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A Teaching Sequence for Learning the Concept of Chemical Equilibrium in Secondary School Education

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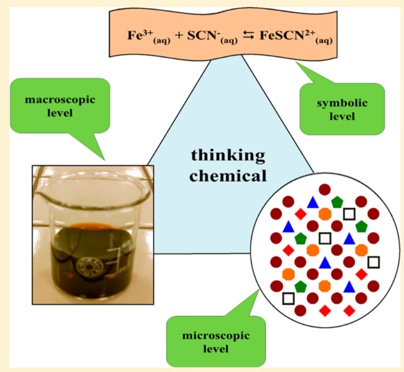
S *Supporting Information*

ABSTRACT: A novel didactic sequence is proposed for the teaching of chemical equilibrium. This teaching sequence takes into account the historical and epistemological evolution of the concept, the alternative conceptions and learning difficulties highlighted by teaching science and research in education, and the need to focus on both the students' learning process and the knowledge to learn.



KEYWORDS: *High School/Introductory Chemistry, Physical Chemistry, Inquiry-Based/Discovery Learning, Equilibrium, Reactions, Student-Centered Learning*

The concept of chemical equilibrium is a central and complex concept in chemistry. It is considered to be one of the most difficult topics in chemistry education.[1,2] Many authors have investigated students' conceptual difficulties with chemical equilibrium, and the most observed misunderstandings have been summarized by several authors: students fail to distinguish between complete and incomplete chemical transformations;[3−7] they believe that the reverse reaction begins only when the forward reaction ends;[3−7] and students have difficulty to grasp the dynamic nature of equilibrium.[8,9] In addition, students believe that the forward and reverse reactions alternate and exist as distinctly separate events when equilibrium is attained (compartmentalized view of equilibrium)[10,11] or even the reactions are carried out in "distinct compartments".[12,13] Sometimes students believe that the equilibrium concentrations of reactants and products are equal or proportional to the stoichiometric coefficients or fail in predicting the direction to which a system evolves, in order to adapt to changes imposed from outside.[14−17]

The task of a high school teacher should be that of helping students to learn the basic concepts of a discipline. Many researchers in science education believe that learning is meaningful when the acquired knowledge is grafted onto what is already known. If such a connection is not established, learning is not meaningful and is purely mnemonic because it has been acquired passively.[18] The design and testing of teaching and learning activities in the classroom that allow for meaningful learning of the concept of chemical equilibrium should take into account the problems that arose and how they were tackled by early scientists, as there are many similarities between some of the alternative conceptions of students on science topics and the ideas of early scientists.[19] The study of the history of chemistry can help teachers design learning activities to help students understand the real nature of science and the complexity of the development of scientific knowledge and to improve their critical thinking skills.[20−24]

Our teaching and learning sequence of chemical equilibrium for secondary school students is based on the following six sections:

- Incomplete chemical transformation
- Opposite chemical transformation
- Systems in dynamic chemical equilibrium
- The evolution of systems (I): from a state of non-equilibrium to a state of equilibrium
- The equilibrium constant
- The evolution of systems (II): from a state of equilibrium to another state of equilibrium.

In this paper we present and discuss the results of the first three sections: from the idea of chemical reaction as a process that proceeds in only one direction to the concept of a system in chemical equilibrium involving two opposite reactions occur-

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ring simultaneously and with the same rate. In a future paper, we will report on the latter three sections of the teaching and learning sequence.

On the basis of previous studies on students' conceptions about chemical equilibrium and the main obstacles to learn it in an appropriate manner,[1−17] we present problematic questions to the students in our teaching sequence that enable students to deal with obstacles and tackle them through a cooperative work of knowledge construction from the whole class. We adopted a teaching strategy from both the epistemological and pedagogical points of view. From the epistemological point of view, the teaching approach refers to the strategy of scientific research in which scientists define a problem, represent it by means of a model, formulate hypotheses, and design a research plan to verify the reasonableness of the adopted model.[25] From the pedagogical point of view, we refer to the allosteric model, according to which learning is a process of construction and reconstruction of the students' mental structure, during which new ways of thinking are tested even with risks to make mistakes.[26,27]

■ DIDACTIC SEQUENCE IN THE CLASSROOM

The proposed learning sequence was designed for students familiar with the concept of a chemical reaction; that is, the reacting substances produce new substances and the process is represented by a model involving a single chemical reaction that proceeds in one direction. The active engagement of students is accomplished in two ways: through discussions and with appropriate experiments. Problematic questions are presented that must be solved by small groups of students, with the help of the teacher, who guides their reasoning through appropriate questions.[25] At the end of the discussion, the teacher proposes a novel concept to the students.

The didactic sequence presented to the students is organized through a collection of worksheets (WS), arranged in a precise order and containing problematic questions and laboratory activities. The teaching sequence was carried out during the 2010−2011 and 2011−2012 school years with three classes of 17-year-old students of a secondary school of scientific and technological lyceum, for a total of 54 students. On average, the time for all activities was 12 lessons of 50 min each, for a total of 10 h. All the students should have studied the following topics: particle model of matter, physical and chemical transformations, stoichiometry, periodic table, chemical bonds, IUPAC nomenclature, traditional nomenclature, ionic dissociations, ionizations, and chemical kinetics.

■ INCOMPLETE CHEMICAL REACTIONS

A system has undergone an incomplete chemical transformation if it is characterized by the presence of all the involved substances (reactants and products) and by the immutability of their concentrations over time. The latter condition is crucial; in fact, the mere presence of all the species involved could be explained by the students assuming that the chemical transformation "*is still ongoing, because it is very slow*". To avoid this type of response, it is necessary that students clearly understand the difference (i) between the chemical reactions in progress and those ended and (ii) between complete chemical reactions ended and those ended but incomplete (in equilibrium) (Figure 1). The overall task of the first section is to help students recognize and distinguish these features of the chemical reactions from an experimental point of view. Five activities were presented and carried out by the students to aid their understanding.

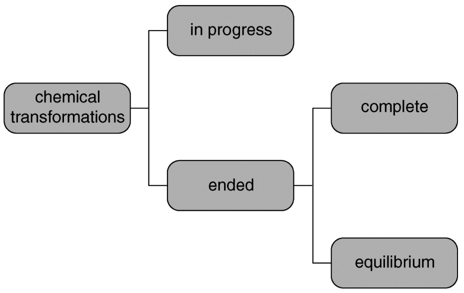

Figure 1. General subdivision of chemical transformation.

Activity 1. Experimental Situation Proposed (WS1 in the Supporting Information)

An aqueous solution of hydrogen chloride is added to an aqueous solution of sodium thiosulfate, affording gaseous sulfur dioxide, an aqueous solution of sodium chloride, a precipitate of solid sulfur, and liquid water.

By mixing the two solutions, colloidal sulfur (a pale yellow suspension) formed and the system became cloudy. Students were asked to write the appropriate reaction scheme, to perform the chemical reaction, and to record, arguing appropriately, when they considered the reaction finished. The majority of the students, 93%, wrote the proper reaction scheme, and the remaining 7% forgot to indicate the physical state of reagent and products or did not balance correctly:

$$Na_2S_2O_{3(aq)} + 2HCl_{(aq)} \rightarrow SO_{2(g)} + 2NaCl_{(aq)} + S_{(s)} + H_2O_{(l)}$$

All students indicated that a reaction could be considered finished when no changes were perceived at a macroscopic level. Examples of students' answers were "we have no more variation of color", "any change no longer occurs", and "ended when no more changes occur, then a dust remains suspended and the system is yellowish and opaque".

Next, students were asked to model the evolution of the system through a microscopic representation of the initial state, during the transformation, and when it is finished. The goal of the delivery was to assess the possible presence a compartmental conception of chemical reactions. A "correct" representation had the following features:

(a) each type of molecule represented by a special icon;
(b) each type of ion in solution represented by a special icon and correct representation of the ions;
(c) icons near and disorderly for the representation of liquids;
(d) icons near and arranged neatly for the representation of solids;
(e) absence of compartmentalization between reactants and products.

An "acceptable" representation had four of the features, a "partially acceptable" representation had three, and a "not acceptable" representation had two of the features (see Figure 2).

None of the representations contained compartmentalization between reactants and products. This result could indicate the students were accustomed, since the first year of high school, to use the particle model of matter to represent homogeneous

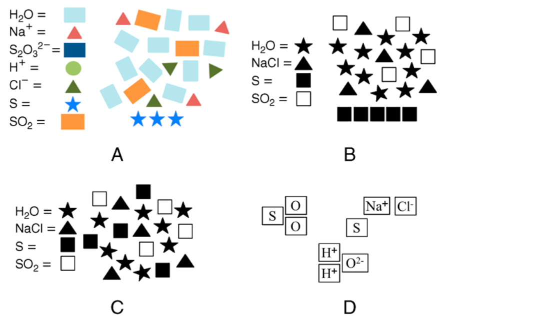

Figure 2. Examples of students' representations of the final state of the activity (WS1): (A) correct (2%), (B) acceptable (38%), (C) partially acceptable (24%), and (D) not acceptable (36%). The evaluation criteria are indicated in the text.

mixtures, heterogeneous mixtures, elements, and compounds in different states of matter (solid, liquid, and gaseous). The discussion of the first part of the worksheet ended quickly because the students had no difficulty in indicating that a reaction could be considered finished when no changes were perceived at a macroscopic level. During the discussion of the second part of the worksheet, some students thought to represent species in ionic form, but for simplicity they did not. The teacher explained to the students that the representation must include all the features described previously. The conclusion proposed by the teacher was *a chemical transformation can be considered finished when the amount of a product is constant.*

Activity 2. Experimental Situation Proposed (WS2 in the Supporting Information)

An aqueous solution of potassium permanganate is mixed with an aqueous solution of sodium oxalate and one of sulfuric acid. Manganese(II) sulfate, potassium sulfate, sodium sulfate, carbon dioxide (all in aqueous solution), and liquid water are obtained.

By mixing the three solutions, a clear colorless mixture was obtained that indicated that the permanganate initially present (which provided a dark purple color of its solution) had been completely consumed. Students were challenged to write the appropriate reaction scheme, to perform the chemical reaction, and to record, arguing appropriately, when they considered the transformation finished. Students succeeded in correctly setting the reaction scheme but were not able to balance it. In fact, this is a redox reaction that needs a balancing technique they did not yet know, and this allowed the teacher to provide the first indications for balancing schemes of redox reactions.

$$2KMnO_{4(aq)} + 5Na_2C_2O_{4(aq)} + 8H_2SO_{4(aq)}$$
$$\rightarrow 2MnSO_{4(aq)} + K_2SO_{4(aq)} + 5Na_2SO_{4(aq)} + 10CO_{2(aq)}$$
$$+ 8H_2O_{(l)}$$

Again, the use of a chemical reaction involving a color change helped students to argue properly when a reaction was finished. All students had no difficulty indicating that reaction was not finished until they perceived changes at the macroscopic level. Examples of students' responses were "*it is not finished because the color is still changing*" and "*every few minutes, the color of the solution continues to change*". Likewise, no student had difficulty indicating that reaction could be considered finished when, at a macroscopic level, changes were not perceived.

Next, students were asked to model the evolution of the system through a microscopic representation of the initial state, during the transformation, and when it is finished (Figure 3).

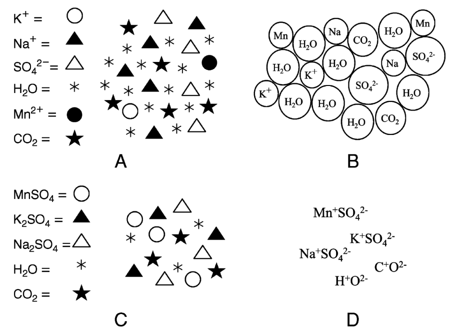

Figure 3. Examples of students' representations concerning the final state of the activity (WS2): (A) correct (31%), (B) acceptable (18%), (C) partially acceptable (13%), and (D) not acceptable (38%). The evaluation criteria are indicated in the text.

Also, in this case, no representation had compartmentalization between reactants and products. In the final discussion, the teacher pointed out that ions were present in solution. After sharing an appropriate way to represent the system in the three states required, the teacher suggested a general conclusion: *a chemical transformation can be considered finished and complete if at least one reactant is completely consumed.*

Activity 3. Experimental Situation Proposed (WS3 in the Supporting Information)

Granular calcium carbonate is introduced in an aqueous solution of hydrogen chloride. Calcium chloride in aqueous solution, gaseous carbon dioxide, and water are obtained.

The worksheet was used to test the degree of concept acquisition in the previous activities. All of the students wrote the reaction scheme correctly, and 96% of the students indicated that as long as there is an evolution of gas, properly referred to as carbon dioxide, the reaction could not be considered concluded, and 71% took into account the simultaneous presence of calcium carbonate.

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$

Examples of students' responses were "*the development of CO_2 in a gaseous state indicates that the reaction is taking place*" and "*there is still the formation of CO_2 as a gas and there is still the presence of $CaCO_3$, which is reacting*". Again, students were asked to model the evolution of the system through a microscopic representation of the initial state, during the transformation, and when it is finished. No representation had compartmentalization between reactants and products, but some students continued to show problems in the representation of the ions in the "aqueous phase" (see an example in Figure 4).

During the discussion, a student said "*no more CO_2 is formed, but I'm not sure that $CaCl_2$ does not continue to form*". Another student replicated "*if a product continue to form, also the other will form, and if one is no more produced, then also the other will not be produced*". After calcium carbonate was completely consumed, the teacher asked students to indicate a way to detect the eventual presence of hydrogen chloride. A student answered promptly "*additional $CaCO_3$ can be added; if solution produces bubbles there is still HCl*". Another student proposed "*and if I use the universal pH indicator paper?*" but he immediately added "*however also the CO_2 reacts with water to*

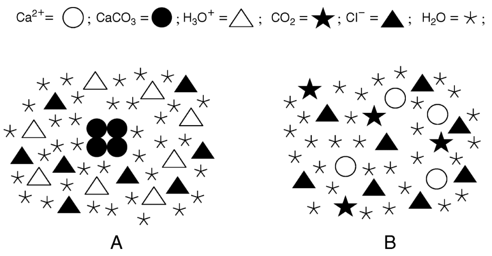

Figure 4. Example of correct representation related to the WS3: (A) initial state and (B) final state.

form an acid, and so the use of the universal pH indicator paper is not a good solution".

By organizing the learning environment in such a way, students were encouraged to ask questions and to mobilize their knowledge in order to seek answers. We think that a teaching practice that is only transmissive cannot get the same results. The conclusion proposed by the teacher was *a chemical transformation can be considered finished and complete if at least one reactant is completely consumed and the amount of a product is constant.*

Activity 4. Experimental Situation Proposed (WS4 in the Supporting Information)

An aqueous solution of iron(III) nitrate is mixed with an aqueous solution of potassium thiocyanate, to afford an aqueous solution of iron(III) thiocyanate and potassium nitrate.[1,22,28]

Students were asked to write the appropriate reaction scheme in the net ionic form, to carry out the chemical reaction, to write down what happens, and to indicate when and why they considered the chemical reaction finished and complete. Most of the students, 94%, correctly wrote the reaction scheme and noted when chemical reaction was concluded. The remaining 6% forgot to indicate the physical state of reagent and products or did not balance correctly. Fifty-two percent of the students wrote that the reaction was instantaneous.

$$Fe^{3+}{}_{(aq)} + SCN^{-}{}_{(aq)} \rightarrow FeSCN^{2+}{}_{(aq)}$$

Similar to previous activities, students were asked to model the evolution of the system, from the microscopic point of view, at the end of the reaction. Such delivery was revised appropriately, after the subsequent empirical evidence. No compartmentalized representation between reactants and products was observed, but still 15% of students did not represent the ions in the "aqueous phase". On the whole, the representations were acceptable (for the evaluation criteria refer to the description in Activity 1).

A second experimental situation was proposed: *a few crystals of iron(III) nitrate are added to a portion of the previous system.* From comparison with a sample of the starting system can be seen the intensification of the red color of the solution. The students, after having noted the empirical event, were invited to provide an explanation. A third experimental situation was proposed: *a few crystals of potassium thiocyanate are added to another portion of the previous system.* From comparison with a sample of the starting system can be seen the intensification of the red color of the solution. The students were invited to supply an explanation. All students realized that in both situations there was an intensification of the red color of solution.

During the discussion, it was noted that the explanations were confusing (*"No precipitate formation", "the concentration change"*). One group suggested that the intensification of the red color depended on the added substances and not the formation of a greater amount of "blood-red" compound (*"The ferric nitrate added to the initial solution has increased its color", "given that in ferric nitrate there is iron, it has increased the color of the solution"*). In another group, students thought that *"iron(III) nitrate reacted with excess KSCN and therefore there is more $FeSCN^{2+}$"; "the potassium thiocyanate reacted with excess $Fe(NO_3)_3$ and therefore there is more $FeSCN^{2+}$"; "on the basis of the outcome of previous experiments, we have hypothesized that in solution an excess of the reagents was present, and then the reaction was concluded but not complete"*; and *"the transformation was not complete because there were still excess of Fe^{3+} and SCN^- reagents"*. In addition, two students expressed their difficulty in accepting the idea that there were transformations concluded in which both reactants are present and that *"an excess of both reagents cannot be present", "if I let for longer time solution A the red color is intensified?"*, and *"how come both reagents are in excess?"*. These statements indicated that it is difficult to accept the idea of incomplete transformation. The teacher asked the students to reflect on the empirical evidence and to recognize that it led to the belief that both reagents are in excess. Students continued to be skeptical, so the teacher invited them to consider the idea of incomplete transformation as a simple working hypothesis. Then, only if they deemed it appropriate they could change their mind. The conclusion proposed by the teacher was *a chemical transformation can be considered concluded and incomplete if the amount of reactants and products is constant and none of the reactants is completely consumed.*

Activity 5. Experimental Situation Proposed (WS4 in the Supporting Information)

An aqueous solution of silver nitrate is mixed with an aqueous solution of iron(II) sulfate, affording solid silver, iron(III) nitrate, and iron(III) sulfate in aqueous solution.

In this activity students were also asked to perform the reactions for ion recognition [iron(II), iron(III), and silver(I)]. It was similar to previous activity (in both cases there were incomplete chemical reactions) and tested what students had actually learned in the previous activities and also introduced, even in sketchy form, the issue of recognition of chemical species in analytical chemistry.

$$3AgNO_{3(aq)} + 3FeSO_{4(aq)}$$
$$\rightarrow 3Ag_{(s)} + Fe(NO_3)_{3(aq)} + Fe_2(SO_4)_{3(aq)}$$

Written in net ionic form:

$$Fe^{2+}{}_{(aq)} + Ag^{+}{}_{(aq)} \rightarrow Ag_{(s)} + Fe^{3+}{}_{(aq)}$$

Except for a group of students, all others noted and wrote on their worksheet that reaction was not complete because none of the reactants was completely consumed. Students who were skeptical during the previous activities about the presence of both reagents then wrote that the transformation is incomplete because *"we have demonstrated the presence of excess reactant ions"*, and *"we have shown that in solution there were still reagents"*. The conclusion proposed by the teacher was *a chemical transformation can be considered concluded and incomplete if the amount of reactants and products is constant and none of the reactants is completely consumed.*

OPPOSITE CHEMICAL REACTIONS

It was necessary to present experimental situations that enable the students to recognize and associate two opposite chemical transformations. This can later facilitate the proper conceptualization of systems in dynamic chemical equilibrium. One activity was performed by the students.

Activity 6. Experimental Situation Proposed (WS6 in the Supporting Information)

Water is added to an alcoholic (isopropyl alcohol) solution containing tetrachlorocobaltate(II) complex anions. Hexahydrated cobalt(II) cationic complexes and chloride anions are produced in aqueous solution.[1,22,28]

Students were asked to write the appropriate reaction scheme, to carry out the chemical transformation, to note what was happening, and to propose a microscopic representation of the system in its final state.

$$[CoCl_4]^{2-}{}_{(aq)} + 6H_2O_{(aq)} \rightarrow [Co(H_2O)_6]^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)}$$

From an empirical point of view, the change from blue ($[CoCl_4]^{2-}{}_{(aq)}$) to pink ($[Co(H_2O)_6]^{2+}{}_{(aq)}$) color was evident. The students had no difficulty in properly writing the reaction scheme and acknowledging that there was a chemical reaction. In the representations of the system at the microscopic level, 33% of students did not take into account the presence of the solvent, isopropyl alcohol. The goal of this activity was not to identify the transformations as incomplete (as made previously) but to recognize when two chemical transformations are opposite.

The second experimental situation was proposed: *about 10 cm^3 of aqueous solution of sodium chloride is added, drop-by-drop, to the previous system.* Students were asked to write down what happens, to propose a microscopic representation of the final system, and to write the reaction scheme. From an empirical point of view, the change of the system from pink to blue was evident. Although students grasped the change of color, they made many errors both in writing the reaction scheme and in the microscopic representation. Thirty-eight percent of students correctly drew the representation and offered meaningful explanation: "*the blue color is due to the formation of $[CoCl_4]^{2-}$*" and "*the two are opposite chemical transformations*". After a brief discussion, a student proposed that two chemical transformations "*are opposite when the reactants of one are the products of the other and vice versa*". The teacher agreed with such statement and considered it as the general conclusion.

SYSTEMS IN DYNAMIC CHEMICAL EQUILIBRIUM

To help the students to understand the state of chemical equilibrium, an experimental report was proposed in which the yield of a given chemical transformation was not 100%. Based on previous activities, students were able, with relative ease, to understand that a yield lower than 100% can be related to the presence of two opposing reactions that occur at the same speed. One activity was performed by the students.

Activity 7. Experimental Situation Proposed (WS7 in the Supporting Information)

Gaseous phosphorus trichloride reacts with dichlorine gas to produce gaseous phosphorus pentachloride. Experimental reports indicate that, while preparing a mixture in stoichiometric amounts of reagents, if the transformation takes place in a closed system, where the reaction conditions are T = 550 °C and P = 2.2 atm, the yield of chemical reaction is equal to 80%.

Students were first asked to write the appropriate reaction scheme and to draw the microscopic representation of both the initial and the final state (Figure 5). All students correctly wrote the reaction scheme:

$$PCl_{3(g)} + Cl_{2(g)} \rightarrow PCl_{5(g)}$$

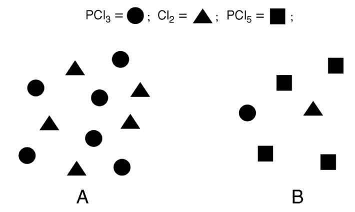

Figure 5. Example of correct representation WS7: (A) initial state and (B) final state.

Seventy-five percent of students correctly represented the initial state, but only 58% were able to correctly represent the final state, that is, with a number of particles, reagents and products, consistent with the yield of reaction. No representation had compartmentalization between reactants and products.

Next, students were asked to indicate at least three reasons to explain why the yield of reaction was not 100%. Many believed that, after a certain time, the energy possessed by the remaining reacting particles was insufficient to cause the reaction, whereas others wrote "*probably PCl_5 either continues to form and to decompose into PCl_3 and Cl_2*", "*the yield is 80% because it is possible that the opposite reaction takes place, thus forming a new reagent*", and "*the opposite reaction $PCl_5 \rightarrow PCl_3 + Cl_2$ occurs*".

During the discussion a student insisted that "*at some point there is not enough energy*" and another denied "*I'm not convinced, in fact the temperature is high and constant.*" The teacher therefore took the opportunity to emphasize that in a system, although it consists of a small number of particles, a certain number of particles always have enough energy to reach the activated complex and to react. Then, students were asked to explain why the concentrations of both reactants and products were constant. During the discussion a student said: "*The speed of the opposite reaction must be equal to that of the direct reaction, because concentrations of reactants and products are constant and the speed with which the reagents are formed is equal to that with which the products are formed*". Finally, the teacher suggested the general conclusions:

- at the end of an incomplete chemical reaction, the system does not suffer any more evolution and is into a state of dynamic chemical equilibrium;
- in a state of dynamic chemical equilibrium, the concentration of reactants and products is constant and different from zero; and
- in a state of dynamic chemical equilibrium, the two opposite reactions occur at the same speed.

HAZARDS

Sodium thiosulfate and calcium carbonate cause irritation to eyes, to skin, and to respiratory and digestive tracts. Hydrogen chloride causes severe respiratory tract, eye, and skin burns, is harmful if inhaled, and is severely corrosive to the eyes. Potassium permanganate, potassium hexacyanoferrate(III), and calcium chloride cause severe irritation to the respiratory tract, digestive tract, eyes, and skin. Sodium oxalate causes central nervous system effects and severe respiratory and digestive tract irritation with possible burns and causes severe skin irritation. Sulfuric acid causes burns to eye, skin, digestive tract, and respiratory tract. Iron(III) nitrate and iron(II) sulfate cause severe irritation to eyes, skin, and respiratory tract, with possible burns. Potassium thiocyanate is harmful by inhalation, in contact with skin, and if swallowed, and contact with acids liberates very toxic gas. Silver nitrate and cobalt(II) chloride hexahydrate causes burns by all exposure routes. Cobalt(II) chloride hexahydrate has possible carcinogenic effects. Isopropyl alcohol causes eye and respiratory tract irritation; breathing vapors may cause drowsiness and dizziness; flammable liquid and vapor. All students must wear safety eye protection and gloves and lab coats. They must follow the general safety precautions required in chemistry laboratories. All reagents and solutions should be handled in a well-ventilated fume hood. Students should also examine the MSDS sheets for the specific hazards associated with the chemicals used in the experiment. All waste must be collected in a designated waste container and disposed properly according to safety regulations.

■ CONCLUSIONS

Our aim was to design and test a teaching sequence that allowed students to participate actively in learning the concept of dynamic chemical equilibrium. The selection and structuring of problematic questions presented to students was based on both historical and epistemological analysis of the concept of chemical equilibrium and on the results of didactical research concerning the misconception and learning difficulties related to chemical equilibrium. The teaching sequence described here was tested on 54 students. If we consider the answers the students gave during the classroom activities and their participation in the activities, it is reasonable to think that, overall, the teaching approach allowed them to actively learn. However, to check if the teaching sequence allowed students to avoid misconceptions and overcome learning difficulties, it is necessary that other teachers would be interested in experiencing our teaching sequence. The didactical sequence described is intended to be used in a school context. Teachers who want to use our proposal can choose other chemical reactions that are better suited to their work situation. We know that in different situations students may show difficulties we have not foreseen and that require much attention, so that further adaptations may be necessary.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed student handout; instructor notes with background, procedures, experimental setup. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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