

IChO 1979

Theory problems and solutions · Leningrad, Soviet Union · 6 theory problems with complete solutions

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Problem 1: Programmed assignment: 20 multiple-choice questions

When carrying out this programmed assignment, encircle those letters which in your opinion correspond to the correct answers to each of the 20 questions.

1. Which element is oxidized in the reaction between ethylene and an aqueous solution of potassium permanganate?

A) carbon, B) hydrogen, C) potassium, D) manganese, E) oxygen.

2. How many litres of CO_2 will approximately be evolved in the reaction of 18 g of potassium hydrogen carbonate with 65 g of 10 % sulphuric acid?

A) 1, B) 2, C) 3, D) 4, E) 5.

3. Which of the following hydrocarbons gives the maximum heat yield on complete combustion of 1 litre of the gas:

A) propane, B) methane, C) acetylene, D) ethylene, E) all give the same yield.

4. How many isomers can have a compound if its formula is $\text{C}_3\text{H}_5\text{Br}$?

A) 1, B) 2, C) 3, D) 4, E) 5.

5. Which of the following hydrocarbons will be the best engine fuel?

A) cyclooctane, B) 2,2-dimethylhexane, C) normal octane, D) 3-ethylhexane, E) 2,2,4-trimethylpentane.

6. With which of the following compounds will an aqueous solution of a higher oxide of element No 33 react?

A) CO_2 , B) K_2SO_4 , C) HCl , D) NaOH , E) magnesium.

7. What must be the minimum concentration (% by mass) of 1 kg of a potassium hydroxide solution for a complete neutralisation of 3.57 moles of nitric acid?

A) 5 %, B) 10 %, C) 15 %, D) 20 %, E) 25 %.

8. How many compounds with the formula $\text{C}_3\text{H}_9\text{N}$ can exist?

A) 1, B) 2, C) 3, D) 4, E) 5.

9. In which of the following compounds has the nitrogen content (in mass %) a maximum value?

A) potassium nitrate, B) barium nitrate, C) aluminium nitrate, D) lithium nitrate, E) sodium nitrate.

10. To which carbon atom (indicate the serial number) will chlorine mainly add in the reaction of HCl with penten-2-oic acid?

A) 1, B) 2, C) 3, D) 4, E) 5.

11. How many moles of water are there per mole of calcium nitrate in a crystallohydrate if the water content is 30.5 % by mass?

A) 1, B) 2, C) 3, D) 4, E) 5.

12. Which of these organic acids is the strongest?

A) benzoic, B) 2-chlorobenzoic, C) 4-methylbenzoic, D) 2-aminobenzoic, E) 4-bromobenzoic.

13. Which of these acids has the highest degree of dissociation?

A) HClO , B) HClO_2 , C) HClO_3 , D) HClO_4 , E) all have the same degree.

14. Which of the salts given below do not undergo hydrolysis?

A) potassium bromide, B) aluminium sulphate, C) sodium carbonate, D) iron(III) nitrate, E) barium sulphate.

15. How many litres of air are approximately required for complete combustion of 1 litre of ammonia?

A) 1, B) 2, C) 3, D) 4, E) 5.

16. Which element is oxidised in the thermal decomposition of sodium hydrogen carbonate?

A) sodium, B) hydrogen, C) oxygen, D) carbon, E) none.

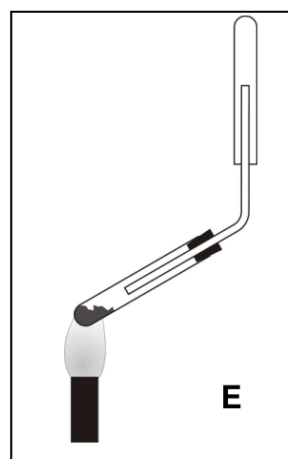
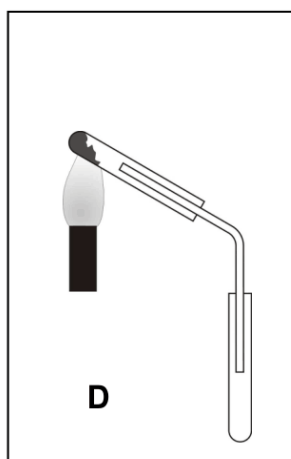
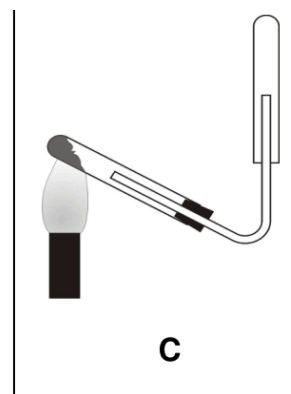
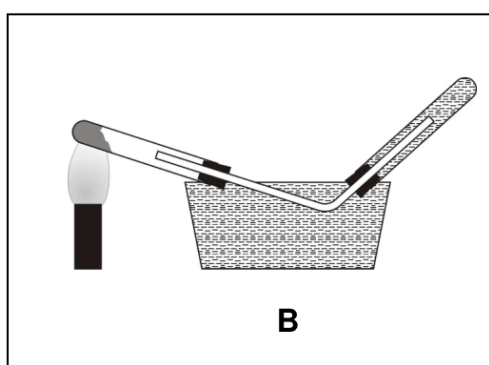
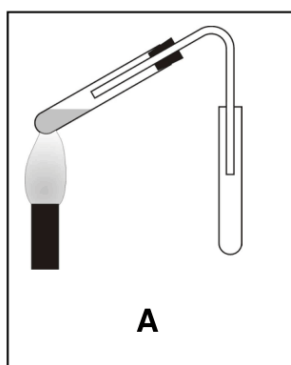
17. Which of the following changes have no effect on the chemical equilibrium in the thermal decomposition of CaCO_3 ?

A) temperature elevation, B) pressure decrease, C) addition of catalyst, D) a change in the CO_2 concentration, E) an increase in the amount of the initial substance.

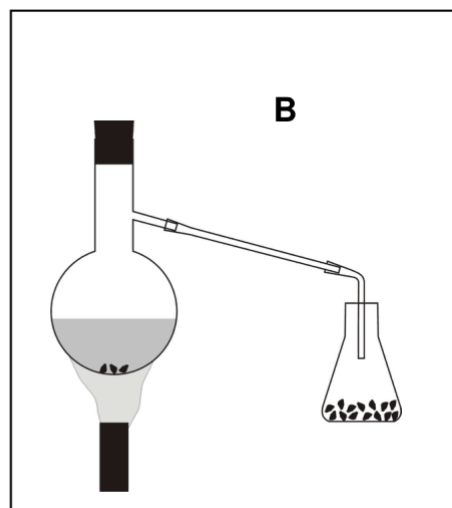
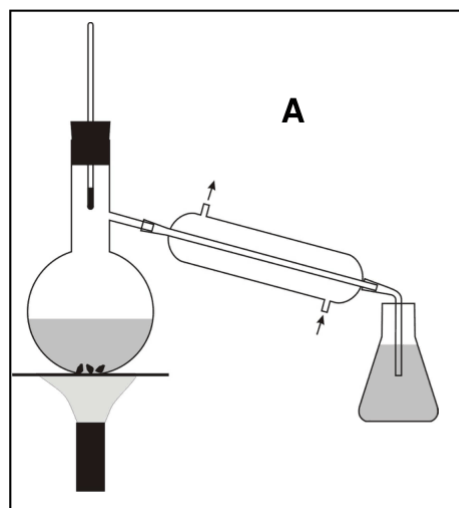
18. Which of the substances given below will be formed at the Pt-anode in the electrolysis of an aqueous solution of aluminium chloride?

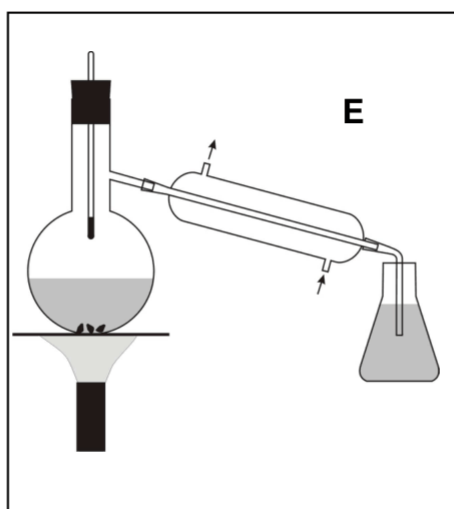
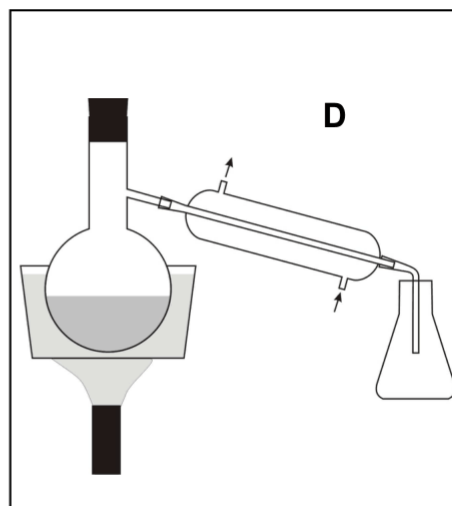
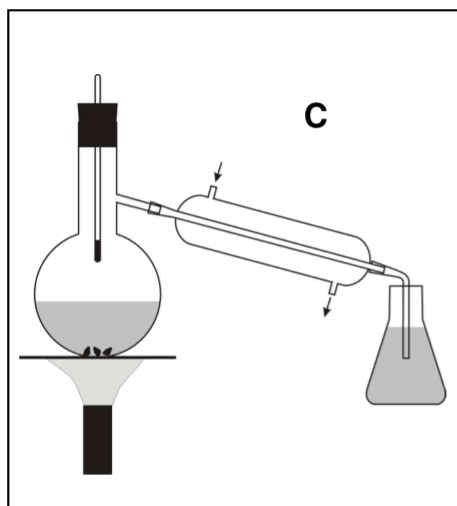
A) aluminium, B) oxygen, C) hydrogen, D) aluminium hydroxide, E) chlorine.

19. The apparatus shown in the figures is intended for preparing ammonia under laboratory conditions. The test tube being heated contains a mixture of NH_4Cl and $\text{Ca}(\text{OH})_2$. Which of the figures is correct?



20. Which of the apparatuses shown in the figures is the best one for the synthesis of bromethane from potassium bromide, concentrated sulphuric acid and ethanol?





Official English text of the problem.

Answers

1. **A — carbon.**
2. **C — approximately 3 L of carbon dioxide, $\text{O}=\text{C}=\text{O}$.**
3. **A — propane, CCC .**
4. **E — 5 isomers, including geometrical isomers.**
5. **E — 2,2,4-trimethylpentane, $\text{CC}(\text{C})(\text{C})\text{CC}(\text{C})\text{C}$.**
6. **D and E — sodium hydroxide, $[\text{Na}^+] \cdot [\text{OH}^-]$, and magnesium.**
7. **D — 20% by mass.**
8. **D — 4 compounds.**
9. **D — lithium nitrate, $[\text{Li}^+] \cdot [\text{O}^-][\text{N}^](=\text{O})[\text{O}^-]$.**
10. **C — carbon atom 3.**
11. **D — 4 waters of crystallisation: calcium nitrate tetrahydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, $[\text{Ca}+2] \cdot [\text{O}^-][\text{N}^](=\text{O})[\text{O}^-] \cdot [\text{O}^-][\text{N}^](=\text{O})[\text{O}^-] \cdot \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O}$.**
12. **B — 2-chlorobenzoic acid, $\text{O}=\text{C}(\text{O})\text{c1ccccc1Cl}$.**
13. **D — perchloric acid, $\text{OCl}(=\text{O})(=\text{O})=\text{O}$.**

14. **A and E — potassium bromide, $[K^+] \cdot [Br^-]$, and barium sulphate, $[Ba^{+2}] \cdot [O^-]S(=O)(=O)[O^-]$.**
15. **D — approximately 4 L of air.**
16. **E — none.**
17. **C and E — addition of a catalyst and increasing the amount of solid calcium carbonate.**
18. **B and E — oxygen, $O=O$, and chlorine, $ClCl$.**
19. **C.**
20. **A.**

Solution

Rounded atomic masses are sufficient for the numerical choices. Gas volumes are compared at the same temperature and pressure; for question 2, the conventional standard molar volume 22.4 L mol^{-1} is used.

SMILES for ionic salts below describe formal ionic composition, not crystal structures. Dot-separated waters in a hydrate do not specify their coordination. Recurring molecular species are water O , carbon dioxide $O=C=O$, hydrogen $[H][H]$, oxygen $O=O$, nitrogen $N\#N$, and ammonia N . The proton, hydronium ion, and hydroxide ion are $[H^+]$, $[OH_3^+]$, and $[OH^-]$, respectively.

1. Oxidation of ethylene — A

Ethylene, or ethene, $C=C$, undergoes oxidation to ethane-1,2-diol, OCO , in the usual dilute aqueous permanganate reaction:



Potassium permanganate has the formal ionic SMILES $[K^+] \cdot [O^-][Mn](=O)(=O)=O$; potassium hydroxide is $[K^+] \cdot [OH^-]$.

Each carbon atom changes oxidation state from -2 in ethylene to -1 in the diol. Thus **carbon is oxidized**. Manganese changes from $+7$ to $+4$, so it is reduced.

2. Carbon dioxide from hydrogen carbonate — C

Potassium hydrogen carbonate is $[K^+].O=C(O)[O^-]$; sulphuric acid is $OS(=O)(=O)O$. The reaction is



Potassium sulphate has the ionic representation $[K^+] \cdot [K^+] \cdot [O^-]S(=O)(=O)[O^-]$.

The solution contains

$$m(\text{H}_2\text{SO}_4) = 65 \text{ g} \times 0.10 = 6.5 \text{ g}.$$

Using $M(\text{KHCO}_3) = 100 \text{ g mol}^{-1}$ and $M(\text{H}_2\text{SO}_4) = 98 \text{ g mol}^{-1}$,

$$n(\text{KHCO}_3) = \frac{18}{100} = 0.180 \text{ mol}, \quad n(\text{H}_2\text{SO}_4) = \frac{6.5}{98} = 0.0663 \text{ mol}.$$

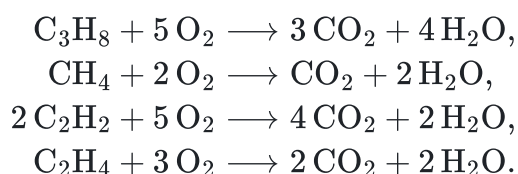
The acid can consume $2(0.0663) = 0.1327 \text{ mol}$ of hydrogen carbonate, so the acid is limiting. Therefore,

$$\begin{aligned} n(\text{CO}_2) &= 0.1327 \text{ mol}, \\ V(\text{CO}_2) &= 0.1327 \times 22.4 = 2.97 \text{ L} \approx 3 \text{ L}. \end{aligned}$$

3. Maximum heat from equal gas volumes — A

At equal temperature and pressure, equal gas volumes contain equal amounts in moles. The relevant comparison is therefore heat released **per mole**, rather than per gram.

The combustion equations are



The structures are propane CCC, methane C, acetylene or ethyne C#C, and ethylene C=C.

Among these particular hydrocarbons, propane has the greatest molar heat of combustion. Its molecule contains more carbon and hydrogen to oxidize than any of the other listed molecules. Consequently, **one litre of propane gives the greatest heat yield.**

4. Isomers of C₃H₅Br — E

Counting bromine as hydrogen, the degree of unsaturation is

$$\text{DBE} = \frac{2(3) + 2 - 5 - 1}{2} = 1.$$

The molecule therefore contains either one double bond or one ring.

Isomer	SMILES
(<i>E</i>)-1-Bromoprop-1-ene	C/C=C/Br
(<i>Z</i>)-1-Bromoprop-1-ene	C/C=C\Br
2-Bromoprop-1-ene	C=C(Br)C
3-Bromoprop-1-ene, or allyl bromide	C=CCBr
Bromocyclopropane	BrC1CC1

In 1-bromoprop-1-ene, each double-bond carbon has two different substituents. Its *E* and *Z* forms have the higher-priority bromine and methyl groups on opposite and the same sides, respectively.

There are therefore **four constitutional isomers but five isomers when geometrical isomerism is included.**

5. Best engine fuel — E

The intended criterion is resistance to knocking in a spark-ignition engine. Branching generally improves the antiknock properties of alkanes.

The listed structures are:

Hydrocarbon	SMILES
Cyclooctane	C1CCCCCCC1
2,2-Dimethylhexane	CC(C)(C)CCCC
Normal octane	CCCCCCCC
3-Ethylhexane	CCC(CC)CCC
2,2,4-Trimethylpentane	CC(C)(C)CC(C)C

2,2,4-Trimethylpentane, commonly called isooctane, is the highly branched reference fuel assigned an octane number of 100. It is the intended best choice.

6. Reactions of the higher oxide of element 33 — D and E

Element 33 is arsenic. Its higher oxide is arsenic(V) oxide, As_2O_5 , which forms arsenic acid, $\text{O}=[\text{As}](\text{O})(\text{O})\text{O}$, in water:



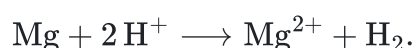
Arsenic(V) oxide is an extended solid; a discrete molecular SMILES would not describe its solid structure.

The acidic solution reacts with sodium hydroxide:

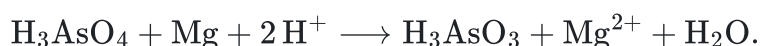


The arsenate ion is $\text{O}=[\text{As}](\text{O}^-)(\text{O}^-)(\text{O}^-)$. The displayed equation represents complete neutralisation; acid salts can form with less hydroxide.

Magnesium also reacts. It is an active reducing metal, and acid reduction can be represented by



The magnesium ion is $[\text{Mg}^{+2}]$. Arsenic(V) itself can also be reduced; for example, a balanced reduction step is



Here arsenious acid, H_3AsO_3 , is $\text{O}=[\text{As}](\text{O})\text{O}$. Further arsenic reduction depends on conditions; a unique final reduction product is not needed to establish that magnesium reacts.

Carbon dioxide and hydrochloric acid, $[\text{H}]\text{Cl}$, are acidic substances, while potassium sulphate provides no conventional reaction driving force in this comparison. Thus **D and E** are selected.

7. Required potassium hydroxide concentration — D

Nitric acid is $\text{O}=[\text{N}^+](\text{O}^-)(\text{O}^-)$. Neutralisation is one-to-one:



Therefore,

$$n(\text{KOH}) = 3.57 \text{ mol}.$$

Using $M(\text{KOH}) = 56 \text{ g mol}^{-1}$,

$$m(\text{KOH}) = 3.57 \times 56 = 199.92 \text{ g} \approx 200 \text{ g}.$$

For $1.00 \text{ kg} = 1000 \text{ g}$ of solution,

$$w(\text{KOH}) = \frac{199.92}{1000} \times 100\% \approx 20.0\%.$$

8. Compounds with formula $\text{C}_3\text{H}_9\text{N}$ — D

The degree of unsaturation is zero:

$$\text{DBE} = \frac{2(3) + 2 + 1 - 9}{2} = 0.$$

The ordinary neutral compounds are saturated, acyclic amines. Distributing three carbon atoms among the substituents on nitrogen gives:

Compound	Type	SMILES
Propan-1-amine	Primary amine	CCCN
Propan-2-amine	Primary amine	CC(N)C
<i>N</i> -Methylethanamine	Secondary amine	CCNC
Trimethylamine	Tertiary amine	CN(C)C

Thus there are **four compounds**.

9. Greatest nitrogen mass fraction — D

For a nitrate of formula $M(\text{NO}_3)_z$,

$$w_{\text{N}} = \frac{14z}{A_{\text{M}} + 62z} \times 100\%.$$

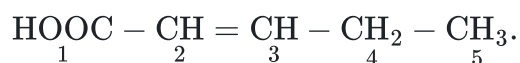
Using rounded atomic masses gives:

Salt	SMILES	Molar mass / g mol^{-1}	Nitrogen / mass %
Potassium nitrate	[K+] . [O-] [N+] (=O) [O-]	101	13.86
Barium nitrate	[Ba+2] . [O-] [N+] (=O) [O-] . [O-] [N+] (=O) [O-]	261	10.73
Aluminium nitrate	[Al+3] . [O-] [N+] (=O) [O-] . [O-] [N+] (=O) [O-] . [O-] [N+] (=O) [O-]	213	19.72
Lithium nitrate	[Li+] . [O-] [N+] (=O) [O-]	69	20.29
Sodium nitrate	[Na+] . [O-] [N+] (=O) [O-]	85	16.47

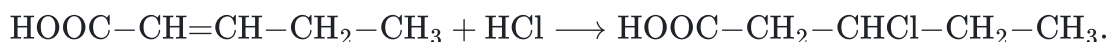
The greatest nitrogen content is therefore that of **lithium nitrate**.

10. Addition of hydrogen chloride to pent-2-enoic acid — C

Pent-2-enoic acid has SMILES CCC=CC(=O)O. Numbering begins at the carboxyl carbon:



The electron-withdrawing carboxyl group makes the β -carbon, carbon 3, the site for chloride addition. The overall reaction is



Thus chlorine attaches mainly to **carbon 3**, giving 3-chloropentanoic acid.

Under achiral conditions the product is racemic. Its two enantiomers are represented by CC[C@H](Cl)CC(=O)O and CC[C@@H](Cl)CC(=O)O. These SMILES specify configuration, but do not depict the electron redistribution during addition.

11. Calcium nitrate hydrate — D

Write the hydrate as $\text{Ca}(\text{NO}_3)_2 \cdot n \text{H}_2\text{O}$. The molar mass of anhydrous calcium nitrate is

$$M(\text{Ca}(\text{NO}_3)_2) = 40 + 2(14 + 3 \times 16) = 164 \text{ g mol}^{-1}.$$

The water mass fraction gives

$$\frac{18n}{164 + 18n} = 0.305.$$

Therefore,

$$18n = 0.305(164 + 18n),$$

$$n = \frac{0.305 \times 164}{18(1 - 0.305)} = 3.998 \approx 4.$$

The hydrate is **calcium nitrate tetrahydrate**. Checking,

$$\frac{4 \times 18}{164 + 4 \times 18} \times 100\% = 30.51\%,$$

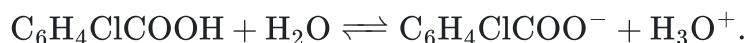
which agrees with the stated 30.5%.

12. Strongest organic acid — B

The structures being compared are:

Acid	SMILES
Benzoic acid	<chem>O=C(O)c1ccccc1</chem>
2-Chlorobenzoic acid	<chem>O=C(O)c1ccccc1Cl</chem>
4-Methylbenzoic acid	<chem>O=C(O)c1ccc(C)cc1</chem>
2-Aminobenzoic acid	<chem>O=C(O)c1ccccc1N</chem>
4-Bromobenzoic acid	<chem>O=C(O)c1ccc(Br)cc1</chem>

The intended strongest acid is **2-chlorobenzoic acid**. Its nearby chlorine substituent produces strong electron withdrawal, together with the characteristic ortho enhancement of benzoic-acid acidity. This favours formation of the carboxylate:



The conjugate base, 2-chlorobenzoate, is O=C([O-])c1ccccc1Cl.

The methyl group donates electron density. An unprotonated amino group also donates by resonance, while the more distant para-bromine substituent has a weaker acid-strengthening effect than ortho-chlorine.

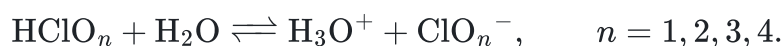
For 2-aminobenzoic acid, zwitterionic equilibria also matter: its zwitterion is O=C([O-])c1ccccc1[NH3+]. Acidity of a separately protonated amino-acid cation must not be confused with dissociation of the net-neutral acid being compared here.

13. Highest degree of dissociation — D

The acids are:

Acid	SMILES
Hypochlorous acid	<chem>OC1</chem>
Chlorous acid	<chem>OC1=O</chem>
Chloric acid	<chem>OC1(=O)=O</chem>
Perchloric acid	<chem>OC1(=O)(=O)=O</chem>

Their dissociation can be written generally as



Increasing the number of oxygen atoms increases electron withdrawal and stabilises the conjugate anion. The acid-strength order is

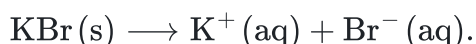


The conjugate anions are hypochlorite $[\text{O}^-]\text{Cl}$, chlorite $[\text{O}^-]\text{Cl}=\text{O}$, chlorate $[\text{O}^-]\text{Cl}(=\text{O})=\text{O}$, and perchlorate $[\text{O}^-]\text{Cl}(=\text{O})(=\text{O})=\text{O}$. These are individual Lewis representations; SMILES does not depict resonance delocalisation.

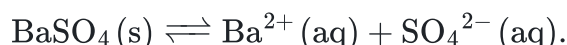
Under the intended comparison at otherwise equal conditions, **perchloric acid** has the greatest tendency to dissociate.

14. Salts that do not undergo hydrolysis — A and E

Potassium bromide is formed from a strong acid and a strong base. Its dissolution supplies potassium ions $[\text{K}^+]$ and bromide ions $[\text{Br}^-]$, neither of which appreciably hydrolyses:



Barium sulphate is likewise treated as a salt of a strong base and strong acid, with no appreciable hydrolysis in this classification. It is also very sparingly soluble:

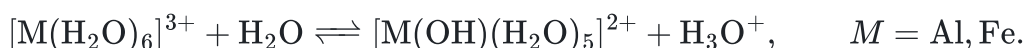


The barium ion is $[\text{Ba}^{+2}]$, and sulphate is $[\text{O}^-]\text{S}(=\text{O})(=\text{O})[\text{O}^-]$.

The other salts do hydrolyse:

- Aluminium(III) and iron(III) aquo ions acidify water by hydrolysis.
- Carbonate is a basic anion and produces hydroxide.

For either trivalent metal, the first hydrolysis step is

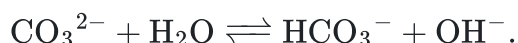


For completeness, dative-bond SMILES for these species are:

Species	SMILES
Hexaaquaaluminium(III)	$\text{O} \rightarrow [\text{Al}^{+3}] (<-\text{O}) (<-\text{O}) (<-\text{O}) (<-\text{O}) <-\text{O}$
Pentaaquahydroxidoaluminium(III)	$[\text{OH}^-] \rightarrow [\text{Al}^{+3}] (<-\text{O}) (<-\text{O}) (<-\text{O}) (<-\text{O}) <-\text{O}$
Hexaaquairon(III)	$\text{O} \rightarrow [\text{Fe}^{+3}] (<-\text{O}) (<-\text{O}) (<-\text{O}) (<-\text{O}) <-\text{O}$
Pentaaquahydroxidoiron(III)	$[\text{OH}^-] \rightarrow [\text{Fe}^{+3}] (<-\text{O}) (<-\text{O}) (<-\text{O}) (<-\text{O}) <-\text{O}$

The six oxygen donors occupy approximately octahedral coordination environments; the SMILES does not encode that spatial arrangement.

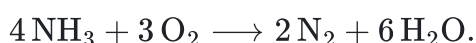
Carbonate hydrolysis is



Carbonate is $\text{O}=\text{C}([\text{O}^-])[\text{O}^-]$, and hydrogen carbonate is $\text{O}=\text{C}(\text{O})[\text{O}^-]$. Thus the correct selections are **A and E**.

15. Air required to burn ammonia — D

Ordinary combustion of ammonia gives nitrogen and water:



At the same temperature and pressure,

$$V(\text{O}_2) = \frac{3}{4}V(\text{NH}_3).$$

Thus 1 L of ammonia requires 0.75 L of oxygen. Taking air as approximately 21% oxygen by volume,

$$V(\text{air}) = \frac{0.75}{0.21} = 3.57 \text{ L}.$$

Using the school approximation of 20% gives 3.75 L. In either case, the nearest answer is 4 L.

16. Thermal decomposition of sodium hydrogen carbonate — E

Sodium hydrogen carbonate is $[\text{Na}^+] \cdot \text{O}=\text{C}(\text{O}) [\text{O}^-]$. It decomposes according to



Sodium carbonate is $[\text{Na}^+] \cdot [\text{Na}^+] \cdot \text{O}=\text{C}([\text{O}^-]) [\text{O}^-]$.

The oxidation states remain:



No oxidation state changes, so **no element is oxidised**.

17. Calcium carbonate decomposition equilibrium — C and E

The equilibrium is



Calcium carbonate and calcium oxide have the formal ionic representations $[\text{Ca}^{+2}] \cdot [\text{O}^-]\text{C}(=\text{O}) [\text{O}^-]$ and $[\text{Ca}^{+2}] \cdot [\text{O}^{2-}]$, respectively.

When both solid phases are present, their activities are unity, so

$$K_p = \frac{p_{\text{CO}_2}}{p^\circ}.$$

Consequently:

- **A:** Increasing temperature favours the endothermic decomposition.
- **B:** Decreasing pressure by expansion lowers the carbon dioxide partial pressure and favours decomposition.
- **C:** A catalyst changes the rates of approach to equilibrium, but not the equilibrium position.
- **D:** Changing carbon dioxide concentration changes the reaction quotient.
- **E:** Adding more pure solid calcium carbonate does not change its activity and therefore does not shift equilibrium, provided the solid phases remain present.

The changes with no effect on equilibrium position are **C and E**.

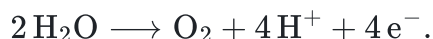
18. Products at the platinum anode — B and E

At an inert platinum anode, chloride oxidation and water oxidation are competing processes in aqueous aluminium chloride.

Chloride ions, $[\text{Cl}^-]$, produce chlorine:



Water oxidation produces oxygen:



Thus **both oxygen and chlorine must be included: B and E**. Their relative production depends on chloride concentration, electrode potential, current density, and mass transport; the problem does not determine their ratio.

Hydrogen formation is a cathodic process, for example



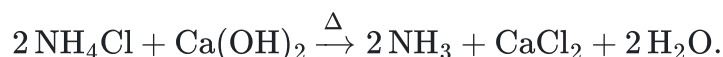
Any aluminium hydroxide formed by local alkalinisation also belongs to the cathodic region:



Aluminium hydroxide is an extended solid, formally represented by $[\text{Al}^{3+}] \cdot [\text{OH}^-] \cdot [\text{OH}^-] \cdot [\text{OH}^-]$. Neither it nor metallic aluminium is an anodic product here.

19. Apparatus for preparing ammonia — C

The preparation reaction is



The salt representations are ammonium chloride $[\text{NH}_4^+] \cdot [\text{Cl}^-]$, calcium hydroxide $[\text{Ca}^{2+}] \cdot [\text{OH}^-] \cdot [\text{OH}^-]$, and calcium chloride $[\text{Ca}^{2+}] \cdot [\text{Cl}^-] \cdot [\text{Cl}^-]$.

The correct apparatus must satisfy three requirements:

1. Ammonia is lighter than air, so it is collected in an **inverted receiver**, displacing air downward.
2. Ammonia is highly soluble in water, so collection over water is unsuitable.
3. The heated generating tube should slope downward toward its mouth, so condensed water does not run back onto the strongly heated end.

Figure C satisfies all three. Figures A and D have upright receivers; B attempts collection over water; E slopes the generating tube so condensate can return to the hot end.

20. Apparatus for preparing bromoethane — A

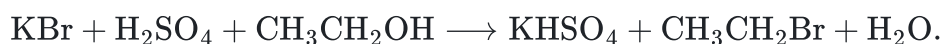
Hydrogen bromide is generated from potassium bromide and sulphuric acid:



It reacts with ethanol:



The overall equation is



The relevant structures are ethanol CCO , hydrogen bromide $[\text{H}]\text{Br}$, bromoethane CCBr , and potassium hydrogen sulphate $[\text{K}^+] \cdot \text{OS}(=\text{O})(=\text{O})[\text{O}^-]$.

Bromoethane is volatile and is distilled as it forms. **Apparatus A** has the appropriate arrangement:

- The thermometer bulb is near the side-arm entrance, where it measures the temperature of the vapour entering the condenser.
- Cooling water enters the **lower, receiver-side connection** and leaves through the **upper, flask-side connection**, keeping the condenser jacket filled.
- The delivery tube extends below the receiving liquid, helping retain the volatile product.

B lacks a water-cooled condenser. C reverses the cooling-water flow and places the thermometer too low. E also places the thermometer too low. D lacks the thermometer and liquid collection arrangement provided in A.

The answers were checked against the official answers published by the organisers.

Problem 2: Gravimetric and titrimetric analysis of a Cd-Sn-Bi-Pb alloy

An alloy comprises the following metals: cadmium, tin, bismuth, and lead. A sample of this alloy weighing 1.2860 g, was treated with a solution of concentrated nitric acid. The individual compound of metal **A** obtained as a precipitate, was separated, thoroughly washed, dried and calcinated. The mass of the precipitate after the calcination to constant mass, was 0.3265 g.

An aqueous ammonia solution was added in excess to the solution obtained after separation of the precipitate. A compound of metal **B** remained in the solution while all the other metals precipitated in the form of sparingly soluble compounds. The solution was first quantitatively separated from the precipitate, and then hydrogen sulphide was passed through the separated solution to saturation. The resulting precipitate containing metal **B** was separated, washed and dried. The mass of the precipitate was 0.6613 g.

The precipitate containing the compounds of metals **C** and **D** was treated with an excess of a NaOH solution. The solution and the precipitate were then quantitatively separated. A solution of HNO₃ was added to the alkaline solution to reach pH 5 – 6, and an excess of K₂CrO₄ solution was added to the resulting transparent solution. The yellow precipitate was separated, washed and quantitatively transferred to a beaker. Finally a dilute H₂SO₄ solution and crystalline KI were added. Iodine produced as a result of the reaction was titrated with sodium thiosulphate solution in the presence of starch as an indicator. 18.46 cm³ of 0.1512 normal Na₂S₂O₃ solution were required.

The last metal contained in the precipitate as a sparingly soluble compound was transformed to an even less soluble phosphate and its mass was found to be 0.4675 g.

2.1 Write all equations of the chemical reactions on which the quantitative analysis of the alloy sample is based. Name metals **A**, **B**, **C**, and **D**. Calculate the mass percentage of the metals in the alloy.

Official English text of the problem.

Answers

- 2.1.** Taking **C** as the metal dissolved by excess sodium hydroxide and **D** as the metal remaining in the residue:

Label	Metal	Analytical product	Mass in sample	Mass percentage
A	Tin	SnO ₂ , weighed after ignition	0.2572 g	20.00%
B	Cadmium	CdS, weighed	0.5145 g	40.01%

Label	Metal	Analytical product	Mass in sample	Mass percentage
C	Lead	PbCrO ₄ , determined iodometrically	0.1928 g	14.99%
D	Bismuth	BiPO ₄ , weighed	0.3214 g	24.99%

The iodometric relation is

$$n(\text{Pb}) = \frac{n(\text{S}_2\text{O}_3^{2-})}{3}.$$

The balanced analytical reactions are given below.

Solution

2.1. Identification, reactions, and composition

The sample mass is $m_0 = 1.2860$ g. Since atomic masses are not supplied, use the conventional values

$$A_r(\text{Sn}) = 118.71, \quad A_r(\text{Cd}) = 112.41, \quad A_r(\text{Pb}) = 207.2, \quad A_r(\text{Bi}) = 208.98, \\ A_r(\text{O}) = 16.00, \quad A_r(\text{S}) = 32.06, \quad A_r(\text{P}) = 30.97.$$

Equations are written in net ionic form where appropriate.

Identification of A: tin

Concentrated nitric acid oxidizes tin to insoluble hydrous tin(IV) oxide, conventionally called *metastannic acid* and represented by the nominal formula H_2SnO_3 :



The other metals enter solution as their nitrate salts:



Ignition converts the hydrous tin precipitate into tin(IV) oxide:



Thus **A is tin**, and the 0.3265 g weighing form is SnO_2 . Each mole contains one mole of tin:

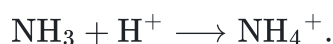
$$m(\text{Sn}) = 0.3265 \text{ g} \times \frac{118.71}{150.71} = 0.2571748 \text{ g}.$$

Therefore,

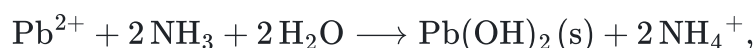
$$w(\text{Sn}) = \frac{0.2571748}{1.2860} \times 100\% = 20.00\%.$$

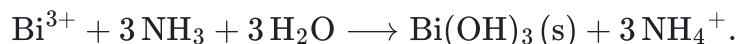
Identification of B: cadmium

Added ammonia first neutralizes residual acid:

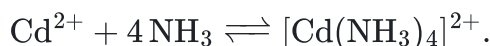


Lead and bismuth precipitate as hydroxides:





Cadmium remains in excess ammonia as the soluble tetraamminecadmium(II) complex:



Passing hydrogen sulfide through the separated ammoniacal solution precipitates cadmium sulfide. Including proton uptake by ammonia, the overall equation is



Thus **B is cadmium**, weighed as CdS:

$$m(\text{Cd}) = 0.6613 \text{ g} \times \frac{112.41}{112.41 + 32.06} = 0.5145479 \text{ g}.$$

Hence,

$$w(\text{Cd}) = \frac{0.5145479}{1.2860} \times 100\% = 40.01\%.$$

Separation of lead and bismuth

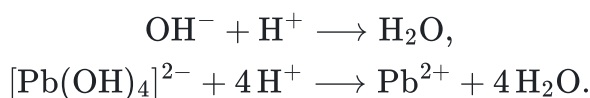
Lead(II) hydroxide is amphoteric and dissolves in excess hydroxide. A conventional hydroxo-complex representation is



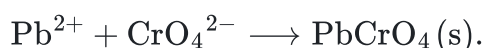
Bismuth(III) hydroxide remains in the precipitate under these conditions. Assigning the soluble branch to **C** and the residue to **D** therefore gives

$$C = \text{Pb}, \quad D = \text{Bi}.$$

Nitric acid neutralizes excess hydroxide and decomposes the lead hydroxo complex:

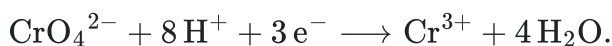


Addition of potassium chromate then precipitates yellow lead(II) chromate:



Iodometric determination of lead

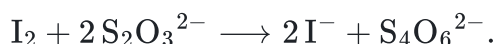
In acid solution, chromium(VI) in the isolated chromate oxidizes iodide to iodine and is reduced to chromium(III). Its reduction half-reaction is



Including precipitation of lead(II) sulfate, the overall reaction with sulfuric acid and iodide is



The liberated iodine is titrated with thiosulfate:



Starch indicates the disappearance of iodine at the endpoint; it does not enter the stoichiometric calculation.

Two moles of lead chromate produce three moles of iodine, which consume six moles of thiosulfate. Consequently,

$$n(\text{Pb}) = n(\text{PbCrO}_4) = \frac{n(\text{S}_2\text{O}_3^{2-})}{3}.$$

In this titration, one mole of thiosulfate corresponds to one redox equivalent, so its 0.1512-normal solution has concentration $0.1512 \text{ mol L}^{-1}$. Keeping guard digits,

$$n(\text{S}_2\text{O}_3^{2-}) = (0.1512 \text{ mol L}^{-1})(18.46 \times 10^{-3} \text{ L}) = 2.791152 \times 10^{-3} \text{ mol}.$$

Thus,

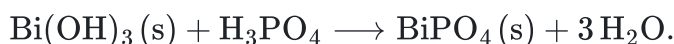
$$\begin{aligned} n(\text{Pb}) &= 9.30384 \times 10^{-4} \text{ mol}, \\ m(\text{Pb}) &= (9.30384 \times 10^{-4} \text{ mol})(207.2 \text{ g mol}^{-1}) = 0.1927756 \text{ g}, \end{aligned}$$

and

$$w(\text{Pb}) = \frac{0.1927756}{1.2860} \times 100\% = 14.99\%.$$

Gravimetric determination of bismuth

The remaining bismuth precipitate is converted to bismuth(III) phosphate. The problem does not specify the phosphate reagent; a balanced representation using phosphoric acid is



Each mole of BiPO_4 contains one mole of bismuth:

$$m(\text{Bi}) = 0.4675 \text{ g} \times \frac{208.98}{208.98 + 30.97 + 4(16.00)} = 0.3214284 \text{ g}.$$

Therefore,

$$w(\text{Bi}) = \frac{0.3214284}{1.2860} \times 100\% = 24.99\%.$$

The independently determined metal masses total

$$0.2571748 + 0.5145479 + 0.1927756 + 0.3214284 = 1.2859267 \text{ g},$$

or 99.9943% of the sample mass. This agrees closely with 1.2860 g; the composition is approximately 20 : 40 : 15 : 25 by mass for tin, cadmium, lead, and bismuth, respectively.

Names and SMILES of the molecular and ionic species

The following notation identifies the species used above. Dative arrows represent ligand-to-metal donation; these SMILES do not specify three-dimensional coordination geometry. The tetraamminecadmium(II) ion is conventionally represented with a tetrahedral arrangement of its four ammonia ligands. Aqueous H^+ denotes a solvated proton.

Species and name	SMILES
HNO_3 , nitric acid	<chem>O[N+](=O)[O-]</chem>
H_2SO_4 , sulfuric acid	<chem>OS(=O)(=O)O</chem>
H_3PO_4 , phosphoric acid	<chem>OP(=O)(O)O</chem>
H_2O , water	<chem>O</chem>
NO_2 , nitrogen dioxide radical	<chem>[O]N=O</chem>
NH_3 , ammonia	<chem>N</chem>

Species and name	SMILES
H ₂ S, hydrogen sulfide	S
I ₂ , iodine	II
H ⁺ , hydrogen ion	[H+]
OH ⁻ , hydroxide ion	[OH-]
NH ₄ ⁺ , ammonium ion	[NH4+]
NO ₃ ⁻ , nitrate ion	[O-][N+](=O)[O-]
Cd ²⁺ , cadmium(II) ion	[Cd+2]
Pb ²⁺ , lead(II) ion	[Pb+2]
Bi ³⁺ , bismuth(III) ion	[Bi+3]
Cr ³⁺ , chromium(III) ion	[Cr+3]
[Cd(NH ₃) ₄] ²⁺ , tetraamminecadmium(II) ion	[NH3]->[Cd+2](<-[NH3])(<-[NH3])<-[NH3]
[Pb(OH) ₄] ²⁻ , tetrahydroxoplumbate(II) ion	[OH-]->[Pb+2](<-[OH-])(<-[OH-])<-[OH-]
CrO ₄ ²⁻ , chromate ion	[O-][Cr](=O)(=O)[O-]
SO ₄ ²⁻ , sulfate ion	[O-]S(=O)(=O)[O-]
I ⁻ , iodide ion	[I-]
S ₂ O ₃ ²⁻ , thiosulfate ion	[O-]S(=O)(=O)[S-]
S ₄ O ₆ ²⁻ , tetrathionate ion	[O-]S(=O)(=O)SSS(=O)(=O)[O-]

The solid analytical compounds have extended structures rather than discrete molecules. Their dot-disconnected SMILES below represent **formal formula units**, not their crystal lattices. In particular, hydrous tin(IV) oxide has no unique molecular SMILES; its entry represents the nominal composition SnO₂ · H₂O.

Solid and name	Formal formula-unit SMILES
H ₂ SnO ₃ , metastannic acid / hydrous tin(IV) oxide	[Sn+4].[O-2].[O-2].O
SnO ₂ , tin(IV) oxide	[Sn+4].[O-2].[O-2]
CdS, cadmium sulfide	[Cd+2].[S-2]
Pb(OH) ₂ , lead(II) hydroxide	[Pb+2].[OH-].[OH-]
Bi(OH) ₃ , bismuth(III) hydroxide	[Bi+3].[OH-].[OH-].[OH-]
PbCrO ₄ , lead(II) chromate	[Pb+2].[O-][Cr](=O)(=O)[O-]
PbSO ₄ , lead(II) sulfate	[Pb+2].[O-]S(=O)(=O)[O-]
BiPO ₄ , bismuth(III) phosphate	[Bi+3].[O-]P(=O)([O-])[O-]

Starch is a polymeric indicator with no single molecular SMILES.

The solution was checked against the official solution.

Problem 3: Chemical processes in five mixtures of reagents (ionic and

organic equations)

Which chemical processes can take place in the interaction of:

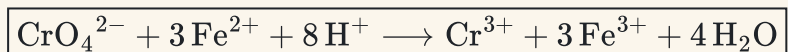
- a) aluminium ammonium sulphate with baryta water,
- b) potassium chromate, ferrous chloride and sulphuric acid,
- c) calcinated soda and sodium hydrogen sulphate,
- d) 4-bromoethyl benzene and chlorine,
- e) n-propyl alcohol, phenol and concentrated sulphuric acid?

Write ionic equations for the reactions that proceed in aqueous solutions. For the other chemical reactions write complete equations and indicate the type of the reaction. Indicate the differences in the reaction conditions for those reactions that may lead to the formation of various substances.

Official English text of the problem.

Answers

- **a)** Barium sulphate and aluminium hydroxide precipitate, and ammonia is liberated. Excess hydroxide dissolves the aluminium hydroxide as tetrahydroxoaluminate.
- **b)** Acidified chromate oxidizes iron(II) to iron(III), while chromium(VI) is reduced to chromium(III):



- **c)** One acid equivalent per carbonate ion gives hydrogen carbonate; two give carbon dioxide and water. Hydrogen sulphate becomes sulphate in both cases.
- **d)** Chlorination with a Lewis-acid catalyst in the dark substitutes the aromatic ring, preferentially ortho to the ethyl group. Photochemical chlorination preferentially substitutes the benzylic position, giving racemic 1-bromo-4-(1-chloroethyl)benzene.
- **e)** Depending on temperature and proportions, possible processes include formation of propyl hydrogen sulphate, intermolecular dehydration to ethers, elimination to propene, and ortho/para sulphonation of phenol. If generated propene remains in contact with phenol and acid, ring alkylation can also give ortho- and para-isopropylphenol.

Names and SMILES for the species and organic products are supplied below.

Solution

SMILES for salts describe ionic formula units; they do not describe crystal lattices. Aqueous metal-ion notation below suppresses coordinated water. Common species are water, H_2O , o; hydrogen ion, H^+ , [H+]; and hydroxide ion, OH^- , [OH-].

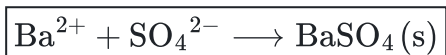
a) Aluminium ammonium sulphate with baryta water

Aluminium ammonium sulphate has the salt formula $\text{NH}_4\text{Al}(\text{SO}_4)_2$, $[\text{NH}_4^+] \cdot [\text{Al}^{3+}] \cdot [\text{O}^-]\text{S}(=\text{O})(=\text{O})[\text{O}^-] \cdot [\text{O}^-]\text{S}(=\text{O})(=\text{O})[\text{O}^-]$. Baryta water is aqueous barium hydroxide, $\text{Ba}(\text{OH})_2$, $[\text{Ba}^{2+}] \cdot [\text{OH}^-] \cdot [\text{OH}^-]$.

The reacting ions are ammonium, $[\text{NH}_4^+]$; aluminium(III), $[\text{Al}^{3+}]$; barium(II), $[\text{Ba}^{2+}]$; sulphate, $[\text{O}^-]\text{S}(=\text{O})(=\text{O})[\text{O}^-]$; and hydroxide.

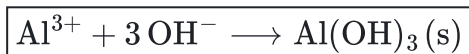
Three processes must be considered.

1. Precipitation of barium sulphate



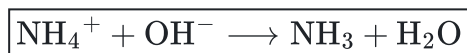
Barium sulphate, $[\text{Ba}^{2+}] \cdot [\text{O}^-]\text{S}(=\text{O})(=\text{O})[\text{O}^-]$, is sparingly soluble.

2. Precipitation of aluminium hydroxide



Aluminium hydroxide, $[\text{Al}^{3+}] \cdot [\text{OH}^-] \cdot [\text{OH}^-] \cdot [\text{OH}^-]$, initially forms a precipitate.

3. Conversion of ammonium to ammonia



The product is ammonia, N . Warming assists its escape from solution.

Aluminium hydroxide is amphoteric. With sufficiently **excess hydroxide**, it dissolves:



The product is tetrahydroxoaluminate, $[\text{Al}^-](\text{O})(\text{O})(\text{O})\text{O}$, with approximately tetrahedral coordination around aluminium. The formal charge placement in this SMILES does not represent aluminium's oxidation state, which remains +3.

Thus the aluminium-containing product depends on the amount of baryta water: a hydroxide precipitate at intermediate alkalinity, and dissolved aluminate in sufficient excess alkali. Barium sulphate remains precipitated.

b) Potassium chromate, ferrous chloride and sulphuric acid

The reagents are:

Name	Formula	SMILES
Potassium chromate	K_2CrO_4	$[\text{K}^+] \cdot [\text{K}^+] \cdot [\text{O}^-][\text{Cr}](=\text{O})(=\text{O})[\text{O}^-]$
Ferrous chloride, or iron(II) chloride	FeCl_2	$[\text{Fe}^{2+}] \cdot [\text{Cl}^-] \cdot [\text{Cl}^-]$
Sulphuric acid	H_2SO_4	$\text{OS}(=\text{O})(=\text{O})\text{O}$

Chromate ion, $[\text{O}^-][\text{Cr}](=\text{O})(=\text{O})[\text{O}^-]$, contains chromium in oxidation state +6. It accepts three electrons to form chromium(III) ion, $[\text{Cr}^{3+}]$. Each iron(II) ion, $[\text{Fe}^{2+}]$, loses one electron to form iron(III) ion, $[\text{Fe}^{3+}]$.

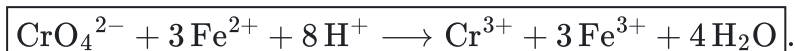
The half-equations are



and

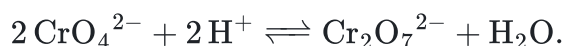


Multiplying the second by three and adding gives



This is an **oxidation–reduction reaction**. The exact stoichiometric requirement is three moles of iron(II) per mole of chromate.

Acidification also shifts the chromate–dichromate equilibrium:



Dichromate ion has SMILES [O-][Cr](=O)(=O)O[Cr](=O)(=O)[O-]. Using this form, the equivalent redox equation is



Potassium ion, [K+], chloride ion, [Cl-], and sulphate are spectator ions in the principal redox reaction. Sufficient acidity also keeps the trivalent-metal products from precipitating as hydroxides.

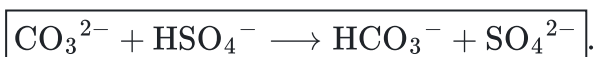
c) Calcinated soda and sodium hydrogen sulphate

“Calcinated soda” means anhydrous sodium carbonate, Na2CO3, [Na+].[Na+].[O-]C(=O)[O-]. Sodium hydrogen sulphate is NaHSO4, [Na+].OS(=O)(=O)[O-].

The relevant ions are carbonate, [O-]C(=O)[O-]; hydrogen sulphate, OS(=O)(=O)[O-]; and the spectator sodium ion, [Na+].

Hydrogen sulphate supplies one acidic proton per ion. Carbonate can accept two protons, successively.

With **one mole of hydrogen sulphate per mole of carbonate**, the net reaction is



The carbon-containing product is hydrogen carbonate, also called bicarbonate, O=C(O)[O-]. Cool conditions favor retaining it in solution.

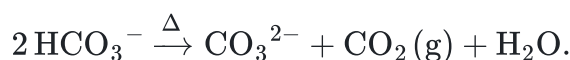
Addition of a second acid equivalent gives



Carbon dioxide has SMILES O=C=O. The overall equation with two acid equivalents is



These are **acid–base reactions**, with gas evolution in the second stage. Heating and allowing carbon dioxide to escape also favor its removal from bicarbonate-containing solutions:



d) 4-Bromoethyl benzene and chlorine

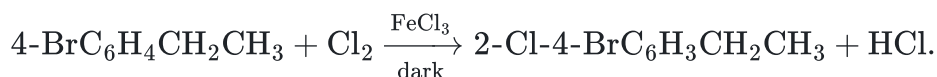
The substrate is interpreted as **1-bromo-4-ethylbenzene**, 4-BrC6H4CH2CH3, CCc1ccc(Br)cc1.

Chlorine is Cl2, ClCl. Hydrogen chloride, HCl, [H]Cl, accompanies each substitution.

The relevant organic products are:

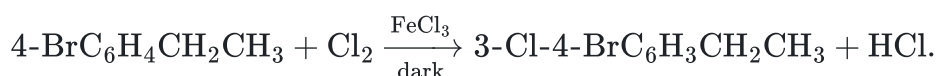
Product	SMILES
4-Bromo-2-chloro-1-ethylbenzene: chlorine ortho to ethyl	<chem>CCc1c(Cl)cc(Br)cc1</chem>
1-Bromo-2-chloro-4-ethylbenzene: chlorine ortho to bromine	<chem>CCc1cc(Cl)c(Br)cc1</chem>
1-Bromo-4-(1-chloroethyl)benzene, the benzylic product	<chem>C[C@H](Cl)c1ccc(Br)cc1</chem> and <chem>C[C@@H](Cl)c1ccc(Br)cc1</chem>
1-Bromo-4-(2-chloroethyl)benzene, the terminal-chain product	<chem>ClCCc1ccc(Br)cc1</chem>
1-Bromo-4-(1,1-dichloroethyl)benzene	<chem>CC(Cl)(Cl)c1ccc(Br)cc1</chem>

Aromatic substitution. In the dark, with a Lewis-acid catalyst such as iron(III) chloride, FeCl_3 , $[\text{Fe}+3] \cdot [\text{Cl}-] \cdot [\text{Cl}-] \cdot [\text{Cl}-]$, electrophilic aromatic substitution occurs:



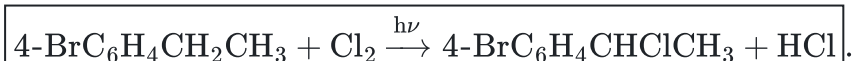
Here the ring positions in the formula are numbered from the ethyl-bearing carbon. Ethyl is an activating ortho/para director. Its para position is occupied, so the equivalent positions 2 and 6 are favored.

Bromine is deactivating but also ortho/para directing. Consequently, the other distinct ring-monochlorination product is possible:



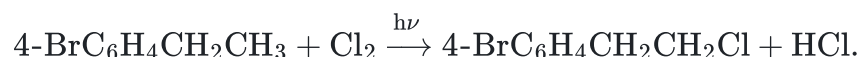
The ethyl-directed product is normally favored; the statement does not determine an exact isomer ratio.

Side-chain substitution. Under irradiation, without the Lewis-acid conditions used for ring chlorination, a radical chain reaction occurs preferentially at the benzylic carbon:

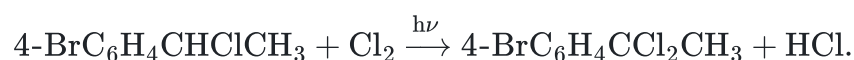


Abstraction of a benzylic hydrogen is favored because the resulting radical is resonance-stabilized. The product has a stereogenic carbon. Formation through a planar radical in an achiral environment gives the **racemic pair** represented by the two stereochemical SMILES above.

Radical chlorination is not perfectly selective; terminal-chain substitution can also occur:



With excess chlorine or prolonged irradiation, further side-chain substitution is possible, for example



Thus light versus Lewis-acid catalysis selects the principal reaction site, while chlorine exposure controls the extent of substitution.

e) n-Propyl alcohol, phenol and concentrated sulphuric acid

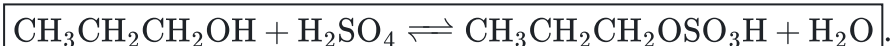
The organic starting materials are propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, ccco, and phenol, $\text{C}_6\text{H}_5\text{OH}$, Oc1ccccc1.

The principal product structures considered below are:

Product	SMILES
Propyl hydrogen sulphate	<chem>CCCOS(=O)(=O)O</chem>
Di-n-propyl ether, or 1-propoxypropane	<chem>CCCOCCC</chem>
n-Propyl phenyl ether, or propoxybenzene	<chem>CCCOc1ccccc1</chem>
Propene	<chem>C=CC</chem>
2-Hydroxybenzenesulphonic acid	<chem>Oc1ccccc1S(=O)(=O)O</chem>
4-Hydroxybenzenesulphonic acid	<chem>Oc1ccc(S(=O)(=O)O)cc1</chem>
2-Isopropylphenol	<chem>CC(C)c1ccccc1O</chem>
4-Isopropylphenol	<chem>CC(C)c1ccc(O)cc1</chem>

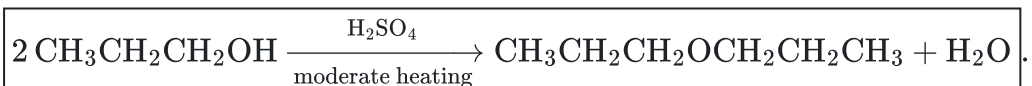
Concentrated sulphuric acid can act as an acid catalyst, a dehydrating reagent, and a sulphonating reagent. Consequently, the mixture does not have one condition-independent product.

Formation of a sulphuric-acid ester. At relatively low temperature, reaction of the alcohol with concentrated sulphuric acid can give propyl hydrogen sulphate:

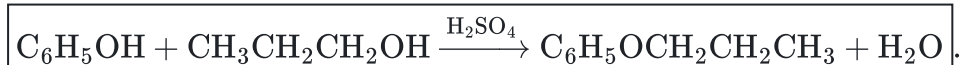


This is **esterification**. A low water content favors the ester; dilution promotes its hydrolysis.

Intermolecular dehydration: ether formation. With excess primary alcohol and moderate heating under acid catalysis, two alcohol molecules can form di-n-propyl ether:

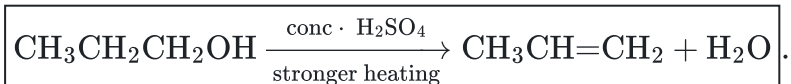


Intermolecular dehydration involving phenol can likewise give the mixed ether:



This is **etherification**, involving substitution at the primary propyl carbon. Phenol's oxygen becomes bonded to that carbon; the aromatic carbon–oxygen bond is retained. In the three-reagent mixture, competing reactions mean that this equation does not imply selective formation of a pure mixed ether.

Intramolecular dehydration: alkene formation. Stronger heating, especially with removal of the gaseous product, favors elimination:

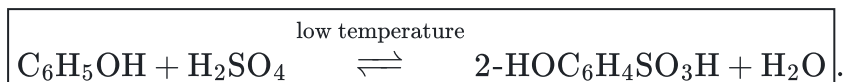


This is an **elimination reaction**. Propene has no *E/Z* stereoisomers because one double-bond carbon bears two hydrogens.

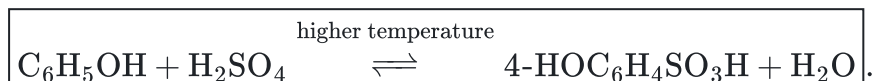
The distinction between ether and alkene formation depends on temperature, acid/alcohol ratio, and product removal; it is not a universal sharp temperature boundary.

Sulphonation of phenol. The hydroxyl group strongly activates the aromatic ring and directs electrophilic substitution to the ortho and para positions.

At low temperature, conventionally around 20 °C, ortho sulphonation is favored:

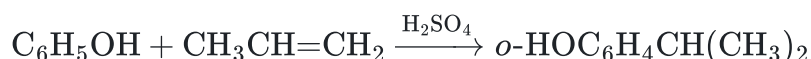


On heating, conventionally around 100 °C, the para product becomes favored:

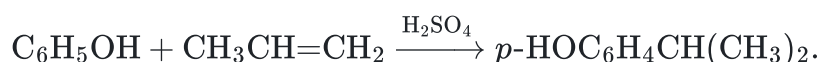


Both reactions are **electrophilic aromatic substitutions**. Sulphonation is reversible; heating allows the product distribution to move toward the less sterically crowded para isomer. These temperatures indicate approximate reaction regimes, not exclusive product boundaries.

Possible ring alkylation when propene is retained. If propene formed by dehydration remains in contact with phenol and acid, it can act as an alkylating reagent. Acid activation favors attachment through the secondary carbon, giving isopropyl substituents:



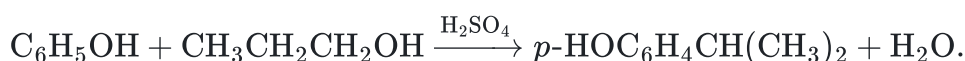
and



These are **electrophilic aromatic substitutions**. Combining alcohol dehydration with either alkylation gives the corresponding complete net equation:



or



Removal of propene favors its isolation; retaining it with phenol permits this additional reaction.

The solution was checked against the official solution.

Problem 4: Formula of a nitrogen-hydrogen compound X from its thermal decomposition

Compound **X** contains nitrogen and hydrogen. Strong heating of 3.2 g of **X** leads to its decomposition without the formation of a solid residue. The resulting mixture of gases is partially absorbed by sulphuric acid (the volume of the gaseous mixture decreased by a factor of 2.8). The non-absorbed gas, that is a mixture of hydrogen and nitrogen, occupies under normal conditions a volume of 1.4 dm³ and has a density of 0.786 g dm⁻³.

Determine the formula of compound **X**.

Official English text of the problem.

Answers

- **Problem 4: Hydrazine**, N_2H_4 , structure $\text{H}_2\text{N}-\text{NH}_2$, SMILES `NN`, fits all the figures **if decomposition is incomplete**: nominally 87.5% decomposes, while the remaining hydrazine vapour is absorbed together with ammonia. Complete decomposition solely into ammonia, nitrogen and hydrogen is inconsistent with the stated data.

Solution

Composition of the non-absorbed gas.

Use the normal molar gas volume $22.4 \text{ dm}^3 \text{ mol}^{-1}$ and molar masses $M(\text{H}_2) = 2$, $M(\text{N}_2) = 28 \text{ g mol}^{-1}$. Hydrogen has SMILES `[H][H]`; nitrogen has SMILES `N#N`.

The amount and mean molar mass of the non-absorbed gas are

$$n_{\text{remaining}} = \frac{1.4}{22.4} = 0.0625 \text{ mol},$$

$$\bar{M} = \rho V_m = 0.786(22.4) = 17.6064 \text{ g mol}^{-1}.$$

If y is its nitrogen mole fraction,

$$28y + 2(1 - y) = 17.6064, \quad y = 0.60025 \approx 0.600.$$

Thus, to the precision relevant here,

$$n(\text{N}_2) = 0.0375 \text{ mol}, \quad n(\text{H}_2) = 0.0250 \text{ mol}.$$

What is absorbed by sulphuric acid?

The volume reduction gives

$$n_{\text{absorbed}} = (2.8 - 1)(0.0625) = 0.1125 \text{ mol}.$$

The mass of the remaining gas is

$$m_{\text{remaining}} = 1.4(0.786) = 1.1004 \text{ g},$$

so the absorbed material must weigh

$$m_{\text{absorbed}} = 3.2 - 1.1004 = 2.0996 \text{ g}.$$

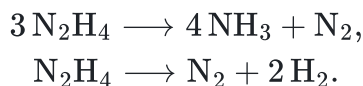
Ammonia, NH_3 , SMILES `N`, is the expected basic decomposition product. However, assigning **all** the absorbed gas to ammonia would give

$$m_{\text{products}} = 1.1004 + (0.1125)(17) = 3.0129 \text{ g},$$

which does not equal the stated 3.2 g. Consequently, that conventional complete-decomposition interpretation does not satisfy all the data.

A consistent hydrazine interpretation.

Hydrazine can give ammonia, nitrogen and hydrogen through the balanced overall reactions



The observed 0.0250 mol of hydrogen corresponds to

$$n_{\text{second reaction}}(\text{N}_2\text{H}_4) = \frac{0.0250}{2} = 0.0125 \text{ mol.}$$

This also produces 0.0125 mol of nitrogen. The other

$$0.0375 - 0.0125 = 0.0250 \text{ mol}$$

of nitrogen can arise from the first reaction, consuming 0.0750 mol of hydrazine and producing 0.100 mol of ammonia.

Therefore,

$$n_{\text{decomposed}}(\text{N}_2\text{H}_4) = 0.0125 + 0.0750 = 0.0875 \text{ mol.}$$

The original sample contains

$$n_0(\text{N}_2\text{H}_4) = \frac{3.2}{32} = 0.100 \text{ mol,}$$

leaving

$$n_{\text{unchanged}}(\text{N}_2\text{H}_4) = 0.0125 \text{ mol}$$

or 0.400 g.

If this unchanged hydrazine is present as vapour before absorption, the figures all agree:

$$n_{\text{absorbed}} = n(\text{NH}_3) + n(\text{N}_2\text{H}_4) = 0.100 + 0.0125 = 0.1125 \text{ mol,}$$

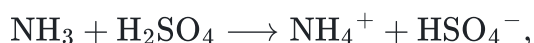
$$m_{\text{absorbed}} = (0.100)(17) + (0.0125)(32) = 2.10 \text{ g,}$$

$$\frac{n_{\text{before}}}{n_{\text{after}}} = \frac{0.100 + 0.0125 + 0.0375 + 0.0250}{0.0375 + 0.0250} = 2.8.$$

The predicted residual density is also correct:

$$\rho = \frac{(0.0375)(28) + (0.0250)(2)}{1.4} = 0.7857 \text{ g dm}^{-3} \approx 0.786 \text{ g dm}^{-3}.$$

Both ammonia and hydrazine are absorbed by sulphuric acid, H_2SO_4 , SMILES OS(=O)(=O)O, through protonation:



The ions are ammonium $[\text{NH}_4^+]$, hydrazinium $[\text{N}_2\text{H}_5^+]$, and hydrogensulfate $\text{OS}(=\text{O})(=\text{O})[\text{O}^-]$.

Thus hydrazine provides an exact numerical fit, with a decomposed fraction

$$\frac{0.0875}{0.100} = 0.875.$$

The solution was checked against the official solution.

Problem 5: Structure of a benzene derivative C_9H_{12} from its bromination products

Benzene derivative **X** has the empirical formula C_9H_{12} . Its bromination in the light leads to the formation of two monobromo derivatives in approximately identical yield. Bromination in the dark in the presence of iron also gives two monobromo derivatives. If the reaction is carried out to a

higher degree, the formation of four dibromo derivatives may occur.

Suggest the structure for compound **X** and for the bromination products. Write schemes for the reactions.

Official English text of the problem.

Answers

The problem has no numbered subparts.

- **Compound X: 4-ethyltoluene (1-ethyl-4-methylbenzene)**, Cc1ccc(CC)cc1.
- **Bromination in light:** the two side-chain products L_1 and L_2 below, in approximately equal yields. L_2 is racemic.
- **Bromination in the dark with iron:** the two ring-monobromination products M_2 and M_3 .
- **Further bromination in the dark with iron:** the four ring-dibromination products D_{23} , D_{25} , D_{26} , and D_{35} .

For all ring-product labels, keep the original methyl group at ring position **1** and the ethyl group at position **4**.

Label	Product name	SMILES
L_1	1-(Bromomethyl)-4-ethylbenzene	<chem>CCc1ccc(CBr)cc1</chem>
L_2	Racemic 1-(1-bromoethyl)-4-methylbenzene	<chem>C[C@H](Br)c1ccc(C)cc1</chem> and <chem>C[C@@H](Br)c1ccc(C)cc1</chem> , in equal amounts
M_2	2-Bromo-4-ethyltoluene	<chem>Cc1c(Br)cc(CC)cc1</chem>
M_3	3-Bromo-4-ethyltoluene	<chem>Cc1cc(Br)c(CC)cc1</chem>
D_{23}	2,3-Dibromo-4-ethyltoluene	<chem>Cc1c(Br)c(Br)c(CC)cc1</chem>
D_{25}	2,5-Dibromo-4-ethyltoluene	<chem>Cc1c(Br)cc(CC)c(Br)c1</chem>
D_{26}	2,6-Dibromo-4-ethyltoluene	<chem>Cc1c(Br)cc(CC)cc1Br</chem>
D_{35}	3,5-Dibromo-4-ethyltoluene	<chem>Cc1cc(Br)c(CC)c(Br)c1</chem>

Solution

Identification of X.

The degree of unsaturation is

$$\text{DBE} = \frac{2(9) + 2 - 12}{2} = 4.$$

The benzene ring accounts for all four degrees of unsaturation. Thus the three carbons outside the ring belong to saturated, acyclic alkyl substituents. They can form one propyl group, an ethyl group plus a methyl group, or three methyl groups.

The possible structures and their numbers of constitutionally distinct ring-monobromination products are:

Candidate	SMILES	Ring-monobromination products
Propylbenzene	<chem>CCCc1ccccc1</chem>	3
Isopropylbenzene (cumene)	<chem>CC(C)c1ccccc1</chem>	3
2-Ethyltoluene	<chem>Cc1ccccc1CC</chem>	4
3-Ethyltoluene	<chem>Cc1cc(CC)ccc1</chem>	4
4-Ethyltoluene	<chem>Cc1ccc(CC)cc1</chem>	2
1,2,3-Trimethylbenzene	<chem>Cc1c(C)c(C)ccc1</chem>	2
1,2,4-Trimethylbenzene	<chem>Cc1c(C)cc(C)cc1</chem>	3
1,3,5-Trimethylbenzene	<chem>Cc1cc(C)cc(C)c1</chem>	1

These counts follow from the equivalence of ring positions under molecular symmetry. In particular, the ethyl and methyl groups are different, so a symmetry operation cannot interchange them.

The observation of two ring-monobromination products leaves **4-ethyltoluene** and **1,2,3-trimethylbenzene**.

For 1,2,3-trimethylbenzene, the available ring positions are 4, 5, and 6, with 4 and 6 equivalent. Introducing two bromines therefore gives only two arrangements:

$$\{4, 5\} \equiv \{5, 6\}, \quad \{4, 6\}.$$

It cannot account for four ring-dibromination products.

For 4-ethyltoluene, the four available positions give four distinct dibromo arrangements, as demonstrated below. Hence

$$X = 4\text{-ethyltoluene.}$$

Bromination in light.

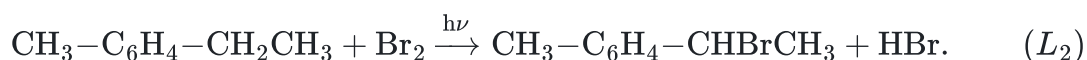
Under the selective benzylic bromination assumed in the problem, light promotes radical substitution at a carbon directly attached to the aromatic ring. X has two different benzylic sites:

- the carbon of its methyl group;
- the methylene carbon of its ethyl group.

The two balanced reactions are



and



The two side chains remain **para** to one another in both equations.

Here molecular bromine is BrBr , and hydrogen bromide is HBr .

In L_2 , the carbon bearing bromine has four different substituents and is stereogenic. Bromination under achiral conditions gives equal amounts of its two enantiomers, whose SMILES appear in the answer table. They constitute **one constitutional product**, so the light reaction gives two constitutional monobromo derivatives overall.

The approximately equal yields of L_1 and L_2 are supplied experimental information; their ratio cannot be calculated from symmetry alone.

Monobromination in the dark with iron.

With iron, $[\text{Fe}]$, bromination in the dark proceeds by electrophilic aromatic substitution.

Numbering the ring with methyl at C1 and ethyl at C4, reflection through these two positions gives

$$2 \longleftrightarrow 6, \quad 3 \longleftrightarrow 5.$$

Consequently, bromination at C2 or C6 gives M_2 , whereas bromination at C3 or C5 gives M_3 .

The following balanced equation applies separately to each product, with the bromine at the position specified in the answer table:



Further bromination: the four dibromo derivatives.

Two ring hydrogens must now be replaced among positions 2, 3, 5, 6. There are initially

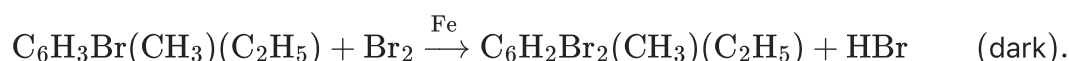
$$\binom{4}{2} = 6$$

pairs, but reflection makes two pairs of arrangements equivalent:

Distinct product	Equivalent choices of brominated positions
D_{23}	$\{2, 3\} \equiv \{5, 6\}$
D_{25}	$\{2, 5\} \equiv \{3, 6\}$
D_{26}	$\{2, 6\}$
D_{35}	$\{3, 5\}$

Thus there are exactly **four constitutional ring-dibromination products**.

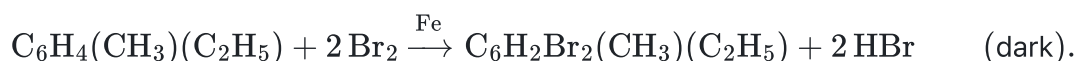
Each further substitution obeys



The possible pathways are:

- From M_2 , substitution at C3, C5, or C6 gives D_{23} , D_{25} , or D_{26} , respectively.
- From M_3 , substitution at C2, C5, or C6 gives D_{23} , D_{35} , or D_{25} , respectively.

The balanced overall reaction, applying separately to each of the four dibromo isomers, is



The solution was checked against the official solution.

Problem 6: Identification of a metal M dissolved in dilute nitric acid

130 g of an unknown metal M were treated with excess of a dilute nitric acid. Excess hot alkaline solution was added to the resulting solution and 1.12 dm³ of a gas evolved (normal conditions).

What metal M was dissolved in the nitric solution?

Official English text of the problem.

Answers

- **Problem 6:** The printed data do **not permit a unique identification**. Zinc, Zn, is a **plausible intended answer** if "130 g" should read "13.0 g," or if "1.12 dm³" should read "11.2 dm³," under the usual assumption that ammonium is the sole nitrate reduction product.

Solution

The expected gas is **ammonia**, NH₃, SMILES N. During dissolution, the metal can reduce nitric acid, HNO₃, SMILES O=[N+]([O-])O, to **ammonium ions**, NH₄⁺, SMILES [NH4+]. Hot alkali then liberates ammonia:



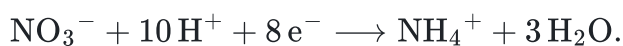
Here OH[−] is the hydroxide ion, SMILES [OH-], and H₂O is water, SMILES o.

Using the standard molar gas volume at normal conditions,

$$n(\text{NH}_3) = \frac{1.12 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.0500 \text{ mol}.$$

Thus the solution contained 0.0500 mol of ammonium ions.

Reduction of nitrate to ammonium requires eight electrons per nitrogen atom:



The nitrate ion has SMILES [O-][N+](=O)[O-]; the hydrogen ion has SMILES [H+].

If ammonium is the only nitrate reduction product, the metal supplied

$$n(\text{e}^-) = 8(0.0500) = 0.400 \text{ mol}.$$

Let z be the metal's oxidation state in the resulting solution and M_{m} its molar mass. Then

$$z \frac{130 \text{ g}}{M_{\text{m}}} = 0.400 \text{ mol},$$

so

$$\boxed{M_{\text{m}} = 325z \text{ g mol}^{-1}}.$$

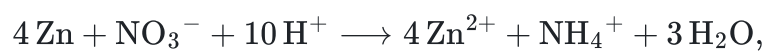
Even $z = 1$ requires a molar mass of 325 g mol^{-1} ; $z = 2$ requires 650 g mol^{-1} . **No known metal fits this result.**

If other nitrate reduction products formed during dissolution, the measured ammonia accounts for only part of the electrons transferred. Their unreported amounts then prevent determination of the metal's molar mass.

For the plausible correction **13.0 g**, the calculation instead gives

$$M_{\text{m}} = 32.5z \text{ g mol}^{-1}.$$

Taking $z = 2$ gives 65.0 g mol^{-1} , identifying **zinc**. Its balanced dissolution equation, written ionically, is



where the zinc(II) ion has SMILES [zn+2]. Consequently,

$$n(\text{NH}_3) = \frac{1}{4} n(\text{Zn}) = \frac{1}{4} \frac{13.0 \text{ g}}{65.0 \text{ g mol}^{-1}} = 0.0500 \text{ mol},$$

which gives the stated 1.12 dm^3 . With **130 g** of zinc, the same model predicts **11.2 dm³**.

The solution was checked against the official solution.