

IChO 1970

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Problem 1: Structure of a gas from its combustion products

An amount of 23 g of gas (density $\rho = 2.05 \text{ g dm}^{-3}$ at STP) when burned, gives 44 g of carbon dioxide and 27 g of water.

Problem:

What is the structural formula of the gas (compound)?

Official English text of the problem.

Answers

1. **Dimethyl ether (methoxymethane)**, $\text{CH}_3\text{—O—CH}_3$, with molecular formula $\text{C}_2\text{H}_6\text{O}$.
SMILES: COC.

Solution

1. Determine the composition and molecular formula.

The combustion products are carbon dioxide ($\text{O}=\text{C}=\text{O}$) and water (H_2O). Using the conventional atomic masses 12, 1, and 16 for carbon, hydrogen, and oxygen:

$$n(\text{CO}_2) = \frac{44 \text{ g}}{44 \text{ g mol}^{-1}} = 1.0 \text{ mol},$$

$$n(\text{H}_2\text{O}) = \frac{27 \text{ g}}{18 \text{ g mol}^{-1}} = 1.5 \text{ mol}.$$

Thus the sample contains 1.0 mol of carbon atoms and $2(1.5) = 3.0$ mol of hydrogen atoms, corresponding to 12 g of carbon and 3 g of hydrogen.

The remaining mass is oxygen:

$$m_{\text{O}} = 23 - 12 - 3 = 8 \text{ g}, \quad n_{\text{O}} = \frac{8 \text{ g}}{16 \text{ g mol}^{-1}} = 0.50 \text{ mol}.$$

The atomic ratio is therefore

$$n_{\text{C}} : n_{\text{H}} : n_{\text{O}} = 1.0 : 3.0 : 0.50 = 2 : 6 : 1,$$

giving the empirical formula $\text{C}_2\text{H}_6\text{O}$, with empirical formula mass 46 g mol^{-1} .

Using the ideal-gas molar volume at conventional STP, $V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}$,

$$M = \rho V_m = (2.05 \text{ g dm}^{-3})(22.4 \text{ dm}^3 \text{ mol}^{-1}) = 45.9 \text{ g mol}^{-1}.$$

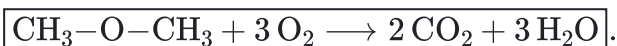
This agrees with the empirical formula mass, so the molecular formula is $\text{C}_2\text{H}_6\text{O}$.

There are two constitutional isomers:

- **Dimethyl ether**, $\text{CH}_3\text{—O—CH}_3$, SMILES coc.
- **Ethanol**, $\text{CH}_3\text{—CH}_2\text{—OH}$, SMILES cco.

Dimethyl ether is gaseous at STP, whereas ethanol is liquid. The stated gaseous state therefore identifies **dimethyl ether**, whose oxygen atom is bonded to two methyl groups.

Its balanced combustion equation, using dioxygen ($\text{O}=\text{O}$), is



Indeed, 23 g is 0.50 mol of dimethyl ether, producing 1.0 mol (44 g) of carbon dioxide and 1.5 mol (27 g) of water.

The solution was checked against the official solution.

Problem 2: Water of crystallisation in two samples of crystalline soda

A sample of crystalline soda (A) with a mass of 1.287 g was allowed to react with an excess of hydrochloric acid and 100.8 cm³ of a gas was liberated (measured at STP).

Another sample of different crystalline soda (B) with a mass of 0.715 g was decomposed by 50 cm³ of 0.2 N sulphuric acid.

After total decomposition of soda, the excess of the sulphuric acid was neutralized which required 50 cm³ of 0.1 N sodium hydroxide solution (by titration on methyl orange indicator).

Problems:

2.1 How many molecules of water in relation to one molecule of Na_2CO_3 are contained in the first sample of soda?

2.2 Have both samples of soda the same composition?

Relative atomic masses: $A_r(\text{Na}) = 23$; $A_r(\text{H}) = 1$; $A_r(\text{C}) = 12$; $A_r(\text{O}) = 16$.

Official English text of the problem.

Answers

- **2.1** Sample A contains **10 molecules of water** (SMILES o) per formula unit of Na_2CO_3 . It is **sodium carbonate decahydrate**, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$; component SMILES: [Na+].[Na+].[O-]C(=O)[O-].O.O.O.O.O.O.O.O.O.O.O.
- **2.2 Yes.** Both samples have the composition $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$.

The hydrate SMILES specifies its constituent ions and water molecules; it does not represent their arrangement in the crystal lattice.

Solution

2.1

Write the composition of sample A as $\text{Na}_2\text{CO}_3 \cdot x \text{H}_2\text{O}$. The given atomic masses yield

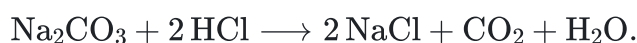
$$M(\text{Na}_2\text{CO}_3) = 2(23) + 12 + 3(16) = 106 \text{ g mol}^{-1},$$

$$M(\text{H}_2\text{O}) = 2(1) + 16 = 18 \text{ g mol}^{-1}.$$

Thus the hydrate has molar mass

$$M_A = (106 + 18x) \text{ g mol}^{-1}.$$

The carbonate component reacts with hydrochloric acid according to



The water of crystallisation enters the solution. The liberated gas is **carbon dioxide**, and one mole of hydrate produces one mole of CO_2 .

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

$$n(\text{CO}_2) = \frac{0.1008 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 4.50 \times 10^{-3} \text{ mol}.$$

Therefore,

$$M_A = \frac{1.287 \text{ g}}{4.50 \times 10^{-3} \text{ mol}} = 286 \text{ g mol}^{-1},$$

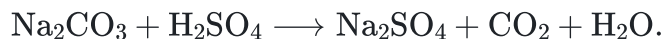
and

$$106 + 18x = 286 \implies \boxed{x = 10}.$$

Sample A is consequently $\boxed{\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}}$.

2.2

The carbonate component of sample B reacts with sulphuric acid:



The excess sulphuric acid is then neutralized:



Normality expresses reactive equivalents per litre. The initial amount of acid, in equivalents, was

$$E_{\text{initial}} = (0.2 \text{ eq L}^{-1})(0.050 \text{ L}) = 0.010 \text{ eq}.$$

The sodium hydroxide titre measures the remaining acid:

$$E_{\text{excess}} = (0.1 \text{ eq L}^{-1})(0.050 \text{ L}) = 0.0050 \text{ eq}.$$

Thus sample B consumed

$$E_B = 0.010 - 0.0050 = 0.0050 \text{ eq}.$$

Each mole of sodium carbonate consumes two acid equivalents, so

$$n_B(\text{Na}_2\text{CO}_3) = \frac{0.0050 \text{ eq}}{2 \text{ eq mol}^{-1}} = 2.5 \times 10^{-3} \text{ mol.}$$

Writing sample B as $\text{Na}_2\text{CO}_3 \cdot y \text{H}_2\text{O}$, its molar mass is

$$M_B = \frac{0.715 \text{ g}}{2.5 \times 10^{-3} \text{ mol}} = 286 \text{ g mol}^{-1}.$$

Hence

$$y = \frac{286 - 106}{18} = 10.$$

Therefore **both samples have the same composition**, $\boxed{\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}}$.

The names and SMILES of the other species appearing in the reactions are:

Species	Formula	SMILES
Sodium carbonate	Na_2CO_3	<chem>[Na+] . [Na+] . [O-] C(=O) [O-]</chem>
Hydrogen chloride, used as aqueous hydrochloric acid	HCl	<chem>Cl</chem>
Sodium chloride	NaCl	<chem>[Na+] . [Cl-]</chem>
Carbon dioxide	CO_2	<chem>O=C=O</chem>
Water	H_2O	<chem>O</chem>
Sulphuric acid	H_2SO_4	<chem>OS(=O)(=O)O</chem>
Sodium sulphate	Na_2SO_4	<chem>[Na+] . [Na+] . [O-] S(=O)(=O) [O-]</chem>
Sodium hydroxide	NaOH	<chem>[Na+] . [OH-]</chem>

The solution was checked against the official solution.

Problem 3: Equilibrium mixture from carbon monoxide and water vapour

Carbon monoxide was mixed with 1.5 times greater volume of water vapours. What will be the composition (in mass as well as in volume %) of the gaseous mixture in the equilibrium state if 80 % of carbon monoxide is converted to carbon dioxide?

Official English text of the problem.

Answers

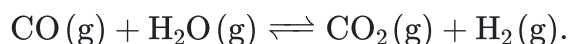
- Problem 3:** The equilibrium mixture has the following composition, including the remaining water vapour:

Component	Mass %	Volume %
Carbon monoxide, CO , <chem>[C-]#[O+]</chem>	10.2	8.0
Water vapour, H_2O , <chem>O</chem>	22.9	28.0

Component	Mass %	Volume %
Carbon dioxide, CO ₂ , O=C=O	64.0	32.0
Hydrogen, H ₂ , [H][H]	2.9	32.0
Total	100.0	100.0

Solution

The balanced equilibrium reaction is



At the same temperature and pressure, ideal-gas volumes are proportional to amounts in moles. Taking the initial water-vapour volume as 1.5 times the carbon-monoxide volume, choose a basis of

$$n_0(\text{CO}) = 1.00 \text{ mol}, \quad n_0(\text{H}_2\text{O}) = 1.50 \text{ mol}.$$

Since 80% of the carbon monoxide reacts, the amount consumed is

$$n_{\text{reacted}}(\text{CO}) = 0.80(1.00 \text{ mol}) = 0.80 \text{ mol}.$$

The reaction consumes an equal amount of water and forms 0.80 mol each of carbon dioxide and hydrogen.

Using the conventional molar masses 28, 18, 44, 2 g mol⁻¹, respectively:

Species	Initial amount / mol	Change / mol	Equilibrium amount / mol	Equilibrium mass / g
CO	1.00	-0.80	0.20	5.60
H ₂ O	1.50	-0.80	0.70	12.60
CO ₂	0	+0.80	0.80	35.20
H ₂	0	+0.80	0.80	1.60
Total	2.50	0	2.50	55.00

The **mass percentages** follow from

$$\text{Mass percentage of } i = \frac{m_i}{55.00 \text{ g}} \times 100\%.$$

Thus, in the order CO, H₂O, CO₂, H₂,

$$\frac{(5.60, 12.60, 35.20, 1.60)}{55.00} \times 100\% \approx (10.2, 22.9, 64.0, 2.9)\%.$$

The **volume percentages** equal the mole percentages:

$$\text{Volume percentage of } i = \frac{n_i}{2.50 \text{ mol}} \times 100\%.$$

Therefore, in the same order,

$$\frac{(0.20, 0.70, 0.80, 0.80)}{2.50} \times 100\% = (8.0, 28.0, 32.0, 32.0)\%.$$

The solution was checked against the official solution.

Problem 4: Alloy of rubidium with another alkali metal

An alloy consists of rubidium and one of the other alkali metals. A sample of 4.6 g of the alloy when allowed to react with water, liberates 2.241 dm³ of hydrogen at STP.

Problems:

4.1 Which alkali metal is the component of the alloy?

4.2 What composition in % by mass has the alloy?

Relative atomic masses:

$A_r(\text{Li}) = 7$; $A_r(\text{Na}) = 23$; $A_r(\text{K}) = 39$; $A_r(\text{Rb}) = 85.5$; $A_r(\text{Cs}) = 133$

Official English text of the problem.

Answers

- **4.1:** Lithium, Li.
- **4.2:** Approximately **24.2% lithium** and **75.8% rubidium** by mass.

Solution

4.1 — Identification of the second metal

All alkali metals react with water according to



where M represents an alkali metal. Thus, two moles of metal atoms produce one mole of hydrogen.

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

$$n(\text{H}_2) = \frac{2.241 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.10004 \text{ mol}.$$

The total amount of metal is therefore

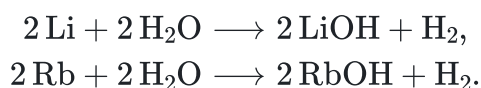
$$n_{\text{metals}} = 2n(\text{H}_2) = 0.20009 \text{ mol}.$$

The mean molar mass of the alloy's metal atoms is

$$\overline{M} = \frac{4.6 \text{ g}}{0.20009 \text{ mol}} \approx 22.99 \text{ g mol}^{-1}.$$

This is a mole-weighted average of the two metals' molar masses. Rubidium has a molar mass of 85.5 g mol^{-1} , so the other metal must have a molar mass **below** 22.99 g mol^{-1} . Of the listed alkali metals, only **lithium**, with $M = 7 \text{ g mol}^{-1}$, satisfies this condition.

The reactions are



The molecular species are water O and hydrogen [H][H]. The products are lithium hydroxide [Li+].[OH-] and rubidium hydroxide [Rb+].[OH-], present as dissociated ions in water.

4.2 — Mass composition

Let x be the mass of lithium. The mass of rubidium is $4.6 \text{ g} - x$. The total amount of metal gives

$$\frac{x}{7 \text{ g mol}^{-1}} + \frac{4.6 \text{ g} - x}{85.5 \text{ g mol}^{-1}} = 0.200089 \text{ mol.}$$

Solving, with guard digits retained,

$$m(\text{Li}) = 1.11533 \text{ g}, \quad m(\text{Rb}) = 3.48467 \text{ g.}$$

Hence the mass percentages are

$$w(\text{Li}) = \frac{1.11533}{4.6} \times 100\% \approx \boxed{24.2\%},$$
$$w(\text{Rb}) = \frac{3.48467}{4.6} \times 100\% \approx \boxed{75.8\%}.$$

The solution was checked against the official solution.

Problem 5: Crystallisation of copper(II) sulphate pentahydrate

An amount of 20 g of copper (II) oxide was treated with a stoichiometric amount of a warm 20% sulphuric acid solution to produce a solution of copper (II) sulphate.

Problem:

How many grams of crystalline copper(II) sulphate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) have crystallised when the solution is cooled to 20°C ?

Relative atomic masses: $A_r(\text{Cu}) = 63.5$; $A_r(\text{S}) = 32$; $A_r(\text{O}) = 16$; $A_r(\text{H}) = 1$

Solubility of CuSO_4 at 20°C : $s = 20.9 \text{ g}$ of CuSO_4 in 100 g of H_2O .

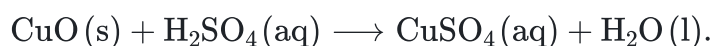
Official English text of the problem.

Answers

- **Problem 5:** $\boxed{32.9 \text{ g}}$ of copper(II) sulphate pentahydrate, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, crystallises.
SMILES: [Cu+2].[O-]S(=O)(=O)[O-].O.O.O.O.O.

Solution

Copper(II) oxide ([Cu+2].[O-2]) reacts with sulphuric acid (OS(=O)(=O)O) to produce copper(II) sulphate ([Cu+2].[O-]S(=O)(=O)[O-]) and water (O):



The SMILES for the ionic compounds specify formula-unit compositions; they do not encode crystal lattices or coordination geometries.

Using the given atomic masses, the molar masses are

$$\begin{aligned}
 M(\text{CuO}) &= 79.5 \text{ g mol}^{-1}, \\
 M(\text{H}_2\text{SO}_4) &= 98 \text{ g mol}^{-1}, \\
 M(\text{H}_2\text{O}) &= 18 \text{ g mol}^{-1}, \\
 M(\text{CuSO}_4) &= 159.5 \text{ g mol}^{-1}, \\
 M(\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}) &= 159.5 + 5(18) = 249.5 \text{ g mol}^{-1}.
 \end{aligned}$$

The amount of copper(II) oxide is

$$n = \frac{20 \text{ g}}{79.5 \text{ g mol}^{-1}} = 0.251572 \text{ mol}.$$

The reaction consumes this same amount of sulphuric acid and produces this amount of both copper(II) sulphate and water. Thus,

$$\begin{aligned}
 m(\text{H}_2\text{SO}_4) &= 0.251572(98) = 24.6541 \text{ g}, \\
 m(\text{CuSO}_4) &= 0.251572(159.5) = 40.1258 \text{ g}, \\
 m(\text{reaction water}) &= 0.251572(18) = 4.52830 \text{ g}.
 \end{aligned}$$

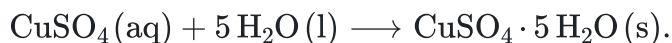
The acid solution contains 20% sulphuric acid by mass, so its mass is

$$m(\text{acid solution}) = \frac{24.6541}{0.20} = 123.2704 \text{ g}.$$

The total water present after reaction includes both the water supplied with the acid and the water formed:

$$m_{\text{water},0} = 0.80(123.2704) + 4.52830 = 103.1447 \text{ g}.$$

On cooling, pentahydrate crystals form:



Crystallisation removes both dissolved salt and water from the solution. Let x be the mass of pentahydrate crystals. These crystals contain

$$\frac{159.5}{249.5}x \text{ of CuSO}_4, \quad \frac{90}{249.5}x \text{ of H}_2\text{O}.$$

The remaining solution is saturated at 20 °C, giving

$$\frac{40.1258 \text{ g} - \frac{159.5}{249.5}x}{103.1447 \text{ g} - \frac{90}{249.5}x} = \frac{20.9}{100}.$$

Therefore,

$$x = \frac{40.1258 - 0.209(103.1447)}{\frac{159.5}{249.5} - 0.209\frac{90}{249.5}} \text{ g} = 32.9295 \text{ g}.$$

Hence the mass crystallised is

$$\boxed{m(\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}) = 32.9 \text{ g}}.$$

The solution was checked against the official solution.

Problem 6: Two oxides of the same metal

Oxide of a certain metal contains 22.55 % of oxygen by mass. Another oxide of the same metal contains 50.48 mass % of oxygen.

Problem:

1. What is the relative atomic mass of the metal?

Official English text of the problem.

Answers

1. The relative atomic mass is approximately **55** ($A_r \approx 54.94$). The metal is **manganese**, Mn.
Relative atomic mass is dimensionless.

Solution

1.

Let the metal have relative atomic mass A and oxidation states n_1 and n_2 in the two oxides. Taking $A_r(\text{O}) = 16.00$, oxygen's oxidation state of -2 gives

$$\frac{m(\text{oxygen})}{m(\text{metal})} = \frac{8n}{A}.$$

The oxygen-to-metal mass ratios are therefore

$$\frac{8n_1}{A} = \frac{22.55}{77.45}, \quad \frac{8n_2}{A} = \frac{50.48}{49.52}.$$

Dividing eliminates A :

$$\frac{n_2}{n_1} = \frac{50.48/49.52}{22.55/77.45} = 3.50117 \approx \frac{7}{2}.$$

The smallest whole-number oxidation states consistent with this ratio are $+2$ and $+7$. Higher proportional pairs would require chemically unreasonable oxidation states for these ordinary metal oxides. Thus the formulas are MO and M_2O_7 .

From the first oxide,

$$\frac{16.00}{A + 16.00} = 0.2255,$$

so

$$A = 16.00 \frac{77.45}{22.55} = 54.95.$$

Independently, the second oxide gives

$$\frac{7(16.00)}{2A + 7(16.00)} = 0.5048,$$

hence

$$A = \frac{7(16.00)}{2} \frac{49.52}{50.48} = 54.94.$$

These results agree within the rounding of the supplied percentages and identify **manganese**, with

$$A_r(\text{Mn}) \approx 54.94 \approx 55.$$

The oxides are:

- **Manganese(II) oxide**, MnO : ionic formula-unit SMILES $[\text{Mn}^{+2}] \cdot [\text{O}^{2-}]$. The solid forms an extended ionic lattice; this notation does not represent a discrete molecule.
- **Manganese(VII) oxide**, Mn_2O_7 : SMILES $\text{O}=[\text{Mn}](=\text{O})(=\text{O})\text{O}[\text{Mn}](=\text{O})(=\text{O})=\text{O}$. A bridging oxygen joins two approximately tetrahedrally coordinated manganese centres.

As a check, $A = 54.94$ gives oxygen contents of 22.5543% and 50.4777%, which round to the stated values.

The solution was checked against the official solution.