11th

International Chemistry Olympiad

6 theoretical problems
2 practical problems

THE ELEVENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
2–11 JULY 1979, LENINGRAD, 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.

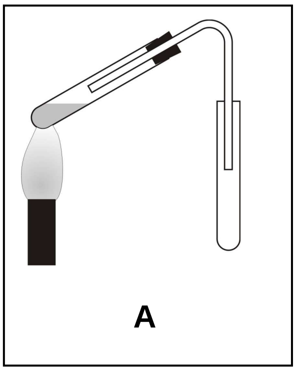
17. Which of the following changes have no effect on the chemical equilibrium in the thermal decomposition of $CaCO_3$?

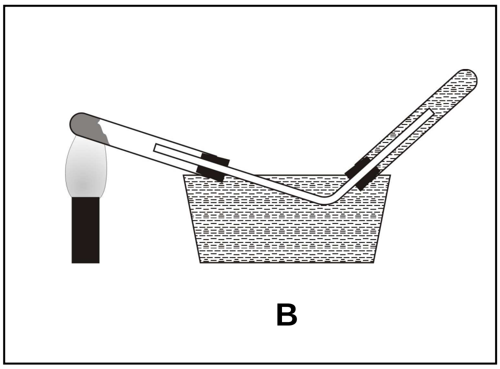
    A) temperature elevation, B) pressure decrease, C) addition of catalyst, D) a change in the CO_2 concentration, E) an increase in the amount of the initial substance.

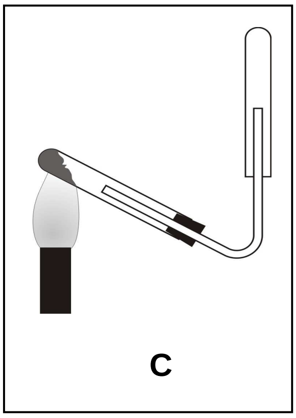
18. Which of the substances given bellow will be formed at the Pt-anode in the electrolysis of an aqueous solution of aluminium chloride?

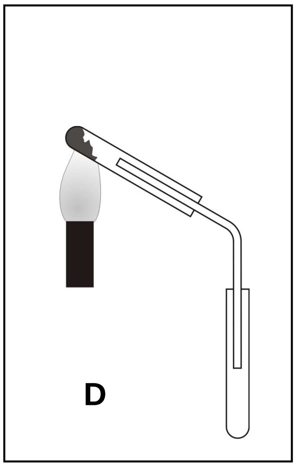
    A) aluminium, B) oxygen, C) hydrogen, D) aluminium hydroxide, E) chlorine.

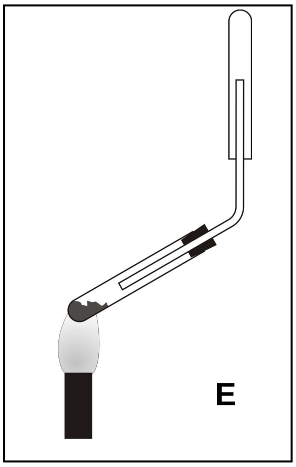
19. The apparatus shown in the figures is intended for preparing ammonia under laboratory conditions. The test tube being heated contains a mixture of NH_4Cl and $Ca(OH)_2$. Which of the figures is correct?



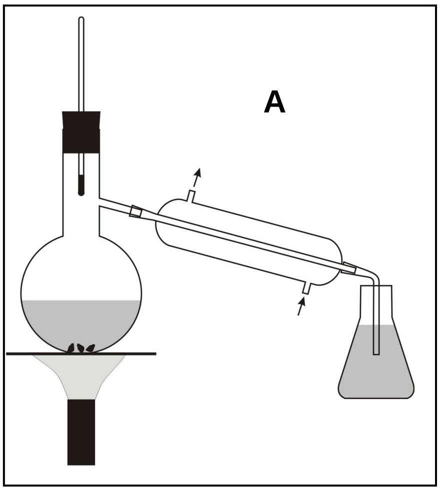


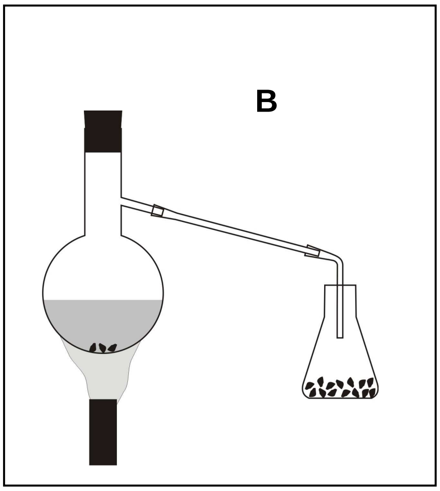


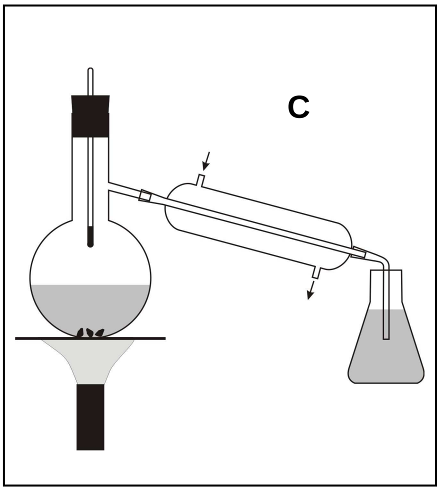


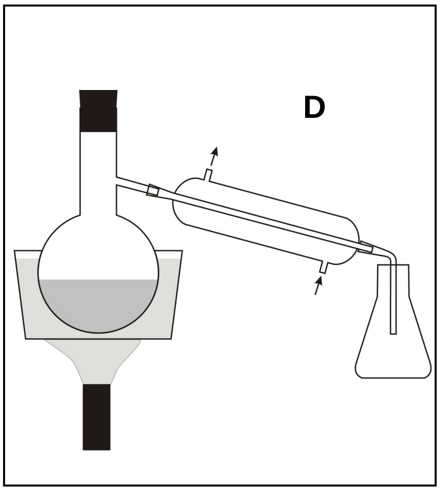


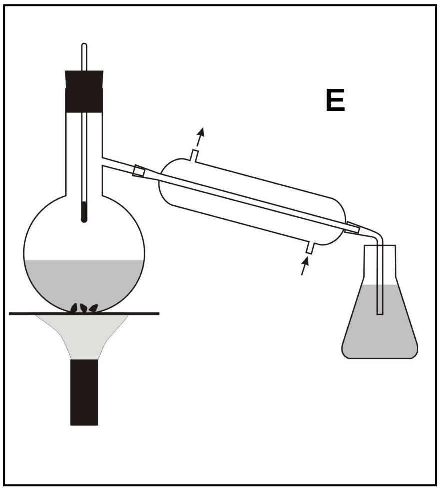
20. Which of the apparatuses shown in the figures is the best one for the synthesis of bromethane from potassium bromide, concentrated sulphuric acid and ethanol?











SOLUTION

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

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.

SOLUTION

2.1 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:

$M(Sn) = 118.7\ g\ mol^{-1}$; $M(SnO_2) = 150.7\ g\ mol^{-1}$

$$\frac{m(Sn)}{m(SnO_2)} = \frac{M(Sn)}{M(SnO_2)}; \qquad m(Sn) = \frac{118.7\ g\ mol^{-1} \times 0.3265\ g}{150.7\ g\ mol^{-1}} = 0.2571\ g$$

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

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

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

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

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

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

Saturating of the solution with hydrogen sulphide:

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

Calculation of the cadmium content in the alloy:

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

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

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

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

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

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

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

$Bi(OH)_3 + NaOH \rightarrow$ 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:

$$w(\mathrm{Pb}) = \frac{c(\mathrm{Na_2S_2O_3}) \times V(\mathrm{Na_2S_2O_3}) \times M(\mathrm{Pb})}{m(\mathrm{alloy}) \times 3}$$

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

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

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:

$M(\mathrm{Bi}) = 209\ \mathrm{g\ mol^{-1}}$; $M(\mathrm{BiPO_4}) = 304\ \mathrm{g\ mol^{-1}}$

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

Percentage of bismuth (metal D) in the alloy:

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

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

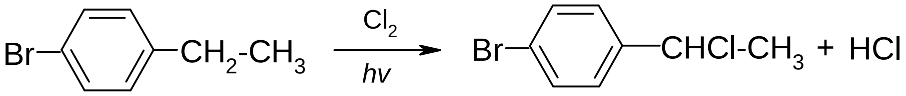
b-3 with high concentrations of Cl^- and H_2SO_4:

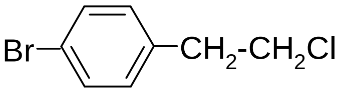
$Cr_2O_7^{2-} + 4\ Cl^- + 6\ H^+ \rightarrow CrO_2Cl_2 + 3\ H_2O$

(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-}: $CO_3^{2-} + H^+ \rightarrow HCO_3^-$

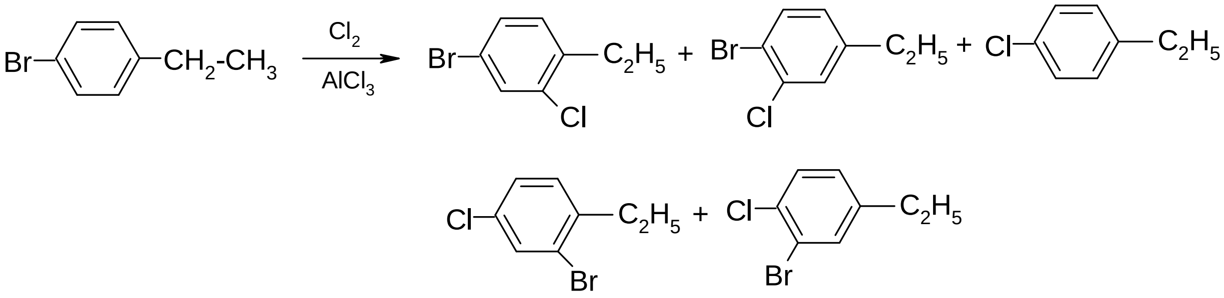
(d) d-1 free radical substitution (upon exposure to light or on heating)



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

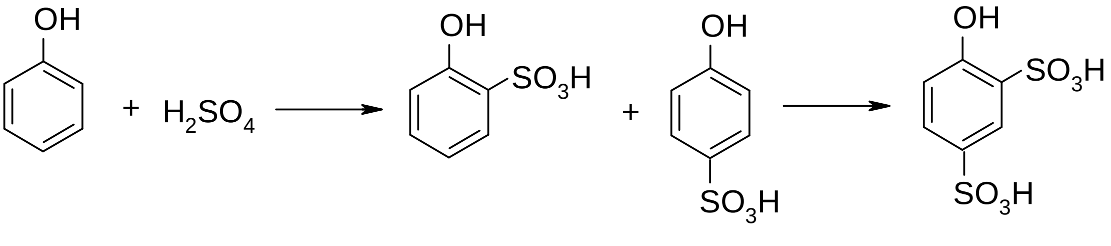
$$2\ C_3H_7OH + H_2SO_4 \xrightarrow[\text{heat}]{} C_3H_7OC_3H_7\ \text{(excess of } C_3H_7OH\text{)} + H_2O$$

e-3

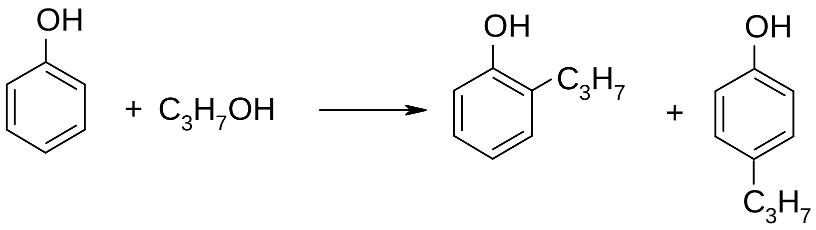
$$3\ CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{H_2SO_4} CH_3CH=CH_2 \xrightarrow[H_2SO_4]{.H_2O} CH_3CH(OH)CH_3$$

(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

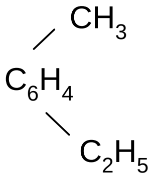
Benzene derivative **X** has the empirical formula C_9H_{12}. Its bromination in the light leads to the formation of two monobromo derivatives in approximately identical yield. Bromination in the dark in the presence of iron also gives two monobromo derivatives. If the reaction is carried out to a higher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

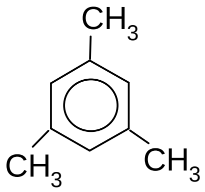


$C_6H_4(CH_3)(C_2H_5)$ II

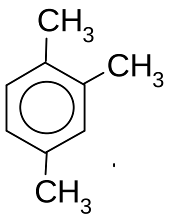
$C_6H_3(CH_3)_3$ III

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.

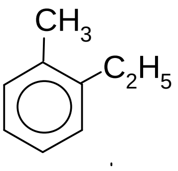


IIIa - Only one monobromo derivative is possible in the bromination of the CH_3 groups.

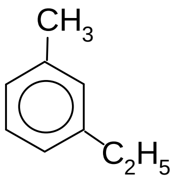


IIIb - Three different monobromo derivatives are possible under the same conditions.

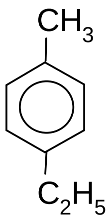
Thus, selection must be made from the following four structures:



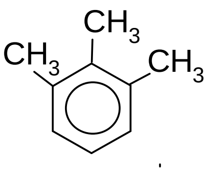
IIa



IIb



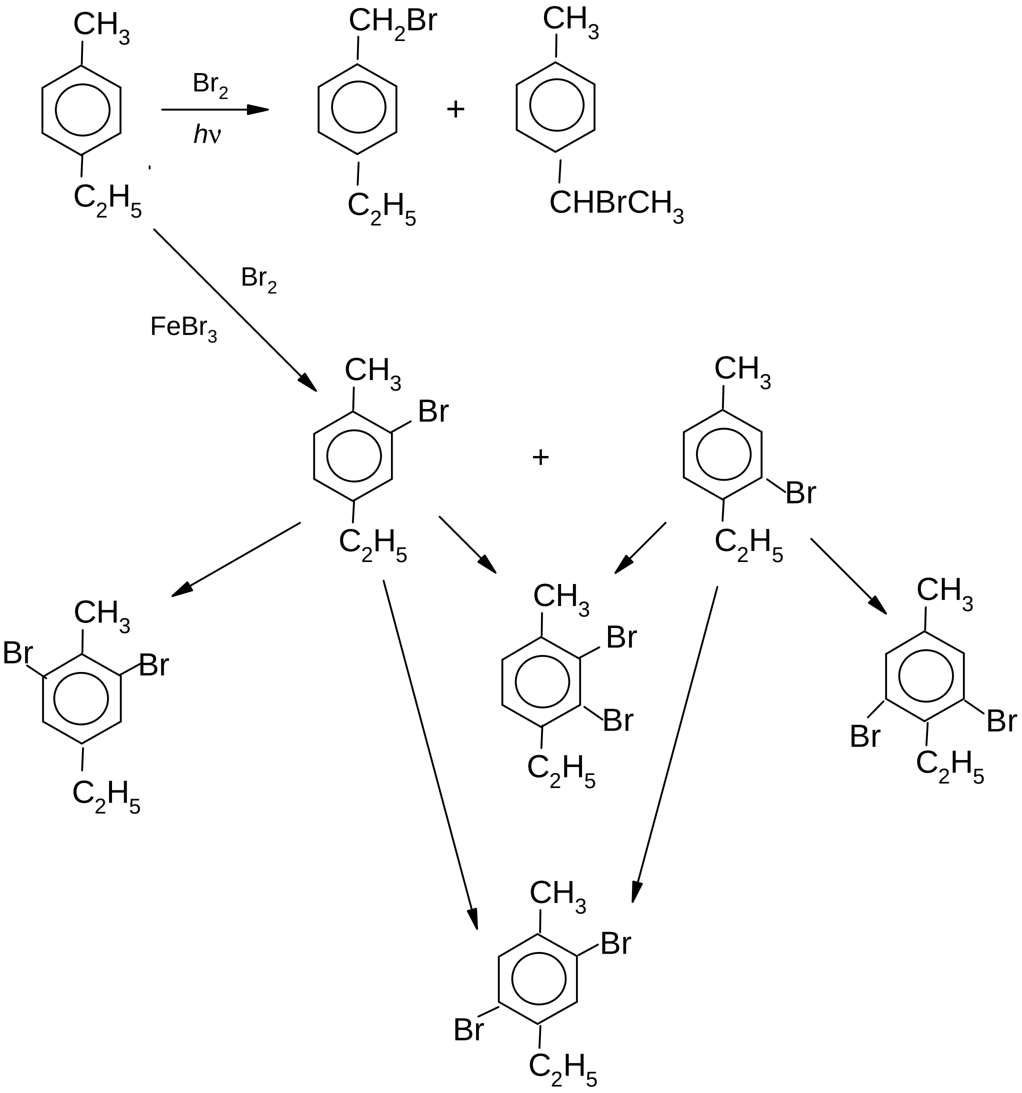
IIc



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

$$\begin{array}{lcl} x & & 1.12\ dm^3 \\ 8\ M & \longrightarrow & n\ NH_3 \\ 8\ A_r(M) & & n\ 22{,}4\ dm^3 \end{array}$$

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.

$8\ A_r(M) \quad \Rightarrow \quad 22.4 \times n$

$13\ g \quad \Rightarrow \quad 1.12\ dm^3$

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

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 (practical)

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 (practical)

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).

12th

6 theoretical problems
3 practical problems

THE TWELFTH
INTERNATIONAL CHEMISTRY OLYMPIAD
13–23 JULY 1980, LINZ, AUSTRIA

THEORETICAL PROBLEMS

PROBLEM 1

The dissociation of (molecular) chlorine is an endothermic process, ΔH = 243.6 kJ mol^{-1}. The dissociation can also be attained by the effect of light.

1.1 At what wavelength can the dissociating effect of light be expected?

1.2 Can this effect also be obtained with light whose wavelength is smaller or larger than the calculated critical wavelength?

1.3 What is the energy of the photon with the critical wavelength?

When light that can effect the chlorine dissociation is incident on a mixture of gaseous chlorine and hydrogen, hydrogen chloride is formed. The mixture is irradiated with a mercury UV-lamp (λ = 253.6 nm). The lamp has a power input of 10 W. An amount of 2 % of the energy supplied is absorbed by the gas mixture (in a 10 litre vessel). Within 2.5 seconds of irradiation 65 millimoles of HCl are formed.

1.4 How large is the quantum yield (= the number of product molecules per absorbed photons)?

1.5 How can the value obtained be (qualitatively) explained? Describe the reaction mechanism.

SOLUTION

1.1 $\lambda_1 = \dfrac{c}{\nu_1}$ from $\Delta H = N_A\, h\, \nu_1$ it follows that

$$\lambda_1 = \frac{c\, N_A\, h}{\Delta H} = \frac{3\,.\,10^8 \times 6.02\,.\,10^{23} \times 6.6\,.\,10^{-34}}{2.436\,.\,10^5} = 4.91\,.\,10^{-7}\ \text{m} = 491\,\text{nm}$$

1.2 Short-wave light is effective, as its photons have a greater energy than required whereas the photons of longer-wavelength light are too poor in energy to affect the dissociation.

1.3 $E_1 = h\,\nu_1 = \dfrac{h\,c}{\lambda_1} = \dfrac{6.6\times10^{-34}\times3\,.\,10^{8}}{4.91\,.\,10^{-7}} = 4.03\,.\,10^{-19}$ J

1.4 The quantum yield $\text{Ø} = \dfrac{\text{the number of HCl molecules formed}}{\text{the number of absorbed photons}}$

$$\text{Ø} = \frac{n(\text{HCl})\times N_A}{\dfrac{E_{tot}}{\dfrac{h\,c}{\lambda_2}}} = \frac{6.5\times10^{-2}\ \times\ 6.02\times10^{23}}{\dfrac{0.2\times2.5}{\dfrac{6.6\times10^{-34}\ \times\ 3\times10^{8}}{2.536\times10^{-7}}}} = 6.1\times10^{4}$$

The energy input = 10 × 0.02 = 0.2 W

1.5 The observed quantum yield is based on a chain mechanism.

The start of reaction chain: $Cl_2 + h\nu \rightarrow 2\ Cl\bullet$

The propagation of the chain: $2\ Cl\bullet + H_2 \rightarrow HCl + 2\ H\bullet$

$H\bullet + Cl_2 \rightarrow HCl + Cl\bullet$

The chain termination mainly by: $2\ H\bullet \rightarrow H_2$

$2\ Cl\bullet \rightarrow Cl_2$

$H\bullet + Cl\bullet \rightarrow HCl$

PROBLEM 2

Water gas equilibrium

The homogeneous gas reaction

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$$

is termed the water gas reaction.

Problems:

2.1 Calculate the Gibbs reaction energy, ΔG^0_{1000}, for the water gas reaction at 1000 K from the reaction enthalpy: $\Delta H^0_{1000} = 35040 \text{ J mol}^{-1}$
and the reaction entropy: $\Delta S^0_{1000} = 32.11 \text{ J mol}^{-1} K^{-1}$.

2.2 What is the value of the equilibrium constant K_p of the water gas reaction at 1000 K?

2.3 What are the values of the equilibrium constants K_x and K_c (x: mole fraction, c: concentration in mol dm^{-3} at the same temperature (1000 K)? (Note: The gas behaves ideally.)

2.4 A mixture of gases containing 35 vol. % of H_2, 45 vol. % of CO and 20 vol. % of H_2O vapours is heated to 1000 K. What is the composition of the mixture after the establishment of the water gas equilibrium?

2.5 Calculate the reaction enthalpy value, ΔH^0_{1400}, at 1400 K from the reaction enthalpy value, ΔH^0_{1000}, and the values of the molar heat, c^0_p, (valid in the temperature range 1000 K to 1400 K)

$$\Delta H^0_{1000} = 35040 \text{ J mol}^{-1}$$

$$c^0_p(CO_2) = 42.31 + 10.09\times10^{-3}\ T\ \text{ J mol}^{-1}\text{ K}^{-1}$$

$$c^0_p(H_2) = 27.40 + 3.20\times10^{-3}\ T\ \text{ J mol}^{-1}\text{ K}^{-1}$$

$$c^0_p(CO) = 28.34 + 4.14\times10^{-3}\ T\ \text{ J mol}^{-1}\text{ K}^{-1}$$

$$c^0_p(H_2O) = 30.09 + 10.67\times10^{-3}\ T\ \text{ J mol}^{-1}\text{ K}^{-1}$$

(It holds that $\int_a^b (c_1 + c_2 x)dx = c_1(b-a) + 0.5\,c_2(b^2-a^2)$)

2.6 What can you say on the basis of the above findings on ΔH^0 about the shift in the water gas equilibrium with increasing temperature?

SOLUTION

2.1 ΔH^0_{1000} = 35040 J

ΔS^0_{1000} = 32.11 J mol^{-1} K^{-1}

$\Delta G^0_{1000} = \Delta H^0_{1000} - T\,\Delta S^0_{1000} = 35040 - 1000 \times 32.11 = 2930$ J

2.2 $\Delta G^0 = -RT \ln K_p$

$$\ln Kp = -\frac{\Delta G^0}{RT} = -\frac{2930}{8314} = -0.352418$$

K_p = 0.7030

2.3 As the numbers of moles do not change in the reaction, the reaction is independent on the concentration and pressure and therefore, $K_x = K_p = K_c$ (dimensionless). Volume fraction and mole fraction are identical in an ideal gas.

2.4 The original composition of the gas:

$x_{0,CO} = 0.45; \quad x_{0,H_2} = 0.35; \quad x_{0,H_2O} = 0.20; \quad x_{0,CO_2} = 0.00;$

If the mole fraction of the CO_2 formed at the equilibrium is denoted as x then the equilibrium concentrations can be obtained from:

$CO: \quad x_{0,CO} - x$

$CO_2: \quad x$

$H_2O: \quad x_{0,H_2O} - x$

$H_2: \quad x_{0,H_2} + x$

$$K_p = K_x = \frac{x_{CO}\ x_{H_2O}}{x_{CO_2}\ x_{H_2}} = \frac{(x_{0,CO} - x)(x_{0,H_2O} - x)}{x\,(x_{0,H_2} + x)} = 0.703$$

$$(x_{0,CO} - x)(x_{0,H_2O} - x) = K\,(x_{0,H_2} + x)\,x$$

$$x_{0,CO}\ x_{0,H_2O} - x(x_{0,H_2O} + x_{0,CO}) + x^2 = K\,x\,x_{0,H_2} + K\,x^2$$

where $K = K_x$

$$x^2\,(1 - K) - x\,(x_{0,H_2O} + x_{0,CO} + K\,x_{0,H_2}) + x_{0,CO}\ x_{0,H_2O} = 0$$

On substitution of the numerical values,

x^2 (1 – 0.703) – x (0.20 + 0.45 + 0.703 × 0.35) + 0.45 × 0.20 = 0

$0.297\,x^2 - 0.89605\,x + 0.09 = 0$

$x^2 - 3.01703\,x + 0.303030 = 0$

$$x_{1,2} = 1.508515 \pm \sqrt{2.275618 - 0.303030} = 1.508515 \pm \sqrt{1.972588}$$

$x = 1.508515 \pm 1.404488 = 0.104027$

(The plus sign leads to a solution that has no physical significance, $x > 1$.)

$x = 0.104$

$x_{CO} = 0.346; \quad x_{H_2} = 0.454; \quad x_{H_2O} = 0.096; \quad x_{CO_2} = 0.104;$

2.5 $\Delta C_p^0 = C_p^0(CO) + C_p^0(H_2O) - C_p^0(CO_2) - C_p^0(H_2)$

$= - 11.28 + 1.52 \times 10^{-3}\ T\ J\ K^{-1}\ mol^{-1}$

$$\Delta H_{1400}^0 = \Delta H_{1000}^0 + \int_{1000}^{1400} C_p^0\, dT = \Delta H_{1000}^0 + \int_{1000}^{1400} (c_1 + c_2 T)\, dT$$

$$= \Delta H_{1000}^0 + c_1 (1400 - 1000) + 0.5\, c_2\, (1.96\times10^6 - 1\times10^6) =$$

$$= \Delta H_{1000}^0 - 11.28\times400 + (1.52\times10^{-3} \times 4.8\times10^5) =$$

$$= \Delta H_{1000}^0 - 4512 + 729.6 =$$

$$= 35040 - 4512 + 729.6 = 31258\ J$$

On the basis of the van't Hoff reaction isobar

$$\frac{\partial \ln K_p}{\partial T} = \frac{\Delta H}{RT^2}$$

2.6 $\ln K_p$ increases with increasing temperature for positive (endothermic) heat of reaction, i.e. the equilibrium shifts with increasing temperature in favour of the reaction products, CO and H_2O.

PROBLEM 3

(Chemistry of ions, stoichiometry, redox reactions)

A white crystalline solid compound **A** exhibits the following reactions:

1) The flame of a Bunsen burner is intensively yellow coloured.
2) An aqueous solution of **A** is neutral. Dropwise addition of sulphurous acid (an SO_2 solution) leads to a deep brown solution that is discoloured in the presence of excess of sulphurous acid.
3) If an $AgNO_3$ solution is added to the discoloured solution obtained by 2) and acidified with HNO_3, a yellow precipitate is obtained that is insoluble on addition of NH_3, but can be readily dissolved by adding CN^- or $S_2O_3^{2-}$.
4) If an aqueous solution of **A** is treated with KI and dilute H_2SO_4 a deep brown solution is formed that can be discoloured by addition of sulphurous acid or a $Na_2S_2O_3$ solution.
5) An amount of 0.1000 g of **A** is dissolved in water, then 0.5 g KI and a few cm^3 of dilute H_2SO_4 are added. The deep brown solution formed is titrated with 0.1000 M $Na_2S_2O_3$ solution until the solution is completely discoloured. The consumption is 37.40 cm^3.

Problems:

3.1 What elements are contained in the compound **A**?

3.2 What compounds can be considered as present on the basis of reactions 1) to 4)? Calculate their molar masses.

3.3 Formulate the reactions corresponding to 2) to 4) for the compounds considered and write the corresponding equations in the ionic form.

3.4 Decide on the basis of 5) which compound is present.

SOLUTION

3.1 The solid must contain Na and I. The yellow colouration of the flame of the Bunsen burner indicates the presence of Na. A yellow silver salt that is dissolved only by strong complexing agents such as CN^- or $S_2O_3^{2-}$, must be AgI.

3.2 Reactions 1) to 4) indicate an Na salt of an oxygen containing acid of iodine:

Both SO_2 and I^- are oxidised. While in the first case I^- is formed with an intermediate of I_2 (or I_3^-, brown solution), in the second I_2 (or I_3^-) is formed.

As the solution of **A** is neutral, $NaIO_3$ and $NaIO_4$ come into consideration.

$M(NaIO_3) = 22.99 + 126.905 + 3 \times 16.000 = 197.895 = 197.90 \text{ g mol}^{-1}$

$M(NaIO_4) = 22.99 + 126.905 + 4 \times 16.000 = 213.895 = 213.90 \text{ g mol}^{-1}$

3.3 $2\, IO_3^- + 4\, H_2O + 5\, SO_2 = 5\, HSO_4^- + 3\, H^+ + I_2$

$I_2 + SO_2 + 2\, H_2O = HSO_4^- + 3\, H^+ + 2\, I^-$

$IO_4^- + 7\, I^- + 8\, H^+ = 4\, I_2 + 4\, H_2O$

$IO_3^- + 5\, I^- + 6\, H^+ = 3\, I_2 + 3\, H_2O$

$I_2 + 2\, S_2O_3^{2-} = 2\, I^- + S_4O_6^{2-}$

3.4 Experiment: 0.1000 g of the compound **A** ...... 3.740×10^{-3} moles $S_2O_3^{2-}$

1st hypothesis: The compound is $NaIO_3$.

1 mole $NaIO_3$ . . . . 197.90 g $NaIO_3$ . . . . 6 moles $S_2O_3^{2-}$

0.1000 g $NaIO_3$ . . . . $\dfrac{0.1000 \times 6}{197.90} = 3.032 \times 10^{-3}$ moles $S_2O_3^{2-}$

The hypothesis is false.

2nd hypothesis: The compound is $NaIO_4$.

mole $NaIO_4$ . . . . 213.90 g $NaIO_4$ . . . . 8 moles $S_2O_3^{2-}$

0.1000 g $NaIO_4$ . . . . $\dfrac{0.1000 \times 8}{213.90} = 3.740 \times 10^{-3}$ moles $S_2O_3^{2-}$

The compound **A** is $NaIO_4$.

PROBLEM 4

(Organic chemistry, stereochemistry)

Carbonic acid **A** with an overall formula of $C_5H_8O_2$ yields two geometric isomers, cis (**A'**) and trans (**A"**). On hydrogenation with Pt/H_2 the same racemic carboxyl acid **B** is obtained from both stereoisomers that can be separated into enantiomers (+)-**B** and (-)-**B**. **A'** and **A"** rapidly react with one mole of bromine in CCl_4 in the dark at 20 ℃ to yield **C**.

Problems:

4.1 What is the constitution of **A** and **B**?

4.2 Write the stereo formulae for **A'** and **A"** and the Fischer projection formulae for the enantiomer **B** (not considering the signs (+) or (-)).

4.3 How many stereo isomers of **C** are simultaneously formed when **A'** and **A"** are treated with bromine?

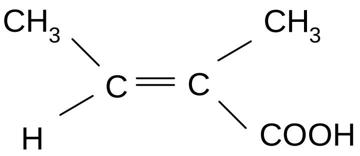
4.4 Briefly, give reasons for your answer to c).

4.5 Write the Fischer projection formulae and one Newman projection formula (conformation) for all the stereoisomers of **C**. Denote those that are mutually enantiomeric and diastereoisomeric.

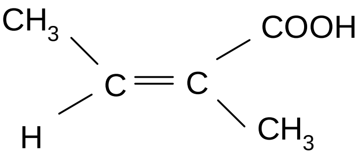
SOLUTION

4.1 **A**: CH_3-CH=C(CH_3)-COOH; **B**: CH_3-CH_2-CH(CH_3)-COOH

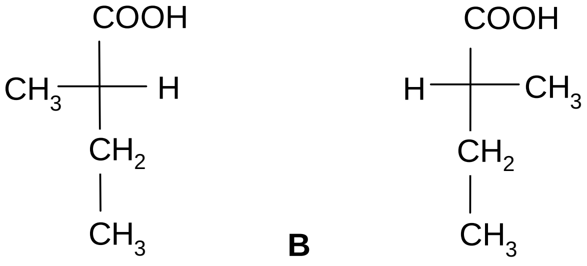
4.2



A'



A"

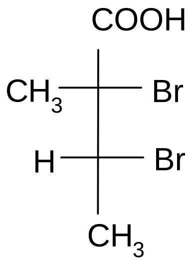


B

4.3 Always two (see e): 1 to 4

4.4 The addition of bromine to the alkene gives trans compound under the given conditions. On the addition, two (non-identical) asymmetrical **C** atoms (chirality centres) are formed yielding together $2^2 = 4$ stereo isomers of which always two are mutually enantiomeric.

4.5 from **A'**:



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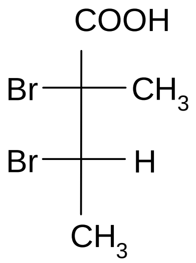
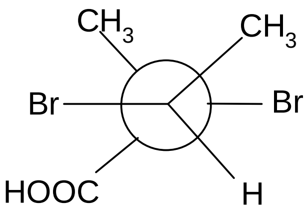
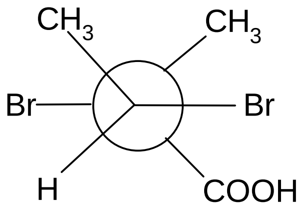
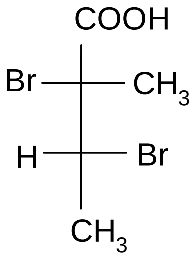






from **A"**:



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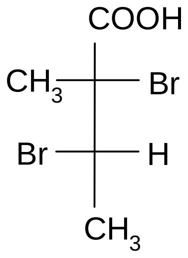
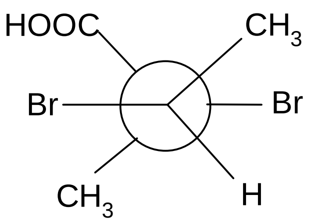
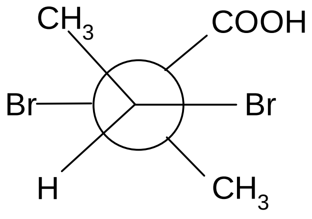






1 and 2 or 3 and 4 are enantiomeric. 1 to 3 and 4, and 2 to 3 and 4 are diastereomeric

PROBLEM 5

(Inorganic chemistry)

From 20 mg of partially methylated disilane, $Si_2H_{6-x}(CH_3)_x$, 27.8 cm^3 of hydrogen are evolved during alkaline hydrolysis at 294 K and 97400 Pa.

5.1 Why the Si-Si bond of the disilane reacts during hydrolysis?

5.2 Why the Si-H bonds of the disilane react during hydrolysis?

5.3 Calculate the degree of substitution x of the methylated disilane.

5.4 Write the complete reaction equation for the hydrolysis.

5.5 How many isomers can form the calculated compound? Give the structural formula for each isomer.

SOLUTION

5.1 The Si-Si bond is coordination unsaturated and thus, has a tendency to react with nucleophilic reagents with the bond breakage.

5.2 Similar to all compounds with negatively polarised hydrogen, this bond also reacts with protons from water with formation of elemental hydrogen.

5.3 $(CH_3)_xSi_2H_{6-x}$

Molecular mass:	2 Si	2×28.086
	(6-x) H	$(6-x) \times 1.008$
	x CH_3	$x \times 15.035$

$$56.172 + 1.008\,(6 - x) + 15.035\,x = 62.22 + 14.027\,x$$

Sample mass**:** 20 mg $\Rightarrow \dfrac{20}{62.22 + 14.027\,x}$ mmol

Hydrogen evolved: $n = \dfrac{pV}{RT}$ mmol H_2 (V in cm^3)

$$n = \frac{0.974 \times 27.8}{0.08314 \times 294} \text{ mmol}$$

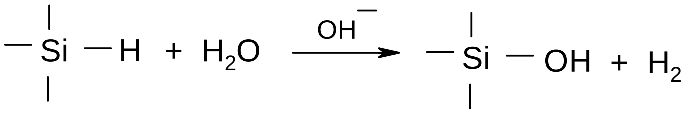
(SiH) (SiSi)

$$(6 - x + 1) \times \frac{20}{62.22 + 14.027\,x} = \frac{0.974 \times 27.8}{0.08314 \times 294}$$

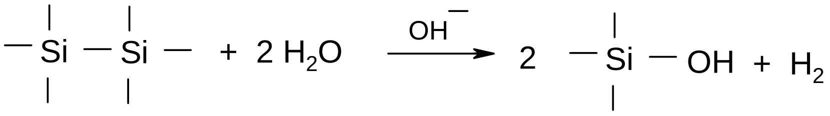
x = 1.9999

Hence, the degree of substitution = 2

5.4



$$-\mathrm{Si}-\mathrm{H} + \mathrm{H_2O} \xrightarrow{\mathrm{OH^-}} -\mathrm{Si}-\mathrm{OH} + \mathrm{H_2}$$



$$-\mathrm{Si}-\mathrm{Si}- + 2\,\mathrm{H_2O} \xrightarrow{\mathrm{OH^-}} 2\ -\mathrm{Si}-\mathrm{OH} + \mathrm{H_2}$$

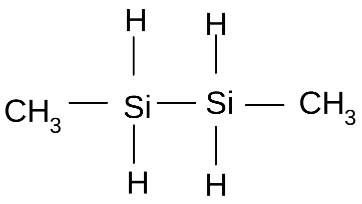
Hence (for a symmetrical isomer):

$Si_2H_4(CH_3)_2 + 6\ H_2O \rightarrow 2\ Si(OH)_3CH_3 + 5\ H_2$ / n

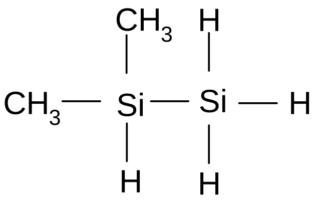
$2\ n\ Si(OH)_3CH_3 \rightarrow [Si_2O_3(CH_3)_2]_n + 3\ n\ H_2O$

$n\ Si_2H_4(CH_3)_2 + 3\ n\ H_2O \rightarrow [Si_2O_3(CH_3)_2]_n + 5\ n\ H_2$

5.5 Two:



$CH_3-SiH_2-SiH_2-CH_3$



$CH_3-Si(CH_3)H-SiH_2-H$

PROBLEM 6

(Organic chemistry, syntheses)

Benzaldehyde and malonic acid reacted in pyridine at 80 ℃ yielding (among others) CO_2 and compound **A** in a yield of ca. 80 % of the theoretical value. Catalytic hydrogenation of 1.48 g **A** on Pt at room temperature and normal pressure yielded **B** with a consumption of 0.25 litre of hydrogen. On reaction of **B** with a polyphosphoric acid (the Friedel-Crafts' conditions) compound **C** can be isolated accompanied by two acidic, isomeric side products. The side products **Da** and **Db** can be formed in a greater amount at a high concentration of **B** in the reaction medium, and can be suppressed by dilution.

The elemental analysis of **C** yields 81.8 % of carbon and 6.1 % of hydrogen. The corresponding values for **Da** and **Db,** identical within the experimental error, are 76.6 % and 6.4 %, respectively. An amount of 2.82 g **Da**, as well as **Db** requires ca. 100 cm^3 0.1 N potassium hydroxide solution for its neutralization. **C** can be purified by distillation (b. p. 243 – 245 ℃) and then exhibits a melting point of 40 ° C and density of 1.09 g/cm^3. The relative molecular mass can be obtained by mass spectrometry and its value is 132.

Using this information solve the following problems:

6.1 The structural formula of **A**.

6.2 The structural formula of **B**.

6.3 The structural formula of **C**.

6.4 The structural formulae of **Da** and **Db**.

6.5 Give an alternative pathway for the synthesis of **A** using the simplest possible starting materials and forming at least one C–C bond.

6.6 Give an alternative pathway for the synthesis of **B** using the simplest possible starting materials and forming at least one C–C bond.

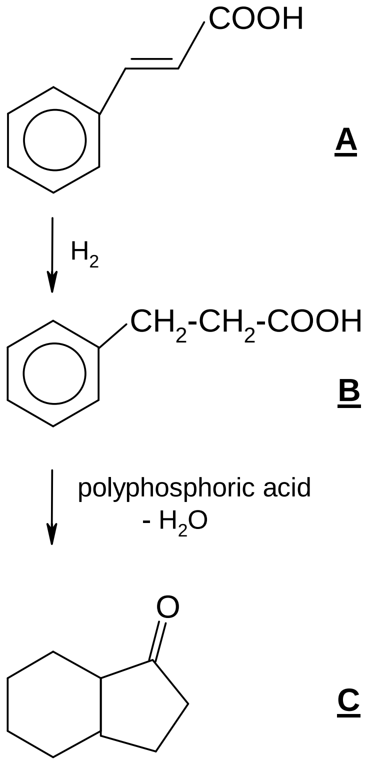
6.7 Give structural formulae for the products of the following reactions:

a) **C** + hydroxylamine (with acid catalysis) →

b) **C** + phenylmagnesium bromide (C_6H_5MgBr) and subsequent treatment under acidic conditions →

c) **C** + benzaldehyde + $C_2H_5O^- \ Na^+$ →

SOLUTION

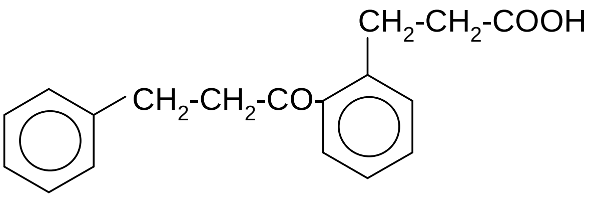


6.1 Condensation

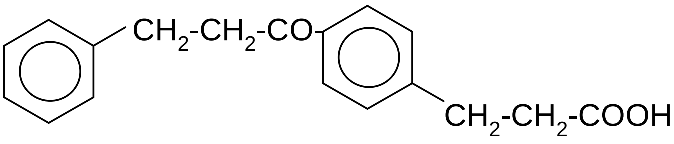
6.2 Hydrogenation

6.3 Intramolecular cyclization

6.4 In addition to **C** two positional isomers **Da** and **Db** are formed.

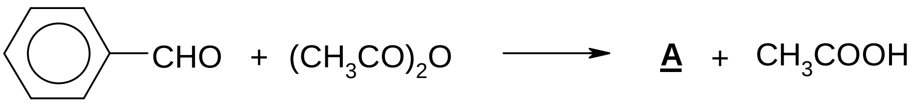


Da

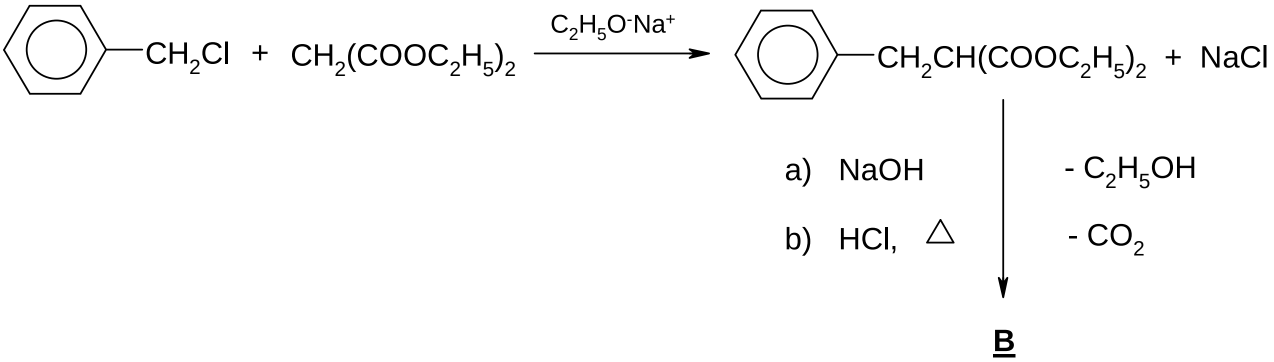


Db

6.5 For example, Perkin reaction: Treatment of benzaldehyde with acetic acid anhydride:

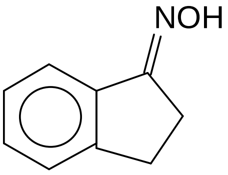


6.6 For example, by malonic ester synthesis



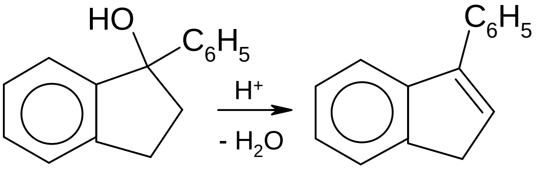
6.7 Reactions a), b), and c) are typical reactions of the carbonyl group.

a)

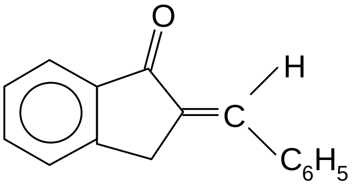


two stereoisomers
(syn and anti)

b)



c)



(**E**)

two stereoisomers

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Qualitative organic analysis

Four different substances that all occur in the nature, are present in 4 test tubes. Find two substances that form basic components of fodders and human foodstuff. Only these two substances are to be identified. Propose the names and structural formulae for those two substances on the basis of combustion tests, solubility experiments, identification of the functional groups and the determination of the melting point.

As an aid the following can be used:

A table of melting points, the Thiele apparatus for melting point determination, a solubility scheme and the following reagents:

diethyl ether, $NaHCO_3$ (5 %), NaOH (2 M), HCl (2 M), H_2SO_4 conc., H_3PO_4 conc., ethanol, Tollens' reagents, (an ammoniac Ag solution), Fehling's solution I and II, phenylhydrazine hydrochloride, β-naphthol, $NaNO_2$ (solid) $Ca(OH)_2$ sat., $FeCl_3$ (5 %), ice, 2,4-dinitrophenylhydrazine, ninhydrine solution (1 % alk.), Seliwanoff's reagent (resorcinol/HCl), phloroglucine.

The requirements: An exact description of the experiments, reaction equations (or reaction schemes where the equation cannot be given) for the reaction required for the identification, the names and the structural formulae of the two test substances.

APPENDIX 1

Determination of the melting point by the Thiele apparatus

A finely pulverized sample is placed in a capillary that is sealed at one side, to a height of 2 – 4 mm. To fill the capillary, it is immersed in the sample. The sample is cautiously wiped off the capillary walls and the content of the capillary is brought to the bottom by cautious tapping. Then the capillary is placed in the opening so that the sample is at the height of the mercury bead of the thermometer. As the heat transmitter, suitable high-boiling silicone oil is used in this apparatus.

To determine the melting point of an unknown organic substance, an approximate melting range is sought first. Thus the heating is carried out according to the figure at about 5 ℃/min. For an exact determination another sample is brought about 10 ℃ below the determined melting range at about 5 ℃/min and then the temperature is very slowly, 1 – 2 ℃/min., brought to complete melting. The temperature, at which the substance is clearly melted, is taken as the melting point.

APPENDIX 2

Tables of melting points (MP, in ℃) and boiling points (BP, in ℃)

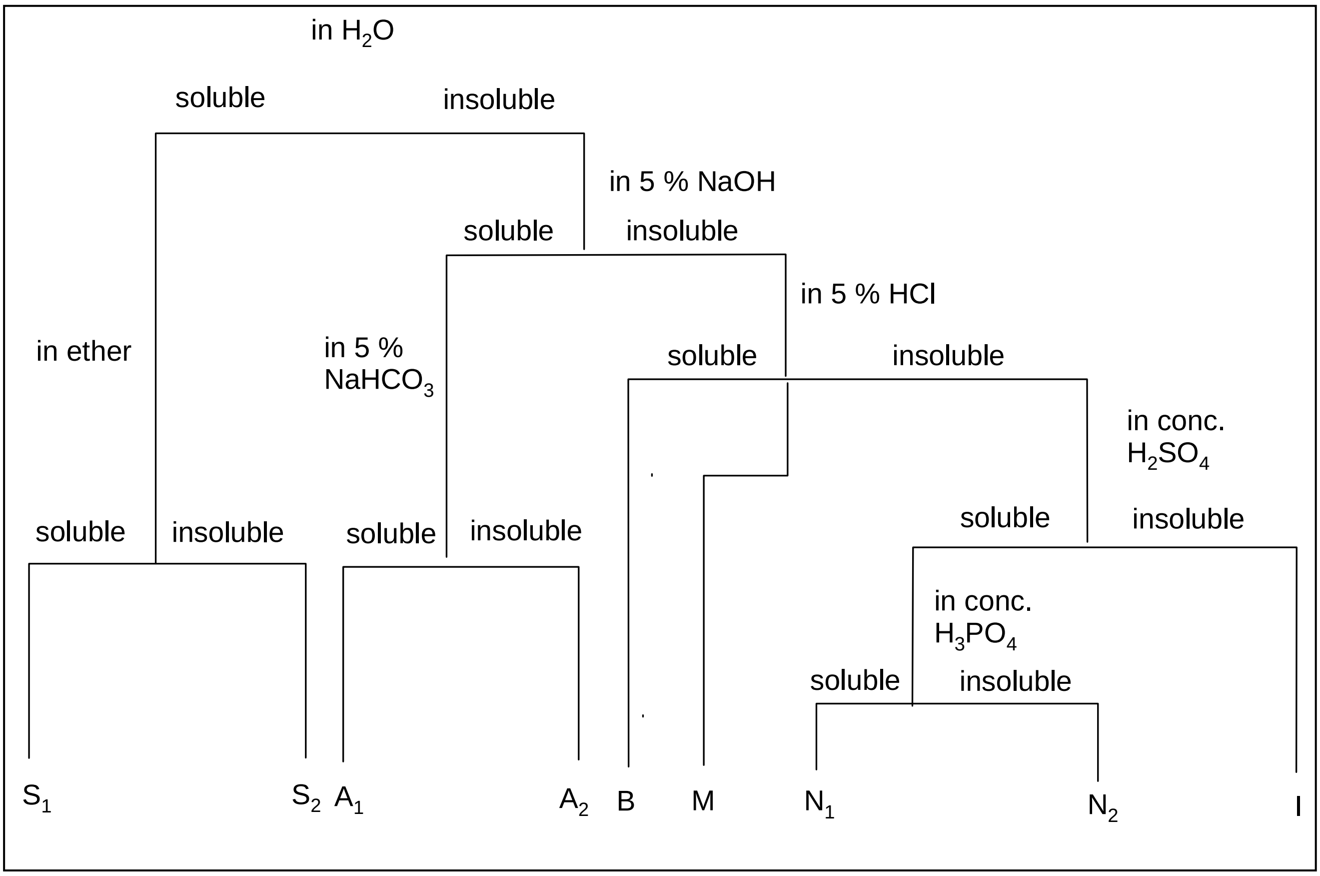
Compound	MP	BP	Compound	MP	BP
ALDEHYDES					
Pentanal	-	103	Acrolein	-	52
Benzaldehyde	-	179	Furfurol	-	161
Salicylaldehyde	-	196	o-Chlorobenzaldehyde	11	214
o-Nitrobenzaldehyde	44	-	α-Naphthaldehyde	34	-
p-Dimetylamino-bemzaldehyde	74	-	Vanillin	81	-
ALCOHOLS					
terc.-Butanol	25	82	Propanol-1	-	97
n-Pentanol	-	136	Ethyleneglycol	-	197
Cyclohexylalcohol	-	160	Butanediol-1,4	-	230
Triphenylcarbinol	165	-	Glycerine	-	290
AMINES					
Diethylamide	-	56	Morpholine	-	130
Cyclohexylamine	-	134	α-Naphthylamine	50	300
Aniline	-	184	p-Bromoaniline	66	-
Diphenylamine	54	-	m-Nitraniline	114	-
o-Phenylenediamine	102	-	p-Aminophenol	186 D	-
ACIDS					
Palmitic acid	63	-	n-Valeric acid	-	186
Stearic acid	70	-	Oleic acid	14	222
Oxalic acid (. 2 H_2O)	101	-	Mandelic acid	118	-
Acetylsalicylic acid	135	-	Benzoic acid	122	-
Phthalic acid	203	-	Malonic acid	135	-
Anthranilic acid	146	-	S-Naphthoic acid	185	-
Glycine	232 D	-	p-Hydroxybenzoic acid	215	-

HALOGENDERIVATIVES					
n-Butyl bromide	-	100	p-Dichlorobenzene	53	-
Cyclohexyl iodide	-	179	p-Bromotoluene	28	185
Trichloroethylene	-	67	Hexachlorobenzene	230	-
KETONES					
Diethyl ketone	-	102	Methylisobutyl ketone	-	118
Cyclohexanone	-	156	Acetophenone	20	202
Benzophenone	49	-	p-Bromoacetophenone	51	-
Benzil	95	-	dl-Camphor	178	-
CARBOHYDRATES					
d-Ribose	95 D	-	β-Maltose	165	-
α-d-Glucose	146	D	β-d-Fructose		
Saccharose	180	-	α-Lactose		
HYDROCARBONS					
n-Heptane	-	99	Pentene-2	-	36
cis-Decaline	-	194	Cyclohexene	-	84
Cumol	-	216	Diphenyl	70	-
Anthracene	216	-	Styrene	-	146
MERCAPTANS – THIOPHENOLS					
n-Amylmercaptan	-	126	p-Thiocresol	-	200
Thiophenol	-	169	p-Bromothiophenol	74	-
PHENOLS					
p-Cresol	36	200	o-Nitrophenol	45	-
α-Naphthol	94	-	Resorcinol	110	-
Pyrocatechol	105	-	β-Naphthol	123	-
Picric acid	122	-	Phloroglucine	218	-
ACID DERIVATIVES					
Acetyl bromide	-	77	Acetamide	82	-
Butyric acid chloride	-	102	N-Methylacetanilide	102	-
4-Nitrobenzoylchloride	73	-	Urea	132	-
Butyric acid ethylester	-	121	Sodium formate	255	-
Malonic acid diethylester	-	199	Al-Acetate	200 – 320 D	-
Palmitic acid cetylester	54	-	Ba-Propionate	ca. 300	-

D after the number denotes decomposition.

APPENDIX 3

Solubility scheme



S_1: Substances with higher volatility;
All low molecular alcohols, aldehydes, ketones, acids, amines, nitriles and acid chlorides.

S_2: Substances with low volatility, often distillable without decomposition: polyols, salts, hydroxyaldehydes and hydroxyketones, carbohydrates, amino- and hydroxyl acids.

A_1: Substances with low volatility: higher molecular acids, nitrophenols.

A_2: Substances with high boiling points: Phenols, primary and secondary nitro compounds, sulfonamides, weak acids.

B: Substances with high boiling points, distillable with water vapour: Basic compounds, amines (with maximum of a few aryl groups), hydrazine.

M: Low volatility substances:
Neutral compounds, tertiary nitro compounds, nitroaniline, azo- and azoxy compounds, nitrito-, nitrato-, sulphuric-, and phosphoric acid esters.

N_1: Substances with small volatility:
Alcohols, aldehydes, methyl ketones and esters with less than 9 C atoms, neutral compounds, ethers, olephins.

N_2: Substances with a very low volatility:
Alcohols, aldehydes, ketones, esters and thioalcohols with more than 9 C atoms, neutral compounds, ethers, olephins.

I: Substances with low boiling point:
Inert compounds, hydrocarbons, halogenoalkanes.

APPENDIX 4

Preparation of the reagents

Tollen's reagent

Mix 0.5 cm^3 2 M NaOH + 1 cm^3 0.1 M $AgNO_3$ in 2 M NH_3.

Fehling's reagent

I: 1.73 g $CuSO_4 . 5 H_2O$ in 25 cm^3 of water

II: 8.5 g Seignette salt + 2.5 g NaOH in 25 cm^3 H_2O

Seliwanoff's reagent

125 g resorcinol is dissolved in 250 cm^3 of diluted HCl (83 cm^3 conc. HCl + 167 cm^3 H_2O), preparing only a necessary amount.

Phenylhydrazine solution

0.5 g of phenylhydrazine hydrochloride + 0.5 cm^3 glacial acetic acid in 2 cm^3 H_2O are shaken until a clear solution is obtained.

2,4-dinitrophenylhydrazine solution,

2 cm^3 of conc. H_2SO_4 are added to 0.4 g of 2,4-dinitrophenylhydrazine and then, with stirring and shaking, 3 cm^3 of H_2O are added. To the warm solution, 10 cm^3 of 95 % ethanol are added.

SOLUTION

In the four test tubes, pure sodium chloride, D-fructose, palmitic acid (hexadecanoic acid), and vanillin were present. D-fructose, as a building block of cane sugar, and palmitic acid, as the building block of most animal and plant fats, were identified.

a) *Fructose*

Melting range: 102 – 105 °C

Combustion test: Carbonizes during combustion with caramel smell.

Solubility: Readily soluble in water, insoluble in diethyl ether.

Identification of the functional groups:

Aldehydic group:

1. With Fehling's reagent

   The oxidation of the carbonyl group with simultaneous reduction of Cu(II) to Cu(I).

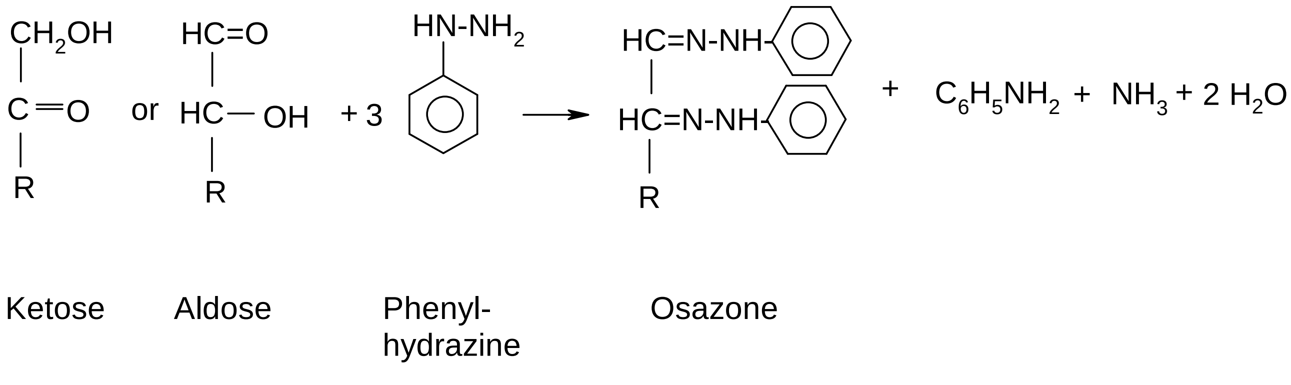
   $–CHO + 2\,[Cu(C_4H_4O_6)_2]^{2-} + 5\,OH^- \rightarrow –COOH + Cu_2O\downarrow + 3\,H_2O + 4\,C_4H_4O_6^{2-}$

2. With Tollen's reagent

   The oxidation to the carboxyl group with simultaneous reduction of Ag(I) to Ag.

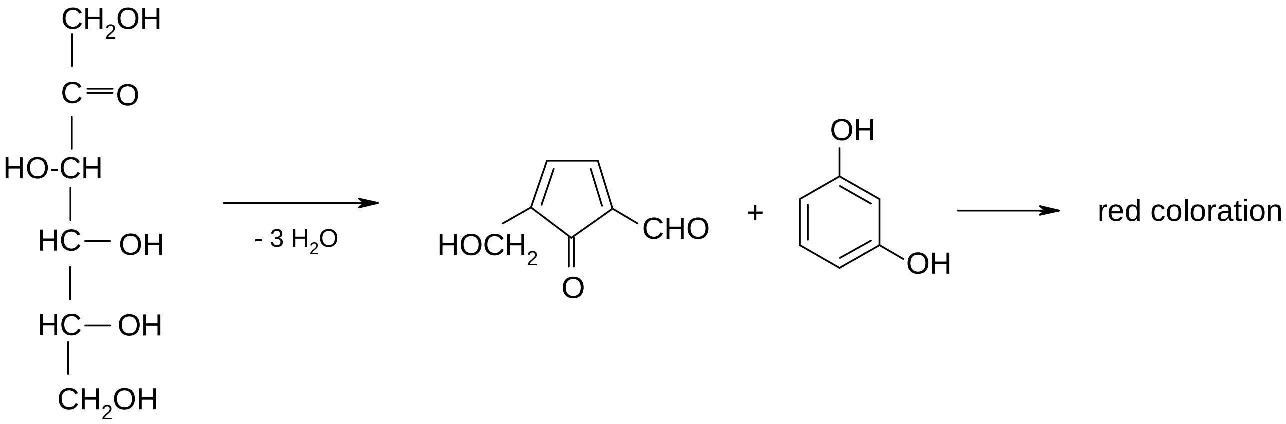
   $–CHO + 2\,[Ag(NH_3)_2]^+ + 2\,OH^- \rightarrow –COOH + 2\,Ag + 4\,NH_3 + H_2O$

Osazone formation (indication of monoses)



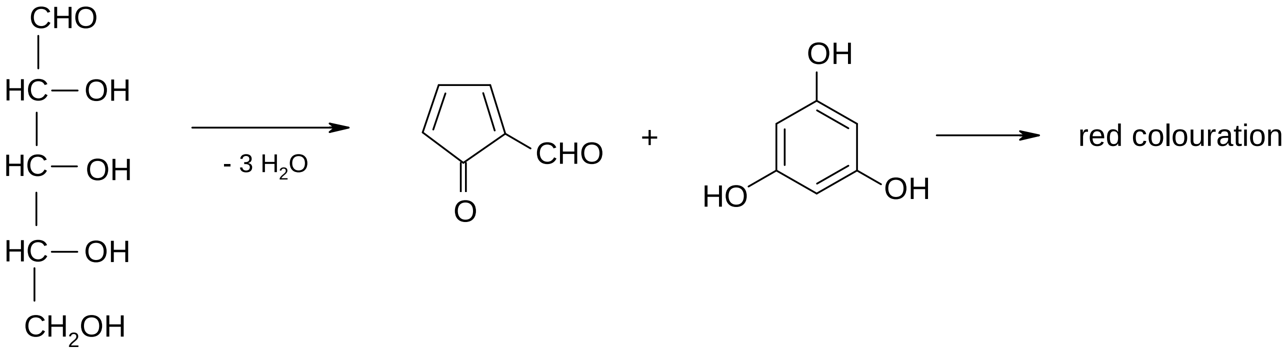
Test for ketohexoses (Saliwanoff's reaction)

Ketohexoses form, with heating in acidic solution, 5-hydroxy-methylfurfural that condenses with resorcinol to red-coloured substances.

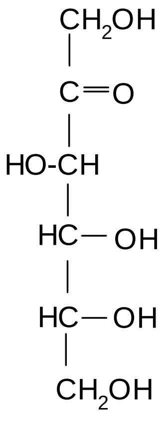


Test for pentoses (Tollens test)

Pentoses, in contrast to hexoses, form furfural in acidic solution that condenses with phloroglucine to give red coloured substances.



Name: The above reactions, the solubility behaviour and the melting range indicate that this substance is D-fructose, a building block of cane sugar.



When giving the configuration, use the Fischer projection.

b) *Palmitic acid*

Melting range: 60 – 63 °C

Combustion test: Burns with yellowish, slightly smoking flame.

Solubility: Insoluble in water, very well soluble in 2 M NaOH, less soluble in 5 % $NaHCO_3$.

Identification of the functional groups:

From alkaline solution a colourless substance is precipitated by Ca^{2+}:

$2\ R\text{-}COO^- + Ca^{2+} \rightarrow (R\text{-}COO)_2Ca$

On the basis of flammability the solubility behaviour and the precipitation of the calcium salt from alkaline solution one can conclude that the substance is an organic carboxyl acid. The melting range indicates palmitic acid = hexadecanoic acid.

$CH_3\text{-}(CH_2)_{14}\text{-}COOH$

PROBLEM 2 (practical)

In 10 reagent bottles are 10 different pure metal samples. By evaluating the solubility and by the following identification, only the six following elements are to be specified by their sample numbers:

calcium, iron, aluminium, zinc, magnesium, tin.

It is expected to specify:

a) the symbol of the identified metal and the corresponding bottle number,

b) a reaction equation for dissolution of each of the six metals,

c) an unambiguous verbal proof or a proof in the form of a chemical equation.

The following chemicals are at disposal:

HCl conc., HCl (2 M), H_2SO_4 (2 M), CH_3COOH (2 M), NaOH (2 M), NH_3 (2 M), NH_4SCN (0.2 M), CH_3COONa (conc.), 3 % H_2O_2, Na_2CO_3 (0.2 M), H_2S (0.1 M), Na_2HPO_4 (0.2 M), $K_4Fe(CN)_6$ (0.2 M), $K_3Fe(CN)_6$ (0.2 M), morin (in CH_3OH), quinalizarine (in C_2H_5OH), urotropine (20 %), dithizone (in CCl_4), $(NH_4)_2C_2O_4$ (0.2 M), distilled water.

SOLUTION

a) See the list at the end.

b) $Ca + 2\ H_2O \rightarrow Ca(OH)_2 + H_2$

$Ca + 2\ H_3O^+ \rightarrow Ca^{2+} + H_2 + 2\ H_2O$

$Fe + 2\ H_3O^+ \rightarrow Fe^{2+} + H_2 + 2\ H_2O$

$Al + 3\ H_3O^+ \rightarrow Al^{3+} + 3/2\ H_2 + 3\ H_2O$

$Al + NaOH + 3\ H_2O \rightarrow Na^+ + [Al(OH)_4]^- + 3/2\ H_2$

$Zn + 2\ H_3O^+ \rightarrow Zn^{2+} + H_2 + 2\ H_2O$

$Zn + 2\ NaOH + 2\ H_2O \rightarrow 2\ Na^+ + [Zn(OH)_4]^{2-} + H_2$

$Mg + 2\ H_2O \rightarrow Mg(OH)_2 + H_2$

$Mg + 2\ H_3O^+ \rightarrow Mg^{2+} + H_2 + 2\ H_2O$

$$Sn + 2\ H_3O^+ \rightarrow Sn^{2+} + H_2 + 2\ H_2O$$

$$Sn + 2\ NaOH + 2\ H_2O \rightarrow 2\ Na^+ + [Sn(OH)_4]^{2-} + H_2$$

c) Ca^{2+}: white precipitate with $(NH_4)_2C_2O_4$;

Fe^{2+}: blue with $K_3[Fe(CN)_6]$
or after oxidation with H_2O_2: blue with $K_4[Fe(CN)_6]$ or red with NH_4SCN, or brown precipitate with NaOH;

Al^{3+}: green fluorescence with morine (in dilute acetic acid);

Zn^{2+}: white precipitate with H_2S (in acetic acid),
with dithizone red coloration of the organic phase;

Mg^{2+}: with quinalizarine light blue lacquer (alkali solution);

Sn^{2+}: with H_2S deep brown precipitate (weakly acidic solution),
blue fluorescence of the outer wall of a glass bottle filled with cold water that was immersed in an Sn^{2+} solution (acidified with HCl),
in the flame of a Bunsen burner ("light test").

PROBLEM 3 (practical)

Titrimetric determination of potassium peroxodisulfate ($K_2S_2O_8$)

A) *Principle*

To the sample ($K_2S_2O_8$) a measured amount of a Fe(II) solution is added in an excess. The excess of the Fe(II) is determined using a standard $KMnO_4$ solution.

B) *Procedures*

1) Determination of the concentration of the Fe(II) solution, $[Fe(NH_4)_2(SO_4)_2]$

To a titration vessel, 25.0 cm^3 Fe(II) solution, 10 cm^3 H_3PO_4 (ca. 3.7 mol dm^{-3}) and 10 cm^3 H_2SO_4 (ca. 1 mol dm^{-3}) are added and titrated with the $KMnO_4$ solution to a pink colouration. The concentration of $KMnO_4$ in the solution is exactly 0.02 mol dm^{-3}. Two titrations are carried out and the consumption of the $KMnO_4$ solution is recorded. The mean value (= V_1) is to be given.

2) Determination of peroxodisulfate in the same solution

   a) The dissolved sample is diluted with distilled water to 100 cm^3 in a standard flask and mixed.

   b) 25.0 cm^3 of this solution are transferred to a titration vessel and mixed with 10 cm^3 H_3PO_4 (ca. 3.7 mol dm^{-3}), 10 cm^3 H_2SO_4 (ca. 1 mol dm^{-3}) and 25.0 cm^3 of the Fe(II) solution. The mixture is allowed to stand for 5 minutes and titrated with the $KMnO_4$ solution (0.02 mol dm^{-3}) to a pink colourization. Two titrations are carried out and the consumption of the $KMnO_4$ solution is recorded. The mean value (= V_2) is to be given.

C) *Calculation and evaluation*

I) Reaction equations: To be given:

Partial equations with electron balance

Overall equations

1) Reaction of peroxodisulfate with Fe(II):

Partial:

a) $S_2O_8^{2-}$ . . . .

b) Fe^{2+} . . . .

c) Overall reaction:

2) Reaction of Fe(II) with permanganate:

Partial:

a) Fe^{2+} . . . .

b) MnO_4^- . . . .

c) Overall reaction:

II) The concentration of the Fe(II) solution

1) Give the consumption of the $KMnO_4$ solution (cm^3) for 25.0 cm^3 of the Fe(II) solution (= V_1); See Procedure 1.

2) Calculate the concentration of the Fe(II) solution in mol dm^{-3}.

III) Determination of $K_2S_2O_8$

1) Give the consumption of the $KMnO_4$ solution in the back-titration of the excess Fe(II) solution in cm^3 (= V_2); See Procedure 2.

2) How many mg $K_2S_2O_8$:

3) Calculate the concentration of $K_2S_2O_8$ in the sample solution in mol dm^{-3}.

SOLUTION

I/1/a $S_2O_8^{2-} + 2\ e^- \rightarrow 2\ SO_4^{2-}$

b) $Fe^{2+} \rightarrow Fe^{3+} + e^-$ /. 2

c) $S_2O_8^{2-} + 2\ Fe^{2+} \rightarrow 2\ SO_4^{2-} + 2\ Fe^{3+}$

I/2/a $Fe^{2+} \rightarrow Fe^{3+} + e^-$ /. 2

$MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$

$5\ Fe^{2+} + MnO_4^- \rightarrow 5\ Fe^{3+} + Mn2^+ + 4\ H_2O$

II/1 V_1 cm^3 $KMnO_4$ (0.02 mol dm^{-3}) / 25 cm^3 Fe(II)

2. $c(Fe^{2+}) = \dfrac{V_1 \times 0.02 \times 5}{25} = \ldots\ldots.$ mol/l

III/1 V_2 cm^3 $KMnO_4$ solution (0.02 mol dm^{-3}) for the back titration

2.

$$\alpha)\quad \frac{(V_1 - V_2)\times 0.02\times 5}{1000}\times\frac{270.33}{2} = \text{........ mg } K_2S_2O_8$$

$$\beta)\quad \frac{25\times c(\text{Fe}^{2+}) - V_2\times 0.02\times 5}{1000}\times\frac{270.33}{2} = \text{........ mg } K_2S_2O_8$$

3.

$$\alpha)\quad \frac{(V_1 - V_2)\times 0.02\times 5}{1000}\times\frac{40}{2} = \text{........ mol } K_2S_2O_8\,/\,\text{dm}^3$$

$$\beta)\quad \frac{25\times c(\text{Fe}^{2+}) - V_2\times 0.02\times 5}{1000}\times\frac{40}{2} = \text{........ mol / dm}^3$$

13th

6 theoretical problems
3 practical problems

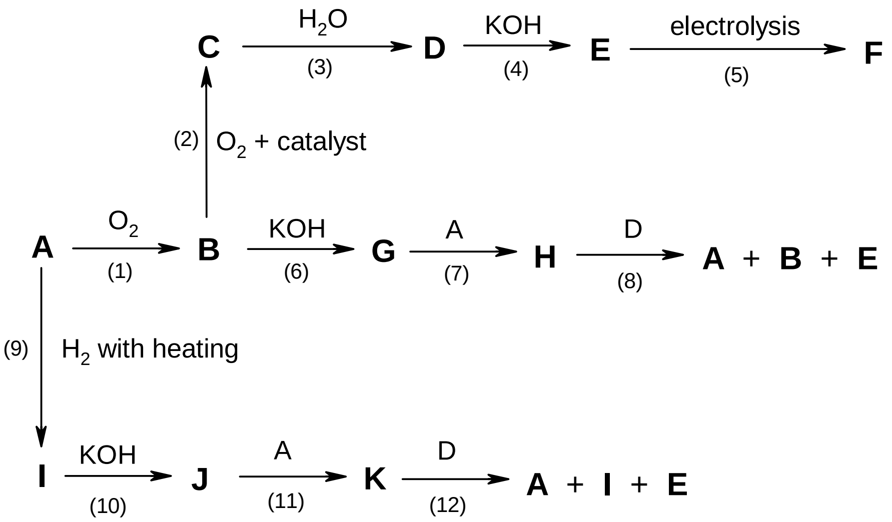
THE THIRTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
13–23 JULY 1981, BURGAS, BULGARIA

THEORETICAL PROBLEMS

PROBLEM 1

The sample **A** participates in the transformations in scheme 1. Only the products containing **A** are shown in the scheme 1.

Scheme 1



a) Substance **A** is a solid and is insoluble in water.

b) Substances **B** and **I** are gases soluble in water.

c) Substances **E**, **F**, **J** and **K** are solid and soluble in water.

d) Aqueous solutions of **B**, **G**, **H**, **I**, **J** and **K** react with **F**, the products in all cases being **E** and **D**.

e) The following transformations occur during the interaction with an aqueous solution of iodine:

$$\mathbf{B} \xrightarrow{(19)} \mathbf{D} \qquad \mathbf{G} \xrightarrow{(20)} \mathbf{E} \qquad \mathbf{H} \xrightarrow{(21)} \mathbf{L}$$

$$\mathbf{I} \xrightarrow[(22)]{} \mathbf{A} \qquad \mathbf{J} \xrightarrow[(23)]{} \mathbf{A} \qquad \mathbf{K} \xrightarrow[(24)]{} \mathbf{A}$$

Write the chemical equations for the above interactions and balance them.

SOLUTION

Schéma:

(1) $S + O_2 \rightarrow SO_2$

(2) $2\ SO_2 + O_2 \rightarrow 2\ SO_3$

(3) $SO_3 + H_2O \rightarrow H_2SO_4$

(4) $2\ KOH + H_2SO_4 \rightarrow K_2SO_4 + 2\ H_2O$

(5) $2\ SO_4^{2-} - 2\ e- \rightarrow S_2O_8^{2-}$

(6) $SO_2 + 2\ KOH \rightarrow K_2SO_3 + H_2O$

(7) $K_2SO_3 + S \rightarrow K_2S_2O_3$

(8) $K_2S_2O_3 + H_2SO_4 \rightarrow K_2SO_4 + S + SO_2 + H_2O$

(9) $H_2 + S \rightarrow H_2S$

(10) $H_2S + 2\ KOH \rightarrow K_2S + 2\ H_2O$

(11) $K_2S + x\ S \rightarrow K_2S_{(x+1)}$

(12) $K_2S_{(x+1)} + H_2SO_4 \rightarrow K_2SO_4 + x\ S + H_2S$

d)

(13) $SO_2 + 2\ H_2O + K_2S_2O_8 \rightarrow K_2SO_4 + 2\ H_2SO_4$

(14) $K_2SO_3 + H_2O + K_2S_2O_8 \rightarrow 2\ K_2SO_4 + H_2SO_4$

(15) $K_2S_2O_3 + 5\ H_2O + 4\ K_2S_2O_8 \rightarrow 5\ H_2SO_4 + 5\ K_2SO_4$

(16) $H_2S + 4\ H_2O + 4\ K_2S_2O_8 \rightarrow 5\ H_2SO_4 + 4\ K_2SO_4$

(17) $K_2S + 4\ H_2O + 4\ K_2S_2O_8 \rightarrow 4\ H_2SO_4 + 5\ K_2SO_4$

(18) $K_2S_{(x+1)} + (4x + 1)\ H_2O + 4\ x\ K_2S_2O_8 \rightarrow 5\ x\ H_2SO_4 + (4x + 1)\ K_2SO_4$ (+S)

e)

(19) $SO_2 + 2\ H_2O + I_2 \rightarrow H_2SO_4 + 2\ HI$

(20) $K_2SO_3 + H_2O + I_2 \rightarrow K_2SO_4 + 2\ HI$

(21) $2\ K_2S_2O_3 + I_2 \rightarrow 2\ KI + K_2S_4O_6$

(22) $H_2S + I_2 \rightarrow 2\ HI + S$

(23) $K_2S + I_2 \rightarrow 2\ KI + S$

(24) $K_2S_x + I_2 \rightarrow 2\ KI + x\ S$

A: S **B**: SO_2 **C**: SO_3 **D**: H_2SO_4

E: K_2SO_4 **F**: $K_2S_2O_8$ **G**: K_2SO_3 **H**: $K_2S_2O_3$

I: H_2S **J**: K_2S **K**: K_2S_x **L**: $K_2S_4O_6$

PROBLEM 2

Maleic acid (H_2A) is a weak dibasic acid. The correlation between the relative quantities of H_2A, HA^-, A^{2-}:

$$\alpha_0 = \frac{c(H_2A)}{c} \qquad \alpha_1 = \frac{c(HA^-)}{c} \qquad \alpha_2 = \frac{c(A^{2-})}{c}$$

and pH values of the solution show that:

a) $\alpha_0 = \alpha_1$ for pH = 1.92

b) $\alpha_1 = \alpha_2$ for pH = 6.22

Find:

2.1 The values of the dissociation constants of maleic acid for the first (K_1) and the second (K_2) degree of dissociation.

2.2 The values of α_0, α_1, and α_2 for pH = 1.92 and pH = 6.22.

2.3 What is the value of pH when α_1 attains a maximum value? Find the maximum value of α.

2.4 Which of the acid-base indicators in the table are suitable for titration of a 0.1 M solution of maleic acid (as a monobasic and as a dibasic acid) with 0.1 M NaOH?

Fill in the table 1 with the correct answers.

All the activity coefficients should be considered equal to 1.

Indicator	pH interval
Methyl green	0.1 – 2.0
Tropeolin 00	1.4 – 3.2
β-Dinitrophenol	2.4 – 4.0
Bromphenol blue	3.0 – 4.6
Congo red	3.0 – 5.2
Methyl red	4.4 – 6.2
Bromphenol red	5.0 – 6.8
Bromthymol blue	6.0 – 7.6
Phenol red	6.8 – 8.0
Cresol red	7.2 – 8.8

Thymol blue	8.0 – 9.6
Phenolphthalein	8.2 – 10.0
Alizarine yellow	10.1 – 12.1
Tropeolin 0	11.0 – 13.0
1,3,5-Trinitrobenzene	12.2 – 14.0

Table 1

2.1		K_1 =
		K_2 =
2.2	pH = 1.92	α_0 =
		α_1 =
		α_2 =
	pH = 6.22	α_0 =
		α_1 =
		α_2 =
2.3		pH =
		α_1 =
2.4	First indicator equivalence point	pH =
		1. 2. 3. 4.
	Second indicator equivalence point	pH =
		1. 2. 3. 4.

SOLUTION

2.1 $\alpha_0 = \alpha_1$

$K_1 = c_{H^+} = 10^{-pH} = 10^{-1.92} = 1.20 \times 10^{-2}$

$\alpha_1 = \alpha_2$

$K_2 = c_{H^+} = 10^{-pH} = 10^{-6.22} = 6.02 \times 10^{-7}$

2.2 $F = c_{H^+}^2 + K_1\, c_{H^+} + K_1\, K_2$

pH = 1.92; $c_{H^+} = 10^{-1.92} = 1.20 \times 10^{-2}$; $F = 2.88 \times 10^{-4}$

$$\alpha_0 = \alpha_1 = \frac{c_{H^+}^2}{F} = \frac{(1.20\,.\,10^{-2})^2}{2.88\,.\,10^{-4}} = 0.500$$

$$\alpha_2 = \frac{K_1\, K_2}{F} = \frac{1.20\,.\,10^{-2} \times 6.02\ .\ 10^{-7}}{2.88\,.\,10^{-4}} = 2.51 \times 10^{-5}$$

pH = 6.22; $c_{H^+} = 10^{-6.22} = 6.02 \times 10^{-7}$; $F = 1.445 \times 10^{-8}$

$$\alpha_0 = \frac{c_{H^+}^2}{F} = \frac{(6.02 \times 10^{-7})^2}{1.445 \times 10^{-8}} = 2.51 \times 10^{-5}$$

$$\alpha_1 = \alpha_2 = \frac{K_1\, K_2}{F} = \frac{1.20 \times 10^{-2} \times\ 6.02 \times 10^{-7}}{1.445 \times 10^{-8}} = 0.500$$

2.3 $$(\alpha)'_{c_{H^+}} = \frac{\left[K_1 F - K_1\, c_{H^+}\,(2c_{H^+} + K_1\right]}{F^2} = 0$$

$$c_{H^+}^2 = K_1 K_2$$

$$c_{H^+} = \sqrt{(1.20 \times 10^{-2} \times\ 6.02 \times 10^{-7}} = 8.50 \times 10^{-5}\ \text{mol dm}^{-3}$$

$F = 1.034 \times 10^{-6}$ pH = 4.07

$$\alpha_1 = \frac{K_1\, c_{H^+}}{F} = \frac{1.20 \times 10^{-2} \times\ 8.50 \times 10^{-5}}{1.034 \times 10^{-6}} = 0.986$$

The pH and the maximum value of α_1 can be estimated either by calculating α_1 for a set of values of c_{H^+} in the interval $1 \times 10^{-5} - 1 \times 10^{-3}$ mol dm^{-3} or from the condition that α_1 can reach a maximum value only when $\alpha_0 = \alpha_2$

2.4 The first equivalence point is found in the region of the α_1 maximum at pH = 4.07 where $c_{HA^-} = c_{NaHA} = \dfrac{0.1}{2} = 0.05\ \text{mol dm}^{-3}$.

The second equivalence point is found in the alkaline region, where:

$$c_{OH^-} = c_{HA^-} \qquad c_{A^{2-}} = \frac{0.1}{3} - c_{OH^-} = 0.0333$$

$$c_{\mathrm{H+}}^2 = \frac{K_2\, c_{\mathrm{HA^-}}}{c_{\mathrm{A^{2-}}}} = \frac{K_2\, c_{\mathrm{OH^-}}}{c_{\mathrm{A^{2-}}}} = \frac{K_2\, K_w}{c_{\mathrm{H^+}}\, c_{\mathrm{A^{2-}}}}$$

$$c_{\mathrm{H^+}} = \sqrt{\frac{K_2\, K_w}{c_{\mathrm{A^{2-}}}}} = \sqrt{\frac{6.02\times10^{-7} \times 1\times10^{-14}}{0.0333}} = 4.25\times10^{-10}\ \mathrm{mol dm^{-3}}$$

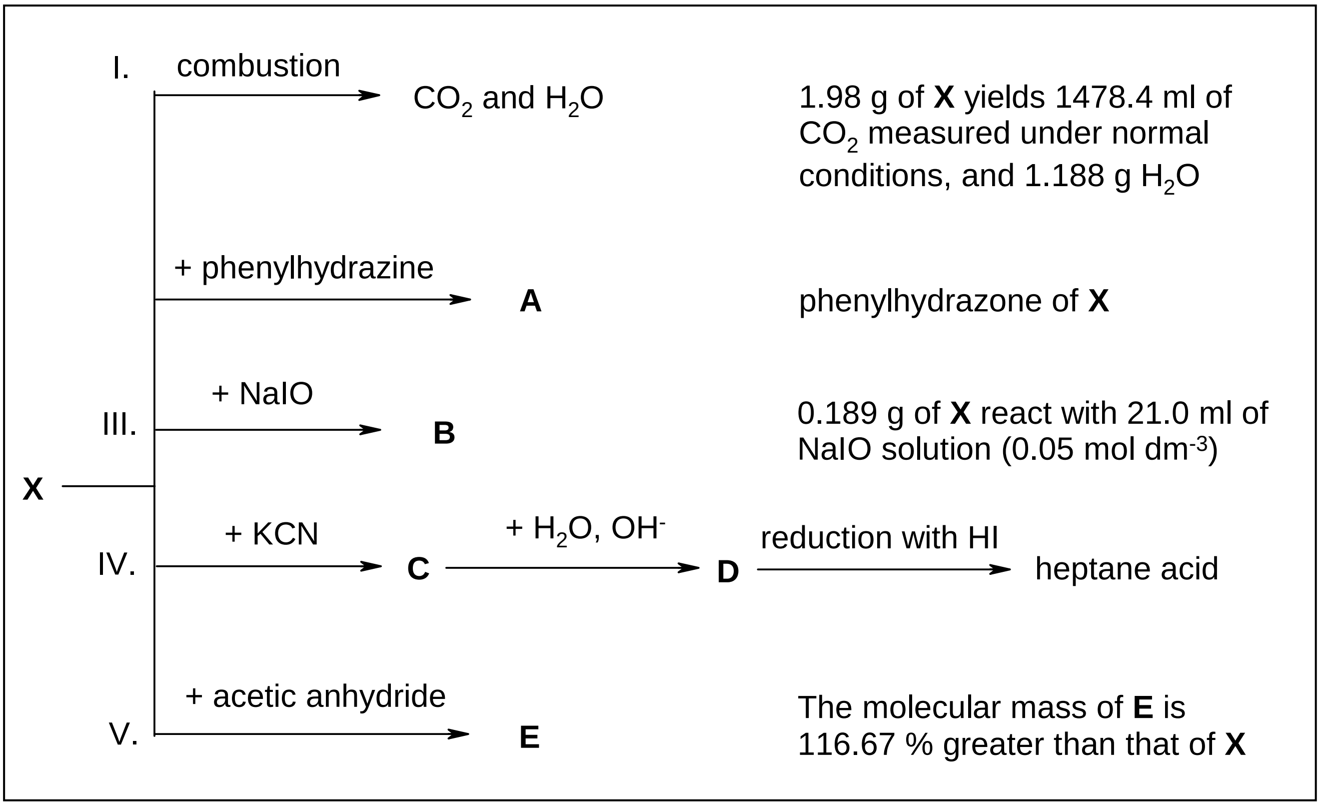
pH = 9.37

Indicators:

Bromphenol blue, Congo red, thymol blue, phenolphthalein.

PROBLEM 3

Compound **X** has been isolated from a neutral product. Different reagents have been used to establish the structure of X. The following results were obtained:



1.98 g of **X** yields 1478.4 ml of CO_2 measured under normal conditions, and 1.188 g H_2O

phenylhydrazone of **X**

0.189 g of **X** react with 21.0 ml of NaIO solution (0.05 mol dm^{-3})

The molecular mass of **E** is 116.67 % greater than that of **X**

3.1 What conclusions can be drawn on the composition and the structure of **X** on the basis of the data obtained from each of the above interactions. The conclusions should be formulated in the most concise and clear way. Fill in the table without describing how you reached your conclusions.

I. ……………………………….

II. ……………………………….

III. ……………………………….

IV. ……………………………….

V. ……………………………….

3.2 Write the formula of substance **X** on the basis of the data about the composition and structure obtained in point 1.

3.3 Write the formulae of substances **A**, **B**, **C**, **D**, and **E** and the formula for heptane acid.

3.4 To what natural substances could this structure correspond? Write the name of the substance and draw the structural formula which best describes its structure properties.

3.5 Give three properties of this compound that do not correspond to the structure found in point 2.

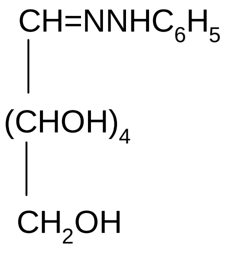
SOLUTION

3.1

Reaction	Yielding
I	The simplest empirical formula, CH_2O
II	Presence of a C=O group
III	Presence of a –CHO group *M*, calculated for a single CHO- 180/n (n – number of CHO groups)
IV	Continuous chain of 6 C atoms 1 CHO, $C_6H_{12}O_6$ (M = 180)
V	5 OH groups

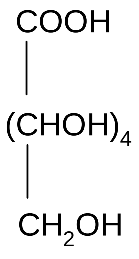
3.2 $HOCH_2(CHOH)_4CHO$

3.3



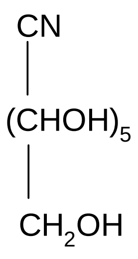
$\begin{array}{l} CH{=}NNHC_6H_5 \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$

A



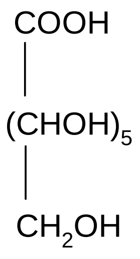
$\begin{array}{l} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$

B



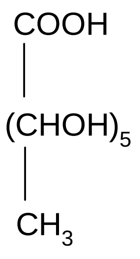
$\begin{array}{l} CN \\ | \\ (CHOH)_5 \\ | \\ CH_2OH \end{array}$

C



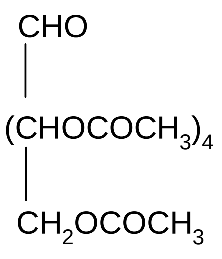
$\begin{array}{l} COOH \\ | \\ (CHOH)_5 \\ | \\ CH_2OH \end{array}$

D



$\begin{array}{l} COOH \\ | \\ (CHOH)_5 \\ | \\ CH_3 \end{array}$

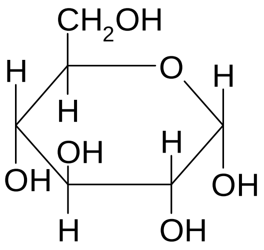
heptane acid



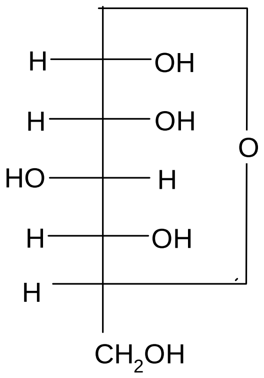
$\begin{array}{l} CHO \\ | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OCOCH_3 \end{array}$

E

3.4 D – (+) – glucose



or



3.5 – does not participate in some reactions typical for aldehydes (e. g. with $NaHSO_3$ or Schiff's reagent),

– the mutarotation phenomenon,

– a stronger reactivity of one of the five OH groups (displayed for example in the interaction with CH_3OH and HCl leading to the methylation of only one OH group).

PROBLEM 4

The thermal decomposition of water

$$H_2O \rightleftharpoons H_2 + ½\,O_2$$

can be traced ($\alpha = 10^{-3}$) at temperature above 1700 K. This process can be realized at temperatures 800 – 900 K as well as through subsequent stages carried out in a cycle. Suggest such a process on the basis of the reactions:

$$CuO(s) + MgCl_2(s) + H_2O(g) \xrightarrow{840\text{ K}} CuCl(s) + MgO(s) + HCl(g) + O_2(g)$$

and

$$Ag(s) + HCl(g) \xrightarrow{430\text{ K}} AgCl(s) + H_2(g)$$

satisfying the following requirements:

a) Only water should be consumed during the process.

b) Oxygen and hydrogen alone should be the end products of the process.

c) In addition to the above substances, a 25 % ammonia solution is needed for the cycle.

d) The temperature for each step in the cycle should not exceed 840 K.

SOLUTION

1. $2\,CuO + 2\,MgCl_2 + H_2O \xrightarrow{840\text{ K}} 2\,CuCl + 2\,MgO + 2\,HCl + 0.5\,O_2$
2. $Ag + 2\,HCl \xrightarrow{430\text{ K}} 2\,AgCl + H_2$
3. $2\,CuCl + 4\,NH_3 \longrightarrow 2\,[Cu(NH_3)_2]^+ + 2\,Cl^-$
4. $2\,AgCl + 4\,NH_3 \longrightarrow 2\,[Ag(NH_3)_2]^+ + 2\,Cl^-$
5. $2\,[Cu(NH_3)_2]^+ + 2\,[Ag(NH_3)_2]^+ \longrightarrow 2\,Ag\downarrow + 2\,[Cu(NH_3)_4]^{2+}$
6. $2\,[Cu(NH_3)_4]^{2+} + 2\,MgO \xrightarrow{\text{boiling}} 2\,CuO\downarrow + 2\,Mg^{2+} + 8\,NH_3\uparrow$
7. $2\,Mg^{2+} + 4\,Cl^- \xrightarrow{\text{evaporation}} 2\,MgCl_2$
8. $H_2O \longrightarrow H_2 + 0.5\,O_2$

PROBLEM 5

Compounds **B** and **C** are structural isomers. They can be obtained when hydrocarbon **A** interacts with chlorine. Hydrocarbon **A** is a basic product of an industrial organic synthesis. It can react with ozone, yielding an ozonide.

Isomer **B** can be used for the technical production of compounds **D** and **E** that are the initial compounds in the production of the fibre nylon:

6,6-$H–[NH(CH_2)_6NHCO(CH_2)_4CO]_n– OH$.

Compound **D** is soluble in bases, **E** in acids.

The reaction between isomer **C** and an alcohol solution of an alkaline base yields monomer **F** which is used for the production of chloroprene (neoprene) rubber

$–[–CH_2CCl = CHCH_2–]_n$.

This method has a technical application.

5.1 Write down the structural formulae of **A**, **B**, **C**, **D**, **E**, **F** and their names in the IUPAC nomenclature.

5.2 Write down the mechanism of the reaction between hydrocarbon **A** and chlorine. What type of reaction is it in terms of its mechanism? Which of the two isomers is obtained in larger quantities under ordinary conditions?

5.3 Write down the equations for:

- the production of **D** and **E** from isomer **B**,
- the production of monomer **F** from isomer **C**,
- the ozonolysis of hydrocarbon **A** and hydrolysis of the ozonide.

5.4 Write down the chemical scheme for an industrial production of hydrocarbon **A** from the hydrocarbon which is main component of natural gas.

5.5 For chloroprene rubber, write down the formulae of the possible steric forms of the elementary unit.

SOLUTION

5.1 **A**: $CH_2=CH-CH=CH_2$

1,3-butadiene

B: $ClCH_2-CH=CH-CH_2Cl$

1,4-dichloro-2-butene

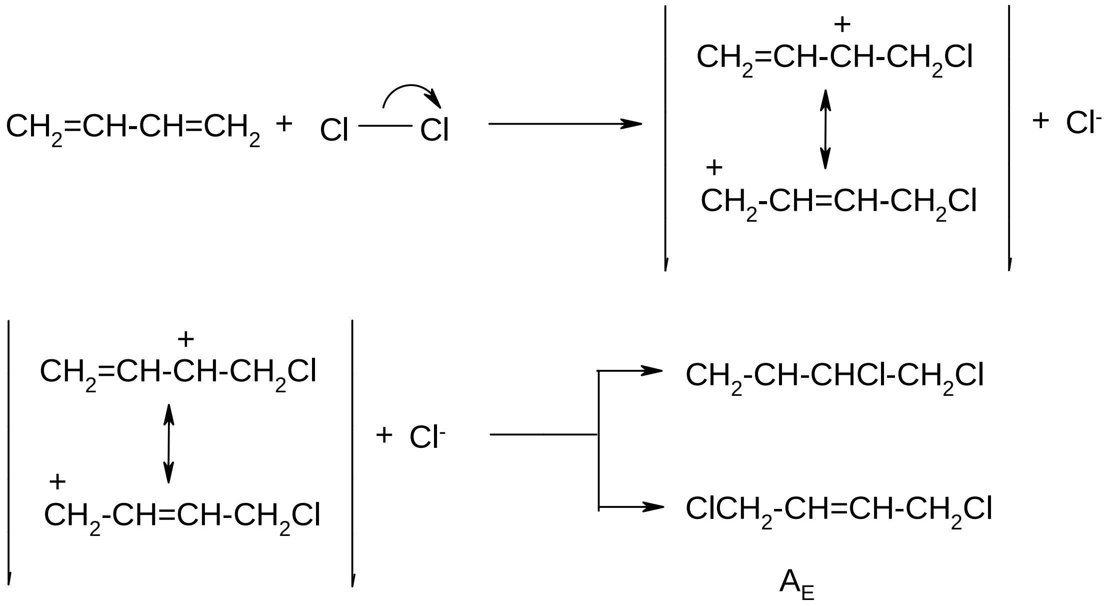
C: $CH_2=CH-CHCl-CH_2Cl$
3,4-dichloro-1-butene

D: $HOOC(CH_2)_4COOH$
hexanedioic acid

E: $H_2N(CH_2)_6NH_2$
1,6-hexandiamine

F: $CH_2=CCl-CH=CH_2$
2-chloro-1,3-butadiene

5.2



1,4-dichloro-2-butene

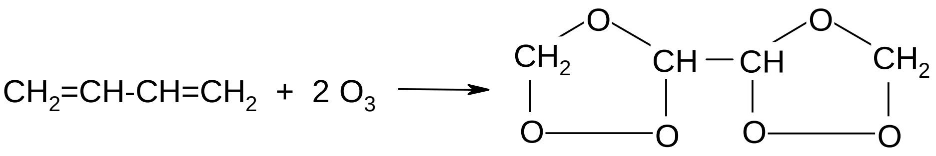
5.3 $ClCH_2CH=CHCH_2Cl + 2\ KCN \longrightarrow NCCH_2CH=CHCH_2CN + 2\ KCl$

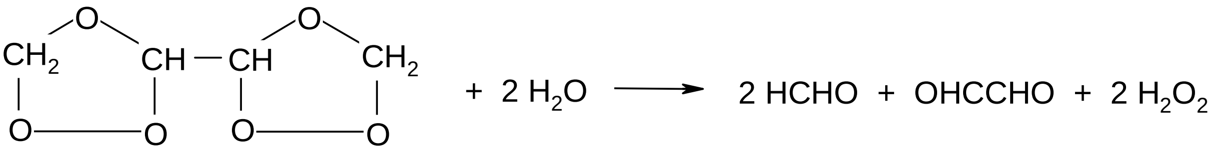
$$NCCH_2CH=CHCH_2CN + H_2 \xrightarrow{\text{cat.}} NCCH_2CH_2CH_2CH_2CN$$

$$NC(CH_2)_4CN + 4\ H_2O \xrightarrow[(HO^- \text{ or } H^+)]{\text{cat.}} HOOC(CH_2)_4COOH + 2\ NH_3$$

$$NC(CH_2)_4CN + 4\ H_2 \longrightarrow H_2N(CH_2)_6NH_2$$

$$CH_2=CHCHClCH_2Cl + OH^- \longrightarrow CH_2=CH–CCl=CH_2 + Cl^- + H_2O$$





5.4

$$CH_4 \xrightarrow[\triangle]{-\,H_2} CH\equiv CH \xrightarrow[Hg^{2+}]{+\,H_2O} CH_3CHO \xrightarrow[OH^-]{+\,CH_3CHO} CH_3CH(OH)CH_2CHO \longrightarrow$$

$$\xrightarrow[Ni]{+\,H_2} CH_3CH(OH)CH_2CH_2OH \xrightarrow{-\,H_2O} CH_2{=}CH\text{-}CH{=}CH_2$$

or

$$CH_4 \xrightarrow[\triangle]{-\,H_2} CH\equiv CH \xrightarrow[OH-]{+\,HCHO} HOCH_2\text{-}C\equiv C\text{-}CH_2OH \longrightarrow$$

$$\xrightarrow[Ni]{+\,H_2} HO(CH_2)_4OH \xrightarrow{-\,H_2O} CH_2{=}CH\text{-}CH{=}CH_2$$

or

$$CH_4 \xrightarrow[\triangle]{-\,H_2} CH\equiv CH \xrightarrow[Cu_2Cl_2\,.\,2\,NH_4Cl]{+\,HC\equiv CH} CH_2{=}CH\equiv CH \longrightarrow$$

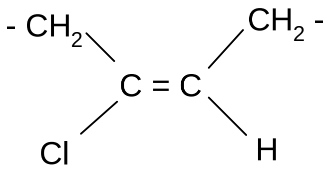
$$\xrightarrow[Zn\,+\,NaOH]{[H]} CH_2{=}CH\text{-}CH{=}CH_2$$

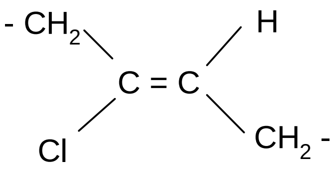
or

$$CH_4 \xrightarrow[\triangle]{-\ H_2} CH\equiv CH \xrightarrow[Hg^{2+}]{+\ H_2O} CH_3CHO \xrightarrow[Ni]{+\ H_2} CH_3CH_2OH \longrightarrow$$

$$\xrightarrow[cat.]{-\ H_2,+\ H_2O} CH_2=CH\text{-}CH=CH_2$$

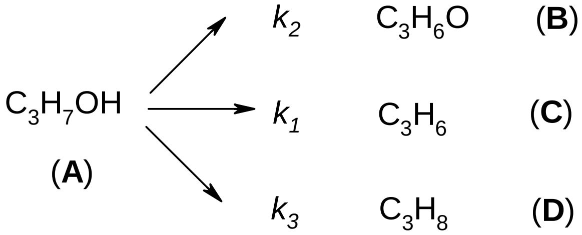
5.5





PROBLEM 6

The catalytic decomposition of isopropanol on the surface of a V_2O_5 catalyst, leading to the products in the scheme, satisfies a first order kinetic equation.



Five seconds after initiation of the reaction at 590 K, the concentrations of the components in the reaction mixture are:

c_A = 28.2 mmol dm^{-3}
c_B = 7.8 mmol dm^{-3}
c_C = 8.3 mmol dm^{-3}
c_D = 1.8 mmol dm^{-3}

6.1 What is the initial concentration c_0 of C_3H_7OH in the system?

6.2 What is the value of the rate constant k for the process:

$$C_3H_7OH \xrightarrow{k} \text{products ?}$$

6.3 What is the interval of time ($\tau_{1/2}$) in which the concentration of C_3H_7OH will reach the value $c = c_0/2$?

6.4 What are the values of rate constants k_1, k_2, and k_3?

6.5 What are the values of concentrations c_B, c_C, c_D at $t = \tau_{1/2}$?

The equation describing the concentration changes of **A** with time t for the first order reaction has the form:

$c_A = c_0 \exp(-k\,t)$

or

$\log (c_0 / c_A) = 0.4343\, k\, t$

or

$\ln (c_0 / c_A) = k\, t$

Fill in the table with the answers obtained.

1	c_0 =
2	k =
3	$\tau_{1/2}$
4	k_1 =
	k_2 =
	k_3 =
5	c_B =
	c_C =
	c_D =

SOLUTION

6.1 $c_0 = c_A + c_B + c_C + c_D = 28.2 + 7.8 + 8.3 + 1.8 = 46.1 \text{ mmol dm}^{-3}$

6.2 $$k = \frac{1}{0.4343\,t}\log\left(\frac{c_0}{c_A}\right) = \frac{1}{0.4343\times 5}\log\left(\frac{46.1}{28.2}\right) = 0.0983\,s^{-1}$$

6.3 $$t = \tau_{1/2} = \frac{1}{0.4343\,k}\log\frac{\frac{c_0}{2}}{c_0} = \frac{1}{0.4343\times 0.0983}\log 2 = 7.05\text{ s}$$

6.4

$$v_1 = \frac{\Delta c_B}{\Delta t} = k_1\,c_A$$

$$v_2 = \frac{\Delta c_C}{\Delta t} = k_2\,c_A$$

$$v_3 = \frac{\Delta c_D}{\Delta t} = k_3\,c_A$$

$v = v_1 + v_2 + v_3 = k\,c_A$

(1) $k_1 + k_2 + k_3 = k = 0.0983\text{ s}^{-1}$

(2) $$\frac{\Delta c_B}{\Delta c_C} = \frac{c_B - 0}{c_C - 0} = \frac{c_B}{c_C} = \frac{k_1}{k_2} = \frac{7.8}{8.3} = 0.940$$

(3) $$\frac{\Delta c_B}{\Delta c_D} = \frac{c_B - 0}{c_D - 0} = \frac{c_B}{c_D} = \frac{k_1}{k_3} = \frac{7.8}{1.8} = 4.33$$

From equations (1) – (3):

k_1 = 0.0428 s^{-1}

k_2 = 0.0455 s^{-1}

k_3 = 0.00988 s^{-1}

6.5 At t = $\tau_{1/2}$ = 7.05 s

(4) $$c_A = \frac{c_0}{2} = c_B + c_C + c_D = 23.05 \text{ mmol dm}^{-3}$$

From equations (2) – (4):

c_B = 10.0 mmol dm^{-3}

c_C = 10.7 mmol dm^{-3}

c_D = 2.32 mmol dm^{-3}

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Fourteen numbered test tubes contain solutions of pure inorganic substances. Each test tube contains only one substance. The samples contain the following ions:

cations K^+, Na^+, Hg_2^{2+}, Ag^+, NH_4^+, Ba^{2+}, Sr^{2+}, Fe^{3+};

anions $OH^–$, NO_3^-, $Cl^–$, $SCN^–$, $I^–$, CO_3^{2-}, $Cr_2O_7^{2-}$, CrO_4^{2-}, $Fe(CN)_6^{4-}$, $Co(NO_2)_6^{3-}$.

Determine the contents of the test tubes. In addition to reactions between samples, the only other possible reagent is a solution of hydrochloric acid with a concentration of 2 mol dm^{-3}.

Fill in the following information on the sheet provided:

1. The chemical formulae of the individual samples and the numbers of the corresponding test tubes.
2. The chemical formulae in ionic form on the basis of which you demonstrated the presence of individual cations present in the samples.

PROBLEM 2 (practical)

Determine the samples in the test tubes using the following reagents: $FeCl_3$ (2.5 % aqueous solution), water, 2,4-dinitrophenylhydrazine, Lucas' reagent ($ZnCl_2$ – HCl), NaOH (5 % aqueous solution), $NaHCO_3$ (5 % aqueous solution), HCl (conc.), Fehling's solution (an alkaline aqueous solution containing Cu^{2+} ions; this is prepared immediately prior to use by mixing identical volumes of Fehling's solutions I and II), Tollen's reagent (prepared immediately prior to use by mixing identical volumes of 10 % solution of $AgNO_3$ and an NaOH solution with a concentration 2 mol dm^{-3}. Finally, ammonia is added dropwise to complete dissolution of silver dioxide.

Write the results of your observations during testing the unknown substances with the reagents into the table provided.

Write the (IUPAC) names and structural formulae for the substances in the test tubes.

Write the chemical equations for the reactions on the basis of which the individual substances were identified. Write only a reaction scheme where this not possible.

PROBLEM 3 (practical)

Volumetric determination of sodium carbonate and sodium hydrogen carbonate simultaneously.

A) *Procedure:*

1. Determination of the precise concentration of an HCl solution (0.1 mol dm^{-3}) using borax $Na_2B_4O_7 . 10 H_2O$ as a standard.

   Principle:

   An aqueous solution of sodium tetraborate reacts with hydrochloric acid to form trihydrogenboric acid.

   Procedure:

   25.00 cm^3 of a standard borax solution with a concentration of about 0.05 mol dm^{-3} (the exact borax concentration is written on the label on the volumetric flask; the solution needs not be diluted with water to a volume of 100 cm^{-3}) is transferred into a titration flask, 1 to 2 drops of methyl red are added and the solution is titrated to the first orange coloration of the yellow solution. The titration should be carried out at least twice. The consumption of hydrochloric acid should be designated by symbol V_1.

2. Volumetric determination of Na_2CO_3 and $NaHCO_3$ simultaneously.

   Procedure:

   The sample in a volumetric flask (250 cm^3) should be diluted to the mark with distilled water from which the carbon dioxide has been removed by boiling, and mix.

   a) Part of the solution (25 cm^3) is titrated with an HCl solution using methyl orange (2 drops) to the first red coloration of the originally yellow solution. The sample is boiled 2 to 3 minutes to release carbon dioxide. Then the solution is cooled and the titration is continued to a clear red coloration of the solution. The titration should be carried out at least twice. The consumption of hydrochloric acid should be designated as V_2 (average of titration values).

   b) A further part of the sample (25.00 cm^3) is transferred to an Erlenmeyer flask and mixed with 25.00 cm^3 of the NaOH solution with a concentration of 0.1 mol dm^{-3}. Add 10 cm^3 of a 10 % solution of $BaCl_2$ and 2 drops of phenolphthalein. Excess hydroxide should be titrated immediately in the presence of a white precipitate formed, using an HCl solution whose precise concentration has been determined

c) in part 1. The consumption of hydrochloric acid should be denoted as V_3 (average values of at least two titrations).

d) Carry out the same titration as in part b) without the sample (blank). The consumption of HCl is designated as V_4 (average of two titrations).

Use the results of the above experiments to calculate the amounts of Na_2CO_3 and $NaHCO_3$ in the sample.

B) Results

The results should be written into the form provided in which you should note the following:

a) The ionic equation for the reaction according to which the concentration of the HCl solution was determined.

b) The ionic equation for the reaction used in the determination of Na_2CO_3 and $NaHCO_3$ simultaneously.

c) The volume of hydrochloric acid consumed in the titration of 25.00 cm^3 of borax solution.

d) Calculation of the HCl concentration (in mol dm^{-3}).

e) Consumption of the HCl solution – V_2, V_3, and V_4.

f) Mass amounts of Na_2CO_3 and $NaHCO_3$ in the sample in grams.

$M(Na_2CO_3) = 105.989$ g mol^{-1}

$M(NaHCO_3) = 84.007$ g mol^{-1}

14th

International Chemistry Olympiad

7 theoretical problems
3 practical problems

THE FOURTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
3–12 JULY 1982, STOCKHOLM, SWEDEN

THEORETICAL PROBLEMS

PROBLEM 1

A. The IUPAC name of the compound $[Co(NH_3)_6]Cl_2$ is

a) cobalt(II) hexaammonia dichlorine,

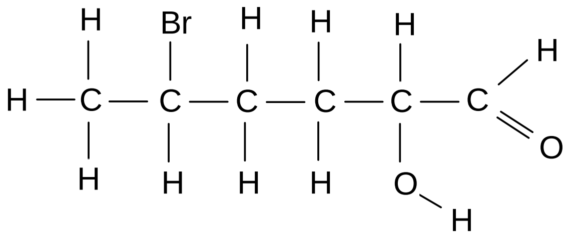
b) cobalt(II) hexaammonia dichloride,

c) hexaamminecobalt(II) chloride.

d) hexaamminedichlorocobalt(II)

e) cobalt(II) chloride-hexaammonia

B. The IUPAC name of the compound



is:

a) 5-bromo-1-hexanoic acid

b) 5-bromo-2-hydroxy-1-hexanal

c) 2-bromo-5-hydroxy-6-hexanal

d) 2-bromo-2-hydroxy-1-hexanal

e) 5-bromo-2-hydroxy-1-hexanone

C. Which of the following acid-base pairs is most suitable for keeping the pH constant at 9 in an aqueous solution?

a) CH_3COOH — CH_3COO^-

b) NH_4^+ — NH_3

c) H_2CO_3 — HCO_3^-

d) $H_2PO_4^-$ — HPO_4^{2-}

e) $H_2C_2O_4$ — $HC_2O_4^-$

D. One of the following statements cannot be correct. State which one.

a) A water-soluble solid contains Mg^{2+}, Cr^{3+}, and Br^-.

b) A solid soluble in a sodium hydroxide solution contains Al^{3+}, K^+, and SO_4^{2-}.

c) A solid soluble in aqueous ammonia solution contains Ag^+, Cu^{2+}, and Cl^-.

d) A solid soluble in nitric acid contains Ba^{2+}, Fe^{2+}, and CO_3^{2-}.

e) A solution neutral to litmus contains Na+, Ca^{2+}, and PO_4^{3-}.

E. Complete the following equation:

$H_3AsO_4 + Zn \rightarrow AsH_3 + Zn^{2+}$

The reaction is carried out in an acid solution. Fill in the missing particles and balance the reaction equation.

F. State the degree of protolysis of acetic acid with concentration of 0.25 mol dm^{-3}.

$K_a(HAc) = 1.8 \times 10^{-5}$.

a) 0.021 %; b) 0.21 %; c) 0.84 %; d) 1.3 %; e) 8.4 %

G. A solution with a volume of 1.00 dm^3 is saturated with lead iodide, PbI_2. The concentration of iodide ions is 2.7 mol dm^{-3}. Determine the solubility product of PbI_2.

a) 3.6×10^{-6}; b) 2.0×10^{-8}; c) 9.8×10^{-9}; d) 2.5×10^{-9}; e) 4.9×10^{-9}.

H. The following standard enthalpies of formation are given:

Compound	ΔH^0
Acetic acid	- 0.50 MJ mol^{-1}
Carbon dioxide	- 0.40 MJ mol^{-1}
Water	- 0.30 MJ mol^{-1}

The ΔH^0 of combustion of acetic acid is:

a) 0.90 MJ mol^{-1}; b) - 0.90 MJ mol^{-1}; c) - 0.20 MJ mol^{-1};

d) - 2.1 MJ mol^{-1}; e) 0.20 MJ mol^{-1}

I. $COCl_2(g)$ is introduced in an empty vessel at a pressure of *a*. It dissociates and the following equilibrium is established at constant temperature:

$2\ COCl_2(g) \rightleftharpoons C(graphite) + CO_2(g) + 2\ Cl_2(g)$

If x represents the partial pressure of $CO_2(g)$ at equilibrium, what is the equilibrium expression?

a) $\frac{4x^3}{(a-2x)^2} = K_p$ b) $\frac{2x^4}{(a-2x)^2} = K_p$ c) $\frac{2x^3}{(a-x)^2} = K_p$

d) $\frac{4x^3}{(a-x)^2} = K_p$ e) $\frac{x^3}{(a-3x)^2} = K_p$

K. For a metal M the following redox data are known:

E^0 = - 0.60 V for $M^{2+}(aq) + e^- \rightarrow M^+(aq)$

E^0 = 0.40 V for $M^{4+}(aq) + 2\,e^- \rightarrow M^{2+}(aq)$

The E^0 for $M^{4+}(aq) + 3\,e^- \rightarrow M^+(aq)$ is then:

a) - 0.20 V b) - 1.00 V c) 1.00 V d) 0.07 V e) - 0.07 V

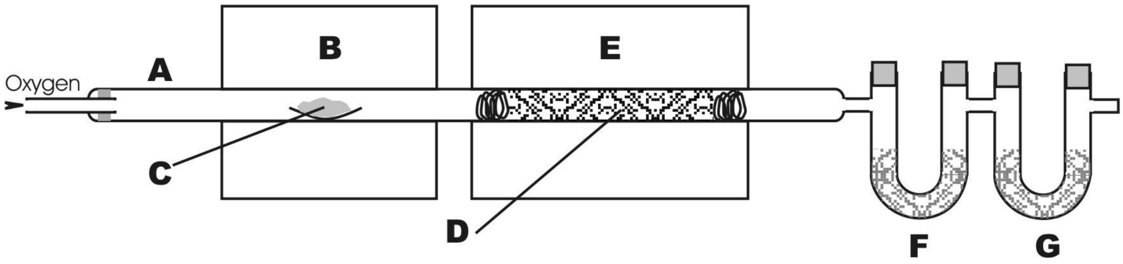
SOLUTION

A. c) B. b) C. b) D. e)

E. $H_3AsO_4 + 4\,Zn + 8\,H^+ \rightarrow AsH_3 + 4\,Zn^{2+} + 4\,H_2O$

F. c) G. c) H. b) I. a) K. d)

PROBLEM 2



Quantitative analysis for carbon and hydrogen was originally carried out using a technique and apparatus (see figure) originally developed in 1831 by the famous chemist Justus Liebig. A carefully weighed sample of organic compound (C) is placed in a combustion tube (A) and vaporized by heating in a furnace (B). The vapours are swept by a stream of oxygen through a heated copper oxide packing (D) and through another furnace (E), which ensures the quantitative oxidation of carbon and hydrogen to carbon dioxide and water. The water vapour is absorbed in a weighed tube (F) containing magnesium perchlorate and the carbon dioxide in another weighed tube (G) containing asbestos impregnated with sodium hydroxide.

A pure liquid sample containing only carbon, hydrogen and oxygen is placed in a 0.57148 g platinum boat, which on reweighing weights 0.61227 g. The sample is ignited and the previously weighed absorption tubes are reweighed. The mass of the water absorption tube has increased from 6.47002 g to 6.50359 g, and the mass of the carbon dioxide tube has increased from 5.46311 g to 5.54466 g.

2.1 Calculate the mass composition of the compound.

2.2 Give the empirical formula of the compound.

To estimate the molar mass of the compound, 1.0045 g was gasified. The volume, measured at a temperature of 350 K and a pressure of 35.0 kPa, was 0.95 dm^3.

2.3 Give the molar mass and the molecular formula of the compound.

2.4 Draw possible structures corresponding to the molecular formula excluding cyclic structures, stereo isomers, peroxides and unsaturated compounds. There are about 15 possibilities. Give 10 of them.

When the compound is heated with a sodium hydroxide solution, two products are formed. Fractional distillation of the reaction mixture yields one of the substances. The other substance is purified by distillation after acidification and appears to be an acid.

2.5 What structures are possible for compound C?

0.1005 g of the acid are dissolved in water and titrated with a sodium hydroxide solution with a concentration of 0.1000 mol dm^{-3}. The indicator changes colour on addition of 16.75 cm^3 of hydroxide solution.

2.6 What was the original substance C?

SOLUTION

2.1 Mass percentage composition: 54.56 % C; 9.21 % H; 36.23 % O

2.2 Empirical formula: C_2H_4O

2.3 Molar mass: 88 g mol^{-1}

Molecular formula: $C_4H_8O_2$

2.4 Possible structures:

1. CH_3-CH_2-CH_2-COOH
2. CH_3-CH(CH_3)-COOH
3. CH_3-O-CO-CH_2-CH_3
4. CH_3-CH_2-O-CO-CH_3
5. CH_3-CH_2-CH_2-O-CO-H
6. CH_3-CH(CH_3)-O-CO-H
7. CH_3-CH_2-CH(OH)-CHO
8. CH_3-CH(OH)-CH_2-CHO
9. CH_2(OH)-CH_2-CH_2-CHO
10. CH_3-C(OH)(CH_3)-CHO
11. CH_2(OH)-CH(CH_3)-CHO
12. CH_3-O-CH_2-CH_2-CHO
13. CH_3-CH_2-O-CH_2-CHO
14. CH_3-O-CH(CH_3)-CHO
15. CH_3-CH_2-CO-CH_2-OH
16. CH_3-CH(OH)-CO-CH_3
17. CH_2(OH)-CH_2-CO-CH_3
18. CH_3-O-CH_2-CO-CH_3

2.5 The possible structures are 3, 4, 5, 6.

2.6 The structure of the compound C is CH_3-CH_2-O-CO-CH_3.

PROBLEM 3

In a chemical factory in which formaldehyde is produced by oxidation of methanol, aqueous solutions containing methanol and formaldehyde are to be analyzed. In order to test the method, experiments are first carried out with known amounts of both methanol and formaldehyde. The following aqueous solutions are used:

Methanol, 5.00 g dm^{-3}
Formaldehyde, 5.00 g dm^{-3}
Potassium dichromate, 3.000×10^{-2} mol dm^{-3}
Ammonium iron(II) sulphate, 0.2000 mol dm^{-3}
Iodine, 0.1000 mol dm^{-3}
Sodium thiosulphate, 0.2000 mol dm^{-3}.

I. 10.00 cm^3 methanol solution and 100.00 cm^3 potassium dichromate solution are mixed, approximately 100 cm^3 concentrated sulphuric acid is added and the solution is allowed to stand for about 30 minutes. Excess dichromate ions are then titrated with iron(II) ions with diphenylamine sulphonic acid as a redox indicator (colour change from red-violet to pale green). The volume of the iron(II) solution consumed is 43.5 cm^3.

II. 10.00 cm^3 of formaldehyde solution and 50.00 cm^3 of iodine solution are mixed. Sodium hydroxide solution is added to alkaline reaction and the mixture is left standing for about 10 minutes. Hydrochloric acid is then added to a neutral reaction, and the excess iodine is determined by titration with thiosulphate, with starch as an indicator. The volume of the thiosulphate solution required is 33.3 cm^{-3}.

3.1 Using the analysis data in I and II calculate the reacting amounts and the molar ratios of methanol/dichromate ions and formaldehyde/iodine.

3.2 Write balanced equations for all reactions described in experiments I and II.

III. It is checked that iodine does not react with methanol. From a solution containing both methanol and formaldehyde, two 10.00 cm^3 samples are taken.

One sample is mixed with 100.00 cm^3 of potassium dichromate solution and concentrated sulphuric acid as in I. Excess dichromate ions consume 4.8 cm^3 of iron(II) solution.

The other sample is mixed with 50.00 cm^3 of iodine solution and treated as in II. Excess iodine consumes 16.50 cm^3 of thiosulphate solution.

3.3 Give balanced equations for the reactions and calculate the contents of methanol and formaldehyde in the solution. Give your answer in g dm^{-3}.

SOLUTION

3.1 Amounts of substance:

methanol	1.56 mol
dichromate ions	3.00 mol
iron(II) ions	8.70 mol

Molar ratio methanol/dichromate: 1 mol $CH_3OH \Rightarrow$ 1 mol $Cr_2O_7^{2-}$

Amounts of substance:

formaldehyde	1.67 mol
iodine	5.00 mol
thiosulphate ions	6.66 mol

Molar ratio formaldehyde/iodine: 1 mol HCHO $\Rightarrow$ 1 mol I_2

3.2 Chemical equations:

$CH_3OH + Cr_2O_7^{2-} + 8\ H^+ \rightarrow CO_2 + 2\ Cr^{3+} + 6\ H_2O$

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

$I_2 + 2\ OH^- \rightarrow IO^- + I^- + H_2O$

$HCHO + IO^- + OH^- \rightarrow HCOO^- + I^- + H_2O$

$IO^- + I^- + 2\ H^+ \rightarrow I_2 + H_2O$

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

In (3), (5), and (6), I_3^- may participate instead of I_2.

As an alternative to (4)

$HCHO + I_2 + 2\ OH^- \rightarrow HCOO^- + 2\ I^- + H_2O$ is acceptable.

3.3 Chemical equations

To the chemical equations above is added

$3\ HCHO + 2\ Cr_2O_7^{2-} + 16\ H^+ \rightarrow 3\ CO_2 + 4\ Cr^{3+} + 11\ H_2O$

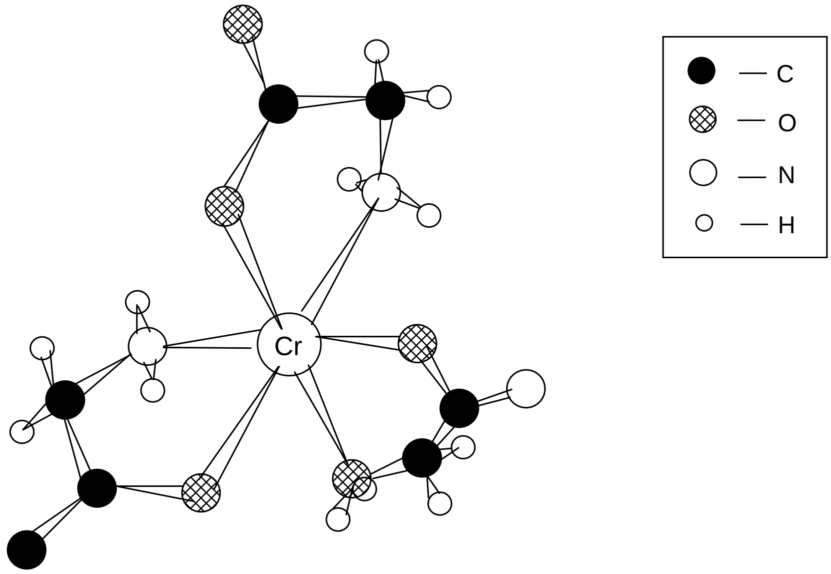
Content of methanol: 1.9 g dm^{-3}

Content of formaldehyde: 10.1 g dm^{-3}

PROBLEM 4

A transition metal atom or ion may be directly bonded to a number of atoms or molecules that surround it (ligands), forming a characteristic pattern. This is the essential structural feature of an important class of so-called coordination or complex compounds. If two or more atoms from one individual ligand form bonds to the same central atom then the ligand is said to form a chelate (Greek chele = crab' claw).

The glycinate ion, $NH_2–CH_2–COO^-$, is a bidentate chelate ligand which can form, for instance, tris-glycinato-chromium(III) complexes. The figure shows one possible structure of such a complex. Oxygen and nitrogen are forced to coordinate to adjacent octahedral positions, as the N – C – C – O chain is too short to "embrace" the chromium ion.



4.1 How many different configurational isomers of the complex are possible, not counting optical isomers?

4.2 Which of these isomers can be further resolved into optical isomers?

Another coordination compound of chromium was analyzed and found to have the following mass composition: 19.5 % Cr, 40.0 % Cl, 4.5 % H, and 36.0 % O. A 0.533 g sample of the compound was dissolved in 100 cm^3 of water, and 10 cm^3 of nitric acid (2 mol dm^{-3}) was added. Excess of silver nitrate solution was then added and the precipitate formed was then filtered, washed, dried and weighed. Its mass was found to be 0.287 g.

When a 1.06 g sample was gently heated to 100 ℃ in a stream of dry air, 0.144 of water was driven off.

The freezing point of a solution prepared from 1.33 g of the compound and 100 cm^3 of water, was found to be –0.18 ℃. (Molar freezing point depression of water is 1.82 K kg mol^{-1}).

Use all the experimental information to solve the following problems:

4.3 Derive the empirical formula of the compound.

4.4 Deduce formula for the compound showing the ligands of the chromium ion. Give molar ratios to support your result.

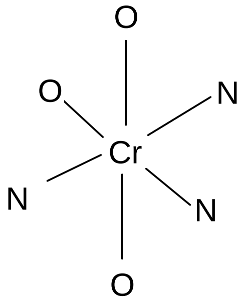
4.5 Sketch all possible steric arrangements of the ligands about the chromium ion.

SOLUTION

4.1 Two geometrical isomers of the complex are possible:

i) the facial, which is the one illustrating the problem,

ii) the meridional, with oxygen and nitrogen positions as shown:



4.2 It is clearly seen that any complex with three bidentate ligands attached octahedrally as shown, lacks mirror symmetry. Hence, both stereoisomers are further resolvable into optical isomers.

4.3 The empirical formula is $CrCl_3H_{12}O_6$.

4.4 The reaction with silver ions indicates that

1 mol $CrCl_3H_{12}O_6$ $\hat{=}$ 1 mol Cl^-

Gentle heating gives

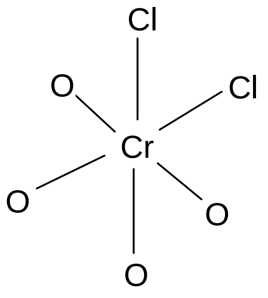
1 mol $CrCl_3H_{12}O_6$ $\hat{=}$ 2 mol H_2O

These results support the coordination $[CrCl_2(H_2O)_4]Cl \cdot 2\,H_2O$.

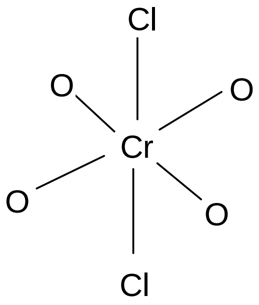
This formula is supported by the freezing point experiment showing that

1 mol $CrCl_3H_{12}O_6$ $\hat{=}$ 2 mol ions in solution

4.5 Possible steric arrangements of the ligands about the chromium atom:



cis-form



trans-form

PROBLEM 5

Iodine is soluble to a certain extent in pure water. It is, however, more soluble in solutions containing iodide ions. By studying the total solubility of iodine as a function of iodide concentration, the equilibrium constants of the following reactions can be determined:

Equation			Equilibrium constants	
$I_2(s)$	$\rightleftharpoons$	$I_2(aq)$	k_1	(1)
$I_2(s) + I^-(aq)$	$\rightleftharpoons$	$I_3^-(aq)$	k_2	(2)
$I_2(aq) + I^-(aq)$	$\rightleftharpoons$	$I_3^-(aq)$	k_3	(3)

5.1 Give the equilibrium equations for (1) – (3).

Solutions of known potassium iodide concentration $[I^-]_{tot}$ were equilibrated with solid iodine. Subsequent titration with sodium thiosulphate solution served to determine the total solubility of iodine $[I_2]_{tot}$.

The experiments yielded the following results:

$[I^-]_{tot}$ / mmol dm^{-3}	10.00	20.00	30.00	40.00	50.00
$[I^-]_{tot}$ / mmol dm^{-3}	5.85	10.53	15.11	19.96	24.82

5.2 Plot $[I_2]_{tot}$ versus $[I^-]_{tot}$ in a diagram.

5.3 Derive a suitable algebraic expression relating $[I_2]_{tot}$ and $[I^-]_{tot}$.

5.4 Use the graph to determine values of the equilibrium constants k_1, k_2, and k_3.

SOLUTION

5.1 Equilibrium equations

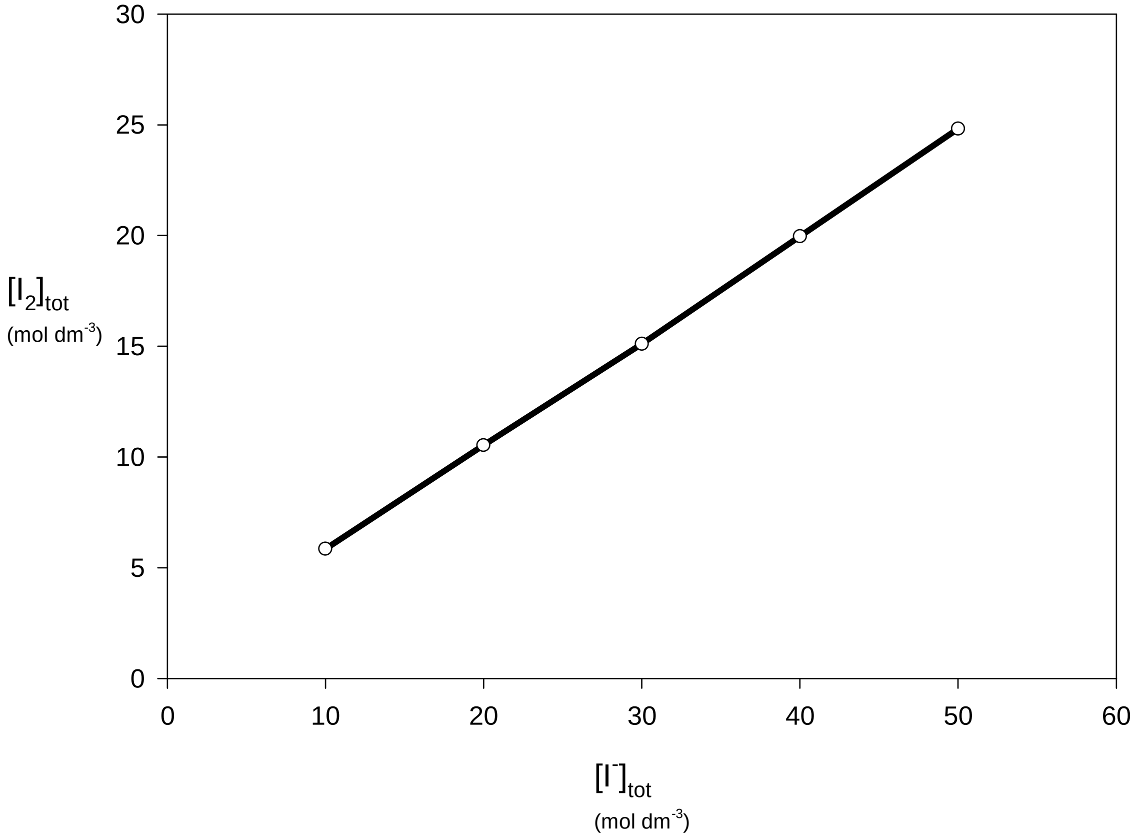
The following relations are valid for the concentrations of the aqueous solutions:

$$\left[I_2\right] = k_1$$

$$\frac{\left[I_3^-\right]}{\left[I^-\right]} = k_2$$

$$\frac{\left[I_3^-\right]}{\left[I_2\right]\left[I^-\right]} = k_3 = \frac{k_2}{k_1}$$

5.2 See diagram on the next page.



5.3 The relation between $[I_2]_{tot}$ and $[I^-]_{tot}$ is as follows:

$$[I_2]_{tot} = k_1 + \frac{k_2}{1 + k_2}[I^-]_{tot}$$

5.4 $k_1 = 1.04 \times 10^{-3}$ mol dm^{-3} $k_2 = 0.90$ $k_3 = 8.6 \times 10^2$ mol^{-1} dm^3

(These values are calculated by the least square method.)

PROBLEM 6

A white solid organic acid, **A,** contains only carbon, hydrogen and oxygen. To obtain an approximate value for the molar mass, 10.0 g of the acid were dissolved in water. Crushed ice was added and vigorous shaking caused a decrease in temperature to – 2.5 °C. The ice was quickly removed. The mass of the solution was 76.1 g, and its pH value was determined to be 1.4. In a handbook the molar freezing point depression constant for water was found to be 1.86 K kg mol^{-1}. A more precise determination of the molar mass of the acid was then carried out. 0.120 g of the acid was titrated with a sodium hydroxide solution with a concentration of 0.100 mol dm^{-3}. Phenolphthalein was used as an indicator, and when 23.4 cm^{3} of hydroxide solution was added the indicator turned red.

6.1 Give the molar mass and the structure of acid **A**.

Liquid **B** dissolves in water up to 10 %. The pH value of the solution is about 4. **B** is not easily oxidized, but following the iodoform reaction and subsequent acidification it is oxidized to acid **A**. 0.10 g of **B** consumes 1.5 g of iodine.

When **B** reacts with sodium, hydrogen is evolved and a metal organic compound is formed. The molar mass of **B** is approximately 100 g mol^{-1}.

6.2 Write the chemical equation for the iodoform reaction and for the reaction with sodium. For the organic molecules structural formulas should be used.

Compound **C** in aqueous solution has a conductivity which differs very little from that of pure water. Alkaline hydrolysis of **C** yields ammonia. 0.120 g of **C** was treated with hot, dilute sodium hydroxide solution and the gas formed was led into 50.0 cm^{3} hydrochloric acid with a concentration of 0.100 mol dm^{-3}. The excess acid was titrated with 10.0 cm^{3} sodium hydroxide solution with a concentration of 0.100 mol dm^{-3}.

Acid hydrolysis of **C** yields carbon dioxide. From the freezing point depression, the molar mass of **C** is estimated to be between 40 g mol^{-1} and 70 g mol^{-1}.

6.3 Give the structure of **C**. Write reaction equations for both the alkaline and the acid hydrolysis.

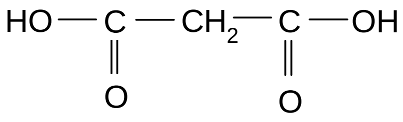
If **C** is allowed to react with the ethyl ester of acid **A** in the presence of a strong alkaline catalyst, ethanol and compound **D** are formed. The composition of **D** is 37.5 % C, 3.1 % H, 21.9 % N, and the reminder is oxygen. The compound is an acid.

6.4 Give the structure for **D**. Which is the "acid" hydrogen atom? Mark it with * in the structure.

SOLUTION

6.1 Molar mass of **A**: 103 g mol^{-1}

Structure of **A**:



$$HO-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OH$$

6.2 $CH_3\text{-}CO\text{-}CH_2\text{-}CO\text{-}CH_3 + 6\ I_2 + 8\ OH^- \rightarrow {}^-O\text{-}CO\text{-}CH_2\text{-}CO\text{-}O^- + 2\ CHI_3 + 6\ I^-$

${}^-O\text{-}CO\text{-}CH_2\text{-}CO\text{-}O^- + 2\ H^+ \rightarrow HO\text{-}CO\text{-}CH_2\text{-}CO\text{-}OH$

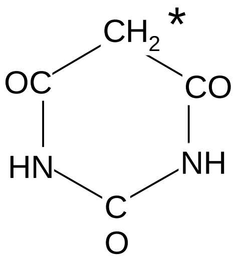
$2\ CH_3\text{-}CO\text{-}CH_2\text{-}CO\text{-}CH_3 + 2\ Na \rightarrow 2\ CH_3\text{-}CO\text{-}\underset{-}{C}H\text{-}CO\text{-}CH_3 + H_2 + 2\ Na^+$

6.3 $H_2N\text{-}CO\text{-}NH_2$

$H_2N\text{-}CO\text{-}NH_2 + 2\ OH^- \rightarrow 2\ NH_3 + CO_3^{2-}$

$H_2N\text{-}CO\text{-}NH_2 + 2\ H^+ + H_2O \rightarrow 2\ NH_4^+ + CO_2\ CO_3^{2-}$

6.4



* - "acid" hydrogen

PROBLEM 7

Calcium oxalate, $CaC_2O_4.H_2O$, is a sparingly soluble salt of analytical and physiological importance. The solubility product is 2.1×10^{-9} at 25 °C. Oxalate ions can protolyse to form hydrogen oxalate ions and oxalic acid. The pK_a values at 25 °C are 1.23 ($H_2C_2O_4$) and 4.28 ($HC_2O_4^-$). At 25 °C the ionic product of water is 1.0×10^{-14}.

7.1 State those expressions for the equilibrium conditions which are of interest for the calculation of the solubility of calcium oxalate monohydrate.

7.2 State the concentration conditions which are necessary for the calculation of the solubility *s* (in mol dm^{-3}) of calcium oxalate in a strong acid of concentration *C*.

7.3 Calculate the solubility (in g dm^{-3}) of calcium oxalate monohydrate in a plant cell in which the buffer system regulates the pH to 6.5.

7.4 Calculate the solubility (in g dm^{-3}) of calcium oxalate monohydrate in hydrochloric acid with a concentration of 0.010 mol dm^{-3}. Give the concentration of hydrogen ions in the solution.

7.5 Calculate the equilibrium concentrations of all other species in solution d).

SOLUTION

7.1 $\left[Ca^{2+}\right]\left[C_2O_4^{2-}\right] = K_s$ (1) $\qquad$ $\left[H^+\right]\left[OH^-\right] = K_w$ (2)

$$\frac{\left[H^+\right]\left[HC_2O_4^-\right]}{\left[H_2C_2O_4\right]} = K_{a1} \quad (3) \qquad \frac{\left[H^+\right]\left[C_2O_4^{2-}\right]}{\left[HC_2O_4^-\right]} = K_{a2} \quad (4)$$

7.2 $$s = \left[Ca^{2+}\right] = \left[C_2O_4^{2-}\right] + \left[HC_2O_4^-\right] + \left[H_2C_2O_4\right] \qquad (5)$$

$$C = \left[H^+\right] + \left[HC_2O_4^-\right] + 2\left[H_2C_2O_4\right] - \left[OH^-\right] \qquad (6)$$

Equations (5) or (6) may be replaced by

$$\left[H^+\right] + 2\left[Ca^{2+}\right] = \left[HC_2O_4^-\right] + 2\left[C_2O_4^{2-}\right] + \left[OH^-\right] + C \qquad (7)$$

7.3 The solubility of calcium oxalate monohydrate is 6.7×10^{-3}. (Calculated according to equation (8)).

7.4 Elimination of the concentrations of oxalate species using equations (1), (3), and (4) yields the following expressions for (5) and (6). (The concentration of hydroxide ions can be neglected.)

$$s_2 = K_s + \frac{\left[H^+\right] K_s}{K_{a2}} + \frac{\left[H^+\right]^2 K_s}{K_{a1} K_{a2}} \qquad (8)$$

$$C = \left[H^+\right] + \frac{\left[H^+\right] K_s}{s\, K_{a2}} + \frac{2\left[H^+\right]^2 K_s}{s\, K_{a1} K_{a2}} \qquad (9)$$

Elimination of *s* from (8) and (9) results in 4th order equation. For this reason, an iterative method is to be preferred. The first approximation is $\left[H^+\right] = C$. This value of $\left[H^+\right]$ can be used to calculate:

i) solubility *s* from (8),

ii) the last two terms in (9), which are corrections. Now a new value for $\left[H^+\right]$ obtained from (9) may be used as a starting value for the next approximation. Two repeated operations give the following value for *s*:

$s = 6.6 \times 10^{-4}$ mol dm^{-3} = 9.6×10^{-2} g dm^{-3}

$\left[H^+\right] = 9.3 \times 10^{-3}$ mol dm^{-3}

7.5

$\left[Ca^{2+}\right] = 6.6\times10^{-4}$ mol dm^{-3}

$\left[C_2O_4^{2-}\right] = 3.2\times10^{-6}$ mol dm^{-3}

$\left[Cl^-\right] = 0.010$ mol dm^{-3}

$\left[HC_2O_4^-\right] = 5.7\times10^{-4}$ mol dm^{-3}

$\left[OH^-\right] = 1.1\times10^{-12}$ mol dm^{-3}

$\left[H_2C_2O_4\right] = 9.0\times10^{-5}$ mol dm^{-3}

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

A pH buffer solution has a well defined acidity which changes only very slightly upon addition of moderate quantities of strong acid or base. The larger is the quantity of acid or base that must be added to a certain volume of a buffer solution in order to change its pH by a specific amount, the better is its action. A buffer solution is prepared by mixing a weak acid and its conjugate base in appropriate amounts in a solution. An example of a useful buffer system in aqueous solution is the phosphate system.

Your task is to prepare a phosphate buffer with properties specified by the following two conditions:

(1) pH = 7.20 in the buffer solution,

(2) pH = 6.80 in a mixture of 50.0 cm^3 of the butter solution and 5.0 cm^3 hydrochloric acid with a concentration of 0.100 mol dm^{-3}.

Chemicals and equipment

Aqueous solution of phosphoric acid, sodium hydroxide solution of known concentration, hydrochloric acid (0.100 mol dm^{-3}), solution of bromocresol green, distilled water.

Burettes, pipettes (25 and 5 cm^3), Erlenmeyer flasks (100 and 250 cm^3), volumetric flask (100 cm^3), beaker, and funnel.

Procedure

Determine the concentration of the phosphoric acid solution by titration with a sodium hydroxide solution using bromocresol green as an indicator (pH range $3.8 < pH < 5.4$).

Make a buffer solution by mixing calculated volumes of phosphoric acid and sodium hydroxide solutions in the volumetric flask and filling the flask to the mark with distilled water.

Mix in an Erlenmeyer flask 50.0 cm^3 of the buffer solution with 5.0 cm^3 of the hydrochloric acid.

Hand in your answer sheet to the referee who will also measure the pH of your two solutions and note your results.

The pK_a values for phosphoric acid are:

pK_{a1} = 1.75, pK_{a2} = 6.73, pK_{a3} = 11.50

SOLUTION

The buffer solution must contain

$H_2PO_4^-$ (concentration **a** mol dm^{-3}) and

HPO_4^{2-} (concentration **b** mol dm^{-3}).

The concentrations should satisfy the condition

$$\frac{\mathbf{b}}{\mathbf{a}} = \frac{10^{-6.73}}{10^{-7.20}}$$

After addition of HCl the condition will be

$$\frac{50.0\,b\ -\ 0.50}{50.0\,a\ +\ 0.50} = \frac{10^{-6.73}}{10^{-6.80}}$$

From these equations,

a = 0.0122 **b** = 0.0361

Total concentration of the phosphate system = 0.0483 mol dm^{-3}

Total concentration of Na^+ = (**a** + 2 **b**) mol dm^{-3} = 0.0844 mol dm^{-3}

If the concentration of both phosphoric acid and sodium hydroxide solution are 0.500 mol dm^{-3}, then 100.0 cm^3 buffer solution will require:

volume of H_3PO_4 solution = $\dfrac{0.0483 \times 0.1000}{0.500\,\text{dm}^3} = 9.7\,\text{cm}^3$

volume of NaOH solution = $\dfrac{0.0844 \times 0.1000}{0.500\,\text{dm}^3} = 16.9\,\text{cm}^3$

PROBLEM 2 (practical)

Each of 8 numbered test tubes contains a solution of one salt. In the solutions the following positive ions can be found (a maximum of one in each test tube):

Ag^+, Al^{3+}, Cu^{2+}, Na^+, NH_4^+, and Zn^{2+}

and the following negative ions (at most one in each test tube)

$Br^–$, $Cl^–$, $I^–$, NO_3^-, $OH^–$, and $S_3O_3^{2-}$.

A test plate, test tubes in a rack, dropping pipettes, indicator paper, and a gas burner are also provided.

Determine by means of mutual reactions which salt is dissolved in each test tube. Confirm your conclusions by carrying out as many reactions as possible. It may be necessary to use combinations of solutions and reagents.

Give a list of numbers and corresponding formulae of the substances, indicate the formation of a precipitate by a downward arrow, and gas evolution by an upward arrow in the square array provided for reporting the reactions.

Write chemical equations for all the reactions observed.

SOLUTION

Numbers of solutions mixed	Chemical equation for the observed reaction
1 + 2	$NH_4^+ + OH^– \rightarrow NH_3(g) + H_2O$
2 + 3	$2\ OH^– + 2\ Ag^+ \rightarrow Ag_2O(s) + H_2O$
2 + 3 + 1	$Ag_2O(s) + 4\ NH_4^+ + 2\ OH^– \rightarrow 2\ Ag(NH_3)_2^+ + 3\ H_2O$
2 + 4	$Zn^{2+} + 2\ OH^– \rightarrow Zn(OH)_2(s) \leftrightarrow Zn(OH)_2(s) + 2\ OH^– \rightarrow Zn(OH)_4^{2-}$
2 + 5	$Al^{3+} + 3\ OH^– \rightarrow Al(OH)_3(s) \leftrightarrow Al(OH)_3(s) + OH^– \rightarrow Al(OH)_4^-$

Reactions to distinguish Zn^{2+} from Al^{3+}:

Numbers of solutions mixed	Chemical equation for the observed reaction
2 + 4 + 1	$Zn(OH)_4^{2-} + 4\ NH_4^+ \rightarrow Zn(NH_3)_4^{2+} + 4\ H_2O$
2 + 5 + 1	$Al(OH)_4^- + 2\ NH_4^+ \rightarrow Al(OH)_3(s) + NH_3 + H_2O$
2 + 6	$Cu^{2+} + 2\ OH^– \rightarrow Cu(OH)_2(s)$

2 + 6 + 1	$Cu(OH)_2(s) + 4\ NH_4^+ + 2\ OH^- \rightarrow Cu(NH_3)_4^{2+} + 4\ H_2O$
3 + 4	$Ag^+ + Cl^- \rightarrow AgCl(s)$
3 + 6	$Ag^+ + Br^- \rightarrow AgBr(s)$
3 + 7	$Ag^+ + I^- \rightarrow AgI(s)$
3 + 8	$2\ Ag+ + S_2O_3^{2-} \rightarrow Ag_2S_2O_3(s) \leftrightarrow Ag_2S_2O_3(s) + 3\,S_2O_3^{2-} \rightarrow$ $\rightarrow 2\,Ag(S_2O_3)_2^{3-}$

Reactions to distinguish Cl^- from Br^- and from I^-

3 + 4 + 1 + 2	$AgCl(s) + 2\ NH_4^+ + 2\ OH^- \rightarrow Ag(NH_3)_2^+ + Cl^- + H_2O$
3 + 4 + 8	$AgCl(s) + 2\ S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-} + Cl^-$
3 + 6 + 1 + 2	AgBr(s) does not dissolve
3 + 6 + 8	$AgBr(s) + 2\ S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-} + Br^-$
3 + 7 + 8	AgI(s) does not dissolve
6 + 7	$2\ Cu^{2+} + 4\ I^- \rightarrow 2\ CuI(s) + I_2$
6 + 7 + 8	$I_2(s) + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

	1	2	3	4	5	6	7	8
1		↑						
2	↑		↓	↓	↓	↓		
3		↓		↓		↓	↓	↓
4		↓	↓					
5		↓						
6		↓	↓				↓	
7			↓			↓		
8			↓					

List of numbers and corresponding formulae for the substances:

1. NH_4NO_3
2. $NaOH$
3. $AgNO_3$
4. $ZnCl_2$
5. $Al(NO_3)_3$
6. $CuBr_2$
7. NaI
8. $Na_2S_2O_3$

PROBLEM 3 (practical)

Determination of the solubility product of lead(II) chloride

Shake solid lead(II) chloride:

a) with water,

b) with three solutions of sodium chloride of different concentrations,

until equilibrium is attained. Then determine the lead ion concentration by titration with EDTA. Calculate the solubility product of lead(II) chloride.

Equipment and chemicals

Volumetric flask (100 cm^3), pipettes (20 cm^3 and 10 cm^3), graduated cylinder (100 cm^3 and 25 cm^3), 4 Erlenmeyer flasks (200 – 250 cm^3) with stoppers, spatula, 4 filter funnels, filter papers, thermometer, 4 Erlenmeyer flasks (100 cm^3), titrating flasks (200 – 250 cm^3), beakers, stand with burette (50 cm^3), burette funnel, wash bottle with distilled water, glass rod.

Standard solutions of sodium chloride (0.1000 mol dm^{-3}) and EDTA (0.01000 mol dm^{-3}), solid lead(II) chloride, xylenol orange solution in a dropping bottle (0.5 % in water), solid hexamine (urotropine), nitric acid (2.5 mol dm^{-3}) in a dropping bottle.

Procedure

1. Prepare 100 cm^3 of sodium chloride solutions with concentrations of 0.0600 mol dm^{-3}, 0.0400 mol dm^{-3}, and 0.0200 mol dm^{-3}, respectively. Place the solutions in Erlenmeyer flasks with stoppers. Place 100 cm^3 of water in the fourth flask with a stopper. Add 5 spatulas of solid lead(II) chloride (about 2 g) to each, stopper the flasks and shake vigorously. Let the flasks stand for 30 minutes. Shake them occasionally. Prepare for filtration and titration in the meanwhile.
2. Measure the temperatures of the lead(II) chloride solutions and report them in the table of results. Filter the solutions through dry filters into small, dry Erlenmeyer flasks.
3. Using a pipette, transfer 10.00 cm^3 of the filtrate into a titration flask. Dilute with approximately 25 cm^3 of water, add 3 drops of xylenol orange (indicator) and 5 drops of nitric acid. Then add 5 spatulas (about 0.5 g) of solid hexamine (a weak base) and swirl gently until the solution is clear. Titrate with EDTA.

4. Calculate the concentration of lead ions and that of chloride ions in the solutions and give the solubility product K_s. Report the results in the table.
5. Answer the questions in the answer sheet.

Questions

3.1 Give the structure of EDTA. Mark those atoms which can coordinate to a metal ion with an asterisk (*).

3.2 Give the equation for the filtration reaction. EDTA may be written as H_2X^{2-}.

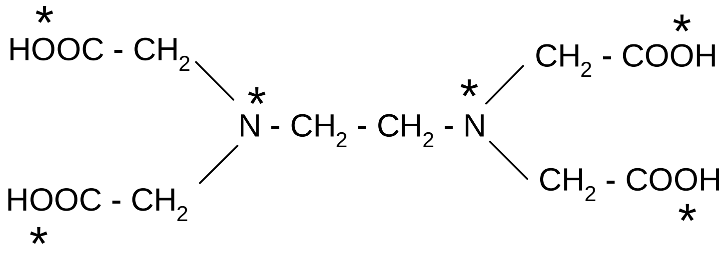
SOLUTION

A typical result:

c(NaCl) (mol dm^{-3})	Temperature (°C)	Volume EDTA solution (cm^3)	[Pb^{2+}] (mol dm^{-3})	[Cl$^-$] (mol dm^{-3})	K_s
0.0600	21	18.7	0.0187	0.0974	1.77×10^{-4}
0.0400	21	22.7	0.0227	0.0854	1.66×10^{-4}
0.0200	21	27.8	0.0278	0.0756	1.59×10^{-4}
-	21	34.2	0.0342	0.0684	1.60×10^{-4}

Answers to the questions:

3.1



3.2 $H_2Y^{2-} + Pb^{2+} \rightarrow PbY^{2-} + 2\,H^+$

15th

7 theoretical problems
3 practical problems

THE FIFTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
2–11 JULY 1983, TIMISOARA, ROMANIA

THEORETICAL PROBLEMS

PROBLEM 1

A) Describe the thermal decomposition of the following ammonium salts in terms of chemical equations:

a) $NH_4ClO_4 \xrightarrow{t\,°C}$

b) $(NH_4)_2SO_4 \xrightarrow{t\,°C}$

c) $(NH_4)_2S_2O_8 \xrightarrow{t\,°C}$

d) $NH_4NO_2 \xrightarrow{t\,°C}$

B) Indicate the right answer:

a) Can the molar mass be determined by measuring the density of a gaseous compound at a given temperature and pressure?

1. Yes, under any conditions.
2. Yes, if the gaseous compound does not dissociate and associate.
3. Yes, if the gaseous compound does not dissociate.
4. Yes, if the gaseous compound does not associate.

b) Is a liquid boiling at a constant temperature (at a given pressure) a pure substance?

1. Yes, if the liquid is not azeotropic.
2. Yes, if the liquid is azeotropic.

C) Complete and balance the following equation: (in H_2O)

$K_2Cr_2O_7 + SnCl_2 +$ .... $\rightarrow CrCl_3 +$ ....+ KCl + ...

D) The solubility of Hg_2Cl_2 in water is 3.0×10^{-5} g/100 ml solution.

a) What is the solubility product?

b) What is the solubility (in mol dm^{-3}) of this substance in a 0.01 M NaCl solution?

c) What is the volume of a 0.01 M NaCl solution which dissolves the same quantity of mercurous chloride as that dissolved in one litre of pure water?

A_r(Hg) = 200.61 A_r(Cl) = 35.45

E) Which of the following groups contains solid compounds at 10 °C?

a) H_2O, NH_3, CH_4

b) F_2, Cl_2, Br_2

c) SO_3, I_2, NaCl

d) Si, S_8, Hg

F) Which of the following salts forms an acidic aqueous solution?

a) CH_3COONa

b) NH_4Cl

c) Na_2HPO_4

d) Na_2CO_3

e) $NaHCO_3$

G) Write the electronic formulas for the following compounds so that the nature of the chemical bonds is evident:

a) $NaClO_3$, b) $HClO_3$, c) SiF_4, d) NH_3, e) CaF_2, f) H_2O

H) Solid perchloric acid is usually written as $HClO_4.H_2O$. Based on experimental data showing four equal bonds, suggest a structure accounting for the experimental result.

I) The compounds of the second row elements with hydrogen are as follows: LiH, BeH_2, B_2H_6, CH_4, NH_3, H_2O, HF.

a) Which compounds are solid at room temperature? Explain.

b) Which of them are ionic?

c) Which are polymeric?

d) Which ones do not react with water under normal conditions?

e) Give products of the following reactions.

$BeH_2 + H_2O \rightarrow$

$B_2H_6 + H_2O \rightarrow$

$B_2H_6 + LiH$

f) Supposing that NH_3, H_2O and HF are acids under some conditions, write their corresponding conjugated bases and arrange them in order of increasing basic strength.

J) The following E^0 values are given for the half-reactions:

$MnO_4^- + 8\,H^+ + 5\,e^- = Mn^{2+} + 4\,H_2O \qquad E_1^0 = 1.52\ V$

$MnO_4^- + 4\,H^+ + 3\,e^- = MnO_2 + 2\,H_2O \qquad E_2^0 = 1.69\ V$

Calculate E^0 for the following reaction:

$MnO_2 + 4\,H^+ + 2\,e^- = Mn^{2+} + 2\,H_2O \qquad E_3^0 = ?$

SOLUTION

A) a) $4\ NH_4ClO_4 \xrightarrow{t\ ^\circ C} 4\ HCl + 6\ H_2O + 2\ N_2 + 5\ O_2$

b) $3\ (NH_4)_2SO_4 \xrightarrow{t\ ^\circ C} SO_2 + N_2 + 4\ NH_3 + 6\ H_2O$

c) $2\ (NH_4)_2S_2O_8 \xrightarrow{t\ ^\circ C} 4\ SO_2 + 2\ N_2 + 8\ H_2O$

d) $NH_4NO_2 \xrightarrow{t\ ^\circ C} N_2 + 2\ H_2O$

B) a) 1, 2, 3, 4

b) 1, 2

C) $K_2Cr_2O_7 + 3\ SnCl_2 + 14\ HCl \rightarrow 2\ CrCl_3 + 3\ SnCl_4 + 2\ KCl + 7\ H_2O$

D) a) $s = 3.0 \times 10^{-5}$ g/100 cm^3 = 3.0×10^{-4} g dm^{-3} =

$$= \frac{3.0 \times 10^{-4}\ \text{g dm}^{-3}}{472\ \text{g mol}^{-1}} = 6.3 \times 10^{-7}\ \text{mol dm}^{-3}$$

$Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2\ Cl^-$

$K_s = 4\ s^3 = 4\ (6.3 \times 10^{-7})^3 = 1.0 \times 10^{-18}$

b) $c(Cl^-) = 0.01$ mol dm^{-3}

$$s = \frac{K_s}{[\text{Cl}^-]^2} = \frac{1.0\times10^{-18}}{(0.01)^2} = 1.0\times10^{-14}$$

$$s = 1.0\times10^{-14}\ \text{mol dm}^{-3}$$

c) The volume of 0.01 M NaCl solution in which dissolves the same quantity of Hg_2Cl_2 as in 1 dm^3 of water, is as follows:

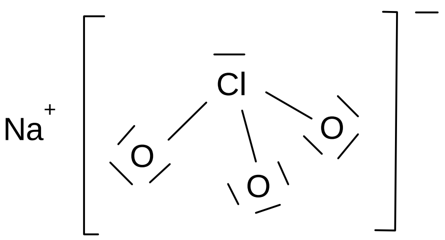
$$V = \frac{6.3\times10^{-7}}{1.0\times10^{-14}} = 6.3\times10^{7}\ \text{dm}^3$$

E) c) SO_3, I_2, NaCl

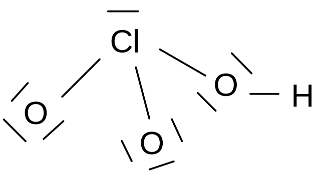
F) b)

G)

a)



b)



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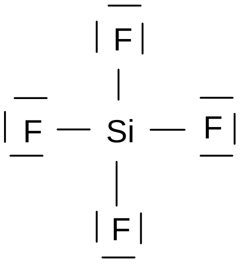

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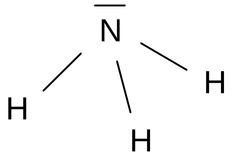
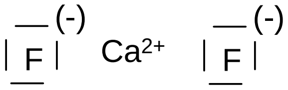
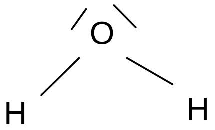


e)

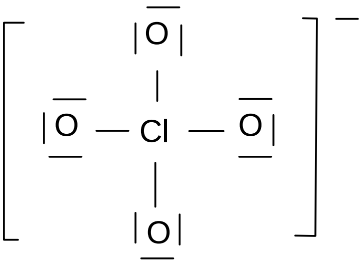


f)



H)

$H_3O^+ + ClO_4^-$ or H_3O^+



I) a) LiH, $(BeH_2)_n$ polymer

b) LiH

c) $(BeH_2)_n$

d) CH_4

e) $BeH_2 + 2\ H_2O \rightarrow Be(OH)_2 + 2\ H_2$

$B_2H_6 + 6\ H_2O \rightarrow 2\ B(OH)_3 + 6\ H_2$

$B_2H_6 + 2\ LiH \rightarrow 2\ Li[BH_4]$

f) $NH_2^- > OH^- > F^-$

J) $MnO_4^- + 4\ H^+ + 3\ e^- = MnO_2 + 2\ H_2O \qquad E_2^0 = 1.69\ V$

$MnO_2 + 4\ H^+ + 2\ e^- = Mn^{2+} + 2\ H_2O \qquad E_3^0 = ?$

$MnO_4^- + 8\ H^+ + 5\ e^- = Mn^{2+} + 4\ H_2O \qquad E_1^0 = 1.52\ V$

$5\,E_1^0 = 3\,E_2^0 + 2\,E_3^0$

$7.60 = 5.07 + 2\,x$

$x = 1.26\ V$

PROBLEM 2

In a gaseous mixture of CO and CO_2, a mass ratio of carbon : oxygen = 1 : 2 was determined.

2.1 Calculate the mass percent composition.

2.2 Calculate the volume percent composition.

2.3 Indicate values of the carbon: oxygen ratios for which both gases cannot be present simultaneously.

SOLUTION

Write x = number of moles of CO in 100 g

y = number of moles of CO_2 in 100 g

$28\,x + 44\,y = 100$

$$\frac{12\,(x+y)}{16\,(x+2y)} = \frac{1}{2}$$

x = 1.389 mol CO

y = 1,389 mol CO_2

2.1 $$\frac{1.389\times 44}{100}\times 100 = 61.11\ \%\,CO_2$$

$$\frac{1.389\times 28}{100}\times 100 = 38.89\ \%\,CO$$

2.2 X = y 50 % CO_2 + 50 % CO (by volume)

2.3 The two gases cannot be simultaneously present in the mixture if:

$$\frac{\text{carbon mass}}{\text{oxygen mass}} = \frac{12}{16}\ \text{which correspeonds to pure CO}$$

$$\frac{12}{32}\ \text{which correspeonds to pure } CO_2$$

PROBLEM 3

A sample containing a mixture of sodium chloride and potassium chloride weights 25 g. After its dissolution in water 840 ml of $AgNO_3$ solution (c = 0.5 mol dm^{-3}) is added. The precipitate is filtered off and a strip of copper weighing 100.00 g is dipped into the filtrate. After a given time interval the strip weights 101.52 g.

Calculate the mass percent composition of the mixture.

SOLUTION

$A_r(Cu) = 63.5$ $A_r(Ag) = 108$

$Cu + 2\ AgNO_3 \rightarrow Cu(NO_3)_2 + 2\ Ag$

y x

x = the quantity of deposited silver

y = the quantity of dissolved copper

$$\frac{63.5}{y} = \frac{2 \times 108}{x}$$

$x - y = 101.52 - 100$ $x = 1.52 + y$

$$\frac{63.5}{y} = \frac{2 \times 108}{1.52 + x} \qquad y = 0.63 \qquad x = 2.15\ \text{g}\ Ag^+$$

Mass of silver nitrate:

$$\frac{840}{1000} \times 0.5 \times 170 = 71.4\ \text{g}\ AgNO_3$$

$$\frac{170\ \text{g}\ AgNO_3}{108\ \text{g}\ Ag} = \frac{71.4}{x} \qquad x = 45.36\ \text{g}\ Ag^+$$

Silver consumed for participation

$45.36 - 2.15 = 43.21$ g Ag^+

Total mass of chloride

$$\frac{108\text{ g }Ag^+}{35.5\text{ g }Cl^-} = \frac{43.2}{x} \qquad x = 14.2\text{ g }Cl^-$$

$M_r(NaCl) = 58.5$ $M_r(KCl) = 74.6$

x = mass of NaCl in the mixture

y = mass of KCl in the mixture

mass of Cl^- in NaCl: $\frac{35.5\ x}{58.5}$

mass of Cl^- in KCl: $\frac{35.5\ y}{74.6}$

$$\frac{35.5\ x}{58.5} + \frac{35.5\ y}{74.6} = 14.2$$

$x + y = 25$

$x = 17.6$ g NaCl 70.4 % NaCl

$y = 7.4$ g KCl 29.6 % KCl

PROBLEM 4

The following data were gathered for the alkaline hydrolysis of certain chlorinated compounds:

a) A certain volume of a solution of the neutral potassium salt of chlorosuccinic acid is mixed with an equal volume of hydroxide solution. The initial concentration of each solution is 0.2 mol dm^{-3}. The potassium hydroxide concentration in the reaction mixture was determined at different time intervals at 25 °C. The following values were obtained:

t (minutes)	10	20	30	45	60	80	100
c(KOH) (mol dm^{-3})	0.085	0.074	0.065	0.056	0.049	0.042	0.036

The experiment was repeated with the same initial solutions at 35 °C. The hydroxide concentration is reduced to one half after 21 minutes.

b) In the hydrolysis of 3-chloro-3-methylhexane with potassium hydroxide, the concentration of potassium hydroxide was found to have been reduced to one half after 32 minutes at 25 °C or 11 minutes at 35 °C, r egardless of the initial reactant concentrations (identical).

c) In the alkaline hydrolysis of 3-chloro-2,4-dimethyl-3-isopropylpentane an identical reaction mechanism as for reaction b was found but the reaction rate was about 100 times faster under the same reaction conditions.

Considering the above data answer the following questions:

4.1 What is the reaction order in cases a, b, and c?

4.2 What is the rate constant at 25 °C for reaction a ? Indicate the units.

4.3 Calculate the activation energies for reactions a and b.

4.4 If in reaction a dipotassium salt of L-chlorosuccinic acid (which is levorotatory,) is used, what type of optical rotation will be exhibited by the corresponding salt of malic acid formed by hydrolysis?

4.5 If the levorotatory isomer is also used in reaction b, what optical rotation will be exhibited by 3-methyl-3-hexanol formed in the hydrolysis reaction?

4.6 Why is the rate of reaction c much faster than that of reaction b when both reactions are of the same type and occur under the same temperature and concentration conditions?

SOLUTION

4.1 For reaction a the reaction order is estimated as follows:

- assuming the first-order reaction:

$$k = \frac{1}{t}\ln\frac{a}{a - x}$$

t (°C)	10	20	30	45	60	80	100
k . 10^2	1.625	1.505	1.436	1.288	1.189	1.084	1.022

k is not constant, hence the reaction is not of the first-order.

- for the second-order reaction (with reactant concentrations equal at time zero):

$$k = \frac{1}{t}\left(\frac{a}{a - x} - \frac{1}{a}\right)$$

t (°C)	10	20	30	45	60	80	100
k	0.176	0.176	0.179	0.175	0.173	0.173	0.178

As *k* has almost a constant value the condition for a second-order reaction is fulfilled.

The half-life of reaction b is independent on the initial concentrations, i. e. it is a first-order reaction:

$$k = \frac{1}{t}\ln\frac{a}{a - x} = \frac{1}{t_{1/2}}\ln\frac{a}{a - \frac{a}{2}} = \frac{1}{t_{1/2}}\ln 2$$

Reaction c has the same mechanism as reaction b. Therefore, it will also be a first-order reaction.

4.2 The rate constant of reaction a is an average of the above calculated values.

$k = 0.176\ \text{dm}^3\ \text{mol}^{-1}\ \text{min}^{-1}$

4.3 In order to determine the activation energy, the rate constant, *k*', at 35 °C is to be calculated.

For the second-order reactions the relationship between the rate constants and half-lives is as follows:

$$k = \frac{1}{t}\left(\frac{a}{a-x} - \frac{1}{a}\right) = \frac{1}{t_{1/2}}\left(\frac{1}{a-\frac{a}{2}} - \frac{1}{a}\right) = \frac{1}{t_{1/2}}\,\frac{1}{a}$$

The half-life at 35 °C and the initial concentration, a = 0.1 mol dm^{-3}, are known. (By mixing equal volumes of the two solutions the concentration of each reacting species is reduced to a half.)

Calculation of the rate constant at 35 °C:

$$k' = \frac{1}{21}\cdot\frac{1}{0.1} = 0.476\ \text{dm}^3\ \text{mol}^{-1}\ \text{min}^{-1}$$

The activation energy of reaction a will be:

$$E_a = R\ln\frac{k'}{k}\cdot\frac{T'\cdot T}{T'-T} = 8314\ \ln\frac{0.476}{0.176}\cdot\frac{308\cdot 298}{308-298} = 7.592\times10^{7}\ \text{J mol}^{-1}$$

For reaction b that is a first-order reaction, the rate constants at the two temperatures are calculated from the half-lives:

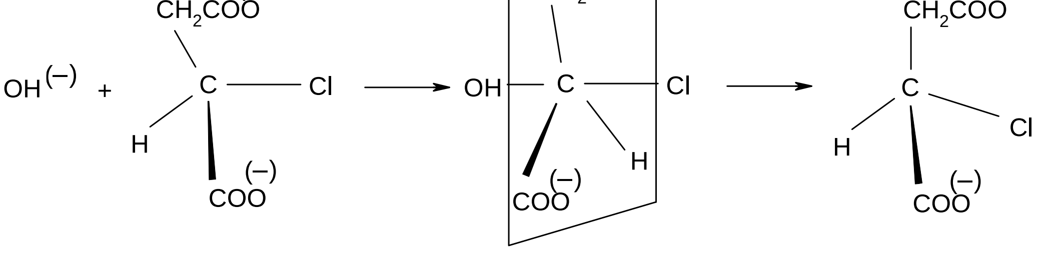
at 25 °C: $k = \frac{\ln 2}{32} = 2.166\times10^{-2}\ \text{min}^{-1}$

at 35 °C: $k' = \frac{\ln 2}{11} = 6.301\times10^{-2}\ \text{min}^{-1}$

Hence the activation energy is:

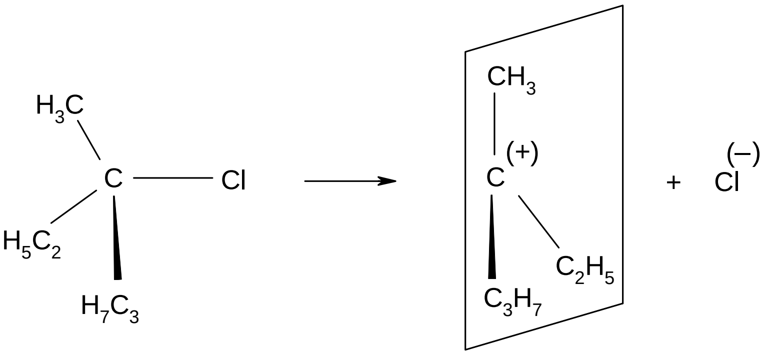
$$E_a = 8314\ \ln\frac{6.301\times10^{-2}}{2.166\times10^{-2}}\cdot\frac{308\cdot 298}{308-298} = 8.149\times10^{7}\ \text{J mol}^{-1}$$

4.4 The product of the hydrolysis reaction a will become dextrorotatory as a result of configuration inversion.



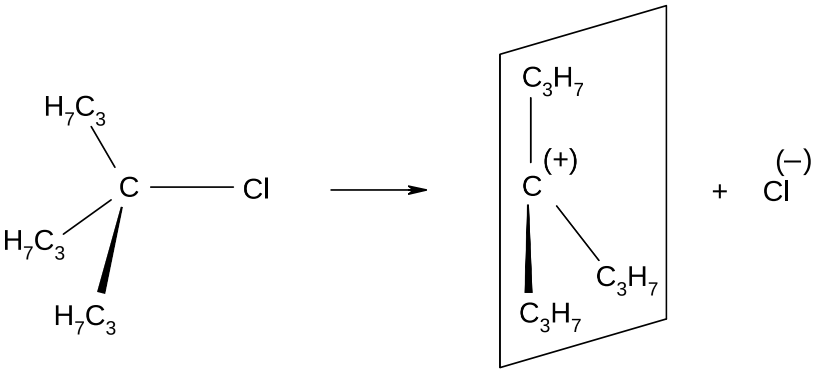
As an S$_N$2 type reaction, it involves a transition state in which the inversion of the configuration of the asymmetric carbon atom occurs. Thus, if the substrate is levorotatory, the product will become dextrorotatory.

4.5 The reaction b is a unimolecular S_N1 reaction and involves the transient formation of an almost stable carbonium ion in the rate-determining step.



The most probable structure of the carbonium ion is planar. The carbonium ion may be attached by the nucleophylic reagent (the OH^- ion) on both sides of the plane with the same probability. The product will result as a racemic mixture, with no optical activity, inactive by intermolecular compensation.

4.6 The same is true for the reaction c, the only difference being a more marked repulsion among bulkier substituents. The tendency towards carbonium ion formation with a planar structure and reduced repulsions is increased.



The rate of the carbonium ion formation, and therefore the overall reaction rate, is consequently increased.

PROBLEM 5

On passing ethanol over a catalyst at 400 K, a dehydration reaction occurs resulting in the formation of ethylene:

$C_2H_5OH(g) \rightarrow C_2H_4(g) + H_2O(g)$

At the above temperature and p_0 = 101.325 kPa, the conversion of ethyl alcohol is 90.6 mol %.

5.1 Calculate the equilibrium constant K_p of the reaction under given conditions.

5.2 Calculate the values of the equilibrium constants K_x and K_c at the above temperature.

5.3 Calculate the ethanol conversion at the following pressures:

$5\ p_0$, $10\ p_0$, $50\ p_0$, $100\ p_0$, and $200\ p_0$.

5.4 Plot the graph for the variation of conversion *vs*. pressure.

SOLUTION

The reaction: $C_2H_5OH \rightarrow C_2H_4 + H_2O$

Moles:

initial: 1 0 0

at equilibrium: 1 – x x x total: 1 + x

	Molar fraction	Partial pressure
Ethanol	$\frac{1-x}{1+x}$	$\frac{1-x}{1+x}\ p$
Ethylene	$\frac{x}{1+x}$	$\frac{x}{1+x}\ p$
Water	$\frac{x}{1+x}$	$\frac{x}{1+x}\ p$

$p = \frac{p'}{p}$ p' – total pressure, p_0 = 101.325 kPa

$$K_p = \frac{p_{C_2H_4} \cdot p_{H_2O}}{p_{C_2H_5OH}} = \frac{\left(\frac{x}{1+x}p\right)\left(\frac{x}{1+x}p\right)}{\frac{1-x}{1+x}p} = \frac{x^2}{1-x^2}p$$

5.1 $p' = 101.325$ kPa

$$K_p = \frac{x^2}{1-x^2} = \frac{0.906^2}{1-0.906^2} = 4.56$$

5.2 $K_x = K_p\, p^{-\Delta n}$; $p' = 101.325$ kPa; $\Delta n = 1$; $K_x = 4.56$

$$K_c = K_p \left(\frac{c_0 RT}{p_0}\right)^{\Delta n} \quad R = 8.314\ \text{J mol}^{-1}\text{K}^{-1};\ c^0 = 1\ \text{mol dm}^{-3};\ T = 400\ K$$

$K_c = 0.139$

5.3 $\dfrac{x^2}{1-x^2} = \dfrac{K_p}{p} = \dfrac{4.56}{p}$

a) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{5} = 0.912$ x = 0.69

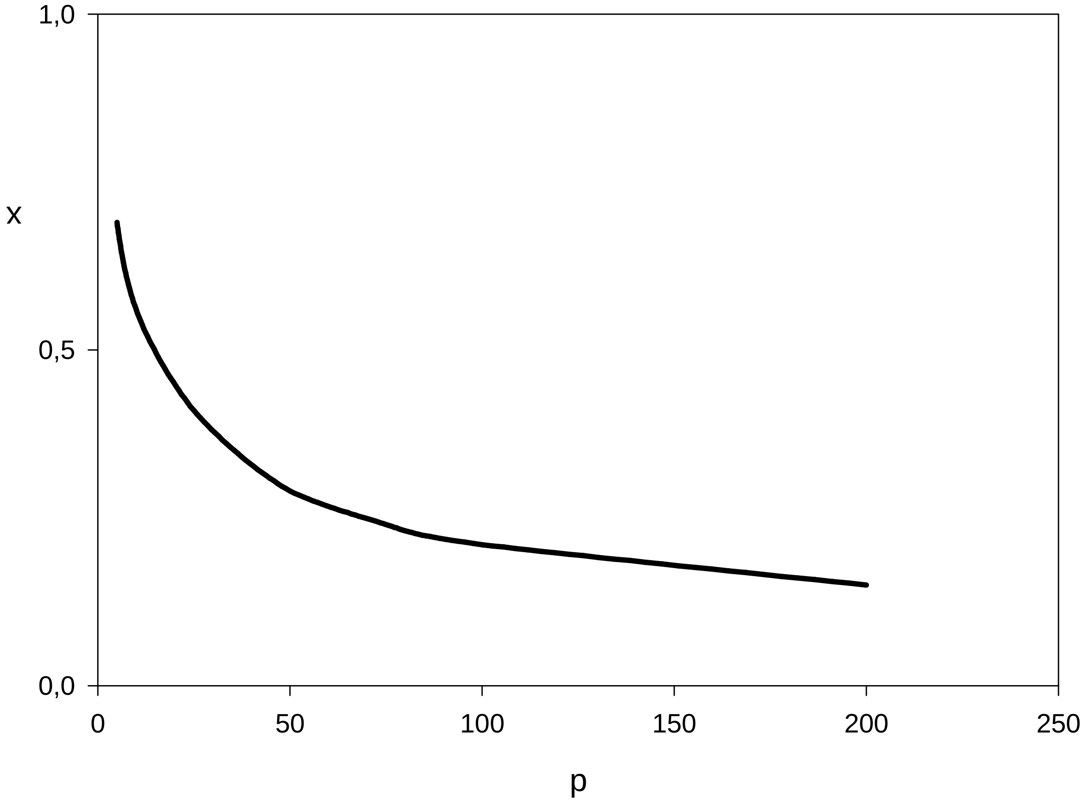
b) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{10} = 0.456$ x = 0.56

c) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{50} = 0.0912$ x = 0.29

d) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{100} = 0.0456$ x = 0.21

e) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{200} = 0.0228$ x = 0.15

5.4



PROBLEM 6

One mole of compound **A** reacts successively with 3 moles of compound **B** in aqueous solution in the presence of a basic catalyst (such as $Ca(OH)_2$):

$\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C}$

$\mathbf{C} + \mathbf{B} \rightarrow \mathbf{D}$

$\mathbf{D} + \mathbf{B} \rightarrow \mathbf{E}$

Hydrogenation of compound **E** yields compound **F**:

$\mathbf{E} + H_2 \rightarrow \mathbf{F}$

F has the composition: C = 44.18 %, H = 8.82 %, O = 47.00 %.

Its molar mass: $M = 136$ g mol^{-1}

Knowing that 13.6 g of **F** reacts with 40.8 g acetic anhydride to form product **G** and acetic acid write down all chemical equations and assign the letters **A**, **B**, **C**, **D**, **E**, **F**, and **G** to particular formulas of compounds.

SOLUTION

The molecular formula of **F**:

$$\text{C : H : O} = \frac{44.18}{12} : \frac{8.82}{1} : \frac{47.00}{16} = 1.25 : 3 : 1 = 5 : 12 : 4$$

$(C_5H_{12}O_4)_n$

Since $M(\mathbf{F}) = 136$

and $(5 \times 12) + (12 \times 1) + (4 \times 16) = 136$

$\mathbf{F} = C_5H_{12}O_4$

Since **F** reacts with acetic anhydride it could be a mono- or polyhydroxy alcohol. If it were a monohydroxy alcohol, 136 g of **F** (1 mol) could react with 102 g (1 mol) of acetic anhydride. In fact 13.6 g of **F** (i. e. 0.1 mol) reacts with 40.8 g of acetic anhydride (40.8 / 102 = 0.4 mol), i. e. **F** is a polyol (tetrahydroxy alcohol).

F is formed by the reduction of **E**, so that **E** has one carbonyl and three OH groups.

E is formed from 3 molecules of **B** and one molecule of **A**.

Since compound **E** has three OH groups and one CO group and the reaction conditions used are typical for aldol condensation, it is clear that **A** is acetaldehyde and **B** is formaldehyde. **C** and **D** are the products of successive aldol condensation of acetaldehyde with formaldehyde:

$$\underset{\textbf{A}}{H_3C\text{-}CH{=}O} + \underset{\textbf{B}}{H_2C{=}O} \rightarrow \underset{\textbf{C}}{HO\text{-}CH_2\text{-}CH_2\text{-}CH{=}O}$$

$$\underset{\textbf{C}}{HO\text{-}CH_2\text{-}CH_2\text{-}CH{=}O} + \underset{\textbf{B}}{H_2C{=}O} \rightarrow \underset{\textbf{D}}{(HO\text{-}CH_2)_2CH\text{-}CH{=}O}$$

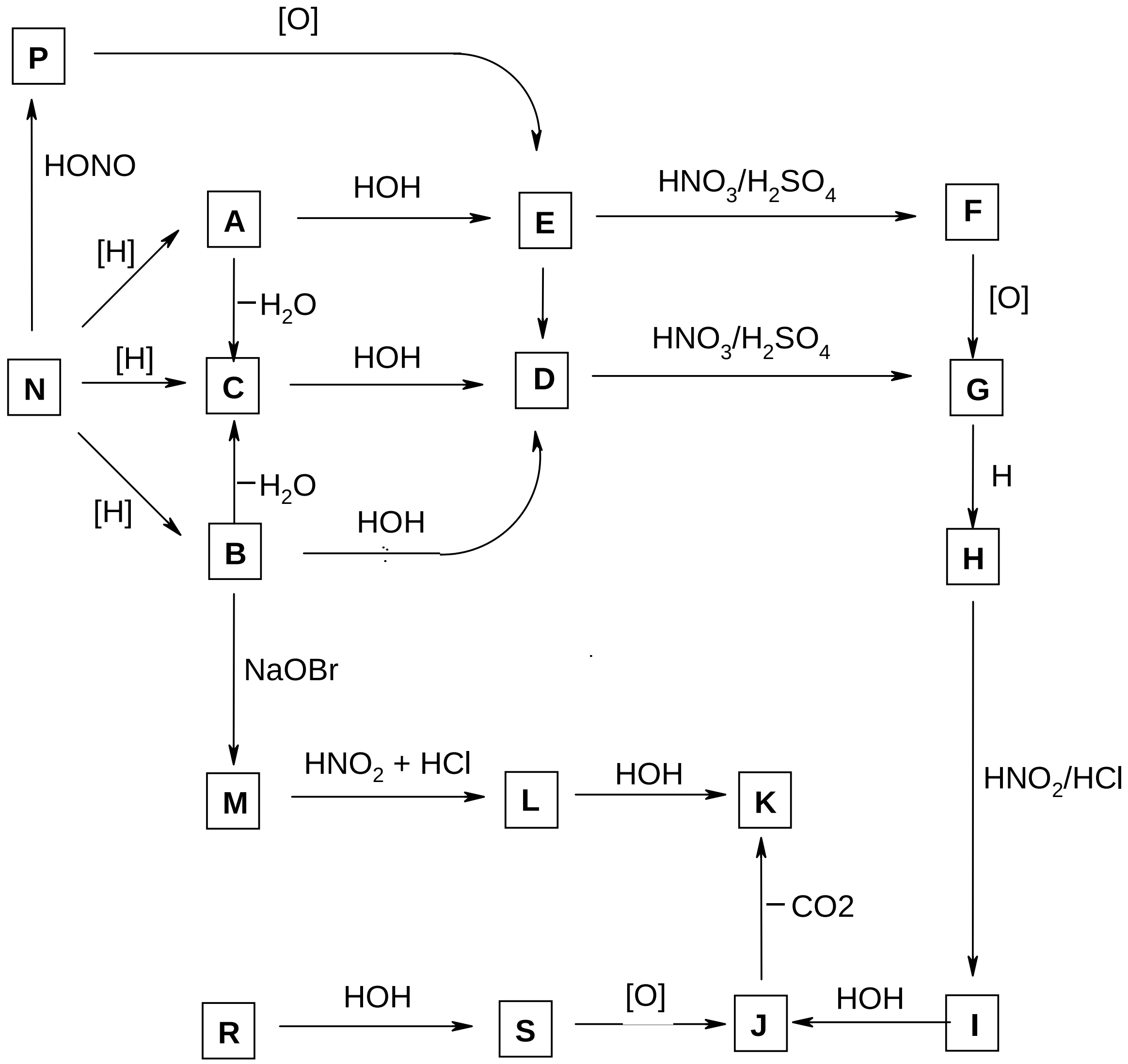
$$\underset{\textbf{D}}{(HO\text{-}CH_2)_2CH\text{-}CH{=}O} + \underset{\textbf{B}}{H_2C{=}O} \rightarrow \underset{\textbf{E}}{(HO\text{-}CH_2)_3C\text{-}CH{=}O}$$

$$\underset{\textbf{E}}{(HO\text{-}CH_2)_3C\text{-}CH{=}O} + H_2 \rightarrow \underset{\textbf{F}}{(HO\text{-}CH_2)_4C}$$

$$(HO\text{-}CH_2)_4C + 4\ (CH_3CO)_2O \rightarrow \underset{\textbf{G}}{(CH_3COO\text{-}CH_2)_4C} + 4\ CH_3COOH$$

PROBLEM 7

Knowing that compounds **A** and **B** are isomers with the molecular formula C_7H_7NO and the relative molecular mass of compound **M** is 93, determine the formulae of compounds **A** to **S** taking in account the reactions given in the following reaction scheme:



SOLUTION

A C_6H_5-CH=N-OH

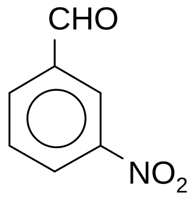
B C_6H_5-CO-NH_2

C C_6H_5-CN

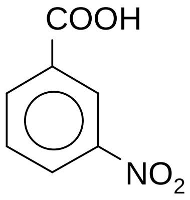
D C_6H_5-COOH

E C_6H_5-CHO

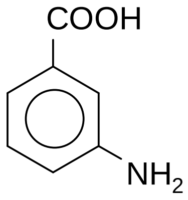
F



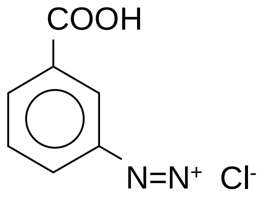
G



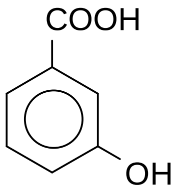
H



I



J



K C_6H_5-OH

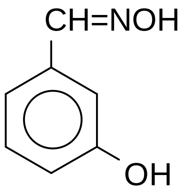
L C_6H_5-N=N$^+$ Cl$^-$

M C_6H_5-NH_2

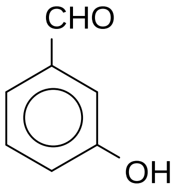
N C_6H_5-CH_2-NH_2

P C_6H_5-CH_2-OH

R



S



PRACTICAL PROBLEMS

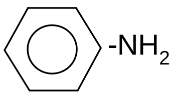
PROBLEM 1 (practical)

In test tubes **A**, **B**, **C**, and **D** there are four benzene derivatives containing one or two functional groups of three distinct types. Identify the functional groups of compounds **A**, **B**, **C**, and **D** using the available reagents.

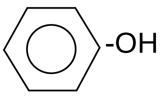
- Justify your choice by writing down the identification reactions.
- Using as reagents the four compounds **A**, **B**, **C**, and **D** synthesize four organic dyes and write the equations for the reactions performed.

SOLUTION

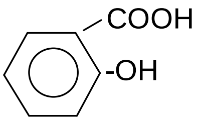
The four compounds are as follows:



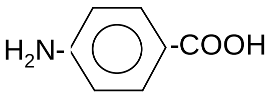
A



B



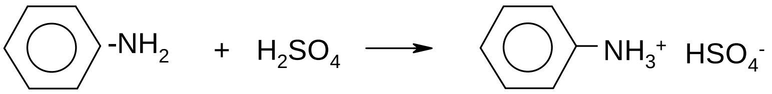
C

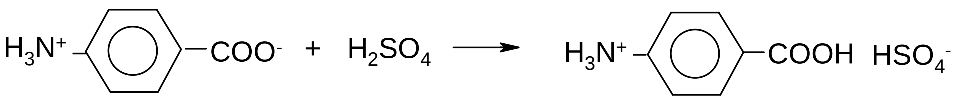


D

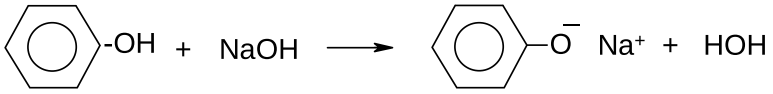
The identification reactions:

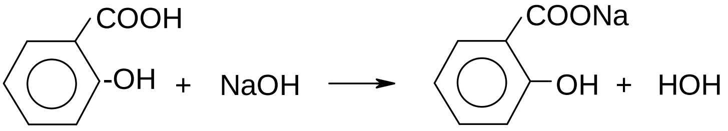
a) With H_2SO_4:

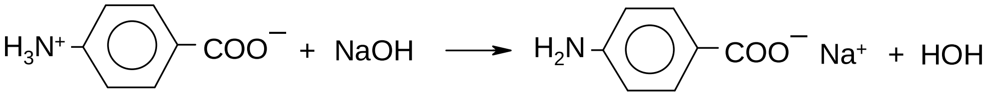




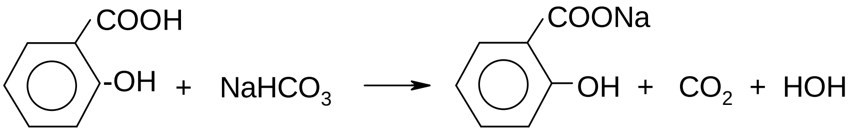
b) With NaOH:

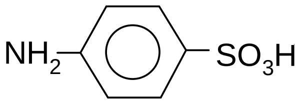


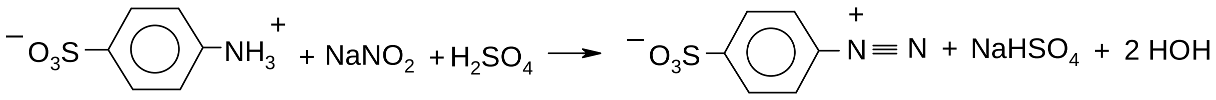


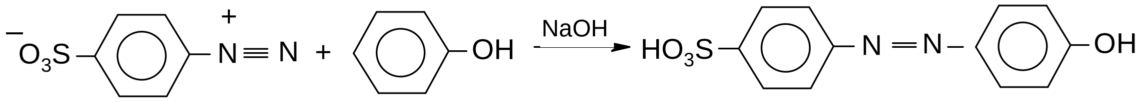


c) With $NaHCO_3$:

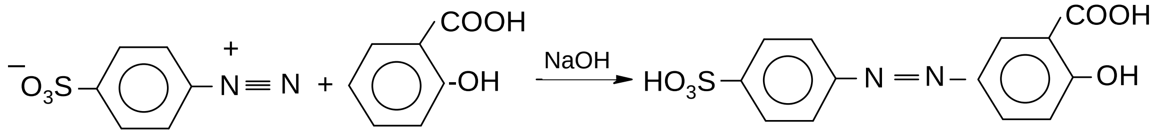


d) With 

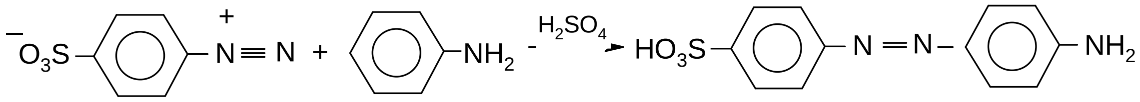




(orange)

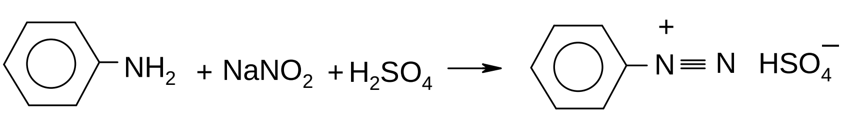


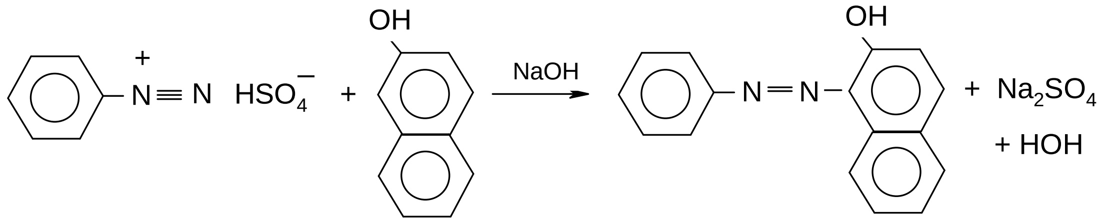
(orange)



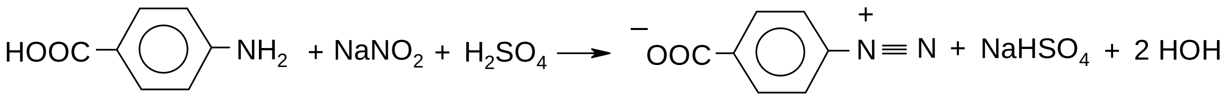
(orange)

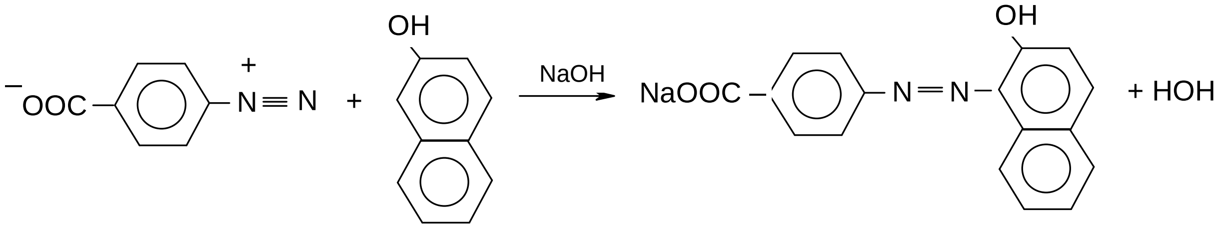
II. e) With β-naphthol:





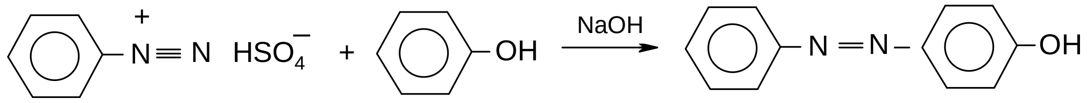
yellow - orange



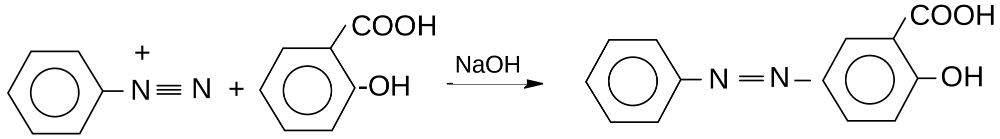


red

The following dyes can be obtained:



(red - orange)



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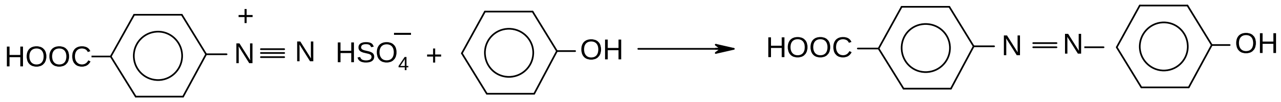
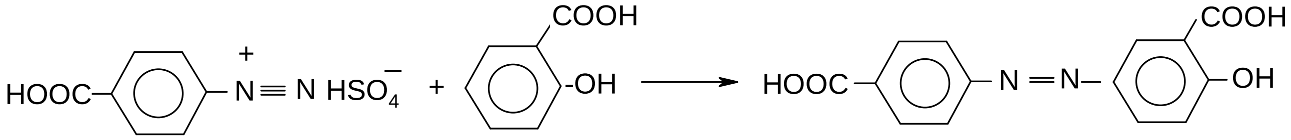


(red - orange)



(red - orange)

PROBLEM 2 (practical)

A solution in a graduated flask contains a mixture of oxalic acid and ammonium oxalate.

One of the bottles denoted X, Y, and Z contains a solution of a calibration substance with reducing character at a concentration of 0.1000 mol dm^{-3}.

You are required to solve the following tasks:

a) Determine the quantity of oxalic acid and of ammonium oxalate in the solution in the graduated flask. (The result will be given in grams.)

b) Write the formula for the substance with reducing character and the equations of the chemical reactions which led to its determination.

In order to carry out the analyses the following solutions are available:
HCl (c = 0.1000 mol dm^{-3}), NaOH (c = 2 mol dm^{-3}), $KMnO_4$ (c = 0.02 mol dm^{-3}), 25 % H_2SO_4, HNO_3 (c = 2 mol dm^{-3}), 5 % $BaCl_2$, 5 % $AgNO_3$, 5 % $Hg_2(NO_3)_2$, phenolphthalein 0.1 %, methyl red 1 %.

c) Describe the procedure used in the individual steps, indicators employed and partial results.

$M_r(H_2C_2O_4) = 90.04$

$M_r((NH_4)_2C_2O_4) = 124.11$

SOLUTION

ANSWER SHEET:

A$_1$ – Identification of the solution with the reducing substance X, Y, Z: $Fe(NH_4)_2(SO_4)_2$

A$_2$ – Identification reactions for the ions of the substance

- $Fe^{2+} + 2\ NaOH \rightarrow Fe(OH)_2 + 2\ Na^+$
- $NH_4^+ + NaOH \rightarrow NH_3\uparrow + H_2O + Na^+$
- $4\ NH_3 + 2\ Hg_2(NO_3)_2 + H_2O \rightarrow O(Hg)_2NH_2.NO_3 + 3\ NH_4OH$
- $SO_4^{2-} + BaCl_2 \rightarrow BaSO_4 + 2\ Cl^-$

B$_1$– Preparation of the 0.1 M NaOH solution

. . . . cm^3 in 200.0 cm^3

B_2 – Concentration of the NaOH in its solution: . . . . M

Indicator used: . . . .

C – Concentration of $KMnO_4$ in its solution . . . . M

D_1 – Mass of oxalic acid in the initial solution . . . . g

Indicator used . . . .

D_2 – Mass of ammonium oxalate in the initial solution . . . . g

Solution

A_1 – 1-2 cm^3 of solution X, Y and Z are put into three test tubes. 6 N H_2SO_4 and a drop of $KMnO_4$ solution are added. The solution which loses colour is the one with reducing character.

A_2 – Establishment of the formula:

. . . . + NaOH – greenish white precipitate $\Rightarrow$ Fe^{2+}

. . . . + NaOH at the upper end of the test-tube, filter paper with a drop of $Hg_2(NO_3)_2$, black spot $\Rightarrow$ NH_4^+

. . . . + $BaCl_2$ – white precipitate $\Rightarrow$ SO_4^{2-}

. . . . + $AgNO_3$ + HNO_3 $\Rightarrow$ Cl^- is absent

Accordingly the substance used is $Fe(NH_4)_2(SO_4)_2$.

The chemical reactions:

$Fe^{2+} + 2\ Na^+ + 2\ OH^- \rightarrow Fe(OH)_2 + 2\ Na^+$

$NH_4^+ + Na^+ + OH^- \rightarrow NH_3 + H_2O + Na^+$

$4\ NH_3 + 2\ Hg_2(NO_3)_2 \rightarrow O(Hg)_2NH_2 . NO_3 + 2\ Hg + 3\ NH_4NO_3$

$SO_4^{2-} + Ba^{2+} + 2\ Cl^- \rightarrow BaSO_4 + 2\ Cl^-$

B_1 – 5 cm^3 2 M solution $\Rightarrow$ 100 cm^3 0.1 M solution

B_2 – *V* cm^3 0.1000 N HCl + 0.1 N NaOH in the presence of phenolphthalein.

C – *V* cm^3 solution X + 10.0 cm^3 H_2SO_4 + H_2O is titrated at elevated temperature with $KMnO_4$.

D_1 – The solution which is to be analyzed is filled to the mark; V cm^3 of this solution is titrated with NaOH in the presence of methyl red. The quantity of oxalic acid (moles and g) is calculated.

D_2 – V cm^3 solution to be analyzed + 10.0 cm^3 6 N H_2SO_4 + H_2O are heated and titrated with $KMnO_4$ solution.

The total amount of oxalate is calculated (in mol).

The difference gives the amount of ammonium oxalate (moles and g).

PROBLEM 3 (practical)

Six test-tubes contain aqueous solutions of $FeSO_4$, H_2SO_4, $Mn(NO_3)_2$, H_2O_2, $Pb(NO_3)_2$, NaOH.

a) Identify the content of each test-tube without using other reagents. Write the results in tabular form. Write the equations for the chemical reactions used for the identification.

b) After identification, perform four reactions each time using three of the identified compounds and write the equations.

SOLUTION

	$FeSO_4$	H_2SO_4	$Mn(NO_3)_2$	H_2O_2	$Pb(NO_3)_2$	NaOH
1) $FeSO_4$		–	–	$Fe(OH)SO_4$ yellowish	$PbSO_4 \downarrow$ white	Fe(OH)2 $\downarrow$ white-greenish $\downarrow$ Fe(OH)3 $\downarrow$ brown-redish
2) H_2SO_4	–		–	–	$PbSO_4 \downarrow$ white	–
3) $Mn(NO_3)_2$	–	–		–	–	$Mn(OH)_2 \downarrow$ white $\downarrow$ $MnMnO_3 \downarrow$ brown black
4) H2O2	$Fe(OH)SO_4$ yellowish	–	–		–	–
5) $Pb(NO_3)_2$	$PbSO_4 \downarrow$ white	$PbSO_4 \downarrow$ white	–	–		–
6) NaOH	$Fe(OH)_2 \downarrow$ white-greenish $\downarrow$ $Fe(OH)_3 \downarrow$ brown-redish	–	$Mn(OH)_2 \downarrow$ white $\downarrow$ $MnMnO_3 \downarrow$ brown black	–	$Pb(OH)_2 \downarrow$ white $\downarrow$ $Pb(OH)_4^{2-}$	

	Reactions	Observation
(1) + (4)	$FeSO_4 + H_2O_2 \rightarrow 2\ Fe(OH)SO_4$	Colour change - yellowish (Fe^{3+})
(1) + (5)	$FeSO_4 + Pb(NO_3)_2 \rightarrow PbSO_4 \downarrow + Fe(NO_3)_2$	Appearance of a white precipitate.
(1) + (6)	$FeSO_4 + 2\ NaOH \rightarrow Fe(OH)_2 \downarrow + Na_2SO_4$ $Fe(OH)_2 + ½\ O_2 + H_2O \rightarrow Fe(OH)_3$	Appearance of a greenish white precipitate $Fe(OH)_2$ which after oxidation by air turns into a reddish brown precipitate $Fe(OH)_3$.
(2) + (5)	$H_2SO_4 + Pb(NO_3)_2 \rightarrow PbSO_4 \downarrow + 2\ HNO_3$	Appearance of a white precipitate $PbSO_4$.
(3) + (6)	$Mn(NO_3)_2 + 2\ NaOH \rightarrow Mn(OH)_2 + 2\ NaNO_3$ $2\ Mn(OH)_2 + ½\ O_2 \rightarrow MnMnO_3 + 2\ H_2O$ $Mn(OH)_2 + ½\ O_2 \rightarrow MnO_2 + H_2O$	Appearance of a white precipitate $Mn(OH)_2$ which after oxidation by air coverts into a brown-black precipitate $MnMnO_3$ which eventually changes into MnO_2 – a black-brown precipitate.
(5) + (6)	$Pb(NO_3)_2 + 2\ NaOH \rightarrow Pb(OH)_2 + 2\ NaNO_3$ $Pb(OH)_2 + 2\ NaOH \rightarrow Na_2Pb(OH)_4$	Appearance of a white precipitate $Pb(OH)_2$ which dissolves in excess reagent.
b)		
(1) + (2) + (4)	$2\ FeSO_4 + H_2O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2\ H_2O$	Colour change → yellowish (Fe^{3+})
(1) + (4) + (6)	$2\ FeSO_4 + H_2O_2 + 4\ NaOH \rightarrow Fe(OH)_3 +$ $+ 2\ Na_2SO_4$	Appearance of a brown-reddish precipitate $Fe(OH)_3$
(3) + (4) + (6)	$Mn(NO_3)_2 + H_2O_2 + 2\ NaOH \rightarrow MnO_2 + 2\ NaNO_3$ $+ 2\ H_2O$	Appearance of a brown precipitate MnO_2
(5) + (4) + (6)	$Pb(NO_3)_2 + H_2O_2 + 2\ NaOH \rightarrow PbO_2 + 2\ NaNO_3$ $+ 2\ H_2O$	Appearance of a brown precipitate PbO_2.