

# 26<sup>th</sup>



International Chemistry Olympiad

**8 theoretical problems**  
**2 practical problems**

# THE TWENTY-SIXTH INTERNATIONAL CHEMISTRY OLYMPIAD 3–11 JULY 1994, OSLO, NORWAY

## THEORETICAL PROBLEMS

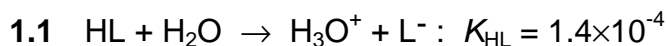
### PROBLEM 1

Lactic acid is formed in the muscles during intense activity (anaerobic metabolism). In the blood, lactic acid is neutralized by reaction with hydrogen carbonate. This will be illustrated by the following calculations:

Lactic acid written as HL is monoprotic, and the acid dissociation constant is  $K_{\text{HL}} = 1.4 \times 10^{-4}$ .

The acid dissociation constants for carbonic acid are:  $K_{\text{a}1} = 4.5 \times 10^{-7}$  and  $K_{\text{a}2} = 4.7 \times 10^{-11}$ . All carbon dioxide remains dissolved during the reactions.

- 1.1 Calculate  $pH$  in a  $3.00 \times 10^{-3}$  M solution of HL.
- 1.2 Calculate the value of the equilibrium constant for the reaction between lactic acid and hydrogen carbonate.
- 1.3  $3.00 \times 10^{-3}$  mol of lactic acid (HL) is added to  $1.00 \text{ dm}^3$  of  $0.024$  M solution of  $\text{NaHCO}_3$  (no change in volume, HL completely neutralized).
  - i) Calculate the value of  $pH$  in the solution of  $\text{NaHCO}_3$  before HL is added.
  - ii) Calculate the value of  $pH$  in the solution after the addition of HL.
- 1.4  $pH$  in the blood of a person changed from 7.40 to 7.00 due to lactic acid formed during physical activity. Let an aqueous solution having  $pH = 7.40$  and  $[\text{HCO}_3^-] = 0.022$  represent blood in the following calculation. How many moles of lactic acid have been added to  $1.00 \text{ dm}^3$  of this solution when its  $pH$  has become 7.00?
- 1.5 In a saturated aqueous solution of  $\text{CaCO}_3(\text{s})$   $pH$  is measured to be 9.95. Calculate the solubility of calcium carbonate in water and show that the calculated value for the solubility product constant  $K_{\text{sp}}$  is  $5 \times 10^{-9}$ .
- 1.6 Blood contains calcium. Determine the maximum concentration of "free" calcium ions in the solution ( $pH = 7.40$ ,  $[\text{HCO}_3^-] = 0.022$ ) given in 1.4.

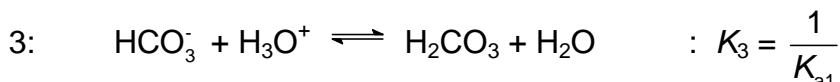
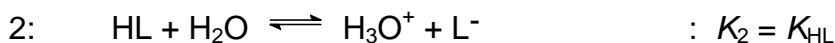
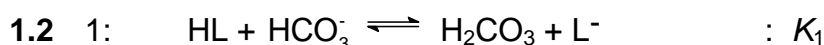
**SOLUTION**

$$c_0 - x \qquad \qquad x \qquad x$$

$$K_a = \frac{x^2}{c_0 - x} = 1.4 \times 10^{-4} \qquad c_0 = 3.00 \times 10^{-3}$$

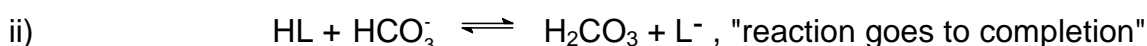
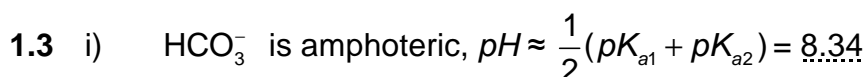
Assumption  $c_0 \gg x$  gives  $x = 6.5 \cdot 10^{-4}$ , not valid

Quadratic formula:  $x = 5.8 \times 10^{-4}$ ,  $[\text{H}_3\text{O}^+] = 5.8 \times 10^{-4}$ ,  $\text{pH} = 3.24$



Reaction 1 = 2 + 3,  $K_1 = K_2 \cdot K_3 = 311 \quad (3.1 \times 10^2)$

$$\text{Alternative: } K_1 = \frac{[\text{H}_2\text{CO}_3][\text{L}^-]}{[\text{HL}][\text{HCO}_3^-]} \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{[\text{H}_3\text{O}^+][\text{L}^-]}{[\text{HL}]} \times \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}$$

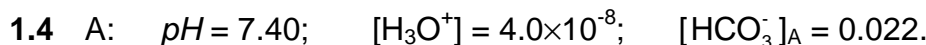


Before: 0.0030 0.024 0 0

After: 0 0.021 0.0030 0.0030

$$\text{Buffer: } \text{pH} \approx \text{p}K_{a1} + \log \frac{0.021}{0.0030} = 6.35 + 0.85 = 7.20$$

$$(\text{Control: } \frac{K_{\text{HL}}}{[\text{H}_3\text{O}^+]} = \frac{[\text{L}^-]}{[\text{HL}]} = 2.2 \times 10^3, \text{ assumption is valid})$$



From  $K_{a1}$ :  $[\text{H}_2\text{CO}_3]_{\text{A}} = 0.0019$ ;

$$(1) [\text{HCO}_3^-]_{\text{B}} + [\text{H}_2\text{CO}_3]_{\text{B}} = 0.0239 \quad (0.024)$$

$$\text{B: } \text{pH} = 7.00; \quad \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.5;$$

$$(2) \quad [\text{HCO}_3^-]_{\text{B}} = 4.5 [\text{H}_2\text{CO}_3]_{\text{B}}$$

$$\text{From (1) and (2):} \quad [\text{HCO}_3^-]_{\text{B}} = 0.0196$$

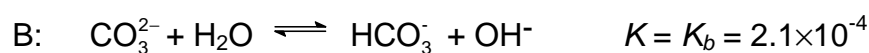
$$[\text{H}_2\text{CO}_3]_{\text{B}} = 0.0043$$

$$n(\text{HL}) = \Delta n(\text{H}_2\text{CO}_3) = \Delta c(\text{H}_2\text{CO}_3) \times 1.00 \text{ dm}^3 = 2.4 \times 10^{-3} \text{ mol}$$

$$1.5 \quad [\text{OH}^-] = 8.9 \times 10^{-5} \quad [\text{H}_2\text{CO}_3] \text{ of no importance}$$



$$c_0 \qquad c_0$$



$$c_0 - x \qquad x \qquad x$$

$$\text{From B:} \quad [\text{HCO}_3^-] = [\text{OH}^-] = 8.9 \times 10^{-5}$$

$$[\text{CO}_3^{2-}] = \frac{[\text{HCO}_3^-][\text{OH}^-]}{K_b} = 3.8 \times 10^{-5}$$

$$[\text{Ca}^{2+}] = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 1.3 \times 10^{-4}$$

$$c_0(\text{Ca}^{2+}) = 1.3 \times 10^{-4} \text{ mol dm}^{-3} = \text{solubility}$$

$$1.6 \quad K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 1.3 \times 10^{-4} \times 3.8 \times 10^{-5} = 4.9 \times 10^{-9} = 5 \times 10^{-9}$$

$$\text{From } K_{a2}: \quad [\text{CO}_3^{2-}] = \frac{K_{a2} [\text{HCO}_3^-]}{[\text{H}_3\text{O}^+]} = 2.6 \times 10^{-5}$$

$$Q = [\text{Ca}^{2+}][\text{CO}_3^{2-}]; \quad \text{Precipitation when } Q > K_{sp} = 5 \times 10^{-9}$$

No precipitation when  $Q < K_{sp}$

Max. concentration of "free"  $\text{Ca}^{2+}$  ions:

$$[\text{Ca}^{2+}]_{\text{max}} = \frac{K_{sp}}{[\text{CO}_3^{2-}]} = 1.9 \times 10^{-4}$$

**PROBLEM 2**

Nitrogen in agricultural materials is often determined by the Kjeldahl method. The method involves a treatment of the sample with hot concentrated sulphuric acid, to convert organically bound nitrogen to ammonium ion. Concentrated sodium hydroxide is then added, and the ammonia formed is distilled into hydrochloric acid of known volume and concentration. The excess hydrochloric acid is then back-titrated with a standard solution of sodium hydroxide, to determine nitrogen in the sample.

- 2.1** 0.2515 g of a grain sample was treated with sulphuric acid, sodium hydroxide was then added and the ammonia distilled into 50.00 cm<sup>3</sup> of 0.1010 M hydrochloric acid. The excess acid was back-titrated with 19.30 cm<sup>3</sup> of 0.1050 M sodium hydroxide. Calculate the concentration of nitrogen in the sample, in percent by mass.
- 2.2** Calculate the *pH* of the solution which is titrated in 2.1 when 0 cm<sup>3</sup>, 9.65 cm<sup>3</sup>, 19.30 cm<sup>3</sup> and 28.95 cm<sup>3</sup> of sodium hydroxide have been added. Disregard any volume change during the reaction of ammonia gas with hydrochloric acid.  $K_a$  for ammonium ion is  $5.7 \times 10^{-10}$ .
- 2.3** Draw the titration curve based on the calculations in b).
- 2.4** What is the *pH* transition range of the indicator which could be used for the back titration.
- 2.5** The Kjeldahl method can also be used to determine the molecular weight of amino acids. In a given experiment, the molecular weight of a naturally occurring amino acid was determined by digesting 0.2345 g of the pure acid and distilling ammonia released into 50.00 cm<sup>3</sup> of 0.1010 M hydrochloric acid. A titration volume of 17.50 cm<sup>3</sup> was obtained for the back titration with 0.1050 M sodium hydroxide. Calculate the molecular weight of the amino acid based on one and two nitrogen groups in the molecule, respectively.

**SOLUTION**

$$\mathbf{2.1} \quad [(50.00 \times 0.1010) - (19.30 \times 0.1050)] \frac{14.01}{1000} \times \frac{100}{0.2515} = 16.84 \% \text{ N}$$

$$\mathbf{2.2} \quad 0 \text{ cm}^3 \text{ added:} \quad [\text{H}^+] = \frac{19.30 \cdot 0.1050}{50} = 0.04053$$

$$pH = 1.39$$

$$9.65 \text{ cm}^3 \text{ added: } [\text{H}^+] = 0.01699$$

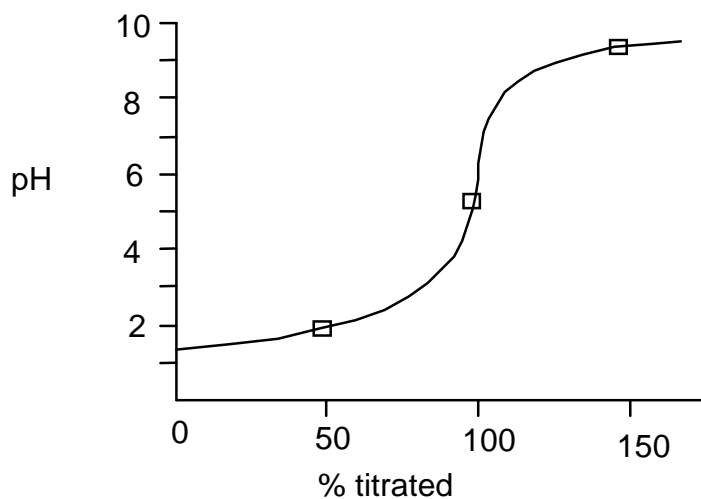
$$pH = 1.77$$

$$19.30 \text{ cm}^3 \text{ added: } [\text{H}^+] = \sqrt{5.7 \cdot 10^{-10} \times \frac{50.000 \times 101019 \times 300 \times 1050}{50 + 19.30}}$$

$$pH = 5.30$$

$$28.95 \text{ cm}^3 \text{ added: } pH = pK_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.24 + \log \frac{1.01}{2.01} = 8.94$$

### 2.3



2.4 Indicator *pH* transition range:  $pH\ 5.3 \pm 1$

$$2.5 \quad [(50.00 \times 0.1010) - (17.50 \times 0.1050)] \frac{14.01}{1000} \times \frac{100}{0.2345} = 19.19\ \% \text{ N}$$

$$1 \text{ N: } M_r = 73.01$$

$$2 \text{ N: } M_r = 146.02$$

### PROBLEM 3

Sulphur forms many different compounds with oxygen and halogens (sulphur as the central atom). These compounds are mainly molecular, and many are easily hydrolysed in water.

- 3.1** Write Lewis structures for molecules  $\text{SCl}_2$ ,  $\text{SO}_3$ ,  $\text{SO}_2\text{ClF}$ ,  $\text{SF}_4$ , and  $\text{SBrF}_5$ .
- 3.2** Carefully draw the geometries of the 5 molecules. (Disregard small deviations from "ideal" angles.)
- 3.3** A compound, consisting of sulphur (one atom per molecule), oxygen and one or more atoms of the elements F, Cl, Br, and I, was examined. A small amount of the substance reacted with water. It was completely hydrolyzed without any oxidation or reduction, and all reaction products dissolved. 0.1 M solutions of a series of test reagents were added to separate small portions of a diluted solution of the substance.

Which ions are being tested for in the following tests?

- Addition of  $\text{HNO}_3$  and  $\text{AgNO}_3$ .
- Addition of  $\text{Ba}(\text{NO}_3)_2$ .
- Adjustment to  $\text{pH} = 7$  with  $\text{NH}_3$  and addition of  $\text{Ca}(\text{NO}_3)_2$ .

Write the equations for the possible reactions in the tests:

- Addition of  $\text{KMnO}_4$  followed by  $\text{Ba}(\text{NO}_3)_2$  to an acid solution of the substance.
- Addition of  $\text{Cu}(\text{NO}_3)_2$ .

- 3.4** In practice, the tests in 3.3 gave the following results:

- A yellowish precipitate.
- No precipitate.
- No visible reaction.
- The main features were that the characteristic colour of permanganate disappeared, and a white precipitate was formed upon addition of  $\text{Ba}(\text{NO}_3)_2$ .
- No precipitate.

Write the formulas of the possible compounds, taking the results of these tests into account.

- 3.5** Finally, a simple quantitative analysis was undertaken:

7.190 g of the substance was weighed out and dissolved in water to give 250.0 cm<sup>3</sup> of a solution. To 25.00 cm<sup>3</sup> of this solution, nitric acid and enough  $\text{AgNO}_3$  was added

to secure complete precipitation. After washing and drying the precipitate weighed 1.452 g. Determine the formula of the compound.

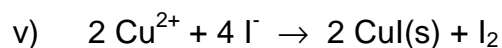
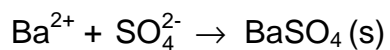
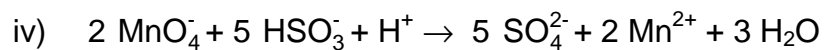
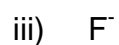
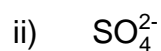
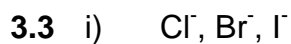
3.6 Write the equation describing the reaction of the substance with water.

If you have not found the formula for the compound, use SOClF.

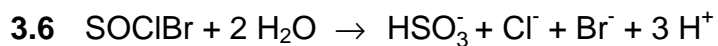
## SOLUTION

|                     | 3.1 | 3.2 |
|---------------------|-----|-----|
| SCl <sub>2</sub>    |     |     |
| SO <sub>3</sub>     |     |     |
| SO <sub>2</sub> ClF |     |     |
| SF <sub>4</sub>     |     |     |
| SBrF <sub>5</sub>   |     |     |





[ $\text{SOClBr}$ : 1.456g, and  $\text{SOBr}_2$ : 1.299g]



**PROBLEM 4**

Platinum(IV) oxide is not found in the nature, but it can be prepared in a laboratory. Solid platinum(IV) oxide is in equilibrium with platinum metal and oxygen gas at 1 atm ( $= 1.01325 \times 10^5$  Pa) and 650 °C.

**4.1** This suggests that the conditions on the Earth, when the minerals we know were formed, were:

[1]  $p(\text{O}_2) = 1$  atm,  $t = 650$  °C;

[2]  $p(\text{O}_2) < 1$  atm,  $t < 650$  °C;

[3]  $p(\text{O}_2) > 1$  atm,  $t < 650$  °C;

[4]  $p(\text{O}_2) < 1$  atm,  $t > 650$  °C;

[5]  $p(\text{O}_2) > 1$  atm,  $t > 650$  °C

Mark the most probable alternative [1] – [5] on the answer sheet. Please note that the marking of only one alternative will be accepted.

**4.2** What are  $\Delta G$  and  $K_p$  for the formation of platinum(IV) oxide at oxygen pressure of 1 atm and temperature of 650 °C?

The preparation of platinum(IV) oxide involves boiling of a solution which contains hexachloroplatinate(IV) ions with sodium carbonate. In this process  $\text{PtO}_2 \cdot n \text{H}_2\text{O}$  is formed and this is in turn converted to platinum(IV) oxide upon subsequent filtering and heat treatment. In the following we assume  $n = 4$ .

$\text{PtO}_2 \cdot 4 \text{H}_2\text{O}$  or  $\text{Pt}(\text{OH})_4 \cdot 2 \text{H}_2\text{O}$  can be dissolved in acids and strong bases.

**4.3** Write the balanced equations for the preparation of platinum(IV) oxide according to the procedure given above.

**4.4** Write the balanced equations for the dissolution of  $\text{PtO}_2 \cdot 4 \text{H}_2\text{O}$  in both hydrochloric acid and sodium hydroxide.

Platinum is mainly found in the nature as the metal (in mixture or in alloying with other precious metals). Platinum is dissolved in aqua regia under the formation of hexachloroplatinate(IV) ions. Aqua regia is a mixture of concentrated hydrochloric and nitric acids in proportion 3 : 1, and of the nitrosylchloride (NOCl) and the atomic chlorine which are formed upon the mixing. The latter is believed to be the active dissolving component.

The hexachloroplatinate(IV) ions can be precipitated as diammonium hexachloroplatinate(IV) and by thermal decomposition of this compound, finely powdered platinum and gaseous products are formed.

- 4.5** Write the balanced equations for the formation of aqua regia and its reaction with platinum.
- 4.6** Write the balanced equation of the thermal decomposition of diammonium hexachloroplatinate(IV) at elevated temperature.

From diammonium hexachloroplatinate(IV) we can prepare  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  which occurs in *cis* ( $\Delta H_f^0 = -467.4 \text{ kJ mol}^{-1}$ ,  $\Delta G_f^0 = -228.7 \text{ kJ mol}^{-1}$ ) and *trans* ( $\Delta H_f^0 = -480.3 \text{ kJ mol}^{-1}$ ,  $\Delta G_f^0 = -222.8 \text{ kJ mol}^{-1}$ ) form.

- 4.7** The occurrence of the isomers shows that  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  has geometry:
- [ 1 ] linear,
  - [ 2 ] planar,
  - [ 3 ] tetrahedral,
  - [ 4 ] octahedral geometry.

Mark the correct alternative of [ 1 ] – [ 4 ] on the answer sheet.

- 4.8** Is the *cis* form or *trans* form thermodynamically more stable?

Platinum is used as a catalyst in modern automobiles. In the catalyst carbon monoxide ( $\Delta H_f^0 = -110.5 \text{ kJ mol}^{-1}$ ,  $\Delta G_f^0 = -137.3 \text{ kJ mol}^{-1}$ ) reacts with oxygen to carbon dioxide ( $\Delta H_f^0 = -393.5 \text{ kJ mol}^{-1}$ ,  $\Delta G_f^0 = -394.4 \text{ kJ mol}^{-1}$ ).

- 4.9** Is the reaction spontaneous at 25 °C?

[ 1 ] yes, or

[ 2 ] no.

Is the reaction:

[ 3 ] endothermic, or

[ 4 ] exothermic?

Calculate  $\Delta S^\circ$  for the reaction.

Establish whether the entropy of the reaction system

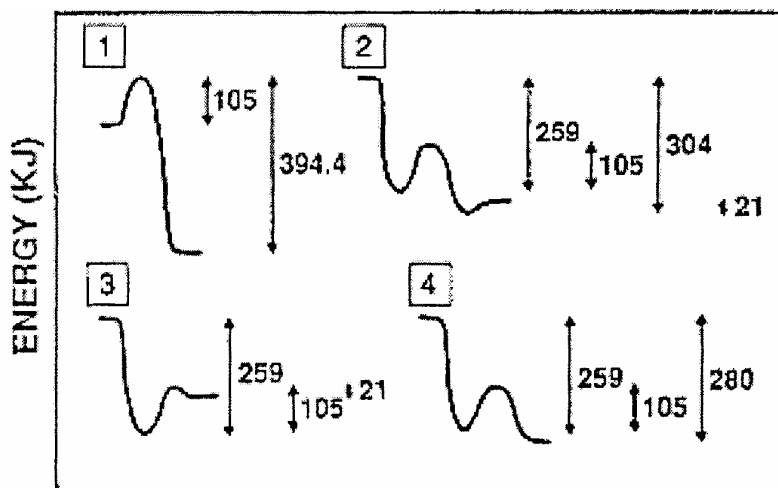
[5] increases, or

[6] decreases.

4.10 Establish an expression for the temperature dependence of the equilibrium constant in this case.

The overall catalytic reaction is simple, whereas the reaction mechanism in the homogeneous phase is very complicated with a large number of reaction steps, and the course is difficult to control owing to a distinct chain character. With platinum as catalyst the significant reaction steps are: (i) Adsorption of CO and adsorption/dissociation of O<sub>2</sub> ( $\Delta H = -259$  kJ per mol CO + O), (ii) their activation (105 kJ per mol CO + O) and (iii) the reaction and the desorption of CO<sub>2</sub> ( $\Delta H = 21$  kJ per mol CO<sub>2</sub>).

A one-dimensional energy-diagram for the platinum catalyzed oxidation of carbon monoxide to dioxide can be represented as:

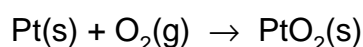


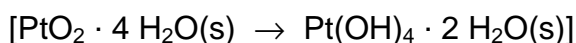
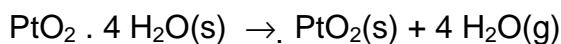
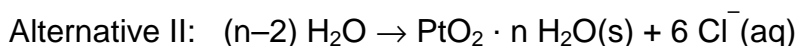
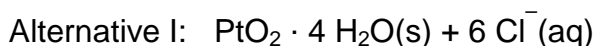
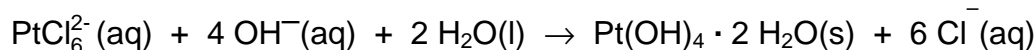
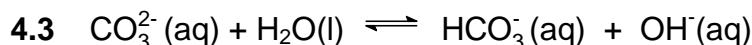
4.11 Mark the correct alternative of [ 1 ] – [ 4 ] on the answer sheet.

## SOLUTION

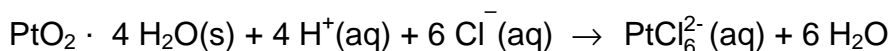
4.1 Correct answer is No 4.

4.2  $\Delta G = 0$  kJ and  $K_p = 1$  according to the chemical equation

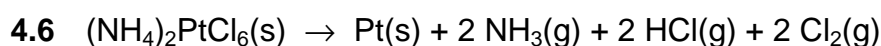
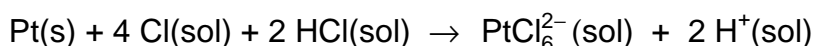
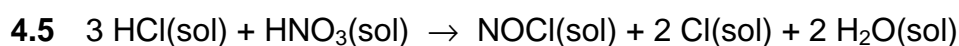
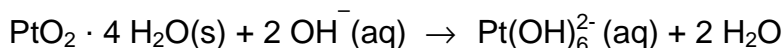




4.4 In hydrochloric acid:



In sodium hydroxide:

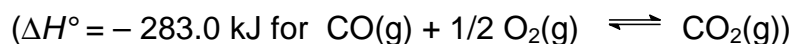


4.7 Correct is No 2.

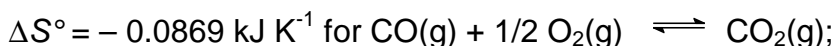
4.8 The cis form is thermodynamically more stable.



[4] The reaction is exothermic.



[6] is correct.



As seen from the sign for  $\Delta S^{\circ}$  as well as for the reaction enthalpy the entropy of the system decreases.

4.10  $\ln K_p = 34037 / T - 10.45$  for  $\text{CO}(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g})$

Alternative:  $K_p = \exp^{(34037 / T - 10.45)}$

4.11 No 2 is correct.

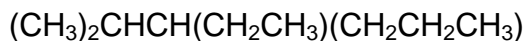
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**PROBLEM 5**

There is only one correct answer to each question

5.1 What is the correct systematic name (IUPAC name) for the compound below?

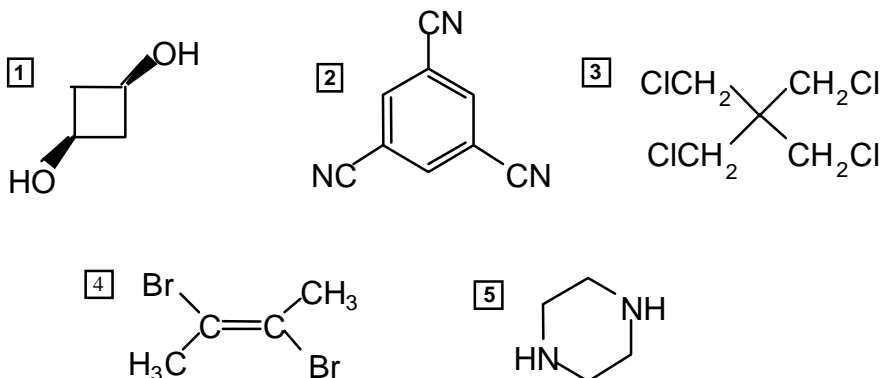


- 1 3-Isopropylhexane
- 2 2-Methyl-3-propylpentane
- 3 Ethyl isopropyl propyl methane
- 4 3-Hexylpropane
- 5 3-Ethyl-2-methylhexane

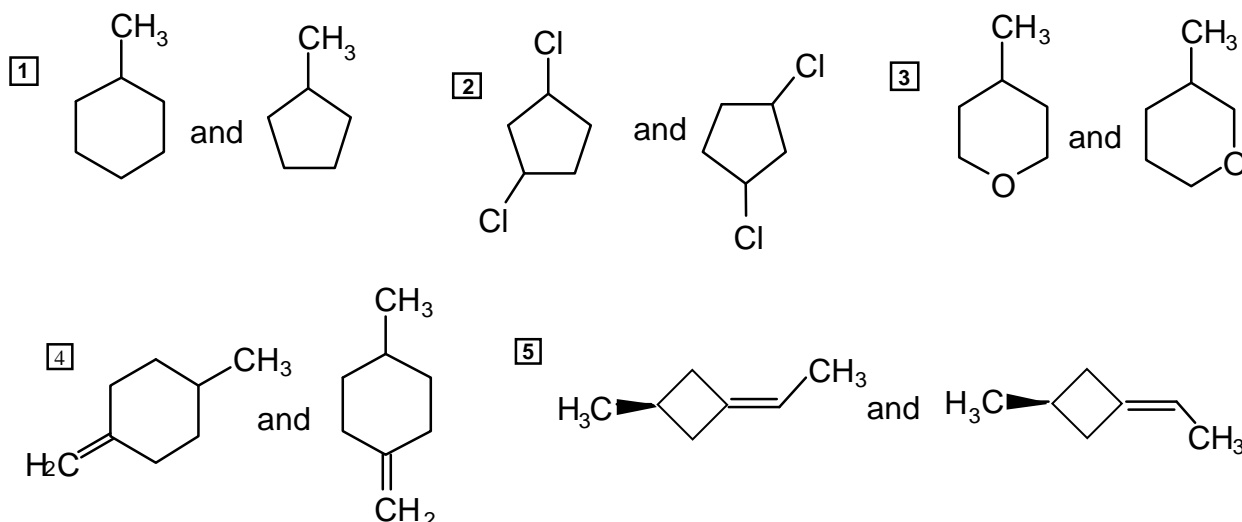
5.2 How many isomers, including stereoisomers, containing only saturated carbon atoms, are there for  $\text{C}_5\text{H}_{10}$ ?

- 1 4 isomers      2 5 isomers      3 6 isomers
- 4 7 isomers      5 8 isomers

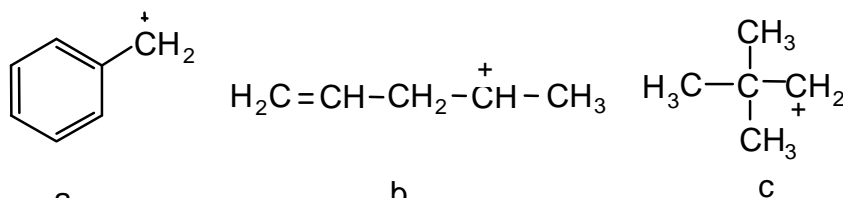
5.3 Which one of the following compounds has a dipole moment significantly different from zero?



5.4 Which of the following is a pair of structural isomers?

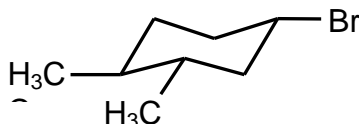


5.5 Which of the following five options is the correct order of relative stabilities of cations a, b and c as written below (most stable first)?



- 1 a>b>c     2 b>c>a     3 c>a>b     4 a>c>b     5 b>a>c

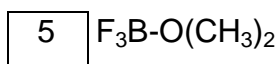
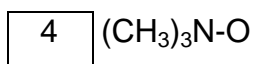
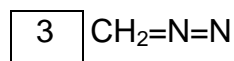
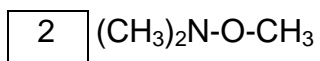
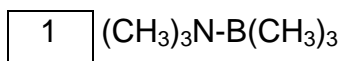
5.6 What is the correct stereochemical descriptor of the optically active compound drawn below?



- 1 1*R*,3*R*,4*R*     2 1*R*,3*R*,4*S*     3 1*R*3*S*,4*R*     4 1*S*,3*S*,4*R*     5 1*S*,3*S*,4*S*



5.7 All the molecules drawn below are neutral compounds. Which one does not contain a formal positive charge and a formal negative charge?



## SOLUTION

|     | 1 | 2 | 3 | 4 | 5 |
|-----|---|---|---|---|---|
| 5.1 | X |   |   |   | X |
| 5.2 |   |   |   | X |   |
| 5.3 | X |   |   |   |   |
| 5.4 |   |   | X |   |   |
| 5.5 | X |   |   |   |   |
| 5.6 |   |   |   |   | X |
| 5.7 |   | X |   |   |   |

## PROBLEM 6

An optical active compound **A** ( $C_{12}H_{16}O$ ) shows amongst other a strong IR-absorption at  $3000 - 3500\text{ cm}^{-1}$ , and two medium signals at  $1580$  and  $1500\text{ cm}^{-1}$ . The compound does not react with 2,4-dinitrophenylhydrazine (2,4-D). Upon treatment with  $I_2/NaOH$ , **A** is oxidized and gives a positive iodoform reaction.

Ozonolysis of **A** (1.  $O_3$ ; 2.  $Zn, H^+$ ) gives **B** ( $C_9H_{10}O$ ) and **C** ( $C_3H_6O_2$ ). Both **B** and **C** give precipitation when treated with 2,4-D, and only **C** gives positive reaction with Tollens reagent. Nitration of **B** ( $HNO_3/H_2SO_4$ ) may give two mono-nitro compounds **D** and **E**, but in practical work only **D** is formed.

Acidification followed by heating of the product formed by the Tollens reaction on **C** gives compound **F** ( $C_6H_8O_4$ ). The compound gives no absorption in IR above  $3100\text{ cm}^{-1}$ .

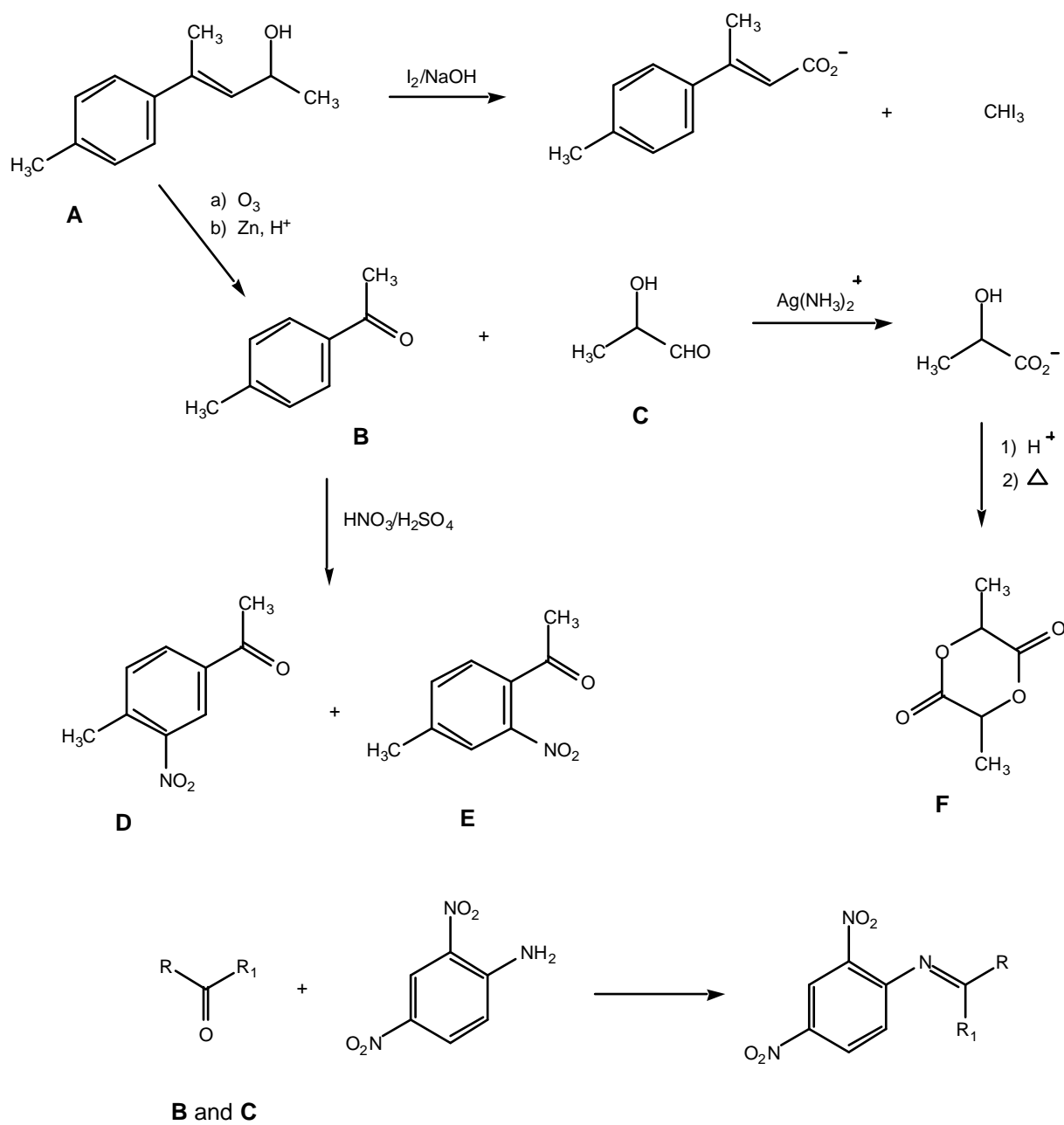
- 6.1** Based on the above information draw the structure formula(e) for the compounds **A – F** and give the overall reaction scheme, including the (2,4-D) and the products of the Tollens and iodoform reactions.
- 6.2** Draw **C** in an R-configuration. Transform this into a Fischer projection formula and state whether it is a **D** or L configuration.

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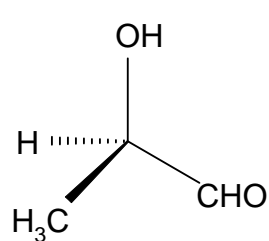
## SOLUTION

(See the next page.)

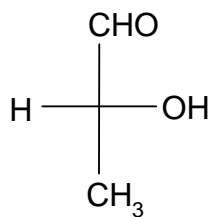
## 6.1



## 6.2



*R*-configuration



*D*-configuration

**PROBLEM 7**

7.1 When an ideal, monatomic gas expands reversibly from a volume  $V_1$  to a volume  $V_2$ , a work

$$w = - \int_{V_1}^{V_2} p \, dV$$

is performed on the system by the surroundings. In this equation,  $w$  is the work and  $p$  is the pressure of the gas.

Determine the performed work when one mole ideal gas expands isothermally from  $V_1 = 1.00 \text{ dm}^3$  to  $V_2 = 20.0 \text{ dm}^3$  at the temperature  $T = 300.0 \text{ K}$ .

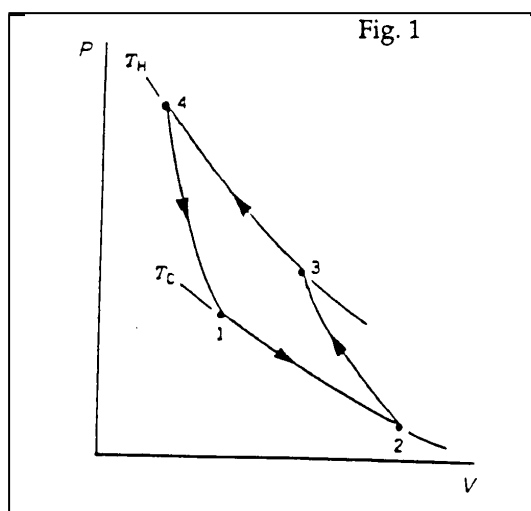
Given: The gas constant  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ .

7.2 Determine how much heat must be added to the gas during the process given under 7.1.

7.3 The gas will perform less work in an adiabatic expansion than in an isothermal expansion. Is this because the adiabatic expansion is characterized by (check the square you think is most important).

|   |                                      |
|---|--------------------------------------|
| 1 | The volume of the gas is constant    |
| 2 | The expansion is always irreversible |
| 3 | No heat is supplied to the gas       |

7.4 The cyclic process shown schematically in Figure 1 shows the four steps in a refrigeration system with an ideal gas as working medium. Identify the isothermal and adiabatic steps in the process. Here,  $T_H$  and  $T_C$  represent high and low temperature, respectively. Specify for each step whether it is adiabatic or isothermal.



## SOLUTION

7.1 Work performed on the gas is

$$w = - \int_{V_1}^{V_2} p \, dV = - RT \int_{V_1}^{V_2} \frac{dV}{V} = - RT \ln \frac{V_2}{V_1}$$

$$= -8,314 \, \text{J K}^{-1} \text{ mol}^{-1} \times 300 \, \text{K} \times \ln \frac{20.00}{1.00} = -7472 \, \text{J mol}^{-1} = -7.47 \, \text{kJ mol}^{-1}$$

7.2 Because this is an isothermal expansion of an ideal monatomic gas, there is no change in internal energy. From the first law of thermodynamics, we then have that  $\Delta U = q + w = 0$

where  $q$  is the amount of supplied heat and  $w$  is performed work. This leads to  $\underline{q} = -w = 7.47 \, \text{kJ mol}^{-1}$ .

7.3 (3) No heat is supplied to the gas.

|     |          |                                     |                                     |                          |                                     |
|-----|----------|-------------------------------------|-------------------------------------|--------------------------|-------------------------------------|
| 7.4 | isotherm | <input checked="" type="checkbox"/> | <input type="checkbox"/>            | <input type="checkbox"/> | <input type="checkbox"/>            |
|     | adiabat  | <input type="checkbox"/>            | <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> |

**PROBLEM 8**

Avogadro's Number:  $6.022 \cdot 10^{23}$

**8.1** An atom of  $^{238}\text{U}$  disintegrates by a series of  $\alpha$ -decays and  $\beta^-$ -decays until it becomes  $^{206}\text{Pb}$ , which is stable.

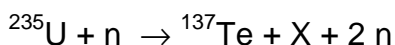
i) How many  $\alpha$ -decays and how many  $\beta^-$ -decays does an atom starting as  $^{238}\text{U}$  undergo before it becomes stable?

ii) One of the following ten nuclides is formed from a series of disintegrations starting at  $^{238}\text{U}$ . Which one ?

$^{235}\text{U}$ ,  $^{234}\text{U}$ ,  $^{228}\text{Ac}$ ,  $^{224}\text{Ra}$ ,  $^{224}\text{Rn}$ ,  $^{220}\text{Rn}$ ,  $^{215}\text{Po}$ ,  $^{212}\text{Po}$ ,  $^{212}\text{Pb}$ ,  $^{211}\text{Pb}$ .

**8.2** In a thermal neutron-induced fission process,  $^{235}\text{U}$  reacts with a neutron and breaks up into energetic fragments and (normally) 2-3 new neutrons.

We consider one single fission event:



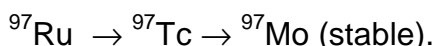
Identify the fragment X.

**8.3** The half-life of  $^{238}\text{U}$  is  $4.5 \times 10^9$  years, the half-life of  $^{235}\text{U}$  is  $7.0 \times 10^8$  years. Natural uranium consists of 99.28 %  $^{238}\text{U}$  and 0.72 %  $^{235}\text{U}$ .

i) Calculate the ratio in natural U between the disintegration rates of these two uranium isotopes.

ii) A mineral contains 50 weight percent uranium. Calculate the disintegration rate of  $^{238}\text{U}$  in 1.0 kg of this mineral.

**8.4** We have the following radioactive sequence:



Halflives:  $^{97}\text{Ru}$ : 2.7 days;  $^{97}\text{Tc}$ :  $2.6 \times 10^6$  years

At  $t = 0$  a radioactive source containing only  $^{97}\text{Ru}$  has a disintegration rate of  $1.0 \times 10^9$  Bq.

i) What is the total disintegration rate of the source at  $t = 6.0$  days?

ii) What is the total disintegration rate of the source at  $t = 6000$  years?

**SOLUTION**

**8.1** i) 8  $\alpha$ 's and 6  $\beta^-$ 's (only  $\alpha$ 's gives  $^{206}\text{Os}$ , to come from Os to Pb requires 6  $\beta^-$ 's).

ii)  $^{234}\text{U}$ , all other answers are incorrect.

8.2 <sup>97</sup>Zr

8.3 i)  $D = \lambda N$ , i.e.  $D_1 / D_2 = \lambda_1 N_1 / \lambda_2 N_2 = \text{abund.}(1)T_{1/2}(2) / \text{abund.}(2)T_{1/2}(1)$   
 $= (99.28 \times 7.0 \times 10^8) / (0.72 \times 4.5 \times 10^9) = 21.4$  (0.047 is also of course correct)

ii)  $N = (m/AW(U)) \times \text{abundance}(238) \times N_A = (500 / 238.01) \times 0.9928 \times 6.022 \times 10^{23}$   
 $= 1.26 \times 10^{24}$

$$D = N \ln 2 / T_{1/2} = 1.26 \times 10^{24} \times \ln 2 / (4.5 \times 10^9 \text{ (y)} \times 3.16 \times 10^7 \text{ (s/y)}) = 6.1 \cdot 10^6 \text{ Bq}$$

8.4 i)  $\lambda = \ln 2 / 2.7(\text{d}) = 0.26 \text{ d}^{-1}$

$$D = D_0 e^{-\lambda t} = 1.0 \times 10^9 \times e^{-(0.26 \times 6.0)} = 2.1 \times 10^8 \text{ Bq}$$

ii) Number of <sup>97</sup>Ru atoms in the source:

$$N = D T_{1/2}({}^{97}\text{Ru}) / \ln 2 = 1.0 \times 10^9 \text{ (Bq)} \times 2.7 \text{ (d)} \times 24 \text{ (h/d)} \times 3600 \text{ (s/h)} / 0.6931 =$$

$$= 3.4 \times 10^{14} \text{ atoms}$$

When all <sup>97</sup>Ru has disintegrated, these atoms have all become <sup>97</sup>Tc, and the disintegration rate of this nuclide is

$$D = N \ln 2 / T_{1/2}({}^{97}\text{Tc}) = (3.4 \times 10^{14} \times 0.6931) / (2.6 \cdot 10^6 \text{ y} \times 3.16 \times 10^7 \text{ s y}^{-1}) =$$

$$= 2.9 \text{ Bq}$$

## PRACTICAL PROBLEMS

### PROBLEM 1 (Practical)

#### Determination of Fatty Acids

A mixture of an unsaturated monoprotic fatty acid and an ethyl ester of a saturated monoprotic fatty acid has been dissolved in ethanol (2.00 cm<sup>3</sup> of this solution contain a total of 1.00 g acid plus ester). By titration the acid number<sup>1)</sup>, the saponification number<sup>2)</sup> and the iodine number<sup>3)</sup> of the mixture shall be determined. The acid number and the saponification number shall be used to calculate the number of moles of free fatty acid and ester present in 1.00 g of the sample. The iodine number shall be used to calculate the number of double bonds in the unsaturated fatty acid.

*Note:* The candidate must be able to carry out the whole exam by using the delivered amount of unknown sample (12 cm<sup>3</sup>). There will be no supplementation.

- 1) Acid number: The mass of KOH in milligram that is required to neutralize *one* gram of the acid plus ester.
- 2) Saponification number: The mass of KOH in milligram that is required to saponify *one* gram of the acid plus ester.
- 3) Iodine number: The mass of iodine (I) in g that is consumed by 100 g of acid plus ester.

Relative atomic masses:

$$A_r(\text{I}) = 126.90 \quad A_r(\text{O}) = 16.00$$

$$A_r(\text{K}) = 39.10 \quad A_r(\text{H}) = 1.01$$

#### 1) Determination of the Acid Number

##### *Reagents and Apparatus*

Unknown sample, 0.1000 M KOH, indicator (phenolphthalein), ethanol/ether (1 : 1 mixture), burette (50 cm<sup>3</sup>), Erlenmeyer flasks (3 x 250 cm<sup>3</sup>), measuring cylinder (100 cm<sup>3</sup>), graduated pipette (2 cm<sup>3</sup>), funnel.



*Procedure:*

Pipette out aliquots (2.00 cm<sup>3</sup>) from the unknown mixture into Erlenmeyer flasks (250 cm<sup>3</sup>). Add first ca. 100 cm<sup>3</sup> of an ethanol/ether mixture (1:1) and then add the indicator (5 drops).

Titrate the solutions with 0.1000 M KOH.

Calculate the acid number.

**2) Determination of the Saponification Number***Reagents and Apparatus*

Unknown sample, 0.5000 M KOH in ethanol, 0.1000 M HCl, indicator (phenolphthalein), volumetric flask (50 cm<sup>3</sup>), round bottom flask (250 cm<sup>3</sup>), Liebig condenser, burette (50 cm<sup>3</sup>), Erlenmeyer flasks (3 x 250 cm<sup>3</sup>), volumetric pipette (25 cm<sup>3</sup>), volumetric pipette (10 cm<sup>3</sup>), graduated pipette (2 cm<sup>3</sup>), funnel, glass rod. The round bottom flask and Liebig condenser are to be found in the fume hoods.

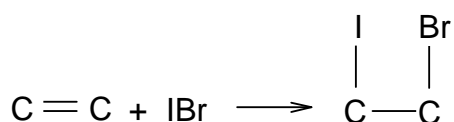
*Procedure*

Pipette out a 2.00 cm<sup>3</sup> aliquot of the unknown sample into a round bottom flask (250 cm<sup>3</sup>) and add 25.0 cm<sup>3</sup> 0.5000 M KOH/EtOH. Reflux the mixture with a heating mantle for 30 min in the fume hood (start the heating with the mantle set to 10, then turn it down to 5 after 7 min.). Bring the flask back to the bench and cool it under tap water. Transfer quantitatively the solution to a 50 cm<sup>3</sup> volumetric flask and dilute to the mark with a 1:1 mixture of ethanol/water. Take out aliquots of 10 cm<sup>3</sup> and titrate with 0.1000 M HCl using phenolphthalein as indicator (5 drops).

Calculate the saponification number.

**3) Determination of the Iodine Number**

In this experiment iodobromine adds to the double bond.



The Hanus solution (IBr in acetic acid) is added in excess. After the reaction is complete, excess iodobromine is reacted with iodide forming I<sub>2</sub>, (IBr + I<sup>-</sup> → I<sub>2</sub> + Br<sup>-</sup>) which in turn is determined by standard thiosulphate solution.

*Warning: Be careful when handling the iodobromine solution. Treat any spill immediately with thiosulphate solution.*

### *Reagents and Apparatus*

Unknown sample, 0.2000 M Hanus solution, dichloro-methane, 15 % KI solution in distilled water, distilled water, 0.2000 M sodium thiosulphate, starch indicator, Erlenmeyer flasks (3 x 500 cm<sup>3</sup>), buret (50 cm<sup>3</sup>), graduated pipette (2 cm<sup>3</sup>), measuring cylinders (10 and 100 cm<sup>3</sup>), volumetric pipette (25 cm<sup>3</sup>), aluminium foil.

### *Procedure*

Pipette out aliquots (1.00 cm<sup>3</sup>) of the unknown mixture into Erlenmeyer flasks (500 cm<sup>3</sup>) and add 10 cm<sup>3</sup> of dichloromethane. With a pipette add 25.0 cm<sup>3</sup> Hanus solution, cover the opening with aluminium foil and place your labelled flasks in the dark in the cupboard (under the fume hood) for 30 min. with occasionally shaking. Add 10 cm<sup>3</sup> of the 15 % KI solution, shake thoroughly and add 100 cm<sup>3</sup> of dist. water. Titrate the solution with 0.2000 M sodium thiosulphate until the solution turns pale yellow. Add starch indicator (3 cm<sup>3</sup>) and continue titration until the blue colour entirely disappears.

Calculate the iodine number.

### **4) Use the results from 1) 2) and 3) to:**

- i) Calculate the amount of ester (in mol) in 1 g of the acid plus ester.
- ii) Calculate the number of double bonds in the unsaturated acid.

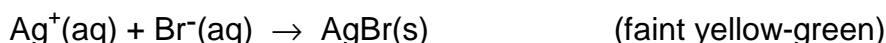
**PROBLEM 2 (Practical)****Volumetric Determination of Bromide by Back-titration with Thiocyanate after Precipitation with Silver Ions in Excess**

*Moments worth considering:*

- The candidates must consider the number of significant figures that will be reasonable in the results.
- The candidates must be able to carry out the whole analysis by using the delivered portions of silver nitrate and potassium thiocyanate. Supplementation of these two solutions will not be available.
- Only *one* 25 cm<sup>3</sup> pipette will be at disposal for each candidate.

**Principle**

Bromide is precipitated as silver bromide after a known amount of silver ions has been added in excess.

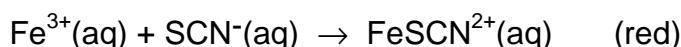


The excess of silver ions is titrated with thiocyanate with a known concentration, after a previous standardization of the thiocyanate solution.

During the titration of the following reaction takes place resulting in the precipitation of silver thiocyanate:



Fe(III) is added as indicator producing a red-coloured ion at the equivalence point:

**a) Procedures**

Every candidate has got a 0.5 dm<sup>3</sup> brown bottle with screw cap, containing the potassium thiocyanate solution (about 0.08 M) and also a 0.25 dm<sup>3</sup> brown bottle with screw cap, containing the silver nitrate solution. The concentration of this solution is 0.1000 M. The exact concentration of the KSCN solution is to be determined by the candidates.

**i) Determination of bromide in the unknown sample solution**

Fill the 250 cm<sup>3</sup> volumetric flask containing the bromide sample solution to the mark with water. Transfer three 25.00 cm<sup>3</sup> portions (pipette) of the sample solution to three Erlenmeyer flasks. Add about 5 cm<sup>3</sup> of 6 M nitric acid (measuring cylinder) to each flask. Transfer 25.00 cm<sup>3</sup> (pipette) of the accurately known silver solution and about 1 cm<sup>3</sup> of iron(III) indicator (ind.) (measuring cylinder) to each solution.

Titrate the contents of the three aliquots with the potassium thiocyanate solution. The end-point of the titration is detected when the solution (including the precipitate) becomes permanently *very faint* brownish. It is important to shake the contents vigorously near the end-point and rinse the walls of the flask with water. The colour should be stable for at least one minute.

**ii) Standardization of the potassium thiocyanate solution**

Transfer 25.00 cm<sup>3</sup> (pipette) of the silver nitrate solution to an Erlenmeyer flask, add about 5 cm<sup>3</sup> of 6 M nitric acid and about 1 cm<sup>3</sup> of the iron(III) indicator solution and about 25 cm<sup>3</sup> of water (use measuring cylinders for these solutions). Titrate the contents with the thiocyanate solution and determine the end-point according to the instruction given in the "Determination" procedure.

Atomic mass:  $A_r(\text{Br}) = 79.90$

**b) Exercise**

At the equivalent point the solution is saturated with respect to both AgBr and AgSCN. Find the molar concentration of free (unprecipitated) Br<sup>-</sup> in this solution:

$$K_{sp}(\text{AgBr}) = 5.00 \times 10^{-13} \quad K_{sp}(\text{AgSCN}) = 1.00 \times 10^{-12}$$

Ignore the effect of *pH* and Fe(III) species.

Note:

On the answer sheet, not only the required final results shall be given, but also exemplifications of how the calculations are carried out.

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