

23rd



International Chemistry Olympiad

**6 theoretical problems
2 practical problems**

THE TWENTY-THIRD INTERNATIONAL CHEMISTRY OLYMPIAD 7–15 JULY 1991, LODZ, POLAND

THEORETICAL PROBLEMS

PROBLEM 1

- 1.1 Show that 0.1 mol of Tl_2S dissolves in a 1 M solution of any strong monoprotic non-coordinating acid.
- 1.2 Show that 0.1 CuS dissolves in a 1 M HNO_3 but not in a 1 M HCl solution.

Information:

Assume that Cu^{2+} ions do not form stable complexes with chloride ions in aqueous solutions.

$$E^0(S/S^{2-}) = -0.48 \text{ V} \quad E^0(NO_3^-/NO_{(aq)}) = 0.96 \text{ V}$$

$$pK_a(H_2S) = 7 \quad pK_a(HS^-) = 13$$

$$K_{sp}(Tl_2S) = 1 \times 10^{-20} \quad K_{sp}(CuS) = 1 \times 10^{-35}$$

Solubility of NO in water (298 K): $2.53 \times 10^{-2} \text{ mol dm}^{-3}$

Solubility of H_2S in water (298 K): 0.1 mol dm^{-3}

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad F = 96\,487 \text{ C mol}^{-1}$$

SOLUTION

1.1 Solubility condition: $[Tl^+]^2 [S^{2-}] \leq 1 \times 10^{-20}$

$$[Tl^+] = c(Tl^+) = 0.2 \text{ mol dm}^{-3}$$

$$c(S^{2-}) = [S^{2-}] + [HS^-] + [H_2S] = [S^{2-}] \left(1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2} \right) = 0.1 \text{ mol dm}^{-3}$$

$$[\text{S}^{2-}] = \frac{0.1}{1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2}} \Rightarrow$$

For a strong monoprotic acid (1 mol dm⁻³) and [H⁺] ≈ 1.

Then

$$1 + 10^{13} [\text{H}^+] \ll 10^{20} [\text{H}^+]^2 \quad \text{and} \quad [\text{S}^{2-}] \approx \frac{0.1}{1 \times 10^{20}}$$

$$[\text{Ti}^+]^2 [\text{S}^{2-}] = \frac{(0.2)^2 \times 0.1}{1 \times 10^{20}} = 4 \times 10^{-23} < K_s(\text{Ti}_2\text{S})$$

Thus, 0.1 mol of Ti₂S dissolves in a 1 M solution of any strong monoprotic non-coordinating acid.

1.2

- Dissolving CuS in 1 M solution HCl (non-oxidizing and non-complexing acid):

$$c(\text{Cu}^{2+}) = 0.1 \text{ mol dm}^{-3}$$

$$[\text{Cu}^{2+}] = 0.1$$

$$c(\text{S}^{2-}) = 0.1 \text{ mol dm}^{-3}$$

Similarly as in part (1.1):

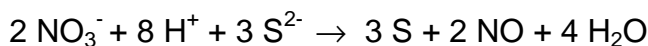
$$[\text{S}^{2-}] = \frac{0.1}{1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2}}$$

$$[\text{S}^{2-}] \approx \frac{0.1}{1 \times 10^{20}}$$

$$[\text{Cu}^{2+}] [\text{S}^{2-}] = \frac{(0.1)^2 \times 0.1}{1 \times 10^{20}} \approx 1 \times 10^{-23} > K_s(\text{CuS})$$

Conclusion: 0.1 mol CuS does not dissolve in 1 M solution HCl.

- When dissolving 0.1 mol CuS in 1 M HNO₃ an additional redox process occurs: the oxidation of S²⁻ to S.



The emf of this reaction is $\Delta E = E_1^0 - E_2^0 = (0.96 + 0.48) = \underline{1.44 \text{ V}}$

$$\log K = \frac{\Delta G}{RT} = \frac{nF}{RT} \Delta E = \frac{n_1 n_2 (E_1^0 - E_2^0)}{0.0591} \cong 144 \quad K = 1 \times 10^{144}$$

The equilibrium constant of this process can also be written in the form:

$$K = \frac{[\text{NO}]^2}{[\text{NO}_3^-]^2 [\text{H}^+]^8 [\text{S}^{2-}]^3}$$

From the above equilibrium follows that $[\text{S}^{2-}] = \sqrt[3]{\frac{K [\text{NO}_3^-]^2 [\text{H}^+]^8}{[\text{NO}]^2}}$

Since $[\text{NO}_3^-] = [\text{H}^+] = 1$

$$[\text{S}^{2-}] = \sqrt[3]{\frac{K}{[\text{NO}]^2}}$$

$c_{\text{CuS}} = [\text{S}] + [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}]$

$$[\text{S}^{2-}] = \frac{c_{\text{CuS}}}{1 + \frac{[\text{H}^+]}{K_1} + \frac{[\text{H}^+]^2}{K_1 K_2} + \sqrt[3]{\frac{K}{[\text{NO}]^2}}}$$

However

$$1 + \frac{[\text{H}^+]}{K_1} + \frac{[\text{H}^+]^2}{K_1 K_2} \ll \sqrt[3]{\frac{K}{[\text{NO}]^2}} = \sqrt[3]{\frac{1 \times 10^{144}}{(0.0253)^2}} = 1.16 \times 10^{49}$$

$$[\text{S}^{2-}] = \frac{0.1}{1.16 \times 10^{49}} = 8.62 \times 10^{-51}$$

$$[\text{Cu}^{2+}] [\text{S}^{2-}] = 0.1 \times 8.62 \times 10^{-51} = 8.62 \times 10^{-52} \ll K_{\text{sp}}(\text{CuS}) (= 1 \times 10^{-35})$$

Conclusion: CuS dissolves in 1 M solution of HNO₃.

PROBLEM 2

A polymer **X** contains 88.25 % C and 11.75 % H. In dilute solutions it reacts with bromine and ozone. The thermal degradation of **X** produces a volatile liquid **Y** in 58 % yield. **Y** starts boiling at 34 °C and contains 88.25 % C and 11.72 % H. Some higher boiling products are formed both from the cracking of **X** and from Diels-Alder type cyclization of **Y**. The vapour of **Y** was 34 times as dense as hydrogen.

The product of bromination of **Y** yields a compound containing 82.5 % bromine by mass. Ozonolysis of **Y** followed by mild reduction gave **A** and **B** in a molar ratio **A** : **B** = 2 : 1. Only compound **B** gave a positive result for the iodoform reaction.

2.1 Determine the molecular formula and the molar mass of **Y**.

2.2 Show the structures of compounds **Y**, **A**, and **B**.

2.3 Give an equation for the reaction of **Y** with bromine.

In the catalytic hydrogenation of 13.6 g of **X**, 0.2 mole of hydrogen was absorbed. Ozonolysis of **X** followed by mild reduction yielded compound **Z** (60.0 % C, 8.0 % H).

2.4 Give the molecular formula of **Z** and the degree of unsaturation of **X**.

Compound **Z** gave a positive reaction with Fehling's solution. Mild oxidation of **Z** gave an acid **C**. A solution of acid **C** was titrated with aqueous KOH solution (phenolphthalein as indicator). 0.001 mol KOH was necessary for neutralization of 0.116 g of **C**.

In the iodoform reaction a probe 2.90 g of **C** yielded 9.85 g of iodoform. In addition, the alkaline filtrate yielded compound **D** upon acidification.

2.5 What is the molar mass of **C** and what functional groups are present in **Z**?

When heated, **D** loses water to form **E**. Both **D** and **E** react with an excess of acidified ethanol to **F** (C₈H₁₄O₄).

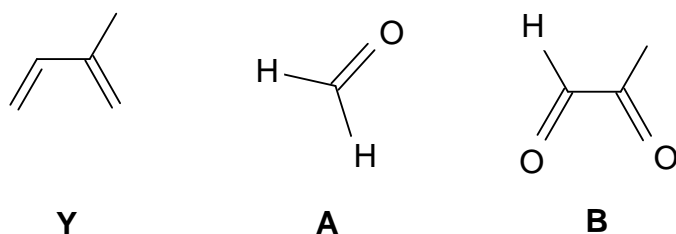
2.6 Sketch the structures of **C**, **D**, **E**, **F** and **Z**.

2.7 **X** exists in isomeric forms which are stereoregular. Show the structure (containing at least 3 monomer units) for two possible stereoisomers of **X**.

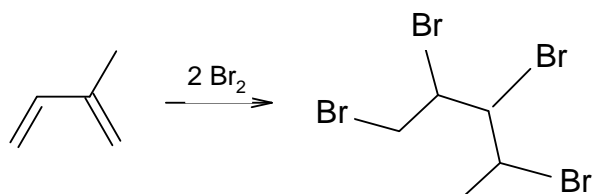
SOLUTION

2.1 $Y = \text{Isoprene, } C_5H_8, M = 68 \text{ g mol}^{-1}$

2.2



2.3

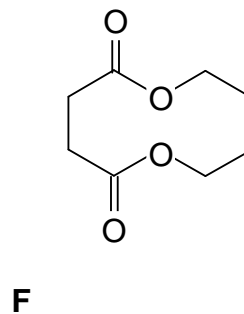
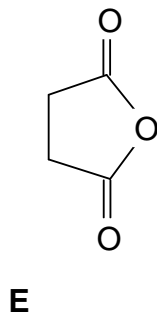
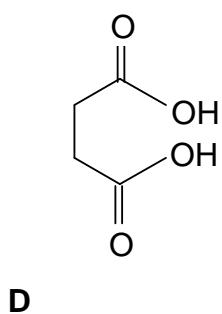
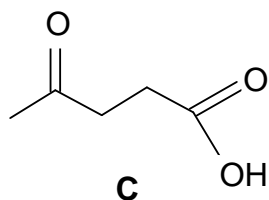


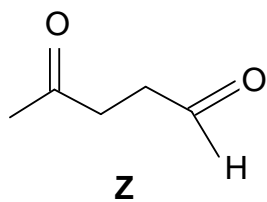
2.4 $Z = C_5H_8O_2$

There is one double bond per monomer unit.

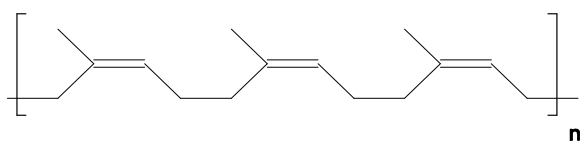
2.5 The molar mass of **C** is 116 g mol^{-1} . **Z** must be a keto aldehyde since it contains an aldehyde functional group and a methyl group next to the carbonyl group.

2.6

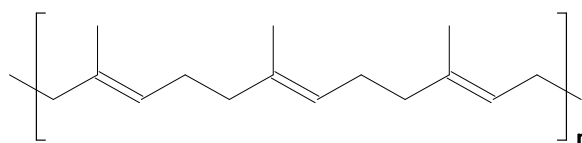




2.7 There are two isomeric form (all cis or all trans) possible:



all-cis (natural caoutchouc)



all-trans

PROBLEM 3

Type II electrodes that are made of a metal covered with a sparingly soluble salt of the metal are dipped into a soluble salt solution containing an anion of the sparingly soluble salt. The silver/silver chloride (Ag, AgCl/Cl⁻) and the calomel electrode (Hg, Hg₂Cl₂/Cl⁻) are examples of such electrodes. The standard emf of a cell built of those electrodes (-) Ag,AgCl/Cl⁻ || Hg₂Cl₂/Hg (+) is $E^0 = 0.0455 \text{ V}$ at $T = 298 \text{ K}$. The temperature coefficient for this cell is $dE^0/dT = 3.38 \times 10^{-4} \text{ V K}^{-1}$.

3.1 Give the equations of the reactions taking place at both the cell electrodes and the overall cell reaction.

3.2 Calculate the Gibbs free energy change (ΔG^0) for the process taking place in the cell at 298 K. What does its sign imply?

3.3 Calculate the enthalpy change for the process taking place at 298 K.

$$\Delta S = n F \Delta E / \Delta T.$$

3.4 Knowing the standard potential of Ag/Ag⁺ electrode is $E^0 = 0.799 \text{ V}$ and the solubility product of AgCl $K_{sp} = 1.73 \times 10^{-10}$, calculate the standard electrode potential value of the silver/silver chloride electrode. Derive an expression showing the dependence between $E^0(\text{Ag}/\text{Ag}^+)$ and $E^0(\text{Ag}, \text{AgCl}/\text{Cl}^-)$.

3.5 Calculate the solubility product of Hg₂Cl₂ knowing that the standard potential of the calomel electrode is $E^0 = 0.798 \text{ V}$.

$$F = 96487 \text{ C mol}^{-1}, \quad R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, \quad T = 298 \text{ K}$$

SOLUTION

3.1 Reduction (calomel electrode (+)): $1/2 \text{ Hg}_2\text{Cl}_2 + e^- \rightarrow \text{Hg} + \text{Cl}^-$
 Oxidation (silver/silver chloride electrode (-)): $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + e^-$
 Summary reaction: $\text{Ag} + 1/2 \text{ Hg}_2\text{Cl}_2 \rightarrow \text{Hg} + \text{AgCl}$

3.2 $\Delta G^0 = -n F E^0 = -96497 \text{ C mol}^{-1} \times 0.0455 \text{ V} = -4.39 \text{ kJ mol}^{-1}$;

Since ΔG^0 is negative, the reaction is spontaneous.

3.3 The change of enthalpy is related to the Gibbs-Helmholtz equation:

$$\begin{aligned}\Delta H &= \Delta G + T\Delta S = -nFE + TnF\left(\frac{\Delta E^0}{\Delta t}\right) = -nF\left(E - T\left(\frac{\Delta E^0}{\Delta t}\right)\right) = \\ &= -96487 \text{ C mol}^{-1} (0.0455 \text{ V} - 298 \text{ K} \times 3.38 \times 10^{-4} \text{ V K}^{-1}) = 5.36 \text{ kJ mol}^{-1}\end{aligned}$$

3.4 For the Ag | Ag⁺ electrode: $E = E^0 + 0.0591 \log[\text{Ag}^+]$

For the Ag, AgCl | Cl⁻ electrode [Ag⁺] is determined by the solubility product:

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]}$$

$$E^0(\text{Ag, AgCl} | \text{Cl}^-) = E^0(\text{Ag} | \text{Ag}^+) + 0.0591 \log K_{sp} = 0.799 - 0.577 = 0.222 \text{ V}$$

3.5 $E^0(\text{Hg, Hg}_2\text{Cl}_2 | \text{Cl}^-) = E^0(\text{Hg} | \text{Hg}^{2+}) + \frac{0.0591}{2} \log K_{sp}(\text{Hg}_2\text{Cl}_2)$

The standard potential of the calomel electrode is equal to $0.0455 + 0.222 = 0.2675 \text{ V}$.

Thus, $\log K_{sp}(\text{Hg}_2\text{Cl}_2)$ can be calculated as:

$$\log K_{sp}(\text{Hg}_2\text{Cl}_2) = \frac{2(0.2675 - 0.798)}{0.0591} = -17.99$$

$$K_{sp} = 1.03 \times 10^{-18}$$

PROBLEM 4

The energy of stable states of the hydrogen atom is given by: $E_n = -2.18 \times 10^{-18} / n^2$ [J] where n denotes the principal quantum number.

4.1 Calculate the energy differences between $n = 2$ (first excited state) and $n = 1$ (ground state) and between $n = 7$ and $n = 1$.

4.2 In what spectral range is the Lyman series lying?

4.3 Can a single photon, emitted in the first and/or sixth line of the Lyman series, ionize:

- another hydrogen atom in its ground state?
- a copper atom in the Cu crystal?

The electron work function of Cu is $\Phi_{\text{Cu}} = 7.44 \times 10^{-19}$ J.

4.4 Calculate the de Broglie wavelength of the electrons emitted from a copper crystal when irradiated by photons from the first line and the sixth line of the Lyman series.

$$h = 6.6256 \times 10^{-34} \text{ J s}; \quad m_e = 9.1091 \times 10^{-31} \text{ kg}; \quad c = 2.99792 \times 10^8 \text{ m s}^{-1}$$

SOLUTION

4.1 $\Delta E_{n \rightarrow 1} = E_n - E_1 = 2.18 \times 10^{-18} (1 - n^2)$

$$\Delta E_{2 \rightarrow 1} = 1.635 \times 10^{-18} \text{ J}$$

$$\Delta E_{7 \rightarrow 1} = 2.135 \times 10^{-18} \text{ J}$$

4.2 The Lyman series is due to $\Delta E_{n \rightarrow 1}$ varying from 1.635×10^{-18} J ($n = 1$) to 2.135×10^{-18} J ($n \rightarrow \infty$), which corresponds to 121.5 nm and to 93.0 nm, respectively. This is in the UV-region.

4.3 a) The ionisation energy is equal to $\Delta E_{\infty \rightarrow 1} = 2.18 \times 10^{-18}$ J. Both $\Delta E_{2 \rightarrow 1}$ and $\Delta E_{7 \rightarrow 1}$ are smaller than $\Delta E_{\infty \rightarrow 1}$ and a single photon emitted from these transitions is not able to ionize a hydrogen atom.

b) Ionization of copper in a Cu-crystal is related to the photoelectric effect:

$$h\nu = \Phi_{\text{Cu}} + E_{\text{kin}} = \Phi_{\text{Cu}} + \frac{1}{2} m_e v^2$$

Because $\Delta E_{2 \rightarrow 1} > \Phi_{\text{Cu}}$ and $\Delta E_{7 \rightarrow 1} > \Phi_{\text{Cu}}$ both photons are indeed able to ionize a Cu-atom in the crystal.

The kinetic energy of the emitted electrons is:

$$\Delta E_{\text{kin}}(2 \rightarrow 1) = \Delta E_{2 \rightarrow 1} - \Phi_{\text{Cu}} = 8.91 \times 10^{-19} \text{ J}$$

$$\Delta E_{\text{kin}}(7 \rightarrow 1) = \Delta E_{7 \rightarrow 1} - \Phi_{\text{Cu}} = 13.91 \times 10^{-19} \text{ J}$$

4.4 The wavelength of an electron is:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2 E_{\text{kin}} m_e}}$$

$$(p = m_e v_e \text{ and } E_{\text{kin}} = \frac{p^2}{2 m_e})$$

$$\Delta E_{2 \rightarrow 1}: \quad \lambda_1 = 4.16 \times 10^{-10} \text{ m} = 4.16 \text{ \AA}$$

$$\Delta E_{7 \rightarrow 1}: \quad \lambda_2 = 5.20 \times 10^{-10} \text{ m} = 5.20 \text{ \AA}$$

PROBLEM 5Halogen derivatives of hydrocarbons

After passing 0.25 mol of hydrocarbon **A** over heated pumice (950 K) in an iron pipe, compound **B** in yield of 80 % (i. e. 15.4 g) and 2.4 dm³ of hydrogen, (295 K, 102 kPa) were obtained.

B and hydrogen are the only products. A mixture of halogen derivatives **C**, **D**, **E**, **F** and **G** is produced from **B** by reaction with a halogen in presence of a Lewis acid. Compounds **C** to **G** contain each one halogen atom more then the preceding compound. For the compounds **C** to **F** only one of the possible isomers is formed. In compound **G** there is no such preference and its three isomers **G**₁, **G**₂ and **G**₃ are found in the mixture. Compounds **C** to **F** racemize easily so that no optical isomerism occurs. However racemization is difficult for **G**₁, **G**₂, and especially for **G**₃. In the mass spectrum of **E** only three isotopic peaks were observed. Their relative intensities are 1: 1: 0.3.

Information:

- $k_{ortho} > k_{para}$ in compound **B**.
- The effect of the first halogen in the ring: $k_{para} > k_{ortho}$.
- Compounds **D** and **F** in one of their conformations have a center of symmetry.
- The contribution of carbon and hydrogen isotopes in the mass spectrum of **E** are negligible.
- Natural abundance of halogen isotopes:
 - $^{19}\text{F} = 100 \%$;
 - $^{35}\text{Cl} = 75.53 \%$; $^{37}\text{Cl} = 24.47 \%$;
 - $^{79}\text{Br} = 50.54 \%$; $^{81}\text{Br} = 49.46 \%$;
 - $^{127}\text{I} = 100 \%$.

5.1 Give the structures of **A**, **B**, **C**, **D**, **E**, **F**, **G**₁, **G**₂ and **G**₃.

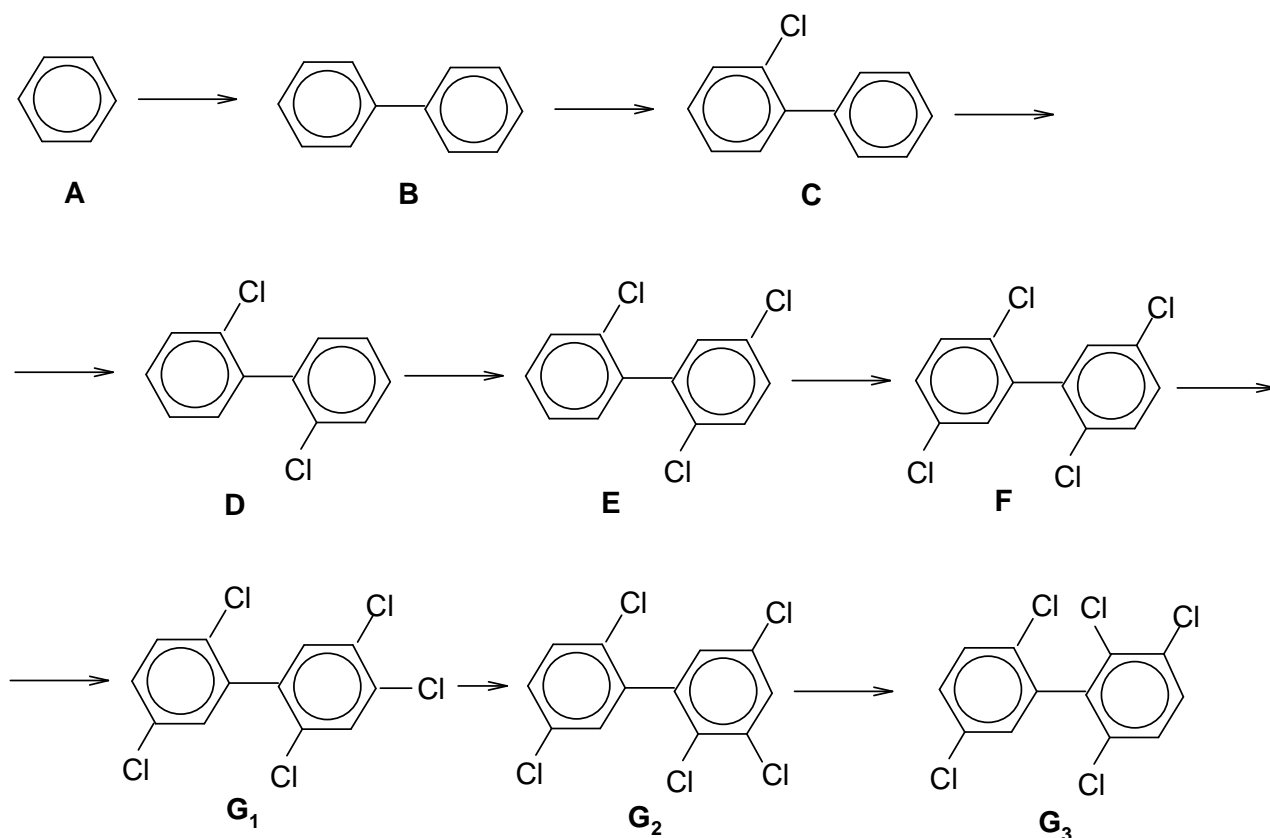
5.2 Explain your choice for the halogen.

5.3 Draw and label stereo-formulas of the rotational isomers of **D** for $\Phi = 0, \pi/2, \pi,$ and $3\pi/2$, where Φ denotes the dihedral or torsional angle in radians and $\vartheta = 0$ describes the configuration with maximal energy.

- 5.4 Draw profiles of the energy changes as a function of the angle of rotation around the C-C bond for compounds **C** and **D**.
- 5.5 Give a sequence of **G**₁, **G**₂, **G**₃ according to their increasing difficulty of racemization. Explain your answer.
- 5.6 Draw stereo-formulas of the enantiomers of **G**₃.
- 5.7 Suggest a chemical reaction or a biological method by which compounds like these can be destroyed.

SOLUTION

5.1



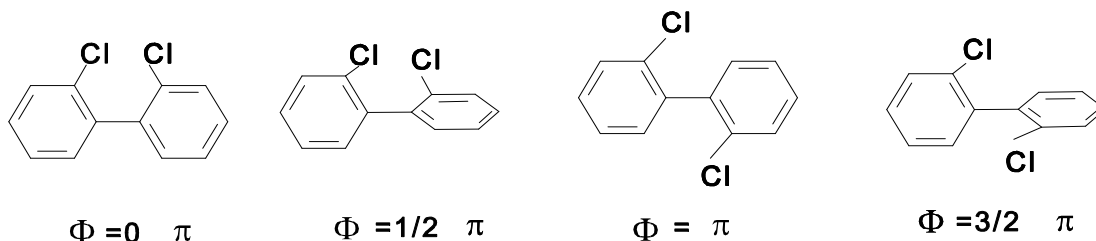
5.2 For the determination of the halogen of **E** we consider the ratio of the isotopic peaks in the mass spectrum.

$$\text{For } \mathbf{E} \ (n = 3) \text{ we have: } (x + y)^3 = x^3 + 3x^2y + 3xy^2 + y^3.$$

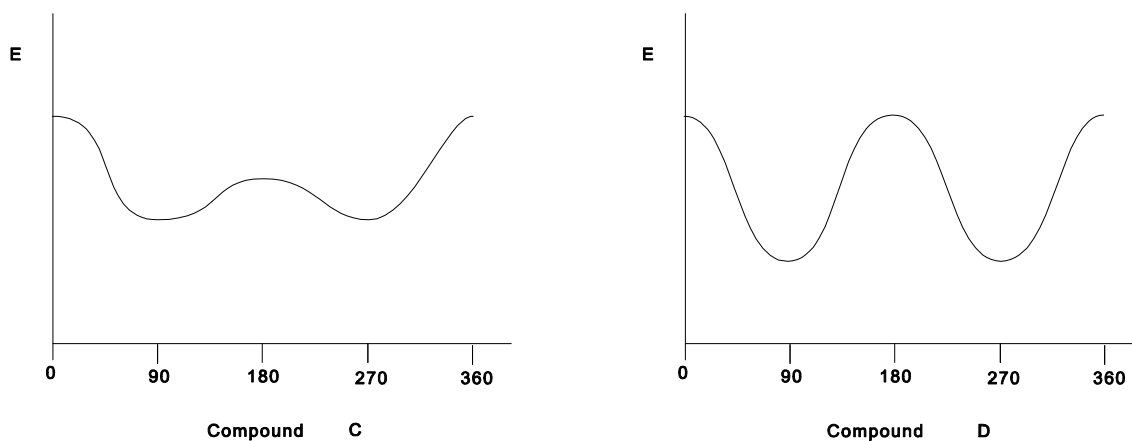
Therefore, with Br we would obtain: $x : y = 50.54 : 49.46 \cong 1 : 1$ hence $(x + y)^3 = 1 + 3 + 3 + 1$ and the ratio would be 1 : 3 : 3 : 1 which is not in agreement with the text.

For chlorine the isotopic ratio is $75.53 : 24.47 \cong 1 : 3$ and therefore $(x + y)^3 = 3^3 + (3 \times 3^2 \times 1) + (3 \times 3 \times 1^2)$, which yields to a ratio of $1 : 1 : 0.33 : 0.04$. So, the X-atom is chlorine.

5.3



5.4

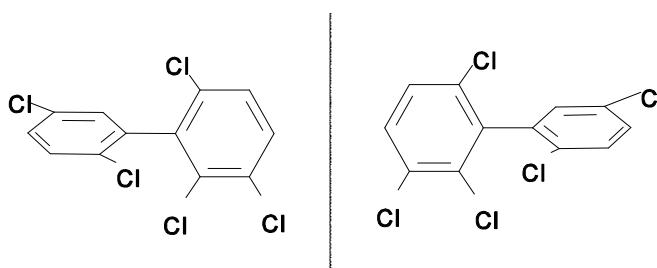


5.5

$$G_1 < G_2 < G_3.$$

Due to the increasing steric hindrance as a result of the interference of the big Van der Waals radii of chlorine, the rotation around the C-C single bond becomes more and more difficult. Therefore racemization is most likely to occur with G_1 , less with G_2 and least with G_3 . This kind of isomerism is called atropisomerism.

5.6



- 5.7** - Complete combustion in chemical incinerator equipped with an afterburner and scrubber.
- Addition of a strong base to obtain corresponding phenols.
 - Transformation into ArOH by OH-radicals in water.
 - Bacteria metabolizing polychlorobiphenyls.
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PROBLEM 6

Sulphuric acid is produced by catalytic oxidation of SO_2 to SO_3 , absorption of SO_3 in concentrated sulphuric acid forming oleum (containing 20 % SO_3 by mass) and appropriate dilution hereafter. The gas leaving the catalyst chamber contains nitrogen, oxygen, a trace of SO_2 and 10 % (by volume) of SO_3 . Sulphur trioxide, SO_3 , is converted into sulphuric acid (98 % by mass) and/or oleum.

- 6.1** Assuming that oleum is the only product formed, calculate the mass of water which is required for 1000 m^3 of gas leaving the catalyst chamber (273 K, 101.3 kPa).
- 6.2** Assuming that only 98 % sulphuric acid is produced, calculate the necessary mass of water and the mass of product produced thereby.
- 6.3** In the industry both oleum and 98 % sulphuric acid are produced in a mass ratio of $x = m_1/m_2$, where m_1 denotes the mass of oleum, m_2 the mass of 98 % sulphuric acid. Find an expression $y = f(x)$ to describe the relation between the mass of water consumed for 1000 m^3 gas (denoted y) and the value of x . Show that the results of 6.1) and 6.2) are in good agreement with your mathematical expression.

SOLUTION

- 6.1** 1000 m^3 of gas contain 4.462 kmol SO_a
 100 kg 20 % oleum contain 0.2498 kmol SO_3 and 0.8157 kmol H_2SO_4
 1.0655 kmol SO_a and 0.8157 kmol (14.70 kg) H_2O are necessary for production of 100 kg 20 % oleum.
 61.56 kg H_2O are necessary for 1000 m^3 of gas.
- 6.2** Assumption that only 98 % sulphuric acid is produced:
 100,0 kg 98 % H_2SO_4 contain 0,9992 kmol H_2SO_4 and 1,1102 kmol H_2O .
 100,0 kg 98 % H_2SO_4 contain 0.9992 kmol SO_3 and 1,1102 kmol (20,01 kg) H_2O .
 89.36 kg H_2O are necessary for 1000 m^3 of gas and 446.56 kg 98 % H_2SO_4 are obtained.
- 6.3** To obtain 1 kg 20 % oleum, 0,1470 kg H_2O are necessary,
 To obtain 1 kg 98 % H_2SO_4 , 0,2001 kg H_2O are necessary.

Thus, for mass of water for production of m_1 kg 20 % oleum and m_2 kg 98 % H_2SO_4 :
 $y = 0,1470 m_1 + 0,2001 m_2$.

Analogically for mass balance of SO_a :

$$4,462 = 1,0655 m_1 + 0,9992 m_2$$

Then:
$$\frac{y}{4.462} = \frac{14.70 m_1 + 20.01 m_2}{1.0655 m_1 + 0.9992 m_2}$$

After substitution: $m_1/m_2 = x$ the above relation may written in the form of a function
 $y = f(x)$:

$$y = \frac{61.65 x + 83.79}{x + 0.9378}$$

Production of oleum: $m_2 = 0$, $y = 61,56$,

production of the acid: $m_1 = 0$, $y = 89,35$,

Results are similar to those obtained in parts **6.1** and **6.2**.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determination of an acid dissociation constant

Reagents:

A solution of a weak monoprotic acid with a concentration of about 0.1 mol dm^{-3} ,
a solution of sodium hydroxide with a concentration of about 0.1 mol dm^{-3} ,
solutions of the indicators: methyl orange and phenolphthalein.

Equipment:

burette 25 cm^3 ,

calibrated pipette 20 cm^3 ,

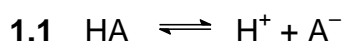
two conical flasks 200 cm^3 ,

access to the *pH*-meter. An assistant will make one measurement only for each participant.

Questions:

- 1.1 Give the expression for the concentration dissociation constant of the acid HA.
- 1.2 Give your reasons for the choice of the indicator.
- 1.3 Give the results of titrations.
- 1.4 Write down your *pH* value (measured by assistant).
- 1.5 Show how you calculate the concentration pK_a value for the acid. Write down the value.

SOLUTION



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (\text{a})$$

1.2 Since the HA is a weak acid the colour transition of the indicator is expected in the basic region ($pH > 7$), and thus phenolphthalein is suitable.

1.3 and 1.4

The results obtained by measuring volumes of the titrand and pH values were expected to be shown in the answer sheet.

1.5 The equation (a) can be transformed to equation (b) as follows:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad (b)$$

When $[A^-] = [HA]$, then $pH = pK_a$

Since the concentration of the sodium hydroxide solution is approximate only, it is not possible to calculate the exact concentration of the acid. Nevertheless, the combination of titration and measuring pH values gives the possibility to find the value of dissociation constant K_a .

PROBLEM 2 (Practical)

Determination of the formation (stability) constants of the complex ions $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Zn}(\text{NH}_3)_4]^{2+}$

Equipment:

Two dry beakers with copper and zinc electrodes,
 three bottles with aqueous solutions of CuSO_4 , ZnSO_4 and NH_3 , respectively,
 one beaker with strips of filter paper for making a salt bridge,
 one beaker with an aqueous solution of KNO_3 ,
 three pipettes for delivering CuSO_4 , ZnSO_4 and NH_3 solutions,
 digital voltmeter for the EMF measurements,
 red and blue leads (conductors) for connecting cell electrodes to the digital voltmeter,
 rubber pipette filler,
 appropriately marked glass stirring rods.

a) Procedure for setting up the Daniell cell:

1. Into the dry beakers containing Cu and Zn electrodes deliver 20 cm³ of CuSO_4 and 20 cm³ of ZnSO_4 using marked pipettes in order to get Cu/Cu^{2+} and Zn/Zn^{2+} half-cells.
2. Wet the filter paper strip with KNO_3 solution. The strip should only be moisten with the solution. Then place the strip ends into the CuSO_4 and ZnSO_4 solutions.
3. Connect the leads to the electrodes (red to Cu electrode and blue to Zn electrode).

a)

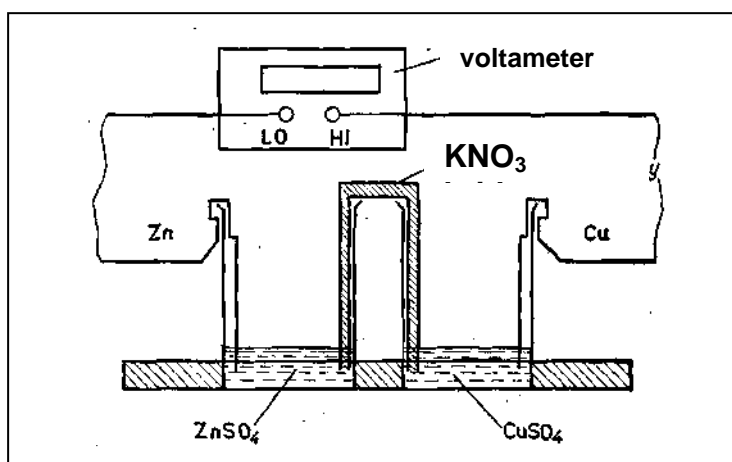


Fig. 1

b) Procedure for the EMF measurement of the Daniell cell (E_A):

Put the appropriately marked glass rods (red - Cu, blue - Zn) into the CuSO_4 and ZnSO_4 solutions. Having stirred the solutions gently with the rods, the rods should be left in the solutions throughout the course of the experiment. Start the EMF measurement of the cell by connecting the red lead to the voltmeter terminal (HI) and the blue one to the negative terminal (LO). If the EMF value changes by no more than 0.001 V, record the EMF (E_A).

c) Procedure for the EMF measurement of the cell (E_B) after the addition of the complexing agent (NH_3 solution) into the Cu/Cu^{2+} half-cell:

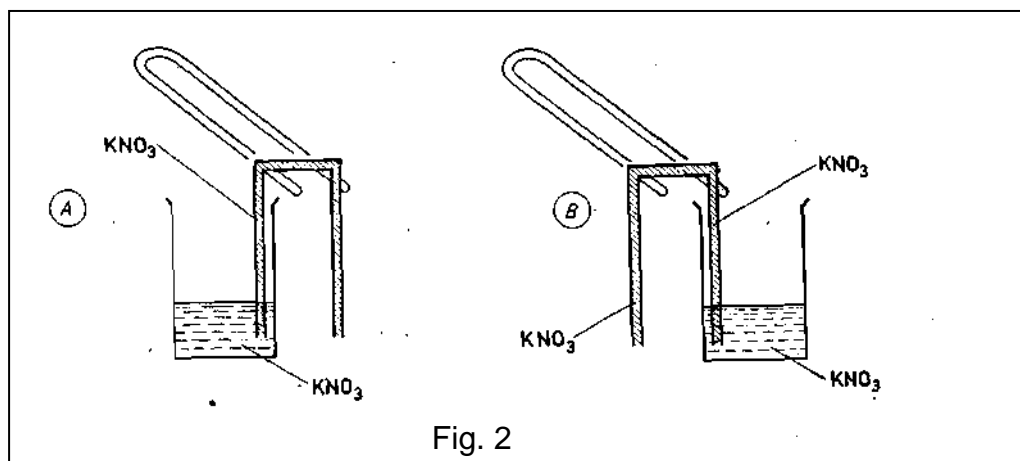


Fig. 2

Pipette 20 cm³ of aqueous NH_3 solution into the CuSO_4 solution. Stir the solution with a glass rod gently until it becomes a clear dark blue. Leave the rod in the solution. Measure and record the new EMF (E_B), in the way described in part b).

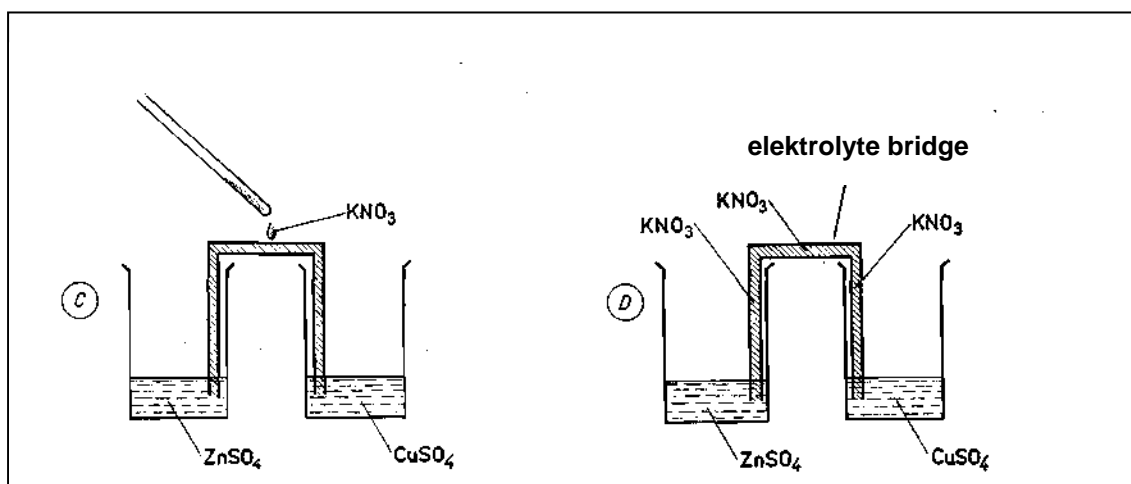


Fig. 3

- d) Procedure for the EMF measurement of the cell (E_C) after the addition of the complexing agent (NH_3 solution) to the Zn/Zn^{2+} half-cell:

Leave the $\text{Cu}/[\text{Cu}(\text{NH}_3)_4]^{2+}$ half-cell unchanged. Add 20 cm^3 of NH_3 solution to the ZnSO_4 half-cell. Carry out the EMF measurement of the cell in the way described in part b). Write down the result (E_C).

Theoretical considerations:

Gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Faraday constant $F = 96\,487 \text{ C mol}^{-1}$

- i) The concentrations of CuSO_4 , ZnSO_4 and NH_3 aqueous solutions written on the bottles are expressed in mol kg^{-1} . Therefore they must be converted into appropriate concentrations expressed in mol dm^{-3} . The densities (d) of the solutions as functions of temperature are respectively:
- CuSO_4 : $d_1 = 1.0923 (\text{kg dm}^{-3}) - 0.0002700 (\text{kg dm}^{-3}\text{K}^{-1}) T$
 ZnSO_4 : $d_2 = 1.0993 (\text{kg dm}^{-3}) - 0.0002900 (\text{kg dm}^{-3}\text{K}^{-1}) T$
 NH_3 : $d_3 = 1.0740 (\text{kg dm}^{-3}) - 0.0002800 (\text{kg dm}^{-3}\text{K}^{-1}) T$
- ii) In order to convert concentrations (c_i) into ionic activities (a_i), we need to calculate activities of the ions using the equation $a_i = f_i \cdot c_i$. The activity coefficient values, f_i , of the ions involved are given in the answer sheet. The activity coefficient of ammonia should be assumed to be 1.
- iii) To simplify the calculations it should be assumed that after the addition of the excess of complexing agent (NH_3) only $\text{Cu}^{2+}_{\text{aq}}$, $\text{Zn}^{2+}_{\text{aq}}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ions exist in the respective solutions.
- iv) Any diffusion potential occurring between both half-cells when the salt bridge is applied may be neglected in practice.

Questions:

- 2.1** Calculate the values of the concentrations of Cu^{2+} and Zn^{2+} ions in the Daniell cell before the introduction of the complexing agent (NH_3).
- 2.2** Calculate the standard EMF value E^0 of your Daniell cell using the Nernst equation.

- 2.3 Calculate the concentrations of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and NH_3 in the B type cell, i.e. after the addition of NH_3 to the Cu/Cu^{2+} half-cell.
- 2.4 Determine the values of the thermodynamic formation (stability) constants K_B and $\ln K_B$ for the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ions.
- 2.5 Calculate the concentrations of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ and NH_3 in the type C cell, i. e. after the addition of NH_3 to the Zn/Zn^{2+} half-cell.
- 2.6 Determine the values of the thermodynamic formation (stability) constant K_C and $\ln K_C$ for $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ions.

SOLUTION

2.1 The mass of the solutions (kg) can be transformed to volumes of the solutions (dm^3) using the given densities. The concentrations are then given in units mol dm^{-3} .

$$2.2 \quad E = \left(E^0(\text{Cu}^{2+}/\text{Cu}) + \frac{RT}{2F} \ln([\text{Cu}^{2+}] \times f_{\text{Cu}^{2+}}) \right) - \left(E^0(\text{Zn}^{2+}/\text{Zn}) + \frac{RT}{2F} \ln([\text{Zn}^{2+}] \times f_{\text{Zn}^{2+}}) \right) - E_{\text{diff}}$$

For $E_{\text{diff}} = 0$:

$$E_A = E^0(\text{Cu}^{2+}/\text{Cu}) - E^0(\text{Zn}^{2+}/\text{Zn}) + \frac{RT}{2F} \ln \frac{[\text{Cu}^{2+}] \times f_{\text{Cu}^{2+}}}{[\text{Zn}^{2+}] \times f_{\text{Zn}^{2+}}}$$

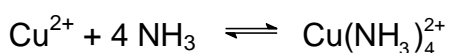
E_A can be measured. All other data required are given in the text of the problem or in the answer sheet.

2.3 Concentrations after the addition of NH_3 :

$$[\text{Cu}(\text{NH}_3)_4^{2+}] = \frac{c(\text{Cu}^{2+}) \times V}{V + V_1}$$

$$[\text{NH}_3] = \frac{(c(\text{NH}_3) \times V_1) - (4 c(\text{Cu}^{2+}) \times V)}{V + V_1}$$

2.4 After the addition of NH_3 the following complex equilibrium is established:



$$\beta_4 = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}] \times f_{\text{Cu}(\text{NH}_3)_4^{2+}}}{[\text{Cu}^{2+}] \times f_{\text{Cu}^{2+}} \times [\text{NH}_3]^4}$$

Then the Nernst equation has the form:

$$E'_1 = E^0(\text{Cu}^{2+}/\text{Cu}) = \frac{RT}{2F} \ln \frac{[\text{Cu}(\text{NH}_3)_4^{2+}] \times f_{\text{Cu}(\text{NH}_3)_4^{2+}}}{\beta_4 \times [\text{NH}_3]^4}$$

$$E_B = E'_1 - E_2 = E^0(\text{Cu}^{2+}/\text{Cu}) - E^0(\text{Zn}^{2+}/\text{Zn}) + \frac{RT}{2F} \ln \frac{[\text{Cu}(\text{NH}_3)_4^{2+}] \times f_{\text{Cu}(\text{NH}_3)_4^{2+}}}{[\text{Zn}^{2+}] \times f_{\text{Zn}^{2+}} \times \beta_4 \times [\text{NH}_3]^4}$$

From the above equation β_4 or $\ln\beta_4$ can be calculated since E_B can be measured, and all other data required are given in the text of the problem or in the answer sheet.

2.5 and 2.6

The procedure in the calculation of β_4 or $\ln\beta_4$ for complex $\text{Zn}(\text{NH}_3)_4^{2+}$ is analogical as that shown in parts (2.3) and (2.4) for complex $\text{Cu}(\text{NH}_3)_4^{2+}$.