

IChO 1989

Theory problems and solutions · Halle, German Democratic Republic · 6 theory problems with complete solutions

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Problem 1: Solubility product of copper(II) iodate by iodometric titration

To determine the solubility product of copper(II) iodate, $\text{Cu}(\text{IO}_3)_2$, by iodometric titration in an acidic solution (25 °C) 30.00 cm³ of a 0.100 molar sodium thiosulphate solution are needed to titrate 20.00 cm³ of a saturated aqueous solution $\text{Cu}(\text{IO}_3)_2$.

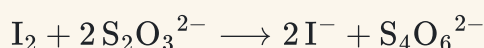
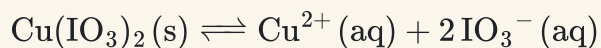
1.1 Write the sequence of balanced equations for the above described reactions.

1.2 Calculate the initial concentration of Cu^{2+} and the solubility product of copper(II) iodate. Activity coefficients can be neglected.

Official English text of the problem.

Answers

• **1.1**



• **1.2**

$$[\text{Cu}^{2+}]_0 = 1.15 \times 10^{-2} \text{ mol dm}^{-3}$$

$$K_{\text{sp}} = 6.14 \times 10^{-6}$$

The corresponding concentration product is $6.14 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}$.

Solution

1.1

Dissolution of copper(II) iodate gives one copper(II) ion and two iodate ions per formula unit, as shown by the first equilibrium above.

For the iodometric determination, excess iodide is added to the acidified sample. **Both dissolved constituents liberate iodine:**

- Iodate oxidizes iodide in acidic solution. Each mole of iodate produces three moles of iodine.

- Copper(II) also oxidizes iodide. Copper(II) is reduced to copper(I), which precipitates as copper(I) iodide. Each mole of copper(II) produces half a mole of iodine.

The liberated iodine is then titrated with thiosulphate. Iodine is reduced to iodide, while thiosulphate is oxidized to tetrathionate. Each mole of iodine consumes two moles of thiosulphate.

The species used in these equations have the following names and SMILES. The salt representations show disconnected constituent ions; SMILES do not describe their crystal lattices or aqueous hydration.

Species	SMILES
Copper(II) iodate	[Cu+2] . [O-] I(=O)=O . [O-] I(=O)=O
Copper(II) ion	[Cu+2]
Iodate ion	[O-] I(=O)=O
Iodide ion	[I-]
Hydrogen ion (proton)	[H+]
Iodine	II
Water	O
Copper(I) iodide	[Cu+] . [I-]
Thiosulphate ion	[O-] S(=O)(=O) [S-]
Tetrathionate ion	[O-] S(=O)(=O) SSS(=O)(=O) [O-]
Sodium thiosulphate	[Na+] . [Na+] . [O-] S(=O)(=O) [S-]

1.2

Let s be the molar solubility of copper(II) iodate in the original saturated solution. Its dissolution stoichiometry gives

$$[\text{Cu}^{2+}]_0 = s, \quad [\text{IO}_3^-]_0 = 2s.$$

For each mole of dissolved copper(II) iodate:

- The two iodate ions produce $2 \times 3 = 6$ moles of iodine, consuming 12 moles of thiosulphate.
- The copper(II) ion produces another $\frac{1}{2}$ mole of iodine, consuming 1 mole of thiosulphate.

Therefore,

$$n(\text{S}_2\text{O}_3^{2-}) = 13 n(\text{Cu}(\text{IO}_3)_2).$$

The amount of thiosulphate used is

$$n(\text{S}_2\text{O}_3^{2-}) = (0.100 \text{ mol dm}^{-3})(30.00 \times 10^{-3} \text{ dm}^3) = 3.00 \times 10^{-3} \text{ mol}.$$

Thus the original 20.00 cm^3 aliquot contains

$$n(\text{Cu}^{2+}) = \frac{3.00 \times 10^{-3}}{13} = 2.30769 \times 10^{-4} \text{ mol}.$$

Its initial copper(II) concentration is consequently

$$s = \frac{2.30769 \times 10^{-4} \text{ mol}}{20.00 \times 10^{-3} \text{ dm}^3} = 0.0115385 \text{ mol dm}^{-3},$$

so

$$[\text{Cu}^{2+}]_0 = 1.15 \times 10^{-2} \text{ mol dm}^{-3}.$$

Using the unrounded value,

$$[\text{IO}_3^-]_0 = 2s = 0.0230769 \text{ mol dm}^{-3}.$$

The solubility concentration product is

$$[\text{Cu}^{2+}]_0 [\text{IO}_3^-]_0^2 = s(2s)^2 = 4s^3,$$

giving

$$4(0.0115385)^3 = 6.14 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}.$$

With activity coefficients neglected and concentrations normalized to the standard concentration $c^\circ = 1 \text{ mol dm}^{-3}$, the dimensionless solubility product is therefore

$$K_{\text{sp}} = 6.14 \times 10^{-6}.$$

The solution was checked against the official solution.

Problem 2: Synthesis gas: compression work and the CO conversion equilibrium

A mixture of gases containing mainly carbon monoxide and hydrogen is produced by the reaction of alkanes with steam:



2.1 Using equations (1) and (2) write down an overall reaction (3) so that the net enthalpy change is zero.

2.2 The synthesis of methanol from carbon monoxide and hydrogen is carried out either

a) in two steps, where the starting mixture corresponding to equation (3) is compressed from $0.1 \times 10^6 \text{ Pa}$ to $3 \times 10^6 \text{ Pa}$, and the mixture of products thereof compressed again from $3 \times 10^6 \text{ Pa}$ to $6 \times 10^6 \text{ Pa}$

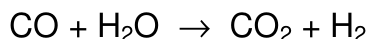
or

b) in one step, where the mixture of products corresponding to equation (3) is compressed from $0.1 \times 10^6 \text{ Pa}$ to $6 \times 10^6 \text{ Pa}$.

Calculate the work of compression, W_a , according to the two step reaction for 100 cm^3 of starting mixture and calculate the difference in the work of compression between the reactions 1 and 2.

Assume for calculations a complete reaction at constant pressure. Temperature remains constant at 500 K , ideal gas behaviour is assumed.

To produce hydrogen for the synthesis of ammonia, a mixture of 40.0 mol CO and 40.0 mol of hydrogen, 18.0 mol of carbon dioxide and 2.0 mol of nitrogen are in contact with 200.0 mol of steam in a reactor where the conversion equilibrium is established.

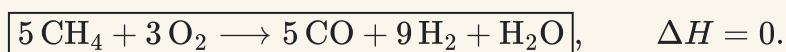


2.3 Calculate the number of moles of each gas leaving the reactor.

Official English text of the problem.

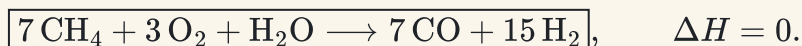
Answers

- **2.1 — Using the enthalpies exactly as printed:**



This is $6(1) - (2)$, requiring reversal of reaction (2). No nonzero combination of both reactions **in the forward direction** has zero enthalpy with the printed positive values.

If equation (1) was intended to have $\Delta H = -36 \text{ kJ mol}^{-1}$:



- **2.2 — Reversible isothermal compression, with work positive when supplied to the gas:**

Enthalpy interpretation	W_a	W_b	Saving, $W_b - W_a$
Values as printed	47.0 J	76.8 J	29.8 J
If $\Delta H_1 = -36 \text{ kJ mol}^{-1}$	47.9 J	81.9 J	34.0 J

- **2.3 — A numerical composition cannot be determined from the data given:** an equilibrium constant or equivalent datum is missing. If x mol undergoes forward conversion,

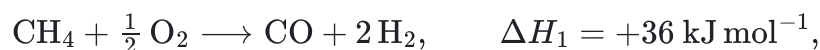
$$\begin{aligned} n_{\text{CO}} &= (40.0 - x) \text{ mol}, \\ n_{\text{H}_2} &= (40.0 + x) \text{ mol}, \\ n_{\text{CO}_2} &= (18.0 + x) \text{ mol}, \\ n_{\text{N}_2} &= 2.0 \text{ mol}, \\ n_{\text{H}_2\text{O}} &= (200.0 - x) \text{ mol}. \end{aligned}$$

Solution

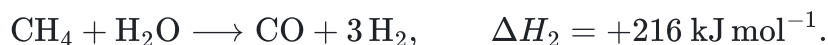
Molecular names and SMILES used here are: methane C; molecular oxygen O=O; carbon monoxide [C-]#[O+]; hydrogen [H][H]; water, including steam, O; methanol CO; carbon dioxide O=C=O; nitrogen N#N; and ammonia N.

2.1

The supplied reactions are



and

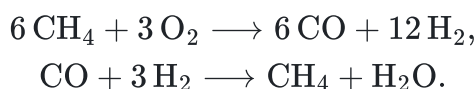


For a linear combination $a(1) + b(2)$ to have zero enthalpy,

$$36a + 216b = 0.$$

Thus $a = -6b$: the two coefficients must have opposite signs.

Choosing $a = 6$ and $b = -1$, multiply reaction (1) by six and reverse reaction (2):



Adding and cancelling gives



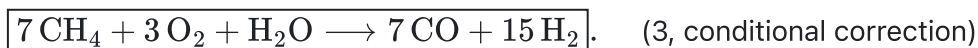
Its enthalpy is

$$\Delta H = 6(36) - 216 = 0.$$

If the first enthalpy was intended to be **negative**, six forward partial-oxidation reactions instead supply the heat for one forward steam-reforming reaction:

$$6(-36) + 216 = 0.$$

Then $6(1) + (2)$ gives



2.2

Methanol formation is



The compression comparison explicitly refers to the reactant and product mixtures of reaction (3). Accordingly:

- Route (a) compresses the reactants to $3 \times 10^6 \text{ Pa}$, completes reaction (3) at that pressure, then compresses its products to $6 \times 10^6 \text{ Pa}$.
- Route (b) completes reaction (3) at the initial pressure, then compresses its products directly to $6 \times 10^6 \text{ Pa}$.

Both routes are compared for the same initial 100 cm^3 reactant charge.

For reversible isothermal compression of an ideal gas, the work supplied is

$$W = - \int_{V_i}^{V_f} p dV = nRT \ln \left(\frac{V_i}{V_f} \right) = nRT \ln \left(\frac{p_f}{p_i} \right).$$

Let n_0 be the initial amount and $r = n_{\text{products}}/n_0$ the mole-number ratio for complete reaction (3).

From the initial state,

$$n_0 RT = p_0 V_0 = (0.1 \times 10^6 \text{ Pa})(100 \times 10^{-6} \text{ m}^3) = 10 \text{ J}.$$

Thus the specified temperature need not be substituted separately.

For route (a),

$$W_a = n_0 RT \ln \left(\frac{3 \times 10^6}{0.1 \times 10^6} \right) + r n_0 RT \ln \left(\frac{6 \times 10^6}{3 \times 10^6} \right) \\ = (10 \text{ J}) [\ln 30 + r \ln 2].$$

For route (b),

$$W_b = r n_0 RT \ln \left(\frac{6 \times 10^6}{0.1 \times 10^6} \right) = (10 \text{ J}) r \ln 60.$$

Therefore,

$$\boxed{W_b - W_a = (10 \text{ J})(r - 1) \ln 30}.$$

Route (a) saves work because fewer moles undergo the initial compression.

With the **printed enthalpies**, reaction (3) converts $5 + 3 = 8$ moles of reactants into $5 + 9 + 1 = 15$ moles of products, so

$$r = \frac{15}{8}.$$

Consequently,

$$W_a = 10 \left[\ln 30 + \frac{15}{8} \ln 2 \right] \text{ J} = \boxed{47.0 \text{ J}},$$

$$W_b = 10 \left(\frac{15}{8} \right) \ln 60 \text{ J} = 76.8 \text{ J},$$

$$\boxed{W_b - W_a = 29.8 \text{ J}}.$$

With the **conditional negative sign for ΔH_1** , reaction (3) converts $7 + 3 + 1 = 11$ moles into $7 + 15 = 22$ moles, giving $r = 2$. Hence

$$\boxed{W_a = 10 [\ln 30 + 2 \ln 2] \text{ J} = 47.9 \text{ J}},$$

$$W_b = 20 \ln 60 \text{ J} = 81.9 \text{ J}, \quad \boxed{W_b - W_a = 34.0 \text{ J}}.$$

These are compressor works; they do not include the expansion work during the constant-pressure chemical reaction.

2.3

The water-gas shift equilibrium is



Let x mol react in the forward direction. Stoichiometry gives:

Gas	Initial amount / mol	Change / mol	Outlet amount / mol
Carbon monoxide, CO	40.0	$-x$	$40.0 - x$
Hydrogen, H ₂	40.0	$+x$	$40.0 + x$
Carbon dioxide, CO ₂	18.0	$+x$	$18.0 + x$
Nitrogen, N ₂	2.0	0	2.0

Gas	Initial amount / mol	Change / mol	Outlet amount / mol
Water vapour, H ₂ O	200.0	− <i>x</i>	200.0 − <i>x</i>

Nitrogen is unchanged. The total gas amount remains 300.0 mol, since the reaction has no net change in gaseous mole number.

For ideal gases, the equilibrium condition is

$$K_p = \frac{p_{\text{CO}_2} p_{\text{H}_2}}{p_{\text{CO}} p_{\text{H}_2\text{O}}} = \frac{(18.0 + x)(40.0 + x)}{(40.0 - x)(200.0 - x)}.$$

The total pressure cancels. Equivalently,

$$(1 - K_p)x^2 + (58.0 + 240.0K_p)x + 720.0 - 8000.0K_p = 0.$$

A supplied value of K_p would determine the physically admissible root, with

$$-18.0 < x < 40.0$$

for a finite positive equilibrium constant. Negative x would signify net reverse conversion.

However, **the problem gives neither K_p nor equivalent data from which it can be calculated.** The initial reaction quotient,

$$Q_{p,0} = \frac{18.0 \times 40.0}{40.0 \times 200.0} = 0.0900,$$

does not establish the equilibrium constant. Therefore, the outlet amounts can only be stated in the parameterized form above. The complete-reaction assumption in 2.2 does not determine this separately specified equilibrium.

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 3: Removal of sulphur dioxide from power-station flue gases

Sulphur dioxide is removed from waste gases of coal power stations by washing with aqueous suspensions of calcium carbonate or calcium hydroxide. The residue formed is recovered.

3.1 Write all reactions as balanced equations.

3.2 How many kilograms of calcium carbonate are daily consumed to remove 95 % of the sulphur dioxide if 10000 m³/h of waste gas (corrected to 0 °C and standard pressure) containing 0.15 % sulphur dioxide by volume are processed? How many kilograms of gypsum are recovered thereby?

3.3 Assuming that the sulphur dioxide is not being removed and equally spread in an atmospheric liquid water pool of 5000 m³ and fully returned on earth as rain, what is the expected pH of the condensed water?

3.4 If a sodium sulphite solution is used for absorption, sulphur dioxide and the sulphite solution can be recovered. Write down the balanced equations and point out possible pathways to increase the recovery of sulphur dioxide from an aqueous solution.

Note:

Protolysis of sulphur dioxide in aqueous solutions can be described by the first step dissociation of sulphurous acid. The dissociation constant $K_{a,1}(\text{H}_2\text{SO}_3) = 10^{-2.25}$.

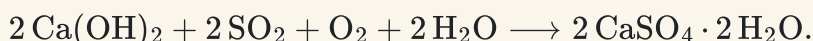
Assume ideal gases and a constant temperature of 0 °C at standard pressure.

$M(\text{CaCO}_3) = 100 \text{ g mol}^{-1}$; $M(\text{CaSO}_4) = 172 \text{ g mol}^{-1}$.

Official English text of the problem.

Answers

- **3.1** Absorption forms calcium sulphite, which is oxidized and recovered as gypsum. The overall equations are



- **3.2** Calcium carbonate consumed: approximately $1.53 \times 10^3 \text{ kg per day}$. Gypsum recovered: approximately $2.63 \times 10^3 \text{ kg per day}$.
- **3.3** For one hour's untreated emissions, $\text{pH} \approx 3.88$.
- **3.4**



Absorption proceeds to the right; regeneration proceeds to the left. Heating and lowering the sulphur dioxide partial pressure promote recovery. Acidification also releases sulphur dioxide, but subsequent neutralization is needed to restore the absorbent.

Solution

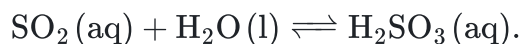
The species used below have the following names and SMILES. For salts, disconnected SMILES components specify composition; they do not describe the crystal lattice or coordination of water in gypsum. Sulphurous acid is the formal aqueous species used in the problem's dissociation model.

Species	Name	SMILES
SO_2	Sulphur dioxide	<chem>O=S=O</chem>
H_2O	Water	<chem>O</chem>
H_2SO_3	Sulphurous acid	<chem>OS(=O)O</chem>
CaCO_3	Calcium carbonate	<chem>[Ca+2].[O-]C(=O)[O-]</chem>
$\text{Ca}(\text{OH})_2$	Calcium hydroxide	<chem>[Ca+2].[OH-].[OH-]</chem>
CaSO_3	Calcium sulphite	<chem>[Ca+2].[O-]S(=O)[O-]</chem>
CO_2	Carbon dioxide	<chem>O=C=O</chem>
O_2	Oxygen	<chem>O=O</chem>
CaSO_4	Calcium sulphate	<chem>[Ca+2].[O-]S(=O)(=O)[O-]</chem>
$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	Gypsum; calcium sulphate dihydrate	<chem>[Ca+2].[O-]S(=O)(=O)[O-].O.O</chem>
H_3O^+	Hydronium ion	<chem>[OH3+]</chem>

Species	Name	SMILES
HSO_3^-	Hydrogen sulphite ion; bisulphite ion	<chem>OS(=O)[O-]</chem>
Na_2SO_3	Sodium sulphite	<chem>[Na+].[Na+].[O-]S(=O)[O-]</chem>
NaHSO_3	Sodium hydrogen sulphite; sodium bisulphite	<chem>[Na+].OS(=O)[O-]</chem>

3.1 — Absorption and gypsum formation

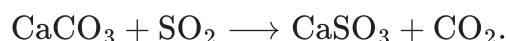
Dissolved sulphur dioxide behaves as an acid, represented formally by



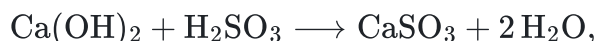
Neutralization by calcium carbonate releases carbon dioxide:



Combining this with the formal hydration step gives



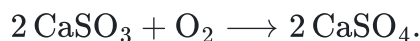
Neutralization by calcium hydroxide gives



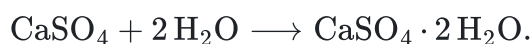
or, after combining with hydration,



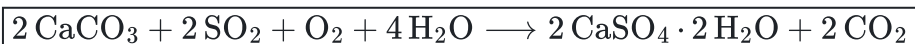
Oxygen from the flue gas or supplied air oxidizes calcium sulphite to calcium sulphate:



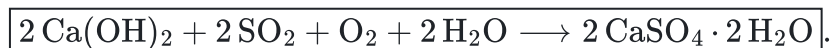
The sulphur oxidation state increases from +4 to +6. The recovered hydrated solid is gypsum:



Thus the overall equations are



and



3.2 — Daily calcium carbonate consumption and gypsum recovery

At 0 °C and conventional standard pressure, the ideal-gas molar volume is

$$V_m \approx 22.4 \text{ L mol}^{-1} = 22.4 \text{ m}^3 \text{ kmol}^{-1}.$$

The volume of sulphur dioxide entering per hour is

$$\dot{V}_{\text{SO}_2} = (10000 \text{ m}^3 \text{ h}^{-1})(0.0015) = 15.0 \text{ m}^3 \text{ h}^{-1}.$$

The volume captured per day is therefore

$$V_{\text{captured}} = (15.0 \text{ m}^3 \text{ h}^{-1})(24 \text{ h day}^{-1})(0.95) = 342 \text{ m}^3 \text{ day}^{-1}.$$

Its amount is

$$n_{\text{captured}} = \frac{342 \text{ m}^3 \text{ day}^{-1}}{22.4 \text{ m}^3 \text{ kmol}^{-1}} = 15.27 \text{ kmol day}^{-1}.$$

The overall reaction shows that one mole of captured sulphur dioxide consumes one mole of calcium carbonate and produces one mole of gypsum. Hence

$$m_{\text{CaCO}_3} = (15.27 \text{ kmol day}^{-1})(100 \text{ kg kmol}^{-1}) \approx \boxed{1.53 \times 10^3 \text{ kg day}^{-1}}.$$

Gypsum is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; the supplied molar mass 172 g mol^{-1} applies to this dihydrate. Thus

$$m_{\text{gypsum}} = (15.27 \text{ kmol day}^{-1})(172 \text{ kg kmol}^{-1}) \approx \boxed{2.63 \times 10^3 \text{ kg day}^{-1}}.$$

3.3 — pH of the rainwater

Taking **one hour** of untreated emissions as the basis, the entire 15.0 m^3 of sulphur dioxide enters the water:

$$n_{\text{SO}_2} = \frac{15.0 \text{ m}^3}{22.4 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}} = 669.6 \text{ mol}.$$

The water volume is

$$5000 \text{ m}^3 = 5.000 \times 10^6 \text{ L}.$$

Consequently, the analytical concentration of dissolved sulphur dioxide, expressed as sulphurous acid, is

$$C = \frac{669.6 \text{ mol}}{5.000 \times 10^6 \text{ L}} = 1.339 \times 10^{-4} \text{ mol L}^{-1}.$$

The prescribed dissociation equilibrium is



Neglecting water's self-ionization and using only the stipulated first dissociation, let

$$x = [\text{H}_3\text{O}^+] = [\text{HSO}_3^-], \quad [\text{H}_2\text{SO}_3] = C - x.$$

Using numerical concentrations in mol L^{-1} ,

$$K_{a,1} = \frac{x^2}{C - x}.$$

The physically meaningful root is

$$x = \frac{-K_{a,1} + \sqrt{K_{a,1}^2 + 4K_{a,1}C}}{2} = 1.309 \times 10^{-4} \text{ mol L}^{-1}.$$

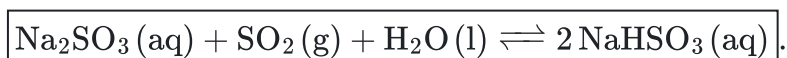
Therefore

$$\boxed{\text{pH} = -\log_{10}\left(\frac{[\text{H}_3\text{O}^+]}{1 \text{ mol L}^{-1}}\right) = 3.88}.$$

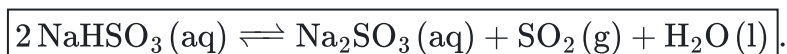
Approximately 97.7% undergoes the first dissociation. Thus the usual weak-acid approximation $x \ll C$ is inappropriate here; the quadratic is needed.

3.4 — Reversible absorption in sodium sulphite

Sodium sulphite absorbs acidic sulphur dioxide to form sodium hydrogen sulphite:



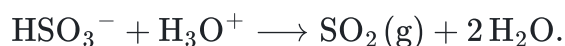
Heating and removing the evolved gas reverse the absorption, regenerating sodium sulphite:



Sulphur remains in oxidation state +4, allowing recovery through this reversible absorption process.

The following changes increase sulphur dioxide release:

- **Raise the temperature.** Heating reduces gas solubility and promotes regeneration from sodium hydrogen sulphite.
- **Lower the sulphur dioxide partial pressure above the solution.** Vacuum operation or continuous removal by steam or an inert gas promotes desorption and shifts the regeneration equilibrium toward the products.
- **Acidify the solution.** Protonation converts hydrogen sulphite into dissolved sulphur dioxide, which can escape:

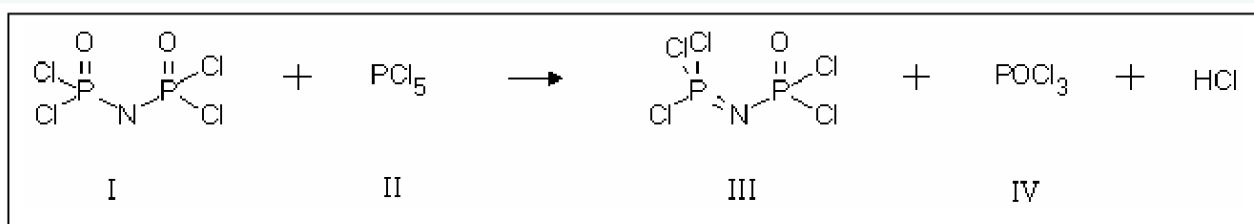


This consumes the absorbent's alkalinity, so additional neutralization is required before sodium sulphite can be reused.

The solution was checked against the official solution.

Problem 4: ^{32}P -labelled PCl_5 : reaction mechanism and solubility of $\text{Mg}(\text{NH}_4)\text{PO}_4$

^{32}P labelled phosphorus pentachloride (half-life $t_{1/2} = 14.3$ days) is used to study the electrophilic attack of a PCl_4^+ cation on nitrogen or on oxygen.



The reaction is carried out in CCl_4 and the solvent and product **IV** distilled off. Samples of **III** (remaining in the distillation flask), of **IV** (in the distillate) and samples of the starting material **II** are hydrolyzed by heating with a strong sodium hydroxide solution. The phosphate ions formed are precipitated as ammonium magnesium phosphate. Purified samples of the three precipitates are then dissolved by known volumes of water and the radioactivity measured.

4.1 Write the balanced equations for the reaction of red phosphorus forming PCl_5

4.2 Write the reaction equations for complete hydrolysis of the compounds **II** and **III** using sodium hydroxide.

4.3 How long does it take in order to lower the initial radioactivity to 10^{-3} of the initial value?

4.4 Write two alternative mechanisms for the reaction of labelled PCl_4^- with the anion of **I**.

4.5 After hydrolysis the precipitated ammonium magnesium phosphates show the following values for radioactivity:

II. 2380 Bq for 128 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$

III. 28 Bq for 153 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$

IV. 2627 Bq for 142 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$

Using these data, what can you say about the nucleophilic centre attacked by PCl_4^- ?

Data: For H_3PO_4 : $pK_1 = 2.2$; $pK_2 = 7.2$; $pK_3 = 12.4$

Solubility product of $\text{Mg}(\text{NH}_4)\text{PO}_4$: $pK_s = 12.6$

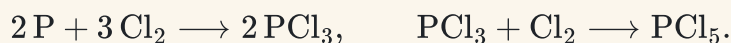
Equilibrium concentration of $\text{NH}_4^+ = 0.1 \text{ mol dm}^{-3}$

4.6 Calculate the solubility for $\text{Mg}(\text{NH}_4)\text{PO}_4$ at pH equal to 10 under idealized conditions (activity coefficients can be neglected).

Official English text of the problem.

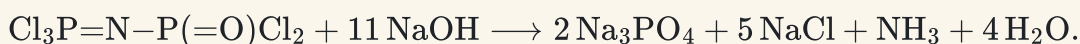
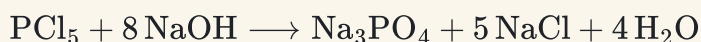
Answers

- **4.1**



Overall: $2 \text{P} + 5 \text{Cl}_2 \longrightarrow 2 \text{PCl}_5$, with red phosphorus as the elemental reactant.

- **4.2**



- **4.3** $t = 142.5 \text{ days} \approx \boxed{143 \text{ days}}$.

- **4.4** Nitrogen attack places the incoming ^{32}P in **III**; oxygen attack places it in **IV**, phosphorus oxychloride. The explicit alternative mechanisms are given below.

- **4.5** The measurements identify **oxygen as the predominantly attacked nucleophilic centre**.

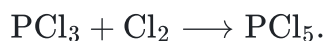
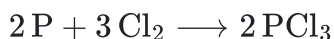
- **4.6** The molar solubility is

$$s \approx 2.5 \times 10^{-5} \text{ mol dm}^{-3}.$$

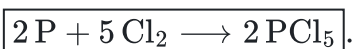
Solution

4.1 — Formation of phosphorus pentachloride

Chlorination first gives phosphorus trichloride; further chlorination gives phosphorus pentachloride:



Multiplying the second equation by two and adding gives



The species are:

Species	Name	SMILES
Cl_2	Chlorine	ClCl

Species	Name	SMILES
PCl_3	Phosphorus trichloride	<chem>ClP(Cl)Cl</chem>
PCl_5	Phosphorus pentachloride	<chem>ClP(Cl)(Cl)(Cl)Cl</chem>
$^{32}\text{PCl}_5$	Phosphorus-32-labelled phosphorus pentachloride	<chem>Cl[32P](Cl)(Cl)(Cl)Cl</chem>

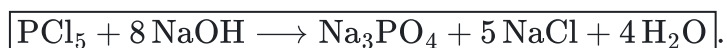
Red phosphorus is an extended covalent allotrope, so it has no unique finite molecular SMILES. [P] represents only an individual phosphorus atom for stoichiometric bookkeeping. The neutral molecular pentachloride has trigonal bipyramidal geometry, which its SMILES does not specify.

4.2 — Complete alkaline hydrolysis

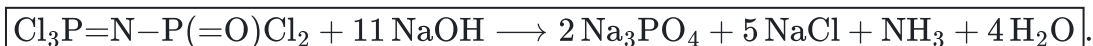
Compound **III** is N-(dichlorophosphoryl)trichlorophosphazene, $\text{Cl}_3\text{P}=\text{N}-\text{P}(=\text{O})\text{Cl}_2$, SMILES O=P(Cl)(Cl)N=P(Cl)(Cl)Cl.

Complete hydrolysis converts each phosphorus atom into orthophosphate and each chlorine atom into chloride. In strongly alkaline solution, the nitrogen of **III** becomes ammonia.

For **II**:



For **III**:



The second equation balances two phosphorus atoms, five chlorine atoms, one nitrogen atom, twelve oxygen atoms and eleven hydrogen atoms on each side.

The additional species are:

Species	Name	SMILES
NaOH	Sodium hydroxide	<chem>[Na+].[OH-]</chem>
Na_3PO_4	Trisodium orthophosphate	<chem>[Na+].[Na+].[Na+].[O-]P(=O)([O-])[O-]</chem>
NaCl	Sodium chloride	<chem>[Na+].[Cl-]</chem>
NH_3	Ammonia	<chem>N</chem>
H_2O	Water	<chem>O</chem>

The disconnected ionic SMILES describe the constituent ions, not their crystal lattices.

4.3 — Radioactive decay

Activity is proportional to the number of undecayed radioactive nuclei:

$$\frac{A(t)}{A_0} = 2^{-t/t_{1/2}}.$$

Therefore,

$$10^{-3} = 2^{-t/(14.3 \text{ days})},$$

and

$$t = (14.3 \text{ days}) \frac{\ln(10^3)}{\ln 2} = 142.5 \text{ days}.$$

Thus approximately ten half-lives are required:

$$t \approx 143 \text{ days}.$$

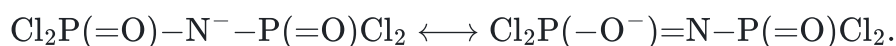
4.4 — Alternative mechanisms and isotope positions

The reacting electrophile is taken to be PCl_4^+ , consistently with the introduction.

Compound **I** is bis(dichlorophosphoryl)amine, $\text{HN}[\text{P}(=\text{O})\text{Cl}_2]_2$, SMILES O=P(Cl)(Cl)NP(=O)(Cl)Cl. Its N–H hydrogen is implicit in the scheme and accounts for the hydrogen chloride byproduct.

Compound **IV** is phosphorus oxychloride, POCl_3 , SMILES O=P(Cl)(Cl)Cl. Hydrogen chloride has SMILES [H]Cl; the solvent, carbon tetrachloride, has SMILES ClC(Cl)(Cl)Cl.

Loss of the N–H proton gives the bis(dichlorophosphoryl)amide anion. Its charge can be represented on nitrogen or on either equivalent oxygen:



These are resonance contributors of the same ion:

- N-centred contributor: O=P(Cl)(Cl)[N-]P(=O)(Cl)Cl.
- O-centred contributor: [O-]P(Cl)(Cl)=NP(=O)(Cl)Cl.

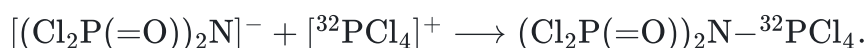
The labelled tetrachlorophosphonium cation is $[\text{}^{32}\text{PCl}_4]^+$, SMILES [32P+](Cl)(Cl)(Cl)Cl. It is tetrahedral and is supplied formally by



where chloride has SMILES [Cl-].

Alternative 1: attack at nitrogen.

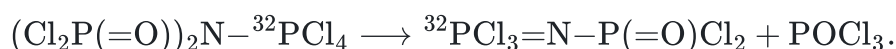
The nitrogen electron pair attacks the labelled phosphorus:



The neutral N-bound adduct is tetrachloro[bis(dichlorophosphoryl)amino]phosphorane, labelled at its tetrachlorophosphorane phosphorus:

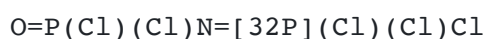


It can collapse as follows:



In this formal elimination, one chloride ligand transfers from the labelled phosphorus to an original dichlorophosphoryl phosphorus. Cleavage of that original phosphorus–nitrogen bond accompanies formation of the $\text{N}=\text{}^{32}\text{P}$ double bond.

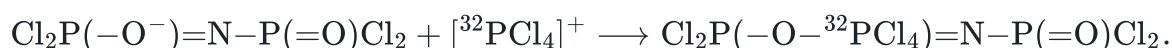
Consequently, the incoming label appears in **III**, at its trichlorophosphazene phosphorus:



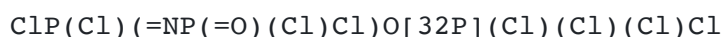
The phosphorus of **IV** comes from **I** and is unlabelled.

Alternative 2: attack at oxygen.

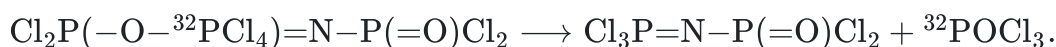
The O-centred resonance contributor attacks the labelled phosphorus:



The O-bound adduct is a dichloro[(dichlorophosphoryl)imino] [(tetrachlorophosphoranyl)oxy]phosphorane, labelled at its tetrachlorophosphoranyl phosphorus:

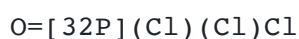


It can collapse according to



Here, chloride transfers from the labelled phosphorus to the original phosphorus bonded to the bridging oxygen. Cleavage of the original phosphorus–oxygen bond accompanies formation of the $\text{O}=\text{}^{32}\text{P}$ double bond.

Thus **III** retains both original, unlabelled phosphorus atoms, while the incoming label appears in **IV**, phosphorus-32-labelled phosphorus oxychloride:



These schemes specify formal electron-flow and atom-mapping alternatives. Their SMILES encode connectivity and isotope positions, but not the electron-pair arrows or transition-state geometry.

4.5 — Identification of the attacked centre

Each formula unit of the precipitate contains one phosphorus atom. Because all three precipitates have the same composition, activity per unit precipitate mass directly compares activity per phosphorus atom.

Define $a_i = A_i/m_i$:

Source	Specific activity a_i , Bq mg ⁻¹	Relative to II
II	$2380/128 = 18.6$	1
III	$28/153 = 0.183$	0.00984
IV	$2627/142 = 18.5$	0.995

The two mechanisms predict different isotope distributions:

- **Nitrogen attack:** one incoming phosphorus atom enters each molecule of **III**, which contains two phosphorus atoms. Its phosphate precipitate should therefore have approximately half the specific activity of that from **II**. **IV** should be unlabelled.
- **Oxygen attack:** the incoming phosphorus atom enters **IV**, so its specific activity should equal that of **II**. **III** should have negligible activity.

The observed pattern closely matches the second prediction:

$$a_{\text{IV}} \approx a_{\text{II}}, \quad a_{\text{III}} \ll a_{\text{II}}.$$

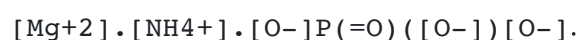
Therefore,

The electrophile attacks predominantly at oxygen.

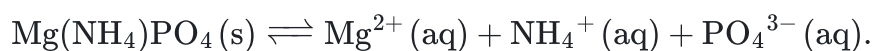
The small residual activity in **III** does not, by itself, establish a definite minor nitrogen-attack pathway.

4.6 — Solubility at pH 10

Ammonium magnesium phosphate is represented by the ionic SMILES



Its dissolution equilibrium is



The ions and phosphate protonation states involved are:

Species	Name	SMILES
Mg^{2+}	Magnesium ion	[Mg+2]
NH_4^+	Ammonium ion	[NH4+]
H^+	Hydrogen ion	[H+]
H_3PO_4	Phosphoric acid	O=P(O)(O)O
H_2PO_4^-	Dihydrogen phosphate ion	O=P(O)(O)[O-]
HPO_4^{2-}	Hydrogen phosphate ion	O=P(O)([O-])[O-]
PO_4^{3-}	Orthophosphate ion	O=P([O-])([O-])[O-]

Let s be the molar solubility. Using the supplied equilibria,

$$[\text{Mg}^{2+}] = s,$$

and the total dissolved phosphate concentration is

$$c_P = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] = s.$$

Only a fraction α_3 of this phosphate is present as PO_4^{3-} . From the three acid dissociation equilibria,

$$\alpha_3 = \frac{[\text{PO}_4^{3-}]}{c_P} = \frac{1}{1 + \frac{[\text{H}^+]}{K_3} + \frac{[\text{H}^+]^2}{K_2 K_3} + \frac{[\text{H}^+]^3}{K_1 K_2 K_3}}.$$

At pH 10, substituting the given pK_i values gives

$$\alpha_3 = \frac{1}{1 + 10^{2.4} + 10^{-0.4} + 10^{-8.2}} = 3.959 \times 10^{-3}.$$

Thus only about 0.396% of the dissolved phosphate is free orthophosphate; most is hydrogen phosphate.

The solubility product is

$$K_s = [\text{Mg}^{2+}][\text{NH}_4^+][\text{PO}_4^{3-}].$$

Using the given equilibrium ammonium concentration directly, and expressing concentrations numerically in mol dm^{-3} ,

$$10^{-12.6} = s(0.1)(\alpha_3 s).$$

Therefore,

$$s = \sqrt{\frac{10^{-12.6}}{0.1(3.959 \times 10^{-3})}} = 2.519 \times 10^{-5} \text{ mol dm}^{-3}.$$

To sensible significant figures,

$$\boxed{s = 2.5 \times 10^{-5} \text{ mol dm}^{-3}}.$$

The solution was checked against the official solution.

Problem 5: Isomeric cyclobutanedicarboxylic acids

Carboxylic acids are a chemically and biologically important class of organic compounds.

5.1 Draw the constitutional (structural) formulae of all isomeric cyclobutanedicarboxylic acids and give the systematic names for these compounds.

5.2 There are three stereoisomers, I, II and III, of cyclobutane-1,2-dicarboxylic acid. Draw perspective or stereo formulas of I, II and III indicating the relative configuration of each molecule.

5.3 Which pairs of stereoisomers I, II and III are diastereoisomers and which are enantiomers of each other?

5.4 Which reaction can be used to determine the relative configuration of diastereoisomers?

5.5 How may the enantiomers of cyclobutane-1,2-dicarboxylic acid be separated?

5.6 Indicate the absolute configurations of each asymmetric centre on the structures of the stereoisomers I, II and III using the Cahn-Ingold-Prelog rules (*R*, *S* system).

Official English text of the problem.

Answers

The statement does not assign particular structures to I–III; the following assignments are used throughout.

- **5.1** The three constitutional isomers are:
 - **Cyclobutane-1,1-dicarboxylic acid:** O=C(O)C1(C(=O)O)CCC1
 - **Cyclobutane-1,2-dicarboxylic acid:** O=C(O)C1C(C(=O)O)CC1
 - **Cyclobutane-1,3-dicarboxylic acid:** O=C(O)C1CC(C(=O)O)C1
- **5.2** The three stereoisomers of cyclobutane-1,2-dicarboxylic acid are:
 - **I:** cis, meso, (1*R*, 2*S*); O=C(O)[C@H]1[C@@H](C(=O)O)CC1
 - **II:** trans, (1*R*, 2*R*); O=C(O)[C@H]1[C@H](C(=O)O)CC1
 - **III:** trans, (1*S*, 2*S*); O=C(O)[C@@H]1[C@@H](C(=O)O)CC1
- **5.3** II and III are enantiomers. I and II, and I and III, are diastereoisomers.
- **5.4** Use **intramolecular dehydration to a cyclic anhydride**. I readily forms **cis-cyclobutane-1,2-dicarboxylic anhydride**, O=C1OC(=O)[C@H]2CC[C@@H]12. II and III cannot form this anhydride while retaining their configurations.
- **5.5** Form diastereomeric salts with a suitable enantiopure base, such as (*S*)-**1-phenylethan-1-amine**, C[C@H](N)c1ccccc1. Separate the salts by fractional crystallization, then acidify each fraction to recover the individual acid enantiomers.
- **5.6** I: 1*R*, 2*S*, equivalently 1*S*, 2*R*; II: 1*R*, 2*R*; III: 1*S*, 2*S*.

Solution

5.1 — Constitutional isomers

Fix one carboxyl group at carbon 1 of a cyclobutane ring. The second carboxyl group can occupy:

1. **The same carbon:** cyclobutane-1,1-dicarboxylic acid.
2. **An adjacent carbon:** cyclobutane-1,2-dicarboxylic acid.
3. **The opposite carbon:** cyclobutane-1,3-dicarboxylic acid.

Position 4 is equivalent to position 2 by reversing the ring numbering, so it gives no additional constitutional isomer.

To draw the structures, draw a square representing the four-carbon ring and attach two —C(=O)OH groups to one vertex, two adjacent vertices, or two opposite vertices, respectively. The connectivity SMILES are given in the answers. All three have molecular formula $\text{C}_6\text{H}_8\text{O}_4$.

5.2 — Stereoisomers and their drawings

Use a square projection with **C1 at the upper left, C2 at the upper right, C3 at the lower right, and C4 at the lower left**. Draw the carboxyl bonds outward: towards the upper left from C1 and towards the upper right from C2.

A **solid wedge** points towards the reader; a **hashed wedge** points away. Draw the hydrogen at each stereocentre with the opposite wedge type to its carboxyl group.

Isomer	Carboxyl bond at C1	Carboxyl bond at C2	Relative configuration
I	Solid wedge	Solid wedge	cis: both groups on the same face
II	Solid wedge	Hashed wedge	trans: groups on opposite faces
III	Hashed wedge	Solid wedge	trans: groups on opposite faces

These descriptions correspond to the stereochemical SMILES in the answers. The actual cyclobutane ring can pucker; the square projection specifies the configurations without specifying a particular puckered conformation.

There are two stereogenic centres, giving the candidate assignments

$$(R, R), \quad (S, S), \quad (R, S), \quad (S, R).$$

The two centres occupy symmetry-equivalent positions. Consequently, the cis assignments (R, S) and (S, R) describe the **same meso compound**, I. Drawing both carboxyl groups as hashed wedges therefore gives another representation of I.

The trans assignments (R, R) and (S, S) describe two distinct, chiral compounds, II and III. Thus there are **three configurational stereoisomers**.

5.3 — Stereochemical relationships

Reflection reverses both stereocentres:

$$(1R, 2R) \longleftrightarrow (1S, 2S).$$

Therefore, **II and III are nonsuperimposable mirror images: enantiomers**.

I has cis substitution, whereas II and III have trans substitution. I is not the mirror image of either trans form. Therefore:

- **I/II**: diastereoisomers.
- **I/III**: diastereoisomers.

5.4 — Determining the relative configuration chemically

Use **cyclic anhydride formation under dehydrating conditions that preserve the stereocentres**.

In **cis** acid **I**, the two carboxyl groups lie on the same face and can undergo intramolecular dehydration. The resulting five-membered anhydride ring contains the two adjacent cyclobutane carbons, the two carbonyl carbons, and the bridging oxygen.

The product is **cis-cyclobutane-1,2-dicarboxylic anhydride**, also named **cis-3-oxabicyclo[3.2.0]heptane-2,4-dione**, with SMILES O=C1OC(=O)[C@H]2CC[C@@H]12.

The balanced dehydration equation is



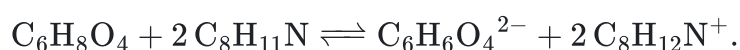
The eliminated molecule is **water**, H_2O .

The **trans** acids have their carboxyl groups on opposite faces. They cannot undergo the corresponding direct closure to this **cis**-fused anhydride while preserving both stereocentres. Thus ready cyclic anhydride formation distinguishes **cis I** from **trans II and III**. Conditions that cause epimerization must be avoided, since anhydride formation after epimerization would not establish the starting configuration.

5.5 — Separating the enantiomers

II and **III** have identical physical properties in an achiral environment, including solubility in an achiral solvent. To resolve them, introduce an enantiopure reagent that converts them into **diastereomeric salts**.

For example, use (*S*)-**1-phenylethan-1-amine**, C[C@H](N)c1ccccc1, as the resolving base. With two equivalents of base per equivalent of dicarboxylic acid, the balanced proton-transfer equation, applicable to either acid enantiomer, is

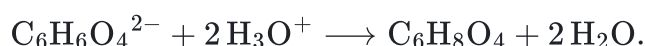


The salt components are:

Ion	Stereochemical SMILES
(<i>S</i>)-1-Phenylethylammonium ion	<chem>C[C@H]([NH3+])c1ccccc1</chem>
(1 <i>R</i> , 2 <i>R</i>)-Cyclobutane-1,2-dicarboxylate	<chem>O=C([O-])[C@H]1[C@H](C(=O)[O-])CC1</chem>
(1 <i>S</i> , 2 <i>S</i>)-Cyclobutane-1,2-dicarboxylate	<chem>O=C([O-])[C@@H]1[C@@H](C(=O)[O-])CC1</chem>

Each salt contains two resolving-base cations and one acid dianion. The two salts are diastereomeric because the base configuration remains fixed while both acid stereocentres are reversed.

Choose a solvent in which the salts have sufficiently different solubilities and separate them by **fractional crystallization**. Acidify each purified salt separately to regenerate its corresponding acid enantiomer. Using **hydronium ion**, [OH3+], the balanced net ionic equation is



This recovers **II** and **III** separately without changing their stereocentres.

5.6 — Absolute configurations by the CIP rules

At either stereocentre, the directly attached atoms are three carbons and one hydrogen. Hydrogen therefore has the lowest priority. Compare the atoms attached to each competing carbon, treating a double bond by the CIP duplicate-atom convention:

Attached group or ring direction	Atoms compared at the next level	Priority
Carboxyl carbon	(O, O, O)	1
Ring path through the other substituted carbon	(C, C, H)	2
Ring path through the neighbouring methylene carbon	(C, H, H)	3
Hydrogen	—	4

Thus the priorities are:

- **At C1:** $\text{—COOH} > \text{path through C2} > \text{path through C4} > \text{H}$.
- **At C2:** $\text{—COOH} > \text{path through C1} > \text{path through C3} > \text{H}$.

With priority 4 directed away, a clockwise $1 \rightarrow 2 \rightarrow 3$ sequence is *R*, and an anticlockwise sequence is *S*. If priority 4 points towards the reader, reverse the assignment.

Applying this to the drawings specified in 5.2:

Isomer	C1	C2	Complete assignment
I	<i>R</i>	<i>S</i>	cis-(1 <i>R</i> , 2 <i>S</i>), meso
II	<i>R</i>	<i>R</i>	trans-(1 <i>R</i> , 2 <i>R</i>)
III	<i>S</i>	<i>S</i>	trans-(1 <i>S</i> , 2 <i>S</i>)

The solution was checked against the official solution.

Problem 6: Fats, fatty acids and phospholipids

Fats (lipids) contain a non-polar (hydrophobic) and a polar (hydrophilic) group. The lipids insoluble in water, have important biological functions.

6.1 Draw the structures of Z-octadec-9-enoic acid (oleic acid), octadecanoic acid (stearic acid), and hexadecanoic acid (palmitic acid).

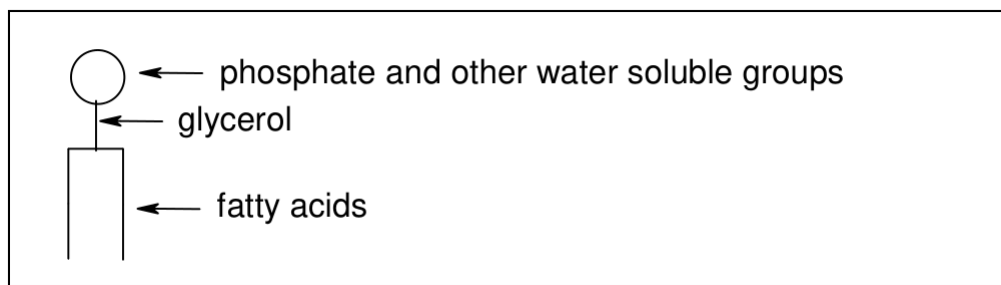
6.2 Using these three fatty acids in part 6.1 draw one possible structure of a triacyl glyceride.

6.3 Write the equation for the hydrolysis reaction of your triacyl glyceride in part 6.2 in aqueous NaOH solution. Give the mechanism of the hydrolysis of one of the fatty acids from your glyceride.

6.4 Which of the following fatty acids, $\text{C}_{21}\text{H}_{43}\text{COOH}$, $\text{C}_{17}\text{H}_{35}\text{COOH}$ or $\text{C}_5\text{H}_{11}\text{COOH}$, is the least soluble in water?

6.5 Phospholipids are an important class of bioorganic compounds. Draw the structure of the phosphatidic acid derived from your triacyl glyceride in part 6.2.

6.6 Phospholipids are frequently characterized by the diagram:



- i) Mark the hydrophilic and hydrophobic groups on a copy of the above diagram.
- ii) Draw two possibilities for the association of six identical molecules of a phospholipid in water using the above diagram.
- iii) Biomembranes consist of a phospholipid bi-layer. Draw such a model for a membrane using the above diagram.
- iv) Such a model (iii) is incomplete. What other bio-macromolecules are contained in such biomembranes?

Official English text of the problem.

Answers

- **6.1**
- **Oleic acid, (9Z)-octadec-9-enoic acid:** CCCCCCCC/C=C\CCCCCCCC(=O)O
- **Stearic acid, octadecanoic acid:** CCCCCCCCCCCCCCCC(=O)O
- **Palmitic acid, hexadecanoic acid:** CCCCCCCCCCCCCCCC(=O)O
- **6.2** One possible structure is **1-oleoyl-2-stearoyl-3-palmitoyl-sn-glycerol:**
CCCCCCCC/C=C\CCCCCCCC(=O)OC[C@H](OC(=O)CCCCCCCCCCCCCCCC)COC(=O)CCCCCCCCCCCCCCCC
- **6.3** Complete alkaline hydrolysis is:

$$\text{C}_{55}\text{H}_{104}\text{O}_6 + 3\text{NaOH} \longrightarrow \text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH} + \text{C}_{17}\text{H}_{33}\text{COONa} + \text{C}_{17}\text{H}_{35}\text{COONa} + \text{C}_{15}\text{H}_{31}\text{COONa}.$$
 The products are:
 - **Glycerol:** OCC(O)CO
 - **Sodium oleate:** CCCCCCCC/C=C\CCCCCCCC(=O)[O-].[Na+]
 - **Sodium stearate:** CCCCCCCCCCCCCCCC(=O)[O-].[Na+]
 - **Sodium palmitate:** CCCCCCCCCCCCCCCC(=O)[O-].[Na+]

The mechanism is hydroxide addition to an ester carbonyl, collapse of the tetrahedral intermediate with loss of a glycerol-derived alkoxide, and proton transfer to form the carboxylate.

- **6.4 Docosanoic acid (behenic acid), $\text{C}_{21}\text{H}_{43}\text{COOH}$, is least soluble:**
CCCCCCCCCCCCCCCCCCCC(=O)O

- **6.5** Retaining the oleoyl and stearoyl groups gives **1-oleoyl-2-stearoyl-sn-glycero-3-phosphoric acid**, a phosphatidic acid:
CCCCCCCC/C=C\CCCCCCCC(=O)OC[C@H](OC(=O)CCCCCCCCCCCCCCCCC)COP(=O)(O)O
- **6.6(i)** The polar head is **hydrophilic**; the two hydrocarbon tails are **hydrophobic**.
- **6.6(ii)** Two schematic arrangements are a **micelle-like cluster**, with six heads facing outward and tails inward, and a **bilayer fragment**, with three molecules in each opposing leaflet.
- **6.6(iii)** A membrane bilayer has polar heads facing the aqueous medium on both sides and hydrocarbon tails packed together in its interior.
- **6.6(iv) Proteins** are the principal additional biomacromolecules. Membranes also bear carbohydrate chains attached to proteins and lipids.

Solution

6.1

Number each fatty acid from its carboxyl carbon, which is C1.

Fatty acid	Condensed structure	Structural interpretation
Oleic acid	$\text{HOOC}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$	Eighteen carbons, with a <i>Z</i> double bond between C9 and C10.
Stearic acid	$\text{HOOC}-(\text{CH}_2)_{16}-\text{CH}_3$	Eighteen carbons and no carbon-carbon double bonds.
Palmitic acid	$\text{HOOC}-(\text{CH}_2)_{14}-\text{CH}_3$	Sixteen carbons and no carbon-carbon double bonds.

For the oleic acid drawing, place the two carbon-chain substituents on the **same side** of the double bond; the two attached hydrogens are consequently on the other side. The $/\text{C}=\text{C}\backslash$ notation in its SMILES specifies this *Z* geometry. It does not prescribe conformations about the remaining single bonds.

6.2

A triacylglycerol has all three hydroxyl groups of glycerol esterified. Use one residue from each acid:

Glycerol position	Attached acyl group
C1	Oleoyl
C2	Stearoyl
C3	Palmitoyl

To draw the chosen structure, place the glycerol carbon chain vertically, with C1 above C2 and C3 below it. Each glycerol oxygen connects to its fatty-acid residue through an ester linkage, $-\text{O}-\text{C}(=\text{O})^-$.

To specify the stereoisomer encoded in the answer, use a Fischer projection with the central hydrogen on the right and the central stearoyloxy substituent on the left. Horizontal bonds project toward the viewer, and vertical bonds project away. Keep the oleoyl double bond *Z*.

The resulting molecular formula is $C_{55}H_{104}O_6$. Other arrangements of the three acyl groups are also acceptable.

6.3

In water, O , sodium hydroxide, $[Na^+].[OH^-]$, supplies the attacking **hydroxide ion**, $[OH^-]$. Each ester group consumes one hydroxide ion, so complete hydrolysis consumes three equivalents.

The balanced equation in the Answers section produces glycerol and the three **sodium carboxylates**. Free fatty acids do not remain as the final products in aqueous alkali.

Consider cleavage of the **palmitoyl ester at glycerol C3**. For the mechanism, let:

- R denote the palmitoyl hydrocarbon chain, $CH_3(CH_2)_{14}$.
- $G-OH$ denote **1-oleoyl-2-stearoyl-sn-glycerol**, the product after removal of the C3 acyl group:

CCCCCCCC/C=C\CCCCCCCC(=O)OC[C@H](OC(=O)CCCCCCCCCCCCCCCC)CO

The reacting ester can then be written as $R-C(=O)-O-G$.

1. Nucleophilic addition



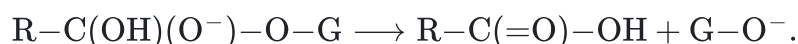
Draw an electron-flow arrow from a lone pair on hydroxide oxygen to the carbonyl carbon, and another from the carbonyl π bond to its oxygen.

The resulting **tetrahedral oxyanion intermediate** is:

CCCCCCCC/C=C\CCCCCCCC(=O)OC[C@H](OC(=O)CCCCCCCCCCCCCCCC)COC(O)([O-])CCCCCCCCCCCCCCCC

Either face of the carbonyl can be attacked; no configuration is specified at this temporary tetrahedral center.

2. Collapse of the tetrahedral intermediate

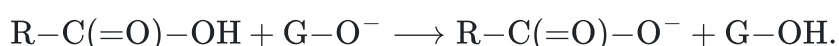


Draw an arrow from the negatively charged oxygen's lone pair toward the carbonyl carbon to restore the carbonyl bond. Simultaneously, move the electrons of the acyl carbon-glycerol oxygen bond onto the leaving oxygen.

This gives palmitic acid, whose SMILES is listed in 6.1, and the **C3 alkoxide of 1-oleoyl-2-stearoyl-sn-glycerol**:

CCCCCCCC/C=C\CCCCCCCC(=O)OC[C@H](OC(=O)CCCCCCCCCCCCCCCC)C[O-]

3. Proton transfer



The alkoxide oxygen accepts the carboxylic acid proton; the acid's oxygen-hydrogen bond electrons remain on its oxygen.

The products of this cleavage are the diacylglycerol defined above and the **palmitate ion**:

CCCCCCCCCCCCCCCC(=O)[O-]

Formation of the resonance-stabilized carboxylate makes saponification effectively irreversible under these conditions. Analogous cleavage of the two remaining ester groups ultimately yields glycerol, oleate and stearate. **Sodium ions**, $[\text{Na}^+]$, provide the counterions.

6.4

Including the carboxyl carbon, the three acids contain 22, 18 and 6 carbon atoms, respectively. They are docosanoic acid, stearic acid and **hexanoic acid**, $\text{CCCCC}(=\text{O})\text{O}$.

All have the same polar carboxyl group, but their nonpolar hydrocarbon chains differ greatly in length. Increasing that chain length makes hydration less favorable. Therefore, the longest-chain acid, **docosanoic acid**, $\text{C}_{21}\text{H}_{43}\text{COOH}$, is the least soluble in water.

6.5

A phosphatidic acid contains two fatty-acid ester groups and one phosphate monoester on the glycerol backbone.

Starting from the chosen triacylglycerol:

- Retain the oleoyl ester at C1.
- Retain the stearyl ester at C2.
- Replace the palmitoyl ester at C3 with a phosphate ester, so the terminal group becomes $-\text{CH}_2-\text{O}-\text{P}(=\text{O})(\text{OH})_2$.

Use the same glycerol stereochemical arrangement as in 6.2 and retain the oleoyl *Z* double bond. This gives the phosphatidic acid whose SMILES appears in the Answers section.

That SMILES depicts the fully protonated acid. Its phosphate head can ionize in aqueous solution.

6.6(i)

On the supplied symbol:

- Label the **circle**, representing phosphate and other polar head groups, **hydrophilic**.
- Label the **two long tail lines**, representing the hydrocarbon portions of the fatty-acid residues, **hydrophobic**.

The glycerol and ester region forms the interface between the polar head and the hydrocarbon tails.

6.6(ii)

Describe the two drawings as follows:

1. **Micellar arrangement:** Place six head circles at equal intervals around a circle. From each head, direct both tails inward toward the common central region. Thus, all six polar heads face the surrounding water while the tails associate internally.
2. **Bilayer fragment:** Place three head circles in an upper horizontal row, with their tails pointing downward. Place three more head circles in a lower row, with their tails pointing upward. The two sets of tails meet in the middle; the upper and lower head groups contact water on opposite sides.

These are schematic associations. Double-tailed phospholipids generally favor bilayers over small spherical micelles.

6.6(iii)

Extend the second arrangement into two continuous opposing leaflets. From top to bottom, the drawing should show:

1. The aqueous medium.
2. A row of polar heads.
3. Tails directed downward.
4. Tails from the opposite leaflet directed upward, meeting the first set in the hydrophobic interior.
5. A second row of polar heads.
6. The aqueous medium on the other side.

The membrane therefore presents hydrophilic surfaces to both aqueous compartments and encloses its hydrocarbon chains within the bilayer.

6.6(iv)

The principal missing biomacromolecules are **proteins**. Integral membrane proteins are embedded in the bilayer, and some span it completely; peripheral proteins associate with its surfaces.

Carbohydrate chains also occur as parts of glycoproteins and glycolipids, commonly on the noncytosolic surface. These names describe classes of substances rather than specified molecular structures, so no unique SMILES can be assigned without their sequences and connectivity.

The solution was checked against the official solution.