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REMEDIATION OF CO_2 IN BOUDOUARD'S REACTION AS AN EXAMPLE OF REVERSIBLE CHEMICAL REACTION

Abstract: One of the fundamental elements of a scientist's work is the ability to lead observations of the phenomena that surround us and based on them making conclusions. These observations are conducted within the so-called scientific experiments. Lessons learned based on the results obtained in experiments allow researchers to better understand the essence of the phenomena occurring in the world around us. Drawing conclusions is not always easy. In order to achieve this skill, we must possess a well-established knowledge in the field of the phenomenon that interests us. The most striking example of how important skills are observation and drawing proper conclusions is the phenomenon of global climate warming. The main parameter influencing temperatures registered on Earth is the concentration of greenhouse gases in the atmosphere, and especially carbon dioxide created from combustion processes. A significant role in studies of the reduction of CO_2 emissions plays chemists. To be sure that conducted by them experiments are optimally designed, it is necessary to ensure them with proper education already at the secondary school level. The main aim of this article was to conduct the study in order to explain chemical issues that create the greatest cognitive difficulties among students. The second aim of the article was to propose a chemical experiment to students that would allow them to find out more about the phenomena governing in the area of problematic issues. The proposed experiment is based on the concept of solubility equilibrium. Results of preliminary tests that have been carried out after applying this experiment on a small group of students, indicated their better understanding of the studied subject.

Keywords: Boudouard reaction, equilibrium constant, inquiry-based science education, chemical experiment

Introduction

Since 1988, employees of Chemical Education Department of the Faculty of Chemistry of the Jagiellonian University have been organizing the Chemical Knowledge Competition for secondary school students. In Poland, studying in secondary schools lasts 3 years and ends with an secondary school-leaving examination. One of the subjects that the students may pass during this exam is chemistry at an extended level. The competition is intended for the second and third grade students from secondary schools of Malopolska Province. Each school year approximately 1300 students take part in the competition. The aim of the competition is to encourage students to be interested in chemistry and enable them to test their knowledge. The scope of material and the formula of the competition tasks were changed in 2014. At present, the competition sheet contains 5 single-choice and 5 multiple-choice tasks, 3 Lowson tasks and 3 open-ended tasks (Fig. 1).

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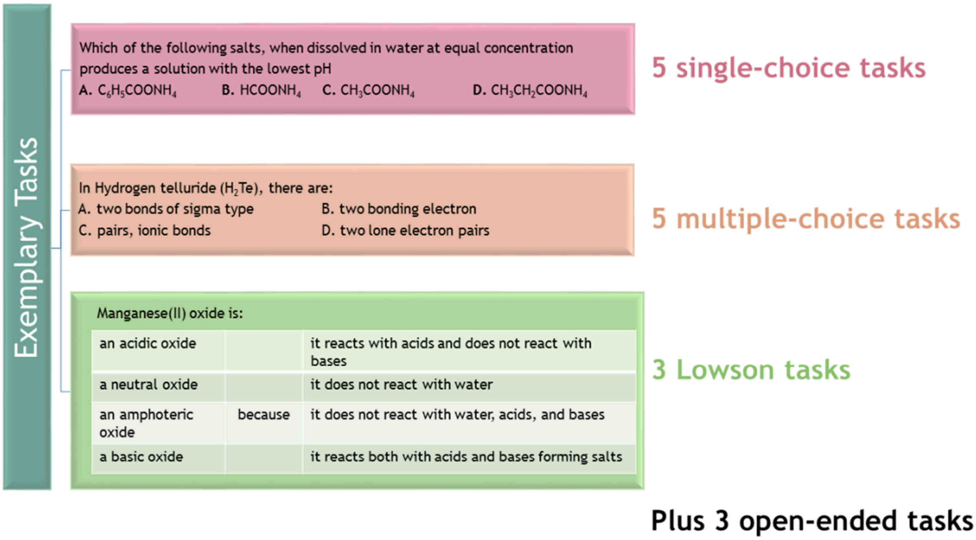

Fig. 1. Exemplary closed tasks from the competition sheet

Students' answers are analysed. On this basis, the most difficult issues for students are chosen and next elaborated in order to create of new methodological solutions. These solutions are presented to teachers and students [1].

Data analysis

Based on all the answers given by the third-grade students of general secondary schools, who have participated in the Chemical Knowledge Competition, the tasks with the greatest index of the wrong answers were selected and next analysed in terms of difficulties faced by students during solving the problem. The research covered 500 competition contestants (337 females and 163 males). It turned out that the biggest challenge for pupils was to answer the questions about the equilibrium established in the system during the so-called Boudouard reaction [2]. Therefore, only these tasks were the subject of further analysis. Boudouard reaction takes place during the gasification of coal and other carbon-rich sources and is very important due to the possibility remediation of CO_2 by reducing it to carbon monoxide, which can be next used to produce hydrogen [3]. The analysis covered only the competition tasks checking the knowledge contained in the following points of the core curriculum:

Student:

- demonstrates the knowledge and understanding of the following concepts: the state of dynamic equilibrium (balance) and equilibrium constant; writes the equilibrium constant expression of a given reaction;
- applies Le Chatelier's principle to the qualitative determination of the impact of change in temperature, concentration of reagents and pressure on the system in a state of dynamic equilibrium.

Results of data analysis

The subject of the analysis were students' answers given to the following competition questions:

Problem 1:

Gaseous carbon monoxide can be obtained by reducing carbon dioxide using elemental carbon.

1a. Assuming that this reaction is reversible one and the system is at equilibrium state, write down the equation of this reaction and equilibrium constant (K_c) expression for this reaction.

1b. State whether the following sentences are true or false.

No.	Question	True	False
I	The efficiency of the reaction will increase if the pressure in the system increases.		
II	Increasing the amount of carbon in the reaction vessel will shift the equilibrium of the reaction to the right.		

Table 1 presents the results of the statistical analysis of the data obtained based on the answers provided by students in competition sheets.

On the basis of the obtained results we can conclude that there were no clear differences between answers given by female and male contestants. As the conducted analysis indicated, writing down the equation of chemical reaction occurring in the given system was not a problem for the students, however, as many as 1/3 of them forgot to mark the state of chemical equilibrium by appropriately written arrows. Difficulties encountered by students in distinguishing between complete and incomplete chemical transformations have already been reported in several works [4-9]. This proves a strong need for a wider explanation of equilibrium processes to pupils.

About half of all respondents were able to write correctly the expression for K_c. More than 1/3 of the rest added the concentration of solid carbon to this expression, which is in a different phase than the other reagents. On average, every tenth student was not able to write down the correct expression for the equilibrium constant. Additionally, nine out of ten those students, who wrote down correctly the expression for the equilibrium constant K_c or input the concentration of carbon into it, answered correctly the question about influence of the pressure changes on the system state. The correct answer to this question was also given by every second student who could not write down the proper expression for K_c. In turn, the most difficult question for participants of the competition was the question about influence of change in the amount of the solid component on the efficiency of the reaction.

As our previous observations have shown, students have no problems with questions concerning single-phase multi-component systems. However, finding correct answer to the question about the equilibrium state in multi-phase multi-component systems causes problem for the majority of them. On the basis of the results obtained, a conclusion can be drawn about a need for designing a chemical experiment that will help pupils understand the essence of the problematic phenomenon. As research indicates, the best way to understand the problem is its visualization [10]. Thus, in the further part of this work we proposed the laboratory classes that would help pupils to understand that addition of solids to the system being in equilibrium state does not affect the efficiency of reaction/process.

Table 1

Results of the statistical data analysis obtained on the basis of the answers given by participants of Chemical Knowledge Competition

The number of students who correctly wrote down the equation of the chemical reaction, remembering to mark the equilibrium state by two arrows pointing in the opposite directions		The number of students who wrote down the equation of the chemical reaction correctly, but did not mark the equilibrium state by two arrows pointing in the opposite directions		The number of students who wrote down the equation of the chemical reaction incorrectly	
Female (N = 337)	Male (N = 163)	Female (N = 337)	Male (N = 163)	Female (N = 337)	Male (N = 163)
196 58 %	109 67 %	131 39 %	50 31 %	10 3 %	4 2 %
The number of students who wrote the equilibrium expression for K_c as follows: $K_c = \frac{[CO]^2}{[CO_2]}$		The number of students who wrote the equilibrium expression for K_c as follows: $K_c = \frac{[CO]^2}{[CO_2] \cdot [C]}$		The number of students who gave other wrong answers to this question.	
Female (N = 327)	Male (N = 159)	Female (N = 327)	Male (N = 159)	Female (N = 327)	Male (N = 159)
177 54 %	87 55 %	124 38 %	49 31 %	26 8 %	23 14 %
The number of students who wrote the K_c properly, and answered correctly to the question 1bI		The number of students who inserted the concentration of the carbon into the K_c expression but answered correctly to the question 1bI		The number of students who wrote the wrong expression for K_c but answered correctly to the question 1bI	
Female (N = 177)	Male (N = 87)	Female (N = 124)	Male (N = 49)	Female (N = 36)	Male (N = 27)
158 89 %	80 92 %	100 81 %	41 87 %	22 61 %	14 52 %
The number of students who wrote the K_c properly, and answered correctly to the questions 1bI and 1bII		The number of students who inserted the concentration of the carbon into the K_c expression, answered correctly to the question 1bI, but answered incorrectly to the question 1bII		The number of students from the whole group of the competition participants of a given sex who answered correctly to the questions 1a and 1bI	
Female (N = 158)	Male (N = 80)	Female (N = 100)	Male (N = 41)	Female (N = 337)	Male (N = 163)
22 14 %	27 34 %	95 95 %	40 98 %	107 32 %	56 34 %
				The number of students from the whole group of the competition participants of a given sex who answered correctly to all the questions	
				Female (N = 337)	Male (N = 163)
				15 (21) 5 %	19 12 %

Background

In any saturated solution that stays in contact with the solid phase of dissolved substance, a state of dynamic equilibrium is established between the substance in the solution and its sediment (in a unit of time the same number of ions goes from the solid phase to the solution as (the number of ions) deposits on the surface of the crystal) [11, 12]. In the experiment proposed below this equilibrium can be described by the equation:

$$CuCl_{2(s)} \rightleftarrows Cu^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \qquad (1)$$

The equilibrium constant for this reaction is expressed as follows:

$$K_c = [Cu^{2+}] \cdot [Cl^{-}]^2 \qquad (2)$$

(simplifying assumptions: the activities of the ions and the ionic strength of the solution are not considered).

Using Le Chatelier's principle in reference to such a reaction, it can be predicted how addition of solid $CuCl_2$ salt or the concentration change of one of the ions affect the efficiency of precipitation of the sediment in the system. These predictions can be next verified based on the proposed chemical experiment.

Experimental procedure

The core of the experiment:

Reagents

1. Saturated solutions of $CuCl_2$, $CuSO_4$ and K_2SO_4 (prepared by dissolving solid salts of $CuCl_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, and K_2SO_4 in distilled water)
2. Concentrated HCl acid

Titration of copper ions

Reagents

1. 0.01 M EDTA
2. Indicator: murexide

Titration of chloride ions

1. 0.1 M $AgNO_3$
2. 0.1 M KSCN
3. (1+1,v/v) HNO_3
4. Indicator: 10 % solution of ammonium iron(III) sulphate dodecahydrate ($NH_4Fe(SO_4)_2 \cdot 12H_2O$) in nitric acid
5. Chloroform

Preparation of reagents

1. Prepare 300 cm^3 of saturated solutions of $CuCl_2$, $CuSO_4$ and K_2SO_4 by dissolving the excess of the corresponding salt or its hydrate in 300 cm^3 of distilled water.
2. Prepare standard solutions of $AgNO_3$ and KSCN from fixanal ampoules.
3. Prepare 0.01 M EDTA solution by dissolving 3.7224 g of $Na_2EDTA \cdot 2H_2O$ into a 1 dm^3 volumetric flask containing about 300 cm^3 of distilled water and fill up to the mark the resulting solution with distilled water.
4. Weigh out about 5 g of $FeNH_4(SO_4)_2 \cdot 12H_2O$. Grind the salt in a mortar to a fine powder. Mix 4 g of this salt with 40 cm^3 of distilled water and a few drops of concentrated nitric acid.
5. All the other reagents i.e. concentrated solutions of HCl and HNO_3, solid salts, murexide and chloroform may be purchased directly from Sigma-Aldrich.

Idea of the experiment

The experiment presented here was designed for a group of maximum 16 students. The experiment requires two 4-5 hour lab sessions. In the first part of the experiment students, by means of a pipette, transfer each time 1 cm^3 of saturated $CuCl_2$ solution into four separate Petri dishes. Next, students add into the first Petri dish 1 cm^3 of concentrated HCl, into the second one 1 cm^3 of saturated $CuSO_4$ solution, into the third one 1 cm^3 of saturated K_2SO_4, and into the fourth one a small amount (ca. 650 mg) of solid $CuCl_2 \cdot 2H_2O$. After that part, they write down their observations into the lab notebooks.

In the second part of the experiment, students pour prepared earlier saturated $CuCl_2$ solution into four separate test tubes. Next, they add 2 cm^3 of concentrated hydrochloride acid to the second tube, 2 cm^3 of saturated $CuSO_4$ solution to the third tube, and 650 mg of solid $CuCl_2 \cdot 2H_2O$ to the fourth tube. The first test tube should contain only a clear saturated $CuCl_2$ solution. The main aim of this experiment is determination of the contents of Cu^{2+} and Cl^- ions in each of the four test tubes.

In turn, during titration experiment students work in pairs. In the first step during the first lab period, one of the students (Student 1) determines the content of Cu^{2+} ions, and the other student (Student 2) determines the content of Cl^- ions in the first test tube. In the second step during the second lab period students exchange their research places. From that moment Student 1 determines the content of Cl^- ions in the third and fourth test tube, and Student 2 determines the content of Cu^{2+} ions in the second and fourth test tube. To determine the contents of Cu^{2+} and Cl^- ions in individual tubes, before titration, each of the tested solutions needs to be diluted with distilled water by dissolving 1 cm^3 of the tested solution into a 1 dm^3 volumetric flask.

Titration of $CuCl_2$ *solution with EDTA (determination of* Cu^{2+} *concentration)*

The chemical reaction of complexation occurring between the sample and titrant:
$Cu^{2+}{}_{(aq)} + (EDTA)^{2-}{}_{(aq)} \rightarrow Cu(EDTA)^{2-}{}_{(aq)} + 2H^+{}_{(aq)}$

1. Rinse the burette first with distilled water, then with small amount of 0.01 mol/dm^3 $Na_2EDTA \cdot 2H_2O$ titrant solution and finally fill it up with this solution. Record the initial volume to 1 decimal place.
2. Transfer precisely 25.00 cm^3 of diluted solution of copper(II) chloride into a clean conical flask using a pipette.
3. Titrate each sample with the standardized EDTA solution (do not forget about constant stirring of titrated solution during the experiment). To see better the endpoint of titration, put a white sheet of paper under the conical flask with titrated solution. Near the endpoint the light yellow solution turns green and then suddenly converts into purplish blue. This moment is the endpoint of the titration (Fig. 2).
4. Record the burette reading.
5. Repeat the titration (procedure 2-4) for one more 25.00 cm^3 sample.
6. Calculate the mass in grams and concentration of copper ions in moles of diluted solution using the following equations:

$$m_{\mathrm{Cu}} = c_{\mathrm{EDTA}} \cdot 63.53 \cdot 40 \text{ [g]} \tag{3}$$

$$n_{\mathrm{Cu}} = \frac{m_{\mathrm{Cu}}}{63.53} \text{ [mol]} \tag{4}$$

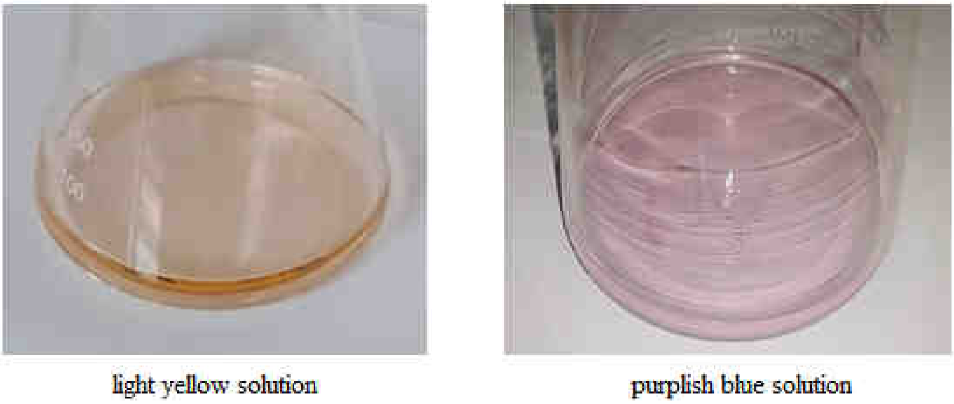

Fig. 2. Colours of the studied solution before and at the endpoint of titration of $CuCl_2$ with EDTA

Titration of $CuCl_2$ *solution by Volhard's method (determination of* Cl^- *concentration)*

The chemical reactions occurring during titration:

$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ white precipitate
$Ag^+_{(aq)} + SCN^-_{(aq)} \rightarrow AgSCN_{(s)}$ white precipitate
$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightarrow [Fe(SCN)]^{2+}_{(aq)}$ dark red complex ion

1. Rinse the burette first with distilled water, then with small amount of the 0.1 mol/dm^3 KSCN titrant solution and finally fill it up with this solution. Record the initial volume to 1 decimal place.
2. Transfer precisely 25.00 cm^3 of diluted copper(II) chloride solution into a clean conical flask using a pipette.
3. Measure 5 cm^3 of (1+1,v/v) HNO_3 acid using a graduated cylinder, place it in the conical flask and then dilute this solution with distilled water to about 50 cm^3.
4. Using a pipette transfer 25.00 cm^3 of standard $AgNO_3$ solution into the conical flask.
5. Under the ventilated hood add at first 3 cm^3 of chloroform and then 1 cm^3 of ammonium iron(III) sulphate to the tested solution using graduated cylinders.
6. Stir the obtained solution in the horizontal position for one minute to precipitate white coloured silver chloride.
7. Titrate the unreacted silver ions with the potassium thiocyanate solution. The endpoint of this titration is the first appearance of creamy-beige colour associated with the presence of a $[Fe(SCN)]^{2+}$ ions and white AgCl precipitate in the solution (see Fig. 3).
8. Record the burette reading.
9. Repeat the titration (procedure 2-8) for one more 25.00 cm^3 sample.
10. Calculate the mass in grams and concentration of chlorine ions in moles of diluted solution using following equations:

$$m_{Cl} = \frac{\left(V_{AgNO_3} \cdot c_{AgNO_3} - V_{KSCN} \cdot c_{KSCN}\right) \cdot 35.46 \cdot 40}{1000} \text{ [g]} \quad (5)$$

$$n_{Cu} = \frac{m_{Cu}}{35.46} \text{ [mol]} \quad (6)$$

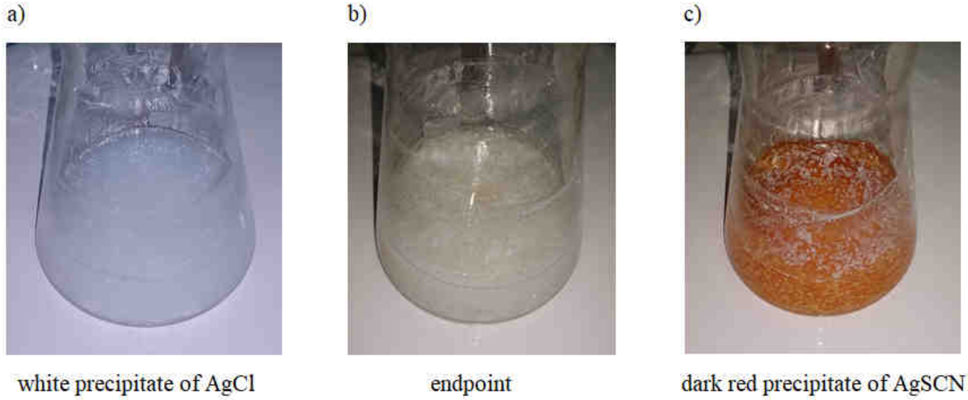

Fig. 3. Colours of the studied solution during titration of $CuCl_2$ by Volhard's method: a) before the endpoint, b) when the endpoint has been reached, and c) after the endpoint of titration

Hazards

Cu(II) salts, whether in a solid state or in solution, have acute toxicity on oral and dermal tissues and can cause irritation to skin, eyes and the respiratory tract [13, 14]. It is necessary to avoid breathing dust, fumes, mist, vapours, or spray of copper(II) sulphate or copper(II) chloride. HCl and HNO_3 concentrated acids have a corrosive effect on human skin [15, 16]. The vapours irritate the respiratory system, eyes, and other mucous membranes. A brief exposure to the solutions of $AgNO_3$ and K_2SO_4 will not produce any immediate side effects other than the purple, brown or black stains on the skin, which are created as a result of an oxidizing properties of $AgNO_3$. Upon a constant exposure of these agents, the side effects including irritation to skin, eyes, and the respiratory tract will be noticeable [17-19]. KSCN is harmful if swallowed or inhaled, and causes irritation to skin, eyes, and the respiratory tract [20]. Chloroform causes moderate eye and skin irritation on contact. Prolonged contact may cause poisoning even through intact skin. Ingestion causes nausea, vomiting, diarrhea, and liver and heart damage [21]. To minimize exposure to chloroform it should be added to the titrated solution under a well ventilated hood. Also, although chloroform is not flammable, it can produce toxic fumes when exposed to flame. Thus, care should be taken to eliminate open flames near areas where chloroform is being used. Personal protective equipment such as goggles and protective gloves should be required to wear to minimize risks throughout the experiment. In case of contact of concentrated solutions with skin or eyes, students should wash the affected area with water immediately. When finished, the remaining solutions should not be drained into the sink; they must be collected into the marked bottles and then properly utilized.

Results of experiment and discussion

In the first part of the experiment a qualitative study was carried out involving the observation of changes taking place in a saturated solution of $CuCl_2$ after adding to it 1 cm^3 of four reagents: concentrated acid $HCl_{(conc)}$, saturated solutions of $CuSO_{4(sat)}$ and $K_2SO_{4(sat)}$, and solid $CuCl_2 \cdot 2H_2O$, respectively. The results of this experiment was shown in Figure 4.

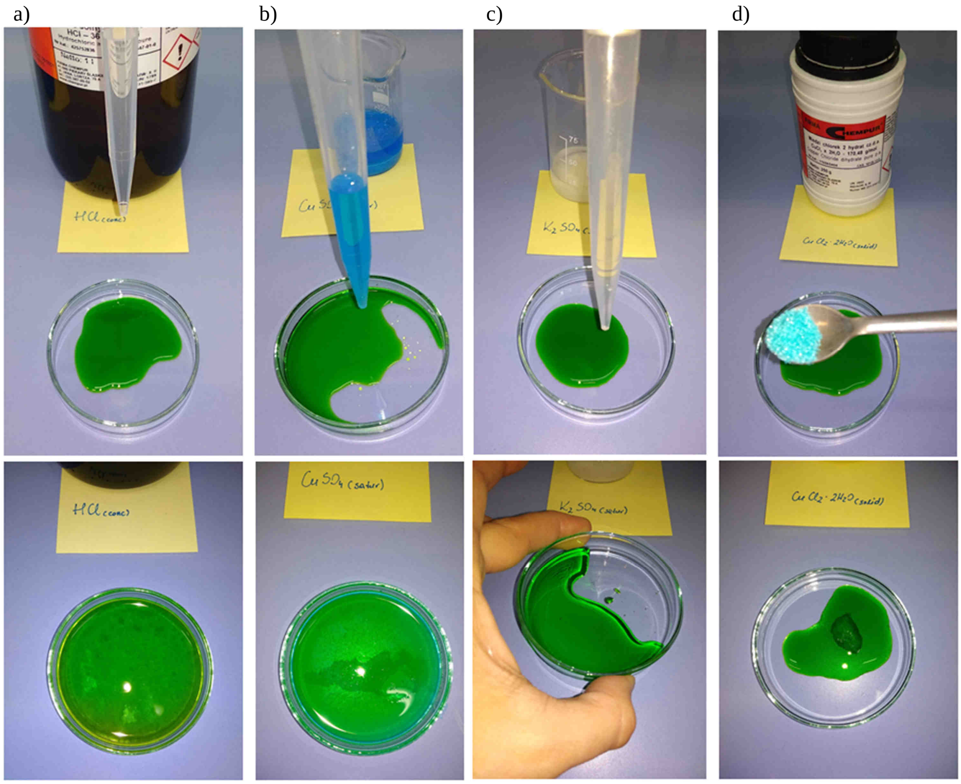

Fig. 4. Observations of changes taking place in a saturated solution of $CuCl_2$ after introducing to it: a) $HCl_{(conc)}$, b) $CuSO_{4(sat)}$, c) $K_2SO_{4(sat)}$, and d) *solid* $CuCl_2 \cdot 2H_2O$

Table 2

Determination of Cu^{2+} ions concentration in solution

Mixture	c_{EDTA} **[mol/dm^3]**	V_{EDTA} **[cm^3]**	**Mass of Cu^{2+} in 1 dm^3 of the tested solution [g/dm^3]**	**Number of copper ions moles in 1 dm^3 of the tested solution [mol/dm^3]**	**Concentration of $CuCl_2$ in the tested solution [mol/dm^3]**
Pure $CuCl_2$ saturated solution	0.01	12.4	315	4.96	4.96
Saturated solution of $CuCl_2$ with addition of 2 cm^3 of concentrated solution of HCl		9.80	249	3.92	3.92
Saturated solution of $CuCl_2$ with addition of 300 mg of solid $CuCl_2 \cdot 2H_2O$		12.4	315	4.96	4.96

As can be seen in Figure 4 addition of concentrated HCl acid or saturated $CuSO_4$ solution into the Petri dishes with saturated $CuCl_2$ solution caused immediate precipitation of the copper(II) chloride sediment. This phenomenon was not observed in Petri dishes with the $CuCl_{2(sat)}$ solutions after addition into them the saturated solution of K_2SO_4 or solid $CuCl_2 \cdot 2H_2O$ salt.

The second part of the experiment included the quantitative indication of changes occurring in the $CuCl_2$ saturated solution under the influence of the disturbance of existing in it equilibrium state. The results of titration of $CuCl_2$ saturated solution before and after adding to it concentrated HCl acid and saturated $CuSO_4$ solution were presented in Tables 2 and 3. Calculations were made according to equations (3)-(4) and (5)-(6), respectively.

Table 3

Determination of Cl^- ions concentration in solution

Mixture	**Constant parameters of titration**	V_{KSCN} **[cm³]**	**Mass of Cl^- in 1 dm³ of the tested solution [g/dm³]**	**Number of Cl^- moles in 1 dm³ of the tested solution [mol/dm³]**	**Concentration of $CuCl_2$ in the tested solution [mol/dm³]**
Pure $CuCl_2$ saturated solution	c_{AgNO_3} = 0.1 M V_{AgNO_3} = 25 cm³ c_{KSCN} = 0.1 M	22.5	355	10.0	5.00
Saturated solution of $CuCl_2$ with addition of 2 cm³ of concentrated solution of $CuSO_4$		23.6	199	5.60	2.80
Saturated solution of $CuCl_2$ with addition of 300 mg of solid $CuCl_2 \cdot 2H_2O$		22.5	355	10.0	5.00

Presented results show influence of changing the concentration of the substances existing in the equilibrium state on the state of multi-phase multi-component system. In proposed experiment these changes are observed only when copper or chlorine ions are introduced into the system. In turn, introducing solid $CuCl_2 \cdot 2H_2O$ reagent into the system does not cause any noticeable changes.

Conclusion

The survey results revealed that students have a huge problem with understanding how change of the amount of the solid component influence the efficiency of the Boudouard's reaction. This indicates the need to present students such proposition of the chemical experiment which enables them to better understand the equilibrium state settling in a multi-phase multi-component system. At the same time, it should be emphasized that planning an experiment that can be performed in a school laboratory and meets the requirements of a multi-phase multi-component system in a state of equilibrium is extremely difficult. The proposed in this work experiment is based on the concept of solubility equilibrium, which until 2017 was not taught at the level of secondary school. Preliminary tests carried out on a small group of students attending schools at that time, indicated a better understanding of the subject. Therefore, the proposition of the experiment will be made available to a wider group of students and their teachers. This will allow them to better understand the issues related to the salt solubility, which have been included in the educational requirements of the new core curriculum since 2017.

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