

## A SIMULATION ON TEACHING VOLHARD METHOD

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### ABSTRACT

Laboratories are important components of chemistry education. Virtual simulations allow students to repeat the experiments as many times as they want and give students the opportunity to learn in their own ways. In this study, a computer assisted teaching material has been developed for tertiary level. This material has been planned to use in Analytical Chemistry Course content in the subject of quantitative methods. This teaching material has been developed by using Flash program and consisted of animations and simulations related to the quantitative determination of chloride by Volhard Method. Even though the quantitative determination of chloride by Volhard Method could be conducted in the laboratory setting, this experiment has been prepared by using simulations to give students the opportunity to repeat the experiment steps when they want, to control the each step, observing the changes on the equivalence point better. Volhard method is one of the methods to be considered as important in chemistry courses and laboratories. It is an important practical experience for students in the laboratory. In this study, the presented simulation has been prepared by considering these harmful effects and insufficient laboratory conditions.

**Keywords:** Computer assisted instruction, face-to-face instruction, Volhard method, science education

### INTRODUCTION

Laboratories are important components of chemistry education. In laboratory applications, students realize practical applications of theoretical knowledge and also they develop their inquiry and scientific processing skills. But, traditional laboratory applications have some limitations. Some experiments cannot be conducted because of technical deficiencies, their hazardous risks or some environmental factors.

Time limitation is one of the problems that students meet in laboratory settings. Students need different time periods even for the same experiment, since they have different personal characteristics. Time limitation is a problem especially for the students who cannot learn easily or have poor motor abilities. Since additional working in the laboratory is not always possible for students, they cannot repeat the experiments or solve the problems which they meet in the laboratory settings.

Computer assisted laboratory applications are alternatives for educators to cope with the mentioned limitations of traditional laboratories. A computerized laboratory experiment is an efficient tool to aid understanding of topics developed in the classroom and in the laboratory (Martinez et al., 2003; Ruiz et al., 2001). Since the real experiment allows teachers and students to reach the desired goals, a virtual experiment could be useful for better understanding of the theoretical information and takes students' attention to the techniques used to perform the measurements (Belletti et al., 2006). Also, simulation experiments give students the opportunity to learn in their own ways. With the help of simulation experiments, students learn the proper usage of the equipments (Belletti et. al., 2006). Moreover, it is possible to organize virtual experiments which cannot usually be done in the laboratory (i. e., with harmful or dangerous chemicals) and the simulation of experiments that would require too many hours or expensive instruments (Belletti et. al, 2006).

In recent years, through the rapid development of computer programs, simulation experiments and computer assisted applications have been developed in chemistry education field. Belletti et. Al. (2006) described the results from a simulation of vapor pressure measurements of a pure liquid as a function of temperature. They used a program called VAPSIM (a simulation of vapor pressure measurements of a pure liquid as a function of temperature). This program was developed with the LabVIEW package they allows students to simulate the vapor pressure measurements of a pure liquid with an isoteniscope apparatus. The program can quickly realize modular and easily modifiable programs and mathematically and graphically elaborate the data simulating a real laboratory experiment.

Victor and Gil (2006) describe Computer Simulations of Salt Solubility which provide an animated, visual interpretation of the different solubilities of related salts based on simple entropy changes associated with dissolution: configurational disorder and thermal disorder. These can also help improve students' conceptual understanding of chemical equilibrium before any quantitative interpretation of equilibrium constants is attempted.

Woodfield et.al. (2005) created a set of sophisticated and realistic laboratory simulations in freshman- and sophomore-level chemistry classes and laboratories called Virtual ChemLab. These simulations were for Inorganic Qualitative Analysis, Organic Synthesis and Organic Qualitative Analysis, Fundamental Experiments in Quantum Chemistry, Gas Properties, Titration Experiments, and Calorimetry. In their study, authors provided a detailed assessment of student responses and described the simulation's pedagogical utility. The evaluation of the organic simulation was conducted to document whether the simulation met the objectives of helping students focus on the principles of organic chemistry, how students used the program, and whether they were satisfied with the simulation.

The authors collected both qualitative and quantitative data from questionnaires, interviews, observations, and assessment of performance. The results displayed the significant jump in the number of A's on the final examination. They concluded that students were able to increase their understanding of organic chemistry more than in previous semesters and terms because of their higher exam scores. Students liked how the organic simulation saved time and looked realistic. Students said that the organic simulation was valuable because it helped improve their problem-solving ability and reinforced chemistry principles they learned previously. Students believed they better understood the chemistry from the combination of experiences they received in the actual and virtual labs. The findings displayed that the organic simulation promoted student learning as demonstrated by observations, improved test scores, and students' self-reports.

Halkides and Herman (2007) introduced Michaelis-Menten Kinetics through simulation. The concept of the steady state is fundamental to enzyme kinetics and the general derivation of the Michaelis-Menten equation assumes that the concentration of the enzyme-substrate complex has achieved steady state (Segel, 1975). Since students have difficulties while learning this, they created a computer tutorial that illustrates the meaning of steady state for the simplest possible case (Michaelis-Menten Software, 2006). In their lectures, they introduce the Michaelis-Menten equation and graph before giving its derivation and then discuss the concepts of the pre-steady state and the steady state in the classroom prior to students working through the tutorial. They give the students a hardcopy of the tutorial and access to a computer on which this program and a spreadsheet program are loaded. Students were asked a number of questions after taking the tutorial. The responses indicated that the students had a better grasp of the term "steady state" and enzyme kinetics. The authors concluded that the determination of kinetic parameters might be especially useful for students who would not otherwise be exposed to saturation enzyme kinetics in a biochemistry laboratory class.

In conclusion simulation experiments can be used for various goals. They can be used for strengthening traditional applications, regulating learning for individual learning preferences (this is one of the learning principles), conducting experiments which are dangerous and have harmful effects on the environment and also teaching students some difficult concepts. They give unlimited repetition opportunity.

### **Why do we need simulations?**

In this study, a computer assisted teaching material has been developed for university level. This material has been planned to use in Analytical Chemistry Course content in the subject of quantitative methods. This teaching material has been developed by using Flash program and consisted of animations and simulations related to the quantitative determination of chloride ion by Volhard Method. Even though the quantitative determination of chloride ion by Volhard Method could be conducted in the laboratory setting, this experiment has been prepared by using simulations to give students the opportunity to repeat the experiment steps when they want, to control the each step, observing the changes on the equivalence point better. In addition it is environmental friendly simulation experiment by considering insufficient safety cautions in laboratory or students' insufficient information about safety in laboratory, and the hazardous effects of the chemicals which used in the experiment on the environment.

The risk information about the chemicals which used for the quantitative determination of chloride ion by Volhard Method has been given below (<http://www.jtbaker.com> 14. 05. 2008).

#### **Hazards Identification of Potassium Permanganete**

##### **Emergency Overview**

**Danger! Strong oxidizer. Contact with other material may cause fire. Corrosive. Causes burns to any area of contact. Harmful if swallowed or inhaled.**

##### **Toxicological Information**

**Investigated as a mutagen, reproductive effector. Oral rat LD50: 750 mg/kg.**

#### **Hazards Identification of Potassium Thiocyanate**

##### **Emergency Overview**

**Warning! Harmful if swallowed or inhaled. Causes irritation to skin, eyes and respiratory tract.**

##### **Toxicological Information**

**Oral rat LD50: 854 mg/kg. Investigated as a mutagen, reproductive effector.**

#### **Hazards Identification of Silver Nitrate**

##### **Emergency Overview**

**Poison! Danger! Corrosive. Causes burns to any area of contact. May be fatal if swallowed. Harmful if inhaled. Strong oxidizer. Contact with other material may cause fire.**

##### **Toxicological Information**

**Oral rat LD50: 1173 mg/kg. Irritation data, rabbit, std Draize: eye: 1 mg, severe. Investigated as a tumorigen, mutagen and reproductive effector.**

#### **Hazards Identification of Ferric Ammonium Sulfate**

##### **Emergency Overview**

**Caution! May cause irritation to skin, eyes, and respiratory tract.**

##### **Toxicological Information**

**No LD50/LC50 information found relating to normal routes of occupational exposure. Investigated as a mutagen.**

#### **Hazards Identification of Nitric Acid**

##### **Emergency Overview**

**Poison! Danger! Strong oxidizer. Contact with other material may cause fire. Corrosive.**

**Liquid and mist cause severe burns to all body tissue. May be fatal if swallowed or inhaled.**

##### **Toxicological Information**

**Nitric acid: Inhalation rat LC50: 244 ppm (NO<sub>2</sub>)/30M; investigated as a mutagen, reproductive effector. Oral (human) LD50: 430 mg/kg.**

## METHOD

### Volhard Method

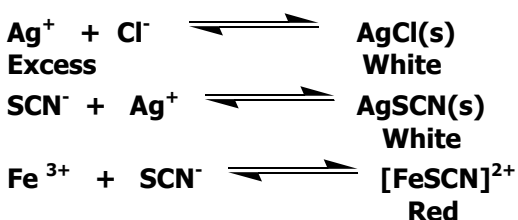
Volhard method in which complex indicator used was developed by a German chemist Jacob Volhard in 1874. In this study, conducting Volhard method, the indicators used in the experiment, the color changes of the indicators at the equivalent point have been presented to the students by using Macro Media Flash 6 program.

This method uses a back titration with potassium thiocyanate to determine the concentration of chloride ions in a solution. This method is first developed for the determination of the concentration of  $\text{Ag}^+$ , but the modified form of the method is suitable for the determination of the concentration of halogen ions. Since the medium is acidic by using  $\text{HNO}_3$ , it prevents the harmful effects seen in other methods in which oxalate, arsenate and carbonate are used. Because these ions form silver salts with poor solubility, but in acidic mediums these salts are not formed.

In this method, the concentration of silver ions can be determined directly and also using back titration the concentration of halogen ions can be determined. To attain this goal, an excess volume of a standardized silver nitrate solution is added to the solution containing chloride ions. The  $\text{Cl}^-$  is precipitated as  $\text{AgCl}$  and then  $\text{AgCl}$  is isolated. Excess of  $\text{Ag}^+$  is back titrated with  $\text{SCN}^-$ . The determination of chloride ions by this method requires great attention since solubility of silver bromide is stronger than silver iodide.

In Volhard method,  $\text{Fe}^{3+}$  ion from  $\text{NH}_4\text{Fe}(\text{SO}_4)_2$  acts as an indicator. When all the silver ions have reacted with  $\text{SCN}^-$ , the slightest excess of thiocyanate ions reacts with  $\text{Fe}^{3+}$  to form a dark red complex.

The equations of the reactions in the determination of the concentration of chloride ions:



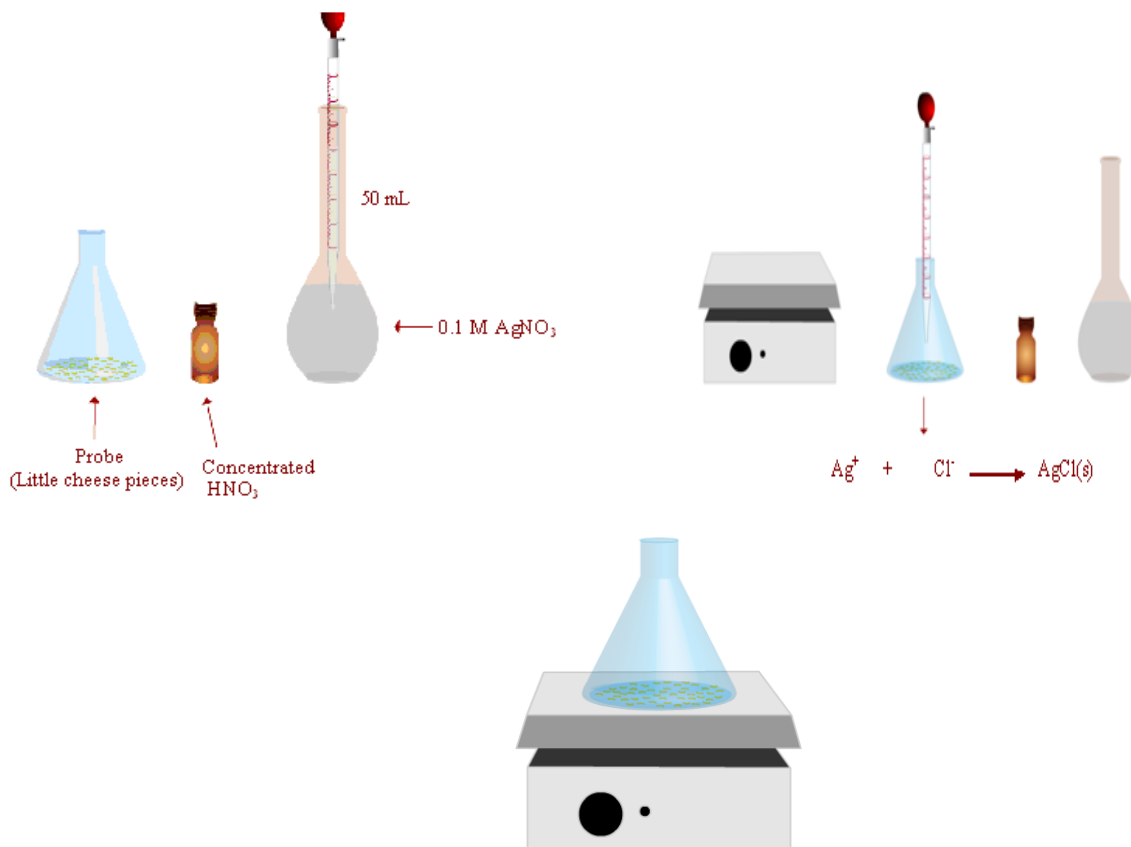
In the titration, the acid medium is necessary to prevent the precipitation of  $\text{Fe}^{3+}$  ions as their hydrated oxides.

### Evaluation of the Educational Experiment

The most important application of Volhard method is the determination of halogen ions directly. For this reason, a student experiment in which the concentration of chloride ions in a cheese probe is determined has been designed. The prepared experiment has been presented to the students with a simulation by using Macro Media Flash 6 program. The prepared simulations can be seen on <http://www.akinkaplan.com.tr/chemistry>

### Preparing the Sample

In this experiment, 6.1632 g cheddar cheese has been grated into small pieces and put into a 500 ml erlen Meyer. 50 mL of 0.1 M  $\text{AgNO}_3$  solution, 20 mL concentrated  $\text{HNO}_3$  and 100 mL of distilled water have been added. This solution has been heated

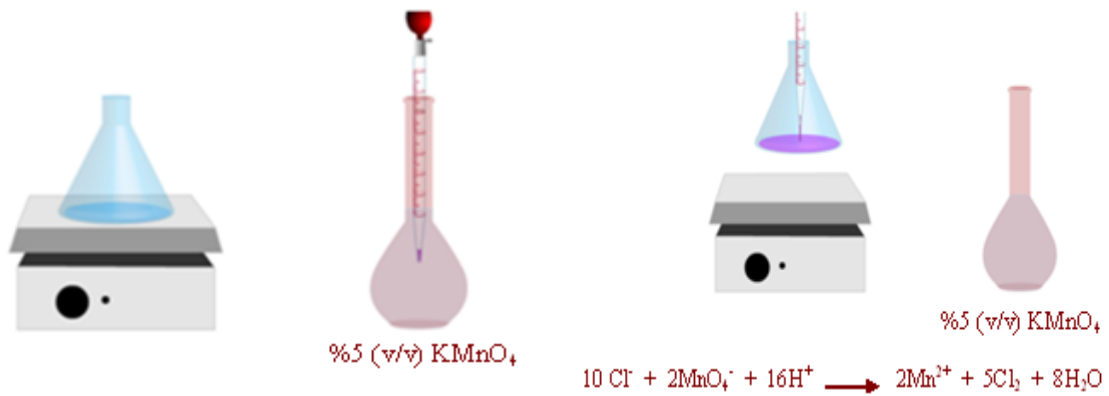


The solution is heated until it boils on the hotplate

**Figure 1:**  
The required materials in the experiment

Volhard method requires strong acid medium and this requirement provides an advantage for this method when compared with other titrimetric methods which analyze halogens since ions like carbonate, oxalate and arsenate have interference effect. As the solution boils, 5 mL of 5% (v/v)  $\text{KMnO}_4$  solution has been added and the cheese particles are completely digested. After the addition of  $\text{KMnO}_4$  solution, a very smelly reaction has occurred. By the addition of  $\text{KMnO}_4$  solution a purple color has been appeared. The boiling of the solution has been continued until the purple color disappeared. And then, another 5 mL of  $\text{KMnO}_4$  solution has been added into the solution. Because of  $\text{KMnO}_4$  addition, a bad smell has occurred.

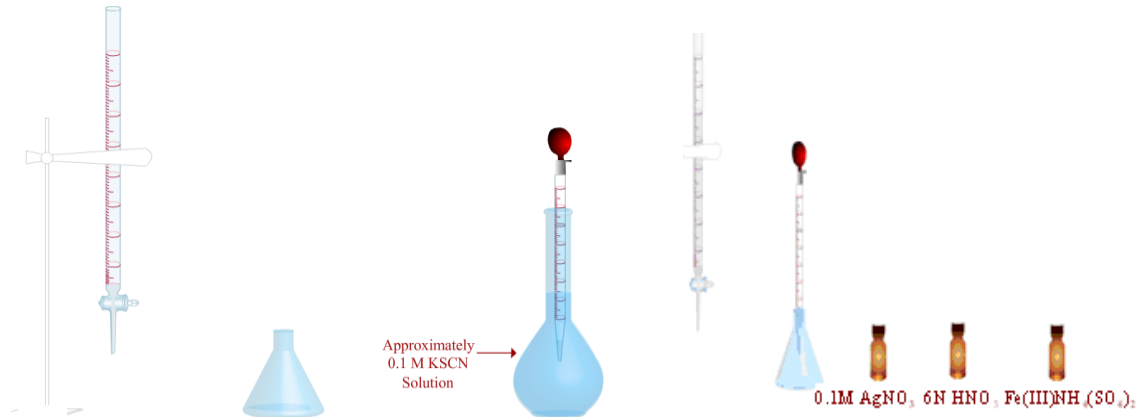
Adding of  $\text{KMnO}_4$  solution has been continued until all the cheese particles are completely digested. As a result of these procedures, a white precipitate of  $\text{AgCl}$  has formed. After cooling the solution, it has been filtered and the solid residue has been washed with distilled water for two or three times and then the filtrate has been put into a flask of 50 mL.

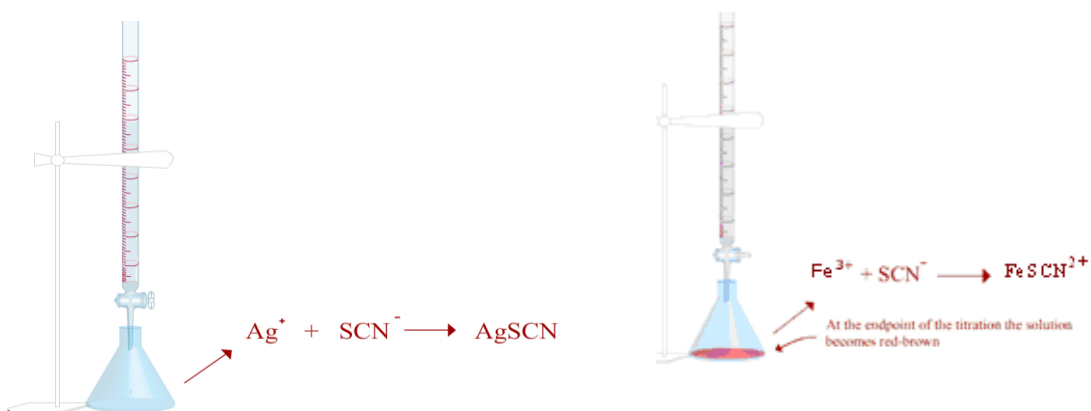


**Figure 2:**  
The preparation steps of the sample

### The procedure of the Experiment

In Volhard method, silver ions have been titrated with a standard thiocyanate solution. Since  $\text{KSCN}$  is a secondary standard matter, the solution of  $\text{KSCN}$  cannot be prepared directly. Therefore, approximately 2.45 g of  $\text{KSCN}$  has been dissolved in a few mL of distilled water and then much more water has been added until 250 mL.

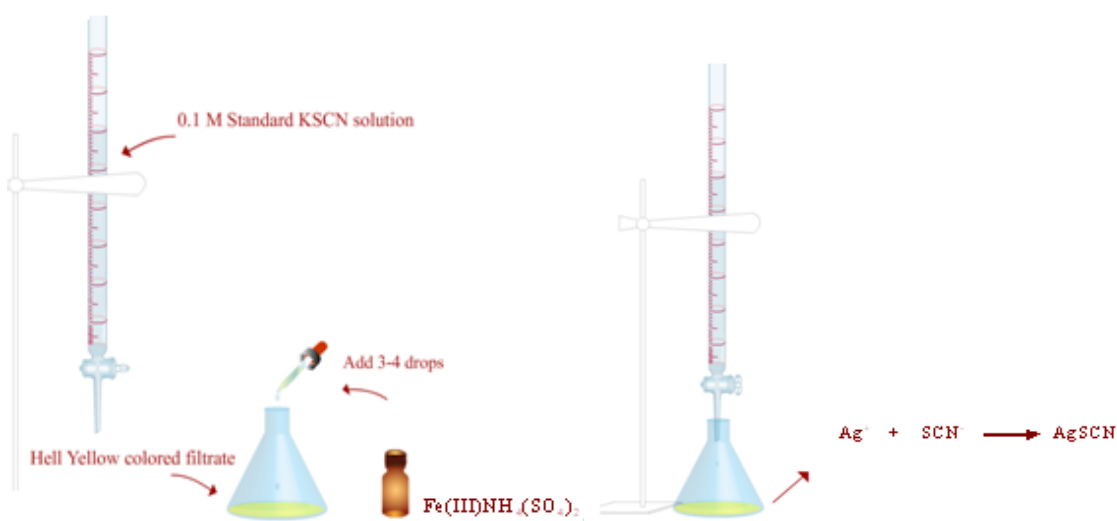




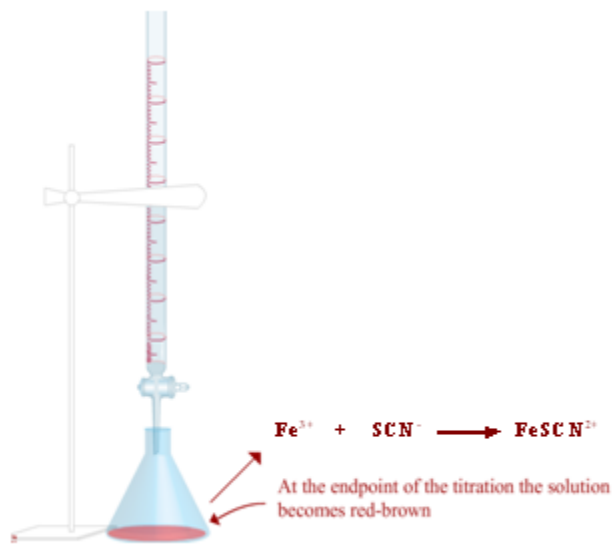
**Figure 3:**  
The steps of the standardization of KSCN solution

Standardized  $\text{AgNO}_3$  solution is poured into an erlen meyer and then some more distilled water has been added until 100 mL. 5 mL of 6 M  $\text{HNO}_3$  and 5 mL of  $\text{NH}_4\text{Fe}(\text{SO}_4)_2$  solution have been added.  $\text{Fe}^{3+}$  ion acts as an indicator. With the excess of thiocyanate ions, the color of the solution turns into red. By using the volume of the KSCN and the concentration of  $\text{AgNO}_3$  solution, the concentration of KSCN has been calculated.

Following the determination of the concentration of KSCN solution, 5 mL of Iron (III) ammonium sulfate indicator has been added into the sample solution and the solution has been shaken strongly. The unreacted silver ions have been titrated with standardized solution of KSCN until the dark red-brown color due to the ferric thiocyanate complex appears for one minute.







**Figure 4:**  
The steps of the titration of the sample

## CONCLUSIONS AND DISCUSSION

An efficient education environment does not contain only text reading and lecturing. Students learn better by thinking, questioning and practicing the given information. For this reason, it has been thought that the simulations have great contributions to the teaching and learning process (Bayrak, 2008).

In the study, teaching the Volhard method through simulations enables students to comprehend the topic in a more visual, interesting and effective way. By this way, the learning process becomes more visual and effective. With the help of simulations, students have opportunity to see the practical usage of the knowledge they learn and also simulations help teachers to lecture more effectively and present the experiment many times they require. Simulations can be used as education tools that support the teaching and they make the learning easier. Victor and Gil' (2006) simulation about the solubility of the salts is a good example for this. In that simulation, students can see the particles (ions and molecules) symbolically. They also see the spaces between the ions and molecules in the solution process. The simulation makes the solubility of the salts visual for the students. By this way make the concepts more concrete.

Each student can follow the simulation steps according to his or her learning speed. This opportunity supported by the simulations will increase student achievement. Additionally, education with simulations would support students' problem solving skills and it contributes to meaningful learning. There are some studies in the literature which aim to make students free in their own learning. For example, Meyer and Sargent (2007) developed a computer visualization package called SymmetryApp to help student learn symmetry and group theory. By using this program students learn in an interactive environment, they make mistakes, but they learn from their own mistakes.

Using simulations in chemistry education would contribute to prevention from the hazardous effects of chemicals as well as the protection of the environment. Belleti et. al. (2006) developed a simulation experiments by considering hazardous effects of the chemicals on students' health. In the real experiment, the vapor pressure of a pure liquid has been measured a function of temperature. This experiment contains some chemical and electrical hazards. The required pure liquids for the experiment are volatile, and can be flammable and contain chemical poisons. For this reasons they are dangerous for the students. Because of these hazard risks, they developed a simulation of this experiment. Laboratory is a vital component of chemistry education; however, in the absence of the required chemicals or the suitable environment for the experiment, using simulations would be a great way facilitating the responsibilities of both the teacher and the learner.

Volhard is one of the methods to be considered as important in chemistry courses and laboratories. It is an important practical experience for students in the laboratory. As mentioned before, the some of the chemicals in the experiment are harmful for human health and environment. In addition to these harmful effects of the chemicals, if laboratory conditions are not sufficient, this experiment cannot be conducted in student laboratories. In this study, the presented simulation has been prepared by considering these harmful effects and in sufficient laboratory conditions.

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