11th

ICHO

International Chemistry Olympiad

6 theoretical problems
2 practical problems

THE ELEVENTH
INTERNATIONAL CHEMISTRY OLYMPIAD

LENINGRAD 1979
SOVIET UNION

THEORETICAL PROBLEMS

PROBLEM 1

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 C_3H_5Br?
   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 C_3H_9N 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.

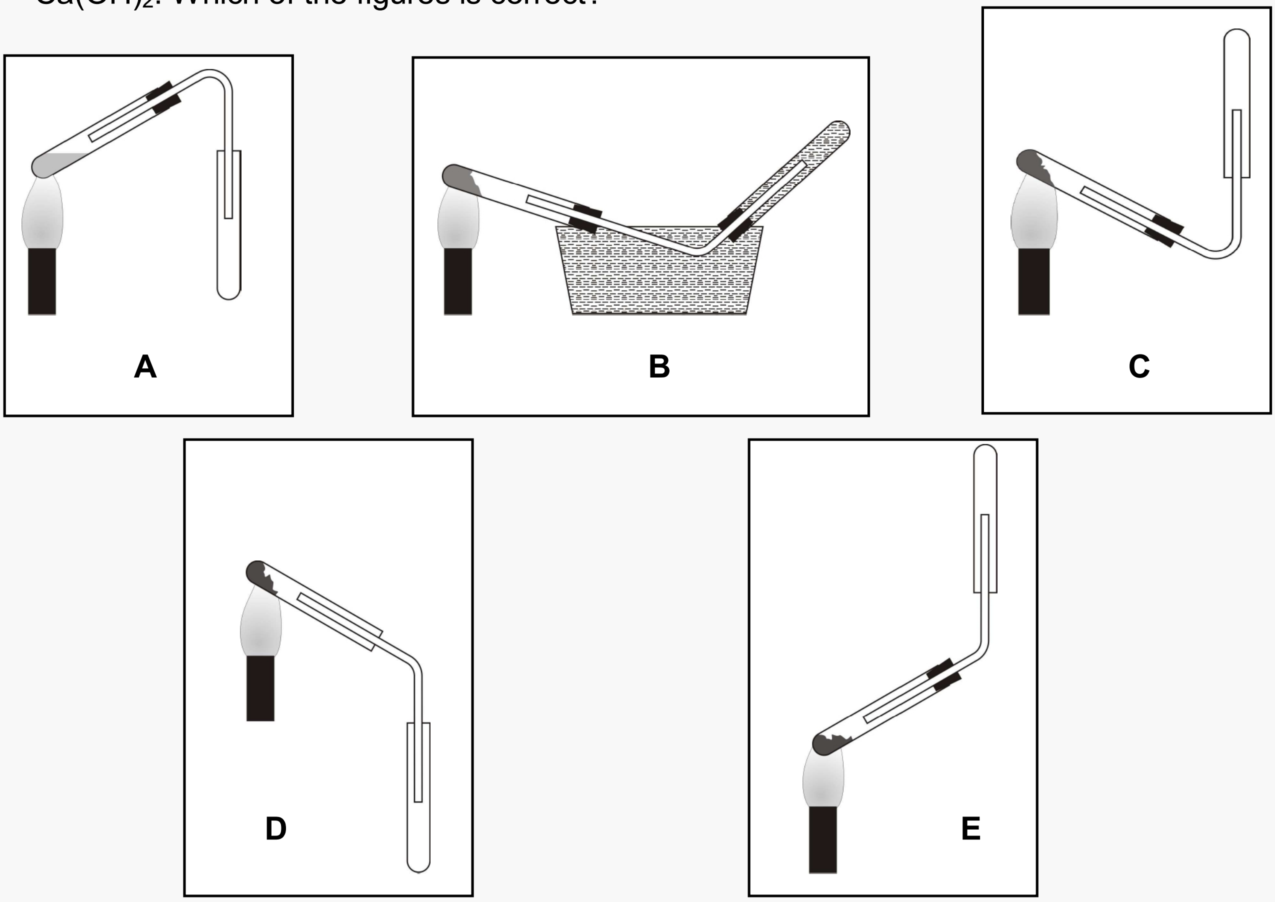
17. Which of the following changes have no effect on the chemical equilibrium in the thermal decomposition of $CaCO_3$?

    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.

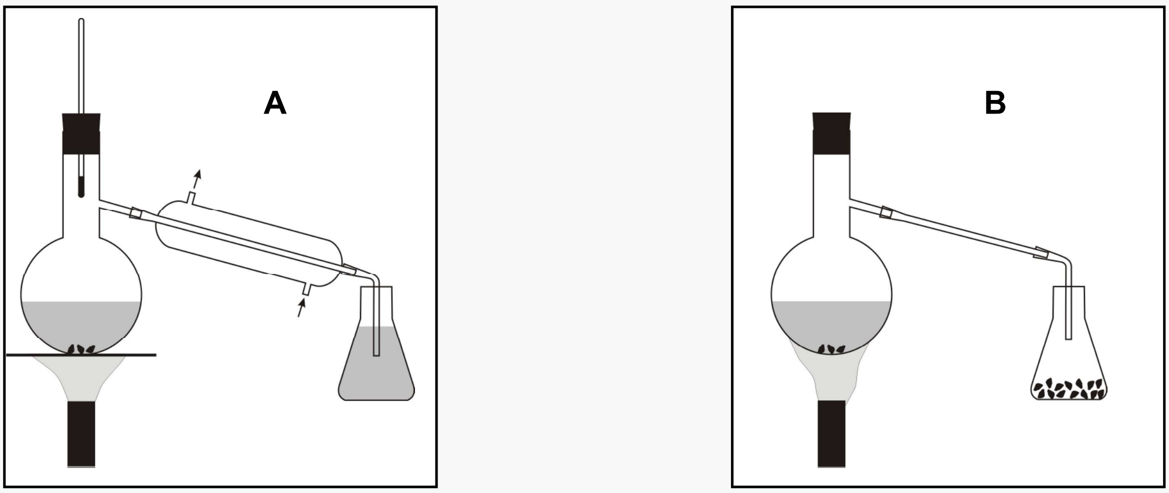
18. Which of the substances given bellow will be formed at the Pt-anode in the electrolysis of an aqueous solution of aluminium chloride?

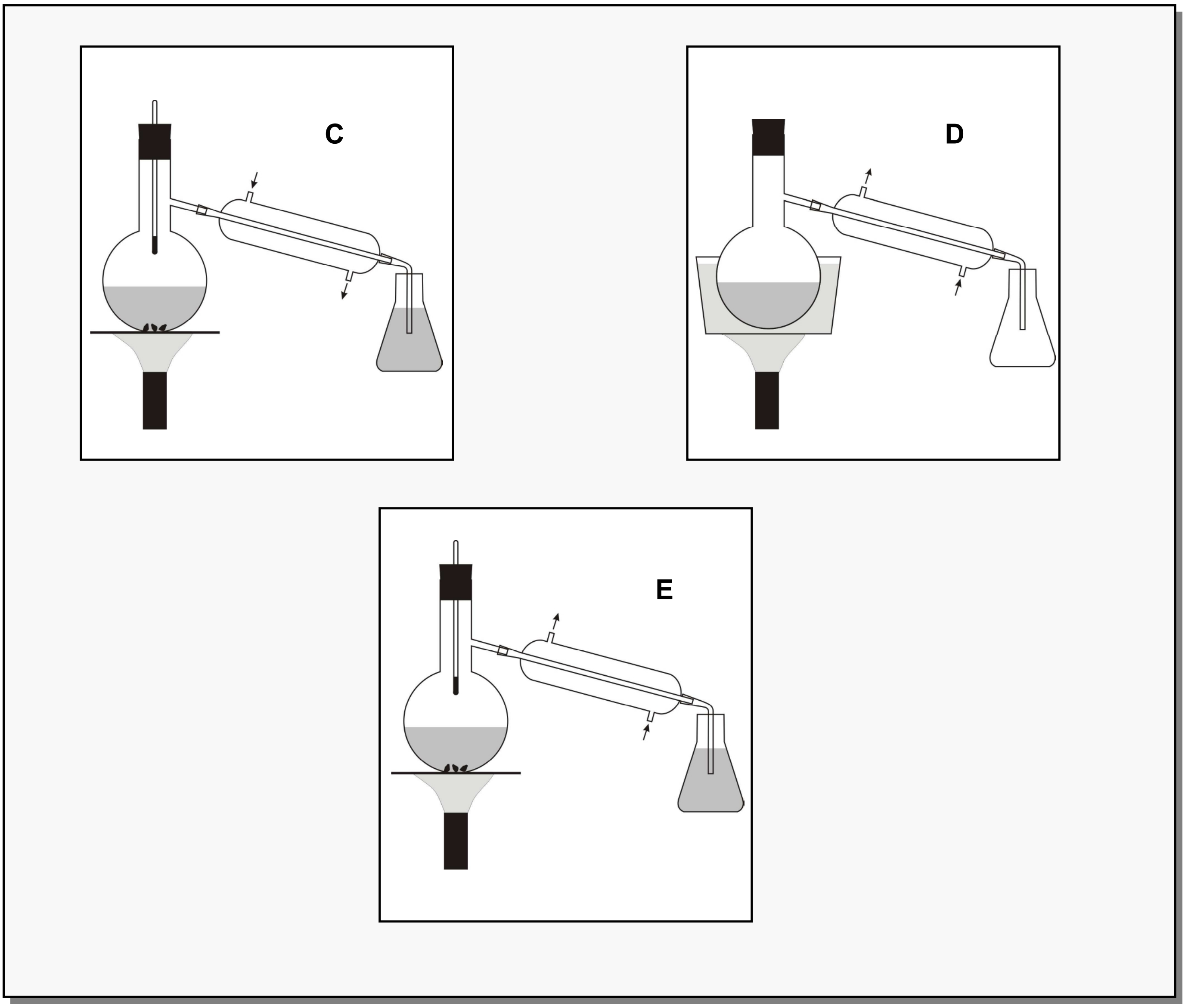
    A) aluminium, B) oxygen, C) hydrogen, D) aluminium hydroxide, E) chlorine.

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 $Ca(OH)_2$. 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?





SOLUTION

1 –	A	6 –	D and E	11 –	D	16 –	E
2 –	C	7 –	D	12 –	B	17 –	C and E
3 –	A	8 –	D	13 –	D	18 –	B and E
4 –	E	9 –	D	14 –	A and E	19 –	C
5 –	E	10 –	C	15 –	D	20 –	A

PROBLEM 2

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 HNO_3 was added to the alkaline solution to reach pH 5 – 6, and an excess of K_2CrO_4 solution was added to the resulting transparent solution. The yellow precipitate was separated, washed and quantitatively transferred to a beaker. Finally a dilute H_2SO_4 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 cm^3 of 0.1512 normal $Na_2S_2O_3$ 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.

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.

SOLUTION

1. The action of nitric acid on the alloy:

$$Sn + 4\,HNO_3 \rightarrow H_2SnO_3 + 4\,NO_2 + H_2O$$

$$Pb + 4\,HNO_3 \rightarrow Pb(NO_3)_2 + 2\,NO_2 + 2\,H_2O$$

$$Bi + 6\,HNO_3 \rightarrow Bi(NO_3)_3 + 3\,NO_2 + 3\,H_2O$$

$$Cd + 4\,HNO_3 \rightarrow Cd(NO_3)_2 + 2\,NO_2 + 2\,H_2O$$

Weight form of tin determination:

$H_2SnO_3 \rightarrow SnO_2 + H_2O$

Calculation of tin content in the alloy:

M(Sn) = 118.7 g mol^{-1}; M(SnO$_2$) = 150.7 g mol^{-1}

$$\frac{m(\text{Sn})}{m(\text{SnO}_2)} = \frac{M(\text{Sn})}{M(\text{SnO}_2)}; \quad m(\text{Sn}) = \frac{118.7 \text{ g mol}^{-1} \times 0.3265 \text{ g}}{150.7 \text{ g mol}^{-1}} = 0.2571 \text{ g}$$

Mass percentage of tin (metal A) in the alloy:

$$w(\text{Sn}) = \frac{0.2571 \text{ g}}{1.2860 \text{ g}} = 0.1999 = 19.99 \text{ \%}$$

1. The reactions taking place in the excess of aqueous ammonia solution:

$Pb(NO_3)_2 + 2\ NH_4OH \rightarrow Pb(OH)_2\downarrow + 2\ NH_4NO_3$

$Bi(NO_3)_3 + 3\ NH_4OH \rightarrow Bi(OH)_3\downarrow + 3\ NH_4NO_3$

$Cd(NO_3)_2 + 4\ NH_4OH \rightarrow [Cd(NH_3)_4](NO_3)_2 + 4\ H_2O$
solution

Saturating of the solution with hydrogen sulphide:

$[Cd(NH_3)_4](NO_3)_2 + 2\ H_2S \rightarrow CdS\downarrow + 2\ NH_4NO_3 + (NH_4)_2S$

3. Calculation of the cadmium content in the alloy:

M(Cd) = 112.4 g mol^{-1}; M(CdS) = 144.5 g mol^{-1}

$$m(\text{Cd}) = \frac{112.4 \text{ g mol}^{-1} \times 0.6613 \text{ g}}{144.5 \text{ g mol}^{-1}} = 0.5143 \text{ g}$$

Mass percentage of cadmium (metal B) in the alloy:

$$w(\text{Cd}) = \frac{0.5143 \text{ g}}{1.2860 \text{ g}} = 0.3999 = 39.99 \text{ \%}$$

4. The reactions taking place in the excess of sodium hydroxide solution:

The action of excess sodium hydroxide on lead(II) and bismuth(III) hydroxides:

$Pb(OH)_2 + 2\ NaOH \rightarrow Na_2[Pb(OH)_4]$
solution

$Bi(OH)_3 + NaOH \rightarrow$ no reaction

Acidification of the solution with nitric acid (pH = 5 – 6):

$Na_2[Pb(OH)_4] + 4\ HNO_3 \rightarrow Pb(NO_3)_2 + 2\ NaNO_3 + 4\ H_2O$

The reaction with K_2CrO_4:

$Pb(NO_3)_2 + K_2CrO_4 \rightarrow PbCrO_4\downarrow + 2\,KNO_3$

The reactions on which the quantitative determination of lead in $PbCrO_4$ precipitate is based:

$2\,PbCrO_4 + 6\,KI + 8\,H_2SO_4 \rightarrow 3\,I_2 + 2\,PbSO_4 + 3\,K_2SO_4 + Cr_2(SO_4)_3 + 8\,H_2O$

$I_2 + 2\,Na_2S_2O_3 \rightarrow 2\,NaI + Na_2S_4O_6$

Percentage of lead (metal C) in the alloy:

$$w(\text{Pb}) = \frac{c(\text{Na}_2\text{S}_2\text{O}_3) \times V(\text{Na}_2\text{S}_2\text{O}_3) \times M(\text{Pb})}{m(\text{alloy}) \times 3}$$

(One Pb^{2+} ion corresponds to one CrO_4^{2-} ion which accepts 3 electrons in the redox reaction considered.)

$$w(\text{Pb}) = \frac{0.1512 \text{ mol dm}^{-3} \times 0.01846 \text{ dm}^3 \times 207.2 \text{ g mol}^{-1}}{1.286 \text{ g} \times 3} = 0.1499 = 14.99\ \%$$

5. In order to convert bismuth(III) hydroxide to phosphate it is necessary:

a) to dissolve the bismuth(III) hydroxide in an acid:

$Bi(OH)_3 + 3\,HNO_3 \rightarrow Bi(NO_3)_3 + 3\,H_2O$

b) to precipitate Bi^{3+} ions with phosphate ions:

$Bi(NO_3)_3 + K_3PO_4 \rightarrow BiPO_4\downarrow + 3\,KNO_3$

Calculation of the bismuth content in the alloy:

$M(\text{Bi}) = 209 \text{ g mol}^{-1}$; $M(\text{BiPO}_4) = 304 \text{ g mol}^{-1}$

$$m(\text{Bi}) = \frac{209 \text{ g mol}^{-1} \times 0.4676 \text{ g}}{304 \text{ g mol}^{-1}} = 0.3215 \text{ g}$$

Percentage of bismuth (metal D) in the alloy:

$$w(\text{Bi}) = \frac{0.3215 \text{ g}}{1.2860 \text{ g}} = 0.2500 = 25.00\ \%$$

Composition of the alloy: % Cd = 40, % Sn = 20, % Pb = 15, % Bi = 25

PROBLEM 3

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.

SOLUTION

(a) a-1 $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$

a-2 $NH_4^+ + OH^- \rightarrow NH_3.H_2O \rightarrow NH_3\uparrow + H_2O$

a-3 $Al^{3+} + 3\ OH^- \rightarrow Al(OH)_3\downarrow$

a-4 $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$

a-5 possibly: $Ba^{2+} + 2\ [Al(OH)_4]^- \rightarrow Ba[Al(OH)_4]_2\downarrow$

(b) b-1 $2\ CrO_4^{2-} + 2\ H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

b-2 $6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \rightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$

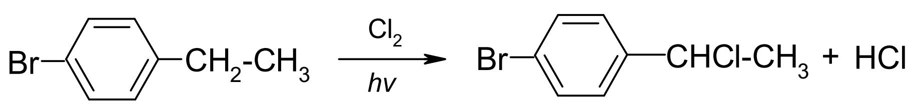
b-3 with high concentrations of Cl^- and H_2SO_4:

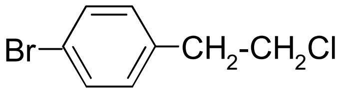
$Cr_2O_7^{2-} + 4\ Cl^- + 6\ H^+ \rightarrow CrO_2Cl_2 + 3\ H_2O$

(c) c-1 with excess of H^+: $CO_3^{2-} + 2\ H^+ \rightarrow H_2O.CO_2 \rightarrow H_2O + CO_2\uparrow$

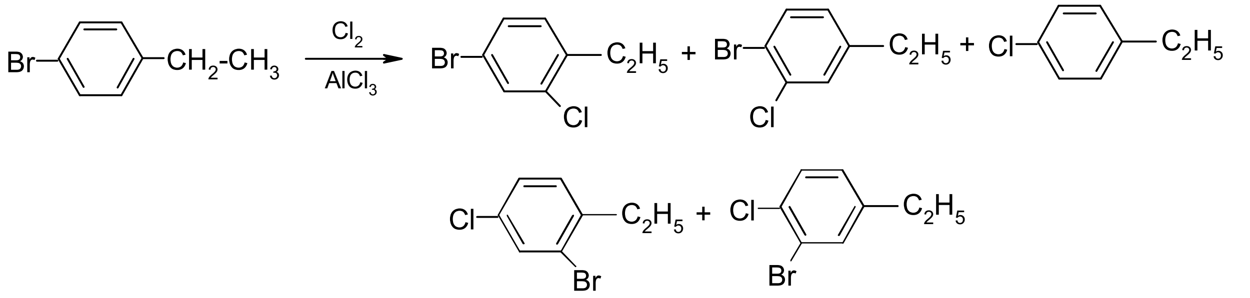
c-2 with excwss of CO_3^{2-}: $CO_3^{2-} + H^+ \rightarrow HCO_3^-$

(d) d-1 free radical substitution (upon exposure to light or on heating)



small quantity of  and polychlorination

d-2 in the presence of electrophilic substitution catalysts:
and as side reaction products:



(e) e-1

$$CH_3CH_2CH_2OH + H_2SO_4 \xrightarrow[\text{heat}]{-\,H_2O} C_3H_7OSO_3H + H_2O \longrightarrow (C_3H_7O)_2SO_2 + H_2O$$

e-2

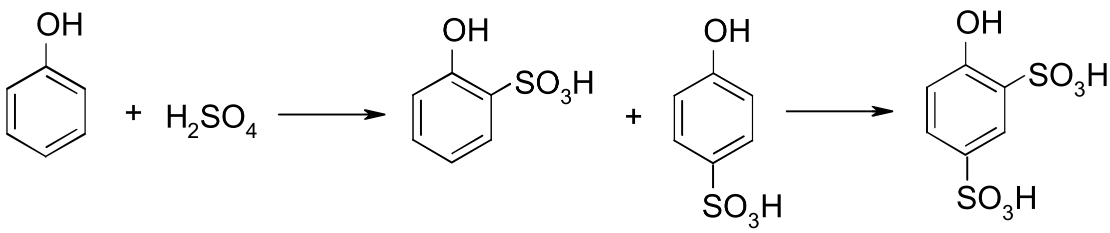
$$2\ C_3H_7OH + H_2SO_4 \xrightarrow[\text{heat}]{} C_3H_7OC_3H_7\ \text{(excess of } C_3H_7OH\text{)} + H_2O$$

e-3

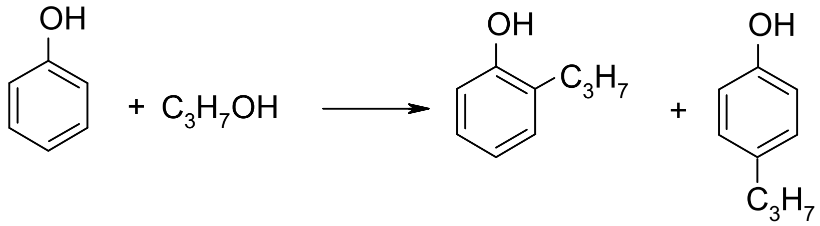
$$3\ CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{H_2SO_4} CH_3CH{=}CH_2 \xrightarrow[H_2SO_4]{.H_2O} CH_3CH(OH)CH_3$$

(in e-1 and e-2)

e-4



e-5



polyalkylation n- and iso-

e-6 partial oxidation of C_3H_7OH and C_6H_5OH with subsequent condensation or esterification

PROBLEM 4

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 dm^3 and has a density of 0.786 g dm^{-3}. Determine the formula of compound **X**.

SOLUTION

If the density of the mixture of N_2 and H_2 is known, its composition can be determined as

$$0.786 \times 22.4 \times (n + 1) = 28\,n + 2$$

Hence n = 1.5. The mass of the mixture is 0.786 g $dm^{-3} \times 1.4 \approx 1.1$ g. Consequently, the mixture of gases absorbed by sulphuric acid (these gases could be NH_3 and N_2H_4) had an average molar mass of

$$\frac{3.2\text{ g} - 1.1\text{ g}}{1.4\text{ dm}^3 \times (2.8 - 1)} \times 22.4\text{ dm}^3\text{ mol}^{-1} \cong 18.67\text{ g mol}^{-1}$$

while NH_3 corresponds to 17 g mol^{-1}.

This means that the absorbed gaseous products consist of a mixture of NH_3 and N_2H_4. The composition of the absorbed fraction is

$$\frac{32 + 17\,n}{n + 1} = 18.67$$

n = 8, i. e. 8 NH_3 + N_2H_4.

As a result, the overall ratio of the components of the mixture is as follows:

8 NH_3 + N_2H_4 + 3 N_2 + 2 H_2 which corresponds to a composition of the initial substance X: N : H = (2 + 8 + 6) : (4 + 24 + 4) = 1 : 2.

The initial substance X is hydrazine N_2H_4.

PROBLEM 5

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.

SOLUTION

The compound with the empirical formula C_9H_{12} can be:

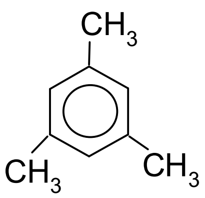
$C_6H_5 - C_3H_7$ I

$C_6H_4(CH_3)(C_2H_5)$ II

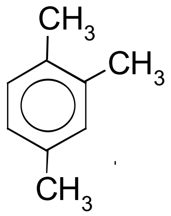
$C_6H_3(CH_3)_3$ III

Under the action of bromine in the light without catalysts, bromination of the aliphatic portion will occur, predominantly on the carbon atoms bonded to the aromatic nucleus. When the reaction is conducted in the dark in presence of iron, the latter is converted to $FeBr_3$ and catalyzes the bromination of the aromatic ring.

Compound **X** cannot be **I** (as then only one monobromo derivative would be formed in the light); it cannot be one of the isomers IIIa, IIIb either.

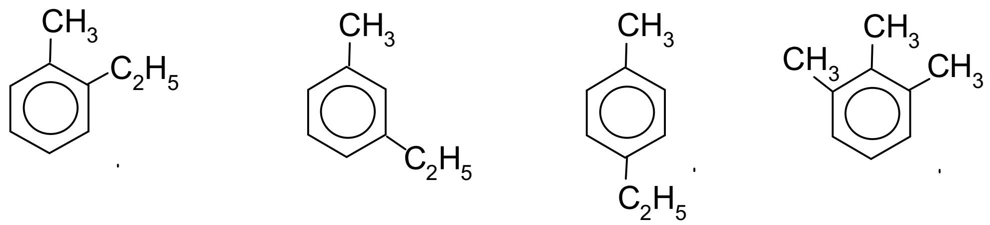


IIIa - Only one monobromo derivative is possible in the bromination of the CH_3 groups.



IIIb - Three different monobromo derivatives are possible under the same conditions.

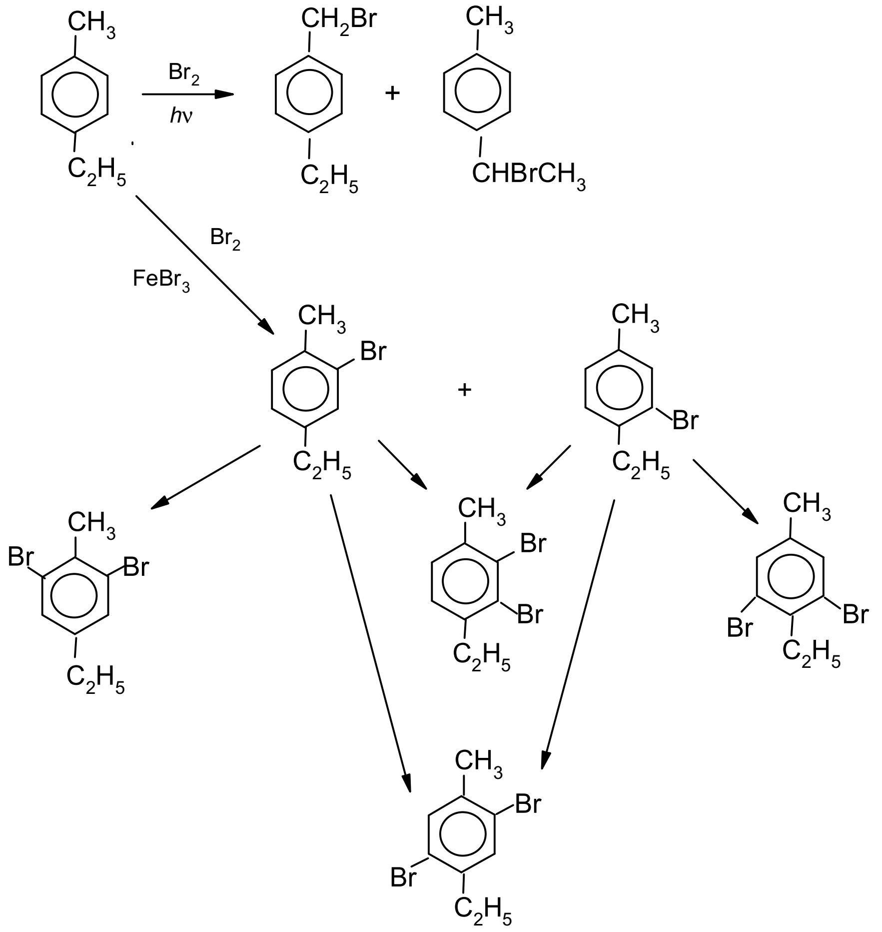
Thus, selection must be made from the following four structures:



IIa IIb IIc IIIc

The condition that two monobromo derivatives can be formed in the dark, rules out structures IIa and IIb. The condition of the possibility of four dibromo derivatives rules out structure IIIc. Hence, the only possible structure of compound **X** is IIc.

The scheme of the bromination reaction (next page):


CH3
Br2
hν
CH2Br
+
CH3
C2H5
C2H5
CHBrCH3
Br2
FeBr3
CH3
Br
+
CH3
Br
C2H5
C2H5
CH3
Br
Br
C2H5
CH3
Br
Br
C2H5
CH3
Br
Br
C2H5
CH3
Br
Br
C2H5

PROBLEM 6

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 dm^3 of a gas evolved (normal conditions).

What metal M was dissolved in the nitric solution?

SOLUTION

The gas that evolved during the reaction with the alkaline solution was ammonia. Therefore, one of the products resulting from dissolution of the metal M in the acid is ammonium nitrate. Thus, the reaction equations will have the form:

$$8\ M + 10\ n\ HNO_3 \rightarrow 8\ M(NO_3)_n + n\ NH_4NO_3 + 3\ n\ H_2O$$

$$n\ NH_4NO_3 + n\ NaOH \rightarrow n\ NH_3 + n\ H_2O + NaNO_3$$

Hence, the scheme:

x	⟶	1.12 dm^3
8 M		n NH_3
8 A_r(M)		n 22,4 dm^3

where n is the valency of the metal (oxidation number of M^{n+}) and A_r(M) is the relative atomic mass of the metal.

8 A_r(M) $\Rightarrow$ 22.4 × n

13 g $\Rightarrow$ 1.12 dm^3

$$A_r(M) = \frac{13\ g \times 22.4\ dm^3 \times n}{8\ g \times 1{,}12\ dm^3} = 32.5\ n$$

If	n = 1	then	A_r(M) = 32.5	no metal
	n = 2		A_r(M) = 65	zinc
	n = 3		A_r(M) = 97,5	none
	n = 4		A_r(M) = 130	none

Answer: The unknown metal is zinc.

PRACTICAL PROBLEMS

PROBLEM 1

10 numbered test tubes, 20 cm^3 each, contain 0.1 M solutions of the following substances: barium chloride, sodium sulphate, potassium chloride, magnesium nitrate, sodium orthophosphate, barium hydroxide, lead nitrate, potassium hydroxide, aluminium sulphate, sodium carbonate. Using only these solutions as reagents, determine in which of the numbered test tubes each of the above given substances, is found.

Draw up a plan of the analysis and write equations of the reactions to be carried out. Do not forget to leave at least 2 cm^3 of the solutions in each test tube for checking. If in the course of the analysis an additional quantity of a solution is needed, you may ask the teacher to give it to you but in such case you will lose some points.

SOLUTION

Table:

	$BaCl_2$	Na_2SO_4	KCl	$Mg(NO_3)_2$	Na_3PO_4	$Ba(OH)_2$	$Pb(NO_3)_2$	KOH	$Al_2(SO_4)_3$	Na_2CO_3
$BaCl_2$		↓	—	—	↓	—	↓	—	↓	↓
Na_2SO_4	↓		—	—	—	↓	↓	—	—	—
KCl	—	—		—	—	—	↓	—	—	—
$Mg(NO_3)_2$	—	—	—		↓	↓	—	↓	—	↓
Na_3PO_4	↓	—	—	↓		↓	↓	—	↓	—
$Ba(OH)_2$	—	↓	—	↓	↓		↓	—	↓	↓
$Pb(NO_3)_2$	↓	↓	↓	—	↓	↓		↓	↓	↓
KOH	—	—	—	↓	—	—	↓		↓	—
$Al_2(SO_4)_3$	↓	—	—	—	↓	↓	↓	↓		↓
Na_2CO_3	↓	—	—	↓	—	↓	↓	—	↓	

Using the table, the entire problem cannot be solved at once: all the precipitates are white and there are substances that form the same number of precipitates. From the number of precipitates only KCl (1), $Mg(NO_3)_2$ (4), and $Pb(NO_3)_2$ (8) can be determined immediately.

Furthermore, Na_2SO_4 and KOH (giving three precipitates each) can be differentiated via the reaction with $Mg(NO_3)_2$ ($Mg(OH)_2$).

$Ba(OH)_2$ and $Al_2(SO_4)_3$ (giving 6 precipitates each): through the reaction with KOH ($Al(OH)_3$).

$BaCl_2$, Na_3PO_4 and Na_2CO_3 (giving 5 precipitates each): first the reaction with Na_2SO_4 indicates $BaCl_2$. Then the reaction with $BaCl_2$: $Al_2(SO_4)_3$ yields $AlCl_3$ ($BaSO_4$ precipitate is flittered off). Evolution of CO_2 and formation of $Al(OH)_3$ in the reaction with $AlCl_3$ solution indicates Na_2CO_3.

PROBLEM 2

Determine the mass of potassium permanganate in the solution you are given. You are provided with hydrochloric acid of a given concentration, a potassium hydroxide solution of an unknown concentration, an oxalic acid solution of an unknown concentration, and a sulphuric acid solution (2 N).

Equipment and reagents:

A burette for titration, indicators (methyl orange, lithmus, phenolphthalein), pipettes (volumes 10, and 15 or 20 cm^3), 2 volumetric flasks (250 cm^3), 2 titration flasks (100 – 150 cm^3).