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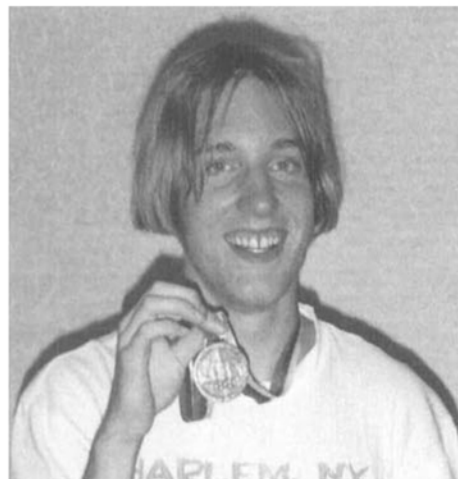
## International Chemistry Olympiad 1996: One Gold Medal for Switzerland

In the 27th International Chemistry Olympiad in Moscow (14.7.–23.7.1996), *Thomas Braschler* from Uettlingen (BE) got one of the 22 gold medals awarded. This is a great achievement for Switzerland, and our second gold medal since we participate in the Chemistry Olympiads. Our first gold medal went to *Lukas Hintermann* in Pittsburgh 1992.

There were 175 competitors in Moscow (24 girls and 151 boys) from 45 countries. The students have to be of high-school level, less than 20 years old and not attending a specialized school. This criteria is difficult to appreciate in some countries, where chemistry may be taught heavily in some selected schools. As everyone knows Swiss chemistry is well known all over the world, despite the fact that chemistry is rated very low in the Swiss school systems. This does not prevent our brightest students from obtaining olympic medals. Of course the family may help: *Thomas's* mother and grandfather had both studied chemistry. Their home laundry should look more like a chemistry lab than a washing room.

Back to Moscow. The students had two examinations each of five hours: a practical and a theoretical one whose descriptions are given below somewhat shortened. Try it ... and don't cheat!

National teams are usually formed by four students and two mentors. Here is the 1996 Swiss team:



Thomas Braschler

- *Beat Amstutz*, Berg (SG), Kantonsschule am Burggraben, born 2.10.1976;
- *Thomas Braschler*, Uettlingen (BE), Gymnasium Bern-Neufeld, born 4.6.1978;
- *Daniel Püntener*, Neuheim (ZG), Kantonsschule Zug, born 5.6.1977;
- *Christophe Schlicht*, Pont-de-la-Morges (VS), Lycée des Creusets, born 7.4.1977.

It may be worth noticing that our gold medalist is also the youngest member of our 1996 team. The mentors were: Dr. *Jochen Müller*, Zürich, Dr. *Blenda Weibel*, Lausanne, and *Marco Ziegler*, Fribourg. Exceptionnally Dr. *Maurice Cosandey* was not present.

The mentors must discuss the tasks, translate them to their native language(s), correct the work of their students and discuss the marks (sometimes vehemently) with the representatives of the organizing country. While the students are working the mentors go sight-seeing and *vice versa*: the Kremlin, the Red Square, the subway, circus, galleries, etc. The students had some disco parties which the mentors did not. Some excursions were scheduled for the whole 'olympic family', i.e. 350 persons: the Sergiev Posad Monastery, boat trip on the Moskwa River, and Kolomenskoje Park.

The Olympiads give chemistry-loving students the opportunity of comparing their knowledge and of socializing with equally minded friends from all over the world. That's also true for the mentors of course.

Next Olympiads will be 1997 Montreal, 1998 Melbourne, 1999 Bangkok, 2000 Copenhagen. Will it be 2001 or 2002 in Switzerland?

B. Weibel

### Problem 1

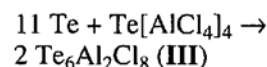
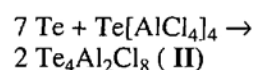
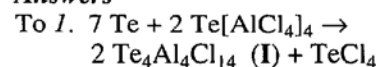
A binary system **A-B** will be studied where **A** is tellurium Te, and **B** is a compound  $\text{TeCl}_4 + 4 \text{AlCl}_3$  or  $\text{Te}[\text{AlCl}_4]_4$ . **A** may react with **B** to produce three com-

pounds **I**, **II**, and **III**, containing 77.8, 87.5, and 91.7 mol-% of **A**, respectively. In these reactions, **II** and **III** are formed without any side products. But when producing **I**, one molecule of  $\text{TeCl}_4$  is liberated when two molecules of **I** are formed.

Compounds **I** and **II** are red purple. Dissolved in  $\text{NaAlCl}_4$ , **I** and **II** are dissociated into three ions. Their molecular masses, as determined by cryoscopy in  $\text{NaAlCl}_4$ , are  $1130 \pm 50$  for **I**, and  $870 \pm 50$  for **II**. Their IR spectra display a band at  $133 \text{ cm}^{-1}$  attributed to a Te-Te bond.  $^{27}\text{Al}$  NMR spectra reveal the same tetrahedral configuration for Al-atoms in both compounds **I** and **II**, but in a different environment.

1. Determine the ratio of Te:Al:Cl in **I**, **II**, and **III**.
2. Write the molecular formulae for **I** and **II**, and the formulae of their ions.
3. Describe the stereochemical formulae of these ions, knowing that cations of **I** and **II** are examples of inorganic aromatic systems.
4. Which of **I** and **II** has the highest thermal stability (noting that  $\text{AlCl}_3$  is extremely volatile)?
5. If any of the compounds **I** and **II** can be transformed into the other by heating, write the corresponding equation.

### Answers



To 2. **I** =  $\text{Te}_4\text{Al}_4\text{Cl}_{14}$ ; **II** =  $\text{Te}_4\text{Al}_2\text{Cl}_8$   
 Ions: **I** =  $[\text{Te}_4]^{2+} + 2 [\text{Al}_2\text{Cl}_7]^-$ ;  
**II** =  $[\text{Te}_4]^{2+} + 2 [\text{AlCl}_4]^-$

To 3.  $\text{AlCl}_4^-$  is a tetrahedron;  $\text{Al}_2\text{Cl}_7^-$  is a double tetrahedron with a common vertex (Cl). The cation  $[\text{Te}_4]^{2+}$  is planar and square.

To 4. **II** is more stable than **I**.

To 5.  $\text{Te}_4[\text{Al}_2\text{Cl}_7]_2 \rightarrow \text{Te}_4[\text{AlCl}_4]_2 + 2 \text{ AlCl}_3$

### Problem 2

Bismuth can be precipitated quantitatively as 8-hydroxyquinoline iodobismuthate  $[\text{C}_9\text{H}_6(\text{OH})\text{NH}]\text{BiI}_4$ , with a molecular mass 862.7.

*Question 1.* How much bismuth is there in 50 mg of the precipitate (minimum amount weighable with precision)?

Here is now an elegant method for titrating bismuth traces.

*Step 1.* Add 50 mg of potassium hexathiocyanatochromate(III)  $K_3[Cr(SCN)_6]$  to 2 ml of a cold and acidic soln. containing traces of bismuth.

*Step 2.* Filtrate and wash the precipitate. Add 5 ml of 10%  $NaHCO_3$ . The precipitate is transformed into a basic bismuth carbonate  $(BiO)_2CO_3$  yielding  $[Cr(SCN)_6]^{3-}$  in soln.

*Step 3.* The acidified filtrate is transferred into a separatory funnel with 0.5 ml of a sat. soln. of iodine in chloroform. The ligand is oxidized into ICN and sulfate ions.

*Step 4.* After 5 min 4 ml of 2M  $H_2SO_4$  is added to the mixture. Some  $I_2$  is produced from ICN and  $I^-$ .

*Step 5.* Iodine is extracted quantitatively by four  $CHCl_3$  portions. The aqueous extract is transferred into a flask. 1 ml of bromine water is added, producing two effects:  $I^-$  is oxidized into iodate  $IO_3^-$  and HCN into BrCN.

*Step 6.* Add 3 ml of 90%  $HCOOH$  to get rid of the bromine excess.

*Step 7.* Add KI in excess (1.5 g) to the acidified soln. Both iodate ions and BrCN are reduced by iodide ions to produce  $I_2$ .

*Step 8.* Titrate the obtained soln. with 0.002M  $Na_2S_2O_3$ .

*Question 2.* Determine the corresponding equations for each step.

*Question 3.* How many moles of thio-sulfate correspond to one mole of the initial Bi?

*Question 4.* What amount of Bi can be determined with 1 ml of 0.002M  $Na_2S_2O_3$ ?

#### Answers

To 1. 12.1 mg

To 2. *Step 1.*  $Bi^{3+} + [Cr(SCN)_6]^{3-} \rightarrow Bi[Cr(SCN)_6]$

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

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

*Step 4.*  $ICN + HI \rightarrow I_2 + HCN$

*Step 5. a)*  $3 Br_2 + I^- + 3 H_2O \rightarrow IO_3^- + 6 Br^- + 6 H^+$

*b)*  $Br_2 + HCN \rightarrow BrCN + Br^- + H^+$

*Step 6.*  $Br_2 + HCOOH \rightarrow CO_2 + 2 Br^- + 2 H^+$

*Step 7. a)*  $IO_3^- + 5 I^- + 6 H^+ \rightarrow 3 I_2 + 3 H_2O$

*b)*  $BrCN + 2 I^- + 2 H^+ \rightarrow I_2 + Br^- + HCN$

To 3. 1 mole of Bi yields 228 moles of thiosulfate.

To 4.  $1.83 \cdot 10^{-6}$  g Bi

#### Problem 3

In 1911, Rutherford observed that 192 mg of  $^{226}Ra$  produced 6.58 mm<sup>3</sup> of helium

in 83 days (at 0° and 1 atm), and that 1 g of  $^{226}Ra$  emits  $3.42 \cdot 10^{10}$   $\alpha$ -particles per second.

1. How many He-atoms are emitted in 83 days neglecting the radon half-life?

2. Determine Avogadro's number from this experiment with the same approximation.

3. The three first terms of the Ra series are:  $Ra \rightarrow Rn \rightarrow RaA$ , with the corresponding rate constants  $k_1$  and  $k_2$ . Determine the relation between the number of radon and radium atoms.

4. How many He-atoms are emitted taking into account radon half-life?

5. Determine Avogadro's number from this experiment taking into account radon half-life.

#### Answers

To 1.  $1.9 \cdot 10^{17}$

To 2.  $6.4 \cdot 10^{23}$

To 3.  $N(Rn) = N(Ra) \cdot k_1/k_2$

To 4.  $1.79 \cdot 10^{17}$

To 5.  $6.09 \cdot 10^{23}$

#### Problem 4

Chromate ions are characterized by the following equilibria:

$HCrO_4^- + H_2O \rightarrow CrO_4^{2-} + H_3O^+$ ;  $pK_1 = 6.50$

$2 HCrO_4^- \rightarrow Cr_2O_7^{2-} + H_2O$ ;  $pK_2 = 1.36$

Ignore any other equilibrium or activity coefficients.

1. Knowing the ionic product of water  $K_w = 10^{-14}$  calculate the equilibrium constants of the following reactions:

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

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

#### Answers

a)  $3.2 \cdot 10^{-8}$ ;

b)  $4.4 \cdot 10^{13}$

2.  $BaCr_2O_7$  is soluble in water.  $BaCrO_4$  has a solubility product  $K_s = 1.2 \cdot 10^{-10}$ .

In which direction will equilibrium 1b be moved in a potassium dichromate soln. if the following reagents are added:

a) KOH,

b) HCl,

c)  $BaCl_2$ ,

d)  $H_2O$ .

#### Answers

a, c, and d to the right; b to the left. Case d is surprising but  $[H_2O]$  must be considered as constant, and dilution favors the right side. Furthermore dilution helps acidity decreasing which also favors the right-hand side of 1b.

3. What is the pH of the following solns.?

a) 0.010M  $K_2CrO_4$ ;

b) 0.010M  $K_2Cr_2O_7$ ;

c) 0.010M  $K_2Cr_2O_7 + 0.10M CH_3COOH$ , knowing that  $K_a$  for acetic acid is  $1.8 \cdot 10^{-5}$ .

#### Answers

a) 9.25; b) 4.20; c) 2.87.

4. Calculate  $[CrO_4^{2-}]$  and  $[Cr_2O_7^{2-}]$  in the mixture from Problem 3c.

#### Answers

$3.0 \cdot 10^{-6}$ ;  $3.7 \cdot 10^{-3}$ .

#### Problem 5

A soln. I contains  $FeSO_4$  and  $Fe_2(SO_4)_3$ . Another soln. II contains  $K_4Fe(CN)_6$  and  $K_3Fe(CN)_6$ , with such concentrations that  $[Fe^{2+}]_I = [Fe(CN)_6^{4-}]_{II}$  and  $[Fe^{3+}]_I = [Fe(CN)_6^{3-}]_{II}$ . Measured with a platinum electrode with respect to a normal hydrogen electrode, their potentials are 0.652 V and 0.242 V, respectively. Transmittance of the soln. II as determined with respect to I at 420 nm is 10.7%. The optical path-length is 5.02 mm. Assume that the only absorbing species at 420 nm is  $Fe(CN)_6^{3-}$  whose extinction coefficient  $\epsilon$  is 1100 l/(mol·cm). The standard potential of  $Fe^{3+}/Fe^{2+}$  is 0.771 V.

1. Write the Nernst equations for the I and II redox systems.

2. What is the dimension and unit of the prelogarithmic factor 0.0590 in these equations?

3. What is the ratio of the stability constants  $b[Fe(CN)_6^{3-}]/b[Fe(CN)_6^{4-}]$ ?

4. What are the minimum and maximum values of the transmittance  $T$  and of the absorbance  $A$ ?

5. What are the concentrations of the ferrous and ferric ions in I?

#### Answers

To 1.  $E_I = E^\circ(Fe^{3+}/Fe^{2+}) + 0.059 \log[Fe^{3+}]/[Fe^{2+}]$

$E_{II} = E^\circ(Fe(CN)_6^{3-}/Fe(CN)_6^{4-}) + 0.059 \log[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}]$

To 2. Volt

To 3.  $b_2/b_1 = 8.9 \cdot 10^6$

To 4.  $T$ : 0–100;  $A$ : 0– $\infty$

To 5.  $[Fe^{3+}] = 1.76 \cdot 10^{-3} M$ ;  $[Fe^{2+}] = 0.183 M$

#### Problem 6

Two hydrocarbons A and B contain 85.7% C mass.

1. What is the general formula for A and B?

Both **A** and **B** react with ozone and yield a single product **C** after subsequent treatment with zinc and acid. Oxidation of **C** gives a carboxylic acid **D**. All H-atoms of this acid **D** are of methyl groups except the carboxylic H. The vapor density of **D** is 9.1 g/l at 0° and 1 atm. Both **A** and **B** react with neutral and cold  $\text{KMnO}_4$ , but **A** reacts quicker and produces only one compound **F**. Oxidation of **B** yields a mixture of two isomers **G1** and **G2**.

2. What are the formula of **A**, **B**, **C**, and **D** (in aqueous and vapor phases)?

3. Write the equation of the transformation of **A** or **B** into **C** and **D**. Write then the equation of **A** and **B** being transformed into **F**, **G1**, and **G2**.

**G1** and **G2** react with acetone in acidic condition forming **H1** and **H2**.

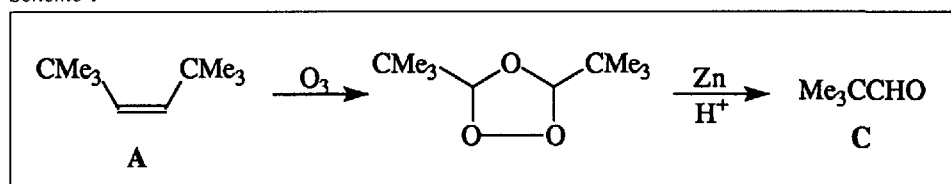
4. Draw the structures of **H1** and **H2**.

5. **A** and **B** react with bromine. One of the products **J** of these reactions is non polar and optically inactive. Draw the stereochemical formula of this product. Mark the chiral atoms according to (*R/S*) nomenclature.

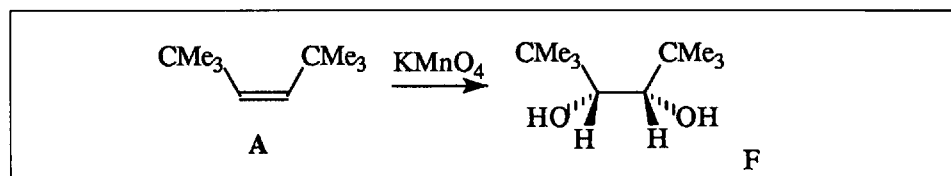
Alkenes react with peroxyacids to form epoxides. This reaction is stereospecific about the double bond. Epoxidation of **A** yields **K**, and **B** produces a mixture of the isomers **L1** and **L2**.

6. Draw the stereochemical formula for **K**, **L1**, and **L2**. Are they optically active?

Scheme 1



Scheme 2



Scheme 3

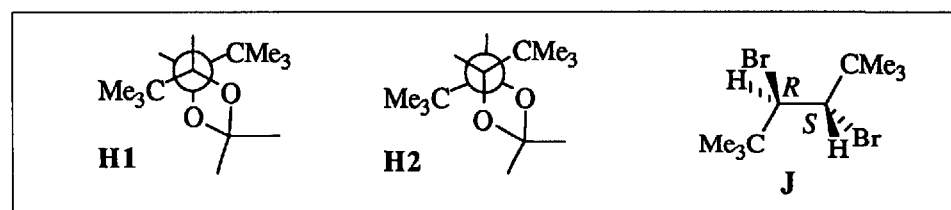
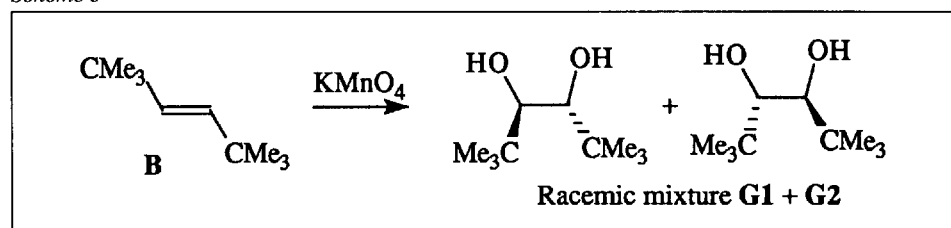


Fig. 1

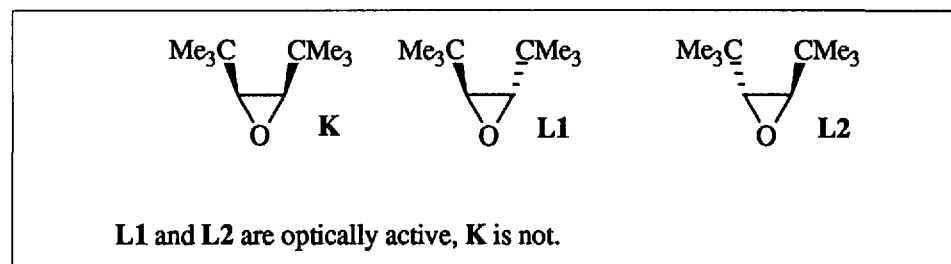


Fig. 2

### Answers

To 1.  $\text{C}_n\text{H}_{2n}$

To 2. **A**: (*Z*)-2,2,5,5-tetramethylhex-3-ene;  
**B**: (*E*)-isomer of **A**; **C**:  $(\text{CH}_3)_3\text{CCHO}$ ;  
**D**:  $(\text{CH}_3)_3\text{CCOOH}$ , dimerized in vapor phase.

To 3. See Scheme 1–3.

To 4 + 5. See Fig. 1

To 6. See Fig. 2

### Practical problem 1: Titration of Copper and Iron Ions

1. **Copper**. Transfer 10.00 ml of the unknown soln. into a flask. Add 20 ml of 5%  $\text{Na}_4\text{P}_2\text{O}_7$ , 7 ml of 1M HCl, and 10 ml of 20% KI. After 5 min in the darkness, titrate with a standardized  $\text{Na}_2\text{S}_2\text{O}_3$  soln. until the color of the suspension changes to pale yellow. Then add 10 drops of a 1% starch soln. Continue the titration until the color becomes clear white.

2. **Iron**. Introduce 10.00 ml of the unknown soln. into a flask. Add 2 ml of 1M HCl and 10 ml of 20% KI. After 5 min in the darkness, titrate with  $\text{Na}_2\text{S}_2\text{O}_3$  soln. until the color of the

suspension changes to pale yellow. Then add 10 drops of 1% starch soln. Continue the titration until the color becomes clear white.

Write the reactions involved. Calculate the mass of copper and iron in the initial solution.

### Practical problem 2: Synthesis and Analysis of Paracetamol

Heat 3.10 g of *p*-aminophenol, 10 ml of  $\text{H}_2\text{O}$ , and 4 ml of acetic anhydride in a 50 ml flask equipped with a reflux condenser for 15 min. Remove the condenser and cool the flask with ice: small white crystals appear on the walls. Filtrate under

vacuum. Wash three times with 2 ml of cold  $\text{H}_2\text{O}$ . Dry in air for 30 min: the product (*p*-hydroxyacetanilide, or paracetamol) contains less than 5% of  $\text{H}_2\text{O}$ . Weigh the product.

Chromatography. Dissolve some crystals in a tube in 1–2 ml of EtOH. Deposit a small spot of the soln. on the starting line of a silica plate. Deposit also a small drop of a soln. made from commercial paracetamol. Dry for 1 min. Immerse the plate in a beaker containing the eluant. At the end remove the plate, mark the front of eluent and allow to dry for 5 min. Examine under UV light. Outline the dark spots with a pencil. Calculate the retention factors. Compare the two analyses.