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CALCULATION OF CONDITIONAL EQUILIBRIUM IN SERIAL MULTIPLE PRECIPITATION OF METAL SULFIDES WITH HYDROGEN SULFIDE STREAM GENERATED FROM SODIUM SULFIDE: A DIDACTIC TOOL FOR CHEMISTRY TEACHING

Renata Bellová, Danica Melicherčíková and Peter Tomčík*
Department of Chemistry and Physics, Faculty of Education, Catholic University in Ružomberok, Hrabovská cesta 1, SK - 034 01 Ružomberok, Slovak Republic

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Hydrogen sulfide is presented in textbooks as toxic, environmentally unacceptable species, however some positive effects in human metabolism were discovered in the last decades. It is important to offer students also some new information about this compound. As didactic tool in this case may serve serial precipitation of Cd^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+} and Pb^{2+} ions forming various colored sulfides in bubblers with chemically generated hydrogen sulfide stream. This experiment has strong and diverse color effect for enhancing the visual perception to motivate students to understand more abstract and complex information about hydrogen sulfide. It also may be helpful in analytical chemistry courses for conditional precipitation equilibrium teaching and calculations.

Keywords: visual perception; laboratory demonstrations; equilibrium.

INTRODUCTION

At adult age, people aim their attention towards scientific discoveries bringing novel facts and observations from distance and closeness or from macroscopic, microscopic or nanoscopic diameter scale. However, at younger age, the perception by human senses, especially sight, is more developed in comparison with research based on abstract models. Color changes attract and enhance the student's attention, motivating the interest, and generate emotions. For these reasons experiments based on colored chemical reactions are successfully used in chemical education.[1,2] Experiments with color effects are used also for chemistry popularization in the frame of various projects organized by educational institutions.

Since 2003, the science literacy of 15-year old students is monitored in a project called PISA. The obtained results showed some educational problems in several countries.[3] This state was consulted also in European Commission with these conclusions:

- The reason of the educational regress in natural sciences is mostly due to the deductive approach based on remembering and understanding without training how to use the obtained information in the concrete standard and non-standard situations
- Inquiry Based Science Education (IBSE) creates the area for student's own research by applying the inductive approach
- It is very convenient conceptually to find the optimal ratio between deductive and inductive approaches

As an example we may mention hydrogen sulfide H_2S. It is well known for its smell like rotten eggs and its high toxicity as nerve agents.[4-6] It irritates the eyes and respiratory tract.[7] H_2S is denser than air and moderately soluble in water with a slight acidic reaction. Hydrogen sulfide concentrations in the range of $8 \times 10^{-4} – 2 \times 10^{-2}$ mg m^{-3} are well detectable by human nose, however at higher concentrations it becomes undetectable due to olfactory nerve paralyzation.[8] This fact is the reason of some sudden deaths, e. g, workers death in sewage canals. Breath irritation is induced by inhaling air containing 0.15 mg dm^{-3} of hydrogen sulfide. If this concentration is higher (around 0.20-0.25 mg dm^{-3}) it is followed by nausea, pain and rustiness. Breathing 0.75 mg dm^{-3} for 15-20 minutes is fatal. Immediate death caused by total breath paralyzation comes by breathing air with hydrogen sulfide concentration of 1.5 mg dm^{-3} because hydrogen sulfide is bonded to Fe in enzymes necessary for breathing in cell mitochondria, blocking oxygen.[9-11]

However, hydrogen sulfide is not just toxic, but has some positive effects on human health. It is present in blood or plasma serum, however biological concentrations of H_2S are very low due to difficulties with its detection. In the literature there are significant differences concerning hydrogen sulfide amounts in biological tissues (from 1×10^{-5} to 3×10^{-4} mol dm^{-3}). At substantially higher concentrations (around 1.2×10^{-2} mol dm^{-3}) H_2S can be found in some mineral waters used in some spa resorts.[12] Hydrogen sulfide is absorbed into the body through skin reducing risk of thrombogenesis, together with positive effects on arthritis, chronic inflammations, borreliosis or chlamydia infections during bath. Last but not least, hydrogen sulfide influences also the immune system and some processes in bone marrow.[13]

At the end of 20th century it was observed that hydrogen sulfide is present in human brain.[14-17] Brain cells are able to take it from sulfur compound like di-allyl-disulfide, di-allyl-trisulfide or S-allyl-cysteine, which are present in garlic or onion. H_2S also positively influences neuron potentiation, which is important for memory.[18-21]

In temporary biological research the hydrogen sulfide is important in the experiments dealing with hibernation, to reduce mortality caused by accidents or other injuries. When laboratory mouses inhaled air with very low concentration of hydrogen sulfide around 0.002-0.008%, their metabolism became very sluggish: breath rate lowered from 120 to 10 breaths per minute, heart beat rate decreased from 600 p min^{-1} to 130 p min^{-1} and the body temperature dropped to 15 °C. In this cirunstance, inhalation of air without hydrogen sulfide normalized the mouses metabolism to previous condition.[22,23] During injuries some blood losses may also occur. If rats had lost 60% of blood and was treated with the solution containing hydrogen sulfide, survival rate was 66%. Without application of hydrogen sulfide the survival rate diminished to only 14%.

To verify whether novel scientific knowledge was incorporated into secondary education we put some questions to 72 students in the first year of university having secondary education in different places of Slovakia. The students had to choose from 12 compounds,

*e-mail: peter.tomcik@ku.sk

including H_2S, and classify them as corrosive (category a), toxic (category b) and/or species important in biological processed in live organisms (category c). One species could be placed into all categories. As can be seen from Figure 1, only 2.9% of the students placed hydrogen sulfide among species important in biological processes.

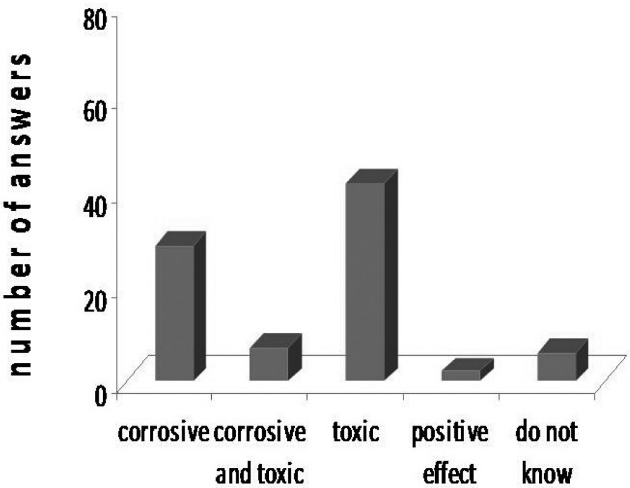

Figure 1. *Brief overview of answers on hydrogen sulfide character*

Therefore, the purpose of this paper is to present novel educational view on hydrogen sulfide as not only toxic, but also as biologically relevant species. The efficient way to force scholars to be more familiar with novel facts are visual impulses, because sensitivity on colors is an universal feature of human visual perception enhancing the effectivity of chemical education. The experiment proposed here is based on multiple colored sulfides formation as a tool to acquire the novel facts about hydrogen sulfide easier.

EXPERIMENTAL

In the experiment proposed here, the following chemicals were used: concentrated hydrochloric acid (p.a., 35%, ρ=1,18 g.cm^{-3}, Penta Prague, CZE), anhydrous Na_2S (extra pure, Aeros Organics, BEL), metallic salts: $CdCl_2.2H_2O$ (p.a, Penta Prague, CZE), $CuSO_4.5H_2O$ (p.a., CentralChem, Bratislava, SVK), $ZnSO_4.7H_2O$ (p.a, CentralChem, Bratislava, SVK) $MnSO_4.H_2O$ (p.a, CentralChem, Bratislava, SVK) and $Pb(NO_3)_2$ (p.a, Penta Prague, CZE), and species for pH value maintaining: acetic acid (pure, 99%, ρ=1,05 g.cm^{-3}, Microchem, Pezinok, SVK) and disodium tetraborate dekahydrate (p.a, CentralChem, Bratislava, SVK).

Hydrogen sulfide was generated from very cheap chemicals: sodium sulfide and hydrochloric acid. 11 g of Na_2S was weighed into reaction vessel and 25 mL of concentrated HCl was carefully added. The generated hydrogen sulfide flowed through 5 bubblers connected serially with 100 mL of 5% solutions (corresponding to approximately 0.2 mol L^{-1}) of Cd^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, and Pb^{2+} (see Graphical Abstract) to form corresponding colored sulfides. The solutions of Zn^{2+} and Mn^{2+} were buffered with 0.3 mol L^{-1} solution of $Na_2B_4O_7.10H_2O$. For the absorption of unreacted excess of hydrogen sulfide, the solution of 20% KOH (CentralChem, Bratislava, SVK) was used. The pH value in each bubbler was checked by Portable pH Meter (Hanna Instruments).

Due to the toxicity of hydrogen sulfide, the experiment should be performed in a fume hood as well as with common laboratory protective tools (gloves, lab coat, and eye shield). The apparatus should be sealed up to avoid unnecessary release of hydrogen sulfide.

RESULTS AND DISCUSSION

The precipitation of metal sulfides is very popular in analytical chemistry due to the simple qualitative detection of high number of metal ions. This fact is relevant also from the educational point of view. The experiments of this type have strong sensational effect and motivation to increase the interest on chemistry.

Hydrogen sulfide is very easy to prepare in laboratory according to the following reaction (equation (1)) of solid Na_2S (instead of the widely used and rather expensive FeS) and concentrated HCl:

$$Na_2S + 2\,HCl \rightarrow 2\,NaCl + H_2S \qquad (1)$$

In water, the hydrogen sulfide behaves as weak acid, releasing protons in two steps:

$$H_2S \Leftrightarrow HS^- + H^+ \qquad K_1 = \frac{[H^+][HS^-]}{[H_2S]} = 9.55\times10^{-8} \qquad (2)$$

$$HS^- \Leftrightarrow S^{2-} + H^+ \qquad K_2 = \frac{[H^+][S^{2-}]}{[HS^-]} = 1.26\times10^{-14} \qquad (3)$$

where K_1 and K_2 are the first and second concentration equilibrium constants for the corresponding steps of hydrogen sulfide dissociation. Many studies published various values of these constants[24] over several orders, e. g., $K_1 \in <1\times10^{-8} - 1.096\times10^{-7}>$, however, the most problematic is the second dissociation constant $K_2 \in <1\times10^{-19} - 1.148\times10^{-12}>$. The sulfide anion S^{2-} is an excellent precipitation agent for many metals forming various colored sulfides. For color reason, we chose five metals (Cd^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+} and Pb^{2+}, see Table 1) which were serially precipitated with hydrogen sulfide. As can be seen from Table 1, for each solubility product value (K_S), its solubility c_{max} in water can be calculated using a well known formula (if we have binary precipitate A_mB_n):

$$c_{max} = \sqrt[m+n]{\frac{K_S}{m^m n^n}}, \text{ for our sulfides: m and n = 1,}$$

$$\text{therefore } c_{max} = \sqrt{K_S} \qquad (4)$$

It is clear that the solubility cannot be attributed only to K_s value, there are also other factors influencing the solubility like temperature and ionic strength. However, as can be seen further from Table 1, soluble products of the reactions stated there are strong acids, and the final value of pH of all five solutions will be low. At low pH values the whole equilibrium should be considered as conditional, where protonization of sulfide anion is assumed as a side reaction influencing strongly the solubility of precipitated sulfides. Sulfide anion protonizes in two steps:

$$S^{2-} + H^+ \Leftrightarrow HS^- \qquad K_1^H = \frac{[HS^-]}{[H^+][S^{2-}]} \qquad (5)$$

$$HS^- + H^+ \Leftrightarrow H_2S \qquad K_2^H = \frac{[H_2S]}{[H^+][HS^-]} \qquad (6)$$

where K_1^H and K_2^H are the first and second protonization constants. In this case, the solubility product is also conditional and is expressed as:

$$K_S' = [M^{2+}][S^{2-}]' \qquad (7)$$

where $[S^{2-}]'$ is the conditional equilibrium concentration of sulfide ion. Practically it can be expressed as a sum of all (deprotonated and

Table 1. Basic view on precipitates used in the described experiment

Precipitation reaction	sulfide color	solubility product (K_S*)	solubility c_{max} in mol L^{-1}
$CdCl_2 + H_2S \rightarrow CdS\downarrow + 2\ HCl$	yellow	9.8×10^{-28}	$c_{max} = 3.1 \times 10^{-14}$
$CuSO_4 + H_2S \rightarrow CuS\downarrow + H_2SO_4$	black	7.7×10^{-37}	$c_{max} = 8.8 \times 10^{-19}$
$ZnSO_4 + H_2S \rightarrow ZnS\downarrow + H_2SO_4$	white	1.5×10^{-23}	$c_{max} = 3.9 \times 10^{-12}$
$MnSO_4 + H_2S \rightarrow MnS\downarrow + H_2SO_4$	pink	8.7×10^{-11}	$c_{max} = 9.3 \times 10^{-6}$
$Pb(NO_3)_2 + H_2S \rightarrow PbS + 2\ HNO_3$	black	1.6×10^{-28}	$c_{max} = 1.3 \times 10^{-14}$

*These numbers were calculated as 10^[-(pKs max + pK_S min)/2] from the set of values taken from various sources:[25-29] CdS – 8×10^{-27} – 1.2×10^{-28}; CuS – 1×10^{-36} – 6×10^{-37}; ZnS – 1.1×10^{-21} – 2×10^{-25}; MnS – 2.5×10^{-10} – 3×10^{-11}; PbS – 2.5×10^{-27}- 1×10^{-29}.

protonated) forms of sulfide anion:

$$[S^{2-}]' = [S^{2-}] + [HS^-] + [H_2S] \quad (8)$$

After expression of $[HS^-]$ and $[H_2S]$ from equations (5) and (6) we will obtain:

$$[S^{2-}]' = [S^{2-}] + K_1^H[H^+][S^{2-}] + K_2^H[H^+][HS^-] \quad (9)$$

or

$$[S^{2-}]' = [S^{2-}] + K_1^H[H^+][S^{2-}] + K_2^H K_1^H[H^+]^2[S^{2-}] \quad (10)$$

Further

$$[S^{2-}]' = [S^{2-}]\,(1 + K_1^H[H^+] + K_2^H K_1^H[H^+]^2) \quad (11)$$

and the conditional equilibrium concentration of sulfide anion is

$$[S^{2-}]' = [S^{2-}]\,\alpha \quad (12)$$

In which

$$\alpha = 1 + K_1^H[H^+] + K_2^H K_1^H[H^+]^2 \quad (13)$$

with α being a sulfide anion protonization side reaction coefficient. This parameter would be also expressed in this form

$$\alpha = 1 + \beta_1[H^+] + \beta_2[H^+]^2 \quad (14)$$

where $\beta_1 = K_1^H$ and $\beta_2 = K_2^H K_1^H$ are association equilibrium constants. Due to some confusions in textbooks we also show parameter α expressed through dissociation constants taking into account the known fact that first protonization constant is an inverse value of second dissociation constant:

$$K_1^H = \frac{1}{K_2} \text{ and } K_2^H = \frac{1}{K_1} \text{ resp. } \beta_1 = \frac{1}{K_2} \text{ and } \beta_2 = \frac{1}{K_1 K_2}$$

$$\alpha = 1 + \frac{1}{K_2}[H^+] + \frac{1}{K_1 K_2}[H^+]^2 \quad (15)$$

In the case of conditional precipitation equilibrium, the conditional solubility product should be recalculated using coefficient α (see equations (7) and (12) and Figure 2)

$$K_S^{'} = \alpha\, K_S \quad (16)$$

From equations (13), (14) and (15) and from Figure 2 it is evident that side reaction coefficient will increase as pH value decreases.

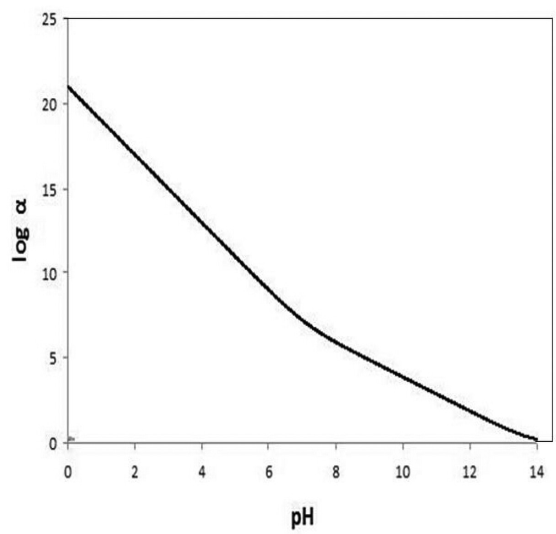

Figure 2. *The dependence of sulfide protonization as side reaction coefficient on pH value*

At low pH it has very high values, therefore it should be expected higher conditional solubility products of chosen sulfides as well as their higher conditional solubilities. It is in good agreement that low value of pH induces dissolution of precipitate. In Table 2, the conditional characteristics for chosen sulfides are calculated. At measured pH value we calculated side reaction coefficients α_{min} using the lowest values of hydrogen sulfide dissociation constants and α_{max} for highest dissociation constants. Then minimal and maximal conditional solubility products were calculated according to equation (16) whereas K_S values were taken from Table 1. The conditional solubilities for $K_S^{'}$ (min) and $K_S^{'}$ (max) were calculated taking into account an excess concentration of unreacted hydrogen sulfide because it contains sulfide ion which strongly influences the solubility. This concentration for our case is given by solubility of hydrogen sulfide in water[30] at 25 °C which is equal to 0.117 mol L^{-1}. Therefore the conditional solubility is equal to

$$c_{max} = \frac{K_S^{'}}{0.117} \quad (17)$$

Finally, the precipitation effectivity was calculated as percentage of the metal present in precipitate according to formula:

$$\% = \frac{c_{starting} - c_{max}}{c_{starting}} 100 \quad (18)$$

These calculations were compared with experimental reality. It is well known that CdS is possible to precipitate very easily even at very low pH values (and in our experiment we also confirmed this

Table 2. Calculated conditional parameters of sulfides precipitation and its comparison with reality

sulfide	pH	α_{min}	α_{max}	K'_S (min)	K'_S (max)	c_{max}(min)	c_{max}(max)	% min	% max	reality
CdS	0,34	1.7×10^{18}	2.1×10^{26}	1.66×10^{-9}	2.06×10^{1}	1.42×10^{-8}	1.76×10^{2}	100	0	nice yellow
CuS	0,40	1.3×10^{18}	1.6×10^{26}	1.00×10^{-18}	1.23×10^{-10}	8.55×10^{-18}	1.05×10^{-9}	100	100	nice black
ZnS	0,46	9.6×10^{17}	1.2×10^{26}	1.44×10^{-5}	1.80×10^{3}	1.23×10^{-4}	1.54×10^{4}	99.9	0	weak white turbidity
MnS	0,23	2.7×10^{18}	3.5×10^{26}	2.35×10^{8}	3.01×10^{16}	2.00×10^{9}	2.60×10^{17}	0	0	no precipitate
PbS	0,52	7.2×10^{17}	9.1×10^{25}	1.15×10^{-10}	1.46×10^{-2}	9.85×10^{-10}	1.24×10^{-1}	100	17	nice black

fact), but we calculated that no precipitate will occur if the highest dissociation constants are used for calculations. Seeing that the value of side reaction coefficient at low pH values is governed by second dissociation constant, according to this approach its value will be slightly higher than the order of 10^{-19}. As for CuS, its solubility product is very low and conditional solubility calculation is not sensitive to dissociation constants values, confirming total formation of black precipitate, which we also got experimentally. The solubility product of MnS is relatively high, therefore no precipitate with hydrogen sulfide stream was obtained in agreement with calculations with both extreme values of dissociation constants. We obtained controversial results with ZnS precipitation. It is well known that zinc sulfide is not precipitated with hydrogen sulfide stream in strong acidic media, but in this experiment we obtained very slight turbidity of the solution in bubbler caused by very low amount of white ZnS. According to theoretical calculations stated in Table 2, if the lowest values of dissociation constant for hydrogen sulfide are used, nice white precipitate should be obtained, in other hand when the highest values are used no precipitate is formed. Concluding, the calculation with lowest values of dissociation constant also does not reflect reality.

To assure formation of nice pink and white precipitate of MnS and ZnS with hydrogen sulfide stream, we suggested to buffer solutions of $ZnSO_4$ and $MnSO_4$ with 0.3 mol L^{-1} sodium tetraborate which reacts with hydrogen sulfide according to equation (19):

$$Na_2B_4O_7 + H_2S + 5\ H_2O \rightarrow 4\ H_3BO_3 + Na_2S \qquad (19)$$

The products of this reaction are very weak trihydrogenboric acid and base Na2S. The pH of the solution is enhanced and side reaction coefficient is decreased as well as conditional solubility of MnS resp. ZnS. This produces very nice pink (MnS) and white (ZnS) precipitates maximizing such visual effects of experiment proposed here (see Graphical Abstract).

PEDAGOGY

The chemical experiment presented in this work was conducted as demonstration in fume hood due to hydrogen sulfide release into laboratory. The students were future chemistry teachers on bachelor level of education in the frame of analytical chemistry. As for interaction between experiment and students they solved the following tasks: write chemical equations of the sulfides precipitation, calculate the amount of the reactants needed for hydrogen sulfide stream generation, calculate the amount of precipitates and pH of solutions in bubblers, find various sources for K_S values and consider their variability. The main aim of this experiment was to motivate students to learn positive and negative facts about hydrogen sulfide as well as the toxicity of the used heavy metals. The students also improved their presentation skills to correctly evaluate the results. Finally, they were able to solve some problem tasks such as why colored sulfides are not precipitated in human body even if hydrogen sulfide is present in it together with some heavy metals.

CONCLUSIONS

In this work, serial precipitation of colored sulfides with one hydrogen sulfide stream was firstly showed, then the possibilities for its use as didactic tool for chemistry teaching were discussed. It is well known that colored sulfides MnS and ZnS are not generally precipitated with acidic hydrogen sulfide stream, however, they may also be consecutively precipitated if the solution is buffered with sodium tetraborate as more suitable species than the commonly used NH_3. The visual effects of this experiment enhanced the interest in chemistry and motivated students to initiate easier the discussions about hydrogen sulfide to be familiar with some novel facts as biologically important compound with positive effects on human health. This fact was unknown until the end of 20th century as well as detection techniques for H_2S in tissues due to substantially lower concentration levels as used in experiment presented here. Furthermore, this experiment was useful for analytical chemistry courses from conditional chemical equilibrium teaching point of view to obtain literacy in data finding about certain compounds, as well as to induce wider discussions about solubility of heavy metals from the environmental point of view.

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