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46th International Chemistry Olympiad

Hanoi, Vietnam

Two Bronze Medals for Switzerland at the 46th International Chemistry Olympiad in Hanoi, Vietnam

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The International Chemistry Olympiad (IChO) is an annual competition between students in secondary education from all over the world. Ever since the first event was held in Prague, Czechoslovakia in 1968 the number of participating countries has steadily increased. At first mainly countries of the Eastern Bloc participated, whereas today 77 countries from all over the world take part in the event.

In 2014 the 46th IChO was held at the Vietnam National University in Hanoi, Vietnam. The event hosted a total number of 524 people, including 291 contestants. Switzerland was represented this year by:

Lukas Lüthy (Alte Kantonsschule Aarau, AG)
Gary Shang (Intenational School of Geneva, GE)
Patrik Willi (Kantonsschule Im Lee, ZH)
Janik Grädel (Alte Kantonsschule Aarau, AG)
accompanied by their mentors:
Peter E. Ludwig (head-mentor, ETH Zurich)
Thanh Phong Lê (mentor, EPF Lausanne)

The competition was won by Singaporean Sun Jiarui, while we are very proud to announce that Switzerland was awarded two bronze medals for the remarkable performance of Lukas Lüthy and Gary Shang. The Swiss Team was accompanied for the second time by a team from Liechtenstein composed of *Simon Eitzinger* and *Saphira Kaiser* (Liechtensteinisches Gymnasium Vaduz), who were mentored by *Alain C. Vaucher* and *Yannick Suter* (both ETH Zurich).

There is more to the event than just the competition though. The IChO brings young chemistry devotees from all over the world together. It enables a cultural exchange on the basis of the common denominator chemistry. In their interactions the young chemists fuel their curiosity further and at the same time form new friendships all over the world. But IChO is just where the effort of a whole year peaks. A year during which students from all over Switzerland come together not only for competition, but also to learn together. Amongst like-minded people they develop an eagerness to learn beyond their curriculum with experienced

The Swiss team with their guides and Zita Ballaman as representative of the Swiss embassy to Hanoi. From left to right: Trần Phượng Thảo, Peter Ludwig, Janik Grädel, Patrik Willi, Gary Shang, Lukas Lüthy, Zita Ballaman, Thanh Phong Lê and Phạm Thanh Hằng.

chemists to support them. Classes in theory as well as in the lab are held by these volunteers and they are also always available for questions. Therefore, the Swiss Chemistry Olympiads (SwissChO) thanks all the members of the organisation, the teachers, organisers and mentors as well as our generous sponsors, who support the students and made the two bronze medals in Hanoi possible.

The next IChO will be held in July 2015 at the Baku branch of Lomonosov Moscow State University in Baku, Azerbaijan.

Example of a Question at the 46th IChO

Task 3: High-valent Silver Compounds

Silver chemistry is dominated by Ag(I) compounds. Compounds of silver in higher oxidation states (from +2 to +5) are not very abundant due to their instability with respect to reduction. High-valent silver compounds are very reactive and can be synthesized from Ag(I) compounds in electrochemical oxidations or in chemical oxidations using powerful oxidizing agents.

1. In some peroxydisulfate ($S_2O_8^{2-}$) oxidations catalyzed by Ag^+, a black solid (**A**) with the composition AgO can be isolated.

1a. Choose the appropriate magnetic behavior of **A** if it existed as $Ag^{II}O$.
☐ diamagnetic
☐ paramagnetic

Single crystal X-ray studies reveal that the lattice of **A** contains two non-equivalent Ag atom sites (in equal proportions) of which one is denoted Ag1 and the other is denoted Ag2. Ag1 shows a linear O atom coordination (O–Ag–O) and Ag2 shows a square-planar O atom coordination. All O atoms are in equivalent environments in the structure. Thus, **A** should be assigned as $Ag^IAg^{III}O_2$ rather than $Ag^{II}O$.

1b. Assign the oxidation number of sites Ag1 and Ag2.

1c. What is the coordination number of O atoms in the lattice of **A**?

1d. How many Ag^I and Ag^{III} bond to one O atom in the lattice of **A**?

1e. Predict the magnetic behavior of **A**. Tick the appropriate box below.
☐ diamagnetic
☐ paramagnetic

1f. Compound **A** can also be formed on warming a solution of Ag^+ with peroxydisulfate. Write down the equation for the formation of **A**.

2. Among the silver oxides which have been crystallographically characterized, the most surprising fact is that compound **A** is not $Ag^{II}O$. Thermochemical cycles are useful to understand this fact. Some standard enthalpy changes (at 298 K) are listed below:

The relationship between the lattice dissociation energy (U_{lat}) and the lattice dissociation enthalpy (ΔH_{lat}) for monoatomic ion lattices is: $\Delta H_{lat} = U_{lat} + nRT - 1/2nRT$, where n is the number of ions in the formula unit.

2a. Calculate U_{lat} at 298 K of $Ag^IAg^{III}O_2$ and $Cu^{II}O$. Assume that they are ionic compounds.

2b. Calculate U_{lat} for the hypothetical compound $Ag^{II}O$. Assume that $Ag^{II}O$ and $Cu^{II}O$ have the same type of lattice, and that $V_m(Ag^{II}O) = V_m(Ag^{II}Ag^{III}{}_2O_4) - V_m(Ag^{III}{}_2O_3)$.

2c. By constructing an appropriate thermodynamic cycle or otherwise, estimate the enthalpy change for the solid state transformation from $Ag^{II}O$ to 1 mole of $Ag^IAg^{III}O_2$.

2d. Indicate which compound is thermodynamically more stable by ticking the appropriate box below.
☐ $Ag^{II}O$
☐ $Ag^IAg^{III}O_2$

The rest of Task 3 and the other problems can be found on *http://www.icho.ch/*

Answers

1a. paramagnetic (Ag^{II} is d^9)
1b. Ag1 is +I and Ag2 is +III
1c. Coordination number of O atoms is 3
1d. one Ag^I and two Ag^{III}
1e. diamagnetic (Ag^I is d^{10}, Ag^{III} is square planar d^8)
1f. $S_2O_8^{2-}{}_{(aq)} + 2Ag^+_{(aq)} + 2H_2O_{(l)} \rightarrow 2SO_4^{2-}{}_{(aq)} + Ag^IAg^{III}O_{2(s)} + 4H^+_{(aq)}$
2a. $U_{lat}(Ag^IAg^{III}O_2) = 9409.9$ kJ·mol^{-1} , $U_{lat}(Cu^{II}O) = 4157.5$ kJ·mol^{-1}
2b. $U_{lat}(Ag^{II}O) = 3733.6$ kJ·mol^{-1}
2c. $\Delta H_{rxn} = 655.7$ kJ/mol
2d. $Ag^IAg^{III}O_2$

Atom	Standard enthalpy of formation (kJ·mol^{-1})	1st ionisation (kJ·mol^{-1})	2nd ionisation (kJ·mol^{-1})	3rd ionisation (kJ·mol^{-1})	1st electron affinity (kJ·mol^{-1})	2nd electron affinity (kJ·mol^{-1})
Cu(g)	337.4	751.7	1964.1	3560.2		
Ag(g)	284.9	737.2	2080.2	3367.2		
O(g)	249.0				–141.0	844.0

Compounds	$\Delta H^{\ominus}_f$ (kJ·mol^{-1})
$Ag^IAg^{III}O_{2\,(s)}$	–24.3
$Cu^{II}O_{(s)}$	–157.3