

IChO 1972

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Problem 1: Mixture of two solid elements

A mixture of two solid elements with a mass of 1.52 g was treated with an excess of hydrochloric acid. A volume of 0.896 dm³ of a gas was liberated in this process and 0.56 g of a residue remained which was undissolved in the excess of the acid.

In another experiment, 1.52 g of the same mixture were allowed to react with an excess of a 10 % sodium hydroxide solution. In this case 0.896 dm³ of a gas were also evolved but 0.96 g of an undissolved residue remained.

In the third experiment, 1.52 g of the initial mixture were heated to a high temperature without access of the air. In this way a compound was formed which was totally soluble in hydrochloric acid and 0.448 dm³ of an unknown gas were released. All the gas obtained was introduced into a one litre closed vessel filled with oxygen. After the reaction of the unknown gas with oxygen the pressure in the vessel decreased by approximately ten times ($T = \text{const}$).

Problem:

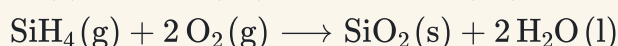
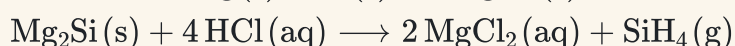
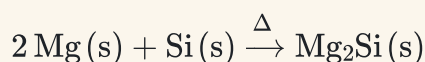
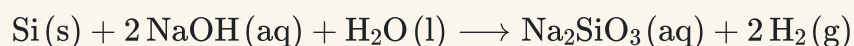
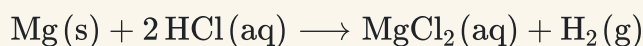
1.1 Write chemical equations for the above reactions and prove their correctness by calculations.

In solving the problem consider that the volumes of gases were measured at STP and round up the relative atomic masses to whole numbers.

Official English text of the problem.

Answers

- 1.1** The mixture contains **0.96 g of magnesium** and **0.56 g of silicon**. The first two experiments release hydrogen, H₂, [H] [H]. Heating produces magnesium silicide, Mg₂Si, which releases silane, SiH₄, [SiH₄], when treated with hydrochloric acid. The reactions are:



The calculated gas volumes are respectively **0.896, 0.896, and 0.448 dm³**. Relative to the original oxygen pressure, the final pressure is approximately $0.104p_0$, a **9.6-fold decrease**, neglecting water vapour.

Solution

1.1

Use the STP molar gas volume

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

and whole-number atomic masses $A_r(\text{Mg}) = 24$ and $A_r(\text{Si}) = 28$.

Identifying the elements.

Each of the first two experiments produces

$$n(\text{H}_2) = \frac{0.896}{22.4} = 0.0400 \text{ mol}.$$

The masses dissolved in acid and alkali are

$$m_{\text{acid}} = 1.52 - 0.56 = 0.96 \text{ g}, \quad m_{\text{alkali}} = 1.52 - 0.96 = 0.56 \text{ g}.$$

Formation of one mole of hydrogen requires two moles of electrons. Thus, if an element loses z electrons per atom, its molar mass M satisfies

$$\frac{M}{z} = \frac{m}{2n(\text{H}_2)}.$$

For the acid-reactive component,

$$\frac{M}{z} = \frac{0.96}{2(0.0400)} = 12 \text{ g mol}^{-1}.$$

Magnesium, which is oxidized from oxidation state 0 to +2, satisfies this relation:

$$\frac{24}{2} = 12.$$

It reacts with hydrochloric acid to form magnesium chloride and hydrogen. The calculated volume is

$$V_{\text{acid}}(\text{H}_2) = \frac{0.96 \text{ g}}{24 \text{ g mol}^{-1}} \times 22.4 \text{ dm}^3 \text{ mol}^{-1} = 0.896 \text{ dm}^3.$$

For the alkali-reactive component,

$$\frac{M}{z} = \frac{0.56}{2(0.0400)} = 7.0 \text{ g mol}^{-1}.$$

Silicon, oxidized from 0 to +4 in silicate, satisfies

$$\frac{28}{4} = 7.$$

Silicon resists hydrochloric acid but reacts with aqueous sodium hydroxide, producing soluble silicate and two moles of hydrogen per mole of silicon:

$$V_{\text{alkali}}(\text{H}_2) = 2 \frac{0.56 \text{ g}}{28 \text{ g mol}^{-1}} \times 22.4 \text{ dm}^3 \text{ mol}^{-1} = 0.896 \text{ dm}^3.$$

Magnesium is not appreciably attacked under the stated alkaline conditions. Consequently, the residues are 0.56 g of silicon after acid treatment and 0.96 g of magnesium after alkali treatment, as required.

Formation and acid treatment of the compound.

The amounts of the elements are

$$n(\text{Mg}) = \frac{0.96}{24} = 0.040 \text{ mol}, \quad n(\text{Si}) = \frac{0.56}{28} = 0.020 \text{ mol}.$$

Their mole ratio is exactly 2 : 1, matching magnesium silicide, Mg_2Si . Both elements are therefore completely consumed on heating.

The product amount and mass are

$$\begin{aligned} n(\text{Mg}_2\text{Si}) &= 0.020 \text{ mol}, \\ m(\text{Mg}_2\text{Si}) &= 0.020(2 \times 24 + 28) = 1.52 \text{ g}. \end{aligned}$$

Treatment with hydrochloric acid converts the magnesium to soluble magnesium chloride and the silicon to silane. One mole of magnesium silicide gives one mole of silane, so

$$\begin{aligned} n(\text{SiH}_4) &= 0.020 \text{ mol}, \\ V(\text{SiH}_4) &= 0.020 \times 22.4 = 0.448 \text{ dm}^3. \end{aligned}$$

This matches the third gas volume and explains the absence of a solid residue.

Reaction with oxygen and the pressure decrease.

Silane burns to solid silicon dioxide and water. With water condensed, both products are removed from the gas phase.

Taking the original oxygen charge as 1.00 dm^3 at STP,

$$n_0(\text{O}_2) = \frac{1.00}{22.4} = 0.04464 \text{ mol}.$$

Combustion consumes

$$n_{\text{consumed}}(\text{O}_2) = 2n(\text{SiH}_4) = 0.0400 \text{ mol}.$$

The remaining oxygen is therefore

$$n_f(\text{O}_2) = 0.04464 - 0.0400 = 0.00464 \text{ mol}.$$

At constant temperature and vessel volume, pressure is proportional to the amount of gas:

$$\frac{p_f}{p_0} = \frac{n_f(\text{O}_2)}{n_0(\text{O}_2)} = \frac{1.00 - 2(0.448)}{1.00} = 0.104.$$

Hence

$$\frac{p_0}{p_f} = \frac{1}{0.104} \approx 9.6,$$

consistent with an approximately tenfold decrease.

The molecular and ionic representations used in the reactions are:

Substance	SMILES
Hydrogen, H_2	[H][H]

Substance	SMILES
Hydrogen chloride, HCl, dissolved to give hydrochloric acid	Cl; formal dissociated representation: [H+] . [Cl-]
Sodium hydroxide, NaOH	[Na+] . [OH-]
Magnesium chloride, MgCl ₂	[Mg+2] . [Cl-] . [Cl-]
Sodium metasilicate, Na ₂ SiO ₃ , formal representation	[Na+] . [Na+] . [O-] [Si] (=O) [O-]
Silane, SiH ₄	[SiH4]
Oxygen, O ₂	O=O
Water, H ₂ O	O

Silane has tetrahedral geometry around silicon. The metasilicate equation and SMILES are conventional composition-level representations; aqueous silicate speciation involves hydration and acid–base equilibria. Magnesium silicide and silicon dioxide (silica) are extended solids, so neither has a unique molecular SMILES; silica contains a network of linked silicon–oxygen tetrahedra.

The solution was checked against the official solution.

Problem 2: Mixture of iron and iron oxides

A mixture of metallic iron with freshly prepared iron (II) and iron (III) oxides was heated in a closed vessel in the atmosphere of hydrogen. An amount of 4.72 g of the mixture when reacted, yields 3.92 g of iron and 0.90 g of water.

When the same amount of the mixture was allowed to react with an excess of a copper(II) sulphate solution, 4.96 g of a solid mixture were obtained.

Problems:

2.1 Calculate the amount of 7.3 % hydrochloric acid ($\rho = 1.03 \text{ g cm}^{-3}$) which is needed for a total dissolution of 4.72 g of the starting mixture.

2.2 What volume of a gas at STP is released?

Relative atomic masses:

$$A_r(\text{O}) = 16; \quad A_r(\text{S}) = 32; \quad A_r(\text{Cl}) = 35.5; \quad A_r(\text{Fe}) = 56; \quad A_r(\text{Cu}) = 64$$

Official English text of the problem.

Answers

- 2.1: 70 g of 7.3 % hydrochloric acid solution**, corresponding to approximately 68 cm^3 .
- 2.2: Hydrogen**, H₂, SMILES [H][H]: 0.448 dm^3 at STP, or approximately 0.45 L.

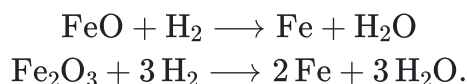
Solution

2.1. Composition of the mixture and acid requirement

Let the initial amounts of metallic iron, iron(II) oxide FeO , and iron(III) oxide Fe_2O_3 be x, y, z mol, respectively.

The oxides can be represented compositionally by the ionic SMILES $[\text{Fe}+2] \cdot [\text{O}-2]$ and $[\text{Fe}+3] \cdot [\text{Fe}+3] \cdot [\text{O}-2] \cdot [\text{O}-2] \cdot [\text{O}-2]$. These represent formal ion proportions, not their crystal structures.

Hydrogen reduces both oxides to iron, producing water, H_2O , SMILES o:



The total amount of iron atoms is therefore

$$x + y + 2z = \frac{3.92}{56} = 0.0700 \text{ mol}.$$

The water yield gives the initial amount of oxygen atoms:

$$y + 3z = \frac{0.90}{18} = 0.0500 \text{ mol}.$$

This agrees with the mass lost by the solid:

$$4.72 - 3.92 = 0.80 \text{ g} = 0.0500 \text{ mol} \times 16 \text{ g mol}^{-1}.$$

In the copper(II) sulphate experiment, metallic iron dissolves while an equimolar amount of copper is deposited. The net ionic equation is



Here copper(II) ion is Cu^{2+} , SMILES $[\text{Cu}+2]$, and iron(II) ion is Fe^{2+} , SMILES $[\text{Fe}+2]$.

With the oxides retained in the solid residue, each mole of metallic iron replaced by copper increases its mass by $64 - 56 = 8$ g. Thus

$$x = \frac{4.96 - 4.72}{64 - 56} = 0.0300 \text{ mol}.$$

Consequently,

$$y + 2z = 0.0700 - 0.0300 = 0.0400, \quad y + 3z = 0.0500,$$

giving

$$\boxed{x = 0.0300, \quad y = 0.0200, \quad z = 0.0100 \text{ mol}}.$$

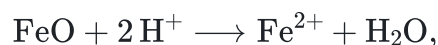
The corresponding masses are

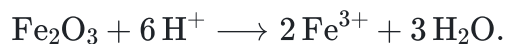
$$m(\text{Fe}) = 1.68 \text{ g}, \quad m(\text{FeO}) = 1.44 \text{ g}, \quad m(\text{Fe}_2\text{O}_3) = 1.60 \text{ g},$$

which sum to 4.72 g.

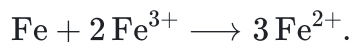
Hydrochloric acid is aqueous hydrogen chloride, HCl , SMILES c1 . It supplies hydrogen ions, H^+ , SMILES $[\text{H}+]$, and chloride ions, Cl^- , SMILES $[\text{Cl}-]$. The hydrogen ions are hydrated in solution; the following equations use conventional net ionic notation.

The oxides dissolve according to

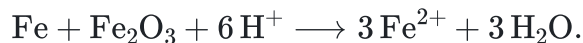




Iron(III) ion, Fe^{3+} , has SMILES [$\text{Fe}+3$]. Crucially, it reacts with metallic iron:



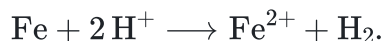
Thus the 0.0100 mol of Fe_2O_3 produces 0.0200 mol of iron(III), consuming 0.0100 mol of metallic iron **without evolving hydrogen**. The combined reaction is



The remaining metal,

$$0.0300 - 0.0100 = 0.0200 \text{ mol},$$

reacts with acid:



Therefore, the total hydrochloric acid requirement is

$$\begin{aligned} n(\text{HCl}) &= 2n(\text{FeO}) + 6n(\text{Fe}_2\text{O}_3) + 2n(\text{remaining Fe}) \\ &= 2(0.0200) + 6(0.0100) + 2(0.0200) \\ &= 0.140 \text{ mol}. \end{aligned}$$

Using $M(\text{HCl}) = 36.5 \text{ g mol}^{-1}$,

$$m(\text{HCl}) = 0.140 \times 36.5 = 5.11 \text{ g}.$$

For a 7.3 % solution by mass,

$$m_{\text{solution}} = \frac{5.11}{0.073} = 70.0 \text{ g},$$

and hence

$$V_{\text{solution}} = \frac{70.0}{1.03} = 67.96 \text{ cm}^3 \approx 68 \text{ cm}^3.$$

2.2. Volume of gas released

The gas is hydrogen. Only the metal remaining after reduction of iron(III) contributes to its yield:

$$n(\text{H}_2) = 0.0300 - 0.0100 = 0.0200 \text{ mol}.$$

Using the conventional STP molar volume $22.4 \text{ dm}^3 \text{ mol}^{-1}$,

$$V(\text{H}_2) = 0.0200 \times 22.4 = 0.448 \text{ dm}^3 = 448 \text{ cm}^3.$$

As a check, the overall dissolution reaction for the determined proportions is



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

Problem 3: Electrolysis of sodium chloride solution with copper electrodes

A volume of 200 cm^3 of a 2-normal sodium chloride solution ($\rho = 1.10\text{ g cm}^{-3}$) was electrolysed at permanent stirring in an electrolytic cell with copper electrodes. Electrolysis was stopped when 22.4 dm^3 (at STP) of a gas were liberated at the cathode.

Problem:

3.1 Calculate the mass percentage of NaCl in the solution after electrolysis.

Relative atomic masses:

$A_r(\text{H}) = 1$; $A_r(\text{O}) = 16$; $A_r(\text{Na}) = 23$; $A_r(\text{Cl}) = 35.5$; $A_r(\text{Cu}) = 64$.

Official English text of the problem.

Answers

- **3.1** 12.7% NaCl by mass in the remaining liquid solution, under the copper(II) hydroxide model described below.

Solution

3.1

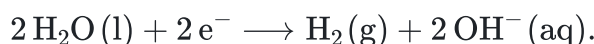
Sodium chloride, NaCl (ionic SMILES $[\text{Na}^+] \cdot [\text{Cl}^-]$), supplies one equivalent per mole, so its initial concentration is 2 mol dm^{-3} . Thus,

$$\begin{aligned}n_0(\text{NaCl}) &= 2\text{ mol dm}^{-3} \times 0.200\text{ dm}^3 = 0.400\text{ mol}, \\m_0(\text{NaCl}) &= 0.400(23 + 35.5) = 23.4\text{ g}.\end{aligned}$$

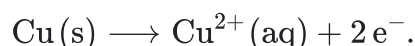
The initial solution mass is

$$m_0(\text{solution}) = \rho V = 1.10\text{ g cm}^{-3} \times 200\text{ cm}^3 = 220\text{ g}.$$

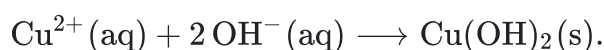
The cathodic gas is **hydrogen**, H_2 , $[\text{H}] [\text{H}]$. In aqueous solution, water, H_2O , O , is reduced rather than sodium ions, Na^+ , $[\text{Na}^+]$. This produces hydroxide ions, OH^- , $[\text{OH}^-]$:



The copper electrode is an active anode. In the conventional copper(II) treatment, copper dissolves as **copper(II) ions**, Cu^{2+} , $[\text{Cu}^{+2}]$:

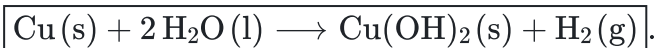


Stirring brings the copper(II) and hydroxide ions together, precipitating **copper(II) hydroxide**, $\text{Cu}(\text{OH})_2$, $[\text{Cu}^{+2}] \cdot [\text{OH}^-] \cdot [\text{OH}^-]$:



The disconnected ionic SMILES indicate composition and charges; they do not depict a crystal lattice.

Adding these reactions gives



Sodium ions and chloride ions, Cl^- , $[\text{Cl}^-]$, are spectators, so the mass of dissolved sodium chloride remains 23.4 g.

Using the molar gas volume at STP,

$$n(\text{H}_2) = \frac{22.4 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 1.00 \text{ mol}.$$

The net reaction therefore consumes 2.00 mol of water:

$$m(\text{water consumed}) = 2.00 \times 18.0 = 36.0 \text{ g}.$$

Consequently, the final **liquid solution** mass, excluding the precipitate, is

$$m_f(\text{solution}) = 220 - 36.0 = 184 \text{ g}.$$

Equivalently, the mass balance includes 64 g of copper entering from the anode, 98 g of hydroxide precipitating, and 2 g of hydrogen escaping:

$$m_f(\text{solution}) = 220 + 64 - 98 - 2 = 184 \text{ g}.$$

Hence,

$$\boxed{w(\text{NaCl}) = \frac{23.4}{184} \times 100\% = 12.7\%}.$$

The solution was checked against the official solution.

Problem 4: Neutralisation heat and final temperature of mixed solutions

Amount of 50 g of a 4 % sodium hydroxide solution and 50 g of a 1.825 % solution of hydrochloric acid were mixed in a heat insulated vessel at a temperature of 20 °C. The temperature of the solution obtained in this way increased to 23.4 °C. Then 70 g of a 3.5 % solution of sulphuric acid at a temperature of 20 °C were added to the above solution.

Problems:

4.1 Calculate the final temperature of the resulting solution.

4.2 Determine the amount of a dry residue that remains after evaporation of the solution.

In calculating the first problem use the heat capacity value $c = 4.19 \text{ J g}^{-1} \text{ K}^{-1}$.

Relative atomic masses:

$$A_r(\text{H}) = 1; \quad A_r(\text{O}) = 16; \quad A_r(\text{Na}) = 23; \quad A_r(\text{S}) = 32; \quad A_r(\text{Cl}) = 35.5.$$

Official English text of the problem.

Answers

- **4.1:** $\boxed{T_f = 24.0 \text{ }^\circ\text{C}}$.

- 4.2: $m_{\text{dry}} = 3.55 \text{ g}$ of anhydrous sodium sulfate, Na_2SO_4 , SMILES $[\text{Na}^+] \cdot [\text{Na}^+] \cdot [\text{O}^-] \text{S}(=\text{O})(=\text{O}) [\text{O}^-]$, assuming complete expulsion of hydrogen chloride during evaporation and drying.

Solution

4.1

The initial reactants are sodium hydroxide, NaOH , SMILES $[\text{Na}^+] \cdot [\text{OH}^-]$, and hydrochloric acid, an aqueous solution of hydrogen chloride, HCl , SMILES Cl .

Their amounts are

$$n(\text{NaOH}) = \frac{(50 \text{ g})(0.04)}{40 \text{ g mol}^{-1}} = 0.0500 \text{ mol},$$

$$n(\text{HCl}) = \frac{(50 \text{ g})(0.01825)}{36.5 \text{ g mol}^{-1}} = 0.0250 \text{ mol}.$$

Neutralisation produces sodium chloride, NaCl , SMILES $[\text{Na}^+] \cdot [\text{Cl}^-]$, and water, H_2O , SMILES O :



Hydrochloric acid is the limiting reactant. Thus 0.0250 mol of water forms, and the same amount of sodium hydroxide remains:

$$n_{\text{remaining}}(\text{NaOH}) = 0.0500 - 0.0250 = 0.0250 \text{ mol}.$$

The heat released in this first reaction is

$$Q_1 = mc\Delta T = (100 \text{ g})(4.19 \text{ J g}^{-1} \text{ K}^{-1})(3.4 \text{ K}) = 1424.6 \text{ J}.$$

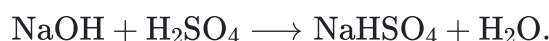
Consequently, the molar enthalpy of neutralisation inferred from the experiment is

$$\Delta_{\text{neut}}H = -\frac{1424.6 \text{ J}}{0.0250 \text{ mol}} \approx -57.0 \text{ kJ mol}^{-1}.$$

The added sulfuric acid, H_2SO_4 , SMILES $\text{OS}(=\text{O})(=\text{O})\text{O}$, has amount

$$n(\text{H}_2\text{SO}_4) = \frac{(70 \text{ g})(0.035)}{98 \text{ g mol}^{-1}} = 0.0250 \text{ mol}.$$

It reacts with the remaining sodium hydroxide in a 1 : 1 molar ratio. The formal salt product is sodium hydrogen sulfate, NaHSO_4 , SMILES $[\text{Na}^+] \cdot [\text{O}^-] \text{S}(=\text{O})(=\text{O})\text{O}$:



A further 0.0250 mol of water forms. Using the same molar neutralisation heat and neglecting dilution effects,

$$Q_2 = Q_1 = 1424.6 \text{ J}.$$

The final heat balance must include warming the added acid solution from 20 °C:

$$(100 \text{ g})c(T_f - 23.4 \text{ °C}) + (70 \text{ g})c(T_f - 20.0 \text{ °C}) = Q_2.$$

Equivalently, all three original solutions started at 20 °C, so

$$(170 \text{ g})c(T_f - 20.0 \text{ °C}) = Q_1 + Q_2.$$

Therefore,

$$T_f - 20.0\text{ }^{\circ}\text{C} = \frac{2849.2\text{ J}}{(170\text{ g})(4.19\text{ J g}^{-1}\text{ K}^{-1})} = 4.0\text{ K},$$

$$\boxed{T_f = 24.0\text{ }^{\circ}\text{C}}.$$

4.2

After mixing, the formal salt amounts are

$$n(\text{NaCl}) = 0.0250\text{ mol}, \quad n(\text{NaHSO}_4) = 0.0250\text{ mol}.$$

During evaporation and sufficiently complete heating, volatile hydrogen chloride can be expelled according to



The two salts are present in exactly the required ratio. Complete hydrogen chloride removal therefore leaves

$$n(\text{Na}_2\text{SO}_4) = 0.0250\text{ mol}.$$

Using the supplied atomic masses,

$$M(\text{Na}_2\text{SO}_4) = 2(23) + 32 + 4(16) = 142\text{ g mol}^{-1},$$

and hence

$$\boxed{m_{\text{dry}} = (0.0250\text{ mol})(142\text{ g mol}^{-1}) = 3.55\text{ g}}.$$

The solution was checked against the official solution.

Problem 5: Hydrocarbon giving a single bromination product

Only one product was obtained by the reaction of bromine with an unknown hydrocarbon. Its density was 5,207 times as great as that of the air.

Problem:

5.1 Determine the structural formula of the unknown hydrocarbon.

Relative atomic masses: $A_r(\text{H}) = 1$; $A_r(\text{C}) = 12$; $A_r(\text{Br}) = 80$.

Official English text of the problem.

Answers

- 5.1** The hydrocarbon is **2,2-dimethylpropane (neopentane)**, $\text{C}(\text{CH}_3)_4$, SMILES: CC(C)(C)C. Its central carbon atom is bonded to four methyl groups.

Solution

5.1

For gases at the same temperature and pressure, the density ratio equals the molar-mass ratio. Taking the usual mean molar mass of air as 29.0 g mol^{-1} , the brominated product has molar mass

$$M_{\text{product}} = 5.207 M_{\text{air}} \approx 5.207 \times 29.0 \approx 151 \text{ g mol}^{-1}.$$

Two bromine atoms alone would contribute 160 g mol^{-1} . Consequently, the product contains **one bromine atom**, and ordinary addition of bromine across a multiple bond is excluded. The reaction is substitution of a hydrogen atom by bromine.

Write the product formula as $\text{C}_n\text{H}_m\text{Br}$. Using the supplied atomic masses,

$$12n + m + 80 = 151, \quad 12n + m = 71.$$

For a neutral molecule containing carbon, hydrogen, and one bromine atom, the maximum hydrogen count is $m = 2n + 1$. Thus

$$0 \leq 71 - 12n \leq 2n + 1,$$

which gives

$$5 \leq n \leq \frac{71}{12} < 6.$$

Therefore $n = 5$ and $m = 11$: the product has formula $\text{C}_5\text{H}_{11}\text{Br}$, and the original hydrocarbon has formula C_5H_{12} .

There are three constitutional isomers of this hydrocarbon:

Hydrocarbon	SMILES	Number of constitutional monobromination products
Pentane	CCCCC	3
2-Methylbutane	CC(C)CC	4
2,2-Dimethylpropane (neopentane)	CC(C)(C)C	1

Pentane has three inequivalent hydrogen positions: the terminal methyl groups, the adjacent methylene groups, and the central methylene group. 2-Methylbutane has four inequivalent hydrogen positions.

In **neopentane**, the central carbon carries no hydrogen, and all four methyl groups are equivalent. Replacing any of its twelve hydrogen atoms therefore gives the same product.

The balanced monobromination equation, under radical conditions, is



Here bromine, BrBr , produces **1-bromo-2,2-dimethylpropane (neopentyl bromide)**, $\text{CC}(\text{C})(\text{C})\text{CBr}$, together with hydrogen bromide, $[\text{H}]\text{Br}$. The organic product is achiral, so no stereochemical distinction is required.

Its molar mass confirms the result:

$$M(\text{C}_5\text{H}_{11}\text{Br}) = (5 \times 12 + 11 \times 1 + 80) \text{ g mol}^{-1} = 151 \text{ g mol}^{-1},$$

$$\frac{151}{29.0} = 5.2069 \approx 5.207.$$

The solution was checked against the official solution.

Problem 6: Organic compounds A-D from elemental analysis and

titration

Organic compound **A** is 41.38 % carbon, 3.45 % hydrogen and the rest is oxygen. Compound **A** when heated with ethanol in the presence of an acid yields a new substance **B** which contains 55.81 % carbon, 6.97 % hydrogen, and oxygen.

The initial compound **A** when allowed to react with hydrobromide yields product **C** which on boiling in water gives substance **D** containing 35.82 % carbon, 4.48 % hydrogen, and oxygen. An amount of 2.68 g of substance **D** required reacting with 20 cm³ of a 2 N solution of potassium hydroxide.

Problems:

6.1 Determine structural formulas of all the above mentioned substances **A**, **B**, **C** and **D**.

Use the finding that compound **A** splits off water when heated.

6.2 Write chemical equations for the above reactions.

Relative atomic masses: $A_r(\text{H}) = 1$; $A_r(\text{C}) = 12$; $A_r(\text{O}) = 16$; $A_r(\text{K}) = 39$.

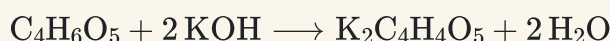
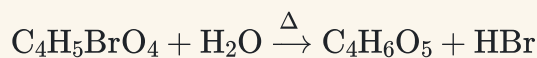
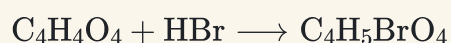
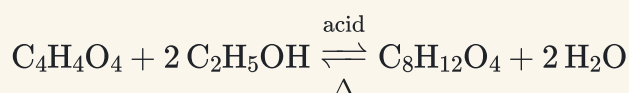
Official English text of the problem.

Answers

- 6.1** The compounds are:

Compound	Identification and molecular formula	Structural SMILES
A	Maleic acid , (<i>Z</i>)-but-2-enedioic acid, C ₄ H ₄ O ₄	<chem>O=C(O)/C=C\C(=O)O</chem>
B	Diethyl maleate , diethyl (<i>Z</i>)-but-2-enedioate, C ₈ H ₁₂ O ₄	<chem>CCOC(=O)/C=C\C(=O)OCC</chem>
C	Racemic 2-bromosuccinic acid , 2-bromobutanedioic acid, C ₄ H ₅ BrO ₄	Equal amounts of <chem>O=C(O)[C@H](Br)CC(=O)O</chem> and <chem>O=C(O)[C@@H](Br)CC(=O)O</chem>
D	Racemic malic acid , 2-hydroxybutanedioic acid, C ₄ H ₆ O ₅	Equal amounts of <chem>O=C(O)[C@H](O)CC(=O)O</chem> and <chem>O=C(O)[C@@H](O)CC(=O)O</chem>

- 6.2** The balanced equations, in molecular form, are:



The last two organic products are dipotassium malate and maleic anhydride, respectively; their structures are specified below.

Solution

6.1 — Identification of A–D

For a 100 g sample of each compound, the oxygen masses are obtained by difference. Dividing the elemental masses by the supplied relative atomic masses gives:

Compound	Oxygen percentage	$n(\text{C})/\text{mol}$	$n(\text{H})/\text{mol}$	$n(\text{O})/\text{mol}$	Simplest ratio and empirical formula
A	55.17	3.4483	3.450	3.4481	1 : 1 : 1, CHO
B	37.22	4.6508	6.970	2.3263	2 : 3 : 1, C ₂ H ₃ O
D	59.70	2.9850	4.480	3.7313	4 : 6 : 5, C ₄ H ₆ O ₅

Establishing the molecular formulas. Acid-catalysed reaction with ethanol indicates esterification. Each carboxyl group esterified gains C₂H₄ overall, while the number of oxygen atoms remains unchanged.

Let A have molecular formula C_{*n*}H_{*n*}O_{*n*}. From B's empirical formula and the unchanged oxygen count, B then has formula C_{2*n*}H_{3*n*}O_{*n*}. The gain of *n* carbon atoms requires esterification of *n*/2 carboxyl groups. Those groups account for all *n* oxygen atoms in A.

A's degree of unsaturation is

$$\text{DBE} = \frac{2n + 2 - n}{2} = \frac{n}{2} + 1.$$

Its *n*/2 carboxyl carbonyls account for all but one degree of unsaturation. The remaining unsaturation is the carbon–carbon double bond that undergoes hydrogen bromide addition.

Addition of hydrogen bromide, followed by hydrolysis of the carbon–bromine bond, amounts to adding one molecule of water across this double bond. Therefore,

$$M_D = M_A + 18 \text{ g mol}^{-1}.$$

The carbon mass per mole is unchanged. Using the carbon percentages,

$$0.4138M_A = 0.3582(M_A + 18),$$

so

$$M_A = \frac{0.3582(18)}{0.4138 - 0.3582} = 115.96 \text{ g mol}^{-1} \approx 116 \text{ g mol}^{-1}.$$

Since A's empirical formula mass is $12 + 1 + 16 = 29$,

$$n = \frac{116}{29} = 4.$$

Consequently,

$$A : \text{C}_4\text{H}_4\text{O}_4, \quad B : \text{C}_8\text{H}_{12}\text{O}_4, \quad C : \text{C}_4\text{H}_5\text{BrO}_4, \quad D : \text{C}_4\text{H}_6\text{O}_5.$$

In particular, A contains $n/2 = 2$ carboxyl groups.

Checking D by titration. The potassium hydroxide supplies

$$n_{\text{eq}} = (20 \times 10^{-3} \text{ L})(2 \text{ eq L}^{-1}) = 0.040 \text{ eq}.$$

Thus D's neutralization equivalent is

$$E_D = \frac{2.68 \text{ g}}{0.040 \text{ eq}} = 67 \text{ g eq}^{-1}.$$

Its molar mass is

$$M_D = 4(12) + 6(1) + 5(16) = 134 \text{ g mol}^{-1}.$$

Therefore, D supplies $134/67 = 2$ acid equivalents per mole, confirming two carboxyl groups. Its fifth oxygen belongs to the alcoholic hydroxyl group introduced by hydrolysis. This alcoholic group is not neutralized in the aqueous carboxylic-acid titration.

Determining connectivity and stereochemistry. The heating clue identifies the arrangement that permits direct formation of a five-membered cyclic anhydride:

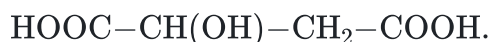


The two carboxyl groups must lie on the **same side** of the double bond. Hence A is **maleic acid**, the *Z* isomer. The trans isomer, fumaric acid, $\text{O}=\text{C}(\text{O})/\text{C}=\text{C}/\text{C}(=\text{O})\text{O}$, lacks the geometry for direct ring closure.

Esterification of both carboxyl groups gives **diethyl maleate B**, retaining the *Z* double bond. Addition of hydrogen bromide gives **2-bromosuccinic acid C**:



Replacing bromine by hydroxyl gives **malic acid D**:

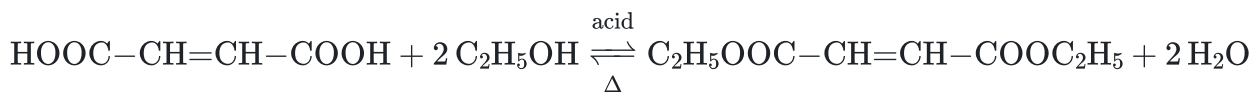


C and D each contain one stereocentre. Because the starting material and reaction conditions are achiral, both products are racemic mixtures, represented by the two enantiomeric SMILES in the answer table.

6.2 — Reaction equations

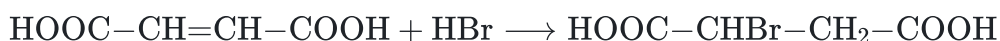
The small-molecule reagents and products are ethanol CCO , hydrogen bromide Br , water O , and potassium hydroxide $[\text{K}^+] \cdot [\text{OH}^-]$.

Esterification, A → B:



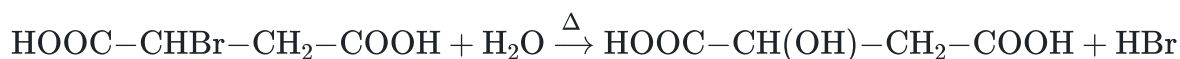
Both alkene structures have *Z* geometry.

Hydrogen bromide addition, A → C:



Hydrogen and bromine add across the double bond. The symmetry of A makes the two alkene carbon atoms equivalent.

Hydrolysis on boiling in water, C → D:



Neutralization of D:

The product is **racemic dipotassium malate**, represented by equal amounts of $[\text{K}^+]$.

$[\text{K}^+] \cdot \text{O}=\text{C}([\text{O}^-])[\text{C}@\text{H}](\text{O})\text{CC}(=\text{O})[\text{O}^-]$ and $[\text{K}^+] \cdot [\text{K}^+] \cdot \text{O}=\text{C}([\text{O}^-])[\text{C}@@\text{H}](\text{O})\text{CC}(=\text{O})[\text{O}^-]$.

Thermal dehydration of A:

The product is **maleic anhydride**, furan-2,5-dione, $\text{O}=\text{C}1\text{OC}(=\text{O})\text{C}=\text{C}1$. It contains a five-membered ring comprising the two alkene carbon atoms, the two carbonyl carbon atoms, and the bridging anhydride oxygen.

The solution was checked against the official solution.