

IChO 2007

Theory problems and solutions · Moscow, Russian Federation · 8 theory problems with complete solutions

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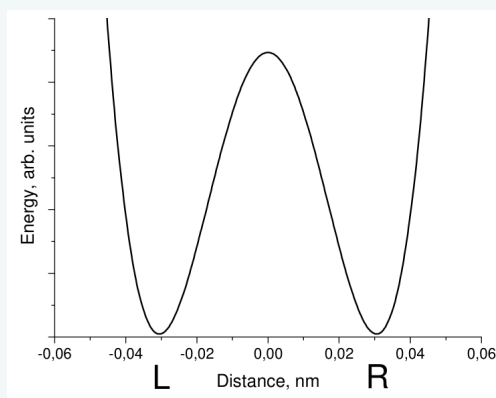
Problem 1: Proton tunneling

Proton tunneling through energy barriers is an important effect, which can be observed in many complex species containing hydrogen bonds (DNA, proteins, etc.). Propanedial (malonaldehyde) is one of the simplest molecules for which intramolecular proton transfer can occur.

1.1 Draw the condensed formula of propanedial and the structures of two of its isomers, which can exist in equilibrium with propanedial.

1.2 In a water solution propanedial is a weak acid, its strength being comparable with that of acetic acid. Specify the acidic hydrogen atom. Explain its acidity (choose one version in the Answer Sheet).

On the plot below an energy profile of the intramolecular proton transfer is given (the dependence of energy on the distance of proton motion (in nm)). Energy curve has a symmetric double-well form.

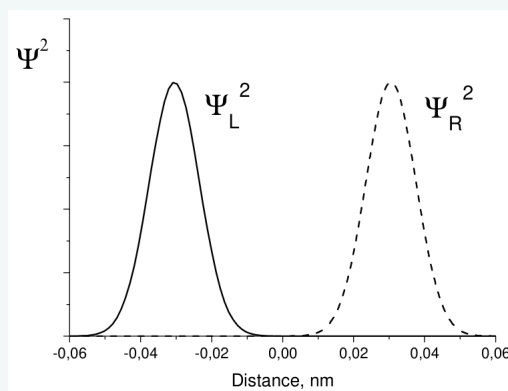


1.3 Draw the structures corresponding to two minima on this curve.

A proton is delocalized between two atoms and oscillates between two minima L and R with an angular frequency $\omega = 6.48 \times 10^{11} \text{ s}^{-1}$. Probability density for a proton depends on time as follows:

$$\Psi^2(x, t) = \frac{1}{2} [\Psi_L^2(x) + \Psi_R^2(x) + (\Psi_L^2(x) - \Psi_R^2(x)) \cos(\omega t)],$$

wavefunctions $\Psi_L(x)$ and $\Psi_R(x)$ describe a proton localized in the left and right wells, respectively:



1.4 Write down the expressions for the probability density at three moments: (a) $t = 0$, (b) $t = \pi/(2\omega)$, (c) $t = \pi/\omega$. Sketch the graphs of these three functions.

1.5 Without calculations, determine the probability of finding the proton in the left well at $t = \pi/(2\omega)$

1.6 How much time is required for a proton to move from one well to another? What is the proton mean speed during the transfer?

1.7 From the energy curve, estimate the uncertainty of the position of proton forming hydrogen bonds. Estimate the minimal uncertainty of the proton speed. Compare this value with that obtained in **1.6** and draw a conclusion about the proton tunneling (choose one of the versions in the Answer Sheet).

Official English text of the problem.

Answers

- **1.1:** Propanedial (malonaldehyde), $\text{OHC}-\text{CH}_2-\text{CHO}$, SMILES O=CCC=O . Its two geometrical enol isomers are **(Z)-3-hydroxyprop-2-enal**, $\text{O}=\text{C}/\text{C}=\text{C}\backslash\text{O}$, and **(E)-3-hydroxyprop-2-enal**, $\text{O}=\text{C}/\text{C}=\text{C}/\text{O}$.
- **1.2:** Either equivalent hydrogen on the central CH_2 group can undergo the first dissociation. In the enol form, the corresponding acidic hydrogen is on OH. The conjugate base, **propanedial enolate**, $\text{O}=\text{C}[\text{CH}-]\text{C}=\text{O}$, is stabilized by delocalization of negative charge over both carbonyl groups.
- **1.3:** The minima are two equivalent, internally hydrogen-bonded arrangements of **(Z)-3-hydroxyprop-2-enal**: L, $\text{O}=\text{C}=\text{C}\backslash\text{C}=\text{O}$, and R, $\text{O}=\text{C}/\text{C}=\text{C}\backslash\text{O}$. With the heavy-atom skeleton held fixed, the proton is bonded to the left oxygen in L and the right oxygen in R; the double bonds shift accordingly.
- **1.4:**
 - (a) $\Psi^2(x, 0) = \Psi_L^2(x)$: the left peak.
 - (b) $\Psi^2\left(x, \frac{\pi}{2\omega}\right) = \frac{1}{2} [\Psi_L^2(x) + \Psi_R^2(x)]$: two equal peaks, each scaled by one-half.
 - (c) $\Psi^2\left(x, \frac{\pi}{\omega}\right) = \Psi_R^2(x)$: the right peak.
- **1.5:** $P_L = 1/2 = 50\%$.
- **1.6:** $t_{\text{transfer}} = 4.85 \times 10^{-12} \text{ s} = 4.85 \text{ ps}$; the mean transfer speed estimated from the graph is $\bar{v} \approx 12 \text{ m s}^{-1}$.
- **1.7:** Using the full separation as the position-uncertainty scale, $\Delta x \sim 0.060 \text{ nm}$, gives $\Delta v_{\text{min}} \sim 5.3 \times 10^2 \text{ m s}^{-1}$, about 40 times the mean transfer speed. A strict rms estimate for two narrow, equally populated peaks gives approximately $1.1 \times 10^3 \text{ m s}^{-1}$. Thus a sharply defined classical velocity and trajectory cannot describe this tunneling transfer.

Solution

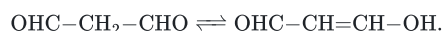
1.1 — Propanedial and its enol isomers

Propanedial contains an aldehyde group at each end of a three-carbon chain:



Its name is **propanedial**, also called **malonaldehyde**, and its SMILES is O=CCC=O .

An aldehyde group can undergo keto–enol tautomerization using a hydrogen from the central carbon:



The product, **3-hydroxyprop-2-enal**, has two different substituents on each carbon of its carbon–carbon double bond, so it has two geometrical isomers:

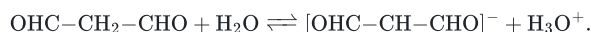
Isomer	SMILES	Required drawing
(Z)-3-hydroxyprop-2-enal	$\text{O}=\text{C}/\text{C}=\text{C}\backslash\text{O}$	Put the CHO and OH substituents on the same side of the carbon–carbon double bond.
(E)-3-hydroxyprop-2-enal	$\text{O}=\text{C}/\text{C}=\text{C}/\text{O}$	Put the CHO and OH substituents on opposite sides of the carbon–carbon double bond.

Both can interconvert with propanedial by tautomerization. Enolization at opposite ends of the symmetrical starting molecule does not produce additional distinct constitutional isomers.

1.2 — Acidic hydrogen and stabilization of the conjugate base

In the dialdehyde structure, identify a hydrogen on the central CH_2 carbon. The two hydrogens are equivalent before dissociation; loss of either gives the same conjugate base.

The aqueous dissociation can be represented as



Here water has SMILES O , hydronium has SMILES $[\text{OH}_3^+]$, and the anion is **propanedial enolate**, represented by $\text{O}=\text{C}[\text{CH}-]\text{C}=\text{O}$.

The anion has three principal resonance contributors:

Location of formal negative charge	SMILES of the contributor
Central carbon	$\text{O}=\text{C}[\text{CH}-]\text{C}=\text{O}$
Left oxygen	$[\text{O}-]\text{C}=\text{CC}=\text{O}$
Right oxygen	$\text{O}=\text{CC}=\text{C}[\text{O}-]$

These are representations of the **same delocalized ion**, not separate species in equilibrium. The negative charge is distributed over a conjugated framework containing both carbonyl groups, with important contributions placing it on electronegative oxygen atoms. This stabilizes the conjugate base and accounts for the acidity.

In the enol tautomer, removal of the hydroxyl hydrogen produces the same delocalized conjugate base. Thus the acidic site is described as a central-carbon hydrogen in the dialdehyde form and the hydroxyl hydrogen in the enol form.

1.3 — Structures at the two minima

The proton transfers between the two oxygens of the internally hydrogen-bonded **(Z)-3-hydroxyprop-2-enal**.

Read the following structures with the oxygen–carbon–carbon–carbon–oxygen skeleton held in the same spatial orientation:

Minimum	Condensed structure	Name and SMILES
L	HO–CH=CH–CHO	(Z)-3-hydroxyprop-2-enal, O/C=C\C=O
R	OHC–CH=CH–OH	(Z)-3-hydroxyprop-2-enal, O=C/C=C\O

For the drawing, bend the approximately planar chain so that the two oxygens face each other, forming a six-membered hydrogen-bonded loop that includes the transferred hydrogen.

- **L:** Draw a covalent bond from the left oxygen to hydrogen and a dotted hydrogen bond to the right oxygen: O–H···O. The left carbon–oxygen bond is single, and the right one is double.
- **R:** Draw the hydrogen covalently bonded to the right oxygen, with a dotted bond to the left: O···H–O. The left carbon–oxygen bond is double, and the right one is single.

The carbon–carbon double bond shifts at the same time. The SMILES encode connectivity and alkene geometry, but the inward-facing conformation and dotted hydrogen bond must be shown separately.

The two arrangements are symmetry-equivalent, explaining the equal depths of the wells. They are not the E and Z isomers from part 1.1.

1.4 — Probability densities and sketches

Rewrite the given expression using the half-angle identities:

$$\Psi^2(x, t) = \cos^2\left(\frac{\omega t}{2}\right) \Psi_L^2(x) + \sin^2\left(\frac{\omega t}{2}\right) \Psi_R^2(x).$$

(a) At $t = 0$:

$$\Psi^2(x, 0) = \Psi_L^2(x).$$

Draw the supplied left-hand peak, centered at approximately -0.030 nm, with its original shape and height.

(b) At $t = \pi/(2\omega)$:

Since $\cos(\omega t) = \cos(\pi/2) = 0$,

$$\Psi^2\left(x, \frac{\pi}{2\omega}\right) = \frac{1}{2} \Psi_L^2(x) + \frac{1}{2} \Psi_R^2(x).$$

Draw two equal peaks centered at approximately -0.030 and $+0.030$ nm. Each component has the original width but half its original height and integrated area $1/2$.

(c) At $t = \pi/\omega$:

Since $\cos(\omega t) = \cos \pi = -1$,

$$\Psi^2\left(x, \frac{\pi}{\omega}\right) = \Psi_R^2(x).$$

Draw the supplied right-hand peak, centered at approximately $+0.030$ nm, with its original shape and height.

1.5 — Probability in the left well

At $t = \pi/(2\omega)$, the density is symmetric between the two wells. The total probability is one, so each well has probability

$$P_L = \frac{1}{2}.$$

1.6 — Transfer time and mean speed

The proton starts in the left-localized state at $t = 0$ and first reaches the right-localized state when $\omega t = \pi$. Therefore,

$$t_{\text{transfer}} = \frac{\pi}{\omega} = \frac{\pi}{6.48 \times 10^{11} \text{ s}^{-1}} = \boxed{4.85 \times 10^{-12} \text{ s}}.$$

This is half the oscillation period.

From the graph, the minima are approximately at -0.030 and $+0.030$ nm, so their separation is

$$d = 0.060 \text{ nm} = 6.0 \times 10^{-11} \text{ m}.$$

The requested distance-over-time estimate is

$$\bar{v} = \frac{d}{t_{\text{transfer}}} = \frac{6.0 \times 10^{-11} \text{ m}}{4.848 \times 10^{-12} \text{ s}} = 12.4 \text{ m s}^{-1} \approx \boxed{12 \text{ m s}^{-1}}.$$

The precision is limited by reading the distance from the graph.

1.7 — Position and velocity uncertainties

The graph gives a characteristic proton-delocalization distance of

$$\Delta x \sim d = 0.060 \text{ nm} = 6.0 \times 10^{-11} \text{ m}.$$

Use the position–momentum uncertainty relation,

$$\Delta x \Delta p_x \geq \frac{\hbar}{2},$$

and, for a nonrelativistic proton, $\Delta p_x = m_p \Delta v_x$. Hence,

$$\Delta v_x \geq \frac{\hbar}{2m_p \Delta x}.$$

Using the standard constants

$$\hbar = 1.055 \times 10^{-34} \text{ J s}, \quad m_p = 1.673 \times 10^{-27} \text{ kg},$$

the graph-based estimate is

$$\Delta v_{\min} \sim \frac{1.055 \times 10^{-34}}{2(1.673 \times 10^{-27})(6.0 \times 10^{-11})} = \boxed{5.3 \times 10^2 \text{ m s}^{-1}}.$$

Compared with part 1.6,

$$\frac{\Delta v_{\min}}{\bar{v}} \approx \frac{525}{12.4} \approx 42.$$

There is a factor-of-two convention to distinguish here. In the exact uncertainty relation, Δx denotes a **standard deviation**, rather than a full spatial span. At equal populations, two narrow peaks centered at $\pm 0.030 \text{ nm}$ have a position standard deviation approximately 0.030 nm . That estimate gives

$$\Delta v_{\min} \sim 1.1 \times 10^3 \text{ m s}^{-1},$$

which leads to the same conclusion.

The velocity uncertainty is much larger than the distance-over-time speed. Thus part 1.6 supplies a characteristic transfer speed, but it does not establish a classical trajectory with a sharply defined velocity through the barrier. The transfer requires a quantum-mechanical description.

The solution was checked against the official solution.

Problem 2: Nanochemistry

Metals of the iron subgroup are effective catalysts of hydrogenation of CO (Fischer-Tropsch reaction)



Catalyst (e.g. cobalt) is often used in the form of solid nanoparticles that have a spherical structure (fig.1). The reduction in size of the catalyst increases catalytic activity significantly. The unwanted side-reaction however involves the oxidation of the catalyst:



Solid cobalt oxide (bulk) is formed in the reaction vessel. This causes an irreversible loss of the catalyst's mass. Solid cobalt oxide can also be deposited on the surface of Co(s). In this case the new spherical layer is formed around the surface of the catalyst (see figure 2) and the catalytic activity drops.

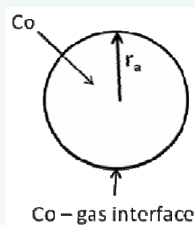


Fig. 1

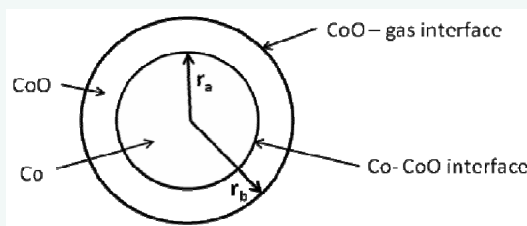


Fig. 2

Let us see how formation of nanoparticles affects the equilibrium of reaction (1).

$$G^0(r) = G^0(\text{bulk}) + \frac{2\sigma}{r}V$$

2.1 Calculate the standard Gibbs energy $\Delta_r G^0(1)$ and the equilibrium constant for the reaction (1) at $T = 500 \text{ K}$.

2.2 Calculate the equilibrium constant for reaction (1) when the cobalt catalyst is dispersed in the form of spherical particles (Fig. 1) of radius:

- (a) 10^{-8} m ,
- (b) 10^{-9} m .

The surface tension at the Co-gas interface is 0.16 J m^{-2} . CoO forms a bulk phase.

The mixture of gases involved in the Fischer-Tropsch (CO, CH₄, H₂, H₂O) reaction was put into a reaction vessel containing the cobalt catalyst. The total pressure is $p = 1 \text{ bar}$, temperature is $T = 500 \text{ K}$. The mole fraction of hydrogen (%) in the mixture is 0.15% .

2.3 At what minimum mole fraction of water (%) in the gas mixture the unwanted spontaneous oxidation of the catalyst becomes possible so that solid bulk CoO may appear in the system? Assume that cobalt catalyst is in the form of

(a) a bulk phase

(b) spherical nanoparticles with $r_a = 1 \text{ nm}$ (Fig. 1).

2.4 What would you suggest to protect Co nanoparticles from the spontaneous oxidation with the formation of bulk CoO at a constant ratio $p(\text{H}_2\text{O})/p(\text{H}_2)$ and a constant temperature:

(a) to increase r_a ;

(b) to decrease r_a ;

(c) change of r_a has no effect.

Assume now that solid cobalt oxide forms a spherical layer around a nanoparticle of cobalt. In this case the nanoparticle contains both a reactant (Co) and a product (CoO) (Fig. 2).

In the following problems denote surface tensions as $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, radii as r_a , r_b , molar volumes as $V(\text{Co})$; $V(\text{CoO})$.

2.5 Write down the expression for the standard molar Gibbs function of CoO.

2.6 Write down the expression for the standard molar Gibbs function of Co.

Hint. If two spherical interfaces surround a nanoparticle, the excess pressure at its centre is given by the expression

$$P_{\text{in}} - P_{\text{ex}} = \Delta P = \Delta P_1 + \Delta P_2 = 2 \frac{\sigma_1}{r_1} + 2 \frac{\sigma_2}{r_2}$$

r_i , σ_i are radius and surface tension at the spherical interface i , respectively.

2.7 Express the standard Gibbs energy of the reaction (1) $\Delta_r G^0(1, r_a, r_b)$ in terms of $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, r_a , r_b , $V(\text{Co})$; $V(\text{CoO})$ and $\Delta_r G^0(1)$.

2.8 When spontaneous oxidation of Co begins the radii of two layers in the nanoparticle (Fig. 2) are almost equal, $r_a = r_b = r_0$, and $\Delta_r G^0(1, r_a, r_b) = \Delta_r G^0(1, r_0)$. Assume that $\sigma_{\text{CoO-gas}} = 2\sigma_{\text{CoO-Co}}$. Which plot in the Answer Sheet describes correctly the dependence of $\Delta_r G^0(1, r_0)$ on r_0 ?

2.9 What would you choose to protect Co nanoparticles from the spontaneous formation of the external layer of CoO at a constant ratio $p(\text{H}_2\text{O})/p(\text{H}_2)$ and a constant temperature:

a) increase r_0

b) decrease r_0

c) change of r_0 has no effect.

Reference data:

Substance	ρ , g cm ⁻³	$\Delta_f G_{500}^0$, kJ mol ⁻¹
Co (s)	8.90	
CoO (s)	5.68	-198.4
H ₂ O (gas)		-219.1

Official English text of the problem.

Answers

For compactness, define

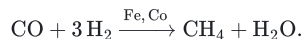
$$\sigma_o = \sigma_{\text{CoO-gas}}, \quad \sigma_i = \sigma_{\text{CoO-Co}}, \quad V_c = V(\text{Co}), \quad V_o = V(\text{CoO}).$$

- 2.1:** $\Delta_r G^0(1) = +20.7 \text{ kJ mol}^{-1}$, $K_{\text{bulk}} = 6.88 \times 10^{-3}$.
- 2.2:** (a) $K(10^{-8} \text{ m}) = 7.24 \times 10^{-3}$; (b) $K(10^{-9} \text{ m}) = 1.14 \times 10^{-2}$.
- 2.3:** Water mole-fraction thresholds: (a) 21.8% ; (b) 13.1% . Forward oxidation is spontaneous above the respective threshold.
- 2.4:** (a) Increase r_a .
- 2.5:** $G_{\text{CoO}}^0 = G_{\text{CoO}}^0(\text{bulk}) + \frac{2\sigma_o V_o}{r_b}$.
- 2.6:** $G_{\text{Co}}^0 = G_{\text{Co}}^0(\text{bulk}) + 2V_c \left(\frac{\sigma_o}{r_b} + \frac{\sigma_i}{r_a} \right)$.
- 2.7:** $\Delta_r G^0(1, r_a, r_b) = \Delta_r G^0(1) + \frac{2\sigma_o}{r_b}(V_o - V_c) - \frac{2\sigma_i V_c}{r_a}$.
- 2.8:** $\Delta_r G^0(1, r_0) = \Delta_r G^0(1) + A/r_0$, where $A = 2\sigma_i(2V_o - 3V_c) > 0$. The curve decreases, is convex upward, and approaches $+20.7 \text{ kJ mol}^{-1}$ from above as r_0 increases.
- 2.9:** (b) Decrease r_0 , under the surface-tension assumption in 2.8.

Solution

The molecular species are carbon monoxide, CO , $[\text{C-}]\#[\text{O+}]$; methane, CH_4 , c ; hydrogen, H_2 , $[\text{H}][\text{H}]$; and water, H_2O , o . Cobalt is a metallic solid: $[\text{Co}]$ represents an individual atom, not its metallic lattice. Cobalt(II) oxide is an ionic solid: $[\text{Co+2}][\text{O-2}]$ records its constituent ions but does not specify its crystal lattice.

The balanced catalytic reaction is



The oxidation equilibrium considered throughout the problem is



For the calculations, use

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, \quad M(\text{Co}) = 58.93 \text{ g mol}^{-1}, \quad M(\text{O}) = 16.00 \text{ g mol}^{-1}.$$

2.1 — Bulk reaction Gibbs energy and equilibrium constant

The standard Gibbs energies of formation of elemental cobalt and hydrogen in their standard states are zero. Therefore,

$$\begin{aligned} \Delta_r G^0(1) &= \Delta_f G^0(\text{CoO}) + \Delta_f G^0(\text{H}_2) - \Delta_f G^0(\text{Co}) - \Delta_f G^0(\text{H}_2\text{O}) \\ &= (-198.4) + 0 - 0 - (-219.1) \\ &= \boxed{+20.7 \text{ kJ mol}^{-1}}. \end{aligned}$$

Since $\Delta_r G^0 = -RT \ln K$,

$$K_{\text{bulk}} = \exp\left(-\frac{20700}{8.314 \times 500}\right) = \boxed{6.88 \times 10^{-3}}.$$

For bulk pure solids, their activities are unity. Treating the gases as ideal,

$$K_{\text{bulk}} = \frac{p(\text{H}_2)/p^0}{p(\text{H}_2\text{O})/p^0} = \frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}.$$

Thus K is dimensionless.

2.2 — Equilibrium constants for cobalt nanoparticles

The molar volume of cobalt is

$$V_c = \frac{M(\text{Co})}{\rho(\text{Co})} = \frac{58.93}{8.90} = 6.621 \text{ cm}^3 \text{ mol}^{-1} = 6.621 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}.$$

The surface correction raises the molar Gibbs energy of the cobalt reactant:

$$G_{\text{Co}}^0(r_a) = G_{\text{Co}}^0(\text{bulk}) + \frac{2\sigma_{\text{Co-gas}}V_c}{r_a}.$$

Because the oxide product remains bulk,

$$\Delta_r G^0(1, r_a) = \Delta_r G^0(1) - \frac{2\sigma_{\text{Co-gas}}V_c}{r_a}.$$

Consequently,

$$K(r_a) = K_{\text{bulk}} \exp\left(\frac{2\sigma_{\text{Co-gas}}V_c}{r_a RT}\right).$$

With $\sigma_{\text{Co-gas}} = 0.16 \text{ J m}^{-2}$:

Part	r_a , m	$2\sigma V_c/r_a$, kJ mol ⁻¹	$\Delta_r G^0(1, r_a)$, kJ mol ⁻¹	$K(r_a)$
(a)	10^{-8}	0.2119	20.488	7.24×10^{-3}
(b)	10^{-9}	2.1188	18.581	1.14×10^{-2}

Smaller cobalt particles have a larger molar Gibbs energy, making their oxidation to bulk oxide more favorable.

2.3 — Minimum water mole fraction

At a specified gas composition,

$$\Delta_r G = \Delta_r G^0 + RT \ln Q, \quad Q = \frac{p(\text{H}_2)}{p(\text{H}_2\text{O})} = \frac{x_{\text{H}_2}}{x_{\text{H}_2\text{O}}}.$$

The total pressure cancels because the reaction consumes and produces equal numbers of gas molecules.

Forward oxidation is favorable when

$$\Delta_r G < 0 \iff Q < K \iff x_{\text{H}_2\text{O}} > \frac{x_{\text{H}_2}}{K}.$$

The critical composition is therefore

$$x_{\text{H}_2\text{O}, \text{crit}} = \frac{x_{\text{H}_2}}{K}, \quad x_{\text{H}_2} = \frac{0.15}{100} = 0.0015.$$

For **(a) bulk cobalt**, using the unrounded equilibrium constant,

$$x_{\text{H}_2\text{O}, \text{crit}} = \frac{0.0015}{0.00687714} = 0.2181,$$

so

$$x_{\text{H}_2\text{O},\text{crit}} = 21.8\%.$$

For **(b) cobalt particles with** $r_a = 1 \text{ nm}$,

$$x_{\text{H}_2\text{O},\text{crit}} = \frac{0.0015}{0.0114490} = 0.1310,$$

so

$$x_{\text{H}_2\text{O},\text{crit}} = 13.1\%.$$

At these thresholds, $\Delta_r G = 0$; strictly spontaneous forward oxidation requires a slightly higher water mole fraction at the stated hydrogen mole fraction.

2.4 — Protecting cobalt against formation of bulk oxide

At fixed temperature and gas-pressure ratio,

$$\Delta_r G = \Delta_r G^0(1) - \frac{2\sigma_{\text{Co-gas}} V_c}{r_a} + RT \ln \frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}.$$

Hence

$$\frac{\partial \Delta_r G}{\partial r_a} = \frac{2\sigma_{\text{Co-gas}} V_c}{r_a^2} > 0.$$

Increasing the particle radius raises the reaction Gibbs energy and suppresses oxidation:

$$\text{Choose (a): increase } r_a.$$

2.5 — Molar Gibbs function of the oxide shell

For the geometry in Fig. 2, the oxide shell lies beneath the outer interface of radius r_b . Its pressure exceeds the external gas pressure by

$$P_{\text{CoO}} - P_{\text{gas}} = \frac{2\sigma_o}{r_b}.$$

At constant temperature, an approximately incompressible phase obeys $dG_m = V_m dP$. Therefore,

$$G_{\text{CoO}}^0 = G_{\text{CoO}}^0(\text{bulk}) + \frac{2\sigma_o V_o}{r_b}.$$

2.6 — Molar Gibbs function of the cobalt core

The cobalt core experiences the pressure increments across both interfaces:

$$P_{\text{Co}} - P_{\text{gas}} = \frac{2\sigma_o}{r_b} + \frac{2\sigma_i}{r_a}.$$

Thus,

$$G_{\text{Co}}^0 = G_{\text{Co}}^0(\text{bulk}) + 2V_c \left(\frac{\sigma_o}{r_b} + \frac{\sigma_i}{r_a} \right).$$

2.7 — Reaction Gibbs energy for a particle with an oxide shell

Subtract the cobalt correction from the oxide correction. The gas contributions remain unchanged:

$$\Delta_r G^0(1, r_a, r_b) = \Delta_r G^0(1) + \frac{2\sigma_o V_o}{r_b} - \left(\frac{2\sigma_o V_c}{r_b} + \frac{2\sigma_i V_c}{r_a} \right).$$

Therefore,

$$\Delta_r G^0(1, r_a, r_b) = \Delta_r G^0(1) + \frac{2\sigma_o}{r_b} (V_o - V_c) - \frac{2\sigma_i V_c}{r_a}.$$

2.8 — Dependence on the initial radius

Set $r_a = r_b = r_0$ and $\sigma_o = 2\sigma_i$:

$$\begin{aligned} \Delta_r G^0(1, r_0) &= \Delta_r G^0(1) + \frac{4\sigma_i}{r_0} (V_o - V_c) - \frac{2\sigma_i V_c}{r_0} \\ &= \Delta_r G^0(1) + \frac{2\sigma_i}{r_0} (2V_o - 3V_c). \end{aligned}$$

The oxide molar volume is

$$V_o = \frac{58.93 + 16.00}{5.68} = 13.192 \text{ cm}^3 \text{ mol}^{-1}.$$

Consequently,

$$2V_o - 3V_c = 2(13.192) - 3(6.621) = 6.520 \text{ cm}^3 \text{ mol}^{-1} > 0.$$

Define

$$A = 2\sigma_i (2V_o - 3V_c) > 0.$$

The required function is

$$\Delta_r G^0(1, r_0) = 20.7 \text{ kJ mol}^{-1} + \frac{A}{r_0},$$

with consistent units used for A/r_0 .

Its derivatives are

$$\frac{d\Delta_r G^0}{dr_0} = -\frac{A}{r_0^2} < 0, \quad \frac{d^2\Delta_r G^0}{dr_0^2} = \frac{2A}{r_0^3} > 0.$$

The required plot has $r_0 > 0$ on the horizontal axis and $\Delta_r G^0(1, r_0)$ on the vertical axis. It decreases steeply at small radii, curves upward, and flattens toward the horizontal asymptote

$$\Delta_r G^0 = +20.7 \text{ kJ mol}^{-1}$$

from above. Within the given mathematical model, it tends to $+\infty$ as $r_0 \rightarrow 0^+$.

2.9 — Protecting cobalt against formation of an oxide shell

Under the assumptions of 2.8,

$$\Delta_r G = \Delta_r G^0(1) + \frac{A}{r_0} + RT \ln \frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}, \quad A > 0.$$

At fixed temperature and gas ratio, decreasing r_0 increases the positive surface contribution A/r_0 . This makes oxide-shell formation less favorable.

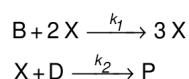
Choose (b): decrease r_0 .

The solution was checked against the official solution.

Problem 3: Unstable chemical reactions

Many chemical reactions display unstable kinetic behavior. At different conditions (concentrations and temperature) such reactions can proceed in various modes: stable, oscillatory or chaotic. Most of these reactions include autocatalytic elementary steps.

Consider a simple reaction mechanism involving autocatalytic step:



(B and D are reagents, X is an intermediate and P is a product).

3.1 Write down the overall reaction equation for this two-step mechanism. Write the rate equation for X.

3.2 Deduce a rate equation using steady-state approximation. Find the orders:

- (i) a partial reaction order with respect to B;
- (ii) a partial reaction order with respect to D;
- (iii) the overall order of a reaction.

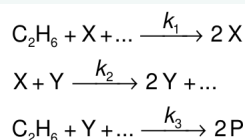
Let the reaction occur in an open system where reagents B and D are being continuously added to the mixture so that their concentrations are maintained constant and equal: $[\text{B}] = [\text{D}] = \text{const.}$

3.3 Without solving the kinetic equation draw the kinetic curve $[\text{X}](t)$ for the cases:

$$1) \quad [\text{X}]_0 > \frac{k_2}{k_1}; \quad 2) \quad [\text{X}]_0 < \frac{k_2}{k_1}.$$

3.4 Without solving the kinetic equation draw the kinetic curve $[\text{X}](t)$ for the case when the reaction proceeds in a closed vessel with the initial concentrations: $[\text{B}]_0 = [\text{D}]_0$, $[\text{X}]_0 > \frac{k_2}{k_1}$.

Much more complex kinetic behavior is possible for the reactions with several intermediates. Consider a simplified reaction mechanism for cold burning of ethane in oxygen:



Under specific conditions this reaction displays oscillatory behavior:

Intermediates are peroxide $\text{C}_2\text{H}_6\text{O}_2$ and aldehyde $\text{C}_2\text{H}_4\text{O}$, P is a stable product.

3.5 Identify X, Y, and P. Fill the blanks in the reaction mechanism.

Behavior of unstable reactions is often controlled by temperature which affects the rate constants. In the above oxidation mechanism oscillations of concentrations are possible only if $k_1 \geq k_2$. Parameters of the Arrhenius equations were determined experimentally:

Step	$A, \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$E_A, \text{ kJ mol}^{-1}$
1	1.0×10^{11}	90
2	3.0×10^{12}	100

3.6 What is the highest temperature at which oscillatory regime is possible? Show your calculations.

Official English text of the problem.

Answers

• 3.1



$$\boxed{\frac{d[\text{X}]}{dt} = k_1[\text{B}][\text{X}]^2 - k_2[\text{D}][\text{X}].}$$

• 3.2 On the nonzero steady-state branch,

$$[\text{X}]_{\text{ss}} = \frac{k_2[\text{D}]}{k_1[\text{B}]}, \quad v = \frac{k_2^2 [\text{D}]^2}{k_1 [\text{B}]}.$$

The orders are -1 with respect to B, 2 with respect to D, and 1 overall.

- **3.3** Write $K = k_2/k_1$. 1. For $[\text{X}]_0 > K$, the curve increases continuously, is concave upward, and becomes unbounded at a finite time in the idealized model. 2. For $0 < [\text{X}]_0 < K$, the curve decreases continuously toward zero. If initially above $K/2$, it first curves downward, passes through an inflection at $K/2$, and then curves upward; if initially at or below $K/2$, it curves upward thereafter.

- **3.4** The curve rises from $[\text{X}]_0$, reaches one maximum, and then decreases toward the horizontal asymptote

$$\boxed{[\text{X}]_{\infty} = [\text{X}]_0.}$$

- **3.5** Using the carbon-skeleton-preserving structural assignments:

Species	Identity	Formula	SMILES
X	Ethyl hydroperoxide	$\text{C}_2\text{H}_5\text{OOH}$	<chem>CCOO</chem>
Y	Ethanal (acetaldehyde)	CH_3CHO	<chem>CC=O</chem>
P	Ethanol	$\text{C}_2\text{H}_5\text{OH}$	<chem>CCO</chem>

The blanks, in order, are **oxygen** O_2 , $\text{O}=\text{O}$; **water** H_2O , O ; and **water** H_2O , O . The completed balanced mechanism is given below.

• 3.6

$$\boxed{T_{\text{max}} = \frac{10\,000}{R \ln 30} \approx 354 \text{ K} \quad (\text{about } 81^\circ \text{C}).}$$

Solution

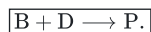
3.1

In this first mechanism, B, D, X, and P are unspecified species, so molecular names and SMILES cannot be assigned.

The steps are



Adding them and cancelling the intermediate gives



Because the steps are elementary, their rates are

$$v_1 = k_1[\text{B}][\text{X}]^2, \quad v_2 = k_2[\text{X}][\text{D}].$$

Each occurrence of the first step produces **one net X**, whereas the second consumes one. Therefore,

$$\boxed{\frac{d[\text{X}]}{dt} = (3 - 2)v_1 - v_2 = k_1[\text{B}][\text{X}]^2 - k_2[\text{D}][\text{X}].}$$

3.2

The steady-state approximation sets the net production rate of the intermediate approximately equal to zero:

$$0 \simeq [\text{X}] (k_1[\text{B}][\text{X}] - k_2[\text{D}]).$$

Besides the zero-concentration solution, the nonzero stationary concentration is

$$[\text{X}]_{\text{ss}} = \frac{k_2[\text{D}]}{k_1[\text{B}]}.$$

Substitution into the product-formation rate gives

$$v = \frac{d[\text{P}]}{dt} = k_2[\text{D}][\text{X}]_{\text{ss}} = \frac{k_2^2 [\text{D}]^2}{k_1 [\text{B}]}.$$

Thus:

$$\boxed{n_{\text{B}} = -1, \quad n_{\text{D}} = 2, \quad n_{\text{overall}} = -1 + 2 = 1.}$$

The other stationary branch, $[X] = 0$, gives zero reaction rate. The nonzero branch yields the requested formal rate law, although it is unstable when the reagent concentrations are held fixed, as the next part shows.

3.3

Define

$$x = [X], \quad x_0 = [X]_0, \quad C = [B] = [D] > 0, \quad K = \frac{k_2}{k_1}.$$

Here K has concentration units. The kinetic equation becomes

$$\dot{x} = Ck_1x(x - K).$$

The stationary concentrations are $x = 0$ and $x = K$. The sign of $\dot{x}$ determines the direction of motion without solving the equation.

For each sketch, put time on the horizontal axis and x on the vertical axis.

Case 1: $x_0 > K$.

Both factors x and $x - K$ are positive, so x increases. Moreover,

$$\ddot{x} = Ck_1(2x - K)\dot{x} > 0.$$

The curve therefore starts above K , rises continuously, and becomes progressively steeper. Its unbounded growth occurs at a finite time: since $x \geq x_0$,

$$\dot{x} \geq Ck_1 \left(1 - \frac{K}{x_0}\right) x^2,$$

so $1/x$ decreases at least at a fixed positive rate until it reaches zero. Thus the idealized sketch has a finite-time vertical asymptote.

Case 2: $0 < x_0 < K$.

Now $\dot{x} < 0$, so the concentration decreases. It approaches zero asymptotically, flattening toward the time axis.

The curvature follows from

$$\ddot{x} = Ck_1(2x - K)\dot{x}.$$

Because $\dot{x} < 0$:

- For $K/2 < x < K$, the curve is concave downward.
- At $x = K/2$, it has an inflection.
- For $0 < x < K/2$, it is concave upward.

Consequently, an initial concentration above $K/2$ gives a decreasing curve with one inflection; an initial concentration at or below $K/2$ gives a curve that is concave upward thereafter.

For completeness, $x_0 = 0$ remains zero, and $x_0 = K$ remains exactly K . The latter stationary state is unstable: a small upward displacement grows, while a small downward displacement leads toward zero.

3.4

In a closed vessel, let

$$b = [B], \quad d = [D], \quad x = [X], \quad b_0 = d_0 = C_0.$$

The equations are

$$\dot{b} = -v_1, \quad \dot{d} = -v_2, \quad \dot{x} = v_1 - v_2.$$

Hence

$$\frac{d}{dt}(x + b - d) = 0.$$

Using the equal initial reagent concentrations,

$$\boxed{x + b - d = x_0, \quad x = x_0 + d - b.}$$

Initially,

$$\dot{x}_0 = C_0x_0(k_1x_0 - k_2) > 0,$$

so the concentration rises.

It cannot subsequently cross below x_0 : at any point where $x = x_0$, conservation requires $b = d$, and therefore

$$\dot{x} = bx_0(k_1x_0 - k_2) > 0$$

while reagents remain.

Since $x \geq x_0 > 0$, both reagents are continuously consumed and tend to zero. For example,

$$\dot{b} \leq -k_1x_0^2b, \quad \dot{d} \leq -k_2x_0d.$$

The conservation relation then gives

$$\boxed{x_\infty = x_0.}$$

There is exactly one maximum. At a stationary point, $v_1 = v_2 = v > 0$, and

$$\ddot{x} = -k_1vx^2 + k_2vx = vx(k_2 - k_1x) < 0,$$

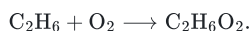
because $x \geq x_0 > K$. Every stationary point is therefore a strict maximum; no intervening minimum is possible.

The requested sketch starts at x_0 , rises to a single peak with a horizontal tangent, then decreases and flattens toward x_0 from above. Its initial concavity is not fixed by the supplied conditions.

3.5

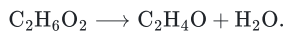
Ethane is C_2H_6 , SMILES `CC`.

In the first step, one molecule of ethane is converted into one additional molecule of X. Addition of oxygen gives



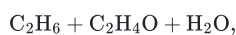
Thus X is the peroxide. Retaining the ethane carbon skeleton gives **ethyl hydroperoxide**, C_2H_5OOH , `CCOO`.

The second step consumes one net peroxide molecule and produces one net molecule of the other intermediate. The balance is



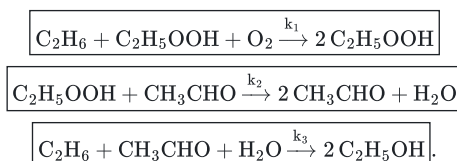
Therefore Y is the aldehyde **ethanal**, CH_3CHO , `CC=O`, and the missing product is water.

In the third step, adding water to ethane and ethanal gives the combined composition



containing four carbon, twelve hydrogen, and two oxygen atoms. Two molecules of P consequently each have formula C_2H_6O . The carbon-skeleton-preserving product is **ethanol**, C_2H_5OH , `CCO`.

The completed mechanism is therefore



All three equations conserve carbon, hydrogen, and oxygen. Adding them cancels both intermediates and water, giving the overall partial oxidation:



3.6

The Arrhenius equation is

$$k_i = A_i \exp\left(-\frac{E_{A,i}}{RT}\right).$$

Thus

$$\frac{k_1}{k_2} = \frac{A_1}{A_2} \exp\left(\frac{E_{A,2} - E_{A,1}}{RT}\right) = \frac{1}{30} \exp\left(\frac{10\,000 \text{ J mol}^{-1}}{RT}\right).$$

The stated condition $k_1 \geq k_2$ requires

$$\frac{10\,000 \text{ J mol}^{-1}}{RT} \geq \ln 30.$$

Therefore,

$$T \leq \frac{10\,000 \text{ J mol}^{-1}}{R \ln 30}.$$

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

$$T_{\max} = \frac{10\,000}{8.314 \ln 30} \text{ K} = 353.6 \text{ K}.$$

Hence

$$\boxed{T_{\max} \approx 354 \text{ K} \approx 81^\circ \text{C}.$$

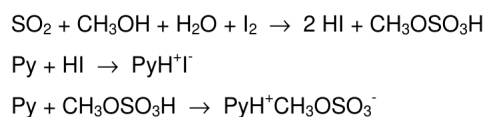
This is the upper temperature allowed by the stated necessary condition; that condition alone does not guarantee oscillations at every lower temperature.

The solution was checked against the official solution.

Problem 4: Determination of water by Fischer titration

Determination of water by Fischer titration

Determination of water by the classical Fischer method involves titration of a sample solution (or suspension) in methanol by a methanolic iodine solution, containing also an excess of SO_2 and pyridine (C_5H_5N , Py) – Fischer reagent. The following reactions occur during the titration:



Iodine content is usually expressed in mg of water reacting with 1 cm^3 of the titrant solution (hereunder T, mg cm^{-3}), which equals the mass of water (mg) reacting with 1.00 cm^3 of the iodine solution. T is determined experimentally by titration of a sample with a known water content. The sample may be, for example, a hydrated compound or a standard solution of water in methanol. In the latter case it should be taken into account that

methanol itself can contain certain amount of water.

In all calculations please use the atomic masses accurate to 2 decimal points.

4.1 Sometimes titration of water is performed in pyridine medium without methanol. How would the reaction of I_2 with SO_2 and H_2O occur in this case? Write down balanced reaction equation.

Calculate the T values of iodine solution in each of the following cases:

4.2 12.20 cm^3 of Fischer reagent solution were used for titration of 1.352 g of sodium tartrate dihydrate $Na_2C_4H_4O_6 \cdot 2H_2O$.

4.3 A known amount of water (21.537 g) was placed into a 1.000 dm^3 volumetric flask which was filled by methanol up to the mark. For titration of 10.00 cm^3 of the obtained solution, 22.70 cm^3 of Fischer reagent solution were needed, whereas 2.20 cm^3 of iodine were used for titration of 25.00 cm^3 of methanol.

4.4 5.624 g of water were diluted by methanol up to a total volume of 1.000 dm^3 (solution **A**); 22.45 cm^3 of this solution were used for titration of 15.00 cm^3 of a Fischer reagent (solution **B**).

Then 25.00 cm^3 of methanol (of the same batch as used for the preparation of solution **A**) and 10.00 cm^3 of solution **B** were mixed, and the mixture was titrated by the solution **A**. 10.79 cm^3 of the latter solution were spent.

4.5 An inexperienced analyst tried to determine water content in a sample of CaO using Fischer reagent. Write down the equation(s) of reaction(s) demonstrating possible sources of errors.

For the titration of 0.6387 g of a hydrated compound $Fe_2(SO_4)_3 \cdot xH_2O$, 10.59 cm^3 of iodine solution ($T = 15.46\text{ mg/cm}^3$) were consumed.

4.6 What other reaction(s), beside those given in the problem, can occur during the titration? Write down the equations of two such processes.

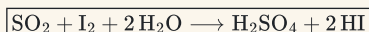
4.7 Write down an equation of the overall reaction of $Fe_2(SO_4)_3 \cdot xH_2O$ with the Fischer reagent.

4.8 Calculate the composition of the hydrate $Fe_2(SO_4)_3 \cdot xH_2O$ ($x = \text{integer}$).

Official English text of the problem.

Answers

- **4.1**



One mole of iodine consumes two moles of water.

- **4.2**

$$T = 17.36\text{ mg cm}^{-3}$$

- **4.3**

$$T \approx 9.870\text{ mg cm}^{-3}$$

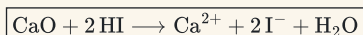
This uses the dilute-solution volume approximation explained below.

- **4.4**

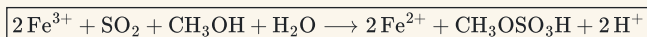
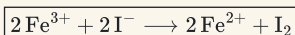
$$T \approx 10.11\text{ mg cm}^{-3}$$

This uses the same volume approximation.

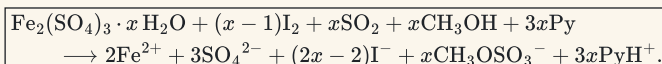
- **4.5** Acid neutralization by calcium oxide generates additional water, causing an erroneously high result. For example,



- **4.6** Iron(III) can oxidize iodide and sulfur dioxide:



- **4.7** An overall equation, with the products written as ions, is



- **4.8**

$$x = 9, \quad Fe_2(SO_4)_3 \cdot 9H_2O$$

The compound is **iron(III) sulfate nonahydrate**.

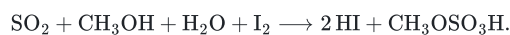
Solution

Names and SMILES for the species used in the equations are collected here once. Disconnected SMILES for ionic compounds describe composition; they do not specify a crystal structure or coordination geometry.

Species	Name	SMILES
H_2O	Water	O

Species	Name	SMILES
CH ₃ OH	Methanol	CO
SO ₂	Sulfur dioxide	O=S=O
I ₂	Iodine	II
Py	Pyridine	n1ccccc1
HI	Hydrogen iodide	[H]I
H ₂ SO ₄	Sulfuric acid	OS(=O)(=O)O
CH ₃ OSO ₃ H	Methyl hydrogen sulfate	COS(=O)(=O)O
H ⁺	Hydrogen ion, or proton	[H+]
I ⁻	Iodide ion	[I-]
PyH ⁺	Pyridinium ion	[nH+]1ccccc1
CH ₃ OSO ₃ ⁻	Methyl sulfate ion	COS(=O)(=O)[O-]
SO ₄ ²⁻	Sulfate ion	[O-]S(=O)(=O)[O-]
Fe ³⁺	Iron(III) ion	[Fe+3]
Fe ²⁺	Iron(II) ion	[Fe+2]
Ca ²⁺	Calcium ion	[Ca+2]
CaO	Calcium oxide	[Ca+2].[O-2]

The given methanolic reaction is



Thus, in the absence of interfering reactions,

$$n(\text{I}_2) = n(\text{H}_2\text{O}), \quad T = \frac{m(\text{H}_2\text{O})}{V_{\text{reagent}}}.$$

The atomic masses used are

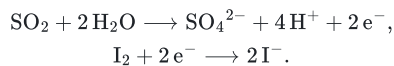
$$\begin{aligned} A_r(\text{H}) &= 1.01, & A_r(\text{C}) &= 12.01, & A_r(\text{O}) &= 16.00, \\ A_r(\text{Na}) &= 22.99, & A_r(\text{S}) &= 32.07, & A_r(\text{Fe}) &= 55.85. \end{aligned}$$

Consequently,

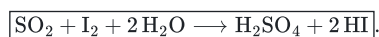
$$M(\text{H}_2\text{O}) = 18.02 \text{ g mol}^{-1}.$$

4.1

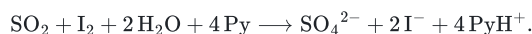
Without methanol, oxidation of sulfur dioxide produces sulfate. The balanced oxidation and reduction half-reactions are



Their sum can be written in molecular form as



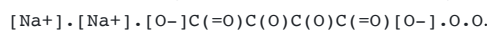
Including neutralization by excess pyridine gives



Two water molecules supply the two additional oxygen atoms required to convert sulfur dioxide into sulfate. In the methanolic reaction, methanol supplies one of these oxygen atoms, so only one water molecule is consumed per iodine molecule.

4.2

Sodium tartrate dihydrate has the composition-only SMILES



The statement does not specify tartrate stereochemistry, so none is assigned in the SMILES.

Its molar mass is

$$\begin{aligned} M(\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}) &= 2(22.99) + 4(12.01) + 4(1.01) + 6(16.00) + 2(18.02) \\ &= 230.10 \text{ g mol}^{-1}. \end{aligned}$$

The mass of crystallization water in the sample is

$$m_w = (1.352 \text{ g}) \frac{2(18.02)}{230.10} = 0.2117605 \text{ g} = 211.7605 \text{ mg}.$$

Therefore,

$$\boxed{T = \frac{211.7605 \text{ mg}}{12.20 \text{ cm}^3} = 17.36 \text{ mg cm}^{-3}}.$$

4.3

For this part and 4.4, use the usual dilute-solution approximation that the methanol contribution to a 1.000 dm³ preparation is approximately the water contained in 1.000 dm³ of the original methanol.

The deliberately added water in the aliquot is

$$m_{\text{added}} = (21.537 \text{ g}) \frac{10.00}{1000} = 0.21537 \text{ g} = 215.37 \text{ mg}.$$

The methanol blank corresponding to the aliquot requires

$$V_{\text{blank}} = (2.20 \text{ cm}^3) \frac{10.00}{25.00} = 0.880 \text{ cm}^3$$

of reagent.

The reagent volume attributable to the deliberately added water is consequently

$$V_{\text{corrected}} = 22.70 - 0.880 = 21.82 \text{ cm}^3.$$

Hence

$$T = \frac{215.37 \text{ mg}}{21.82 \text{ cm}^3} \approx 9.870 \text{ mg cm}^{-3}.$$

4.4

Let c_m be the water concentration in the original methanol, and c_A the total water concentration in solution A, both in mg cm^{-3} .

Under the stated volume approximation,

$$c_A = \frac{5624 \text{ mg}}{1000 \text{ cm}^3} + c_m = 5.624 \text{ mg cm}^{-3} + c_m.$$

The first titration gives

$$(15.00 \text{ cm}^3)T = (22.45 \text{ cm}^3)c_A.$$

In the second experiment, water from the added methanol consumes part of the iodine initially present in solution B. Solution A consumes the remainder:

$$(10.00 \text{ cm}^3)T = (25.00 \text{ cm}^3)c_m + (10.79 \text{ cm}^3)c_A.$$

Eliminating T ,

$$c_m = \frac{10.00(22.45/15.00) - 10.79}{25.00} c_A = 0.1670667 c_A.$$

Thus

$$c_A = \frac{5.624}{1 - 0.1670667} = 6.752041 \text{ mg cm}^{-3},$$

and

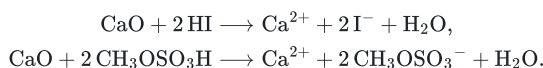
$$c_m = 1.128041 \text{ mg cm}^{-3}.$$

Finally,

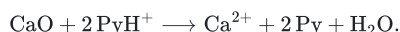
$$T = \frac{22.45}{15.00} c_A = 10.10555 \text{ mg cm}^{-3} \approx 10.11 \text{ mg cm}^{-3}.$$

4.5

Calcium oxide is a basic oxide. It reacts with acidic components of the reagent system and generates water. Two examples, with the calcium salts written as ions, are



The corresponding reaction with protonated pyridine is



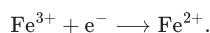
The newly generated water consumes additional iodine. Combining the first equation with the Fischer reaction makes the interference explicit:



Thus even anhydrous calcium oxide can consume iodine. Each mole of calcium oxide reacting through this process produces one mole of apparent water, giving an erroneously high water determination.

4.6

Iron(III) is an additional oxidizing agent in the sample. Its reduction is

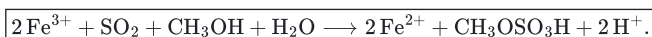


It can accept electrons from iodide:



This regenerates iodine from iodide formed during the Fischer reaction.

Iron(III) can also accept electrons directly from sulfur dioxide. Written consistently with the methyl hydrogen sulfate product specified for the methanolic medium,

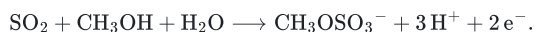


Here sulfur is oxidized from +4 to +6, releasing two electrons, while two iron(III) ions each accept one electron.

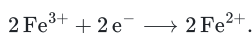
These are alternative routes for reduction of the same iron(III): each formula unit of the hydrate accepts two electrons in total through its two iron ions.

4.7

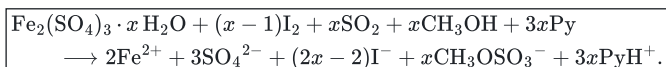
Including dissociation of methyl hydrogen sulfate, the sulfur oxidation half-reaction is



For x waters of hydration, this process releases $2x$ electrons. Reduction of the two iron(III) ions consumes two electrons:



The remaining $2x - 2$ electrons reduce $x - 1$ iodine molecules. Pyridine binds the $3x$ protons produced. Therefore,



The three sulfate ions originally present in the hydrate are retained. Both atoms and charge balance; the total product charge is

$$2(2) + 3(-2) - (2x - 2) - x + 3x = 0.$$

The analytical consequence is

$$\boxed{n(\text{I}_2) = (x - 1) n(\text{hydrate})}.$$

4.8

The anhydrous iron(III) sulfate formula unit has composition-only SMILES

[Fe+3].[Fe+3].[O-]S(=O)(=O)[O-].[O-]S(=O)(=O)[O-].[O-]S(=O)(=O)[O-].

Its molar mass is

$$M_0 = 2(55.85) + 3[32.07 + 4(16.00)] = 399.91 \text{ g mol}^{-1}.$$

The iodine consumed corresponds to an apparent water mass of

$$m_{\text{equiv}} = (15.46 \text{ mg cm}^{-3})(10.59 \text{ cm}^3) = 163.7214 \text{ mg}.$$

Because the reagent titer is based on the ordinary 1 : 1 iodine–water reaction,

$$n(\text{I}_2) = \frac{0.1637214 \text{ g}}{18.02 \text{ g mol}^{-1}} = 0.009085538 \text{ mol}.$$

Meanwhile,

$$n(\text{hydrate}) = \frac{0.6387 \text{ g}}{(399.91 + 18.02x) \text{ g mol}^{-1}}.$$

Using the stoichiometry established in 4.7,

$$0.009085538 = \frac{0.6387(x - 1)}{399.91 + 18.02x}.$$

Solving,

$$x = \frac{0.6387 + (0.009085538)(399.91)}{0.6387 - (0.009085538)(18.02)} = 8.9943.$$

Since x must be an integer,

$$\boxed{x = 9, \quad \text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}}.$$

The compound is **iron(III) sulfate nonahydrate**, with composition-only SMILES

[Fe+3].[Fe+3].[O-]S(=O)(=O)[O-].[O-]S(=O)(=O)[O-].[O-]S(=O)(=O)[O-].O.O.O.O.O.O.O.O.O.

The formula and this SMILES specify nine waters per formula unit. They do not establish which waters coordinate iron or the hydrate's crystal geometry.

The solution was checked against the official solution.

Problem 5: A mysterious mixture (organic hide-and-seek game)

An equimolar mixture **X** of three colorless organic liquids **A**, **B**, **C** was treated by water containing a drop of hydrochloric acid at heating to give (after separation from water) a 1 : 2 (molar ratio) mixture of acetic acid and ethanol without any other components. A catalytic amount (one-two drops) of concentrated sulfuric acid was added to the mixture after hydrolysis and after a long reflux (boiling with reflux condenser) a compound **D**, a volatile liquid with pleasant smell, was formed in 85% yield. Compound **D** is not identical with any of **A**, **B**, **C**.

5.1 Draw the structure of compound **D**?

5.2 Which class of organic compounds does **D** belong to? Choose the proper variant from those given in the Answer Sheet.

5.3 Even if the reflux is continued twice as long, the yield of **D** would not exceed 85%. Calculate the expected yield of **D** if 1 : 1 (molar ratio) mixture of ethanol and acetic acid is taken. Assume that: a) volumes do not change during the reactions; b) all concomitant factors, such as solvent effects, non-additivity of volumes, variation of temperature, etc. are negligible. If you cannot make a quantitative estimate, please indicate whether the yield will be: a) the same (85 %); b) higher than 85 %; c) lower than 85 %.

¹H NMR spectra of compounds **A**, **B**, **C** look very similar and each shows singlet, triplet and quartet with the ratio of integral intensities equal to 1 : 3 : 2.

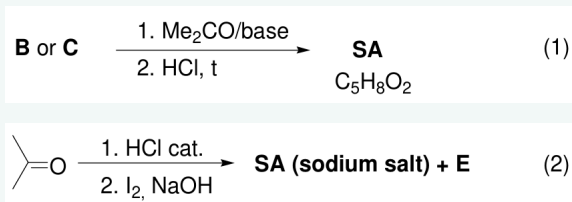
The same mixture **X** was subjected to alkaline hydrolysis. **A** remained unchanged, and was separated. After acidification and short boiling the remaining solution gave 2 : 3 (molar ratio) mixture of acetic acid and ethanol with evolution of gas.

The mixture **X** (3.92 g) was dissolved in diethyl ether and underwent hydrogenation in the presence of Pd on charcoal catalyst. 0.448 dm³ (standard conditions) of hydrogen were absorbed, but after the reaction **A** and **C** were isolated unchanged (3.22 g of mixture were recovered) while neither **B**, nor any other organic compounds, except diethyl ether, could be identified after hydrogenation.

5.4 Determine and draw the structures of **A**, **B**, and **C**.

5.5 Which intermediate compounds are formed during the acidic hydrolysis of **C** and the basic hydrolysis of **B**.

The reaction of either **B** or **C** with acetone (in the presence of a base) with subsequent acidification by dilute HCl at gentle heating gives the same product, senecioic acid (**SA**), a compound widely occurring in Nature. Alternatively, senecioic acid can be obtained from acetone by treating it with concentrated HCl and subsequent oxidation of the intermediate product by iodine in alkaline solution. The latter reaction gives, besides sodium salt of senecioic acid, a heavy yellow precipitate **E** (see the scheme 2).



5.6 Determine the structure of senecioic acid and draw the reaction scheme leading to senecioic acid from acetone.

5.7 Give structure of **E**

Official English text of the problem.

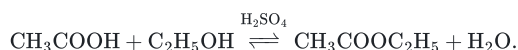
Answers

- 5.1: **D** is **ethyl acetate (ethyl ethanoate)**, $\text{CH}_3\text{C}(=\text{O})\text{OCH}_2\text{CH}_3$, SMILES CCOC(=O)C.
- 5.2: **D** is a **carboxylic ester**.
- 5.3: The expected equilibrium yield is approximately **67%** (calculated conversion 0.6718); therefore choose **c**), **lower than 85%**.
- 5.4: **A** is **triethyl orthoacetate**, $\text{CH}_3\text{C}(\text{OC}_2\text{H}_5)_3$, CC(OC)(OC)OC; **B** is **ethoxyethyne (ethyl ethynyl ether)**, $\text{HC}\equiv\text{C}-\text{OC}_2\text{H}_5$, CCOC\#C; **C** is **diethyl malonate**, $\text{CH}_2(\text{COOC}_2\text{H}_5)_2$, CCOC(=O)CC(=O)OCC.
- 5.5: **C** gives **malonic acid**, $\text{O}=\text{C}(\text{O})\text{CC}(=\text{O})\text{O}$, before decarboxylation. For **B**, hydration gives **ethyl acetate**, $\text{CCOC}(=\text{O})\text{C}$, which is saponified to **acetate ion**, $\text{CC}(=\text{O})[\text{O}^-]$, before acidification.
- 5.6: **SA** is **3-methylbut-2-enoic acid (senecioic acid)**, $(\text{CH}_3)_2\text{C}=\text{CHCOOH}$, CC(C)=CC(=O)O. Acetone undergoes aldol condensation to **mesityl oxide**, $\text{CC}(=\text{O})\text{C}=\text{C}(\text{C})\text{C}$; haloform cleavage gives **sodium senecioate**, $\text{CC}(=\text{O})\text{C}=\text{C}(\text{O}^-)[\text{Na}^+]$, followed by acidification.
- 5.7: **E** is **iodoform (triiodomethane)**, CHI_3 , SMILES IC(I)I.

Solution

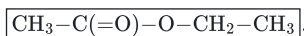
5.1 – Identification and structure of **D**

Acetic acid, $\text{CC}(=\text{O})\text{O}$, and ethanol, CCO , undergo acid-catalysed Fischer esterification:



Thus **D** is **ethyl acetate**, $\text{CCOC}(=\text{O})\text{C}$, a volatile liquid with a pleasant smell. Water has SMILES O.

For the requested drawing, draw a carbonyl carbon bonded to a methyl group and an oxygen atom; that oxygen is bonded to an ethyl group:



5.2 – Compound class

The characteristic linkage is $-\text{C}(=\text{O})-\text{O}^-$, with carbon groups on both sides. Therefore **D** is a **carboxylic ester**.

5.3 – Equilibrium yield with equimolar reactants

The yield ceases to increase because esterification reaches equilibrium. The catalyst accelerates attainment of equilibrium but does not change its position.

Take initial amounts of 1.00 mol acetic acid and 2.00 mol ethanol, with no initial ester or water after the stated separation. An 85% yield corresponds to an extent of reaction of 0.85 mol.

Species	Initial amount / mol	Equilibrium amount / mol
Acetic acid	1.00	0.15
Ethanol	2.00	1.15
Ethyl acetate	0	0.85
Water	0	0.85

Under the stated assumptions,

$$K_c = \frac{[\text{ethyl acetate}][\text{water}]}{[\text{acetic acid}][\text{ethanol}]}.$$

The volume factors cancel, giving

$$K_c = \frac{0.85^2}{(1 - 0.85)(2 - 0.85)} = \frac{0.7225}{0.1725} = 4.1884.$$

Now start with 1.00 mol of each reactant. Let y be the fraction converted:

$$K_c = \frac{y^2}{(1 - y)^2}.$$

Hence

$$\frac{y}{1 - y} = \sqrt{K_c}, \quad y = \frac{\sqrt{K_c}}{1 + \sqrt{K_c}} = 0.6718.$$

Therefore,

$$\boxed{\text{Yield} \approx 67\%}.$$

Removing the initial excess of ethanol lowers the equilibrium conversion. The appropriate qualitative choice is **c**).

5.4 — Identification of A, B and C

The structures are:

Compound	Name and SMILES	Description of the required drawing
A	Triethyl orthoacetate, CC(OCC)(OCC)OCC	A tetrahedral central carbon bonded to one methyl group and three ethoxy groups through oxygen: $\text{CH}_3\text{C}(\text{OC}_2\text{H}_5)_3$.
B	Ethoxyethyne, CCOC#C	A terminal carbon-carbon triple bond attached to an ethoxy oxygen: $\text{H}-\text{C}\equiv\text{C}-\text{O}-\text{CH}_2\text{CH}_3$.
C	Diethyl malonate, CCOC(=O)CC(=O)OCC	A methylene group between two ester carbonyl groups, each ester bearing an ethyl group.

These assignments satisfy all the independent observations.

Hydrogenation identifies B.

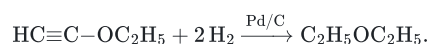
The mass of **B** in the sample is

$$m_B = 3.92 - 3.22 = 0.70 \text{ g}.$$

Using the conventional molar gas volume at standard conditions,

$$n(\text{H}_2) = \frac{0.448 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.0200 \text{ mol}.$$

Diethyl ether, CCOC, is the only organic product that could be hidden in the solvent. Ethoxyethyne gives exactly this product upon complete hydrogenation:



Hydrogen has SMILES [H][H]. Consequently,

$$n_B = \frac{0.0200}{2} = 0.0100 \text{ mol},$$

and

$$M_B = \frac{0.70 \text{ g}}{0.0100 \text{ mol}} = 70 \text{ g mol}^{-1}.$$

This agrees with ethoxyethyne, $\text{C}_4\text{H}_6\text{O}$:

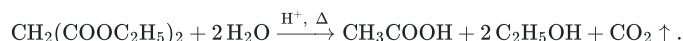
$$M(\text{C}_4\text{H}_6\text{O}) = 4(12) + 6(1) + 16 = 70 \text{ g mol}^{-1}.$$

The acid/base behaviour identifies A and C.

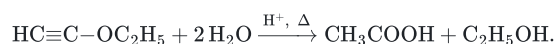
An orthoester is hydrolysed by aqueous acid but survives alkaline treatment. The orthoester that gives acetic acid and ethanol is **triethyl orthoacetate, A**:



For **C**, two equivalent ethoxy groups and a methylene singlet suggest a malonic ester. Hydrolysis followed by decarboxylation gives acetic acid, ethanol and carbon dioxide, $\text{O}=\text{C}=\text{O}$:



For **B**, the overall acidic hydrolysis is



Thus one mole of each starting compound gives:

Starting compound	Acetic acid / mol	Ethanol / mol
A	1	3
B	1	1
C	1	2
Total	3	6

The ratio is therefore $3 : 6 = 1 : 2$, as required. Carbon dioxide escapes and is not an additional component of the recovered liquid mixture.

In the alkaline experiment, **A** remains unchanged. After acidification and heating, **B** and **C** together give

$$n(\text{acetic acid}) : n(\text{ethanol}) = (1 + 1) : (1 + 2) = 2 : 3,$$

with carbon dioxide evolved from the malonic-acid intermediate.

The NMR integrations agree.

Compound	Singlet	Triplet	Quartet	Integration ratio
A	Central-carbon methyl: 3H	Three ethyl methyl groups: 9H	Three ethoxy methylene groups: 6H	3 : 9 : 6 = 1 : 3 : 2
B	Terminal acetylenic proton: 1H	Ethyl methyl: 3H	Ethoxy methylene: 2H	1 : 3 : 2
C	Methylene between carbonyl groups: 2H	Two ethyl methyl groups: 6H	Two ethoxy methylene groups: 4H	2 : 6 : 4 = 1 : 3 : 2

The ethyl groups give their usual triplet and quartet. The remaining protons have no adjacent proton-bearing carbon that would produce ordinary vicinal splitting.

The remaining masses agree.

Because the mixture is equimolar,

$$n_A = n_C = n_B = 0.0100 \text{ mol.}$$

For **A**, $\text{C}_8\text{H}_{18}\text{O}_3$, $M_A = 162 \text{ g mol}^{-1}$; for **C**, $\text{C}_7\text{H}_{12}\text{O}_4$, $M_C = 160 \text{ g mol}^{-1}$. Therefore,

$$m_A + m_C = 0.0100(162 + 160) = 3.22 \text{ g,}$$

and

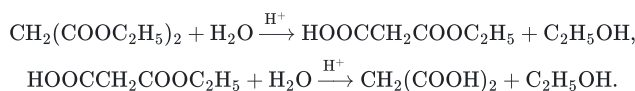
$$m_X = 0.0100(162 + 70 + 160) = 3.92 \text{ g.}$$

Both reproduce the measured masses.

5.5 — Hydrolysis intermediates

For **C**, the important intermediate before decarboxylation is **malonic acid (propanedioic acid)**, $\text{O}=\text{C}(\text{O})\text{CC}(\text{O})\text{O}$.

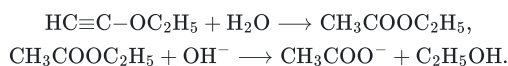
Stepwise ester hydrolysis can first give **ethyl hydrogen malonate**, $\text{CCOC}(\text{O})\text{CC}(\text{O})\text{O}$:



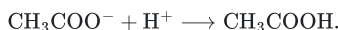
Malonic acid then decarboxylates:



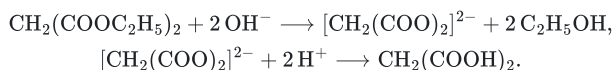
For **B**, hydration gives **ethyl acetate**, **D**, $\text{CCOC}(\text{O})\text{C}$, followed by saponification to **acetate ion**, $\text{CC}(\text{O})[\text{O}^-]$. The stepwise stoichiometry is



Here hydroxide ion has SMILES $[\text{OH}^-]$. Acidification subsequently gives



For completeness, **C** initially gives **malonate ion**, $\text{O}=\text{C}([\text{O}^-])\text{CC}(\text{O})[\text{O}^-]$, under alkaline conditions:



The resulting malonic acid undergoes the decarboxylation shown above.

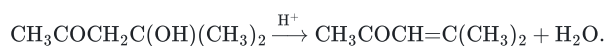
5.6 — Senecioic acid and its synthesis from acetone

The yellow precipitate formed with iodine and alkali indicates a **haloform reaction**. A methyl ketone is cleaved to a carboxylate and iodoform.

Acetone, $\text{CC}(\text{O})\text{C}$, first undergoes acid-catalysed self-aldol addition to **diacetone alcohol (4-hydroxy-4-methylpentan-2-one)**, $\text{CC}(\text{O})\text{CC}(\text{C})(\text{C})\text{O}$:



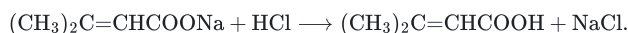
Dehydration produces **mesityl oxide (4-methylpent-3-en-2-one)**, $\text{CC}(\text{O})\text{C}=\text{C}(\text{C})\text{C}$:



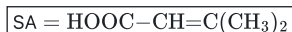
Its methyl ketone group undergoes haloform cleavage:



The carboxylate product is **sodium 3-methylbut-2-enoate**, $\text{CC}(\text{C})=\text{CC}(\text{O})[\text{O}^-] \cdot [\text{Na}^+]$. Acidification gives senecioic acid:



Therefore,

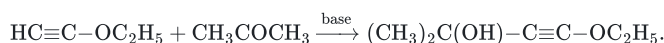


is **3-methylbut-2-enoic acid**, $\text{CC}(\text{C})=\text{CC}(\text{O})\text{O}$.

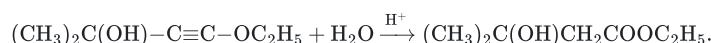
For the requested drawing, place a carboxyl group on one end of an alkene: its adjacent alkene carbon bears one hydrogen, while the other alkene carbon bears two methyl groups. There is **no E/Z stereochemistry**, because one alkene carbon has two identical methyl substituents.

The reactions of **B** and **C** independently support this structure.

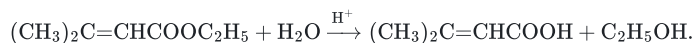
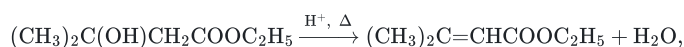
For **B**, base-promoted addition to acetone gives **4-ethoxy-2-methylbut-3-yn-2-ol**, CCOC#CC(C)(C)O:



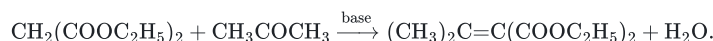
Hydration of the ethoxyalkyne gives **ethyl 3-hydroxy-3-methylbutanoate**, CCOC(=O)CC(C)(C)O:



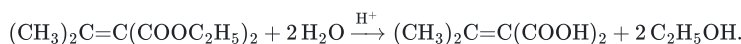
Dehydration gives **ethyl senecioate**, CCOC(=O)C=C(C)C, which hydrolyses to SA:



For **C**, Knoevenagel condensation with acetone gives **diethyl 2-(propan-2-ylidene)malonate**, CCOC(=O)C(=C(C)C)C(=O)OCC:



Hydrolysis gives **2-(propan-2-ylidene)malonic acid**, O=C(O)C(=C(C)C)C(=O)O:



Decarboxylation yields the same acid:



5.7 – Identification and structure of E

The heavy yellow precipitate is **iodoform (triiodomethane)**:



Draw a tetrahedral carbon atom with three single bonds to iodine atoms and one single bond to hydrogen. It is the haloform product of the balanced reaction in **5.6**.

The solution was checked against the official solution.

Problem 6: Silicates as the base of the Earth crust

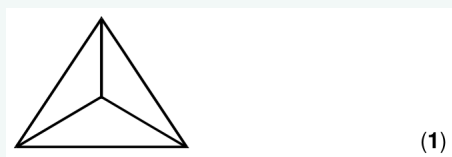
Silica and compounds derived from it, silicates, constitute ca. 90 % of the Earth crust substances. Silica gives rise to a beautiful material – glass. Nobody knows exactly how glass was discovered. There is a well-favored story related to Phoenician sailors who fused occasionally sea sand and soda ash. It is likely that they discovered the secret of “liquid glass” (LGL) – sodium metasilicate (Na_2SiO_3) soluble in water.

6.1 The solution of LGL was used earlier as office glue. Write down the net ionic equation accounting for the ability of LGL to set in air.

Hydrolysis of LGL in water allows obtaining a colloidal solution of silicic acid.

6.2 Complete the Table in the Answer Sheet. Write down the net ionic equations matching the processes enumerated in the Table. For each process check the “Yes” box if it leads to changes of pH. Otherwise check the “No” box.

The structure of species occurring in aqueous solutions of silicates is rather complex. However, it is possible to distinguish the main building block of all species – orthosilicate tetrahedron (SiO_4^{4-} , **1**):



For $[\text{Si}_3\text{O}_9]^{n-}$ ion found in aqueous solutions of silicates:

6.3 Determine the charge (n).

6.4 Determine the number of oxygen atoms bridging adjacent tetrahedra.

6.5 Depict its structure joining together several tetrahedra (1). Take into account that any adjacent tetrahedron shares one vertex.

Charged monolayers with the composition $[\text{Si}_4\text{O}_{10}]^{m-}$ are found in kaolinite (clay).

6.6 Using the same strategy as in **6.3 - 6.5**, depict a fragment of the layered structure joining 16 tetrahedra (1). Note that 10 tetrahedra have shared vertices with 2 neighbours each, and the rest 6 have shared vertices with 3 neighbours each.

Being placed into the LGL solution, salts of transition metals give rise to fancy “trees” tinted relevant to the colour of the salt of the corresponding transition metal. Crystals of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ produce “trees” of blue colour, whereas those of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ form green “trees”.

6.7 Determine the pH of 0.1 M aqueous solution of copper sulphate at 25 °C assuming that its hydrolysis occurs in small degree only. Use the value of the first acidity constant of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ $K_a^I = 1 \times 10^{-7}$.

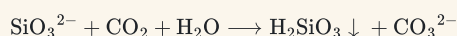
6.8 Write down equation of a reaction between aqueous solutions of CuSO_4 and sodium metasilicate (LGL). Take into account the pH values of aqueous solutions of the salts.

Official English text of the problem.

Answers

Names and SMILES representations are supplied with the corresponding explanations in the Solution.

• **6.1**



Here H_2SiO_3 denotes hydrated silica gel.

• **6.2**

Process	Net ionic equation	Changes pH?
(a) Protonation	$\text{SiO}_4^{4-} + \text{H}_2\text{O} \rightleftharpoons \text{HSiO}_4^{3-} + \text{OH}^-$	Yes
(b) Hydration	$\text{SiO}_4^{4-} + 2 \text{H}_2\text{O} \rightleftharpoons [\text{SiO}_4(\text{H}_2\text{O})_2]^{4-}$	No
(c) Polycondensation	$2 \text{SiO}_4^{4-} + \text{H}_2\text{O} \rightleftharpoons \text{Si}_2\text{O}_7^{6-} + 2 \text{OH}^-$	Yes

• **6.3** $n = 6$; the ion is $[\text{Si}_3\text{O}_9]^{6-}$.

• **6.4** Three bridging oxygen atoms.

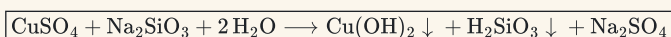
• **6.5** A closed ring of **three corner-sharing tetrahedra**, containing an alternating six-membered $\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}$ ring.

• **6.6** $m = 4$. Draw a patch of **four fused hexagonal rings containing 16 tetrahedra**, with **19 shared oxygen vertices**. Ten tetrahedra have two neighbours and six have three; an exact drawing prescription is given below.

• **6.7**

$$\text{pH} \approx 4.0$$

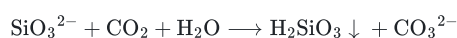
• **6.8**



Solution

6.1 — Setting of liquid glass in air

Atmospheric carbon dioxide acidifies the alkaline silicate solution. Protonation of silicate produces hydrated silica, which forms a gel and hardens as water is lost:



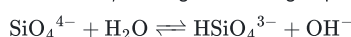
The equation balances both atoms and charge: each side has total charge -2 .

The species are carbon dioxide $\text{O}=\text{C}=\text{O}$, water O , carbonate ion $[\text{O}-]\text{C}(=\text{O})[\text{O}-]$, and metasilicate ion, formally $[\text{O}-][\text{Si}](=\text{O})[\text{O}-]$.

Here **metasilicic acid**, H_2SiO_3 , with formal formula-unit SMILES $\text{O}=[\text{Si}](\text{O})\text{O}$, is conventional shorthand for hydrated, polymeric silica. The actual gel contains an extended network of $\text{Si}-\text{O}-\text{Si}$ bonds and has no unique molecular SMILES.

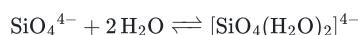
6.2 — Protonation, hydration, and polycondensation

(a) Protonation. An orthosilicate oxygen accepts a proton from water, forming a $\text{Si}-\text{OH}$ group:



Hydroxide ions are produced, so this process **changes pH: Yes**, increasing it.

(b) Hydration. Two water molecules coordinate to silicon:



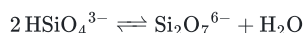
This hydration step neither releases nor consumes protons or hydroxide ions. Thus **changes pH: No**, for the process as written.

(c) Polycondensation. The simplest condensation product is the disilicate ion, containing one bridging oxygen:



Consequently, **changes pH: Yes**, increasing it.

The hydroxide production follows explicitly by combining twice the protonation reaction in (a) with condensation of the resulting silanol groups:



Although this last silanol-condensation equation releases only water, the **overall process starting from orthosilicate ions** releases two hydroxide ions.

The relevant structural representations are:

Species	Name	SMILES
SiO_4^{4-}	Orthosilicate ion	$[\text{O}-][\text{Si}](\text{O}-)(\text{O}-)(\text{O}-)$
HSiO_4^{3-}	Hydrogen orthosilicate ion	$\text{O}[\text{Si}](\text{O}-)(\text{O}-)(\text{O}-)$
$[\text{SiO}_4(\text{H}_2\text{O})_2]^{4-}$	Hydrated orthosilicate ion	$[\text{OH}2+][\text{Si}-2](\text{O}-)(\text{O}-)(\text{O}-)(\text{O}-)(\text{O}-)(\text{OH}2+)$
$\text{Si}_2\text{O}_7^{6-}$	Disilicate, or pyrosilicate, ion	$[\text{O}-][\text{Si}](\text{O}-)(\text{O}-)(\text{O}-)\text{O}[\text{Si}](\text{O}-)(\text{O}-)(\text{O}-)$
OH^-	Hydroxide ion	$[\text{OH}-]$

The hydrate's SMILES uses single bonds with formal charge separation to represent the two water-to-silicon donor bonds; its total charge is -4 . Its six-coordinate silicon has an idealized octahedral environment. The other silicon centres in this table are tetrahedral. These geometries are not encoded by the SMILES.

6.3 — Charge of the trisilicate ion

Silicon has oxidation state $+4$, and oxygen has oxidation state -2 . Therefore,

$$q = 3(+4) + 9(-2) = -6.$$

Thus

$$n = 6, \quad [\text{Si}_3\text{O}_9]^{6-}.$$

6.4 — Number of bridging oxygen atoms

Let B be the number of bridging oxygens and T the number of nonbridging oxygens.

There are nine distinct oxygen atoms:

$$B + T = 9.$$

Three tetrahedra have $3 \times 4 = 12$ oxygen-vertex incidences. Each bridging oxygen belongs to two tetrahedra, so

$$2B + T = 12.$$

Subtracting gives

$$B = 3, \quad T = 6.$$

6.5 — Structure of the trisilicate ion

There are three tetrahedra and three shared corners. Since each pair of adjacent tetrahedra shares only one corner, the tetrahedra form a closed triangular arrangement.

To draw it:

1. Place three tetrahedra around a central opening.
2. Make each tetrahedron share one distinct oxygen vertex with each of the other two.
3. Leave the other two oxygen vertices of each tetrahedron unshared.

The resulting **cyclotrisilicate ion**, $[\text{Si}_3\text{O}_9]^{6-}$, has SMILES:

[O-][Si]1([O-])O[Si]([O-])([O-])O[Si]([O-])([O-])O1

Its ring backbone alternates three silicon atoms and three bridging oxygen atoms. Six additional, nonbridging oxygens carry the formal negative charges. Each silicon remains tetrahedral; the SMILES does not specify ring conformation.

6.6 — The silicate layer and its 16-tetrahedron fragment

First, the charge per stated composition unit is

$$q = 4(+4) + 10(-2) = -4,$$

so

$$m = 4.$$

In the extended sheet, each tetrahedron shares three oxygen corners with three neighbouring tetrahedra. Its fourth corner is unshared with other silicon tetrahedra. Therefore the number of distinct oxygens per silicon is

$$\frac{3}{2} + 1 = \frac{5}{2},$$

giving the composition $[\text{Si}_4\text{O}_{10}]^{4-}$. Per four silicon atoms, there are six bridging oxygens and four oxygens unshared with other silicon tetrahedra.

A suitable finite patch consists of **four fused hexagonal rings**. The following prescription specifies the drawing exactly:

- Draw an outer cycle of 14 tetrahedra, labelled consecutively $1, 2, \dots, 14$, with 14 joined back to 1.
- Place tetrahedra 15 and 16 inside this boundary.
- Add the five connections $3-15$, $13-15$, $15-16$, $6-16$, and $10-16$.
- Represent every connection by **one shared oxygen corner**.

The four hexagonal rings then have the vertex sequences

$$\begin{aligned} &1 - 2 - 3 - 15 - 13 - 14 - 1, \\ &3 - 4 - 5 - 6 - 16 - 15 - 3, \\ &6 - 7 - 8 - 9 - 10 - 16 - 6, \\ &10 - 11 - 12 - 13 - 15 - 16 - 10. \end{aligned}$$

Tetrahedra 3, 6, 10, 13, 15, 16 each have three neighbours; the remaining ten each have two. The number of shared oxygens is consequently

$$B = \frac{10(2) + 6(3)}{2} = 19.$$

For the polyhedral drawing, keep the three potentially shared corners of each tetrahedron in the basal plane, with its fourth corner pointing to the same side of the sheet.

An infinite layer has no single finite molecular SMILES. The **fully deprotonated 16-tetrahedron silicate-sheet fragment** just specified can, however, be represented by:

[O-][Si]1([O-])O[Si]([O-])([O-])O[Si]2([O-])O[Si]([O-])([O-])O[Si]([O-])([O-])O[Si]3([O-])O[Si]([O-])([O-])O[Si]([O-])([O-])O[Si]([O-])([O-])O[Si]4([O-])O[Si]([O-])([O-])O[Si]([O-])([O-])O[Si]([O-])(O[Si]([O-])(O2)O[Si]([O-])(O3)O4)O[Si]([O-])([O-])O1

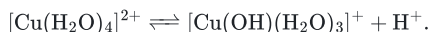
As an isolated fragment, this has 19 bridging and 26 nonbridging oxygens:

$$N_O = 16(4) - 19 = 45, \quad q = 16(4) - 45(2) = -26.$$

Thus its isolated formula is $[\text{Si}_{16}\text{O}_{45}]^{26-}$. The boundary oxygens account for the difference between this finite fragment's composition and the periodic layer composition.

6.7 — pH of the copper(II) sulfate solution

In the specified model, the **tetraaquacopper(II) ion**, $\text{O} \rightarrow [\text{Cu}+2] (<- \text{O}) (<- \text{O}) <- \text{O}$, undergoes its first acid dissociation:



The product is the **triaquahydroxidocopper(II) ion**, $[\text{OH}-] \rightarrow [\text{Cu}+2] (<- \text{O}) (<- \text{O}) <- \text{O}$. The proton is represented formally by $[\text{H}+]$. These dative-bond SMILES specify oxygen-to-copper coordination connectivity, without fixing coordination geometry or the surrounding solvent structure.

Let the initial copper concentration be

$$c_0 = 0.1 \text{ mol L}^{-1},$$

and let the hydrogen-ion concentration produced be x . In the usual ideal, single-equilibrium treatment,

$$K_a^I = \frac{x^2}{c_0 - x}.$$

Because hydrolysis is small, $c_0 - x \approx c_0$. Using molar concentrations,

$$[\text{H}^+] \approx \sqrt{K_a^I c_0} = \sqrt{(1 \times 10^{-7})(0.1)} = 1 \times 10^{-4} \text{ mol L}^{-1}.$$

Therefore,

$$\text{pH} = -\log_{10} \left(\frac{[\text{H}^+]}{1 \text{ mol L}^{-1}} \right) = 4.0.$$

The fraction hydrolysed is

$$\frac{x}{c_0} = \frac{10^{-4}}{0.1} = 10^{-3} = 0.1\%,$$

which confirms the assumed small degree of hydrolysis.

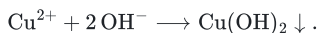
6.8 — Reaction of copper(II) sulfate with liquid glass

The copper(II) solution is acidic through cation hydrolysis, whereas metasilicate solution is alkaline through anion hydrolysis. Mixing them promotes mutual hydrolysis, producing copper(II) hydroxide and hydrated silica.

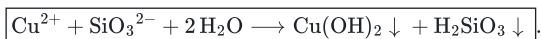
One way to express the coupled processes is



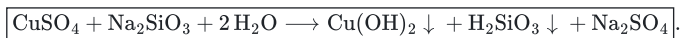
and



The overall net ionic equation is



Including the spectator ions gives



Copper(II) hydroxide is the blue precipitate, and H_2SiO_3 denotes the hydrated silica gel discussed in 6.1.

The copper(II) ion is $[\text{Cu}+2]$; the spectator ions are sodium $[\text{Na}+]$ and sulfate $[\text{O-}]\text{S}(=\text{O})(=\text{O})[\text{O-}]$. Composition SMILES for the ionic substances are:

Substance	SMILES
Copper(II) sulfate	$[\text{Cu}+2] \cdot [\text{O-}]\text{S}(=\text{O})(=\text{O})[\text{O-}]$
Sodium metasilicate	$[\text{Na}+] \cdot [\text{Na}+] \cdot [\text{O-}][\text{Si}](=\text{O})[\text{O-}]$
Copper(II) hydroxide	$[\text{Cu}+2] \cdot [\text{OH-}] \cdot [\text{OH-}]$
Sodium sulfate	$[\text{Na}+] \cdot [\text{Na}+] \cdot [\text{O-}]\text{S}(=\text{O})(=\text{O})[\text{O-}]$

These disconnected-ion SMILES specify composition; they do not describe solid-state coordination networks.

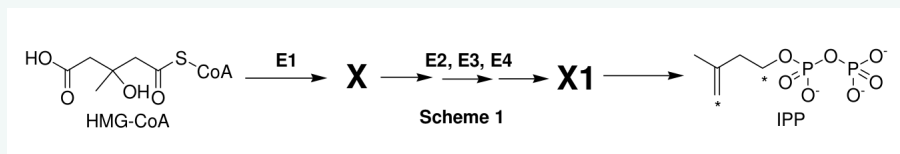
The solution was checked against the official solution.

Problem 7: Atherosclerosis and intermediates of cholesterol biosynthesis

Cholesterol is a lipid wide-spread in living nature. Disruption of its metabolism leads to atherosclerosis and related potentially fatal diseases.

Substances **X** and **Y** are two key intermediates of cholesterol biosynthesis in animals.

X is an optically active monocarboxylic acid composed of atoms of only three elements. It is formed in organisms from (S)-3-hydroxy-3-methylpentanedioyl-coenzyme A (HMG-CoA). This reaction is catalyzed by enzyme **E1** (which catalyses two types of reactions) and does not involve water as a substrate. **X** is further metabolized into **X1** through a three-stage process requiring enzymes **E2**, **E3**, **E4**, which catalyze reactions of one and the same (and only one) type. Finally, **X1** spontaneously (non-enzymatically) decomposes to give isopentenyl pyrophosphate (3-methylbut-3-enyl diphosphate, IPP) and inorganic products:

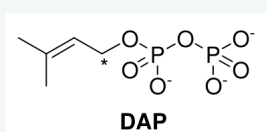


Scheme 1

7.1 In the Answer Sheet, choose the reaction type(s) for **E1** and **E3**.

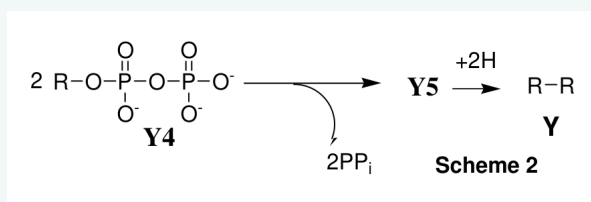
7.2 Draw the structure of **X** with stereochemical details and indicate absolute configuration (R or S) of the stereocenter.

Y is an unsaturated acyclic hydrocarbon. Its reductive ozonolysis leads to a mixture of only three organic substances **Y1**, **Y2** and **Y3** in a molar ratio of 2:4:1. **Y** is formed as a result of a number of successive coupling reactions of two isomeric substances: IPP and dimethyl allyl pyrophosphate (3-methylbut-2-enyl diphosphate, DAP) with subsequent reduction of a double bond in the final coupling product **Y5**. Carbon atoms IPP and DAP involved in the formation of C-C bonds during biosynthesis of **Y** are marked with asterisks.



7.3 Write down the overall reaction equation for reductive ozonolysis of DAP, if dimethyl sulfide is used as the reducing agent.

The product of the final coupling reaction (hydrocarbon **Y5**) is formed when two hydrocarbon residues (R) of intermediate **Y4** are combined:



Scheme 2

At each coupling stage but that shown in Scheme 2, pyrophosphate is released in a molar ratio of 1 : 1 to the coupling product.

7.4 Determine molecular formula of **Y**, if it is known that **Y2** and **Y3** contain 5 and 4 carbon atoms, respectively.

7.5 Calculate the number of IPP and DAP molecules needed to give **Y5**, if it is known that all carbon atoms of isomeric pyrophosphates are incorporated into **Y**.

7.6 Draw the product of coupling reaction of one IPP molecule with one DAP molecule (C-C bond can be formed only by carbon atoms marked with asterisks), if it is known that subsequent reductive ozonolysis of the product of the coupling reaction gives **Y1**, **Y2** and one more product, the latter containing phosphorus.

The only double bond reduced in **Y5** during its metabolism into **Y** was formed in the reaction described in Scheme 2. All double bonds in **Y** and **Y4** exist in trans configuration.

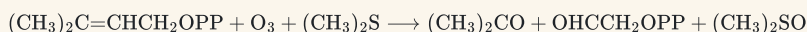
7.7 Draw structures of **Y** and **Y4** with stereochemical details.

Official English text of the problem.

Answers

In the condensed structures below, --OPP denotes the diphosphate ester group $\text{--O--P(=O)(O}^-\text{)--O--P(=O)(O}^-\text{)O}^-$. Its charge is included implicitly.

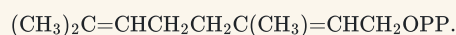
- 7.1 E1:** reduction and elimination of the CoA thiol fragment—nonhydrolytic cleavage of the thioester C—S bond. **E3:** phosphorylation.
- 7.2 X** is **(R)-mevalonic acid**, or **(3R)-3,5-dihydroxy-3-methylpentanoic acid**, $\text{C}_6\text{H}_{12}\text{O}_4$.
SMILES: C[C@H](O)(CCO)CC(=O)O
- 7.3**



The products are **acetone**, **2-oxoethyl diphosphate**, and **dimethyl sulfoxide**.

- 7.4** $\text{Y} = \text{C}_{30}\text{H}_{50}$.
- 7.5** Each molecule of **Y5** requires 4 IPP molecules + 2 DAP molecules.

- 7.6 The product is **geranyl diphosphate, (2E)-3,7-dimethylocta-2,6-dien-1-yl diphosphate**:



SMILES: CC(C)=CCC/C(C)=C/COP(=O)([O-])OP(=O)([O-])[O-]

- 7.7 Y is **all-trans-squalene**, with *E* configurations at positions 6, 10, 14, 18.

SMILES: CC(C)=CCC/C(C)=C/CC/C(C)=C/CC/C=C(C)/CC/C=C(C)/CCC=C(C)C

Y4 is (2E,6E)-farnesyl diphosphate, or (2E,6E)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl diphosphate.

SMILES: CC(C)=CCC/C(C)=C/CC/C(C)=C/COP(=O)([O-])OP(=O)([O-])[O-]

Solution

7.1 — Reaction types

The thioester end of HMG-CoA is converted into a primary alcohol. The functional-group balance is



where *A* represents the unchanged remainder of the substrate and $[\text{H}]$ denotes formal hydrogen equivalents.

This transformation involves reduction of the acyl carbon and cleavage of its bond to sulfur. Mechanistically, reduction of the thioester produces an aldehyde with elimination of the CoA thiol fragment; further reduction gives the primary alcohol. The overall thioester cleavage is a hydrogenolysis, and no water is consumed.

Thus **E1 performs reduction and elimination/nonhydrolytic C–S cleavage**.

The three subsequent steps are phosphorylations:

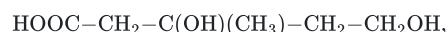
1. **E2** phosphorylates the terminal primary alcohol.
2. **E3** adds a second phosphoryl group to form the diphosphate ester.
3. **E4** phosphorylates the tertiary hydroxyl group.

The last phosphorylation makes that oxygen substituent a suitable leaving group. Subsequent loss of phosphate and decarboxylation produces IPP.

Therefore **E3 catalyzes phosphorylation**.

7.2 — Identification and absolute configuration of X

Reduction of the thioester group gives



which is **mevalonic acid**. Its stereocenter is C3.

The CIP priorities in the product are



In the starting HMG-CoA, the thioester-containing side chain has higher priority than the carboxylic-acid-containing side chain: the comparison ultimately encounters sulfur versus oxygen. After reduction, the carboxylic-acid-containing chain has higher priority than the hydroxyethyl chain.

Consequently, priorities 2 and 3 exchange places while the spatial arrangement at C3 is retained. The starting *S* descriptor therefore becomes *R*.

The required drawing is **(R)-mevalonic acid**, SMILES C[C@H](O)(CCO)CC(=O)O. An unambiguous Fischer projection has:

- CH_2COOH above the stereocenter;
- $\text{CH}_2\text{CH}_2\text{OH}$ below;
- CH_3 on the left;
- OH on the right.

As usual for a Fischer projection, the horizontal bonds point toward the viewer and the vertical bonds point away.

7.3 — Reductive ozonolysis of DAP

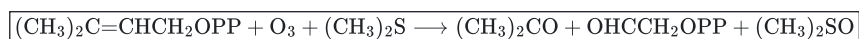
DAP is **3-methylbut-2-en-1-yl diphosphate**:

SMILES: CC(C)=CCOP(=O)([O-])OP(=O)([O-])[O-]

Its alkene has two methyl groups on one carbon and one hydrogen plus a diphosphate-bearing side chain on the other:



Reductive cleavage therefore produces a ketone at the dimethyl-substituted carbon and an aldehyde at the other carbon. Dimethyl sulfide accepts the remaining oxygen atom from ozone:



The named species and their SMILES are:

Species	Name	SMILES
O_3	Ozone	<chem>[O-][O+]=O</chem>
$(\text{CH}_3)_2\text{S}$	Dimethyl sulfide	<chem>CSC</chem>
$(\text{CH}_3)_2\text{CO}$	Acetone, or propanone	<chem>CC(=O)C</chem>
OHCCH_2OPP	2-Oxoethyl diphosphate	<chem>O=CCOP(=O)([O-])OP(=O)([O-])[O-]</chem>
$(\text{CH}_3)_2\text{SO}$	Dimethyl sulfoxide	<chem>CS(=O)C</chem>

The equation conserves every atom and the diphosphate ester's charge. Each alkene consumes one molecule each of ozone and dimethyl sulfide.

7.4 — Molecular formula of Y

The DAP-derived terminal $(\text{CH}_3)_2\text{C}=\text{}$ groups yield acetone on ozonolysis. Hence **Y1 is acetone**, containing three carbon atoms.

The final coupling joins two prenyl chains, each with one such terminal group. One molecule of **Y** therefore gives two acetone molecules, so the stated ratio corresponds to

$$2 \text{ Y1} + 4 \text{ Y2} + 1 \text{ Y3}$$

per molecule of **Y**.

Since reductive ozonolysis preserves the carbon atoms in these organic fragments,

$$N_{\text{C}} = 2(3) + 4(5) + 1(4) = 30.$$

There are seven fragments. Cleaving each double bond in an acyclic carbon skeleton increases the number of separate fragments by one, so

$$N_{\text{double bonds}} = 7 - 1 = 6.$$

An acyclic hydrocarbon with 30 carbon atoms and six double bonds has

$$N_{\text{H}} = 2(30) + 2 - 2(6) = 50.$$

Thus

$$\boxed{\text{Y} = \text{C}_{30}\text{H}_{50}}.$$

7.5 — Numbers of IPP and DAP molecules

Both IPP and DAP contain five carbon atoms. No carbon is lost during assembly, and the final reduction changes only the hydrogen count. Therefore six five-carbon building blocks are required:

$$N_{\text{IPP}} + N_{\text{DAP}} = \frac{30}{5} = 6.$$

The two identical residues in Scheme 2 each contain 15 carbon atoms, hence three five-carbon units.

Each residue has one DAP-derived terminal dimethyl-substituted alkene. The remaining two units extend that chain and come from IPP. Thus each **Y4** is assembled from

$$1 \text{ DAP} + 2 \text{ IPP}.$$

For two molecules of **Y4**,

$$\boxed{N_{\text{DAP}} = 2, \quad N_{\text{IPP}} = 4}.$$

This also satisfies the diphosphate balance: four ordinary coupling steps release four diphosphates, and the final coupling releases two more, accounting for all six starting diphosphate groups.

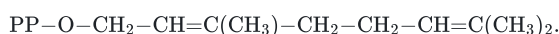
7.6 — Coupling one IPP with one DAP

IPP is **3-methylbut-3-en-1-yl diphosphate**:



Numbering from the carbon bearing the diphosphate ester, the required new bond joins **C1 of DAP to C4 of IPP**, the terminal methylene carbon.

The DAP diphosphate group leaves, while the IPP diphosphate group is retained. Formation of the new bond and loss of a proton relocate the IPP double bond from C3–C4 to C2–C3. The product is



This is **geranyl diphosphate**, with the stereochemical SMILES given in the Answers.

Its reductive ozonolysis gives



The three organic fragments are:

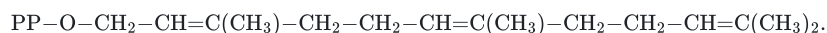
- **Y1: acetone**, $\text{CC}(=\text{O})\text{C}$;
- **Y2: 4-oxopentanal**, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CHO}$, $\text{CC}(=\text{O})\text{CCC}=\text{O}$;
- **2-oxoethyl diphosphate**, $\text{O}=\text{CCOP}(=\text{O})([\text{O}-])\text{OP}(=\text{O})([\text{O}-])[\text{O}-]$.

Their carbon counts are $3 + 5 + 2 = 10$, as required.

Ozonolysis determines the connectivity but does not distinguish alkene geometries. The later trans requirement for **Y4**, whose existing double bonds are retained during chain extension, selects the **2E** geranyl structure.

7.7 — Structures and stereochemistry of Y and Y4

Adding a second IPP unit to geranyl diphosphate gives the 15-carbon intermediate **farnesyl diphosphate, Y4**:



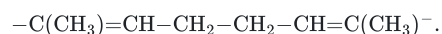
For the required drawing, place the double bonds at C2–C3 and C6–C7 in the *E* configuration. The terminal C10–C11 double bond has two identical methyl substituents at C11 and therefore has no *E/Z* designation.

Thus **Y4 is (2E,6E)-farnesyl diphosphate**:



In Scheme 2, the two farnesyl residues join through the carbons that originally bore diphosphate. The newly formed double bond is subsequently reduced. Therefore, to draw **Y**, replace the two terminal C₁–O bonds of two **Y4** molecules with a **C1–C1' single bond**, retaining all pre-existing alkene configurations.

The central segment is consequently



The resulting hydrocarbon is **squalene**, specifically

(6E,10E,14E,18E)-2,6,10,15,19,23-hexamethyltetracos-2,6,10,14,18,22-hexaene:



Its ozonolysis provides a direct structural check:

Product	Origin in squalene	Molecules per molecule of Y	SMILES
Y1: acetone	Two terminal dimethyl-substituted alkene carbons	2	<chem>CC(=O)C</chem>
Y2: 4-oxopentanal	Four intervening five-carbon segments	4	<chem>CC(=O)CCC=O</chem>
Y3: butane-1,4-dial , or succinaldehyde	Central four-carbon segment	1	<chem>O=CCCC=O</chem>

The balanced overall check is

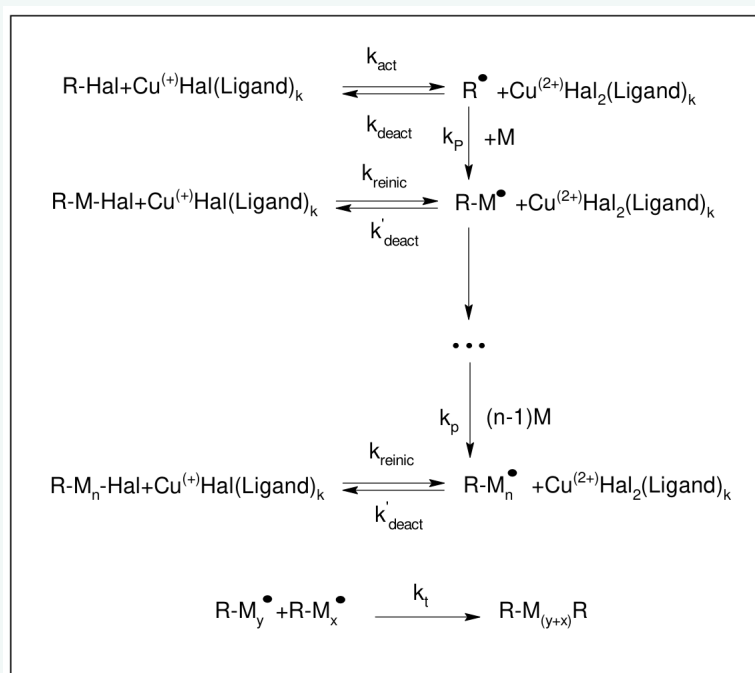


This reproduces the required 2 : 4 : 1 ratio and the specified carbon counts.

The solution was checked against the official solution.

Problem 8: ATRP allows new polymers

ATRP (Atom Transfer Radical Polymerization) is one of the most promising novel approaches towards polymer synthesis. This modification of radical polymerization is based on a redox reaction of organic halides with complexes of transition metals, Cu (I) in particular. The process can be described by the following scheme (M – monomer, Hal – halogen):



The reaction rate constants are:

k_{act} – all activation reactions, k_{deact} – all reversible deactivation reactions, k_p – chain propagation, and k_t – irreversible termination.

8.1 Write down expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t). Write down generalized equation assuming just one reacting species $\text{R}'\text{X}$.

Consider that the total number of polymeric chains is equal to that of initiator molecules. Assume that at each moment throughout polymerization all chains are of the same length.

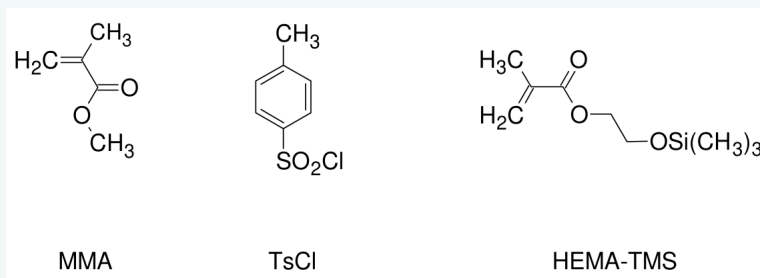
8.2 Compare the rate of deactivation to the rates of ATRP elementary stages.

Dependence of monomer concentration ($[\text{M}]$) on reaction time (t) for ATRP is:

$$\ln \left(\frac{[\text{M}]}{[\text{M}]_0} \right) = -k_p [\text{R}^\bullet] t,$$

$[\text{M}]_0$ – initial monomer concentration, k_p – rate constant of propagation, $[\text{R}^\bullet]$ – concentration of active radicals.

To prepare a polymer sample by using ATRP, catalytic amounts of CuCl , organic ligand (L) and 31.0 mmol of monomer (methylmethacrylate, or MMA) were mixed. The reaction was initiated by adding 0.12 mmol of tosyl chloride (TsCl). Polymerization was conducted for 1400 s. k_p is $1616 \text{ L mol}^{-1} \text{ s}^{-1}$, and the steady state concentration of radicals is $1.76 \times 10^{-7} \text{ mol dm}^{-3}$.



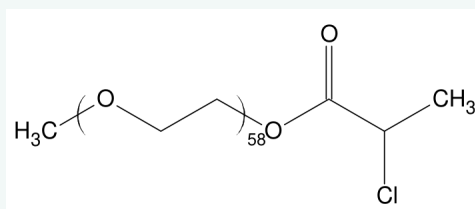
8.3 Calculate mass (m) of the polymer obtained.

In another experiment the time of MMA polymerization was changed, all the rest reaction conditions being the same. The mass of the obtained polymer was 0.73 g. Then 2-(trimethylsilyloxy)ethyl methacrylate, HEMA-TMS (23.7 mmol) was added to the mixture and polymerization was continued for another 1295 s. MMA and HEMA-TMS reactivities are the same under reaction conditions.

8.4 Calculate degree of polymerization (DP) of the obtained polymer.

8.5 Depict the structure of the obtained polymer (including end groups), showing MMA and HEMA-TMS units as A and B, respectively. If necessary, use the symbols in the copolymer structure representation: block (block), stat (statistical), alt (alternating), grad (gradient), graft (grafted). For example, $(\text{A}_{65}\text{-graft-C}_{100})\text{-stat-B}_{34}$ means that chains of polymer C are grafted on units A in the statistical copolymer of A and B.

ATRP was applied to synthesize two block copolymers, P_1 and P_2 . One block in both block-copolymers was the same and was synthesized from mono-(2-chloropropionyl)-polyethylene oxide used as a macroinitiator:



The other block in P_1 consisted of styrene (C), and in P_2 of p-chloromethylstyrene (D) units.

^1H NMR spectra of the macroinitiator, P_1 and P_2 are given below. Integral intensities of characteristic signals can be found in the table.

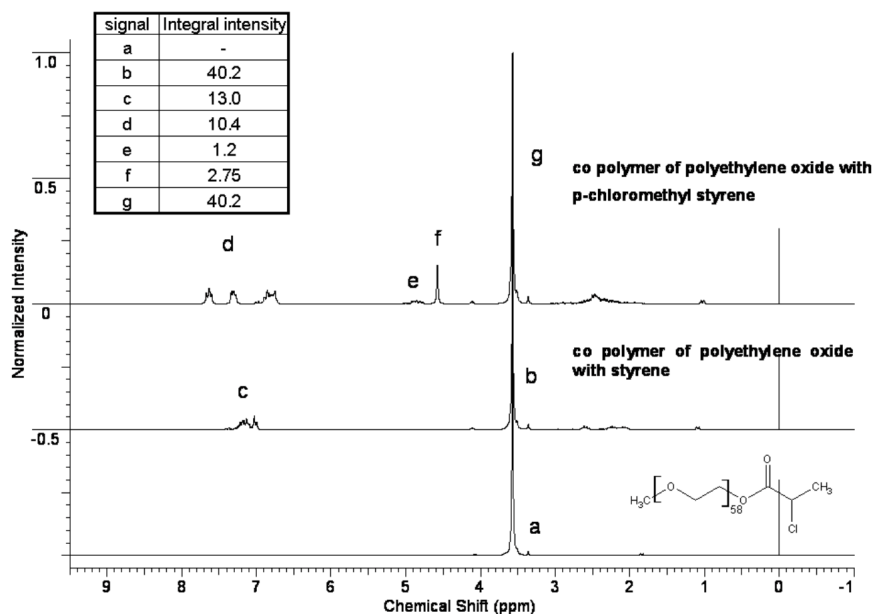
8.6 Assign ^1H NMR signals to substructures given in the Answer Sheet.

8.7 Determine molar fractions of units C and D and molecular weights of P_1 and P_2 .

8.8 Write down all possible reactions of activation occurring during the synthesis of P_1 and P_2 . You may use R symbol to depict any unchanged part of the macromolecule, but you should specify what substructure you use it for.

8.9 Draw the structure of P_1 and one of possible structures of P_2 representing poly(ethylene oxide) chain by a wavy line and showing units of co-monomers as C and D, respectively.

signal	Integral intensity
a	-
b	40.2
c	13.0
d	10.4
e	1.2
f	2.75
g	40.2



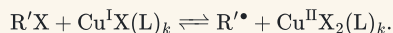
Official English text of the problem.

Answers

- 8.1

$$\begin{aligned}
 v_{\text{act}} &= k_{\text{act}}[\text{R}'\text{X}][\text{Cu}^{\text{I}}\text{X}(\text{L})_k], \\
 v_{\text{deact}} &= k_{\text{deact}}[\text{R}'\bullet][\text{Cu}^{\text{II}}\text{X}_2(\text{L})_k], \\
 v_p &= k_p[\text{R}'\bullet][\text{M}], \\
 v_t &= k_t[\text{R}'\bullet]^2.
 \end{aligned}$$

Here v_t counts termination events; radical disappearance by termination is $2v_t$. The activation–deactivation equation is



- 8.2

$$v_{\text{deact}} \simeq v_{\text{act}}, \quad v_{\text{deact}} \gg v_p, \quad v_{\text{deact}} \gg v_t.$$

- 8.3 Including the retained initiator-derived end groups,

$$m = 1.04 \text{ g.}$$

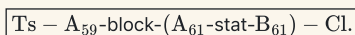
Neglecting their mass gives 1.02 g.

- 8.4 Consistently including end-group mass,

$$\text{DP} \approx 181.$$

The approximation that neglects end-group mass gives approximately 183.

- 8.5



Subscripts are rounded average numbers of units. The initiating end is a tosyl group; the dormant growing end bears chlorine.

- 8.6 **a, b, g:** PEO methylene protons; **c:** styrene aromatic protons; **d:** p-chloromethylstyrene aromatic protons; **e:** terminal benzylic $-\text{CH}(\text{Cl})^-$ protons; **f:** pendant benzylic $-\text{CH}_2\text{Cl}$ protons.

- 8.7

$$n_C \simeq n_D \simeq 15, \quad x_C = x_D \simeq 0.205$$

and

$$M(P_1) \simeq 4.24 \times 10^3 \text{ g mol}^{-1}, \quad M(P_2) \simeq 4.97 \times 10^3 \text{ g mol}^{-1}.$$

- 8.8 Both syntheses permit activation of the macroinitiator's α -chloroester and of dormant benzylic chain ends. P_2 additionally permits activation of the benzyl chloride group in free D and in incorporated D units. The balanced reactions appear below.
- 8.9 P_1 is a linear PEO–polystyrene block copolymer, with approximately 58 EO and 15 C units. P_2 can contain a branched, approximately 15-unit D portion attached to PEO, because pendant chloromethyl groups can initiate additional arms. An explicit idealized example is described below.

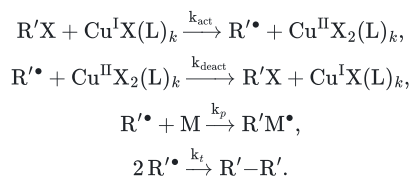
Solution

SMILES containing * describe fragments, with * marking attachment to the rest of a molecule. A statistical polymer does not have one unique finite SMILES; its repeat units and end groups must therefore be specified separately. Stereochemical configurations and polymer tacticity are not determined by the problem.

8.1 — Elementary reactions and rate laws

Let $R'X$ represent any dormant initiator or polymer chain, and let $R'^{\bullet}$ represent its active radical.

The elementary reactions are



Mass action gives

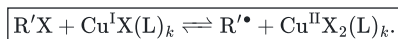
$$\begin{aligned} v_{act} &= k_{act}[R'X][Cu^I X(L)_k], \\ v_{deact} &= k_{deact}[R'^{\bullet}][Cu^{II} X_2(L)_k], \\ v_p &= k_p[R'^{\bullet}][M], \\ v_t &= k_t[R'^{\bullet}]^2. \end{aligned}$$

These rates have units $\text{mol L}^{-1} \text{s}^{-1}$. With v_t defined as the number of coupling events per unit volume and time, the balance for the total active-radical concentration is

$$\frac{d[R'^{\bullet}]}{dt} = v_{act} - v_{deact} - 2v_t.$$

Propagation does not appear in this balance because one radical enters and one radical leaves each propagation event.

The generalized reversible activation equation is



Neglecting termination, the overall chain-growth equation is



For the chloride system, copper(I) chloride has the ionic SMILES representation $[Cu+].[Cl-]$, and copper(II) chloride $[Cu+2].[Cl-].[Cl-]$. These represent compositions, not the actual ligand-bound catalyst structures. Since L is unspecified, neither a complete catalyst SMILES nor its coordination geometry can be determined.

8.2 — Required relative rates

At steady radical concentration,

$$v_{act} = v_{deact} + 2v_t.$$

The assumption that the number of polymer molecules remains equal to the number of initiator molecules requires negligible coupling termination. Hence

$$v_t \ll v_{deact}, \quad v_{act} \simeq v_{deact}.$$

For all chains to grow nearly equally, an activated chain should usually be deactivated before adding many monomers. Frequent activation–deactivation cycles distribute growth among the chains. Thus

$$v_{deact} \gg v_p.$$

Together,

$$v_{deact} \simeq v_{act}, \quad v_{deact} \gg v_p, \quad v_{deact} \gg v_t.$$

These are comparisons of reaction rates, not simply of the corresponding rate constants.

8.3 — Mass of the first polymer

The relevant molecules are:

Molecule	Formula	SMILES	Approximate molar mass
Methyl methacrylate, MMA; methyl 2-methylprop-2-enoate	$C_5H_8O_2$	<chem>C=C(C)C(=O)OC</chem>	$100.114 \text{ g mol}^{-1}$
Tosyl chloride; 4-methylbenzenesulfonyl chloride	$C_7H_7ClO_2S$	<chem>Cc1ccc(S(=O)(=O)Cl)cc1</chem>	$190.636 \text{ g mol}^{-1}$

The effective first-order constant is

$$k_{obs} = k_p[R'^{\bullet}] = (1616)(1.76 \times 10^{-7}) = 2.84416 \times 10^{-4} \text{ s}^{-1}.$$

After 1400 s, the fraction of MMA consumed is

$$f_1 = 1 - e^{-k_{obs}t} = 1 - e^{-0.3981824} = 0.328460.$$

Therefore,

$$n_{\text{MMA,consumed}} = (31.0 \text{ mmol})(0.328460) = 10.1823 \text{ mmol}.$$

The mass contributed by the repeat units is

$$m_{\text{repeat}} = (10.1823 \times 10^{-3})(100.114) = 1.01939 \text{ g}.$$

In the supplied mechanism, the initiating organic group and the terminal chlorine are retained in the polymer. Their combined mass per chain equals the mass of one TsCl molecule. Thus

$$m_{\text{ends}} = (0.120 \times 10^{-3})(190.636) = 0.022876 \text{ g},$$

and

$$m = 1.01939 + 0.022876 = 1.04226 \text{ g} \approx 1.04 \text{ g}.$$

If end-group mass is neglected, the result is instead 1.02 g.

8.4 — Degree of polymerization after the second feed

The second monomer is **2-(trimethylsilyloxy)ethyl methacrylate**, HEMA-TMS, SMILES C=C(C)C(=O)OCCO[Si](C)(C)C.

The first-stage polymer mass in this experiment is 0.73 g. Subtracting the end-group contribution gives the amount of MMA already incorporated:

$$n_{A,1} = \frac{0.730 - 0.022876}{100.114} = 7.06318 \times 10^{-3} \text{ mol}.$$

Thus the remaining MMA is

$$n_{A,\text{remaining}} = 31.0 - 7.06318 = 23.9368 \text{ mmol}.$$

The newly added amount of B is 23.7 mmol.

Because the monomers have equal reactivities, each undergoes the same fractional conversion during the additional 1295 s:

$$f_2 = 1 - e^{-(2.84416 \times 10^{-4})(1295)} = 1 - e^{-0.36831872} = 0.308103.$$

Consequently,

$$\Delta n_A = (23.9368)(0.308103) = 7.37501 \text{ mmol},$$

$$\Delta n_B = (23.7)(0.308103) = 7.30205 \text{ mmol}.$$

The total number of incorporated monomer units, expressed as an amount, is

$$n_{\text{units}} = 7.06318 + 7.37501 + 7.30205 = 21.7402 \text{ mmol}.$$

There are 0.120 mmol of polymer chains, so

$$\text{DP} = \frac{21.7402}{0.120} = 181.17 \approx 181.$$

For comparison, neglecting end-group mass and using $M_{\text{MMA}} \approx 100 \text{ g mol}^{-1}$ gives

$$n_{A,1} = 7.30 \text{ mmol}, \quad n_{A,\text{remaining}} = 23.7 \text{ mmol},$$

and

$$\text{DP} = \frac{7.30 + 2(23.7)(0.308103)}{0.120} = 182.53 \approx 183.$$

8.5 — Sequence and end groups

The average numbers of units incorporated per chain are

$$N_{A,1} = \frac{7.06318}{0.120} = 58.86,$$

$$N_{A,2} = \frac{7.37501}{0.120} = 61.46, \quad N_{B,2} = \frac{7.30205}{0.120} = 60.85.$$

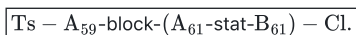
The first segment contains only A. MMA remains present when B is added, so the second segment contains both monomers.

Equal reactivities mean that neither monomer is preferentially consumed. Their ratio remains constant during this stage, producing a statistical segment, approximately equimolar in A and B.

The polymer is therefore **tosyl-initiated, chlorine-terminated poly(methyl methacrylate)-block-poly(methyl methacrylate-stat-HEMA-TMS)**:



With rounded subscripts,



The structures needed to draw it are:

Component	Structure or meaning	SMILES fragment
A, an MMA repeat unit	$-\text{CH}_2-\text{C}(\text{CH}_3)(\text{C}(=\text{O})\text{OCH}_3)-$	<chem>*CC(C)(C(=O)OC)*</chem>
B, a HEMA-TMS repeat unit	$-\text{CH}_2-\text{C}(\text{CH}_3)(\text{C}(=\text{O})\text{OCH}_2\text{CH}_2\text{OSi}(\text{CH}_3)_3)-$	<chem>*CC(C)(C(=O)OCCO[Si](C)(C)C)*</chem>
Tosyl initiating end	4-Methylbenzenesulfonyl group, attached through sulfur	<chem>Cc1ccc(S(=O)(=O)*)cc1</chem>
Chlorine-capped terminal A unit	Chlorine bonded to the substituted backbone carbon	<chem>*CC(C)(Cl)C(=O)OC</chem>
Chlorine-capped terminal B unit	Same terminal arrangement, with the B ester substituent	<chem>*CC(C)(Cl)C(=O)OCCO[Si](C)(C)C</chem>

Draw the tosyl sulfur bonded to the first backbone methylene. At the other end, attach chlorine to the substituted carbon of whichever monomer was incorporated last. The statistical sequence does not specify whether the final unit is A or B.

Under the end-group-mass-neglecting convention, the corresponding rounded notation is $\text{Ts} - \text{A}_{61}\text{-block-}(\text{A}_{61}\text{-stat-B}_{61}) - \text{Cl}$.

8.6 — NMR assignments

The monomers in this part are:

- **Styrene**, ethenylbenzene: C=Cc1ccccc1.
- **p-Chloromethylstyrene**, 1-(chloromethyl)-4-ethenylbenzene: C=Cc1ccc(CCl)cc1.

Their polymerized repeat-unit fragments are:

- C, a styrene unit: *CC(c1ccccc1)*.
- D, a p-chloromethylstyrene unit with an unactivated pendant group: *CC(c1ccc(CC1)cc1)*.

The assignments are:

Signal	Approximate shift	Assignment and reasoning
a	3.6 ppm	PEO $-\text{OCH}_2\text{CH}_2-$ protons in the macroinitiator
b	3.6 ppm	The same PEO protons in P_1
c	Around 7 ppm	The five aromatic protons per C unit
d	Around 7 ppm	The four aromatic protons per para-disubstituted D ring
e	About 4.9 ppm	Benzylic terminal methine, $-\text{CH}_2-\text{CH}(\text{Cl})-\text{Ar}$, one proton per such end
f	About 4.6 ppm	Pendant benzyl chloride, $\text{Ar}-\text{CH}_2\text{Cl}$, two protons per unactivated group
g	3.6 ppm	PEO protons in P_2

The PEO repeat fragment is *OCC*. A representative D-derived terminal chloromethine fragment is *CC(Cl)c1ccc(CCl)cc1; the pendant benzyl chloride substructure is *c1ccc(CCl)cc1.

Oxygen shifts the PEO methylene signals downfield from ordinary aliphatic protons. Aromatic protons occur around 7 ppm. Carbon bonded both to chlorine and to an aromatic ring gives the characteristic benzylic signals e and f.

8.7 — Composition and molecular weights

Each EO repeat contributes four protons to the PEO signal. Each C unit contributes five aromatic protons; each D unit contributes four.

For P_1 ,

$$\frac{N_C}{58} = \frac{I_c/5}{I_b/4},$$

so

$$N_C = 58 \frac{13.0/5}{40.2/4} = 15.005 \approx 15.$$

For P_2 ,

$$\frac{N_D}{58} = \frac{I_d/4}{I_a/4},$$

giving

$$N_D = 58 \frac{10.4/4}{40.2/4} = 15.005 \approx 15.$$

Therefore,

$$x_C = \frac{15}{58+15} = 0.2055, \quad x_D = \frac{15}{58+15} = 0.2055.$$

Both copolymers contain approximately 20.5% styrene-derived repeat units on a molar basis.

The macroinitiator is **monomethyl poly(ethylene glycol) 2-chloropropanoate**, with the structure



Its formula is $C_{120}H_{239}ClO_{60}$, and its SMILES is:



Its molar mass is approximately

$$M_{\text{macro}} = 2677.6 \text{ g mol}^{-1}.$$

Addition polymerization retains the atoms of the monomers, so

$$M(P_1) = M_{\text{macro}} + 15M(\text{C}_8\text{H}_8) = 2677.6 + 15(104.14),$$

$$M(P_1) \approx 4.24 \times 10^3 \text{ g mol}^{-1}.$$

Likewise,

$$M(P_2) = M_{\text{macro}} + 15M(\text{C}_9\text{H}_9\text{Cl}) = 2677.6 + 15(152.61),$$

$$M(P_2) \approx 4.97 \times 10^3 \text{ g mol}^{-1}.$$

Branching changes connectivity but does not change this mass sum, provided the initiator and monomer atoms are retained.

8.8 — All types of activation

Write



This is an illustrative allowed connectivity. The spectrum does not uniquely determine the arrangement of the branches.

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.