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Problem 1: Peroxo compounds

1.1 Explain by means of generally used international symbols and formulas which compounds are named as peroxo compounds. Write summary formulas for six of them.

1.2 Write chemical equations for two methods of quantitative determination of the content of peroxide in calcium(II) peroxide.

1.3 By means of chemical equations express the following chemical reactions:

a) $[\mathrm{Cr(H_2O)_6}]\mathrm{Cl_3}$ dissolved in water, is mixed with an excess of sodium hydroxide solution. A clear green solution is formed. The colour of the solution changes to yellow when an aqueous hydrogen peroxide solution is added.

b) If an aqueous solution of a violet manganese compound is mixed with a hydrogen peroxide solution, the resulting solution is decolourised and a gas is released from it.

Official English text of the problem.

Answers

- **1.1** Peroxo compounds contain an oxygen–oxygen single-bonded peroxide group, formally $\mathrm{{O_2}^{2-}}$, with oxygen in oxidation state -1. Six examples are $\mathrm{H_2O_2}$, $\mathrm{Na_2O_2}$, $\mathrm{CaO_2}$, $\mathrm{BaO_2}$, $\mathrm{H_2SO_5}$, and $\mathrm{H_2S_2O_8}$. Their names and SMILES are given below.
- **1.2** Release hydrogen peroxide by acidification:

  $$\mathrm{CaO_2 + 2\,H^+ \longrightarrow Ca^{2+} + H_2O_2}.$$

  Determine it by **permanganometry**:

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

  or by **iodometry**, followed by thiosulfate titration:

  $$\mathrm{H_2O_2 + 2\,I^- + 2\,H^+ \longrightarrow I_2 + 2\,H_2O},$$
  $$\mathrm{I_2 + 2\,{S_2O_3}^{2-} \longrightarrow 2\,I^- + {S_4O_6}^{2-}}.$$
- **1.3(a)** Using hexahydroxidochromate(III) to represent the dissolved green chromium(III) species:

  $$\mathrm{[Cr(H_2O)_6]^{3+} + 6\,OH^- \longrightarrow [Cr(OH)_6]^{3-} + 6\,H_2O},$$
  $$\mathrm{2\,[Cr(OH)_6]^{3-} + 3\,H_2O_2 \longrightarrow 2\,{CrO_4}^{2-} + 2\,OH^- + 8\,H_2O}.$$

  The yellow product is chromate(VI).

- **1.3(b)** The violet species is permanganate. In an acidic medium, hydrogen peroxide reduces it to nearly colourless manganese(II), releasing dioxygen:

$$2\,\mathrm{MnO_4^-} + 5\,\mathrm{H_2O_2} + 6\,\mathrm{H^+} \longrightarrow 2\,\mathrm{Mn^{2+}} + 5\,\mathrm{O_2}\uparrow + 8\,\mathrm{H_2O}.$$

Solution

1.1 — Meaning and examples of peroxo compounds

The defining structural feature is an **oxygen–oxygen single bond** belonging to a peroxide group. In the peroxide ion, $\mathrm{O_2^{2-}}$, SMILES `[O-][O-]`, each oxygen has oxidation state -1. The same oxidation state occurs for the two peroxide oxygens in hydrogen peroxide and in covalently bound peroxo groups.

Thus, peroxo compounds include both ionic peroxides and molecular compounds containing a peroxide linkage.

Compound	Summary formula	SMILES
Hydrogen peroxide	$\mathrm{H_2O_2}$	`OO`
Sodium peroxide	$\mathrm{Na_2O_2}$	`[Na+].[Na+].[O-][O-]`
Calcium(II) peroxide	$\mathrm{CaO_2}$	`[Ca+2].[O-][O-]`
Barium(II) peroxide	$\mathrm{BaO_2}$	`[Ba+2].[O-][O-]`
Peroxomonosulfuric acid	$\mathrm{H_2SO_5}$	`OOS(=O)(=O)O`
Peroxodisulfuric acid	$\mathrm{H_2S_2O_8}$	`OS(=O)(=O)OOS(=O)(=O)O`

The last two structures contain, respectively, the linkages $\mathrm{S-O-O-H}$ and $\mathrm{S-O-O-S}$. Only their peroxide oxygens have oxidation state -1; their other oxygens have oxidation state -2.

For ionic solids, dot-separated SMILES specify the ions and formula-unit stoichiometry; they do not describe the crystal lattice.

1.2 — Two quantitative peroxide assays

Acid converts the peroxide group in calcium peroxide into hydrogen peroxide:

$$\mathrm{CaO_2} + 2\,\mathrm{H^+} \longrightarrow \mathrm{Ca^{2+}} + \mathrm{H_2O_2}.$$

Consequently, one mole of calcium peroxide supplies one mole of hydrogen peroxide for either assay.

Method 1: acidic permanganate titration

Hydrogen peroxide acts as a reducing agent. Its oxygen is oxidized from -1 to 0, while manganese is reduced from $+7$ to $+2$.

The half-equations are

$$\mathrm{H_2O_2} \longrightarrow \mathrm{O_2} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-},$$
$$\mathrm{MnO_4^-} + 8\,\mathrm{H^+} + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}} + 4\,\mathrm{H_2O}.$$

Multiplying the first by five and the second by two, then cancelling electrons and excess hydrogen ions, gives

$$\boxed{2\,\mathrm{MnO_4^-} + 5\,\mathrm{H_2O_2} + 6\,\mathrm{H^+} \longrightarrow 2\,\mathrm{Mn^{2+}} + 5\,\mathrm{O_2} + 8\,\mathrm{H_2O}}.$$

A standardized permanganate solution is added until a faint pink colour persists, indicating a slight excess of permanganate.

If its concentration is c_{Mn} and the volume consumed is V_{Mn},

$$\boxed{n_{\mathrm{peroxide}} = \frac{5}{2} c_{\mathrm{Mn}} V_{\mathrm{Mn}}}.$$

Method 2: iodometry

Here hydrogen peroxide acts as an oxidizing agent. In acid solution it oxidizes iodide to iodine:

$$\boxed{\mathrm{H_2O_2 + 2\,I^- + 2\,H^+ \longrightarrow I_2 + 2\,H_2O}}.$$

The liberated iodine is titrated with standardized thiosulfate solution:

$$\boxed{\mathrm{I_2 + 2\,{S_2O_3}^{2-} \longrightarrow 2\,I^- + {S_4O_6}^{2-}}}.$$

One mole of peroxide therefore liberates one mole of iodine and consumes two moles of thiosulfate. For thiosulfate concentration c_{thio} and consumed volume V_{thio},

$$\boxed{n_{\mathrm{peroxide}} = \frac{1}{2} c_{\mathrm{thio}} V_{\mathrm{thio}}}.$$

In both expressions, using c in $\mathrm{mol\,L^{-1}}$ and V in L gives the peroxide amount in mol. No numerical titration data are supplied.

The additional molecular and ionic species used in these assays are:

Species	Name	SMILES
$\mathrm{H^+}$	Hydrogen ion, proton	`[H+]`
$\mathrm{Ca^{2+}}$	Calcium(II) ion	`[Ca+2]`
$\mathrm{H_2O}$	Water	`O`
$\mathrm{O_2}$	Dioxygen	`O=O`
$\mathrm{MnO_4^-}$	Permanganate ion	`[O-][Mn](=O)(=O)=O`
$\mathrm{Mn^{2+}}$	Manganese(II) ion	`[Mn+2]`
$\mathrm{I^-}$	Iodide ion	`[I-]`
$\mathrm{I_2}$	Iodine	`II`
$\mathrm{{S_2O_3}^{2-}}$	Thiosulfate ion	`[O-]S(=O)(=O)[S-]`
$\mathrm{{S_4O_6}^{2-}}$	Tetrathionate ion	`[O-]S(=O)(=O)SSS(=O)(=O)[O-]`

Permanganate is tetrahedral. Its SMILES gives one formal bonding representation, without describing resonance delocalization. The dioxygen SMILES does not encode its triplet ground state.

1.3(a) — Chromium(III) in excess alkali, followed by oxidation

The starting salt supplies the hexaaquachromium(III) ion. Addition of hydroxide first produces chromium(III) hydroxide:

$$\mathrm{[Cr(H_2O)_6]^{3+} + 3\,OH^- \longrightarrow Cr(OH)_3(s) + 6\,H_2O}.$$

Chromium(III) hydroxide is amphoteric. In excess hydroxide it dissolves to form a green hydroxo complex, conventionally represented here as hexahydroxidochromate(III):

$$\mathrm{Cr(OH)_3(s) + 3\,OH^- \longrightarrow [Cr(OH)_6]^{3-}}.$$

Adding these equations gives

$$\boxed{[\mathrm{Cr(H_2O)_6}]^{3+} + 6\,\mathrm{OH^-} \longrightarrow [\mathrm{Cr(OH)_6}]^{3-} + 6\,\mathrm{H_2O}}.$$

Hydrogen peroxide then oxidizes chromium from $+3$ to $+6$. In alkaline solution the chromium(VI) product is yellow chromate.

The oxidation half-equation is

$$[\mathrm{Cr(OH)_6}]^{3-} + 2\,\mathrm{OH^-} \longrightarrow \mathrm{CrO_4}^{2-} + 4\,\mathrm{H_2O} + 3\,\mathrm{e^-},$$

and the peroxide reduction half-equation is

$$\mathrm{H_2O_2} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{OH^-}.$$

Two chromium centres release six electrons, which are accepted by three hydrogen peroxide molecules. Combining the half-equations gives

$$\boxed{2\,[\mathrm{Cr(OH)_6}]^{3-} + 3\,\mathrm{H_2O_2} \longrightarrow 2\,\mathrm{CrO_4}^{2-} + 2\,\mathrm{OH^-} + 8\,\mathrm{H_2O}}.$$

The green-to-yellow change therefore indicates oxidation of chromium(III) to chromium(VI).

Species	Name	SMILES
$\mathrm{OH^-}$	Hydroxide ion	`[OH-]`
$[\mathrm{Cr(H_2O)_6}]^{3+}$	Hexaaquachromium(III) ion	`[Cr+3](<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])<-[OH2]`
$\mathrm{Cr(OH)_3}$	Chromium(III) hydroxide	`[Cr+3].[OH-].[OH-].[OH-]`
$[\mathrm{Cr(OH)_6}]^{3-}$	Hexahydroxidochromate(III) ion	`[Cr+3](<-[OH-])(<-[OH-])(<-[OH-])(<-[OH-])(<-[OH-])<-[OH-]`
$\mathrm{CrO_4}^{2-}$	Chromate(VI) ion	`[O-][Cr](=O)(=O)[O-]`

The donor-arrow SMILES describe oxygen-to-chromium coordination. Both six-coordinate chromium(III) complexes are represented as **octahedral**; chromate is **tetrahedral**. The disconnected chromium hydroxide SMILES is a stoichiometric representation of the solid, not a discrete molecular structure.

1.3(b) — Reduction of permanganate by hydrogen peroxide

The characteristic violet colour identifies the permanganate ion, $\mathrm{MnO_4^-}$. Its reduction to dilute, nearly colourless manganese(II) accounts for the decolourisation.

Hydrogen peroxide is the reducing agent and is oxidized to dioxygen, explaining the gas evolution. The half-equations are the same as those used in the permanganate assay in 1.2, giving

$$\boxed{2\,\mathrm{MnO_4^-} + 5\,\mathrm{H_2O_2} + 6\,\mathrm{H^+} \longrightarrow 2\,\mathrm{Mn^{2+}} + 5\,\mathrm{O_2}\uparrow + 8\,\mathrm{H_2O}}.$$

Thus, each two moles of permanganate consume five moles of hydrogen peroxide and produce five moles of dioxygen. Sufficient acidity is required for this equation to describe the stated outcome.

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 2: Formula of a crystallohydrate

> A sample of 2.3793 g of crystallohydrate of the type $\mathrm{M}_x\mathrm{A}_y \cdot z\,\mathrm{H_2O}$, where M is a metal, reacted with an excess of $\mathrm{SOCl_2}$. Gaseous products formed by the reaction were introduced into a barium chloride solution containing hydrochloric acid and hydrogen peroxide. Small quantities of $\mathrm{SOCl_2}$

carried by the gaseous products were removed by freezing out. The mass of the precipitate that is deposited from the solution, was 14.004 g. It was found to contain 13.74 mass % of sulphur.

In another experiment, 1.1896 g of the initial substance were dissolved in water and the solution was diluted to a volume of 100 cm^3. One fifth of this solution required to react with 10 cm^3 of a 0.2-molar $\mathrm{AgNO_3}$ solution. The mass of the precipitate formed by the titration was 0.28664 g. (The end point of the titration was determined by the conductometric method.)

Problems:

2.1 Calculate the summary formula of the crystallohydrate. (Use the relative atomic mass values given in the attached Periodical Table of Elements.)

2.2 If you know that the sample can contain a maximum of seven moles of water per one mole of the crystallohydrate, give an example of another possible hydrate that cannot come into consideration due to the given limitation.

Official English text of the problem.

Answers

- **2.1** $\boxed{\mathrm{CoCl_2 \cdot 6\,H_2O}}$, **cobalt(II) chloride hexahydrate**. Compositional SMILES: `[Co+2].[Cl-].[Cl-].O.O.O.O.O.O`.
- **2.2** A formal different-metal candidate is $\boxed{\mathrm{SnCl_4 \cdot 12\,H_2O}}$, **tin(IV) chloride dodecahydrate**, which exceeds the limit because $12 > 7$. Compositional SMILES: `[Sn+4].[Cl-].[Cl-].[Cl-].[Cl-].O.O.O.O.O.O.O.O.O.O.O.O`. **However, this is only a near-candidate: it does not match all the numerical data at their stated precision.** That discrepancy is quantified below.

These disconnected SMILES express composition; they do not specify metal coordination, water positions, or crystal structure.

Solution

2.1 — Identification of the anion

The amount of silver nitrate in the titration is

$$n(\mathrm{AgNO_3}) = (0.2\ \mathrm{mol\,dm^{-3}})(0.010\ \mathrm{dm^3}) = 0.0020\ \mathrm{mol}.$$

Silver nitrate, `[Ag+].[O-][N+](=O)[O-]`, supplies silver(I) ions, `[Ag+]`. The precipitate mass per mole of silver supplied is

$$\frac{0.28664\ \mathrm{g}}{0.0020\ \mathrm{mol}} = 143.32\ \mathrm{g\,mol^{-1}}.$$

Subtracting the molar mass of silver gives

$$143.32 - 107.87 = 35.45\ \mathrm{g\,mol^{-1}},$$

which identifies chloride, $\mathrm{Cl^-}$, `[Cl-]`. The precipitate is therefore **silver chloride**, AgCl, `[Ag+].[Cl-]`:

$$\mathrm{Ag^+ + Cl^- \longrightarrow AgCl(s)}.$$

The entire 1.1896 g sample contains

$$n(\mathrm{Cl^-}) = 5(0.0020) = 0.0100\ \mathrm{mol}.$$

Consequently, the 2.3793 g sample contains

$$n(\mathrm{Cl^-}) = 0.0100\,\frac{2.3793}{1.1896} = 0.02000084\ \mathrm{mol} \simeq 0.02000\ \mathrm{mol}.$$

Determination of the water

The barium precipitate is **barium sulfate**, $\mathrm{BaSO_4}$, `[Ba+2].[O-]S(=O)(=O)[O-]`. Its calculated sulfur content is

$$w(\mathrm{S}) = \frac{32.06}{137.34 + 32.06 + 4(16.00)} = \frac{32.06}{233.40} = 0.13736,$$

or 13.736%, agreeing with the reported 13.74%.

Thionyl chloride consumes the water of crystallization:

$$\mathrm{SOCl_2 + H_2O \longrightarrow SO_2 + 2\,HCl}.$$

Hydrogen peroxide oxidizes the sulfur dioxide, and barium sulfate precipitates. The combined absorption reaction is

$$\mathrm{SO_2 + H_2O_2 + BaCl_2 \longrightarrow BaSO_4(s) + 2\,HCl}.$$

The molecular species and reagent compositions in these equations are:

Name	Formula	SMILES
Thionyl chloride	$\mathrm{SOCl_2}$	`O=S(Cl)Cl`
Water	$\mathrm{H_2O}$	`O`
Sulfur dioxide	$\mathrm{SO_2}$	`O=S=O`
Hydrogen chloride	HCl	`Cl`
Hydrogen peroxide	$\mathrm{H_2O_2}$	`OO`
Barium chloride	$\mathrm{BaCl_2}$	`[Ba+2].[Cl-].[Cl-]`

Thus, one mole of crystal water produces one mole of sulfur dioxide and ultimately one mole of barium sulfate:

$$n(\mathrm{H_2O}) = n(\mathrm{BaSO_4}) = \frac{14.004\ \mathrm{g}}{233.40\ \mathrm{g\,mol^{-1}}} = 0.06000\ \mathrm{mol}.$$

Removing entrained thionyl chloride is essential: otherwise its hydrolysis in the absorbing solution would produce additional sulfate and overestimate the crystal water.

The water-to-chloride ratio is therefore

$$\frac{n(\mathrm{H_2O})}{n(\mathrm{Cl^-})} = \frac{0.06000}{0.02000084} = 2.99987 \simeq 3.$$

Hence there are **three water molecules per chloride ion**.

Identification of the metal

Using $M(\mathrm{H_2O}) = 18.016\ \mathrm{g\,mol^{-1}}$, the masses in the 2.3793 g sample are

$$m(\mathrm{H_2O}) = 0.06000(18.016) = 1.08096\ \mathrm{g},$$
$$m(\mathrm{Cl}) = 0.02000084(35.45) = 0.70903\ \mathrm{g},$$

and therefore

$$m_M = 2.3793 - 1.08096 - 0.70903 = 0.58931\ \mathrm{g}.$$

The metal mass per mole of chloride is

$$E_M = \frac{0.58931\ \mathrm{g}}{0.02000084\ \mathrm{mol}} = 29.464\ \mathrm{g\,mol^{-1}}.$$

For an ordinary metal chloride MCl_q, where the metal has oxidation state $+q$,

$$A_\mathrm{r}(M) \simeq 29.464q, \qquad z = 3q.$$

For $q = 2$,

$$A_\mathrm{r}(M) \simeq 58.929,$$

which identifies **cobalt**, $A_\mathrm{r}(\mathrm{Co}) \simeq 58.93$, present as the cobalt(II) ion, `[Co+2]`. The number of waters is then

$$z = 3(2) = 6.$$

Therefore,

$$\boxed{\mathrm{CoCl_2 \cdot 6\,H_2O}}.$$

Its calculated molar mass provides a check:

$$M = 58.93 + 2(35.45) + 6(18.016) = 237.926\ \mathrm{g\,mol^{-1}},$$

so 2.3793 g is approximately 0.01000 mol, containing 0.02000 mol chloride and 0.06000 mol water, as required.

2.2 — A different metal and higher valence

The analytical relations are

$$A_\mathrm{r}(M) \simeq 29.464q, \qquad z = 3q.$$

The seven-water restriction therefore permits only $q = 1$ or $q = 2$ for a simple chloride hydrate. A tetravalent metal would require twelve waters:

$$\mathrm{MCl_4 \cdot 12\,H_2O}.$$

A formal different-metal example is **tin(IV) chloride dodecahydrate**, $\mathrm{SnCl_4 \cdot 12\,H_2O}$. Its twelve waters exclude it under the stated restriction.

There is, however, a numerical inconsistency if this is claimed to satisfy the original analyses exactly. The inferred atomic mass for a tetravalent metal is

$$A_\mathrm{r}(M) = 4(29.464) = 117.857,$$

whereas tin has $A_\mathrm{r}(\mathrm{Sn}) \simeq 118.69$.

For the measured 0.0100 mol chloride in the second experiment, the proposed tin hydrate would have mass

$$\begin{aligned} m &= \frac{0.0100}{4}\left[118.69 + 4(35.45) + 12(18.016)\right] \\ &= 1.191705\ \mathrm{g}, \end{aligned}$$

rather than 1.1896 g. The difference, approximately 2.1 mg, exceeds rounding of the reported sample mass.

Thus $\mathrm{SnCl_4 \cdot 12\,H_2O}$ supplies a **formal higher-valence example excluded by the hydration limit**, but cannot honestly be described as an exact second solution of all the supplied measurements.

The solution was checked against the official solution.

Problem 3: Technical iron(II) sulphide and hydrochloric acid

A sample of 5 g of a technical iron(II) sulphide FeS, which contains 5 % metallic iron reacted with hydrochloric acid.

Problems:

3.1 Calculate the volume of the gaseous products at STP conditions.

3.2 What is the composition (in volume %) of the gaseous mixture?

Official English text of the problem.

Answers

- **3.1** The total gas volume is $1.31\ \mathrm{L}$ at STP: $1.21\ \mathrm{L}$ of hydrogen sulphide, $\mathrm{H_2S}$ (SMILES `S`), and $0.100\ \mathrm{L}$ of hydrogen, $\mathrm{H_2}$ (SMILES `[H][H]`).
- **3.2** The mixture contains $92.4\%\ \mathrm{H_2S}$ and $7.6\%\ \mathrm{H_2}$ by volume.

Solution

3.1

Assume complete reaction with sufficient hydrochloric acid. The two components react according to

$$\mathrm{FeS + 2\,HCl \longrightarrow FeCl_2 + H_2S\uparrow}$$
$$\mathrm{Fe + 2\,HCl \longrightarrow FeCl_2 + H_2\uparrow}\,.$$

Acid protonates the sulphide component to produce hydrogen sulphide. Metallic iron is oxidized to iron(II), reducing hydrogen ions to hydrogen gas. Thus, each mole of FeS produces one mole of $\mathrm{H_2S}$, and each mole of metallic iron produces one mole of $\mathrm{H_2}$.

For chemical identification, hydrogen chloride has SMILES `Cl`; hydrochloric acid is its aqueous solution. Formal ionic representations of iron(II) sulphide and iron(II) chloride are `[Fe+2].[S-2]` and `[Fe+2].[Cl-].[Cl-]`, respectively. These specify ionic constituents, without representing crystal structure or aqueous solvation.

The component masses are

$$m(\mathrm{Fe}) = 5.00\ \mathrm{g} \times 0.05 = 0.250\ \mathrm{g},$$
$$m(\mathrm{FeS}) = 5.00 - 0.250 = 4.750\ \mathrm{g}.$$

Using the rounded molar masses $M(\mathrm{Fe}) = 56.0\ \mathrm{g\,mol^{-1}}$ and $M(\mathrm{FeS}) = 88.0\ \mathrm{g\,mol^{-1}}$,

$$n(\mathrm{H_2S}) = \frac{4.750}{88.0} = 0.0539773\ \mathrm{mol},$$

$$n(\mathrm{H_2}) = \frac{0.250}{56.0} = 0.00446429\ \mathrm{mol}.$$

At conventional STP, $0\,^\circ\mathrm{C}$ and $1\ \mathrm{atm}$, take the ideal-gas molar volume as $22.4\ \mathrm{L\,mol^{-1}}$. Therefore,

$$V(\mathrm{H_2S}) = 0.0539773 \times 22.4 = 1.20909\ \mathrm{L},$$
$$V(\mathrm{H_2}) = 0.00446429 \times 22.4 = 0.10000\ \mathrm{L}.$$

Hence,

$$\boxed{V_{\text{total}} = 1.30909\ \mathrm{L} \approx 1.31\ \mathrm{L}}.$$

3.2

For ideal gases at the same temperature and pressure, volume fractions equal mole fractions:

$$\text{Volume \% of } \mathrm{H_2S} = \frac{0.0539773}{0.0539773 + 0.00446429} \times 100 = 92.3611\%.$$

The remaining gas is hydrogen:

$$\text{Volume \% of } \mathrm{H_2} = 100 - 92.3611 = 7.6389\%.$$

Thus,

$$\boxed{\mathrm{H_2S}: 92.4\% \qquad \mathrm{H_2}: 7.6\% \quad \text{by volume}}.$$

The solution was checked against the official solution.

Problem 4: Four natural nitrogen-containing substances

Four often occurring natural substances have the following summary (empirical) formulas:

$\mathrm{C_2H_5O_2N}$	**(A)**	$\mathrm{C_3H_7O_2N}$	**(C)**
$\mathrm{C_3H_7O_2N}$	**(B)**	$\mathrm{C_9H_{11}O_2N}$	**(D)**

The given substances when allowed to react with an alkali hydroxide solution yield alkali salts. However, in a neutral or acidic solution the reaction takes place on the nitrogen atom.

Problems:

4.1 Write structural formulas for the compounds **A**, **B**, **C**, and **D**.

4.2 Which of the given substances are optically active and which ones are inactive?

4.3 Write the formula of the functional group which is typical of certain natural substances and which is contained also in the product formed by the reaction of two molecules of compound **A**. Give the name of the natural substances to which belongs the above mentioned product.

4.4 A cyclic organic compound being of technical importance contains also the functional group mentioned in passage 3.

a) Write the structural formula of this cyclic compound.

b) Write the characteristic part of the structural formula of a macromolecular substance that can be obtained from the mentioned compound.

c) Write the characteristic part of the structural formula of an isomeric macromolecular substance that is also technically important.

d) Give the name for the group of compounds to which belong the above mentioned macromolecular substances.

Official English text of the problem.

Answers

The following uses the conventional amino-acid assignments, with **B** as α-alanine and **C** as β-alanine. These assignments are not uniquely determined by the supplied information. The stereochemical SMILES show the usual natural L forms where applicable.

In fragment SMILES, `*` marks attachment to the rest of the structure.

- **4.1**

Compound	Name	Condensed structural formula	SMILES
A	Glycine	$\mathrm{H_2N-CH_2-COOH}$	`NCC(=O)O`
B	α-Alanine; usual natural form: L-(S)-alanine	$\mathrm{CH_3-CH(NH_2)-COOH}$	`N[C@@H](C)C(=O)O`
C	β-Alanine, or 3-aminopropanoic acid	$\mathrm{H_2N-CH_2-CH_2-COOH}$	`NCCC(=O)O`
D	Phenylalanine; usual natural form: L-(S)-phenylalanine	$\mathrm{C_6H_5-CH_2-CH(NH_2)-COOH}$	`N[C@@H](Cc1ccccc1)C(=O)O`

- **4.2 B and D** are chiral and optically active when nonracemic. **A and C** are achiral and optically inactive.
- **4.3** The functional group is the **amide, or peptide, linkage**, $\mathrm{-C(=O)-NH^-}$, fragment SMILES `*C(=O)N*`. Two glycine molecules form **glycylglycine**, `NCC(=O)NCC(=O)O`, a **dipeptide**. Peptides and proteins contain this linkage.
- **4.4(a) ε-Caprolactam**, `O=C1CCCCCN1`: a seven-membered ring containing one NH, five $\mathrm{CH_2}$ groups, and one carbonyl carbon.
- **4.4(b) Nylon-6**, also called polycaprolactam:

  $$\left[\mathrm{-NH-(CH_2)_5-CO^-}\right]_n.$$

  Repeat-fragment SMILES: `*NCCCCCC(=O)*`.
- **4.4(c) Nylon-6,6**, or poly(hexamethylene adipamide):

  $$\left[\mathrm{-NH-(CH_2)_6-NH-CO-(CH_2)_4-CO^-}\right]_n.$$

  Repeat-fragment SMILES: `*NCCCCCCNC(=O)CCCCC(=O)*`.
- **4.4(d)** Both polymers are **polyamides**.

Solution

4.1 — Identification and structural formulas

The intended interpretation is that the substances are **amino acids**, containing an acidic carboxyl group and a basic amino group.

The carboxyl group explains formation of alkali salts. For example, glycine reacts with sodium hydroxide, `[Na+].[OH-]`, to give sodium glycinate, `[Na+].NCC(=O)[O-]`, and water, `O`:

$$\mathrm{H_2N{-}CH_2{-}COOH + NaOH \longrightarrow H_2N{-}CH_2{-}COONa + H_2O.}$$

The amino group can accept a proton. Using the uncharged structural representation, reaction with hydrogen chloride, `Cl`, gives glycine hydrochloride, `[Cl-].[NH3+]CC(=O)O`:

$$\mathrm{H_2N{-}CH_2{-}COOH + HCl \longrightarrow [H_3N{-}CH_2{-}COOH]Cl.}$$

These equations describe the acid–base functionality shared by the proposed structures. Near neutral pH, glycine exists predominantly as its **zwitterion**, `[NH3+]CC(=O)[O-]`. Consequently, acidification of that zwitterion protonates its carboxylate group; the preceding equation uses the conventional uncharged drawing.

The structural assignments follow as follows:

- **A:** A carboxyl group accounts for one carbon and both oxygen atoms. The remaining carbon can bear the amino group, giving aminoacetic acid, **glycine**, $\mathrm{H_2N{-}CH_2{-}COOH}$. Its formula is $\mathrm{C_2H_5O_2N}$.
- **B and C:** A three-carbon amino acid can have its amino group on carbon 2 or carbon 3, numbering from the carboxyl carbon. These structures are **α-alanine** and **β-alanine**, respectively, both with formula $\mathrm{C_3H_7O_2N}$.
- **D:** The degree of unsaturation, treating the supplied formula as molecular, is

  $$\mathrm{DBE} = \frac{2(9) + 2 + 1 - 11}{2} = 5.$$

  A phenyl ring accounts for four degrees of unsaturation and a carboxyl carbonyl for the fifth. The common natural amino acid **phenylalanine**, $\mathrm{C_6H_5{-}CH_2{-}CH(NH_2){-}COOH}$, has exactly the required formula $\mathrm{C_9H_{11}O_2N}$.

The structural and stereochemical SMILES are given in the answer table.

4.2 — Optical activity

For **B**, the α-carbon is bonded to four different substituents:

$$\mathrm{-NH_2}, \qquad \mathrm{-COOH}, \qquad \mathrm{-CH_3}, \qquad \mathrm{-H}.$$

For **D**, the corresponding substituents are:

$$\mathrm{-NH_2}, \qquad \mathrm{-COOH}, \qquad \mathrm{-CH_2{-}C_6H_5}, \qquad \mathrm{-H}.$$

Each molecule therefore has one stereogenic carbon and exists as a pair of enantiomers. Their usual natural L forms both have the S configuration.

In **A**, the amino-bearing carbon has two identical hydrogen substituents. In **C**, both noncarbonyl carbons are methylene groups. Neither molecule is chiral.

Thus **B and D are capable of optical activity**, while **A and C are inactive**. A racemic sample of B or D would also be optically inactive.

4.3 — Condensation of two molecules of A

Under peptide-forming conditions, the carboxyl group of one glycine molecule combines with the amino group of another, eliminating one water molecule:

$$2\,\mathrm{H_2N{-}CH_2{-}COOH} \longrightarrow \mathrm{H_2N{-}CH_2{-}CO{-}NH{-}CH_2{-}COOH} + \mathrm{H_2O}.$$

The product is **glycylglycine**, a dipeptide. The newly formed linkage is

$$\boxed{\mathrm{-C(=O)-NH^-}}.$$

To draw it, show a carbonyl carbon directly bonded to an NH nitrogen, with the carbonyl carbon and nitrogen each connected to the remaining molecular structure.

This is an **amide linkage**, called a **peptide linkage** when it joins amino-acid residues. Glycylglycine belongs to the **peptides**; the same linkage connects amino-acid residues in proteins.

4.4(a) — The technically important cyclic compound

The intended industrial cyclic amide is **ε-caprolactam**, `O=C1CCCCCN1`.

Its ring can be described by the sequence

$$\mathrm{-NH-(CH_2)_5-C(=O)^-},$$

with the carbonyl carbon bonded back to the nitrogen. Thus the ring contains seven atoms: one nitrogen, five methylene carbons, and one carbonyl carbon. The oxygen lies outside the ring.

4.4(b) — Polymer obtained from the cyclic compound

Ring-opening polymerization of ε-caprolactam gives **nylon-6**:

$$\boxed{\left[\mathrm{-NH-(CH_2)_5-CO^-}\right]_n}.$$

Each repeat contains one amide linkage and five consecutive methylene groups.

For a linear chain with amino and carboxyl end groups, the overall hydrolytic polymerization can be balanced explicitly as

$$n\,\mathrm{C_6H_{11}NO} + \mathrm{H_2O} \longrightarrow \mathrm{H{-}[NH{-}(CH_2)_5{-}CO]_n{-}OH},$$

where $\mathrm{C_6H_{11}NO}$ denotes ε-caprolactam. The terminal $\mathrm{H^-}$ and $\mathrm{-OH}$ complete the amino and carboxyl end groups.

4.4(c) — An isomeric technically important polymer

The corresponding industrial example is **nylon-6,6**:

$$\boxed{\left[\mathrm{-NH-(CH_2)_6-NH-CO-(CH_2)_4-CO^-}\right]_n}.$$

It is formed from:

- **Hexane-1,6-diamine**, also called hexamethylenediamine, `NCCCCCCN`;
- **Adipic acid**, or hexanedioic acid, `O=C(O)CCCCC(=O)O`.

For a linear chain formed from n molecules of each monomer, the balanced condensation is

$$\begin{aligned} n\,\mathrm{H_2N{-}(CH_2)_6{-}NH_2} + n\,\mathrm{HOOC{-}(CH_2)_4{-}COOH} \\ \longrightarrow \mathrm{H{-}[NH{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_4{-}CO]_n{-}OH} \\ + (2\,\mathrm{n}\text{-}1)\,\mathrm{H_2O}. \end{aligned}$$

The $2n$ monomer molecules are joined by $2n-1$ amide bonds, releasing $2n-1$ water molecules.

One nylon-6 repeat has composition $\mathrm{C_6H_{11}NO}$. Two such repeats therefore have composition $\mathrm{C_{12}H_{22}N_2O_2}$, identical to one nylon-6,6 repeat. Their atomic connectivity differs, explaining the requested isomeric relationship.

4.4(d) — Classification

Both synthetic polymers contain recurring $\mathrm{-CO-NH^-}$ linkages in their main chains and are therefore **polyamides**.

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 5: Organic compounds A-H from an ester C6H12O3

a) Compounds **B** and **E** are formed when an organic substance **A** (summary formula $\mathrm{C_6H_{12}O_3}$) reacts with a sodium hydroxide solution (saponification).

b) Substance **B** can be oxidised in a two-step process to a substance **C**.

c) Substance **C** when reacted with bromine yields a substitution product **D** which can be hydrolysed by the reaction with sodium hydroxide solution to produce a substance **E**.

d) Substance **E** when allowed to react with a stoichiometric amount of hydrochloric acid gives a compound **F** (40.0 % C, 6.66 % H, the rest is oxygen).

e) Substance **F** is an important product of metabolism in biological processes.

f) Compound **F** when allowed to stand, splits off one mole of water from two moles of the substance that results in the formation of an unstable compound **G**.

g) Substance **F** can also be obtained from a compound **H** containing nitrogen, by one-step reaction with nitrous acid. Assuming the quantitative course of the reaction, 4.5 g of substance **F** are formed from 4.45 g of substance **H**.

Problems:

5.1 Write all equations for the above mentioned chemical reactions.

5.2 Give structural formulas of the organic compounds **A – H**.

Official English text of the problem.

Answers

- **5.1.** The balanced equations, labelled according to the statement, are:

(a) Saponification

$$\mathrm{CH_3CH(OH)C(=O)OCH_2CH_2CH_3 + NaOH \longrightarrow CH_3CH_2CH_2OH + CH_3CH(OH)COONa}$$

(b) Two successive oxidations

$$\mathrm{CH_3CH_2CH_2OH + [O] \longrightarrow CH_3CH_2CHO + H_2O}$$
$$\mathrm{CH_3CH_2CHO + [O] \longrightarrow CH_3CH_2COOH}$$

(c) Bromination and alkaline hydrolysis

$$\mathrm{CH_3CH_2COOH + Br_2 \longrightarrow CH_3CH(Br)COOH + HBr}$$
$$\mathrm{CH_3CH(Br)COOH + 2\,NaOH \longrightarrow CH_3CH(OH)COONa + NaBr + H_2O}$$

(d) Acidification

$$\mathrm{CH_3CH(OH)COONa + HCl \longrightarrow CH_3CH(OH)COOH + NaCl}$$

(f) Intermolecular esterification

$$\mathrm{2\,CH_3CH(OH)COOH \rightleftharpoons CH_3CH(OH)C(=O)OCH(CH_3)COOH + H_2O}$$

(g) Deamination with nitrous acid

$$\mathrm{CH_3CH(NH_2)COOH + HNO_2 \longrightarrow CH_3CH(OH)COOH + N_2 + H_2O}$$

Here $[\mathrm{O}]$ denotes one oxygen-atom equivalent supplied by an oxidant. The intermediate in (b) is **propanal**, CCC=O. Statement (e) supplies identification evidence and specifies no additional reaction.

- **5.2.** The organic compounds are:

Compound	Name	Condensed structural formula	SMILES
A	Propan-1-yl 2-hydroxypropanoate; n-propyl lactate	$\mathrm{CH_3CH(OH)C(=O)OCH_2CH_2CH_3}$	`CC(O)C(=O)OCCC`
B	Propan-1-ol	$\mathrm{CH_3CH_2CH_2OH}$	`CCCO`
C	Propanoic acid	$\mathrm{CH_3CH_2COOH}$	`CCC(=O)O`
D	2-Bromopropanoic acid	$\mathrm{CH_3CH(Br)COOH}$	`CC(Br)C(=O)O`
E	Sodium 2-hydroxypropanoate; sodium lactate	$\mathrm{CH_3CH(OH)COO^-, Na^+}$	`CC(O)C(=O)[O-].[Na+]`
F	2-Hydroxypropanoic acid; lactic acid	$\mathrm{CH_3CH(OH)COOH}$	`CC(O)C(=O)O`
G	Lactoyllactic acid; 2-[(2-hydroxypropanoyl)oxy]propanoic acid	$\mathrm{CH_3CH(OH)C(=O)OCH(CH_3)COOH}$	`CC(O)C(=O)OC(C)C(=O)O`
H	2-Aminopropanoic acid; alanine	$\mathrm{CH_3CH(NH_2)COOH}$	`CC(N)C(=O)O`

Solution

5.1. Reaction sequence and identification

Saponification in (a) identifies **A** as an ester: **B** is its alcohol component, and **E** is the sodium salt of its acid component.

The two-step oxidation in (b) is the characteristic sequence primary alcohol $\rightarrow$ aldehyde $\rightarrow$ carboxylic acid. This preserves the carbon skeleton. Bromination, hydrolysis and acidification in (c)–(d) also preserve that skeleton. Thus **B**, **C**, **D**, **E** and **F** all contain the same number of carbon atoms.

If that number is n, the ester **A** contains n carbons from its alcohol component and n from its acid component. Therefore,

$$2n = 6, \qquad n = 3.$$

The three-carbon primary alcohol **B** is consequently **propan-1-ol**. Its oxidation first gives **propanal** and then **propanoic acid C**, as shown in the two balanced equations for (b).

In (c), α-bromination of propanoic acid replaces a hydrogen on the carbon adjacent to the carboxyl group, giving **2-bromopropanoic acid D**. This is understood as the usual Hell–Volhard–Zelinsky reaction under suitable phosphorus-assisted conditions, for example using phosphorus tribromide, `BrP(Br)Br`, followed by aqueous workup.

Treatment of **D** with aqueous sodium hydroxide replaces bromine by a hydroxy group and neutralizes the carboxyl group. Hence **two equivalents of sodium hydroxide** are required: one for substitution and one for neutralization. The product **E** is sodium lactate.

In (d), one equivalent of hydrochloric acid protonates the carboxylate group, yielding **lactic acid F**. Its composition can be checked independently. For a $100\ \mathrm{g}$ sample, using the usual rounded atomic molar masses,

$$n(\mathrm{C}) = \frac{40.0\ \mathrm{g}}{12\ \mathrm{g\,mol^{-1}}} \approx 3.33\ \mathrm{mol},$$
$$n(\mathrm{H}) = \frac{6.66\ \mathrm{g}}{1\ \mathrm{g\,mol^{-1}}} = 6.66\ \mathrm{mol},$$
$$n(\mathrm{O}) = \frac{53.34\ \mathrm{g}}{16\ \mathrm{g\,mol^{-1}}} \approx 3.33\ \mathrm{mol}.$$

Thus the atomic ratio is approximately

$$\mathrm{C} : \mathrm{H} : \mathrm{O} = 1 : 2 : 1.$$

The empirical formula is $\mathrm{CH_2O}$. Since **F** has three carbon atoms, its molecular formula is $\mathrm{C_3H_6O_3}$, consistent with lactic acid and the metabolic clue in (e).

In (f), lactic acid contains both an alcohol group and a carboxyl group. The carboxyl group of one molecule esterifies the alcohol group of another, eliminating one molecule of water. The resulting **G**, lactoyllactic acid, has formula

$$\mathrm{C_6H_{10}O_5}.$$

It is an **open-chain monoester dimer**, retaining one free alcohol group and one free carboxyl group. Its formation is reversible by hydrolysis. Formation of a cyclic diester would require elimination of two water molecules from two lactic acid molecules.

In (g), nitrous acid converts a primary amino group into a hydroxy group, with evolution of nitrogen. Replacing the hydroxy group of lactic acid by an amino group therefore identifies **H** as **alanine**.

Using rounded atomic molar masses,

$$M(\mathrm{H}) = M(\mathrm{C_3H_7NO_2}) = 89\ \mathrm{g\,mol^{-1}}, \qquad M(\mathrm{F}) = M(\mathrm{C_3H_6O_3}) = 90\ \mathrm{g\,mol^{-1}}.$$

The balanced deamination equation gives a $1 : 1$ molar conversion:

$$n(\mathrm{H}) = \frac{4.45\ \mathrm{g}}{89\ \mathrm{g\,mol^{-1}}} = 0.0500\ \mathrm{mol}.$$

Consequently,

$$m(\mathrm{F}) = 0.0500\ \mathrm{mol} \times 90\ \mathrm{g\,mol^{-1}} = 4.50\ \mathrm{g},$$

which agrees with the stated $4.5\ \mathrm{g}$.

For completeness, the inorganic species in the equations are sodium hydroxide `[Na+].[OH-]`, water `O`, bromine `BrBr`, hydrogen bromide `Br`, sodium bromide `[Na+].[Br-]`, hydrogen chloride (aqueous hydrochloric acid) `Cl`, sodium chloride `[Na+].[Cl-]`, nitrous acid `ON=O`, and nitrogen `N#N`.

5.2. Structural formulas

The structures are given in the answer table. In particular, joining the carboxyl group of lactic acid to the alcohol component propan-1-ol gives **A**, n-propyl lactate. Its molecular formula provides a final check:

$$\mathrm{C_3H_6O_3} + \mathrm{C_3H_8O} - \mathrm{H_2O} = \mathrm{C_6H_{12}O_3}.$$

E is an ionic sodium carboxylate; the sodium is not covalently bonded to the organic skeleton. **G** contains an ester linkage between the two lactic acid units.

No stereochemistry is specified in the problem, so the SMILES leave absolute configurations unspecified. Under ordinary achiral conditions, bromination of **C** produces racemic **D**.

The solution was checked against the official solution.

Problem 6: Gas thermometer

Temperature in a larger room should be measured by means of a gaseous thermometer. A glass tube with the internal volume of 80 cm³ was for this purpose filled with nitrogen at a temperature of 20 °C and a pressure of 101.325 kPa. The tube was then slowly and steadily moved throughout the room. Due to the thermal expansion the gas at the higher temperature escapes from the tube and is captured above the liquid whose vapour pressure is negligible. The total volume of the gas escaped from the tube was 35 cm³ at a temperature of 20 °C and a pressure of 101.325 kPa.

Problems:

6.1 How many moles of nitrogen were used to fill the glass tube?

6.2 How many moles of nitrogen escaped from the tube at the higher temperature?

6.3 Calculate the average temperature in the room under investigation if the thermal expansion of the glass tube is assumed to be negligible.

6.4 Does anything change if instead of pure nitrogen, a mixture containing 50 volume % of nitrogen and 50 volume % of hydrogen is used?

Official English text of the problem.

Answers

- **6.1** Initially, $3.33 \times 10^{-3}\,\mathrm{mol}$ of nitrogen, $\mathrm{N_2}$, `N#N`.
- **6.2** Escaped nitrogen: $1.46 \times 10^{-3}\,\mathrm{mol}$.
- **6.3** The inferred room temperature is approximately $\boxed{521\ \mathrm{K} = 248\ ^\circ\mathrm{C}}$.
- **6.4** The inferred temperature and total mole amounts are unchanged for an ideal, nonreacting mixture. For a mixture that remains well mixed, nitrogen and hydrogen, $\mathrm{H_2}$, `[H][H]`, each contribute $1.66 \times 10^{-3}\,\mathrm{mol}$ initially and $7.28 \times 10^{-4}\,\mathrm{mol}$ to the escaped gas.

Solution

Treat the gases as ideal and take their pressure during expansion to remain equal to the stated atmospheric pressure. Use

$$pV = nRT, \qquad R = 8.314\ \text{kPa}\,\text{L}\,\text{mol}^{-1}\,\text{K}^{-1},$$

with the reference temperature

$$T_0 = 20 + 273.15 = 293.15\ \text{K}.$$

6.1

The initial volume of nitrogen is

$$V_0 = 80\ \text{cm}^3 = 0.080\ \text{L}.$$

Therefore,

$$n_0 = \frac{pV_0}{RT_0} = \frac{(101.325\ \text{kPa})(0.080\ \text{L})}{(8.314\ \text{kPa}\,\text{L}\,\text{mol}^{-1}\,\text{K}^{-1})(293.15\ \text{K})} = 3.3259 \times 10^{-3}\ \text{mol}.$$

Thus,

$$\boxed{n_0 \approx 3.33 \times 10^{-3}\ \text{mol}}.$$

6.2

The escaped gas is measured at the same reference temperature and pressure. Since the collecting liquid has negligible vapour pressure, no vapour-pressure correction is required.

$$n_{\text{escaped}} = \frac{pV_{\text{escaped}}}{RT_0} = \frac{(101.325\ \text{kPa})(0.035\ \text{L})}{(8.314\ \text{kPa}\,\text{L}\,\text{mol}^{-1}\,\text{K}^{-1})(293.15\ \text{K})} = 1.4551 \times 10^{-3}\ \text{mol}.$$

Hence,

$$\boxed{n_{\text{escaped}} \approx 1.46 \times 10^{-3}\ \text{mol}}.$$

6.3

The amount remaining in the tube is

$$n_{\text{remaining}} = n_0 - n_{\text{escaped}} = 1.8708 \times 10^{-3}\ \text{mol}.$$

Because both measured volumes refer to the same temperature and pressure,

$$\frac{n_{\text{remaining}}}{n_0} = \frac{80 - 35}{80} = \frac{45}{80}.$$

The glass tube retains its volume of $80\ \text{cm}^3$. Applying the ideal gas law to its initial and heated states gives

$$pV_0 = n_0RT_0 = n_{\text{remaining}}RT.$$

Consequently,

$$T = T_0\frac{n_0}{n_{\text{remaining}}} = 293.15\ \text{K} \times \frac{80}{45} = 521.16\ \text{K}.$$

Converting to Celsius,

$$t = (521.16 - 273.15)\ ^\circ\text{C} = 248.01\ ^\circ\text{C}.$$

Thus the intended thermometer result is

$$\boxed{T \approx 521\ \mathrm{K}, \qquad t \approx 248\ ^\circ\mathrm{C}}.$$

6.4

For an ideal mixture of nitrogen, $\mathrm{N_2}$, `N#N`, and hydrogen, $\mathrm{H_2}$, `[H][H]`,

$$pV = (n_{\mathrm{N_2}} + n_{\mathrm{H_2}})RT.$$

At a common temperature and pressure, volume fractions equal mole fractions. The specified mixture therefore has

$$x_{\mathrm{N_2}} = x_{\mathrm{H_2}} = 0.50.$$

The ideal gas law depends on the **total amount of gas**, irrespective of its molecular identity. Thus the initial total amount, escaped total amount, and inferred temperature remain unchanged.

The amount of nitrogen itself is halved. Assuming the escaping gas has the same composition as the well-mixed gas in the tube, each constituent has

$$n_{i,0} = \frac{n_0}{2} \approx 1.66 \times 10^{-3}\ \mathrm{mol},$$

and

$$n_{i,\mathrm{escaped}} = \frac{n_{\mathrm{escaped}}}{2} \approx 7.28 \times 10^{-4}\ \mathrm{mol}.$$

The solution was checked against the official solution.

Problem 7: Lead accumulator

The density of a sulphuric acid solution in a charged lead accumulator should be equal to $\rho = 1.28\ \mathrm{g\,cm^{-3}}$ which corresponds to the solution containing 36.87 % of $\mathrm{H_2SO_4}$ by mass. In a discharged lead accumulator it should not decrease under the value of $\rho = 1.10\ \mathrm{g\,cm^{-3}}$ which corresponds to the 14.35 % solution of sulphuric acid.

(Faraday's constant F is equal to $26.8\ \mathrm{Ah\,mol^{-1}}$.)

Problems:

7.1 Write the equation for a total electrochemical reaction that takes place in the lead accumulator when it is charged and discharged.

7.2 Calculate the masses of $\mathrm{H_2O}$ and $\mathrm{H_2SO_4}$ being consumed or formed according to the equation in No 1.

7.3 Calculate the mass of $\mathrm{H_2SO_4}$ that is required to be added to a led accumulator with a capacity of 120 Ah if the content of $\mathrm{H_2SO_4}$ is to be in the range as given in the task.

7.4 Calculate the difference in volumes of the sulphuric acid solutions in a charged and a discharged lead accumulator with a capacity of 120 Ah.

Official English text of the problem.

Answers

- **7.1** Discharge:
$$\mathrm{Pb} + \mathrm{PbO_2} + 2\,\mathrm{H_2SO_4} \longrightarrow 2\,\mathrm{PbSO_4} + 2\,\mathrm{H_2O}.$$
Charging proceeds by the reverse reaction.
- **7.2** Per reaction as written, corresponding to $53.6\ \mathrm{Ah}$, discharge **consumes** $196\ \mathrm{g}$ **of** $\mathrm{H_2SO_4}$ and **forms** $36.0\ \mathrm{g}$ **of** $\mathrm{H_2O}$. Equivalently, these amounts are 3.66 and $0.672\ \mathrm{g\,Ah^{-1}}$, respectively. For $120\ \mathrm{Ah}$, they are $439\ \mathrm{g}$ and $80.6\ \mathrm{g}$. Charging reverses consumption and formation.
- **7.3** The minimum initial quantity of pure $\mathrm{H_2SO_4}$ is
$$\boxed{m(\mathrm{H_2SO_4}) = 634\ \mathrm{g}},$$
contained in approximately $1.72\ \mathrm{kg}$ of charged electrolyte.
- **7.4**
$$\boxed{V_{\mathrm{charged}} - V_{\mathrm{discharged}} = 1.06 \times 10^{2}\ \mathrm{cm^3} = 0.106\ \mathrm{L}}.$$
The electrolyte volume decreases on discharge.

Solution

7.1

During discharge, metallic lead is oxidized from oxidation state 0 to $+\mathrm{II}$, while lead in lead(IV) oxide is reduced from $+\mathrm{IV}$ to $+\mathrm{II}$. Lead(II) sulfate forms at both electrodes.

The discharge half-reactions are:

$$\begin{aligned}\text{Negative electrode:}\quad & \mathrm{Pb\,(s)} + \mathrm{SO_4{}^{2-}\,(aq)} \longrightarrow \mathrm{PbSO_4\,(s)} + 2\,\mathrm{e^-},\\ \text{Positive electrode:}\quad & \mathrm{PbO_2\,(s)} + 4\,\mathrm{H^+\,(aq)} + \mathrm{SO_4{}^{2-}\,(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{PbSO_4\,(s)} + 2\,\mathrm{H_2O\,(l)}.\end{aligned}$$

Adding them gives the overall discharge reaction:

$$\boxed{\mathrm{Pb\,(s)} + \mathrm{PbO_2\,(s)} + 2\,\mathrm{H_2SO_4\,(aq)} \longrightarrow 2\,\mathrm{PbSO_4\,(s)} + 2\,\mathrm{H_2O\,(l)}}.$$

During charging, an external source drives the reverse reaction:

$$\boxed{2\,\mathrm{PbSO_4\,(s)} + 2\,\mathrm{H_2O\,(l)} \longrightarrow \mathrm{Pb\,(s)} + \mathrm{PbO_2\,(s)} + 2\,\mathrm{H_2SO_4\,(aq)}}.$$

The molecular and ionic species used here are sulphuric acid, `OS(=O)(=O)O`; water, `O`; sulfate ion, `[O-]S(=O)(=O)[O-]`; and hydrogen ion, `[H+]`. The aqueous hydrogen ion denotes a solvated proton. Lead, lead(IV) oxide, and lead(II) sulfate are extended solid phases; molecular SMILES do not describe their crystal lattices.

7.2

Use the molar masses

$$M(\mathrm{H_2SO_4}) = 98.0\ \mathrm{g\,mol^{-1}}, \qquad M(\mathrm{H_2O}) = 18.0\ \mathrm{g\,mol^{-1}}.$$

For the overall reaction as written, two moles of electrons pass through the external circuit. The corresponding charge is

$$Q_0 = (2\ \text{mol})(26.8\ \text{Ah mol}^{-1}) = 53.6\ \text{Ah}.$$

At this reaction extent, discharge consumes

$$m(\text{H}_2\text{SO}_4) = (2\ \text{mol})(98.0\ \text{g mol}^{-1}) = 196\ \text{g}$$

and forms

$$m(\text{H}_2\text{O}) = (2\ \text{mol})(18.0\ \text{g mol}^{-1}) = 36.0\ \text{g}.$$

Thus one mole of acid is consumed and one mole of water is formed per mole of electrons transferred. For a charge Q,

$$m_{\text{acid consumed}} = \frac{Q}{F} M(\text{H}_2\text{SO}_4), \qquad m_{\text{water formed}} = \frac{Q}{F} M(\text{H}_2\text{O}).$$

Per ampere-hour, these amounts are

$$\frac{98.0}{26.8} = 3.66\ \text{g Ah}^{-1}, \qquad \frac{18.0}{26.8} = 0.672\ \text{g Ah}^{-1}.$$

For the $120\ \text{Ah}$ discharge considered in the following parts,

$$n(e^-) = \frac{120\ \text{Ah}}{26.8\ \text{Ah mol}^{-1}} = 4.47761\ \text{mol}.$$

Consequently,

$$\begin{aligned} a \equiv m_{\text{acid consumed}} &= 4.47761(98.0) = 438.806\ \text{g}, \\ b \equiv m_{\text{water formed}} &= 4.47761(18.0) = 80.5970\ \text{g}. \end{aligned}$$

Charging consumes the same mass of water and regenerates the same mass of acid.

7.3

Let m_c be the mass of electrolyte in the charged accumulator. Its initial acid mass is

$$m_{\text{acid},c} = 0.3687 m_c.$$

After discharge, the acid mass is $0.3687 m_c - a$. Since acid is consumed and water is formed, the total electrolyte mass becomes

$$m_d = m_c - a + b = m_c - 358.209\ \text{g}.$$

The minimum initial quantity is obtained when the $120\ \text{Ah}$ discharge reaches exactly the permitted lower acid concentration:

$$\frac{0.3687 m_c - a}{m_c - a + b} = 0.1435.$$

Rearranging,

$$m_c = \frac{a - 0.1435(a - b)}{0.3687 - 0.1435} = \frac{438.806 - 0.1435(358.209)}{0.2252} = 1720.26\ \text{g}.$$

The required initial mass of pure sulphuric acid is therefore

$$m_{\text{acid},c} = 0.3687(1720.26) = 634.261\ \text{g},$$

or

$$\boxed{m_{\text{acid},c} = 634\ \text{g}}.$$

As a check, after discharge the electrolyte contains

$$634.261 - 438.806 = 195.455\ \text{g}$$

of acid in $1362.05\ \mathrm{g}$ of solution, giving

$$\frac{195.455}{1362.05} \times 100\% = 14.35\%.$$

7.4

Using the given densities and retaining extra digits until the final subtraction,

$$V_c = \frac{m_c}{\rho_c} = \frac{1720.26\ \mathrm{g}}{1.28\ \mathrm{g\,cm^{-3}}} = 1343.95\ \mathrm{cm^3}.$$

The discharged electrolyte mass is

$$m_d = 1720.26 - 438.806 + 80.5970 = 1362.05\ \mathrm{g},$$

so its volume is

$$V_d = \frac{m_d}{\rho_d} = \frac{1362.05\ \mathrm{g}}{1.10\ \mathrm{g\,cm^{-3}}} = 1238.23\ \mathrm{cm^3}.$$

Hence

$$\boxed{V_c - V_d = 105.725\ \mathrm{cm^3} \approx 1.06 \times 10^2\ \mathrm{cm^3}}.$$

The solution was checked against the official solution.