15th

ICHO

International Chemistry Olympiad

7 theoretical problems
3 practical problems

THE FIFTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD

TIMISOARA 1983
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:

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

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

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}

$$s = \frac{K_s}{[Cl^-]^2} = \frac{1.0 \times 10^{-18}}{(0.01)^2} = 1.0 \times 10^{-14}$$

$s = 1.0 \times 10^{-14}$ 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:

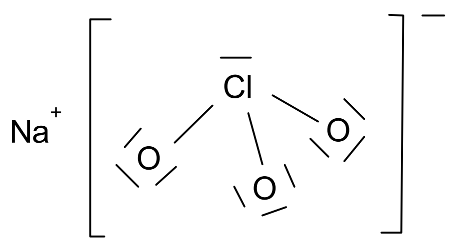
$$V = \frac{6.3 \times 10^{-7}}{1.0 \times 10^{-14}} = 6.3 \times 10^{7}\ \text{dm}^3$$

E) c) SO_3, I_2, NaCl

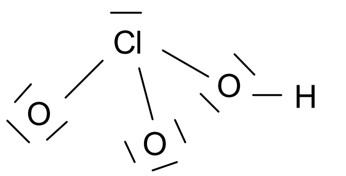
F) b) NH_4Cl

G)

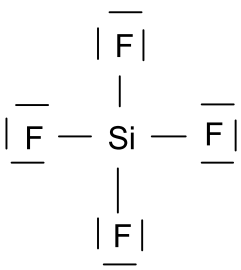
a)



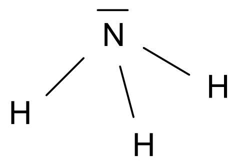
b)



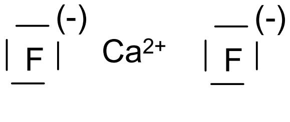
c)



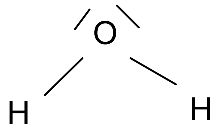
d)



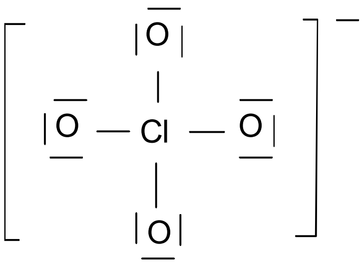
e)



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.

a) Calculate the mass percent composition.

b) Calculate the volume percent composition.

c) 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

a) $$\frac{1.389 \times 44}{100} \times 100 = 61.11\ \%\ CO_2$$

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

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

c) 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

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

Mass of silver nitrate:

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

$$\frac{170 \text{ g } AgNO_3}{108 \text{ g Ag}} = \frac{71.4}{x}$$ x = 45.36 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, regardl ess 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:

1. What is the reaction order in cases a, b, and c?
2. What is the rate constant at 25 °C for reaction a? Indicate the units.
3. Calculate the activation energies for reactions a and b.
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?

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?
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

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
$k \cdot 10^2$	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.

2. The rate constant of reaction a is an average of the above calculated values.
   k = 0.176 $dm^3\ mol^{-1}\ min^{-1}$
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 ℃ and the initial concentratio n, 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 ℃:

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

The activation energy of reaction a will be:

$$E_a = R\ln\frac{k'}{k}\times\frac{T'\cdot T}{T'-T} = 8314\ \ln\frac{0.476}{0.176}\times\frac{308\times298}{308-298} = 7.592\times10^7\ \text{J mol}^{-1}$$

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

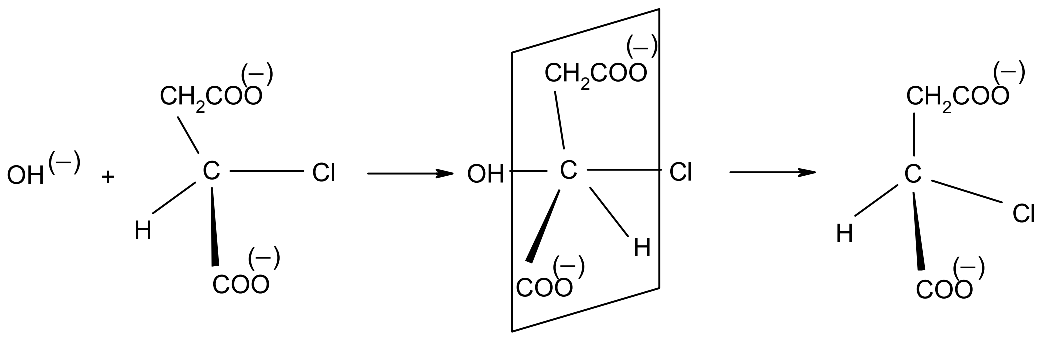
at 25 ℃: $k = \frac{\ln 2}{32} = 2.166\times10^{-2}\ \text{min}^{-1}$

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

Hence the activation energy is:

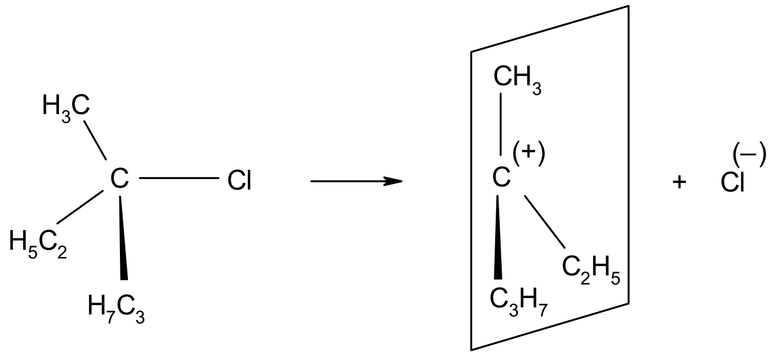
$$E_a = 8314\ \ln\frac{6.301\times10^{-2}}{2.166\times10^{-2}}\times\frac{308\times298}{308-298} = 8.149\times10^7\ \text{J mol}^{-1}$$

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



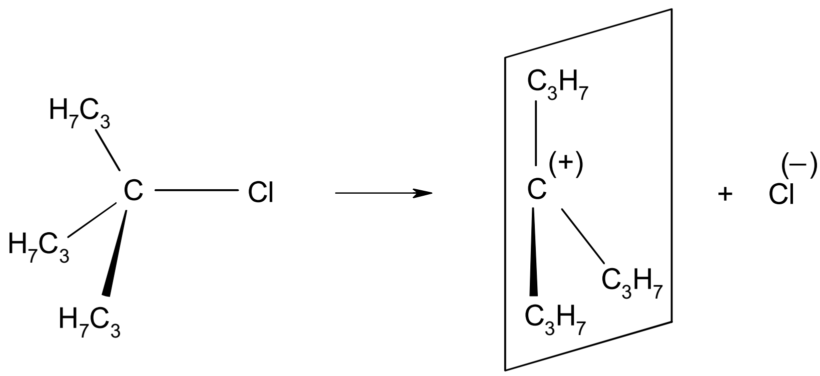
As an S_N2 type reaction, it involves a transition state in which the inversion of the configuration of the asymmetric carbon atom occurs. Thus, if the substrate is levorotatory, the product will become dextrorotatory.

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.

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 %.

1. Calculate the equilibrium constant K_p of the reaction under given conditions.
2. Calculate the values of the equilibrium constants K_x and K_c at the above temperature.
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.
4. Plot the graph for the variation of conversion *vs*. pressure.

SOLUTION

The reaction: $C_2H_5OH \rightarrow C_2H_4 + H_2O$

Moles:

	C_2H_5OH	C_2H_4	H_2O	
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	$\frac{x}{1+x}$	$\frac{x}{1+x}\,p$

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

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

1. $p' = 101.325$ kPa

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

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

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

$K_c = 0.139$

3. $$\frac{x^2}{1-x^2} = \frac{K_p}{p} = \frac{4.56}{p}$$

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

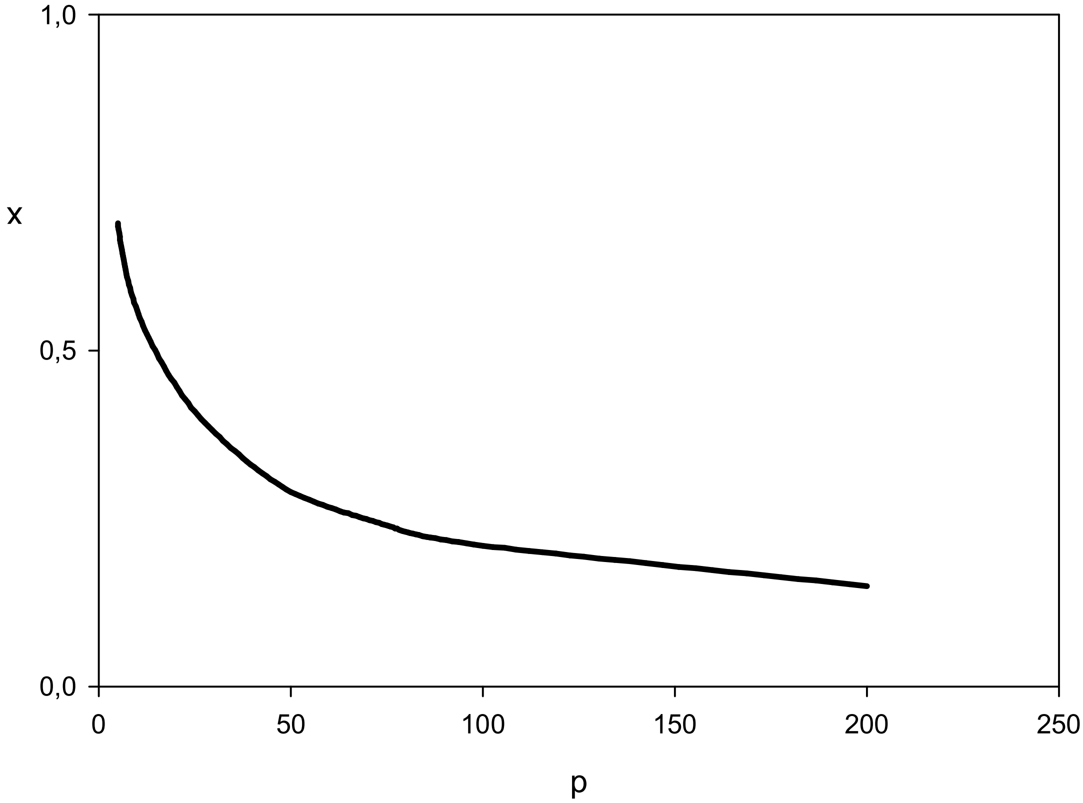
b) $\frac{x^2}{1-x^2} = \frac{4.56}{10} = 0.456$ x = 0.56

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

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

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

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 $Ca(OH)_2$):

A + **B** $\rightarrow$ **C**

C + **B** $\rightarrow$ **D**

D + **B** $\rightarrow$ **E**

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

E + H_2 $\rightarrow$ **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**:

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

$(C_5H_{12}O_4)_n$

Since M(**F**) = 136

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

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:

$H_3C\text{-}CH{=}O + H_2C{=}O \rightarrow HO\text{-}CH_2\text{-}CH_2\text{-}CH{=}O$

A **B** **C**

$HO\text{-}CH_2\text{-}CH_2\text{-}CH{=}O + H_2C{=}O \rightarrow (HO\text{-}CH_2)_2CH\text{-}CH{=}O$

C **B** **D**

$(HO\text{-}CH_2)_2CH\text{-}CH{=}O + H_2C{=}O \rightarrow (HO\text{-}CH_2)_3C\text{-}CH{=}O$

D **B** **E**

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

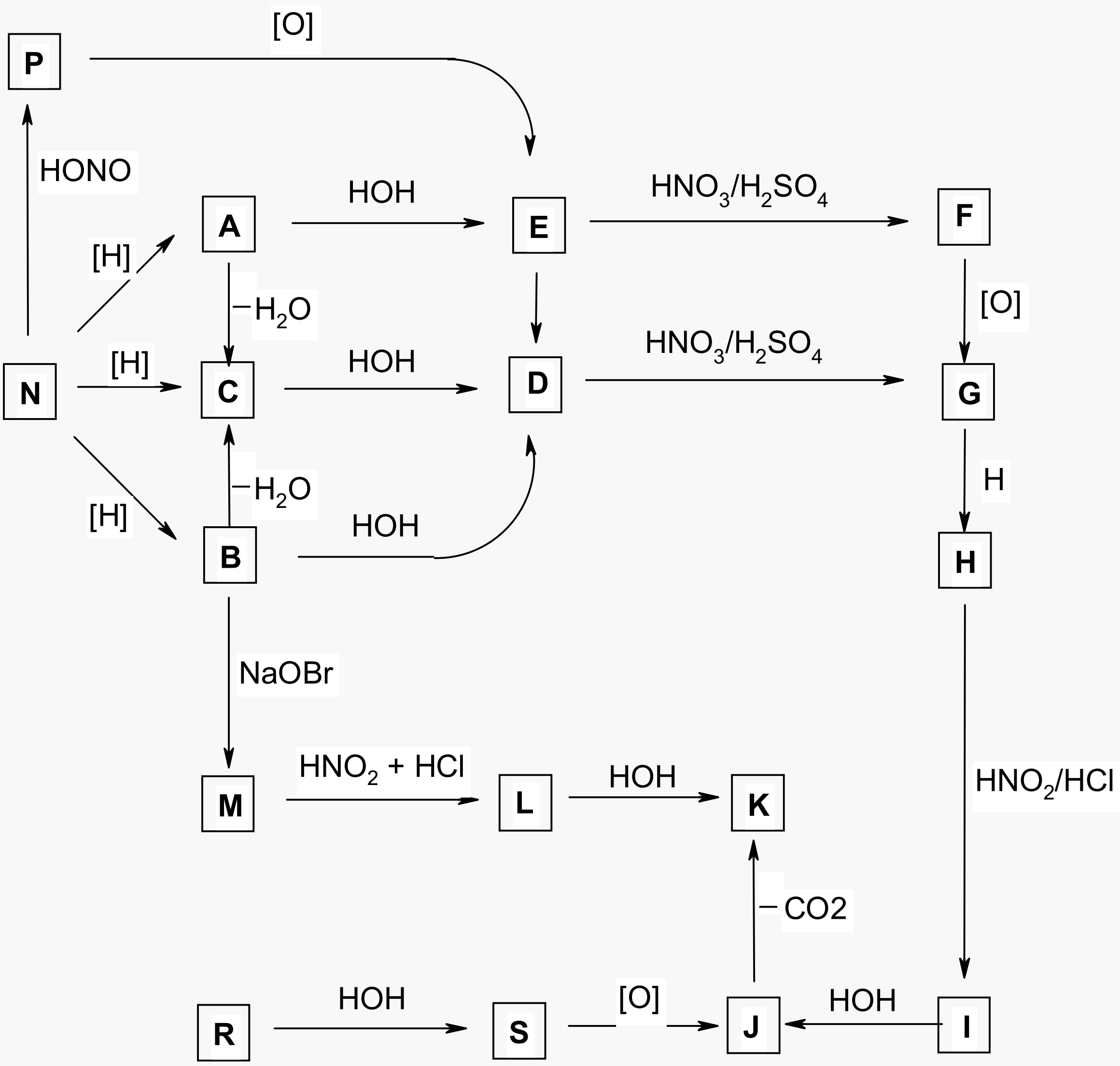
E **F**

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

G

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

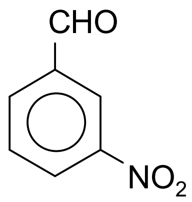
B C_6H_5-CO-NH_2

C C_6H_5-CN

D C_6H_5-COOH

E C_6H_5-CHO

F



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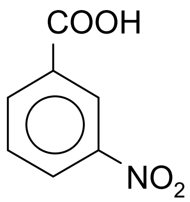

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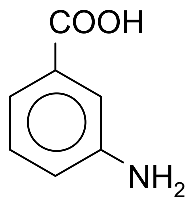

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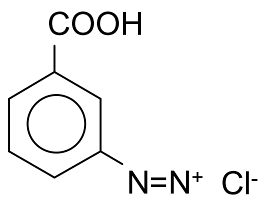

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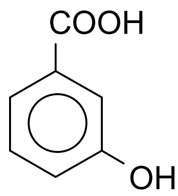


K C_6H_5-OH

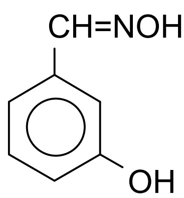
L C_6H_5-N=N^+ Cl^-

M C_6H_5-NH_2

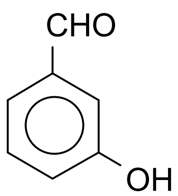
N C_6H_5-CH_2-NH_2

P C_6H_5-CH_2-OH

R



S



PRACTICAL PROBLEMS

PROBLEM 1

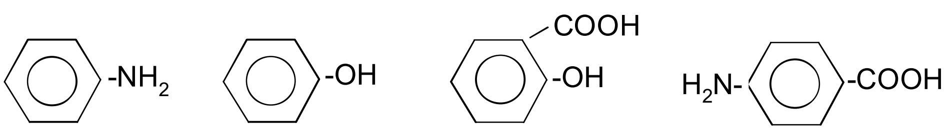
In test tubes **A**, **B**, **C**, and **D** there are four benzene derivatives containing one or two functional groups of three distinct types. Identify the functional groups of compounds **A**, **B**, **C**, and **D** using the available reagents.

– 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

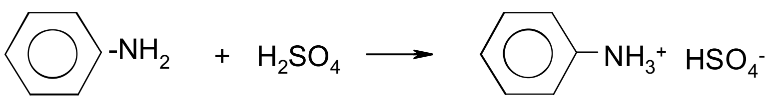
The four compounds are as follows:

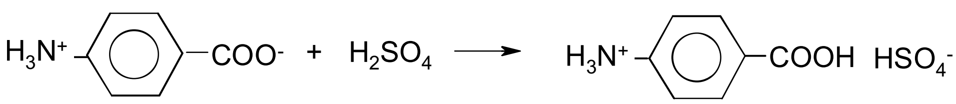


A **B** **C** **D**

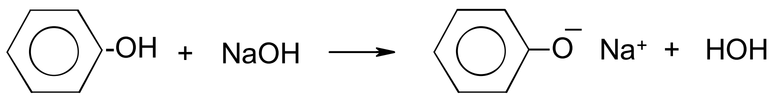
The identification reactions:

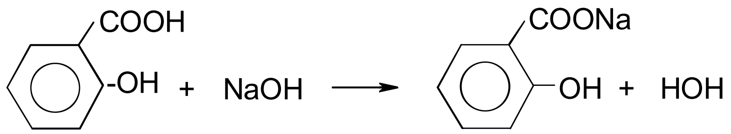
a) With H_2SO_4:

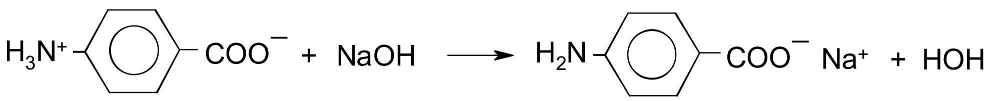




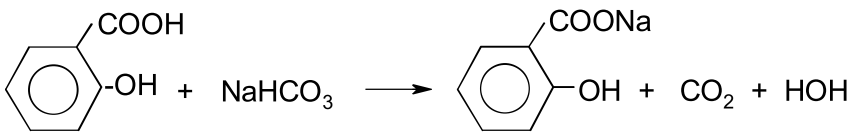
b) With NaOH:

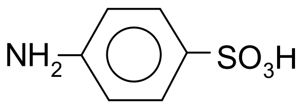


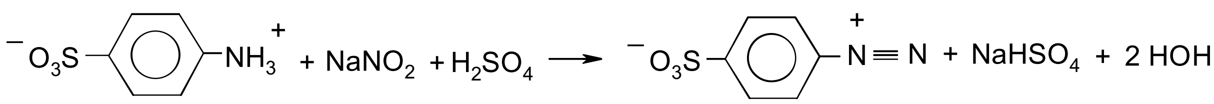


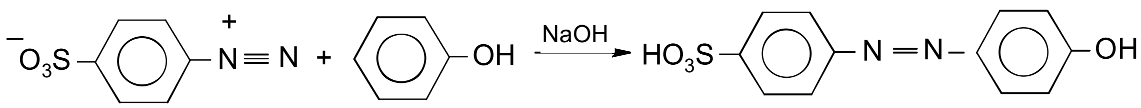


c) With $NaHCO_3$:

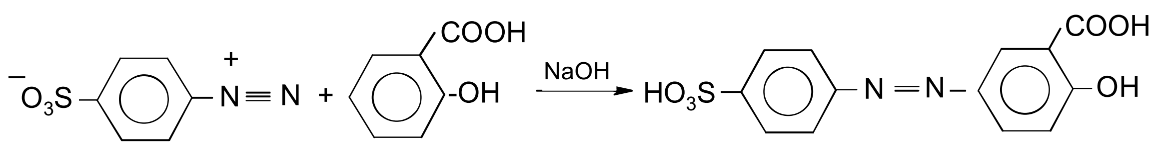


d) With 

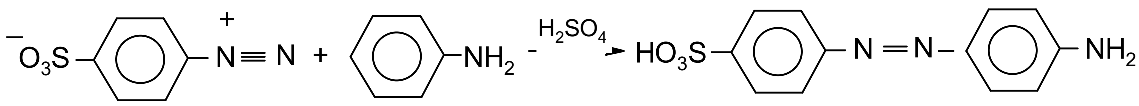




(orange)

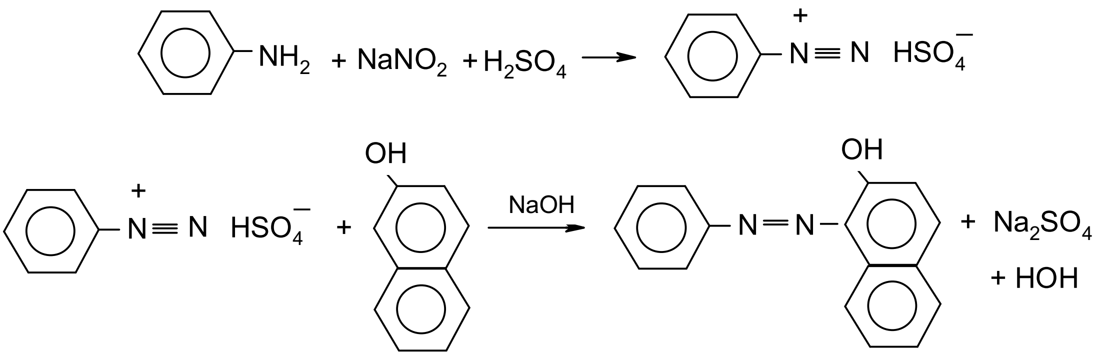


(orange)

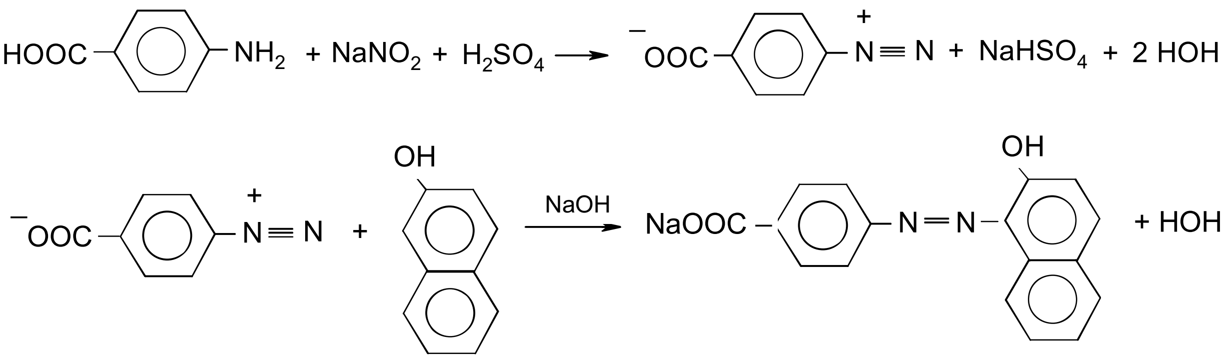


(orange)

II. e) With β-naphthol:

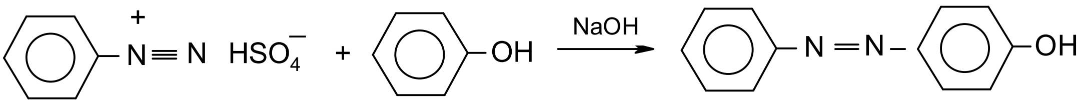


yellow - orange

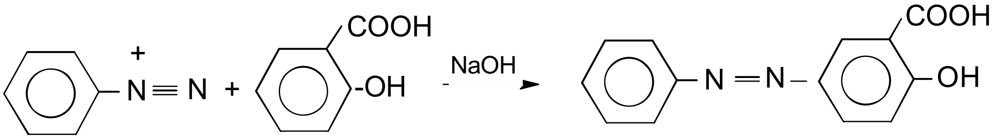


red

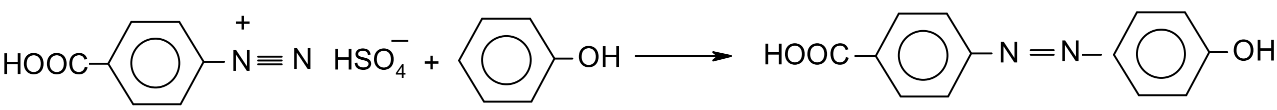
The following dyes can be obtained:



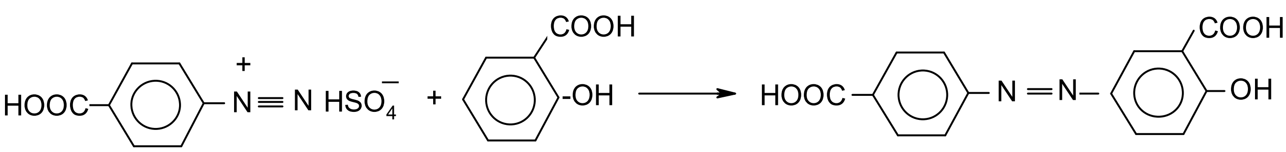
(red - orange)



(red - orange)



(red - orange)



(red - orange)

PROBLEM 2

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

S o l u t i o n

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* cm3 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

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	$PbSO_4$ ↓ white	Fe(OH)2 ↓ white-greenish ↓ Fe(OH)3 ↓ brown-redish
2) H_2SO_4	–		–	–	$PbSO_4$ ↓ white	–
3) $Mn(NO_3)_2$	–	–		–	–	$Mn(OH)_2$ ↓ white ↓ $MnMnO_3$ ↓ brown black
4) H2O2	$Fe(OH)SO_4$ yellowish	–	–		–	–
5) $Pb(NO_3)_2$	$PbSO_4$ ↓ white	$PbSO_4$ ↓ white	–	–		–
6) NaOH	$Fe(OH)_2$ ↓ white-greenish ↓ $Fe(OH)_3$ ↓ brown-redish	–	$Mn(OH)_2$ ↓ white ↓ $MnMnO_3$ ↓ brown black	–	$Pb(OH)_2$ ↓ white ↓ $Pb(OH)_4^{2-}$	

	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.