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-dinitrophenyl-hydrazine, 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 ℃)

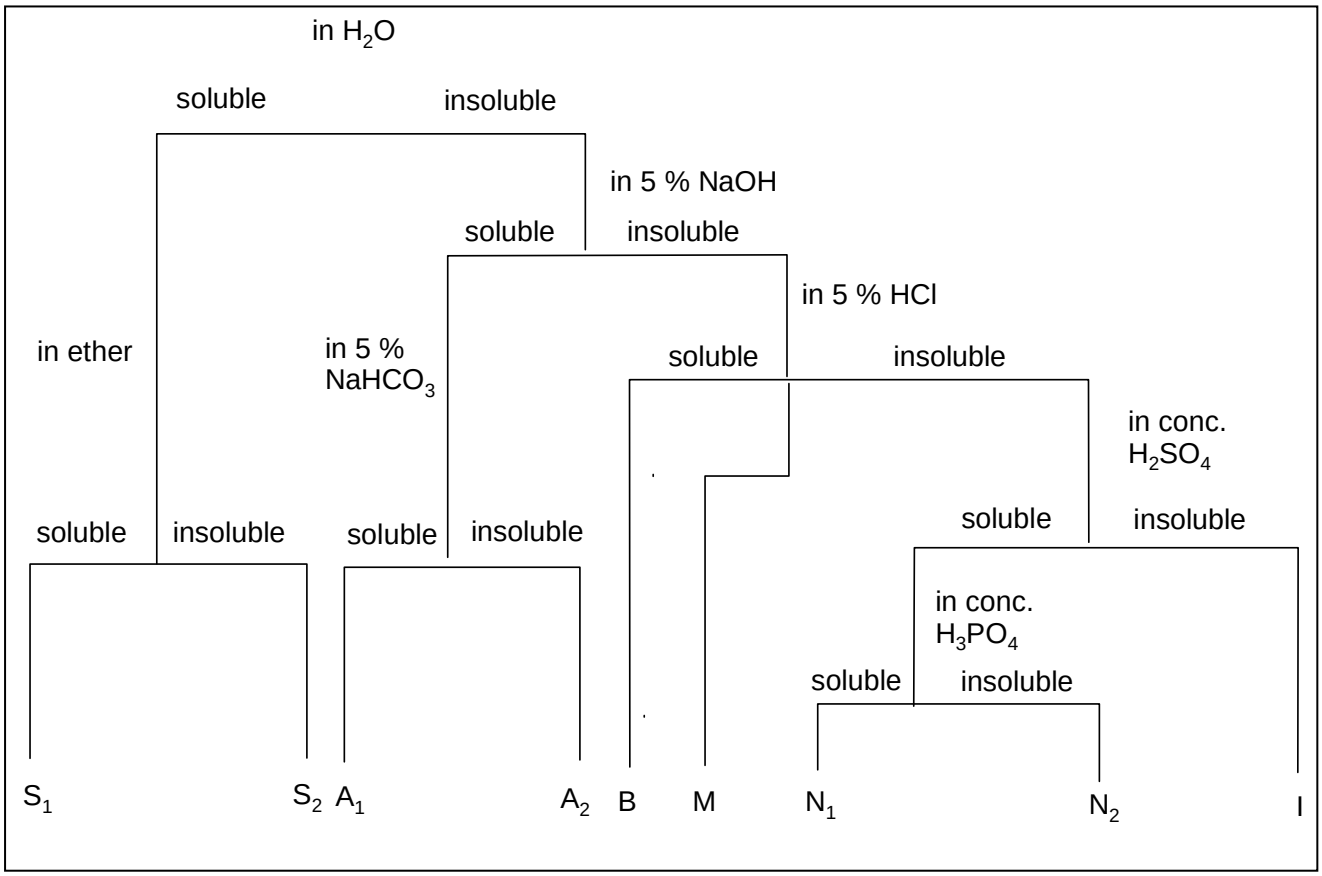
Compound	MP	BP	Compound	MP	BP
ALDEHYDES					
Pentanal	-	103	Acrolein	-	52
Benzaldehyde	-	179	Furfurol	-	161
Salicylaldehyde	-	196	o-Chlorobenzaldehyde	11	214
o-Nitrobenzaldehyde	44	-	α-Naphthaldehyde	34	-
p-Dimetylamino-bemzaldehyde	74	-	Vanillin	81	-
ALCOHOLS					
terc.-Butanol	25	82	Propanol-1	-	97
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 ℃

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).

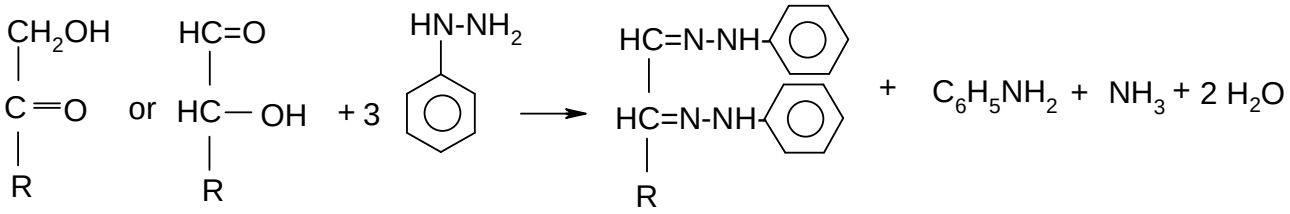
   $-CHO + 2\ [Cu(C_4H_4O_6)_2]^{2-} + 5\ OH^- \rightarrow -COOH + Cu_2O\downarrow + 3\ H_2O + 4\ C_4H_4O_6^{2-}$

2. With Tollen's reagent

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

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

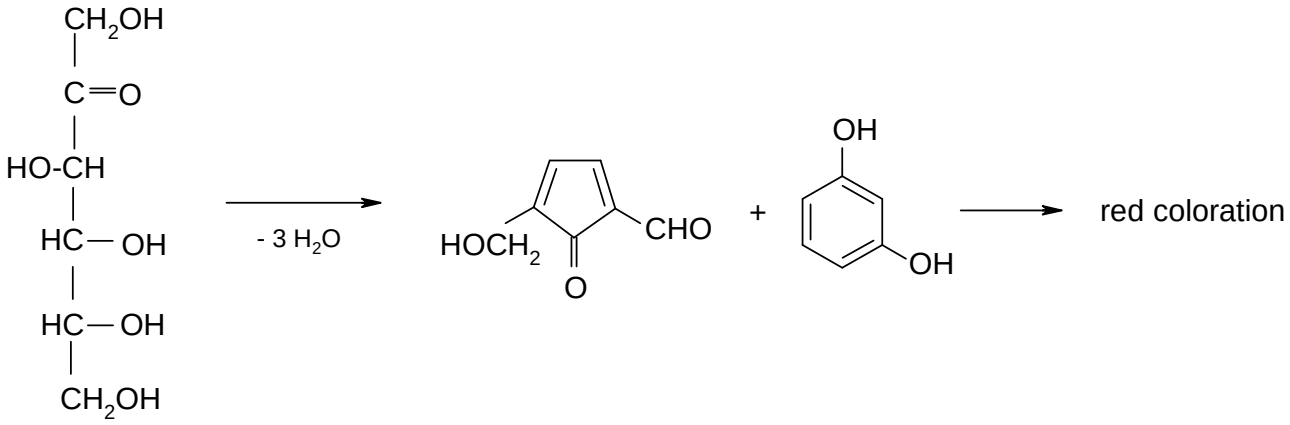
Osazone formation (indication of monoses)



Ketose Aldose Phenyl-hydrazine Osazone

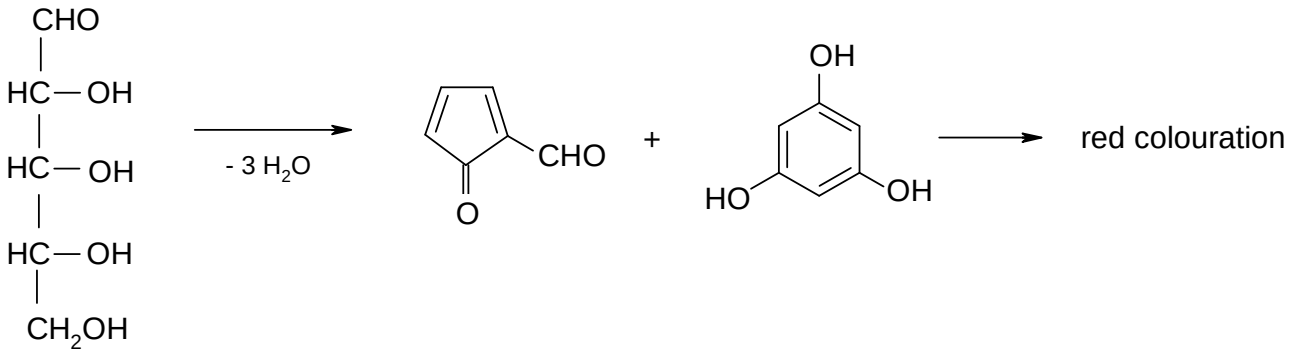
Test for ketohexoses (Saliwanoff's reaction)

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

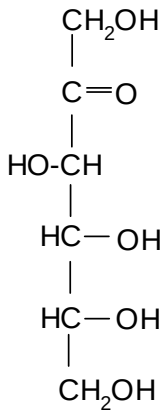


Test for pentoses (Tollens test)

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 ℃

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

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

2.

α) $\frac{(V_1 - V_2)\times 0.02\times 5}{1000}\times\frac{270.33}{2}$ = …… mg $K_2S_2O_8$

β) $\frac{25\times c(Fe^{2+}) - V_2\times 0.02\times 5}{1000}\times\frac{270.33}{2}$ = …… mg $K_2S_2O_8$

3.

α) $\frac{(V_1 - V_2)\times 0.02\times 5}{1000}\times\frac{40}{2}$ = …… mol $K_2S_2O_8$ / dm^3

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