

# 12<sup>th</sup>



**6 theoretical problems  
3 practical problems**

# THE TWELFTH INTERNATIONAL CHEMISTRY OLYMPIAD

**LINZ 1980  
AUSTRIA**

## THEORETICAL PROBLEMS

### PROBLEM 1

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

*1<sup>st</sup> question:* At what wavelength can the dissociating effect of light be expected?

*2<sup>nd</sup> question:* Can this effect also be obtained with light whose wavelength is smaller or larger than the calculated critical wavelength?

*3<sup>d</sup> question:* What is the energy of the photon with the critical wavelength?

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

*4<sup>th</sup> question:* How large is the quantum yield (= the number of product molecules per absorbed photons)?

*5<sup>th</sup> question:* How can the value obtained be (qualitatively) explained? Describe the reaction mechanism.

### SOLUTION

1.  $\lambda_1 = \frac{c}{\nu_1}$  from  $\Delta H = N_A h \nu_1$  it follows that

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

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

$$3. \quad E_1 = h \nu_1 = \frac{h c}{\lambda_1} = \frac{6.6 \times 10^{-34} \times 3 \cdot 10^8}{4.91 \cdot 10^{-7}} = 4.03 \cdot 10^{-19} \text{ J}$$

4. The quantum yield  $\phi = \frac{\text{the number of HCl molecules formed}}{\text{the number of absorbed photons}}$

$$\phi = \frac{\frac{n(\text{HCl}) \times N_A}{E_{tot}}}{\frac{h c}{\lambda_2}} = \frac{6.5 \times 10^{-2} \times 6.02 \times 10^{23}}{\frac{0.2 \times 2.5}{6.6 \times 10^{-34} \times 3 \times 10^8}} = 6.1 \times 10^4$$

The energy input =  $10 \times 0.02 = 0.2 \text{ W}$

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

The start of reaction chain:  $\text{Cl}_2 + h\nu \rightarrow 2 \text{Cl}\bullet$

The propagation of the chain:  $2 \text{Cl}\bullet + \text{H}_2 \rightarrow \text{HCl} + 2 \text{H}\bullet$

$\text{H}\bullet + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}\bullet$

The chain termination mainly by:  $2 \text{H}\bullet \rightarrow \text{H}_2$

$2 \text{Cl}\bullet \rightarrow \text{Cl}_2$

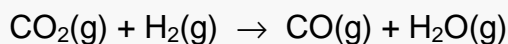
$\text{H}\bullet + \text{Cl}\bullet \rightarrow \text{HCl}$

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## PROBLEM 2

### Water gas equilibrium

The homogeneous gas reaction



is termed the water gas reaction.

Problems:

- Calculate the Gibbs reaction energy,  $\Delta G_{1000}^0$ , for the water gas reaction at 1000 K from the reaction enthalpy:  $\Delta H_{1000}^0 = 35040 \text{ J mol}^{-1}$  and the reaction entropy:  $\Delta S_{1000}^0 = 32.11 \text{ J mol}^{-1} \text{ K}^{-1}$ .
- What is the value of the equilibrium constant  $K_p$  of the water gas reaction at 1000 K?
- What are the values of the equilibrium constants  $K_x$  and  $K_c$  ( $x$ : mole fraction,  $c$ : concentration in  $\text{mol dm}^{-3}$  at the same temperature (1000 K)? (Note: The gas behaves ideally.)
- A mixture of gases containing 35 vol. % of  $\text{H}_2$ , 45 vol. % of  $\text{CO}$  and 20 vol. % of  $\text{H}_2\text{O}$  vapours is heated to 1000 K. What is the composition of the mixture after the establishment of the water gas equilibrium?
- Calculate the reaction enthalpy value,  $\Delta H_{1400}^0$ , at 1400 K from the reaction enthalpy value,  $\Delta H_{1000}^0$ , and the values of the molar heat,  $c_p^0$ , (valid in the temperature range 1000 K to 1400 K)

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

$$c_p^0(\text{CO}_2) = 42.31 + 10.09 \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$c_p^0(\text{H}_2) = 27.40 + 3.20 \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$c_p^0(\text{CO}) = 28.34 + 4.14 \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$c_p^0(\text{H}_2\text{O}) = 30.09 + 10.67 \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\left( \text{It holds that } \int_a^b (c_1 + c_2 x) dx = c_1(b-a) + 0.5 c_2 (b^2 - a^2) \right)$$

- What can you say on the basis of the above findings on  $\Delta H^0$  about the shift in the water gas equilibrium with increasing temperature?

**SOLUTION**

a)  $\Delta H^{\circ}_{1000} = 35040 \text{ J}$   
 $\Delta S^{\circ}_{1000} = 32.11 \text{ J mol}^{-1} \text{ K}^{-1}$   
 $\Delta G^{\circ}_{1000} = \Delta H^{\circ}_{1000} - T \Delta S^{\circ}_{1000} = 35040 - 1000 \times 32.11 = 2930 \text{ J}$

b)  $\Delta G^{\circ} = -RT \ln K_p$   
 $\ln K_p = -\frac{\Delta G^{\circ}}{RT} = -\frac{2930}{8314} = -0.352418$

$K_p = 0.7030$

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

d) The original composition of the gas:

$x_{0,\text{CO}} = 0.45; \quad x_{0,\text{H}_2} = 0.35; \quad x_{0,\text{H}_2\text{O}} = 0.20; \quad x_{0,\text{CO}_2} = 0.00;$

If the mole fraction of the  $\text{CO}_2$  formed at the equilibrium is denoted as  $x$  then the equilibrium concentrations can be obtained from:

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

$\text{CO}_2: \quad x$

$\text{H}_2\text{O}: \quad x_{0,\text{H}_2\text{O}} - x$

$\text{H}_2: \quad x_{0,\text{H}_2} + x$

$$K_p = K_x = \frac{x_{\text{CO}} x_{\text{H}_2\text{O}}}{x_{\text{CO}_2} x_{\text{H}_2}} = \frac{(x_{0,\text{CO}} - x)(x_{0,\text{H}_2\text{O}} - x)}{x(x_{0,\text{H}_2} + x)} = 0.703$$

$$(x_{0,\text{CO}} - x)(x_{0,\text{H}_2\text{O}} - x) = K(x_{0,\text{H}_2} + x)x$$

$$x_{0,\text{CO}} x_{0,\text{H}_2\text{O}} - x(x_{0,\text{H}_2\text{O}} + x_{0,\text{CO}}) + x^2 = K x x_{0,\text{H}_2} + K x^2$$

where  $K = K_x$

$$x^2(1 - K) - x(x_{0,\text{H}_2\text{O}} + x_{0,\text{CO}} + K x_{0,\text{H}_2}) + x_{0,\text{CO}} x_{0,\text{H}_2\text{O}} = 0$$

On substitution of the numerical values,

$$x^2(1 - 0.703) - x(0.20 + 0.45 + 0.703 \times 0.35) + 0.45 \times 0.20 = 0$$

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

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

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

$$x = 1.508515 \pm 1.404488 = 0.104027$$

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

$$x = 0.104$$

$$x_{\text{CO}} = 0.346; \quad x_{\text{H}_2} = 0.454; \quad x_{\text{H}_2\text{O}} = 0.096; \quad x_{\text{CO}_2} = 0.104;$$

e)

$$\Delta C_p^0 = C_p^0(\text{CO}) + C_p^0(\text{H}_2\text{O}) - C_p^0(\text{CO}_2) - C_p^0(\text{H}_2)$$

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

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

$$= \Delta H_{1000}^0 + c_1 (1400 - 1000) + 0.5 c_2 (1.96 \times 10^6 - 1 \times 10^6) =$$

$$= \Delta H_{1000}^0 - 11.28 \times 400 + (1.52 \times 10^{-3} \times 4.8 \times 10^5) =$$

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

$$= 35040 - 4512 + 729.6 = 31258 \text{ J}$$

On the basis of the van't Hoff reaction isobar

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

$\ln K_p$  increases with increasing temperature for positive (endothermic) heat of reaction, i.e. the equilibrium shifts with increasing temperature in favour of the reaction products, CO and H<sub>2</sub>O.

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### PROBLEM 3

(Chemistry of ions, stoichiometry, redox reactions)

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

- 1) The flame of a Bunsen burner is intensively yellow coloured.
- 2) An aqueous solution of **A** is neutral. Dropwise addition of sulphurous acid (an  $\text{SO}_2$  solution) leads to a deep brown solution that is discoloured in the presence of excess of sulphurous acid.
- 3) If an  $\text{AgNO}_3$  solution is added to the discoloured solution obtained by 2) and acidified with  $\text{HNO}_3$ , a yellow precipitate is obtained that is insoluble on addition of  $\text{NH}_3$ , but can be readily dissolved by adding  $\text{CN}^-$  or  $\text{S}_2\text{O}_3^{2-}$ .
- 4) If an aqueous solution of **A** is treated with  $\text{KI}$  and dilute  $\text{H}_2\text{SO}_4$  a deep brown solution is formed that can be discoloured by addition of sulphurous acid or a  $\text{Na}_2\text{S}_2\text{O}_3$  solution.
- 5) An amount of 0.1000 g of **A** is dissolved in water, then 0.5 g  $\text{KI}$  and a few  $\text{cm}^3$  of dilute  $\text{H}_2\text{SO}_4$  are added. The deep brown solution formed is titrated with 0.1000 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution until the solution is completely discoloured. The consumption is  $37.40 \text{ cm}^3$ .

Problems:

- a) What elements are contained in the compound **A**?
- b) What compounds can be considered as present on the basis of reactions 1) to 4)? Calculate their molar masses.
- c) Formulate the reactions corresponding to 2) to 4) for the compounds considered and write the corresponding equations in the ionic form.
- d) Decide on the basis of 5) which compound is present.

### SOLUTION

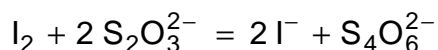
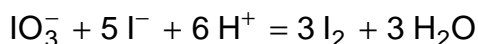
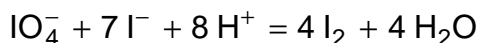
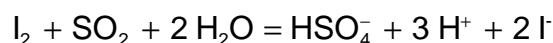
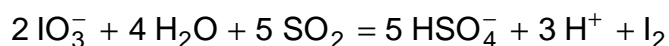
- a) The solid must contain Na and I. The yellow colouration of the flame of the Bunsen burner indicates the presence of Na. A yellow silver salt that is dissolved only by strong complexing agents such as  $\text{CN}^-$  or  $\text{S}_2\text{O}_3^{2-}$ , must be  $\text{AgI}$ .
- b) Reactions 1) to 4) indicate an Na salt of an oxygen containing acid of iodine:

Both  $\text{SO}_2$  and  $\text{I}^-$  are oxidised. While in the first case  $\text{I}^-$  is formed with an intermediate of  $\text{I}_2$  (or  $\text{I}_3^-$ , brown solution), in the second  $\text{I}_2$  (or  $\text{I}_3^-$ ) is formed.

As the solution of **A** is neutral,  $\text{NaIO}_3$  and  $\text{NaIO}_4$  come into consideration.

$$M(\text{NaIO}_3) = 22.99 + 126.905 + 3 \times 16.000 = 197.895 = 197.90 \text{ g mol}^{-1}$$

$$M(\text{NaIO}_4) = 22.99 + 126.905 + 4 \times 16.000 = 213.895 = 213.90 \text{ g mol}^{-1}$$



d) Experiment: 0.1000 g of the compound **A** .....  $3.740 \times 10^{-3}$  moles  $\text{S}_2\text{O}_3^{2-}$

1<sup>st</sup> hypothesis: The compound is  $\text{NaIO}_3$ .

1 mole  $\text{NaIO}_3$  . . . . 197.90 g  $\text{NaIO}_3$  . . . . 6 moles  $\text{S}_2\text{O}_3^{2-}$

$$0.1000 \text{ g NaIO}_3 \text{ . . . . } \frac{0.1000 \times 6}{197.90} = 3.032 \times 10^{-3} \text{ moles S}_2\text{O}_3^{2-}$$

The hypothesis is false.

2<sup>nd</sup> hypothesis: The compound is  $\text{NaIO}_4$ .

1 mole  $\text{NaIO}_4$  . . . . 213.90 g  $\text{NaIO}_4$  . . . . 8 moles  $\text{S}_2\text{O}_3^{2-}$

$$0.1000 \text{ g NaIO}_4 \text{ . . . . } \frac{0.1000 \times 8}{213.90} = 3.740 \times 10^{-3} \text{ moles S}_2\text{O}_3^{2-}$$

The compound **A** is  $\text{NaIO}_4$ .

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## PROBLEM 4

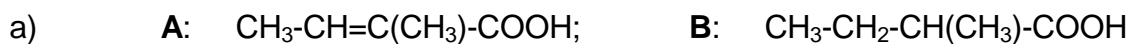
(Organic chemistry, stereochemistry)

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

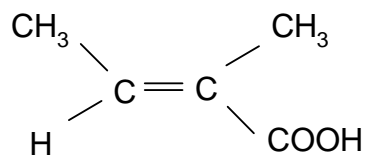
Problems:

- What is the constitution of **A** and **B**?
- Write the stereo formulae for **A'** and **A''** and the Fischer projection formulae for the enantiomer **B** (not considering the signs (+) or (-)).
- How many stereo isomers of **C** are simultaneously formed when **A'** and **A''** are treated with bromine?
- Briefly, give reasons for your answer to c).
- Write the Fischer projection formulae and one Newman projection formula (conformation) for all the stereoisomers of **C**. Denote those that are mutually enantiomeric and diastereoisomeric.

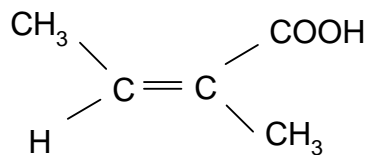
## SOLUTION



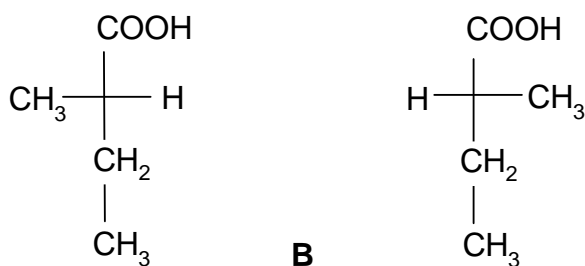
b)



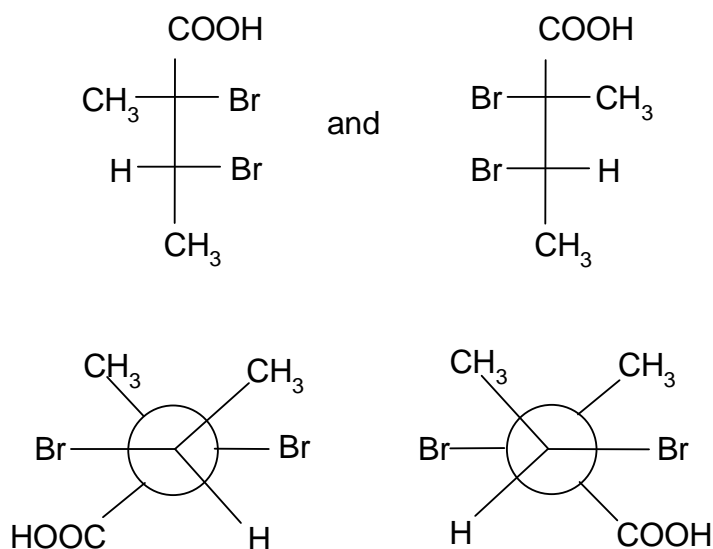
**A'**



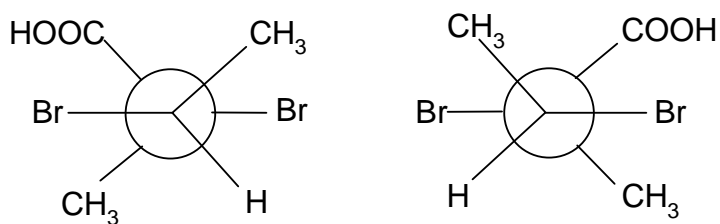
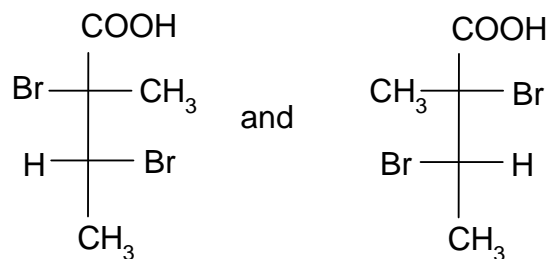
**A''**



- c) Always two (see e): 1 to 4
- d) The addition of bromine to the alkene gives trans compound under the given conditions. On the addition, two (non-identical) asymmetrical **C** atoms (chirality centres) are formed yielding together  $2^2 = 4$  stereo isomers of which always two are mutually enantiomeric.
- e) from **A'**:



from A":



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

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## PROBLEM 5

(Inorganic chemistry)

From 20 mg of partially methylated disilane,  $\text{Si}_2\text{H}_{6-x}(\text{CH}_3)_x$ ,  $27.8 \text{ cm}^3$  of hydrogen are evolved during alkaline hydrolysis at 294 K and 97400 Pa.

- Why the Si-Si bond of the disilane reacts during hydrolysis?
- Why the Si-H bonds of the disilane react during hydrolysis?
- Calculate the degree of substitution  $x$  of the methylated disilane.
- Write the complete reaction equation for the hydrolysis.
- How many isomers can form the calculated compound? Give the structural formula for each isomer.

## SOLUTION

- The Si-Si bond is coordination unsaturated and thus, has a tendency to react with nucleophilic reagents with the bond breakage.
- Similar to all compounds with negatively polarised hydrogen, this bond also reacts with protons from water with formation of elemental hydrogen.
- $(\text{CH}_3)_x\text{Si}_2\text{H}_{6-x}$

$$\begin{aligned} \text{Molecular mass:} \quad & 2 \text{ Si} \quad 2 \times 28.086 \\ & (6-x) \text{ H} \quad (6-x) \times 1.008 \\ & x \text{ CH}_3 \quad x \times 15.035 \\ & 56.172 + 1.008 (6 - x) + 15.035 x = 62.22 + 14.027 x \end{aligned}$$

$$\text{Sample mass: } 20 \text{ mg} \Rightarrow \frac{20}{62.22 + 14.027 x} \text{ mmol}$$

$$\text{Hydrogen evolved: } n = \frac{pV}{RT} \text{ mmol H}_2 \text{ (V in cm}^3\text{)}$$

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

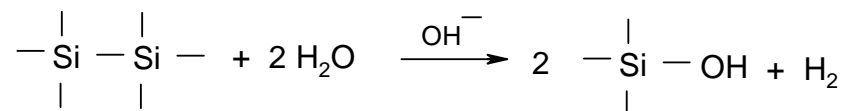
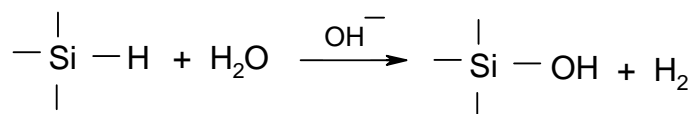
(SiH) (SiSi)

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

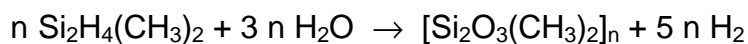
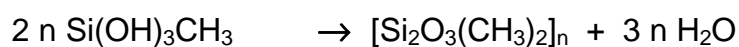
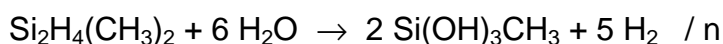
$$x = 1.9999$$

Hence, the degree of substitution = 2

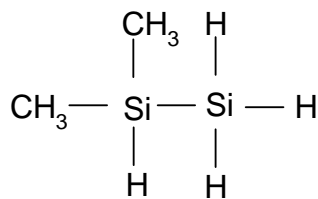
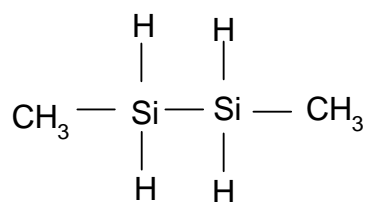
d)



Hence (for a symmetrical isomer):



e) Two:



## PROBLEM 6

(Organic chemistry, syntheses)

Benzaldehyde and malonic acid reacted in pyridine at 80 °C yielding (among others) CO<sub>2</sub> and compound **A** in a yield of ca. 80 % of the theoretical value. Catalytic hydrogenation of 1.48 g **A** on Pt at room temperature and normal pressure yielded **B** with a consumption of 0.25 litre of hydrogen. On reaction of **B** with a polyphosphoric acid (the Friedel-Crafts' conditions) compound **C** can be isolated accompanied by two acidic, isomeric side products. The side products **Da** and **Db** can be formed in a greater amount at a high concentration of **B** in the reaction medium, and can be suppressed by dilution.

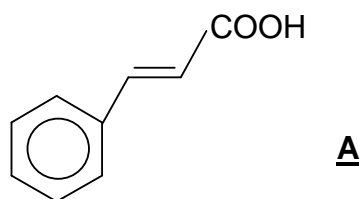
The elemental analysis of **C** yields 81.8 % of carbon and 6.1 % of hydrogen. The corresponding values for **Da** and **Db**, identical within the experimental error, are 76.6 % and 6.4 %, respectively. An amount of 2.82 g **Da**, as well as **Db** requires ca. 100 cm<sup>3</sup> 0.1 N potassium hydroxide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

Using this information solve the following problems:

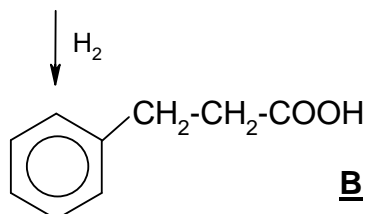
1. The structural formula of **A**.
2. The structural formula of **B**.
3. The structural formula of **C**.
4. The structural formulae of **Da** and **Db**.
5. Give an alternative pathway for the synthesis of **A** using the simplest possible starting materials and forming at least one C–C bond.
6. Give an alternative pathway for the synthesis of **B** using the simplest possible starting materials and forming at least one C–C bond.
7. Give structural formulae for the products of the following reactions:
  - a) **C** + hydroxylamine (with acid catalysis) →
  - b) **C** + phenylmagnesium bromide (C<sub>6</sub>H<sub>5</sub>MgBr) and subsequent treatment under acidic conditions →
  - c) **C** + benzaldehyde + C<sub>2</sub>H<sub>5</sub>O<sup>−</sup> Na<sup>+</sup> →

**SOLUTION**

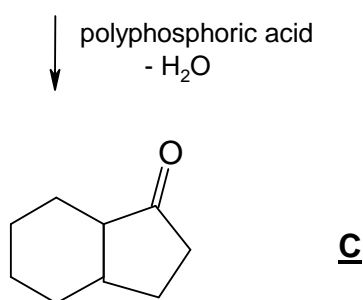
1. Condensation



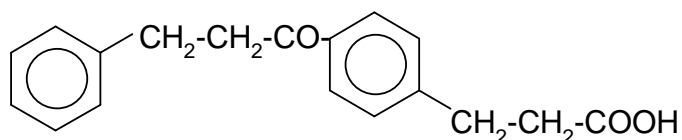
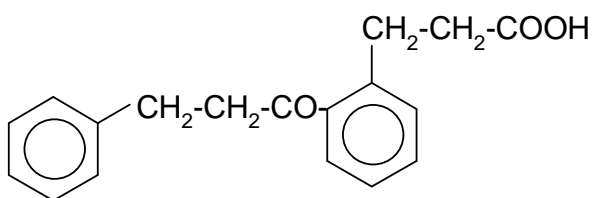
2. Hydrogenation



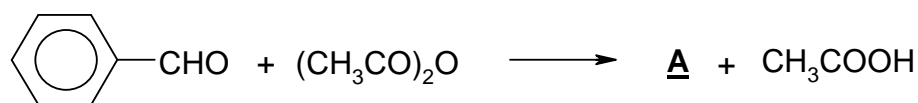
3. Intramolecular cyclization



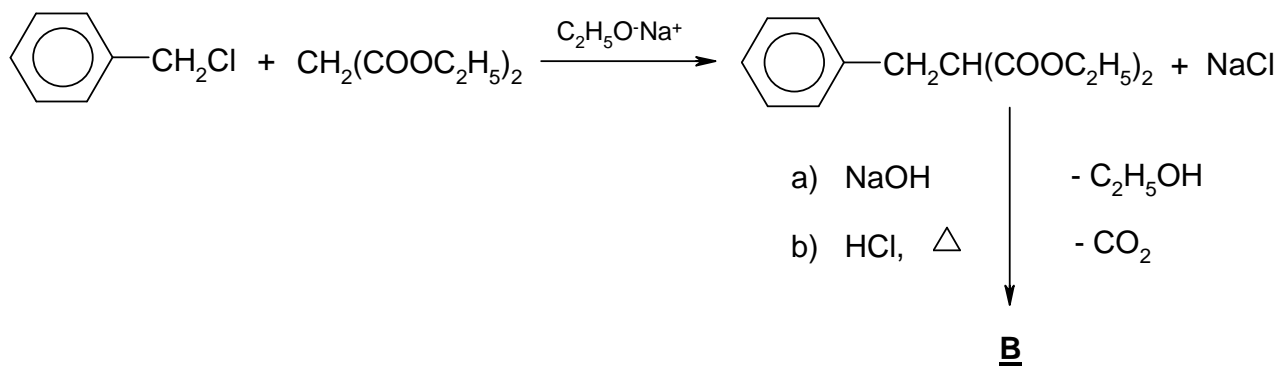
4. In addition to **C** two positional isomers **Da** and **Db** are formed.



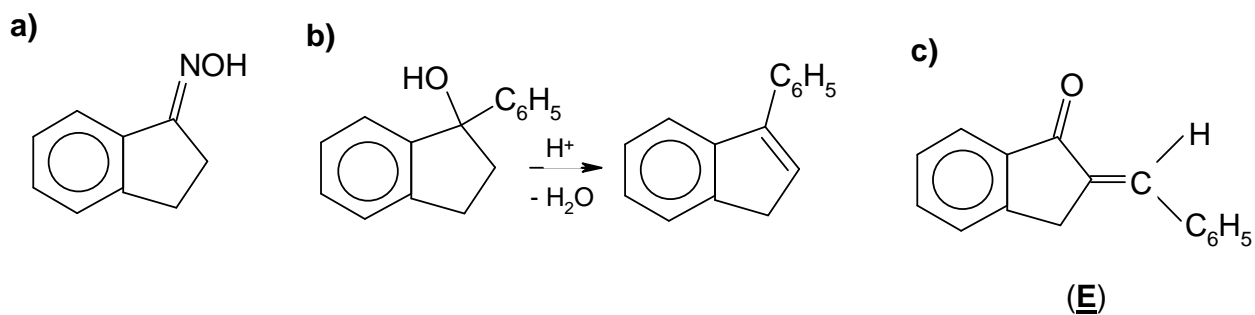
5. For example, Perkin reaction: Treatment of benzaldehyde with acetic acid anhydride:



6. For example, by malonic ester synthesis



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



two stereoisomers  
(syn and anti)

two stereoisomers



## PRACTICAL PROBLEMS

### PROBLEM 1

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,  $\text{NaHCO}_3$  (5 %),  $\text{NaOH}$  (2 M),  $\text{HCl}$  (2 M),  $\text{H}_2\text{SO}_4$  conc.,  $\text{H}_3\text{PO}_4$  conc., ethanol, Tollens' reagents, (an ammoniac Ag solution), Fehling's solution I and II, phenylhydrazine hydrochloride,  $\beta$ -naphthol,  $\text{NaNO}_2$  (solid)  $\text{Ca}(\text{OH})_2$  sat.,  $\text{FeCl}_3$  (5 %), ice, 2,4-dinitrophenylhydrazine, ninhydrine solution (1 % alk.), Seliwanoff's reagent (resorcinol/ $\text{HCl}$ ), 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 °C/min. For an exact determination another sample is brought about 10 °C below the determined melting range at about 5 °C/min and then the temperature is very slowly, 1 – 2 °C/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 °C) and boiling points (BP, in °C)

Compound	MP	BP	Compound	MP	BP
<b>ALDEHYDES</b>					
Pentanal	-	103	Acrolein	-	52
Benzaldehyde	-	179	Furfural	-	161
Salicylaldehyde	-	196	o-Chlorobenzaldehyde	11	214
o-Nitrobenzaldehyde	44	-	α-Naphthaldehyde	34	-
p-Dimethylamino-benzaldehyde	74	-	Vanillin	81	-
<b>ALCOHOLS</b>					
tert.-Butanol	25	82	Propanol-1	-	97
n-Pentanol	-	136	Ethylene glycol	-	197
Cyclohexylalcohol	-	160	Butanediol-1,4	-	230
Triphenylcarbinol	165	-	Glycerine	-	290
<b>AMINES</b>					
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	-
<b>ACIDS</b>					
Palmitic acid	63	-	n-Valeric acid	-	186
Stearic acid	70	-	Oleic acid	14	222
Oxalic acid (. 2 H <sub>2</sub> O)	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	-

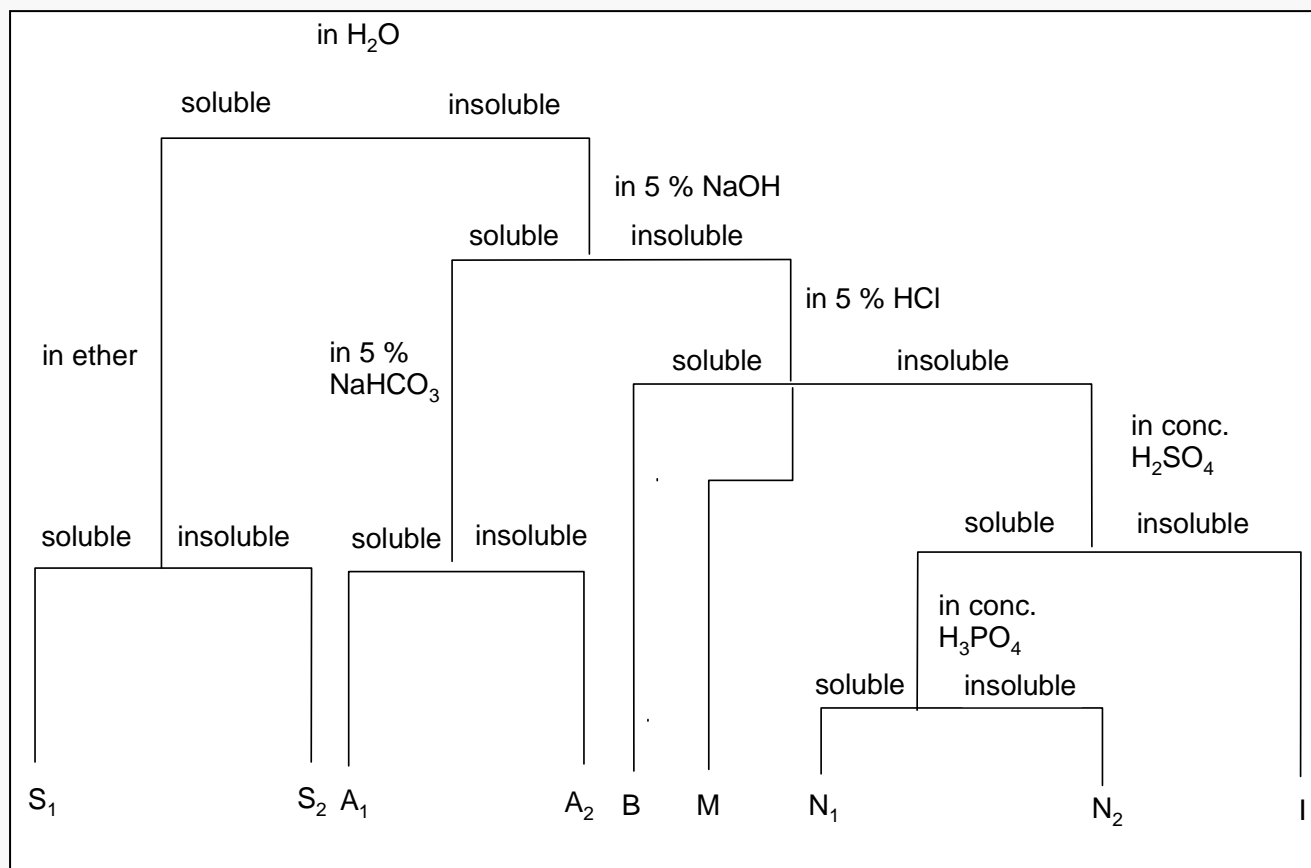
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Linz 1980, Austria

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	-	$\beta$ -Maltose	165	-
$\alpha$ -d-Glucose	146	D	$\beta$ -d-Fructose		
Saccharose	180	-	$\alpha$ -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	-
$\alpha$ -Naphthol	94	-	Resorcinol	110	-
Pyrocatechol	105	-	$\beta$ -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<sub>1</sub>: Substances with higher volatility;

All low molecular alcohols, aldehydes, ketones, acids, amines, nitriles and acid chlorides.

S<sub>2</sub>: Substances with low volatility, often distillable without decomposition: polyols, salts, hydroxyaldehydes and hydroxyketones, carbohydrates, amino- and hydroxyl acids.

A<sub>1</sub>: Substances with low volatility: higher molecular acids, nitrophenols.

A<sub>2</sub>: 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-, nitrate-, sulphuric-, and phosphoric acid esters.

N<sub>1</sub>: Substances with small volatility:

Alcohols, aldehydes, methyl ketones and esters with less than 9 C atoms, neutral compounds, ethers, olefins.

N<sub>2</sub>: Substances with a very low volatility:

Alcohols, aldehydes, ketones, esters and thioalcohols with more than 9 C atoms, neutral compounds, ethers, olefins.

I: Substances with low boiling point:

Inert compounds, hydrocarbons, halogenoalkanes.

#### APPENDIX 4

##### Preparation of the reagents

###### *Tollen's reagent*

Mix 0.5 cm<sup>3</sup> 2 M NaOH + 1 cm<sup>3</sup> 0.1 M AgNO<sub>3</sub> in 2 M NH<sub>3</sub>.

###### *Fehling's reagent*

I: 1.73 g CuSO<sub>4</sub> · 5 H<sub>2</sub>O in 25 cm<sup>3</sup> of water

II: 8.5 g Seignette salt + 2.5 g NaOH in 25 cm<sup>3</sup> H<sub>2</sub>O

###### *Seliwanoff's reagent*

125 g resorcinol is dissolved in 250 cm<sup>3</sup> of diluted HCl (83 cm<sup>3</sup> conc. HCl + 167 cm<sup>3</sup> H<sub>2</sub>O), preparing only a necessary amount.

###### *Phenylhydrazine solution*

0.5 g of phenylhydrazine hydrochloride + 0.5 cm<sup>3</sup> glacial acetic acid in 2 cm<sup>3</sup> H<sub>2</sub>O are shaken until a clear solution is obtained.

###### *2,4-dinitrophenylhydrazine solution,*

2 cm<sup>3</sup> of conc. H<sub>2</sub>SO<sub>4</sub> are added to 0.4 g of 2,4-dinitrophenylhydrazine and then, with stirring and shaking, 3 cm<sup>3</sup> of H<sub>2</sub>O are added. To the warm solution, 10 cm<sup>3</sup> of 95 % ethanol are added.

**SOLUTION**

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

a) *Fructose*

Melting range: 102 – 105 °C

Combustion test: Carbonizes during combustion with caramel smell.

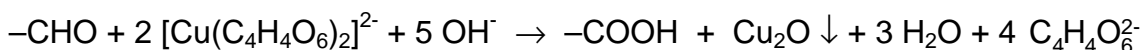
Solubility: Readily soluble in water, insoluble in diethyl ether.

Identification of the functional groups:

Aldehydic group:

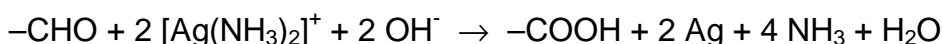
1. With Fehling's reagent

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

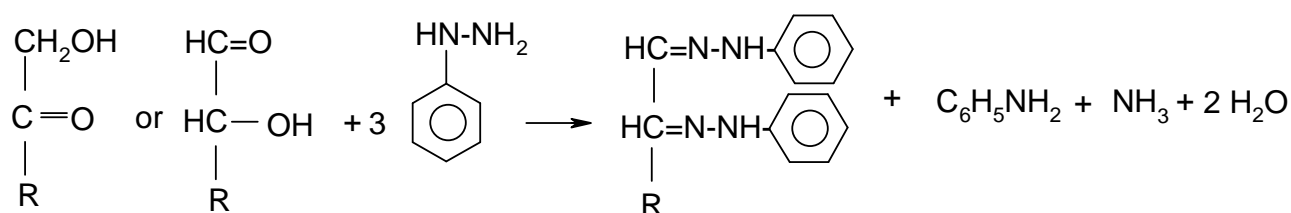


2. With Tollen's reagent

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



Osazone formation (indication of monoses)



Ketose

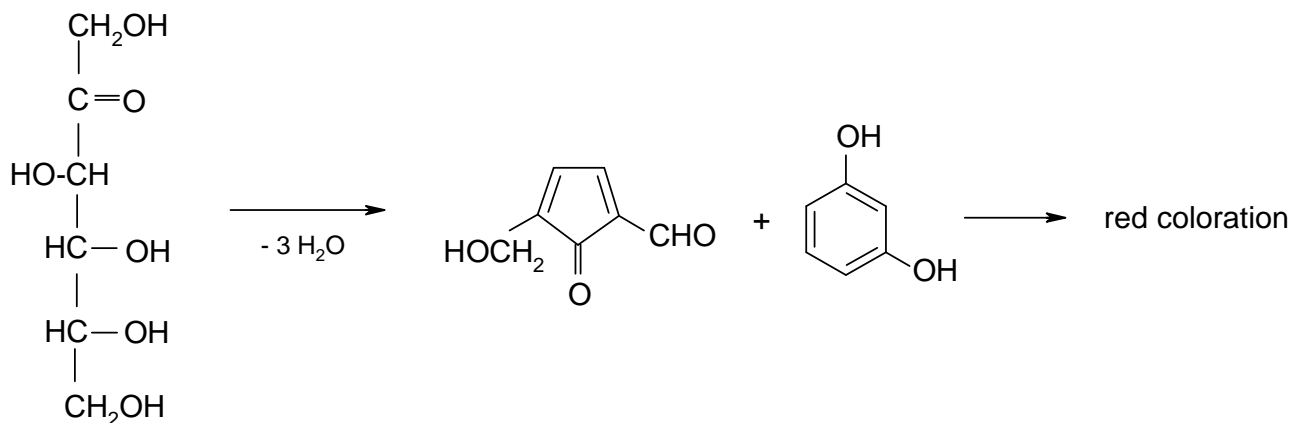
Aldose

Phenyl-  
hydrazine

Osazone

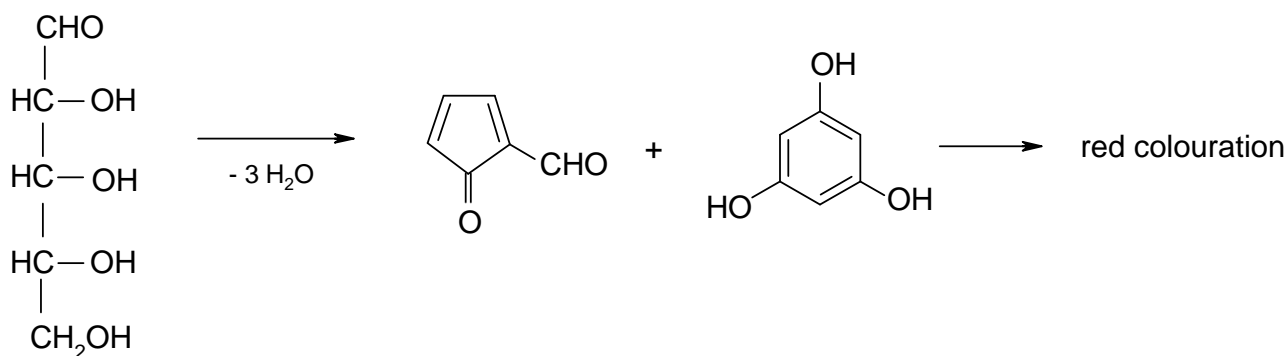
Test for ketohexoses (Saliwanoff's reaction)

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

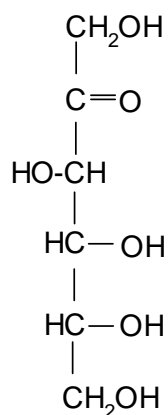


Test for pentoses (Tollens test)

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*

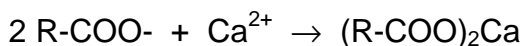
Melting range: 60 – 63 °C

Combustion test: Burns with yellowish, slightly smoking flame.

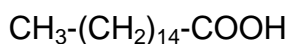
Solubility: Insoluble in water, very well soluble in 2 M NaOH, less soluble in 5 % NaHCO<sub>3</sub>.

Identification of the functional groups:

From alkaline solution a colourless substance is precipitated by Ca<sup>2+</sup>:



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.





## PROBLEM 2

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:

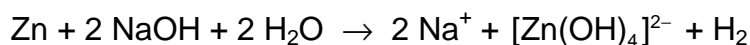
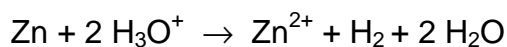
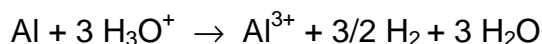
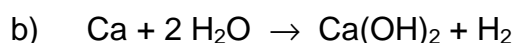
- the symbol of the identified metal and the corresponding bottle number,
- a reaction equation for dissolution of each of the six metals,
- an unambiguous verbal proof or a proof in the form of a chemical equation.

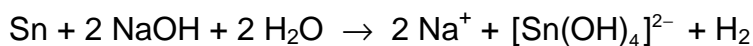
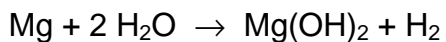
The following chemicals are at disposal:

HCl conc., HCl (2 M), H<sub>2</sub>SO<sub>4</sub> (2 M), CH<sub>3</sub>COOH (2 M), NaOH (2 M), NH<sub>3</sub> (2 M), NH<sub>4</sub>SCN (0.2 M), CH<sub>3</sub>COONa (conc.), 3 % H<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> (0.2 M), H<sub>2</sub>S (0.1 M), Na<sub>2</sub>HPO<sub>4</sub> (0.2 M), K<sub>4</sub>Fe(CN)<sub>6</sub> (0.2 M), K<sub>3</sub>Fe(CN)<sub>6</sub> (0.2 M), morin (in CH<sub>3</sub>OH), quinalizarine (in C<sub>2</sub>H<sub>5</sub>OH), urotropine (20 %), dithizone (in CCl<sub>4</sub>), (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (0.2 M), distilled water.

## SOLUTION

a) See the list at the end.





- c)  $\text{Ca}^{2+}$ : white precipitate with  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ;  
 $\text{Fe}^{2+}$ : blue with  $\text{K}_3[\text{Fe}(\text{CN})_6]$   
or after oxidation with  $\text{H}_2\text{O}_2$ : blue with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  or red with  $\text{NH}_4\text{SCN}$ , or  
brown precipitate with  $\text{NaOH}$ ;  
 $\text{Al}^{3+}$ : green fluorescence with morine (in dilute acetic acid);  
 $\text{Zn}^{2+}$ : white precipitate with  $\text{H}_2\text{S}$  (in acetic acid),  
with dithizone red coloration of the organic phase;  
 $\text{Mg}^{2+}$ : with quinalizarine light blue lacquer (alkali solution);  
 $\text{Sn}^{2+}$ : with  $\text{H}_2\text{S}$  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  $\text{Sn}^{2+}$  solution (acidified with  $\text{HCl}$ ),  
in the flame of a Bunsen burner ("light test").
-

### PROBLEM 3

#### *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<sup>3</sup> Fe(II) solution, 10 cm<sup>3</sup>  $H_3PO_4$  (ca. 3.7 mol dm<sup>-3</sup>) and 10 cm<sup>3</sup>  $H_2SO_4$  (ca. 1 mol dm<sup>-3</sup>) 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<sup>-3</sup>. 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<sup>3</sup> in a standard flask and mixed.

b) 25.0 cm<sup>3</sup> of this solution are transferred to a titration vessel and mixed with 10 cm<sup>3</sup>  $H_3PO_4$  (ca. 3.7 mol dm<sup>-3</sup>), 10 cm<sup>3</sup>  $H_2SO_4$  (ca. 1 mol dm<sup>-3</sup>) and 25.0 cm<sup>3</sup> 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<sup>-3</sup>) 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*

##### l) 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:



c) Overall reaction:

II) The concentration of the Fe(II) solution

1) Give the consumption of the  $\text{KMnO}_4$  solution ( $\text{cm}^3$ ) for  $25.0 \text{ cm}^3$  of the Fe(II) solution (=  $V_1$ ); See Procedure 1.

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

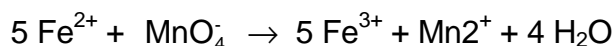
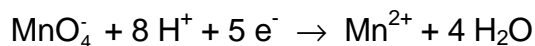
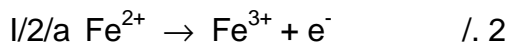
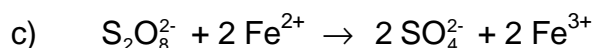
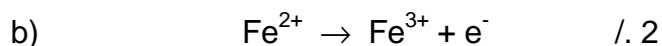
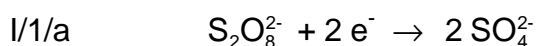
III) Determination of  $\text{K}_2\text{S}_2\text{O}_8$

1) Give the consumption of the  $\text{KMnO}_4$  solution in the back-titration of the excess Fe(II) solution in  $\text{cm}^3$  (=  $V_2$ ); See Procedure 2.

2) How many mg  $\text{K}_2\text{S}_2\text{O}_8$ :

3) Calculate the concentration of  $\text{K}_2\text{S}_2\text{O}_8$  in the sample solution in  $\text{mol dm}^{-3}$ .

### SOLUTION



II/1  $V_1 \text{ cm}^3 \text{ KMnO}_4 (0.02 \text{ mol dm}^{-3}) / 25 \text{ cm}^3 \text{ Fe(II)}$

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

III/1  $V_2 \text{ cm}^3 \text{ KMnO}_4$  solution ( $0.02 \text{ mol dm}^{-3}$ ) for the back titration

2.

$$\alpha) \frac{(V_1 - V_2) \times 0.02 \times 5}{1000} \times \frac{270.33}{2} = \dots\dots\dots \text{mg K}_2\text{S}_2\text{O}_8$$

$$\beta) \frac{25 \times c(\text{Fe}^{2+}) - V_2 \times 0.02 \times 5}{1000} \times \frac{270.33}{2} = \dots\dots\dots \text{mg K}_2\text{S}_2\text{O}_8$$

3.

$$\alpha) \frac{(V_1 - V_2) \times 0.02 \times 5}{1000} \times \frac{40}{2} = \dots\dots\dots \text{mol K}_2\text{S}_2\text{O}_8 / \text{dm}^3$$

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

---