

IChO 2002

Theory problems and solutions · Groningen, The Netherlands · 10 theory problems with complete solutions

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Problem 1: Oxygen in Your Life

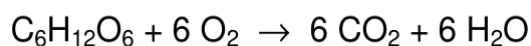
Theme 1 - Chemistry of Life

Life runs on chemistry. Understanding and monitoring life processes receive much attention in chemistry.

PROBLEM 1

OXYGEN IN YOUR LIFE

Oxygen is of vital importance for all of us. Oxygen enters the body via the lungs and is transported to the tissues in our body by blood. There it can deliver energy by the oxidation of sugars:

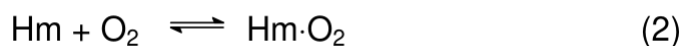


This reaction releases 400 kJ of energy per mol of oxygen. O_2 uptake by blood is at four heme (Hm) groups in the protein hemoglobin (Hb).

Free Hm consists of an Fe^{2+} ion attached to four N atoms of a porphyrin²⁻ ligand. Oxygen can bind at the coordination site of Fe^{2+} giving a $\text{Hm} \cdot \text{O}_2$ complex. Carbon monoxide can be complexed similarly, giving a $\text{Hm} \cdot \text{CO}$ complex. CO is a poison as it binds more strongly to Hm than O_2 does. The equilibrium constant K_1 for the reaction:



is 10 000 times larger than the equilibrium constant K_2 for the reaction:



Each Hb molecule can take up four molecules of O_2 . Blood in contact with O_2 absorbs a fraction of this amount, depending on the oxygen pressure, as shown in Figure 1 (curve 1). Also shown are the curves (2) and (3) for blood with two kinds of deficient Hb. These occur in patients with certain hereditary diseases.

Relevant data: O_2 pressure in lungs is 15 kPa; in the muscles it is 2 kPa. The maximum flow of blood through heart and lungs is $4 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$. The red cells in blood occupy 40 % of the blood volume; inside the cells the concentration of Hb is 340 kg m^{-3} ; Hb has a molar mass of 64 kg mol^{-1} . $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. $T = 298 \text{ K}$.

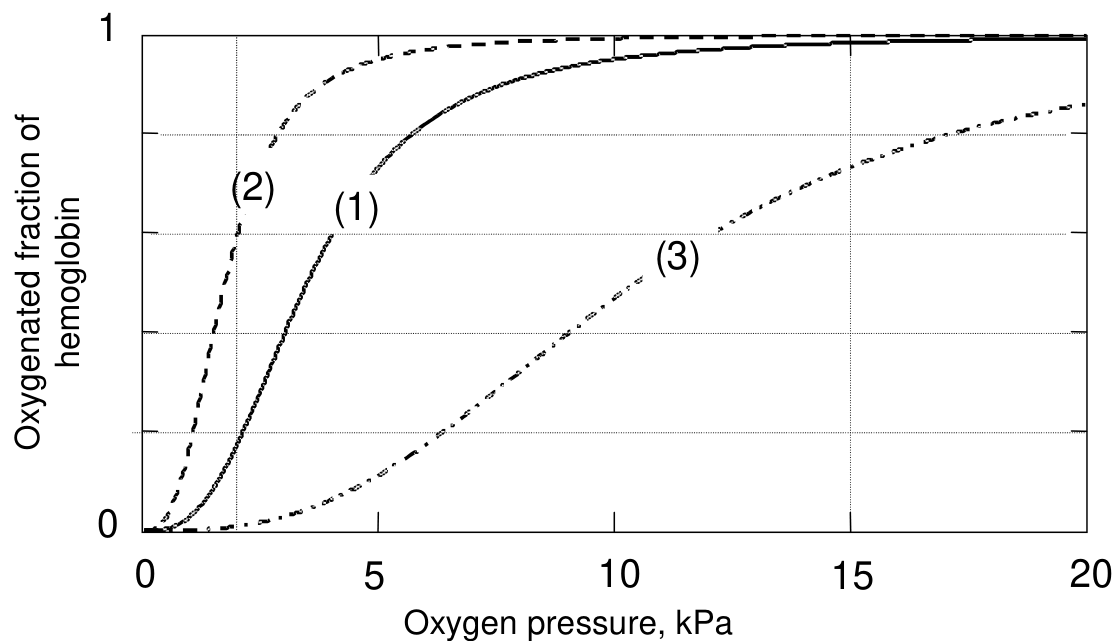


Figure 1

1.1 Using the relation between K and the standard Gibbs energy ΔG^0 for a reaction, calculate the difference between the ΔG^0 values for the heme reactions (1) and (2).

1.2 Estimate from Figure 1 (to 2 significant figures) how many moles of O_2 are deposited in muscle tissue when one mole of Hb travels from the lungs to the muscles and back again for the three different types of Hb.

1.3 The special S-shaped uptake curve 1 is the result of subtle structural features of Hb. The deficient Hb shown in curve 2 is not optimal because:

- ☐ The binding with O_2 is too weak.
- ☐ The binding with O_2 is too strong.
- ☐ The maximum oxygen capacity is too low.
- ☐ The deficiency is caused by carbon monoxide poisoning.

1.4 Calculate how much oxygen (in mol s^{-1}) can be deposited in tissue by blood with normal Hb (1).

1.5 Calculate the maximum power that the body can produce (assuming it is limited by oxygen transfer).

Official English text of the problem.

Answers

- **1.1:** $\Delta G_1^0 - \Delta G_2^0 = -22.8 \text{ kJ mol}^{-1}$. The standard Gibbs energy of carbon monoxide binding is lower by 22.8 kJ mol^{-1} .
- **1.2:** Approximately $3.2, 1.6, 2.9 \text{ mol}$ of O_2 per mole of Hb for curves (1), (2), and (3), respectively.

- 1.3: Select the **second** box: "The binding with O₂ is too strong."
- 1.4: $2.7 \times 10^{-3} \text{ mol s}^{-1}$ of O₂.
- 1.5: $1.1 \times 10^3 \text{ W} = 1.1 \text{ kW}$.

Solution

The small molecules involved in the binding comparison are molecular oxygen (dioxygen), O₂, SMILES O=O, and carbon monoxide, CO, SMILES [C-]#[O+]. Hm denotes the heme binding site defined in the problem; its detailed structure is unnecessary for these calculations.

1.1

For the binding equilibria



and



the standard Gibbs energy is related to the equilibrium constant by

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

Subtracting the values for reactions (1) and (2),

$$\begin{aligned} \Delta G_1^\circ - \Delta G_2^\circ &= -RT \ln \left(\frac{K_1}{K_2} \right) \\ &= -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \ln(10\,000) \\ &= -2.2819 \times 10^4 \text{ J mol}^{-1} \\ &= \boxed{-22.8 \text{ kJ mol}^{-1}}. \end{aligned}$$

The negative sign means that carbon monoxide binding has the more favorable standard Gibbs energy.

1.2

Let $f(p)$ be the oxygenated fraction shown in Figure 1. Since each Hb molecule can bind four oxygen molecules, one mole of Hb carries $4f(p)$ moles of O₂.

Thus, the amount released in the muscles during one complete circulation is

$$n_{\text{released}} = 4[f(15 \text{ kPa}) - f(2 \text{ kPa})] \quad \text{mol of O}_2 \text{ per mol of Hb.}$$

Approximate readings from the graph give:

Hb curve	Fraction in lungs, $f(15)$	Fraction in muscles, $f(2)$	Oxygen deposited per mole of Hb
(1), normal	0.98	0.18	$4(0.98 - 0.18) = \boxed{3.2 \text{ mol}}$
(2), deficient	1.00	0.60	$4(1.00 - 0.60) = \boxed{1.6 \text{ mol}}$
(3), deficient	0.74	0.01	$4(0.74 - 0.01) = 2.92 \approx \boxed{2.9 \text{ mol}}$

Returning to the lungs restores the oxygen loading for the next circulation.

1.3

Curve (2) reaches high oxygenation at a lower oxygen pressure than normal Hb, indicating stronger oxygen binding. At the muscle oxygen pressure of 2 kPa, it remains about 60% oxygenated, so much of its oxygen remains bound instead of being delivered to the tissue.

Therefore, select:

☒ **The binding with O₂ is too strong.**

Its oxygenation in the lungs is essentially complete; the deficiency concerns oxygen release.

1.4

The concentration of Hb given in the problem applies to the red cells, which occupy 40% of the blood volume. The Hb concentration in whole blood is therefore

$$c_{\text{Hb}} = \frac{0.40(340 \text{ kg m}^{-3})}{64 \text{ kg mol}^{-1}} = 2.125 \text{ mol m}^{-3}.$$

At the maximum blood flow, the molar flow of Hb is

$$\begin{aligned}\dot{n}_{\text{Hb}} &= (4 \times 10^{-4} \text{ m}^3 \text{ s}^{-1})(2.125 \text{ mol m}^{-3}) \\ &= 8.50 \times 10^{-4} \text{ mol s}^{-1}.\end{aligned}$$

Normal Hb delivers approximately 3.2 moles of oxygen per mole of Hb, so

$$\begin{aligned}\dot{n}_{\text{O}_2} &= (8.50 \times 10^{-4} \text{ mol Hb s}^{-1}) \left(3.2 \frac{\text{mol O}_2}{\text{mol Hb}} \right) \\ &= 2.72 \times 10^{-3} \text{ mol s}^{-1} \\ &\approx \boxed{2.7 \times 10^{-3} \text{ mol s}^{-1}}.\end{aligned}$$

1.5

The energy released is 400 kJ per mole of oxygen consumed. Using the unrounded intermediate oxygen-delivery rate,

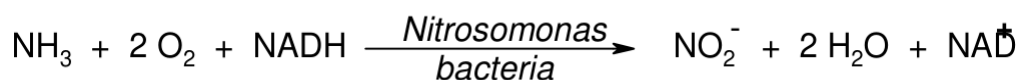
$$\begin{aligned}P_{\text{max}} &= \dot{n}_{\text{O}_2} (400 \text{ kJ mol}^{-1}) \\ &= (2.72 \times 10^{-3} \text{ mol s}^{-1})(400 \text{ kJ mol}^{-1}) \\ &= 1.088 \text{ kJ s}^{-1} \\ &\approx \boxed{1.1 \text{ kW}}.\end{aligned}$$

This is the maximum chemical-energy release rate under the stated oxygen-transfer limitation.

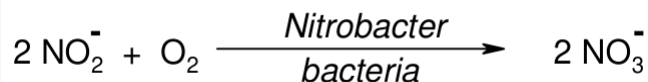
The solution was checked against the official solution.

Problem 2: Nitrogen Cycle in Nature

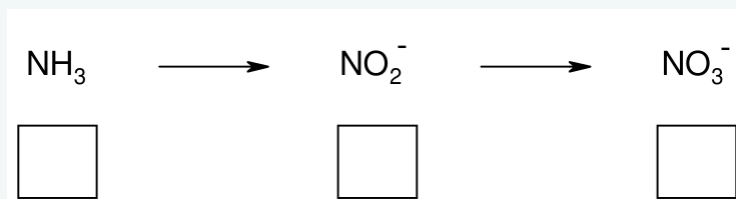
Ammonia is a toxic substance to marine animals at levels exceeding 1 ppm. Nitrifying bacteria play an important role in the conversion of NH₃ first to nitrite and then to nitrate, the storage form of nitrogen in the soil.



NADH is the biochemical reducing agent of the coenzyme nicotinamide dinucleotide (NAD), NAD^+ is the oxidized form of the coenzyme NAD.



2.1 Give the oxidation states of N in the following series: (Use the boxes below the compounds)



The spectrophotometric analysis of nitrite is based on a reaction with an indicator. The coloured product then obtained has an absorbance maximum at $\lambda = 543 \text{ nm}$. For quantitative analyses a calibration curve has to be made, in which absorbance at the maximum absorbance wavelength $\lambda = 543 \text{ nm}$ is plotted against nitrite concentration in a series of standards.

2.2 The measurements are performed at the wavelength with the maximum absorbance because:

- ☐ There is no interference of impurities.
- ☐ There is no contribution of stray light.
- ☐ There is optimal accuracy of the measurement.
- ☐ None of these statements.

Mark the correct answer.

The absorption is measured with a single beam spectrophotometer. However 5 % of the light, the so-called stray light I_s , strikes the detector directly (see Figure 2).

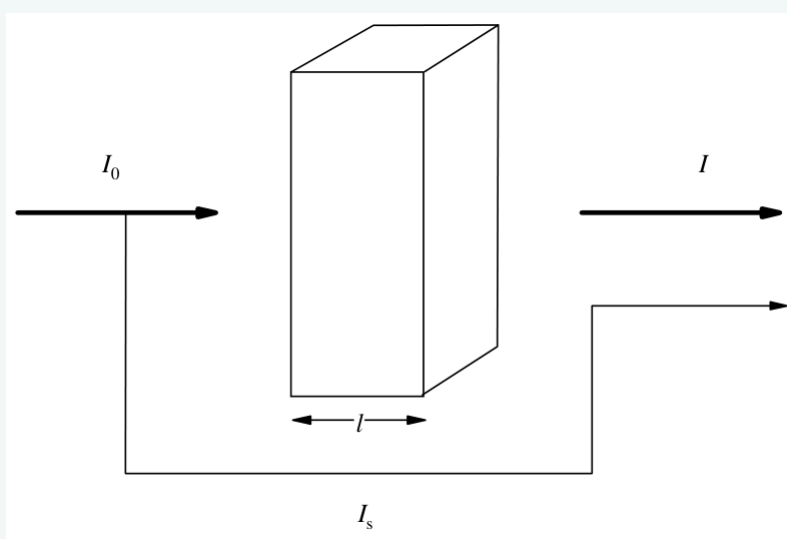


Figure 2

2.3 Calculate the value of the absorbance A shown by the spectrophotometer if $\epsilon = 6\,000\text{ M}^{-1}\text{ cm}^{-1}$, $l = 1\text{ cm}$ and $c = 1 \times 10^{-4}\text{ M}$

For a nitrite determination in water the following data have been measured.

Table 1

concentration of nitrite nitrogen (ppm)	absorbance at 543 nm (1.000 cm cell)
blank	0.003 (due to impurities in the solvent)
0.915	0.167
1.830	0.328

2.4 Determine (show calculation) from the data given above, using the values corrected for the solvent impurities, the slope m and the intercept b of the calibration curve $A = mc + b$.

The duplicate analyses of a water sample are given below. The measurements have been performed at a wavelength of 543 nm and in a 2.000 cm cell.

Table 2

water sample	absorbance
analysis 1	0.562
analysis 2	0.554

For the calculation of the concentration of the nitrite nitrogen (c in ppm) the equation obtained by the method of least squares

$$\text{corrected absorbance} = 0.1769c + 0.0015 \quad (\text{a})$$

may be applied, using the measurements in a 1.000 cm cell.

2.5 Calculate the average nitrite nitrogen concentration in ppm and $\mu\text{g cm}^{-3}$.

Hint: Take the blank from problem 2.4.

Official English text of the problem.

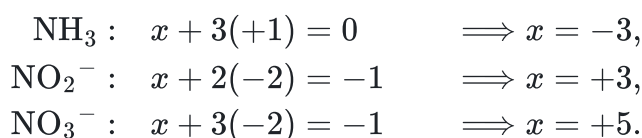
Answers

- **2.1:** Ammonia, NH_3 , SMILES N: **-3**; nitrite ion, NO_2^- , SMILES O=N[O-]: **+3**; nitrate ion, NO_3^- , SMILES [O-][N+](=O)[O-]: **+5**.
- **2.2:** Select the **third** statement: "There is optimal accuracy of the measurement."
- **2.3:** $A = 0.540$.
- **2.4:** $m = 0.176\text{ ppm}^{-1}$, $b = 0.003$.
- **2.5:** $\bar{c} = 1.55\text{ ppm} = 1.55\text{ }\mu\text{g cm}^{-3}$, expressed as nitrogen and scaling the solvent blank with path length. The alternative blank interpretation, subtracting 0.003 unchanged from each 2.000 cm reading, gives **1.56** in both units.

Solution

2.1

The sum of oxidation states equals the overall charge. Hydrogen has oxidation state +1 and oxygen has oxidation state −2 in these species. Writing x for the oxidation state of nitrogen:



Fill the left, middle and right boxes with **−3, +3 and +5**, respectively.

The ionic SMILES given above represent individual resonance contributors; the actual nitrogen–oxygen bonding is delocalized.

2.2

The Beer–Lambert law is

$$A = \epsilon lc.$$

At the absorption maximum, ϵ is greatest, so the concentration sensitivity,

$$\frac{\partial A}{\partial c} = \epsilon l,$$

is greatest. For a given small absorbance uncertainty, this reduces the uncertainty in the inferred concentration.

Also, at a smooth absorption maximum,

$$\frac{d\epsilon}{d\lambda} = 0,$$

so small wavelength-setting errors have a smaller effect on absorbance. These considerations support the **third statement**. Measuring at the maximum does not eliminate impurity absorption or stray light.

2.3

The absorbance of the light passing through the solution is

$$A_{\text{true}} = \epsilon lc = (6000 \text{ M}^{-1} \text{ cm}^{-1})(1 \text{ cm})(1 \times 10^{-4} \text{ M}) = 0.600.$$

Its transmittance is therefore

$$T_{\text{true}} = 10^{-0.600} = 0.2511886.$$

As shown by the branching diagram, 5% of the incident light bypasses the cell, while 95% passes through it. The total fraction reaching the detector is

$$T_{\text{measured}} = 0.05 + 0.95T_{\text{true}} = 0.05 + 0.95(0.2511886) = 0.2886292.$$

Thus,

$$A_{\text{measured}} = -\log_{10}(0.2886292) = 0.5396597 \approx 0.540.$$

The stray light increases the detected intensity and consequently lowers the displayed absorbance.

2.4

Subtract the solvent blank from each standard:

$$A_1 = 0.167 - 0.003 = 0.164, \quad A_2 = 0.328 - 0.003 = 0.325.$$

The slope of the line through the two corrected standards is

$$m = \frac{A_2 - A_1}{c_2 - c_1} = \frac{0.325 - 0.164}{(1.830 - 0.915) \text{ ppm}} = 0.175956 \text{ ppm}^{-1}.$$

Its intercept is

$$b = A_1 - mc_1 = 0.164 - (0.175956 \text{ ppm}^{-1})(0.915 \text{ ppm}) = 0.003.$$

Hence,

$$m = 0.176 \text{ ppm}^{-1}, \quad b = 0.003$$

and the calibration line is

$$A = (0.175956 \text{ ppm}^{-1})c + 0.003.$$

Absorbance and b are dimensionless. Subtracting the solvent blank does not force the line through the two measured standards to have zero intercept.

2.5

Use the supplied least-squares calibration,

$$A_{\text{corrected}, 1 \text{ cm}} = (0.1769 \text{ ppm}^{-1})c + 0.0015.$$

The sample readings were obtained in a 2.000 cm cell, whereas both this calibration and the tabulated solvent blank refer to 1.000 cm.

Under the Beer–Lambert law, the solvent-impurity absorbance scales with path length. Thus the blank in the 2.000 cm cell is

$$A_{\text{blank}, 2 \text{ cm}} = 0.003 \frac{2.000}{1.000} = 0.006.$$

Subtracting this blank and then halving is equivalent to halving the readings first and subtracting 0.003:

$$A_{1,\text{corrected}, 1 \text{ cm}} = \frac{0.562}{2} - 0.003 = 0.278,$$
$$A_{2,\text{corrected}, 1 \text{ cm}} = \frac{0.554}{2} - 0.003 = 0.274.$$

Therefore,

$$c_1 = \frac{0.278 - 0.0015}{0.1769 \text{ ppm}^{-1}} = 1.56303 \text{ ppm},$$
$$c_2 = \frac{0.274 - 0.0015}{0.1769 \text{ ppm}^{-1}} = 1.54042 \text{ ppm}.$$

The average is

$$\bar{c} = \frac{1.56303 + 1.54042}{2} = 1.55172 \text{ ppm} \approx 1.55 \text{ ppm}.$$

For dilute water, taking $\rho \approx 1.00 \text{ g cm}^{-3}$,

$$1 \text{ ppm} = 1 \text{ mg kg}^{-1} \approx 1 \text{ mg L}^{-1} = 1 \mu\text{g cm}^{-3}.$$

Consequently,

$$\bar{c} = 1.55 \mu\text{g cm}^{-3}.$$

Both results are **nitrite nitrogen concentrations**, so no conversion to the total mass of the nitrite ion is required.

The solution was checked against the official solution.

Problem 3: Inulin, a New Renewable Raw Material

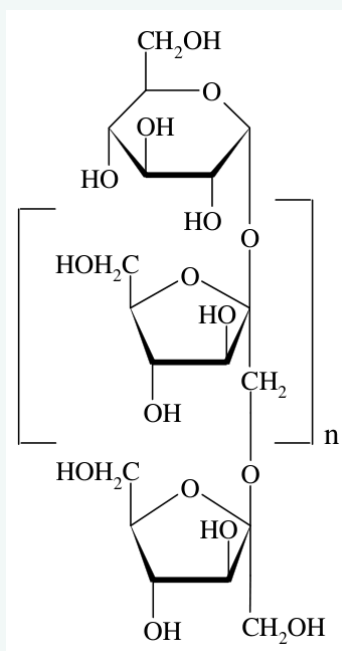
Theme II - Chemistry of Industrial Relevance

In our daily life we use many products that are produced on an industrial scale. Mastering the underlying chemistry is at the heart of this business.

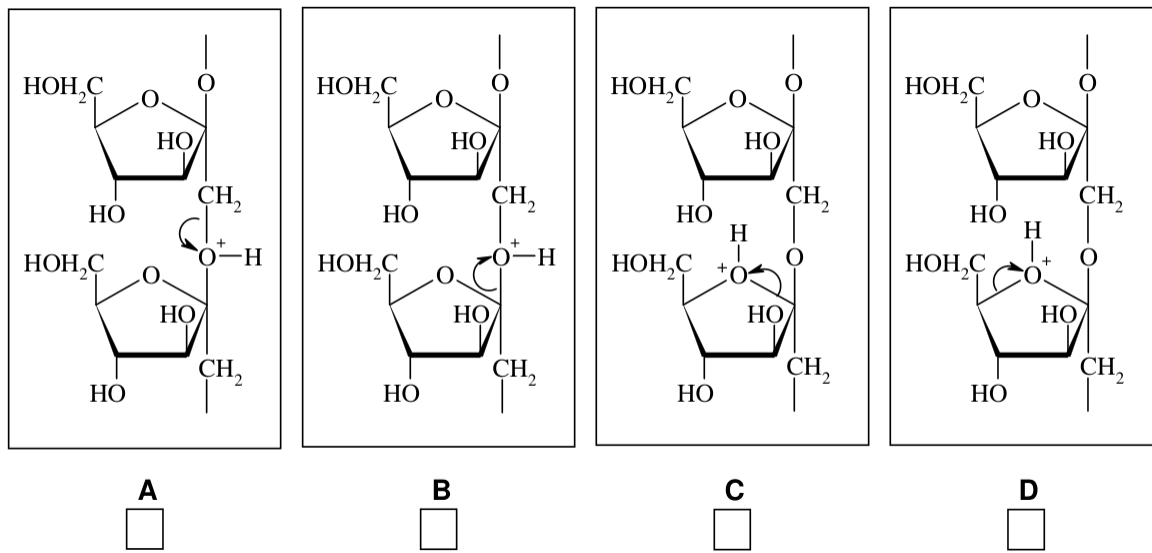
PROBLEM 3

Inulin, a New Renewable Raw Material

Inulin, which is produced from chicory roots in Belgium and The Netherlands, is used as a food additive as it has a beneficial effect on the intestinal flora. It is also used as source of fructose which is 1.9 times sweeter than sucrose, and for the production of mannitol which is used in chewing gum. Inulin is a linear polymer of fructose units with a glucose unit at one end; its Haworth projection formula is shown at the left. In this problem inulin has 10 fructose units ($n = 9$).



3.1 Inulin may be hydrolyzed under H^+ -catalysis conditions. Of the four options below (**A**, **B**, **C** and **D**) indicate which C-O bond cleavage is most likely to occur.



Mark the correct cleavage mechanism for the most efficient hydrolysis.

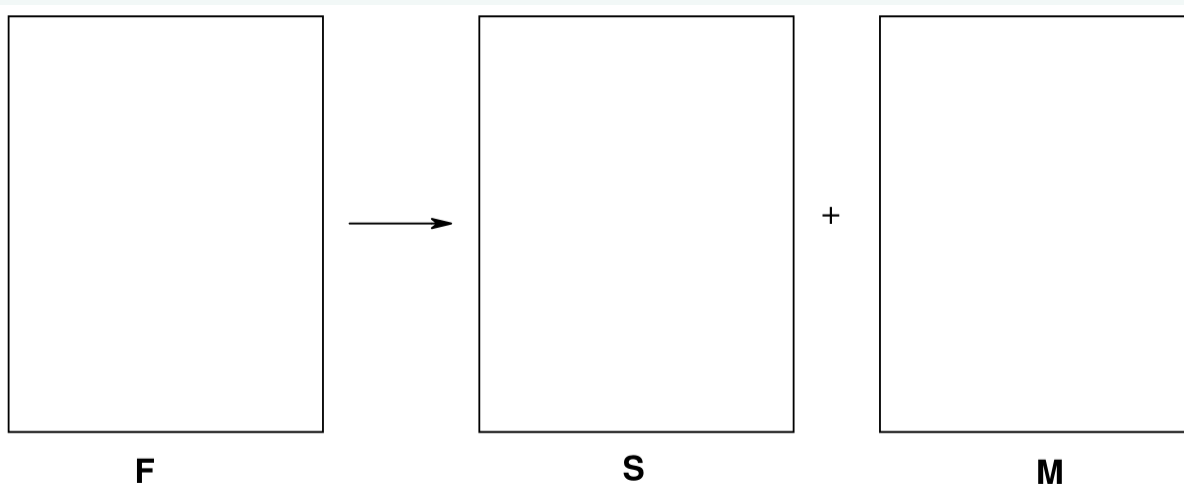
Hydrolysis with isotopically labelled water can provide information about the mechanism of hydrolysis using modern NMR techniques, which can “see” deuterium (^2H) and the oxygen isotope ^{17}O .

3.2 Indicate which labelled water can best be used for this purpose. Mark the correct answer.

- ☐ $^2\text{H}_2\text{O}$
- ☐ H_2^{17}O
- ☐ $^2\text{H}_2^{17}\text{O}$
- ☐ None of them.

Upon catalytic hydrogenation glucose gives sorbitol (**S**), whilst fructose (**F**) gives mannitol (**M**) and sorbitol (**S**).

3.3 Draw the Fischer projections of fructose (**F**), sorbitol (**S**) and mannitol (**M**).



1.00 mol of inulin in 2.00 kg of water with added catalysts, is subjected to hydrolysis and hydrogenation at 95°C in a one step process. The selectivity of the hydrogenation of fructose to mannitol / sorbitol is 7 / 3.

3.4 How many moles of mannitol and sorbitol are obtained?

M:**S:**

After completion of the reactions the catalysts are removed and the reaction mixture is cooled to 25 °C. The solubility of **M** is 0.40 mol kg⁻¹ in water at 25 °C and the solubility of **S** is so high that it will not precipitate.

3.5 Calculate how many moles of **M** will precipitate.

Official English text of the problem.

Answers

- **3.1: B** — cleavage of the protonated glycosidic bond at the anomeric carbon, C2, of fructose.
- **3.2:** H₂¹⁷O, oxygen-17-labelled water, [17OH2].
- **3.3:** The required structures are:
- **F:** D-fructose, OCC(=O) [C@@H](O) [C@H](O) [C@H](O)CO.
- **S:** Sorbitol (D-glucitol), OC[C@H](O) [C@@H](O) [C@H](O) [C@H](O)CO.
- **M:** D-mannitol, OC[C@@H](O) [C@@H](O) [C@H](O) [C@H](O)CO.

Their Fischer projections are specified in part 3.3 below. - **3.4:**

$n(\text{M}) = 7.00 \text{ mol}$, $n(\text{S}) = 4.00 \text{ mol}$. - **3.5:** 6.27 mol of mannitol precipitates.

Solution

3.1 — Acid-catalysed bond cleavage

The fructose residues are connected through glycosidic bonds between anomeric C2 of one residue and the oxygen attached to C1 of another.

In **B**, the bridging oxygen is protonated, and the bond between this oxygen and anomeric C2 breaks. The curved arrow indicates that the bonding electron pair moves onto the protonated oxygen. This produces an alcohol on the departing fragment and an **oxocarbenium centre** on the fructose residue. The positive charge is stabilised by electron donation from the adjacent ring oxygen.

Water, O, then attacks the anomeric carbon. Subsequent deprotonation produces the anomeric hydroxyl group and regenerates the acid catalyst, represented by H⁺, [H+].

The alternatives explain the preference:

- **A** would generate an unstabilised primary carbocation at C1.
- **C** opens the fructofuranose ring without directly breaking the connection between the two residues.
- **D** breaks the ring at a non-anomeric carbon, without the favourable oxocarbenium stabilisation obtained in B.

Thus **B** directly cleaves the polymer chain through the favourable anomeric pathway.

3.2 — Choice of isotopically labelled water

Choose **oxygen-17-labelled water**, H_2^{17}O , $[\text{}^{17}\text{OH}_2]$.

In mechanism B, the oxygen of the attacking water becomes the oxygen of the newly formed hydroxyl group at fructose C2. The original bridging oxygen remains attached to C1 of the other fragment. Consequently, the location of the oxygen isotope identifies where water enters during hydrolysis.

Deuterated water, $^2\text{H}_2\text{O}$, $[\text{}^2\text{H}]\text{O}[\text{}^2\text{H}]$, is less informative because hydroxyl hydrogens readily exchange with the solvent. Deuterium would therefore appear at many hydroxyl groups, independently of glycosidic bond cleavage.

Doubly labelled water, $^2\text{H}_2^{17}\text{O}$, $[\text{}^2\text{H}][\text{}^{17}\text{O}][\text{}^2\text{H}]$, would provide the useful oxygen label, but its deuterium labels add no necessary positional information. The best choice is therefore the oxygen-only label.

3.3 — Fischer projections and hydrogenation

Use a vertical six-carbon chain, numbered **C1 at the top to C6 at the bottom**, with CH_2OH at both ends. The required arrangements are:

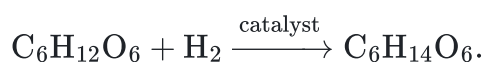
Carbon	D-fructose, F	Sorbitol, S	Mannitol, M
C2	Carbonyl, $\text{C}=\text{O}$	OH on the right	OH on the left
C3	OH on the left	OH on the left	OH on the left
C4	OH on the right	OH on the right	OH on the right
C5	OH on the right	OH on the right	OH on the right

At every stereogenic carbon, hydrogen occupies the horizontal position opposite OH. In the fructose projection, draw the carbonyl oxygen to the right of C2 with a double bond. As usual for Fischer projections, horizontal bonds point towards the viewer and vertical bonds point away. The stereochemical SMILES are given in the Answers section.

Hydrogenation of fructose reduces its C2 ketone and creates a new stereogenic centre. The two possible C2 configurations give sorbitol and mannitol, while the configurations at C3, C4 and C5 remain unchanged.

For comparison, D-glucose has open-chain SMILES $\text{O}=\text{C}[\text{C}@\text{H}](\text{O})[\text{C}@@\text{H}](\text{O})[\text{C}@\text{H}](\text{O})[\text{C}@\text{H}](\text{O})\text{CO}$. Reducing its C1 aldehyde to CH_2OH gives sorbitol without creating a new stereogenic centre.

Molecular hydrogen is H_2 , $[\text{H}][\text{H}]$. Each individual hydrogenation—glucose to sorbitol, fructose to sorbitol, or fructose to mannitol—has the balanced stoichiometry

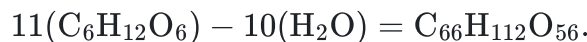


One mole of fructose therefore yields one mole of total hexitol products.

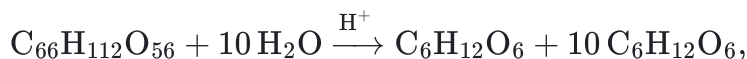
3.4 — Amounts of mannitol and sorbitol

Each inulin molecule contains one glucose residue and ten fructose residues: **11 monosaccharide residues joined by 10 glycosidic bonds**.

The molecular formula follows from condensation of the eleven monosaccharides:



The balanced hydrolysis is



where the first product term is glucose and the second is fructose. Thus, 1.00 mol of inulin produces

$$n(\text{glucose}) = 1.00 \text{ mol}, \quad n(\text{fructose}) = 10.0 \text{ mol}.$$

The fructose hydrogenation selectivity is

$$\text{M} : \text{S} = 7 : 3.$$

Hence

$$n(\text{M}) = 10.0 \text{ mol} \times \frac{7}{10} = \boxed{7.00 \text{ mol}},$$

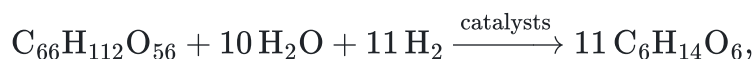
and the fructose-derived sorbitol is

$$n(\text{S; from fructose}) = 10.0 \text{ mol} \times \frac{3}{10} = 3.00 \text{ mol}.$$

The glucose supplies another 1.00 mol of sorbitol:

$$n(\text{S}) = 3.00 + 1.00 = \boxed{4.00 \text{ mol}}.$$

The combined hydrolysis and hydrogenation balance is



with the eleven product moles distributed as seven moles of mannitol and four moles of sorbitol.

3.5 — Precipitation of mannitol

Hydrolysis consumes ten moles of water per mole of inulin:

$$n(\text{water consumed}) = 10(1.00 \text{ mol}) = 10.0 \text{ mol}.$$

Using $M(\text{H}_2\text{O}) = 18.0 \text{ g mol}^{-1}$, the remaining water mass is

$$\begin{aligned} m(\text{water}) &= 2.00 \text{ kg} - (10.0 \text{ mol})(18.0 \text{ g mol}^{-1}) (10^{-3} \text{ kg g}^{-1}) \\ &= 1.82 \text{ kg}. \end{aligned}$$

Hydrogenation does not change this water balance.

At 25 °C, the amount of mannitol that remains dissolved is

$$n(\text{M; dissolved}) = (0.40 \text{ mol kg}^{-1})(1.82 \text{ kg}) = 0.728 \text{ mol}.$$

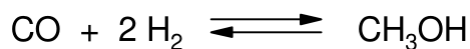
Retaining these digits until the final subtraction,

$$\begin{aligned} n(\text{M; precipitated}) &= 7.00 - 0.728 \\ &= 6.272 \text{ mol} \\ &\approx \boxed{6.27 \text{ mol}}. \end{aligned}$$

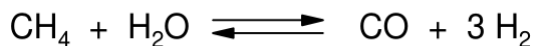
The solution was checked against the official solution.

Problem 4: Production of Methanol

Methanol (CH_3OH) is a chemical that is used for the production of additives in gasoline and many common plastics. A factory, producing methanol, is based on the reaction:



Hydrogen and CO are obtained by the reaction:



The three units of the factory, namely, the "reformer" for the hydrogen / carbon monoxide production, the "methanol reactor" and a "separator" to separate methanol from CO and H_2 , are schematically shown in Figure 1. Four positions are indicated by α , β , γ and δ .

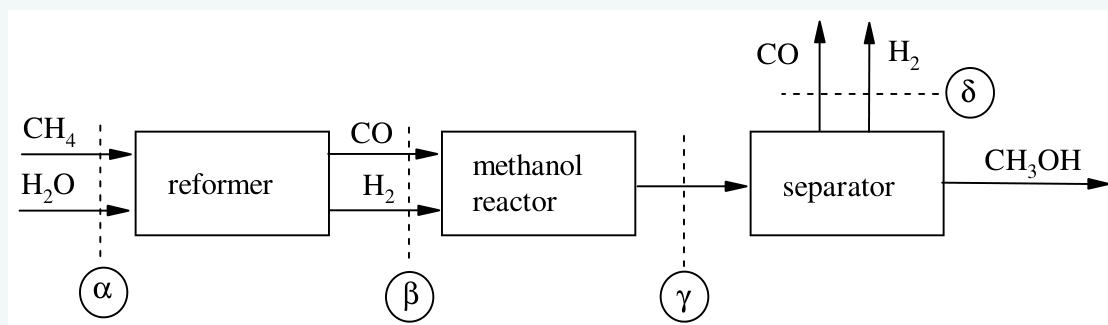


Figure 1

The flow of methanol at position γ is $n[\text{CH}_3\text{OH}, \gamma] = 1000 \text{ mol s}^{-1}$. The factory is so designed that $2/3$ of the CO is converted to methanol. Excess CO and H_2 at position δ are used to heat the first reactor. Assume that the reformer reaction goes to completion.

4.1 Calculate the flow of CO and H_2 at position β .

4.2 Calculate the flow of CO and H_2 at position γ .

4.3 Calculate the flows of CH_4 and H_2O needed at position α .

4.4 At point γ all species are gases. Calculate the partial pressures in MPa for CO, H_2 and CH_3OH at position γ using the equation:

$$p_i = p \frac{n_i}{n_{\text{tot}}}$$

wherein n_i is the flow and p_i the partial pressure of the compound i , n_{tot} is the total flow at the position considered, and p the total pressure in the system. ($p = 10 \text{ MPa}$)

When the methanol reactor is large enough the reaction goes to equilibrium. The partial pressures at point γ obey the equation:

$$K_p = \frac{p_{\text{CH}_3\text{OH}} p_0^2}{p_{\text{CO}} p_{\text{H}_2}^2}$$

wherein p_0 is a constant (0.1 MPa) and K_p is a function of temperature as is shown in Figure 2 (the vertical scale is logarithmic).

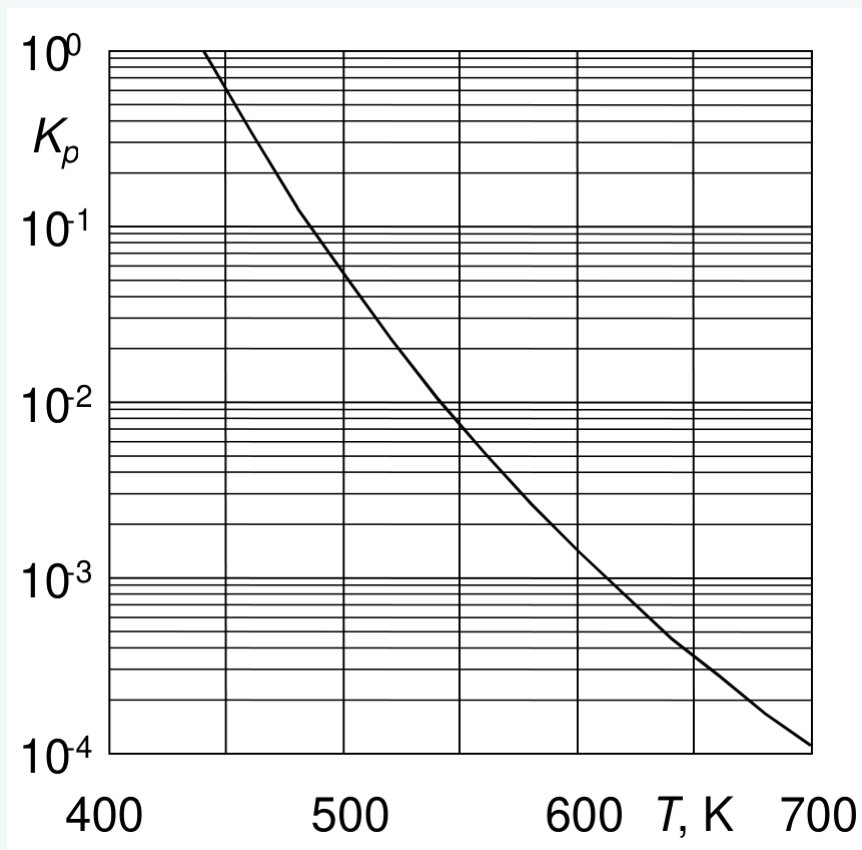


Figure 2

4.5 Calculate K_p and indicate at which temperature T the reaction must be operated to achieve this equilibrium.

Official English text of the problem.

Answers

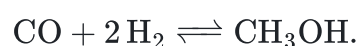
Molecular names and SMILES used below: carbon monoxide, CO, [C-]#[O+]; hydrogen, H₂, [H][H]; methane, CH₄, c; water, H₂O, o; methanol, CH₃OH, co.

- **4.1:** $n[\text{CO}, \beta] = 1.50 \times 10^3 \text{ mol s}^{-1}$; $n[\text{H}_2, \beta] = 4.50 \times 10^3 \text{ mol s}^{-1}$.
- **4.2:** $n[\text{CO}, \gamma] = 5.00 \times 10^2 \text{ mol s}^{-1}$; $n[\text{H}_2, \gamma] = 2.50 \times 10^3 \text{ mol s}^{-1}$.
- **4.3:** $n[\text{CH}_4, \alpha] = n[\text{H}_2\text{O}, \alpha] = 1.50 \times 10^3 \text{ mol s}^{-1}$.
- **4.4:** At γ , $p_{\text{CO}} = 1.25 \text{ MPa}$, $p_{\text{H}_2} = 6.25 \text{ MPa}$, and $p_{\text{CH}_3\text{OH}} = 2.50 \text{ MPa}$.
- **4.5:** $K_p = 5.12 \times 10^{-4}$, dimensionless; $T \approx 640 \text{ K}$, read from Figure 2.

Solution

4.1 — Flows entering the methanol reactor

The balanced methanol synthesis reaction is



Each mole of methanol formed consumes one mole of carbon monoxide. Thus, producing 1000 mol s^{-1} of methanol consumes 1000 mol s^{-1} of carbon monoxide. Since this represents $2/3$ of the incoming carbon monoxide,

$$\frac{2}{3} n[\text{CO}, \beta] = 1000 \text{ mol s}^{-1},$$

giving

$$n[\text{CO}, \beta] = 1500 \text{ mol s}^{-1}.$$

The balanced reforming reaction, taken to completion as instructed, is



It produces three moles of hydrogen for each mole of carbon monoxide. Therefore,

$$n[\text{H}_2, \beta] = 3 n[\text{CO}, \beta] = 3(1500),$$

$$n[\text{H}_2, \beta] = 4500 \text{ mol s}^{-1}.$$

4.2 — Flows leaving the methanol reactor

Subtract the quantities consumed in forming methanol:

$$n[\text{CO}, \gamma] = (1500 - 1000) \text{ mol s}^{-1} = 500 \text{ mol s}^{-1},$$

$$n[\text{H}_2, \gamma] = (4500 - 2 \times 1000) \text{ mol s}^{-1} = 2500 \text{ mol s}^{-1}.$$

The methanol flow is the given 1000 mol s^{-1} .

4.3 — Required methane and water feeds

The reforming reaction consumes one mole each of methane and water per mole of carbon monoxide produced. Complete reforming must supply 1500 mol s^{-1} of carbon monoxide, so the required stoichiometric feeds are

$$n[\text{CH}_4, \alpha] = 1500 \text{ mol s}^{-1},$$

$$n[\text{H}_2\text{O}, \alpha] = 1500 \text{ mol s}^{-1}.$$

4.4 — Partial pressures at γ

The total gas flow is

$$n_{\text{tot}, \gamma} = (500 + 2500 + 1000) \text{ mol s}^{-1} = 4000 \text{ mol s}^{-1}.$$

Using $p_i = p n_i / n_{\text{tot}}$ at $p = 10 \text{ MPa}$,

$$p_{\text{CO}} = (10 \text{ MPa}) \frac{500}{4000} = 1.25 \text{ MPa},$$

$$p_{\text{H}_2} = (10 \text{ MPa}) \frac{2500}{4000} = 6.25 \text{ MPa},$$

$$p_{\text{CH}_3\text{OH}} = (10 \text{ MPa}) \frac{1000}{4000} = 2.50 \text{ MPa}.$$

These partial pressures sum to 10.00 MPa , as required.

4.5 — Equilibrium constant and temperature

Substitute the partial pressures and $p_0 = 0.1 \text{ MPa}$ into the given expression:

$$\begin{aligned}
 K_p &= \frac{p_{\text{CH}_3\text{OH}} p_0^2}{p_{\text{CO}} p_{\text{H}_2}^2} \\
 &= \frac{(2.50 \text{ MPa})(0.1 \text{ MPa})^2}{(1.25 \text{ MPa})(6.25 \text{ MPa})^2} \\
 &= \boxed{5.12 \times 10^{-4}}.
 \end{aligned}$$

The pressure units cancel, so K_p is dimensionless.

On the logarithmic vertical axis of Figure 2, this value lies between 10^{-3} and 10^{-4} , at

$$\log_{10} K_p = -3.291.$$

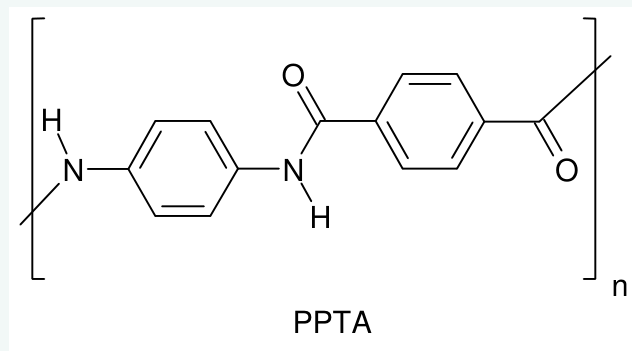
Following this level horizontally to the curve and then vertically down to the temperature axis gives

$$\boxed{T \approx 640 \text{ K}}.$$

The solution was checked against the official solution.

Problem 5: Aramids, High-performance Polymeric Materials

Aromatic polyamides (aramids) are high strength, high performance polymer fibers that find use in composite materials, bullet-proof vests, high quality skis, safety helmets, etc. Aramid PPTA is marketed under the names Kevlar® (DuPont) and Twaron® (Teijin), and amongst others manufactured in the north of The Netherlands. The PPTA chains are neatly packed into fibers with a sheet type structure.

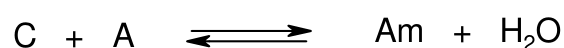


PPTA

5.1 Draw the structure of these sheets (three chains suffice).

For a polymerisation of equimolar amounts of two monomers the average chain length is $\overline{P}_n$, the degree of conversion is p , which equals the fraction of functional groups that have reacted, the total number of chains is N_t and the total initial number of monomers is U_0 .

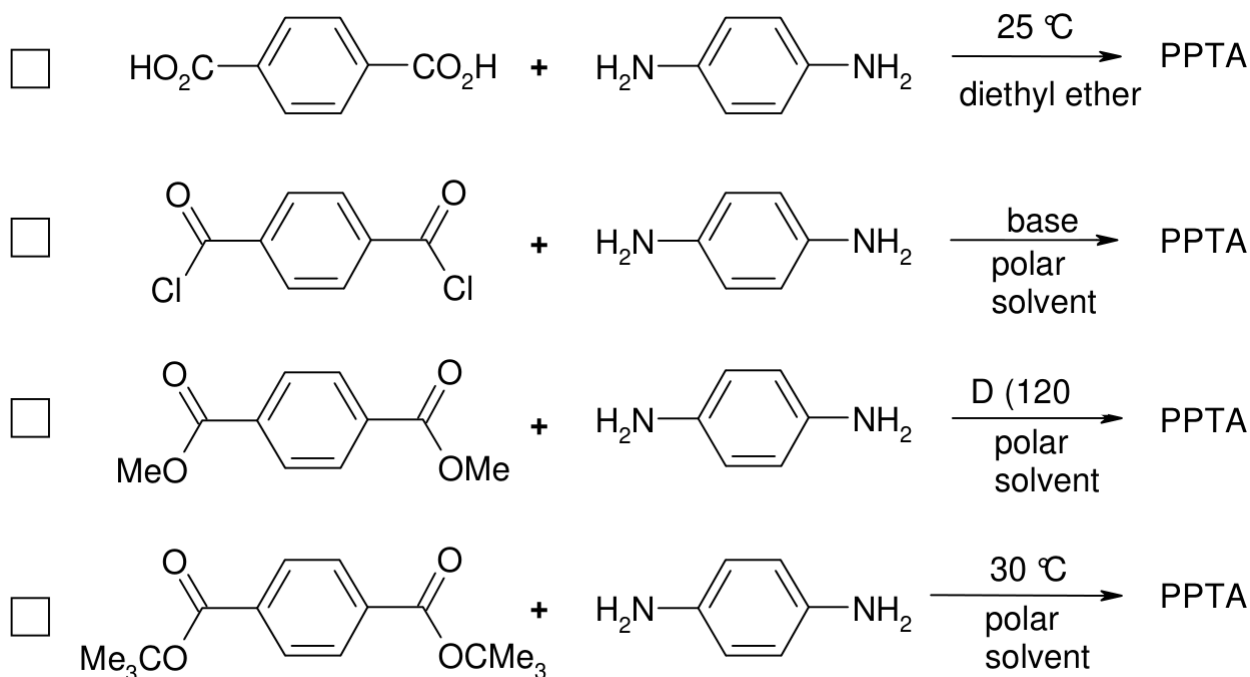
Assuming that the polymerization equilibrium can fully be described by:



where C stands for any $-\text{CO}_2$ group, A stands for any $-\text{NH}_2$ group and Am stands for any amide group.

5.2 Calculate the degree of conversion needed to obtain an average chain length of 500.

5.3 For the synthesis of PPTA the following possibilities are considered. Which of the following reactions will work? Mark the correct answer(s).



5.4 Another type of aramid can be produced from 4-aminobenzoic acid (4-aminobenzene-carboxylic acid) by heating.

(a) Give the structure of this aramid ($n = 4$)

(b) Calculate the average chain length at equilibrium (reaction is carried out in a closed vessel). The equilibrium constant $K = 576$.

Official English text of the problem.

Answers

- 5.1:** Three extended, parallel PPTA chains joined into a sheet by repeated interchain $\text{N}-\text{H} \cdots \text{O}=\text{C}$ hydrogen bonds. The repeat-fragment SMILES and drawing description are given below.
- 5.2:** $p = 0.998 = 99.8\%$.
- 5.3:** Mark **the second and third reactions**: terephthaloyl chloride with the diamine, and heated dimethyl terephthalate with the diamine.
- 5.4(a):** The linear poly(p-benzamide) tetramer:



where R is para-phenylene. Its explicit SMILES is given below.

- **5.4(b):** $\overline{P}_n = 25$ monomer residues per chain, with equilibrium conversion $p = 0.960$.

Solution

5.1 — Hydrogen-bonded sheets

PPTA is **poly(p-phenylene terephthalamide)**. Its repeating fragment has SMILES

[*]Nc1ccc(NC(=O)c2ccc(C(=O)[*])cc2)cc1.

The two [*] atoms indicate continuation into neighbouring repeat units; this notation describes the covalent connectivity.

To draw the requested sheet:

1. Draw three extended PPTA chains with parallel chain axes and predominantly trans amide groups.
2. Align adjacent chains so that an amide N-H group directed into the gap faces a carbonyl oxygen on the neighbouring chain.
3. Draw a dashed hydrogen bond from that hydrogen to the oxygen:



4. Repeat these contacts along both gaps, so that the middle chain hydrogen-bonds to both outer chains.

The nearly linear donor–hydrogen–acceptor contacts hold the chains together within the sheet. Their spatial arrangement and the amide conformations are not specified by the SMILES.

5.2 — Conversion required for a chain length of 500

Each monomer is bifunctional, so the initial number of functional groups is $2U_0$. At conversion p , the number of reacted functional groups is $2U_0p$.

Each new amide linkage consumes two functional groups. Consequently, the number of linkages formed is U_0p . For linear polymerization without cyclization, each linkage reduces the number of separate molecules by one:

$$N_t = U_0 - U_0p = U_0(1 - p).$$

The number-average chain length therefore obeys the Carothers equation:

$$\overline{P}_n = \frac{U_0}{N_t} = \frac{1}{1 - p}.$$

Thus,

$$500 = \frac{1}{1 - p} \implies p = 1 - \frac{1}{500} = \boxed{0.998 = 99.8\%}.$$

Here chain length counts individual original monomer residues.

5.3 — Suitable synthesis routes

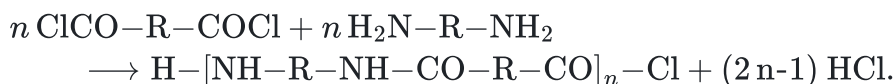
The common diamine is **p-phenylenediamine**, also called benzene-1,4-diamine, SMILES

Nc1ccc(N)cc1.

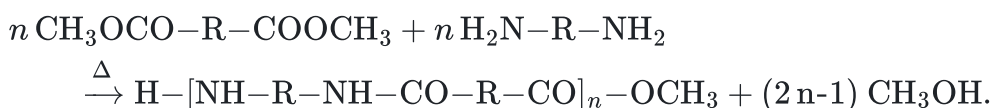
Scheme, from top to bottom	Carbonyl-containing monomer and SMILES	Works under the indicated conditions?	Reason
1	Terephthalic acid , <chem>O=C(O)c1ccc(C(=O)O)cc1</chem>	No	At 25 °C, the unactivated carboxylic acid and amine primarily undergo acid–base interaction. These conditions do not provide effective dehydrative amidation.
2	Terephthaloyl chloride , <chem>O=C(Cl)c1ccc(C(=O)Cl)cc1</chem>	Yes	Acid chlorides readily acylate amines. The base captures the acid produced and maintains the amine's nucleophilicity.
3	Dimethyl terephthalate , <chem>COC(=O)c1ccc(C(=O)OC)cc1</chem>	Yes	Heating enables ester aminolysis: amide bonds form with elimination of methanol.
4	Di-tert-butyl terephthalate , <chem>CC(C)(C)OC(=O)c1ccc(C(=O)OC(C)(C)C)cc1</chem>	No	The hindered, unactivated tert-butyl ester does not undergo effective aminolysis with this aromatic diamine at 30 °C.

For balanced polymerization equations, let *R* denote **para-phenylene**, or benzene-1,4-diyl, fragment SMILES [*]c1ccc([*])cc1. In the condensed structures below, CO denotes a carbonyl group, C(=O).

A representative finite chain containing *n* molecules of each monomer has $2n - 1$ newly formed amide bonds. The acid-chloride route is therefore



The corresponding methyl-ester route is



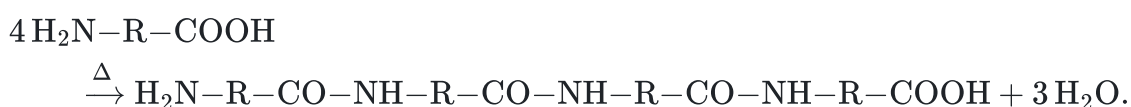
These equations retain the end groups explicitly: the leading hydrogen completes an amino end group, while the other end retains an acid chloride or methyl ester group.

The byproducts are **hydrogen chloride**, SMILES Cl, and **methanol**, SMILES CO, respectively. In the second scheme, the added base captures the hydrogen chloride.

5.4(a) — Aramid from 4-aminobenzoic acid

The monomer is **4-aminobenzoic acid**, SMILES Nc1ccc(C(=O)O)cc1. Its amino group reacts with another molecule's carboxyl group, producing **poly(p-benzamide)**.

Four monomers form three amide bonds and release three molecules of **water**, SMILES O:



The **linear 4-aminobenzoic acid tetramer** has SMILES

Nc1ccc(C(=O)Nc2ccc(C(=O)Nc3ccc(C(=O)Nc4ccc(C(=O)O)cc4)cc3)cc2)cc1.

The requested drawing should show four benzene rings, each substituted in the para positions, connected successively by three $-\text{C}(=\text{O})-\text{NH}^-$ links. One end is an amino group and the other is a carboxylic acid group. Its molecular formula is $\text{C}_{28}\text{H}_{22}\text{N}_4\text{O}_5$.

5.4(b) — Equilibrium chain length in a closed vessel

Use the stated functional-group equilibrium:



Let c_0 be the initial monomer concentration, in mol L^{-1} . Taking the starting monomer to contain no water, each amide linkage produces one water molecule, which remains in the closed vessel.

At conversion p ,

$$[\text{C}] = [\text{A}] = c_0(1 - p), \quad [\text{Am}] = [\text{H}_2\text{O}] = c_0p.$$

Under the problem's equilibrium model,

$$K = \frac{[\text{Am}][\text{H}_2\text{O}]}{[\text{C}][\text{A}]} = \frac{(c_0p)^2}{[c_0(1 - p)]^2} = \left(\frac{p}{1 - p} \right)^2.$$

Therefore,

$$\frac{p}{1 - p} = \sqrt{576} = 24, \quad p = \frac{24}{25} = 0.960.$$

Applying the chain-count relation from 5.2,

$$\boxed{\overline{P}_n = \frac{1}{1 - p} = 25}.$$

Thus the equilibrium average is **25 monomer residues per chain**.

The solution was checked against the official solution.

Problem 6: Phospholipids in Membranes

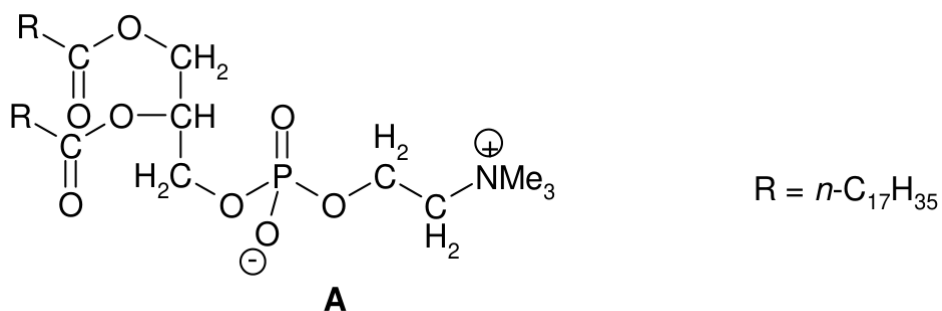
Theme III - Chemistry of Functional Molecules in Nature

A challenge in chemistry is to discover what nature does and how the structures of biologically active molecules are related to what they do.

PROBLEM 6

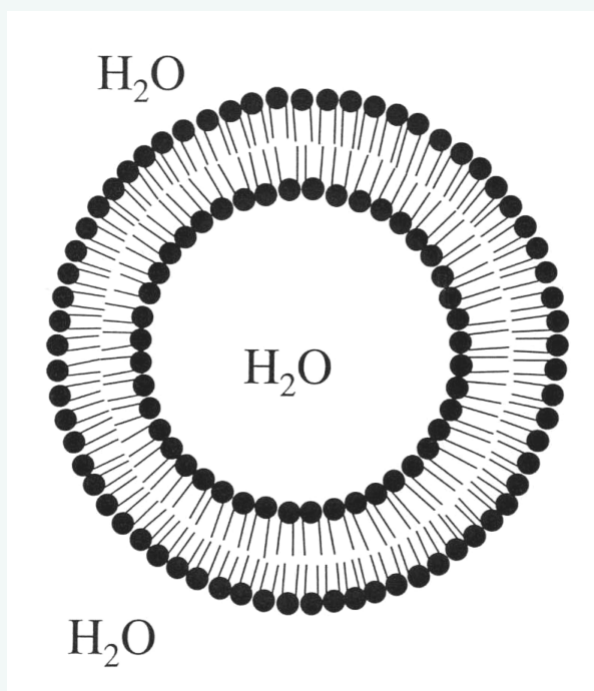
Phospholipids in Membranes

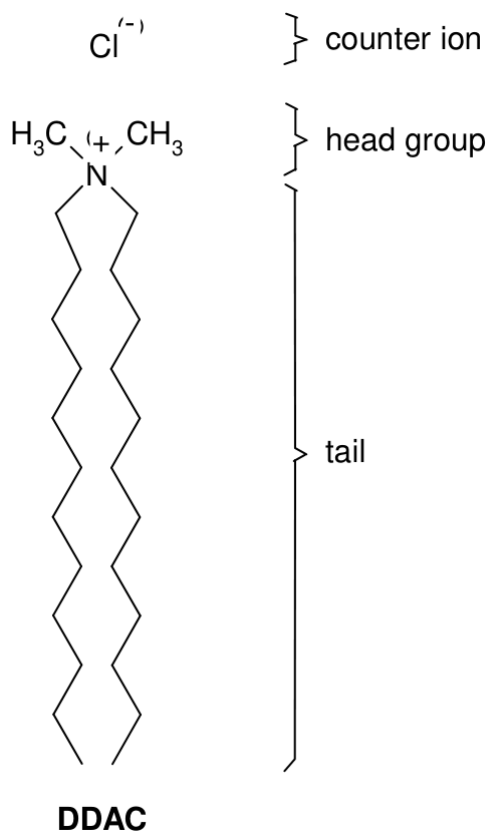
Biological cell membranes are complex, functional, non-covalent molecular assemblies, largely consisting of lipids and proteins. Their function is of vital importance for life processes. They separate the cell from its environment and also determine the specific flow of information between the cell contents and the environment. Phospholipids are among the most important components of cell membranes. An example is compound **A**.



Upon dispersion in water (above a low critical concentration) compound **A** forms closed bilayer structures, called liposomes, which are employed as model compounds for aspects of the chemistry of the structurally much more complex cell membranes. Liposomes are globular aggregates with the polar or ionic head groups in contact with water and with the alkyl tails sequestered in a hydrophobic core. The bilayer structure encloses an aqueous inner compartment.

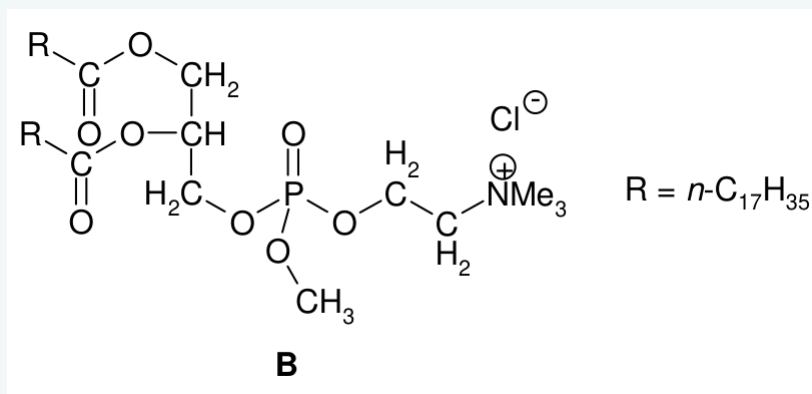
Double-tailed *synthetic* surfactants also form closed bilayer assemblies similar to liposomes but now called vesicles. An example is di-*n*-dodecyldimethylammonium chloride (**DDAC**).





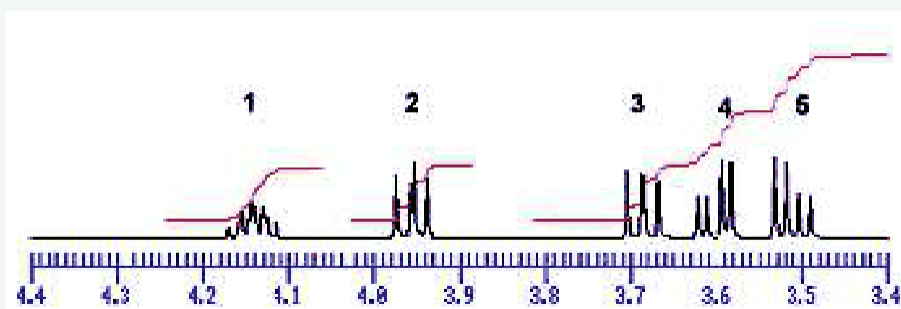
6.1 (a) How many stereoisomers are possible for compound **A**?

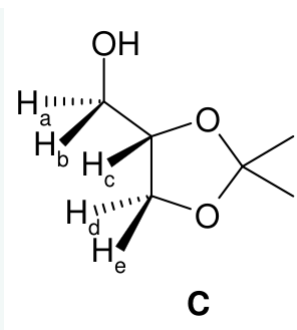
(b) How many stereoisomers are possible for the trialkylphosphate **B**?



A precursor for the synthesis of compound **A** is the acetonide **C** derived from glycerol. Part of the ^1H -NMR spectrum of compound **C** is shown below.

6.2 Which signal number in the ^1H -NMR spectrum corresponds to proton H_c ?





The bilayer of a liposome can be characterized by V (the volume of the hydrocarbon chains), a_0 (optimal cross-sectional surface area of the head groups of the phospholipid in the aggregate) and l_c (the maximum chain length that the alkyl group can assume). A good approximation for unbranched alkyl tails containing n carbon atoms yields:

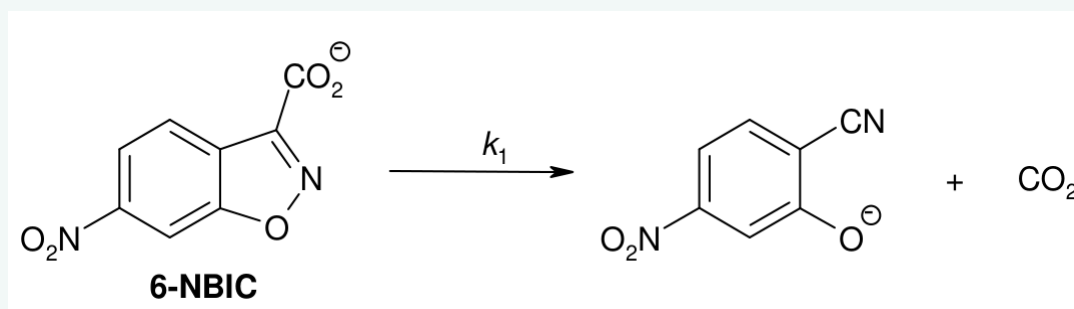
$$V = (27.4 + 26.99n) \times 10^{-3} \text{ nm}^3$$

$$l_c = (0.154 + 0.1265n) \text{ nm}$$

For very large n values, the intertail interactions dominate over the head group repulsions.

6.3 Calculate the minimum cross-sectional surface area of the head groups for such very large n values.

Vesicles formed from **DDAC** (above its critical vesicle concentration, c_{vc}) catalyse the unimolecular decarboxylation of 6-nitro-benzisoxazole-3-carboxylate (**6-NBIC**).



In water at 25 °C $k_1 = 3.1 \times 10^{-6} \text{ s}^{-1}$. At the concentration c_1 of **DDAC** at which **6-NBIC** becomes fully bound to the vesicles, $k_1 = 2.1 \times 10^{-3} \text{ s}^{-1}$.

6.4 Sketch a plot of k_1 vs. **[DDAC]** for **[DDAC]** = 0 $\rightarrow$ $3c_1$.

6.5 The main reason for the efficient catalysis of the decarboxylation of **6-NBIC** by **DDAC** vesicles is:

- ☐ The decarboxylation is catalysed by the Cl^- ions bound to the surface of the vesicles.
- ☐ Efficient loss of hydration of the carboxylate group of vesicle-bound 6-NBIC.
- ☐ Strong binding of CO_2 in the interior of the vesicle.
- ☐ Strong binding of the organic reaction product to the vesicles relative to that of 6-NBIC.

Mark the correct answer.

Official English text of the problem.

Answers

- **6.1(a): 2 stereoisomers**, an enantiomeric pair.
- **6.1(b): 4 stereoisomers**, comprising two enantiomeric pairs.
- **6.2: Signal 1**, at approximately $\delta = 4.14$ ppm.
- **6.3:** $a_{0,\min} = 0.2134 \text{ nm}^2$ per head group.
- **6.4:** Begin at $3.1 \times 10^{-6} \text{ s}^{-1}$; above the cvc, rise toward $2.1 \times 10^{-3} \text{ s}^{-1}$, reaching the plateau by c_1 . Remain at this plateau through $3c_1$.
- **6.5: The second option:** efficient loss of hydration of the carboxylate group of vesicle-bound 6-NBIC.

Solution

6.1(a) — Stereoisomers of A

Compound **A** is distearoylphosphatidylcholine. Its central glycerol carbon is attached to four different groups: hydrogen, an ester oxygen, an esterified terminal methylene group, and a phosphorylated terminal methylene group. It is therefore stereogenic.

The phosphorus atom is **not** an additional stereogenic center. Its two non-esterified oxygen atoms are constitutionally equivalent: the drawing with one double bond and one negatively charged oxygen represents one resonance contributor. The trimethylammonium nitrogen is also not stereogenic, because three of its substituents are identical methyl groups.

There is consequently one stereogenic center:

$$N_{\text{stereoisomers}} = 2^1 = \boxed{2}.$$

The two enantiomers are:

Configuration at the glycerol carbon	Isomeric SMILES
<i>R</i> -distearoylphosphatidylcholine	<chem>C[N+](C)(C)CCOP(=O)([O-])OC[C@H](OC(=O)CCCCCCCCCCCCCCCC)COC(=O)CCCCCCCCCCCCCCCC</chem>
<i>S</i> -distearoylphosphatidylcholine	<chem>C[N+](C)(C)CCOP(=O)([O-])OC[C@@H](OC(=O)CCCCCCCCCCCCCCCC)COC(=O)CCCCCCCCCCCCCCCC</chem>

6.1(b) — Stereoisomers of B

Compound **B** is the phosphate O-methyl ester of distearoylphosphatidylcholine, as its chloride salt.

The glycerol stereogenic center remains. Phosphorus now has four different oxygen-containing ligands: an oxo oxygen, a methoxy group, the choline-derived group, and the glycerol-derived group. Its approximately tetrahedral arrangement therefore introduces a second stereogenic center.

There is no internal symmetry that produces a meso form, so

$$N_{\text{stereoisomers}} = 2^2 = \boxed{4}.$$

Writing configurations in the order (**glycerol carbon, phosphorus**):

Configuration	Isomeric SMILES
(R, R)	<chem>CO[P@](=O)(OCC[N+](C)(C)C)OC[C@H](OC(=O)CCCCCCCCCCCCCCCCC)COC(=O)CCCCCCCCCCCCCCCCC.[Cl-]</chem>
(S, R)	<chem>CO[P@](=O)(OCC[N+](C)(C)C)OC[C@@H](OC(=O)CCCCCCCCCCCCCCCCC)COC(=O)CCCCCCCCCCCCCCCCC.[Cl-]</chem>
(R, S)	<chem>CO[P@@](=O)(OCC[N+](C)(C)C)OC[C@H](OC(=O)CCCCCCCCCCCCCCCCC)COC(=O)CCCCCCCCCCCCCCCCC.[Cl-]</chem>
(S, S)	<chem>CO[P@@](=O)(OCC[N+](C)(C)C)OC[C@@H](OC(=O)CCCCCCCCCCCCCCCCC)COC(=O)CCCCCCCCCCCCCCCCC.[Cl-]</chem>

The enantiomeric pairs are $(R, R)/(S, S)$ and $(R, S)/(S, R)$.

6.2 — Assignment of H_c

Compound **C** is glycerol acetonide, also called **solketal** or **(2,2-dimethyl-1,3-dioxolan-4-yl)methanol**. The depicted enantiomer is S , with SMILES CC1(C)OC[C@H](CO)O1.

The methine proton H_c has four vicinal proton neighbors:

$$H_a, \quad H_b, \quad H_d, \quad H_e.$$

The two protons within each methylene group are diastereotopic and need not have equal coupling constants to H_c . Thus H_c can give a doublet of doublets of doublets of doublets, with overlapping or unresolved lines producing a complex multiplet.

Each of the other labeled protons instead has one geminal partner and one vicinal methine neighbor, giving a simpler principal splitting pattern.

The complex multiplet at approximately 4.14 ppm, labeled **1**, therefore corresponds to H_c :

Signal 1.

6.3 — Minimum head-group area

In the limiting, densely packed arrangement, the hydrocarbon volume associated with one head group occupies a column of cross-sectional area a_0 and chain projection l :

$$V = a_0 l.$$

Because the chain projection cannot exceed l_c ,

$$a_0 \geq \frac{V}{l_c}.$$

The smallest area corresponds to maximum chain extension. Using V as defined in the problem:

$$\begin{aligned}
 a_{0,\min} &= \lim_{n \rightarrow \infty} \frac{(27.4 + 26.99n) \times 10^{-3} \text{ nm}^3}{(0.154 + 0.1265n) \text{ nm}} \\
 &= \frac{26.99 \times 10^{-3}}{0.1265} \text{ nm}^2 \\
 &= 0.213359 \dots \text{ nm}^2.
 \end{aligned}$$

Hence

$$a_{0,\min} = 0.2134 \text{ nm}^2 \text{ per head group}.$$

6.4 — Rate constant versus DDAC concentration

DDAC is **di-*n*-dodecyldimethylammonium chloride**, SMILES CCCCCCCCCCCC[N+](C)(C)CCCCCCCCCCCC.[Cl-].

Let f_b be the fraction of substrate bound to vesicles. Under the usual rapid-exchange description, the observed first-order rate constant is

$$k_1 = (1 - f_b)k_w + f_b k_v,$$

where

$$k_w = 3.1 \times 10^{-6} \text{ s}^{-1}, \quad k_v = 2.1 \times 10^{-3} \text{ s}^{-1}.$$

Draw the horizontal axis as $[\text{DDAC}]$, extending from 0 to $3c_1$, and the vertical axis as k_1 , in s^{-1} . The curve should have these features:

1. **From zero to the cvc:** an approximately horizontal baseline at $3.1 \times 10^{-6} \text{ s}^{-1}$.
2. **Above the cvc:** a monotonic rise as an increasing fraction of 6-NBIC binds to vesicles.
3. **At c_1 :** the curve reaches the full-binding value $2.1 \times 10^{-3} \text{ s}^{-1}$.
4. **From c_1 to $3c_1$:** a horizontal plateau at $2.1 \times 10^{-3} \text{ s}^{-1}$.

Because the reaction is unimolecular, additional vesicles do not increase the intrinsic rate constant once all substrate is bound. The plateau is approximately

$$\frac{k_v}{k_w} = \frac{2.1 \times 10^{-3}}{3.1 \times 10^{-6}} \approx 6.8 \times 10^2$$

times the aqueous value. On a linear vertical scale, the initial baseline therefore lies very close to zero.

6.5 — Origin of the catalytic effect

The relevant reactant and products are:

Species	SMILES
6-Nitro-1,2-benzisoxazole-3-carboxylate, 6-NBIC	<chem>O=C([O-])c1noc2cc([N+](=O)[O-])ccc12</chem>
2-Cyano-5-nitrophenolate	<chem>N#Cc1ccc([N+](=O)[O-])cc1[O-]</chem>
Carbon dioxide	<chem>O=C=O</chem>

Their balanced molecular-formula equation is



The transformation involves decarboxylation and opening of the heterocyclic ring: formation of the nitrile group accompanies cleavage of the nitrogen–oxygen bond, whose electron pair moves onto the oxygen that becomes the phenolate oxygen.

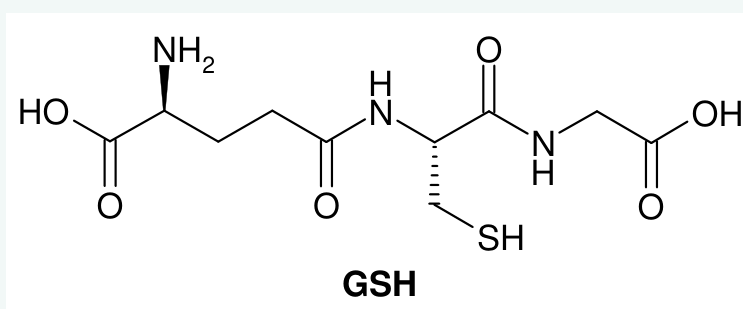
In water, SMILES O, hydrogen bonding strongly stabilizes the localized carboxylate charge of the reactant. Binding at the vesicle interface reduces this hydration. The reactant consequently loses more solvation stabilization than the transition state, in which charge is being redistributed during decarboxylation and ring opening. This lowers the activation free energy and accelerates the reaction.

Therefore, mark:

The solution was checked against the official solution.

Problem 7: Glutathione, an Essential Mini-Peptide

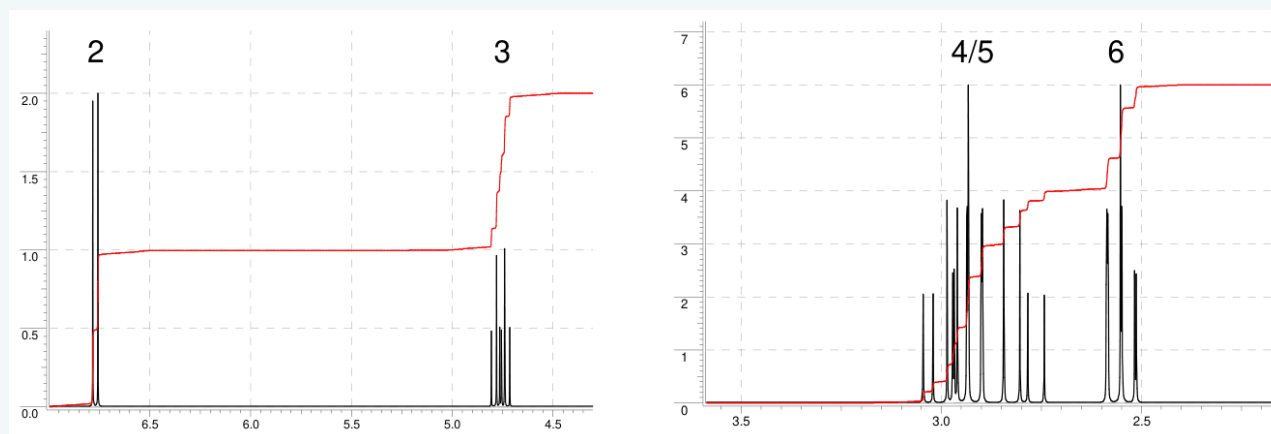
Glutathione, abbreviated as GSH, is a small peptide that is present in almost all tissues of animals. GSH fulfils important biological functions, such as detoxification of electrophilic chemicals and reduction of (organic) peroxides in blood. An electrophilic compound reacts irreversibly with GSH, especially in the liver, to give a primary product that is converted by a series of biotransformations into a so-called *mercapturic acid*, which is excreted via the urine. Oxidants react with GSH to give the disulfide GSSG, which can be enzymatically reverted to GSH with reductases. The ratio GSH/GSSG in most cells is ≥ 500 .



7.1 (a) How many amino acid residues are present in GSH?

(b) Draw the structures of the corresponding amino acids and mark the chiral centers with an asterisk.

A mercapturic acid **A** isolated from urine of a person who has been exposed to acrylonitrile ($\text{H}_2\text{C}=\text{CH}-\text{CN}$) has the molecular formula $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_3\text{S}$. The ^1H -NMR spectrum of **A** in $(\text{CD}_3)_2\text{SO}$ is shown in Figure 1. When the product is pretreated with D_2O , the signals at δ 12.8 and δ 6.8 are no longer present and the signal 3 is simplified.



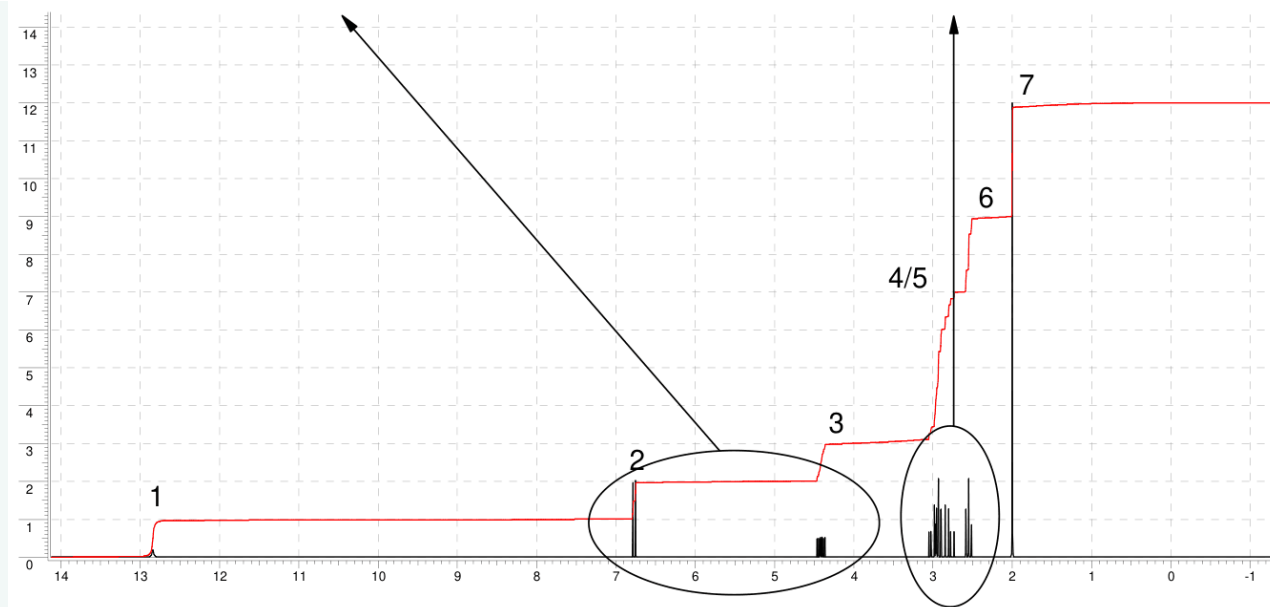


Figure 1

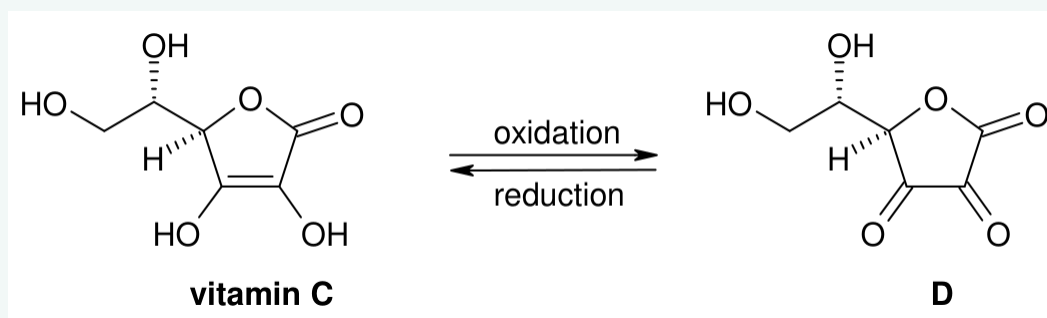
7.2 (a) The NMR-signals correspond with protons in the following groups: CH, CH₂, CH₃, OH and NH. Indicate the appropriate proton group in the boxes for the signals 1 – 7.

Signals	1	2	3	4/5	6	7
Protons						

(b) How many carbon atoms are present in compound **A** that do not carry any protons?

(c) Draw the structure of compound **A**.

Vitamin C (ascorbic acid) reacts with oxidants to give dehydroascorbic acid **D**



7.3 Eating fresh fruit and vegetables is healthy

- ☐ because vitamin C forms a complex with GSH.
- ☐ because vitamin C reacts with electrophilic compounds.
- ☐ because vitamin C removes oxidants and prevents undesired depletion of GSH.
- ☐ for many reasons, but none of them has anything to do with GSH.

Official English text of the problem.

Answers

- **7.1(a): Three amino acid residues.**
- **7.1(b):**
- **L-Glutamic acid:** N[C@@H](CCC(=O)O)C(=O)O. Mark its α -carbon with an asterisk; it has *S* configuration.
- **L-Cysteine:** N[C@@H](CS)C(=O)O. Mark its α -carbon with an asterisk; it has *R* configuration.
- **Glycine:** NCC(=O)O. It has **no chiral center**.
- **7.2(a):** 1 : OH; 2 : NH; 3 : CH; 4/5 : two CH₂ groups; 6 : CH₂; 7 : CH₃.
- **7.2(b): Three:** the carboxyl carbon, the amide carbonyl carbon, and the nitrile carbon.
- **7.2(c): N-Acetyl-S-(2-cyanoethyl)-L-cysteine,** CC(=O)N[C@@H](CSCC#N)C(=O)O. Its α -carbon has *R* configuration.
- **7.3:** Select the **third statement**: "because vitamin C removes oxidants and prevents undesired depletion of GSH."

Solution

7.1(a)

GSH is **γ -L-glutamyl-L-cysteinylglycine**, with SMILES N[C@@H](CCC(=O)N[C@@H](CS)C(=O)NCC(=O)O)C(=O)O.

The two amide linkages connect one glutamic acid residue, one cysteine residue, and one glycine residue. Thus, GSH contains **three amino acid residues**. The glutamyl linkage uses glutamic acid's side-chain carboxyl group.

7.1(b)

The free amino acids have the following structures. An asterisk above a CH group marks its carbon atom.

Amino acid	Structure with chiral center marked	Configuration
L-Glutamic acid	$\text{HOOC} - \overset{*}{\text{CH}}(\text{NH}_2) - \text{CH}_2 - \text{CH}_2 - \text{COOH}$	<i>S</i>
L-Cysteine	$\text{HOOC} - \overset{*}{\text{CH}}(\text{NH}_2) - \text{CH}_2 - \text{SH}$	<i>R</i>
Glycine	$\text{H}_2\text{N} - \text{CH}_2 - \text{COOH}$	Achiral

The α -carbon of glutamic acid and that of cysteine each bear four different substituents. Glycine's α -carbon bears two identical hydrogen atoms and therefore is not chiral.

L-Cysteine has *R* configuration because its sulfur-containing side chain has higher CIP priority than its carboxyl group; this does not change its designation as an L-amino acid.

7.2(a)

The integral increases give the proton counts:

Signal	Approximate δ / ppm	Number of protons	Assignment
1	12.8	1	Carboxylic-acid OH
2	6.8	1	Amide NH
3	4.8	1	CH
4/5	2.7–3.1	4 combined	Two CH ₂ groups
6	2.55	2	CH ₂
7	2.0	3	CH ₃

Signals 1 and 2 disappear after treatment with D₂O, identifying exchangeable hydrogens. The very downfield signal at δ 12.8 is characteristic of a carboxylic-acid proton. Signal 2 is consequently the NH proton.

Signal 3 integrates to one proton and is assigned to the amino-acid α -CH. Its simplification after deuterium exchange shows that part of its original splitting arose from coupling to the neighboring NH proton.

The remaining integrals identify three methylene groups and one methyl group. The total is

$$1 + 1 + 1 + 4 + 2 + 3 = 12$$

hydrogens, agreeing with C₈H₁₂N₂O₃S.

7.2(b)

The carbon-bound hydrogens belong to one CH, three CH₂, and one CH₃ group. These account for

$$1 + 3 + 1 = 5$$

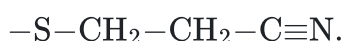
carbon atoms. Since **A** contains eight carbon atoms, the number without attached hydrogens is

$$\boxed{8 - 5 = 3}.$$

In the identified structure, these are the two carbonyl carbons and the nitrile carbon.

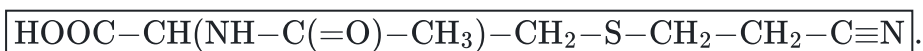
7.2(c)

Acrylonitrile, C=CC#N, is an activated alkene. Conjugate addition of the cysteine sulfur of GSH to its terminal alkene carbon produces the fragment



The cysteine portion supplies the carboxylic-acid group, the α -CH, and another methylene group attached to sulfur. Removal of the glutamyl and glycyl portions and acetylation of the remaining amino group produce the mercapturic acid.

The methyl signal near δ 2.0, together with the amide NH, supports an N-acetyl group, $-\text{NH}-\text{C}(=\text{O})-\text{CH}_3$. Combining these fragments gives



Thus, **A** is **N-acetyl-S-(2-cyanoethyl)-L-cysteine**, CC(=O)N[C@@H](CSCCC#N)C(=O)O. Draw the α -carbon in the *R* configuration retained from the cysteine residue of GSH.

The structure accounts for every signal:

- The carboxylic-acid and amide hydrogens give signals 1 and 2.
- The α -CH gives signal 3.

- The two sulfur-adjacent methylene groups give the overlapping signals 4/5.
- The methylene adjacent to the nitrile gives signal 6.
- The acetyl methyl group gives signal 7.

Its hydrogen count is $1_{\text{OH}} + 1_{\text{NH}} + 1_{\text{CH}} + 6_{\text{CH}_2} + 3_{\text{CH}_3} = 12$. Its three oxygen atoms belong to the carboxylic acid and amide, and its two nitrogen atoms belong to the amide and nitrile.

As a further check, the degree of unsaturation is

$$\text{DBE} = \frac{2(8) + 2 + 2 - 12}{2} = 4.$$

The two carbonyl groups contribute two units, and the nitrile triple bond contributes two more.

7.3

Select the **third statement**.

Vitamin C, **L-ascorbic acid**, OC[C@H](O)[C@H]1OC(=O)C(O)=C1O, reduces oxidants while being oxidized to **dehydroascorbic acid D**, OC[C@H](O)[C@H]1OC(=O)C(=O)C1=O, as depicted in the problem. The corresponding balanced oxidation half-reaction is



By donating electrons to oxidants, vitamin C reduces the amount of GSH that must be consumed in removing them, helping preserve reduced glutathione.

The solution was checked against the official solution.

Problem 8: Lighting Lamps

Theme IV - Chemistry Related to Light and Energy

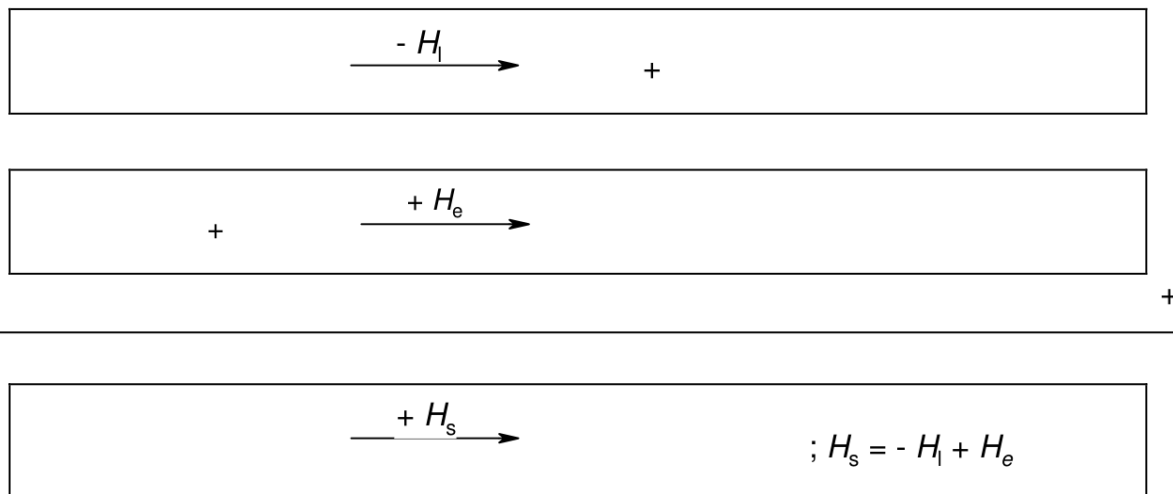
Chemistry plays a major role in meeting our needs of light and energy. Our life is unthinkable without artificial light and energy for mobility.

PROBLEM 8

LIGHTING LAMPS

Since 1891 lighting lamps have been manufactured in The Netherlands. The improvement today in comparison to the first lamp is enormous, especially with the introduction of the gas discharge lamps. The life-time has increased by orders of magnitude. The colour is also an important aspect. Rare earth metal compounds like CeBr_3 are now included to reach a colour temperature of 6000 K in the lamp. These compounds are ionic solids at room temperature, and upon heating they sublime partially to give a vapour of neutral metal halide molecules. To achieve a high vapour pressure, the sublimation enthalpy should be as low as possible.

8.1 Give a thermochemical cycle (Law of Hess) for sublimation of CeBr_3 , via a vapour of mononuclear ions. ($H_1 = H_{\text{lattice}}$; $H_e = H_{\text{electrostatic}}$; $H_s = H_{\text{sublimation}}$; H is not absolute, H means ΔH)



The lattice energy of the solid can be calculated using the Born–Landé formula:

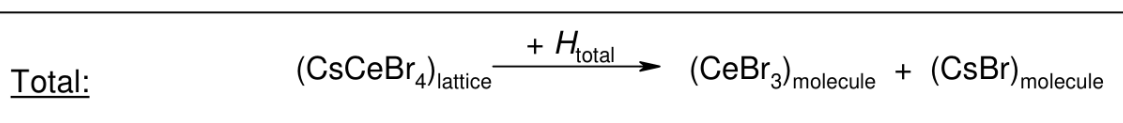
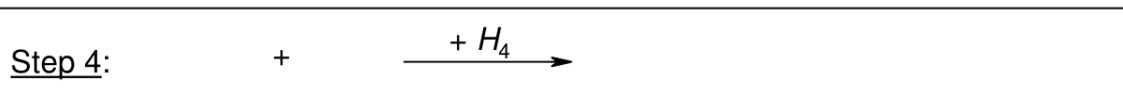
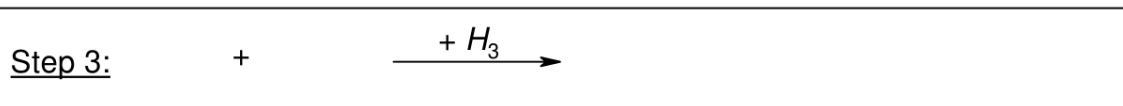
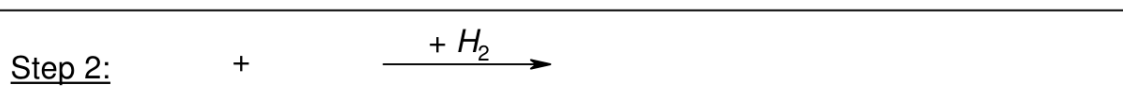
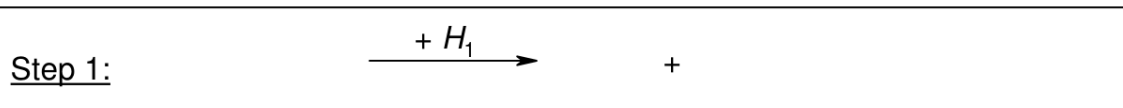
$$H_l = f \frac{Z_+ Z_- A e^2}{r_+ + r_-} \left(1 - \frac{1}{n} \right)$$

The factor $f e^2$ (necessary in order to calculate the lattice energy in kJ mol^{-1}) amounts to 139 when the ionic radii are substituted in nm. The Madelung constant A for the lattice is 2.985. The Born exponent n is 11. The charges of the ions Z_+ and Z_- are integer numbers (Z_- is negative). For the calculation of the energy of gaseous CeBr_3 (when formed from ions) the same Born–Landé formula can be used without A . The structure of CeBr_3 in the gas phase is planar triangular. The radius of Ce^{3+} is 0.115 nm and of Br^- is 0.182 nm.

8.2 Calculate the enthalpy of sublimation of CeBr_3 (in integers; be aware of the signs!)

Attempts to make a better lamp have been undertaken by adding a stoichiometric amount of CsBr to the CeBr_3 in the lamp leading at room temperature to solid CsCeBr_4 . When the sublimation temperature decreases the life time of the lamp will increase likewise. The CsCeBr_4 lattice has a NaCl structure with Cs^+ as cations and tetrahedral CeBr_4^- as complex anions. Sublimation of CsCeBr_4 leads to a vapour of CsBr and CeBr_3 molecules.

8.3 Give the reaction equations of the thermochemical cycle (Law of Hess) for this process in which some steps involve CeBr_4^- ions, mononuclear ions and/or neutral molecules in the gas phase.



8.4 Calculate the enthalpy of sublimation of CsCeBr_4 (in integers).

Use the Born–Landé formula for all steps in the process and report the separate energies also (be aware of the signs!). The Madelung constant for NaCl is 1.75. The Cs–Ce distance in the lattice is 0.617 nm. The CeBr_4^- anion is a tetrahedron in which the ratio between the edge and the distance between a corner of the tetrahedron and the centre of gravity (body-radius) amounts to $(2\sqrt{6})/3 = 1.633$. The Born exponent of CsBr is 11. The radius of Cs^+ is 0.181 nm.

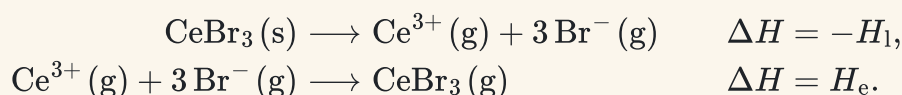
8.5 Conclusion in relation to the previous answers: Was adding CsBr a good idea? Mark the correct answer.

- ☐ Adding CsBr is counterproductive.
- ☐ Adding CsBr has no influence.
- ☐ Adding CsBr is advantageous.
- ☐ From these data no clear answer can be given.

Official English text of the problem.

Answers

• 8.1



Thus $\text{CeBr}_3(\text{s}) \longrightarrow \text{CeBr}_3(\text{g})$, with

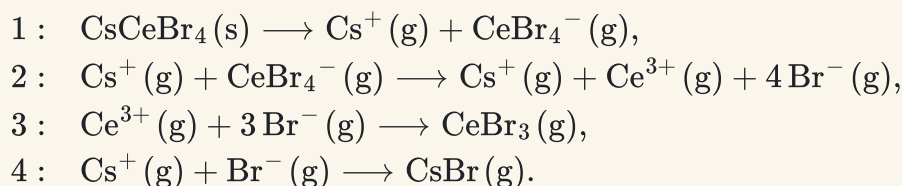
$$\boxed{H_s = -H_1 + H_e}.$$

• 8.2

$$H_1 = -3810, \quad H_e = -3092, \quad \boxed{H_s = +718 \text{ kJ mol}^{-1}}.$$

All listed energies are in kJ mol^{-1} .

• 8.3 A consistent ordering of the four steps is



Their sum is



• 8.4 For the ordering above:

$$\boxed{H_1 = +358, \quad H_2 = +3542, \quad H_3 = -3092, \quad H_4 = -348 \quad (\text{kJ mol}^{-1})}$$

$$\boxed{H_{\text{total}} = +460 \text{ kJ mol}^{-1}}.$$

• 8.5 Mark "Adding CsBr is advantageous."

Solution

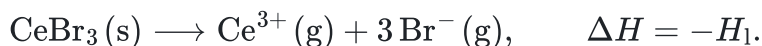
8.1 — Thermochemical cycle for cerium(III) bromide

The species are cerium(III) ions, Ce^{3+} , SMILES [Ce+3]; bromide ions, Br^- , SMILES [Br-]; and neutral gaseous cerium(III) bromide, CeBr_3 , connected SMILES [Ce](Br)(Br)Br. The gas molecule is trigonal planar, with Ce at the centre and three Br atoms at the vertices of an equilateral triangle. SMILES does not specify this geometry.

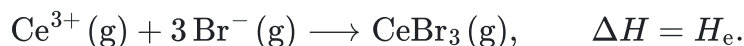
Solid cerium(III) bromide is an extended ionic lattice; its formula-unit composition can be represented by [Ce+3].[Br-].[Br-].[Br-].

The given Born–Landé expression uses signed ionic charges. Consequently, $H_1 < 0$ describes formation of the lattice from separated gaseous ions. Breaking the lattice therefore requires $-H_1 > 0$.

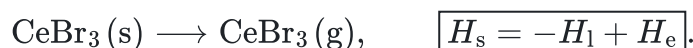
Fill the first reaction box with



Fill the second box with association of the gaseous ions into a neutral molecule:



Adding these equations cancels all gaseous ions. The bottom box is therefore



8.2 — Sublimation enthalpy of cerium(III) bromide

Define the common factor

$$C = fe^2 \left(1 - \frac{1}{n}\right) = 139 \left(1 - \frac{1}{11}\right) = 126.3636 \text{ kJ nm mol}^{-1}.$$

The Ce–Br separation is

$$r = 0.115 + 0.182 = 0.297 \text{ nm.}$$

Using the given lattice expression once per mole of CeBr_3 ,

$$H_1 = C \frac{(3)(-1)(2.985)}{0.297} = -3810.06 \text{ kJ mol}^{-1}.$$

For the gaseous molecule, sum the energies of every distinct ion pair, using the prescribed expression without a Madelung constant.

There are three attractive Ce–Br pairs. There are also three repulsive Br–Br pairs, whose separation follows from the 120° Br–Ce–Br angle:

$$d_{\text{Br–Br}} = \sqrt{r^2 + r^2 - 2r^2 \cos 120^\circ} = \sqrt{3} r = 0.514419 \text{ nm.}$$

Thus

$$\begin{aligned} H_e &= C \left[3 \frac{(3)(-1)}{r} + 3 \frac{(-1)(-1)}{\sqrt{3} r} \right] \\ &= \frac{126.3636}{0.297} \left(-9 + \frac{3}{\sqrt{3}} \right) \\ &= -3092.27 \text{ kJ mol}^{-1}. \end{aligned}$$

The attractive contribution is $-3829.20 \text{ kJ mol}^{-1}$, while bromide–bromide repulsion contributes $+736.93 \text{ kJ mol}^{-1}$.

Hess's law gives

$$\begin{aligned} H_s &= -(-3810.06) + (-3092.27) \\ &= 717.78 \text{ kJ mol}^{-1}. \end{aligned}$$

Therefore, to the requested integer,

$$\boxed{H_s(\text{CeBr}_3) = +718 \text{ kJ mol}^{-1}}.$$

8.3 — Thermochemical cycle for caesium tetrabromidocerate(III)

The additional species are:

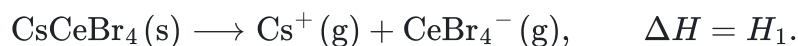
Species	Name	SMILES	Geometry
Cs^+	Caesium ion	[Cs+]	Monatomic
CeBr_4^-	Tetrabromidocerate(III) ion	[Ce-](Br)(Br)(Br)Br	Ce at the centre of a regular tetrahedron of Br atoms
CsBr(g)	Caesium bromide molecule	[Cs]Br	Diatomic

The connected SMILES encode connectivity and overall charge. In particular, the formal charge on [Ce-] does not denote the oxidation state: Ce is +3 in CeBr_4^- . The tetrahedral geometry must be stated separately.

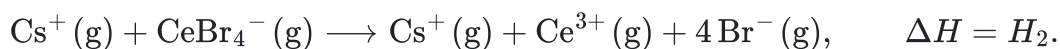
Solid caesium tetrabromidocerate(III), CsCeBr_4 , has the formula-unit representation [Cs+] · [Ce-](Br)(Br)(Br)Br. Its extended rock-salt lattice consists of caesium cations and tetrahedral complex anions.

Fill the four reaction boxes as follows.

1. Separate the lattice into gaseous constituent ions:



2. Dissociate the complex anion into mononuclear ions:



The caesium ion is a spectator and contributes zero net enthalpy to this step.

3. Form one gaseous cerium(III) bromide molecule:



4. Form one gaseous caesium bromide molecule:



All intermediate ions cancel on addition:



$$\boxed{H_{\text{total}} = H_1 + H_2 + H_3 + H_4}.$$

8.4 — Sublimation enthalpy of caesium tetrabromidocerate(III)

Use $C = 126.3636 \text{ kJ nm mol}^{-1}$ throughout.

For **step 1**, the lattice contains ions of charges $+1$ and -1 . Their separation is the given Cs–Ce distance, 0.617 nm . Reversing lattice formation gives

$$H_1 = -C \frac{(+1)(-1)(1.75)}{0.617} = +358.41 \text{ kJ mol}^{-1},$$

so

$$\boxed{H_1 = +358 \text{ kJ mol}^{-1}}.$$

For **step 2**, calculate the energy of forming the tetrahedral complex anion from its mononuclear ions, then reverse the sign.

The four Ce–Br distances are $r = 0.297 \text{ nm}$. Each of the six Br–Br pairs lies along an edge of the tetrahedron, so

$$d_{\text{Br-Br}} = 1.633r = 1.633(0.297) = 0.485001 \text{ nm}.$$

The complex-ion formation energy is

$$\begin{aligned} E_4 &= C \left[4 \frac{(3)(-1)}{r} + 6 \frac{(-1)(-1)}{1.633r} \right] \\ &= \frac{126.3636}{0.297} \left(-12 + \frac{6}{1.633} \right) \\ &= -3542.34 \text{ kJ mol}^{-1}. \end{aligned}$$

Dissociation is the reverse process:

$$H_2 = -E_4 = +3542.34 \text{ kJ mol}^{-1},$$

$$\boxed{H_2 = +3542 \text{ kJ mol}^{-1}}.$$

For **step 3**, the formation of gaseous CeBr_3 was calculated in 8.2:

$$H_3 = -3092.27 \text{ kJ mol}^{-1}, \quad \boxed{H_3 = -3092 \text{ kJ mol}^{-1}}.$$

For **step 4**, the caesium–bromide separation is

$$r_{\text{Cs-Br}} = 0.181 + 0.182 = 0.363 \text{ nm}.$$

There is one attractive ion pair and no Madelung factor:

$$H_4 = C \frac{(+1)(-1)}{0.363} = -348.11 \text{ kJ mol}^{-1},$$
$$\boxed{H_4 = -348 \text{ kJ mol}^{-1}}.$$

Adding the unrounded values,

$$\begin{aligned} H_{\text{total}} &= 358.41 + 3542.34 - 3092.27 - 348.11 \\ &= 460.37 \text{ kJ mol}^{-1}. \end{aligned}$$

Therefore,

$$\boxed{H_s(\text{CsCeBr}_4) = +460 \text{ kJ mol}^{-1}}.$$

This value is per mole of solid CsCeBr_4 , producing one mole each of gaseous CeBr_3 and CsBr .

8.5 — Effect of adding caesium bromide

Both sublimation processes produce one mole of gaseous CeBr_3 per mole of starting cerium-containing solid, but

$$460 \text{ kJ mol}^{-1} < 718 \text{ kJ mol}^{-1}.$$

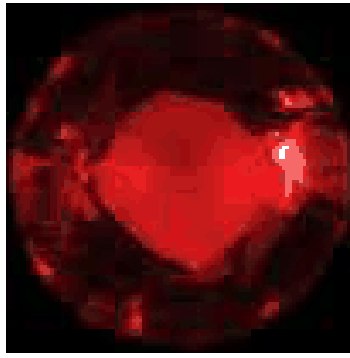
According to the enthalpy criterion specified in the problem, adding CsBr therefore makes vaporization more favourable and permits operation at a lower temperature, increasing lamp life.

Mark the **third option**: “Adding CsBr is advantageous.”

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 9: Red Ruby

Ruby crystals have a deep red colour and are well known for their use in jewellery. Not many people know that the heart of the first laser, built in 1960 by Maiman, was a big ruby crystal. The red colour of ruby originates from the absorption of light by Cr^{3+} ions that are incorporated in colourless aluminium oxide (Al_2O_3) crystals. The Cr^{3+} ion has 3 electrons in the $3d$ shell and the absorption of light is due to electronic transitions between $3d$ orbitals of lower and higher energy.



9.1 Indicate which of the four absorption spectra belongs to ruby.

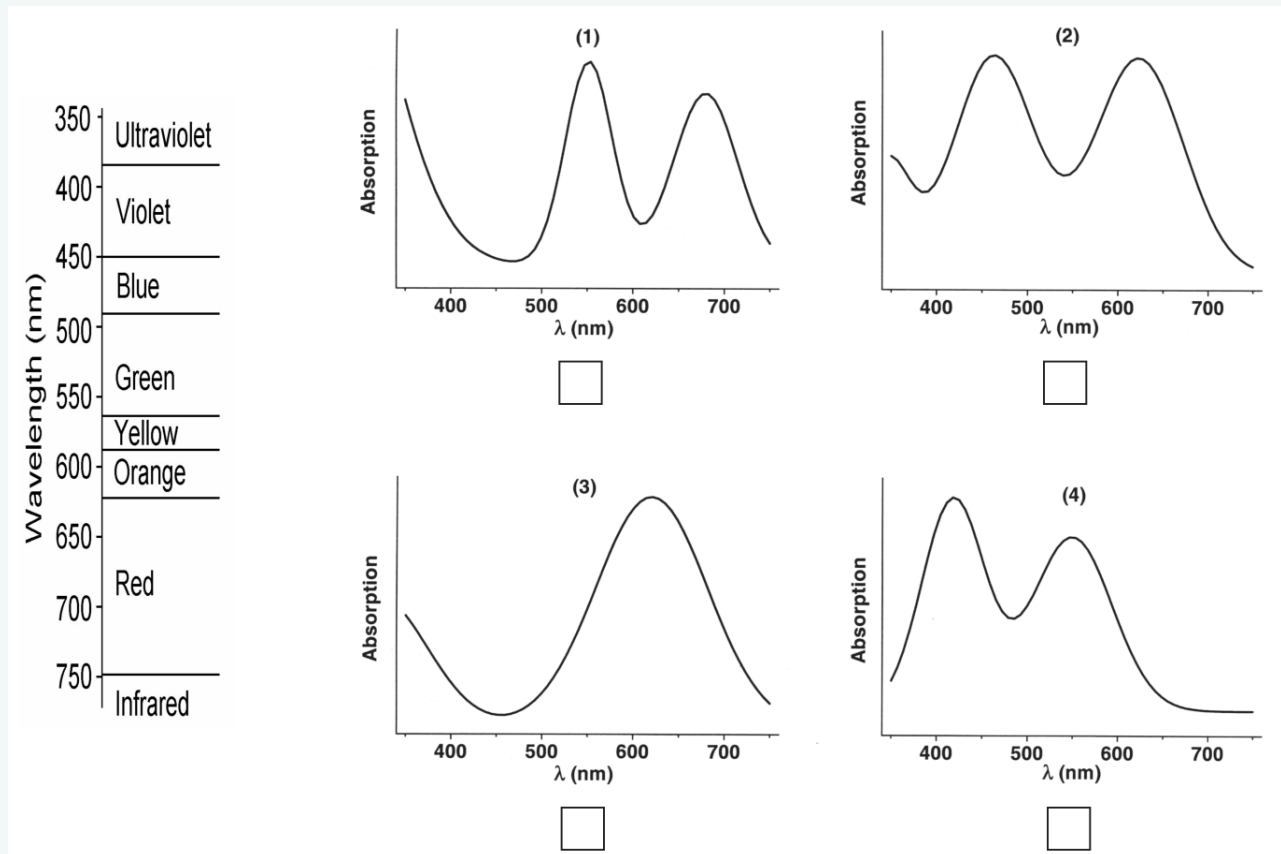


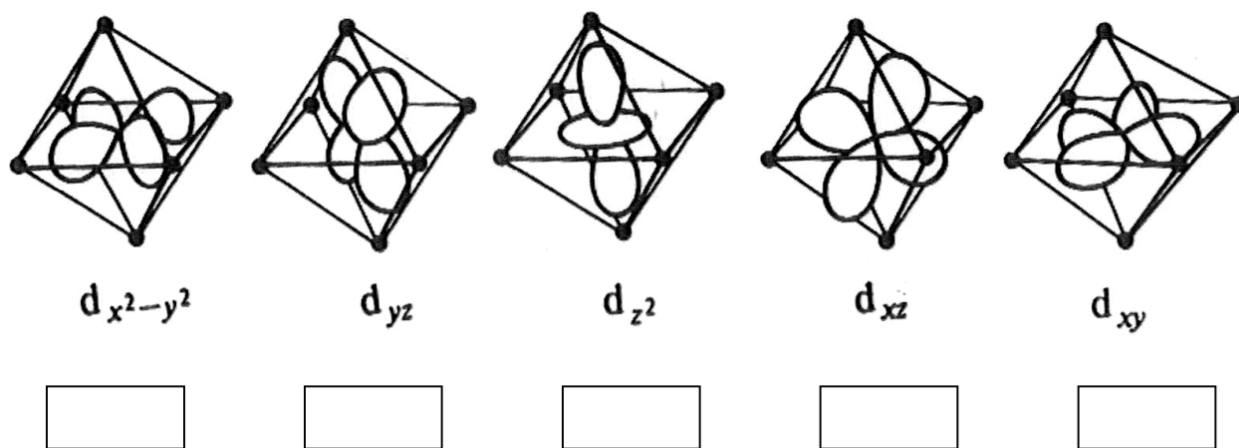
Figure 1

The rod used in ruby lasers is a cylinder with a length of 15.2 cm and a diameter of 1.15 cm. The amount of Cr^{3+} ions is 0.050 mass %. The density of Al_2O_3 is 4.05 g cm^{-3} . The atomic mass of $\text{Cr} = 52 \text{ u}$. ($1 \text{ u} = 1.67 \times 10^{-27} \text{ kg}$).

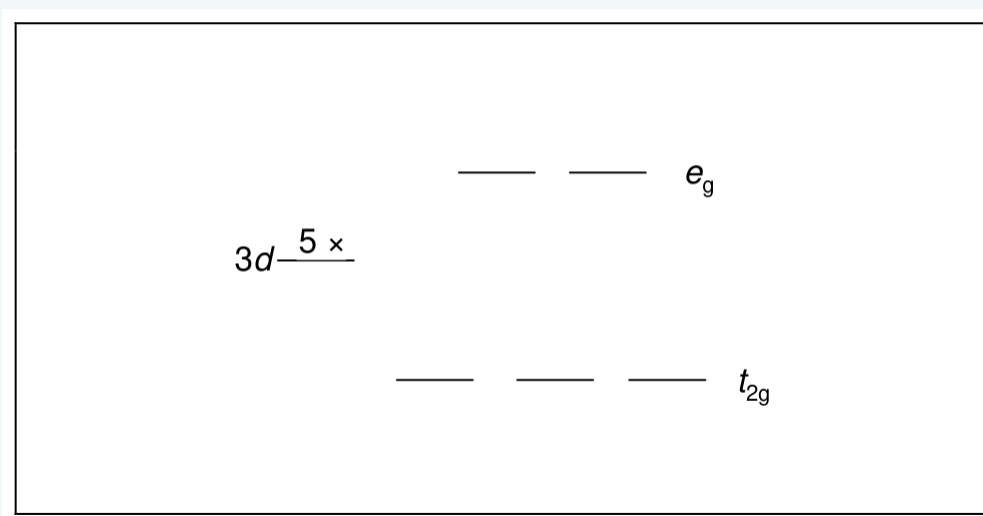
9.2 Calculate how many Cr^{3+} ions are in this laser rod.

In rubies the Cr^{3+} ions are coordinated by an octahedron of 6 oxygen ions. The shape of the five $3d$ orbitals is shown below. The box below shows the splitting of the five $3d$ orbitals into a group of three orbitals at lower energy (t_{2g}) and a group of two at higher energy (e_g).

9.3 Indicate in the boxes below which of the $3d$ orbitals (d_{z^2} , d_{xy} , d_{yz} , $d_{x^2-y^2}$, d_{xz}) belong to the t_{2g} group and which belong to the e_g group.



9.4 Indicate with arrows the distribution and the direction of the magnetic spin moment of the three $3d$ electrons of Cr^{3+} over the five d orbitals in the lowest energy state of Cr^{3+} .



The ruby is placed on a (non-magnetic) scale. When the scale is in balance (Figure 2) a magnet is placed directly under the side with the ruby.

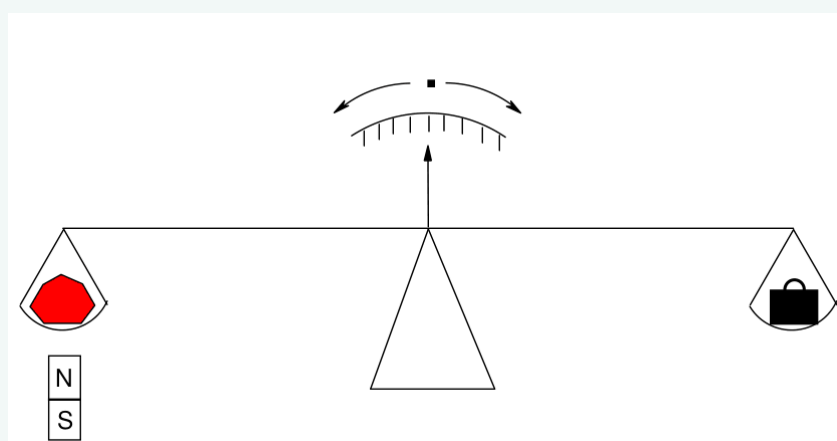


Figure 2

9.5 Indicate what will happen with the ruby (mark the correct answer)

- ☐ The magnet attracts the ruby (the ruby moves down)
- ☐ The magnet has no influence on the ruby (the ruby does not move)

- ☐ The magnet repels the ruby (the ruby moves up)
- ☐ The magnet has an oscillating effect on the ruby (the ruby moves up and down)

Official English text of the problem.

Answers

- **9.1:** Spectrum **(4)**.
- **9.2:** 3.7×10^{20} chromium(III) ions, Cr^{3+} , SMILES $[\text{Cr}+3]$.
- **9.3:** $t_{2g} : d_{xy}, d_{yz}, d_{xz}; e_g : d_{z^2}, d_{x^2-y^2}$. Fill the boxes from left to right with $e_g, t_{2g}, e_g, t_{2g}, t_{2g}$.
- **9.4:** $t_{2g}^3 e_g^0$: one electron in each t_{2g} orbital, all three with parallel spins; both e_g orbitals empty.
- **9.5:** The magnet attracts the ruby (the ruby moves down).

Solution

9.1

Ruby appears red because it absorbs other visible wavelengths more strongly than red wavelengths.

Spectrum **(4)** has strong absorption in the violet–blue and green regions, with very little absorption in the red region, especially at approximately 650–750 nm. Thus red light is preferentially transmitted, giving the crystal its red colour. Mark the box beneath spectrum **(4)**.

9.2

The cylindrical rod has volume

$$V = \pi \left(\frac{d}{2} \right)^2 L = \pi \left(\frac{1.15 \text{ cm}}{2} \right)^2 (15.2 \text{ cm}) = 15.79 \text{ cm}^3.$$

Using the supplied density, its mass is

$$m_{\text{rod}} = \rho V = (4.05 \text{ g cm}^{-3})(15.79 \text{ cm}^3) = 63.94 \text{ g}.$$

The chromium mass fraction is

$$w = \frac{0.050}{100} = 5.0 \times 10^{-4}.$$

Therefore, retaining guard digits,

$$m_{\text{Cr}} = w m_{\text{rod}} = (5.0 \times 10^{-4})(63.94 \text{ g}) = 0.03197 \text{ g} = 3.197 \times 10^{-5} \text{ kg}.$$

Using the given atomic mass for each chromium(III) ion,

$$m_{\text{ion}} = (52)(1.67 \times 10^{-27} \text{ kg}) = 8.684 \times 10^{-26} \text{ kg}.$$

Hence

$$N = \frac{m_{\text{Cr}}}{m_{\text{ion}}} = \frac{3.197 \times 10^{-5} \text{ kg}}{8.684 \times 10^{-26} \text{ kg}} = 3.682 \times 10^{20}.$$

The chromium mass percentage is given to two significant figures, so

$$N = 3.7 \times 10^{20} \text{ chromium(III) ions.}$$

9.3

Each chromium(III) ion, Cr^{3+} ([Cr+3]), is surrounded by six oxide ions, O^{2-} ([O-2]), in an octahedral arrangement. These individual-ion SMILES do not encode the coordination geometry of the crystal.

Taking the metal–oxygen directions as the Cartesian axes:

- The d_{z^2} and $d_{x^2-y^2}$ orbitals point directly toward the surrounding ions. Their electrons experience greater electrostatic repulsion, so these orbitals form the higher-energy e_g group.
- The d_{xy} , d_{yz} , and d_{xz} orbitals point between those directions. They experience less repulsion and form the lower-energy t_{2g} group.

Thus,

$$t_{2g} = \{d_{xy}, d_{yz}, d_{xz}\}, \quad e_g = \{d_{z^2}, d_{x^2-y^2}\}.$$

The drawings are ordered $d_{x^2-y^2}$, d_{yz} , d_{z^2} , d_{xz} , d_{xy} , so write in the boxes, from left to right:

$$e_g, \quad t_{2g}, \quad e_g, \quad t_{2g}, \quad t_{2g}.$$

9.4

The three $3d$ electrons occupy the three lower-energy t_{2g} orbitals. Hund's rule requires singly occupied degenerate orbitals with parallel spins before pairing occurs.

The ground-state occupation is therefore

$$t_{2g}^3 e_g^0.$$

On the answer-sheet diagram, put **one upward arrow on each of the three lower t_{2g} lines**, and leave **both upper e_g lines empty**. Three downward arrows would describe the equivalent opposite orientation.

There are three unpaired electrons, with total spin

$$S = 3 \left(\frac{1}{2} \right) = \frac{3}{2}.$$

9.5

The three unpaired electrons give the chromium(III) centres a paramagnetic response. In the treatment intended by the problem, the ruby is consequently attracted toward the stronger magnetic field near the magnet.

Since the magnet is underneath the ruby, the magnetic force is downward. Select the first option:

The magnet attracts the ruby (the ruby moves down).

The solution was checked against the official solution.

Problem 10: Vehicle Traction Batteries

Battery-powered electric vehicles (EV's) are likely to become increasingly common in the next 50 years because of growing concern over pollution caused by vehicles using combustion engines. The reason for the current meagre commercial success of EV's is that the battery specifications must have a performance and cost profile comparable to conventionally powered vehicles.

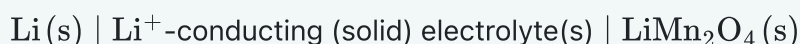
Lead-acid batteries are extensively used as portable power sources for vehicles and traction. A lead-acid battery capable of efficient recharging has an energy density of 45 Wh/kg.

In the current evolution of EV batteries, the most promising long-term solution is the rechargeable light weight lithium-ion battery. Such batteries are under intensive investigation worldwide and hold also promise for the storage of electricity from solar cells. Their weight is 1/3 of a lead-acid battery. Lithium is used as a negative electrode. It has a high specific capacity and electrode potential. A common positive electrode material is the environmentally benign spinel-type LiMn_2O_4 . The spinel structure comprises a matrix of cubic close-packed oxide ions, stabilised by lithium ions in tetrahedral sites and manganese ions in octahedral sites. In LiMn_2O_4 half of the manganese ions has an oxidation state +3 and half the oxidation state +4.

A lead-acid battery is represented by:



A lithium battery is represented by:



Upon discharge the insertion product $\text{Li}_2\text{Mn}_2\text{O}_4$ is formed. Charging the battery leads to the products Li(s) and LiMn_2O_4 .

10.1 Give the electrochemical reactions at the electrodes of the lead-acid battery during discharge.

10.2 Give the electrochemical reactions at the electrodes of the lithium-ion battery upon discharge.

10.3 Give the coordination numbers of the lithium ions and of the manganese ions in the spinel structure of LiMn_2O_4 .

A typical family car of 1000 kg requires at least 5 kWh of energy to move 50 km, which corresponds with the consumption of about 5.0 litres or 3.78 kg of petrol. This conventional car has a petrol tank volume of 50 L. The weight of the tank is 10 kg. The fuel consumption is 10 km L^{-1} .

10.4 Calculate the extra weight of the car if the petrol tank is replaced by an equivalent battery in an EV based on **(a)** lead-acid battery and **(b)** lithium battery. Assume that in all cases the engine efficiency is the same. Calculate:

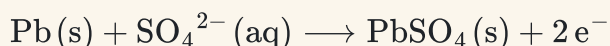
(a) Extra weight of a lead-acid battery car.

(b) Extra weight of a lithium battery car.

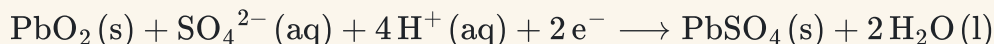
Official English text of the problem.

Answers

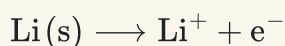
- **10.1** Negative electrode (anode):



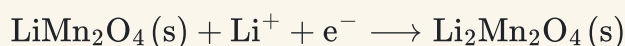
Positive electrode (cathode):



- **10.2** Negative electrode (anode):



Positive electrode (cathode):



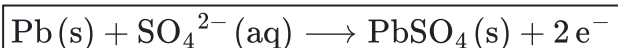
- **10.3** Lithium ions: **4**, tetrahedral coordination. Manganese ions: **6**, octahedral coordination.
- **10.4(a)** Nominal minimum extra mass: approximately 1.1×10^3 kg; the calculation gives 1063.3 ... kg.
- **10.4(b)** Nominal minimum extra mass: approximately 3.2×10^2 kg; the calculation gives 322.6 ... kg.

Solution

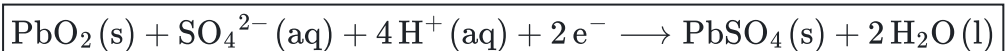
10.1 — Lead-acid battery

During discharge, oxidation occurs at the negative electrode and reduction occurs at the positive electrode.

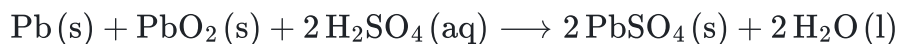
At the negative electrode, lead metal is oxidized from oxidation state 0 to +2. It combines with sulfate to form solid lead(II) sulfate:



At the positive electrode, lead in lead(IV) oxide is reduced from +4 to +2, also forming lead(II) sulfate. Oxygen is balanced with water and hydrogen with hydrogen ions:



Each half-reaction transfers two electrons. Adding them gives the overall discharge reaction, written using sulfuric acid:



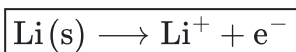
The molecular and ionic species used here have the following names and SMILES:

Species	Name	SMILES
SO_4^{2-}	Sulfate ion	[O-]S(=O)(=O)[O-]
H^+	Hydrogen ion (proton)	[H+]
H_2O	Water	O
H_2SO_4	Sulfuric acid	OS(=O)(=O)O

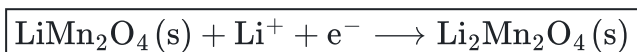
The aqueous hydrogen-ion notation represents a solvated proton. The metallic and crystalline electrode materials have extended structures, whose lattices are not specified by molecular SMILES.

10.2 — Lithium battery

At the negative electrode, lithium metal is oxidized to a lithium ion, releasing one electron:



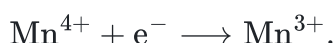
The lithium ion passes through the solid electrolyte. At the positive electrode, lithium-ion insertion and electron uptake convert lithium manganese oxide into the stated insertion product:



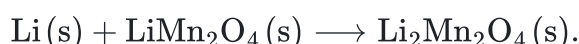
To identify the reduction, use charge neutrality. Taking lithium as +1 and oxygen as -2, the sum of the manganese oxidation states is:

$$\begin{aligned}\text{LiMn}_2\text{O}_4 : \quad & 8 - 1 = 7, \\ \text{Li}_2\text{Mn}_2\text{O}_4 : \quad & 8 - 2 = 6.\end{aligned}$$

Thus, the initial manganese(III)/manganese(IV) pair becomes two manganese(III) centres. One electron is accepted per formula unit, formally:



The overall discharge reaction is therefore:



The ions are lithium ion, Li^+ , [$\text{Li}+$]; manganese(III) ion, Mn^{3+} , [$\text{Mn}+3$]; and manganese(IV) ion, Mn^{4+} , [$\text{Mn}+4$]. The manganese ions occupy sites within the oxide lattice; these SMILES specify their formal charges but do not describe that lattice.

10.3 — Coordination numbers

The coordination number is the number of nearest neighbouring oxide ions around a cation. An oxide ion, O^{2-} , has SMILES [$\text{O}-2$].

- Lithium ions occupy **tetrahedral sites**: each has four nearest oxide-ion neighbours at the vertices of a tetrahedron. Hence,

$$\boxed{\text{CN}(\text{Li}^+) = 4}.$$

- Manganese ions occupy **octahedral sites**: each has six nearest oxide-ion neighbours at the vertices of an octahedron. Hence,

$$\boxed{\text{CN}(\text{Mn}^{3+}) = \text{CN}(\text{Mn}^{4+}) = 6}.$$

These coordination geometries are properties of the crystal structure and are not conveyed by the individual-ion SMILES.

10.4 — Extra vehicle mass

An equivalent battery must provide the energy needed for the range obtained from a full petrol tank:

$$R = (50 \text{ L})(10 \text{ km L}^{-1}) = 500 \text{ km}.$$

Using the stated minimum energy requirement,

$$E_{\min} = \frac{5 \text{ kWh}}{50 \text{ km}} (500 \text{ km}) = 50 \text{ kWh} = 5.0 \times 10^4 \text{ Wh}.$$

The petrol mass in the full tank is

$$m_{\text{petrol}} = (50 \text{ L}) \left(\frac{3.78 \text{ kg}}{5.0 \text{ L}} \right) = 37.8 \text{ kg}.$$

Replacing the tank and its fuel removes

$$m_{\text{removed}} = 10 + 37.8 = 47.8 \text{ kg}.$$

Consequently,

$$\Delta m = m_{\text{battery}} - 47.8 \text{ kg}.$$

The equal-efficiency assumption requires no additional relative efficiency correction. The calculation uses the stated energy consumption; the problem gives no relation for correcting it as vehicle mass increases.

10.4(a) — Lead-acid battery

With an energy density of 45 Wh kg^{-1} ,

$$m_{\text{lead-acid}} = \frac{5.0 \times 10^4 \text{ Wh}}{45 \text{ Wh kg}^{-1}} = 1111.1 \dots \text{ kg}.$$

Therefore,

$$\Delta m_{\text{lead-acid}} = 1111.1 \dots - 47.8 = 1063.3 \dots \text{ kg} \approx 1.1 \times 10^3 \text{ kg}.$$

10.4(b) — Lithium battery

For the same stored energy, the lithium battery has one-third the mass of the lead-acid battery:

$$m_{\text{lithium}} = \frac{1111.1 \dots}{3} = 370.37 \dots \text{ kg}.$$

Therefore,

$$\Delta m_{\text{lithium}} = 370.37 \dots - 47.8 = 322.57 \dots \text{ kg} \approx 3.2 \times 10^2 \text{ kg}.$$

These are nominal minimum estimates because the stated energy requirement is "at least" 5 kWh per 50 km.

The solution was checked against the official solution.