28th

ICHO

International Chemistry Olympiad

7 theoretical problems
2 practical problems

THE TWENTY-EIGHTH
INTERNATIONAL CHEMISTRY OLYMPIAD
14−23 JULY 1996, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

PROBLEM 1

The stereoregular polymerization of unsaturated hydrocarbons is usually considered as one of the most important for the industrial organic chemistry. The salts of big nonlinear cations carrying a sufficiently high charge to attack the electron density distributed along the π-bonds of the olefin molecules are usually used as the catalysts in these processes. Chloroaluminate anions (like $AlCl_4^-$) possessing a highly delocalized negative charge are used usually as the anions. The necessity to develop new catalysts of this kind urged the chemists to study the interaction in the system A - B, where A = Te(cryst.) and B = (TeCl$_4$ + 4 AlCl$_3$). The second component B was considered as an analog of Te(IV) chloroaluminate Te[AlCl$_4$]$_4$ which, however, cannot be isolated as an individual compound. It was found out that the interaction of the components A and B can lead to the formation of three new compounds (**I**, **II** and **III**) in the systems containing initially 77.8, 87.5 and 91.7 mol. % of the component A, respectively. It was also noticed that while in the case of compounds **II** and **III** no side products were formed, the formation of **I** was accompanied by the evolution of 1 mole of volatile TeCl$_4$ per two moles of **I**.

The compounds **I** and **II** attracted a particular interest of investigators. They both have pinkish-purple color and both dissociate into three ions as the conductivity studies in melted NaAlCl$_4$ showed. The cryoscopic measurements in NaAlCl$_4$ melt enabled to determine the molecular weights of these compounds being equal to 1126 $\pm$ 43 g mol^{-1} and 867 $\pm$ 48 g mol^{-1} for **I** and **II**, respectively. In the IR spectra of both compounds there is only one band observed which can be attributed to a vibration mode of a bond formed by Te atom. This band lies at 133 cm^{-1} and is therefore so low in energy that this bond undoubtedly is a kind of Te – Te interaction. The ^{27}Al NMR data for the complexes **I** and **II** show that in each compound there is only one type of tetrahedrally coordinated

---

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

591

aluminum. However, the observed chemical shifts of aluminium for the compounds **I** and **II** are different, thus manifesting that Al atoms are different in them.

1.1   Determine Te : Al : Cl minimal atomic ratio for the complexes **I**, **II** and **III**.

1.2   Write the molecular-formulae of the compounds **I** and **II**.

1.3   Write the formulae of the anions and cations in compounds **I** and **II**.

1.4   Draw stereochemical formulae of cations and anions in the structures of **I** and **II** assuming that the cations in **I** and **II** are examples of inorganic aromatic systems.

1.5   Which compound has a higher thermal stability, **I** or **II**, taking into account that $AlCl_3$ is extremely volatile compound.

1.6   If one of the compounds **I** or **II** can be transformed into the other by heating, write the corresponding reaction equation.

_____

SOLUTION

1.1   Te : Al : Cl ratios:

Compound I   2 : 2 : 7

Compound II   2 : 1 : 4

Compound III   3 : 1 : 4

solution:

The determination of the Te : Al : Cl ratios can be made using the data on the content of Te(cryst.) thus:

77.8 % of Te(cryst.) corresponds to Te(cryst.) + 2 $TeCl_4$ + 8 $AlCl_3$ and the minimum atomic ratio for the composition from which the excess of $TeCl_4$ is not substracted is Te : Al : Cl = 9 : 8 : 32, where the contents of Al and Cl are even and can be divided by 4, while that of Te exceeding the analogous even number by 1. Substracting one mole of $TeCl_4$ from the obtained ratio and dividing by 2 we obtain 4 Te + 4 Al + 14 Cl and the ratio is Te : Al : Cl = 2 : 2 : 7, which can be then verified by comparison with the molecular weight given 87.5 % of Te(cryst.) corresponds to 7 Te(cryst.) + $TeCl_4$ + 4 $AlCl_3$ = 8 Te + 4 Al + 16 Cl and the ratio is Te : Al : Cl = 2 : 1 : 4. 91.7 % of Te(cryst.) corresponds to 11 Te(cryst.) + $TeCl_4$ + 4 $AlCl_3$ = 12 Te + 4 Al + 16 Cl and the ratio is Te : Al : Cl = 3 : 1 : 4.

1.2   The molecular formulae of compounds **I** and **II**:

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

592

Compound **I**: $Te_4Al_4Cl_{14}$

Compound **II**: $Te_4Al_2Cl_8$

Molecular formulae can be deduced from the data on molar weights. Both correspond to double simplest formula.

For compound I: 2 ($Te_2Al_2Cl_7$) gives calculated M_r = 1114.7 while experimental value is 1126 ± 43.

For compound II: 2 (Te_2AlCl_4) gives calculated M_r = 848 while experimental value is 867 ± 48.

1.3   Cations and anions in compounds I and II:

Compound **I**: $[Te_4]^{2+}$ $[Al_2Cl_7]^-$

Compound **II**: $[Te_4]^{2+}$ $[AlCl_4]^-$

The compositions of the ions included in the structures of **I** and **II** can be determined by taking into consideration that both **I** and **II** are tri-ionic electrolytes, and the fact that all the tellurium atoms should be equivalent according to IR and are bonded only to each other. The Al atoms are in both compounds tetrahedrally coordinated and equivalent. At least in one case this can be $AlCl_4^-$ anion which seems probable for **II**, which therefore can be formulated as $[Te_4]^{2+}[AlCl_4]_2^-$. As according to similar colouration the cations are likely to be the same in both cases, the structure of **I** should contain $[Te_4]^{2+}$ cations and $[Al_2Cl_7]^-$ anions, which seems also to be in a good agreement with NMR data, assigning to Al atoms in **I** with a different tetrahedral geometry than that in **II**.

1.4   The geometry of the cation:

$[Te_4]^{2+}$ is a plane square due to proclaimed aromaticity.

The plane square configuration appears to be more favourable because the cation is mentioned to be aromatic, which means planar and possessing equal bond lengths for the sides of the corresponding aromatic ring.
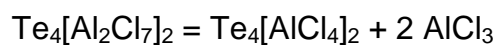

The geometry of anions:

$AlCl_4^-$ is a single tetrahedron;

$Al_2Cl_7^-$ - there are two tetrahedra sharing a common vertex (a chlorine atoms).

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

593

1.5 The thermal stability of **II** should be higher than that of **I**. They both are ionic compounds with high melting points, but compound **I** can be transformed into **II** by the elimination of $AlCl_3$. which is a volatile solid and can be relatively easily removed on heating.

1.6 The reaction equation:

$Te_4[Al_2Cl_7]_2 = Te_4[AlCl_4]_2 + 2\ AlCl_3$

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

594

PROBLEM 2

The detection limit is one of the basic parameters in quantitative analysis of trace amounts of elements. The detection limit is expressed as the least mass of an element which can be determined by a given method with a given accuracy.

As an example we shall consider the method used for the determination of microscopic amounts of bismuth. In 1927 German chemist Berg suggested to precipitate bismuth as a practically insoluble salt: 8-hydroxyquinolinium tetraiodobismuthate $[C_9H_6(OH)NH][BiI_4]$ ($M_r = 862.7$).

2.1 a)   Draw the structural formulae of the cation and anion of this salt.

   b)   What is the oxidation state of Bi atom in this compound?

2.2 Evaluate the smallest mass of bismuth (in *mg*), which can be determined reliably by Berg method, if the smallest mass of precipitate which can be reliably measured is 50.0 mg.

For the determination of trace amounts of bismuth R. Belcher and co-workers from Birmingham developed a multiplicative method. According to this method a chain of reactions followed by a titration of the final product is carried out. A detailed description follows.

Step 1:   To a given small amount (≈ 2 cm^3) of cold acidified solution containing trace amounts of Bi^{3+} 50 mg of potassium hexathiocyanatochromate(III) ($K_3[Cr(SCN)_6]$) is added in the cold, that leads to practically quantitative precipitation of bismuth.

2.3 Write a balanced net ionic equation of this reaction.

Step 2:   The precipitate is filtered off, washed by cold water, and treated with 5 cm^3 of 10 % solution of sodium hydrogen carbonate. Upon this treatment the initial precipitate transforms into the precipitate of oxobismuth(III) carbonate $(BiO)_2CO_3$ with liberation of hexathiocyanatochromate(III) ions into solution.

2.4 Write a balanced net ionic equation of this reaction.

Step 3:   To the slightly acidified filtrate transferred to a separatory funnel 0.5 cm^3 of saturated iodine solution in chloroform are added, and the mixture is vigorously shaken. Iodine oxidizes the ligand of the complex ion to ICN and sulphate ion.

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

595

2.5   Write a balanced net ionic equation of this reaction.

Step 4:   Upon 5 minutes 4 cm^3 of 2 M H$_2$SO$_4$ solution are added to the mixture. The acidification leads to the reaction of coproportionation with the evolution of molecular iodine.

2.6   Write a balanced net ionic equation of the reaction occurred on acidification.

Step 5:   Iodine is quantitatively extracted by 4 portions of chloroform. Aqueous layer is transferred to a flask, to which 1 cm^3 of bromine water is added, and the mixture is mixed for 5 minutes.

2.7   Write the balanced net ionic equations of the reactions occurred upon the addition of bromine water. Note that an excess of bromine can react with hydrogen cyanide to give BrCN, and iodide is oxidized into IO$_3^-$.

Step 6:   To eliminate an excess of molecular bromine 3 cm^3 of 90 % methanoic (formic) acid is added to the mixture.

2.8   Write a balanced net ionic equation of this reaction.

Step 7:   To the slightly acidic solution an excess (1.5 g) of potassium iodide is added.

2.9   Write the balanced net ionic equations of the reactions occurred upon the addition of KI, taking into consideration that iodide reacts with BrCN in a similar manner as with ICN to form molecular iodine.

Step 8:   The resulting solution is titrated by a standard 0.00200 M Na$_2$S$_2$O$_3$ solution. The results thus obtained are used to calculate the content of bismuth in the sample taken for analysis.
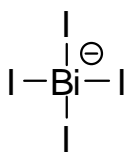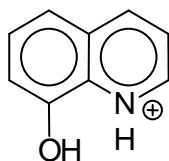
2.10 a)   How many moles of thiosulphate are equivalent to 1 mol of bismuth in the initial sample?

   b)   What is the least mass of bismuth which can be determined by this method (assume that reliable determination requires no less than 1 cm^3 of standard 0.00200 M Na$_2$S$_2$O$_3$ solution)?
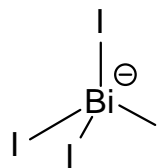
2.11 By how many times the multiplicative method just described is more sensitive than Berg's gravimetric method?

_____

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

596

SOLUTION
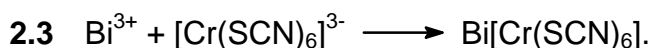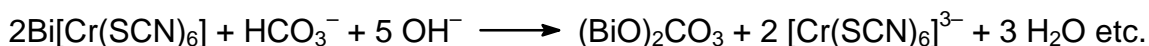
2.1 a)

Cation   Anion

b)

The oxidation number of bismuth in 8-hydroxyquinolinium tetraiodobismuthate: **III**

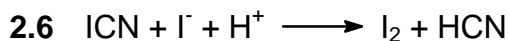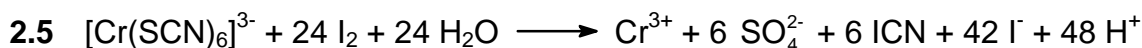**2.2** The smallest mass of bismuth determined reliably by Berg method, 12.1 mg.

Molar mass of the precipitate is 862.7 g, which contains 209.0 g of bismuth. Thus, 0.0500 g of the precipitate correspond to 1.21×10^{-2} g = 12.1 mg of bismuth.
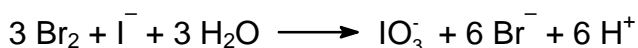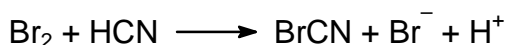
2.3 $Bi^{3+} + [Cr(SCN)_6]^{3-} \longrightarrow Bi[Cr(SCN)_6]$.

2.4 $2\ Bi[Cr(SCN)_6] + 6\ HCO_3^- \longrightarrow (BiO)_2CO_3 + 2\ [Cr(SCN)_6]^{3-} + 3\ H_2O + 5\ CO_2$

or

$2Bi[Cr(SCN)_6] + HCO_3^- + 5\ OH^- \longrightarrow (BiO)_2CO_3 + 2\ [Cr(SCN)_6]^{3-} + 3\ H_2O$ etc.
(variations are possible)

2.5 $[Cr(SCN)_6]^{3-} + 24\ I_2 + 24\ H_2O \longrightarrow Cr^{3+} + 6\ SO_4^{2-} + 6\ ICN + 42\ I^- + 48\ H^+$

2.6 $ICN + I^- + H^+ \longrightarrow I_2 + HCN$

2.7 a)

$3\ Br_2 + I^- + 3\ H_2O \longrightarrow IO_3^- + 6\ Br^- + 6\ H^+$

b)

$Br_2 + HCN \longrightarrow BrCN + Br^- + H^+$

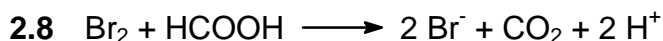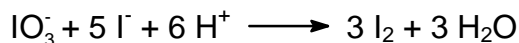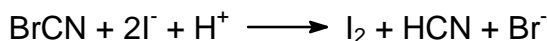*Comment*: From reaction 2.5 it is evident that considerably more of ions I^- are formed than of ICN molecules. Therefore, after the completion of reaction 2. 6 an excess of I^- ions will be left.

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

597

2.8 $Br_2 + HCOOH \longrightarrow 2\ Br^- + CO_2 + 2\ H^+$

2.9 a)

$IO_3^- + 5\ I^- + 6\ H^+ \longrightarrow 3\ I_2 + 3\ H_2O$

b)

$BrCN + 2I^- + H^+ \longrightarrow I_2 + HCN + Br^-$
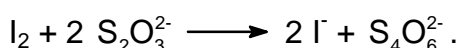
2.10 a)

228 moles of thiosulphate correspond to 1 mole of bismuth.

b)

The least mass of bismuth, $1.83 \cdot 10^{-3}$ mg

Solution:

a)

Titration of iodine by thiosulphate involves the reaction:

$I_2 + 2\ S_2O_3^{2-} \longrightarrow 2\ I^- + S_4O_6^{2-}$.

Assume that the initial solution contained 1 mole of Bi. In the reaction 5 each mole of Bi leads to the formation of 42 moles of iodide (for convenience divide all coefficients of reaction 4 by 2), of which 6 moles of iodide-ion was consumed in reaction 2.6. Thus, 36 moles of iodide was consumed in reaction 2.7a) to give 36 moles of IO_3^-, which in reaction 2.9a) gave $36 \times 3 = 108$ moles of I_2, which take $108 \times 2 = 216$ moles of thiosulphate for titration. However, that is not all. Indeed, 6 moles of HCN are generated per mole of Bi^{3+} according to reactions 2.5 and 2.6. The oxidation of HCN by bromine in reaction 2.7b) gives 6 moles of BrCN, which in its turn in reaction 2.9b) gives 6 moles of iodine taking 12 more moles of thiosulphate. Thus, total amount of thiosulphate is $216 + 12 = 228$.

b)

$1.00\ cm^3$ of 0.00200 M thiosulphate solution contains 2.00×10^{-6} mole of $Na_2S_2O_3$, which corresponds to $209.0 \times 2.00 \times 10^{-6}\ /\ 228 = 1.83 \times 10^{-6}$ g $= 1.83 \times 10^{-3}$ mg $= 1.83\ \mu g$.

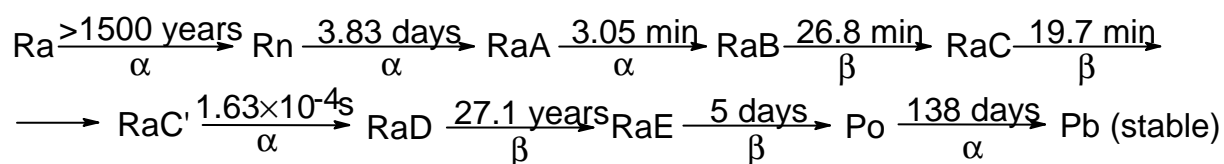**2.11** $\dfrac{\text{Detection limit of gravimetric method}}{\text{Detection limit of multiplicated method}} = 6600$

The multiplicative method is more sensitive than the gravimetric method by 12.1 mg $/\ 1.83 \times 10^{-3}$ mg $= 6600$ times.

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

598

PROBLEM 3

In 1908 Rutherford together with H.Geiger measured the rate of emission of α-particles (*x*) by radium (in the nature this element is represented by a single nuclide $^{226}_{88}Ra$) and found that 1.00 g of radium emits *x* = 3.42×10^{10} α - particles per second.

In 1911 Rutherford and American physical chemist B.Boltwood measured the rate of formation of helium from radium. This experiment permits to obtain the most accurate value of Avogadro's number available at that time, given that the value of molar volume of ideal gas was well established. To achieve this goal a sample of radium salt purified from decay products and containing *m* = 192 mg of Ra was put into a device and the volume of the evolved helium was measured. After 83 days (*t* = 83.0 days) of the experiment 6.58 mm^3 of He was collected (V_{He} = 6.58 mm^3 corrected to 0° C and 1 atm).

To understand the results of this experiment we shall need the kinetic scheme of radioactive decay of Ra which is given below (half-lives are over the arrows, the type of decay is below the arrows).

$$Ra \xrightarrow[\alpha]{>1500 \text{ years}} Rn \xrightarrow[\alpha]{3.83 \text{ days}} RaA \xrightarrow[\alpha]{3.05 \text{ min}} RaB \xrightarrow[\beta]{26.8 \text{ min}} RaC \xrightarrow[\beta]{19.7 \text{ min}}$$

$$\longrightarrow RaC' \xrightarrow[\alpha]{1.63\times10^{-4}s} RaD \xrightarrow[\beta]{27.1 \text{ years}} RaE \xrightarrow[\beta]{5 \text{ days}} Po \xrightarrow[\alpha]{138 \text{ days}} Pb \text{ (stable)}$$

(RaA -RaE are intermediate products of radon decay).

3.1 Write the first six radioactive decays using a modern notation showing atomic and mass numbers of all nuclei involved.

As a rough first approximation half-lives of all radium decay products, except those of RaD and Po, may be assumed to be negligible compared to the time of measurement *t*. Using this approximation perform the following calculations.

3.2 a) How many helium atoms were formed from each decayed radium atom after 83 days?

b) How many helium atoms were formed in total during the experiment?

3.3 Calculate an approximate value of Avogadro's number from the above data.

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

599

For a more accurate computation of Avogadro's number the half-life of radon $T_{1/2}(\text{Rn}) = 3.83$ days cannot be neglected as it is comparable with the duration of experiment t and not all of radon atoms decayed to the end of experiment.

3.4 Choose which of the plots given below displays the time dependence of the number N_{Rn} of radon atoms in the course of the experiment.
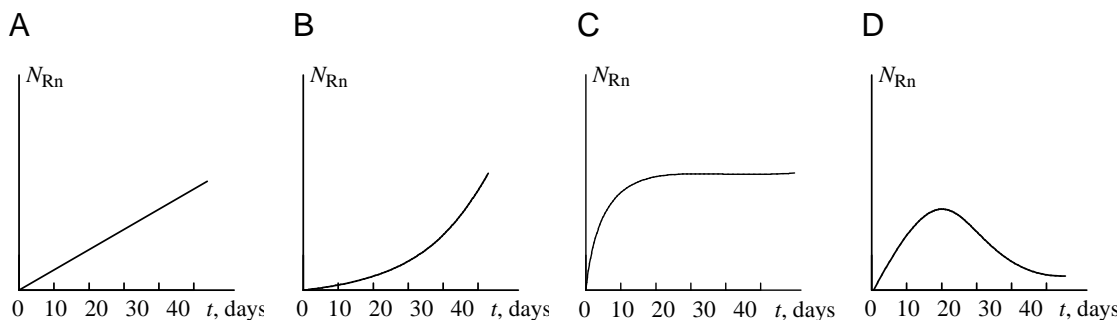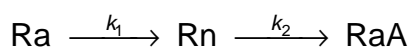

3.5 Choose which of the plots given below shows the time dependence of the volume of helium in the course of the experiment.
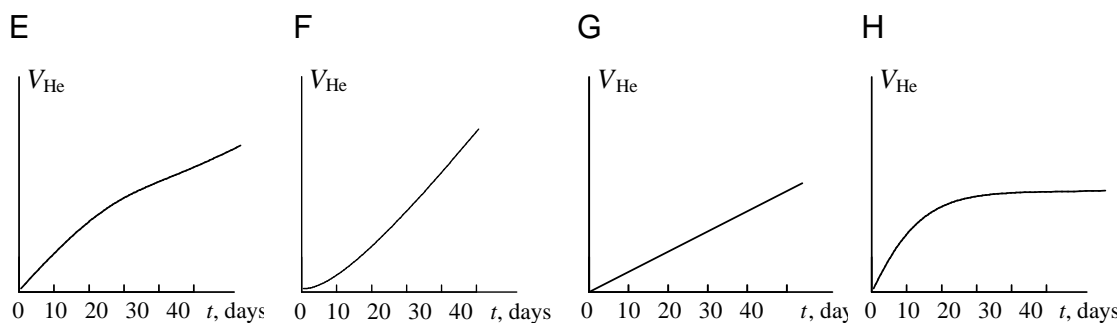
3.6 Choose the relation between the decay rate k of any given nuclide and its half-life $T_{1/2}$.

3.7 a) Using a short kinetic scheme

$$\text{Ra} \xrightarrow{k_1} \text{Rn} \xrightarrow{k_2} \text{RaA}$$

(where k_1 and k_2 are the rate constants of the corresponding reactions) and the plot which you have selected in question 4, write a relation between the number of radon atoms at the end of experiment N'_{Rn} and the number of radium atoms N_{Ra}.
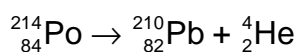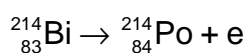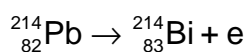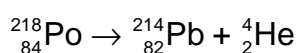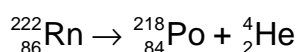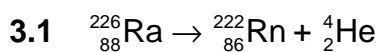
b) Calculate N'_{Rn} using the rate of radium decay given above ($x = 3.42 \times 10^{10}$ α-particles per gram of radium per second).

3.8 How many helium atoms could be formed from radon atoms remaining at the end of experiment N'_{Rn}, if all these atoms had decayed to RaD?

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

600

3.9 Using the solutions of the above questions calculate a better approximation to:

a) the number of helium atoms formed;

b) the Avogadro's number.

_____

SOLUTION

3.1 $^{226}_{88}Ra \rightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$

$^{222}_{86}Rn \rightarrow {}^{218}_{84}Po + {}^{4}_{2}He$

$^{218}_{84}Po \rightarrow {}^{214}_{82}Pb + {}^{4}_{2}He$

$^{214}_{82}Pb \rightarrow {}^{214}_{83}Bi + e$

$^{214}_{83}Bi \rightarrow {}^{214}_{84}Po + e$

$^{214}_{84}Po \rightarrow {}^{210}_{82}Pb + {}^{4}_{2}He$

3.2 a) The correct answer: 4

b) Number of helium atoms (rough 1.9×10^{17} estimate)

$N_{He} = 4\ x\ m\ t = 1.9 \times 10^{17}$

3.3 The first estimate of Avogadro's number: 6.4×10^{23} mol^{-1}

Solution: The Avogadro's number N_A is the number of particles in one mole.

$N_A = N_{He} / v_{He}$, where N_{He} is number of helium atoms, and v_{He} is the number of moles of helium formed within time t. If we assume that all radon atoms formed from radium atoms decayed during the time of experiment (this assumption follows from the assumption that radon half-life can be neglected in comparison with 83 days, that introduces an error of about 5 %), then we obtain that during time t the number of helium atom emitted is $N_{He} = 4xmt$, and

$$N_A = \frac{4\ x\ m\ t}{v_{He}} = \frac{4 \times 3.42 \times 10^{10} \times 0.192 \times (83 \times 24 \times 3600)}{\dfrac{6.58 \times 10^{-6}}{22.4}} = 6.4 \times 10^{23}\ \text{mol}^{-1}.$$

3.4 Correct answer: **C.**

The number of radon atoms reaches a quasi-stationary state which is sometimes called as the radioactive equilibrium.

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

601

3.5 Correct answer: **F.**

In the beginning helium is formed only from α-particles emitted by radium, but to the end of the experiment α-particles are emitted both by radium and by decay products, the amount of which is four times that of radium.

3.6 Underline the correct answer:

$k = 1 / T_{1/2}$	$\underline{k = \ln 2 / T_{1/2}}$	$k = \ln 2 \cdot T_{1/2}$	$k = \pi / T_{1/2}$

3.7 a) Underline the correct answer:

$\underline{N'_{Rn} = k_1 \cdot N_{ra} / k_2}$	$N'_{Rn} = k_2 \cdot N_{Ra} / k_1$	$N'_{Rn} = k_1 \cdot N_{Ra} / 2k_2$	$N'_{Rn} = k_1 \cdot N_{Ra} / 3k_2$

The number of radon atoms reaches a quasi-stationary state, at which the rate of formation is equal to the rate of decay $k_2 N'_{Rn} = k_1 N_{Ra}$, whence $N'_{Rn} = k_1 \cdot N_{Ra} / k_2$

b) $N'_{Rn} = 3.14 \times 10^{15}$

The rate of radium decay is $k_1 N_{Ra} = xm$, whence

$$N'_{Rn} = \frac{xm}{\dfrac{\ln 2}{T_{1/2(Rn)}}} = \frac{3.42 \times 10^{10} \times 0.192}{\dfrac{0.693}{3.83 \times 24 \times 3600}} = 3.14 \times 10^{15}$$

3.8 Underline the correct answer:

$4N'_{Rn}$	$2N'_{Rn}$	$5N'_{Rn}$	N'_{Rn}	$\underline{3N'_{Rn}}$

3.9 a) A more accurate estimate of the number of helium atoms: 1.79×10^{17}

$$N_{He} = 4\,xmt - 3N'_{Rn} = 1.9 \times 10^{17} - 3 \times 3.14 \times 10^{15} = 1.79 \times 10^{17}$$

b) A more accurate estimate of Avogadro's number (mol^{-1}): 6.09×10^{23}

$$N_{\text{Å}} = \frac{N_{He}}{n(He)} = \frac{1.79 \times 10^{17}}{\dfrac{6.58 \times 10^{-6}}{22.4}} = 6.09 \times 10^{23}$$

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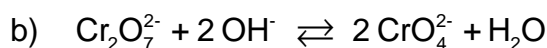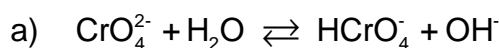ICHO International Information Centre, Bratislava, Slovakia

602

PROBLEM 4

The precipitation is widely used in classical methods of the quantitative and qualitative analysis for the separation of ions. The possibility of separation is determined by the equilibrium concentrations of all species in a solution to be analyzed.

Potassium dichromate is one of the most widely used precipitating reagents. The following equilibria are established in aqueous solutions of Cr(VI).

$$HCrO_4^- \rightleftarrows H^+ + CrO_4^{2-} \qquad \log K_1 = -6.50$$

$$2\,HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O \qquad \log K_2 = 1.36$$

4.1 Calculate the equilibrium constants

   a) $CrO_4^{2-} + H_2O \rightleftarrows HCrO_4^- + OH^-$

   b) $Cr_2O_7^{2-} + 2\,OH^- \rightleftarrows 2\,CrO_4^{2-} + H_2O$

   The ionic product of water $K_W = 1.0 \times 10^{-14}$.

4.2 In what direction shall the equilibrium state 1b shift upon the addition of the following reagents to the aqueous solution of potassium dichromate?

   a) KOH

   b) HCl

   c) BaCl$_2$

   d) H$_2$O

   The solubility product of BaCrO$_4$ is 1.2×10^{-10}. BaCr$_2$O$_7$ is well soluble in water.

4.3 Calculate the pH value of the following solutions

   a)   0.010 M K$_2$CrO$_4$

   b)   0.010 M K$_2$Cr$_2$O$_7$

   c)   0.010 M K$_2$Cr$_2$O$_7$ + 0.100 M CH$_3$COOH

   Dissociation constant of acetic acid $K_a = 1.8 \times 10^{-5}$.

4.4 Calculate the equilibrium concentrations of the following ions in the solution of 0.010 M K$_2$Cr$_2$O$_7$ + 0.100 M CH$_3$COOH

   a) CrO_4^{2-}

   b) $Cr_2O_7^{2-}$

   Pb^{2+} and Ag$^+$ form poorly soluble compounds with chromate and dichromate ions. The solubility products of these compounds are indicated below.

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

603

PbCrO$_4$ K_{s1} = 1.2×10^{-14}

Ag$_2$CrO$_4$ K_{s2} = 1.3×10^{-12}

Ag$_2$Cr$_2$O$_7$ K_{s3} = 1.1×10^{-10}

To the aqueous solution of the mixture of 1.0×10^{-3} M Pb(NO$_3$)$_2$ and 2.0×10^{-4} M AgNO$_3$ an equal volume of 0.020 M solution of K$_2$Cr$_2$O$_7$ in 0.200 M CH$_3$COOH was added.

4.5   a)   Shall Pb^{2+} be precipitated?

     b)   Shall Ag$^+$ be precipitated?

     c)   Shall a quantitative separation of Pb^{2+} and Ag$^+$ ions be thus achieved?

The quantitative precipitation is achieved if the residual concentration of the ion being precipitated is not higher than 1×10^{-6} M.

_____

SOLUTION

4.1

   a)

Equilibrium constant = 3.2×10^{-8}

$$\frac{[HCrO_4^-][OH^-]}{[CrO_4^{2-}]} = \frac{[HCrO_4^-][OH^-][H^+]}{[CrO_4^{2-}][H^+]} = \frac{K_w}{K_1}$$

$$\frac{1.0\times10^{-14}}{3.16\times10^{-7}} = 3.2\times10^{-8}$$

   b)   Equilibrium constant > 4.4×10^{13}

$$\frac{K_1^2}{K_2\,K_w^2} = \frac{\left(\dfrac{\left[CrO_4^{\,2-}\right]\left[H^+\right]}{\left[HCrO_4^{\,-}\right]}\right)^2}{\dfrac{\left[HCrO_4^{\,-}\right]^2}{\dfrac{\left[Cr_2O_7^{\,2-}\right]}{\left(\left[H^+\right]\left[OH^-\right]\right)^2}}} = \frac{10^{-2\times6.50}}{10^{1.36}\times10^{-2\times14.00}} = 10^{13.64} = 4.4\times10^{13}$$

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

604

4.2 Place a checkmark at the correct answer

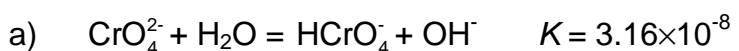| The equilibrium will	shift to left	shift to right	not shift
a)		☑	
b)	☑		
c)		☑	
d)		☑	

Calculations:

In case a) and b) the answer is self-evident.

c) BaCl$_2$ shifts the equilibrium to the right due to the binding of chromate ion into a poorly soluble compound
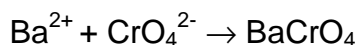
Ba^{2+} + CrO$_4$$^{2-}$ → BaCrO$_4$

d) This answer may appear as strange, as water is among the products specified in the right part of the equilibrium equation. However, this is too formal. Actually in dilute aqueous solutions the concentration of water may be regarded as fairly constant and the addition of water would not affect it. Nevertheless, the addition of water to dichromate solution leads to the dilution, which in its turn shifts the dichromate ion dissociation equilibrium to the right. Second, in the aqueous solution of K$_2$Cr$_2$O$_7$ the value of pH < 7 due to the processes described in the problem statement (cf. also the solution to 3b). With the dilution of any aqueous solution pH is varying towards 7, that in this case means the increase of pH. This also shifts the equilibrium to the right.

4.3 a) $pH = 9.25$

b) $pH = 4.20$

c) $pH = 2.87$

Calculations:

a) $CrO_4^{2-} + H_2O = HCrO_4^- + OH^-$ $K = 3.16 \times 10^{-8}$

$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^-] + 2\,[Cr_2O_7^{2-}] \approx [CrO_4^{2-}]$,

$[HCrO_4^-] \approx [OH^-]$

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

605

$[OH^-]^2/c_{Cr} = K$, $[OH^-] = \sqrt{K\,c_{Cr}} = \sqrt{3.16 \times 10^{-8} \times 0.01} = 1.78 \times 10^{-5}$
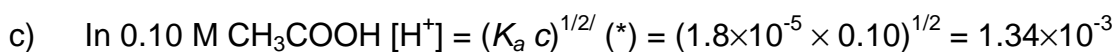
$[H^+] = 5.65 \cdot 10^{-10}$, $pH = 9.25$

b) $Cr_2O_7^{2-} + H_2O = 2\ HCrO_4^-$ $K = 1/K_2 = 4.37 \times 10^{-2}$

$HCrO_4^- = H^+ + CrO_4^{2-}$ $K = K_1 = 3.16 \times 10^{-7}$

$[H^+] \approx [CrO_4^{2-}] \Rightarrow [H^+] = \sqrt{K_1[HCrO_4^{2-}]}$

$[HCrO_4^-] = ?$

$c_{Cr} = 2.0 \cdot 10^{-2}$ M (**) $= [CrO_4^{2-}] + [HCrO_4^-] + 2\,[Cr_2O_7^{2-}] \approx [HCrO_4^-] + 2\,[Cr_2O_7^{2-}]$

$[HCrO_4^-] = x$; $K_2 = [Cr_2O_7^{2-}]/[HCrO_4^-]^2 = (c_{Cr} - x)/2x^2$; $2\,K_2x^2 + x - c_{Cr} = 0$

hence $[H^+] = (3.16 \times 10^{-7} \times 1.27 \times 10^{-2})^{1/2} = 6.33 \times 10^{-5}$; $pH = 4.20$

c) In 0.10 M CH_3COOH $[H^+] = (K_a\,c)^{1/2}$ (*) $= (1.8 \times 10^{-5} \times 0.10)^{1/2} = 1.34 \times 10^{-3}$

$pH = 2.87$

4.4 Equilibrium concentrations

a)	3.0×10^{-6}
b)	3.7×10^{-3}

Calculations:

The different methods can be used.

Method 1.

a)

$[HCrO_4^-] = 1.3 \times 10^{-2}$ (*)

$[CrO_4^{2-}] = K_1[HCrO_4^-]/[H^+] = 3.16 \times 10^{-7} \times 1.3 \times 10^{-2}/1.34 \times 10^{-3} = 3.0 \times 10^{-6}$

b)

$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^-] + 2\,[Cr_2O_7^{2-}]$

$[Cr_2O_7^{2-}] = \frac{1}{2}(c_{Cr} - [CrO_4^{2-}] - [HCrO_4^-]) = \frac{1}{2}\,(2.0 \times 10^{-2} - 3.0 \times 10^{-6} - 1.3 \times 10^{-2}) = 3.7 \times 10^{-3}$

or otherwise

$[Cr_2O_7^{2-}] = K_2[HCrO_4^-]^2 = 22.9 \times (1.3 \times 10^{-2})^2 = 3.9 \times 10^{-3}$

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

606

Method 2

a)

$[CrO_4^{2-}] = x$; $[HCrO_4^-] = x[H^+] / K_1$

$[Cr_2O_7^{2-}] = K_2[HCrO_4^-] = x^2 K_2 [H^+]^2 / K_1^2$

$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^-] + 2[Cr_2O_7^{2-}] = 2K_2 [H^+]^2 / K_1^2 x^2 + (1 + [H^+] / K_1)x$

$K_1 = 3.16 \times 10^{-7}$; $K_2 = 22.9$; $[H^+] = 1.34 \times 10^{-3}$

$8.24 \times 10^8 x^2 + 4.24 \times 10^3 x - 2.0 \times 10^{-2} = 0$

$x = 3.0 \times 10^{-6}$

b)

$[Cr_2O_7^{2-}] = K_2[HCrO_4^-] = K_2 [H^+]^2 / K_1^2 [CrO_4^{2-}]^2 = 4.12 \times 10^8 \times (3.0 \times 10^{-6})^2 = 3.7 \times 10^{-3}$

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

607

PROBLEM 5

Potentiometric and spectrophotometric methods are widely used for the determination of equilibrium concentrations and equilibrium constants in solution. Both methods are frequently used in combination to achieve simultaneous determination of several species.

Solution **I** contains a mixture of $FeCl_2$ (aq)$_)$ and $FeCl_3$(aq), and solution **II** contains a mixture of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. The concentrations of iron-containing species satisfy the relations $[Fe^{2+}]_I = [Fe(CN)_6^{4-}]_{II}$ and $[Fe^{3+}]_I = [Fe(CN)_6^{3-}]_{II}$. The potential of platinum electrode immersed into the solution **I** is 0.652 V, while the potential of platinum electrode immersed into solution II is 0.242 V. The transmittance of the solution **II** measured relative to the solution **I** at 420 nm is 10.7 % (optical pathlength l = 5.02 mm). The complexes $Fe(CN)_6^{4-}$, $Fe(H_2O)_6^{3+}$, and $Fe(H_2O)_6^{2+}$ do not absorb light at 420 nm.

Molar absorption at this wavelength $\varepsilon([Fe(CN)_6^{3-}]) = 1100$ M^{-1} cm^{-1}.

Standard redox potential for $Fe(H_2O)_6^{3+} / Fe(H_2O)_6^{2+}$ is 0.771 *V*.

The factor before the logarithm in the Nernst equation is 0.0590.

5.1 Write Nernst equations for redox systems of

    a)   solution **I**,

    b)   solution **II**.

5.2 What are the units of the pre-logarithm factor 0.0590 in the Nernst equation?

5.3 Calculate the ratio of the stability constants $\beta[Fe(CN)_6^{3-}] / \beta[Fe(CN)_6^{4-}]$.

5.4 What is the absolute range of variation for the following physical values

    a)   transmittance *T*;

    b)   absorbance *A*.

5.5 Sketch the graphs of concentration dependences satisfying the Lambert-Beer law for

    a)   absorbance *A*;

    b)   transmittance *T*;

    c)   molar absorption ε.

5.6 Calculate the concentrations of

    a) Fe^{2+} in solution **I**;

    b) Fe^{3+} in solution **II**.

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

608

5.7 Mixing solutions **I** and **II** gives intense blue colour. What species is characterized by this colour? Write the reaction equation.

_____

SOLUTION

5.1 Nernst equations:

a) $E_I = E°(Fe^{3+}/Fe^{2+}) + 0.0590 \log \dfrac{\left[Fe^{3+}\right]}{\left[Fe^{2+}\right]}$

b) $E_I = E°(Fe(CN)_6^{3-}/ Fe(CN)_6^{4-}) + 0.0590 \log \dfrac{\left[Fe(CN)_6^{3-}\right]}{\left[Fe(CN)_6^{4-}\right]}$

5.2 The units of pre-logarithm factor: V

5.3 The ratio of stability constants

$\beta\{Fe(CN)_6^{3-}\} / \beta\{Fe(CN)_6^{4-}\} = 8.90 \times 10^6$

Calculations:

$E_{II} = E°(Fe(CN)_6^{3-}/Fe(CN)_6^{4-}) + 0.0590 \log[Fe(CN)_6^{3-}/Fe(CN)_6^{4-}] =$

$= E°(Fe^{3+}/Fe^{2+}) + 0.0590 \log(\beta_1 / \beta_2) + 0.0590 \log([CN^-]^6/[CN^-]^6) +$

$+ 0.0590 \log[Fe(CN)_6^{3-}/Fe(CN)_6^{4-}] = 0.242$

(where β_1 and β_2 are stability constants for $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$, respectively.)

$[Fe(CN)_6^{3-}] / [Fe(CN)_6^{4-}] = [Fe^{3+}] / [Fe^{2+}]$, therefore

$\Delta E = E_{II} - E_I = 0.0590 \cdot \log (\beta_1 / \beta_2)$, and $\beta_2/\beta_1 = 8.90 \times 10^6$.

5.4 The ranges of variation:

a)   from 0 to 100

b)   from 0 to ∞

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

609

5.5

a)	b)	c)

5.6 a) Using Bouger-Lambert-Beer law

$A = \varepsilon l c = \varepsilon l c [Fe(CN)_6^{3-}] = 0.971$;

$c[Fe(CN)_6^{3-}] = 0.971/(1100 \times 0.502) = 1.76 \times 10^{-3} \, M = c[Fe^{3+}]$

b) using Nernst's equation

$E = E°(Fe^{3+}/Fe^{2+}) + 0.0590 \log[Fe^{3+}]_l/[Fe^{2+}]_l =$

$= 0.771 + 0.0590 \log [Fe^{3+}]_l/[Fe^{2+}]_l = 0.652 \, V.$

hence,

$[Fe^{3+}]_l/[Fe^{2+}]_l = 9.62 \times 10^{-3}$;

$[Fe^{2+}]_l = 1.76 \times 10^{-3}/9.62 \times 10^{-3} = 0.183 \, M.$

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

610

PROBLEM 6

Two isomeric hydrocarbons A and B contain 85.7 mass % of carbon.

6.1 Write a general formula which satisfies this condition.

The hydrocarbons **A** and **B** possess the following properties. The reaction of each of the compounds with ozone with subsequent treatment of the product with zinc dust in the presence of acid gives a single organic product **C**. The oxidation of compound **C** gives a single product, the carboxylic acid **D**. According to spectral data all hydrogen atoms in this acid except the one in carboxylic group are contained in methyl groups. The density of vapours of **D** corrected to normal conditions (0 °C, 1 atm) is 9. 1 g dm^{-3}.

Compound **A** is more reactive than compound **B** in the reaction with cold neutral potassium permanganate. A single compound **F** is formed from **A**, and a 1 : 1 mixture of isomers **G1** and **G2** is formed from **B**.

6.2 Draw the structural formulae of the compound **D** both in aqueous solution and in vapour phase.

6.3 Write the formula of compound **C**.

6.4 Draw the structures of isomers **A** and **B**.

6.5 a) Write the reactions of the transformation of **A** or **B** into **C** and **D**.

    b) Write the reactions of the transformation of **A** and **B** into **F**, **G1** and **G2**.

6.6 Compounds **G1** and **G2** readily react with acetone in the presence of acids and form compounds **H1** and **H2**. Draw the structures of **H1** and **H2**.

6.7 Compounds **A** and **B** react with bromine. One of the products of these reactions is non-polar (dipole moment of this molecule is practically equal to zero) and optically inactive. Draw the stereochemical formula of this product, and write the reaction of its formation. Determine the absolute configuration of chiral atoms in this molecule (if any) and mark them according to *R,S* nomenclature by *R* or *S* letters.

Alkenes react with peroxoacids with the addition of oxygen to double bond to form a three-member oxygen-containing ring. This epoxidation reaction is highly stereospecific to retain the relative positions of substituents at the bond to which the oxygen atom is attached.

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

611

The epoxidation of compound **A** by peroxoacetic acid yields a single compound **K**. Under the same conditions **B** gives a mixture of isomers **L1** and **L2** (the ratio is 1:1).

6.8 Is the compound **K** optically active? Draw the stereochemical formula of **K**. Are the individual compounds **L1** and **L2** optically active? Draw the stereochemical formulae of **L1** and **L2**.
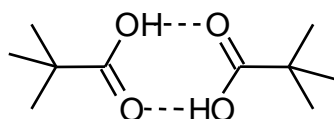
_____

SOLUTION

6.1 The general formula: C_nH_{2n}

6.2 Compound **D**:

In aqueous solution: $(CH_3)_3CCOOH$

In vapours:

Dimeric structure in vapour phase is guessed using the value of vapour density.

The relative molar weight in vapour phase is $9.1 \times 22.4 = 204$ which is close to double value of the molar weight of $(CH_3)_3CCOOH$. Possibly, as other simple fat acids, this acid is also dimerized in vapours.

6.3 Compound **C**: $(CH_3)_3CCHO$

6.4 **A**:

B:

6.5   A ⟶ C ⟶ D

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

612
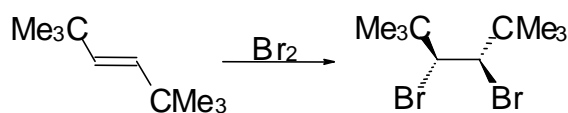
A ⟶ F

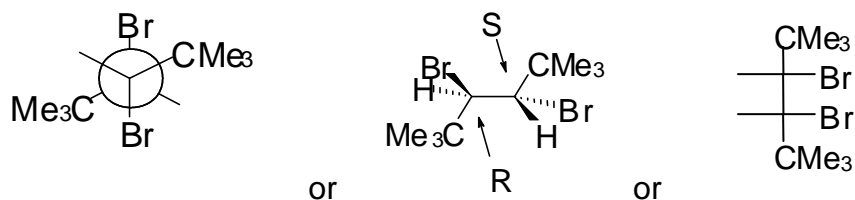
B ⟶ G1 + G2

racemic mixture

6.6 H1:

H2:

6.7 Non-polar bromination product (either of three types of structures may be given)

or   or

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

613

6.8   K:

Me₃C̲   C̲Me₃

O

☑ NO; The molecule is not optically active.

L1:

Me₃C   CMe₃

O

☑ YES; The molecule is optically active.

L2:

Me₃C   CMe₃

O

☑ YES; The molecule is optically active.

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

614

PROBLEM 7

Stereochemistry of organic compounds can sometimes be determined by studying their chemical behaviour. The stereochemical configuration of one of the isomers of 5-norbornene-2,3-dicarboxylic acids (compound **X**)

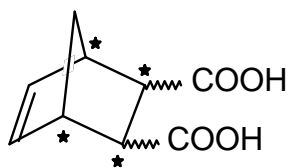(no stereochemistry is shown) was established by the following experiments.

On heating this substance decomposes producing water and a new compound **Y**. Compound **Y** slowly dissolves in excess of aqueous NaOH with the formation of product **X₁** same to that is formed in the reaction of **X** with NaOH. The resulting solution of **X₁** is treated by I₂ to give compounds containing iodine. Acidification of the solution leads to a mixture of two isomeric compounds, **A** and **B** in the 3 : 1 ratio. The titration of 0.3913 g of compound **A** by 0.1000 M aqueous solution of NaOH in the presence of phenolphthalein takes 12.70 cm3 of alkali. The same amount of 0.1000 M solution of NaOH is required for the titration of 0.3913 g of compound **B**. On heating compound **A** slowly transforms into compound **C**, which contains no iodine and is able to react with water. Under the same conditions compound **B** does not undergo this transformation, but on heating with hydrochloric acid slowly transforms into **A**.

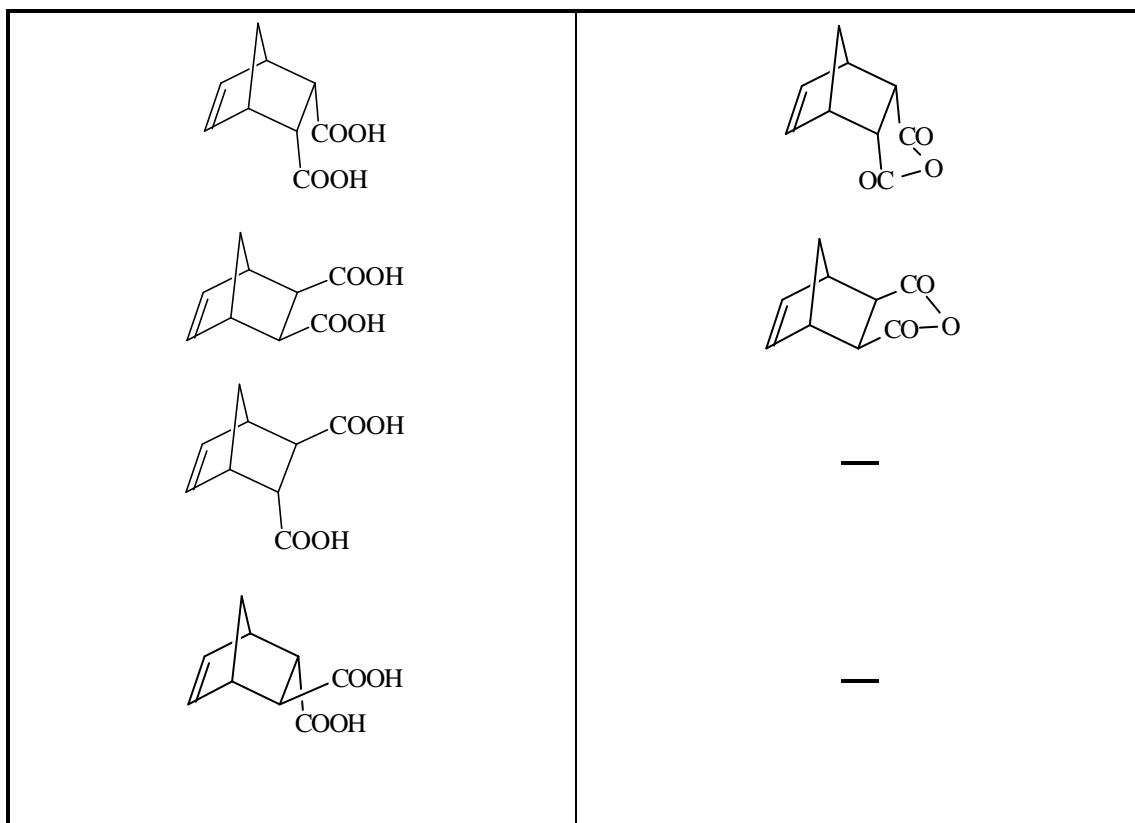*All reactions must be written as balance equations. No mechanisms are required.*

7.1 Mark by asterisks (*) the asymmetric carbon atoms in the structure of 5-norbornene-2,3-dicarboxylic acids.

7.2 Draw the stereochemical formulas of all stereoisomers of compound **X**, and the structures of products of their dehydration in those cases when it is possible.

7.3 Write the reactions of NaOH with a stereoisomer of **X** and a stereoisomer of **Y**.

7.4 Calculate the molar mass of compound **A**. Write the reactions leading from **X₁** to **A**.

7.5 Write the reaction of the formation of **C** from **A** and the reaction of **C** with water.

7.6 Draw the stereochemical formula of compound **X** which satisfies all of the data given in the problem.

7.7 Write the reactions leading from **B** to **A**.

7.8 Are the compounds **A** and **B** diastereomers?

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
Edited by Anton Sirota,
ICHO International Information Centre, Bratislava, Slovakia
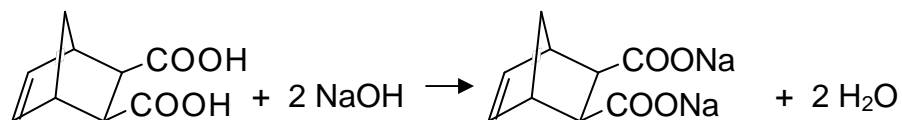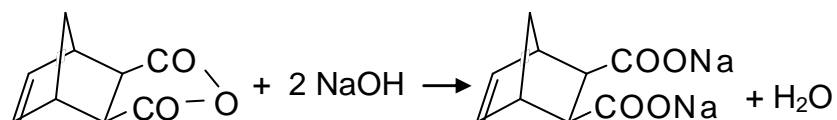
615

SOLUTION

7.1

7.2 Fill in left column with the structures of stereoisomers of **X**, and the right column with the corresponding structures of dehydration products (when such structure does not exist write a minus.

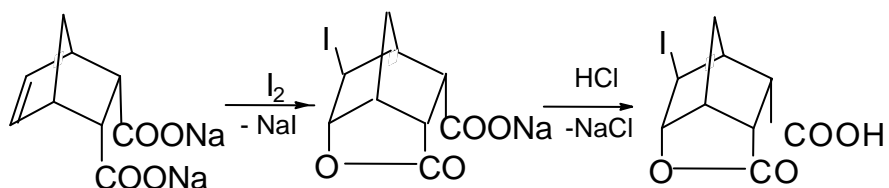**7.3** The reaction of a stereoisomer of **X** with NaOH:

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

616

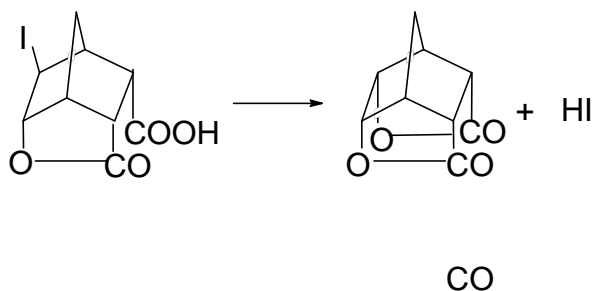The reaction of a stereoisomer of **Y** with alkali:

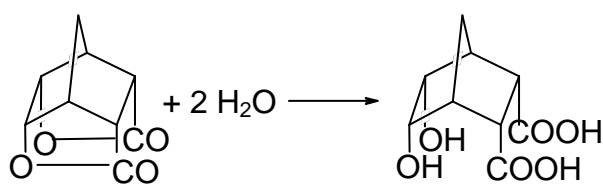**7.4** The molar mass of **A**:   308 g mol^{-1}
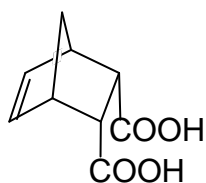
The reactions leading from **X$_1$** to **A**

7.5 The transformation of **A** to **C**:

The reaction of **C** with water:

7.6 The structure of compound **X**:

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

617

7.7 The transformation of **B** to **A**:

7.8 ☑ No, **A** and **B** are not diastereomers.

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

618

PRACTICAL PROBLEMS

PROBLEM 1   (Practical)

Iodometric Determination of the Concentration of Copper(II) and Iron(III) in a Sample of Technological Solution

Reagents

- $K_2Cr_2O_7$, 0.008333 M
- KI, 20 % by mass.
- HCl, 1 M
- H_2SO_4, 1 M
- $Na_4P_2O_7$, 5 % by mass.
- Starch, 1 % by mass.
- $Na_2S_2O_3$ (should be standardized)
- The solution to be analyzed in 100 cm^3 volumetric flask.

Procedure

1.   Standardization of $Na_2S_2O_3$ solution

    (1)   10 cm^3 of 1 M solution of H_2SO_4 and 2 cm^3 of 20 % KI solution are placed into an Erlenmeyer flask (the solution remains colourless).

    (2)   10.00 cm^3 of $K_2Cr_2O_7$ solution is added.

    (3)   The Erlenmeyer flask is covered with a watch glass and kept in a dark place for 3 to 5 min.

    (4)   100 cm^3 of water is added to the flask.

    (5)   The mixture is titrated immediately with $Na_2S_2O_3$ solution until the colour of mixture changes to pale yellow. Then 10 drops of starch solution are added. The titration continues until blue colour disappears completely.

    (6)   It is recommended to repeat the titration (steps 1 through 5) two more times.

Do the following and fill in the answer sheet form

1.1   Write the reactions involved in the procedure of standardization of $Na_2S_2O_3$ solution

1.2   Calculate the concentration of $Na_2S_2O_3$ solution, and write your calculations.

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

619

2. The determination of copper

(1) The solution to be analyzed in a 100 cm^3 volumetric flask is diluted with water to the mark and stirred

(2) A 10.00 cm^3 aliquot of the solution is placed into an Erlenmeyer flask.

(3) 20 cm^3 of 5 % solution of Na$_4$P$_2$O$_7$, 7 cm^3 of 1 M solution of HCl, and 10 cm^3 of 20 % solution of KI are added. A precipitate may form upon the addition of Na$_4$P$_2$O$_7$.

(4) The Erlenmeyer flask is covered with a watch glass and left in a dark place for 3 - 5 min.

(5) The mixture is titrated immediately with Na$_2$S$_2$O$_3$ solution until the colour of suspension changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until the colour of suspension becomes clear white.

(6) It is recommended to repeat the titration (steps 2 through 5) two more times.

Do the following and fill in the answer sheet form

1.3 Write the reactions involved in the procedure of determination of Cu^{2+} ion.

1.4 Calculate the mass of copper in the solution under analysis, and write your calculations.

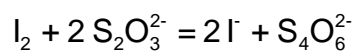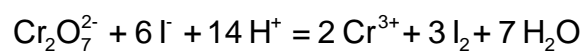## 3. The determination of total amount of copper and iron

(1) A 10.00 cm^3 aliquot of the solution prepared in the item 2(1) is placed into an Erlenmeyer flask.

(2) 2 cm^3 of 1 M HCl solution and 10 cm^3 of 20 % KI solution are added.

(3) The Erlenmeyer flask is covered with a watch glass and kept in a dark place for 3 to 5 min.

(4) The mixture is titrated immediately with Na$_2$S$_2$O$_3$ solution until the colour of suspension changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until the colour of suspension becomes clear white.

(5) It is recommended to repeat the titration (steps 1 through 4) two more times.

Do the following and fill in the answer sheet form

1.5 Write the reactions involved in the procedure of determination of Fe^{3+} ion.

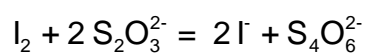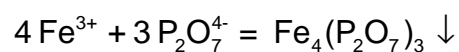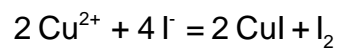**1.6** Calculate the mass of iron in the solution under analysis, and write your calculations.

_____

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

620

SOLUTION

1.1

Equations:

$$Cr_2O_7^{2-} + 6\,I^- + 14\,H^+ = 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O$$

$$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$$

i

1.3

Equations:

$$2\,Cu^{2+} + 4\,I^- = 2\,CuI + I_2$$

$$4\,Fe^{3+} + 3\,P_2O_7^{4-} = Fe_4(P_2O_7)_3 \downarrow$$

$$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$$

1.5

Equations:

$$2\,Fe^{3+} + 2\,I^- = 2\,Fe^{2+} + I_2$$

$$2\,Cu^{2+} + 4\,I^- = 2\,CuI + I_2$$

$$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$$

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 2
Edited by Anton Sirota,
ICHO International Information Centre, Bratislava, Slovakia
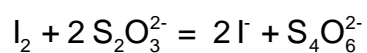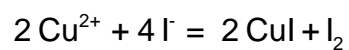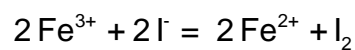
621

PROBLEM 2   (Practical)

Qualitative Determination of Paracetamol in a Sample of Unknown Drug

Introduction

Three organic compounds are most widely used as pain relieving drugs: acetylsalicylic acid (ortho-acetoxybenzoic acid), phenacetine (*para*-ethoxyacetanilide), and paracetamol (*para*-hydroxyacetanilide). Paracetamol is now the most popular, being the base of a large number of well known patented pharmaceuticals (panadol, solpadeine, coldrex, calpol, efferalgan etc.), as it is now considered as the safest and highly efficient drug.

You were given a sample of unknown drug which claims to contain paracetamol. Your task is to prove or disprove this claim experimentally. To do this you shall have to prepare an authentic sample of *para*-hydroxyacetanilide, and run a thin layer chromatography test.

Reagents

- *Para*-aminophenol, 3.10 *g* in a weighing beaker
- Acetic anhydride, 4.00 cm^3 in an Erlenmeyer flask
- Ethanol
- Eluent (heptane : ethyl acetate : ethanol = 41 : 47 : 12 by volume)
- Sample of unknown drug in a test tube, 1 % solution in ethanol
- Water (use tap water for all purposes)

Procedure

Preparation of para-hydroxyacetanilide

A 50 cm^3 round bottom flask is equipped with reflux condensor and installed on a laboratory stand over a hot plate. Note that the space between the top of hot plate and the bottom of flask be about 1-1.5 cm. Use two clamps to properly support the flask and condenser. Remove the hot plate. Do not switch on the hot plate until you finish with adding reagents and reassembling the apparatus. With reflux condensor temporarily removed, 3.10 g of *para*-aminophenol is placed to the flask using a funnel (use a glass rod

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

622

to push it through the funnel, if necessary). Water (10 cm^3) is then added through the same funnel. The condenser is mounted back, and acetic anhydride (4.00 cm^3) is carefully poured to the reaction mixture through the condenser (*attention*! acetic anhydride has a strong irritating smell. In case of spill immediately wash hands with water and ask the supervisor to help with the disposal of spilled compound). Carefully stir the contents by slightly relieving clamps and waving the flask 2 - 3 times. Be careful as the mixture and the flask gets very hot due to the reaction heat. Place back the hot plate and switch it on. The reaction mixture is heated for 15 minutes beginning from the time when you switch on the hot plate. Then, the heater is switched off and removed from the apparatus. The mixture is allowed to cool first by immersing the flask into a bath with cold tap water. You may do this immediately after you remove the plate as the flask is made of highly durable glass. After approximately five minutes unattach the condenser and pour the contents into an empty 100 cm^3 pyrex glass beaker. Put the beaker into a metal dish filled with ice and water. Accurately rub the walls of beaker with spatula and observe the crystallization of crude product as small white crystals.

Assemble a suction filtration device: put the frit filter onto a rubber ring and a heavy-wall flask. Connect the flask to a suction vacuum pump and turn on water in the pump by turning tap. (*Attention*! Never turn off the water tap if your device is under vacuum. First always disconnect the flask from vacuum pump by carefully pulling off the rubber tubing from the inlet.)

The crystalline precipitate is quantitatively moved onto a filter by spatula. Remaining solid can be washed with small portions of ice cold water (as small as possible, as the compound possesses an essential solubility in water, and the losses of dissolved compound must not outweigh the losses due to incomplete transfer of product to the filter). The product in the filter is carefully washed with 2 - 3 portions of 2 - 3 cm^3 of cold water by a) connecting the vacuum suction flask to the atmosphere; b) addition of water and careful mixing it with the precipitate using a spatula; c) reapplying vacuum; d) pressing the precipitate with flat tip of a glass rod to squeeze out as much water as possible.

Several crystals of material are used for chromatography test (see below). All other precipitate is moved to a sheet of filtering paper in a Petri dish, and spread out over the filter in a thin layer, and allowed to dry on a shelf to exclude accidental spill. For rapid drying it is critical to spread it as thin as possible, to break all large pieces, and to stir it

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

623

and spread again every 3-5 minutes to expose all wet crystals to air. It is established after a numerous repetition of this procedure, that after 30 min the product contains no more than 5 % of water. Such wetness is considered as insignificant for evaluating the results of the preparation.

Chromatography test

(If for some reason you have failed to obtain *para*-hydroxyacetanilide, you can obtain a sample for chromatography from your supervisor.)

While still wet several crystals of the material obtained by you are dissolved in a tube in 1 - 2 cm^3 of ethanol. The unknown drug is already dissolved in ethanol and given to you as 1 % solution. These solutions are used for thin layer chromatography, as follows:

Prepare a sheet of chromatography plate covered with silica. Using a sharp pencil draw a start line and marks for sample spots. A small spot of each solution is placed on a chromatography plate using a capillary. The spots are allowed to dry for 1-2 minutes.

The plate is immersed into a beaker containing the eluent and allowed to be eluted. Use forceps to move the plate in and out of the beaker. After the elution, remove the plate from the flask, mark the front of eluent, and allow it to dry under the hood for 5 minutes. Examine the chromatogram under UV light in a special cabinet. Outline the dark spots (if there are any) with a sharp pencil.
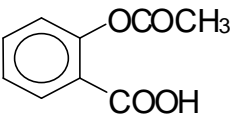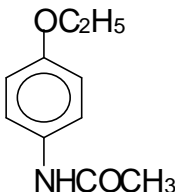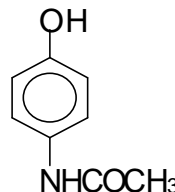
Weighting of sample

After you complete the chromatography, your product usually is almost dry and is ready for weighting. Ask you supervisor to weight an empty weighing beaker. Put the dry product into a weighted beaker and give it to the supervisor for weighting. Weights are written in your answer sheet by the supervisor. Calculate the weight of the product.

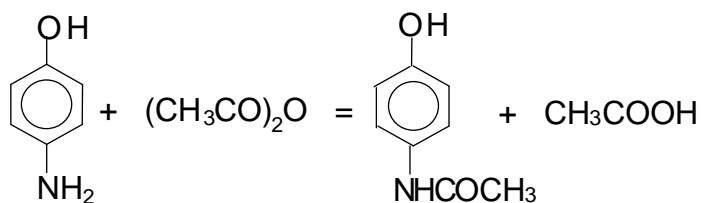**Do the following and fill in the answer sheet form**

2.1 Draw the structures of three main pain relieving drugs mentioned above.

2.2 Draw the reaction equation involved in the preparation of *para*-hydroxyacetanilide. Calculate the stoichiometric amounts of reagents needed for the reaction. How much acetic anhydride is taken in excess over the stoichiometry? The density of acetic anhydride is 1.08 g cm^{-3}.

2.3 Calculate the yield of product obtained by you.

2.4 Calculate and compare the values of R_f of unknown drug and your product.

2.5 Is it likely that paracetamol is contained in the sample of drug?

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

624

SOLUTION

2.1

Acetylsalicylic acid	Phenacetine	Paracetamol
OCOCH$_3$ COOH	OC$_2$H$_5$ NHCOCH$_3$	OH NHCOCH$_3$

2.2

OH + (CH$_3$CO)$_2$O = OH + CH$_3$COOH
NH$_2$ NHCOCH$_3$

2.5 Yes, the sample is likely to contain paracetamol.

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

625