

IChO 1974

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Problem 1: From electrolytic hydrogen to methyl orange

By electrochemical decomposition of water, there are in an electric circuit a voltmeter, platinum electrodes and a battery containing ten galvanic cells connected in series, each of it having the voltage of 1.5 V and internal resistance of 0.4 Ω . The resistance of the voltmeter is 0.5 Ω and the polarisation voltage of the battery is 1.5 V. Electric current flows for 8 hours, 56 minutes and 7 seconds through the electrolyte. Hydrogen obtained in this way was used for a synthesis with another substance, thus forming a gaseous substance **A** which can be converted by oxidation with oxygen via oxide to substance **B**.

By means of substance **B** it is possible to prepare substance **C** from which after reduction by hydrogen substance **D** can be obtained. Substance **D** reacts at 180 °C with a concentration solution of sulphuric acid to produce sulphanilic acid. By diazotization and successive copulation with p-N,N-dimethylaniline, an azo dye, methyl orange is formed.

Problems:

1. Write chemical equations for all the above mentioned reactions.
2. Calculate the mass of product **D**.
3. Give the exact chemical name for the indicator methyl orange. Show by means of structural formulas what changes take place in dependence on concentration of H_3O^+ ions in the solution.

Relative atomic masses: $A_r(\text{N}) = 14$; $A_r(\text{O}) = 16$; $A_r(\text{C}) = 12$; $A_r(\text{H}) = 1$.

Official English text of the problem.

Answers

1. The substances are:

Label	Identity	SMILES
A	Ammonia, NH_3	<chem>N</chem>
B	Nitric acid, HNO_3	<chem>O=[N+]([O-])O</chem>
C	Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$	<chem>O=[N+]([O-])c1ccccc1</chem>
D	Aniline, $\text{C}_6\text{H}_5\text{NH}_2$	<chem>Nc1ccccc1</chem>

Aniline is sulfonated to sulfanilic acid, which is diazotized and coupled with N,N-dimethylaniline to give methyl orange. All balanced equations appear in Solution 1.

2. $m(\mathbf{D}) \approx 31 \text{ g}$, assuming quantitative conversion and an additional hydrogen supply for the reduction of **C**.
3. Methyl orange is **sodium 4-[[4-(dimethylamino)phenyl]diazenyl]benzenesulfonate**, also called sodium 4-[(4-dimethylaminophenyl)azo]benzenesulfonate. Its usual *E* form has SMILES
CN(C)c1ccc(/N=N/c2ccc(S(=O)(=O)[O-])cc2)cc1.[Na+].

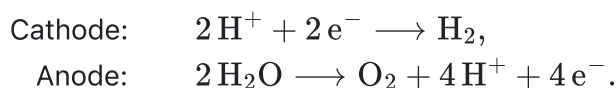
Its azo anion is **yellow**; increasing the hydronium concentration produces the **red protonated form**, whose resonance contributors are shown in Solution 3.

Solution

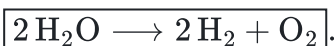
1. Identification and balanced reaction equations

Working backwards, sulfanilic acid is an aniline derivative with a sulfonic acid group para to the amino group. Therefore **D** is aniline. Hydrogenation of nitrobenzene gives aniline, identifying **C**. Nitrobenzene can be prepared by nitrating benzene with nitric acid, identifying **B**. Finally, ammonia is synthesized from hydrogen and nitrogen and can be oxidized through nitrogen oxides to nitric acid, identifying **A**.

Electrolysis of water. Water (O) produces hydrogen ($[\text{H}][\text{H}]$) and oxygen ($\text{O}=\text{O}$). Using the conventional aqueous proton notation, H^+ ($[\text{H}+]$), the electrode reactions are

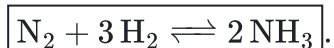


Thus,

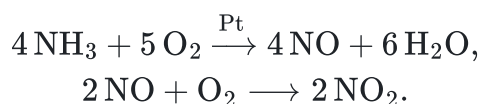


The proton notation suppresses its hydration in water.

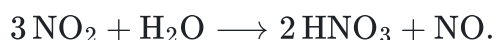
Synthesis of ammonia, A. Hydrogen reacts with nitrogen ($\text{N}\equiv\text{N}$), using an iron catalyst at elevated temperature and pressure:



Conversion of A into nitric acid, B. Catalytic oxidation first gives nitrogen monoxide ($[\text{N}]=\text{O}$), which is oxidized further to nitrogen dioxide ($\text{O}=[\text{N}+][\text{O}-]$):



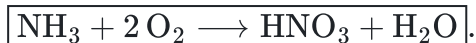
Absorption in water gives nitric acid and regenerates nitrogen monoxide:



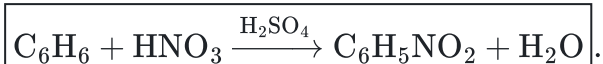
The regenerated nitrogen monoxide is reoxidized. Consequently, absorption with sufficient oxygen has the overall equation



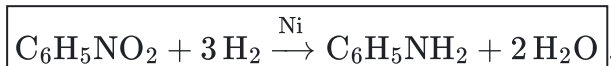
The net conversion of ammonia into nitric acid is therefore



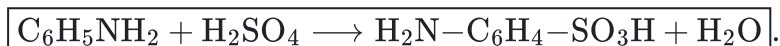
Preparation of nitrobenzene, C. Benzene (c1ccccc1) is nitrated with nitric acid in the presence of concentrated sulfuric acid (OS(=O)(=O)O):



Reduction to aniline, D. Catalytic hydrogenation, for example over nickel, gives



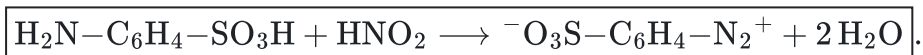
Sulfonation of aniline. Heating with concentrated sulfuric acid at 180 °C produces sulfanilic acid, or 4-aminobenzenesulfonic acid: Nc1ccc(S(=O)(=O)O)cc1.



The amino and sulfonic acid groups occupy positions 1 and 4. Sulfanilic acid commonly exists as the zwitterion [NH3+]c1ccc(S(=O)(=O)[O-])cc1; the equation above uses its neutral structural representation.

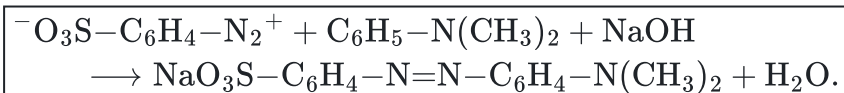
Diazotization. Nitrous acid (O=NO) converts the amino group into a diazonium group in acidic solution at approximately 0–5 °C. The product is 4-diazoniobenzenesulfonate, an inner salt: [N+]c1ccc(S(=O)(=O)[O-])cc1.

Its balanced net formation is



The diazonium and sulfonate groups remain para to each other.

Azo coupling and formation of methyl orange. N,N-Dimethylaniline (CN(C)c1ccccc1) couples at the carbon para to its dimethylamino group. Coupling followed by neutralization with sodium hydroxide ([Na+].[OH-]) has the combined equation



Both benzene rings in the product are para-disubstituted. The product is the sodium salt methyl orange identified in Answer 3.

2. Mass of aniline

Treating the stated resistances as series resistances, the total electromotive force and resistance are

$$\begin{aligned}\mathcal{E} &= 10(1.5 \text{ V}) = 15 \text{ V}, \\ R &= 10(0.4 \Omega) + 0.5 \Omega = 4.5 \Omega.\end{aligned}$$

The polarization voltage opposes the applied electromotive force. Hence

$$I = \frac{\mathcal{E} - E_{\text{pol}}}{R} = \frac{15 - 1.5}{4.5} = 3.0 \text{ A}.$$

The electrolysis time is

$$t = 8(3600) + 56(60) + 7 = 32167 \text{ s}.$$

Therefore the charge passed is

$$Q = It = (3.0 \text{ A})(32167 \text{ s}) = 96501 \text{ C}.$$

Using the standard Faraday constant $F \approx 96500 \text{ C mol}^{-1}$, and assuming complete current efficiency, two moles of electrons produce one mole of hydrogen:

$$n(\text{H}_2) = \frac{Q}{2F} = \frac{96501}{2(96500)} \approx 0.500 \text{ mol}.$$

Ammonia synthesis gives

$$n(\text{NH}_3) = \frac{2}{3}n(\text{H}_2) \approx \frac{1}{3} \text{ mol}.$$

The subsequent stoichiometric relationships are

$$n(\text{NH}_3) = n(\text{HNO}_3) = n(\text{C}_6\text{H}_5\text{NO}_2) = n(\text{C}_6\text{H}_5\text{NH}_2),$$

assuming quantitative conversion, adequate other reagents, and additional hydrogen for the nitrobenzene reduction.

Aniline has molecular formula $\text{C}_6\text{H}_7\text{N}$, so

$$M(\text{C}_6\text{H}_7\text{N}) = 6(12) + 7(1) + 14 = 93 \text{ g mol}^{-1}.$$

Thus,

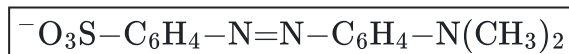
$$m(\mathbf{D}) = \left(\frac{1}{3} \text{ mol} \right) (93 \text{ g mol}^{-1}) \approx 31 \text{ g}.$$

3. Methyl orange: name, structures and indicator equilibrium

The exact chemical name is **sodium 4-{[4-(dimethylamino)phenyl]diazenyl}benzenesulfonate**, with the usual *E* azo configuration:

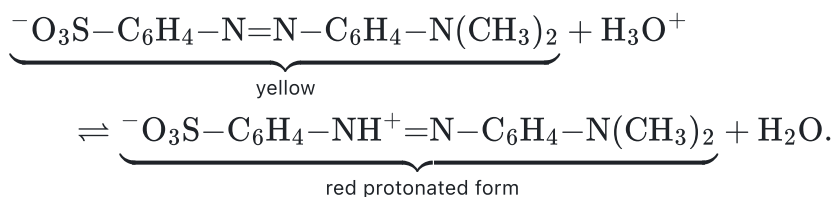
CN(C)c1ccc(/N=N/c2ccc(S(=O)(=O)[O-])cc2)cc1.[Na+].

The sodium ion, Na^+ ([Na+]), is a spectator. Omitting it, the yellow methyl-orange anion is



with SMILES CN(C)c1ccc(/N=N/c2ccc(S(=O)(=O)[O-])cc2)cc1.

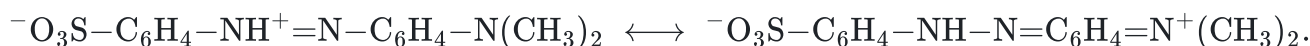
Hydronium, H_3O^+ ([OH3+]), protonates the azo nitrogen attached to the sulfonated ring:



This protonated methyl-orange zwitterion has the azo-form SMILES

CN(C)c1ccc(/N=[NH+]/c2ccc(S(=O)(=O)[O-])cc2)cc1.

Its positive charge is delocalized. An important alternative resonance contributor is the para-quinoid form:



The **para-quinoid resonance contributor of protonated methyl orange** has SMILES

C[N+](C)=C1C=CC(=NNc2ccc(S(=O)(=O)[O-])cc2)C=C1.

To draw this contributor precisely, keep the sulfonated ring aromatic. In the other ring, place the azo-derived nitrogen at carbon 1 and the dimethylamino nitrogen at carbon 4. Draw exocyclic double bonds from these two carbons to their respective nitrogens, and internal ring double bonds between carbons 2–3 and 5–6. The dimethylamino nitrogen carries the positive charge; the proton remains on the nitrogen attached to the sulfonated ring.

These are resonance contributors of the same protonated species. SMILES records each contributor separately; it does not itself show the delocalization of electrons between them.

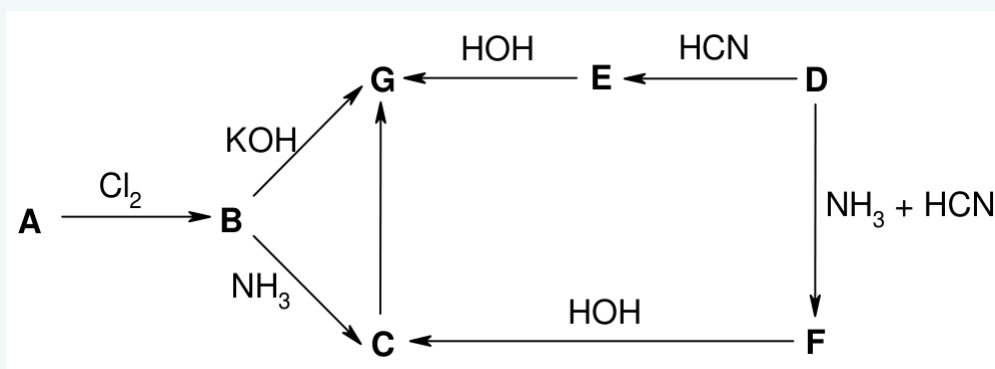
Consequently:

- Increasing $[\text{H}_3\text{O}^+]$ favors the protonated form and gives a **red** solution.
- Decreasing $[\text{H}_3\text{O}^+]$ favors the azo anion and gives a **yellow** solution.
- Intermediate proportions produce the **orange** transition color.

The solution was checked against the official solution.

Problem 2: Reaction scheme leading to substance G

Substance **G** can be prepared by several methods according to the following scheme:



Compound **A** is 48.60 mass % carbon, 8.10 % hydrogen, and 43.30 % oxygen. It reacts with a freshly prepared silver(I) oxide to form an undissolved salt. An amount of 1.81 g of silver(I) salt is formed from 0.74 g of compound **A**.

Compound **D** contains 54.54 mass % of carbon, 9.09 % of hydrogen, and 36.37 % of oxygen. It combines with NaHSO_3 to produce a compound containing 21.6 % of sulphur.

Problems:

1. Write summary as well as structural formulas of substances **A** and **D**.
2. Write structural formulas of substances **B**, **C**, **E**, **F**, and **G**.
3. Classify the reactions in the scheme marked by arrows and discuss more in detail reactions **B** → **G** and **D** → **E**.
4. Write structural formulas of possible isomers of substance **G** and give the type of isomerism.

Relative atomic masses:

$$A_r(\text{C}) = 12; \quad A_r(\text{H}) = 1; \quad A_r(\text{O}) = 16; \quad A_r(\text{Ag}) = 108; \quad A_r(\text{Na}) = 23; \quad A_r(\text{S}) = 32.$$

Answers

1. A and D:

Substance	Name	Molecular formula	Condensed structural formula	SMILES
A	Propanoic acid (propionic acid)	C ₃ H ₆ O ₂	CH ₃ CH ₂ COOH	CCC(=O)O
D	Ethanal (acetaldehyde)	C ₂ H ₄ O	CH ₃ CHO	CC=O

2. The remaining compounds:

Substance	Name	Condensed structural formula	SMILES
B	2-Chloropropanoic acid	CH ₃ CHClCOOH	CC(Cl)C(=O)O
C	2-Aminopropanoic acid (alanine)	CH ₃ CH(NH ₂)COOH	CC(N)C(=O)O
E	2-Hydroxypropanenitrile (acetaldehyde cyanohydrin)	CH ₃ CH(OH)CN	CC(O)C#N
F	2-Aminopropanenitrile	CH ₃ CH(NH ₂)CN	CC(N)C#N
G	2-Hydroxypropanoic acid (lactic acid)	CH ₃ CH(OH)COOH	CC(O)C(=O)O

These SMILES leave stereochemistry unspecified. Under achiral reaction conditions, the chiral products are obtained as racemates.

3. Reaction classifications:

Arrow	Classification
A → B	Substitution: chlorination at the carbon adjacent to the carboxyl group
B → G	Nucleophilic substitution: replacement of chlorine by hydroxyl
B → C	Nucleophilic substitution by ammonia; ammonolysis
C → G	Nitrosative deamination, replacing the amino group by hydroxyl
D → E	Nucleophilic addition to a carbonyl group; cyanohydrin formation
E → G	Hydrolysis of a nitrile to a carboxylic acid
D → F	Condensation followed by cyanide addition; the aminonitrile-forming stage of the Strecker synthesis
F → C	Hydrolysis of a nitrile to a carboxylic acid

The missing reagent for **C → G** is nitrous acid, HNO₂, ON=O. Aqueous potassium hydroxide initially gives a lactate salt in **B → G**; acidification gives free **G**.

4. G has two optical isomers, which are enantiomers:

Isomer	Stereochemical SMILES
(<i>S</i>)-2-Hydroxypropanoic acid	<chem>C[C@H](O)C(=O)O</chem>
(<i>R</i>)-2-Hydroxypropanoic acid	<chem>C[C@@H](O)C(=O)O</chem>

Within the hydroxycarboxylic-acid family, **3-hydroxypropanoic acid**, HOCH2CH2COOH, OCCC(=O)O, is also a **positional constitutional isomer** of **G**.

Solution

1. Identification of A and D

For **A**, a 100 g sample contains

$$n(\text{C}) = \frac{48.60}{12} = 4.050 \text{ mol},$$

$$n(\text{H}) = \frac{8.10}{1} = 8.10 \text{ mol}, \quad n(\text{O}) = \frac{43.30}{16} = 2.70625 \text{ mol}.$$

Thus,

$$n(\text{C}) : n(\text{H}) : n(\text{O}) = 1.4965 : 2.9931 : 1 \approx 3 : 6 : 2.$$

The empirical formula is therefore $\text{C}_3\text{H}_6\text{O}_2$, with empirical-formula mass

$$3(12) + 6(1) + 2(16) = 74 \text{ g mol}^{-1}.$$

Formation of a silver salt with silver(I) oxide identifies a carboxylic acid. An integer multiple of this empirical formula, $\text{C}_{3k}\text{H}_{6k}\text{O}_{2k}$, has only one degree of unsaturation:

$$\text{DBE} = 1 + 3k - \frac{6k}{2} = 1.$$

Consequently, it can contain only one carboxyl group. Formation of its silver salt replaces one acidic hydrogen per molecule by silver, increasing the molar mass by

$$108 - 1 = 107 \text{ g mol}^{-1}.$$

Hence,

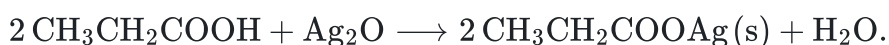
$$n(\text{A}) = \frac{(1.81 - 0.74) \text{ g}}{107 \text{ g mol}^{-1}} = 0.0100 \text{ mol},$$

and

$$M(\text{A}) = \frac{0.74 \text{ g}}{0.0100 \text{ mol}} = 74 \text{ g mol}^{-1}.$$

The molecular formula equals the empirical formula. The three-carbon carboxylic acid is **propanoic acid**, CCC(=O)O.

The salt-forming reaction is



Here silver(I) oxide is represented ionically by $[\text{Ag}^+] \cdot [\text{Ag}^+] \cdot [\text{O}^{2-}]$, silver propanoate by $\text{CCC}(=\text{O})[\text{O}^-] \cdot [\text{Ag}^+]$, and water by O . These ionic SMILES specify composition rather than solid-state coordination.

The silver salt has molar mass

$$M(\text{C}_3\text{H}_5\text{O}_2\text{Ag}) = 36 + 5 + 32 + 108 = 181 \text{ g mol}^{-1},$$

so the predicted salt mass is

$$0.0100 \text{ mol} \times 181 \text{ g mol}^{-1} = 1.81 \text{ g},$$

exactly reproducing the stated yield.

For **D**, the corresponding amounts in 100 g are

$$\frac{54.54}{12} : \frac{9.09}{1} : \frac{36.37}{16} = 4.545 : 9.09 : 2.273125 \approx 2 : 4 : 1.$$

Its empirical formula is therefore $\text{C}_2\text{H}_4\text{O}$, with empirical-formula mass 44 g mol^{-1} .

Addition of sodium hydrogensulfite, NaHSO_3 , $[\text{Na}^+] \cdot [\text{O}^-]\text{S}(=\text{O})\text{O}$, indicates a carbonyl compound. Any integer multiple of $\text{C}_2\text{H}_4\text{O}$ also has only one degree of unsaturation, so there is one carbonyl group and one hydrogensulfite unit is added per molecule.

Since

$$M(\text{NaHSO}_3) = 23 + 1 + 32 + 3(16) = 104 \text{ g mol}^{-1},$$

the sulfur mass fraction in the adduct gives

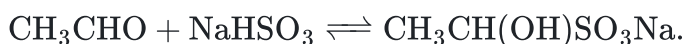
$$\frac{32}{M(\text{D}) + 104} = 0.216.$$

Therefore,

$$M(\text{D}) = \frac{32}{0.216} - 104 = 44.1 \text{ g mol}^{-1} \approx 44 \text{ g mol}^{-1}.$$

Thus **D** has molecular formula $\text{C}_2\text{H}_4\text{O}$. A two-carbon carbonyl compound must be the aldehyde **ethanal**, $\text{CC}=\text{O}$.

Its addition reaction is



The product is **sodium 1-hydroxyethane-1-sulfonate**, $\text{CC}(\text{O})\text{S}(=\text{O})(=\text{O})[\text{O}^-] \cdot [\text{Na}^+]$. Its molar mass is 148 g mol^{-1} , giving

$$w(\text{S}) = \frac{32}{148} \times 100\% = 21.6\%.$$

2. Identification of B, C, E, F, and G

Starting from **D** provides the most direct identification of **G**.

Addition of **hydrogen cyanide**, $\text{C}\equiv\text{N}$, to ethanal places hydroxyl and cyano groups on the former carbonyl carbon. The product **E** is therefore **2-hydroxypropanenitrile**:



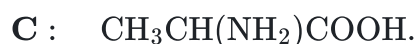
Hydrolysis converts the nitrile carbon into the carboxyl carbon without changing the carbon skeleton. Thus **G** is **2-hydroxypropanoic acid**:



To produce this **G** by replacing chlorine with hydroxyl, **B** must have chlorine on carbon 2:



Replacing that chlorine by an amino group using **ammonia**, N , gives **C**, **alanine**:



Finally, ethanal reacts with ammonia and hydrogen cyanide to form the corresponding aminonitrile **F**:



Hydrolysis of its nitrile group gives alanine, independently confirming both **F** and **C**.

3. Balanced equations and reaction mechanisms

The equations below use neutral organic molecular forms unless a salt is explicitly shown. Nitrile hydrolysis requires suitable aqueous acidic or alkaline conditions, usually with heating; protonation states during the reaction depend on pH.

A → B: α-chlorination



This is substitution of an α hydrogen by chlorine, under the usual conditions for α-halogenation of a carboxylic acid. Chlorine has SMILES ClCl ; hydrogen chloride has SMILES Cl .

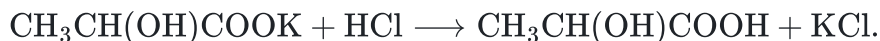
B → G: hydrolytic nucleophilic substitution

With aqueous **potassium hydroxide**, $[\text{K}^+] \cdot [\text{OH}^-]$, neutralization and chlorine displacement give

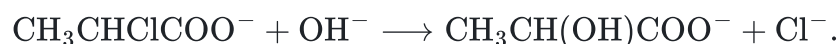


The organic product in the alkaline solution is **potassium lactate**, $\text{CC}(\text{O})\text{C}(=\text{O})[\text{O}^-] \cdot [\text{K}^+]$. Potassium chloride is $[\text{K}^+] \cdot [\text{Cl}^-]$.

Acidification then gives free lactic acid:



One equivalent of hydroxide neutralizes the carboxyl group; another effects substitution. The substitution can be represented ionically as



The participating ions are:

- **2-Chloropropanoate:** $\text{CC}(\text{Cl})\text{C}(=\text{O})[\text{O}^-]$
- **Hydroxide:** $[\text{OH}^-]$
- **Lactate:** $\text{CC}(\text{O})\text{C}(=\text{O})[\text{O}^-]$
- **Chloride:** $[\text{Cl}^-]$

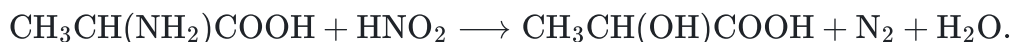
In a direct S_N2 description, an oxygen lone pair of hydroxide attacks the α carbon from the side opposite chlorine. The carbon–chlorine bonding pair moves onto chlorine as the carbon–oxygen bond forms. Such a direct displacement inverts an individual stereocentre. Because **B** is formed racemically under achiral conditions, this route gives racemic **G**.

B → C: ammonolysis



This is nucleophilic substitution. One ammonia molecule supplies the amino group, while another accepts the released proton. **Ammonium chloride** has SMILES $[\text{NH}_4^+] \cdot [\text{Cl}^-]$.

C → G: nitrosative deamination



Nitrous acid, $\text{ON}=\text{O}$, replaces the amino group by hydroxyl with evolution of **nitrogen**, $\text{N}\equiv\text{N}$. This supplies the reagent omitted from the vertical arrow in the scheme.

D → E: cyanohydrin formation



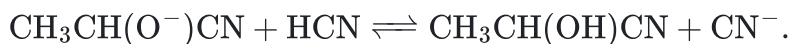
This is nucleophilic addition to the carbonyl group. The mechanism proceeds in two steps.

First, **cyanide ion**, $[\text{C}^-]\equiv\text{N}$, attacks the electrophilic carbonyl carbon through its carbon atom. The carbonyl π -electron pair moves onto oxygen:



The intermediate is the **cyanohydrin alkoxide**, $\text{CC}([\text{O}^-])\text{C}\equiv\text{N}$.

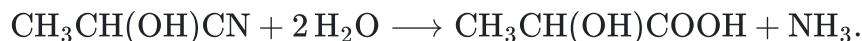
Second, the alkoxide takes a proton from hydrogen cyanide:



Cyanide is regenerated. The net changes are formation of a carbon–carbon bond and conversion of the carbonyl group into an alcohol group.

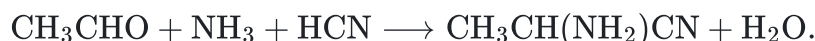
The carbonyl carbon is initially trigonal planar. Attack on its two faces is equally probable in an achiral environment, producing the two enantiomers of E in equal amounts. Subsequent nitrile hydrolysis therefore gives racemic G.

E → G: nitrile hydrolysis



The nitrile group is hydrolysed, through an amide intermediate, to a carboxyl group.

D → F: aminonitrile formation



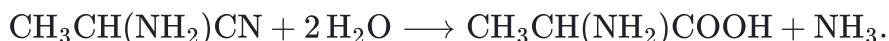
This is the aminonitrile-forming stage of the Strecker synthesis. It comprises condensation of ethanal with ammonia, followed by cyanide addition. The condensation intermediate is **ethanimine**, $\text{CC}=\text{N}$:



followed overall by



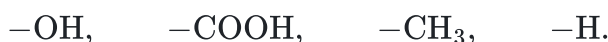
F → C: nitrile hydrolysis



The nitrile group becomes a carboxyl group while the amino group is retained, yielding alanine.

4. Isomerism of G

The central carbon of lactic acid is attached to four different groups:



It is therefore a stereogenic centre. There are exactly two stereoisomers of this connectivity: (*S*)-**lactic acid**, $\text{C}[\text{C}@\text{H}](\text{O})\text{C}(=\text{O})\text{O}$, and (*R*)-**lactic acid**, $\text{C}[\text{C}@@\text{H}](\text{O})\text{C}(=\text{O})\text{O}$. They are nonsuperimposable mirror images: **optical isomers, or enantiomers**.

Their Fischer projections can be specified precisely as follows. Put the carboxyl group at the top and the methyl group at the bottom:

Isomer	Left horizontal group	Right horizontal group
(<i>S</i>)-Lactic acid	OH	H
(<i>R</i>)-Lactic acid	H	OH

In these projections, horizontal bonds point toward the observer and vertical bonds point away. The priority order is hydroxyl > carboxyl > methyl > hydrogen.

The enantiomers have equal and opposite optical rotations under identical measurement conditions. Their equimolar mixture is optically inactive.

If constitutional isomers are also intended, the other saturated hydroxycarboxylic acid with formula $\text{C}_3\text{H}_6\text{O}_3$ is:

Name	Structure	SMILES	Relationship to G
3-Hydroxypropanoic acid	$\text{HOCH}_2\text{CH}_2\text{COOH}$	<chem>occc(=O)O</chem>	Positional isomer; achiral

Allowing different functional-group arrangements gives further constitutional isomers. Examples include **methoxyethanoic acid**, $\text{CH}_3\text{OCH}_2\text{COOH}$, cocc(=O)O, and **methyl 2-hydroxyethanoate (methyl glycolate)**, $\text{HOCH}_2\text{COOCH}_3$, coc(=O)CO. These illustrate **functional-group isomerism**.

The solution was checked against the official solution.

Problem 3: Acid-base reactions of 0.2 M solutions A-H

The following 0.2 molar solutions are available:

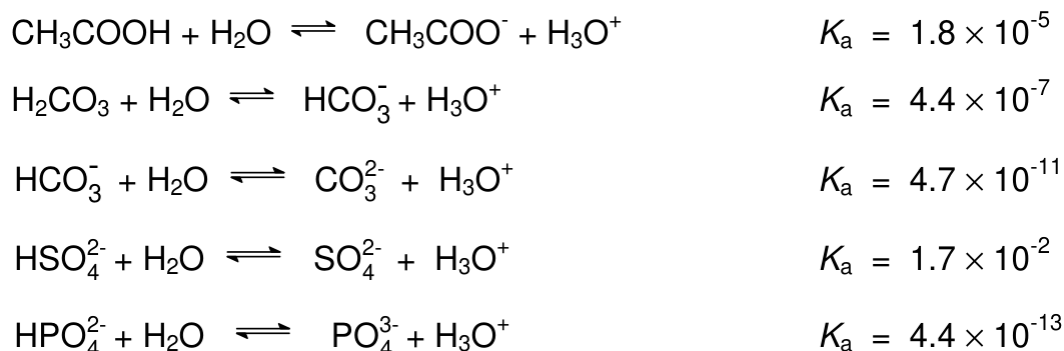
A: HCl	B: HSO_4^-	C: CH_3COOH	D: NaOH
E: CO_3^{2-}	F: CH_3COONa	G: HPO_4^{2-}	H: H_2SO_4

Problems:

- Determine the concentration of H_3O^+ ions in solution **C**.
- Determine pH value in solution **A**.
- Write an equation for the chemical reaction that takes place when substances **B** and **E** are allowed to react and mark conjugate acid-base pairs.
- Compare acid-base properties of substances **A**, **B**, and **C** and determine which one will show the most basic properties. Explain your decision.
- Write a chemical equation for the reaction between substances **B** and **G**, and explain the shift of equilibrium.
- Write a chemical equation for the reaction between substances **C** and **E**, and explain the shift of equilibrium.
- Calculate the volume of **D** solution which is required to neutralise 20.0 cm^3 of **H** solution.

8. What would be the volume of hydrogen chloride being present in one litre of **A** solution if it were in gaseous state at a pressure of 202.65 kPa and a temperature of 37 °C?

Ionisation constants:



Relative atomic masses:

$A_r(\text{Na}) = 23$; $A_r(\text{S}) = 32$; $A_r(\text{O}) = 16$.

Official English text of the problem.

Answers

- $[\text{H}_3\text{O}^+] = 1.9 \times 10^{-3} \text{ mol dm}^{-3}$.
- $\text{pH} = 0.70$.
- $\text{HSO}_4^- + \text{CO}_3^{2-} \rightleftharpoons \text{SO}_4^{2-} + \text{HCO}_3^-$. Conjugate pairs: $\text{HSO}_4^-/\text{SO}_4^{2-}$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$.
- Acid strength: $A > B > C$. **C has the highest pH and is least acidic; B is amphoteric.**
These distinguish two possible readings of "most basic properties."
- $\text{HSO}_4^- + \text{HPO}_4^{2-} \rightleftharpoons \text{SO}_4^{2-} + \text{H}_2\text{PO}_4^-$, favouring the products. The constant needed to calculate its equilibrium constant is not supplied.
- $\text{CH}_3\text{COOH} + \text{CO}_3^{2-} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{HCO}_3^-$, with $K = 3.8 \times 10^5$, strongly favouring the products. With sufficient acid, further reaction releases CO_2 .
- $V_D = 40.0 \text{ cm}^3$.
- $V \approx 2.54 \text{ dm}^3$, treating the gas as ideal.

Solution

The species names and SMILES used in the answers and calculations are collected below. SMILES represent connectivity and formal charges; they do not show aqueous solvation, resonance delocalisation, or the direction of proton transfer. Dots separate ionic components of salts.

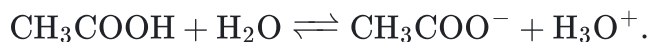
Species	Name	SMILES
HCl	Hydrogen chloride	Cl
HSO_4^-	Hydrogen sulfate ion	O=S(=O)(O)[O-]

Species	Name	SMILES
CH ₃ COOH	Acetic acid	CC(=O)O
NaOH	Sodium hydroxide	[Na+] . [OH-]
CO ₃ ²⁻	Carbonate ion	O=C([O-])[O-]
CH ₃ COONa	Sodium acetate	CC(=O)[O-].[Na+]
HPO ₄ ²⁻	Hydrogen phosphate ion	O=P(O)([O-])[O-]
H ₂ SO ₄	Sulfuric acid	O=S(=O)(O)O
H ₂ O	Water	O
H ₃ O ⁺	Hydronium ion	[OH3+]
Cl ⁻	Chloride ion	[Cl-]
CH ₃ COO ⁻	Acetate ion	CC(=O)[O-]
SO ₄ ²⁻	Sulfate ion	O=S(=O)([O-])[O-]
HCO ₃ ⁻	Hydrogen carbonate ion	O=C(O)[O-]
H ₂ CO ₃	Carbonic acid	O=C(O)O
CO ₂	Carbon dioxide	O=C=O
H ₂ PO ₄ ⁻	Dihydrogen phosphate ion	O=P(O)(O)[O-]
PO ₄ ³⁻	Phosphate ion	O=P([O-])([O-])[O-]
Na ₂ SO ₄	Sodium sulfate	[Na+] . [Na+] . [O-]S(=O)(=O)[O-]

The calculations use the usual concentration approximation for aqueous equilibria.

1. Hydronium concentration in C

Acetic acid dissociates according to



Let $c_0 = 0.2 \text{ mol dm}^{-3}$ and let $x = [\text{H}_3\text{O}^+]$. Neglecting the very small contribution from water,

$$[\text{CH}_3\text{COO}^-] = x, \quad [\text{CH}_3\text{COOH}] = c_0 - x.$$

Thus

$$K_a = \frac{x^2}{c_0 - x} = 1.8 \times 10^{-5}.$$

Solving the quadratic gives

$$x = \frac{-K_a + \sqrt{K_a^2 + 4K_ac_0}}{2} = 1.8884 \times 10^{-3} \text{ mol dm}^{-3}.$$

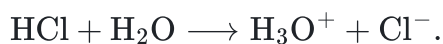
Therefore,

$$[\text{H}_3\text{O}^+] \approx 1.9 \times 10^{-3} \text{ mol dm}^{-3}.$$

The approximation $x \approx \sqrt{K_ac_0}$ gives the same rounded result. Only 0.94% of the acid dissociates, so that approximation is justified.

2. pH of A

Hydrogen chloride is a strong acid and is essentially completely ionised:



Consequently,

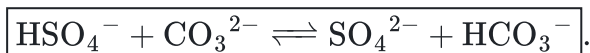
$$[\text{H}_3\text{O}^+] = 0.2 \text{ mol dm}^{-3},$$

and

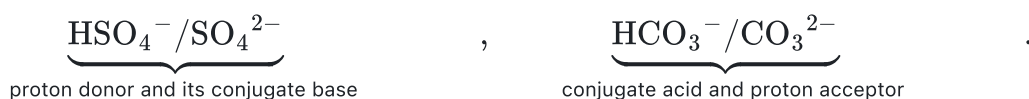
$$\boxed{\text{pH} = -\log_{10}(0.2) = 0.699 \approx 0.70}.$$

3. Reaction between B and E; conjugate pairs

Hydrogen sulfate donates a proton to carbonate:



The conjugate acid–base pairs, written acid first, are

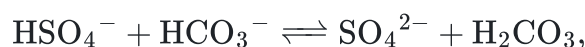


The equilibrium constant for this proton transfer is

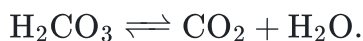
$$K = \frac{K_a(\text{HSO}_4^-)}{K_a(\text{HCO}_3^-)} = \frac{1.7 \times 10^{-2}}{4.7 \times 10^{-11}} = 3.6 \times 10^8.$$

Hence the reaction strongly favours the products.

If at least two equivalents of hydrogen sulfate are supplied per carbonate ion, a second proton transfer is possible:



followed by

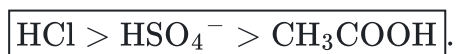


The additional conjugate pair is $\text{H}_2\text{CO}_3/\text{HCO}_3^-$. With carbon dioxide escaping, the overall reaction is



4. Acid–base properties of A, B, and C

Their acid strengths decrease in the order



Hydrogen chloride is a strong acid. Hydrogen sulfate has $K_a = 1.7 \times 10^{-2}$, whereas acetic acid has the much smaller $K_a = 1.8 \times 10^{-5}$.

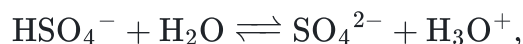
For equal analytical concentrations, their approximate hydronium concentrations and pH values are:

Solution	$[\text{H}_3\text{O}^+]$, mol dm ⁻³	pH
A	0.200	0.70
B	0.0504	1.30
C	0.00189	2.72

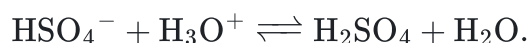
For B, the value follows from $x^2/(0.2 - x) = 1.7 \times 10^{-2}$.

Thus, **if “most basic” means the highest pH among the three solutions, the answer is C**. All three solutions are nevertheless acidic.

There is a separate distinction: **B is amphotropic** in the usual aqueous acid–base classification. It can donate a proton,



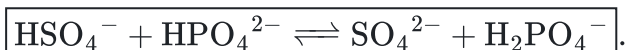
or accept a proton in a sufficiently acidic medium,



Consequently, B is the answer if the intended identification is the species displaying both acid and base behaviour. Amphotropic character alone does not establish a ranking of intrinsic proton-acceptor basicity.

5. Reaction between B and G

Hydrogen sulfate acts as the proton donor and hydrogen phosphate as the proton acceptor:

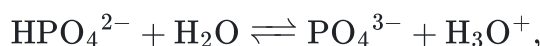


The equilibrium favours the products because dihydrogen phosphate is a weaker acid than hydrogen sulfate: proton transfer produces the weaker acid–base pair.

The equilibrium constant would be

$$K = \frac{[\text{SO}_4^{2-}][\text{H}_2\text{PO}_4^-]}{[\text{HSO}_4^-][\text{HPO}_4^{2-}]} = \frac{K_a(\text{HSO}_4^-)}{K_a(\text{H}_2\text{PO}_4^-)}.$$

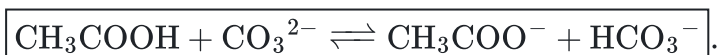
However, $K_a(\text{H}_2\text{PO}_4^-)$ is not supplied. The listed value 4.4×10^{-13} describes



and cannot be used as the denominator for the requested reaction. Thus the direction stated above uses the qualitative acid-strength relationship; a numerical equilibrium constant cannot be calculated from the supplied table alone.

6. Reaction between C and E

Acetic acid transfers a proton to carbonate:

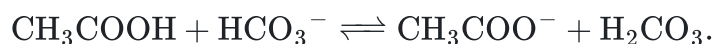


Its equilibrium constant is

$$K = \frac{K_a(\text{CH}_3\text{COOH})}{K_a(\text{HCO}_3^-)} = \frac{1.8 \times 10^{-5}}{4.7 \times 10^{-11}} = \boxed{3.8 \times 10^5}.$$

Therefore, the equilibrium lies strongly to the right. Acetic acid is much stronger than hydrogen carbonate as a proton donor.

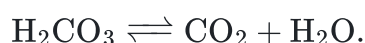
With additional acetic acid, hydrogen carbonate also accepts a proton:



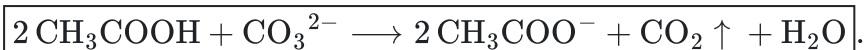
For this step,

$$K = \frac{1.8 \times 10^{-5}}{4.4 \times 10^{-7}} \approx 41,$$

so it also favours the products. Carbon dioxide formation and escape drive the reaction further:

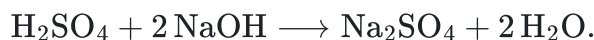


With two acid equivalents per carbonate ion, the overall reaction is



7. Volume of D needed to neutralise H

Complete neutralisation requires two moles of sodium hydroxide per mole of sulfuric acid:



The amount of sulfuric acid is

$$n(\text{H}_2\text{SO}_4) = 0.2 \text{ mol dm}^{-3} \times 20.0 \times 10^{-3} \text{ dm}^3 = 4.00 \times 10^{-3} \text{ mol}.$$

Therefore,

$$n(\text{NaOH}) = 8.00 \times 10^{-3} \text{ mol},$$

and

$$V_D = \frac{8.00 \times 10^{-3} \text{ mol}}{0.2 \text{ mol dm}^{-3}} = 0.0400 \text{ dm}^3.$$

Thus,

$$\boxed{V_D = 40.0 \text{ cm}^3}.$$

The common molarity cancels, so the required base volume is exactly twice the acid volume under the stated conditions.

8. Volume of gaseous hydrogen chloride

One litre of solution A contains the equivalent of

$$n(\text{HCl}) = 0.2 \text{ mol dm}^{-3} \times 1 \text{ dm}^3 = 0.2 \text{ mol}.$$

Using the ideal-gas equation,

$$V = \frac{nRT}{p},$$

with

$$T = 37 + 273.15 = 310.15 \text{ K}, \quad R = 8.314 \text{ kPa dm}^3 \text{ mol}^{-1} \text{ K}^{-1},$$

gives

$$V = \frac{(0.2)(8.314)(310.15)}{202.65} \text{ dm}^3 = 2.5449 \text{ dm}^3.$$

Hence,

$$\boxed{V \approx 2.54 \text{ dm}^3},$$

or about 2.5 L.

The solution was checked against the official solution.

Problem 4: Mixture of two oxygen-containing organic compounds

A mixture contains two organic compounds, **A** and **B**. Both of them have in their molecules oxygen and they can be mixed together in arbitrary ratios. Oxidation of this mixture on cooling yields the only substance **C** that combines with NaHSO_3 . The ratio of the molar mass of the substance being formed in the reaction with NaHSO_3 to that of substance **C**, is equal to 2.7931.

The mixture of substances **A** and **B** is burned in the presence of a stoichiometric amount of air (20 % O_2 and 80 % of N_2 by volume) in an eudiometer to produce a mixture of gases with a total volume of 5.432 dm^3 at STP. After the gaseous mixture is bubbled through a $\text{Ba}(\text{OH})_2$ solution, its volume is decreased by 15.46 %.

Problems:

4.1 Write structural formulas of substance **A** and **B**.

4.2 Calculate the molar ratio of substances **A** and **B** in the mixture.

$$A_r(\text{C}) = 12; \quad A_r(\text{O}) = 16; \quad A_r(\text{S}) = 32; \quad A_r(\text{Na}) = 23.$$

Official English text of the problem.

Answers

- 4.1** The intended compounds are **A: propan-2-ol**, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, SMILES CC(O)C, and **B: propan-2-one (acetone)**, CH_3COCH_3 , SMILES CC(=O)C. The labels may be interchanged.
- 4.2** With these labels,

$$n(\text{A}) : n(\text{B}) \approx 1 : 4.$$

Direct use of the printed percentage gives 1 : 3.94; the simple ratio 1 : 4 reproduces the reported percentage after rounding.

Solution

4.1 — Identification of the compounds

An aldehyde or ketone ordinarily adds one formula unit of sodium hydrogensulfite, NaHSO_3 , SMILES [Na+].[O-]S(=O)O, per carbonyl group, without eliminating another molecule.

Taking $A_r(\text{H}) = 1$,

$$M(\text{NaHSO}_3) = 23 + 1 + 32 + 3(16) = 104 \text{ g mol}^{-1}.$$

For a monocarbonyl compound **C**,

$$\frac{M(\text{C}) + 104}{M(\text{C})} = 2.7931,$$

so

$$M(\text{C}) = \frac{104}{1.7931} = 58.0001 \dots \text{ g mol}^{-1} \approx 58.0 \text{ g mol}^{-1}.$$

The ordinary aldehyde and ketone candidates with this molar mass have formula C_3H_6O :

- Propanal, CH_3CH_2CHO , SMILES CCC=O.
- Propan-2-one (acetone), CH_3COCH_3 , SMILES CC(=O)C.

Under the conventional oxidation conditions intended here, an aldehyde undergoes further oxidation. Propanal would give propanoic acid, SMILES CCC(=O)O:



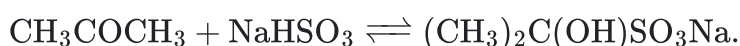
Acetone, however, survives mild oxidation. Thus the intended mixture consists of acetone and the secondary alcohol that oxidizes to acetone: propan-2-ol.

Assigning **A** to propan-2-ol and **B** to acetone,



Here $[O]$ denotes an oxygen atom equivalent supplied by the unspecified oxidant; water has SMILES O. The original acetone remains, so the sole organic product is **C = B**, acetone. These two liquids are mutually miscible in all proportions.

Acetone forms the bisulfite addition compound:



The product is **sodium 2-hydroxypropane-2-sulfonate**, SMILES CC(C)(O)S(=O)(=O)[O-].[Na+]. Its formula is $C_3H_7NaO_4S$, and

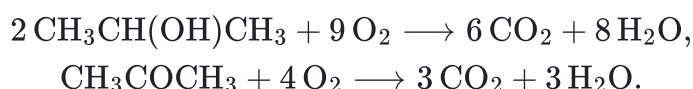
$$M = 3(12) + 7 + 23 + 4(16) + 32 = 162 \text{ g mol}^{-1}.$$

This verifies the stated ratio:

$$\frac{162}{58} = 2.793103 \dots \approx 2.7931.$$

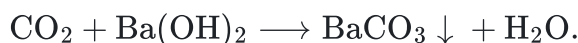
4.2 — Molar ratio

The balanced combustion equations are



The relevant gases are oxygen, SMILES O=O; nitrogen, SMILES N#N; and carbon dioxide, SMILES O=C=O. Taking the reported STP gas volumes as dry, combustion water is excluded. Because the air is stoichiometric, no oxygen remains: the measured gases are carbon dioxide and nitrogen.

Barium hydroxide removes carbon dioxide:



Barium hydroxide has formula-unit SMILES [Ba+2].[OH-].[OH-]; barium carbonate has formula-unit SMILES [Ba+2].[O-]C(=O)[O-].

Consequently,

$$\begin{aligned} V(CO_2) &= 0.1546(5.432) = 0.8397872 \text{ dm}^3 \approx 0.8398 \text{ dm}^3, \\ V(N_2) &= 5.432 - 0.8397872 \approx 4.592 \text{ dm}^3. \end{aligned}$$

Let $x = n(A)$ and $y = n(B)$, both in moles. The combustion equations give

$$n(\text{CO}_2) = 3x + 3y, \quad n(\text{O}_2) = \frac{9}{2}x + 4y.$$

The air contains four moles of nitrogen per mole of oxygen, so

$$n(\text{N}_2) = 4 \left(\frac{9}{2}x + 4y \right) = 18x + 16y.$$

Gas volume fractions equal mole fractions at the same temperature and pressure. Therefore,

$$0.1546 = \frac{3x + 3y}{(3x + 3y) + (18x + 16y)} = \frac{3(x + y)}{21x + 19y}.$$

Rearranging,

$$\begin{aligned} 3.2466x + 2.9374y &= 3x + 3y, \\ 0.2466x &= 0.0626y, \end{aligned}$$

and hence

$$\frac{y}{x} = \frac{0.2466}{0.0626} = 3.9393 \dots$$

Thus the printed numbers give $n(A) : n(B) = 1 : 3.94$. To check the intended simple ratio 1 : 4,

$$\frac{V(\text{CO}_2)}{V_{\text{total}}} = \frac{3(1 + 4)}{21 + 19(4)} = \frac{15}{97},$$

which corresponds to

$$15.4639 \dots \% = 15.46\% \quad \text{after rounding.}$$

At the stated total volume, this gives

$$V(\text{CO}_2) = \frac{15}{97}(5.432) = 0.840 \text{ dm}^3,$$

consistent with the absorption data. Therefore,

$$n(\text{propan-2-ol}) : n(\text{acetone}) \approx 1 : 4.$$

The solution was checked against the official solution.

Problem 5: Mixture of two metals: hydrides, hydroxides and a precipitate

A mixture of two metals found in Mendelejev's periodical table in different groups, reacted with 56 cm³ of hydrogen on heating (measured at STP conditions) to produce two ionic compounds. These compounds were allowed to react with 270 mg of water but only one third of water reacted. A basic solution was formed in which the content of hydroxides was 30 % by mass and at the same time deposited a precipitate with a mass that represented 59.05 % of a total mass of the products formed by the reaction. After filtration the precipitate was heated and its mass decreased by 27 mg.

When a stoichiometric amount of ammonium carbonate was added to the basic solution, a slightly soluble precipitate was obtained, at the same time ammonia was liberated and the content of hydroxides in the solution decreased to 16.81 %.

Problem:

5.1 Determine the metals in the starting mixture and their masses.

Official English text of the problem.

Answers

- **5.1** The intended composition is **sodium, Na: approximately 23 mg**, and **calcium, Ca: approximately 80 mg**.

Solution

5.1

Use the conventional STP molar volume $22\,400\text{ cm}^3\text{ mol}^{-1}$ and rounded molar masses.

The formation of ionic hydrides suggests an alkali metal A and an alkaline-earth metal B , forming AH and BH_2 . Their hydrolysis produces the corresponding hydroxides and hydrogen.

The hydrogen consumed in hydride formation is

$$n(\text{H}_2) = \frac{56}{22\,400} = 2.50 \times 10^{-3}\text{ mol}.$$

Thus the hydrides contain 5.00 mmol of hydride hydrogen. Each mole of hydride hydrogen consumes one mole of water during hydrolysis, agreeing with

$$m(\text{H}_2\text{O})_{\text{reacted}} = \frac{270}{3} = 90\text{ mg}, \quad n(\text{H}_2\text{O})_{\text{reacted}} = \frac{90}{18} = 5.00\text{ mmol}.$$

The unreacted water therefore has mass

$$270 - 90 = 180\text{ mg}.$$

The hydroxides formed contain a total of 5.00 mmol of hydroxide groups.

Identification of the precipitated hydroxide.

Let S be the mass of dissolved hydroxides. The initial solution contains 30% hydroxides by mass:

$$\frac{S}{S + 180} = 0.30, \quad S = 77.14\text{ mg} \simeq 77\text{ mg}.$$

Interpret the stated 59.05% as the precipitate's fraction of the **combined hydroxide products**. If its mass is P ,

$$\frac{P}{P + S} = 0.5905, \quad P = \frac{0.5905}{0.4095}(77.14) = 111.24\text{ mg}.$$

An alkaline-earth hydroxide loses one mole of water per mole on heating to its oxide. Consequently,

$$n(\text{B}(\text{OH})_2)_{\text{precipitated}} = \frac{27\text{ mg}}{18\text{ mg mmol}^{-1}} = 1.50\text{ mmol}.$$

Its inferred molar mass is

$$M(\text{B}(\text{OH})_2) = \frac{111.24\text{ mg}}{1.50\text{ mmol}} = 74.16\text{ g mol}^{-1},$$

so

$$M(B) \simeq 74.16 - 2(17) = 40.16 \text{ g mol}^{-1}.$$

This identifies **calcium**. The thermal reaction is



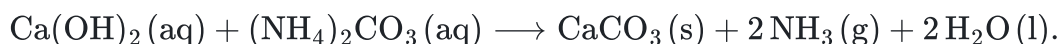
The precipitate contains $2(1.50) = 3.00$ mmol of hydroxide groups, leaving 2.00 mmol in solution.

Identification of the dissolved alkali metal and determination of the amounts.

Write the dissolved amounts as x mmol of Ca(OH)_2 and y mmol of AOH . Then

$$y + 2x = 2.00.$$

The carbonate addition is interpreted as stoichiometric for the dissolved calcium:



For x mmol of calcium hydroxide, this removes approximately $74x$ mg of dissolved hydroxide and produces $36x$ mg of water. The remaining hydroxide is AOH .

Using $S \simeq 77$ mg, the final mass fraction gives

$$\frac{77 - 74x}{180 + 36x + 77 - 74x} \simeq 0.1681.$$

Therefore,

$$x \simeq 0.500, \quad y = 2.00 - 2x \simeq 1.00.$$

The remaining alkali hydroxide has mass

$$m(\text{AOH}) \simeq 77 - 74(0.500) = 40.0 \text{ mg}.$$

Hence

$$M(\text{AOH}) \simeq \frac{40.0 \text{ mg}}{1.00 \text{ mmol}} = 40.0 \text{ g mol}^{-1},$$

and

$$M(A) \simeq 40.0 - 17.0 = 23.0 \text{ g mol}^{-1}.$$

Thus A is **sodium**.

The original metal amounts are consequently

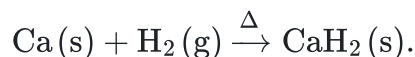
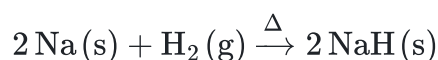
$$n(\text{Na}) \simeq 1.00 \text{ mmol}, \quad n(\text{Ca}) \simeq 1.50 + 0.500 = 2.00 \text{ mmol}.$$

Their masses are

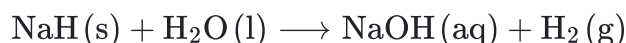
$$\boxed{m(\text{Na}) \simeq 23 \text{ mg}}, \quad \boxed{m(\text{Ca}) \simeq 80 \text{ mg}}.$$

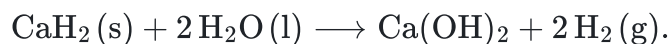
Reaction equations and numerical checks.

Hydride formation:



Hydrolysis:





The proposed amounts consume

$$n(\text{H}_2) = \frac{1.00}{2} + 2.00 = 2.50 \text{ mmol},$$

corresponding to 56 cm^3 , and

$$n(\text{H}_2\text{O}) = 1.00 + 2(2.00) = 5.00 \text{ mmol} = 90 \text{ mg}.$$

The first filtrate contains approximately 40 mg of sodium hydroxide, 37 mg of calcium hydroxide and 180 mg of water:

$$w_{\text{hydroxides}} = \frac{40 + 37}{40 + 37 + 180} \times 100\% = 29.96\% \simeq 30\%.$$

The 1.50 mmol calcium hydroxide precipitate weighs approximately 111 mg and loses 27 mg of water on heating.

Carbonate precipitation removes the dissolved calcium hydroxide and generates 18 mg of water. The final solution therefore contains 40 mg of sodium hydroxide and 198 mg of water:

$$w_{\text{hydroxides,final}} = \frac{40}{40 + 198} \times 100\% = 16.8067\% \simeq 16.81\%.$$

The molecular and ionic substances used above have the following SMILES. For ionic compounds, these specify the constituent ions, not the crystal lattice or aqueous hydration.

Substance	Formula	SMILES
Hydrogen	H_2	[H][H]
Water	H_2O	O
Sodium hydride	NaH	[Na+].[H-]
Calcium hydride	CaH_2	[Ca+2].[H-].[H-]
Sodium hydroxide	NaOH	[Na+].[OH-]
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	[Ca+2].[OH-].[OH-]
Calcium oxide	CaO	[Ca+2].[O-2]
Ammonium carbonate	$(\text{NH}_4)_2\text{CO}_3$	[NH4+].[NH4+].[O-]C(=O)[O-]
Calcium carbonate	CaCO_3	[Ca+2].[O-]C(=O)[O-]
Ammonia	NH_3	N

The solution was checked against the official solution.