A Bronze Medal for Switzerland at the 33rd Chemistry Olympiad

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Abstract: At the 33rd International Chemistry Olympiad in Munmai (India), Switzerland won a bronze medal.

Keywords: International Chemistry Olympiad · Swiss students

Delegations from 53 countries took part in the 33rd International Chemistry Olympiad, which was organized in Mumbai (Bombay), 5–15 July, 2001. Thanks to Daniel Torricelli, 19 years old, from Kloten ZH, Switzerland won a bronze medal (Fig. 1 and 2).

The International Chemistry Olympiad is an annual competition for high school students younger than 20 years old. Participating countries send their four best students to this competition that lasts ten days. Two of the ten days are devoted to competitions, one for practical work in a laboratory, and one for solving theoretical problems. After correction and grading, the best students are awarded gold, silver, and bronze medals like in the real Olympic games. The best 10% are awarded gold, the next 20% silver, and 30% bronze.

In the present Olympiad, the best result was obtained by a Chinese, and the second by a Russian. The most successful countries were China, Korea, and Russia, with three gold medals and one silver medal each. The surprise came from Germany and Austria which used to pile up gold medals and which achieved only one silver and one bronze each.

The four members of the Swiss team were:
– Karin Birbaum, b. 1982, 6340 Baar, Kantonsschule Zug
– Martin Kotyrba, b. 1982, 5313 Klingnau, Kantonsschule Baden
– Ulrich Neuenschwander, b. 1983, 8624 Grüt, Kantonsschule Zürich-Wetzikon
– Daniel Torricelli, b. 1982, 8302 Kloten, Kantonsschule Zürich-Oerlikon.

Each delegation is headed by two mentors who meet at the beginning of the Olympiad to create and define the problems of the Olympiad. The level of these problems is usually so high that the contestants have to be seriously trained in advance in their original countries. In Switzerland the preparation was done in winter weekends followed by one week in April at the Gymnase de Chamblandes, Pully-Lausanne.

The two Swiss mentors were Thomas Bark, University of Fribourg, and Maurice Cosandey, Gymnase de Chamblandes, 1009 Pully. Mentors were hosted in one of the best luxury hotels in Mumbai ($90/night).

After the competition the mentors and the candidates had a lot of opportunities for sightseeing and visiting parks, museums, industries, *etc.* around Mumbai.

The next Olympiad will be in 2002 in the Netherlands, 2003 in Greece, 2004 in Switzerland, 2005 in Taiwan, 2006 in Korea, 2007 in Turkey, 2008 in England, and 2009 in Singapore.

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Fig. 1. The bronze medal.

Fig. 2. Reverse side of the bronze medal with a text in sanskrit.

Theoretical Problems

The theoretical problems of the 2001 Olympiad are presented along with their answers.

Problem 1. H-atom

The observed wavelengths in the line spectrum of the H atom are expressed in terms of the famous Balmer's empirical formula:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right); n = 3,4,5,...$$

$$R_H = \frac{m_e e^4}{8 \varepsilon_0^2 h^3 c} = 109678 cm^{-1}$$

where R_H is the Rydberg constant. This formula can be generalized to any one-electron atom or ion.

1.1. Calculate the largest wavelength in the Balmer's series of the He$^+$ ion.

1.2. A formula analogous to Balmer's formula applies to the series of spectral lines which arises from transitions to the lowest energy level of H atom. Write this formula and use it to determine the ground state energy of the H atom in eV.

1.3. A 'muonic H atom' is like a H atom if the electron is replaced by a heavier particle, the muon. The mass of the muon is 207 times the mass of the electron, while its charge is the same as that of the electron. Determine the lowest energy and the radius of the first orbit of the 'muonic H atom', knowing the radius a_0 of the first Bohr orbit of a H atom.

$$a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2} = 53 pm$$

The classical picture of an orbit in Bohr's theory has now been replaced by the quantum mechanical notion of an orbital. The orbital 1s for the ground state of a H atom is given by:

$$\Psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

where r is the distance of the electron from the nucleus.

1.4. Consider a spherical shell of radius a_0 and thickness 0.1 pm. Estimate the probability of finding the electron in this shell.

1.5. The H_2 molecule can dissociate through two different channels:

$H_2 \rightarrow H + H$

$H_2 \rightarrow H^+ + H^-$

The energy of the separated H^+ and H^- is –14.3 eV, and the energy of the molecule H_2 is –31.9 eV, assuming 2 protons and 2 electrons have zero energy. Calculate the dissociation energies of H_2 for the two processes.

1.6. Calculate the energy change for the process $H^- \rightarrow H + e^-$.

1.7. Assuming that the Bohr energy formula is valid for each electron with nuclear charge Z replaced by Z_{eff}, calculate Z_{eff} for H^-.

Problem 2. Phosphoric Acid

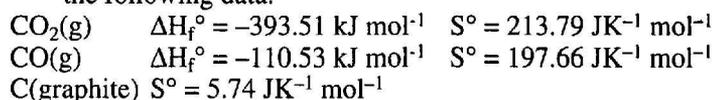2.1. The pK_a values of the three successive dissociations of phosphoric acid at 25 °C are: $pK_{1a} = 2.12$; $pK_{2a} = 7.21$; $pK_{3a} = 12.32$. Write down the conjugate base of dihydrogen phosphate ion and determine its pK_b value.

2.2. Many drinks contain small amounts of phosphoric acid. A cola having a density of 1.00 g ml^{-1} contains 0.050% by weight of phosphoric acid. What is its pH, ignoring the 2nd and the 3rd dissociation of the acid?

2.3. Determine the fractional concentrations of all the different phosphate species present in a solution of phosphoric acid 0.00100 M at pH 7.

2.4. In a given soil water with pH = 7.0, zinc phosphate was found to be the only source of zinc and phosphate. Calculate the concentration of Zn^{2+} and PO_4^{3-} ions in the solution. K_{sp} for zinc phosphate is 9.1×10^{-33}.

Problem 3. Thermodynamics

3.00 mol CO_2 expands isothermally (in thermal contact with the surroundings, at a temperature 15.0 °C) against a fixed external pressure of 1.00 bar. The initial and final volume of the gas are 10.0 and 30.0 l, respectively.

3.1. Calculate the sign of the change of entropy of the system ΔS_{sys} and of the surroundings ΔS_{sur}.

3.2. Calculate ΔS_{sys} assuming CO_2 to be an ideal gas.

3.3. Calculate ΔS_{sur}.

3.4. Calculate the change in entropy of the universe. Does your answer agree with the Second Law of Thermodynamics?

The critical point of CO_2 is 73.8 bar and 31 °C. The triple point of CO_2 is 5.18 bar and –56.6 °C. At 1.01 bar, CO_2 sublimes at –78.5 °C.

3.5. Suppose CO_2 gas is taken at 4.0 bar and 10 °C then cooled at constant pressure. Does it goes to the liquid state then to the solid state, or does it go to the solid state without going through the liquid phase?

3.6. Starting with the same T and P value as in 3.5., CO_2 is compressed isothermally. Does it go first to the liquid phase, or direct to the solid phase?

3.7. Calculate the molar enthalpy change of sublimation of CO_2.

3.8. CO gas can be obtained by reacting CO_2 with graphite. Show that the equilibrium constant is < 1 at 298 K, using the following data.

$CO_2(g)$ $\Delta H_f^\circ = -393.51$ kJ mol^{-1} $S^\circ = 213.79$ JK^{-1} mol^{-1}
$CO(g)$ $\Delta H_f^\circ = -110.53$ kJ mol^{-1} $S^\circ = 197.66$ JK^{-1} mol^{-1}
C(graphite) $S^\circ = 5.74$ JK^{-1} mol^{-1}

3.9. Estimate the temperature at which the reaction would have an equilibrium constant equal to 1.

3.10. The reaction in 3.8. is carried out between CO_2 and excess hot graphite at about 800 °C and a total pressure of 5.0 bar. The dimensionless equilibrium constant Kp is 10.0. Calculate the partial pressure of CO at equilibrium.

Problem 4. Radioactivity

Monazite contains about 9% ThO_2 and 0.35% U_3O_8. ^{208}Pb and ^{206}Pb are the stable end-products of ^{232}Th and ^{238}U respectively. All the lead (Pb) found in monazite is of radiogenic origin. The isotopic ratio $^{208}Pb/^{232}Th$, measured by mass spectrometry in a monazite sample was found to be 0.104. The half-lives of ^{232}Th and ^{238}U are $1.41 \cdot 10^{10}$ years and $4.47 \cdot 10^9$ years, respectively.

4.1. Calculate the age of the monazite sample.

4.2. Estimate the ratio $^{206}Pb/^{238}U$ in the monazite sample.

4.3. Thorium-232 can absorb a neutron. The resulting isotope forms ^{233}U by successive beta decays. Write the nuclear reactions for the formation of ^{233}U from ^{232}Th. In nuclear fission of ^{233}U, a complex mixture of fission products is

formed. The fission product ^{101}Mo undergoes radioactive decay as shown below:

$$^{101}_{42}\text{Mo} \xrightarrow{t_{1/2} = 14.6 \text{ min}} {}^{101}_{43}\text{Tc} \xrightarrow{t_{1/2} = 14.3 \text{ min}} {}^{101}_{44}\text{Ru} \text{ (stable)}$$
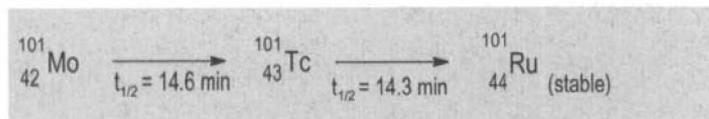
4.4. A freshly prepared radiochemically pure sample of ^{101}Mo contains 50,000 atoms initially. How many atoms of ^{101}Mo, ^{101}Tc, ^{101}Ru will be present in the sample after 14.6 min?

Problem 5. Halogen Chemistry

5A. Photography

A black and white photographic plate contains a coating of silver bromide and gelatine on a support of cellulose acetate.

5.1. Write the photochemical reaction that occurs when light falls on AgBr(s) coated on a film.

5.2. During the development process, unexposed AgBr is washed away by complexation of Ag(I) by sodium thiosulfate solution. Write down this chemical equation.

5.3. These washings are often disposed of as waste. However, metallic silver can be recovered from them by adding cyanide, followed by zinc. Write down the equations involved.

5B. Shapes, Spectra, and Reactivity

5.4. Fluorine reacts with other halogens, Cl_2, Br_2, and I_2 giving a tetra-atomic, hexa-atomic and an octa-atomic molecule, respectively. Write the formulae and 3-dimensional structures of these interhalogen molecules on the basis of the VSEPR theory.

5.5. A mixture of iodine vapor and chlorine gas when fed into a mass spectrometer gave two sets (A and B) of mass spectral peaks corresponding to molecular ions of two chemical species at m/z equal to: A: (162, 164); B: (464, 466, 468, 470, 472, 474, 476). Identify the molecular species corresponding to m/z = 162, 164, 466 and 476, indicating clearly the lone pairs on iodine atoms.

5.6. In aqueous medium chlorine oxidizes sodium thiosulphate to an ion containing the highest oxidation state of sulphur. Write down the equation for this reaction.

5.7. Write down the Lewis dot structure of the thiosulphate ion. Circle the sulphur atom that has the lower oxidation state.

5.8. Chlorine dioxide reacts with sodium hydroxide. Balance the equation.

5.9. Chlorine is used for manufacturing bleaching powder. Write the chemical equation for its formation.

5.10. What is the oxidation state of chlorine in bleach?

5C. Alkali Metal Halides and X-ray Crystallography.

The radius ratio (r^+/r^-) of ions from alkali metal halides is given in the Table below.

	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
Cl$^-$	0.33	0.52	0.74	0.82	0.93
Br$^-$	0.31	0.49	0.68	0.76	0.87
I$^-$	0.28	0.44	0.62	0.69	0.78

The electrostatic component of lattice energy of alkali halides does not change with radius ratio r^+/r^- for NaCl-type and CsCl-type crystal structures, if this ratio passes from 0 to a critical value to be determined later on. For higher values of r^+/r^- the energy increases when r^+/r^- tends towards 1.

5.11. Why is the energy leveling off at low values of r^+/r^-? Is it cation–cation contact along the face diagonal? Is it anion–anion contact along the diagonal? Is it cation–anion contact along the cell edge?

5.12. Which among the halides LiBr, NaBr and RbBr is likely to undergo phase transition from NaCl-type to CsCl-type with change of temperature or pressure?

5.13. Determine the radius ratio at which the energy of the CsCl-type structure levels off.

5.14. Crystallography of KCl will be performed using Cu Kα X-rays ($\lambda = 154$ pm). Given that
– diffraction at $\theta = 14.2°$ takes place from the planes (hkl) with $h^2 + k^2 + l^2 = 4$
– reflections in a fcc structure can only occur from planes with 'all odd' or 'all even' hkl indices
– the distance d_{hkl} between adjacent planes (hkl) is related to the lattice parameter a by the following expression: $d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2}$.
Calculate the lattice parameter a for KCl.

5.15. Calculate the distance in pm to the 2nd and the 3rd nearest neighbors of a K$^+$ ion in the KCl lattice.

5.16. Determine the lowest value of diffraction angle θ possible for the KCl structure.

Problem 6. Organic Chemistry

The rhizomes of ginger (Zingiber officinale) have medicinal and flavoring properties. The pungency of ginger is due to many substituted aromatic compounds. Three of them will be discussed: Zingerone $C_{11}H_{14}O_3$, Gingerol $C_{17}H_{26}O_4$, and Shogaol $C_{17}H_{24}O_3$.

6.1. Zingerone reacts with FeCl$_3$ and 2,4-dinitrophenylhydrazine, but does not react with Tollens' reagent. Which functional group does it contain?

6.2. The NMR spectrum of Zingerone displays the following features: a) two singlets at $\delta = 2.04$ and 3.81 (both with intensities 3); b) two closely spaced triplets of equal intensity at $\delta = 2.69$ and 2.71 (total intensity 4); c) two doublets with similar chemical shifts and one singlet at $\delta = 6.4–6.8$ (total intensity 3); d) one broad singlet interchangeable with D_2O (intensity 1) at $\delta = 5.90$. Zingerone on bromination with bromine water gives only one ring monobrominated product. The IR spectrum of Zingerone indicates the presence of a weak intramolecular hydrogen bond. The same is present even after Clemmensen reduction (Zn-Hg/HCl) of Zingerone. A table of NMR displacements is available in an appendix.

6.2.i. What is the side chain in Zingerone?

6.2.ii. What are the remaining substituents on the ring?

6.2.iii. What are the relative positions of the substituents on the ring?

6.3. Draw the structure of Zingerone.

6.4. Imagine a synthesis for Zingerone starting from A + B(C_3H_6O) producing C in the presence of NaOH, which is then reduced by H_2 on Raney Nickel to produce Zingerone.

Zingerone can be converted into Gingerol by the following reaction sequence

$$\text{Zingerone} \xrightarrow[\text{(ii) LDA, -78°C}]{\text{(i) Me}_3\text{SiCl / (Me}_3\text{Si)}_2\text{NH}} \text{D} \xrightarrow[\text{(ii) H}_2\text{O / H}^+]{\text{(i) hexanal}} \text{Gingerol}$$

(Zingerone: $C_{11}H_{14}O_3$; Gingerol: $C_{17}H_{26}O_4$)

Note that $Me_3SiCl/(Me_3Si)_2NH$ is used to convert –OH into –$OSiMe_3$, and that the group $SiMe_3$ can be removed by acid hydrolysis. Note that LDA is lithium diisopropylamide, a strong, very hindered, non-nucleophilic base.

6.5.i.   What is the structure of D?

6.5.ii. What is the structure of Gingerol?

6.5.iii. Draw the Fischer structure of the (*R*)-enantiomer of Gingerol, with H on the left.

6.5.iv. In the sequence 6.5., about 2% of another constitutional isomer E of Gingerol is obtained. Draw the likely structure of E.

6.5.v. Will the compound E be formed as a) a pair of enantiomers, or b) a mixture of diastereoisomers, or c) a mixture of an enantiomeric pair and a meso isomer?

6.5.vi. When heated with a mild acid such as $KHSO_4$, Gingerol ($C_{17}H_{26}O_4$) gives Shogaol ($C_{17}H_{24}O_3$). Draw the structure of Shogaol.

6.6.   Turmeric (Curcuma longa) is a commonly used spice in Indian food. Its main constituent, Curcumin ($C_{21}H_{20}O_6$) is responsible for the yellow color and the taste of turmeric. Chemically speaking it is related to Gingerol, but it exhibits an keto-enol tautomerism. The NMR spectrum of the keto form of curcumin shows aromatic signals similar to Gingerol. It also shows a singlet around δ 3.5 (2 H) and two doublets (2 H each) in the region δ 6–7 with J = 16 Hz. It can be synthesized by condensing two moles of A (refer to § 6.4) with one mole of pentan-2,4-dione.

6.6.i.   Draw the structure of Curcumin.

6.6.ii. Draw the enol form of Curcumin.

6.6.iii. Why is Curcumin yellow? Is it due to the presence of a phenyl ring, a carbonyl group, an extended conjugation, or an hydroxyl group?

Laboratory task 1. Synthesis of 2-iodobenzoic acid from 2-aminobenzoic acid.

The procedure consists of diazotation of 1 g of 2-aminobenzoic acid followed by reaction with KI, purification, and weighing.

Laboratory task 2. Complexometric titration of a mixture Mg + Mn.

First a mixture containing about 6–8 mg Mg (x mol) and 20–28 mg Mn (y mol) in 5–10 ml is titrated at pH 10 with EDTA 0.05 M and Eriochrome T until the color changes from red to blue. This gives the total Mg + Mn (or x + y). After this first operation an excess of NaF (1.5 g) is added to transform Mg in MgF_2, (and to produce x mol free EDTA). Then 20.0 ml of a standard Mn solution (0.0500 M) is added (z mol). When the solution is red again, the excess of Mn in the solution is titrated against EDTA 0.05 M. This second titration corresponds to (z–x) mol Mn.

Laboratory task 3. Kinetics of the oxidation of ethanol by Cr(VI).

At t = 0, 1 ml ethanol is added into 100 ml $K_2Cr_2O_7$ 0.037 M in HCl 3.6 M. A burette is filled with this reacting mixture. At every 10 min, 10.0 ml of this solution are drawn in a flask containing 4 ml KI 3% which quenches the oxidation of ethanol and produces I_2. The amount of I_2 is determined with $Na_2S_2O_3$ 0.01 M. By reporting the logarithm of remaining [Cr(VI)] against time the student should obtain a straight line. So the reaction is first order, with a rate constant to be determined k = 0.030 min^{-1}.

Answers to Theoretical Problems

1.1. 164 nm; 1.2. 13.6 eV; 1.3. E = –2.82 keV; r = 0.26 pm; 1.4. Prob = 5.4 10^{-4}; 1.5. 4.7 eV, 17.6 eV; 1.6. 0.7 eV; 1.7. Z_{eff} = 0.7.
2.1. $H_2PO_4^-$; pK_{2b} = 6.79; 2.2. pH 2.46; 2.3. f(H_3PO_4) = 8.1 10^{-6}; f($H_2PO_4^-$) = 0.62; f(HPO_4^{2-}) = 0.38; f(PO_4^{3-}) = 1.8 10^{-6}; 2.4. [Zn^{2+}] = 9·10^{-5}; [PO_4^{3-}] = 1.1·10^{-10};
3.1. ΔS_{sys} > 0, ΔS_{sur} < 0; 3.2. ΔS_{sys} = 27.4 JK^{-1}; 3.3. ΔS_{sur} = –6.9 JK^{-1}; 3.4. $\Delta S_{universe}$ = 20.5 JK^{-1}; 3.5. No liquid; 3.6. Liquid first; 3.7. ΔH = 26 kJ mol^{-1}; 3.8. ΔG = 119 kJ mol^{-1}; so K < 1; 3.9. 980 K; 3.10. p(CO) = 3.63 bar.
4.1. 2.0·10^9 y; 4.2. x = 0.366; 4.3. ^{232}Th – ^{233}Th –^{233}Pa –^{233}U; 4.4. ^{101}Mo: 25000 atoms; ^{101}Tc: 1710 atoms; ^{101}Ru: 790 atoms.
5.1. AgBr → Ag + Br; 5.2. AgBr + 2 $Na_2S_2O_3$ → Na_3Ag (S_2O_3)$_2$ + NaBr; 5.3. Ag(S_2O_3)$_2^{3-}$ + 2 CN$^-$ → Ag(CN)$_2^-$ + 2 $S_2O_3^{2-}$; 2 Ag(CN)$_2^-$ + Zn → 2 Ag + Zn(CN)$_4^{2-}$; 5.4. ClF$_3$, BrF$_5$, IF$_7$; 5.5. 162 = I^{35}Cl; 164 = I^{37}Cl; 466 = I$_2^{35}$Cl$_5^{37}$Cl; 476 = I$_2^{37}$Cl$_6$; 5.6. 4 Cl$_2$ + $S_2O_3^{2-}$ + 5 H_2O → 8 Cl$^-$ + 2 SO$_4^{2-}$+ 10 H$^+$; 5.7. S–S bond. 5.8. 2 ClO$_2$+ 2 NaOH → NaClO$_2$ + NaClO$_3$ + H_2O. 5.9. 2 Cl$_2$ + 2 Ca(OH)$_2$ → CaCl$_2$ + Ca(ClO)$_2$ + 2 H_2O. 5.10. –1 and +1.   5.11. anion–anion diagonal.   5.12. RbBr.   5.13. 0.732. 5.14. a = 628 pm;(hkl) = 200. 5.15. 444 pm; 544 pm. 5.16. (hkl) = 111; θ =12.2°.
6.1. Ketone and phenol. 6.2.i. $CH_2CH_2COCH_3$. 6.2.ii. OH, OCH$_3$. 6.2.iii.1,2,4.

6.6.iii. Extended conjugation