22nd

ICHO

International Chemistry Olympiad

7 theoretical problems
4 practical problems

THE TWENTY-SECOND
INTERNATIONAL CHEMISTRY OLYMPIAD
8–17 JULY 1990, PARIS, FRANCE

THEORETICAL PROBLEMS

PROBLEM 1

PHOSPHORIC ACID

The elemental phosphorus is present in the nature as phosphate in a complex mineral apatite. This mineral contains, in addition to phosphate, silica and the following ions: Ca^{2+}, CO_3^{2-}, SO_4^{2-}, SiO_3^{2-}, and F^-.

Let us assume that this mineral is a mixture of tricalcium phosphate, $Ca_3(PO_4)_2$, calcium sulphate, calcium fluoride, calcium carbonate and silica.

For uses as fertilizer the calcium bis(dihydrogenphosphate), $Ca(H_2PO_4)_2$, which is soluble in water, has been prepared. For this purpose, apatite is treated with a mixture of phosphoric and sulphuric acid. At the same time this operation eliminates the majority of impurities.

The elemental analysis of an apatite gave the following results in which, except of fluorine, the elemental composition is expressed as if the elements were in the form of oxides:

	CaO	P_2O_5	SiO_2	F	SO_3	CO_2
% by mass	47.3	28.4	3.4	3.4	3.5	6.1

Operation 1 - A sample of m_0 of this mineral is treated with 50.0 cm^3 of a solution containing 0.500 mol dm^{-3} phosphoric and 0.100 mol dm^{-3} sulphuric acids. The mixture is completely dehydrated by heating up to about 70 °C avoiding temperature rising above 90 °C. This operation is carried out under the hood since toxic gaseous substances are emitted. The dry residue is ground and weighed; m_1 is the mass of the residue obtained.

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429

In these conditions only dihydrogenphosphate, $Ca(H_2PO_4)_2$, is formed while silica and silicate do not react.

Operation 2 - 1.00 g of this residue is treated with 50.0 cm^3 of water at 40 ℃, then filtered, dried and weighed. The mass of the residue obtained is m_2. This new residue is mainly containing gypsum, $CaSO_4 \cdot 2\,H_2O$, whose solubility can be considered as constant between 20 ℃ and 50 ℃ and is equal to 2.3 g dm^{-3}.

1.1 Write the balanced equations for the reactions that are involved.

1.2 From what mass of apatite should one start if all the reactions are stoichiometric?

Starting with m_0 of obtained apatite, $m_1 = 5.49$ g of residue are obtained.

1.3 What mass should theoretically be obtained?

1.4 This result is due to the presence of products that are not expected to be found in the residue. Give two of them that under these experimental conditions can plausibly account for the data.

Traditionally, in industry the analysis and the yield are expressed as percentage of oxide. The phosphorous content is expressed as if it were P_2O_5.

If n_2 is the amount of a soluble product obtained, n_1 the amount of a substance added as acid, n_0 the amount of apatite added, the yield is:
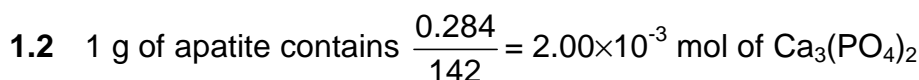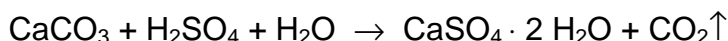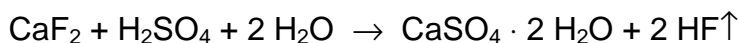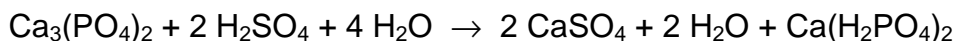
$$r_{exp} = \frac{n_2}{n_1 + n_0}\,100$$

$m_2 = 0.144$ g of residue is obtained on the filter.

1.5 Calculate r_{exp}.

1.6 The experimental yield is over 100 %. Calculate a value of r nearer to the real yield.

Relative atomic masses of P: 31; Ca: 40; O: 16; H: 1; F: 19; C: 12; Si: 28; S: 32.

Values of pK: $\dfrac{HSO_4^-}{SO_4^{2-}} = 2$ $\dfrac{HF}{F^-} = 3$ $\dfrac{H_3PO_4}{H_2PO_4^-} = 2$ $\dfrac{H_2PO_4^-}{HPO_4^{2-}} = 7$ $\dfrac{HPO_4^{2-}}{PO_4^{3-}} = 12$

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430

SOLUTION

1.1 $Ca_3(PO_4)_2 + 4\,H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2\,HF$

$CaCO_3 + 2\,H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + CO_2\uparrow + H_2O$

$Ca_3(PO_4)_2 + 2\,H_2SO_4 + 4\,H_2O \rightarrow 2\,CaSO_4 + 2\,H_2O + Ca(H_2PO_4)_2$

$CaF_2 + H_2SO_4 + 2\,H_2O \rightarrow CaSO_4 \cdot 2\,H_2O + 2\,HF\uparrow$

$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2\,H_2O + CO_2\uparrow$

1.2 1 g of apatite contains $\dfrac{0.284}{142} = 2.00 \times 10^{-3}$ mol of $Ca_3(PO_4)_2$

$\dfrac{0.034}{2+19} = 0.89 \times 10^{-3}$ mol of CaF_2

$\dfrac{0.061}{44} = 1.39 \times 10^{-3}$ mol of $CaCO_3$

$\dfrac{0.035}{80} = 0.44 \times 10^{-3}$ mol of $CaSO_4$

$\dfrac{0.473}{56} - \dfrac{3 \times 0.284}{142} - \dfrac{0.034}{38} - \dfrac{0.061}{44} - \dfrac{0.035}{80} = 2.72 \times 10^{-4}$ mol CaO that remain.

The amount of H_3PO_4 needed to react with 1 g of apatite is equal to $n(H_3PO_4) = 4\,n(Ca_3(PO_4)_2) + 2\,n(CaF_2) + 2\,n(CaCO_3) = 12.56 \times 10^{-3}$ mol.

50 cm^3 of the acid contains 25×10^{-3} mol of H_3PO_4, therefore 25 / 12.56 = <u>1.99 g</u> apatite is needed to neutralize the H_3PO_4 present.

The amount of H_2SO_4 needed to react with 1 g of apatite can be calculated in the same way:

$n(H_2SO_4) = 2\,n(Ca_3(PO_4)_2) + n(CaF_2) + n(CaCO_3) = 6.28 \times 10^{-3}$ mol. 50 cm^3 of the acid contains 5.00×10^{-3} mol of sulphuric acid. Therefore 5 / 6.28 = 0.80 g of apatite is needed to neutralize the H_2SO_4.

The total amount of apatite is $m_0 = 1.99 + 0.80 =$ <u>2.79 g</u>

1.3 Formation of $Ca(H_2PO_4)_2$:

1.99 g of apatite needed to neutralize the H_3PO_4 contains $1.9 \times 2.00 \times 10^{-3}$ mol of $Ca_3(PO_4)_2$, thus $3 \times 2 \times 2 \times 10^{-3} = 1.2 \times 10^{-2}$ mol of dihydrogen phosphate is being formed.

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431

From CaF_2, $1.99 \times 0.89 = 1.80$ mol and from $CaCO_3$, $1.99 \times 1.39 = 2.77$ mol of $Ca(H_2PO_4)_2$ are formed.

0.8 g of apatite that reacts with 50 cm^3 of the sulphuric acid yields $2 \times 0.8 \times 10^{-3} = 1.6 \times 10^{-3}$ mol of $Ca(H_2PO_4)_2$.

$m(Ca(H_2PO_4)_2 = 18.07 \times 10^{-3}$ mol $= 4.230$ g

Formation of gypsum: $n(CaSO_4) = n(H_2SO_4) = 5.00 \times 10^{-3}$ mol $\triangleq 0.86$ g

The amount of $CaSO_4$ that was already present in 1 g of apatite and yielded gypsum is $0.434 \times 10^{-3} \times 172 = 0.075$ g. There remain also 0.034 g of silica, and thus the theoretical mass of the residue should be:

$m_{th} = 4.230 + 0.86 + (0.0753 + 0.034) \times 2.79 = \underline{5.39 \text{ g}}$

1.4 The difference of 0.1 g may be due to water and unreacted CaF_2 in the residue.

1.5 The second reaction is intended to dissolve $Ca(H_2PO_4)_2$, while all the other products remain on the filter.

According to the yielded residue of 0.144 g, 1 g of residue contains $1 - 0.144 = 0.856$ g of soluble product. If it were all $Ca(H_2PO_4)_2$ it would correspond to $0.856 / 234 = 3.66 \times 10^{-3}$ mol. For 5.49 g of residue it is 0.0201×10^{-3} mol of soluble product (n_2). The amount of acid used is $0.500 / 20 = 0.025$ mol H_3PO_4 (equals 0.0125 mol P_2O_5) and 0.005 mol H_2SO_4. The amount of $Ca_3(PO_4)_2$ in 2.79 g apatite is 0.00558 mol (equals 0.00558 mol P_2O_5). So, $r_{exp} = 100 \times [0.0201/(0.0125 + 0.00558)] = \underline{111 \%}$

Since 50 cm^3 water dissolve 0.115 g of gypsum, the real quantity of $Ca(H_2PO_4)_2$ is $0.856 - 0.115 = 0.741$ mol, so that the real yield gives: $r_{exp} = 100 \times [0.0174/(0.0125 + 0.00558)] = \underline{96 \%.}$

1.6 The theoretical value for r_{exp} is: $r_{exp} = 100 \times [4.23/234 / (0.0125 + 0.00558)] = 100 \%$, so this calculation makes sense.

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432

PROBLEM 2

IONIC SOLUTIONS – AQUEOUS SOLUTIONS OF COPPER SALTS

<u>This part is about the acidity of the hydrated Cu^{2+} ion and the precipitation of the hydroxide.</u>

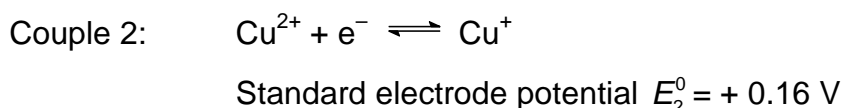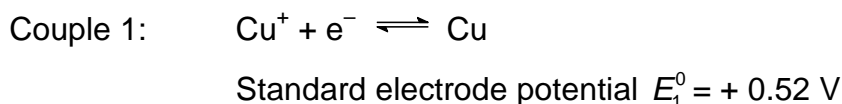Consider a 1.00×10^{-2} mol dm^{-3} solution of copper(II) nitrate. The *pH* of this solution is 4.65.

2.1   Give the equation for the formation of the conjugate base of the hydrated Cu^{2+} ion.

2.2   Calculate the *pK$_a$* of the corresponding acid-base pair.

The solubility product of copper(II) hydroxide is $K_{sp} = 1 \times 10^{-20}$.

2.3   At what *pH* value hydroxide $Cu(OH)_2$ precipitates from the solution under consideration? Justify your calculation showing that the conjugate base of this hydrated Cu^{2+} ion is present in negligible quantity.

<u>Disproportionation of copper(I) ions</u>

The Cu^+ ion is involved in two redox couples:

Couple 1: $Cu^+ + e^- \rightleftharpoons Cu$

Standard electrode potential $E_1^0 = + 0.52$ V

Couple 2: $Cu^{2+} + e^- \rightleftharpoons Cu^+$

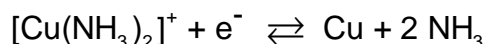Standard electrode potential $E_2^0 = + 0.16$ V

2.4   Write down the equation for the disproportionation of copper(I) ions and calculate the corresponding equilibrium constant.

2.5   Calculate the composition of the solution (in mol dm^{-3}) obtained on dissolving 1.00×10^{-2} mol of copper(I) in 1.0 dm^3 of water.

2.6   Apart from Cu^+ ions, name two chemical species which also disproportionate in aqueous solution; write down the equations and describe the experimental conditions under which disproportionation is observed.

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433

Consider the stability of copper(I) oxide, Cu_2O, in contact with a 1.00×10^{-2} mol dm^{-3} solution of Cu^{2+} ions. The solubility product of copper(I) oxide is $K_{sp} = [Cu^+][OH^-] = 1 \times 10^{-15}$

2.7 Calculate the *pH* value at which Cu_2O becomes stable. Quote a simple experiment allowing the observation of the precipitation of Cu_2O.

Complex formation involving Cu^+ and Cu^{2+} ions

2.8 The dissociation constant of the complex ion $[Cu(NH_3)_2]^+$ is $K_D = 1 \times 10^{-11}$. Calculate the standard electrode potential of the couple:
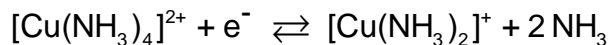
$$[Cu(NH_3)_2]^+ + e^- \rightleftarrows Cu + 2\,NH_3$$

2.9 The standard electrode potential of the couple

$$[Cu(NH_3)_4]^{2+} + 2\,e^- \rightleftarrows Cu + 4\,NH_3$$
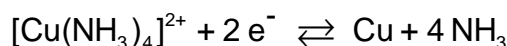
$$E_3^0 = -0{,}02 \text{ V.}$$
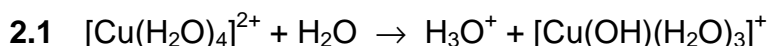
Calculate the dissociation constant for the complex ion $[Cu(NH_3)_4]^{2+}$.

2.10 Deduce from it the standard electrode potential of the couple:

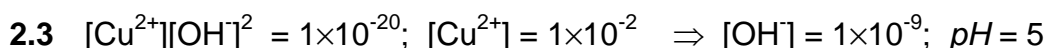$$[Cu(NH_3)_4]^{2+} + e^- \rightleftarrows [Cu(NH_3)_2]^+ + 2\,NH_3$$

Does the disproportionation of the cation $[Cu(NH_3)_2]^+$ take place?

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SOLUTION

2.1 $[Cu(H_2O)_4]^{2+} + H_2O \rightarrow H_3O^+ + [Cu(OH)(H_2O)_3]^+$

2.2 $K_a = \dfrac{[H_3O^+]\left[[Cu(OH)(H_2O)_3]^+\right]}{\left[[Cu(H_2O)_4]^{2+}\right]} = \dfrac{[H_3O^+]^2}{\left[[Cu(H_2O)_4]^{2+}\right]} = \dfrac{(2.24 \times 10^{-5})^2}{1 \times 10^{-2}} = 5.01 \times 10^{-8}$

$pK_a = 7.30$

2.3 $[Cu^{2+}][OH^-]^2 = 1 \times 10^{-20}$; $[Cu^{2+}] = 1 \times 10^{-2} \Rightarrow [OH^-] = 1 \times 10^{-9}$; $\underline{pH = 5}$

$\left[[Cu(OH)(H_2O)_3]^+\right] : \left[[Cu(H_2O)_4]^{2+}\right] = K_a : 10^{-pH} = 1 \times 10^{-7.3} : 1 \times 10^{-5} = 1 : 200$

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434

2.4 $2\,Cu^+ \rightarrow Cu^{2+} + Cu$
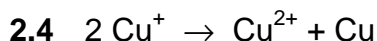
$$K = \frac{[Cu^{2+}]}{[Cu^+]^2}$$
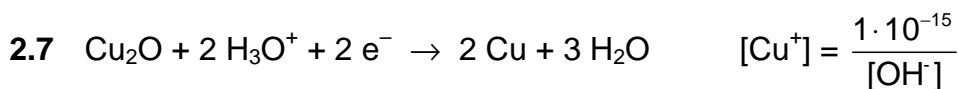
$0.52 - 0.16 = 0.059 \log K$ (Nernst equation) $\Rightarrow K = 1\times10^6$

2.5 At equilibrium: $[Cu^+] + 2\,[Cu^{2+}] = 1\times10^{-2}$ and $[Cu^{2+}] = 1\times10^6\,[Cu^+]$ so that the following equation is obtained:

$2\times10^6\,[Cu^+]^2 + [Cu^+] - 1\times10^{-2} = 0$

with the solution

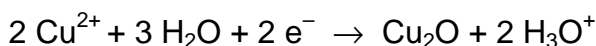$[Cu^+] = \underline{7.07\times10^{-5}}$ and $[Cu^{2+}] = \underline{4.96\times10^{-3}}$.

2.6 Other disproportionation reactions:

$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$ (catalyzed by $KMnO_4$, Fe^{3+} etc.)

$Cl_2 + OH^- \rightarrow HCl + ClO^-$ (basic conditions)

2.7 $Cu_2O + 2\,H_3O^+ + 2\,e^- \rightarrow 2\,Cu + 3\,H_2O$ $[Cu^+] = \dfrac{1\cdot10^{-15}}{[OH^-]}$

$E_1 = 0.52 + \dfrac{0.059}{2} \log\left([Cu^+][H_3O^+]^2\right) = 0.49 - 0.0885\,pH$

$2\,Cu^{2+} + 3\,H_2O + 2\,e^- \rightarrow Cu_2O + 2\,H_3O^+$

$E_2 = 0.16 + \dfrac{0.059}{2} \log \dfrac{1\times10^{-4}}{[Cu^+][H_3O^+]^2} = 0.07 + 0.0885\,pH$

Cu_2O is stable when $E_2 > E_1$ i.e. $0.42 < 0.177$ pH, or pH > 2.4

Cu_2O can be obtained by the reduction of Cu^{2+} in acid or basic media, e.g. by Fehling's solution or reducing sugars.
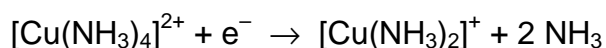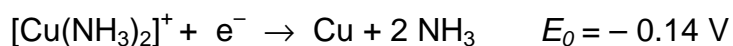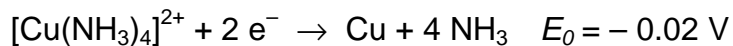
2.8 $[Cu(NH_3)_2]^+ \rightleftharpoons Cu^+ + 2\,NH_3$
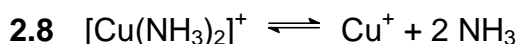
$$K_D = \frac{[Cu^+]\,[NH_3]^2}{\left[[Cu(NH_3)_2{}^+]\right]} = 1\times10^{-11}$$

Knowing $E_0(Cu^+/Cu) = 0.52$ V, the $E^0([Cu(NH_3)_2]^+ / Cu^+)$ becomes:

$E_{f1} = 0.52 - 0.06\,pK_D = -\underline{0.14\ V}$

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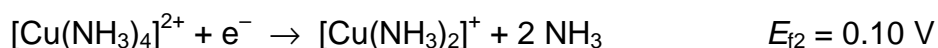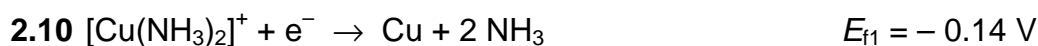ICHO International Information Centre, Bratislava, Slovakia

435

2.9 The standard *emf* of a Cu^{2+}/Cu cell is thus: E^0 = (0.5 + 0.16)/2 = 0.33 V and E_3^0 = 0.33 − 0.03 pK_2.

Thereout: pK_2 = (0.33 − E_3^0) / 0.03 = (0.33 − (− 0.02)) / 0.03 = <u>12</u>

$[Cu(NH_3)_4]^{2+}$ + 2 e$^−$ → Cu + 4 NH$_3$ E_0 = − 0.02 V

$[Cu(NH_3)_2]^+$ + e$^−$ → Cu + 2 NH$_3$ E_0 = − 0.14 V

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$[Cu(NH_3)_4]^{2+}$ + e$^−$ → $[Cu(NH_3)_2]^+$ + 2 NH$_3$

Since only ΔG^0 is additive and from $\Delta G^0 = − n F E^0$ it follows:

E_{f2} = 2 × (− 0.02) − (− 0.14) = 0.10 V

2.10 $[Cu(NH_3)_2]^+$ + e$^−$ → Cu + 2 NH$_3$ E_{f1} = − 0.14 V

$[Cu(NH_3)_4]^{2+}$ + e$^−$ → $[Cu(NH_3)_2]^+$ + 2 NH$_3$ E_{f2} = 0.10 V

Since E_{f1} < E_{f2} the $[Cu(NH_3)_2]^+$ ion doesn't disproportionate (the *emf* would be − 0.14 − 0.10 = − 0.24 V)

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436

PROBLEM 3

ORGANIC SYNTHESIS – SYNTHESIS OF HALOPERIDOL

Haloperidol is a powerful neuroleptic prescribed in cases of psychomotoric disorder and for the treatment of various psychoses. A synthesis of this compound is proposed.

3.1 Give a scheme for the preparation of methyl 4-chlorobenzoate starting from benzene and all necessary inorganic substances. Diazomethane (H_2CN_2) must be used in your synthesis.

γ-Butyrolactone (**J**) is a cyclic ester represented below.

J
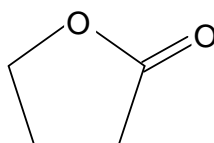
3.2 How can γ-butyrolactone **J** be converted into 4-hydroxybutanoic acid (**K**)?

3.3 Convert **K** into 4-chlorobutanoyl chloride (**L**).

The reactions described below do not correspond to those used in the industrial synthesis of haloperidol for which the route is quite complex.

Methyl 4-chlorobenzoate is treated with an excess of vinylmagnesium bromide in anhydrous ether. **M** is obtained after hydrolysis. When **M** is treated with an excess of hydrogen bromide in anhydrous conditions in the presence of benzoyl peroxide, **N** is obtained. **N** reacts with ammonia to form 4-(4-chlorophenyl)-4-hydroxypiperidine (**O**).

3.4 Write down the structure of **M**, **N** and **O** and indicate the mechanism of the reaction leading to **M**.

In the presence of a moderate amount of aluminium chloride, **L** reacts with fluoro-benzene to yield mainly a ketone **P** ($C_{10}H_{10}OFCl$).

3.5 Sketch the structure of **P** and indicate the mechanism.

3.6 Give a chemical and physical test method for the determination of the carbonyl group. How can you make sure that the carbonyl group does not belong to an aldehyde group?
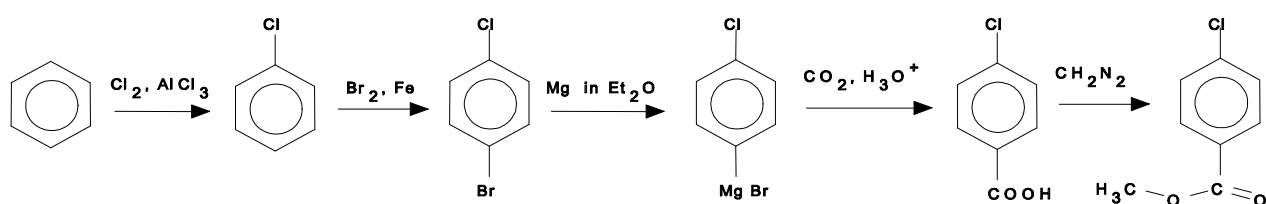
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437

P reacts with **O** in basic media in a 1 : 1 molar ratio to give **H** that contains only one chlorine atom on the aromatic ring.

3.7 Give the structure of **H** which is haloperidol.
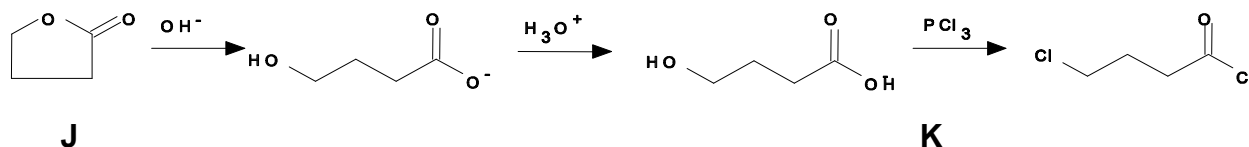
3.8 State the multiplicity of each resonance in the ^{1}H NMR spectrum of **K**. Assume that all coupling constants between protons and adjacent carbons are identical.

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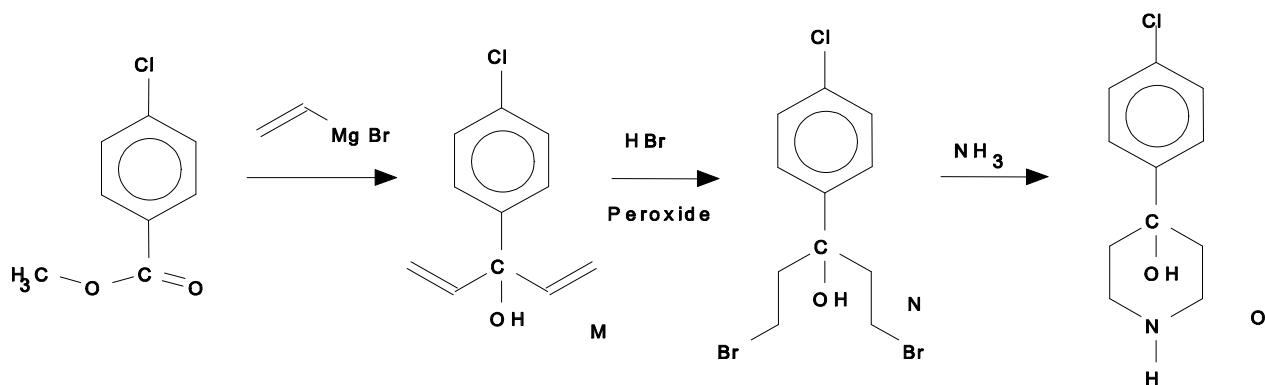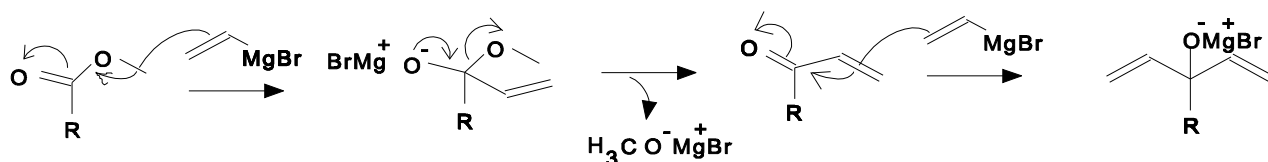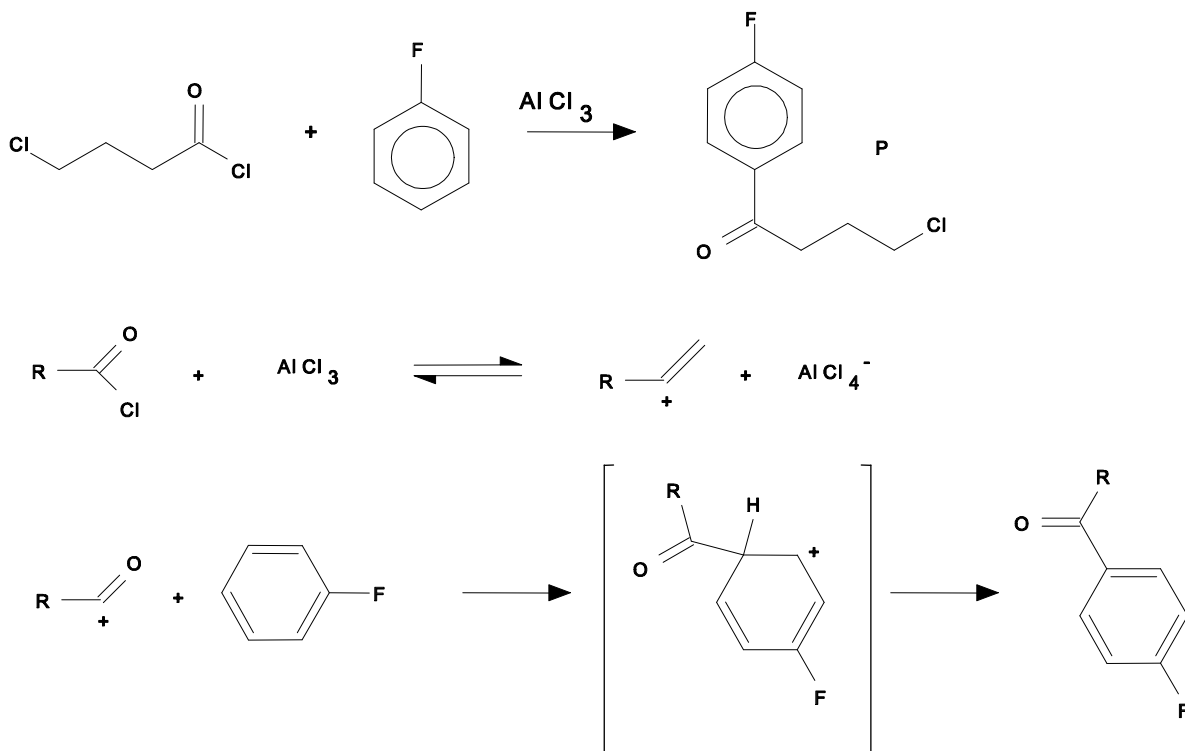# SOLUTION

3.1

3.2 and 3.3

3.4

Mechanism of the Grignard reaction:

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438

3.5

3.6 Chemical test: carbonyl groups react with phenylhydrazines to phenylhydrazones with a sharp, specific melting point.

Physical test: IR-absorption at 1740 cm^{-1}

A possibility to distinguish between ketones and aldehydes is the Tollens-test (silver mirror). Ketones cannot be reduced whereas aldehydes easily reduce the silver ions to elementary silver.

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439

3.7

Haloperidol
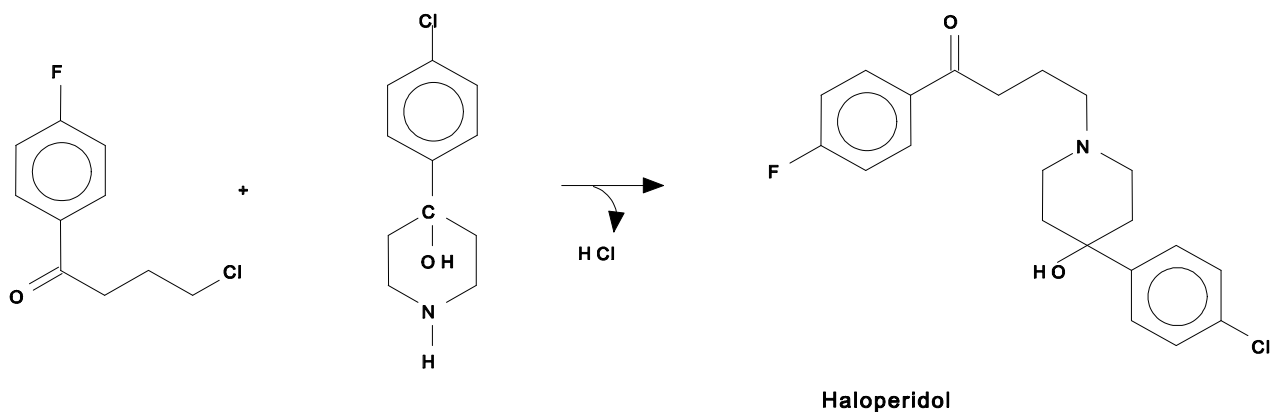
3.8
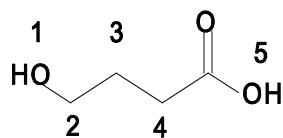
proton1:singulet

proton2:triplet

proton3:quintuplet

proton4:triplet

proton5:singulet

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440

PROBLEM 4

CHEMICAL THERMODYNAMICS

The production of zinc from zinc sulphide proceeds in two stages: the roasting of zinc sulphide in the air and the reduction of the zinc oxide formed by carbon monoxide. In this problem we will consider the roasting of zinc sulphide.

This operation consists in burning zinc sulphide in the air. The equation of the reaction taking place is as follows:

$$ZnS(s) + 3/2\ O_2(g) \rightarrow ZnO(s) + SO_2(g) \qquad \Delta_r H^0_{1350} = -448.98\ kJ\ mol^{-1}$$
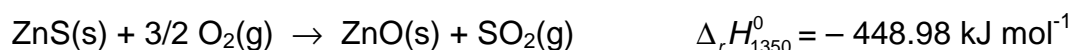
Industrially this reaction is carried out at 1350 K.

4.1 Show that the reaction can be self-sustaining, i.e. that the heat produced is sufficient to bring the reactants from ambient temperature to the reaction temperature.

Suppose that the zinc containing mineral contains only zinc sulphide, ZnS.

4.2 Starting with a stoichiometric mixture of one mole zinc blend only and a necessary quantity of the air at 298 K, calculate the temperature to which the mixture will raise by the heat evolved during the roasting of the mineral at 1350 K under standard pressure. Is the reaction self-sustaining? Air is considered to be a mixture of oxygen and nitrogen in a volume ratio equal to 1 : 4.

In fact, zinc blend is never pure and is always mixed with a gangue that can be assumed to be entirely silica SiO_2.

4.3 Assuming that the gangue does not react during the roasting, calculate the minimum ZnS content of the mineral for which the reaction would be self-sustaining at 1350 K despite the presence of silica. Give the answer is grams of ZnS per hundred grams of zinc blend.

Data:

Standard molar heat capacities averaged over the temperature range considered (in $J\ K^{-1}\ mol^{-1}$):

ZnS (solid):   58.05   ZnO (solid):   51.64

SO_2 (gas):   51.10 O_2 (gas):   34.24

N_2 (gas):   30.65 SiO_2 (solid):   72.50

Molar masses (in $g\ mol^{-1}$):   ZnS: 97.5 SiO_2: 60.1

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
Edited by Anton Sirota
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441

SOLUTION

4.1 The heat given off heats 1 mol of ZnS, 1.5 mol of O_2 and 6 mol of N_2. Therefore:

$$\Delta_r H_{1350}^0 = \int_{298}^{T} [c_p(ZnS) + 1.5\, c_p(O_2) + 6\, c_p(N_2)]\, dT = 293.3(T - 298) = 448\,980 \text{ J mol}^{-1}$$

Thus $\underline{T \approx 1830 \text{ K}}$, which indicates that the reaction is self-sustaining.

4.2 If n denotes the quantity (in moles) of SiO_2 per mol of ZnS, the heat given off heats 1 mol of ZnS, n mol of SiO_2, 1.5 mol of O_2 and 6 mol of N_2 from 298 to 1350 K:

$$\Delta_r H^o = \int_{298}^{1350} \sum (n_i \times c_{p(i)})\, dT = \int_{298}^{1350} (293.3 + 72.5\, n)\, dT$$

Wherefrom: $448\,980 = (293.3 + 72.5\, n)(1350 - 298)$, so $\underline{n = 1.84 \text{ mol}}$

4.3 By mass, we have 110.6 g of SiO_2 per 97.5 g of ZnS, or 46.9 g of ZnS per 100 g of mineral. Thus, the minimum tolerated ZnS content in the mineral is $\underline{46.9\ \%}$.

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Edited by Anton Sirota
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442

PROBLEM 5

CHEMICAL KINETICS

Nitramide NO_2NH_2 decomposes slowly in aqueous solution according to the reaction:

$$NO_2NH_2 \rightarrow N_2O(g) + H_2O$$

The experimental kinetic law is as follows:

$$\frac{d[N_2O]}{dt} = k\frac{[NO_2NH_2]}{[H_3O^+]}$$

5.1 What is the apparent order of this reaction in a buffered solution?

5.2 Which of the following mechanisms is the most appropriate for the interpretation of this kinetic law? Justify your answer.
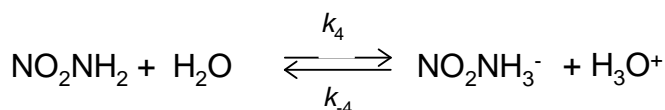
Mechanism 1:

$$NO_2NH_2 \xrightarrow{k_1} N_2O + H_2O \qquad\qquad \text{(rate limiting step)}$$

Mechanism 2:

$$NO_2NH_2 + H_3O^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NO_2NH_3^+ + H_2O \qquad \text{(rapid equilibrium)}$$

$$NO_2NH_3^+ \xrightarrow{k_3} N_2O + H_3O^+ \qquad\qquad \text{(rate limiting step)}$$

Mechanism 3:

$$NO_2NH_2 + H_2O \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} NO_2NH_3^- + H_3O^+$$

$$NO_2NH^- \xrightarrow{k_5} N_2O + OH^- \qquad\qquad \text{(rate limiting step)}$$

$$H_3O^+ + OH^- \xrightarrow{k_6} 2\,H_2O \qquad\qquad \text{(very fast reaction)}$$
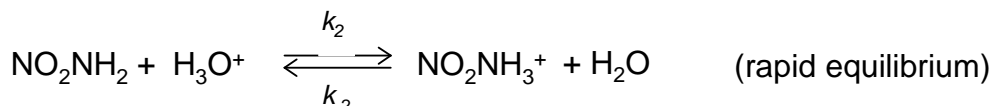
5.3 Show the relationship between the experimentally observed rate constant and the rate constants of the selected mechanism.

5.4 Show that hydroxyl ions catalyze the decomposition of nitramide.

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Edited by Anton Sirota
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443

The decomposition is studied in a buffered solution of a constant volume V at a constant temperature by measuring the partial pressure of the gas N_2O, considered to be insoluble in water, in a constant volume of the same value V above the solution. The following results are obtained:

t(min)	0	5	10	15	20	25
p(Pa)	0	6800	12400	17200	20800	24000

After a sufficiently long time, the pressure stabilises at 40000 Pa.

5.5 Express the pressure p as a function of time and the constant $k`$ such that

$$k` = \frac{k}{[H_3O^+]} \ .$$

5.6 Verify graphically that the kinetic law is confirmed by these experimental results.

5.7 Calculate k' giving its units.

_____

SOLUTION

5.1 In a buffer solution $[H_3O^+]$ is constant and the reaction is of the first order:

$v = k' [NO_2NH_2]$

5.2 The rate laws of the three mechanisms proposed are:

$v_1 = k_1 [NO_2NH_2]$

$v_2 = k_3 [NO_2NH_3^+] = \dfrac{k_3 k_2}{k_{-2}} [NO_2NH_2] [H_3O^+]$

$v_3 = k_5 [NO_2NH^-] = \dfrac{k_5 k_4}{k_{-4}} \dfrac{[NO_2NH_2]}{[H_3O^+]}$

Thus, it is the third mechanism that is correct.

5.3 $k = \dfrac{k_5 k_4}{k_{-4}}$

5.4 Noting that $[H_3O^+] = K_e / [OH^-]$ it follows that $v = k / K_e [NO_2NH_2] [OH^-]$, which shows the catalytic role of OH^-.

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
Edited by Anton Sirota
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444

5.5 $d[N_2O]$ can be expressed by the change of pressure $dp(N_2O)/RT$ (according to $pV = nRT$). We obtain:

$$v = \frac{d[N_2O]}{dt} = \frac{1}{RT}\frac{dp(N_2O)}{dt} = \frac{1}{RT}\frac{dp}{dt} = k\frac{[NO_2NH_2]}{[H_3O^+]}$$

We also know that $V[NO_2NH_2] = n(NO_2NH_2)_{init} - n(N_2O) = n(N_2O)_\infty - n(N_2O)$ from which

$$\frac{dp}{dt} = \frac{k}{[H_3O^+]} \times \frac{RT}{V} \times (n(N_2O)_\infty - n(N_2O))$$

and thus

$$\frac{dp}{dt} = \frac{k}{[H_3O^+]} \times (p_\infty - p) = k'(p_\infty - p)$$

Integration gives $p = p_\infty (1 - e^{-k't})$

wherefrom: $e^{-k't} = 1 - p/p_\infty$

5.6
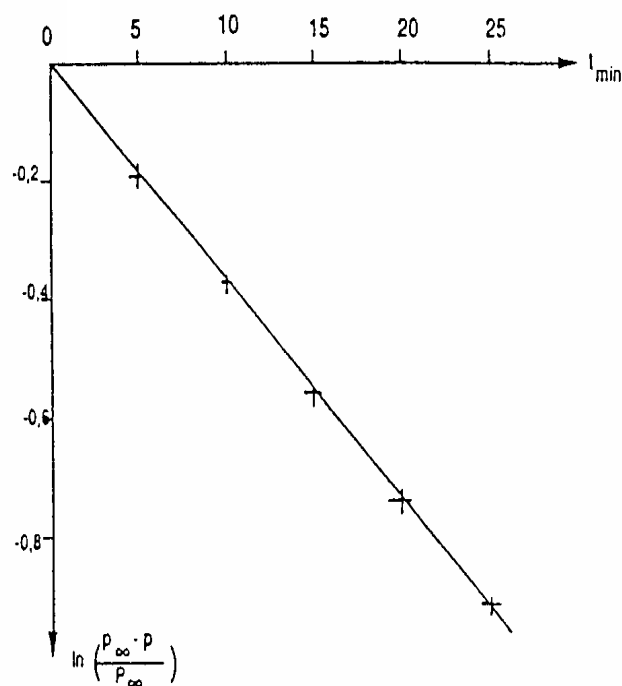
5.7 The graph of $f(x) = \ln(1 - p/p_\infty) = -k't$ is a straight line with the slope k' shown in Fig. k' was determined to be 3.7×10^{-2} min^{-1}.

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445

PROBLEM 6

BIO-ORGANIC CHEMISTRY

The reaction of dehydrogenation of succinate to fumarate is a one step in the tricarboxylic Krebs cycle, catalysed by the enzyme succinic dehydrogenase. Flavine-adenine-dinucleotide, FAD, acts as a coenzyme. The equation of the process:

Succinate   Fumarate
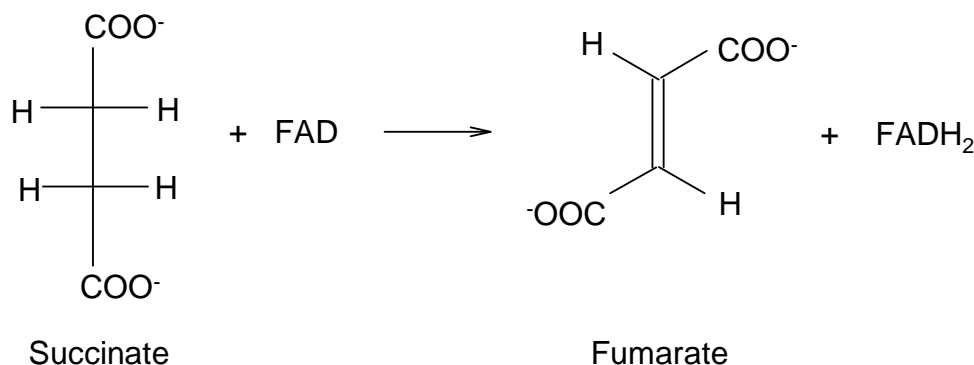
The stereochemistry of the dehydrogenation of succinate to fumarate has been studied. Consider the enzymatic reaction with the 2,3-dideuteriosuccinates related to the acids or obtained by catalytic deuteration (in the presence of palladium on coal) of fumaric and maleic acids.
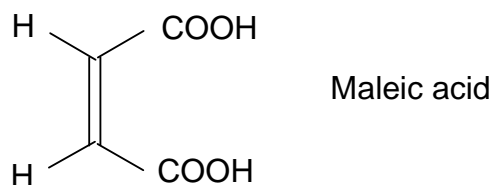
Maleic acid

6.1 Using Fischer formulae, write down structures for all the possible stereoisomers obtained by catalytic deuteration of maleic and fumaric acids. How many isomers are there? Indicate those that are optically active. Establish a stereochemical relationship between them (compare the isomers two by two). Using Newman projections show the most stable conformation of each isomer.

The proportion of dideuterated fumarate (obtained when each of the above 2-3 dideuterated succinates is submitted to the enzymatic reaction) is 4 % when using fumaric acid as starting molecule, but 48.5 % when using maleic acid.

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446

It is assumed that at the active site, the enzymatic dehydrogenation occurs on the succinate, in the most stable conformation as proposed in 6.1. The dehydrogenation stereochemistry can be *syn* or *anti*.

6.2 On the basis of the Newman projections of the most stable conformations of each isomer and the above facts, determine the percentage of dideuterated fumarate formed by *syn* and *anti* dehydrogenation.

(Assume that the percentages of dideuterated fumarate are 0 or 50 %, respectively.)

6.3 Show the stereochemistry of the enzymatic dehydrogenation.

In the following step of the Krebs cycle and in the presence of fumarase enzyme, fumarate adds on a water molecule to yield (*S*)-malate (also called as L-malate).
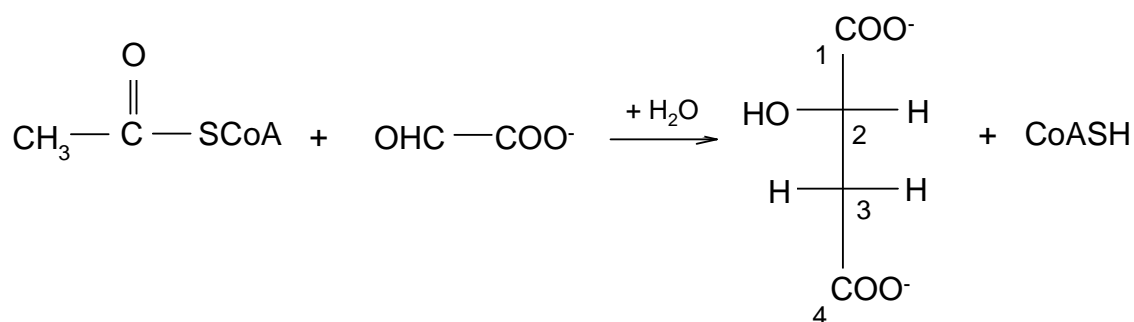
Fischer projection of (*S*)-malate:
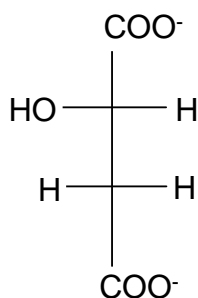
6.4 The 2,3-dideuterofumarate reacts with fumarase to (2*S*,3*S*)-2,3-dideuteromalate (through addition of water). Show the stereochemical pathway of the reaction. Use the schematic drawing below to answer this question.

2,3-dideuteriofumarate

(2S,3S)-2,3-dideuteriomalate
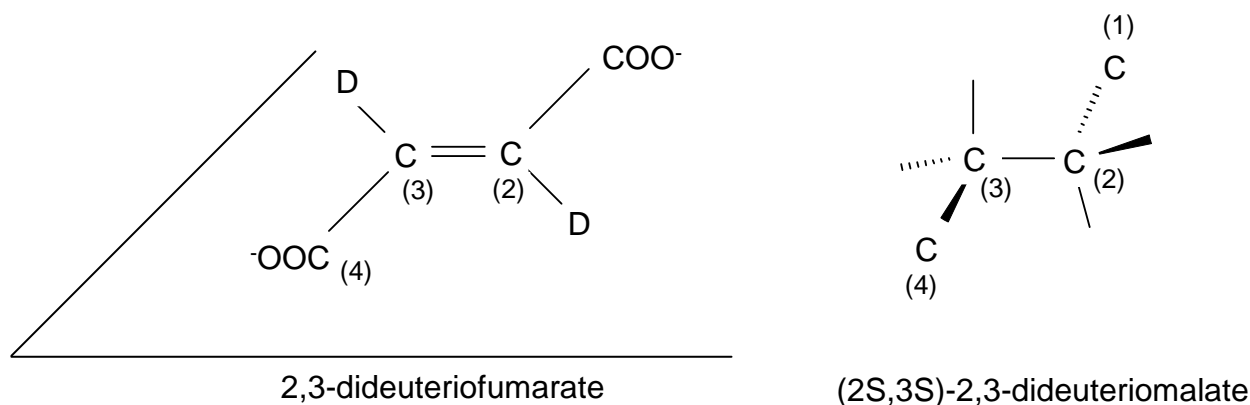
The acetylcoenzyme A, CH$_3$COSCoA reacts with glyoxylate, OHC-CO$_2$-, in the presence of malate synthetase enzyme to (*S*)-malate.

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447

A similar reaction can proceed between an ester CH_3COOR' (similar to the thioester $CH_3COSCoA$) and an aldehyde $R''CHO$ (similar to the glyoxylate) in the presence of $R'\text{-}O^-$ ions. It leads to a β-hydroxyester.
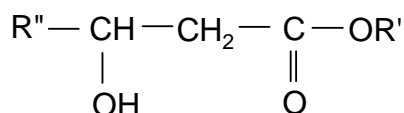
(R'-O⁻ enter the reaction as a base to produce an intermediate carbanion from the ester)

6.5 Write the steps of the mechanism.

The enzymatic reaction is carried out using acetylcoenzyme A which is obtained from acetic acid CHDTCOOH having R-configuration.
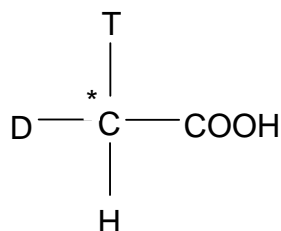
(tritium $T = {}_1^3H$, deuterium $D = {}_1^2H$)

The formed (*S*)-malate is dehydrated (the reverse reaction of question 6.4) by an enzymatic reaction.

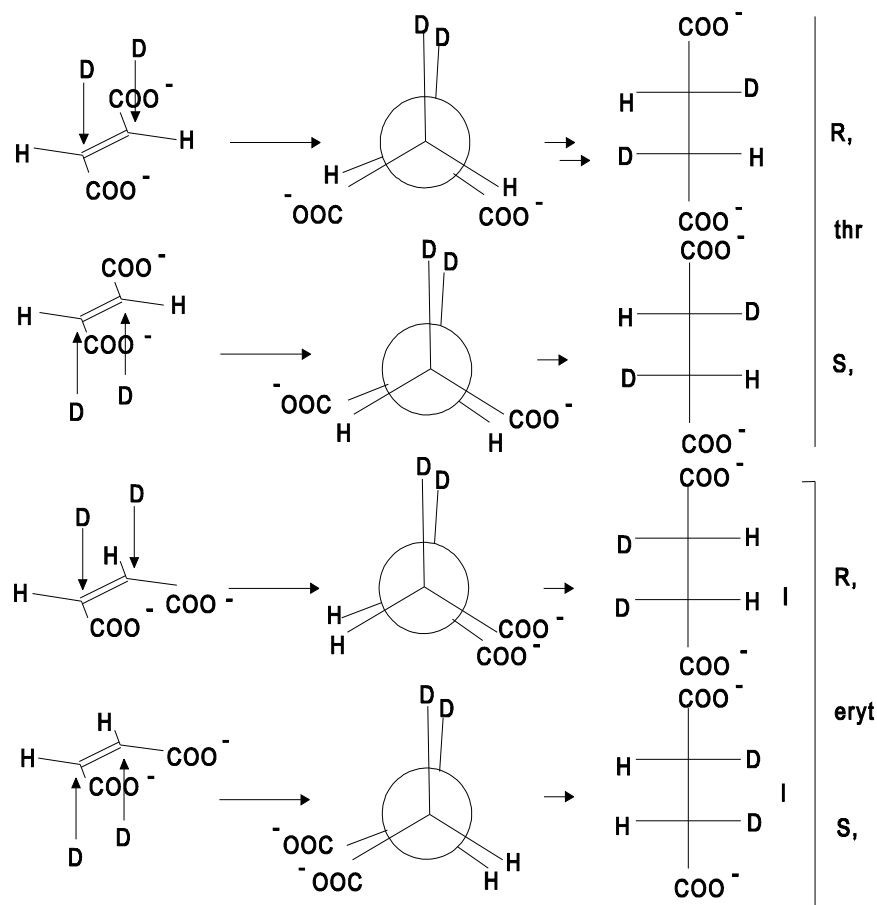**6.6** What enzyme can be used?

The major product is monotritiated fumarate (79%) with 21 % untritiated fumarate.

6.7 Write down the Fischer projections of the two possible structures of the major product (*S*)-malate arising from the acetylcoenzyme A which has a labelled acetyl group with *R*-configuration.
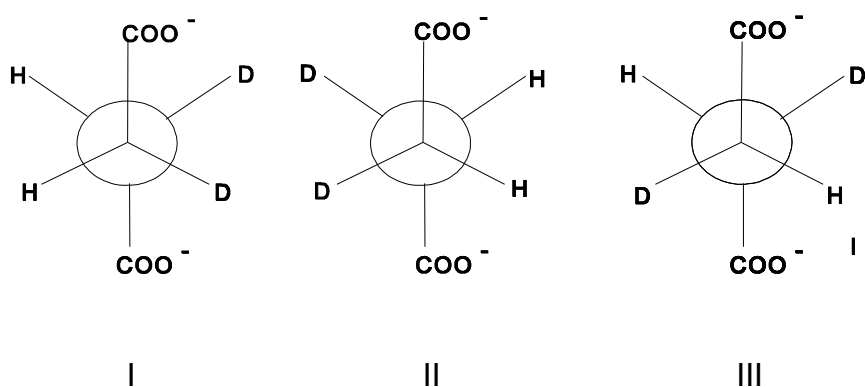
6.8 What would be the products if the starting material has a labelled acetyl group with *S*-configuration**?**

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448

SOLUTION

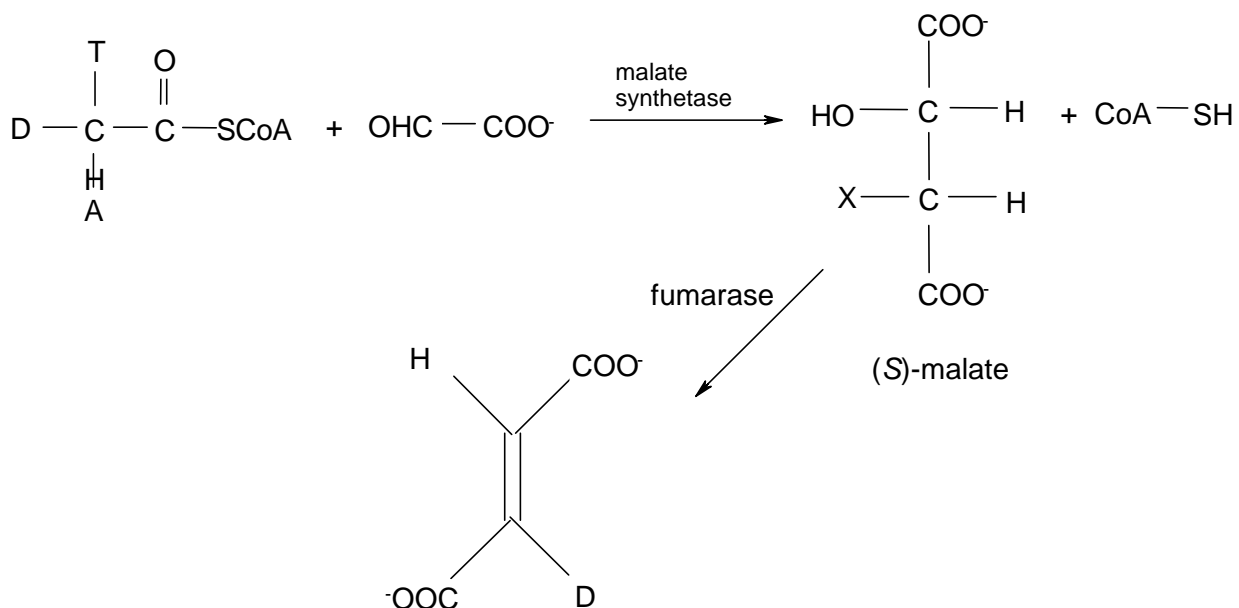**6.1** There are three isomers. The catalytic deuteration is a syn deuteration.

The most stable conformation for succinates is the anti form, since the distance between the bulky COO^- groups is maximal:

I	II	III

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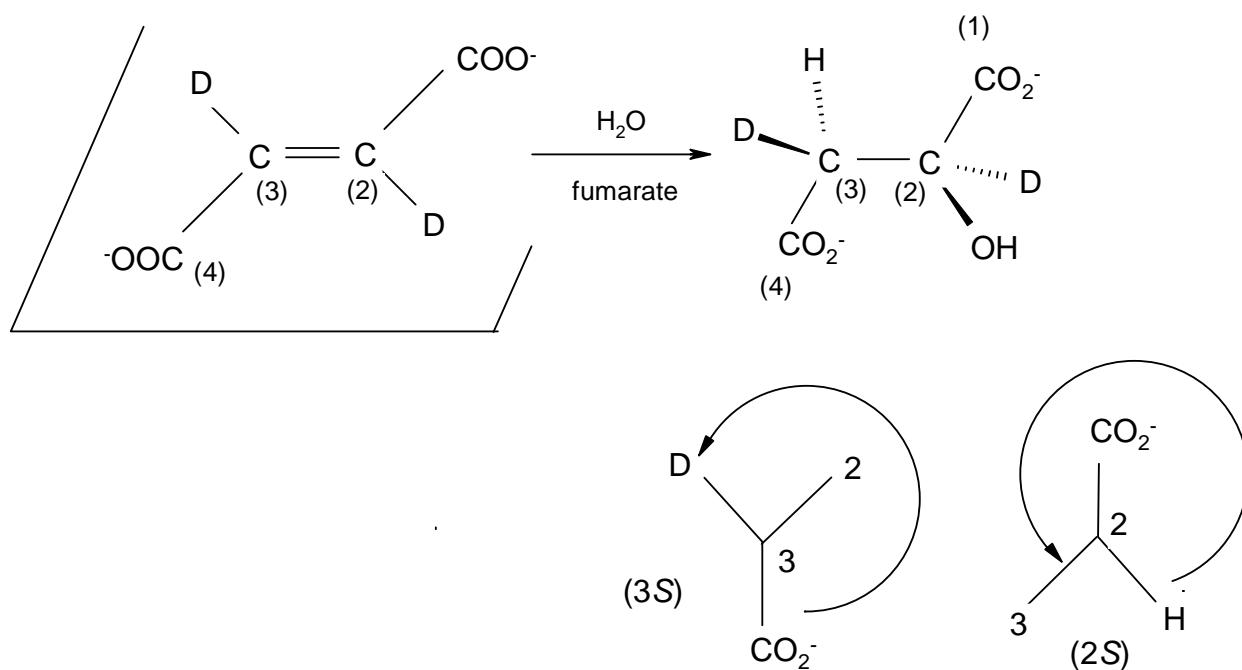ICHO International Information Centre, Bratislava, Slovakia

449

I and II are enantiomeres, II and III are a meso isomer, thus there are in total three isomers (two enantiomers and one meso form). Each threo and the meso form are diastereomers.

6.2 Considering the Newman projections of the three isomers it is clear that *syn* elimination of I and II leads either to fumarate containing no D or to dideuterated fumarate (percentage of dideuterated fumarate is thus 50 %) whereas *anti* elimination leads to monodeuterated fumarate. Concerning the experiment 4 % of dideuterated fumarate indicates that *anti* elimination occurs. *Syn* - elimination of the meso-form only leads to monodeuterated fumarate, whereas *anti*-elimination gives 50 % normal and 50% dideuterated fumarate. This is in accordance with the experiment where 48.5% of dideuterated fumarate are obtained after enzymatic dehydrogenation of the meso isomer formed from maleic acid.

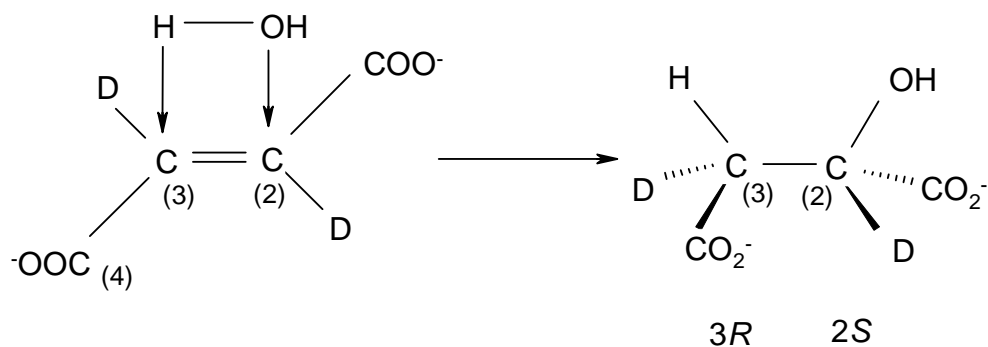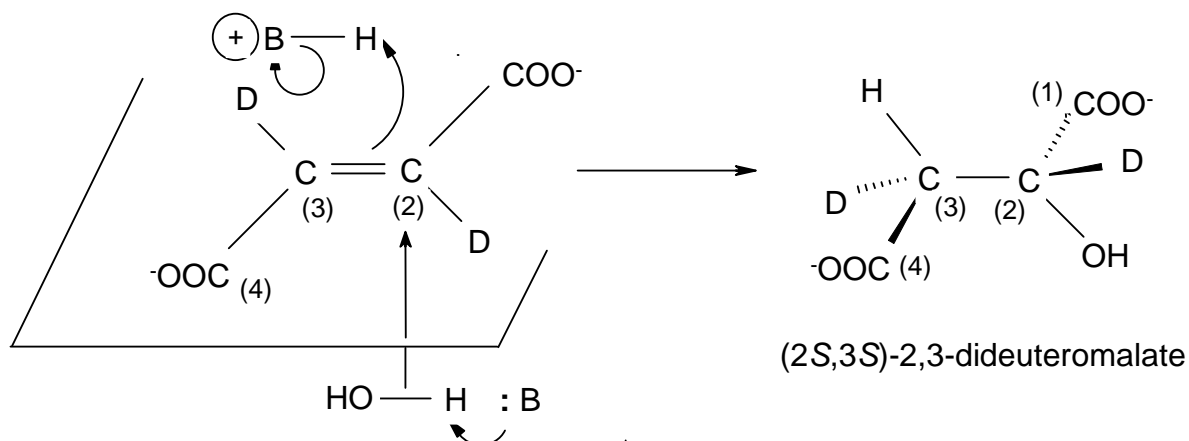**6.3** The enzymatic dehydrogenation is a anti elimination as shown above.

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450

6.4

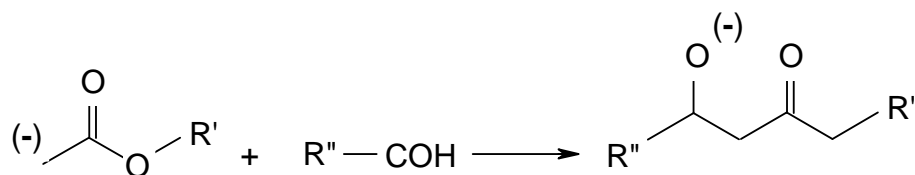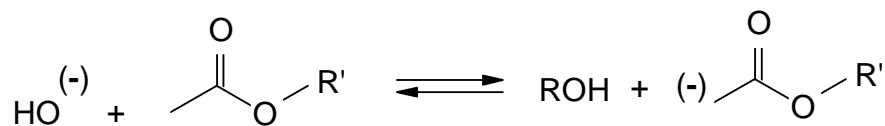Stereospecific addition, *syn* or *anti*

Syn addition:

Syn addition would yield 2*S*, 3*R* or 2*R*, 3*S*

Anti addition:

(2*S*,3*S*)-2,3-dideuteromalate

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Edited by Anton Sirota
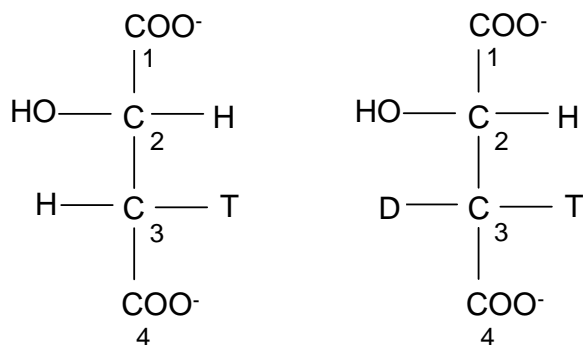ICHO International Information Centre, Bratislava, Slovakia

451

6.5
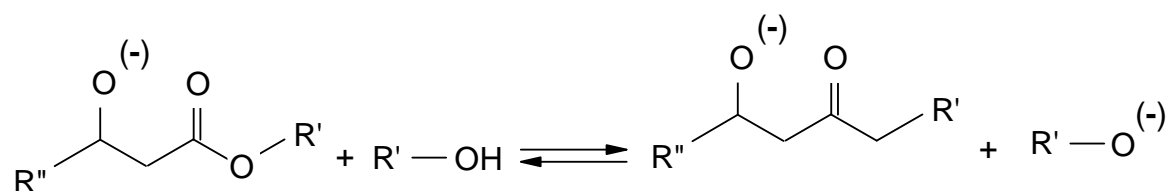
6.6 We would have (2*R*) (3*R*) if the enzyme did not produce enantiospecific addition. Thus: enantiospecific addition *anti*.

6.7 Thus Y = T and X = H or D; then the two Fischer projections are:

6.8 Starting from an acetyl group of *S* configuration one obtains a configuration inversion of carbon 3 for L-malate and two possible structures are:

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452

major products | minor product

79 % non tritiated fumarate

21 % monotritiated fumarate

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453

PROBLEM 7

In this problem tick the appropriate box in the tables of the answer sheet.

Hydrogenation of benzene to cyclohexane is performed in continuous reactors. The reaction is as follows:

$C_6H_6 + 3 H_2 \rightleftarrows C_6H_{12}$ (catalyst) $\Delta H^0 = 214$ kJ mol^{-1} at 200 °C
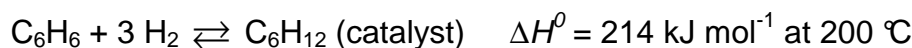
Two basic types of continuous reactors are examined: a continuous plug flow reactor and a continuous stirred reactor.
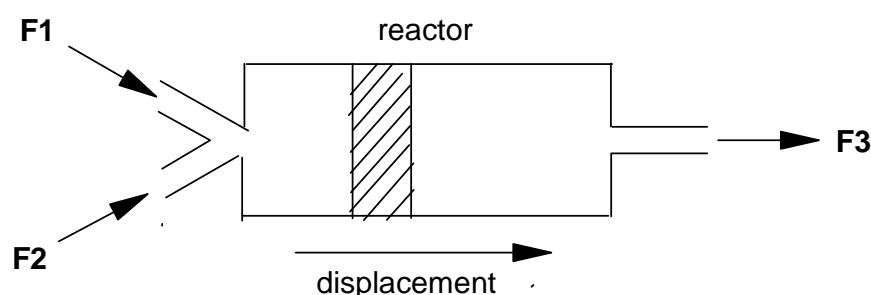
The continuous plug flow reactor (Fig. 1)

Fig. 1

The reagents are introduced and mixed at the inlet of the reactor (flow F1 and F2). Each slice of the reaction medium (marked zone in the diagram) moves along inside the plug flow reactor without mixing with the others and exits from the reactor (flow F3). When the flow has stabilized, concentrations and conditions are time-independent but dependent on the location in the reactor.

The continuous stirred reactor (Fig. 2)

reactor
Fig. 2

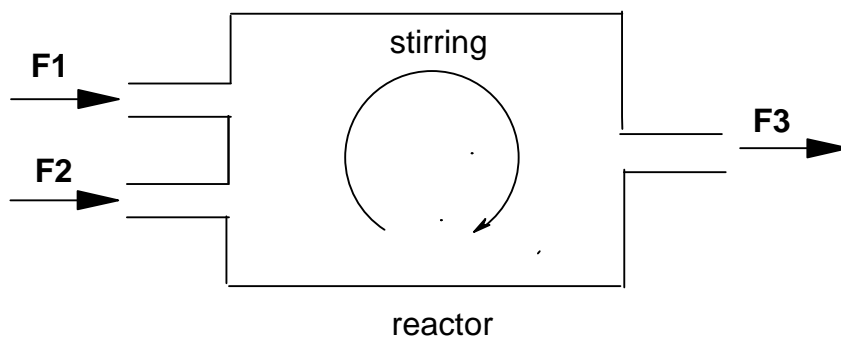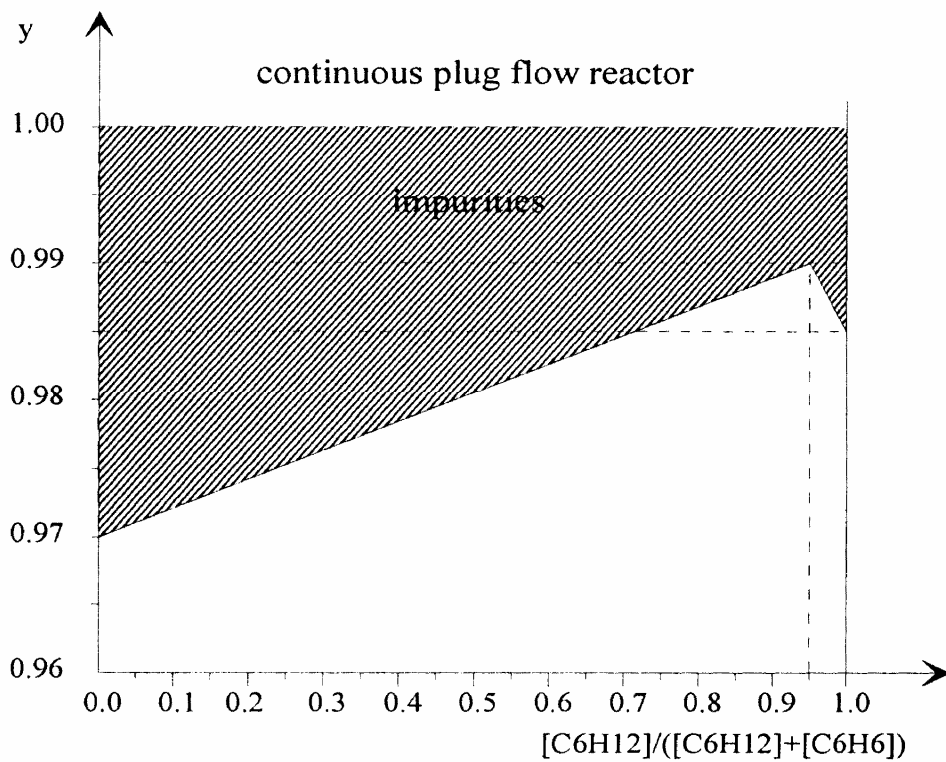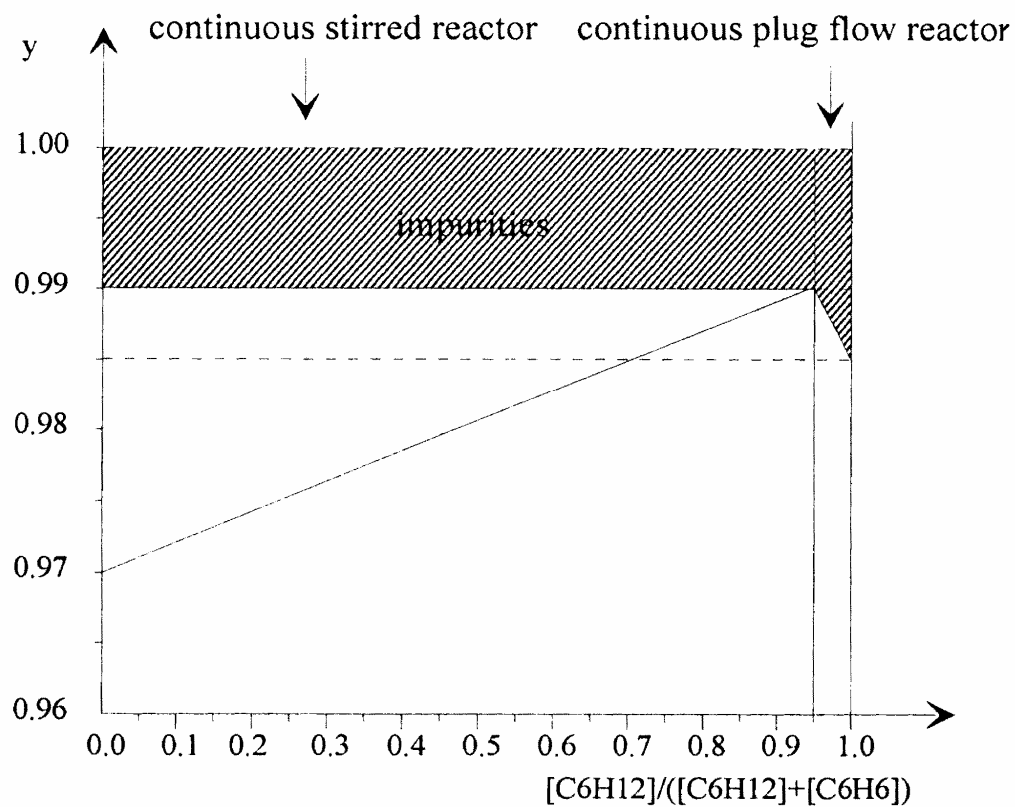The reagents are introduced into the reactor (flows F1 and F2). Inside the reactor they are stirred perfectly and instantaneously. When the flow is stabilized, concentrations and conditions are time-independent and identical at every point of the reactor.

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454

The differential yield of hydrogenation (Y) is given by $Y = -\dfrac{d([C_6H_{12}])}{d([C_6H_6])}$.

The proportion of benzene already hydrogenated is given by $p = \dfrac{[C_6H_{12}]}{[C_6H_{12}] + [C_6H_6]}$.

The relationship between p and Y is shown in Fig. 3.

Fig. 3

The aim is to hydrogenate almost all the benzene, i.e. $0.9 \leq p \leq 1$ with the best mean yield

$Y = -\dfrac{\Delta[C_6H_{12}]}{\Delta[C_6H_6]}$.

7.1 What is the value of p in a continuous stirred reactor leading to the maximal mean yield of hydrogenation? What is the maximal value of Y?

7.2 For a continuous plug flow reactor, give a rough value of Y for $0.9 \leq p \leq 1$:

Y = 0.97, 0.98, 0.99 or 1.00 ?

7.3 Represent by grey shading in the graph (Fig. 3) the quantities of benzene lost in installation P (plug flow reactor) and installation MP (stirred reactor + plug flow reactor).

7.4 Give the amount of annual benzene lost in installation P and MP assuming an annual consumption of 100 000 tons of benzene.

_____

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455

SOLUTION

7.1 In the continuous stirred reactor, concentrations are time independent and identical at every point. This means that the differential yield y for a given p is identical to the mean yield Y. A maximum mean yield is therefore obtained for y_{max}. From the Fig. 1 it's seen that $y_{max} = 0.99$ with p = 0.95.

7.2 In a continuous plug flow reactor concentrations are time-independent but dependent upon the location in the reactor. We shall consider a thin slice dx of the reactor at the entrance and at the end of the reactor. At the entrance $[C_6H_6] = 1$ and $[C_6H_{12}] = 0$, thus p = 0 and y = 0.97. At the outlet of the reactor we have: $[C_6H_6] = 0$ and $[C_6H_{12}] = 1$. So, p = 1 and y = 0.985. The mean yield is now the average of y over all p, which is 0.98, as one can easily see from the Fig. 1.

7.3 In the plug flow reactor, the quantity of benzene lost (not hydrogenated) is 1 – p. Fig. 1 shows the area that represents the amount of benzene that is not hydrogenated and therefore lost. For the installation MP we first have the amount of benzene lost in the continuous stirred reactor which is always 1 – 0.99 = 0.01 independent from p up to a point p = 0.95. At p > 0.95 to the continuous plug reactor has the same loss of benzene as already indicated in the Fig 1 below.

7.4 In the plug reactor the percentage of benzene lost is 2 % (the best mean yield is 0.98), therefore the amount of benzene annually lost is 2000 tons.

In a MP installation, the yield of hydrogenation is 0.99 (except for 0.95 < p < 1 where it slightly decreases to 0.985, but this can be neglected) and therefore, the overall mean yield of hydrogenation is also 0.99.

The amount of benzene annually lost is therefore 1000 tons.

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456

Figure 1

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
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457

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis involving Carbanions Chalcone

The aim of this experiment is to condense acetophenone and benzaldehyde in a mixed aldol condensation. After spontaneous dehydratation, an α,β - unsaturated ketone is obtained: the chalcone, 1,3-diphenylprop-2-en-1-on.
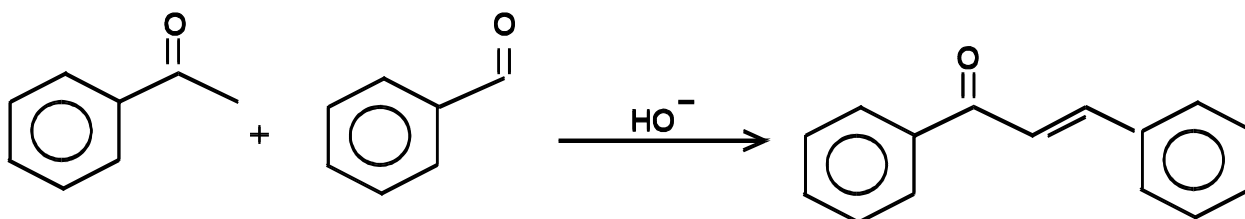
a) *Starting the condensation reaction*

In a 250 cm^3 ground neck Erlenmeyer (conical) flask, dissolve about 5 g of potassium hydroxide, KOH, (50 pellets) in 30 cm^3 of water, then add slowly under stirring 20 cm^3 of ethanol. From the automatic dispensers, add 9.6 g (0.08 mol = 9.5 cm^3) of acetophenone and 8.5 g (0.08 mol = 8.5 cm^3) of benzaldehyde. Set up a condenser in the vertical reflux position and reflux vigorously while stirring the mixture with the magnetic stirrer for an hour.

b) *Isolation of the crude chalcone*

After refluxing, cool the contents of the Erlenmeyer flask in an ice bath. The chalcone should crystallize. If crystals do not appear, scratch the inside wall of the flask with a glass rod. Collect the crystals in a Büchner funnel, wash them with a little ice cold ethanol, then air dry and weigh the crystals.

c) *Recrystallization of the chalcone*

Recrystallize this crude chalcone from ethanol, using a 100 cm^3 beaker. Use the heating plate located in the hood (fume chamber). When the crystallization is over (wait long enough and scratch if necessary), collect the crystals in a Büchner funnel, and air dry them.

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458

Give your entire product to the supervisor who will measure its mass and melting-point.
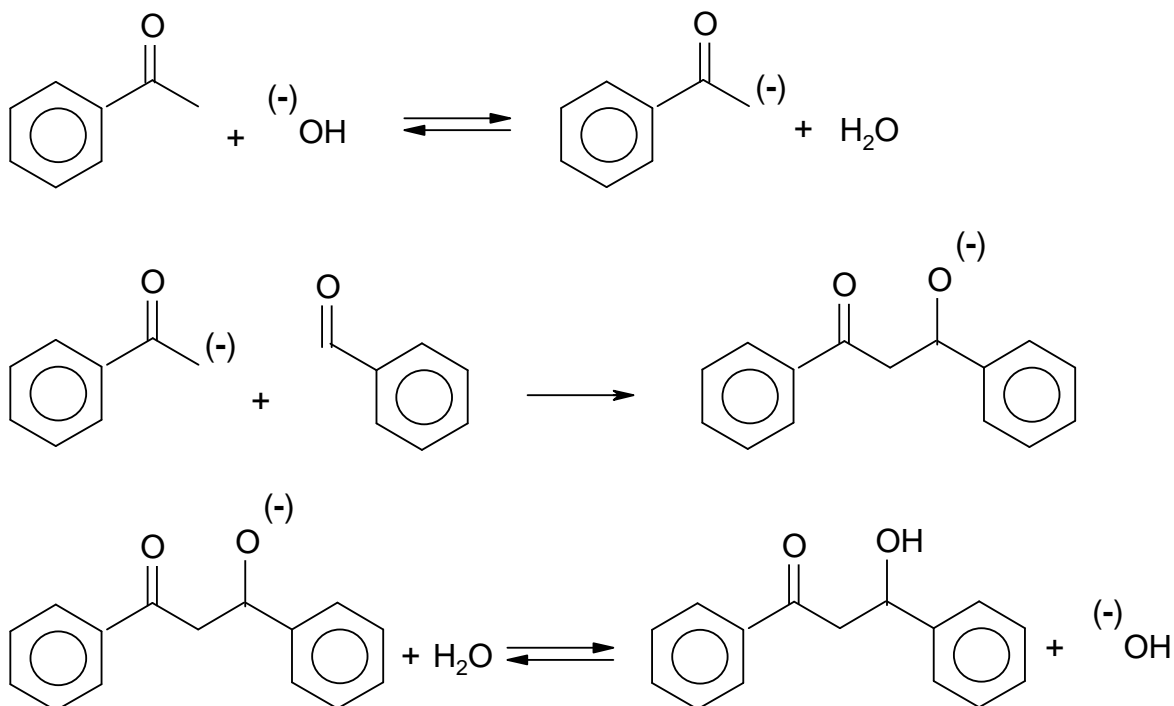
Do not breathe the vapour while recrystallizing and measuring the melting point. It contains irrigating chalcone!!!
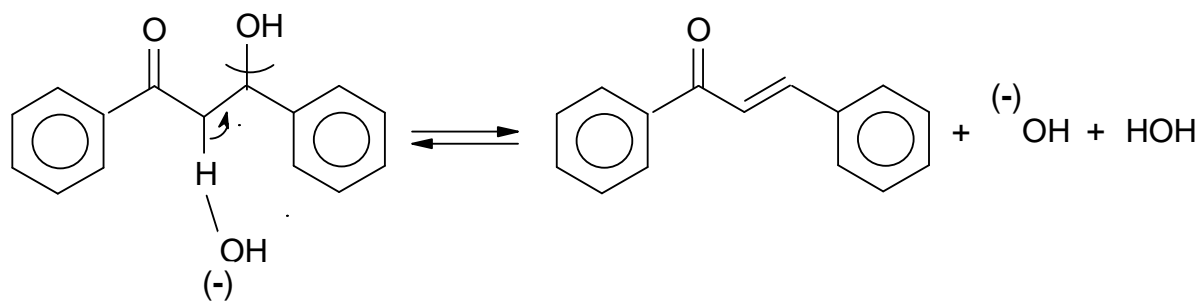
Questions:

1.1 Write the mechanism for this reaction.

1.2 Give the mass of the crystals of the crude chalcon obtained and calculate the yield of crude product.

1.3 Calculate the yield of recrystallized product based on starting material and calculate the efficiency of the recrystallization process.

SOLUTION

1.1

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
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459

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
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460

PROBLEM 2 (Practical)

Qualitative Analysis

Equipment:

Five flasks are labelled 2.1 through 2.5. Each contains an aqueous solution of a colourless metal nitrate. Except for silver nitrate, the concentrations of the nitrates used to prepare these solutions, are all 0.1 mol dm^{-3}.

The solutions are: aluminium(III) nitrate

calcium(II) nitrate

lead(II) nitrate
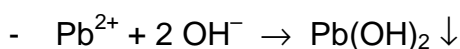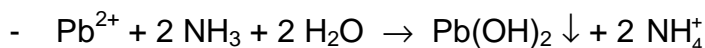
silver(I) nitrate

zinc(II) nitrate

Moreover, available are pH indicator paper and the following three reagents of a concentration of about 5 mol dm^{-3}, contained in flasks labelled 2.6 through 2.8.

2.6 : hydrochloric acid,

2.7 : aqueous ammonia solution,

2.8 : sodium hydroxide solution.

Beware: these solutions are all concentrated and corrosive.

Tasks:

2.1 Carry out reactions between each reagent and each solution. For each of the solutions 2.1 through 2.5, record your observations for each reaction observed.

2.2 Write the name of the cation contained in each of the solutions 2.1 through 2.5 in the corresponding space on the answer sheet.

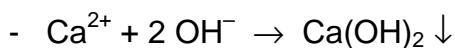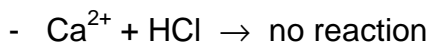**2.3** For each cation identified, write the equation for each reaction observed.

_____
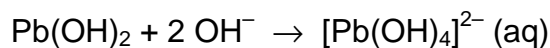
SOLUTION

2.1 Aluminium(III) nitrate

- $Al^{3+} + HCl \rightarrow$ no reaction

- $Al^{3+} + 3\,NH_3 + 3\,H_2O \rightarrow Al(OH)_3 \downarrow + 3\,NH_4^+$

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

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
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461

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

calcium(II) nitrate

- $Ca^{2+} + HCl \rightarrow$ no reaction
- $Ca^{2+} + 2\,OH^- \rightarrow Ca(OH)_2 \downarrow$

lead(II) nitrate

- $Pb^{2+} + 2\,Cl^- \rightarrow PbCl_2 \downarrow$ (in cold solutions)
- $Pb^{2+} + 2\,NH_3 + 2\,H_2O \rightarrow Pb(OH)_2 \downarrow + 2\,NH_4^+$
- $Pb^{2+} + 2\,OH^- \rightarrow Pb(OH)_2 \downarrow$

  $Pb(OH)_2 + 2\,OH^- \rightarrow [Pb(OH)_4]^{2-}$ (aq)

silver(I) nitrate

- $Ag^+ + Cl^- \rightarrow AgCl \downarrow$
- $Ag^+ + NH_3 + H_2O \rightarrow AgOH \downarrow + NH_4^+$ (or Ag_2O)

  $AgOH + 2\,NH_3 \rightarrow [Ag(NH_3)_2]^+$ (aq) $+ OH^-$
- $Ag^+ + OH^- \rightarrow AgOH \downarrow$

  $2\,AgOH \rightarrow Ag_2O + H_2O$

zinc(II) nitrate

- $Zn^{2+} + HCl \rightarrow$ no reaction
- $Zn^{2+} + 2\,NH_3 + 2\,H_2O \rightarrow Zn(OH)_2 \downarrow + 2\,NH_4^+$

  $Zn(OH)_2 + 4\,NH_3 \rightarrow [Zn(NH_3)_4]^{2+}$(aq) $+ 2\,OH^-$
- $Zn^{2+} + 2\,OH^- \rightarrow Zn(OH)_2 \downarrow$

  $Zn(OH)_2 + 2\,OH^- \rightarrow [Zn(OH)_4]^-$ (aq)

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
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462

PROBLEM 3   (Practical)

Titration of Oxygen Dissolved in Water

(Winkler's method)

In aqueous alkaline solution, dissolved oxygen oxidizes manganese(II) hydroxide to hydrated manganese(III) oxide (written as $Mn(OH)_3$ for simplification). In acidic solution, manganese(III) ions oxidize iodide ions to iodine. The iodine formed is titrated with a sodium thiosulphate solution.

Data:

Redox couple	Electrode potentials (in V)	
	at $pH = 0$	at $pH = 14$
Mn^{3+} / Mn^{2+}	1.51	
$Mn(OH)_3 / Mn(OH)_2$		0.13
O_2 / H_2O	1.23	0.39
I_2 / I^-	0.62	0.62
$S_4O_6^{2-} / S_2O_3^{2-}$	0.09	0.09

Solubility products: $K_{sp}(Mn(OH)_2) = 1 \times 10^{-13}$

$K_{sp}(Mn(OH)_3) = 1 \times 10^{-36}$

Gas constant: $R = 8.315$ J K^{-1}mol^{-1}

Procedure:

Preliminary remarks: To reduce volume variations, the reagents are added either as solids (sodium hydroxide pellets ...), or as concentrated solutions (sulphuric acid).

1.   The water to be tested is stored in a large container located on the general-use bench. Place two glass beads into a 250 cm^3 ground top Erlenmeyer (conical) flask. Fill it to the rim with the water to be tested. At this stage of the manipulation the

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
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463

Erlenmeyer flask should be standing in the basin provided to avoid overflow of water onto the bench. Measure the temperature of the water.

2. Add to the water, avoiding any loss of reagent:

   a) 2 g of manganese(II) chloride, preweighed within a decigram and contained in the bag.

   b) about 8 pellets of sodium hydroxide (yielding a basic medium, *pH* = 14). The pellets will be found on the general-use bench.

3. Stopper the Erlenmeyer flask, avoiding air bubbles, and swirl it until complete dissolution of the sodium hydroxide and of the manganese chloride has occurred. A brown precipitate forms.

4. Let the flask stand for at least 30 minutes.

5. Open the Erlenmeyer flask, add concentrated sulphuric acid dropwise, stirring with a glass rod until the solution is definitely acidic (check with the *pH* indicator paper); make sure that nearly all the precipitate has disappeared.
   Sulphuric acid will be found on the general-use bench.

6. Add to the Erlenmeyer flask 3 g of potassium iodide, preweighed within a decigram and contained in a bag. Stopper the flask and shake it until the potassium iodide has dissolved. The solution should now be clear.

7. Remove a 50 cm^3 sample of the solution and titrate it with a X mol dm^{-3} sodium thiosulphate solution (the numerical value of X will be shown on the board). For this titration, the endpoint can be determined using the indicator thiodene which is equivalent to starch. A small quantity of this solid indicator should be dissolved in the solution being titrated just prior to the endpoint.
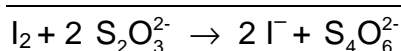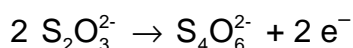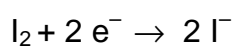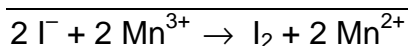
Questions:

3.1 Justify that the oxidation of manganese(II) by dissolved oxygen is possible only in alkaline solution.

3.2 Write the equation of the reaction between:

   - dissolved oxygen and manganese(II) hydroxide (in alkaline solution),

   - manganese(III) ions and iodide ions,

   - iodine and thiosulphate.
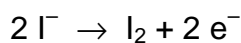
3.3 Record the volume of thiosulphate required to reach the endpoint.

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
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ICHO International Information Centre, Bratislava, Slovakia

464

3.4 Derive an expression that relates the dissolved oxygen concentration in water (expressed as mol dm^{-3}) to the volume in cm^3 of thiosulphate added at the endpoint. Determine that concentration for the water tested.

Deduce the volume of oxygen (in cm^3), determined at 0 ^{o}C and at a pressure of 101,325 Pa, contained in a litre of water (measured at ambient temperature). Give the temperature of the water.
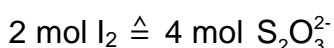
_____

SOLUTION

3.1 E^0(O$_2$/H$_2$O) > E^0(Mn(III)/Mn(II) at pH = 14

3.2 O$_2$ + 4 e$^-$ + 2 H$_2$O → 4 OH$^-$

Mn(OH)$_2$ + HO$^-$ → Mn(OH)$_3$ + e$^-$

_____

O$_2$ + 4 Mn(OH)$_2$ + 2 H$_2$O → 4 Mn(OH)$_3$

2 I$^-$ → I$_2$ + 2 e$^-$

Mn^{3+} + e$^-$ → Mn^{2+}

_____

2 I$^-$ + 2 Mn^{3+} → I$_2$ + 2 Mn^{2+}

I$_2$ + 2 e$^-$ → 2 I$^-$

2 S$_2$O$_3^{2-}$ → S$_4$O$_6^{2-}$ + 2 e$^-$

_____

I$_2$ + 2 S$_2$O$_3^{2-}$ → 2 I$^-$ + S$_4$O$_6^{2-}$
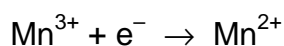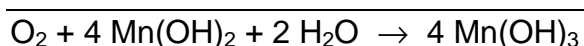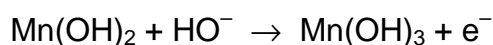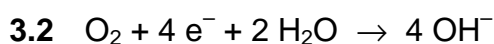
3.4 1 mol O$_2$ ≙ 4 mol Mn(II) ≙ 4 mol Mn(III)

4 mol Mn(III) ≙ 4 mol I$^-$ ≙ 2 mol I$_2$

2 mol I$_2$ ≙ 4 mol S$_2$O$_3^{2-}$

$c($S$_2$O$_3^{2-}$) × $V($S$_2$O$_3^{2-}$) = 4 × c(O2) × 50

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
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465
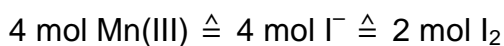
PROBLEM 4   (Practical)

Kinetics of an S$_N$1 Reaction

In an aqueous ethanolic solution, *tert*-butyl chloride (2-chloro-2-methylpropane) undergoes an S$_N$1 nucleophilic substitution reaction leading to the formation of 2-methylpropan-2-ol and hydrochloric acid:

tert-BuCl + H$_2$O = *tert*-BuOH + HCl
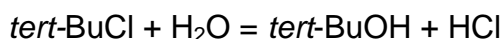
The rate of the reaction is given by

$$\frac{d[\text{HCl}]}{dt} = k_1 [tert\,\text{BuCl}]$$

The aim of this experiment is to determine the rate constant k_1 at ambient temperature.

Procedure:

1. Using a pipette transfer 2.0 cm^3 of *tert*-butyl chloride (flask 4.1 on the general-use bench) into a clean and dry 250 cm^3 ground neck Erlenmeyer (conical) flask.

2. As soon as possible add 148 cm^3 (measure with the graduated cylinder) of the aqueous ethanol solution standing on the general-use bench (flask 4.2).

3. Stopper the Erlenmeyer flask and stir vigorously using the magnetic stirrer. Start your timer. Note carefully the temperature, T(0), of the solution.

4. After approximately 5, 15, 25, 35, 45, 55 min (determined accurately), transfer 10.0 cm^3 samples using a pipette into 20 cm^3 of a mixture of ice and acetone (propanone).

    Add 2 drops of bromothymol blue and titrate the liberated acid with a solution of Y mol dm^{-3} aqueous sodium hydroxide (Y will be shown on the board).

Questions:

4.1 The concentrations of *tert*-BuCl at time $t = 0$ and at time t are linked by the following relationship:

$$\ln \frac{[\text{tertBuCl}]_0}{[\text{tertBuCl}]_t} = k_1.t$$

Establish the theoretical expression:

$$\ln \frac{V_\infty}{V_\infty - V} = k_1\, t$$

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
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466

where V stands for the volume of sodium hydroxide used at time t and $V(8)$ for the corresponding value at $t(8)$.

$$t_\infty = t(8); \quad V_\infty = V(8)$$

4.2 Calculate $V(8)$ (density of *tert*-BuCl at 20 $^{\circ}$C: 850 kg m^{-3}, molar mass of *tert*-BuCl: 92.5 g mol^{-1}).

4.3 Fill in the table on the answer sheet whose columns will be:

t(min), V(cm^3), V_∞, V, $\dfrac{V_\infty}{V_\infty - V}$, $\ln \dfrac{V_\infty}{V_\infty - V}$

Draw the curve

$$\ln \frac{V_\infty}{V_\infty - V} = f(t)$$

4.4 Determine the value of k_1 (give the value of $t(0)$).

_____

SOLUTION

4.1 $\quad$ t-BuCl + H$_2$O $\rightarrow$ t-BuOH + HCl

$t = 0$ $\quad$ (t-BuCl)$_0$

t $\quad$ (t-BuCl) $\quad$ (t-BuCl)$_0$ − (t-BuCl)

$t(8)$ $\quad\quad\quad\quad$ (t-BuCl)$_0$

$$\frac{d(\text{HCl})}{dt} = -\frac{(t-\text{BuCl})}{dt} = k_1\,(t-\text{BuCl})$$

$$\ln \frac{(t-BuCl)_0}{(t-BuCl)} = k_1\, t$$

t:

$$c(\text{HCl}) = c_0(\text{t-BuCl}) - c(\text{t-BuCl}) = \frac{V(\text{NaOH}) \times c(\text{NaOH})}{V(\text{HCl})} = \frac{V \times Y \times 10^{-2}}{10}$$

$t(8)$

$$c(\text{HCl}) = c_0(\text{t-BuCl}) = \frac{a\,Y}{10}$$

$$c(\text{t-BuCl}) = \frac{(a-V)\,Y}{10}$$

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
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467

$$\ln \frac{c_0(\text{t-BuCl})}{c(\text{t-BuCl})} = \ln \frac{a}{a-V} = k_1\, t$$

4.2 $n_0(\text{t-BuCl}) = \dfrac{1.70}{92.5}$ $M(\text{t-BuCl}) = 92.5 \text{ g mol}^{-1}$

$\text{Y} \times \text{a} \times 10^{-3} = \dfrac{10}{150} \times n_0(\text{t-BuCl})$

$\text{a}_{(ml)} = \dfrac{170}{\text{Y} \times 10^{-3} \times 15 \times 92.5}$

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
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468