

IChO 2004

Theory problems and solutions · Kiel, Germany · 8 theory problems with complete solutions

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Problem 1: Thermodynamics

For his 18th birthday party in February Peter plans to turn a hut in the garden of his parents into a swimming pool with an artificial beach. In order to estimate the costs for heating the water and the house, Peter obtains the data for the natural gas composition and its price.

1.1 Write down the chemical equations for the complete combustion of the main components of natural gas, methane and ethane, given in Table 1. Assume that nitrogen is inert under the chosen conditions.

Calculate the reaction enthalpy, the reaction entropy, and the Gibbs energy under standard conditions ($1.013 \cdot 10^5$ Pa, 25.0 °C) for the combustion of methane and ethane according to the equations above assuming that all products are gaseous.

The thermodynamic properties and the composition of natural gas can be found in Table 1.

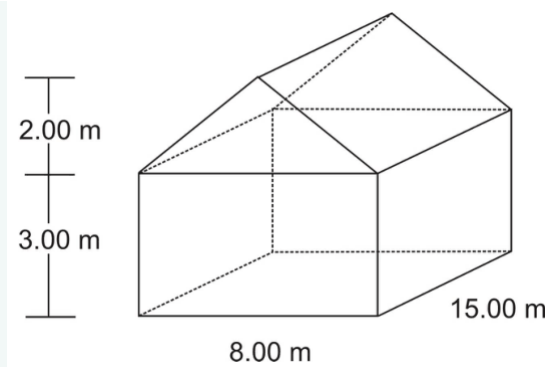
1.2 The density of natural gas is 0.740 g dm^{-3} (1.013×10^5 Pa, 25.0 °C) specified by PUC, the public utility company.

a) Calculate the amount of methane and ethane (in moles) in 1.00 m^3 of natural gas (natural gas, methane, and ethane are not ideal gases!).

b) Calculate the combustion energy which is released as thermal energy during the burning of 1.00 m^3 of natural gas under standard conditions assuming that all products are gaseous. (If you do not have the amount from 1.2a) assume that 1.00 m^3 natural gas corresponds to 40.00 mol natural gas.)

According to the PUC the combustion energy will be 9.981 kWh per m^3 of natural gas if all products are gaseous. How large is the deviation (in percent) from the value you obtained in b)

The swimming pool inside the house is 3.00 m wide, 5.00 m long and 1.50 m deep (below the floor). The tap water temperature is 8.00 °C and the air temperature in the house (dimensions given in the figure below) is 10.0 °C. Assume a water density of $\rho = 1.00 \text{ kg dm}^{-3}$ and air behaving like an ideal gas.



1.3 Calculate the energy (in MJ) which is required to heat the water in the pool to $22.0\text{ }^{\circ}\text{C}$ and the energy which is required to heat the initial amount of air (21.0 % of O_2 , 79.0 % of N_2) to $30.0\text{ }^{\circ}\text{C}$ at a pressure of $1.013 \times 10^5\text{ Pa}$.

In February, the outside temperature is about $5\text{ }^{\circ}\text{C}$ in Northern Germany. Since the concrete walls and the roof of the house are relatively thin (20.0 cm) there will be a loss of energy. This energy is released to the surroundings (heat loss released to water and/or ground should be neglected). The heat conductivity of the wall and roof is $1.00\text{ W K}^{-1}\text{ m}^{-1}$.

1.4 Calculate the energy (in MJ) which is needed to maintain the temperature inside the house at $30.0\text{ }^{\circ}\text{C}$ during the party (12 hours).

1.00 m^3 of natural gas as delivered by PUC costs 0.40 € and 1.00 kWh of electricity costs 0.137 €. The rent for the equipment for gas heating will cost him about 150.00 € while the corresponding electrical heaters will only cost 100.00 €.

1.5 What is the total energy (in MJ) needed for Peter's "winter swimming pool" calculated in 1.3 and 1.4? How much natural gas will he need, if the gas heater has an efficiency of 90.0 %? What are the different costs for the use of either natural gas or electricity? Use the values given by PUC for your calculations and assume 100 % efficiency for the electric heater.

Table 1: Composition of natural gas

Chemical Substance	mol fraction x	$\Delta_f H^0\text{ (kJ mol}^{-1}\text{)}^{-1}$	$S^0\text{ (J mol}^{-1}\text{ K}^{-1}\text{)}^{-1}$	$C_p^0\text{ (J mol}^{-1}\text{ K}^{-1}\text{)}^{-1}$
$\text{CO}_2\text{ (g)}$	0.0024	-393.5	213.8	37.1
$\text{N}_2\text{ (g)}$	0.0134	0.0	191.6	29.1
$\text{CH}_4\text{ (g)}$	0.9732	-74.6	186.3	35.7
$\text{C}_2\text{H}_6\text{ (g)}$	0.0110	-84.0	229.2	52.5
$\text{H}_2\text{O (l)}$	–	-285.8	70.0	75.3
$\text{H}_2\text{O (g)}$	–	-241.8	188.8	33.6
$\text{O}_2\text{ (g)}$	–	0.0	205.2	29.4

Equation:

$$J = E \times (A \times \Delta t)^{-1} = \lambda_{\text{wall}} \times \Delta T \times d^{-1}$$

J energy flow E along a temperature gradient (wall direction z) per area A and time Δt

d wall thickness

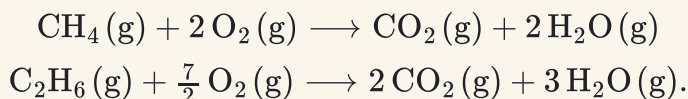
λ_{wall} heat conductivity

ΔT difference in temperature between the inside and the outside of the house

Official English text of the problem.

Answers

- 1.1 The balanced combustion equations are



The thermodynamic quantities at 298.15 K, **per mole of fuel**, are:

Fuel	$\Delta_r H^\circ / \text{kJ mol}^{-1}$	$\Delta_r S^\circ / \text{J mol}^{-1} \text{K}^{-1}$	$\Delta_r G^\circ / \text{kJ mol}^{-1}$
Methane C	-802.5	-5.3	-800.9
Ethane CC	-1428.4	+46.6	-1442.3

- 1.2(a) In 1.00 m^3 of natural gas:

$$n(\text{CH}_4) = 43.9 \text{ mol}, \quad n(\text{C}_2\text{H}_6) = 0.496 \text{ mol}.$$

- 1.2(b) The heat released is

$$Q = 35.9 \text{ MJ} = 9.97 \text{ kWh}.$$

Using unrounded intermediate values, PUC's value is approximately 0.086% **higher**, or about 0.1%.

- 1.3

$$Q_{\text{water}} = 1.32 \times 10^3 \text{ MJ}, \quad Q_{\text{air}} = 12.0 \text{ MJ}.$$

- 1.4

$$Q_{\text{loss}} = 1.56 \times 10^3 \text{ MJ}.$$

- 1.5 The total heat requirement and natural-gas volume are

$$Q_{\text{total}} = 2.88 \times 10^3 \text{ MJ}, \quad V_{\text{gas}} = 89.2 \text{ m}^3.$$

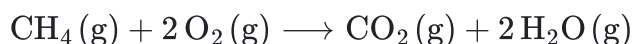
Including equipment rental, the estimated costs are **€185.68 for gas** and **€209.77 for electricity**. Gas heating saves approximately **€24.09**.

Solution

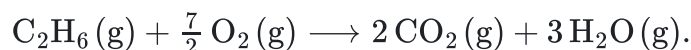
The molecular identities used throughout are methane c (CH_4), ethane CC (C_2H_6), oxygen O=O (O_2), carbon dioxide O=C=O (CO_2), water o (H_2O), and nitrogen N#N (N_2). SMILES do not specify physical phase; gaseous and liquid water are distinguished by the phase labels.

1.1 — Combustion equations and thermodynamic quantities

Complete combustion converts the carbon atoms into carbon dioxide and the hydrogen atoms into water. Balancing carbon, hydrogen, and then oxygen gives



and



Nitrogen remains unchanged under the stated assumption. Each equation is written for one mole of fuel.

For either reaction,

$$\begin{aligned}\Delta_{\text{r}}H^{\circ} &= \sum_{\text{products}} \nu_i \Delta_{\text{f}}H_i^{\circ} - \sum_{\text{reactants}} \nu_i \Delta_{\text{f}}H_i^{\circ}, \\ \Delta_{\text{r}}S^{\circ} &= \sum_{\text{products}} \nu_i S_i^{\circ} - \sum_{\text{reactants}} \nu_i S_i^{\circ},\end{aligned}$$

and, at $T = 25.0 + 273.15 = 298.15\text{ K}$,

$$\Delta_{\text{r}}G^{\circ} = \Delta_{\text{r}}H^{\circ} - T\Delta_{\text{r}}S^{\circ}.$$

For **methane**, using the data for gaseous water,

$$\begin{aligned}\Delta_{\text{r}}H^{\circ} &= [-393.5 + 2(-241.8)] - [-74.6 + 2(0)] \\ &= \boxed{-802.5\text{ kJ mol}^{-1}}, \\ \Delta_{\text{r}}S^{\circ} &= [213.8 + 2(188.8)] - [186.3 + 2(205.2)] \\ &= \boxed{-5.3\text{ J mol}^{-1}\text{ K}^{-1}}, \\ \Delta_{\text{r}}G^{\circ} &= -802.5 - (298.15)(-5.3 \times 10^{-3}) \\ &= \boxed{-800.9\text{ kJ mol}^{-1}}.\end{aligned}$$

For **ethane**,

$$\begin{aligned}\Delta_{\text{r}}H^{\circ} &= [2(-393.5) + 3(-241.8)] - [-84.0 + \frac{7}{2}(0)] \\ &= \boxed{-1428.4\text{ kJ mol}^{-1}}, \\ \Delta_{\text{r}}S^{\circ} &= [2(213.8) + 3(188.8)] - [229.2 + \frac{7}{2}(205.2)] \\ &= \boxed{+46.6\text{ J mol}^{-1}\text{ K}^{-1}}, \\ \Delta_{\text{r}}G^{\circ} &= -1428.4 - (298.15)(46.6 \times 10^{-3}) \\ &= \boxed{-1442.3\text{ kJ mol}^{-1}}.\end{aligned}$$

1.2(a) — Amounts of methane and ethane

The supplied density gives the mass directly:

$$m = \rho V = (0.740\text{ g dm}^{-3})(1000\text{ dm}^3) = 740\text{ g}.$$

Use the conventional molar masses

$$\begin{aligned}M(\text{CO}_2) &= 44.01\text{ g mol}^{-1}, & M(\text{N}_2) &= 28.02\text{ g mol}^{-1}, \\ M(\text{CH}_4) &= 16.04\text{ g mol}^{-1}, & M(\text{C}_2\text{H}_6) &= 30.07\text{ g mol}^{-1}.\end{aligned}$$

The mean molar mass is the mole-fraction-weighted average, including the noncombustible components:

$$\begin{aligned}\bar{M} &= \sum_i x_i M_i \\ &= 0.0024(44.01) + 0.0134(28.02) + 0.9732(16.04) + 0.0110(30.07) \\ &= 16.42199 \text{ g mol}^{-1}.\end{aligned}$$

Hence

$$n_{\text{total}} = \frac{740}{16.42199} = 45.0615 \text{ mol}.$$

The individual amounts are

$$\begin{aligned}n(\text{CH}_4) &= x_{\text{CH}_4} n_{\text{total}} = 0.9732(45.0615) = 43.8539 \text{ mol} \approx \boxed{43.9 \text{ mol}}, \\ n(\text{C}_2\text{H}_6) &= x_{\text{C}_2\text{H}_6} n_{\text{total}} = 0.0110(45.0615) = 0.495677 \text{ mol} \approx \boxed{0.496 \text{ mol}}.\end{aligned}$$

These mass and mole-fraction relationships do not require ideal-gas behaviour.

1.2(b) — Heat of combustion and comparison with PUC

At constant pressure, the heat released is the negative of the combustion enthalpy. Only methane and ethane contribute to the combustion heat:

$$\begin{aligned}Q_{\text{released}} &= -[n(\text{CH}_4)\Delta_r H_{\text{CH}_4}^\circ + n(\text{C}_2\text{H}_6)\Delta_r H_{\text{C}_2\text{H}_6}^\circ] \\ &= (43.8539)(802.5) + (0.495677)(1428.4) \\ &= 35900.8 \text{ kJ} \\ &= 35.9008 \text{ MJ}.\end{aligned}$$

Since 1 kWh = 3.600 MJ,

$$Q_{\text{released}} = \frac{35.9008}{3.600} = 9.97243 \text{ kWh}.$$

Thus, to three significant figures,

$$\boxed{Q_{\text{released}} = 35.9 \text{ MJ} = 9.97 \text{ kWh}}.$$

Taking the calculated value as the reference, as requested,

$$\begin{aligned}\text{deviation} &= \frac{Q_{\text{PUC}} - Q_{\text{calculated}}}{Q_{\text{calculated}}} \times 100\% \\ &= \frac{9.981 - 9.97243}{9.97243} \times 100\% \\ &= \boxed{0.0859\%}.\end{aligned}$$

PUC's value is therefore approximately 0.09% higher; this very small difference is about 0.1%.

1.3 — Heating the water and the initial air

The supplied heat capacities are treated as constant over the temperature intervals.

For the **pool water**,

$$V_{\text{water}} = (3.00)(5.00)(1.50) = 22.5 \text{ m}^3 = 2.25 \times 10^4 \text{ dm}^3.$$

Its mass is

$$m_{\text{water}} = (1.00 \text{ kg dm}^{-3})(2.25 \times 10^4 \text{ dm}^3) = 2.25 \times 10^4 \text{ kg}.$$

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

$$n_{\text{water}} = \frac{2.25 \times 10^7 \text{ g}}{18.02 \text{ g mol}^{-1}} = 1.24861 \times 10^6 \text{ mol}.$$

The temperature increase is

$$\Delta T_{\text{water}} = 22.0 - 8.00 = 14.0 \text{ K}.$$

Therefore,

$$\begin{aligned} Q_{\text{water}} &= n_{\text{water}} C_{p,\text{water}} \Delta T_{\text{water}} \\ &= (1.24861 \times 10^6)(75.3)(14.0) \text{ J} \\ &= 1316.29 \text{ MJ} \\ &\approx \boxed{1.32 \times 10^3 \text{ MJ}}. \end{aligned}$$

For the **air**, the building consists of a rectangular prism topped by a triangular prism. Its volume is

$$\begin{aligned} V_{\text{air}} &= (8.00)(15.00)(3.00) + \frac{1}{2}(8.00)(2.00)(15.00) \\ &= 360 + 120 \\ &= 480 \text{ m}^3. \end{aligned}$$

The pool is below floor level, so its volume is not subtracted.

At the initial temperature $T_i = 283.15 \text{ K}$, the ideal-gas law, with $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, gives

$$n_{\text{air}} = \frac{pV}{RT_i} = \frac{(1.013 \times 10^5)(480)}{(8.314)(283.15)} = 2.06549 \times 10^4 \text{ mol}.$$

The molar heat capacity of the mixture is

$$\begin{aligned} C_{p,\text{air}} &= 0.210 C_p(\text{O}_2) + 0.790 C_p(\text{N}_2) \\ &= 0.210(29.4) + 0.790(29.1) \\ &= 29.163 \text{ J mol}^{-1} \text{ K}^{-1}. \end{aligned}$$

The question specifies heating the initial amount of air at constant pressure, so C_p applies:

$$\begin{aligned} Q_{\text{air}} &= n_{\text{air}} C_{p,\text{air}} (30.0 - 10.0) \\ &= (2.06549 \times 10^4)(29.163)(20.0) \text{ J} \\ &= 12.0472 \text{ MJ} \\ &\approx \boxed{12.0 \text{ MJ}}. \end{aligned}$$

1.4 — Heat loss during the party

Heat passes through the four walls, including the two triangular gables, and the two sloping roof faces.

The rectangular wall area is

$$A_{\text{rectangular}} = 2(15.00)(3.00) + 2(8.00)(3.00) = 138.0 \text{ m}^2.$$

The combined area of the triangular gables is

$$A_{\text{gables}} = 2 \left[\frac{1}{2}(8.00)(2.00) \right] = 16.0 \text{ m}^2.$$

The sloping distance from an eave to the ridge is

$$s = \sqrt{(8.00/2)^2 + (2.00)^2} = \sqrt{20.00} = 4.47214 \text{ m}.$$

Thus the roof area is

$$A_{\text{roof}} = 2(15.00)(4.47214) = 134.164 \text{ m}^2.$$

The total area conducting heat to the outside is

$$A = 138.0 + 16.0 + 134.164 = 288.164 \text{ m}^2.$$

The temperature difference, thickness, and duration are

$$\Delta T = 30.0 - 5 = 25 \text{ K}, \quad d = 0.200 \text{ m}, \quad \Delta t = 12(3600) = 43200 \text{ s}.$$

Rearranging the supplied heat-flow equation,

$$Q_{\text{loss}} = \frac{\lambda A \Delta T \Delta t}{d}.$$

Therefore,

$$\begin{aligned} Q_{\text{loss}} &= \frac{(1.00)(288.164)(25)(43200)}{0.200} \text{ J} \\ &= 1.556086 \times 10^9 \text{ J} \\ &= 1556.09 \text{ MJ} \\ &\approx \boxed{1.56 \times 10^3 \text{ MJ}}. \end{aligned}$$

This is the heat that must be supplied during the party to maintain the indoor temperature.

1.5 — Total energy, gas consumption, and costs

Adding the results without prematurely rounding,

$$\begin{aligned} Q_{\text{total}} &= Q_{\text{water}} + Q_{\text{air}} + Q_{\text{loss}} \\ &= 1316.287 + 12.047 + 1556.086 \\ &= 2884.42 \text{ MJ} \\ &\approx \boxed{2.88 \times 10^3 \text{ MJ}}. \end{aligned}$$

For **gas heating**, use PUC's specified energy content:

$$q_{\text{gas}} = 9.981 \text{ kWh m}^{-3} = 35.9316 \text{ MJ m}^{-3}.$$

At 90.0% efficiency, each cubic metre supplies

$$q_{\text{useful}} = 0.900(35.9316) = 32.33844 \text{ MJ m}^{-3}.$$

Hence

$$V_{\text{gas}} = \frac{2884.42}{32.33844} = 89.1948 \text{ m}^3 \approx \boxed{89.2 \text{ m}^3}.$$

The fuel charge is

$$C_{\text{gas,fuel}} = (89.1948 \text{ m}^3)(0.40 \text{ € m}^{-3}) = 35.68 \text{ €}.$$

Including equipment rental,

$$\boxed{C_{\text{gas,total}} \approx 35.68 + 150.00 = 185.68 \text{ €}}.$$

For **electric heating**, the 100% efficiency means the required electrical energy is

$$E_{\text{electricity}} = \frac{2884.42}{3.600} = 801.228 \text{ kWh}.$$

The electricity charge is

$$C_{\text{electricity,energy}} = (801.228)(0.137) = 109.77 \text{ €}.$$

Including equipment rental,

$$C_{\text{electricity,total}} \approx 109.77 + 100.00 = 209.77 \text{ €}.$$

The estimated saving from choosing gas is

$$209.77 - 185.68 = 24.09 \text{ €}.$$

The solution was checked against the official solution.

Problem 2: Kinetics at catalyst surfaces

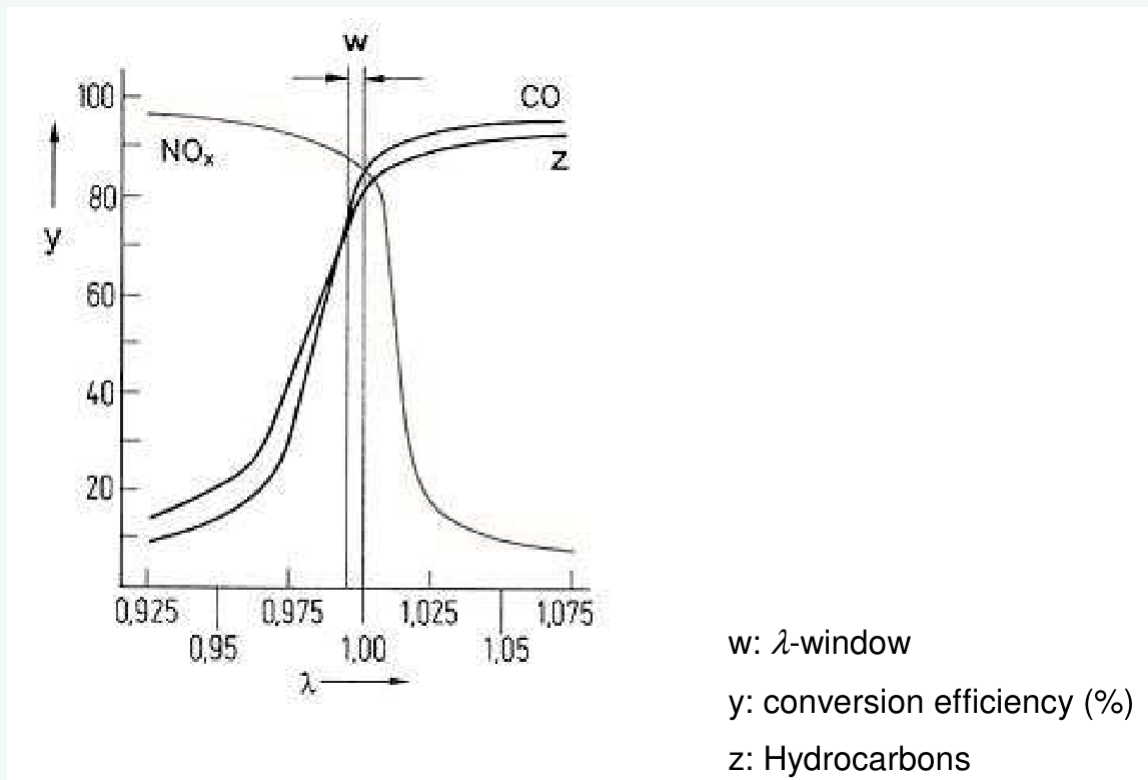
Apart from other compounds the exhaust gases of an Otto engine are the main pollutants carbon monoxide, nitrogen monoxide and uncombusted hydrocarbons, as, for example, octane. To minimize them they are converted to carbon dioxide, nitrogen and water in a regulated three-way catalytic converter.

2.1 Complete the chemical reaction equations for the reactions of the main pollutants in the catalyst.

To remove the main pollutants from the exhaust gas of an Otto engine optimally, the λ -value is determined by an electro-chemical element, the so called lambda probe. It is located in the exhaust gas stream between engine and the three-way catalytic converter.

The lambda value is defined as

$$\lambda = \frac{\text{amount of air at the inlet}}{\text{amount of air necessary for complete combustion}}.$$



2.2 Decide the questions on the answer sheet concerning the λ probe.

The adsorption of gas molecules on a solid surface can be described in a simple model by using the Langmuir isotherm:

$$\theta = \frac{K \times p}{1 + K \times p}$$

where θ is the fraction of surface sites that are occupied by the gas molecules, p is the gas pressure and K is a constant.

The adsorption of a gas at 25 °C may be described by using the Langmuir isotherm with $K = 0.85 \text{ kPa}^{-1}$.

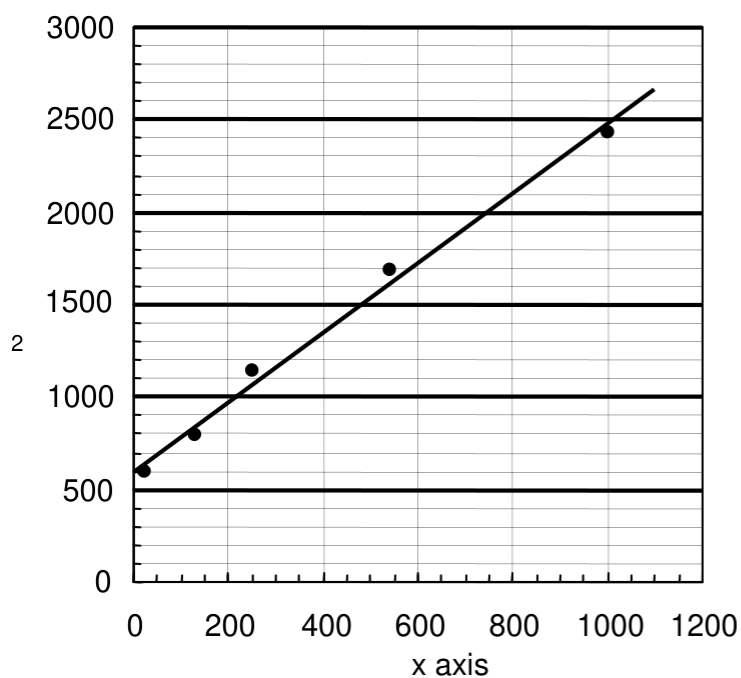
2.3 a) Determine the surface coverage θ at a pressure of 0.65 kPa.

b) Determine the pressure p at which 15 % of the surface is covered.

c) The rate r of the decomposition of gas molecules at a solid surface depends on the surface coverage θ (reverse reaction neglected): $r = k\theta$

Give the order of the decomposition reaction at low and at high gas pressures assuming the validity of the Langmuir isotherm given above (products to be neglected).

d) Data for the adsorption of another gas on a metal surface (at 25 °C)



x axis: $p \cdot (\text{Pa})^{-1}$

y axis: $p \cdot V_a^{-1} \cdot (\text{Pa cm}^{-3})^{-1}$

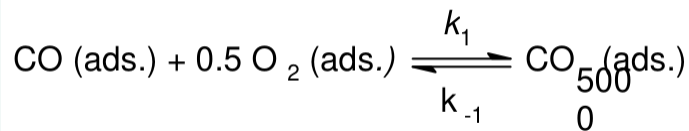
V_a is the gas volume that has been adsorbed.

If the Langmuir isotherm can be applied, determine the gas volume $V_{a,\text{max}}$ needed for a complete coverage of the metal surface and the product $KV_{a,\text{max}}$.

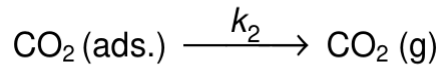
Hint: Set $\theta = V_a/V_{a,\text{max}}$.

Assume that the catalytic oxidation of CO on a Pd surface with equal surface sites proceeds in the following way:

In a first step adsorbed CO and adsorbed O_2 form adsorbed CO_2 in a fast equilibrium,



In a slow second step, CO_2 is then desorbed from the surface:



2.4 Derive the formula for the reaction rate of the $\text{CO}_2 \text{ (g)}$ - formation as a function of the partial pressures of the reaction components.

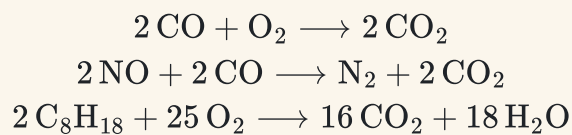
Hint: Use the Langmuir isotherm with the proper number of gas components

$$\theta_i = \frac{K_i \times p_i}{1 + \sum_j K_j \times p_j} \quad \text{j: relevant gas components}$$

Official English text of the problem.

Answers

- **2.1**



- **2.2** Simultaneous removal of the three pollutants requires operation within the narrow λ -window near $\lambda = 1$, slightly on the fuel-rich side in the diagram.

$\lambda < 1$: fuel-rich, insufficient air.

$\lambda > 1$: fuel-lean, excess air.

The probe supplies an oxygen-dependent voltage used to regulate the air–fuel ratio. The individual answer-sheet statements are unavailable.

- **2.3(a)** $\theta \approx 0.36$, or approximately 36% coverage.
- **2.3(b)** $p \approx 0.21 \text{ kPa}$.
- **2.3(c)** First order at low pressure, $Kp \ll 1$; zero order at high pressure, $Kp \gg 1$.
- **2.3(d)** From the plotted straight line:

$$V_{a,\max} \approx 0.53 \text{ cm}^3, \quad KV_{a,\max} \approx 1.7 \times 10^{-3} \text{ cm}^3 \text{ Pa}^{-1}.$$

• 2.4

$$r = \frac{k_1 k_2}{k_{-1}} \frac{K_{\text{CO}} p_{\text{CO}} \sqrt{K_{\text{O}_2} p_{\text{O}_2}}}{D^{3/2}}$$

For reactant-only competitive adsorption,

$$D = 1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2}.$$

If gaseous carbon dioxide is also included as a competing adsorbate, use

$$D = 1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2} + K_{\text{CO}_2} p_{\text{CO}_2}.$$

The distinction is discussed below.

Solution

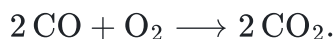
The molecular and ionic identities used in the solution are:

Name	Formula	SMILES
Carbon monoxide	CO	[C-]#[O+]
Nitrogen monoxide, or nitric oxide	NO	[N]=O
Octane, represented by <i>n</i> -octane	C ₈ H ₁₈	CCCCCCCC
Carbon dioxide	CO ₂	O=C=O
Dinitrogen	N ₂	N#N
Water	H ₂ O	O
Dioxygen	O ₂	O=O
Oxide ion	O ²⁻	[O-2]

All octane isomers have the same combustion stoichiometry. These SMILES describe the molecular identities; they do not specify adsorption geometries on palladium. The conventional dioxygen SMILES also does not specify its triplet electronic ground state.

2.1 — Reactions in the catalytic converter

Carbon monoxide is oxidized to carbon dioxide:



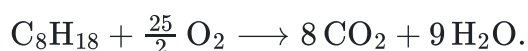
Carbon changes from oxidation state +2 to +4.

Nitrogen monoxide is reduced to nitrogen, with carbon monoxide supplying the reducing equivalents:

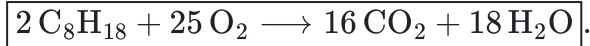


Each nitrogen atom changes from +2 to 0, accepting two electrons. Each carbon atom changes from +2 to +4, supplying two electrons. Thus the required mole ratio of nitrogen monoxide to carbon monoxide is 1 : 1.

Complete oxidation of one octane molecule produces eight carbon dioxide molecules and nine water molecules:



The products contain $16 + 9 = 25$ oxygen atoms. Multiplying by two gives integer coefficients:



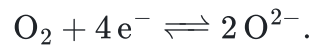
2.2 — Lambda probe and operating window

The definition of λ directly gives:

Condition	Air–fuel mixture	Consequence for conversion
$\lambda < 1$	Fuel-rich; less air than required for complete combustion	Nitrogen monoxide reduction is favoured, but oxidation of carbon monoxide and hydrocarbons is limited by oxygen availability.
$\lambda \approx 1$	Approximately stoichiometric	A narrow range permits efficient simultaneous oxidation and reduction.
$\lambda > 1$	Fuel-lean; excess air	Carbon monoxide and hydrocarbon oxidation are favoured, while nitrogen monoxide reduction becomes inefficient.

In the diagram, the operating window is the narrow band between the two marked vertical lines immediately below and approximately at $\lambda = 1$. The falling curve represents nitrogen oxides; the two rising curves represent carbon monoxide and hydrocarbons.

A conventional oxygen-ion-conducting lambda probe is an electrochemical oxygen concentration cell. Its electrode equilibrium is



Oxide ions move through the solid electrolyte, and electrons move through the external circuit.

With reference air on one side and exhaust gas on the other, the ideal cell voltage, with the reference electrode taken as positive, is

$$E = \frac{RT}{4F} \ln \left(\frac{p_{\text{O}_2, \text{reference}}}{p_{\text{O}_2, \text{exhaust}}} \right).$$

Here T is the probe's operating temperature.

Fuel-rich exhaust has a very low oxygen partial pressure and gives a relatively high voltage. Lean exhaust has a higher oxygen partial pressure and gives a lower voltage. This signal allows the engine controller to adjust the fuel supply and keep λ within the operating window.

2.3(a) — Surface coverage

Using

$$\theta = \frac{Kp}{1 + Kp},$$

the dimensionless product is

$$Kp = (0.85 \text{ kPa}^{-1})(0.65 \text{ kPa}) = 0.5525.$$

Therefore,

$$\theta = \frac{0.5525}{1.5525} = 0.35588.$$

To two significant figures,

$$\theta = 0.36, \quad \text{coverage} = 36\%.$$

2.3(b) — Pressure for 15% coverage

Rearranging the Langmuir equation,

$$\begin{aligned}\theta(1 + Kp) &= Kp, \\ \theta &= Kp(1 - \theta),\end{aligned}$$

so

$$p = \frac{\theta}{K(1 - \theta)}.$$

At $\theta = 0.15$,

$$p = \frac{0.15}{(0.85 \text{ kPa}^{-1})(0.85)} = 0.20761 \text{ kPa}.$$

Thus,

$$\boxed{p = 0.21 \text{ kPa}}.$$

2.3(c) — Limiting reaction orders

Substitution of the Langmuir isotherm into $r = k\theta$ gives

$$r = \frac{kKp}{1 + Kp}.$$

At low pressure, $Kp \ll 1$:

$$r \approx kKp.$$

The rate is proportional to pressure, so the reaction is **first order**.

At high pressure, $Kp \gg 1$:

$$r \approx k.$$

The surface is almost completely covered. Increasing the pressure produces essentially no further increase in coverage or rate, so the reaction is **zero order**.

The continuous transition can be expressed through the apparent order:

$$n = \frac{d \ln r}{d \ln p} = \frac{1}{1 + Kp}.$$

2.3(d) — Maximum adsorbed volume

With the supplied identification

$$\theta = \frac{V_a}{V_{a,\max}},$$

the Langmuir equation becomes

$$V_a = V_{a,\max} \frac{Kp}{1 + Kp}.$$

Rearrangement gives the straight-line form

$$\boxed{\frac{p}{V_a} = \frac{1}{KV_{a,\max}} + \frac{p}{V_{a,\max}}}.$$

Thus a plot of p/V_a against p has

$$\text{slope } m = \frac{1}{V_{a,\max}}, \quad \text{intercept } b = \frac{1}{KV_{a,\max}}.$$

The graph's abscissa is pressure in pascals, and its ordinate is p/V_a in Pa cm^{-3} . Reading the drawn line approximately,

$$b \approx 600 \text{ Pa cm}^{-3},$$

and, using its ordinate near $p = 1000 \text{ Pa}$,

$$m \approx \frac{(2500 - 600) \text{ Pa cm}^{-3}}{1000 \text{ Pa}} = 1.9 \text{ cm}^{-3}.$$

Consequently,

$$V_{a,\max} = \frac{1}{m} \approx \frac{1}{1.9 \text{ cm}^{-3}} = \boxed{0.53 \text{ cm}^3},$$

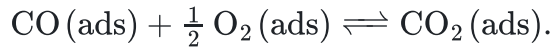
and

$$KV_{a,\max} = \frac{1}{b} \approx \frac{1}{600 \text{ Pa cm}^{-3}} = \boxed{1.7 \times 10^{-3} \text{ cm}^3 \text{ Pa}^{-1}}.$$

These are graphical estimates for the second gas.

2.4 — Rate of carbon dioxide formation

The stipulated surface equilibrium is



Using the mass-action interpretation of this equilibrium, its forward and reverse rates are

$$v_1 = k_1 \theta_{\text{CO}} \theta_{\text{O}_2}^{1/2}, \quad v_{-1} = k_{-1} \theta_{\text{CO}_2}.$$

Because this step is fast compared with desorption,

$$k_1 \theta_{\text{CO}} \theta_{\text{O}_2}^{1/2} \approx k_{-1} \theta_{\text{CO}_2},$$

giving

$$\theta_{\text{CO}_2} = \frac{k_1}{k_{-1}} \theta_{\text{CO}} \theta_{\text{O}_2}^{1/2}.$$

The slow step is



so, in the same surface-coverage rate convention used in 2.3(c),

$$r = k_2 \theta_{\text{CO}_2} = \frac{k_1 k_2}{k_{-1}} \theta_{\text{CO}} \theta_{\text{O}_2}^{1/2}.$$

Write the common competitive-adsorption denominator as

$$D = 1 + \sum_j K_j p_j.$$

The supplied isotherm then gives

$$\theta_{\text{CO}} = \frac{K_{\text{CO}} p_{\text{CO}}}{D}, \quad \theta_{\text{O}_2} = \frac{K_{\text{O}_2} p_{\text{O}_2}}{D}.$$

Substitution yields

$$r = \frac{k_1 k_2}{k_{-1}} \frac{K_{\text{CO}} p_{\text{CO}} \sqrt{K_{\text{O}_2} p_{\text{O}_2}}}{D^{3/2}}.$$

The denominator exponent is $1 + \frac{1}{2} = \frac{3}{2}$.

For the reactant-only competitive Langmuir approximation,

$$r = \frac{k_1 k_2}{k_{-1}} \frac{K_{\text{CO}} p_{\text{CO}} \sqrt{K_{\text{O}_2} p_{\text{O}_2}}}{(1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2})^{3/2}}.$$

If the instruction "relevant gas components" includes competitive adsorption of gaseous carbon dioxide, the formal three-component expression instead is

$$r = \frac{k_1 k_2}{k_{-1}} \frac{K_{\text{CO}} p_{\text{CO}} \sqrt{K_{\text{O}_2} p_{\text{O}_2}}}{(1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2} + K_{\text{CO}_2} p_{\text{CO}_2})^{3/2}}.$$

Setting the product-adsorption contribution to zero recovers the reactant-only expression.

The solution was checked against the official solution.

Problem 3: Monovalent alkaline earth compounds?

In the past there have been several reports on compounds of monovalent calcium. Until recently the nature of these "compounds" was not known but they are still of great interest to solid state chemists.

Attempts to reduce CaCl_2 to CaCl have been made with

(a) Calcium (b) Hydrogen (c) Carbon

3.1 Give the corresponding reaction equations that could potentially lead to the formation of CaCl .

After an attempt to reduce CaCl_2 with the stoichiometric 1 : 1 molar amount of Ca one obtains an inhomogeneous grey substance. A closer look under the microscope reveals silvery metallic particles and colourless crystals.

3.2 What substance are the metallic particles and the colourless crystals?

When CaCl_2 is attempted to be reduced with elemental hydrogen a white product forms.

Elemental analysis shows that the sample contains 52.36 % (by mass) of calcium and 46.32 mass % of chlorine.

3.3 Determine the empirical formula of the compound formed.

When CaCl_2 is attempted to be reduced with elemental carbon a red crystalline product forms.

The molar ratio of Ca and Cl determined by elemental analysis is $n(\text{Ca}) : n(\text{Cl}) = 1.5 : 1$.

During the hydrolysis of the red crystalline substance the same gas is evolved as during the hydrolysis of Mg_2C_3 .

3.4 a) Show the two acyclic constitutional isomers of the gas that are formed by hydrolysis.

b) What compound is formed by the reaction of CaCl_2 with carbon?

(Provided that monovalent calcium does not exist.)

As none of these attempts lead to the formation of CaCl more consideration has to be given as to the hypothetical structure of CaCl . One can assume that CaCl is likely to crystallize in a simple crystal structure.

It is the radius ratio of cation $r(\text{M}^{m+})$ and anion $r(\text{X}^{x-})$ of salts that often determines the crystal structure of a particular compound as shown for MX compounds in the table below.

Coordination number of M	Surrounding of X	Radius ratio $r_{\text{M}}/r_{\text{X}}$	Structure type	estimated $\Delta_{\text{L}}H^0$ for CaCl
3	Triangular	0.155 – 0.225	BN	$-663.8 \text{ kJ mol}^{-1}$
4	Tetrahedral	0.225 – 0.414	ZnS	$-704.8 \text{ kJ mol}^{-1}$
6	Octahedral	0.414 – 0.732	NaCl	$-751.9 \text{ kJ mol}^{-1}$
8	Cubic	0.732 – 1.000	CsCl	$-758.4 \text{ kJ mol}^{-1}$

$\Delta_{\text{L}}H^0(\text{CaCl})$ is defined for the reaction $\text{Ca}^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{CaCl}(\text{s})$

3.5 a) What type of structure is CaCl likely to have?

$[r(\text{Ca}^+) \approx 120 \text{ pm (estimated)}, r(\text{Cl}^-) \approx 167 \text{ pm}]$

Not only the lattice energy $\Delta_{\text{L}}H^0$ for CaCl is important for the decision whether CaCl is thermodynamically stable or not. In order to decide whether it is stable against decomposition into its elements, the standard enthalpy of formation $\Delta_{\text{f}}H^0$ of CaCl has to be known.

b) Calculate the value of $\Delta_{\text{f}}H^0(\text{CaCl})$ with the aid of a Born-Haber-cycle.

heat of fusion	$\Delta_{\text{fusion}}H^0(\text{Ca})$		9.3 kJ mol^{-1}
ionization enthalpy	$\Delta_{1. \text{IE}}H(\text{Ca})$	$\text{Ca} \longrightarrow \text{Ca}^+$	$589.7 \text{ kJ mol}^{-1}$
ionization enthalpy	$\Delta_{2. \text{IE}}H(\text{Ca})$	$\text{Ca}^+ \longrightarrow \text{Ca}^{2+}$	$1145.0 \text{ kJ mol}^{-1}$
heat of vaporization	$\Delta_{\text{vap}}H^0(\text{Ca})$		$150.0 \text{ kJ mol}^{-1}$
dissociation energy	$\Delta_{\text{diss}}H(\text{Cl}_2)$	$\text{Cl}_2 \longrightarrow 2 \text{ Cl}$	$240.0 \text{ kJ mol}^{-1}$
enthalpy of formation	$\Delta_{\text{f}}H^0(\text{CaCl}_2)$		$-796.0 \text{ kJ mol}^{-1}$
electron affinity	$\Delta_{\text{EA}}H(\text{Cl})$	$\text{Cl} + \text{e}^- \longrightarrow \text{Cl}^-$	$-349.0 \text{ kJ mol}^{-1}$

To decide whether CaCl is thermodynamically stable to disproportionation into Ca and CaCl_2 the standard enthalpy of this process has to be calculated. (The change of the entropy ΔS is very small in this case, so its influence is negligible.)

3.6 Does the disproportionation of CaCl take place from a thermodynamic point of view? Base your decision on a calculation!

Official English text of the problem.

Answers

- **3.1 (a)** $\text{CaCl}_2 + \text{Ca} \longrightarrow 2 \text{ CaCl}$.
- **3.1 (b)** $2 \text{ CaCl}_2 + \text{H}_2 \longrightarrow 2 \text{ CaCl} + 2 \text{ HCl}$.

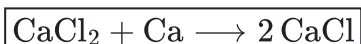
- **3.1 (c)** $4 \text{CaCl}_2 + \text{C} \longrightarrow 4 \text{CaCl} + \text{CCl}_4$.
- **3.2** Metallic particles: calcium, Ca. Colourless crystals: calcium chloride, CaCl_2 .
- **3.3** Calcium hydride chloride, CaHCl , containing divalent calcium.
- **3.4 (a)** Propyne, $\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$, SMILES CC#C; and propadiene (allene), $\text{H}_2\text{C}=\text{C}=\text{CH}_2$, SMILES C=C=C.
- **3.4 (b)** Calcium carbide chloride, $\text{Ca}_3\text{C}_3\text{Cl}_2$.
- **3.5 (a)** The NaCl (rock-salt) structure, with coordination number 6 and octahedral coordination.
- **3.5 (b)** $\Delta_f H^\circ(\text{CaCl}) = -231.9 \text{ kJ mol}^{-1}$.
- **3.6** Yes. For $2 \text{CaCl}(\text{s}) \longrightarrow \text{Ca}(\text{s}) + \text{CaCl}_2(\text{s})$, $\Delta_r H^\circ = -332.2 \text{ kJ mol}^{-1}$. With the stated negligible entropy contribution, disproportionation is thermodynamically favorable.

Solution

SMILES below describe discrete molecules or formal constituent ions. They do not specify the extended crystal lattices of the solids.

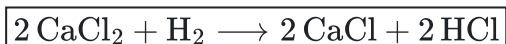
3.1 — Hypothetical reactions forming calcium(I) chloride

(a) Calcium



Calcium in oxidation state $+II$ gains one electron, while elemental calcium loses one electron. Both would therefore become calcium(I).

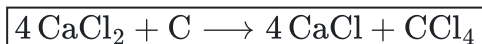
(b) Hydrogen



The two hydrogen atoms change from oxidation state 0 to $+I$, supplying the two electrons needed to reduce two calcium atoms from $+II$ to $+I$.

The molecular species are hydrogen, SMILES [H][H], and hydrogen chloride, SMILES [H]Cl.

(c) Carbon



Carbon changes from oxidation state 0 to $+IV$, supplying four electrons to reduce four calcium atoms from $+II$ to $+I$. Carbon tetrachloride has SMILES C1C(Cl)(Cl)Cl.

These equations express the proposed formation of CaCl ; they do not establish that it actually occurs.

3.2 — Identification of the two phases

The silvery particles are **calcium metal**, Ca, and the colourless crystals are **calcium chloride**, CaCl_2 .

A mixture containing one mole of each has two moles of calcium atoms and two moles of chlorine atoms. Thus its overall atomic ratio is 1 : 1, even though it consists of separate elemental-calcium and calcium-chloride phases. That bulk ratio alone is not evidence for a homogeneous CaCl compound.

Calcium chloride contains calcium(II) ions, Ca^{2+} , SMILES [Ca+2], and chloride ions, Cl^- , SMILES [Cl-].

3.3 — Empirical formula of the white product

The mass percentage not accounted for by calcium and chlorine is assigned to hydrogen:

$$w(\text{H}) = 100.00 - 52.36 - 46.32 = 1.32\%.$$

Using standard approximate atomic molar masses, $M(\text{Ca}) = 40.08$, $M(\text{Cl}) = 35.45$, and $M(\text{H}) = 1.008 \text{ g mol}^{-1}$, a 100.00 g sample contains:

Element	Mass	Amount
Calcium	52.36 g	$52.36/40.08 = 1.306 \text{ mol}$
Chlorine	46.32 g	$46.32/35.45 = 1.307 \text{ mol}$
Hydrogen	1.32 g	$1.32/1.008 = 1.31 \text{ mol}$

Consequently,

$$n(\text{Ca}) : n(\text{Cl}) : n(\text{H}) \approx 1 : 1 : 1,$$

and the empirical formula is



This is **calcium hydride chloride**. Its constituent ions are calcium(II), chloride, and hydride, H^- , SMILES [H-]. Their charges balance as

$$(+2) + (-1) + (-1) = 0.$$

A formal ionic SMILES for this composition is [Ca+2].[H-].[Cl-].

The corresponding balanced reaction is

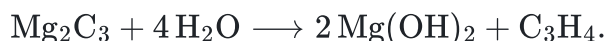


Hydrogen forms both hydride and hydrogen chloride; calcium remains in oxidation state $+II$.

3.4 (a) — The two acyclic hydrolysis products

In magnesium carbide, Mg_2C_3 , two magnesium(II) ions require a three-carbon carbide unit with total charge $4-$. This is formally the **tricarbon(4-) ion**, C_3^{4-} ; one Lewis-form SMILES is [C-2]=C=[C-2]. This representation specifies a formal bond and charge assignment, not coordination within the solid.

Hydrolysis supplies four hydrogen atoms to this unit:



Here water has SMILES O; magnesium(II), Mg^{2+} , has SMILES [Mg+2]; and hydroxide, OH^- , has SMILES [OH-].

The hydrocarbon therefore has molecular formula C_3H_4 . Its degree of unsaturation is

$$\frac{2(3) + 2 - 4}{2} = 2.$$

For an acyclic three-carbon molecule, the two possibilities are a triple bond or two cumulated double bonds:

Name	Structure	SMILES
Propyne	$\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$	<chem>CC#C</chem>
Propadiene (allene)	$\text{H}_2\text{C}=\text{C}=\text{CH}_2$	<chem>C=C=C</chem>

The triple-bonded portion of propyne is linear. In propadiene, the three-carbon skeleton is linear and the two terminal CH_2 groups lie in perpendicular planes; the SMILES alone does not display this geometry.

3.4 (b) — Formula of the red crystalline compound

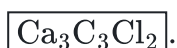
The measured calcium-to-chlorine ratio is

$$n(\text{Ca}) : n(\text{Cl}) = 1.5 : 1 = 3 : 2.$$

Three calcium(II) ions and two chloride ions have net charge

$$3(+2) + 2(-1) = +4.$$

The hydrolysis result identifies the remaining anion as a C_3^{4-} unit. One such unit exactly balances this charge, giving



Thus the product is a **calcium(II) carbide chloride**, with formal ionic composition



Its balanced hydrolysis can be written



This accounts for both the elemental ratio and the three-carbon hydrocarbon evolved.

3.5 (a) — Predicted crystal structure

Using the supplied radii,

$$\frac{r(\text{Ca}^+)}{r(\text{Cl}^-)} = \frac{120 \text{ pm}}{167 \text{ pm}} = 0.719.$$

This lies within the table's interval

$$0.414 \leq \frac{r_{\text{M}}}{r_{\text{X}}} \leq 0.732.$$

The predicted structure is therefore the NaCl , **or rock-salt, structure**. Each calcium(I) ion is surrounded octahedrally by six chloride ions, and each chloride ion has six calcium(I) nearest neighbours.

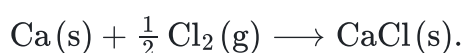
Calcium(I), Ca^+ , has SMILES [Ca+]. The formal ionic composition of hypothetical calcium(I) chloride is [Ca+] . [Cl-]; its octahedral crystal coordination must be described separately.

The appropriate lattice-formation enthalpy is

$$\boxed{\Delta_{\text{L}}H^\circ = -751.9 \text{ kJ mol}^{-1}}.$$

3.5 (b) — Born–Haber calculation

The standard formation reaction is



Molecular chlorine has SMILES ClCl; a gaseous chlorine atom is represented by [Cl], and a gaseous calcium atom by [Ca].

The following steps sum to the formation reaction:

Step	Reaction	Enthalpy contribution, kJ mol^{-1}
Fusion of calcium	$\text{Ca(s)} \longrightarrow \text{Ca(l)}$	+9.3
Vaporization of calcium	$\text{Ca(l)} \longrightarrow \text{Ca(g)}$	+150.0
First ionization of calcium	$\text{Ca(g)} \longrightarrow \text{Ca}^+(\text{g}) + \text{e}^-$	+589.7
Atomization of half a mole of chlorine	$\frac{1}{2} \text{Cl}_2(\text{g}) \longrightarrow \text{Cl}(\text{g})$	$+\frac{1}{2}(240.0) = +120.0$
Electron attachment to chlorine	$\text{Cl}(\text{g}) + \text{e}^- \longrightarrow \text{Cl}^-(\text{g})$	-349.0
Formation of the ionic lattice	$\text{Ca}^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{CaCl(s)}$	-751.9

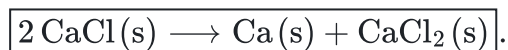
By Hess's law,

$$\begin{aligned}
 \Delta_f H^\circ(\text{CaCl}) &= \Delta_{\text{fusion}} H^\circ + \Delta_{\text{vap}} H^\circ + \Delta_{1. \text{IE}} H^\circ \\
 &\quad + \frac{1}{2} \Delta_{\text{diss}} H^\circ(\text{Cl}_2) + \Delta_{\text{EA}} H^\circ(\text{Cl}) + \Delta_{\text{L}} H^\circ \\
 &= 9.3 + 150.0 + 589.7 + 120.0 - 349.0 - 751.9 \\
 &= \boxed{-231.9 \text{ kJ mol}^{-1}}.
 \end{aligned}$$

The second ionization enthalpy is not used because the hypothetical compound contains calcium(I).

3.6 — Disproportionation

The balanced disproportionation reaction is



One calcium(I) centre is reduced to elemental calcium, while the other is oxidized to calcium(II).

The standard formation enthalpy of elemental calcium in its standard state is zero. Therefore,

$$\begin{aligned}
 \Delta_r H^\circ &= \Delta_f H^\circ(\text{Ca}) + \Delta_f H^\circ(\text{CaCl}_2) - 2\Delta_f H^\circ(\text{CaCl}) \\
 &= 0 - 796.0 - 2(-231.9) \\
 &= \boxed{-332.2 \text{ kJ mol}^{-1}}.
 \end{aligned}$$

This is per mole of reaction as written, consuming two moles of CaCl; equivalently, it is -166.1 kJ per mole of CaCl.

With the problem's assumption that the entropy contribution is negligible,

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ \approx -332.2 \text{ kJ mol}^{-1} < 0.$$

Thus **disproportionation is thermodynamically favorable**. Although formation of hypothetical CaCl from its elements is exothermic, the mixture of calcium metal and calcium chloride is still more favorable.

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

Problem 4: Determining atomic masses

The reaction of the element X with hydrogen leads to a class of compounds that is analogous to hydrocarbons. 5.000 g of X form 5.628 g of a molar 2 : 1 mixture of the stoichiometric X-analogues of methane and ethane, respectively.

4.1 Determine the molar mass of X from this information. Give the chemical symbol of X, and the 3D-structure of the two products.

The following more complex case is of great historical interest.

The mineral Argyrodite is a stoichiometric compound that contains silver (oxidation state +1), sulphur (oxidation state -2) and an unknown element Y (oxidation state +4). The ratio between the masses of silver and Y in Argyrodite is $m(\text{Ag}) : m(\text{Y}) = 11.88 : 1$. Y forms a reddish brown lower sulfide (oxidation state of Y is +2) and a higher white sulfide (oxidation state of Y is +4). The coloured lower sulfide is the sublimate obtained by heating Argyrodite in a flow of hydrogen. The residues are Ag_2S and H_2S . To convert 10.0 g of Argyrodite completely, 0.295 dm^3 of hydrogen are needed at 400 K and 100 kPa.

4.2 Determine the molar mass of Y from this information. Give the chemical symbol of Y, and the empirical formula of Argyrodite.

The atomic masses are correlated with spectroscopic properties. To determine the vibrational frequency $\tilde{\nu}$ expressed in wave numbers of chemical bonds in IR spectra chemists use Hooke's law which focuses on the frequency of the vibration (attention to units!):

$$\tilde{\nu} = \frac{1}{2\pi c} \cdot \sqrt{\frac{k}{\mu}}$$

$\tilde{\nu}$ - vibrational frequency of the bond, in wavenumbers (cm^{-1})

c - speed of light

k - force constant, indicating the strength of the bond ($\text{N m}^{-1} = \text{kg s}^{-2}$)

μ reduced mass in AB_4 , which is given by

$$\mu = \frac{3 m(A) m(B)}{3 m(A) + 4 m(B)}$$

$m(A), m(B)$ - the masses of the two bond atoms

The vibrational frequency of the C—H bond of methane is known to be 3030.00 cm^{-1} .

The vibrational frequency of the Z-analogue of methane is known to be 2938.45 cm^{-1} . The bond enthalpy of a C—H bond in methane is $438.4 \text{ kJ mol}^{-1}$. The bond enthalpy of a Z—H bond in the Z-analogue of methane is known to be $450.2 \text{ kJ mol}^{-1}$.

4.3 Determine the force constant k of a C—H bond using Hooke's law.

Estimate the force constant k of a Z—H bond, assuming that there is a linear proportionality between force constant and bond enthalpy.

Determine the atomic mass of Z from this information.

Give the chemical symbol of Z.

Answers

- **4.1:** $M(X) \approx 28.1 \text{ g mol}^{-1}$; $X = \text{Si}$, silicon. The products are **silane**, SiH_4 , SMILES $[\text{SiH}_4]$, with tetrahedral geometry, and **disilane**, Si_2H_6 , SMILES $[\text{SiH}_3][\text{SiH}_3]$, with approximately tetrahedral coordination at each silicon and a preferred staggered conformation.
- **4.2:** $M(Y) \approx 72.6 \text{ g mol}^{-1}$; $Y = \text{Ge}$, germanium. Argyrodite has empirical formula $\boxed{\text{Ag}_8\text{GeS}_6}$.
- **4.3:** $k_{\text{C-H}} = 490.4 \text{ N m}^{-1}$; $k_{\text{Z-H}} \approx 503.6 \text{ N m}^{-1}$. The estimated atomic mass is $m(Z) \approx 73.4 \text{ u}$, identifying $Z = \text{Ge}$. Its methane analogue is **germane**, GeH_4 , SMILES $[\text{GeH}_4]$.

Solution

The problem gives no table of constants. The calculations use the standard reference molar masses

$$M(\text{H}) = 1.008, \quad M(\text{C}) = 12.01, \quad M(\text{Ag}) = 107.87, \quad M(\text{S}) = 32.06 \text{ g mol}^{-1},$$

together with

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, \quad c = 2.99792458 \times 10^{10} \text{ cm s}^{-1}, \quad 1 \text{ u} = 1.66054 \times 10^{-27} \text{ kg}.$$

4.1

Methane, CH_4 , SMILES C , and ethane, C_2H_6 , SMILES CC , have the stoichiometric X-analogues XH_4 and X_2H_6 .

Let their amounts be $2t$ and t , respectively. The mixture therefore contains

$$n(X) = 2t + 2t = 4t, \quad n(\text{H atoms}) = 4(2t) + 6t = 14t.$$

The mass gained is the mass of hydrogen:

$$m(\text{H}) = 5.628 - 5.000 = 0.628 \text{ g}.$$

Consequently,

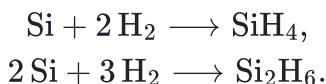
$$t = \frac{0.628 \text{ g}}{14(1.008 \text{ g mol}^{-1})} = 0.04450 \text{ mol},$$

and

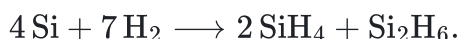
$$M(X) = \frac{5.000 \text{ g}}{4t} = 28.09 \text{ g mol}^{-1} \approx \boxed{28.1 \text{ g mol}^{-1}}.$$

This identifies **silicon**, $\boxed{\text{Si}}$.

The balanced formation equations, with hydrogen H_2 , SMILES $[\text{H}][\text{H}]$, are



For the specified mixture, their combined stoichiometry is



The requested three-dimensional structures are:

- **Silane**, SiH_4 , SMILES `[SiH4]`: silicon lies at the centre of a regular tetrahedron, with the four hydrogen atoms at its vertices. The bond angles are approximately 109.5° .
- **Disilane**, Si_2H_6 , SMILES `[SiH3][SiH3]`: a single silicon–silicon bond joins two groups, each containing silicon bonded to three hydrogen atoms. Each silicon has approximately tetrahedral coordination. In the preferred staggered conformation, looking along the silicon–silicon bond, the three rear hydrogen atoms are rotated by 60° relative to the three front hydrogen atoms.

The SMILES specify connectivity; the tetrahedral geometry and staggered conformation are supplied by these descriptions.

4.2

Y is reduced from oxidation state $+4$ to $+2$, requiring two electrons per Y atom. Oxidation of one hydrogen molecule supplies these two electrons. Thus,

$$n(\text{Y}) = n(\text{H}_2).$$

Using the ideal-gas equation, with $1 \text{ kPa dm}^3 = 1 \text{ J}$,

$$n(\text{H}_2) = \frac{pV}{RT} = \frac{(100 \text{ kPa})(0.295 \text{ dm}^3)}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(400 \text{ K})} = 8.8706 \times 10^{-3} \text{ mol}.$$

Let $n = n(\text{Y})$ and $M = M(\text{Y})$. The mass ratio gives

$$m(\text{Y}) = nM, \quad m(\text{Ag}) = 11.88nM,$$

so

$$n(\text{Ag}) = \frac{11.88nM}{M(\text{Ag})}.$$

Charge neutrality, using the stated oxidation states, requires the amounts of atoms in the mineral to satisfy

$$n(\text{Ag}) + 4n(\text{Y}) = 2n(\text{S}).$$

Hence,

$$n(\text{S}) = n \left(\frac{11.88M}{2M(\text{Ag})} + 2 \right).$$

Adding the masses of all three elements gives

$$10.0 \text{ g} = nM + 11.88nM + n \left(\frac{11.88M}{2M(\text{Ag})} + 2 \right) M(\text{S}).$$

Therefore,

$$M = \frac{\frac{10.0 \text{ g}}{n} - 2M(\text{S})}{12.88 + \frac{11.88M(\text{S})}{2M(\text{Ag})}} \approx \boxed{72.6 \text{ g mol}^{-1}}.$$

This identifies **germanium**, $\boxed{\text{Ge}}$. The reddish brown lower sulfide is germanium(II) sulfide, GeS , and the white higher sulfide is germanium(IV) sulfide, GeS_2 .

The silver-to-germanium atomic ratio is

$$\frac{n(\text{Ag})}{n(\text{Ge})} = \frac{11.88M(\text{Ge})}{M(\text{Ag})} \approx \frac{11.88(72.6)}{107.87} \approx 8.$$

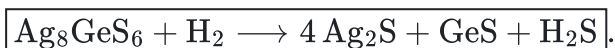
Charge neutrality then gives

$$\frac{n(\text{S})}{n(\text{Ge})} = \frac{8 + 4}{2} = 6.$$

Thus the empirical formula is



The balanced conversion is



Here Ag_2S is silver(I) sulfide, and H_2S is hydrogen sulfide, SMILES s. The solid sulfides and argyrodite have extended structures, so a discrete-molecule SMILES would not describe their solid-state structures.

4.3

For methane, use the reduced-mass expression supplied for AB_4 :

$$\mu_{\text{CH}_4} = \frac{3m(\text{C})m(\text{H})}{3m(\text{C}) + 4m(\text{H})}.$$

Substituting atomic masses,

$$\mu_{\text{CH}_4} = \frac{3(12.01)(1.008)}{3(12.01) + 4(1.008)} \text{ u} = 0.9065508 \text{ u} = 1.50536 \times 10^{-27} \text{ kg}.$$

Rearranging Hooke's law,

$$k = 4\pi^2 c^2 \tilde{\nu}^2 \mu.$$

Because the wavenumber is in cm^{-1} , use c in cm s^{-1} :

$$k_{\text{C-H}} = 4\pi^2 (2.99792458 \times 10^{10} \text{ cm s}^{-1})^2 (3030.00 \text{ cm}^{-1})^2 (1.50536 \times 10^{-27} \text{ kg}).$$

Thus,

$$\boxed{k_{\text{C-H}} = 490.4 \text{ N m}^{-1}}.$$

Under the assumed proportionality between force constant and bond enthalpy,

$$\frac{k_{\text{Z-H}}}{k_{\text{C-H}}} = \frac{450.2}{438.4}.$$

Using the unrounded first result,

$$\boxed{k_{\text{Z-H}} \approx 503.6 \text{ N m}^{-1}}.$$

The reduced mass of the Z-analogue follows from

$$\frac{\mu_{\text{ZH}_4}}{\mu_{\text{CH}_4}} = \frac{k_{\text{Z-H}}}{k_{\text{C-H}}} \left(\frac{\tilde{\nu}_{\text{C-H}}}{\tilde{\nu}_{\text{Z-H}}} \right)^2.$$

Therefore,

$$\mu_{\text{ZH}_4} = 0.9065508 \left(\frac{450.2}{438.4} \right) \left(\frac{3030.00}{2938.45} \right)^2 \text{ u} = 0.9898645 \text{ u}.$$

Writing $m_Z = m(Z)$ and $m_H = m(\text{H})$,

$$\mu_{\text{ZH}_4} = \frac{3m_Z m_H}{3m_Z + 4m_H}.$$

Solving for m_Z ,

$$m_Z = \frac{4\mu_{\text{ZH}_4} m_H}{3(m_H - \mu_{\text{ZH}_4})}.$$

Retaining guard digits because the denominator contains a small difference,

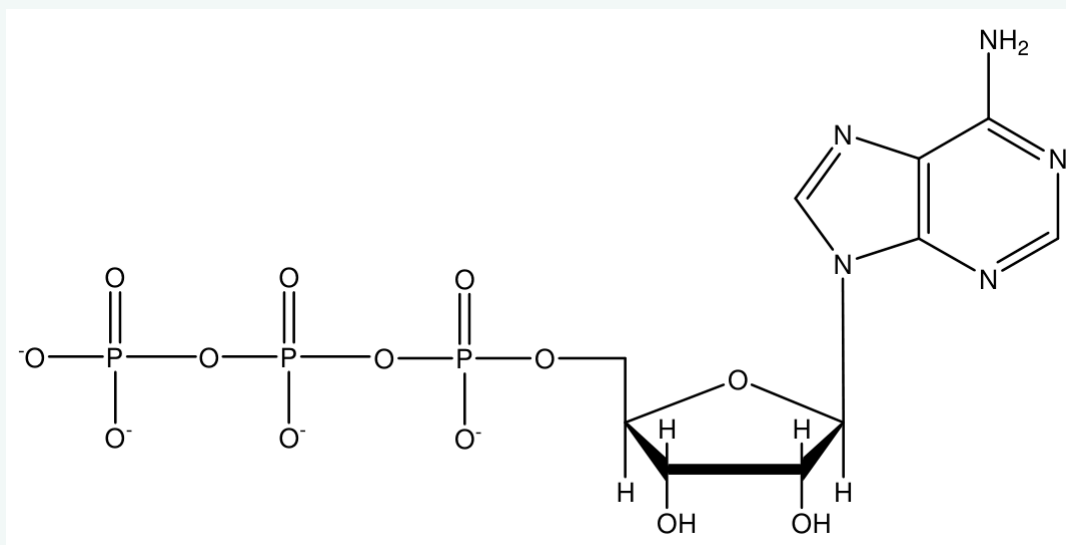
$$m_Z = \frac{4(0.9898645)(1.008)}{3(1.008 - 0.9898645)} \text{ u} \approx \boxed{73.4 \text{ u}}.$$

This estimated mass identifies $Z = \text{Ge}$, consistent with the germanium mass determined in 4.2. The methane analogue is **germane**, GeH_4 , SMILES [GeH4], with tetrahedral geometry.

The inferred 73.4 u is an estimate: the assumed proportionality between bond enthalpy and force constant is approximate.

The solution was checked against the official solution.

Problem 5: Biochemistry with Thermodynamics



Structure of ATP^{4-}

Shifting chemical equilibria with ATP:

Animals use free energy from the oxidation of their food to maintain concentrations of ATP, ADP, and phosphate far from equilibrium. In red blood cells the following concentrations have been measured:

$$\begin{aligned} c(\text{ATP}^{4-}) &= 2.25 \text{ mmol dm}^{-3} \\ c(\text{ADP}^{3-}) &= 0.25 \text{ mmol dm}^{-3} \\ c(\text{HPO}_4^{2-}) &= 1.65 \text{ mmol dm}^{-3} \end{aligned}$$

Free energy stored in ATP can be released according to the following reaction:



As the pH is close to 7 in most living cells, biochemists use $\Delta G'^{\circ}$ instead of ΔG° . The standard state of $\Delta G'^{\circ}$ is defined as having a constant pH of 7. In equations with $\Delta G'^{\circ}$ and K' for reactions at $pH = 7$ the concentration of H^+ is therefore omitted. Standard concentration is 1 mol dm^{-3} .

5.1 Calculate the actual $\Delta G'$ of reaction (1) in the red blood cell at 25°C and $pH = 7$.

In living cells many so-called "anabolic" reactions take place, which are at first sight thermodynamically unfavourable because of a positive ΔG . The phosphorylation of glucose is an example:



5.2 Calculate first the equilibrium constant K' of reaction (2) and then the ratio $c(\text{glucose 6-phosphate})/c(\text{glucose})$ in the red blood cell in chemical equilibrium at 25°C and $pH = 7$.

To shift the equilibrium to a higher concentration of glucose 6-phosphate, reaction (2) is coupled with hydrolysis of ATP:



5.3 Calculate $\Delta G'^{\circ}$ and K' of reaction (3).

What is now the ratio $c(\text{glucose 6-phosphate})/c(\text{glucose})$ in the red blood cell in chemical equilibrium at 25°C and $pH = 7$?

ATP synthesis:

An adult person ingests about 8000 kJ of energy ($\Delta G'$) per day with the food.

5.4 a) What will be the mass of ATP that is produced per day if half of this energy is used for ATP synthesis? Assume a $\Delta G'$ of -52 kJ mol^{-1} for reaction (1), and a molecular weight of 503 g mol^{-1} for ATP.

b) What mass of ATP does the human body contain on average if the mean lifetime of an ATP molecule until its hydrolysis is 1 min?

c) What happens to the rest of the free energy, which is not used for ATP synthesis? Mark on the answer sheet.

In animals the energy obtained by the oxidation of food is used to pump protons out of specialized membrane vesicles, the mitochondria. ATP-synthase, an enzyme, will allow protons to re-enter the mitochondria if ATP is simultaneously synthesized from ADP and phosphate.

5.5 a) How many protons (H^+) are in a spherical mitochondrion with a diameter of $1 \mu\text{m}$ at $pH = 7$?

b) How many protons have to enter into each of the 1000 mitochondria of a liver cell via the ATP-synthase to allow the production of a mass of 0.2 fg of ATP per cell? Assume that 3 protons have to enter for the synthesis of 1 molecule of ATP.

Official English text of the problem.

Answers

- **5.1:** $\Delta G' = -51.8 \text{ kJ mol}^{-1}$.
- **5.2:** $K'_2 = 3.82 \times 10^{-3}$; $c(\text{glucose 6-phosphate})/c(\text{glucose}) = 6.31 \times 10^{-6}$.
- **5.3:** $\Delta G'_3 = -16.7 \text{ kJ mol}^{-1}$; $K'_3 = 8.43 \times 10^2$;
 $c(\text{glucose 6-phosphate})/c(\text{glucose}) \approx 7.6 \times 10^3$.
- **5.4(a):** Approximately 39 kg of ATP produced per day.
- **5.4(b):** Approximately 27 g of ATP present on average.
- **5.4(c):** The remaining energy is dissipated as heat.
- **5.5(a):** Approximately **32 free protons** per mitochondrion.
- **5.5(b):** Approximately 7.2×10^2 **protons** must enter each mitochondrion.

Solution

Use

$$T = 298.15 \text{ K}, \quad R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, \quad N_A = 6.022 \times 10^{23} \text{ mol}^{-1}.$$

Activities are approximated by $a_i = c_i/c^\circ$, with $c^\circ = 1 \text{ mol dm}^{-3}$; water has unit activity. At the fixed pH of 7, the proton activity is already incorporated into the primed thermodynamic quantities.

The chemical species used below have the following structural representations. The glucose SMILES show open-chain D forms, avoiding an arbitrary choice of anomer.

Species	SMILES
Adenosine 5'-triphosphate(4-), ATP ⁴⁻	<chem>Nc1ncnc2c1ncn2[C@H]1O[C@H](COP(=O)([O-])OP(=O)([O-])OP(=O)([O-])[O-])[C@H](O)[C@H]1O</chem>
Adenosine 5'-diphosphate(3-), ADP ³⁻	<chem>Nc1ncnc2c1ncn2[C@H]1O[C@H](COP(=O)([O-])OP(=O)([O-])[O-])[C@H](O)[C@H]1O</chem>
Hydrogen phosphate, HPO ₄ ²⁻	<chem>O=P([O-])([O-])O</chem>
D-Glucose, C ₆ H ₁₂ O ₆	<chem>O=C[C@H](O)[C@H](O)[C@H](O)[C@H](O)CO</chem>
D-Glucose 6-phosphate(2-), C ₆ H ₁₁ O ₉ P ²⁻	<chem>O=C[C@H](O)[C@H](O)[C@H](O)[C@H](O)COP(=O)([O-])[O-]</chem>
Water, H ₂ O	<chem>O</chem>
Proton, H ⁺	<chem>[H+]</chem>

5.1 — Actual free energy of ATP hydrolysis

Reaction (1) is



Its transformed reaction quotient is

$$Q'_1 = \frac{[c(\text{ADP}^{3-})/c^\circ][c(\text{HPO}_4^{2-})/c^\circ]}{c(\text{ATP}^{4-})/c^\circ}.$$

Converting the supplied concentrations to mol dm^{-3} ,

$$Q'_1 = \frac{(0.25 \times 10^{-3})(1.65 \times 10^{-3})}{2.25 \times 10^{-3}} = 1.833 \times 10^{-4}.$$

Therefore,

$$\begin{aligned}\Delta G'_1 &= \Delta G_1^{\circ'} + RT \ln Q'_1 \\ &= -30.5 + (8.314 \times 10^{-3})(298.15) \ln(1.833 \times 10^{-4}) \\ &= \boxed{-51.8 \text{ kJ mol}^{-1}}.\end{aligned}$$

5.2 — Uncoupled glucose phosphorylation

Reaction (2), written with molecular formulas, is



The standard free energy gives

$$\Delta G_2^{\circ'} = -RT \ln K'_2,$$

so

$$K'_2 = \exp\left(-\frac{13800}{8.314 \times 298.15}\right) = \boxed{3.82 \times 10^{-3}}.$$

This is a dimensionless equilibrium constant:

$$K'_2 = \frac{c(\text{glucose 6-phosphate})/c^\circ}{[c(\text{glucose})/c^\circ][c(\text{HPO}_4^{2-})/c^\circ]}.$$

At the supplied phosphate concentration,

$$\begin{aligned}\frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} &= K'_2 \frac{c(\text{HPO}_4^{2-})}{c^\circ} \\ &= (3.821 \times 10^{-3})(1.65 \times 10^{-3}) \\ &= \boxed{6.31 \times 10^{-6}}.\end{aligned}$$

Thus the equilibrium strongly favours unphosphorylated glucose under these conditions.

5.3 — Glucose phosphorylation coupled to ATP hydrolysis

Adding reactions (1) and (2) cancels water and hydrogen phosphate. The resulting hexokinase-catalysed reaction is



Standard reaction free energies are additive:

$$\begin{aligned}\Delta G_3^{\circ'} &= \Delta G_1^{\circ'} + \Delta G_2^{\circ'} \\ &= -30.5 + 13.8 \\ &= \boxed{-16.7 \text{ kJ mol}^{-1}}.\end{aligned}$$

Consequently,

$$K'_3 = \exp\left(\frac{16700}{8.314 \times 298.15}\right) = \boxed{8.43 \times 10^2}.$$

At fixed pH,

$$K'_3 = \frac{c(\text{glucose 6-phosphate}) c(\text{ADP}^{3-})}{c(\text{glucose}) c(\text{ATP}^{4-})}.$$

Hence

$$\begin{aligned} \frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} &= K'_3 \frac{c(\text{ATP}^{4-})}{c(\text{ADP}^{3-})} \\ &= (8.431 \times 10^2) \frac{2.25}{0.25} \\ &= 7.588 \times 10^3 \\ &\approx \boxed{7.6 \times 10^3}. \end{aligned}$$

These ratios describe equilibrium of the specified reaction with the supplied metabolite concentrations maintained. Coupling changes the net reaction and its free energy; hexokinase catalyses that reaction without changing its equilibrium constant.

5.4(a) — Daily ATP production

ATP synthesis reverses reaction (1):



Its assumed free-energy requirement is therefore

$$\Delta G'_{\text{synthesis}} = +52 \text{ kJ mol}^{-1}.$$

The daily energy allocated to synthesis is

$$E_{\text{synthesis}} = \frac{8000}{2} = 4000 \text{ kJ}.$$

Thus

$$n_{\text{ATP, daily}} = \frac{4000 \text{ kJ}}{52 \text{ kJ mol}^{-1}} = 76.9 \text{ mol},$$

and

$$\begin{aligned} m_{\text{ATP, daily}} &= (76.9 \text{ mol})(503 \text{ g mol}^{-1}) \\ &= 3.87 \times 10^4 \text{ g} \\ &\approx \boxed{39 \text{ kg}}. \end{aligned}$$

This is the mass synthesized through repeated turnover during one day.

5.4(b) — Average ATP mass in the body

At steady state, the average amount present equals the production rate multiplied by the mean lifetime:

$$m_{\text{pool}} = \dot{m}_{\text{synthesis}} \tau.$$

Since one day contains 1440 min,

$$m_{\text{pool}} = \frac{3.869 \times 10^4 \text{ g}}{1440 \text{ min}} (1 \text{ min}) = 26.9 \text{ g} \approx \boxed{27 \text{ g}}.$$

5.4(c) — Fate of the remaining free energy

The remaining energy, about 4000 kJ per day in this model, is **dissipated as heat**, contributing to maintenance of body temperature. This is the answer to select on the missing answer sheet.

5.5(a) — Free protons inside one mitochondrion

At pH 7,

$$c(\text{H}^+) = 10^{-7} \text{ mol dm}^{-3}.$$

The radius is

$$r = \frac{1 \mu\text{m}}{2} = 5.0 \times 10^{-7} \text{ m}.$$

The spherical volume is

$$\begin{aligned} V &= \frac{4\pi r^3}{3} \\ &= \frac{4\pi}{3} (5.0 \times 10^{-7} \text{ m})^3 \\ &= 5.236 \times 10^{-19} \text{ m}^3 \\ &= 5.236 \times 10^{-16} \text{ dm}^3. \end{aligned}$$

The mean number of free protons is

$$\begin{aligned} N(\text{H}^+) &= c(\text{H}^+) V N_A \\ &= (10^{-7}) (5.236 \times 10^{-16}) (6.022 \times 10^{23}) \\ &= 31.5. \end{aligned}$$

Thus there are approximately

$32 \text{ free protons per mitochondrion}$

on average.

5.5(b) — Proton entry required for ATP production

The ATP mass produced per cell is

$$0.2 \text{ fg} = 0.2 \times 10^{-15} \text{ g}.$$

The corresponding number of ATP molecules is

$$N_{\text{ATP, cell}} = \frac{0.2 \times 10^{-15} \text{ g}}{503 \text{ g mol}^{-1}} (6.022 \times 10^{23} \text{ mol}^{-1}) = 2.394 \times 10^5.$$

Each molecule requires entry of three protons. Distributing the production equally among 1000 mitochondria gives

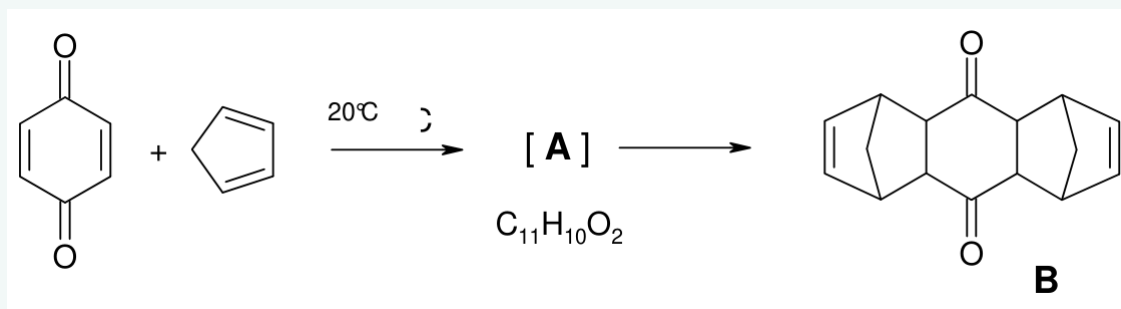
$$\begin{aligned} N_{\text{protons, each}} &= \frac{3N_{\text{ATP, cell}}}{1000} \\ &= \frac{3(2.394 \times 10^5)}{1000} \\ &= 7.18 \times 10^2 \\ &\approx \boxed{7.2 \times 10^2 \text{ protons}}. \end{aligned}$$

This is cumulative proton entry during ATP production. Proton pumping and buffering make it compatible with the small instantaneous free-proton population calculated in 5.5(a).

The solution was checked against the official solution.

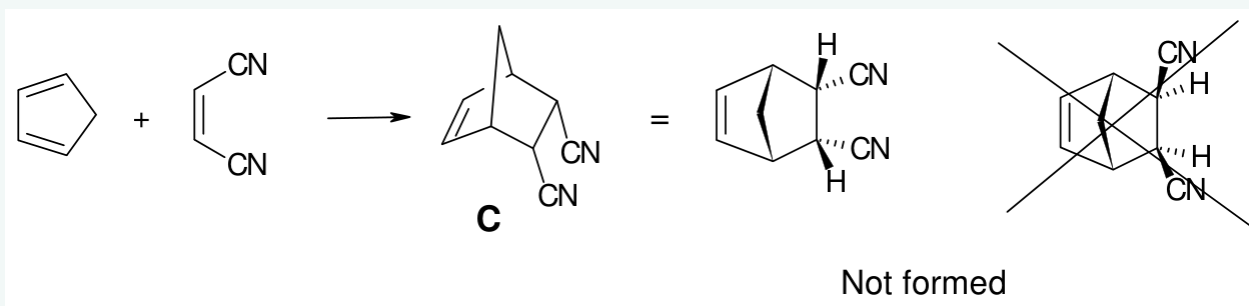
Problem 6: Diels-Alder Reactions

The Diels-Alder reaction, a concerted [4+2]-cycloaddition between a diene and an olefin to yield a cyclohexene, was discovered in 1928 here in Kiel. Prof. Otto Diels and his coworker Kurt Alder mixed *p*-benzoquinone with an excess of cyclopentadiene and obtained the following result:



6.1 Draw the structure of **A** (without stereochemical information).

The Diels-Alder reaction is a concerted, one-step reaction that proceeds with high stereospecificity. For example, only a single stereoisomer **C** is formed in the following reaction



If you use the *E*-isomer of the alkene instead, you will obtain two other stereoisomers **D1** and **D2**.

6.2 Give the structures of **D1** and **D2**.

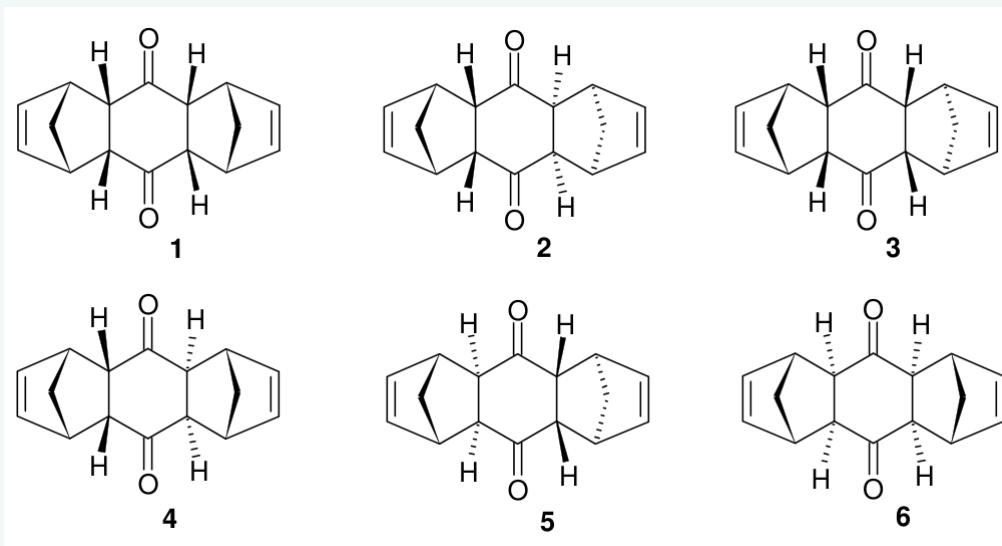
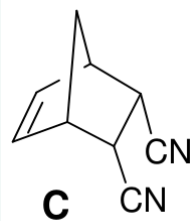
Accordingly, in the original reaction (formation of **B** from cyclopentadiene and benzoquinone) Diels and Alder found only one of the following six conceivable stereoisomers of **B** (see next page).

Hints:

- keep the stereospecific formation of **C** in mind

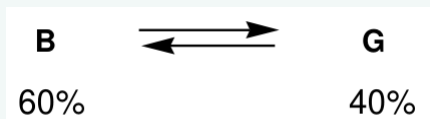
and

- the sterically less hindered isomer forms.



6.3 Which single isomer of the six stereoisomers 1-6 of **B** shown above did they isolate?

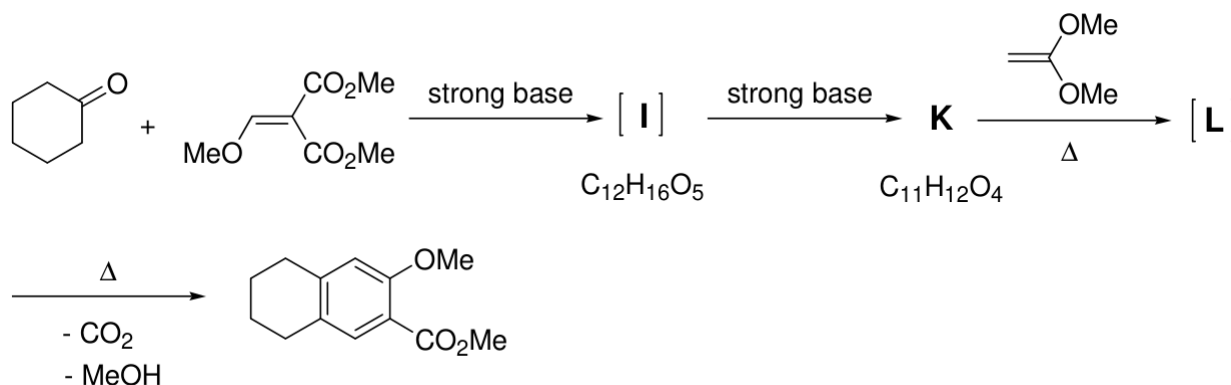
After prolonged heating (15h, 120 °C) of the originally isolated stereoisomer **B** (melting point mp: 157 °C), Diels and Alder obtained two new stereoisomers **E** (mp: 153 °C) and **F** (mp: 163 °C). Equilibration of **B** with a catalytic amount of a strong base at 25 °C gave a further stereoisomer **G** (mp: 184 °C).



6.4 Decide the questions on the answer sheet concerning the Diels-Alder reaction.

Hint: You do not need to know, which of the six stereoisomers 1 – 6 (shown above) corresponds to either **E**, **F** or **G** in order to answer this question.

The Diels-Alder reaction plays also an important role in the following reaction sequence.



6.5 Draw the structures for **I**, **K** and **L**.

Hints:

- **K** has only one methyl group.
- **L** is the Diels-Alder adduct of **K** and the alkene shown.

Official English text of the problem.

Answers

- **6.1 — A:** The mono-Diels-Alder adduct, **tricyclo[6.2.1.0^{2,7}]undeca-4,9-diene-3,6-dione**, $C_{11}H_{10}O_2$.
SMILES, without stereochemistry: O=C1C=CC(=O)C2C3C=CC(C3)C12.
- **6.2 — D1 and D2:** The two enantiomers of **trans-bicyclo[2.2.1]hept-5-ene-2,3-dicarbonitrile**, formed as a racemate. Each has one endo and one exo cyano group.
 - **D1**, the (2*R*, 3*R*) enantiomer: N#C[C@H]1[C@H](C#N)[C@H]2C=C[C@@H]1C2.
 - **D2**, the (2*S*, 3*S*) enantiomer: N#C[C@@H]1[C@@H](C#N)[C@H]2C=C[C@@H]1C2.
 The labels D1 and D2 may be interchanged.
- **6.3 — B: Isomer 2**, the **anti-endo,endo bis(cyclopentadiene) adduct of *p*-benzoquinone**, $C_{16}H_{16}O_2$. Its two methylene bridges lie on opposite faces.
Stereochemical SMILES: O=C1[C@H]2[C@H]3C=C[C@H](C3)[C@H]2C(=O)[C@@H]2[C@@H]3C=C[C@@H](C3)[C@H]12.
- **6.4:** The intended interpretation is **kinetic endo selectivity in the initial formation of B**, followed by **reversible equilibration on heating**. At 120 °C, the equilibrium abundance is **F > E > B**; at 25 °C, **B is favored over G**. Melting points do not determine this equilibrium ordering. The exact answer-sheet questions are unavailable.
- **6.5:**
- **I: Dimethyl 2-[(2-oxocyclohexyl)methylidene]propanedioate**, $C_{12}H_{16}O_5$, shown in its keto form:
COC(=O)C(=CC1CCCCC1=O)C(=O)OC.

- **K: Methyl 2-oxo-5,6,7,8-tetrahydro-2H-chromene-3-carboxylate**, a fused α -pyrone, $C_{11}H_{12}O_4$:
COC(=O)C1=CC2=C(CCCC2)OC1=O.
- **L: The racemic tricyclic lactone Diels–Alder adduct of K and 1,1-dimethoxyethene**, $C_{15}H_{20}O_6$. The carbon bearing both methoxy groups bonds to the ester-bearing terminus of K's diene. Its two enantiomeric SMILES are:
COC(=O)[C@]12C=C3CCCC[C@@]3(C(C1(OC)OC)OC2=O
COC(=O)[C@@]12C=C3CCCC[C@]3(C(C1(OC)OC)OC2=O.

Solution

6.1 — Formation of the mono-adduct A

The reactants are **cyclopenta-1,3-diene**, C1=CC=CC1, and **1,4-benzoquinone**, O=C1C=CC(=O)C=C1.

One double bond of benzoquinone acts as the dienophile. Cycloaddition forms two carbon–carbon σ bonds, while the two internal carbons of the original diene retain a double bond. The other benzoquinone double bond remains available for the second cycloaddition.

The atom balance is



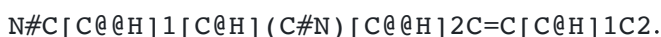
Thus **A** is the mono-adduct specified in the Answers.

To draw it, retain the six-membered quinone ring with both carbonyl groups. Convert one of its double bonds into the shared single bond of a fused norbornene unit; leave the opposite quinone double bond unchanged. Do not add stereochemical wedges or dashes.

6.2 — Retention of the alkene configuration

The illustrated dienophile is **maleonitrile**, or **(Z)-but-2-enedinitrile**, N#C/C=C\C#N. Its two cyano groups are cis.

The illustrated product **C** is **cis-endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarbonitrile**:



A Diels–Alder reaction is suprafacial on both reacting π systems. Consequently, substituents that are cis on the dienophile remain cis in the product, and trans substituents remain trans.

The alternative reagent is **fumaronitrile**, or **(E)-but-2-enedinitrile**, N#C/C=C/C#N. It therefore gives a norbornene product with **trans cyano groups**:



One cyano group is endo and the other exo. The two possible products are mirror images, **D1** and **D2**, whose stereochemical SMILES are given above. With achiral reagents and conditions, they form in equal amounts.

For the requested drawings, use the same norbornene framework as C:

- In one drawing, place the upper cyano group on a solid wedge and the lower one on a hashed wedge.
- In the other, reverse those two cyano-group orientations.

- At each substituted carbon, the hydrogen points opposite to its cyano group.

The cis/trans retention is **stereospecificity**. Selection of the particular cis product C over the other cis arrangement is the additional **endo selectivity** illustrated by the problem.

6.3 — Selection of isomer 2

A second cyclopentadiene molecule adds to the remaining quinone-derived double bond:



The overall reaction is



Applying the endo relationship illustrated by C to both additions leaves **isomers 1 and 2** as the endo,endo possibilities.

Candidate	Relationship of the two methylene bridges	Consequence
1	Same face, syn	Greater crowding
2	Opposite faces, anti	Less crowding

The second cyclopentadiene approaches the less obstructed face of the mono-adduct. Therefore,

$$\boxed{\text{B} = \text{isomer 2}}.$$

In the supplied projection of isomer 2, the left bridge and both left fusion hydrogens are solid wedges; the right bridge and both right fusion hydrogens are dashed. This is the configuration encoded in B's SMILES above.

6.4 — Conclusions supported by the equilibration experiments

The printed **E + F** denotes a mixture of stereoisomers, not a reaction producing one molecule of each from one molecule of B. The balanced interconversions are separately



All four species have formula $\text{C}_{16}\text{H}_{16}\text{O}_2$. E, F and G are stereoisomers of the same bis-adduct skeleton; its stereo-unspecified SMILES is

O=C1C2C3C=CC(C3)C2C(=O)C2C3C=CC(C3)C12.

Their individual configurations need not be assigned to interpret the experiments.

Kinetic and thermodynamic interpretation. The original addition selects endo,endo B. This is the intended example of kinetic endo selectivity. Prolonged heating permits equilibration, for which F is the predominant product. Thermal interconversion can occur through retro-Diels–Alder cleavage and readdition.

Base provides another route to stereochemical equilibration through removal and return of hydrogens adjacent to the carbonyl groups. A catalyst changes the rate of equilibration, not the equilibrium constant for a specified reaction at a fixed temperature.

Equilibrium ratios. With the usual ideal-mixture interpretation of the percentages,

$$K_{\text{B} \rightarrow \text{E}} = \frac{20}{10} = 2, \quad K_{\text{B} \rightarrow \text{F}} = \frac{70}{10} = 7 \quad \text{at } 120^\circ\text{C},$$

whereas

$$K_{B \rightarrow G} = \frac{40}{60} = \frac{2}{3} \quad \text{at } 25^\circ\text{C}.$$

For completeness, the corresponding standard Gibbs-energy differences follow from

$$\Delta G^\circ = -RT \ln K.$$

Using the standard gas constant $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$:

Conversion	Temperature	K	ΔG°
B $\rightarrow$ E	393.15 K	2	$-2.27 \text{ kJ mol}^{-1}$
B $\rightarrow$ F	393.15 K	7	$-6.36 \text{ kJ mol}^{-1}$
E $\rightarrow$ F	393.15 K	3.5	$-4.10 \text{ kJ mol}^{-1}$
B $\rightarrow$ G	298.15 K	2/3	$+1.01 \text{ kJ mol}^{-1}$

Thus, under that interpretation,

$$G_F^\circ < G_E^\circ < G_B^\circ \quad \text{at } 120^\circ\text{C},$$

and

$$G_B^\circ < G_G^\circ \quad \text{at } 25^\circ\text{C}.$$

Melting point is not a sufficient stability criterion. G has the highest quoted melting point, yet the B/G equilibrium favors B. Melting points concern solid–liquid equilibrium and cannot by themselves rank the isomers in the reacting mixture.

The two experiments occur at different temperatures and involve different sets of equilibrating species. They do **not** establish a single ordering of B, E, F and G at one common temperature, nor do they determine activation energies, reaction enthalpies or entropies.

6.5 — Identification of I, K and L

The starting materials are:

Substance	Name	SMILES
Cyclic ketone	Cyclohexanone	<chem>O=C1CCCCC1</chem>
Activated alkene	Dimethyl 2-(methoxymethylidene)propanedioate	<chem>COC=C(C(=O)OC)C(=O)OC</chem>
Later dienophile	1,1-Dimethoxyethene	<chem>C=C(OC)OC</chem>

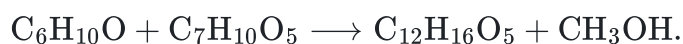
Formation of I. Strong base generates the cyclohexanone enolate; its oxygen-anionic resonance form is [O-]C1=CCCCC1.

The enolate carbon attacks the methoxy-bearing carbon of the activated alkene. Elimination of **methoxide**, C[O-], restores the activated double bond. The resulting ketone has the side chain



attached to an α -carbon of cyclohexanone. This is **I**, dimethyl 2-[(2-oxocyclohexyl)methylidene]propanedioate.

The neutral organic atom balance, expressing the formal loss of **methanol**, CO, is



For the drawing, start with cyclohexanone and attach the side chain above to either equivalent α -carbon. The SMILES in the Answers leaves the configuration of this enolizable center unspecified.

Formation of K. Further deprotonation at that α -carbon gives a conjugated enolate. An oxygen-anionic representation of the **I-derived enolate** is



Its oxygen attacks one methyl ester carbonyl intramolecularly. Methoxide elimination closes a six-membered lactone ring, giving the fused **α -pyrone K**:



One methyl ester has become the lactone; the other remains a methyl ester. Consequently, **K has exactly one methyl group**, as required.

For a precise drawing, number the α -pyrone oxygen 1, its carbonyl carbon 2, and the remaining ring carbons 3–6. K has:

- a methyl ester at C3;
- double bonds C3=C4 and C5=C6;
- the four-methylene chain of the original cyclohexanone ring joining C5 and C6.

Formation of L. The conjugated diene in K is C3=C4–C5=C6. It undergoes cycloaddition with 1,1-dimethoxyethene:



The final aromatic product fixes the required regiochemistry. To obtain adjacent methoxy and ester substituents:

- form a bond between **C3 of K** and the dienophile carbon bearing **both methoxy groups**;
- form a bond between **C6 of K** and the dienophile's **methylene carbon**;
- leave the residual double bond at **C4=C5**;
- retain the lactone bridge C3–C2(=O)–O1–C6.

This gives **L**, with the connectivity and relative stereochemistry encoded by the two enantiomeric SMILES in the Answers. Addition to either face of K produces the racemic pair.

Conversion of L to the aromatic product. Heating expels **carbon dioxide**, $\text{O}=\text{C}=\text{O}$, from the lactone bridge. Loss of methanol from the dimethoxy-containing portion then completes aromatization:



The product is **methyl 3-methoxy-5,6,7,8-tetrahydronaphthalene-2-carboxylate**,
COC(=O)c1cc2c(cc1OC)CCCC2.

One methoxy group of the dienophile remains attached to the aromatic ring, adjacent to the methyl ester. The complete neutral organic balance is



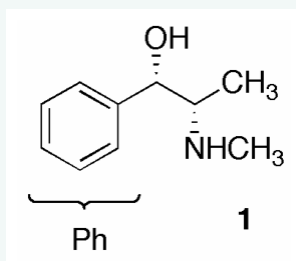
The solution was checked against the official solution.

Problem 7: Stereochemistry in Drugs

The Cahn-Ingold-Prelog rules are used to specify the stereochemistry of molecules.

7.1 Order the groups on the answer sheet according to their priority in the Cahn-Ingold-Prelog (CIP)-system.

Pseudoephedrine (**1**) is a constituent in many common drugs against colds, e.g. in nasal sprays.



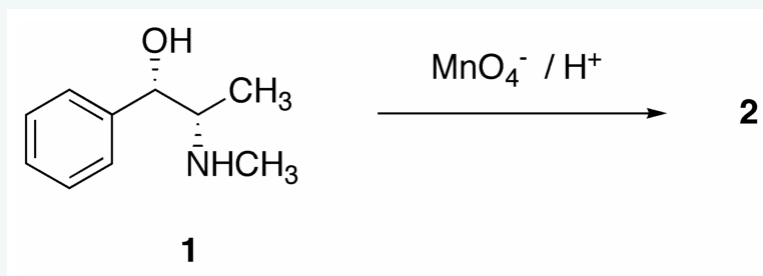
7.2 Mark the stereocenters in **1** with an asterisk * on the answer sheet.

Order the substituents on each stereocenter in **1** according to their priority and determine their absolute configuration (*R* or *S*).

7.3 Draw a Newman or a sawhorse representation of **1**.

Draw a Fischer representation of **1**.

Treatment of **1** with acidic permanganate solutions under mild conditions yields the stimulant Methcathinone **2**:



7.4 Draw the stereochemically correct structure of compound **2** and a balanced redox equation of the reaction. Indicate in your equation the particular oxidation number on all atoms which undergo a change in their formal oxidation numbers.

The treatment of **2** with LiAlH_4 results exclusively in compound **3**, which differs from **1** in its melting point.



7.5

- Draw the stereochemically correct structure of **3**.
- Decide the statements on the answer sheet concerning isomers.
- Draw a structural model to rationalize the exclusive formation of **3** from **2**.

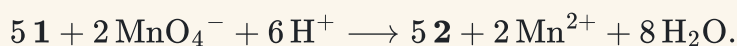
Answers

Throughout, C_1 is the carbon attached directly to phenyl and bearing the alcohol or carbonyl group; C_2 is the adjacent carbon bearing methylamino.

- **7.1:** The answer-sheet group list is missing, so its exact ordering cannot be recovered. For the substituent types visible in this problem, decreasing CIP priority is
 $-\text{OH} > -\text{NHCH}_3 > -\text{CH}(\text{OH})\text{Ph} > -\text{CH}(\text{NHCH}_3)\text{CH}_3 > -\text{Ph} > -\text{CH}_3 > -\text{H}$.
- **7.2:** Mark C_1 and C_2 . Both are *S*.
- At C_1 : $\text{OH} > \text{CH}(\text{NHCH}_3)\text{CH}_3 > \text{Ph} > \text{H}$.
- At C_2 : $\text{NHCH}_3 > \text{CH}(\text{OH})\text{Ph} > \text{CH}_3 > \text{H}$.

Compound **1** is **(1*S*,2*S*)-pseudoephedrine**, or **(1*S*,2*S*)-2-(methylamino)-1-phenylpropan-1-ol**, CN[C@@H](C)[C@@H](O)c1ccccc1.

- **7.3:** One valid staggered Newman projection, looking from C_1 toward C_2 , has front groups phenyl at 12 o'clock, hydroxyl at 4 o'clock and hydrogen at 8 o'clock; rear groups methylamino at 2 o'clock, methyl at 6 o'clock and hydrogen at 10 o'clock. For a Fischer projection with phenyl at the top and methyl at the bottom, put hydroxyl on the right at C_1 and methylamino on the left at C_2 .
- **7.4:** Compound **2** is **(2*S*)-methcathinone**, or **(2*S*)-2-(methylamino)-1-phenylpropan-1-one**, CN[C@@H](C)C(=O)c1ccccc1. The balanced redox equation is



The changing oxidation numbers are $C_1 : 0 \rightarrow +\text{II}$ and manganese $+\text{VII} \rightarrow +\text{II}$.

- **7.5(a):** Compound **3** is **(1*R*,2*S*)-ephedrine**, or **(1*R*,2*S*)-2-(methylamino)-1-phenylpropan-1-ol**, CN[C@@H](C)[C@H](O)c1ccccc1. In the original drawing, reverse only the hydroxyl-bearing stereocenter.
- **7.5(b):** **1** and **3** are **diastereomers**, specifically C_1 **epimers**. The alcohol connectivity admits four configurational stereoisomers, comprising two enantiomeric pairs; none is meso.
- **7.5(c):** An oxygen–nitrogen chelate to aluminium constrains the ketone conformation. Hydride approaches the carbonyl from the face opposite the C_2 methyl group—the **Si face** in the model described below—giving $C_1 = R$ while retaining $C_2 = S$.

Solution

7.1 — CIP priorities

CIP comparison proceeds as follows:

1. Compare the atomic numbers of the atoms directly attached to the stereocenter. Higher atomic number gives higher priority.
2. For isotopes of the same element, higher mass number gives higher priority.
3. If the directly attached atoms tie, compare their outward attached atoms, arranged in decreasing atomic number, until the first difference.
4. Treat multiple bonds using duplicate atoms for the purpose of comparison.

The missing answer-sheet list prevents a specific answer for its unknown groups. However, all the substituent types needed for the supplied structures can be ranked:

Decreasing priority	Group	Fragment SMILES	First relevant comparison
1	Hydroxyl	[*]O	Directly attached oxygen
2	Methylamino	[*]NC	Directly attached nitrogen
3	Hydroxy(phenyl)methyl	[*]C(O)c1ccccc1	Carbon followed by (O, C, H)
4	1-(Methylamino)ethyl	[*]C(NC)C	Carbon followed by (N, C, H)
5	Phenyl	[*]c1ccccc1	Carbon followed by (C, C, C)
6	Methyl	[*]C	Carbon followed by (H, H, H)
7	Hydrogen	[*][H]	Directly attached hydrogen

Here [*] denotes the attachment point in a fragment SMILES. The phenyl comparison includes the duplicate carbon arising from its aromatic bonding.

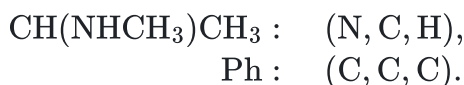
7.2 — Stereocenters and absolute configurations

The side chain is



Both methine carbons have four different substituents, so place an asterisk on each. The secondary amine nitrogen undergoes rapid pyramidal inversion and is not counted as an additional configurationally stable stereocenter.

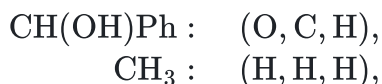
At C_1 , oxygen has highest priority and hydrogen lowest. The two carbon substituents are distinguished by



Because nitrogen outranks carbon,



At C_2 , nitrogen has highest priority. The remaining carbon groups give



and hence



In the supplied drawing, both the hydroxyl bond and the methylamino bond are hashed wedges pointing away from the viewer. The omitted hydrogen therefore points toward the viewer at each center.

At each center, the visible $1 \rightarrow 2 \rightarrow 3$ sequence is clockwise. Since priority 4 points toward the viewer, reverse that result: both centers are S .

Thus **1** is $(1S, 2S)$.

7.3 — Newman and Fischer representations

For the **Newman projection**, look along the $C_1 - C_2$ bond from the alcohol-bearing carbon toward the amino-bearing carbon. Draw C_1 as the central point and C_2 as the rear circle.

Carbon	Substituent	Clock position
Front, C_1	Phenyl	12
Front, C_1	Hydroxyl	4
Front, C_1	Hydrogen	8
Rear, C_2	Methylamino	2
Rear, C_2	Methyl	6
Rear, C_2	Hydrogen	10

This is a staggered conformer with phenyl and methyl anti. Its two configurations are S, S . The clock positions specify conformation, which the ordinary stereochemical SMILES does not encode.

For the **Fischer projection**, draw the vertical chain in the order



with phenyl at the top and methyl at the bottom. Place the horizontal substituents as follows:

Center	Left	Right
C_1	H	OH
C_2	NHCH ₃	H

Horizontal bonds point toward the viewer; vertical bonds point away. This gives the required S, S configuration.

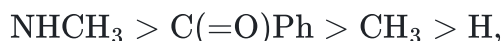
7.4 — Oxidation product and redox balance

Oxidation converts the secondary alcohol into a ketone:



The carbonyl carbon is trigonal planar, so C_1 ceases to be a stereocenter. No bond at C_2 is broken, and its spatial configuration is retained.

Its CIP priorities also retain their order:



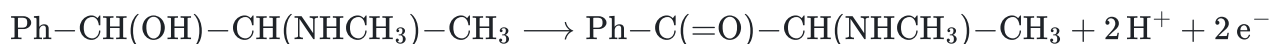
because the carbonyl substituent presents (O, O, C), whereas methyl presents (H, H, H). Thus **2** is the $2S$ ketone.

To draw **2**, replace the alcohol-bearing carbon in the original skeleton with a carbonyl group. Keep the methylamino bond at C_2 hashed away from the viewer, with its hydrogen toward the viewer.

For the changing oxidation numbers:

- At the alcohol carbon, one C–O bond contributes +1, one C–H bond contributes –1, and the carbon–carbon bonds contribute zero. Therefore C_1 initially has oxidation number 0.
- In the ketone, the C=O bond contributes +2, so C_1 becomes +II.
- Manganese changes from +VII in permanganate to +II.

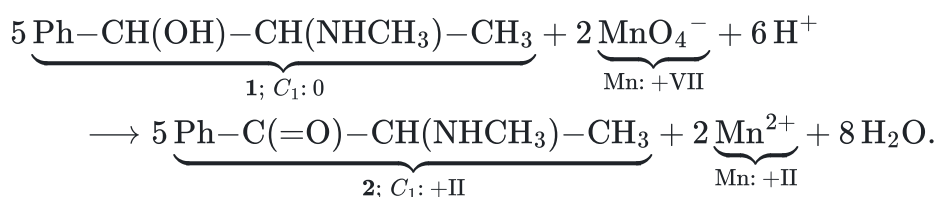
The half-equations are



and



Multiplying the first by 5 and the second by 2 gives the balanced equation, with every changing oxidation number identified:



Five alcohol molecules lose ten electrons, and two permanganate ions gain ten electrons. Both sides have net charge +4.

The inorganic species are **permanganate**, $[\text{O}-][\text{Mn}](=\text{O})(=\text{O})=\text{O}$; **hydrogen ion**, $[\text{H}^+]$; **manganese(II) ion**, $[\text{Mn}^{2+}]$; and **water**, O .

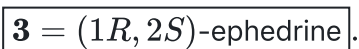
The equation uses the neutral organic structures shown in the problem. In the acidic medium, their amines are protonated: **protonated (1S,2S)-pseudoephedrine**, $\text{C}[\text{NH}_2^+][\text{C}@\text{H}](\text{C})[\text{C}@\text{H}](\text{O})\text{c1ccccc1}$, and **protonated (2S)-methcathinone**, $\text{C}[\text{NH}_2^+][\text{C}@\text{H}](\text{C})\text{C}(=\text{O})\text{c1ccccc1}$. Using these forms on both sides leaves the redox coefficients unchanged.

7.5(a) — Identification of compound 3

Reduction restores the alcohol group and creates a new stereocenter at C_1 . The existing $C_2 = S$ center remains unchanged. The two possible alcohol configurations are therefore



The first is the starting compound **1**. Since the problem specifies a different compound with a different melting point, the product is



For the requested drawing, retain the original carbon skeleton and the hashed methylamino bond. Change the hydroxyl bond from a hashed wedge to a solid wedge toward the viewer; its hydrogen now points away.

Equivalently, in a Fischer projection with phenyl at the top and methyl at the bottom:

Center	Left	Right
C_1	OH	H
C_2	NHCH ₃	H

7.5(b) — Isomer relationships

Compounds **1** and **3** have identical connectivity and differ at exactly one of their two stereocenters. Therefore they are **diastereomers**, specifically **epimers at C_1** .

The complete configurational stereoisomer set is:

Configuration	Name	SMILES
(1 <i>S</i> , 2 <i>S</i>)	(1 <i>S</i> , 2 <i>S</i>)-Pseudoephedrine, 1	<chem>CN[C@@H](C)[C@@H](O)c1ccccc1</chem>
(1 <i>R</i> , 2 <i>R</i>)	(1 <i>R</i> , 2 <i>R</i>)-Pseudoephedrine	<chem>CN[C@H](C)[C@H](O)c1ccccc1</chem>
(1 <i>R</i> , 2 <i>S</i>)	(1 <i>R</i> , 2 <i>S</i>)-Ephedrine, 3	<chem>CN[C@@H](C)[C@H](O)c1ccccc1</chem>
(1 <i>S</i> , 2 <i>R</i>)	(1 <i>S</i> , 2 <i>R</i>)-Ephedrine	<chem>CN[C@H](C)[C@@H](O)c1ccccc1</chem>

The enantiomeric pairs are



There is no internal symmetry allowing a meso form, so all four are chiral. Pure enantiomers have the same melting point under the same achiral conditions; diastereomers can have different melting points. The sign of optical rotation cannot be inferred simply from an *R* or *S* descriptor.

Compound **2** has one stereocenter and therefore two enantiomers. Its mirror image is **(2*R*)-methcathinone**, CN[C@H](C)C(=O)c1ccccc1. It is not an isomer of either alcohol: its formula is $C_{10}H_{13}NO$, whereas **1** and **3** have formula $C_{10}H_{15}NO$.

7.5(c) — Structural model for stereoselective reduction

The reagent is **lithium aluminium hydride**, $[Li^+].[AlH_4^-]$. A suitable model is **chelation-controlled reduction**: the carbonyl oxygen and amino nitrogen bind a common aluminium center, forming a five-membered ring containing aluminium, oxygen, C_1 , C_2 , and nitrogen.

Describe the model drawing as follows:

1. Draw the five-membered chelate approximately in the page, with aluminium at the top, oxygen upper left, nitrogen upper right, C_1 lower left, and C_2 lower right. Retain the carbonyl double bond between C_1 and oxygen.
2. Draw phenyl outward from C_1 , toward the lower left in the plane.
3. At C_2 , draw methyl on a solid wedge toward the viewer and hydrogen on a hashed wedge away. This arrangement gives $C_2 = S$.
4. Draw hydride attack at C_1 from behind the page, opposite the protruding methyl group.

Viewed from the front, the carbonyl substituent priorities are oxygen first, C_2 second, and phenyl third. Their clockwise order identifies the front as the **Re face**. The rear is consequently the **Si face**, which is less hindered by the C_2 methyl group.

Transfer of **hydride**, $[H^-]$, to this Si face moves the carbonyl π -electron pair onto oxygen. Protonation during work-up gives the alcohol. The newly introduced hydrogen points away in this drawing, and the remaining priorities run clockwise, so the new center is $C_1 = R$.

The product is therefore (1*R*, 2*S*)-**3**. The chelate geometry, attack direction, and electron movements are specified by this model; ordinary SMILES encode the product's configuration but do not encode those mechanistic details.

The solution was checked against the official solution.

Problem 8: Colloids

The combination of an inorganic and an organic component on a nanometer scale yields materials with excellent properties. Thus the synthesis of hybrid nanoparticles is of interest.

($T = 298.15\text{ K}$ throughout whole problem)

Solution **A** is an aqueous solution of CaCl_2 with a concentration of 1.780 g dm^{-3} .

Solution **B** is an aqueous solution of Na_2CO_3 with a concentration of 1.700 g dm^{-3} .

$$pK_{a1}(\text{H}_2\text{CO}_3) = 6.37 \quad pK_{a2}(\text{HCO}_3^-) = 10.33$$

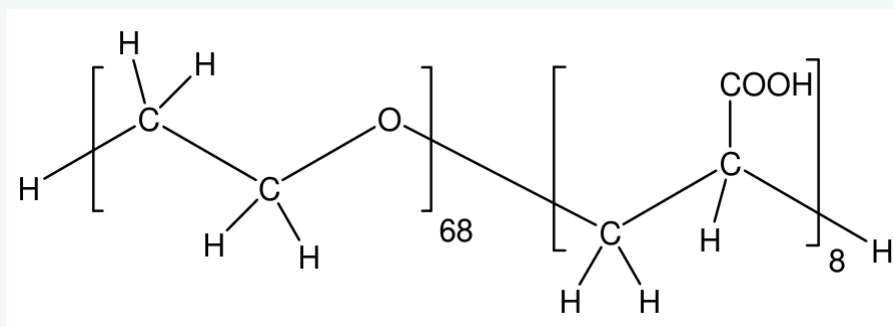
8.1 Calculate the pH of solution **B** using reasonable assumptions.

100 cm^3 of solution **A** and 100 cm^3 of solution **B** are mixed to form solution **C**. Solution **C** is adjusted to $pH\ 10$. A precipitate forms.

$$K_{sp}(\text{Ca}(\text{OH})_2) = 6.46 \times 10^{-6} \quad K_{sp}(\text{CaCO}_3) = 3.31 \times 10^{-9}$$

8.2 Show by calculation for each of the compounds $\text{Ca}(\text{OH})_2$ and CaCO_3 whether it can be found in the precipitate or not.

In a similar experiment 100 cm^3 of solution **A** additionally contain 2 g of a copolymer consisting of two water soluble blocks: a poly(ethylene oxide) block and a poly(acrylic acid) block:



The polymer does not undergo any chemical reaction (except protolysis of the acid) and yet has a strong effect: after mixing of the two solutions (**A+B**) no precipitate can be observed. Small calcium carbonate particles with the polymer chains attached to their surface form. The attached polymers prevent further crystal growth and the hybrid particles remain in solution.

8.3 Circle the block of the polymer (on the answer sheet) that attaches to the surface of the growing calcium carbonate crystal.

To characterize the hybrid particles they are separated from the preparation solution and transferred into 50 cm^3 of an aqueous NaOH solution ($c(\text{NaOH}) = 0.19\text{ mol dm}^{-3}$). The solution is diluted by the addition of 200 cm^3 of water. Assume that the new solution contains

only the hybrid particles and no additional calcium or carbonate ions. All acidic groups participate in the acid-base equilibrium.

- For the new solution, a pH of 12.30 is measured.
- In electron microscopy you only can see the inorganic particles (not the polymer): Spherical particles of 100 nm diameter are observed.
- The molar mass of the hybrid particles (inorganic and organic part together) is determined to be $M = 8.01 \cdot 10^8 \text{ g mol}^{-1}$.
- The charge of the particles is found to be $Z = -800$ (number of unit charges).

$(pK_a(\text{COOH}, \text{copolymer}) = 4.88)$

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?

8.5 Calculate which modification of calcium carbonate has been formed.

Modification	density
Calcite	2.71 g cm^{-3}
Vaterite	2.54 g cm^{-3}
Aragonite	2.95 g cm^{-3}

Official English text of the problem.

Answers

- **8.1:** $pH \approx 11.24$. The usual small-hydrolysis approximation gives 11.27.
- **8.2:** Calcium carbonate, CaCO_3 , $[\text{Ca}^{+2}] \cdot [\text{O}^{2-}]\text{C}(=\text{O})[\text{O}^{2-}]$, **precipitates**. Calcium hydroxide, $\text{Ca}(\text{OH})_2$, $[\text{Ca}^{+2}] \cdot [\text{OH}^{-}] \cdot [\text{OH}^{-}]$, **does not precipitate**.
- **8.3:** Circle the **right-hand poly(acrylic acid) block**, containing eight repeat units. Its acid-form repeat-unit SMILES is $[*]\text{CC}(\text{C}(=\text{O})\text{O})[*]$; its deprotonated form is $[*]\text{CC}(\text{C}(=\text{O})[\text{O}^{-}])[*]$.
- **8.4:** The formal acid-base calculation gives $m_{\text{polymer}} \approx 2.0 \text{ g}$, essentially **100%** of the initial polymer.
- **8.5:** The individual-particle data give $\rho \approx 2.54 \text{ g cm}^{-3}$, identifying **vaterite**, a calcium carbonate polymorph.

The results for 8.4 and 8.5 cannot both satisfy the overall material balance with all the supplied data. The titration in 8.4 gives $4.512 \times 10^{-3} \text{ mol}$ of carboxylate charges, that is $5.640 \times 10^{-6} \text{ mol}$ of particles with 800 charges each; at the stated molar mass this would be $4.52 \times 10^3 \text{ g}$ of hybrid, whereas the initial calcium and polymer allow only about 2.16 g.

Solution

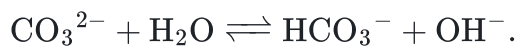
Use $K_w = 1.00 \times 10^{-14}$ at 298.15 K, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$, and standard atomic molar masses. Activities are approximated by concentrations, and volume changes other than the stated mixing and dilution are neglected.

8.1 — pH of solution B

The analytical concentration of sodium carbonate, $[\text{Na}^+] \cdot [\text{Na}^+] \cdot [\text{O}^-] \text{C}(=\text{O}) [\text{O}^-]$, is

$$C_B = \frac{1.700 \text{ g dm}^{-3}}{105.99 \text{ g mol}^{-1}} = 0.01604 \text{ mol dm}^{-3}.$$

Carbonate, $[\text{O}^-] \text{C}(=\text{O}) [\text{O}^-]$, reacts with water, O , to give hydrogen carbonate, $\text{OC}(=\text{O}) [\text{O}^-]$, and hydroxide, $[\text{OH}^-]$:



The corresponding base constant is

$$K_b = \frac{K_w}{K_{a2}} = \frac{10^{-14}}{10^{-10.33}} = 2.138 \times 10^{-4}.$$

Further hydrolysis to carbonic acid, $\text{OC}(=\text{O})\text{O}$,



has $K'_b = K_w/K_{a1} = 2.34 \times 10^{-8}$ and is negligible here. Water autoionization also contributes negligibly to the hydroxide concentration.

Let $x = [\text{OH}^-] \approx [\text{HCO}_3^-]$. Then

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

so

$$x = \frac{-K_b + \sqrt{K_b^2 + 4K_b C_B}}{2} = 1.748 \times 10^{-3} \text{ mol dm}^{-3}.$$

Therefore,

$$pOH = 2.7575, \quad \boxed{pH = 11.2425 \approx 11.24}.$$

If carbonate depletion is also neglected,

$$x \approx \sqrt{K_b C_B}, \quad pH \approx \frac{pK_w + pK_{a2} + \log C_B}{2} = 11.27.$$

The quadratic calculation avoids this last approximation: about 10.9% of the carbonate undergoes hydrolysis.

8.2 — Composition of the precipitate

For calcium chloride, $[\text{Ca}^{+2}] \cdot [\text{Cl}^-] \cdot [\text{Cl}^-]$,

$$c_A = \frac{1.780}{110.98} = 0.01604 \text{ mol dm}^{-3}.$$

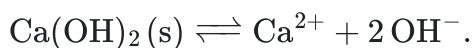
Mixing equal volumes halves both analytical concentrations:

$$C_{\text{Ca}} = 8.019 \times 10^{-3} \text{ mol dm}^{-3}, \quad C_{\text{carbonate}} = 8.020 \times 10^{-3} \text{ mol dm}^{-3}.$$

At $pH = 10$,

$$[\text{OH}^-] = 10^{-4} \text{ mol dm}^{-3}.$$

For calcium hydroxide, the dissolution equilibrium is



The concentration of calcium(II) ions, $[\text{Ca}^{2+}]$, cannot exceed C_{Ca} . Thus the largest possible ion product is

$$Q_{\text{Ca(OH)}_2} \leq (8.019 \times 10^{-3})(10^{-4})^2 = 8.019 \times 10^{-11}.$$

Since

$$8.019 \times 10^{-11} \ll 6.46 \times 10^{-6},$$

Ca(OH)_2 cannot precipitate.

For calcium carbonate, carbonate protonation must be considered. At $pH = 10$,

$$\frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = 10^{pK_{a2}-pH} = 10^{0.33} = 2.138.$$

Also,

$$\frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = 10^{6.37-10} = 2.34 \times 10^{-4},$$

so carbonic acid makes a negligible contribution. Before precipitation, therefore,

$$[\text{CO}_3^{2-}] \approx \frac{8.020 \times 10^{-3}}{1 + 2.138} = 2.56 \times 10^{-3} \text{ mol dm}^{-3}.$$

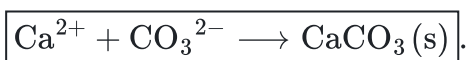
The initial ion product is

$$Q_{\text{CaCO}_3} = (8.019 \times 10^{-3})(2.56 \times 10^{-3}) = 2.05 \times 10^{-5}.$$

Because

$$2.05 \times 10^{-5} \gg 3.31 \times 10^{-9},$$

calcium carbonate precipitates:



Its precipitation further lowers the calcium concentration, reinforcing the exclusion of calcium hydroxide.

8.3 — Polymer block attached to the crystal

Circle the **entire right-hand bracketed block with subscript 8**, containing the pendant COOH groups.

This is the poly(acrylic acid) block:

- Acid-form repeat unit: $[\text{*}] \text{CC}(\text{C}(=\text{O})\text{O}) [\text{*}]$.
- Deprotonated polyacrylate repeat unit: $[\text{*}] \text{CC}(\text{C}(=\text{O})[\text{O}^-]) [\text{*}]$.

The negatively charged carboxylate groups adsorb at calcium sites on the growing crystal surface. The hydrated poly(ethylene oxide) block, repeat-unit SMILES $[\text{*}] \text{CCO} [\text{*}]$, extends into the surrounding water and provides steric stabilization.

Here $[\text{*}]$ marks continuation of the polymer chain; the repeat counts are eight for the acrylic acid block and 68 for the ethylene oxide block. The drawing specifies no tacticity. These fragment SMILES do not describe the spatial arrangement of the adsorbed chains.

8.4 — Amount of retained polymer

The intended titration balance attributes the consumption of added hydroxide to the polymer's acidic groups:



where R denotes the polymer backbone.

At the measured pH,

$$\frac{[\text{RCOO}^-]}{[\text{RCOOH}]} = 10^{12.30-4.88} = 2.63 \times 10^7.$$

Consequently, the fraction of deprotonated acid groups is

$$\alpha = \frac{1}{1 + 10^{4.88-12.30}} = 0.999999962 \approx 1.$$

The added sodium hydroxide, $[\text{Na}^+] \cdot [\text{OH}^-]$, supplies

$$n_{\text{OH}^-,0} = (0.050 \text{ dm}^3)(0.19 \text{ mol dm}^{-3}) = 9.50 \times 10^{-3} \text{ mol}.$$

The final volume is

$$V = 0.050 + 0.200 = 0.250 \text{ dm}^3.$$

Since $pOH = 14.00 - 12.30 = 1.70$,

$$[\text{OH}^-]_{\text{final}} = 10^{-1.70} = 1.995 \times 10^{-2} \text{ mol dm}^{-3},$$

and hence

$$n_{\text{OH}^-, \text{final}} = (0.250)(1.995 \times 10^{-2}) = 4.988 \times 10^{-3} \text{ mol}.$$

Thus the amount of deprotonated carboxyl groups inferred from this balance is

$$n_{\text{carboxylate}} = 9.50 \times 10^{-3} - 4.988 \times 10^{-3} = 4.512 \times 10^{-3} \text{ mol}.$$

Each polymer chain has eight acidic groups, so

$$n_P = \frac{n_{\text{carboxylate}}}{8\alpha} = 5.640 \times 10^{-4} \text{ mol}.$$

The depicted chain contains 68 ethylene oxide repeat units, eight acrylic acid repeat units, and two terminal hydrogen atoms. Its acid-form molar mass is approximately

$$M_P = 68(44.052) + 8(72.062) + 2(1.008) = 3574 \text{ g mol}^{-1}.$$

Therefore,

$$m_P = n_P M_P = (5.640 \times 10^{-4})(3574) = 2.016 \text{ g}.$$

With the precision of the supplied measurements,

$m_P \approx 2.0 \text{ g},$	retained fraction $\approx 100\%.$
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The small calculated excess over the initial 2 g is consistent with rounding: complete neutralization of exactly 2.000 g would give $pH \approx 12.303$.

8.5 — Calcium carbonate modification

For a neutral, stoichiometric calcium carbonate core, the negative particle charge is attributed to the polymer's deprotonated carboxyl groups. Each chain contributes approximately eight negative unit charges. Thus the number of attached chains per particle is

$$N_P = \frac{|Z|}{8\alpha} \approx \frac{800}{8} = 100.$$

Allowing for loss of the acidic hydrogen atoms, the organic contribution per mole of hybrid particles is

$$M_{\text{organic}} \approx 100(3574 - 8(1.008)) = 3.57 \times 10^5 \text{ g mol}^{-1}.$$

The inorganic contribution is therefore

$$M_{\text{inorganic}} = 8.01 \times 10^8 - 3.57 \times 10^5 = 8.0064 \times 10^8 \text{ g mol}^{-1}.$$

Electron microscopy gives the **inorganic** diameter. Hence

$$r = 50 \text{ nm} = 5.00 \times 10^{-6} \text{ cm},$$

and the inorganic volume per particle is

$$V_{\text{inorganic}} = \frac{4\pi r^3}{3} = 5.236 \times 10^{-16} \text{ cm}^3.$$

The inorganic mass per particle is

$$m_{\text{inorganic}} = \frac{M_{\text{inorganic}}}{N_A} = 1.330 \times 10^{-15} \text{ g}.$$

Therefore,

$$\rho = \frac{m_{\text{inorganic}}}{V_{\text{inorganic}}} = \frac{1.330 \times 10^{-15}}{5.236 \times 10^{-16}} \approx 2.54 \text{ g cm}^{-3}.$$

This matches the tabulated density of vaterite:

The individual-particle data identify vaterite.

Vaterite, calcite, and aragonite all have the ionic composition represented by $[\text{Ca}^{+2}] \cdot [\text{O}^-] \text{C}(=\text{O})$ $[\text{O}^-]$. This SMILES does not distinguish their crystal lattices.

The solution was checked against the official solution.