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Problem 1: Salts M2S2Ox of sulphur oxoacids

Compare three salts of a composition $\mathrm{M_2S_2O_x}$ where x are three different small integers and M is an alkali metal. To each of the three salts apply some of the following assertions:

a) The $\mathrm{O-O}$ bond is characteristic for the anion.
b) The $\mathrm{S-S}$ bond is characteristic for the anion.
c) The $\mathrm{S-O-S}$ bond is characteristic for the anion.
d) It is formed by thermal decomposition of hydrogen sulphate.
e) It is formed by anodic oxidation of hydrogen sulphate.
f) It is formed by the reaction of an aqueous solution of sulphite with sulphur.
g) Its aqueous solution dissolves silver bromide.
h) Neutralisation of its aqueous solution with hydroxide MOH yields sulphate $\mathrm{M_2SO_4}$.
i) In aqueous solution, it is able to oxidise Mn(II) salt to permanganate.

Problems:

1.1 Fill in the correct x values in the formulas given in the Table and indicate in the corresponding square by appropriate letters those assertions that may be applied to each of the given salts:

$\mathrm{M_2S_2O_{\square}}$					
$\mathrm{M_2S_2O_{\square}}$					
$\mathrm{M_2S_2O_{\square}}$					

1.2 Write structural formulas of the anions of the above three salts and assign σ-bonds and π-bonds in them.

1.3 Write the chemical equations expressing the processes involved in the assertions under the letters d, e, f, g, h, i.

Official English text of the problem.

Answers

- **1.1**

Salt	x	Applicable assertions
Thiosulphate, $\mathrm{M_2S_2O_3}$	3	**b, f, g**
Disulphate (pyrosulphate), $\mathrm{M_2S_2O_7}$	7	**c, d, h**

Salt	x	Applicable assertions
Peroxodisulphate, $\mathrm{M_2S_2O_8}$	8	**a, e, i**

These can occupy the three answer-sheet rows in the order shown; unused assertion boxes remain blank.

- **1.2**

The following SMILES specify conventional Lewis structures of the anions. The unspecified alkali-metal counterions are omitted.

Anion	SMILES	σ-bonds	Formal π-bonds
Thiosulphate, $\mathrm{S_2O_3^{2-}}$	`[O-]S(=O)(=O)[S-]`	4	2
Disulphate, $\mathrm{S_2O_7^{2-}}$	`[O-]S(=O)(=O)OS(=O)(=O)[O-]`	8	4
Peroxodisulphate, $\mathrm{S_2O_8^{2-}}$	`[O-]S(=O)(=O)OOS(=O)(=O)[O-]`	9	4

- **1.3**

d) Thermal condensation:

$$2\,\mathrm{MHSO_4} \xrightarrow{\Delta} \mathrm{M_2S_2O_7} + \mathrm{H_2O}$$

e) Anodic oxidation:

$$2\,\mathrm{HSO_4^-} \longrightarrow \mathrm{S_2O_8^{2-}} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-}$$

f) Reaction with sulphur:

$$8\,\mathrm{M_2SO_3} + \mathrm{S_8} \xrightarrow{\text{warm aqueous solution}} 8\,\mathrm{M_2S_2O_3}$$

g) Dissolution by complex formation:

$$\mathrm{AgBr\,(s)} + 2\,\mathrm{S_2O_3^{2-}\,(aq)} \longrightarrow \mathrm{[Ag(S_2O_3)_2]^{3-}\,(aq)} + \mathrm{Br^-\,(aq)}$$

h) Neutralisation:

$$\mathrm{M_2S_2O_7} + 2\,\mathrm{MOH} \longrightarrow 2\,\mathrm{M_2SO_4} + \mathrm{H_2O}$$

i) Oxidation of manganese(II):

$$2\,\mathrm{Mn^{2+}} + 5\,\mathrm{S_2O_8^{2-}} + 8\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{MnO_4^-} + 10\,\mathrm{SO_4^{2-}} + 16\,\mathrm{H^+}$$

Solution

1.1 Identification of the salts

Thiosulphate, $\mathrm{M_2S_2O_3}$. Adding sulphur to aqueous sulphite introduces a terminal sulphur atom bonded directly to the central sulphur atom. The resulting thiosulphate anion therefore contains an $\mathrm{S{-}S}$ bond and satisfies **b** and **f**. It also forms a soluble silver(I) complex, allowing its solution to dissolve silver bromide: **g**.

Disulphate, $\mathrm{M_2S_2O_7}$. Heating two formula units of an alkali-metal hydrogen sulphate eliminates one water molecule. The resulting anion contains two sulphur centres joined through a bridging oxygen atom, giving an $\mathrm{S{-}O{-}S}$ linkage. Thus **c** and **d** apply. In water, disulphate hydrolyses to hydrogen sulphate; neutralisation then produces sulphate, accounting for **h**.

Peroxodisulphate, $\mathrm{M_2S_2O_8}$. This anion contains two sulphate-derived groups connected by an $\mathrm{O{-}O}$ peroxide bond. It is produced by anodic oxidation of hydrogen sulphate, so **a** and **e** apply. Its strong oxidising action allows manganese(II) to be converted into permanganate, giving **i**.

1.2 Structures and bond assignments

A suitable set of conventional Lewis structural formulas is:

$$\text{Thiosulphate:} \quad \mathrm{S^{-}{-}S(=O)_2{-}O^{-}}$$

$$\text{Disulphate:} \quad \mathrm{O^{-}{-}S(=O)_2{-}O{-}S(=O)_2{-}O^{-}}$$

$$\text{Peroxodisulphate:} \quad \mathrm{O^{-}{-}S(=O)_2{-}O{-}O{-}S(=O)_2{-}O^{-}}$$

In these formulas, each $\mathrm{S(=O)_2}$ indicates two separate terminal oxygen atoms, each drawn with a double bond to sulphur. Every single bond is a σ-bond; each double bond contains one σ-bond and one π-bond.

- **Thiosulphate:** three $\mathrm{S{-}O}$ connections and one $\mathrm{S{-}S}$ connection give **four σ-bonds**. The two drawn $\mathrm{S{=}O}$ double bonds supply **two π-bonds**.
- **Disulphate:** each sulphur has four oxygen neighbours, giving **eight σ-bonds** in total. The bridging oxygen participates in two single $\mathrm{S{-}O}$ bonds. Four terminal $\mathrm{S{=}O}$ double bonds supply **four π-bonds**.
- **Peroxodisulphate:** eight $\mathrm{S{-}O}$ connections and the peroxide $\mathrm{O{-}O}$ connection give **nine σ-bonds**. Four terminal $\mathrm{S{=}O}$ double bonds supply **four π-bonds**.

The central sulphur atoms have approximately tetrahedral arrangements of their four neighbours; the written formulas do not imply planar structures. The double bonds and terminal charges are formal Lewis assignments: resonance delocalises bonding and charge over terminal oxygen positions, so the drawings do not imply permanently localised π-bonds.

1.3 Explanation and balancing of the reactions

d) Thermal decomposition of hydrogen sulphate

Two hydrogen sulphate units condense with loss of one water molecule. The remaining oxygen connects the two sulphur centres, producing disulphate:

$$\mathrm{2\,MHSO_4 \xrightarrow{\Delta} M_2S_2O_7 + H_2O}$$

e) Anodic oxidation of hydrogen sulphate

Oxidation releases electrons at the anode:

$$\mathrm{2\,HSO_4^{-} \longrightarrow S_2O_8^{2-} + 2\,H^{+} + 2\,e^{-}}$$

The equation conserves both atoms and charge: each side has net charge -2. Sulphur remains in oxidation state $+6$; formation of the peroxide bond changes two oxygen atoms from oxidation state -2 to -1.

f) Reaction of sulphite with sulphur

Sulphite incorporates one additional sulphur atom per anion. Writing elemental sulphur as cyclooctasulphur gives the integer-balanced ionic equation:

$$\mathrm{8\,SO_3^{2-} + S_8 \longrightarrow 8\,S_2O_3^{2-}}$$

Cyclooctasulphur has SMILES `S1SSSSSSS1`; its ring normally adopts a puckered crown conformation, which this SMILES does not specify.

g) Dissolution of silver bromide

Excess thiosulphate binds silver(I), forming **bis(thiosulphato)argentate(I)**, $[\mathrm{Ag(S_2O_3)_2}]^{3-}$.

Its dative-bond SMILES is:

`[O-]S(=O)(=O)[S-]->[Ag+]<-[S-]S(=O)(=O)[O-]`

The arrows represent donation from the terminal sulphur atoms to silver(I). The conventional two-coordinate depiction has an approximately linear sulphur–silver–sulphur arrangement; the SMILES records connectivity, not this angle.

Complex formation lowers the free silver-ion concentration, shifting the dissolution equilibrium towards dissolved silver:

$$\mathrm{AgBr\,(s) + 2\,{S_2O_3}^{2-}\,(aq) \longrightarrow [Ag(S_2O_3)_2]^{3-}\,(aq) + Br^-\,(aq)}$$

The net charge is -4 on both sides.

h) Neutralisation of aqueous disulphate

Disulphate first hydrolyses:

$$\mathrm{{S_2O_7}^{2-} + H_2O \longrightarrow 2\,HSO_4^-}$$

Hydrogen sulphate is then neutralised:

$$\mathrm{HSO_4^- + OH^- \longrightarrow {SO_4}^{2-} + H_2O}$$

Adding the first equation to twice the second gives:

$$\mathrm{{S_2O_7}^{2-} + 2\,OH^- \longrightarrow 2\,{SO_4}^{2-} + H_2O}$$

Restoring the alkali-metal counterions gives the molecular equation in the Answers.

i) Oxidation of manganese(II) to permanganate

Manganese changes from oxidation state $+2$ to $+7$, losing five electrons per manganese atom:

$$\mathrm{Mn^{2+} + 4\,H_2O \longrightarrow MnO_4^- + 8\,H^+ + 5\,e^-}$$

Each peroxodisulphate ion accepts two electrons:

$$\mathrm{{S_2O_8}^{2-} + 2\,e^- \longrightarrow 2\,{SO_4}^{2-}}$$

Multiplying the manganese half-reaction by two and the peroxodisulphate half-reaction by five cancels ten electrons:

$$\mathrm{2\,Mn^{2+} + 5\,{S_2O_8}^{2-} + 8\,H_2O \longrightarrow 2\,MnO_4^- + 10\,{SO_4}^{2-} + 16\,H^+}$$

Thus the required molar ratio is **five peroxodisulphate ions to two manganese(II) ions**. This oxidation is commonly performed in acidic solution with warming and a silver(I) catalyst.

For completeness, the remaining chemical species used in these equations are identified below. The silver bromide SMILES represents its constituent ions, not its crystal lattice.

Species	Formula	SMILES
Hydrogen sulphate ion	$\mathrm{HSO_4^-}$	`OS(=O)(=O)[O-]`
Sulphite ion	$\mathrm{{SO_3}^{2-}}$	`[O-]S(=O)[O-]`

Species	Formula	SMILES
Sulphate ion	SO_4^{2-}	`[O-]S(=O)(=O)[O-]`
Water	H_2O	`O`
Hydroxide ion	OH^-	`[OH-]`
Hydrogen ion, representing aqueous acidity	H^+	`[H+]`
Silver bromide	$AgBr$	`[Ag+].[Br-]`
Silver(I) ion	Ag^+	`[Ag+]`
Bromide ion	Br^-	`[Br-]`
Manganese(II) ion	Mn^{2+}	`[Mn+2]`
Permanganate ion	MnO_4^-	`[O-][Mn](=O)(=O)=O`

The solution was checked against the official solution.

Problem 2: Permanganate and hydrogen peroxide

The reaction of permanganate ions with hydrogen peroxide in an acidic solution gives Mn(II) salt and at the same time oxygen is released:

$$2\,MnO_4^- + 1\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 3\,O_2 + 4\,H_2O$$

$$2\,MnO_4^- + 3\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 4\,O_2 + 6\,H_2O$$

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O$$

$$2\,MnO_4^- + 7\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 6\,O_2 + 10\,H_2O$$

Problems:

1. The possible ratios of the reactants in the above equations express:

a) all equations □
b) only some of the equations □
c) only one equation □
d) none □

Indicate the correct assertion by a cross in the corresponding square and explain your decision.

2. Which of the reactants is an oxidising agent and which is a reducing one?
3. How much potassium permanganate is needed to release 112 cm^3 of oxygen at STP conditions from an excess of hydrogen peroxide in acidic solution?

Official English text of the problem.

Answers

1. **c) only one equation:** the third equation. Place a cross in the square beside **c)**. The reacting mole ratio is
$$n(\mathrm{MnO_4^-}) : n(\mathrm{H_2O_2}) = 2 : 5.$$
2. **Oxidising agent:** permanganate ion, $\mathrm{MnO_4^-}$, `[O-][Mn](=O)(=O)=O`.
Reducing agent: hydrogen peroxide, $\mathrm{H_2O_2}$, OO.
3. $0.316\ \mathrm{g}$ of potassium permanganate, $\mathrm{KMnO_4}$, `[K+].[O-][Mn](=O)(=O)=O`.

Solution

The other species used below are hydrogen ion, $\mathrm{H^+}$, `[H+]`; manganese(II) ion, $\mathrm{Mn^{2+}}$, `[Mn+2]`; dioxygen, $\mathrm{O_2}$, O=O; and water, $\mathrm{H_2O}$, O. Potassium permanganate contains potassium ions, $\mathrm{K^+}$, `[K+]`, and permanganate ions. Permanganate is tetrahedral; its SMILES gives a formal bond representation rather than the geometry or resonance delocalisation.

1. Selecting the reaction equation

All four proposed equations balance atoms and total charge. To identify the equation describing the stated redox reaction, we must consider the oxidation and reduction processes.

Manganese changes from oxidation state $+7$ in permanganate to $+2$, accepting five electrons per manganese atom. Its reduction half-reaction in acidic solution is
$$\mathrm{MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O}.$$
Hydrogen peroxide is oxidised to dioxygen. Each oxygen atom changes from oxidation state -1 to 0, so each peroxide molecule supplies two electrons:
$$\mathrm{H_2O_2 \longrightarrow O_2 + 2\,H^+ + 2\,e^-}.$$
Multiplying the reduction half-reaction by two and the oxidation half-reaction by five transfers ten electrons in each direction. Adding and cancelling electrons and excess hydrogen ions gives
$$\boxed{\mathrm{2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O}}.$$
Thus **the third equation** expresses the stoichiometry of this redox reaction, and the correct choice is **c)**.

2. Identifying the oxidising and reducing agents

- **Permanganate is the oxidising agent:** it accepts electrons and is itself reduced, with manganese changing from $+7$ to $+2$.
- **Hydrogen peroxide is the reducing agent:** it supplies electrons and is itself oxidised, with oxygen changing from -1 to 0.

Hydrogen ions provide the acidic medium; their oxidation state does not change.

3. Calculating the required potassium permanganate

Using the conventional STP molar gas volume,

$$V_m = 22.4\,\mathrm{dm^3\,mol^{-1}},$$

the amount of oxygen is

$$n(\mathrm{O_2}) = \frac{112 \times 10^{-3}\,\mathrm{dm^3}}{22.4\,\mathrm{dm^3\,mol^{-1}}} = 5.00 \times 10^{-3}\,\mathrm{mol}.$$

The balanced equation produces five moles of oxygen for every two moles of permanganate. Each mole of potassium permanganate supplies one mole of permanganate ions, so

$$n(\mathrm{KMnO_4}) = \frac{2}{5} n(\mathrm{O_2}) = 2.00 \times 10^{-3}\,\mathrm{mol}.$$

Using rounded standard atomic masses,

$$M(\mathrm{KMnO_4}) = 39.1 + 54.9 + 4(16.0) = 158.0\,\mathrm{g\,mol^{-1}}.$$

Therefore,

$$m(\mathrm{KMnO_4}) = (2.00 \times 10^{-3}\,\mathrm{mol})(158.0\,\mathrm{g\,mol^{-1}}) = \boxed{0.316\,\mathrm{g}}.$$

The solution was checked against the official solution.

Problem 3: Isomeric cyclobutanedicarboxylic acids

The letters **A, B, C, D,** and **E** represent isomeric cyclobutane dicarboxylic acid, one of them being a racemic form.

It was shown that:

a) only compound **C** forms a cyclic anhydride easily,

b) **B** yields a cyclic anhydride only at higher temperatures,

c) of all the acids under investigation, only **A** releases carbon dioxide when heated,

d) **D** and **E** do not change at higher temperatures,

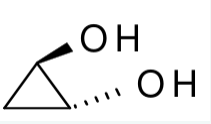
e) 2 moles of diethyl ester of malonic acid when reacted with sodium ethoxide (EtONa), are transformed to sodium salt which by reaction with methylene iodide ($\mathrm{CH_2I_2}$) yields a tetraester $\mathrm{C_{15}H_{24}O_8}$. This new ester gives a tetraester $\mathrm{C_{16}H_{24}O_8}$ in the reaction with 2 moles of sodium ethoxide and 1 mole of methylene iodide. The last mentioned tetraester is transformed by alkaline hydrolysis and subsequent acidification to a tetracarboxylic acid which when heated, gives a mixture of **B** and **E**.

Problems:

3.1 Give formulas corresponding to the letters **A, B, C, D,** and **E**. Mark the group which is above the plane of the cycle

, that under the plane with

For example:



3.2 Express processes a), b), and c) by chemical equations.

Official English text of the problem.

Answers

- **3.1** The assignments are:

Letter	Identity	SMILES
A	Cyclobutane-1,1-dicarboxylic acid	`O=C(O)C1(C(=O)O)CCC1`
B	**cis**-Cyclobutane-1,3-dicarboxylic acid	`O=C(O)[C@H]1C[C@@H](C(=O)O)C1`
C	**cis**-Cyclobutane-1,2-dicarboxylic acid, the **meso** form	`O=C(O)[C@H]1[C@@H](C(=O)O)CC1`
D	**trans**-Cyclobutane-1,2-dicarboxylic acid, a **1:1 racemate** of the $(1R,2R)$ and $(1S,2S)$ enantiomers	`O=C(O)[C@H]1[C@H](C(=O)O)CC1` and `O=C(O)[C@@H]1[C@@H](C(=O)O)CC1`
E	**trans**-Cyclobutane-1,3-dicarboxylic acid	`O=C(O)[C@H]1C[C@H](C(=O)O)C1`

For the requested drawings, number an idealized square cyclobutane ring clockwise:

Letter	Positions of the two carboxyl groups	Wedge/dash representation
A	Both at carbon 1	One solid wedge and one hashed wedge
B	Carbons 1 and 3	Both solid wedges
C	Carbons 1 and 2	Both solid wedges
D	Carbons 1 and 2	One solid wedge and one hashed wedge; show its mirror image alongside it, in equal proportion
E	Carbons 1 and 3	One solid wedge and one hashed wedge

- **3.2** The balanced reactions are:

$$\text{a) C:}\quad \mathrm{C_6H_8O_4} \xrightarrow{\text{mild heating}} \mathrm{C_6H_6O_3 + H_2O}$$

$$\text{b) B:}\quad \mathrm{C_6H_8O_4} \xrightarrow{\text{higher temperature}} \mathrm{C_6H_6O_3 + H_2O}$$

$$\text{c) A:}\quad \mathrm{C_6H_8O_4} \xrightarrow{\Delta} \mathrm{C_5H_8O_2 + CO_2}$$

The organic products, respectively, are:

Process	Product	SMILES
a)	Cyclic anhydride of cis-cyclobutane-1,2-dicarboxylic acid	`O=C1OC(=O)[C@H]2CC[C@@H]12`

Process	Product	SMILES
b)	Cyclic anhydride of cis-cyclobutane-1,3-dicarboxylic acid	`O=C1OC(=O)[C@H]2C[C@@H]1C2`
c)	Cyclobutanecarboxylic acid	`O=C(O)C1CCC1`

The small-molecule products are water, `O`, and carbon dioxide, `O=C=O`.

Solution

3.1 — Identification of the five acids

There are three possible arrangements of two carboxyl groups on a cyclobutane ring: **1,1**, **1,2**, and **1,3**. The 1,2- and 1,3-arrangements each have cis and trans forms. Counting an enantiomeric pair as one racemic form gives the five substances in the question.

Identification of A.
The 1,1-isomer contains two carboxyl groups attached to the same carbon, the characteristic arrangement of a substituted malonic acid. It can lose one carboxyl group as carbon dioxide on heating, replacing that group by hydrogen. Consequently,

A is cyclobutane-1,1-dicarboxylic acid.

The synthesis in observation e) determines which positional isomers **B** and **E** are.

The starting reagents are diethyl malonate, `CCOC(=O)CC(=O)OCC`; sodium ethoxide, `[Na+].CC[O-]`; and diiodomethane (methylene iodide), `C(I)I`. Ethanol, `CCO`, and sodium iodide, `[Na+].[I-]`, are the coproducts of the alkylation steps.

Ethoxide removes an acidic methylene proton from each of two diethyl malonate molecules. Their carbon atoms then replace the two iodides of one diiodomethane molecule, giving the linkage

$$(\mathrm{EtO_2C})_2\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH}(\mathrm{CO_2Et})_2.$$

Here Et denotes an ethyl group. The product is **tetraethyl propane-1,1,3,3-tetracarboxylate**, `CCOC(=O)C(CC(C(=O)OCC)C(=O)OCC)C(=O)OCC`. The balanced net reaction is

$$2\,\mathrm{C_7H_{12}O_4} + 2\,\mathrm{NaOC_2H_5} + \mathrm{CH_2I_2} \longrightarrow \mathrm{C_{15}H_{24}O_8} + 2\,\mathrm{C_2H_5OH} + 2\,\mathrm{NaI}.$$

Its molecular formula agrees with the stated $\mathrm{C_{15}H_{24}O_8}$.

Each terminal malonate carbon still bears one hydrogen. Removing these two hydrogens with two equivalents of ethoxide allows a second diiodomethane molecule to link the same two carbons through another methylene group. This closes a four-membered ring:

- Ring carbons 1 and 3 are the original malonate carbons, each bearing two ester groups.
- Ring carbons 2 and 4 are the two methylene groups introduced from diiodomethane.

The product is therefore **tetraethyl cyclobutane-1,1,3,3-tetracarboxylate**, `CCOC(=O)C1(C(=O)OCC)CC(C(=O)OCC)(C(=O)OCC)C1`:

$$\mathrm{C_{15}H_{24}O_8} + 2\,\mathrm{NaOC_2H_5} + \mathrm{CH_2I_2} \longrightarrow \mathrm{C_{16}H_{24}O_8} + 2\,\mathrm{C_2H_5OH} + 2\,\mathrm{NaI}.$$

Hydrolysis and acidification replace the four ethoxy groups by hydroxyl groups, producing **cyclobutane-1,1,3,3-tetracarboxylic acid**, `O=C(O)C1(C(=O)O)CC(C(=O)O)(C(=O)O)C1`.

The overall ester-to-acid conversion is

$$\mathrm{C_{16}H_{24}O_8} + 4\,\mathrm{H_2O} \xrightarrow[\text{then acidification}]{\text{alkaline hydrolysis}} \mathrm{C_8H_8O_8} + 4\,\mathrm{C_2H_5OH}.$$

Heating removes one carboxyl group from each geminal pair:

$$\mathrm{C_8H_8O_8} \xrightarrow{\Delta} \mathrm{C_6H_8O_4} + 2\,\mathrm{CO_2}.$$

The remaining carboxyl groups are necessarily at **positions 1 and 3**. Their relative orientations can be cis or trans; the stated product mixture therefore establishes that **B and E are the two cyclobutane-1,3-dicarboxylic acids**. No mixture ratio is specified.

Distinguishing B and E.
In the cis-1,3-isomer, both carboxyl groups lie on the same face of the ring and can form an oxygen bridge by dehydration. The constrained bridged anhydride requires higher temperature. The trans-1,3-isomer has the groups on opposite faces and remains unchanged under the stated conditions. Thus,

B is cis-1,3; E is trans-1,3.

Distinguishing C and D.
The remaining substances are the cis- and trans-1,2-isomers. Adjacent carboxyl groups on the same face can readily form a five-membered anhydride ring, so

C is cis-1,2; D is trans-1,2.

The cis-1,2-isomer has opposite configurations at its two stereogenic carbons and is meso. The trans-1,2-isomer has the enantiomeric configurations $(1R, 2R)$ and $(1S, 2S)$, making **D the racemic form**.

The square drawings in the Answers section specify relative configurations. Actual cyclobutane rings are puckered; the wedges and hashes indicate the two ring faces, rather than asserting a perfectly planar conformation.

3.2 — Equations and explanation of the thermal reactions

a) Easy anhydride formation by C

$$\mathrm{C_6H_8O_4} \xrightarrow{\text{mild heating}} \mathrm{C_6H_6O_3} + \mathrm{H_2O}.$$

The reactant is cis-cyclobutane-1,2-dicarboxylic acid; the product is its cyclic anhydride, whose structure is given above. The two adjacent carboxyl groups lie on the same face. Dehydration joins their carbonyl carbons through an oxygen atom, forming a **five-membered anhydride ring fused to the cyclobutane ring**.

b) Anhydride formation by B at higher temperature

$$\mathrm{C_6H_8O_4} \xrightarrow{\text{higher temperature}} \mathrm{C_6H_6O_3} + \mathrm{H_2O}.$$

The reactant is cis-cyclobutane-1,3-dicarboxylic acid; the product is its cyclic anhydride. Here the bridge spans opposite ring carbons. An anhydride-containing circuit is **six-membered**, but it is constrained within a bridged bicyclic framework. This less favorable geometry accounts for the higher temperature required.

Although the two anhydrides have the same molecular formula, their connectivities differ, as their SMILES show.

c) Decarboxylation of A

$$\mathrm{C_6H_8O_4} \xrightarrow{\Delta} \mathrm{C_5H_8O_2} + \mathrm{CO_2}.$$

Cyclobutane-1,1-dicarboxylic acid undergoes malonic-acid-type decarboxylation to give cyclobutanecarboxylic acid. One carboxyl group is replaced by hydrogen, while the cyclobutane ring remains intact. One mole of **A** therefore releases one mole of carbon dioxide.

The solution was checked against the official solution.

Problem 4: Hydrolysis of an optically active ester C6H12O2

An optically active ester (11.6 g) having the summary formula $\mathrm{C_6H_{12}O_2}$, was hydrolysed by heating with an excess of aqueous sodium hydroxide solution. After terminating the hydrolysis the alkaline reaction mixture was several times extracted with ether. The aqueous solution was not optically active. The united ether extracts were dried with anhydrous magnesium sulphate. The ether solution was filtrated, ether was distilled off from it and the residue was redistilled. 7.4 g (100 %) of a liquid boiling at 100 °C was obtained.

Problems:

1. Write the structural formula of the ester.
2. What would be the structure of an ester with identical summary formula, i. e. $\mathrm{C_6H_{12}O_2}$, if the aqueous solution after the alkaline hydrolysis obtained in the above mentioned way, were optically active?
3. Write down equations for the alkaline hydrolysis of both esters with sodium hydroxide solution.

Official English text of the problem.

Answers

The stereochemical SMILES below depict representative enantiomers. Replacing `@` by `@@` gives the corresponding opposite enantiomers, which are equally consistent with the information supplied.

1. **Butan-2-yl ethanoate (sec-butyl acetate)**, `CC(=O)O[C@H](C)CC`:
$$\mathrm{CH_3C(=O)OCH(CH_3)CH_2CH_3}.$$
2. **Methyl 2-methylbutanoate**, `COC(=O)[C@H](C)CC`:
$$\mathrm{CH_3CH_2CH(CH_3)C(=O)OCH_3}.$$
3. The balanced hydrolysis equations are:
$$\mathrm{CH_3C(=O)OCH(CH_3)CH_2CH_3 + NaOH \longrightarrow CH_3COONa + CH_3CH(OH)CH_2CH_3}$$
$$\mathrm{CH_3CH_2CH(CH_3)C(=O)OCH_3 + NaOH \longrightarrow CH_3CH_2CH(CH_3)COONa + CH_3OH}.$$

The first reaction produces **sodium ethanoate**, `[Na+].CC(=O)[O-]`, and **butan-2-ol**, `O[C@H](C)CC`. The second produces **sodium 2-methylbutanoate**, `[Na+].[O-]C(=O)[C@H](C)CC`, and **methanol**, `CO`. The reagent is **sodium hydroxide**, `[Na+].[OH-]`.

Solution

1. Identification of the original ester

Alkaline hydrolysis of an ester produces one mole of alcohol and one mole of sodium carboxylate per mole of ester. The neutral alcohol is recovered from the organic extracts, while the sodium carboxylate remains in the aqueous solution.

Using the usual integer atomic masses, the ester's molar mass is

$$M_{\text{ester}} = \left[6(12) + 12(1) + 2(16)\right]\,\text{g mol}^{-1} = 116\,\text{g mol}^{-1}.$$

Thus,

$$n_{\text{ester}} = \frac{11.6\,\text{g}}{116\,\text{g mol}^{-1}} = 0.100\,\text{mol}.$$

Hydrolysis and alcohol recovery are quantitative, so

$$n_{\text{alcohol}} = 0.100\,\text{mol}, \qquad M_{\text{alcohol}} = \frac{7.4\,\text{g}}{0.100\,\text{mol}} = 74\,\text{g mol}^{-1}.$$

The ester has one degree of unsaturation:

$$\text{DBE} = \frac{2(6) + 2 - 12}{2} = 1.$$

Its carbonyl group accounts for this completely; consequently, the alcohol fragment is saturated and acyclic. A saturated monohydric alcohol has formula $\text{C}_k\text{H}_{2k+2}\text{O}$, giving

$$M_{\text{alcohol}} = (14k + 18)\,\text{g mol}^{-1}.$$

Therefore,

$$k = \frac{74 - 18}{14} = 4,$$

so the alcohol has molecular formula $\text{C}_4\text{H}_{10}\text{O}$.

Four of the ester's six carbon atoms belong to the alcohol fragment, leaving two in the acid fragment. The latter must therefore be the ethanoate group, which is achiral. The ester's optical activity must arise from the four-carbon alcohol fragment.

Among the saturated four-carbon alcohols, only **butan-2-ol**, `O[C@H](C)CC`, is chiral. Its hydroxyl-bearing carbon has four different substituents: hydroxyl, hydrogen, methyl and ethyl. Its boiling point is consistent with the stated $100\,^{\circ}\text{C}$.

The ester is therefore **butan-2-yl ethanoate**, `CC(=O)O[C@H](C)CC`. Hydrolysis leaves achiral sodium ethanoate in the aqueous phase, explaining its optical inactivity.

2. Identification when the aqueous solution is optically active

After extraction of the alcohol, optical activity in the aqueous solution requires a chiral, nonracemic carboxylate.

The smallest saturated, acyclic monocarboxylic acid capable of having a stereogenic carbon is **2-methylbutanoic acid**, `O=C(O)[C@H](C)CC`:

$$\mathrm{CH_3CH_2CH(CH_3)COOH}.$$

Its stereogenic carbon bears hydrogen, methyl, ethyl and carboxyl groups, all different. This acid fragment contains five carbon atoms.

Since the ester contains six carbon atoms altogether, only one remains for the alcohol-derived group. That group must be methyl. The required ester is consequently **methyl 2-methylbutanoate**, `COC(=O)[C@H](C)CC`.

Its hydrolysis produces optically active sodium 2-methylbutanoate in the aqueous phase and achiral methanol as the alcohol.

3. Hydrolysis equations and stereochemical outcome

On heating with aqueous sodium hydroxide, the first ester undergoes:

$$\boxed{\mathrm{CH_3C(=O)OCH(CH_3)CH_2CH_3 + NaOH \longrightarrow CH_3COONa + CH_3CH(OH)CH_2CH_3}}$$

The ester's acyl–oxygen bond is cleaved; the bond between oxygen and the stereogenic carbon remains intact. Thus, the stereogenic centre is retained in butan-2-ol.

For the second ester:

$$\boxed{\mathrm{CH_3CH_2CH(CH_3)C(=O)OCH_3 + NaOH \longrightarrow CH_3CH_2CH(CH_3)COONa + CH_3OH}}$$

Here the stereogenic centre remains in the acid-derived product, sodium 2-methylbutanoate. Both equations consume one mole of sodium hydroxide per mole of ester and are balanced in atoms and charge.

The solution was checked against the official solution.

Problem 5: Solubility of two copper(I) salts in a buffer

Two copper(I) salts of the organic acids HA and HB, slightly soluble in water, form a saturated solution in buffer of a given pH.

Problems:

5.1 What will be the concentration of $\mathrm{Cu^+}$ cations in the solution if the solubility products of the two salts are $K_\mathrm{s}(\mathrm{CuA})$ and $K_\mathrm{s}(\mathrm{CuB})$ and the ionisation constants of the acids are $K_\mathrm{a}(\mathrm{HA})$ and $K_\mathrm{a}(\mathrm{HB})$?

Official English text of the problem.

Answers

- **5.1**

$$\boxed{[\mathrm{Cu^+}] = \sqrt{K_\mathrm{s}(\mathrm{CuA})\left(1 + \frac{h}{K_\mathrm{a}(\mathrm{HA})}\right) + K_\mathrm{s}(\mathrm{CuB})\left(1 + \frac{h}{K_\mathrm{a}(\mathrm{HB})}\right)}}$$

  Here $h = [\mathrm{H^+}] = 10^{-\mathrm{pH}}\,\mathrm{mol\,L^{-1}}$ in the ideal-solution approximation, with equilibrium constants expressed in concentration form.

Solution

5.1

Let $c = [\mathrm{Cu^+}]$, the concentration of the copper(I) ion (`[Cu+]`), and $h = [\mathrm{H^+}]$, the concentration of the hydrogen ion, or proton (`[H+]`).

The structures of the organic acids HA and HB, their conjugate-base anions $\mathrm{A^-}$ and $\mathrm{B^-}$, and their salts are unspecified, so unique names and SMILES cannot be assigned to them.

We use the intended equilibrium model: the solution is saturated with respect to both salts, the buffer fixes the pH without supplying either acid residue, and copper remains as free $\mathrm{Cu^+}$.

The dissolution equilibria are

$$\mathrm{CuA\,(s)} \rightleftharpoons \mathrm{Cu^+\,(aq)} + \mathrm{A^-\,(aq)}, \qquad \mathrm{CuB\,(s)} \rightleftharpoons \mathrm{Cu^+\,(aq)} + \mathrm{B^-\,(aq)}.$$

Consequently,

$$K_\mathrm{s}(\mathrm{CuA}) = c[\mathrm{A^-}], \qquad K_\mathrm{s}(\mathrm{CuB}) = c[\mathrm{B^-}],$$

and hence

$$[\mathrm{A^-}] = \frac{K_\mathrm{s}(\mathrm{CuA})}{c}, \qquad [\mathrm{B^-}] = \frac{K_\mathrm{s}(\mathrm{CuB})}{c}.$$

The acid dissociation equilibria are

$$\mathrm{HA\,(aq)} \rightleftharpoons \mathrm{H^+\,(aq)} + \mathrm{A^-\,(aq)}, \qquad \mathrm{HB\,(aq)} \rightleftharpoons \mathrm{H^+\,(aq)} + \mathrm{B^-\,(aq)}.$$

Their constants give

$$[\mathrm{HA}] = \frac{h[\mathrm{A^-}]}{K_\mathrm{a}(\mathrm{HA})}, \qquad [\mathrm{HB}] = \frac{h[\mathrm{B^-}]}{K_\mathrm{a}(\mathrm{HB})}.$$

Every mole of either salt dissolved supplies one mole of copper and one mole of the corresponding acid residue. Protonation preserves the total amount of each residue. Thus the material balance is

$$c = [\mathrm{A^-}] + [\mathrm{HA}] + [\mathrm{B^-}] + [\mathrm{HB}].$$

Substituting the equilibrium expressions,

$$c = \frac{K_\mathrm{s}(\mathrm{CuA})}{c}\left(1 + \frac{h}{K_\mathrm{a}(\mathrm{HA})}\right) + \frac{K_\mathrm{s}(\mathrm{CuB})}{c}\left(1 + \frac{h}{K_\mathrm{a}(\mathrm{HB})}\right).$$

Multiplying by c and taking the positive square root yields

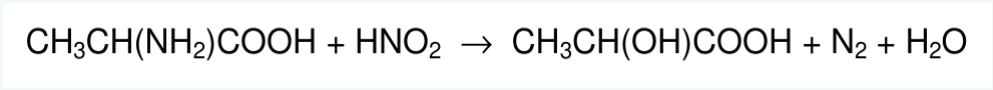
$$\boxed{[\mathrm{Cu^+}] = \left[K_\mathrm{s}(\mathrm{CuA})\left(1 + \frac{h}{K_\mathrm{a}(\mathrm{HA})}\right) + K_\mathrm{s}(\mathrm{CuB})\left(1 + \frac{h}{K_\mathrm{a}(\mathrm{HB})}\right)\right]^{1/2}}.$$

In concentration form, h/K_a is dimensionless and each K_s has units $\mathrm{mol^2\,L^{-2}}$, giving the required concentration in $\mathrm{mol\,L^{-1}}$. No numerical values are supplied.

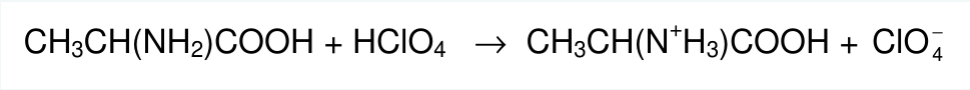
The solution was checked against the official solution.

Problem 6: Determination of glycine

Amino acids can be determined by measuring the volume of nitrogen released in their reaction with nitrous acid (Van Slyke's method), for example:



Another method consists of the reaction of amino acids with a volumetric solution of perchloric acid, for example:



The excess of the perchloric acid is determined then by titration with a volumetric solution of sodium acetate (carried out in a non-aqueous solution).

50.0 cm³ of a 0.100-normal solution of perchloric acid were added to a sample of glycine in glacial acetic acid. The excess of the perchloric acid was determined after the reaction by titration with 0.150-normal volumetric solution of sodium acetate. The consumption was 16.0 cm³.

Problem:

6.1 What would be the volume of the nitrogen released at a pressure of 102 658 Pa and a temperature of 20 °C when assumed that the same quantity of sample were analysed by the Van Slyke's method?

Official English text of the problem.

Answers

- **6.1** The volume of nitrogen, `N#N`, is $\boxed{61.7\,\mathrm{cm^3}}$ at the stated pressure and temperature.

Solution

6.1

Glycine, `NCC(=O)O`, consumes one mole of perchloric acid per mole, forming the glycinium ion, `[NH3+]CC(=O)O`:

$$\mathrm{NH_2CH_2COOH + HClO_4 \longrightarrow [NH_3CH_2COOH]^+ + {ClO_4}^-}.$$

Here perchloric acid is `OCl(=O)(=O)=O`, and the perchlorate ion is `[O-]Cl(=O)(=O)=O`.

The remaining perchloric acid reacts with sodium acetate, `CC(=O)[O-].[Na+]`, in a 1:1 molar ratio:

$$\mathrm{HClO_4 + CH_3COONa \longrightarrow CH_3COOH + NaClO_4}.$$

The products are acetic acid, `CC(=O)O`, and sodium perchlorate, `[Na+].[O-]Cl(=O)(=O)=O`.

Normality gives the concentration in equivalents per litre. The amounts of acid initially added and remaining after reaction with glycine are therefore

$$\begin{aligned} q_{\text{added}} &= (0.100\,\text{eq}\,\text{L}^{-1})(50.0\times10^{-3}\,\text{L}) = 5.00\times10^{-3}\,\text{eq},\\ q_{\text{remaining}} &= (0.150\,\text{eq}\,\text{L}^{-1})(16.0\times10^{-3}\,\text{L}) = 2.40\times10^{-3}\,\text{eq}. \end{aligned}$$

Since each mole of glycine consumes one equivalent,

$$n_{\text{glycine}} = \frac{(5.00-2.40)\times10^{-3}\,\text{eq}}{1\,\text{eq}\,\text{mol}^{-1}} = 2.60\times10^{-3}\,\text{mol}.$$

In Van Slyke's method, glycine reacts with nitrous acid, `ON=O`, to form glycolic acid (2-hydroxyacetic acid), `OCC(=O)O`, nitrogen, `N#N`, and water, `O`:

$$\mathrm{NH_2CH_2COOH + HNO_2 \longrightarrow HOCH_2COOH + N_2 + H_2O}.$$

Thus, one mole of glycine releases one mole of nitrogen gas; the second nitrogen atom comes from nitrous acid:

$$n(\mathrm{N_2}) = n_{\text{glycine}} = 2.60\times10^{-3}\,\text{mol}.$$

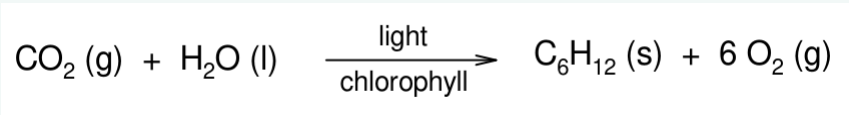
Treating nitrogen as an ideal gas, with $T = 20 + 273.15 = 293.15\,\text{K}$,

$$\begin{aligned} V &= \frac{nRT}{p}\\ &= \frac{(2.60\times10^{-3}\,\text{mol})(8.31446\,\text{Pa}\,\text{m}^3\,\text{mol}^{-1}\,\text{K}^{-1})(293.15\,\text{K})}{102\,658\,\text{Pa}}\\ &= 6.1731\times10^{-5}\,\text{m}^3 = \boxed{61.7\,\text{cm}^3}. \end{aligned}$$

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

Problem 7: Photosynthesis reversed in a galvanic cell

Photosynthesis by be summarised by the overall equation:



for which values of ΔH and ΔS at $25\,^\circ\text{C}$ are as follows:

$$\Delta H = 2.816\times10^6\,\text{J}, \qquad \Delta S = -182\,\text{J}\,\text{K}^{-1} \quad \text{or}$$

$\Delta H = 2.816\times10^6\,\text{J}\,\text{mol}^{-1}, \quad \Delta S = -182\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$ if ΔH and ΔS values are related to one mole of reaction changes.

Imagine that there have been devised electrodes that would allow selective reduction of oxygen to water and oxidation of glucose to carbon dioxide in a galvanic cell, i. e a reverse process when compared with that of the photosynthetic reaction.

Problems:

7.1 What will be the electromotive force of the cell in which light energy would be transformed to electric energy by means of the photosynthetic reaction?

Note: In the envelope you can find the relation between the electromotive force and the change of free enthalpy of the reaction. (Attention: If you open the envelope you lose some points.)

7.2 In case we would want to quantify the symbol "light" in the equation of photosynthesis, we would ask: how many moles of photons with wavelength for example $500\,\mathrm{nm}$ take part in the above reaction? Calculate.

7.3 Calculate, what would be the electric power of a square swimming pool with a side of $10\,\mathrm{m}$ containing green algae capable of the photosynthetic reaction if under average illumination a current of $1\,\mathrm{mA}$ can be expected from the area of $1\,\mathrm{cm}^2$.

Official English text of the problem.

Answers

- **7.1:** $\boxed{E = 1.24\,\mathrm{V}}$.
- **7.2:** $\boxed{\text{Approximately } 12\,\mathrm{mol} \text{ of photons per mole of glucose}}$. The ideal free-energy estimate is $12.00\,\mathrm{mol}$; an enthalpy-only estimate gives $11.77\,\mathrm{mol}$.
- **7.3:** $\boxed{P = 1.24 \times 10^3\,\mathrm{W} = 1.24\,\mathrm{kW}}$, assuming the cell supplies the calculated voltage at the stated current.

Solution

The prose identifies the product as glucose. Correcting the apparent errors in the printed scheme, the balanced photosynthetic reaction is

$$6\,\mathrm{CO_2\,(g)} + 6\,\mathrm{H_2O\,(l)} \xrightarrow[\text{chlorophyll}]{\text{light}} \mathrm{C_6H_{12}O_6\,(s)} + 6\,\mathrm{O_2\,(g)}.$$

The supplied thermodynamic quantities therefore refer to the formation of one mole of glucose.

The species used below are glucose, represented as open-chain D-glucose by `O=C[C@H](O)[C@@H](O)[C@H](O)[C@H](O)CO`; carbon dioxide `O=C=O`; water `O`; dioxygen `O=O`; and the hydrogen ion (proton) `[H+]`. The open-chain glucose SMILES specifies its carbon stereochemistry, but does not describe its cyclic solid-state form or crystal structure.

7.1 — Electromotive force

The galvanic cell carries out the reverse reaction:

$$\mathrm{C_6H_{12}O_6\,(s)} + 6\,\mathrm{O_2\,(g)} \longrightarrow 6\,\mathrm{CO_2\,(g)} + 6\,\mathrm{H_2O\,(l)}.$$

Written in acidic form for balancing, the electrode reactions are:

$$\begin{aligned}\text{Anode:}\quad & \mathrm{C_6H_{12}O_6\,(s) + 6\,H_2O\,(l) \longrightarrow 6\,CO_2\,(g) + 24\,H^+\,(aq) + 24\,e^-},\\ \text{Cathode:}\quad & \mathrm{6\,O_2\,(g) + 24\,H^+\,(aq) + 24\,e^- \longrightarrow 12\,H_2O\,(l)}.\end{aligned}$$

Thus $n = 24$ moles of electrons are transferred per mole of glucose. Equivalently, the six carbon atoms increase their mean oxidation number from 0 in glucose to $+4$ in carbon dioxide, releasing $6 \times 4 = 24$ electrons.

At $T = 298.15\,\mathrm{K}$, the Gibbs energy change for photosynthesis is

$$\begin{aligned}\Delta G_{\mathrm{photo}} &= \Delta H_{\mathrm{photo}} - T\Delta S_{\mathrm{photo}}\\ &= 2.816 \times 10^{6} - (298.15)(-182)\\ &= 2.8702633 \times 10^{6}\,\mathrm{J\,mol^{-1}}.\end{aligned}$$

Reversing the reaction changes its sign:

$$\Delta G_{\mathrm{cell}} = -2.8702633 \times 10^{6}\,\mathrm{J\,mol^{-1}}.$$

The maximum electrical work gives the relation

$$\Delta G_{\mathrm{cell}} = -nFE.$$

Using $F = 96485\,\mathrm{C\,mol^{-1}}$,

$$E = \frac{2.8702633 \times 10^{6}\,\mathrm{J\,mol^{-1}}}{24(96485\,\mathrm{C\,mol^{-1}})} = 1.2395\,\mathrm{J\,C^{-1}}.$$

Therefore,

$$\boxed{E = 1.24\,\mathrm{V}}.$$

7.2 — Amount of photons

The energy of a photon is

$$\varepsilon_\gamma = \frac{hc}{\lambda}.$$

Using $h = 6.62607 \times 10^{-34}\,\mathrm{J\,s}$, $c = 2.99792 \times 10^{8}\,\mathrm{m\,s^{-1}}$, and $\lambda = 500 \times 10^{-9}\,\mathrm{m}$,

$$\varepsilon_\gamma = \frac{(6.62607 \times 10^{-34})(2.99792 \times 10^{8})}{500 \times 10^{-9}} = 3.97289 \times 10^{-19}\,\mathrm{J}.$$

With $N_{\mathrm{A}} = 6.02214 \times 10^{23}\,\mathrm{mol^{-1}}$, one mole of these photons carries

$$E_{\gamma,\mathrm{m}} = N_{\mathrm{A}}\varepsilon_\gamma = 2.39253 \times 10^{5}\,\mathrm{J\,mol^{-1}} = 239.253\,\mathrm{kJ\,mol^{-1}}.$$

If photon energy is ideally converted into the chemical free energy required for photosynthesis, the amount needed to form one mole of glucose is

$$n_\gamma = \frac{2.8702633 \times 10^{6}\,\mathrm{J}}{2.39253 \times 10^{5}\,\mathrm{J\,mol^{-1}}} = 11.9968\,\mathrm{mol}.$$

Hence,

$$\boxed{n_\gamma \approx 12.0\,\mathrm{mol}\quad \text{per mole of glucose}}.$$

If the question instead intends a simple comparison with the reaction enthalpy, it gives

$$n_{\gamma,H} = \frac{2.816 \times 10^{6}\,\mathrm{J}}{2.39253 \times 10^{5}\,\mathrm{J\,mol^{-1}}} = 11.77\,\mathrm{mol},$$

which also rounds to approximately $12\,\mathrm{mol}$. The free-energy calculation includes the entropy contribution relevant to reversible electrical work. These energy estimates do not determine the actual biological photon requirement.

7.3 — Electric power of the pool

The illuminated area is

$$A = (10\,\mathrm{m})^2 = 100\,\mathrm{m}^2 = 1.00 \times 10^6\,\mathrm{cm}^2.$$

At the specified current density,

$$I = \left(1.00 \times 10^{-3}\,\mathrm{A\,cm^{-2}}\right)\left(1.00 \times 10^6\,\mathrm{cm}^2\right) = 1.00 \times 10^3\,\mathrm{A}.$$

Assuming uniform illumination and neglecting voltage losses,

$$P = EI = (1.2395\,\mathrm{V})(1.00 \times 10^3\,\mathrm{A}) = 1.2395 \times 10^3\,\mathrm{W}.$$

Thus,

$$\boxed{P \approx 1.24\,\mathrm{kW}}.$$

The solution was checked against the official solution.

Problem 8: Carbon monoxide and haemoglobin

Among other factors, deterioration of the environment is manifested also by air pollution with carbon monoxide. Its most powerful source are combustion engines. The toxicity of carbon monoxide is caused by the fact that it forms with the blood dye - haemoglobin (Hb), the compound carbonyl haemoglobin (HbCO):

$$\mathrm{Hb} + \mathrm{CO} \rightarrow \mathrm{HbCO}$$

The chemical bond in carbonyl haemoglobin is about 200 times stronger than that in oxyhaemoglobin ($\mathrm{HbO_2}$) originating under common conditions. Consequently, haemoglobin cannot be used in oxygen transfer. The lack of oxygen starts to be felt from 50 ppm carbon monoxide in the air, i. e. 10 % carbonyl haemoglobin in blood.

Air oxygen dissolves in blood in the lungs and its concentration under common conditions is kept at $1.6 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}$ by breathing. The concentration of haemoglobin in the blood of lung capillaries is also constant and is equal to $8 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}$

Problems:

8.1 Calculate the rate of oxyhaemoglobin formation if the rate constant is $k = 2.1 \times 10^6\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ (at $37\,^\circ\mathrm{C}$ – normal body temperature).

8.2 In some cases (carbon monoxide poisoning) an increase of the rate of oxyhaemoglobin formation up to $1.1 \times 10^{-4}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$ is needed.

a) Calculate the required concentration of oxygen assuming that the concentration of haemoglobin in blood is constant.

b) Suggest of practical solution on the assumption that the concentration of oxygen in blood is proportional to the pressure of oxygen entering the lungs.

Official English text of the problem.

Answers

- **8.1:** $v = 2.7 \times 10^{-5}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$.
- **8.2(a):** $[\mathrm{O_2}] = 6.5 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}$.
- **8.2(b):** Increase the inhaled oxygen **partial pressure** to approximately 4.1 times its normal value, using oxygen-enriched gas or a pressure chamber. With unchanged air composition, the required absolute total pressure is 4.1 times normal.

Solution

The small molecules involved are oxygen (dioxygen), $\mathrm{O_2}$, SMILES `O=O`, and carbon monoxide, CO, SMILES `[C-]#[O+]`. Haemoglobin (Hb), oxyhaemoglobin ($\mathrm{HbO_2}$), and carbonyl haemoglobin (HbCO) are represented by the problem's simplified protein-binding notation. Their full molecular structures are not specified, so unique complete SMILES cannot be supplied for these protein species.

8.1

In the simplified model used by the problem, oxygen associates with haemoglobin:

$$\mathrm{Hb} + \mathrm{O_2} \longrightarrow \mathrm{HbO_2}.$$

The bimolecular formation rate is

$$v = k[\mathrm{Hb}][\mathrm{O_2}].$$

Substituting the given values,

$$\begin{aligned} v &= \left(2.1 \times 10^{6}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}\right)\left(8 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}\right)\left(1.6 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}\right) \\ &= 2.688 \times 10^{-5}\,\mathrm{mol\,dm^{-3}\,s^{-1}}. \end{aligned}$$

Thus,

$$\boxed{v \approx 2.7 \times 10^{-5}\,\mathrm{mol\,dm^{-3}\,s^{-1}}}.$$

8.2(a)

At the same temperature, k is unchanged. With haemoglobin concentration held constant, rearranging the rate law gives

$$[\mathrm{O_2}]_{\text{required}} = \frac{v_{\text{required}}}{k[\mathrm{Hb}]}.$$

Therefore,

$$\begin{aligned} {}_{\text{required}} &= \frac{1.1 \times 10^{-4}\,\mathrm{mol\,dm^{-3}\,s^{-1}}}{\left(2.1 \times 10^{6}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}\right)\left(8 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}\right)} \\ &= 6.5476 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}. \end{aligned}$$

Hence,

$$\boxed{[\mathrm{O_2}]_{\text{required}} \approx 6.5 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}}.$$

8.2(b)

By the stipulated proportionality between dissolved oxygen concentration and inhaled oxygen partial pressure,

$$\frac{p_{\mathrm{O_2,required}}}{p_{\mathrm{O_2,normal}}} = \frac{[\mathrm{O_2}]_{\text{required}}}{[\mathrm{O_2}]_{\text{normal}}} = \frac{6.5476 \times 10^{-6}}{1.6 \times 10^{-6}} \approx 4.1.$$

Thus,

$$\boxed{p_{\mathrm{O_2,required}} \approx 4.1\, p_{\mathrm{O_2,normal}}}.$$

A practical solution is to administer oxygen-enriched inhaled gas, increasing its oxygen partial pressure. Alternatively, a pressure chamber can increase the pressure of inhaled air. Since

$$p_{\mathrm{O_2}} = x_{\mathrm{O_2}} P,$$

where $x_{\mathrm{O_2}}$ is the oxygen mole fraction and P is the absolute total pressure, using air of unchanged composition requires $P_{\text{required}} \approx 4.1 P_{\text{normal}}$.

The solution was checked against the official solution.