

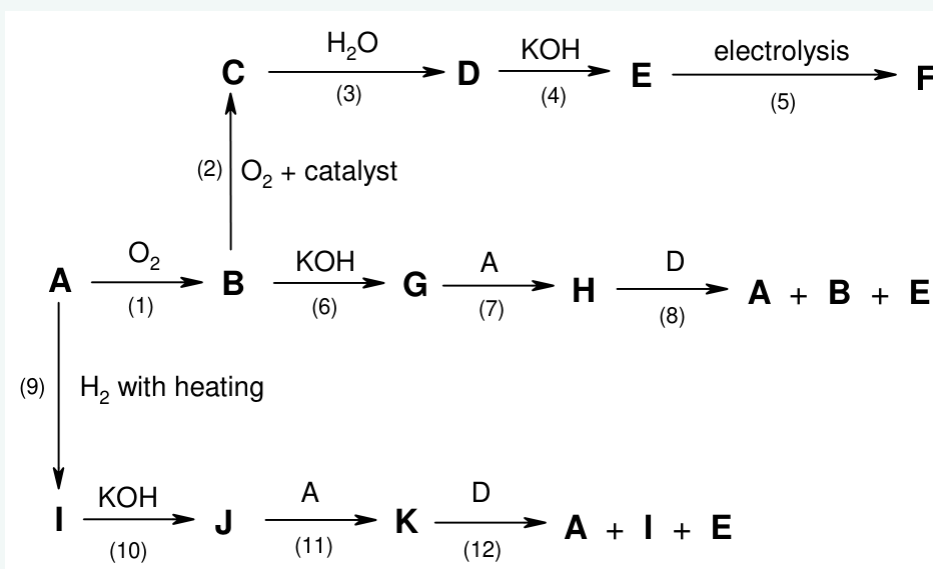
IChO 1981

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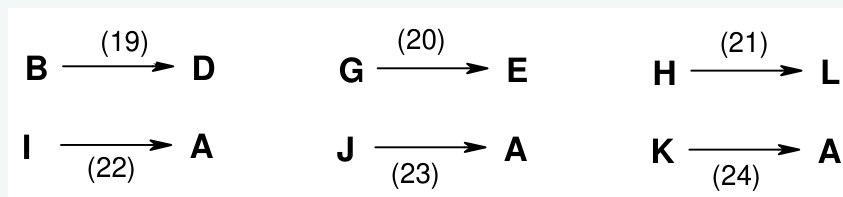
Problem 1: Reaction scheme of a substance A and its compounds (substances A-L)

The sample **A** participates in the transformations in scheme 1. Only the products containing **A** are shown in the scheme 1.



Scheme 1

- Substance **A** is a solid and is insoluble in water.
- Substances **B** and **I** are gases soluble in water.
- Substances **E**, **F**, **J** and **K** are solid and soluble in water.
- Aqueous solutions of **B**, **G**, **H**, **I**, **J** and **K** react with **F**, the products in all cases being **E** and **D**.
- The following transformations occur during the interaction with an aqueous solution of iodine:



Write the chemical equations for the above interactions and balance them.

Official English text of the problem.

Answers

The substances are identified below. **K is a potassium polysulfide, K_2S_n , with $n \geq 2$; its exact chain length is not specified.**

Label	Formula	Name and SMILES
A	S , ordinarily molecular S_8	Sulfur; cyclooctasulfur: <chem>S1SSSSSSS1</chem>
B	SO_2	Sulfur dioxide: <chem>O=S=O</chem>
C	SO_3	Sulfur trioxide: <chem>O=S(=O)=O</chem>
D	H_2SO_4	Sulfuric acid: <chem>OS(=O)(=O)O</chem>
E	K_2SO_4	Potassium sulfate: <chem>[K+] . [K+] . [O-]S(=O)(=O)[O-]</chem>
F	$K_2S_2O_8$	Potassium peroxodisulfate, also called potassium persulfate: <chem>[K+] . [K+] . [O-]S(=O)(=O)OOS(=O)(=O)[O-]</chem>
G	K_2SO_3	Potassium sulfite: <chem>[K+] . [K+] . [O-]S(=O)[O-]</chem>
H	$K_2S_2O_3$	Potassium thiosulfate: <chem>[K+] . [K+] . [O-]S(=O)(=O)[S-]</chem>
I	H_2S	Hydrogen sulfide: <chem>[SH2]</chem>
J	K_2S	Potassium sulfide: <chem>[K+] . [K+] . [S-2]</chem>
K	K_2S_n	Potassium polysulfide; for $n = 2$, potassium disulfide: <chem>[K+] . [K+] . [S-]</chem> <chem>[S-]</chem>
L	$K_2S_4O_6$	Potassium tetrathionate: <chem>[K+] . [K+] . [O-]S(=O)(=O)SSS(=O)(=O)[O-]</chem>

For a general polysulfide, insert $n - 2$ neutral s atoms between the two terminal [S-] atoms in K's SMILES. The disconnected ionic SMILES do not describe crystal lattices. The sulfur-ring SMILES does not specify the usual crown conformation of S_8 .

Other species appearing in the equations are water O, dioxygen O=O, dihydrogen [H][H], potassium hydroxide [K+] . [OH-], iodine I I, hydrogen iodide [H] I (hydroiodic acid in aqueous solution), and potassium iodide [K+] . [I-].

Elemental sulfur is written conventionally as S in the equations, so its coefficients count sulfur atom equivalents.

Scheme 1: reactions (1)–(12)

- (1) S + O2 -> SO2
- (2) 2 SO2 + O2 >>[catalyst] 2 SO3
- (3) SO3 + H2O -> H2SO4
- (4) H2SO4 + 2 KOH -> K2SO4 + 2 H2O
- (5) 2 K2SO4 + 2 H2O >>[electrolysis] K2S2O8 + 2 KOH + H2
- (6) SO2 + 2 KOH -> K2SO3 + H2O
- (7) K2SO3 + S -> K2S2O3
- (8) K2S2O3 + H2SO4 -> S + SO2 + K2SO4 + H2O
- (9) S + H2 >>[Delta] H2S
- (10) H2S + 2 KOH -> K2S + 2 H2O

- (11) $\text{K}_2\text{S} + (n - 1) \text{S} \longrightarrow \text{K}_2\text{S}_n$
- (12) $\text{K}_2\text{S}_n + \text{H}_2\text{SO}_4 \longrightarrow (n - 1) \text{S} + \text{H}_2\text{S} + \text{K}_2\text{SO}_4$

d): reactions with F

The six interactions are numbered (13)–(18) below in the printed order **B, G, H, I, J, K**.

- (13) $\text{SO}_2 + \text{K}_2\text{S}_2\text{O}_8 + 2 \text{H}_2\text{O} \longrightarrow \text{K}_2\text{SO}_4 + 2 \text{H}_2\text{SO}_4$
- (14) $\text{K}_2\text{SO}_3 + \text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \longrightarrow 2 \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4$
- (15) $\text{K}_2\text{S}_2\text{O}_3 + 4 \text{K}_2\text{S}_2\text{O}_8 + 5 \text{H}_2\text{O} \longrightarrow 5 \text{K}_2\text{SO}_4 + 5 \text{H}_2\text{SO}_4$
- (16) $\text{H}_2\text{S} + 4 \text{K}_2\text{S}_2\text{O}_8 + 4 \text{H}_2\text{O} \longrightarrow 4 \text{K}_2\text{SO}_4 + 5 \text{H}_2\text{SO}_4$
- (17) $\text{K}_2\text{S} + 4 \text{K}_2\text{S}_2\text{O}_8 + 4 \text{H}_2\text{O} \longrightarrow 5 \text{K}_2\text{SO}_4 + 4 \text{H}_2\text{SO}_4$
- (18)



e): reactions with aqueous iodine

- (19) $\text{SO}_2 + \text{I}_2 + 2 \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + 2 \text{HI}$
- (20) $\text{K}_2\text{SO}_3 + \text{I}_2 + \text{H}_2\text{O} \longrightarrow \text{K}_2\text{SO}_4 + 2 \text{HI}$
- (21) $2 \text{K}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{K}_2\text{S}_4\text{O}_6 + 2 \text{KI}$
- (22) $\text{H}_2\text{S} + \text{I}_2 \longrightarrow \text{S} + 2 \text{HI}$
- (23) $\text{K}_2\text{S} + \text{I}_2 \longrightarrow \text{S} + 2 \text{KI}$
- (24) $\text{K}_2\text{S}_n + \text{I}_2 \longrightarrow n \text{S} + 2 \text{KI}$

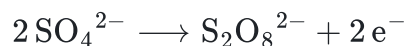
Solution

a)–c): identification of A and its compounds

The combination of an insoluble solid element, a water-soluble gaseous oxide, and a water-soluble gaseous hydrogen compound identifies **A as sulfur**. Its combustion product **B** is sulfur dioxide, while its product with heated hydrogen, **I**, is hydrogen sulfide.

(1)–(4). Burning sulfur produces sulfur dioxide. Catalytic oxidation raises sulfur's oxidation state from +4 to +6, identifying **C as sulfur trioxide**. Hydration then gives **D, sulfuric acid**. Complete neutralization with potassium hydroxide gives **E, potassium sulfate**.

(5). Electrolysis can oxidatively couple sulfate ions to form **F, potassium peroxodisulfate**. Under conditions favoring this anodic reaction, the half-equations are



and, for reduction of water at the cathode,



Here sulfate ion has SMILES $[\text{O}-]\text{S}(=\text{O})(=\text{O})[\text{O}-]$, peroxodisulfate ion has SMILES $[\text{O}-]\text{S}(=\text{O})(=\text{O})\text{OOS}(=\text{O})(=\text{O})[\text{O}-]$, and hydroxide ion has SMILES $[\text{OH}-]$.

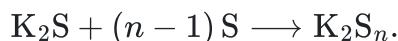
Adding these half-equations and restoring potassium ions, $[\text{K}+]$, gives equation **(5)**. Hydrogen and potassium hydroxide are absent from the scheme because they contain no sulfur.

(6)–(8). Complete neutralization of sulfur dioxide gives **G, potassium sulfite**. Sulfite combines with elemental sulfur to form **H, potassium thiosulfate**. Its acid decomposition produces sulfur and sulfur dioxide:



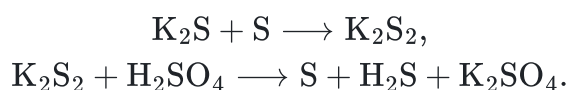
This accounts exactly for the three sulfur-containing products shown in reaction **(8)**: **A + B + E**.

(9)–(12). Hydrogen and heated sulfur form **I, hydrogen sulfide**. Complete neutralization gives **J, potassium sulfide**. Incorporating additional sulfur produces **K, potassium polysulfide**:



Acidification liberates one equivalent of hydrogen sulfide and leaves the remaining $n - 1$ sulfur equivalents as elemental sulfur. Potassium forms potassium sulfate. Thus reaction **(12)** gives precisely **A + I + E**.

For the simplest representative, $n = 2$, reactions **(11)** and **(12)** become



The identified potassium salts are consistent with the solid, water-soluble substances specified in **c)**.

d), (13)–(18): oxidation by peroxodisulfate

Peroxodisulfate contains an O–O bond. Its two peroxide oxygen atoms have oxidation state -1 , while its sulfur atoms remain at $+6$. Reduction breaks the peroxide linkage and produces sulfate:



Thus each formula unit of **F** accepts **two electrons**. All sulfur in the reacting compounds is oxidized to sulfate, giving the following electron balances:

Reaction	Reactant	Initial sum of sulfur oxidation states	Final sum	Electrons released	Required equivalents of F
(13)	B , SO_2	+4	+6	2	1
(14)	G , K_2SO_3	+4	+6	2	1
(15)	H , $\text{K}_2\text{S}_2\text{O}_3$	+4	+12	8	4
(16)	I , H_2S	−2	+6	8	4
(17)	J , K_2S	−2	+6	8	4
(18)	K , K_2S_n	−2	+6 n	6 n + 2	3 n + 1

For thiosulfate, the two sulfur atoms have oxidation states $+5$ and -1 . Their combined increase to $+6$, $+6$ releases eight electrons, explaining the coefficient 4 for peroxodisulfate in **(15)**.

After fixing the oxidant coefficient, potassium balance determines the amount of **E**, sulfur balance determines the amount of **D**, and hydrogen and oxygen balances determine the water coefficient. For example, in **(15)**:

- One thiosulfate and four peroxodisulfates supply ten potassium atoms, requiring five potassium sulfates.
- They supply ten sulfur atoms altogether, leaving five sulfur atoms for five sulfuric acids.
- Five water molecules supply the required ten hydrogen atoms and complete the oxygen balance.

For general polysulfide in **(18)**, the required oxidant amount is

$$\frac{6n + 2}{2} = 3n + 1.$$

Potassium balance then gives $3n + 2$ potassium sulfates; the remaining sulfur gives $4n$ sulfuric acids, requiring $4n$ waters. In particular, for potassium disulfide,



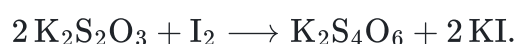
These balances produce **E and D** in every case, as required.

e), (19)–(24): oxidation by iodine

Each iodine molecule accepts two electrons to form two iodide ions, whose SMILES is [I-].

(19)–(20). Sulfur dioxide and sulfite both contain sulfur at +4. Oxidation to sulfate, with sulfur at +6, releases two electrons per sulfur atom. Consequently, each consumes one iodine molecule. Balancing hydrogen and oxygen with water gives equations **(19)** and **(20)**.

(21). Iodine converts thiosulfate into **L**, **potassium tetrathionate**:

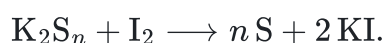


The terminal sulfur atoms of two thiosulfate ions form a new sulfur–sulfur bond. Each changes oxidation state from -1 to 0 , releasing two electrons in total. The oxygen-bearing sulfur atoms remain at $+5$.

Tetrathionate therefore has a chain of four sulfur atoms, with each terminal sulfur bonded to three oxygen atoms. This connectivity is represented by L's SMILES in the identification table.

(22)–(23). Iodine oxidizes sulfur in hydrogen sulfide or potassium sulfide from -2 to elemental sulfur at 0 . Each formula unit releases two electrons and therefore consumes one iodine molecule. Hydrogen iodide or potassium iodide supplies the corresponding nonsulfur product.

(24). A polysulfide chain has a total sulfur oxidation-state sum of -2 , regardless of its length. Converting all n sulfur atoms to elemental sulfur therefore releases only two electrons per polysulfide ion. Hence one iodine molecule produces n sulfur equivalents:



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

Problem 2: Dissociation of maleic acid and the choice of acid-base indicators

Maleic acid (H_2A) is a weak dibasic acid. The correlation between the relative quantities of H_2A , HA^- , A^{2-} :

$$\alpha_0 = \frac{c(\text{H}_2\text{A})}{c} \quad \alpha_1 = \frac{c(\text{HA}^-)}{c} \quad \alpha_2 = \frac{c(\text{A}^{2-})}{c}$$

and pH values of the solution show that:

a) $\alpha_0 = \alpha_1$ for pH = 1.92

b) $\alpha_1 = \alpha_2$ for pH = 6.22

Find:

2.1 The values of the dissociation constants of maleic acid for the first (K_1) and the second (K_2) degree of dissociation.

2.2 The values of α_0 , α_1 , and α_2 for pH = 1.92 and pH = 6.22.

2.3 What is the value of pH when α_1 attains a maximum value? Find the maximum value of α .

2.4 Which of the acid-base indicators in the table are suitable for titration of a 0.1 M solution of maleic acid (as a monobasic and as a dibasic acid) with 0.1 M NaOH?

Fill in the table 1 with the correct answers.

All the activity coefficients should be considered equal to 1.

Indicator	pH interval
Methyl green	0.1 – 2.0
Tropeolin 00	1.4 – 3.2
β -Dinitrophenol	2.4 – 4.0
Bromphenol blue	3.0 – 4.6
Congo red	3.0 – 5.2
Methyl red	4.4 – 6.2
Bromphenol red	5.0 – 6.8
Bromthymol blue	6.0 – 7.6
Phenol red	6.8 – 8.0
Cresol red	7.2 – 8.8
Thymol blue	8.0 – 9.6
Phenolphthalein	8.2 – 10.0
Alizarine yellow	10.1 – 12.1
Tropeolin 0	11.0 – 13.0
1,3,5-Trinitrobenzene	12.2 – 14.0

Table 1

2.1		$K_1 =$
		$K_2 =$
2.2	pH = 1.92	$\alpha_0 =$
		$\alpha_1 =$
		$\alpha_2 =$
	pH = 6.22	$\alpha_0 =$
		$\alpha_1 =$
		$\alpha_2 =$
2.3		pH =

		$\alpha_1 =$
2.4	First indicator equivalence point	pH =
		1. 2. 3. 4.
	Second indicator equivalence point	pH =
		1. 2. 3. 4.

Official English text of the problem.

Answers

- **2.1:** $K_1 = 1.2 \times 10^{-2}, \quad K_2 = 6.0 \times 10^{-7}$.

- **2.2:**

pH	α_0	α_1	α_2
1.92	0.49999	0.49999	2.5×10^{-5}
6.22	2.5×10^{-5}	0.49999	0.49999

- **2.3:** $\text{pH} = 4.07, \quad \alpha_{1,\text{max}} = 0.986 \text{ (98.6\%)}$.

- **2.4:** Using the listed transition intervals:

- **First equivalence point:** $\text{pH} \approx 4.12$; bromphenol blue and Congo red. The usual simplified ampholyte approximation gives pH 4.07.

- **Second equivalence point:** $\text{pH} \approx 9.37$; thymol blue and phenolphthalein.

SMILES identifying these indicators are supplied in Solution 2.4.

Solution

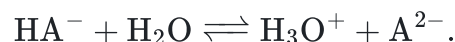
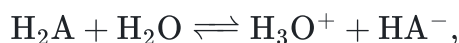
2.1 — Dissociation constants

The acid and its conjugate bases are:

Symbol	Name	SMILES
H_2A	Maleic acid, (Z)-but-2-enedioic acid	<chem>O=C(O)/C=C\C(=O)O</chem>
HA^-	Hydrogen maleate ion	<chem>O=C(O)/C=C\C(=O)[O-]</chem>
A^{2-}	Maleate ion	<chem>O=C([O-])/C=C\C(=O)[O-]</chem>

These SMILES encode the *Z* alkene geometry; they do not specify a particular conformation of the carboxyl groups. Other species used below are water O , hydronium $[\text{OH}_3^+]$, hydroxide $[\text{OH}^-]$, and sodium hydroxide $[\text{Na}^+] \cdot [\text{OH}^-]$, whose sodium ion $[\text{Na}^+]$ is a spectator.

The successive dissociations are



Write $h = [\text{H}_3\text{O}^+]$. Equilibrium expressions below use molar concentrations, with the 1 mol L^{-1} standard state implicit. Then

$$K_1 = \frac{h[\text{HA}^-]}{[\text{H}_2\text{A}]} = h \frac{\alpha_1}{\alpha_0}, \quad K_2 = \frac{h[\text{A}^{2-}]}{[\text{HA}^-]} = h \frac{\alpha_2}{\alpha_1}.$$

When $\alpha_0 = \alpha_1$, $K_1 = h$. Consequently,

$$pK_1 = 1.92, \quad \boxed{K_1 = 10^{-1.92} = 1.2023 \times 10^{-2} \approx 1.2 \times 10^{-2}}.$$

Similarly, $\alpha_1 = \alpha_2$ implies $K_2 = h$, giving

$$pK_2 = 6.22, \quad \boxed{K_2 = 10^{-6.22} = 6.0256 \times 10^{-7} \approx 6.0 \times 10^{-7}}.$$

2.2 — Distribution fractions

The analytical concentration is

$$c = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}], \quad \alpha_0 + \alpha_1 + \alpha_2 = 1.$$

The equilibrium ratios give

$$[\text{HA}^-] = \frac{K_1}{h} [\text{H}_2\text{A}], \quad [\text{A}^{2-}] = \frac{K_1 K_2}{h^2} [\text{H}_2\text{A}].$$

Therefore, defining $D = h^2 + K_1 h + K_1 K_2$,

$$\boxed{\alpha_0 = \frac{h^2}{D}, \quad \alpha_1 = \frac{K_1 h}{D}, \quad \alpha_2 = \frac{K_1 K_2}{D}}.$$

Let

$$r = \frac{K_2}{K_1} = 10^{-4.30} = 5.0119 \times 10^{-5}.$$

At **pH 1.92**, $h = K_1$, so

$$(\alpha_0, \alpha_1, \alpha_2) = \frac{(1, 1, r)}{2 + r}.$$

Thus

$$\alpha_0 = \alpha_1 = 0.49998747, \quad \alpha_2 = 2.50587 \times 10^{-5}.$$

At **pH 6.22**, $h = K_2$, so

$$(\alpha_0, \alpha_1, \alpha_2) = \frac{(r, 1, 1)}{2 + r}.$$

Thus

$$\alpha_0 = 2.50587 \times 10^{-5}, \quad \alpha_1 = \alpha_2 = 0.49998747.$$

2.3 — Maximum hydrogen maleate fraction

Rewrite the expression for α_1 as

$$\alpha_1 = \frac{1}{1 + h/K_1 + K_2/h}.$$

For positive h , the arithmetic–geometric mean inequality gives

$$\frac{h}{K_1} + \frac{K_2}{h} \geq 2\sqrt{\frac{K_2}{K_1}},$$

with equality precisely when

$$\frac{h}{K_1} = \frac{K_2}{h}, \quad h = \sqrt{K_1 K_2}.$$

This minimizes the denominator and hence gives the global maximum:

$$\text{pH}_{\max} = \frac{pK_1 + pK_2}{2} = \frac{1.92 + 6.22}{2} = 4.07.$$

The maximum fraction is

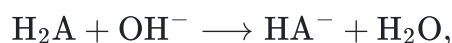
$$\alpha_{1,\max} = \frac{1}{1 + 2\sqrt{K_2/K_1}} = \frac{1}{1 + 2(10^{-2.15})} = 0.98603876 \approx 0.986.$$

At this pH, the remaining fractions are equal:

$$\alpha_0 = \alpha_2 = \frac{1 - \alpha_{1,\max}}{2} \approx 0.00698.$$

2.4 — Equivalence points and indicators

The two neutralization stages are



Let the initial acid volume be V_0 . Since acid and titrant both have concentration 0.1 mol L^{-1} , the first and second equivalence points require titrant volumes V_0 and $2V_0$, respectively.

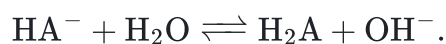
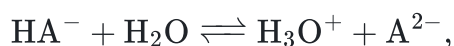
Use the conventional value $K_w = 1.0 \times 10^{-14}$ at 25°C .

First equivalence point.

Dilution gives

$$C_1 = \frac{0.1V_0}{2V_0} = 0.050 \text{ mol L}^{-1}.$$

The solution contains predominantly the amphiprotic hydrogen maleate ion. Its acid and base reactions are



The familiar ampholyte approximation is

$$h \approx \sqrt{K_1 K_2}, \quad \text{pH} \approx \frac{pK_1 + pK_2}{2} = 4.07.$$

For the stated concentration, a small correction is warranted because $K_1/C_1 \approx 0.24$. At this equivalence point, $[\text{Na}^+] = C_1$, so charge balance requires

$$h + C_1 = \frac{K_w}{h} + C_1\alpha_1 + 2C_1\alpha_2.$$

Using the distribution fractions,

$$h - \frac{K_w}{h} = C_1(\alpha_2 - \alpha_0) = C_1 \frac{K_1K_2 - h^2}{h^2 + K_1h + K_1K_2}.$$

Solving this equation gives

$$\boxed{\text{pH}_{\text{eq},1} = 4.1174 \approx 4.12.}$$

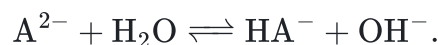
Both 4.07 and 4.12 fall within the listed intervals of **bromphenol blue** and **Congo red**.

Second equivalence point.

The analytical maleate concentration is now

$$C_2 = \frac{0.1V_0}{3V_0} = \frac{0.1}{3} = 0.0333 \text{ mol L}^{-1}.$$

Maleate hydrolyses:



Its base dissociation constant is

$$K_b = \frac{K_w}{K_2} = \frac{10^{-14}}{6.0256 \times 10^{-7}} = 1.6596 \times 10^{-8}.$$

Writing $x = [\text{OH}^-]$, the weak-base approximation gives

$$K_b = \frac{x^2}{C_2 - x} \approx \frac{x^2}{C_2},$$

$$x \approx \sqrt{K_b C_2} = \sqrt{(1.6596 \times 10^{-8})(0.03333)} = 2.3520 \times 10^{-5} \text{ mol L}^{-1}.$$

Here $x/C_2 \approx 7.1 \times 10^{-4}$, confirming the approximation. Hence

$$\text{pOH} = 4.6286, \quad \boxed{\text{pH}_{\text{eq},2} = 14.00 - 4.6286 \approx 9.37.}$$

This lies within the intervals of **thymol blue** and **phenolphthalein**.

The indicator entries in Table 1 are therefore:

Equivalence point	pH	Indicator	Listed transition interval
First	4.12, or 4.07 in the simplified approximation	Bromphenol blue	3.0–4.6
First	Same	Congo red	3.0–5.2
Second	9.37	Thymol blue	8.0–9.6
Second	Same	Phenolphthalein	8.2–10.0

These occupy two indicator lines in each box; the remaining lines can be left blank.

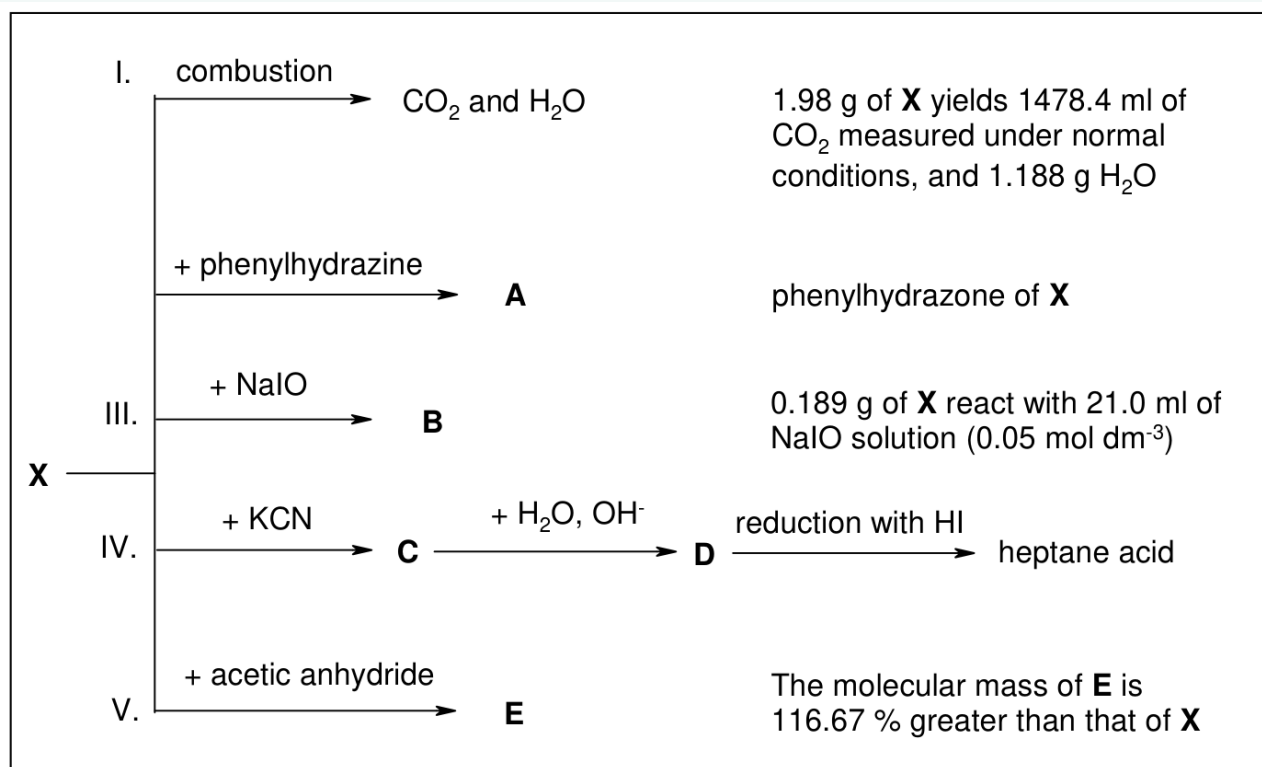
The following SMILES identify the selected compounds. For the three phthalein/sulfonephthalein indicators, neutral closed-ring reference forms are shown; Congo red is shown as its usual disodium salt. Their solution forms change with pH.

Indicator	SMILES
Bromphenol blue (bromophenol blue)	<chem>O=S1(=O)OC(c2cc(Br)c(O)c(Br)c2)(c2cc(Br)c(O)c(Br)c2)c2ccccc21</chem>
Congo red	<chem>[Na+].[Na+].Nc1c(/N=N/c2ccc(-c3ccc(/N=N/c4cc(S(=O)(=O)[O-])c5ccccc5c4N)cc3)cc2)cc(S(=O)(=O)[O-])c2ccccc12</chem>
Thymol blue	<chem>O=S1(=O)OC(c2cc(C(C)C)c(O)cc2C)(c2cc(C(C)C)c(O)cc2C)c2ccccc21</chem>
Phenolphthalein	<chem>O=C1OC(c2ccc(O)cc2)(c2ccc(O)cc2)c2ccccc21</chem>

The solution was checked against the official solution.

Problem 3: Structure of a natural compound X from its reactions

Compound **X** has been isolated from a neutral product. Different reagents have been used to establish the structure of **X**. The following results were obtained:



3.1 What conclusions can be drawn on the composition and the structure of **X** on the basis of the data obtained from each of the above interactions. The conclusions should be formulated in the most concise and clear way. Fill in the table without describing how you reached your conclusions.

I.	
II.	
III.	

IV.	
V.	

3.2 Write the formula of substance **X** on the basis of the data about the composition and structure obtained in point 1.

3.3 Write the formulae of substances **A**, **B**, **C**, **D**, and **E** and the formula for heptane acid.

3.4 To what natural substances could this structure correspond? Write the name of the substance and draw the structural formula which best describes its structure properties.

3.5 Give three properties of this compound that do not correspond to the structure found in point 2.

Official English text of the problem.

Answers

• 3.1

Interaction	Conclusion
I	Empirical formula: CH_2O .
II	X contains a reactive carbonyl group.
III	X has one aldehyde group; its molar mass is 180 g mol^{-1} , giving $\text{C}_6\text{H}_{12}\text{O}_6$.
IV	X has an unbranched six-carbon skeleton, with the carbonyl group at an end.
V	X has five acetyltable hydroxyl groups.

- 3.2** The open-chain structure is an **aldohexose**, 2,3,4,5,6-pentahydroxyhexanal:



SMILES: O=CC(O)C(O)C(O)C(O)CO. The configuration is not determined by the experiments.

- 3.3** The products are as follows. Neutral parent acids are shown for **B** and **D**; their carboxylates occur under alkaline conditions. Stereochemistry unspecified by the data is deliberately omitted.

Product	Name and molecular formula	SMILES
A	Aldohexose phenylhydrazone, $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_5$	<chem>OCC(O)C(O)C(O)C(O)C=NNc1ccccc1</chem>
B	2,3,4,5,6-Pentahydroxyhexanoic acid, an aldonic acid, $\text{C}_6\text{H}_{12}\text{O}_7$	<chem>O=C(O)C(O)C(O)C(O)C(O)CO</chem>
C	Aldohexose cyanohydrin, 2,3,4,5,6,7- hexahydroxyheptanenitrile, $\text{C}_7\text{H}_{13}\text{NO}_6$	<chem>N#CC(O)C(O)C(O)C(O)C(O)CO</chem>
D	2,3,4,5,6,7-Hexahydroxyheptanoic acid, $\text{C}_7\text{H}_{14}\text{O}_8$	<chem>O=C(O)C(O)C(O)C(O)C(O)C(O)CO</chem>

Product	Name and molecular formula	SMILES
E	Penta- <i>O</i> -acetyl derivative, C ₁₆ H ₂₂ O ₁₁ ; shown here as 1,2,3,4,6-penta- <i>O</i> -acetyl-D-glucopyranose, with its anomer unspecified	<chem>CC(=O)OC[C@H]1OC(OC(C)=O)[C@H](OC(C)=O)[C@@H](OC(C)=O)[C@H]1OC(C)=O</chem>
"Heptane acid"	Heptanoic acid, CH ₃ (CH ₂) ₅ COOH, C ₇ H ₁₄ O ₂	<chem>CCCCCCC(=O)O</chem>

The provisional open-chain drawing of **E** is discussed in the solution.

- **3.4** Natural compounds consistent with the open-chain connectivity include:

Compound	Open-chain stereochemical SMILES
D-Glucose	<chem>O=C[C@H](O)[C@@H](O)[C@H](O)[C@H](O)CO</chem>
D-Mannose	<chem>O=C[C@@H](O)[C@@H](O)[C@H](O)[C@H](O)CO</chem>
D-Galactose	<chem>O=C[C@H](O)[C@@H](O)[C@@H](O)[C@H](O)CO</chem>

Taking **D-glucose** as the representative, its predominant structures are the cyclic hemiacetals:

- **α-D-Glucopyranose:** OC[C@H]1O[C@H](O)[C@H](O)[C@@H](O)[C@@H]1O
- **β-D-Glucopyranose:** OC[C@H]1O[C@@H](O)[C@H](O)[C@@H](O)[C@@H]1O

In a conventional Haworth drawing, the hydroxyl groups at C2, C3 and C4 point **down, up and down**, respectively; the C5 hydroxymethyl group points **up**. The anomeric C1 hydroxyl points **down in α** and **up in β**.

- **3.5** Three properties unexplained by the open-chain formula alone are: 1. The existence of distinct **α and β anomers**. 2. **Mutarotation** in aqueous solution. 3. The failure of glucose pentaacetate to form an oxime with **hydroxylamine**, NO, showing that it has no free aldehyde group.

Solution

3.1 — Conclusions from the individual reactions

Use the conventional values $V_m = 22.4 \text{ L mol}^{-1}$ at normal conditions and atomic masses 12, 1, 16 for carbon, hydrogen and oxygen.

I. Combustion analysis

The amounts of **carbon dioxide**, O=C=O, and **water**, O, are

$$n(\text{CO}_2) = \frac{1.4784 \text{ L}}{22.4 \text{ L mol}^{-1}} = 0.0660 \text{ mol},$$

$$n(\text{H}_2\text{O}) = \frac{1.188 \text{ g}}{18.0 \text{ g mol}^{-1}} = 0.0660 \text{ mol}.$$

Consequently,

$$n(\text{C}) = 0.0660 \text{ mol}, \quad n(\text{H}) = 2(0.0660) = 0.132 \text{ mol}.$$

Their masses are

$$m_{\text{C}} = 0.792 \text{ g}, \quad m_{\text{H}} = 0.132 \text{ g}.$$

Taking the remaining mass as oxygen,

$$m_{\text{O}} = 1.980 - 0.792 - 0.132 = 1.056 \text{ g},$$

$$n(\text{O}) = \frac{1.056}{16.0} = 0.0660 \text{ mol}.$$

Thus

$$n_{\text{C}} : n_{\text{H}} : n_{\text{O}} = 1 : 2 : 1,$$

giving the empirical formula $\boxed{\text{CH}_2\text{O}}$. The mass percentages are 40.0% carbon, 6.67% hydrogen and 53.3% oxygen.

II. Phenylhydrazone formation

Phenylhydrazine, NNc1ccccc1, condenses with an aldehyde or ketone carbonyl group, replacing its oxygen by a phenylhydrazone group with elimination of water.

Therefore this experiment establishes a reactive carbonyl group, but by itself does not distinguish an aldehyde from a ketone.

III. Oxidation by sodium hypoiodite

The reagent is **sodium hypoiodite**, $[\text{Na}^+] \cdot [\text{O}^-]\text{I}$, NaIO. In the intended aldehyde oxidation, one mole of hypoiodite oxidizes one mole of aldehyde groups to carboxyl groups.

$$n(\text{NaIO}) = (0.05 \text{ mol L}^{-1})(21.0 \times 10^{-3} \text{ L}) = 1.05 \times 10^{-3} \text{ mol}.$$

For one aldehyde group per molecule,

$$M_{\text{X}} = \frac{0.189 \text{ g}}{1.05 \times 10^{-3} \text{ mol}} = 180 \text{ g mol}^{-1}.$$

Since the empirical-formula mass is 30 g mol^{-1} ,

$$\frac{180}{30} = 6, \quad \boxed{\text{X} : \text{C}_6\text{H}_{12}\text{O}_6}.$$

The unbranched chain-extension result in IV independently supports the terminal aldehyde assignment.

IV. Cyanide addition, hydrolysis and reduction

Cyanide addition introduces **one additional carbon atom** at the original carbonyl carbon. Hydrolysis converts the nitrile carbon into a carboxyl carbon. Subsequent reduction removes the alcoholic oxygen atoms without changing the carbon skeleton.

The final product is unbranched seven-carbon heptanoic acid. Hence **X** has an unbranched six-carbon skeleton, and its carbonyl group is terminal. An internal ketone would give a branched carboxylic-acid skeleton after this sequence.

V. Acetylation

Each hydroxyl hydrogen replaced by an acetyl group increases the molar mass by

$$\Delta M_{\text{per OH}} = 43 - 1 = 42 \text{ g mol}^{-1}.$$

The stated increase is 116.67%, so

$$M_E = 2.1667M_X \approx 390 \text{ g mol}^{-1}.$$

Therefore the number of acetylated hydroxyl groups is

$$N_{\text{OH}} = \frac{390 - 180}{42} = \boxed{5}.$$

The reagent, **acetic anhydride**, $\text{CC}(=\text{O})\text{OC}(\text{C})=\text{O}$, therefore converts **X** into a pentaacetate.

3.2 — Structure of X

The combined evidence gives:

- Six carbons in an unbranched chain.
- One terminal aldehyde group.
- Five hydroxyl groups.
- Molecular formula $\text{C}_6\text{H}_{12}\text{O}_6$.

The corresponding ordinary polyhydroxyaldehyde structure is



This is the open-chain connectivity of an aldohexose. Its four stereogenic centres are not assigned by the experiments.

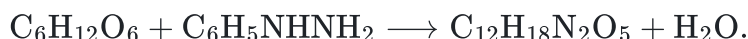
The balanced combustion equation, using **dioxygen**, $\text{O}=\text{O}$, is



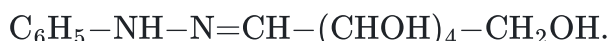
3.3 — Products and balanced equations

A: phenylhydrazone

Condensation occurs at the aldehyde group:



The product has the connectivity



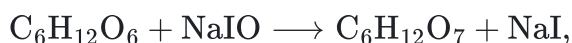
The problem explicitly identifies a phenylhydrazone; no further reaction with excess phenylhydrazine is required.

B: aldonic acid or aldionate

Only the aldehyde group is oxidized:



The balanced equation written with the neutral acid product is



where **sodium iodide** is $[\text{Na}^+] \cdot [\text{I}^-]$.

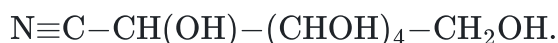
If the solution is maintained alkaline, the product is the **aldonate ion**, $\text{O}=\text{C}([\text{O}^-])\text{C}(\text{O})\text{C}(\text{O})\text{C}(\text{O})\text{C}(\text{O})\text{CO}$, and the balanced ionic equation is



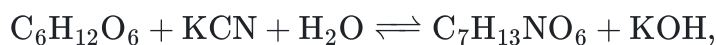
Here **hypoiodite**, **hydroxide** and **iodide** have SMILES $[\text{O}-]\text{I}$, $[\text{OH}-]$ and $[\text{I}-]$, respectively.

C: cyanohydrin

The **cyanide ion**, $[C-]\#N$, attacks the carbonyl carbon; protonation gives



For aqueous **potassium cyanide**, $[K+].[C-]\#N$, a balanced representation is



where **potassium hydroxide** is $[K+].[OH-]$.

Addition creates a new stereogenic centre at the former aldehyde carbon. The data do not specify its configuration, so two epimeric cyanohydrins are possible.

D: chain-extended hydroxy acid

Alkaline nitrile hydrolysis gives the **2,3,4,5,6,7-hexahydroxyheptanoate ion**,

$O=C([O-])C(O)C(O)C(O)C(O)C(O)CO$, and **ammonia**, N :



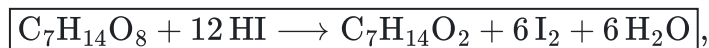
The corresponding neutral acid is



On treatment with **hydrogen iodide**, I , the carboxylate is first protonated:

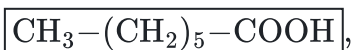


Vigorous reduction replaces all six alcoholic hydroxyl groups by hydrogen:



where **iodine** is I_2 .

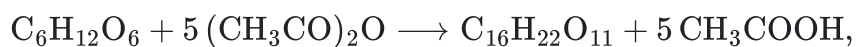
The product is therefore



heptanoic acid. This explains both the additional carbon and the unbranched skeleton.

E: pentaacetate

The balanced acetylation equation is



with **acetic acid**, $CC(=O)O$, as the coproduct.

Mechanical acetylation of the provisional open-chain drawing gives the **open-chain penta-O-acetyl aldohexose**:



SMILES: $O=CC(OC(=O)C)C(OC(=O)C)C(OC(=O)C)C(OC(=O)C)COC(=O)C$.

However, actual glucose normally gives a **cyclic glucopyranose pentaacetate**, as represented in the answer table. Both drawings have molecular formula $C_{16}H_{22}O_{11}$; consequently, the mass increase alone cannot distinguish them.

3.4 — Natural compounds and the appropriate structural drawing

The reactions establish the aldohexose connectivity, which fits D-glucose, D-mannose, D-galactose and other aldohexoses. They do not select a particular configuration.

For representative **D-glucose**, the open-chain Fischer configuration has the hydroxyl groups at C2–C5 arranged **right, left, right, right**, with the aldehyde at the top.

Its predominant molecular structures are six-membered cyclic hemiacetals. The C5 hydroxyl oxygen adds intramolecularly to the C1 aldehyde carbon:

- The C5 oxygen becomes the ring oxygen.
- The former carbonyl oxygen becomes the C1 hydroxyl group.
- C1 becomes a new stereogenic centre, producing the α and β anomers.
- No water is eliminated during hemiacetal formation.

For the requested drawing, place the ring oxygen at the upper right of a Haworth hexagon, followed clockwise by C1, C2, C3, C4 and C5. Draw:

Position	Substituent direction
C1	Hydroxyl down for α ; up for β
C2	Hydroxyl down
C3	Hydroxyl up
C4	Hydroxyl down
C5	Hydroxymethyl up

The hydrogen at each position points in the opposite direction.

Both anomers predominantly adopt the ${}^4C_1$ chair conformation. In β -D-glucopyranose, all hydroxyl and hydroxymethyl substituents are equatorial; in α -D-glucopyranose, the anomeric hydroxyl is axial. The SMILES specify configuration but do not themselves specify this preferred chair conformation.

3.5 — Three properties requiring the cyclic structure

1. Two anomeric forms.

The α and β forms have the same configurations at C2–C5 but differ at C1. The open-chain aldehyde carbon is planar and cannot supply this additional stereogenic centre. Hemiacetal formation does.

2. Mutarotation.

A solution prepared from either pure anomer changes its optical rotation as the anomers interconvert through the small equilibrium population of the open-chain form:



The rotation becomes constant when equilibrium is reached.

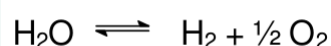
3. The pentaacetate does not form an oxime with hydroxylamine.

Acetylation of five hydroxyl groups in the open-chain model would leave an aldehyde group available for oxime formation. In the actual cyclic pentaacetate, the anomeric carbon is an acetal carbon, and there is no free aldehyde group. This explains the negative reaction.

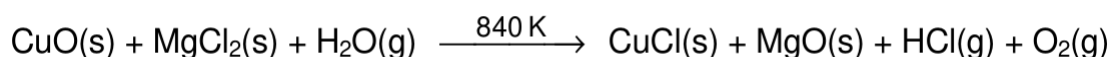
The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 4: Thermochemical cycle for the decomposition of water at moderate temperature

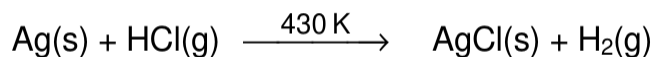
The thermal decomposition of water



can be traced ($\alpha = 10^{-3}$) at temperature above 1700 K. This process can be realized at temperatures 800 – 900 K as well as through subsequent stages carried out in a cycle. Suggest such a process on the basis of the reactions:



and



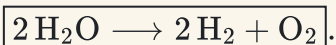
satisfying the following requirements:

- Only water should be consumed during the process.
- Oxygen and hydrogen alone should be the end products of the process.
- In addition to the above substances, a 25 % ammonia solution is needed for the cycle.
- The temperature for each step in the cycle should not exceed 840 K.

Official English text of the problem.

Answers

- a)** Regenerate the copper(II) oxide, magnesium chloride, silver, and ammonia using the cycle below. Its net reaction is



- b)** The only net products are hydrogen, $[\text{H}][\text{H}]$, and oxygen, $\text{O}=\text{O}$, in the molar ratio 2 : 1.

- **c)** Aqueous ammonia, N , enables copper(I) chloride to reduce silver chloride to silver, forming a copper(II) ammine complex. Removing ammonia in the presence of magnesium oxide regenerates the copper oxide and magnesium chloride.
- **d)** Use 840 K for the first supplied reaction and 430 K for the second. Complex formation and the regeneration operations can be conducted below 840 K.

Names and SMILES for the remaining species are collected in the solution.

Solution

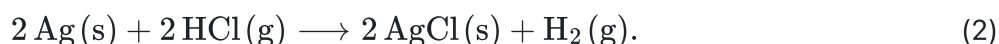
a) Constructing a closed cycle

First balance the supplied oxygen-producing reaction:



This step takes place at 840 K. Four copper centres change from oxidation state +2 to +1, accepting four electrons in total. Formation of one molecule of oxygen from oxygen in oxidation state -2 releases four electrons.

Separate the hydrogen chloride from the oxygen and use it in the second supplied reaction, at 430 K:

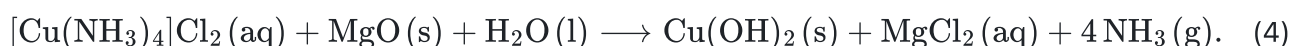


To close the cycle, the copper(I) chloride and silver chloride must regenerate copper(II) and metallic silver. Their reaction in aqueous ammonia accomplishes this:



Here copper(I) supplies the electron needed to reduce silver(I); ammonia stabilizes the resulting copper(II) complex.

Next add the magnesium oxide from reaction (1) and remove ammonia by warming. As the ammine complex dissociates, magnesium oxide supplies the basic conditions needed to precipitate copper(II) hydroxide. The overall equation is

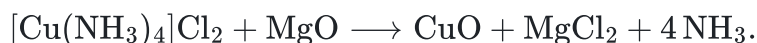


Capture the ammonia in recycled water to restore the ammonia solution. On warming, copper(II) hydroxide gives copper(II) oxide:



Filter off the copper(II) oxide and recover magnesium chloride from the solution. For its return as an anhydrous solid, dehydration should use a circulating hydrogen chloride atmosphere to suppress hydrolysis. Hydrogen chloride is already an intermediate in the cycle and is recovered for reuse.

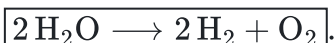
Thus reactions (4) and (5), taken together, regenerate both oxides/chlorides needed for closure:



Add the reactions in the proportions

$$(1) + 2(2) + 4(3) + 4(4) + 4(5).$$

After ammonia recovery and the solvent/phase-recovery operations, every auxiliary substance cancels:



Only water is consumed.

b) Identifying the final products

Reaction (1) releases oxygen; reaction (2) releases hydrogen. Collect these streams separately, retaining hydrogen chloride and ammonia within the process.

For every 2 mol of water consumed,

$$n(\text{H}_2) = 2 \text{ mol}, \quad n(\text{O}_2) = 1 \text{ mol}.$$

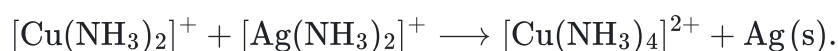
Silver, copper compounds, magnesium compounds, chloride, and ammonia all circulate within the cycle.

c) Explaining the role of the 25 % ammonia solution

Ammonia dissolves the sparingly soluble copper(I) and silver(I) chlorides through ammine-complex formation:



The dissolved complexes undergo the electron-transfer reaction



The copper centre changes from +1 to +2, while the silver centre changes from +1 to 0. Ligand redistribution provides four ammonia ligands around copper(II). Adding the two dissolution equations gives reaction (3).

Ammonia therefore enables silver regeneration and stabilizes the copper(II) intermediate. It is subsequently released in reaction (4), captured, and reused.

d) Meeting the temperature limit

Operation	Temperature or suitable condition
Oxygen evolution, reaction (1)	840 K, as supplied
Hydrogen evolution, reaction (2)	430 K, as supplied
Ammine formation and silver recovery, reaction (3)	Ordinary temperature
Ammonia removal and hydroxide precipitation, reaction (4)	Warming the aqueous mixture
Copper(II) hydroxide decomposition, reaction (5)	Gentle heating, readily below 840 K
Magnesium chloride recovery	Evaporation and dehydration below 840 K, with recycled hydrogen chloride suppressing hydrolysis

The ammonia and water vapours are recovered by cooling and absorption. No step requires a temperature above the stated maximum.

The following SMILES identify the species used. For ionic solids, disconnected-ion SMILES represent composition and formal charges, not the crystal lattice.

Species	Name	SMILES
H ₂ O	Water	O
H ₂	Hydrogen	[H][H]

Species	Name	SMILES
O ₂	Oxygen	O=O
HCl	Hydrogen chloride	Cl
NH ₃	Ammonia	N
CuO	Copper(II) oxide	[Cu+2].[O-2]
CuCl	Copper(I) chloride	[Cu+].[Cl-]
MgO	Magnesium oxide	[Mg+2].[O-2]
MgCl ₂	Magnesium chloride	[Mg+2].[Cl-].[Cl-]
Ag	Silver	[Ag]
AgCl	Silver chloride	[Ag+].[Cl-]
Cu(OH) ₂	Copper(II) hydroxide	[Cu+2].[OH-].[OH-]
Cl ⁻	Chloride ion	[Cl-]
[Cu(NH ₃) ₂] ⁺	Diamminecopper(I) ion	[NH3]->[Cu+]<-[NH3]
[Ag(NH ₃) ₂] ⁺	Diamminesilver(I) ion	[NH3]->[Ag+]<-[NH3]
[Cu(NH ₃) ₄] ²⁺	Tetraamminecopper(II) ion	[NH3]->[Cu+2](<-[NH3])(<-[NH3])<-[NH3]
[Cu(NH ₃) ₄]Cl ₂	Tetraamminecopper(II) chloride	[NH3]->[Cu+2](<-[NH3])(<-[NH3])<-[NH3].[Cl-].[Cl-]

The two-coordinate copper(I) and silver(I) ammine complexes are approximately linear. In aqueous copper(II) solution, the four ammonia ligands occupy approximately equatorial positions, with axial water coordination omitted from the shorthand formula. The SMILES do not specify these coordination geometries or oxygen's triplet electronic ground state.

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

Problem 5: Chlorination of hydrocarbon A: intermediates for nylon and chloroprene rubber

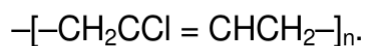
Compounds **B** and **C** are structural isomers. They can be obtained when hydrocarbon **A** interacts with chlorine. Hydrocarbon **A** is a basic product of an industrial organic synthesis. It can react with ozone, yielding an ozonide.

Isomer **B** can be used for the technical production of compounds **D** and **E** that are the initial compounds in the production of the fibre nylon:



Compound **D** is soluble in bases, **E** in acids.

The reaction between isomer **C** and an alcohol solution of an alkaline base yields monomer **F** which is used for the production of chloroprene (neoprene) rubber



This method has a technical application.

5.1 Write down the structural formulae of **A**, **B**, **C**, **D**, **E**, **F** and their names in the IUPAC nomenclature.

5.2 Write down the mechanism of the reaction between hydrocarbon **A** and chlorine. What type of reaction is it in terms of its mechanism? Which of the two isomers is obtained in larger quantities under ordinary conditions?

5.3 Write down the equations for:

- the production of **D** and **E** from isomer **B**,
- the production of monomer **F** from isomer **C**,
- the ozonolysis of hydrocarbon **A** and hydrolysis of the ozonide.

5.4 Write down the chemical scheme for an industrial production of hydrocarbon **A** from the hydrocarbon which is main component of natural gas.

5.5 For chloroprene rubber, write down the formulae of the possible steric forms of the elementary unit.

Official English text of the problem.

Answers

• 5.1

Label	Structural formula	IUPAC name	SMILES
A	$CH_2=CH-CH=CH_2$	Buta-1,3-diene	<chem>C=CC=C</chem>
B	$ClCH_2-CH=CH-CH_2Cl$	1,4-Dichlorobut-2-ene	<chem>ClCC=CCC1</chem>
C	$CH_2=CH-CHCl-CH_2Cl$	3,4-Dichlorobut-1-ene	<chem>C=CC(Cl)CC1</chem>
D	$HOOC(CH_2)_4COOH$	Hexanedioic acid (adipic acid)	<chem>O=C(O)CCCC(=O)O</chem>
E	$H_2N(CH_2)_6NH_2$	Hexane-1,6-diamine	<chem>NCCCCCN</chem>
F	$CH_2=C(Cl)-CH=CH_2$	2-Chlorobuta-1,3-diene (chloroprene)	<chem>C=C(Cl)C=C</chem>

- **5.2** Electrophilic addition gives **B** by 1,4-addition and **C** by 1,2-addition through a delocalized allylic intermediate. **B** is the thermodynamically favoured product and the intended ordinary-condition prediction, subject to the qualification below.
- **5.3** Cyanide substitution followed by hydrogenation converts **B** into hexanedinitrile, $N\#CCCCC\#N$. Hydrolysis gives **D**; reduction gives **E**. Alcoholic base converts **C** into **F** by elimination of hydrogen chloride. Complete ozonolysis gives two molecules of methanal, $C=O$, and one of ethanedial, $O=CC=O$; formal ozonide hydrolysis also produces hydrogen peroxide, OO .

- **5.4** One industrial synthesis sequence is methane (C) → ethyne (C≡C) → ethanal (CC=O) → ethanol (CCO) → **A**, with the last step being the Lebedev process.
- **5.5** The specified 1,4-repeat has two configurations:
- **cis-1,4**, with the backbone methylene groups on the same side: *C/C(Cl)=C\C*, corresponding to **E**.
- **trans-1,4**, with those groups on opposite sides: *C/C(Cl)=C/C*, corresponding to **Z**.

Solution

5.1 — Identification of A–F

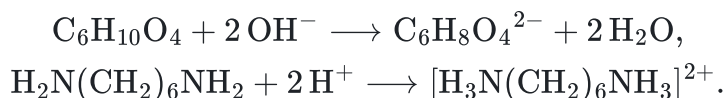
The nylon-6,6 repeat, represented by *NCCCCCNC(=O)CCCC(=O)*, contains a six-carbon diamine fragment and a six-carbon dicarboxylic-acid fragment. Here and below, * marks continuation into the polymer.

Cleaving the amide connections identifies the two monomers:



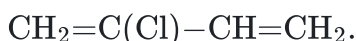
The acid is **D**, hexanedioic acid, because it dissolves in bases by forming salts. The diamine is **E**, hexane-1,6-diamine, because its amino groups are protonated by acids.

For example,



The species used here are hydroxide ion, [OH[−]]; water, O; hydrogen ion, [H⁺]; hexanedioate ion, O=C([O[−]])CCCC(=O)[O[−]]; and hexane-1,6-diaminium ion, [NH₃⁺]CCCCCC[NH₃⁺].

The displayed chloroprene-rubber repeat results from 1,4-polymerization of **F**, 2-chlorobuta-1,3-diene:



Since **F** is obtained by eliminating hydrogen chloride from **C**, the appropriate precursor is



namely 3,4-dichlorobut-1-ene.

This is the 1,2-addition product of chlorine to **A**, buta-1,3-diene. Its corresponding 1,4-addition product is **B**, 1,4-dichlorobut-2-ene. Substitution of the two terminal chlorine atoms in **B** by cyanide introduces two additional carbon atoms, giving the six-carbon skeleton needed for both nylon monomers.

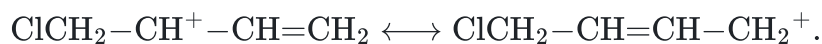
The names, condensed structures and SMILES of all six compounds are given in the answer table.

5.2 — Chlorination mechanism and product preference

Chlorine, Cl₂, undergoes **electrophilic addition** to the conjugated diene.

Number the carbon atoms of **A** consecutively from 1 to 4. In the usual ionic representation:

1. The π electrons of the C₁=C₂ bond attack the electrophilic end of polarized chlorine.
2. The chlorine–chlorine bond breaks heterolytically, producing chloride ion, [Cl[−]].
3. The resulting chlorinated allylic cation has two principal resonance contributors:

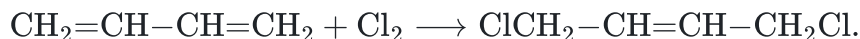


These are the C2-charged contributor, $\text{ClC}[\text{CH}^+]\text{C}=\text{C}$, and the C4-charged contributor, $\text{ClCC}=\text{C}[\text{CH}_2^+]$, of the same delocalized allylic cation. To draw the resonance electron flow, move the $\text{C3}=\text{C4}$ π -electron pair into the C2--C3 bond.

Chloride attack at C2 gives the **1,2-adduct C**:



Chloride attack at C4 gives the **1,4-adduct B**:



The internal, disubstituted double bond of **B** is more stable than the terminal, monosubstituted double bond of **C**. Consequently, **B is favoured under thermodynamic control** and is the ordinary-condition prediction used here. Kinetic conditions can favour **C**; temperature, medium and reversibility affect the actual ratio.

5.3 — Required reaction equations

Production of D and E from B

First replace both terminal chlorine atoms by cyanide groups:



The organic product is **hex-3-enedinitrile**, $\text{N}\#\text{CCC}=\text{CCC}\#\text{N}$. Potassium cyanide is $[\text{K}^+].[\text{C}^-]\#\text{N}$, and potassium chloride is $[\text{K}^+].[\text{Cl}^-]$.

Catalytic hydrogenation of its carbon-carbon double bond gives **hexanedinitrile**, also called adiponitrile, $\text{N}\#\text{CCCCCC}\#\text{N}$:



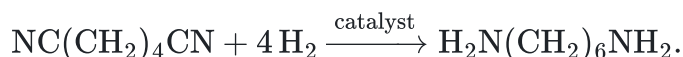
Dihydrogen has SMILES $[\text{H}][\text{H}]$.

Acidic hydrolysis of both nitrile groups gives **D**:



Hydrogen chloride is $[\text{H}]\text{Cl}$, and ammonium chloride is $[\text{NH}_4^+].[\text{Cl}^-]$. Including the acid explicitly accounts for the nitrogen product as ammonium rather than free ammonia.

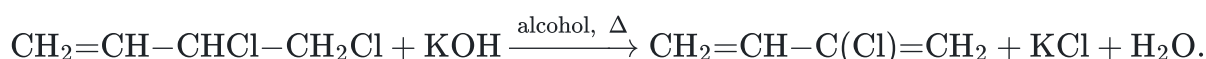
Alternatively, hydrogenation of both nitrile groups gives **E**:



Each nitrile carbon becomes a terminal methylene carbon, so the diamine contains six methylene groups.

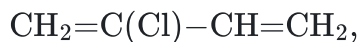
Production of F from C

Using potassium hydroxide, $[\text{K}^+].[\text{OH}^-]$, in ethanol, CCO :



This is a base-induced **dehydrochlorination**. With the numbering of **C**, the base removes hydrogen from C3 while chlorine leaves C4; the new $\text{C3}=\text{C4}$ bond completes the conjugated diene.

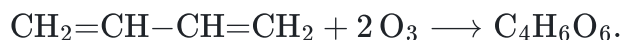
The product written from the opposite end is



which is **F**, chloroprene.

Ozonolysis of A and hydrolysis of the ozonide

Complete ozonolysis consumes two equivalents of ozone, $[\text{O}-][\text{O}+]=\text{O}$:



A formal structural representation of the **butadiene bis(ozonide)** is $\text{O1OC}(\text{C2OOCO2})\text{OC1}$. Each original double bond is incorporated into a five-membered 1,2,4-trioxolane ring, and the original central carbon-carbon bond connects the two rings. No particular ozonide stereoisomer is implied.

Formal hydrolysis is



The products are:

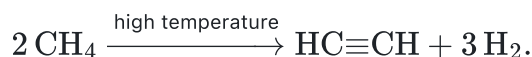
- **Methanal (formaldehyde)**, $\text{C}=\text{O}$: one molecule from each terminal methylene group.
- **Ethanedial (glyoxal)**, $\text{O}=\text{CC}=\text{O}$: the two central carbons remain connected.
- **Hydrogen peroxide**, OO .

These are the primary carbonyl cleavage products. A reductive work-up removes peroxide and preserves the aldehydes; an oxidizing work-up can oxidize them further.

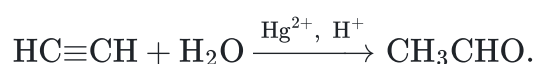
5.4 — Industrial synthesis of A from methane

The principal hydrocarbon in natural gas is **methane**, C . A route through ethanol uses the following balanced reactions.

First, high-temperature cracking gives **ethyne (acetylene)**, $\text{C}\equiv\text{C}$:



Hydration of ethyne gives **ethanal (acetaldehyde)**, $\text{CC}=\text{O}$:

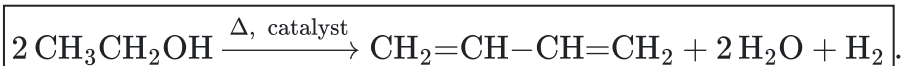


The catalyst notation denotes mercury(II) ion, $[\text{Hg}+2]$, in acidic solution.

Hydrogenation gives **ethanol**, CCO :

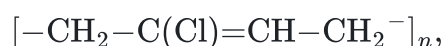


Finally, the industrial **Lebedev process**, using a heated oxide catalyst, converts ethanol into **A**, buta-1,3-diene:



5.5 — Steric forms of the chloroprene-rubber repeat

For the stated 1,4-repeat,



the remaining double bond permits two geometrical configurations.

Form	Precise drawing description	Repeat-fragment SMILES	CIP configuration
cis-1,4	Draw the double bond horizontally, with both backbone methylene groups below it. Chlorine and hydrogen are then above it.	<chem>*C/C(C1)=C\C*</chem>	E
trans-1,4	Draw one backbone methylene group below the double bond and the other above it. Chlorine is opposite the first methylene group; hydrogen is opposite the second.	<chem>*C/C(C1)=C/C*</chem>	Z

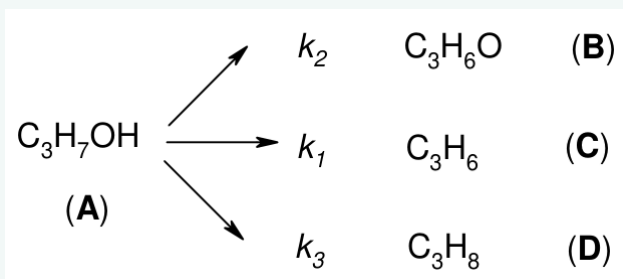
The apparent reversal between cis/trans and E/Z follows from the priority rules. At the chlorine-bearing alkene carbon, chlorine has higher priority than the backbone carbon. At the other alkene carbon, the backbone carbon has higher priority than hydrogen.

Thus, **cis backbone groups give E**, while **trans backbone groups give Z**. The SMILES encode these double-bond configurations; they do not specify the overall conformation of the polymer chain.

The solution was checked against the official solution.

Problem 6: Kinetics of the catalytic decomposition of isopropanol on V2O5

The catalytic decomposition of isopropanol on the surface of a V_2O_5 catalyst, leading to the products in the scheme, satisfies a first order kinetic equation.

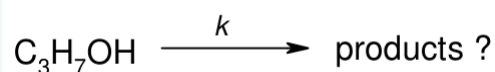


Five seconds after initiation of the reaction at 590 K, the concentrations of the components in the reaction mixture are:

$$\begin{aligned}
 c_A &= 28.2 \text{ mmol dm}^{-3} \\
 c_B &= 7.8 \text{ mmol dm}^{-3} \\
 c_C &= 8.3 \text{ mmol dm}^{-3} \\
 c_D &= 1.8 \text{ mmol dm}^{-3}
 \end{aligned}$$

6.1 What is the initial concentration c_0 of C_3H_7OH in the system?

6.2 What is the value of the rate constant k for the process:



6.3 What is the interval of time ($\tau_{1/2}$) in which the concentration of C_3H_7OH will reach the value $c = c_0/2$?

6.4 What are the values of rate constants k_1 , k_2 , and k_3 ?

6.5 What are the values of concentrations c_B , c_C , c_D at $t = \tau_{1/2}$?

The equation describing the concentration changes of **A** with time t for the first order reaction has the form:

$$c_A = c_0 \exp(-kt)$$

or

$$\log(c_0/c_A) = 0.4343 kt$$

or

$$\ln(c_0/c_A) = kt$$

Fill in the table with the answers obtained.

1	$c_0 =$
2	$k =$
3	$\tau_{1/2}$
4	$k_1 =$
	$k_2 =$
	$k_3 =$
5	$c_B =$
	$c_C =$
	$c_D =$

Official English text of the problem.

Answers

- **6.1:** $c_0 = 46.1 \text{ mmol dm}^{-3}$.
- **6.2:** $k = 9.83 \times 10^{-2} \text{ s}^{-1}$.
- **6.3:** $\tau_{1/2} = 7.05 \text{ s}$, measured from initiation.
- **6.4:** $k_1 = 4.56 \times 10^{-2} \text{ s}^{-1}$, $k_2 = 4.28 \times 10^{-2} \text{ s}^{-1}$, $k_3 = 9.88 \times 10^{-3} \text{ s}^{-1}$.
- **6.5:** At $t = \tau_{1/2}$, $c_B = 10.0 \text{ mmol dm}^{-3}$, $c_C = 10.7 \text{ mmol dm}^{-3}$, and $c_D = 2.32 \text{ mmol dm}^{-3}$.

Solution

6.1 — Initial concentration

The substrate **A** is isopropanol (propan-2-ol), CC(O)C. Dehydrogenation of this secondary alcohol gives the ketone **B**, acetone (propan-2-one), CC(=O)C; dehydration gives the alkene **C**, propene, C=CC. The saturated product **D**, C3H8, is propane, CCC.

The stated kinetic scheme consists of three parallel, irreversible pathways. Initially the products are absent. Each molecule of A consumed yields one molecule of B , C , or D , retaining all three carbon atoms. Thus, at constant volume,

$$c_0 = c_A + c_B + c_C + c_D.$$

Using the concentrations at $t = 5$ s,

$$c_0 = (28.2 + 7.8 + 8.3 + 1.8) \text{ mmol dm}^{-3} = \boxed{46.1 \text{ mmol dm}^{-3}}.$$

6.2 — Overall rate constant

The three pathways contribute additively to the disappearance of A :

$$-\frac{dc_A}{dt} = (k_1 + k_2 + k_3)c_A = kc_A.$$

Therefore,

$$k = k_1 + k_2 + k_3.$$

The integrated first-order equation gives

$$k = \frac{1}{t} \ln \left(\frac{c_0}{c_A} \right).$$

Hence, at 590 K,

$$k = \frac{1}{5 \text{ s}} \ln \left(\frac{46.1}{28.2} \right) = 0.0982982 \text{ s}^{-1} \approx \boxed{9.83 \times 10^{-2} \text{ s}^{-1}}.$$

6.3 — Half-life

At the half-life, $c_A = c_0/2$, so

$$\frac{c_0}{2} = c_0 e^{-k\tau_{1/2}}.$$

Consequently,

$$\tau_{1/2} = \frac{\ln 2}{k} = \frac{0.693147}{0.0982982 \text{ s}^{-1}} = \boxed{7.05 \text{ s}}.$$

This is the elapsed time from the start of the reaction.

6.4 — Individual rate constants

The diagram assigns k_2 to B , k_1 to C , and k_3 to D . Their formation rates are therefore

$$\frac{dc_B}{dt} = k_2 c_A, \quad \frac{dc_C}{dt} = k_1 c_A, \quad \frac{dc_D}{dt} = k_3 c_A.$$

For example, integrating the first equation with $c_B(0) = 0$ gives

$$c_B(t) = k_2 \int_0^t c_0 e^{-kt'} dt' = \frac{k_2}{k} c_0 (1 - e^{-kt}) = \frac{k_2}{k} (c_0 - c_A).$$

Similarly,

$$c_C = \frac{k_1}{k} (c_0 - c_A), \quad c_D = \frac{k_3}{k} (c_0 - c_A).$$

The concentration of A consumed after five seconds is

$$c_0 - c_A = 46.1 - 28.2 = 17.9 \text{ mmol dm}^{-3}.$$

Thus,

$$k_1 = k \frac{c_C}{c_0 - c_A} = (0.0982982) \frac{8.3}{17.9} \text{ s}^{-1} \approx \boxed{4.56 \times 10^{-2} \text{ s}^{-1}},$$

$$k_2 = k \frac{c_B}{c_0 - c_A} = (0.0982982) \frac{7.8}{17.9} \text{ s}^{-1} \approx \boxed{4.28 \times 10^{-2} \text{ s}^{-1}},$$

$$k_3 = k \frac{c_D}{c_0 - c_A} = (0.0982982) \frac{1.8}{17.9} \text{ s}^{-1} \approx \boxed{9.88 \times 10^{-3} \text{ s}^{-1}}.$$

The unrounded values satisfy $k_1 + k_2 + k_3 = k$.

6.5 — Product concentrations at the half-life

At $t = \tau_{1/2}$, the concentration of A consumed is

$$c_0 - c_A = \frac{c_0}{2} = 23.05 \text{ mmol dm}^{-3}.$$

Because all three products form directly from the same reactant by first-order pathways, their proportions remain constant:

$$c_B : c_C : c_D = k_2 : k_1 : k_3 = 7.8 : 8.3 : 1.8.$$

Therefore,

$$c_B(\tau_{1/2}) = \frac{7.8}{17.9} (23.05) = 10.0441 \text{ mmol dm}^{-3} \approx \boxed{10.0 \text{ mmol dm}^{-3}},$$

$$c_C(\tau_{1/2}) = \frac{8.3}{17.9} (23.05) = 10.6880 \text{ mmol dm}^{-3} \approx \boxed{10.7 \text{ mmol dm}^{-3}},$$

$$c_D(\tau_{1/2}) = \frac{1.8}{17.9} (23.05) = 2.31788 \text{ mmol dm}^{-3} \approx \boxed{2.32 \text{ mmol dm}^{-3}}.$$

The unrounded product concentrations sum to $23.05 \text{ mmol dm}^{-3} = c_0/2$, as required.

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.