefficient is $715 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. At 350 nm, only I_3^- absorbs and its molar absorption coefficient is $11000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The optical path length was 0.874 cm.



7.8 Write balanced chemical equations for the reactions that occur in the region where the absorbance increases at 465 nm, and in the region where the absorbance decreases at 465 nm.

Calculate the expected time for the maximum absorbance of the kinetic curve measured at 465 nm.

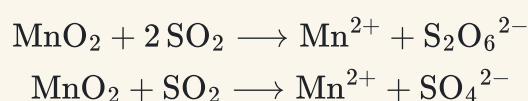
Estimate the expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm.

Official English text of the problem.

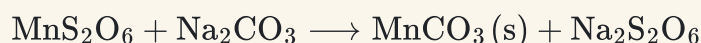
Answers

Species names and SMILES are supplied in the corresponding Solution parts and apply to all equations below.

- **7.1**



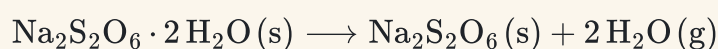
- **7.2**



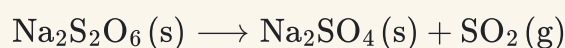
Carbonate also precipitates any residual dissolved barium as barium carbonate.

- **7.3** The crystals are **sodium dithionate dihydrate**, $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$.

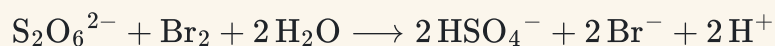
At 130 °C:



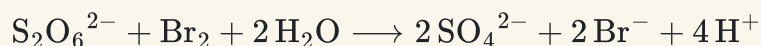
The subsequent decomposition at 300 °C is:



• 7.4



Equivalently:

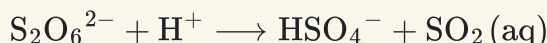


- 7.5 Orders in Br_2 , H^+ , and $\text{S}_2\text{O}_6^{2-}$: **0, 1, and 1**, respectively.

$$v = k[\text{H}^+][\text{S}_2\text{O}_6^{2-}], \quad k \approx 2.56 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 75 °C.

- 7.6 The absorbing species is **dissolved sulfur dioxide**, $\text{SO}_2(\text{aq})$.

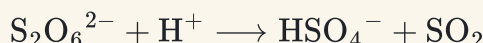


• 7.7

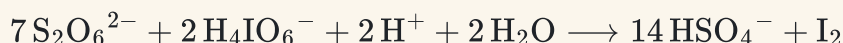
$$k_{\text{obs}} = 1.79 \times 10^{-5} \text{ s}^{-1}$$

$$k = \frac{k_{\text{obs}}}{[\text{H}^+]} \approx 2.56 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

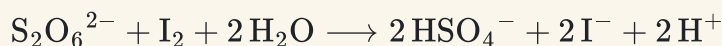
A consistent rate-determining reaction is:



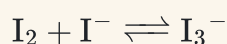
- 7.8 During increasing absorbance, the overall reaction is:



During decreasing absorbance:



The transient triiodide signal results from:



The predicted peak time and slope ratio are:

$$t_{\text{max}} \approx 1.9 \times 10^3 \text{ s} \approx 32 \text{ min}$$

$$|m_{\text{increase}}| : |m_{\text{decrease}}| \approx 1 : 7$$

Thus the signed ratio $m_{\text{increase}}/m_{\text{decrease}} \approx -1/7$.

Solution

Dot-separated SMILES for salts and hydrates specify their ionic composition, not their crystal structure or hydration geometry.

7.1 — Formation of dithionate and sulphate

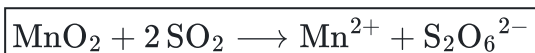
The relevant species are:

Species	SMILES
Dithionate ion, $\text{S}_2\text{O}_6^{2-}$	[O-]S(=O)(=O)S(=O)(=O)[O-]
Sulfur dioxide, SO_2	O=S=O

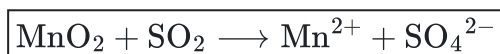
Species	SMILES
Sulphate ion, SO_4^{2-}	[O-]S(=O)(=O)[O-]
Manganese(II) ion, Mn^{2+}	[Mn+2]
Manganese(IV) oxide, MnO_2	[Mn+4].[O-2].[O-2]

The manganese dioxide SMILES is a formal ionic formula-unit representation of an extended solid. Dithionate contains an S–S bond joining two approximately tetrahedral sulfur centres.

Manganese is reduced from +4 to +2, accepting two electrons. Sulfur starts at +4 in sulfur dioxide. Formation of dithionate raises each of two sulfur atoms to +5, supplying the required two electrons:



Alternatively, oxidation of one sulfur atom to +6 supplies two electrons and produces sulphate:



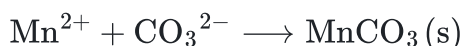
Both equations balance atoms and charge without additional water or hydrogen ions.

7.2 — Addition of sodium carbonate

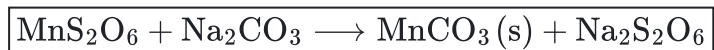
The additional species are:

Species	SMILES
Manganese(II) dithionate, MnS_2O_6	[Mn+2].[O-]S(=O)(=O)S(=O)(=O)[O-]
Sodium carbonate, Na_2CO_3	[Na+].[Na+].[O-]C(=O)[O-]
Carbonate ion, CO_3^{2-}	[O-]C(=O)[O-]
Manganese(II) carbonate, MnCO_3	[Mn+2].[O-]C(=O)[O-]
Sodium dithionate, $\text{Na}_2\text{S}_2\text{O}_6$	[Na+].[Na+].[O-]S(=O)(=O)S(=O)(=O)[O-]
Barium ion, Ba^{2+}	[Ba+2]
Barium carbonate, BaCO_3	[Ba+2].[O-]C(=O)[O-]

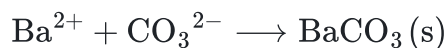
After removal of sulphate, carbonate precipitates the remaining dissolved manganese(II):



The corresponding salt equation shows the formation of soluble sodium dithionate:



Any soluble barium remaining from the previous addition is also removed:



7.3 — Composition and thermal decomposition

The additional species are:

Species	SMILES
Sodium dithionate dihydrate, $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2 \text{H}_2\text{O}$	[Na+].[Na+].[O-]S(=O)(=O)S(=O)(=O)[O-].O.O
Water, H_2O	O
Sodium sulphate, Na_2SO_4	[Na+].[Na+].[O-]S(=O)(=O)[O-]

Species	SMILES
Barium sulphate, BaSO ₄	[Ba+2].[O-]S(=O)(=O)[O-]

Let the crystals be Na₂S₂O₆ · n H₂O. Using standard rounded atomic masses,

$$M(\text{Na}_2\text{S}_2\text{O}_6) = 206.10 \text{ g mol}^{-1}, \quad M(\text{H}_2\text{O}) = 18.016 \text{ g mol}^{-1}.$$

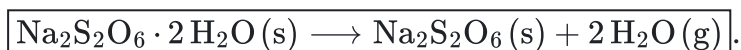
The absence of a barium precipitate after heating to 130 °C is consistent with retention of dithionate. Assigning the first mass loss to water gives

$$\frac{18.016n}{206.10 + 18.016n} = 0.1488.$$

Hence

$$n = \frac{0.1488(206.10)}{18.016(1 - 0.1488)} = 1.9998 \approx 2.$$

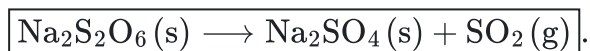
Thus the crystals are **sodium dithionate dihydrate**, and dehydration is



The hydrate molar mass is approximately 242.132 g mol⁻¹. After the 300 °C treatment, the mass remaining per mole of original hydrate is

$$(1 - 0.4134)(242.132) = 142.03 \text{ g}.$$

This matches one mole of sodium sulphate, $M \approx 142.04 \text{ g mol}^{-1}$. The anhydrous dithionate therefore decomposes by disproportionation:



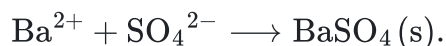
One sulfur atom changes from +5 to +6, and the other from +5 to +4. Starting from the original crystals, the overall reaction is



Its predicted total mass loss is

$$\frac{64.06 + 2(18.016)}{242.132} \times 100\% = 41.34\%.$$

The sulphate residue explains the white precipitate:



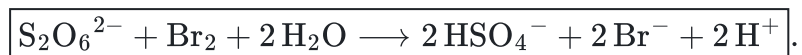
7.4 — Oxidation by bromine

The additional species are:

Species	SMILES
Bromine, Br ₂	BrBr
Bromide ion, Br ⁻	[Br-]
Hydrogen ion, H ⁺	[H+]
Hydrogen sulphate ion, HSO ₄ ⁻	OS(=O)(=O)[O-]

The hydrogen-ion notation represents aqueous acidity; it does not describe proton solvation.

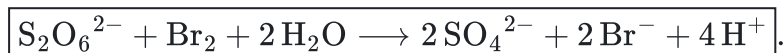
Oxidation of the two sulfur atoms from +5 to +6 releases two electrons. One bromine molecule accepts these electrons to form two bromide ions. Writing hydrogen sulphate as the sulfur product in acidic solution gives



Using



the equivalent sulphate-form equation is



7.5 — Rate law and rate constant

Write the empirical rate law as

$$v = k[\text{Br}_2]^a[\text{H}^+]^b[\text{S}_2\text{O}_6^{2-}]^c.$$

The independently varied concentrations establish the orders:

- Changing bromine from 0.100 to 0.500 mmol dm⁻³ leaves the rate essentially unchanged, so $a = 0$.
- Increasing dithionate fivefold, from 0.0100 to 0.0500 mol dm⁻³, changes the rate from 129 to 640, approximately fivefold. Thus $c = 1$.
- Increasing hydrogen-ion concentration fivefold, from 0.100 to 0.500 mol dm⁻³, changes the rate from 128 to 640, exactly fivefold within the reported values. Thus $b = 1$.

Therefore,

$$\boxed{v = k[\text{H}^+][\text{S}_2\text{O}_6^{2-}]}.$$

Using the first experiment,

$$k = \frac{640 \times 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}}{(0.500 \text{ mol dm}^{-3})(0.0500 \text{ mol dm}^{-3})} = \boxed{2.56 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}.$$

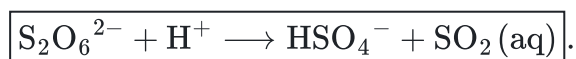
The overall empirical order is two.

7.6 — Reaction without an oxidant

The absorbing species is **sulfur dioxide**, SO₂ (aq), SMILES o=s=o.

Dithionate can disproportionate: one sulfur atom is oxidized from +5 to +6, producing hydrogen sulphate, while the other is reduced to +4. In the strongly acidic medium, the latter product is predominantly dissolved sulfur dioxide.

The balanced equation is



Hydrogen sulphate does not absorb at 275 nm according to the statement, so the growing band is assigned to the sulfur dioxide product.

7.7 — Half-life and the rate-determining reaction

Hydrogen ion is in large excess over dithionite, so its concentration remains approximately constant. Consequently,

$$-\frac{d[\text{S}_2\text{O}_6^{2-}]}{dt} = k[\text{H}^+][\text{S}_2\text{O}_6^{2-}] = k_{\text{obs}}[\text{S}_2\text{O}_6^{2-}],$$

where

$$k_{\text{obs}} = k[\text{H}^+].$$

The half-life is

$$t_{1/2} = 10(3600) + 45(60) = 38700 \text{ s}.$$

For first-order decay,

$$k_{\text{obs}} = \frac{\ln 2}{t_{1/2}} = \frac{0.693147}{38700} = \boxed{1.79 \times 10^{-5} \text{ s}^{-1}}.$$

The corresponding second-order constant is

$$k = \frac{1.79 \times 10^{-5}}{0.70} = \boxed{2.56 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}.$$

This agrees with the bromine result and with the constants for the other oxidants. Together with the zero order in bromine, this supports a common slow reaction that does not involve the oxidant:



The released sulfur dioxide is then rapidly oxidized. For example, with bromine,



Adding these two reactions gives the overall equation in 7.4. This is a consistent kinetic mechanism; the rate data alone do not uniquely establish its microscopic elementary steps.

7.8 — Periodate, iodine formation, and iodine consumption

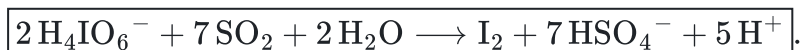
The additional species are:

Species	SMILES
Tetrahydrogen orthoperiodate ion, H_4IO_6^-	[O-][I+](O)(O)(O)(O)[O-]
Iodine, I_2	I I
Iodide ion, I^-	[I-]
Triiodide ion, I_3^-	I[I-]I

The periodate SMILES is a charge-separated representation; iodine has six oxygen neighbours in an approximately octahedral arrangement. Triiodide is linear and has three-centre, four-electron bonding, which the single-bond SMILES does not fully describe.

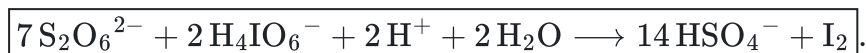
Increasing absorbance at 465 nm.

The slow reaction in 7.7 supplies sulfur dioxide. Periodate rapidly oxidizes this sulfur dioxide while being reduced to iodine:



The stoichiometry follows from electron balance: two iodine atoms each fall from oxidation state +7 to 0, accepting fourteen electrons; seven sulfur dioxide molecules each supply two electrons.

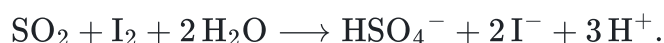
Adding seven occurrences of the slow dithionate decomposition gives



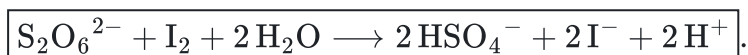
Thus **seven dithionate ions produce one iodine molecule**, and the 465 nm absorbance rises.

Decreasing absorbance at 465 nm.

Once periodate is exhausted, newly generated sulfur dioxide reduces iodine:

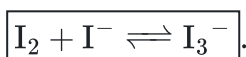


Including the slow dithionate decomposition gives

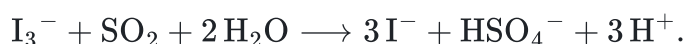


Now **one dithionate ion consumes one iodine molecule**.

As iodide accumulates, some remaining iodine forms triiodide:



This accounts for the transient 350 nm signal. Triiodide is ultimately reduced as well:



Time of maximum iodine absorbance.

The maximum occurs approximately when all periodate has been converted to iodine. The required amount of decomposed dithionate per unit volume is

$$\Delta[\text{S}_2\text{O}_6^{2-}] = \frac{7}{2}[\text{H}_4\text{IO}_6^-]_0 = \frac{7}{2}(5.3 \times 10^{-4}) = 1.855 \times 10^{-3} \text{ mol dm}^{-3}.$$

This is only

$$\frac{1.855 \times 10^{-3}}{0.0519} \times 100\% = 3.57\%$$

of the initial dithionate, so an approximately constant rate is appropriate:

$$v \simeq (2.56 \times 10^{-5})(0.728)(0.0519) = 9.67 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}.$$

Therefore,

$$t_{\max} \simeq \frac{1.855 \times 10^{-3}}{9.67 \times 10^{-7}} = \boxed{1.9 \times 10^3 \text{ s} \approx 32 \text{ min}}.$$

Allowing for dithionate depletion while holding acidity constant gives the modest refinement

$$t_{\max} = \frac{-\ln\left(1 - \frac{(7/2)[\text{H}_4\text{IO}_6^-]_0}{[\text{S}_2\text{O}_6^{2-}]_0}\right)}{k[\text{H}^+]} \approx 1.95 \times 10^3 \text{ s}.$$

Both estimates are consistent with the graph.

The expected peak height provides an independent stoichiometric check. Neglecting the small amount of triiodide near the iodine maximum,

$$[\text{I}_2]_{\text{max}} \simeq \frac{5.3 \times 10^{-4}}{2} = 2.65 \times 10^{-4} \text{ mol dm}^{-3}.$$

Beer–Lambert’s law then gives

$$A_{465, \text{max}} = \epsilon l [\text{I}_2]_{\text{max}} = (715)(0.874)(2.65 \times 10^{-4}) \approx 0.166,$$

matching the plotted maximum.

The apparently large triiodide absorbance does not imply a similarly large concentration: its peak $A_{350} \approx 0.19$ corresponds to only

$$[\text{I}_3^-]_{\text{max}} \approx \frac{0.19}{11000(0.874)} \approx 2.0 \times 10^{-5} \text{ mol dm}^{-3}.$$

Ratio of slopes.

Let v denote the approximately constant rate of dithionate decomposition. Ignoring the transient redistribution into triiodide,

$$\left(\frac{d[\text{I}_2]}{dt} \right)_{\text{increase}} = \frac{v}{7}, \quad \left(\frac{d[\text{I}_2]}{dt} \right)_{\text{decrease}} = -v.$$

Because $A_{465} = \epsilon l [\text{I}_2]$, the same ratio applies to the absorbance slopes:

$$\boxed{\frac{m_{\text{increase}}}{m_{\text{decrease}}} \approx -\frac{1}{7}}.$$

Thus the decreasing region is expected to be approximately **seven times steeper in magnitude**.

Triiodide formation and the small decline in dithionate concentration cause departures from this simple estimate.

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

Problem 8: Photochemistry of cerium(III) chloride solutions

Ms. Z was a bright student, whose research project was to measure the complexation of all lanthanide(III) ions with newly designed complexing ligands. One day she monitored the UV-VIS absorption with Ce(III) and a particularly poor complexing ligand in a spectrophotometer. She noticed that some small bubbles had formed in the closed cell by the end of the 12-hour experiment. Soon she realized that the presence of the ligand is not necessary to see the bubble formation, and continued her experiments with an acidified CeCl_3 solution. Bubble formation never occurred when she just kept the solution in the spectrophotometer without turning on the instrument. Next, Ms. Z used a small quartz flask, in which she dipped a chloride ion selective electrode and could also withdraw samples regularly for spectrophotometric measurements. She calibrated the chloride ion selective electrode using two different NaCl solutions and obtained the following results:

$c_{\text{NaCl}} \text{ (mol/dm}^3\text{)}$	$E \text{ (mV)}$
0.1000	26.9
1.000	−32.2

8.1 Give a formula to calculate the chloride ion concentration of an unknown sample based on the electrode voltage reading (E).

Ms. Z also determined the molar absorption coefficient for Ce^{3+} ($\epsilon = 35.2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 295 nm, and, as a precaution, also for Ce^{4+} ($\epsilon = 3967 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

8.2 Give a formula to calculate the Ce^{3+} concentration from an absorbance reading at 295 nm (A) measured in a solution containing CeCl_3 (cuvette path length: 1.000 cm).

Ms. Z prepared a solution which contained $0.0100 \text{ mol/dm}^3 \text{ CeCl}_3$ and $0.1050 \text{ mol/dm}^3 \text{ HCl}$, and began her experiment by turning on a quartz lamp. HCl does not absorb at 295 nm.

8.3 What were the expected initial absorbance ($A_{295 \text{ nm}}$) and voltage (E) readings?

Before the quantitative experiment Ms. Z collected the gas formed into a carefully neutralized solution of methyl orange (acid-base and redox indicator). Although she saw bubbles going through the solution, the colour did not change or fade even after a day.

8.4 Give the formula of two gases, comprised of elements in the illuminated sample, which could not be present given the results of this experiment.

During her quantitative experiment she recorded the absorbance and voltage values regularly. The uncertainty of the spectrophotometric measurements is ± 0.002 and the accuracy of the voltage measurements is $\pm 0.3 \text{ mV}$.

time (min)	0	120	240	360	480
$A_{295 \text{ nm}}$	0.3496	0.3488	0.3504	0.3489	0.3499
$E \text{ (mV)}$	19.0	18.8	18.8	19.1	19.2

8.5 Estimate the average rate of change in the concentrations of Ce^{3+} , Cl^- , and H^+ .

$$d[\text{Ce}^{3+}]/dt = d[\text{Cl}^-]/dt = d[\text{H}^+]/dt = ?$$

The following day, Ms. Z used an intense monochromatic light beam (254 nm) with an intensity of 0.0500 W. She passed this light through a 5-cm long quartz photoreactor filled with the same acidic CeCl_3 solution she had used before. She measured the molar absorption coefficient for Ce^{3+} ($\epsilon = 2400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 254 nm.

8.6 What percentage of the light is absorbed in this experimental setup?

The equipment allowed her to lead the gas first through a drying tube that removed traces of water vapour and then into a closed chamber, whose volume was 68 cm^3 . The chamber was equipped with a high-precision manometer and an igniter. She first filled the chamber with dry argon to a pressure of 102165 Pa and then she turned on the lamp. In 18.00 hours, the pressure reached 114075 Pa. The temperature of the equipment was 22.0°C .

8.7 Estimate the amount of substance of the gas collected in the chamber.

At this point, Ms. Z turned off the light and pressed the ignition button. When the chamber cooled down to the initial temperature, the final pressure was 104740 Pa.

8.8 Suggest the formula(s) of the gas(es) formed and collected, and give the balanced equation for the original chemical reaction taking place under illumination.

8.9 What would be the final pressure after the ignition if the chamber was being filled for 24 hours before ignition?

8.10 Estimate the quantum yield of product formation in the Ce(III) solution.

Official English text of the problem.

Answers

- **8.1** For chloride ion, Cl^- ([Cl-]):

$$[\text{Cl}^-] = 10^{-(E/\text{mV}+32.2)/59.1} \text{ mol dm}^{-3}.$$

- **8.2** For cerium(III) ion, Ce^{3+} ([Ce+3]), in the initial solution:

$$[\text{Ce}^{3+}] = \frac{A}{35.2} \text{ mol dm}^{-3}.$$

- **8.3** $A_{295 \text{ nm}} = 0.352$, $E = 19.2 \text{ mV}$.

- **8.4** Hydrogen chloride, HCl ([H]Cl), and chlorine, Cl_2 (ClCl).

- **8.5** All three average rates are indistinguishable from zero:

$$\frac{d[\text{Ce}^{3+}]}{dt} \simeq \frac{d[\text{Cl}^-]}{dt} \simeq \frac{d[\text{H}^+]}{dt} \simeq 0 \text{ mol dm}^{-3} \text{ min}^{-1}.$$

Here H^+ denotes the hydrogen ion or proton ([H+]).

- **8.6** $100(1 - 10^{-120})\% \simeq 100\%$.

- **8.7** $n_{\text{gas}} \simeq 3.3 \times 10^{-4} \text{ mol}$.

- **8.8** Hydrogen, H_2 ([H][H]), and oxygen, O_2 (o=o), in a 2 : 1 molar ratio. Water (o) undergoes photochemical decomposition:



under illumination, with cerium(III) acting as photocatalyst.

- **8.9** $p_{\text{final}} = 104740 \text{ Pa}$.

- **8.10** Counting both gaseous products:

$$\Phi_{\text{gas}} = 0.048 \text{ molecules per absorbed photon}.$$

The individual product yields are

$$\Phi_{\text{H}_2} = 0.032, \quad \Phi_{\text{O}_2} = 0.016.$$

Solution

The SMILES specify chemical species and connectivity; they do not depict aqueous solvation or cerium coordination geometry. The oxygen SMILES o=o does not encode its ground-state triplet spin.

8.1

The chloride electrode has a logarithmic concentration response:

$$E = a + b \log_{10} \left(\frac{[\text{Cl}^-]}{1 \text{ mol dm}^{-3}} \right).$$

The two calibration concentrations differ by a factor of ten, giving

$$b = \frac{-32.2 - 26.9}{\log_{10}(1.000) - \log_{10}(0.1000)} = -59.1 \text{ mV}.$$

At $1.000 \text{ mol dm}^{-3}$, the logarithm is zero, so $a = -32.2 \text{ mV}$. Therefore,

$$\frac{E}{\text{mV}} = -32.2 - 59.1 \log_{10} \left(\frac{[\text{Cl}^-]}{1 \text{ mol dm}^{-3}} \right),$$

and hence

$$[\text{Cl}^-] = 10^{-(E/\text{mV} + 32.2)/59.1} \text{ mol dm}^{-3}.$$

8.2

The Beer–Lambert law is

$$A = \varepsilon \ell c.$$

For a solution whose cerium is present as cerium(III),

$$[\text{Ce}^{3+}] = \frac{A}{(35.2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})(1.000 \text{ cm})},$$

so

$$[\text{Ce}^{3+}] = \frac{A}{35.2} \text{ mol dm}^{-3}.$$

If cerium(IV), Ce^{4+} ($[\text{Ce}^{4+}]$), were also present, its contribution would have to be included:

$$A = \ell (\varepsilon_3 [\text{Ce}^{3+}] + \varepsilon_4 [\text{Ce}^{4+}]).$$

8.3

Cerium(III) chloride, CeCl_3 ($[\text{Ce}^{3+}] \cdot [\text{Cl}^-] \cdot [\text{Cl}^-] \cdot [\text{Cl}^-]$), supplies three chloride ions per cerium ion. Dissolved hydrogen chloride supplies one chloride ion per formula unit. Thus,

$$[\text{Cl}^-]_0 = 3(0.0100) + 0.1050 = 0.1350 \text{ mol dm}^{-3}.$$

The initial absorbance is

$$A_0 = (35.2)(1.000)(0.0100) = \boxed{0.352}.$$

The initial electrode voltage is

$$E_0 = -32.2 - 59.1 \log_{10}(0.1350) = 19.197 \dots \text{ mV},$$

or

$$\boxed{E_0 = 19.2 \text{ mV}.}$$

8.4

The two excluded gases are:

- **Hydrogen chloride**, HCl: its dissolution would acidify the carefully neutralized indicator solution and change the methyl-orange colour.
- **Chlorine**, Cl₂: it would oxidatively bleach the indicator; its reaction with water also acidifies the solution.

The absence of either a colour change or fading excludes these gases at detectable amounts in this qualitative experiment.

8.5

A constant absorbance and a constant electrode voltage are compatible with every reading at the stated uncertainties. In particular, the endpoint changes are only

$$\Delta A = 0.3499 - 0.3496 = 0.0003, \quad \Delta E = 19.2 - 19.0 = 0.2 \text{ mV}.$$

Neither establishes a concentration trend.

The absorbance also rules out detectable net conversion of cerium(III) into cerium(IV). Let $c_T = c_3 + c_4$ be the conserved total cerium concentration. Then

$$A = \ell [\varepsilon_3 c_T + (\varepsilon_4 - \varepsilon_3) c_4].$$

Since

$$\varepsilon_4 - \varepsilon_3 = 3967 - 35.2 = 3931.8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1},$$

even a small accumulation of cerium(IV) would increase the absorbance appreciably. The measurements show no detectable net change in the cerium oxidation-state distribution.

The constant electrode voltage similarly indicates no detectable change in chloride concentration. At this acidity, charge balance gives

$$[\text{H}^+] + 3[\text{Ce}^{3+}] + 4[\text{Ce}^{4+}] = [\text{Cl}^-].$$

Consequently, the hydrogen-ion concentration also remains constant within the experimental resolution:

$$\boxed{\frac{d[\text{Ce}^{3+}]}{dt} \simeq \frac{d[\text{Cl}^-]}{dt} \simeq \frac{d[\text{H}^+]}{dt} \simeq 0 \text{ mol dm}^{-3} \text{ min}^{-1}.$$

8.6

At 254 nm, the absorbance through the photoreactor is

$$A_{254} = (2400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})(5 \text{ cm})(0.0100 \text{ mol dm}^{-3}) = 120.$$

Because $A = -\log_{10}(I/I_0)$,

$$\frac{I}{I_0} = 10^{-120}.$$

Therefore, the absorbed percentage is

$$\boxed{100(1 - 10^{-120})\% \simeq 100\%.$$

Essentially all incident light is absorbed.

8.7

The amount of argon, Ar ($[\text{Ar}]$), remains unchanged. At constant volume and temperature, the pressure increase is therefore due to the newly collected gas:

$$\Delta p = 114075 - 102165 = 11910 \text{ Pa.}$$

Using

$$V = 68 \times 10^{-6} \text{ m}^3, \quad T = 22.0 + 273.15 = 295.15 \text{ K},$$

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

$$n_{\text{gas}} = \frac{\Delta p V}{RT} = \frac{(11910)(68 \times 10^{-6})}{(8.314)(295.15)} = 3.300 \times 10^{-4} \text{ mol.}$$

Thus, to the precision of the stated volume,

$$n_{\text{gas}} \simeq 3.3 \times 10^{-4} \text{ mol.}$$

8.8

The gas mixture reacts on ignition, as shown by the substantial pressure decrease. Hydrogen is combustible, while oxygen provides the oxidant required for combustion in the initially argon-filled chamber. Both gases are consistent with the unchanged methyl-orange indicator.

The solution measurements show no detectable net consumption of cerium(III), chloride, or hydrogen ions. The consistent overall process is therefore light-driven water decomposition:



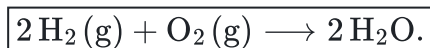
Cerium(III) absorbs the light and is regenerated overall. The gases are produced in the molar ratio

$$n_{\text{H}_2} : n_{\text{O}_2} = 2 : 1.$$

Their amounts after 18 hours are consequently

$$n_{\text{H}_2} = \frac{2}{3} n_{\text{gas}} \simeq 2.2 \times 10^{-4} \text{ mol},$$
$$n_{\text{O}_2} = \frac{1}{3} n_{\text{gas}} \simeq 1.1 \times 10^{-4} \text{ mol.}$$

Ignition reverses the overall reaction:



After cooling, the newly formed water is distributed between liquid and vapour.

8.9

The argon partial pressure returns to its original value when the chamber returns to its original temperature. Thus, after the 18-hour experiment, the water-vapour contribution is

$$p_{\text{H}_2\text{O}} = 104740 - 102165 = 2575 \text{ Pa.}$$

Combustion produces two water molecules for every three molecules of collected gas. If all this water remained gaseous, its pressure contribution would be

$$p_{\text{H}_2\text{O, all vapour}} = \frac{2}{3}(11910) = 7940 \text{ Pa.}$$

The observed contribution is substantially smaller, so some water has condensed. Liquid water is therefore present, and the vapour is saturated at the final temperature.

Collecting the gases for 24 hours produces more water upon ignition. At the same final temperature, the additional water increases the amount of liquid while the equilibrium vapour pressure stays the same. Hence,

$$p_{\text{final, 24h}} = 102165 + 2575 = 104740 \text{ Pa.}$$

8.10

The quantum yield is the number of product molecules formed per absorbed photon. From 8.6, essentially all incident photons are absorbed.

The light energy supplied in 18.00 hours is

$$Q = Pt = (0.0500 \text{ J s}^{-1})(18.00 \times 3600 \text{ s}) = 3240 \text{ J.}$$

Using $h = 6.626 \times 10^{-34} \text{ J s}$ and $c = 2.998 \times 10^8 \text{ m s}^{-1}$, the energy of one 254-nm photon is

$$E_{\gamma} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34})(2.998 \times 10^8)}{254 \times 10^{-9}} = 7.82 \times 10^{-19} \text{ J.}$$

The amount of absorbed photons, with $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$, is

$$n_{\gamma} = \frac{Q}{N_A E_{\gamma}} = 6.88 \times 10^{-3} \text{ mol.}$$

Counting all newly formed gas molecules,

$$\Phi_{\text{gas}} = \frac{n_{\text{H}_2} + n_{\text{O}_2}}{n_{\gamma}} = \frac{3.300 \times 10^{-4}}{6.88 \times 10^{-3}} = \boxed{0.048}.$$

This means approximately **4.8 gas molecules per 100 absorbed photons**.

For each product separately,

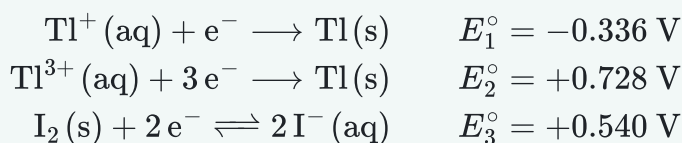
$$\Phi_{\text{H}_2} = \frac{2}{3} \Phi_{\text{gas}} = 0.032, \quad \Phi_{\text{O}_2} = \frac{1}{3} \Phi_{\text{gas}} = 0.016.$$

The solution was checked against the official solution.

Problem 9: Thallium iodides

Thallium exists in two different oxidation states: Tl^+ and Tl^{3+} . Iodide ions can combine with iodine to form tri-iodide ions (I_3^-) in aqueous solutions,

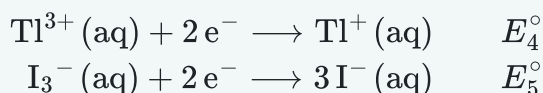
The standard redox potentials for some relevant reactions are:



The equilibrium constant for the reaction $\text{I}_2 (\text{s}) + \text{I}^- (\text{aq}) \longrightarrow \text{I}_3^- (\text{aq})$: $K_1 = 0.459$.

Use $T = 25^\circ \text{C}$ throughout this problem.

9.1 Calculate the redox potentials E_4° and E_5° for the following reactions:



9.2 Write empirical formulae for all theoretically possible neutral compounds that contain one thallium ion and any number of iodide and/or tri-iodide ion(s) as anion(s).

There is an empirical formula that could belong to two different compounds. Which one? Based on the standard redox potentials, which of the two isomers mentioned above is the stable one at standard conditions? Write the chemical reaction for the isomerisation of the other isomer of thallium iodide.

Complex formation can shift this equilibrium. The cumulative complex formation constant for the reaction $\text{Tl}^{3+} + 4\text{I}^- \longrightarrow \text{TlI}_4^-$ is $\beta_4 = 10^{35.7}$

9.3 Write the reaction that takes place when a solution of the more stable isomer of thallium iodide is treated with an excess of KI. Calculate the equilibrium constant K_2 for this reaction.

If the solution of the more stable isomer is treated with a strong basic reagent precipitation of a black substance can be observed. After the water content of the precipitate is removed, the remaining material contains 89.5% thallium (by mass).

9.4 What is the empirical formula of this compound? Show your calculations. Write a balanced equation for its formation.

Official English text of the problem.

Answers

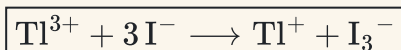
• **9.1**

$$E_4^\circ = +1.260 \text{ V}, \quad E_5^\circ = +0.550 \text{ V}.$$

• **9.2** The possible empirical formulae are

$$\text{TII}, \text{TII}_3, \text{TII}_5, \text{TII}_7, \text{TII}_9.$$

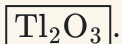
There are six ionic compositions because TII_3 can be thallium(III) iodide or thallium(I) triiodide. **Thallium(I) triiodide is the stable isomer**, with formal ionic SMILES $[\text{Tl}^+] \cdot \text{I}^- [\text{I}^-] \text{I}^-$.



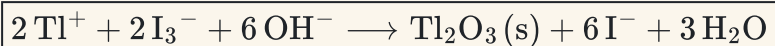
• **9.3** Tetraiodothallate(III), $[\text{TII}_4]^-$, SMILES $[\text{Tl}^+](\text{I})(\text{I})(\text{I})\text{I}$, forms:

$$\text{Tl}^+ + \text{I}_3^- + \text{I}^- \rightleftharpoons [\text{TII}_4]^-, \quad K_2 \approx 5.0 \times 10^{11}.$$

- **9.4** The dried precipitate is **thallium(III) oxide**:



Its formal ionic formula-unit SMILES is $[\text{Tl}+3] \cdot [\text{Tl}+3] \cdot [\text{O}-2] \cdot [\text{O}-2] \cdot [\text{O}-2]$.



Solution

We use

$$T = 298.15 \text{ K}, \quad R = 8.31446 \text{ J mol}^{-1} \text{ K}^{-1}, \quad F = 96485.3 \text{ C mol}^{-1}.$$

The species used below include thallium(I) ion $[\text{Tl}+]$, thallium(III) ion $[\text{Tl}+3]$, iodide ion $[\text{I}-]$, iodine I_2 , and triiodide ion $[\text{I}-]\text{I}$. Triiodide is linear; the SMILES does not describe its three-centre, four-electron bonding fully.

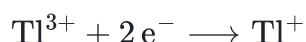
For ionic solids, dot-separated SMILES specify formal ionic formula units, not discrete molecules or crystal lattices.

9.1 — Standard reduction potentials

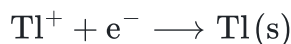
Potentials must be combined through Gibbs energies:

$$\Delta_r G^\circ = -nFE^\circ.$$

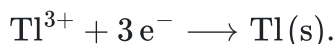
Adding



and



gives



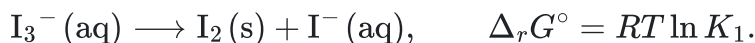
Consequently,

$$-3FE_2^\circ = -2FE_4^\circ - FE_1^\circ,$$

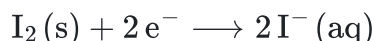
so

$$E_4^\circ = \frac{3E_2^\circ - E_1^\circ}{2} = \frac{3(0.728) - (-0.336)}{2} = \boxed{1.260 \text{ V}}.$$

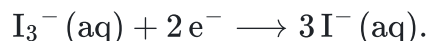
For the second potential, reverse the triiodide formation reaction:



Adding this to



gives the required half-reaction:



Therefore,

$$-2FE_5^\circ = RT \ln K_1 - 2FE_3^\circ,$$

and

$$\begin{aligned}
 E_5^\circ &= E_3^\circ - \frac{RT}{2F} \ln K_1 \\
 &= 0.540 - \frac{(8.31446)(298.15)}{2(96485.3)} \ln(0.459) \\
 &= 0.550003 \text{ V}.
 \end{aligned}$$

Thus,

$$E_5^\circ = +0.550 \text{ V}.$$

9.2 — Possible compounds and the stable isomer

Both permitted anions, I^- and I_3^- , carry charge -1 . A neutral compound therefore needs one anion per Tl^+ , or three anions per Tl^{3+} .

If m is the number of iodide ions and n the number of triiodide ions per thallium ion, neutrality requires

$$m + n = z,$$

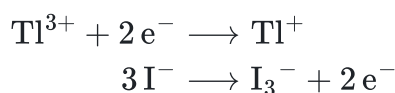
where $z = 1$ or 3 . The total number of iodine atoms is $m + 3n$.

This gives every permitted combination:

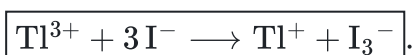
Empirical formula	Ionic contents per formula unit	Name and formal formula-unit SMILES
TlI	Tl^+, I^-	Thallium(I) iodide — $[\text{Tl}^+].[\text{I}^-]$
TlI_3	$\text{Tl}^+, \text{I}_3^-$	Thallium(I) triiodide — $[\text{Tl}^+].[\text{I}^-] \text{I}$
TlI_3	$\text{Tl}^{3+}, 3 \text{I}^-$	Thallium(III) iodide — $[\text{Tl}^{3+}].[\text{I}^-].[\text{I}^-].[\text{I}^-]$
TlI_5	$\text{Tl}^{3+}, 2 \text{I}^-, \text{I}_3^-$	Thallium(III) diiodide triiodide — $[\text{Tl}^{3+}].[\text{I}^-].[\text{I}^-].[\text{I}^-] \text{I}$
TlI_7	$\text{Tl}^{3+}, \text{I}^-, 2 \text{I}_3^-$	Thallium(III) iodide bis(triiodide) — $[\text{Tl}^{3+}].[\text{I}^-].[\text{I}^-] \text{I} . [\text{I}^-] \text{I}$
TlI_9	$\text{Tl}^{3+}, 3 \text{I}_3^-$	Thallium(III) tris(triiodide) — $[\text{Tl}^{3+}].[\text{I}^-] \text{I} . [\text{I}^-] \text{I} . [\text{I}^-] \text{I}$

The duplicated empirical formula is therefore TlI_3 .

To determine the preferred isomer, combine thallium(III) reduction with iodide oxidation:



The net reaction is



Its standard cell potential is

$$E_{\text{cell}}^\circ = E_4^\circ - E_5^\circ = 1.260 - 0.550 = +0.710 \text{ V},$$

and hence

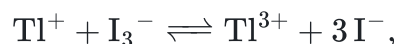
$$\Delta_r G^\circ = -2FE_{\text{cell}}^\circ \approx -137 \text{ kJ mol}^{-1}.$$

The negative Gibbs energy establishes that **thallium(I) triiodide is favored** in the standard-state comparison requested. The isomerisation converts thallium(III) iodide into thallium(I) triiodide.

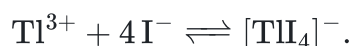
9.3 — Reaction with excess iodide

Potassium iodide, KI, has formula-unit SMILES [K+] . [I-]; its potassium ion [K+] is a spectator.

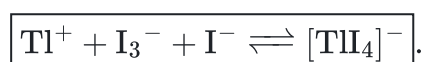
Complex formation stabilizes thallium(III). Add the reverse of the preceding redox reaction,



to



Cancelling Tl^{3+} and three iodide ions gives



The product is tetraiodothallate(III), [Tl-](I)(I)(I)I, with tetrahedral coordination. In this covalent SMILES representation the central atom has formal charge -1 ; the thallium **oxidation state remains** $+3$. SMILES does not specify the tetrahedral bond angles.

Let K_{iso} denote the equilibrium constant for the forward isomerisation in 9.2. Then

$$\ln K_{\text{iso}} = \frac{2F(E_4^\circ - E_5^\circ)}{RT},$$

or, at 298.15 K,

$$\log_{10} K_{\text{iso}} = \frac{2(E_4^\circ - E_5^\circ)}{0.059159 \text{ V}} \approx 24.003.$$

Because the complex formation reaction is added to the **reverse** isomerisation,

$$K_2 = \frac{\beta_4}{K_{\text{iso}}}.$$

Thus,

$$\log_{10} K_2 = 35.7 - 24.003 = 11.697,$$

$$\boxed{K_2} = \boxed{4.98 \times 10^{11} \approx 5.0 \times 10^{11}}.$$

This dimensionless thermodynamic equilibrium constant is very large, explaining why excess iodide produces the thallium(III) complex.

9.4 — Identification and formation of the black precipitate

Precipitation in strongly basic solution followed by removal of water suggests a metal oxide. For the dried oxide, consider 100.0 g of material:

$$m(\text{Tl}) = 89.5 \text{ g}, \quad m(\text{O}) = 10.5 \text{ g}.$$

Using $M(\text{Tl}) = 204.38 \text{ g mol}^{-1}$ and $M(\text{O}) = 16.00 \text{ g mol}^{-1}$,

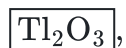
$$n(\text{Tl}) = \frac{89.5}{204.38} = 0.4379 \text{ mol},$$

$$n(\text{O}) = \frac{10.5}{16.00} = 0.6563 \text{ mol}.$$

Therefore,

$$n(\text{Tl}) : n(\text{O}) = 1 : 1.499 \approx 2 : 3.$$

The empirical formula is



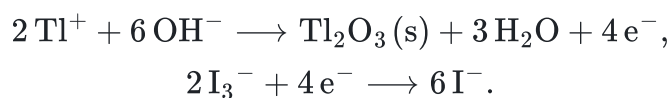
thallium(III) oxide. Its formal ionic representation contains thallium(III) and oxide ions, the latter having SMILES [O-2].

The calculated thallium mass fraction confirms the identification:

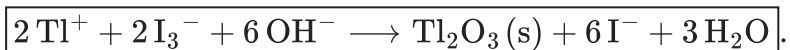
$$w(\text{Tl}) = \frac{2(204.38)}{2(204.38) + 3(16.00)} = 0.894912 = \boxed{89.49\%},$$

which agrees with the stated 89.5%.

Formation of this oxide oxidizes thallium(I) to thallium(III), while triiodide is reduced to iodide. In basic solution the balanced half-reactions are



Here hydroxide ion has SMILES [OH-], and water has SMILES O. Adding the half-reactions gives



This equation describes formation of the dry oxide; water associated with the initially hydrated precipitate is removed during drying.

The solution was checked against the official solution.