

IChO 2013

Theory problems and solutions · Moscow, Russia · 8 theory problems with complete solutions

eulersolve.org/icho/2013/

Problem 1: Clathrate gun

The only gun that is able to kill all living people in one shot

On the floors of oceans and seas there are vast reserves of methane in the form of clathrate compounds called methane hydrates. These reserves can be mined and serve as a source of energy or raw materials for organic synthesis. However, scientists are seriously worried about the possibility of spontaneous decomposition of hydrates caused by the raising ocean temperature. It is believed that if a sufficient amount of methane is released into the atmosphere, the oceans will warm up quicker due to the greenhouse effect, further accelerating the decomposition of clathrates. Due to the explosion of the resulting methane-air mixture and/or changes in the composition of the atmosphere, all living creatures may become extinct. This apocalyptic scenario is called a clathrate gun.



Upon decomposition of 1.00 g of a methane hydrate with a fixed composition at 25 °C and atmospheric (101.3 kPa) pressure, 205 cm³ of methane is released.

1.1 Determine n (not necessarily integer) in the formula of methane hydrate, $\text{CH}_4 \cdot n \text{H}_2\text{O}$.

Real methane hydrate has a non-stoichiometric composition close to $\text{CH}_4 \cdot 6 \text{H}_2\text{O}$. At atmospheric pressure, methane hydrate decomposes at -81°C . However, under high pressures (e.g. on the ocean floor) it is stable at much higher temperatures.

Decomposition of methane hydrate produces gaseous methane and solid or liquid water depending on temperature.

1.2 Write down the equation of decomposition of 1 mol of $\text{CH}_4 \cdot 6 \text{H}_2\text{O}$ producing solid water (ice) $\text{H}_2\text{O}(\text{s})$.

The enthalpy of this process equals $17.47 \text{ kJ mol}^{-1}$. Assume that the enthalpies do not depend on temperature and pressure, the volume change upon decomposition of hydrate is equal to the volume of released methane, and methane is an ideal gas.

1.3 At what external pressure does decomposition of methane hydrate into methane and ice take place at $-5\text{ }^{\circ}\text{C}$?

1.4 What is the minimum possible depth of pure liquid water at which methane hydrates can be stable?

To answer this question, you should first deduce at which minimum temperature methane hydrate can coexist with liquid water. Choose the correct answer.

☐ 272.9 K ☐ 273.15 K ☐ 273.4 K

Large methane hydrate stocks on the floor of Baikal lake, the largest freshwater lake in Russia and in the world, have been discovered in July 2009 by the crew of a deep-submergence vehicle «Mir-2». During the ascent from the depth of 1400 m methane hydrate samples started to decompose at the depth of 372 m.

1.5 Determine the temperature in Baikal lake at the depth of 372 m. The enthalpy of fusion of ice is equal to 6.01 kJ mol^{-1} .

Total amount of methane in hydrates on the Earth is no less than $5 \cdot 10^{11}$ tons.

1.6 By how many degrees would the Earth atmosphere heat up, if such amount of methane is burned by reacting with atmospheric oxygen?

The enthalpy of combustion of methane is -889 kJ mol^{-1} , the total heat capacity of the Earth's atmosphere is about $4 \cdot 10^{21}\text{ J K}^{-1}$.

Official English text of the problem.

Answers

- **1.1:** $n \approx 5.74$.
- **1.2:** $\text{CH}_4 \cdot 6\text{H}_2\text{O (s)} \longrightarrow \text{CH}_4\text{ (g)} + 6\text{H}_2\text{O (s)}$.
- **1.3:** $P \approx 2.25\text{ MPa}$, absolute pressure.
- **1.4:** Tick 272.9 K. The minimum depth is $h_{\min} \approx 252\text{ m}$, or approximately 250 m.
- **1.5:** $T \approx 277.3\text{ K} \approx 4.2\text{ }^{\circ}\text{C}$.
- **1.6:** $\Delta T \approx 7\text{ K}$, equivalent to a temperature rise of approximately $7\text{ }^{\circ}\text{C}$.

Solution

The molecular species used below are methane C, water O, dioxygen O=O, and carbon dioxide O=C=O. Methane hydrate is an extended clathrate lattice rather than a discrete molecule. The disconnected SMILES `C.O.O.O.O.O.O` records its approximate $\text{CH}_4 \cdot 6\text{H}_2\text{O}$ composition, but does not describe the water cages or hydrogen bonding. SMILES also does not distinguish liquid water from ice.

Use the standard constants and approximations

$$R = 8.31446\text{ J mol}^{-1}\text{ K}^{-1}, \quad \rho_{\text{water}} = 1.00 \times 10^3\text{ kg m}^{-3}, \quad g = 9.81\text{ m s}^{-2},$$

with molar masses $M(\text{CH}_4) = 16.04\text{ g mol}^{-1}$ and $M(\text{H}_2\text{O}) = 18.015\text{ g mol}^{-1}$. All pressures below are absolute.

1.1

The amount of methane released is obtained from the ideal-gas equation:

$$\nu_{\text{CH}_4} = \frac{PV}{RT} = \frac{(101.3 \times 10^3 \text{ Pa})(205 \times 10^{-6} \text{ m}^3)}{(8.31446 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = 8.3771 \times 10^{-3} \text{ mol}.$$

Each formula unit of hydrate contains one methane molecule. Hence its mass satisfies

$$1.00 \text{ g} = \nu_{\text{CH}_4} [M(\text{CH}_4) + nM(\text{H}_2\text{O})].$$

Therefore,

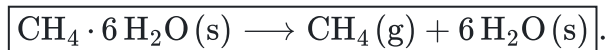
$$n = \frac{\frac{1.00}{8.3771 \times 10^{-3}} - 16.04}{18.015} = 5.7359,$$

so

$$\boxed{n = 5.74}.$$

1.2

One mole of hydrate releases one mole of methane and six moles of water:



For this decomposition into methane and ice,

$$\Delta_r H_{\text{ice}} = +17.47 \text{ kJ mol}^{-1}.$$

1.3

Along the decomposition-equilibrium curve, the Clapeyron equation gives

$$\frac{dP}{dT} = \frac{\Delta_r H}{T \Delta_r V}.$$

For one mole of hydrate, one mole of methane is released. Under the stated volume approximation,

$$\Delta_r V = \frac{RT}{P}.$$

Thus,

$$\frac{dP}{P} = \frac{\Delta_r H}{R} \frac{dT}{T^2}.$$

Integrating with constant enthalpy,

$$\boxed{\ln \frac{P}{P_0} = \frac{\Delta_r H}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}.$$

The known equilibrium point is

$$T_0 = 273.15 - 81 = 192.15 \text{ K}, \quad P_0 = 101.3 \text{ kPa}.$$

At -5°C , $T = 268.15 \text{ K}$, so

$$P = (101.3 \text{ kPa}) \exp \left[\frac{17470}{8.31446} \left(\frac{1}{192.15} - \frac{1}{268.15} \right) \right].$$

Therefore,

$$P = 2.247 \times 10^3 \text{ kPa} \approx 2.25 \text{ MPa}.$$

A pressure above this equilibrium value favors the hydrate, which occupies much less volume than its gaseous decomposition product.

1.4

The minimum depth occurs where the hydrate-decomposition boundary meets the ice–liquid–water melting boundary. At lower pressures, the temperatures required to stabilize hydrate would leave the water frozen.

Ice occupies more volume than the same amount of liquid water. Consequently,

$$\Delta V_{\text{fus}} = V_{\text{liquid}} - V_{\text{ice}} < 0,$$

and the melting-curve slope is

$$\frac{dT_m}{dP} = \frac{T_m \Delta V_{\text{fus}}}{\Delta H_{\text{fus}}} < 0.$$

Pressure therefore lowers the melting temperature below 273.15 K. The appropriate choice is

$$T_m = 272.9 \text{ K}.$$

At this boundary, the equilibrium pressure can be calculated using decomposition into ice:

$$P_m = (101.3 \text{ kPa}) \exp \left[\frac{17470}{8.31446} \left(\frac{1}{192.15} - \frac{1}{272.9} \right) \right] = 2.5753 \times 10^6 \text{ Pa}.$$

Hydrostatic pressure includes the atmospheric pressure at the surface:

$$P_m = P_{\text{atm}} + \rho g h_{\text{min}}.$$

Hence,

$$h_{\text{min}} = \frac{2.5753 \times 10^6 - 1.013 \times 10^5}{(1.00 \times 10^3)(9.81)} \text{ m} = 252.2 \text{ m}.$$

Thus,

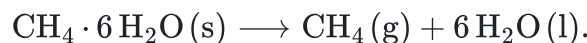
$$h_{\text{min}} \approx 252 \text{ m} \approx 250 \text{ m}.$$

1.5

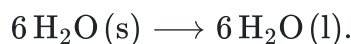
At 372 m, the external pressure is

$$P_{372} = P_{\text{atm}} + \rho g h = 101300 + (1000)(9.81)(372) = 3.75062 \times 10^6 \text{ Pa}.$$

Here the decomposition products contain liquid water:



To obtain its enthalpy, add the melting of six moles of ice to the reaction in 1.2:



By Hess's law, per mole of hydrate,

$$\Delta_r H_{\text{liquid}} = 17.47 + 6(6.01) = 53.53 \text{ kJ mol}^{-1}.$$

The ice and liquid–water decomposition branches meet at the boundary used in 1.4:

$$T_m = 272.9 \text{ K}, \quad P_m = 2.5753 \times 10^6 \text{ Pa}.$$

Integrating along the liquid-water branch,

$$\ln \frac{P_{372}}{P_m} = \frac{\Delta_r H_{\text{liquid}}}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right).$$

Solving for T ,

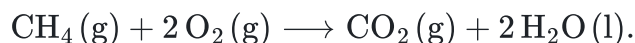
$$T = \left[\frac{1}{272.9} - \frac{8.31446}{53530} \ln \left(\frac{3.75062 \times 10^6}{2.5753 \times 10^6} \right) \right]^{-1} \approx 277.32 \text{ K}.$$

Therefore,

$$t = T - 273.15 \approx 4.17^\circ \text{C} \approx 4.2^\circ \text{C}.$$

1.6

The balanced combustion equation, with liquid water as product, is



The stated methane mass is

$$m = 5 \times 10^{11} \text{ tons} = 5 \times 10^{17} \text{ g}.$$

Its amount is

$$\nu_{\text{CH}_4} = \frac{5 \times 10^{17} \text{ g}}{16.04 \text{ g mol}^{-1}} = 3.1172 \times 10^{16} \text{ mol}.$$

The heat released is

$$Q = \nu_{\text{CH}_4} |\Delta_c H| = (3.1172 \times 10^{16})(889 \times 10^3) = 2.7712 \times 10^{22} \text{ J}.$$

Assigning this heat to the atmosphere gives

$$\Delta T = \frac{Q}{C_{\text{atm}}} = \frac{2.7712 \times 10^{22} \text{ J}}{4 \times 10^{21} \text{ J K}^{-1}} = 6.93 \text{ K}.$$

Given the approximate inventory and heat capacity,

$$\Delta T \approx 7 \text{ K},$$

equivalent to a rise of approximately 7°C for the quoted methane amount.

The solution was checked against the official solution.

Problem 2: Break down photosynthesis – the Hill reaction

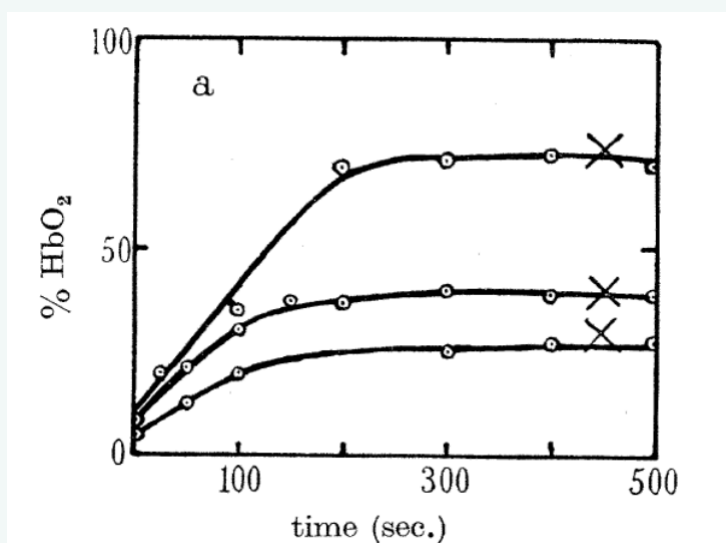
In the history of photosynthesis research, there were some breakthrough experiments which added much to our knowledge of this very complex process. One of such experiments was performed in 1930s by an English biochemist Robert Hill. In this problem, we consider some of his data together with the data of more recent experiments.

2.1 In plants, under illumination, carbon dioxide is reduced to carbohydrates (denote as $\{\text{CH}_2\text{O}\}$) and oxygen is produced. Write the overall equation of photosynthesis in plants.

Much of the photosynthesis takes place in chloroplasts – organelles found in plant cells and containing chlorophyll – the light-absorbing substance. Hill isolated chloroplasts from the cells by grinding the leaves in the sucrose solutions. The cell-free chloroplasts did not produce oxygen under illumination even in the presence of CO_2 . However, upon adding potassium ferrioxalate $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ (with the excess of potassium oxalate) to the chloroplast suspension Hill observed oxygen liberation under illumination even without CO_2 .

2.2 Hill's experiment enabled to determine the source of oxygen during photosynthesis. Write the formulas of the oxidant and the reducing agent in the photosynthesis inside the plant cells and in the cell-free chloroplasts (the Hill reaction).

Hill measured the amount of evolved oxygen using muscle haemoglobin (Hill denoted it Hb) which binds all molecular oxygen in a 1 : 1 ratio to form HbO_2 . The initial concentration of Hb was $0.6 \cdot 10^{-4} \text{ mol dm}^{-3}$. Kinetic curves corresponding to different ferrioxalate concentrations are shown in the figure (the upper curve corresponds to $2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$).



The fraction of bound haemoglobin HbO_2 (with respect to the initial amount of Hb) as a function of time. Crosses denote the end of the reaction

(Figure 2a from the original Hill's paper: *R. Hill. Oxygen produced by isolated chloroplasts. – Proc. R. Soc. B, 1939, v. 127, pp. 192-210.*)

2.3 a. From the figure, estimate the Fe / O_2 mole ratio at the end of the reaction. Do not take into account the iron from Hb .

b. Write the equation of Hill reaction assuming that it proceeds with a high yield.

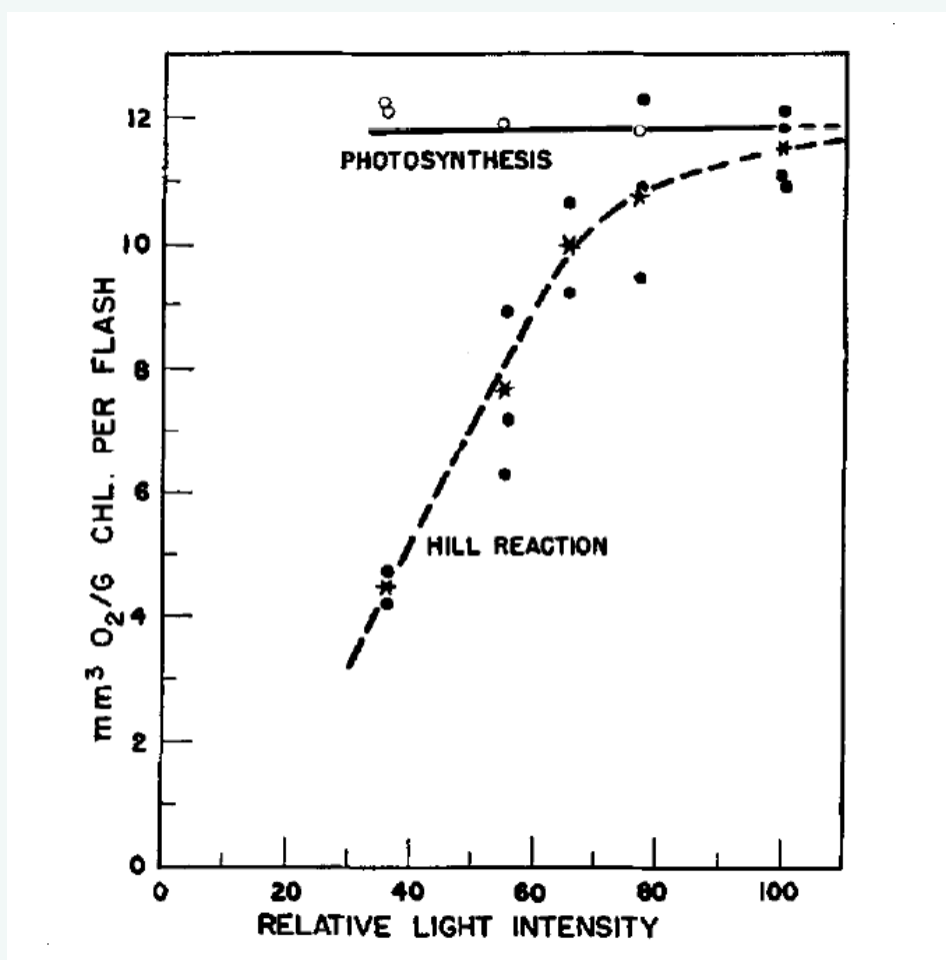
c. Using the table of standard electrode potentials, determine the Gibbs energy of the Hill reaction at $T = 298 \text{ K}$, oxygen pressure 1 mm Hg , $\text{pH} = 8$ and standard concentrations of other species. Is this reaction spontaneous at such conditions?

Half-reaction	$E^\circ, \text{ V}$
$\text{O}_2 + 4 \text{H}^+ + 4 \text{e} \longrightarrow 2 \text{H}_2\text{O}$	+1.23
$\text{CO}_2 + 4 \text{H}^+ + 8 \text{e} \longrightarrow \{\text{CH}_2\text{O}\} + \text{H}_2\text{O}$	-0.01
$\text{Fe}^{3+} + \text{e} \longrightarrow \text{Fe}^{2+}$	+0.77
$\text{Fe}^{3+} + 3 \text{e} \longrightarrow \text{Fe}^0$	-0.04

Half-reaction	E° , V
$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} + e \longrightarrow [\text{Fe}(\text{C}_2\text{O}_4)_3]^{4-}$	+0.05
$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{4-} + 2e \longrightarrow \text{Fe} + 3\text{C}_2\text{O}_4^{2-}$	-0.59

Now, the name "Hill reaction" denotes photochemical oxidation of water by any oxidant other than carbon dioxide which is sensitized by plant cells or isolated chloroplasts.

In another experiment (1952), quinone in an acid solution was used as an oxidant in the Hill reaction initiated by light flashes in the *Chlorella* algae. Experimental data are shown in the figure. The volume of oxygen (in mm^3 , at temperature 10°C and pressure 740 mm Hg) per one gram of chlorophyll per one flash was determined as a function of light intensity for natural photosynthesis and for isolated chloroplasts. It was found that the maximum yield of oxygen is the same for natural photosynthesis and the Hill reaction.



(Figure 1 from: H. Ehrmantraut, E. Rabinovitch. *Kinetics of Hill reaction*. – *Archives of Biochemistry and Biophysics*, 1952, v. 38, pp. 67-84)

- 2.4 a.** Determine the reaction order of a photochemical Hill reaction with respect to light intensity at low and high intensity. For each case choose one of the following three values: 0, 1 or 2.
- b.** How many chlorophyll molecules participate in the formation of one oxygen molecule in the saturation limit of the Hill reaction? (The molecular mass of chlorophyll is about 900 Da).

The quantum requirement of the light redox reactions is defined as the average number of light photons (not necessarily integer) needed for the transfer of one electron from a reducing agent to an oxidant. The isolated chloroplasts were irradiated during 2 hours by a monochromatic light (wavelength 672 nm) with the energy input 0.503 mJ s^{-1} , and the total volume of oxygen formed was 47.6 mm^3 (under the same conditions as in question 4).

2.5 Calculate the quantum requirement for the Hill reaction.

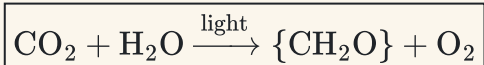
2.6 Try to make conclusions from the above experiments (questions 2.2 – 2.5). Tick the relevant boxes.

	Yes	No
In natural photosynthesis, water oxidation and CO_2 reduction are separated in space.		
In chloroplasts, O_2 is produced from CO_2 .		
Oxidation of water in chloroplasts requires light illumination.		
Most of chlorophylls in chloroplasts participate directly in the photochemical O_2 production.		
In isolated chloroplasts, every absorbed photon causes transfer of one electron.		

Official English text of the problem.

Answers

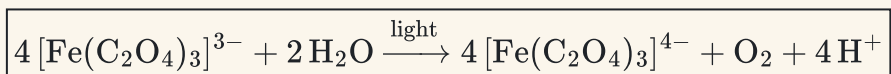
• 2.1



- **2.2** In plant cells: oxidant CO_2 , reducing agent H_2O . In Hill's experiment: oxidant $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, reducing agent H_2O .

- **2.3(a)** The graph gives approximately $n(\text{Fe})/n(\text{O}_2) = 4.4$. The ideal stoichiometric ratio is 4 : 1.

• 2.3(b)



- **2.3(c)** $\Delta_r G \approx +256 \text{ kJ mol}^{-1}$, per mole of reaction as written, producing one mole of O_2 . The reaction is **not thermodynamically spontaneous** under the stated conditions.

- **2.4(a)** Low light intensity: $\boxed{1}$. High light intensity: $\boxed{0}$.

- **2.4(b)** Approximately $\boxed{2.2 \times 10^3}$ chlorophyll molecules per oxygen molecule produced per saturating flash.

- **2.5** $\boxed{2.55}$ photons per transferred electron, interpreting the stated energy input as absorbed light energy.

- **2.6** In the order printed: $\boxed{\text{Yes; No; Yes; No; No}}$, with the interpretive qualifications stated below.

Names and SMILES for the molecular species in these answers are provided at the start of the solution.

Solution

The relevant species are:

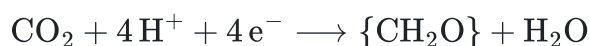
Formula	Name	SMILES
CO ₂	Carbon dioxide	O=C=O
H ₂ O	Water	O
O ₂	Dioxygen	O=O
H ⁺	Hydrogen ion, or proton	[H+]
C ₂ O ₄ ²⁻	Oxalate ion	[O-]C(=O)C(=O)[O-]
[Fe(C ₂ O ₄) ₃] ³⁻	Tris(oxalato)ferrate(III), or ferrioxalate	[Fe+3]123(<-[O-]C(=O)C(=O)[O-]->1)(<-[O-]C(=O)C(=O)[O-]->2)<-[O-]C(=O)C(=O)[O-]->3
[Fe(C ₂ O ₄) ₃] ⁴⁻	Tris(oxalato)ferrate(II)	[Fe+2]123(<-[O-]C(=O)C(=O)[O-]->1)(<-[O-]C(=O)C(=O)[O-]->2)<-[O-]C(=O)C(=O)[O-]->3

The extended SMILES for the iron complexes use arrows for oxygen-to-iron coordinate bonds. Each oxalate ligand is bidentate, giving six oxygen donors in an approximately octahedral arrangement. Neither a particular Δ nor Λ configuration is specified by the problem or encoded here. These bond arrows do not represent the electron flow of the redox reaction.

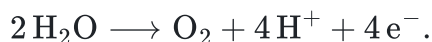
The notation {CH₂O} is a carbohydrate composition unit, not a uniquely specified molecule, so it has no unique SMILES. Likewise, the unspecified chlorophyll of approximate molecular mass 900 Da does not identify a unique molecular structure.

2.1 — Overall photosynthesis equation

Carbon dioxide is reduced to carbohydrate, while water is oxidized to oxygen. The balanced half-reactions are



and



Adding them and cancelling the electrons, protons and one water molecule gives



This equation is written per carbon atom incorporated into carbohydrate.

2.2 — Oxidants and reducing agents

An oxidant accepts electrons and is reduced; a reducing agent supplies electrons and is oxidized.

System	Oxidant	Reducing agent
Overall photosynthesis in plant cells	CO ₂	H ₂ O
Hill reaction with ferrioxalate	[Fe(C ₂ O ₄) ₃] ³⁻	H ₂ O

In photosynthesis, carbon's average oxidation state decreases from +4 in carbon dioxide to 0 in the carbohydrate composition unit. Oxygen in water increases in oxidation state from −2 to 0.

In Hill's experiment, the iron centre in ferrioxalate accepts an electron, changing from oxidation state +3 to +2. Water still supplies the electrons and the evolved oxygen. Oxygen evolution without carbon dioxide shows that carbon dioxide is not required as the oxygen source.

2.3(a) — Experimental iron-to-oxygen ratio

At the endpoint, the upper curve shows approximately 75% of the initial haemoglobin bound to oxygen. Because binding is 1 : 1,

$$c(\text{O}_2) \approx 0.75 c_0(\text{Hb}) = 0.75(0.6 \times 10^{-4}) = 4.5 \times 10^{-5} \text{ mol dm}^{-3}.$$

Each ferrioxalate ion contains one iron atom, so the initial concentration of iron supplied by ferrioxalate is

$$c(\text{Fe}) = 2.0 \times 10^{-4} \text{ mol dm}^{-3}.$$

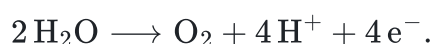
Thus

$$\boxed{\frac{n(\text{Fe})}{n(\text{O}_2)} \approx \frac{2.0 \times 10^{-4}}{4.5 \times 10^{-5}} = 4.4}.$$

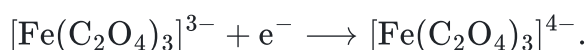
The graph therefore supports an ideal ratio of approximately four iron centres per oxygen molecule. For a 4 : 1 stoichiometry, the theoretical oxygen concentration is $5.0 \times 10^{-5} \text{ mol dm}^{-3}$; the graph corresponds to about 90% of that amount.

2.3(b) — Balanced Hill reaction

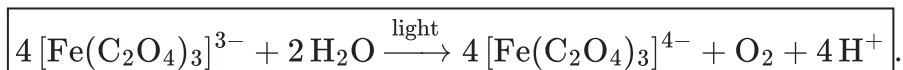
Formation of one oxygen molecule from water releases four electrons:



The inferred four iron centres per oxygen molecule therefore each accept one electron:



Multiplying this reduction half-reaction by four and adding gives



Both sides have total charge −12, and all atoms are balanced.

2.3(c) — Gibbs energy under the specified conditions

The relevant standard reduction potentials are

$$E_{\text{ferrioxalate}}^\circ = +0.05 \text{ V}, \quad E_{\text{O}_2/\text{H}_2\text{O}}^\circ = +1.23 \text{ V}.$$

For ferrioxalate reduction coupled to water oxidation,

$$E_{\text{cell}}^\circ = 0.05 - 1.23 = -1.18 \text{ V}.$$

Four electrons are transferred per reaction as written. Using $F = 96485 \text{ C mol}^{-1}$,

$$\Delta_r G^\circ = -4FE_{\text{cell}}^\circ = +455.4 \text{ kJ mol}^{-1}.$$

The reaction quotient is

$$Q = \frac{a([\text{Fe}(\text{C}_2\text{O}_4)_3]^{4-})^4 a(\text{H}^+)^4 (p_{\text{O}_2}/p^\circ)}{a([\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-})^4 a(\text{H}_2\text{O})^2}.$$

Under the stated conditions, the complex activities and water activity are unity, while

$$a(\text{H}^+) = 10^{-8}, \quad \frac{p_{\text{O}_2}}{p^\circ} = \frac{1}{760}$$

using $p^\circ = 1 \text{ atm}$. Therefore,

$$Q = \frac{10^{-32}}{760}.$$

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

$$\begin{aligned} \Delta_r G &= \Delta_r G^\circ + RT \ln Q \\ &= 455.4 + \frac{8.314(298)}{1000} \ln \left(\frac{10^{-32}}{760} \right) \\ &= \boxed{+256.4 \text{ kJ mol}^{-1}}. \end{aligned}$$

The positive Gibbs energy means that the chemical reaction is not spontaneous under these conditions. Light supplies energy to drive it.

2.4(a) — Dependence on light intensity

For flashes of fixed duration, the oxygen yield indicates how the photochemical reaction responds to intensity I .

At low intensity, the rising portion of the Hill-reaction curve is approximately linear:

$$Y_{\text{O}_2} \propto I,$$

so the apparent order is **1**.

At high intensity, the curve approaches a plateau. Increasing intensity produces essentially no further increase in oxygen yield:

$$Y_{\text{O}_2} \propto I^0,$$

so the apparent order is **0**.

2.4(b) — Chlorophyll molecules per oxygen molecule

The saturation yield is approximately

$$V_{\text{O}_2} = 12 \text{ mm}^3$$

per gram of chlorophyll per flash.

Convert the experimental conditions:

$$T = 283.15 \text{ K}, \quad p = \frac{740}{760}(101325) = 9.866 \times 10^4 \text{ Pa},$$

$$V_{\text{O}_2} = 12 \times 10^{-9} \text{ m}^3.$$

The ideal-gas equation gives

$$n(\text{O}_2) = \frac{pV}{RT} = \frac{(9.866 \times 10^4)(12 \times 10^{-9})}{8.314(283.15)} = 5.03 \times 10^{-7} \text{ mol}.$$

One gram of chlorophyll contains approximately

$$n(\text{chlorophyll}) = \frac{1 \text{ g}}{900 \text{ g mol}^{-1}} = 1.11 \times 10^{-3} \text{ mol.}$$

The molecular ratio equals the molar ratio:

$$\frac{N(\text{chlorophyll})}{N(\text{O}_2)} = \frac{1.11 \times 10^{-3}}{5.03 \times 10^{-7}} \approx \boxed{2.2 \times 10^3}.$$

Thus about 2200 chlorophyll molecules are associated with the production of one oxygen molecule per saturating flash. This is an effective pigment-to-output ratio; it does not mean that all these pigments directly perform the oxygen-forming redox chemistry.

2.5 — Quantum requirement

The total light energy supplied is

$$E_{\text{light}} = (0.503 \times 10^{-3} \text{ J s}^{-1})(2 \times 3600 \text{ s}) = 3.6216 \text{ J.}$$

Using

$$h = 6.626 \times 10^{-34} \text{ J s}, \quad c = 2.998 \times 10^8 \text{ m s}^{-1}, \quad N_A = 6.022 \times 10^{23} \text{ mol}^{-1},$$

the energy of one 672 nm photon is

$$\varepsilon_{\gamma} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34})(2.998 \times 10^8)}{672 \times 10^{-9}} = 2.956 \times 10^{-19} \text{ J.}$$

The amount of photons is consequently

$$n_{\gamma} = \frac{E_{\text{light}}}{N_A \varepsilon_{\gamma}} = 2.034 \times 10^{-5} \text{ mol.}$$

At the same pressure and temperature as in 2.4,

$$n(\text{O}_2) = \frac{(9.866 \times 10^4)(47.6 \times 10^{-9})}{8.314(283.15)} = 1.995 \times 10^{-6} \text{ mol.}$$

Each oxygen molecule corresponds to four electrons transferred from water:

$$n_e = 4n(\text{O}_2) = 7.979 \times 10^{-6} \text{ mol.}$$

Hence the quantum requirement is

$$q = \frac{n_{\gamma}}{n_e} = \frac{2.034 \times 10^{-5}}{7.979 \times 10^{-6}} = \boxed{2.55 \text{ photons per electron}}.$$

Equivalently, approximately 10.2 photons are required per oxygen molecule formed. The reciprocal electron yield is about 0.392 net electrons transferred per photon.

2.6 — Conclusions

Statement	Box to tick	Reason
In natural photosynthesis, water oxidation and CO ₂ reduction are separated in space.	Yes	This is the intended biological interpretation: water oxidation occurs at the thylakoid membrane, while carbon fixation occurs in the stroma. Hill's experiment demonstrates that oxygen evolution can operate with an alternative electron acceptor.

Statement	Box to tick	Reason
In chloroplasts, O ₂ is produced from CO ₂ .	No	Oxygen evolution occurs without carbon dioxide. Water is the oxygen source and electron donor.
Oxidation of water in chloroplasts requires light illumination.	Yes	The observed process is photochemical; the positive Gibbs energy calculated in 2.3(c) is consistent with its need for an energy input.
Most of chlorophylls in chloroplasts participate directly in the photochemical O ₂ production.	No	The large pigment-to-oxygen ratio is consistent with many chlorophyll molecules collecting and transferring excitation energy to a much smaller number of reaction centres.
In isolated chloroplasts, every absorbed photon causes transfer of one electron.	No	On the absorbed-energy interpretation of 2.5, approximately 2.55 photons are required per net electron transferred, giving only about 0.392 electron per photon.

The solution was checked against the official solution.

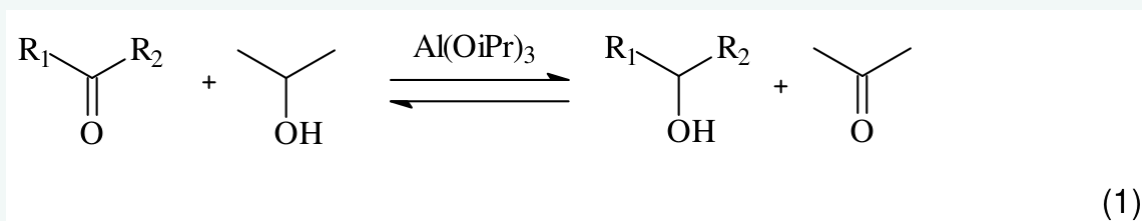
Problem 3: Meerwein-Schmidt-Ponndorf-Verley reaction

In the table for 3.3, A–F are editorial labels identifying the six structures in reading order.

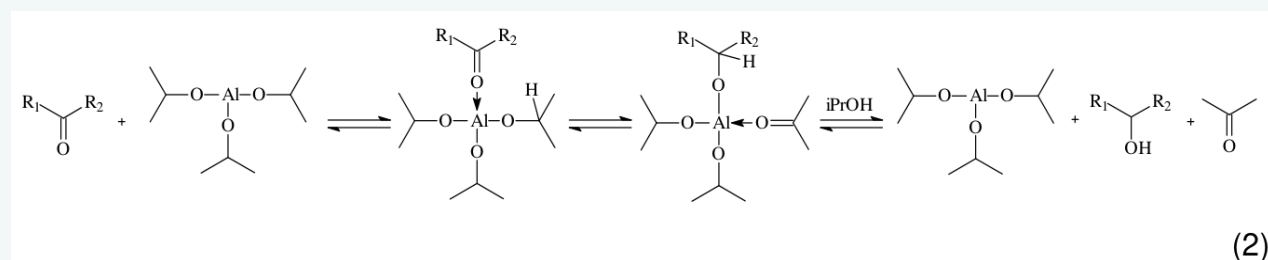
PROBLEM 3

Meerwein-Schmidt-Ponndorf-Verley reaction

Meerwein-Schmidt-Ponndorf-Verley (MSPV) reaction is a useful tool for reduction of carbonyl compounds to alcohols. The reaction is the reduction of carbonyl compounds by low molecular weight alcohols in the presence of alkoxides of aluminium or other metals:



The mechanism of the reaction includes coordination of carbonyl compound by aluminium alkoxide, hydride transfer in the inner sphere of the complex and subsequent transalkoxylation. It can be schematically represented as follows (transalkoxylation is shown as a one-step process for brevity):



The reaction is reversible and shifting the equilibrium to the desired product requires some excess of the reductant. In some cases (e. g. in the case of reduction of aromatic aldehydes and ketones) the equilibrium constant is so large that the reverse reaction can be neglected.

The table below contains standard entropies and standard enthalpies of formation of liquid substances at 298 K. The boiling points of the substances at 1 bar are also given.

Substance	$\Delta_f H_{298}^\circ, \text{ kJ mol}^{-1}$	$S_{298}^\circ, \text{ J mol}^{-1} \text{ K}^{-1}$	$t_{\text{vap}}, ^\circ\text{C}$
Acetone	-248.4	200.4	56
Isopropanol	-318.1	180.6	82
Cyclohexanone	-271.2	229.0	156
Cyclohexanol	-348.2	203.4	161

3.1 a Calculate the minimum isopropanol to cyclohexanone mass ratio which is required to reach a 99 % yield of reaction at 298 K. Assume that:

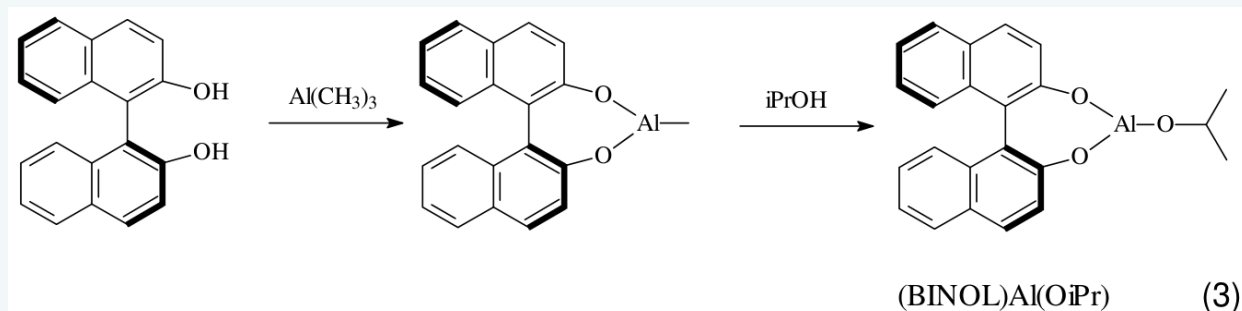
- i) the reaction mixture eventually gets at equilibrium,
- ii) no products are initially present.

3.1 b Choose the appropriate way(s) to increase the cyclohexanol yield. Tick the relevant boxes.

Increase the temperature up to 50 °C using a reflux	☐
Increase the temperature up to 60 °C, evaporating (distilling) the acetone	☐
Add some ethanol to the reaction mixture	☐
Add some ethanal to the reaction mixture	☐

3.2 Often the rate-limiting step in the MSPV reaction is the hydride transfer or the alcoholysis of the alkoxide after hydride transfer. For these two cases, using the above mechanism (2), derive an expression for the rate of reaction as a function of current concentrations of a carbonyl compound, isopropanol and a catalyst. In both cases determine the rate orders in the reactants and the catalyst. Assume that all reaction steps before the limiting step are fast and reversible. Use equilibrium approximation, if necessary. For brevity use the following notation: **A** for carbonyl compound, **B** for isopropanol, **C** for catalyst. Denote intermediates as you wish.

MSPV reaction can be used to obtain chiral alcohols, if the chiral catalyst is employed. For instance, Campbell et al. used the catalyst based on the chiral 2,2'-dihydroxy-1,1'-binaphthyl (BINOL), which is synthesized *in situ* from binaphtol and trimethylaluminium:

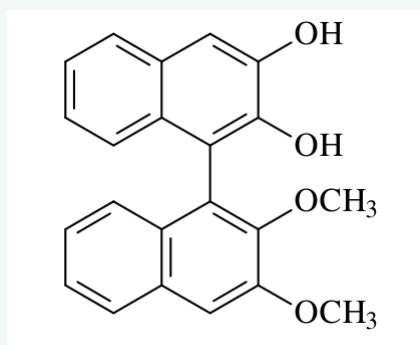


The chirality of BINOL is due to the sterically hindered rotation around the C—C bond. Though perfectly stable at room temperature, BINOL may racemize when heated.

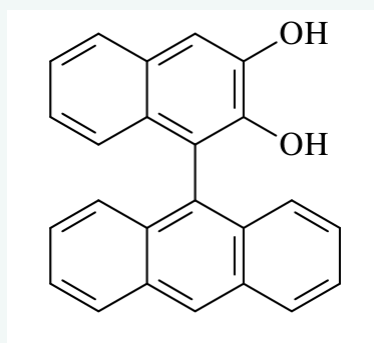
3.3 Which of the phenols below can form stable (at room temperature) enantiomers so that they can be used in the same fashion to produce a chiral catalyst? Tick the relevant boxes.

Substance	Can be used	Substance	Can be used
A		B	
C		D	
E		F	

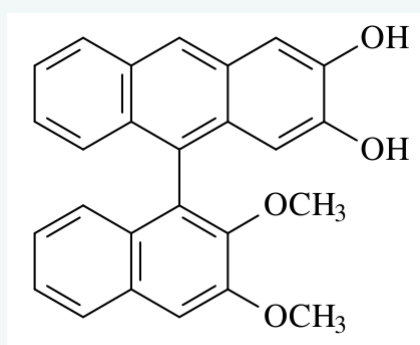
A:



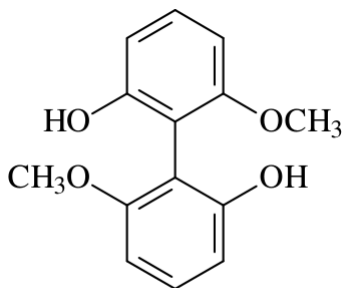
B:



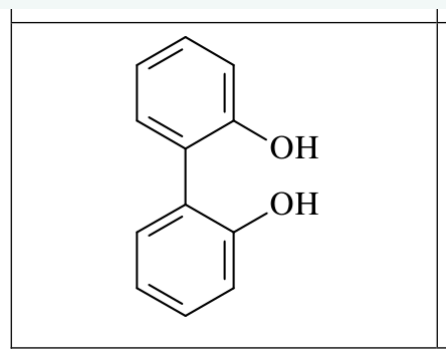
C:



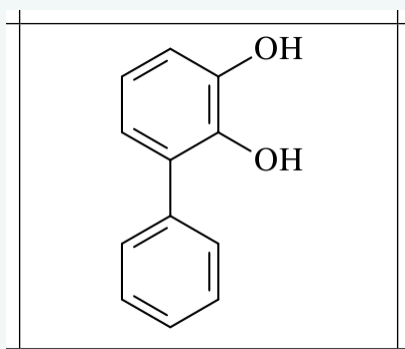
D:



E:



F:



Enantiomeric excess, ee , is used to characterize the enantiomeric purity of the substance. This quantity equals to the ratio of the difference of concentrations of enantiomers R and S to their sum:

$$ee = \frac{[R] - [S]}{[R] + [S]}$$

Enantiomeric excess of the pure R isomer is unity, ee of the racemic mixture is zero.

3.4 When using the enantiomerically pure (BINOL)Al(OiPr) as a catalyst for reduction of α -bromoacetophenone, the ee of the product equals 81 %. What is the ee of the product if the catalyst ee equals 50 %? Provide your calculation with an illustration or derivation of the final formula.

Official English text of the problem.

Answers

- **3.1 a:** The minimum initial mass ratio is

$$\frac{m(\text{isopropanol})}{m(\text{cyclohexanone})} \approx 6.94 : 1.$$

- **3.1 b:** Tick **distilling off acetone at 60 °C** and **adding ethanol**. Leave the other two boxes unticked.
- **3.2:** With $[C]$ denoting free catalyst:
- Hydride transfer limiting:

$$v = k_H K_1 [A][C], \quad (n_A, n_B, n_C) = (1, 0, 1).$$

- Alcoholysis limiting:

$$v = k_{\text{alc}} K_1 K_2 [A][B][C], \quad (n_A, n_B, n_C) = (1, 1, 1).$$

- **3.3:** Tick **A, C and D**: the **top-left, middle-left and middle-right** structures.
- **3.4:**

$$ee_{\text{product}} = 0.81(0.50) = 0.405 = 40.5\%.$$

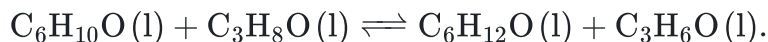
Solution

3.1 a

The reacting substances are:

- Cyclohexanone: O=C1CCCCC1
- Isopropanol, or propan-2-ol: CC(O)C
- Cyclohexanol: OC1CCCCC1
- Acetone, or propan-2-one: CC(=O)C

The balanced reaction is



From the supplied formation enthalpies,

$$\begin{aligned} \Delta_r H^\circ &= (-348.2 - 248.4) - (-271.2 - 318.1) \\ &= -7.3 \text{ kJ mol}^{-1}. \end{aligned}$$

Similarly,

$$\begin{aligned} \Delta_r S^\circ &= (203.4 + 200.4) - (229.0 + 180.6) \\ &= -5.8 \text{ J mol}^{-1} \text{ K}^{-1}. \end{aligned}$$

Consequently, at 298 K,

$$\begin{aligned} \Delta_r G^\circ &= \Delta_r H^\circ - T\Delta_r S^\circ \\ &= -7.300 - 298(-0.0058) \\ &= -5.5716 \text{ kJ mol}^{-1}. \end{aligned}$$

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

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left(\frac{5571.6}{8.314(298)}\right) = 9.4765.$$

Assume ideal liquid-mixture behaviour, so activities can be represented by mole fractions. Because the reaction has equal total stoichiometric coefficients on both sides, the total-mole factors cancel.

Take initially 1.000 mol cyclohexanone and b mol isopropanol. At 99 % conversion:

Substance	Initial amount / mol	Equilibrium amount / mol
Cyclohexanone	1.000	0.010
Isopropanol	b	$b - 0.990$
Cyclohexanol	0	0.990
Acetone	0	0.990

Thus,

$$K = \frac{(0.990)^2}{0.010(b - 0.990)}.$$

Solving,

$$b = 0.990 + \frac{0.990^2}{0.010(9.4765)} = 11.3324.$$

Using molar masses 60.10 g mol^{-1} for isopropanol and 98.15 g mol^{-1} for cyclohexanone,

$$\frac{m(\text{isopropanol})}{m(\text{cyclohexanone})} = \frac{11.3324(60.10)}{1.000(98.15)} = 6.939.$$

Therefore,

$$m(\text{isopropanol}) : m(\text{cyclohexanone}) \approx 6.94 : 1.$$

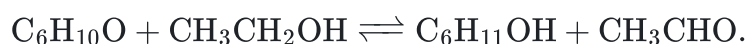
This is the minimum because any smaller initial isopropanol charge gives an equilibrium conversion below 99 %.

3.1 b

Proposed change	Tick?	Reason
Heat to 50 °C under reflux	No	The forward reaction is exothermic, so heating decreases its equilibrium constant. Reflux returns volatile substances to the mixture.
Heat to 60 °C while distilling acetone	Yes	Removing acetone, a reaction product, shifts the reaction towards cyclohexanol. Acetone has the lowest listed boiling point, 56 °C.
Add ethanol	Yes	Ethanol supplies an additional reducing alcohol and is oxidized to ethanal.
Add ethanal	No	Ethanal is a hydrogen acceptor and promotes oxidation of alcohols, opposing the desired reduction.

The additional substances are ethanol CCO and ethanal, or acetaldehyde, CC=O .

Their coupled transfer-hydrogenation reaction is



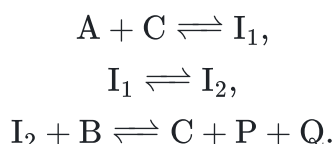
Adding ethanol favours the forward direction. Adding ethanal favours the reverse direction, consuming cyclohexanol.

For heating alone, the sign also follows from the van 't Hoff equation:

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2} < 0.$$

3.2

Let P denote the product alcohol and Q acetone. The mechanism can be written schematically as



Here:

- A is the carbonyl substrate, generic SMILES [*:1]C(=O)[*:2].
- B is isopropanol, CC(O)C.
- C is aluminium triisopropoxide, CC(C)O[Al](OC(C)C)OC(C)C.
- P is the corresponding alcohol, generic SMILES [*:1]C(O)[*:2].
- Q is acetone, CC(=O)C.
- I_1 is the carbonyl–aluminium coordination complex, represented schematically by CC(C)O[Al](OC(C)C)(OC(C)C)<-O=C([*:1])[*:2].
- I_2 is the mixed aluminium alkoxide with coordinated acetone after hydride transfer, represented by CC(C)O[Al](OC(C)C)(OC([*:1])[*:2])<-O=C(C)C.

The wildcard groups denote the substrate substituents. These SMILES describe the monomeric connectivity used in the problem; $<-$ denotes oxygen-to-aluminium coordination. They do not show the cyclic arrangement during hydride transfer.

In that transfer, the coordinated isopropoxide donates its carbon-bound hydrogen to the substrate carbonyl carbon while becoming acetone. The substrate carbonyl oxygen becomes an alkoxide oxygen. Free hydride need not be released.

Define the pre-equilibrium constants

$$K_1 = \frac{[I_1]}{[A][C]}, \quad K_2 = \frac{[I_2]}{[I_1]}.$$

Hydride transfer is rate-limiting.

The first coordination step is at equilibrium:

$$[I_1] = K_1[A][C].$$

Hydride transfer occurs within I_1 , so its forward rate is

$$v = k_H[I_1] = k_H K_1[A][C].$$

Hence the orders are

$$\boxed{n_A = 1, \quad n_B = 0, \quad n_C = 1}.$$

Free isopropanol does not participate in this limiting step: the hydrogen donor is already an isopropoxide ligand on the catalyst.

Alcoholysis is rate-limiting.

Both preceding steps are at equilibrium:

$$[I_2] = K_2[I_1] = K_1K_2[A][C].$$

The limiting step involves I_2 and one molecule of isopropanol:

$$v = k_{\text{alc}}[I_2][B] = k_{\text{alc}}K_1K_2[A][B][C].$$

Therefore,

$$\boxed{n_A = 1, \quad n_B = 1, \quad n_C = 1}.$$

These expressions refer to **free catalyst concentration** and to forward rates, or net rates when the reverse reaction is negligible.

If catalyst concentration instead means total catalyst loading C_T , binding can produce saturation. For hydride transfer limiting, neglecting the rapidly consumed downstream intermediate,

$$C_T \simeq [C] + [I_1], \quad v = \frac{k_H K_1 [A] C_T}{1 + K_1 [A]}.$$

For alcoholysis limiting,

$$C_T = [C] + [I_1] + [I_2], \quad v = \frac{k_{\text{alc}} K_1 K_2 [A] [B] C_T}{1 + K_1 [A] (1 + K_2)}.$$

Thus the reaction remains first order in total catalyst, while its apparent substrate order can decrease from one towards zero as binding saturates.

3.3

Stable biaryl enantiomers require both:

1. A stereogenic axis: the two paths around the aromatic framework at **each** end of the axis must be distinguishable.
2. Sufficiently hindered rotation to prevent rapid interconversion at room temperature.

The following SMILES specify connectivity. Ordinary SMILES do not reliably distinguish these biaryl axial configurations; the two stable atropisomers must additionally be designated (R_a) and (S_a). The flat drawings do not select one of them.

- **A — top left: tick.**

2',3'-Dimethoxy-[1,1'-binaphthalene]-2,3-diol, c1(-
c2c(OC)c(OC)cc3ccccc23)c(O)c(O)cc2ccccc12.

Both ends of the binaphthyl axis have distinguishable ring paths. The crowded ortho and peri environments strongly hinder rotation, allowing stable atropisomers.

- **B — top right: leave unticked.**

1-(Anthracen-9-yl)naphthalene-2,3-diol, c1(-
c2c3ccccc3cc3ccccc23)c(O)c(O)cc2ccccc12.

The two paths through the unsubstituted anthracen-9-yl group are symmetry-equivalent. Thus the connecting bond does not constitute a stereogenic axis, despite its steric crowding.

- **C — middle left: tick.**

9-(2,3-Dimethoxynaphthalen-1-yl)anthracene-2,3-diol, c1(-c2c(OC)c(OC)cc3ccccc23)c2cc(O)c(O)cc2cc2ccccc12.

Unlike B, the anthracene fragment has hydroxyl substituents on only one terminal ring, making its two paths different. The naphthalene end also has distinct paths, and rotation is strongly hindered.

- **D — middle right: tick.**

6,6'-Dimethoxy-[1,1'-biphenyl]-2,2'-diol, COc1cccc(O)c1-c1c(O)cccc1OC.

Each ring has different ortho substituents, hydroxyl and methoxy, so the axis is stereogenic. Occupation of all four ortho positions provides the rotational hindrance needed for stable enantiomers.

- **E — bottom left: leave unticked.**

[1,1'-Biphenyl]-2,2'-diol, Oc1cccc1-c1cccc1O.

Twisted conformations can be chiral, but the two hydroxyl groups alone do not sufficiently hinder rotation. The mirror-image conformations interconvert too readily at room temperature.

- **F — bottom right: leave unticked.**

[1,1'-Biphenyl]-2,3-diol, c1(-c2ccccc2)c(O)c(O)ccc1.

The unsubstituted phenyl end has equivalent ring paths, so the connecting bond is not a stereogenic axis.

The completed answer-sheet pattern is therefore

Row	Left box	Right box
Top	✓	
Middle	✓	✓
Bottom		

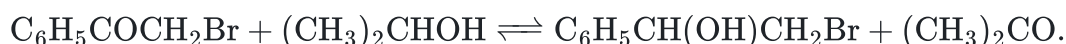
3.4

The substrate is **2-bromo-1-phenylethan-1-one**, commonly called α -bromoacetophenone or phenacyl bromide: O=C(CBr)c1ccccc1.

Reduction gives **2-bromo-1-phenylethan-1-ol**:

- (*R*)-enantiomer: O[C@@H](CBr)c1ccccc1
- (*S*)-enantiomer: O[C@H](CBr)c1ccccc1

The balanced reaction is



BINOL is **[1,1'-binaphthalene]-2,2'-diol**, Oc1ccc2ccccc2c1-c1c(O)ccc2ccccc12.

Its catalyst is **aluminium isopropoxide chelated by binaphthalene-2,2'-diolate**, represented by CC(C)O[Al]1OCC2CCC3CCCC3C2-c2c(O)CCC3CCCC323. Its axial configuration must additionally be specified as discussed in 3.3.

Assume the two catalyst enantiomers act independently and have equal total activity. They then give equal and opposite product selectivities.

Call the catalyst enantiomer that favours R C_+ , and its mirror image C_- . With pure C_+ , the product fractions satisfy

$$f_R + f_S = 1, \quad f_R - f_S = 0.81.$$

Therefore,

$$f_R = \frac{1 + 0.81}{2} = 0.905, \quad f_S = \frac{1 - 0.81}{2} = 0.095.$$

Pure C_- gives the reversed proportions.

A catalyst ee of 50 % means

$$f_{C_+} = \frac{1 + 0.50}{2} = 0.75, \quad f_{C_-} = \frac{1 - 0.50}{2} = 0.25.$$

The product fractions are consequently

$$\begin{aligned} f_R &= 0.75(0.905) + 0.25(0.095) = 0.7025, \\ f_S &= 0.75(0.095) + 0.25(0.905) = 0.2975. \end{aligned}$$

Thus,

$$ee_{\text{product}} = \frac{0.7025 - 0.2975}{0.7025 + 0.2975} = 0.405.$$

More generally, if e_0 is the product ee obtained with pure catalyst and e_C is the catalyst ee ,

$$\begin{aligned} f_R &= \frac{1 + e_C}{2} \frac{1 + e_0}{2} + \frac{1 - e_C}{2} \frac{1 - e_0}{2} = \frac{1 + e_C e_0}{2}, \\ f_S &= \frac{1 - e_C e_0}{2}. \end{aligned}$$

Hence

$$ee_{\text{product}} = e_C e_0 = 40.5\%.$$

The solution was checked against the official solution.

Problem 4: A simple inorganic experiment

Compound **A** which contains metal **X** is a colourless crystalline solid and highly soluble in water. It is used as a reagent in analysis and gives in alkali media a binary compound **B** containing 6.9 % (mass) of oxygen. Under heating **A** decomposes with a mass loss of 36.5 %.

4.1 Determine the metal **X** and compounds **A** and **B**.

Upon adding some amount of sodium thiosulfate to the solution of **A** the colour immediately becomes red, then changes to reddish-brown, and after some minutes a dark-brown precipitate **C** forms (reaction 1). The solution over it is colourless. Being heated on air at 600 °C, **C** gives a grey powder **X** (reaction 2), so as 0.90 g of residue can be obtained from 1.10 g of **C**. A gas evolved by heating **C** in vacuum (reaction 3) can be absorbed by calcium hydroxide suspension (reaction 4). Being stored for a long time under saturated solution of barium perchlorate in HClO_4 ($c = 0.1 \text{ mol dm}^{-3}$), the colour of the precipitate becomes lighter, while the use of magnesium perchlorate does not give such an effect.

4.2 What is **C**? Write the equations of the reactions 1 – 4.

The compound **C** being stored under the mother liquor (containing an excess of **A**) changes its colour to yellow due to the transformation into **D**. If barium ions are added to the suspension of **C** in the mother liquor, a mixture of **D** and of a white precipitate is formed.

4.3 Propose the formula of **D**, taking into account that it contains 77.5 mass % of **X**. Give the equation of **D** formation.

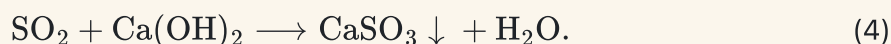
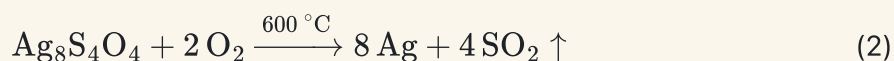
Official English text of the problem.

Answers

- **4.1:** **X** is silver, Ag; **A** is silver(I) nitrate, AgNO₃; **B** is silver(I) oxide, Ag₂O.
- **4.2:** **C** is silver(I) sulfide sulfate,



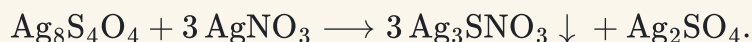
The reactions are:



- **4.3:** **D** is silver(I) sulfide nitrate,



Its formation can be written:



Solution

4.1 — Identification of **X**, **A** and **B**

An oxide formed when alkali is added to a soluble metal salt is consistent with **B**. For a monovalent metal oxide, X₂O, the oxygen mass fraction gives

$$\frac{16.0}{2M(\text{X}) + 16.0} = 0.069,$$

hence

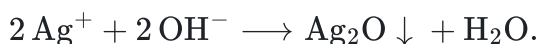
$$M(\text{X}) = \frac{16.0}{2} \left(\frac{1}{0.069} - 1 \right) \approx 108 \text{ g mol}^{-1}.$$

This identifies silver. Its oxide, Ag₂O, contains

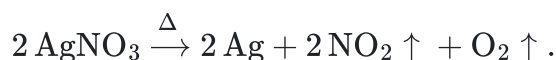
$$w(\text{O}) = \frac{16.0}{2(108) + 16.0} \times 100\% = 6.90\%,$$

in agreement with the stated 6.9%.

Silver nitrate is a colourless, water-soluble analytical reagent. Its precipitation with alkali is



On heating, silver nitrate decomposes:



Using rounded molar atomic masses 108, 14.0, 16.0 g mol⁻¹ for silver, nitrogen and oxygen, respectively,

$$M(\text{AgNO}_3) = 170 \text{ g mol}^{-1}.$$

The predicted mass loss is therefore

$$\frac{170 - 108}{170} \times 100\% = 36.5\%,$$

which confirms **A** as AgNO₃.

4.2 — Identification of C and reactions 1–4

The silver mass fraction in **C** is

$$w(\text{Ag}) = \frac{0.90 \text{ g}}{1.10 \text{ g}} \approx 0.818.$$

Pure silver sulfide would contain

$$\frac{216}{216 + 32.0} \times 100\% = 87.1\%$$

silver, so **C** is not simply Ag₂S.

The barium experiment indicates a sulfate component: barium can remove sulfate as white, sparingly soluble BaSO₄, whereas magnesium sulfate remains soluble. Together with the dark sulfide-containing precipitate, this suggests a compound containing both Ag₂S and Ag₂SO₄.

Let there be r sulfide formula units per sulfate formula unit. Using $M(\text{S}) = 32.0 \text{ g mol}^{-1}$,

$$M(\text{Ag}_2\text{S}) = 248 \text{ g mol}^{-1}, \quad M(\text{Ag}_2\text{SO}_4) = 312 \text{ g mol}^{-1}.$$

Consequently,

$$\frac{216(r + 1)}{248r + 312} = \frac{0.90}{1.10},$$

which gives $r = 3$. Thus

$$\boxed{\text{C} = \text{Ag}_8\text{S}_4\text{O}_4 = 3\text{Ag}_2\text{S} \cdot \text{Ag}_2\text{SO}_4}.$$

The predicted silver residue is

$$1.10 \text{ g} \times \frac{8(108)}{8(108) + 4(32.0) + 4(16.0)} = 0.90 \text{ g}.$$

The lightening in the barium experiment is explained by

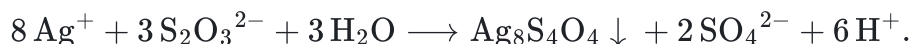


White barium sulfate forms alongside the remaining dark silver sulfide.

For **reaction 1**, thiosulfate undergoes disproportionation. The underlying balanced transformation is



Three such transformations produce three sulfide ions and three sulfate ions. Precipitation of eight silver ions incorporates all three sulfides and one sulfate into **C**, leaving two sulfates in solution:



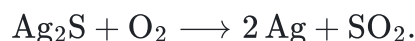
For **reaction 3**, heating in vacuum permits internal oxidation–reduction between the sulfate component and one sulfide component:



The other two sulfide components remain, giving



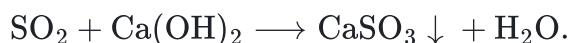
For **reaction 2**, oxygen in air also allows the remaining silver sulfide to yield silver:



Adding this reaction twice to the vacuum decomposition gives



The evolved gas is therefore sulfur dioxide. Its absorption by calcium hydroxide gives calcium sulfite, **reaction 4**:



4.3 — Identification and formation of **D**

The mother liquor contains excess silver nitrate. The sulfate released during formation of **D** can account for the additional white barium sulfate precipitate. A natural candidate is therefore a silver sulfide–silver nitrate compound.

Let its composition be $\text{Ag}_2\text{S} \cdot x \text{AgNO}_3$. Its silver mass fraction must satisfy

$$\frac{216 + 108x}{248 + 170x} = 0.775.$$

Solving,

$$x = \frac{216 - 0.775(248)}{0.775(170) - 108} \approx 1.00.$$

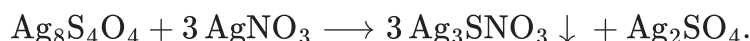
Thus

$$\boxed{\text{D} = \text{Ag}_3\text{SNO}_3 = \text{Ag}_2\text{S} \cdot \text{AgNO}_3}.$$

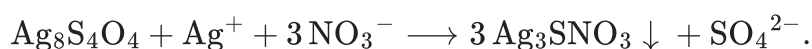
Its calculated silver content is

$$\frac{3(108)}{3(108) + 32.0 + 14.0 + 3(16.0)} \times 100\% = \frac{324}{418} \times 100\% = 77.5\%.$$

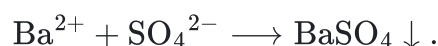
Formation of **D** is represented by



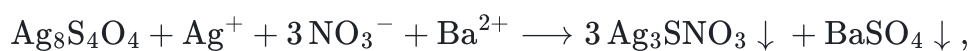
Writing dissolved silver sulfate as ions and cancelling silver ions gives the net ionic form



If barium ions are present, the released sulfate precipitates:



The combined reaction is



explaining the mixture of yellow **D** and white barium sulfate.

Names and SMILES

The identified compounds are extended ionic solids. Their formulas specify the proportions of the constituent ions below; these SMILES do not describe their crystal lattices or coordination geometries.

Molecule or ion	SMILES
Silver(I) ion, Ag^+	[Ag+]
Oxide ion, O^{2-}	[O-2]
Sulfide ion, S^{2-}	[S-2]
Nitrate ion, NO_3^-	[O-] [N+] (=O) [O-]
Sulfate ion, SO_4^{2-}	[O-] S (=O) (=O) [O-]
Thiosulfate ion, $\text{S}_2\text{O}_3^{2-}$	[O-] S (=O) (=O) [S-]
Sulfite ion, SO_3^{2-}	[O-] S (=O) [O-]
Hydroxide ion, OH^-	[OH-]
Hydrogen ion (proton), H^+	[H+]
Calcium ion, Ca^{2+}	[Ca+2]
Barium ion, Ba^{2+}	[Ba+2]
Magnesium ion, Mg^{2+}	[Mg+2]
Water, H_2O	O
Sulfur dioxide, SO_2	O=S=O
Nitrogen dioxide, NO_2 , a radical	[O-] [N+] =O
Dioxygen, O_2	O=O

The solution was checked against the official solution.

Problem 5: Simple estimates of graphene properties

Graphene is a two-dimensional, one atom thick carbon material (Fig. 1 a). Many layers of graphene stack together to form graphite (Fig. 1 b).

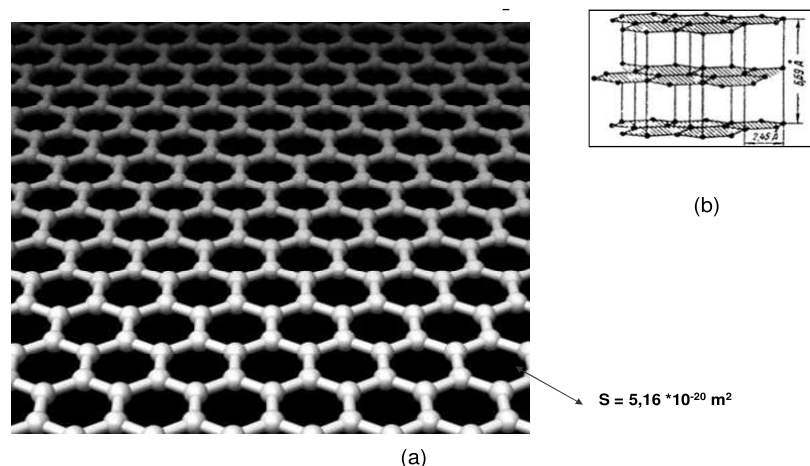


Fig. 1. (a) The structure of graphene. Spheres are carbon atoms. They are arranged in hexagons. The area of one carbon hexagon is $5.16 \cdot 10^{-20} \text{ m}^2$. (b) Crystal lattice of graphite. Three graphene layers are shown.

Such atomic structure was long considered to be unstable. However, in 2004 Andrey Geim and Konstantin Novoselov have reported production of the first samples of this unusual material. This groundbreaking invention was awarded by Nobel prize in 2010.

Experimental studies of graphene are still restricted. Production of massive portions of the new substance still is a challenging synthetic problem. Many properties of graphene were estimated. Usually, there is not enough information for rigorous calculations, so we have to make assumptions and neglect unimportant factors. In this problem, you will estimate the adsorption properties of graphene.

5.1 Estimate the specific surface of graphene open for adsorption in units $\text{m}^2 \text{ g}^{-1}$. Consider that graphene plane is separated from any other solid or liquid substance.

The single layer of nitrogen molecules adsorbed on the outer surface of graphite is shown in Fig. 2. Assume that the same arrangement of nitrogen molecules is formed on a graphene surface.

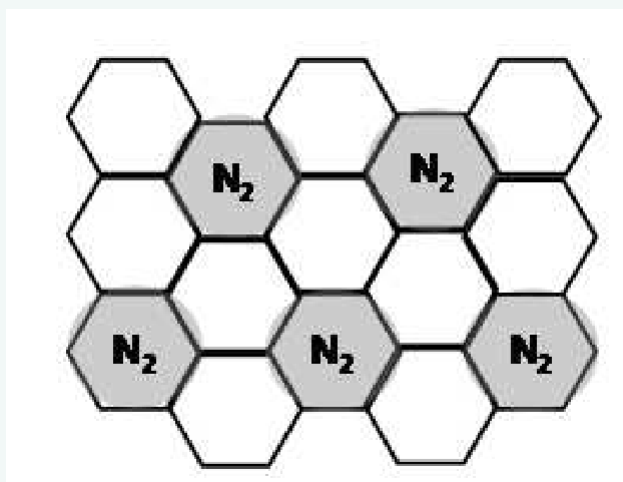


Fig. 2. Nitrogen molecules N_2 (grey circles) on the outer surface of graphite

5.2 How many grams of nitrogen can be adsorbed on 1 gram of graphene assuming that the graphene layer is placed onto the surface of a solid support? Estimate the volume occupied by these nitrogen molecules after the complete desorption from 1 g of graphene (pressure 1 bar, temperature 298 K).

Let us consider adsorption as a common chemical equilibrium



(A_{gas} are molecules A in the gaseous state, A_{ads} are the same molecules on the surface)

with the equilibrium constant K :

$$K = \frac{n_{A_{\text{ads}}} (\text{mol m}^{-2})}{p_{A_{\text{gas}}} (\text{bar})}$$

(Such an assumption holds if a small number of molecules is adsorbed on the surface.)

Adsorption properties of graphene can be estimated from the data for adsorption on a regular three-dimensional graphite. The enthalpy of adsorption (ΔH° of reaction (1)) of any molecule A on graphene is on average by 10 % less negative compared to that on graphite. On graphite, the adsorbed molecule is bound more strongly due to the interaction with the lower graphene layers in the lattice (Fig. 1 b) and hence the enthalpy of adsorption is more negative. The standard entropies of adsorption on graphene and graphite are assumed to be the same.

5.3 How many moles, n , of CCl_4 are adsorbed on 1 g of graphene at $p(\text{CCl}_4) = 10^{-4}$ bar if $2.0 \cdot 10^{-7}$ mol of CCl_4 are adsorbed on 1 m^2 of graphite at $p(\text{CCl}_4) = 6.6 \cdot 10^{-5}$ bar? Assume that graphene is placed onto the surface of a solid support and the interaction of CCl_4 with the support does not change the enthalpy of adsorption of CCl_4 on graphene. The temperature in both cases is 293 K. ΔH° of adsorption of CCl_4 on graphite is -35.1 kJ/mol .

The graphene films are expected to be sensitive gas detectors. If 10^9 particles of a gas are adsorbed on 1 cm^2 of a graphene surface this is enough to measure an electrical resistivity change of the graphene layer and to detect the presence of a gas in the environment.

5.4 Determine the minimal content of ethane, C_2H_6 , in the air (in mol. %) at atmospheric pressure ($T = 293 \text{ K}$) at which a graphene sensor will detect this gas. The known data for the adsorption of alkanes on graphite are shown in Fig 3. Assume that air doesn't affect the adsorption properties of ethane.

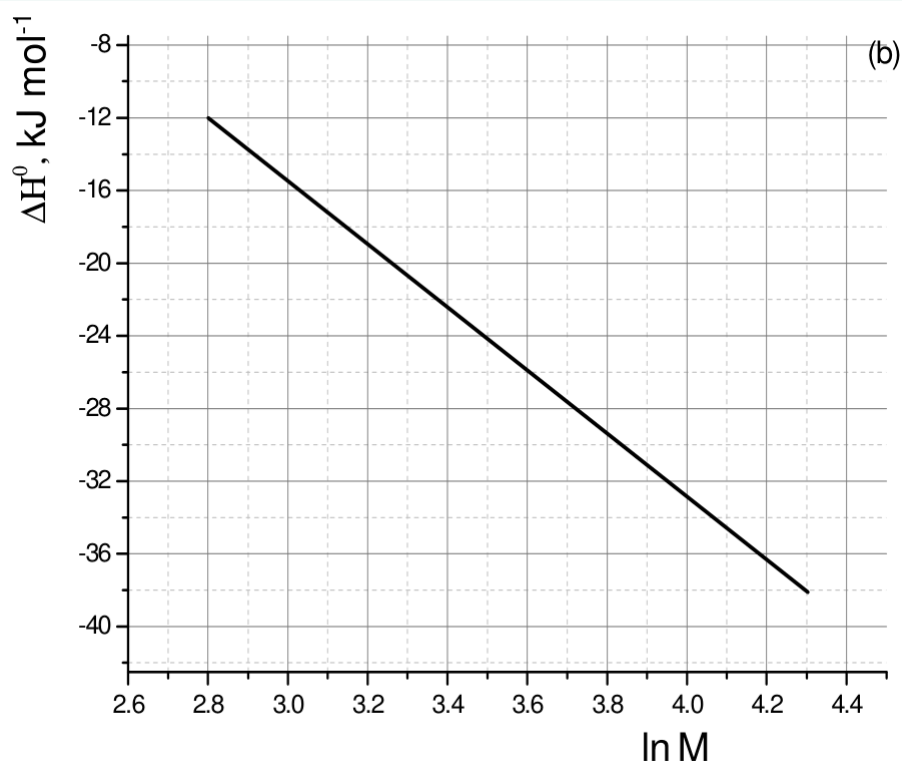
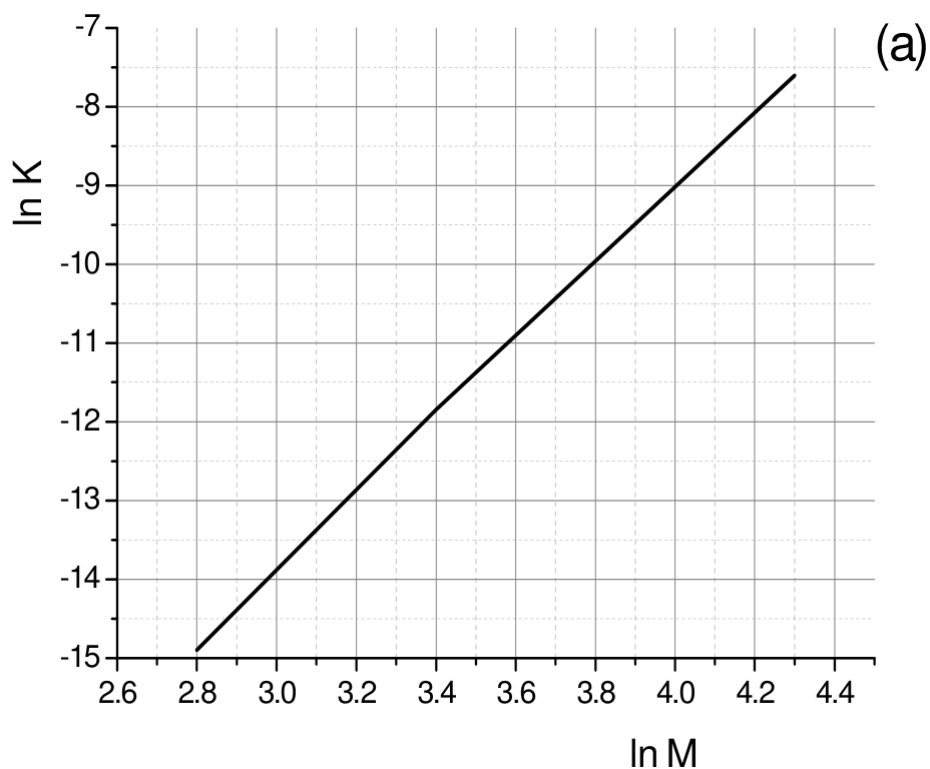


Fig. 3

Thermodynamic properties for adsorption of alkanes on a graphite surface.

(a) $\ln K$ [$\text{mol m}^{-2} \text{bar}^{-1}$] as a function of $\ln M$ (M - molar mass of alkane in g mol^{-1});

(b) ΔH° of adsorption as a function of $\ln M$.

Linear dependences are assumed in both cases

Official English text of the problem.

Answers

- **5.1:** $2.59 \times 10^3 \text{ m}^2 \text{ g}^{-1}$, counting both exposed faces.
- **5.2:** Nitrogen, N_2 , SMILES $\text{N}\#\text{N}$: 0.389 g adsorbed per gram of supported graphene; after desorption, 0.344 L at 1 bar and 298 K.
- **5.3:** Carbon tetrachloride, CCl_4 , SMILES $\text{ClC}(\text{Cl})(\text{Cl})\text{Cl}$: $9.3 \times 10^{-5} \text{ mol}$ adsorbed.
- **5.4:** Ethane, C_2H_6 , SMILES CC : approximately $6.6 \times 10^{-4} \text{ mol. \%}$, or about 7 ppm by mole, subject to graphical reading precision.

Solution

Use $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$, and the approximate molar masses $M(\text{C}) = 12.0$, $M(\text{N}_2) = 28.0$, and $M(\text{C}_2\text{H}_6) = 30.0 \text{ g mol}^{-1}$.

5.1

Each carbon hexagon has six vertices, and each carbon atom belongs to three adjacent hexagons. Thus, neglecting sheet edges, one hexagon accounts for

$$\frac{6}{3} = 2 \text{ carbon atoms.}$$

Its corresponding mass is

$$m_{\text{hex}} = \frac{2M(\text{C})}{N_A}.$$

Both faces of the isolated graphene sheet are accessible, so the adsorption area corresponding to one hexagon is $2S$. Therefore,

$$a_{\text{both}} = \frac{2S}{2M(\text{C})/N_A} = \frac{SN_A}{M(\text{C})}.$$

Substitution gives

$$a_{\text{both}} = \frac{(5.16 \times 10^{-20} \text{ m}^2)(6.022 \times 10^{23} \text{ mol}^{-1})}{12.0 \text{ g mol}^{-1}} = 2.59 \times 10^3 \text{ m}^2 \text{ g}^{-1}.$$

For subsequent parts involving a solid support, only one face is accessible:

$$a_{\text{one}} = \frac{a_{\text{both}}}{2} = 1.295 \times 10^3 \text{ m}^2 \text{ g}^{-1}.$$

5.2

The repeating arrangement in Fig. 2 places one nitrogen molecule over every three carbon hexagons. Since each hexagon accounts for two carbon atoms, this means

$$1 \text{ adsorbed } \text{N}_2 \text{ molecule per } 6 \text{ carbon atoms.}$$

Only the upper face of supported graphene is accessible. Consequently, for 1 g of graphene,

$$n(\text{N}_2) = \frac{1}{6} \frac{1.00 \text{ g}}{12.0 \text{ g mol}^{-1}} = 1.389 \times 10^{-2} \text{ mol.}$$

The adsorbed nitrogen mass is

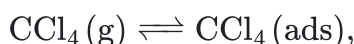
$$m(\text{N}_2) = n(\text{N}_2)M(\text{N}_2) = (1.389 \times 10^{-2})(28.0) = \boxed{0.389 \text{ g}}.$$

After complete desorption, treating the nitrogen as an ideal gas,

$$V = \frac{nRT}{p} = \frac{(1.389 \times 10^{-2} \text{ mol})(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1 \text{ bar}} = \boxed{0.344 \text{ L}}.$$

5.3

For the adsorption equilibrium



let Γ denote the adsorbed amount per unit area. The given equilibrium relation is

$$\Gamma = Kp.$$

The graphite data give

$$K_{\text{graphite}} = \frac{2.0 \times 10^{-7} \text{ mol m}^{-2}}{6.6 \times 10^{-5} \text{ bar}} = 3.03 \times 10^{-3} \text{ mol m}^{-2} \text{ bar}^{-1}.$$

The adsorption enthalpy on graphene is 10% less negative:

$$\Delta H_{\text{graphene}}^{\circ} = 0.90(-35.1) = -31.59 \text{ kJ mol}^{-1}.$$

Because the adsorption entropies are equal,

$$\Delta G_{\text{graphene}}^{\circ} - \Delta G_{\text{graphite}}^{\circ} = \Delta H_{\text{graphene}}^{\circ} - \Delta H_{\text{graphite}}^{\circ} = +3.51 \text{ kJ mol}^{-1}.$$

Using consistent standard states for both surfaces,

$$\ln \frac{K_{\text{graphene}}}{K_{\text{graphite}}} = -\frac{3510}{8.314 \times 293} = -1.441.$$

Thus,

$$K_{\text{graphene}} = (3.03 \times 10^{-3})e^{-1.441} = 7.17 \times 10^{-4} \text{ mol m}^{-2} \text{ bar}^{-1}.$$

The weaker adsorption on graphene correctly gives the smaller equilibrium constant. At the specified pressure,

$$\Gamma_{\text{graphene}} = (7.17 \times 10^{-4})(10^{-4}) = 7.17 \times 10^{-8} \text{ mol m}^{-2}.$$

One gram of supported graphene exposes $1.295 \times 10^3 \text{ m}^2$, so

$$n = \Gamma_{\text{graphene}}A = (7.17 \times 10^{-8})(1.295 \times 10^3) = \boxed{9.3 \times 10^{-5} \text{ mol}}.$$

5.4

For ethane,

$$\ln M = \ln(30.0) = 3.40.$$

Reading Fig. 3 at this abscissa gives approximately

$$\ln K_{\text{graphite}} \approx -12.0, \quad \Delta H_{\text{graphite}}^{\circ} \approx -22 \text{ kJ mol}^{-1}.$$

Here K is expressed in the units specified by the graph. Applying the same enthalpy correction as in 5.3,

$$\Delta H_{\text{graphene}}^{\circ} \approx 0.90(-22) = -19.8 \text{ kJ mol}^{-1},$$

and hence

$$\ln \frac{K_{\text{graphene}}}{K_{\text{graphite}}} = -\frac{2200}{8.314 \times 293} = -0.903.$$

Therefore,

$$\begin{aligned}\ln K_{\text{graphene}} &\approx -12.903, \\ K_{\text{graphene}} &\approx 2.49 \times 10^{-6} \text{ mol m}^{-2} \text{ bar}^{-1}.\end{aligned}$$

The detection threshold is 10^9 molecules per square centimetre. Since $1 \text{ cm}^2 = 10^{-4} \text{ m}^2$,

$$\Gamma_{\min} = \frac{10^9}{(10^{-4} \text{ m}^2)N_{\text{A}}} = 1.66 \times 10^{-11} \text{ mol m}^{-2}.$$

Using $\Gamma = Kp$, the minimum ethane partial pressure is

$$p_{\min} = \frac{1.66 \times 10^{-11}}{2.49 \times 10^{-6}} \approx 6.67 \times 10^{-6} \text{ bar}.$$

For an ideal gas mixture, mole fraction equals partial pressure divided by total pressure. Taking atmospheric pressure as 1.01325 bar,

$$x_{\min} = \frac{p_{\min}}{P} \approx 6.58 \times 10^{-6}.$$

Thus the minimum molar percentage is

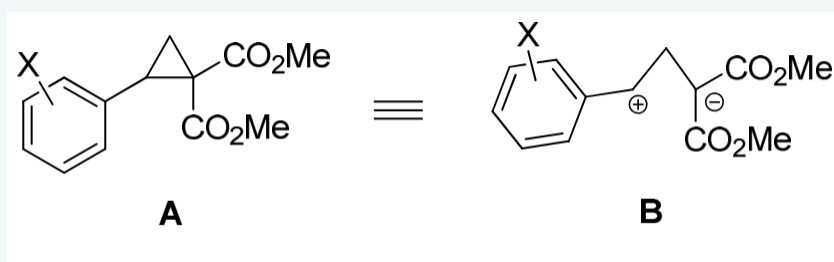
$$100x_{\min} \approx 6.6 \times 10^{-4} \text{ mol. \%},$$

equivalent to approximately 7 ppm by mole.

The solution was checked against the official solution.

Problem 6: Cyclopropanes. So simple. So fancy...

Cyclopropanes bearing donor and acceptor substituents at the neighbouring C-atoms, for example, **A**, demonstrate high reactivity behaving similar to 1,3-zwitterion **B**.



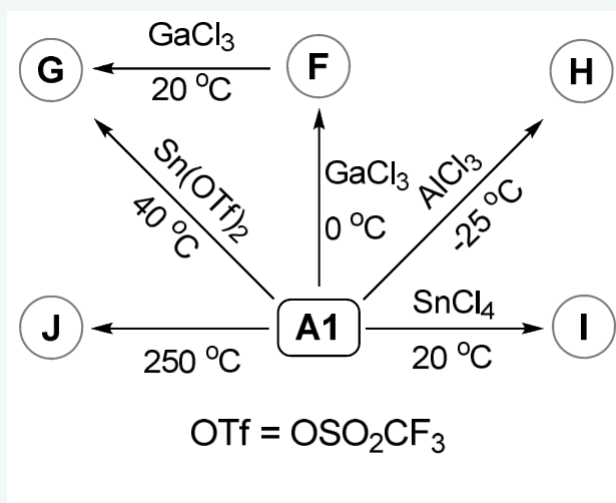
Thus, **A1** ($X = 4\text{-OMe}$) undergoes the three-membered ring opening in the Lewis acid-catalyzed reaction with 1,3-dimethoxybenzene as a nucleophile giving the product **C**.

6.1 Write down structural formula of **C**.

A1 participates in cycloadditions, annulations, oligomerizations, and other processes. Thus, [3+2]-cycloaddition between **A1** and 4-methoxybenzaldehyde leads to a five-membered ring in **D**. Complete decarboxylation of **D** produces **E** ($\text{C}_{18}\text{H}_{20}\text{O}_3$), the molecule of the latter having a plane of symmetry.

6.2 Write down structural formulae of **D** and **E** indicating their stereochemistry.

Also, **A**, can undergo various transformations in the absence of any reaction partners except catalysts. Some transformations typical of **A1** are shown in the Scheme below.



To determine the structures of **F – J**, a set of physico-chemical data was obtained (see Table for some results). It was found that:

- F** and **G** are structural isomers of **A1**;
- G** is formed as the most stable stereoisomer;
- H** and **I** are structural isomers;
- H** is formed as a single diastereomer with C_2 axis of symmetry (the molecule looks the same after rotation through the angle of 180°);
- I** is formed as a mixture of two diastereomers;
- J** is naphthalene derivative.

In the process leading to **I**, one molecule of **A1** demonstrates the described above common reactivity (analogous to that of **B**). The other molecule of **A1** behaves differently. Also, the latter behaviour is demonstrated by cyclopropane **A2** (dimethyl 2-(3,4,5-trimethoxyphenyl)cyclopropane-1,1-dicarboxylate) when treated with SnCl_4 in CH_3NO_2 affording **K** as a mixture of two diastereomers. The major isomer has the centre of symmetry. Similar reactivity is shown by **A2** in $\text{Sn}(\text{OTf})_2$ -catalyzed reaction with **G** furnishing **L**.

6.3 Write down the structural formulae of **F – J**, and those of **L** and the major isomer of **K**.

Ratio of the number of hydrogen-containing groups

	Non-aromatic CH	Non-aromatic CH ₂	Non-aromatic CH ₃	Non-aromatic OH	Aromatic	Composition
F	1	1	1+1+1	0	4 in total	C 63.62%, H 6.11%
G	1+1+1	0	2+1	0	4 in total	C 63.62%, H 6.11%

	Non-aromatic CH	Non-aromatic CH ₂	Non-aromatic CH ₃	Non-aromatic OH	Aromatic	Composition
H	1	1	1+1+1	0	4 in total	C 63.62%, H 6.11%
I	1+1+1	1+1	2+1+1+1+1	0	7 in total	C 63.62%, H 6.11%
J	0	0	1+1	1	5 in total	C 67.22%, H 5.22%
K	1+1	1	2+1+1+1	0	1	C 59.24%, H 6.23%
L	1+1+1+1+1	1	2+2+1+1+1+1	0	5 in total	C 61.21%, H 6.18%

Official English text of the problem.

Answers

For **D** and **H**, one enantiomer is represented explicitly; its mirror image is equally compatible with the statement. **E** and the major isomer of **K** are meso compounds.

- **6.1 — C:** Dimethyl 2-[2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)ethyl]propanedioate.

COC(=O)C(CC(c1ccc(OC)cc1)c1ccc(OC)cc1OC)C(=O)OC

- **6.2 — D:** Dimethyl **cis**-2,5-bis(4-methoxyphenyl)oxolane-3,3-dicarboxylate. Both aryl groups lie on the same face of the five-membered ring.

COC1CCC([C@H]2CC(C(=O)OC)(C(=O)OC)[C@@H](C3CCC(OC)CC3)O2)CC1

E: **cis**-2,5-Bis(4-methoxyphenyl)oxolane, the meso (*2R*, *5S*) stereoisomer.

COC1CCC([C@H]2CC[C@@H](C3CCC(OC)CC3)O2)CC1

- **6.3 — F:** Dimethyl 2-[2-(4-methoxyphenyl)ethylidene]propanedioate.

COC(=O)C(=CCc1ccc(OC)cc1)C(=O)OC

G: Dimethyl 2-[(*E*)-2-(4-methoxyphenyl)ethenyl]propanedioate.

COC(=O)C(/C=C/c1ccc(OC)cc1)C(=O)OC

H: Tetramethyl **cis**-2,5-bis(4-methoxyphenyl)cyclohexane-1,1,4,4-tetracarboxylate. Both aryl groups are on the same face; the configurations are (*2R*, *5R*) or (*2S*, *5S*).

COC1CCC([C@H]2CC(C(=O)OC)(C(=O)OC)[C@@H](C3CCC(OC)CC3)CC2(C(=O)OC)C(=O)OC)CC1

I: Dimethyl 1-[2,2-bis(methoxycarbonyl)ethyl]-6-methoxy-4-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene-2,2-dicarboxylate, as two diastereomers. One representative of each is:

COC(=O)C(C[C@H]1c2ccc(OC)cc2[C@H](c2ccc(OC)cc2)CC1(C(=O)OC)C(=O)OC)C(=O)OC
COC(=O)C(C[C@H]1c2ccc(OC)cc2[C@@H](c2ccc(OC)cc2)CC1(C(=O)OC)C(=O)OC)C(=O)OC

These represent the (1*S*, 4*S*) and (1*S*, 4*R*) configurations; their respective mirror images are also possible.

J: Methyl 1-hydroxy-7-methoxynaphthalene-2-carboxylate.

COC(=O)c1ccc2ccc(OC)cc2c1O

L: Dimethyl 2-{1-[2,2-bis(methoxycarbonyl)ethyl]-4,5,6-trimethoxy-3-(4-methoxyphenyl)indan-2-yl}propanedioate. Its relative stereochemistry is not specified by the supplied data.

COC(=O)C(CC1c2cc(OC)c(OC)c(OC)c2C(c2ccc(OC)cc2)C1C(C(=O)OC)C(=O)OC)C(=O)OC

Major K: *trans*-9,10-Bis[2,2-bis(methoxycarbonyl)ethyl]-1,2,3,5,6,7-hexamethoxy-9,10-dihydroanthracene, the centrosymmetric meso isomer. The two side chains lie on opposite faces of the central ring.

COC(=O)C(C[C@H]1c2cc(OC)c(OC)c(OC)c2[C@H](CC(C(=O)OC)C(=O)OC)c2cc(OC)c(OC)c(OC)c21)C(=O)OC
COC(=O)C(C[C@@H]1c2cc(OC)c(OC)c(OC)c2[C@@H](CC(C(=O)OC)C(=O)OC)c2cc(OC)c(OC)c(OC)c21)C(=O)OC

Solution

The starting compounds are:

Compound	Name	SMILES
A1	Dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate	<chem>COC(=O)C1(C(=O)OC)CC1c1ccc(OC)cc1</chem>
A2	Dimethyl 2-(3,4,5-trimethoxyphenyl)cyclopropane-1,1-dicarboxylate	<chem>COC(=O)C1(C(=O)OC)CC1c1cc(OC)c(OC)c(OC)c1</chem>

Their formulas are respectively $C_{14}H_{16}O_5$ and $C_{16}H_{20}O_7$.

For tracking connectivity, label the cyclopropane carbons:

- *a*: the carbon bearing both ester groups;
- *b*: the methylene carbon;
- *c*: the aryl-bearing methine carbon.

Cleavage of the *a* — *c* bond gives the formal reactivity represented by **B**: nucleophilic character at *a*, stabilized by the two ester groups, and electrophilic character at benzylic carbon *c*.

For **A1**, this formal ring-opened benzylic-cation/malonate-anion equivalent can be written as:

COC(=O)[C-](C[CH+]1c1ccc(OC)cc1)C(=O)OC

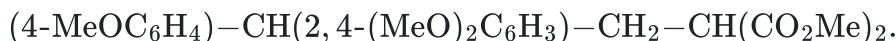
This is a description of reactivity; it does not require an independently existing, freely solvated zwitterion.

6.1 — Formation of C

The aromatic partner is 1,3-dimethoxybenzene, COc1cc(OC)ccc1.

Its positions 4 and 6 are equivalent and activated by both methoxy groups: each is ortho to one methoxy group and para to the other. Attack there also avoids the more crowded position between the two methoxy groups.

The aromatic ring attacks electrophilic carbon *c*. Rearomatization and protonation of carbon *a* give **C**, whose carbon chain is



Thus, the incoming aromatic fragment is **2,4-dimethoxyphenyl** when numbered from its new attachment point.

The balanced reaction is



The aromatic hydrogen displaced in forming the new carbon–carbon bond ultimately supplies the hydrogen gained by the malonate carbon. No small-molecule coproduct is required.

6.2 — Formation and stereochemistry of D and E

The aldehyde is 4-methoxybenzaldehyde, COc1ccc(C=O)cc1.

In the formal [3+2]-cycloaddition:

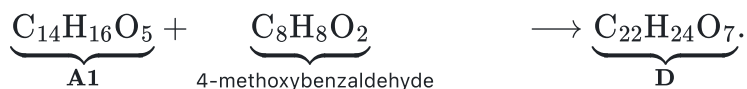
1. Carbon *a* bonds to the aldehyde carbonyl carbon.
2. The aldehyde oxygen bonds to benzylic carbon *c*.

The resulting five-membered ring follows the sequence



Numbering the oxolane ring from oxygen gives aryl substituents at positions 2 and 5 and the two ester groups at position 3. Therefore **D** is the oxolane-3,3-dicarboxylate specified in the answers.

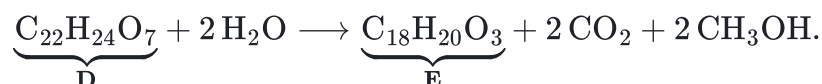
The balanced addition is



Complete removal of both ester-derived carboxyl groups gives a 2,5-diaryloxolane. Its stated plane of symmetry selects the **cis, meso** stereoisomer **E**. In a symmetric conformation, the plane passes through the ring oxygen and the midpoint of the opposite carbon–carbon bond, interchanging positions 2 and 5.

Consequently, the two aryl substituents in **D** must also be **cis**. In a ring drawing, draw both aryl bonds as wedges, or both as dashed bonds.

Writing the conversion as ester hydrolysis followed by complete decarboxylation gives the balanced net equation



Here water is O, carbon dioxide is O=C=O, and methanol is CO.

The formula of **E** is exactly the supplied C₁₈H₂₀O₃. Its two ester-free ring methylene groups also distinguish it from **D**.

Although the representative SMILES for **D** has *R, R* configurations and **E** is *R, S*, this does **not** imply inversion during decarboxylation: removal of the ester substituents changes the CIP priority ordering.

6.3 — Composition and hydrogen-count checks

Elemental analysis fixes empirical composition, but cannot by itself distinguish a compound from an atom-conserving dimer. The group counts and symmetry supply that information.

Using rounded atomic molar masses 12.01, 1.01, and 16.00 g mol⁻¹ for carbon, hydrogen, and oxygen reproduces the reported percentages. For example,

$$M(\mathbf{A1}) = 14(12.01) + 16(1.01) + 5(16.00) = 264.30 \text{ g mol}^{-1},$$

$$w_C = \frac{14(12.01)}{264.30} \times 100\% = 63.62\%, \quad w_H = \frac{16(1.01)}{264.30} \times 100\% = 6.11\%.$$

The complete checks are:

Product	Molecular formula	<i>M</i> , g mol ⁻¹	Calculated C	Calculated H
F, G	C ₁₄ H ₁₆ O ₅	264.30	63.62%	6.11%
H, I	C ₂₈ H ₃₂ O ₁₀	528.60	63.62%	6.11%
J	C ₁₃ H ₁₂ O ₄	232.25	67.22%	5.22%
K	C ₃₂ H ₄₀ O ₁₄	648.72	59.24%	6.23%
L	C ₃₀ H ₃₆ O ₁₂	588.66	61.21%	6.18%

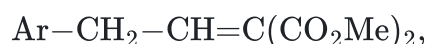
The actual group totals in the proposed molecules are:

Product	Non-aromatic CH	CH ₂	CH ₃	Aromatic H	OH
F	1	1	3	4	0
G	3	0	3	4	0
H	2	2	6	8	0
I	3	2	6	7	0
J	0	0	2	5	1
K	4	2	10	2	0
L	5	1	8	5	0

For the symmetric dimers **H** and **K**, the problem's tabulated ratios correspond to half these molecular totals.

F and G: ring opening and alkene isomerization

The one methine and one methylene group of **F** fit

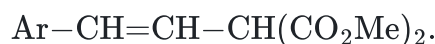


where **Ar** denotes 4-methoxyphenyl.

Relative to the original *c* – *b* – *a* carbon sequence, the net change transfers a hydrogen from *b* to *c* and forms the *b* = *a* double bond.

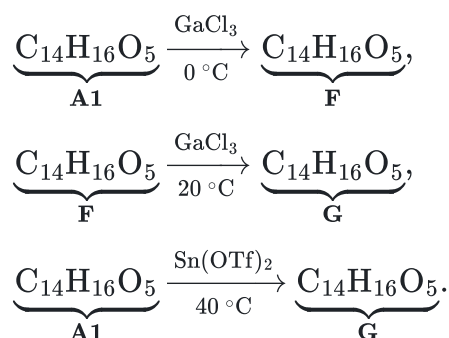
The two ester groups occupy different positions relative to the alkene's hydrogen and benzyl substituent, accounting for two distinct ester-methyl entries, in addition to the aromatic methoxy group.

Double-bond migration gives **G**:



This structure has three methine groups and no methylene group. Its alkene is conjugated with the aromatic ring. The more stable geometrical isomer is *E*, with the aryl and malonate substituents on opposite sides of the double bond.

All three transformations are atom-conserving isomerizations:



H: coupling of two ordinary three-carbon units

Two molecules of **A1** can combine through their normal donor-acceptor reactivity. The new bonds connect *a* of each molecule to *c* of the other:

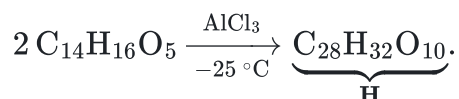


The resulting six-membered ring has the sequence



It therefore contains two geminal diester-bearing carbons, two methylene carbons, and two aryl-bearing methine carbons: precisely the cyclohexane structure **H**.

The C_2 symmetry clue selects the **cis** relationship between the two aryl groups, corresponding to the *R, R/S, S* enantiomeric pair. A flattened ring drawing should show both aryl bonds wedged or both dashed. This specifies relative configuration, not a unique cyclohexane conformation.



I: aromatic-ring participation by one cyclopropane

The alternative reactivity involves the aromatic carbon **ortho to the cyclopropyl substituent**. Instead of using the malonate carbon as the second bond-forming terminus, the molecule uses this aromatic carbon.

The participating three-carbon sequence is now



Aromatic substitution supplies a proton that ultimately converts the ester-bearing terminus into $\text{CH}(\text{CO}_2\text{Me})_2$. Thus, the benzylic carbon retains a $-\text{CH}_2\text{CH}(\text{CO}_2\text{Me})_2$ side chain.

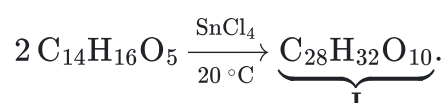
For **I**, one molecule uses its ordinary $c - b - a$ unit and the other uses this aromatic three-carbon unit. Their union produces a six-membered ring fused to the latter molecule's benzene ring: a **tetralin** skeleton.

Numbering that tetralin ring gives:

- position 1: $-\text{CH}_2\text{CH}(\text{CO}_2\text{Me})_2$;
- position 2: two methoxycarbonyl groups;
- position 4: 4-methoxyphenyl;
- position 6: methoxy.

One aromatic hydrogen is replaced, reducing the aromatic total from eight to seven. The product has three non-aromatic methines and two methylenes, matching the table.

Positions 1 and 4 are stereogenic, allowing the two stated relative configurations.



J: cyclization to a naphthol

The composition and hydrogen counts require:

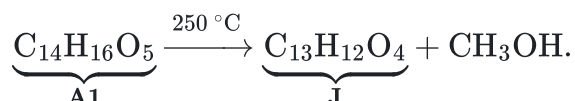
- a naphthalene nucleus;
- one aromatic methoxy group;
- one methyl ester;
- one phenolic hydroxyl group.

The corresponding formula is $\text{C}_{13}\text{H}_{12}\text{O}_4$. Compared with **A1**, the difference is exactly methanol:



The connectivity can be followed from the open-chain skeleton of **G**. An aromatic ortho carbon forms a bond to one ester carbonyl carbon, closing a six-membered ring. Methanol elimination and aromatizing proton transfer give the naphthol.

Tracing the atoms places the hydroxyl group at position 1, the remaining ester at position 2, and the original para-methoxy substituent at position 7.



The resulting structure has five aromatic hydrogens, two methyl groups, one hydroxyl group, and no non-aromatic methine or methylene groups.

L: annulation of A2 with G

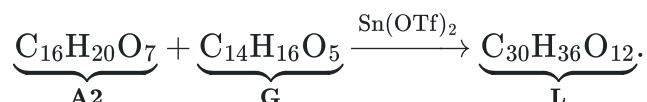
Here **A2** supplies the aromatic three-carbon unit described for **I**, while **G** supplies its two alkene carbons. Their combination therefore forms a five-membered ring fused to the trimethoxy-substituted benzene ring: an **indane**.

The regioselectivity follows benzylic stabilization. Bond formation between the benzylic electrophilic carbon of opened **A2** and the alkene carbon of **G** adjacent to its malonate group leaves positive character at the aryl-bearing alkene carbon. Intramolecular aromatic attack then closes the ring.

The indane substituents are consequently:

- position 1: $-\text{CH}_2\text{CH}(\text{CO}_2\text{Me})_2$, from **A2**;
- position 2: $-\text{CH}(\text{CO}_2\text{Me})_2$, from **G**;
- position 3: 4-methoxyphenyl, from **G**;
- positions 4, 5, and 6: methoxy groups, from **A2**.

The balanced reaction is



The three saturated indane carbons and the two malonate methines account for all five non-aromatic CH groups. Only the side chain at position 1 contains a methylene group. Aromatic substitution leaves five aromatic hydrogens.

Major K: aromatic participation by both molecules

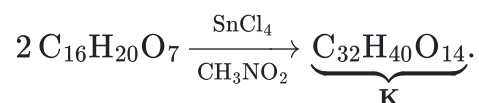
When two molecules of **A2** both use their aromatic three-carbon units, each benzylic carbon forms a bond to an ortho carbon of the other aromatic ring.

This closes the central six-membered ring of a **9,10-dihydroanthracene**. Both original malonate-bearing fragments remain as $-\text{CH}_2\text{CH}(\text{CO}_2\text{Me})_2$ side chains at positions 9 and 10.

Each aromatic ring loses one hydrogen through substitution. The product therefore has:

- two aromatic hydrogens altogether;
- two central-ring methines;
- two malonate methines;
- two side-chain methylene groups;
- ten methyl groups.

The stated centre of symmetry selects the **trans** arrangement of the two side chains. In a conventional drawing, one side-chain bond is wedged and the other dashed. Inversion through the centre exchanges positions 9 and 10 and the two substituted aromatic rings. This is the meso stereoisomer encoded in the answer.



For completeness, the reaction auxiliaries are gallium(III) chloride, $\text{Cl}[\text{Ga}](\text{Cl})\text{Cl}$; aluminium(III) chloride, $\text{Cl}[\text{Al}](\text{Cl})\text{Cl}$; tin(IV) chloride, $\text{Cl}[\text{Sn}](\text{Cl})(\text{Cl})\text{Cl}$; tin(II) triflate, $[\text{Sn}+2].\text{O}=\text{S}(=\text{O})([\text{O}-])\text{C}(\text{F})(\text{F})\text{F}$; and nitromethane, $\text{C}[\text{N}+](=\text{O})[\text{O}-]$. These SMILES do not specify their solution coordination structures.

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

Problem 7: Diverse permanganatometry

The amount of many reducing agents can be determined by permanganatometric titration in alkaline medium allowing permanganate ion reduction to manganate.

7.1 Write down the ionic reaction equation for titration of formate with permanganate in an aqueous NaOH solution with a concentration of $\sim 0.5 \text{ mol dm}^{-3}$.

Titration with permanganate in alkaline medium is often supplemented by addition of a barium salt, which leads to precipitation of manganate as BaMnO_4 .

7.2 Which side redox processes involving manganate is suppressed by the barium salt? Write down an example of equation of the corresponding reaction.

A volume of 10.00 cm^3 (V_{Mn}) of KMnO_4 solution with a concentration of $0.0400 \text{ mol dm}^{-3}$ (c_{Mn}) was placed in each of flasks **A**, **B**, and **C** and different reactions were conducted in each flask.

A sample solution containing crotonic acid (CA) $\text{CH}_3\text{--CH=CH--COOH}$, an alkali and barium nitrate (both in an excess) were added to flask **A**, and the reaction mixture was incubated for 45 min. It is known that crotonic acid loses 10 electrons under the experiment conditions.

7.3 a Write down the total ionic equation for the reaction.

A volume of 8.00 cm^3 (V_{CN}) of potassium cyanide solution ($c_{\text{CN}} = 0.0100 \text{ mol dm}^{-3}$) was then added to the incubated mixture. This resulted in completion of the following reaction:



BaMnO_4 precipitate was then filtered off, and the excess of cyanide in the filtrate was titrated with AgNO_3 solution ($c_{\text{Ag}} = 0.0050 \text{ mol dm}^{-3}$) till detectable precipitation was observed. Note that both CN^- and CNO^- are analogs of halide ions, but CNO^- affords soluble silver salt.

7.3 b Give the formula for the complex formed when Ag^+ ions were initially added to the cyanide solution (until the precipitate was formed).

7.3 c Give the formula of the precipitate formed.

7.3 d Derive the formula for calculating the amount of substance of crotonic acid in the sample solution. Calculate the mass of crotonic acid (in mg) if 5.40 cm^3 (V_{Ag}) of the silver salt solution was consumed for the titration to the endpoint.

Another sample of crotonic acid and alkali (in an excess) were added to flask **B**, this mixture lacking barium salt. An excess of **KI** (instead of cyanide) was added as a reducing agent. The mixture was then acidified and the iodine evolved was titrated with a thiosulfate solution ($c_{\text{S}} = 0.1000 \text{ mol dm}^{-3}$). 4.90 cm^3 (V_{S1}) of the titrant was used to reach the endpoint.

7.4 Derive the formula for calculating the amount of substance of crotonic acid in this experiment. Calculate the mass of crotonic acid (in mg).

A sample containing tin(II) was added to flask **C**, and the medium was adjusted to weak alkaline. Tin(II) was quantitatively oxidized to $\text{Sn}(\text{OH})_6^{2-}$, whereas a precipitate formed as a result of permanganate reduction. The precipitate was isolated, washed off, dried at 250°C , weighed (the

mass of the water-free precipitate (m_{prec}), representing a binary compound, was of 28.6 mg), and dissolved in H_2SO_4 in the presence of an excess of potassium iodide. The evolved iodine was titrated with 0.1000 M thiosulfate solution. 2.5 cm^3 (V_{S_2}) of the latter was consumed to attain the endpoint.

7.5 a Write down the reaction of precipitation. Confirm it with calculations.

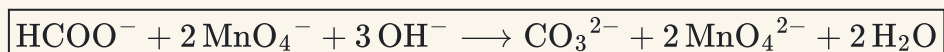
7.5 b Calculate the mass of tin in the sample (in mg) referred to the metal.

Official English text of the problem.

Answers

Species names and SMILES are collected in the solution. In the calculation formulas below, volumes are in dm^3 .

• **7.1**



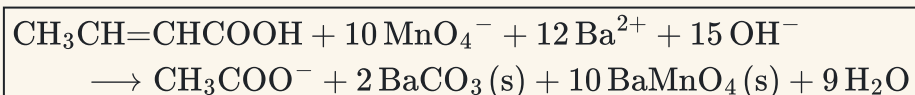
- **7.2** Precipitation suppresses secondary reactions of dissolved manganate: further reduction and disproportionation. Examples are



and



• **7.3 a**



- **7.3 b** Dicyanidoargentate(I), $[\text{Ag}(\text{CN})_2]^-$, a linear complex.
- **7.3 c** Silver cyanide, $\text{AgCN}(\text{s})$. The endpoint precipitate can equivalently be written $\text{Ag}[\text{Ag}(\text{CN})_2]$, with the composition of two formula units of AgCN .

• **7.3 d**

$$n_{\text{CA,A}} = \frac{c_{\text{Mn}}V_{\text{Mn}} - 2c_{\text{CN}}V_{\text{CN}} + 4c_{\text{Ag}}V_{\text{Ag}}}{10}$$

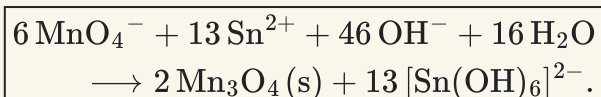
$$n_{\text{CA,A}} = 3.48 \times 10^{-5} \text{ mol}, \quad m_{\text{CA,A}} = 3.00 \text{ mg}$$

• **7.4**

$$n_{\text{CA,B}} = \frac{5c_{\text{Mn}}V_{\text{Mn}} - c_{\text{S}}V_{\text{S1}}}{10}$$

$$n_{\text{CA,B}} = 1.51 \times 10^{-4} \text{ mol}, \quad m_{\text{CA,B}} = 13.0 \text{ mg}$$

- **7.5 a** The precipitate is manganese(II,III) oxide, Mn_3O_4 :



- **7.5 b**

$$m_{\text{Sn}} = 96.4 \text{ mg}$$

using the precipitate mass after identifying its composition.

Solution

For the mass conversions, conventional molar masses are used:

$$M_{\text{CA}} = 86.09 \text{ g mol}^{-1}, \quad M_{\text{Mn}} = 54.94 \text{ g mol}^{-1}, \quad M_{\text{O}} = 16.00 \text{ g mol}^{-1}, \quad M_{\text{Sn}} = 118.71 \text{ g mol}^{-1}.$$

The species used below have the following names and SMILES. For extended solids, the disconnected SMILES express formula-unit composition, not the crystal lattice. Coordination SMILES use arrows for donor–metal bonds; these do not specify geometry.

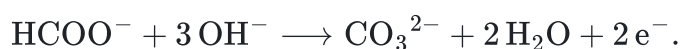
Species	Name	SMILES
$\text{CH}_3\text{CH}=\text{CHCOOH}$	Crotonic acid, conventionally (<i>E</i>)-but-2-enoic acid	<chem>C/C=C/C(=O)O</chem>
HCOO^-	Formate	<chem>[H]C(=O)[O-]</chem>
CH_3COO^-	Acetate	<chem>CC(=O)[O-]</chem>
CO_3^{2-}	Carbonate	<chem>[O-]C(=O)[O-]</chem>
MnO_4^-	Permanganate	<chem>[O-][Mn](=O)(=O)=O</chem>
MnO_4^{2-}	Manganate(VI)	<chem>[O-][Mn](=O)(=O)[O-]</chem>
OH^-	Hydroxide	<chem>[OH-]</chem>
H_2O	Water	<chem>O</chem>
Ba^{2+}	Barium ion	<chem>[Ba+2]</chem>
BaMnO_4	Barium manganate(VI)	<chem>[Ba+2].[O-][Mn](=O)(=O)[O-]</chem>
BaCO_3	Barium carbonate	<chem>[Ba+2].[O-]C(=O)[O-]</chem>
MnO_2	Manganese(IV) oxide	<chem>[Mn+4].[O-2].[O-2]</chem>
CN^-	Cyanide	<chem>[C-]#N</chem>
CNO^-	Cyanate	<chem>N#C[O-]</chem>
Ag^+	Silver(I) ion	<chem>[Ag+]</chem>
$[\text{Ag}(\text{CN})_2]^-$	Dicyanidoargentate(I)	<chem>N#[C-]>[Ag+]<-[C-]#N</chem>
AgCN	Silver cyanide	<chem>[Ag+].[C-]#N</chem>
H^+	Hydrogen ion	<chem>[H+]</chem>
I^-	Iodide	<chem>[I-]</chem>
I_2	Iodine	<chem>II</chem>
$\text{S}_2\text{O}_3^{2-}$	Thiosulfate	<chem>[O-]S(=O)(=O)[S-]</chem>
$\text{S}_4\text{O}_6^{2-}$	Tetrathionate	<chem>[O-]S(=O)(=O)SSS(=O)(=O)[O-]</chem>

Species	Name	SMILES
Mn^{2+}	Manganese(II) ion	[Mn+2]
Sn^{2+}	Tin(II) ion	[Sn+2]
$[\text{Sn}(\text{OH})_6]^{2-}$	Hexahydroxidostannate(IV)	[Sn+4] (<- [OH-]) (<- [OH-]) (<- [OH-]) (<- [OH-]) (<- [OH-]) <- [OH-]
Mn_3O_4	Manganese(II,III) oxide	[Mn+2] . [Mn+3] . [Mn+3] . [O-2] . [O-2] . [O-2] . [O-2]

The silver complex has linear carbon–silver–carbon coordination. The tin(IV) complex has octahedral coordination by six hydroxide ligands. The printed condensed formula of crotonic acid does not specify alkene geometry; that geometry does not affect any calculation here.

7.1

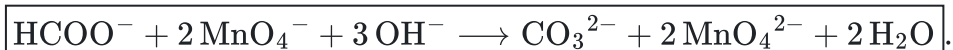
Carbon is oxidized from +2 in formate to +4 in carbonate, releasing two electrons:



Each permanganate ion accepts one electron:

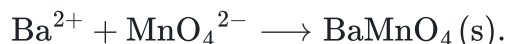


Multiplying the second half-reaction by two and adding gives



7.2

Barium removes dissolved manganate by precipitation:



This suppresses further reduction of manganese(VI), for example by formate:



It also suppresses manganate disproportionation into manganese(VII) and manganese(IV):



These secondary reactions would otherwise disturb the intended one-electron reduction of permanganate to manganate.

7.3 a

Oxidative cleavage of crotonic acid leaves its methyl-containing two-carbon fragment as acetate. The other two carbon atoms are oxidized to carbonate.

Reading from the methyl end, the carbon oxidation numbers change as follows:



The total increase is

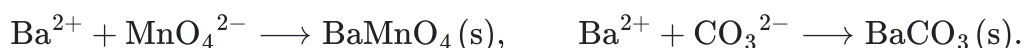
$$0 + 4 + 5 + 1 = 10,$$

consistent with the stated ten-electron oxidation.

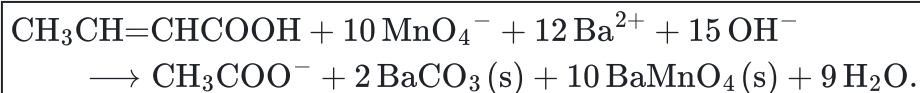
The oxidation half-reaction is



Ten permanganate ions accept these ten electrons. Excess barium precipitates both manganate and carbonate:

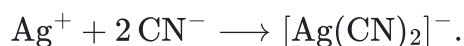


Thus the total ionic equation is



7.3 b

Initially, excess cyanide keeps added silver in the soluble complex:



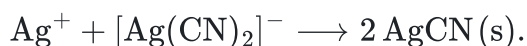
The complex is therefore



with two carbon-bound cyanide ligands and linear coordination.

7.3 c

Once the free cyanide has been consumed by complex formation, further silver produces silver cyanide:



Hence



Writing the endpoint precipitate as $\text{Ag}[\text{Ag}(\text{CN})_2]$ gives the same overall composition. Cyanate does not produce the endpoint precipitate because its silver salt is soluble, as specified.

7.3 d

Define the initially added amounts:

$$n_{\text{Mn},0} = c_{\text{Mn}} V_{\text{Mn}}, \quad n_{\text{CN},0} = c_{\text{CN}} V_{\text{CN}}.$$

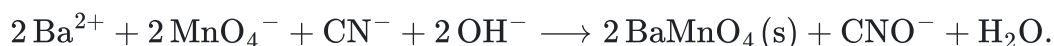
The silver titration measures the remaining cyanide. From the 1 : 2 silver-to-cyanide complexation ratio,

$$n_{\text{CN},\text{remaining}} = 2c_{\text{Ag}} V_{\text{Ag}}.$$

Therefore cyanide consumed by residual permanganate is

$$n_{\text{CN},\text{reacted}} = c_{\text{CN}} V_{\text{CN}} - 2c_{\text{Ag}} V_{\text{Ag}}.$$

The given reaction is



Thus two moles of residual permanganate consume one mole of cyanide:

$$n_{\text{Mn},\text{residual}} = 2(c_{\text{CN}} V_{\text{CN}} - 2c_{\text{Ag}} V_{\text{Ag}}).$$

Crotonic acid consumes ten moles of permanganate per mole, giving

$$\boxed{n_{\text{CA},\text{A}} = \frac{c_{\text{Mn}} V_{\text{Mn}} - 2c_{\text{CN}} V_{\text{CN}} + 4c_{\text{Ag}} V_{\text{Ag}}}{10}}.$$

Numerically,

$$n_{\text{Mn},0} = 0.0400(0.01000) = 4.00 \times 10^{-4} \text{ mol},$$

$$n_{\text{CN},0} = 0.0100(0.00800) = 8.00 \times 10^{-5} \text{ mol},$$

$$n_{\text{Ag}} = 0.0050(0.00540) = 2.70 \times 10^{-5} \text{ mol}.$$

Consequently,

$$n_{\text{CA},A} = \frac{4.00 \times 10^{-4} - 2(8.00 \times 10^{-5}) + 4(2.70 \times 10^{-5})}{10} = 3.48 \times 10^{-5} \text{ mol}.$$

The mass is

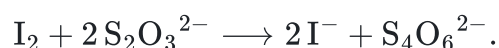
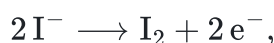
$$m_{\text{CA},A} = (3.48 \times 10^{-5})(86.09) \text{ g} = \boxed{3.00 \text{ mg}}.$$

7.4

After acidification in excess iodide, manganese is reduced to manganese(II). Relative to this final state, each initial permanganate ion has a five-electron oxidizing capacity:



Crotonic acid has already supplied ten electrons per molecule. The remaining oxidizing capacity is measured by iodometry:



Thus one mole of thiosulfate corresponds to one mole of electrons transferred from iodide to the remaining manganese oxidants.

Conservation of electron equivalents gives

$$5c_{\text{Mn}}V_{\text{Mn}} = 10n_{\text{CA},B} + c_{\text{S}}V_{\text{S1}}.$$

Hence

$$n_{\text{CA},B} = \frac{5c_{\text{Mn}}V_{\text{Mn}} - c_{\text{S}}V_{\text{S1}}}{10}.$$

This balance remains valid when manganese undergoes intermediate reductions or disproportionation, because these redistribute its oxidation states without changing the overall electron balance.

Substitution gives

$$n_{\text{CA},B} = \frac{5(0.0400)(0.01000) - (0.1000)(0.00490)}{10} = 1.51 \times 10^{-4} \text{ mol}.$$

Therefore

$$m_{\text{CA},B} = (1.51 \times 10^{-4})(86.09) \text{ g} = \boxed{13.0 \text{ mg}}.$$

7.5 a

The dried binary precipitate is a manganese oxide. Its composition must be determined from both its mass and its oxidizing capacity.

Let n_{Mn} and n_{O} denote the amounts of manganese and oxygen atoms in the precipitate. Oxygen has oxidation number -2 , so reducing all manganese to $+2$ requires

$$2n_{\text{O}} - 2n_{\text{Mn}}$$

moles of electrons.

The thiosulfate amount is

$$n_{\text{S}_2\text{O}_3} = (0.1000)(0.0025) = 2.5 \times 10^{-4} \text{ mol.}$$

Since each mole of thiosulfate corresponds to one electron equivalent,

$$2(n_{\text{O}} - n_{\text{Mn}}) = 2.5 \times 10^{-4} \text{ mol,}$$

or

$$n_{\text{O}} = n_{\text{Mn}} + 1.25 \times 10^{-4} \text{ mol.}$$

The precipitate mass gives

$$54.94n_{\text{Mn}} + 16.00n_{\text{O}} = 0.0286,$$

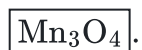
with amounts in mol and mass in g. Substitution yields

$$n_{\text{Mn}} = \frac{0.0286 - 16.00(1.25 \times 10^{-4})}{54.94 + 16.00} = 3.7496 \times 10^{-4} \text{ mol,}$$
$$n_{\text{O}} = 4.9996 \times 10^{-4} \text{ mol.}$$

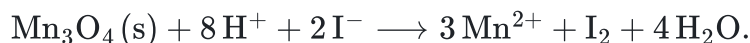
Thus

$$\frac{n_{\text{O}}}{n_{\text{Mn}}} \approx \frac{4}{3},$$

identifying the precipitate as



It contains one manganese(II) and two manganese(III) ions per formula unit. Its iodometric dissolution is



Each mole of oxide therefore produces one mole of iodine and consumes two moles of thiosulfate. With

$$M(\text{Mn}_3\text{O}_4) = 3(54.94) + 4(16.00) = 228.82 \text{ g mol}^{-1},$$

the measured mass corresponds to

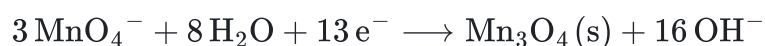
$$n(\text{Mn}_3\text{O}_4) = \frac{0.0286}{228.82} = 1.24989 \times 10^{-4} \text{ mol.}$$

The predicted thiosulfate volume is

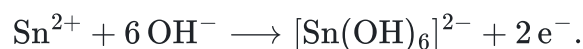
$$V_{\text{S}_2} = \frac{2(1.24989 \times 10^{-4})}{0.1000} = 2.4998 \times 10^{-3} \text{ dm}^3 \approx 2.5 \text{ cm}^3,$$

in agreement with the observation.

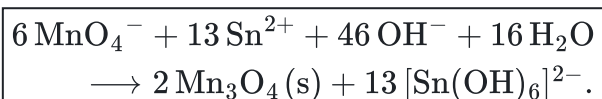
For precipitation, the half-reactions are



and



Multiplying these by two and thirteen, respectively, gives



Here Sn^{2+} represents the analytical tin(II) input in the net ionic balance; its hydrolysis in alkaline solution does not alter the electron stoichiometry.

7.5 b

The precipitation equation gives

$$n(\text{Sn}) = \frac{13}{2} n(\text{Mn}_3\text{O}_4).$$

Using the measured precipitate mass,

$$n(\text{Sn}) = \frac{13}{2} \frac{0.0286}{228.82} = 8.12429 \times 10^{-4} \text{ mol.}$$

Therefore

$$m(\text{Sn}) = (8.12429 \times 10^{-4})(118.71) \text{ g} = \boxed{96.4 \text{ mg}}.$$

As a consistency check, the precipitate contains

$$3n(\text{Mn}_3\text{O}_4) \approx 0.375 \text{ mmol}$$

of manganese, whereas 0.400 mmol of permanganate was initially added. Approximately 0.0250 mmol of permanganate therefore remains in excess.

The solution was checked against the official solution.

Problem 8: Unique life of archaea

Archaea (or archaeobacteria) are single-celled microorganisms. They significantly differ from bacteria and eukaryotes at the molecular level.

Enzymatic reaction of methylamine with water is the major energy source for some archaea. In a particular experiment, an archaea strain was cultivated at pH 7 under anaerobic (oxygen free) conditions with the nutrient medium containing $^{13}\text{CH}_3\text{NH}_2$ as the only energy source. After a certain incubation period, the gas over the archaea culture was sampled and analyzed. It was found that the gas contains two substances, **A** and **B**, in a molar ratio of 1 : 3 correspondingly (the sample density relative to H_2 is 12.0).

8.1 Calculate the volume fractions (in %) of **A** and **B** in the mixture.

8.2 Determine **A** and **B** if there are no nitrogen atoms in the gas collected.

8.3 Write down the equation of enzymatic reaction of methylamine with water described in the above experiment using predominant form of each species.

Enzymes containing the residue of α -amino acid **X**, are found in many archaea capable of methylamine utilization. It is known that **X**:

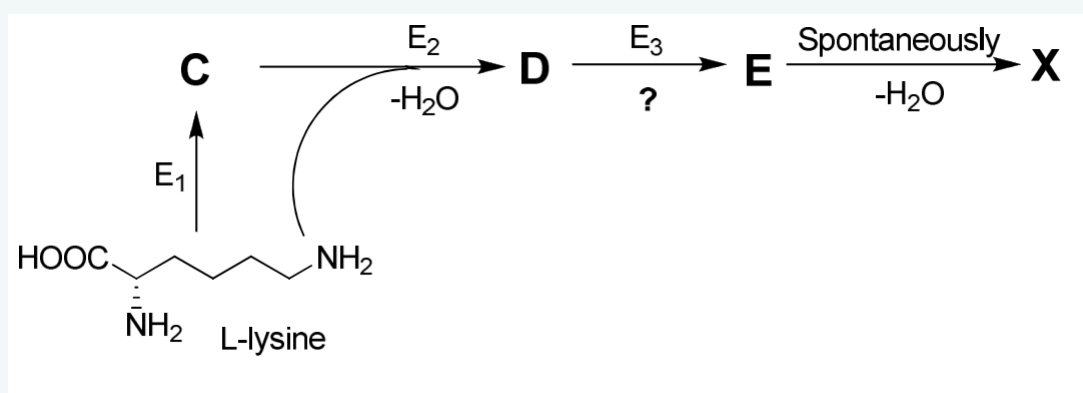
- is composed of atoms of 4 elements;
- contains 18.8 mass % of oxygen;
- possesses the single individual tRNA and is incorporated into proteins of archaea during translation.

Amino acid *L*-lysine (see the structure in scheme below) was identified as the **X** precursor in archaea. All carbon and nitrogen atoms found in **X** originate from two starting lysine molecules. Different isotope-labelled *L*-lysines were introduced into a model system to clarify the biosynthetic pathways of **X**. The results are summarized in the table.

Isotope composition of <i>L</i> -lysine	Molar mass (rounded to integer) of the X residue [RCH(NH ₂)CO], bound to tRNA, (g mol ⁻¹)
Normal	238
All carbons ¹³ C, all nitrogens ¹⁵ N	253
ε-amino group with ¹⁵ N	239

8.4 Determine the molecular formula of **X**.

X is biosynthesized in archaea according to the following scheme (*E*₁, *E*₂, and *E*₃ – enzymes):



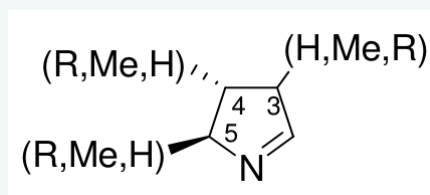
At the first step, lysine is transformed into its structural isomer (α-amino acid, **C**), whereas **D** contains a peptide bond, and **E** a formyl group –CHO. All reaction coefficients in the above scheme are equal to 1.

8.5 i) Give the chemical formula of **C**, **D** and **E**.

ii) From the reaction types given hereunder, choose (tick) **only one** corresponding to the enzyme *E*₃ catalyzed reaction.

- ☐ Oxidative deamination
- ☐ Decarboxylation
- ☐ Intermolecular deamination
- ☐ Hydroxylation
- ☐ Peptide bond hydrolysis

X contains the following fragment:

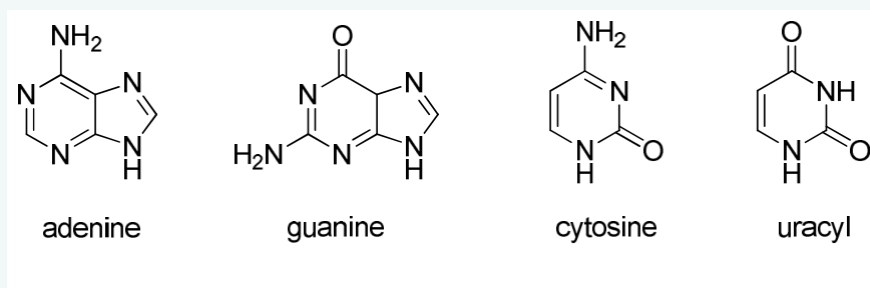


R is a massive substituent ($M > 100 \text{ g mol}^{-1}$). The 3rd carbon atom is non-asymmetric. The 4th and 5th carbon atoms are stereogenic centres. All carbon atoms in the cycle are bound with at least one hydrogen atom. Each substituent (H, Me and R) is found only once.

8.6 Determine the positions of substituents H, Me, and R.

8.7 Draw structural formulae of **C** and **X** with stereochemical details. Mark every stereocenter of **X** with either *R* or *S*.

Only one codon is responsible for the incorporation of **X** residues into proteins in archaea. The nitrogen bases forming this codon contain two exocyclic amino groups and three exocyclic oxygen atoms in total.



8.8 Determine the nucleotide composition of the codon by filling in the hereunder table. Write down the number of each nitrogen base in the codon encoding **X**. Tick only **one** box in each line.

The number of bases in the codon

Nitrogen base	1	2	3	0 or 1	1 or 2
A					
C					
G					
U					

The fragment of mRNA coding sequence given below contains the codons encoding **X** residue incorporation into an archaea enzyme:

5' ... AAUAGAAUUAGCGGAACAGAGGGUGAC ... 3'

8.9 a Using the table of the genetic code, decide how many amino acid residues are incorporated into the enzyme chain due to this fragment translation.

8.9 b Write down the amino acid sequence translated from this fragment. Note that **more than one X residue** is found in the fragment.

Fill in the boxes below with the amino acid abbreviations (from N- to C-terminus).

Note that the number of boxes is excessive. If there is more than one possibility, write all separated by "/". If the translation is stopped in a particular position, write "STOP" and leave all the boxes to the right empty.

--	--	--	--	--	--	--	--	--	--

(a) RNA codons for the twenty amino acids

Second base

First base	U	C	A	G	Third base
U	Phe	Ser	Tyr	Cys	U
U	Phe	Ser	Tyr	Cys	C
U	Leu	Ser	STOP	STOP	A
U	Leu	Ser	STOP	Trp	G
C	Leu	Pro	His	Arg	U
C	Leu	Pro	His	Arg	C
C	Leu	Pro	Gln	Arg	A
C	Leu	Pro	Gln	Arg	G
A	Ile	Thr	Asn	Ser	U
A	Ile	Thr	Asn	Ser	C
A	Ile	Thr	Lys	Arg	A
A	Met (start)	Thr	Lys	Arg	G
G	Val	Ala	Asp	Gly	U
G	Val	Ala	Asp	Gly	C
G	Val	Ala	Glu	Gly	A
G	Val	Ala	Glu	Gly	G

Amino Acids Abbreviations:

Ala = Alanine

Arg = Arginine

Asp = Aspartic acid

Asn = Asparagine

Cys = Cysteine

Glu = Glutamic Acid

Gln = Glutamine

Gly = Glycine

His = Histidine

Ile = Isoleucine

Leu = Leucine

Lys = Lysine

Met = Methionine

Phe = Phenylalanine

Pro = Proline

Ser = Serine

Thr = Threonine

Amino Acids Abbreviations:

Trp = Tryptophan

Tyr = Tyrosine

Val = Valine

Official English text of the problem.

Answers

- **8.1:** $A = 25\%$, $B = 75\%$ by volume.
- **8.2:** **A** is carbon dioxide- ^{13}C , $^{13}\text{CO}_2$, $\text{O}=[^{13}\text{C}]=\text{O}$; **B** is methane- ^{13}C , $^{13}\text{CH}_4$, $[^{13}\text{CH}_4]$.
- **8.3:**



- **8.4:** $\text{C}_{12}\text{H}_{21}\text{N}_3\text{O}_3$. **X** is pyrrolysine, $\text{N}[\text{C}@\text{H}] (\text{CCCCNC}(=\text{O}))$
 $[\text{C}@\text{H}]1\text{N}=\text{CC}[\text{C}@\text{H}]1\text{C}(=\text{O})\text{O}$.
- **8.5 i:** $\text{C} : \text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$; $\text{D} : \text{C}_{12}\text{H}_{26}\text{N}_4\text{O}_3$; $\text{E} : \text{C}_{12}\text{H}_{23}\text{N}_3\text{O}_4$. Their names and structural SMILES are given in the solution.
- **8.5 ii: Oxidative deamination.**
- **8.6:** $3 : \text{H}$; $4 : \text{Me}$; $5 : \text{R}$.
- **8.7:** **C** is (2*R*, 3*R*)-2,5-diamino-3-methylpentanoic acid, $\text{N}[\text{C}@\text{H}] ([\text{C}@\text{H}] (\text{C})\text{CCN})\text{C}(=\text{O})\text{O}$.
X has three stereocentres: the lysine α -carbon is *S*, and ring positions 4 and 5 are both *R*.
- **8.8:** Tick **1** for A, **0 or 1** for C, **0 or 1** for G, and **1** for U. Exactly one of C and G is present.
- **8.9 a:** 8 amino acid residues, reading UGA as selenocysteine in this enzyme-coding fragment.
- **8.9 b:** From N- to C-terminus:



Here X is pyrrolysine and Sec is selenocysteine. Fill eight boxes and leave the remaining two empty.

Solution**8.1**

At the same temperature and pressure, gas volumes are proportional to amounts in moles. Thus

$$\phi_A = \frac{1}{1+3} \times 100\% = 25\%, \quad \phi_B = \frac{3}{1+3} \times 100\% = 75\%.$$

8.2

The reference gas is dihydrogen, H_2 , $[\text{H}][\text{H}]$. Using the integer atomic masses appropriate to the supplied data,

$$\overline{M} = D_{\text{H}_2} M_{\text{H}_2} = 12.0 \times 2.00 = 24.0 \text{ g mol}^{-1}.$$

Since $n_A : n_B = 1 : 3$,

$$\frac{M_A + 3M_B}{4} = 24.0 \text{ g mol}^{-1}.$$

The substrate is methylamine- ^{13}C , $[\text{}^{13}\text{CH}_3]\text{N}$. Its carbon has oxidation state -2 . Disproportionation can oxidize one carbon to $+4$ in carbon dioxide and reduce three carbons to -4 in methane: the first releases six electrons, while the other three consume two electrons each.

For the labelled products,

$$\begin{aligned} M(^{13}\text{CO}_2) &= 13 + 2(16) = 45 \text{ g mol}^{-1}, \\ M(^{13}\text{CH}_4) &= 13 + 4(1) = 17 \text{ g mol}^{-1}. \end{aligned}$$

Their mean molar mass is

$$\frac{45 + 3(17)}{4} = 24.0 \text{ g mol}^{-1},$$

which matches the measured density. Therefore **A** is labelled carbon dioxide and **B** is labelled methane, with the identities and SMILES given above.

8.3

At pH 7, the predominant aqueous forms are methylammonium rather than methylamine, ammonium rather than ammonia, and hydrogen carbonate rather than dissolved carbon dioxide.

The additional species in the equation are:

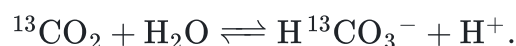
Species	Name	SMILES
$^{13}\text{CH}_3\text{NH}_3^+$	Methylammonium- ^{13}C	<chem>[13CH3][NH3+]</chem>
H_2O	Water	<chem>O</chem>
$\text{H}^{13}\text{CO}_3^-$	Hydrogen carbonate- ^{13}C	<chem>O[13C](=O)[O-]</chem>
NH_4^+	Ammonium	<chem>[NH4+]</chem>
H^+	Hydrogen ion, conventionally representing a solvated proton	<chem>[H+]</chem>

The balanced equation is



Both sides contain four carbon atoms, thirty hydrogen atoms, four nitrogen atoms and three oxygen atoms; both have total charge $+4$.

The gaseous oxidized product remains carbon dioxide. Its relationship to the predominant dissolved form is



8.4

The specified tRNA-bound residue is the acyl group $\text{RCH}(\text{NH}_2)\text{CO}$. Recovering the free amino acid adds an OH group, of molar mass 17 g mol^{-1} . Hence

$$M_X = 238 + 17 = 255 \text{ g mol}^{-1}.$$

An α -amino acid already contains C, H, N and O, so these are its four elements. Its number of oxygen atoms is

$$n_{\text{O}} = \frac{0.188(255)}{16} = 2.996 \approx 3.$$

Each replacement of ^{12}C by ^{13}C , or ^{14}N by ^{15}N , raises the rounded molar mass by 1 g mol^{-1} . Thus

$$n_{\text{C}} + n_{\text{N}} = 253 - 238 = 15.$$

Two lysine molecules supply at most twelve carbons and four nitrogens. Selective labelling of both starting ϵ -amino groups raises the product mass by only one unit, so exactly one of those two nitrogen atoms is retained. Including the two possible α -amino nitrogens gives

$$n_{\text{N}} \leq 3, \quad n_{\text{C}} \leq 12.$$

Their sum is fifteen, so both upper bounds must be attained:

$$n_{\text{C}} = 12, \quad n_{\text{N}} = 3.$$

The remaining mass is hydrogen:

$$n_{\text{H}} = \frac{255 - 12(12) - 3(14) - 3(16)}{1} = 21.$$

Therefore

$$\boxed{X = \text{C}_{12}\text{H}_{21}\text{N}_3\text{O}_3}.$$

The oxygen percentage checks:

$$\frac{48}{255} \times 100\% = 18.82\% \approx 18.8\%.$$

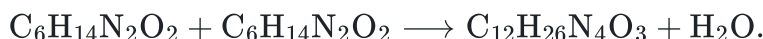
8.5 i

L-Lysine is (2*S*)-2,6-diaminohexanoic acid, $\text{N}[\text{C}(\text{H})_4](\text{CCCCN})\text{C}(=\text{O})\text{O}$, with molecular formula $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$.

Because **C** is a structural isomer of lysine,

$$\boxed{C = \text{C}_6\text{H}_{14}\text{N}_2\text{O}_2}.$$

Condensation of one molecule of **C** with one lysine molecule eliminates one water molecule:



Therefore

$$\boxed{D = \text{C}_{12}\text{H}_{26}\text{N}_4\text{O}_3}.$$

Since **E** loses one water molecule to produce **X**,



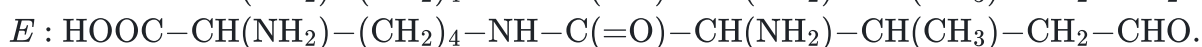
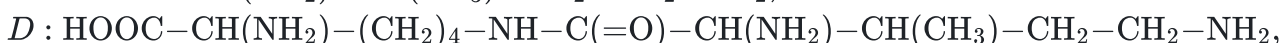
and hence

$$\boxed{E = \text{C}_{12}\text{H}_{23}\text{N}_3\text{O}_4}.$$

The structures, with the stereochemistry established in 8.6–8.7, are as follows. These SMILES represent neutral free-acid forms.

Compound	Name	SMILES
C	(2 <i>R</i> , 3 <i>R</i>)-2,5-Diamino-3-methylpentanoic acid; 3-methyl-D-ornithine	<chem>N[C@H]([C@H](C)CCN)C(=O)O</chem>
D	<i>N</i> ^ε -[(2 <i>R</i> ,3 <i>R</i>)-2,5-diamino-3-methylpentanoyl]-L-lysine	<chem>N[C@@H](CCCCNC(=O)[C@H](N)[C@H](C)CCN)C(=O)O</chem>
E	<i>N</i> ^ε -[(2 <i>R</i> ,3 <i>R</i>)-2-amino-3-methyl-5-oxopentanoyl]-L-lysine	<chem>N[C@@H](CCCCNC(=O)[C@H](N)[C@H](C)CC=O)C(=O)O</chem>

Their condensed connectivities are

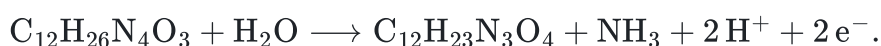


The amide in **D** joins the carboxyl group of **C** to the ε-amino group of the second lysine molecule.

8.5 ii

The terminal aminomethyl group in **D** becomes the aldehyde group in **E**. This is **oxidative deamination**.

Writing the neutral molecular forms, its oxidation half-reaction is



Here NH_3 is ammonia, N . The electron acceptor is not specified in the problem.

The retained amino group of **E** then attacks its aldehyde carbon intramolecularly. Condensation eliminates water and forms the five-membered imine ring of **X**.

8.6

Position 3 is a saturated ring carbon with two different ring paths. A methyl or R substituent there would produce a stereogenic methine carbon. Since position 3 is expressly non-asymmetric, its indicated substituent must be **H**, making it a methylene group.

The remaining substituents, Me and R, occupy positions 4 and 5.

Reverse the final imine-forming condensation conceptually: the imine carbon at position 2 becomes the aldehyde, while the ring nitrogen becomes an amino group attached to position 5. Because precursor **C** is an **α-amino acid**, its carboxyl-derived carbonyl must be attached directly to that amino-bearing carbon. Thus the large carboxamide substituent is at position 5:



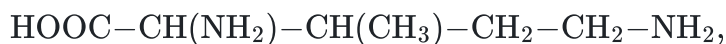
This is the lysine-derived carboxamide substituent, represented with its ring attachment marked by [*] as [*]C(=O)NCCCC[C@H](N)C(=O)O. Its composition is $\text{C}_7\text{H}_{13}\text{N}_2\text{O}_3$, corresponding to approximately 173 g mol^{-1} , consistent with the stated mass condition.

Consequently,



8.7

For **C**, the required structure is



with configurations $\boxed{2R, 3R}$.

A precise Fischer-projection description is: put the carboxyl group at the top and the $\text{CH}_2\text{CH}_2\text{NH}_2$ chain at the bottom; place the amino group on the right at C2 and the methyl group on the right at C3, with hydrogen on the left at both centres. Its stereochemical SMILES is $\text{N}[\text{C}@\text{H}](\text{C}[\text{C}@\text{H}] (\text{C})\text{CCN})\text{C}(=\text{O})\text{O}$.

For **X**, retain the five-membered ring orientation shown in the question:

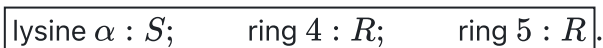
- The double bond joins N1 and C2.
- C3 is a methylene group.
- C4 bears methyl on the **dashed bond**, directed away from the viewer.
- C5 bears R on the **solid wedge**, directed toward the viewer.
- The lysine α -carbon retains its *S* configuration.

The CIP priorities establish the ring configurations:

Centre	Priorities, highest to lowest	Configuration
Ring C4	Ring path through C5; ring path through C3; methyl; H	<i>R</i>
Ring C5	Ring N; carbonyl carbon of R; ring C4; H	<i>R</i>
Lysine α -carbon	Amino N; carboxyl carbon; side-chain carbon; H	<i>S</i>

For example, at ring C5 the carbonyl carbon has the comparison list (O, O, N), which outranks the (C, C, H) list of ring C4.

Thus **X is pyrrolysine**, with



Its complete stereochemical SMILES is



The wedges specify configuration; they do not require a particular fixed ring conformation.

8.8

The functional-group counts in the four bases are:

Base	Name and SMILES	Exocyclic amino groups	Exocyclic oxygen atoms
A	Adenine, Nc1ncnc2[nH]cnc12	1	0
C	Cytosine, Nc1cc[nH]c(=O)n1	1	1
G	Guanine, $\text{Nc1nc2[nH]cnc2c(=O)[nH]1}$	1	1
U	Uracil, $\text{O=c1cc[nH]c(=O)[nH]1}$	0	2

Let their numbers in the codon be a, c, g, u . A codon contains three bases:

$$a + c + g + u = 3.$$

The two amino groups give

$$a + c + g = 2,$$

so $u = 1$. The three oxygen atoms give

$$c + g + 2u = 3,$$

hence $c + g = 1$, and therefore $a = 1$.

The completed table is

Nitrogen base	1	2	3	0 or 1	1 or 2
A	✓				
C				✓	
G				✓	
U	✓				

Thus the codon contains one A, one U, and either one C or one G. This determines composition, but not yet order.

8.9 a

A candidate X codon must contain exactly the bases AUC or AUG in some order. Checking the three reading frames, the first two contain no complete codons with either composition. The third frame gives

$$5' \dots AA \mid UAG \mid AAU \mid UAG \mid CGG \mid AAC \mid AGA \mid GGG \mid UGA \mid C \dots 3'.$$

UAG occurs twice, whereas UGA occurs once. Since only one codon encodes X and more than one X residue occurs in the fragment,

$$\boxed{\text{X codon} = \text{UAG}}.$$

There are **eight complete codons**. The leading AA and trailing C are incomplete codons and contribute no residues to the requested count.

Since the fragment belongs to the coding sequence of the enzyme, the final complete codon, UGA, is read as **selenocysteine** in this enzyme-coding fragment. Therefore

$$\boxed{8 \text{ amino acid residues are incorporated}}.$$

8.9 b

The translation is

Complete codon	Residue
UAG	X, pyrrolysine
AAU	Asn
UAG	X, pyrrolysine
CGG	Arg
AAC	Asn
AGA	Arg
GGG	Gly
UGA	Sec

Hence, from N- to C-terminus,

$$\boxed{\text{X} - \text{Asn} - \text{X} - \text{Arg} - \text{Asn} - \text{Arg} - \text{Gly} - \text{Sec}}.$$

The additional amino acids are identified below. The SMILES describe their neutral free amino acids; incorporation into the protein gives the corresponding peptide residues.

Abbreviation	Name	SMILES
Asn	L-Asparagine	<chem>N[C@@H](CC(=O)N)C(=O)O</chem>
Arg	L-Arginine	<chem>N[C@@H](CCCNC(=N)N)C(=O)O</chem>
Gly	Glycine	<chem>NCC(=O)O</chem>
Sec	L-Selenocysteine, with <i>R</i> configuration at its α -carbon	<chem>N[C@@H](C[SeH])C(=O)O</chem>

Fill the first eight answer boxes with this sequence and leave the final two empty.

The solution was checked against the official solution.