

Implementing an Equilibrium Law Teaching Sequence for Secondary School Students To Learn Chemical Equilibrium

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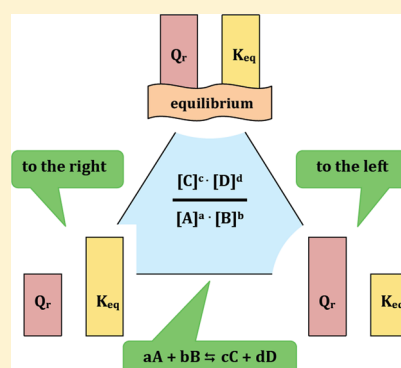
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Supporting Information

ABSTRACT: A didactic sequence is proposed for the teaching of chemical equilibrium law. In this approach, we have avoided the kinetic derivation and the thermodynamic justification of the equilibrium constant. The equilibrium constant expression is established empirically by a trial-and-error approach. Additionally, students learn to use the criterion of comparison between equilibrium constant and reaction quotient to predict the direction of reaction. The teaching sequence takes into account the alternative conceptions and learning difficulties highlighted by teaching and research in science education and the need to focus on both the students' learning process and the knowledge on how to learn.



KEYWORDS: High School/Introductory Chemistry, Equilibrium, Reactions, Student-Centered Learning, Inorganic Chemistry, Misconceptions/Discrepant Events, Learning Theories

INTRODUCTION

Students' misunderstandings and conceptual difficulties on chemical equilibrium have been reviewed by several authors: students fail to distinguish between complete and incomplete chemical transformations;^{1–5} they believe that the reverse reaction begins only when the direct reaction ends;^{1–5} and they have difficulty with grasping the dynamic nature of equilibrium.^{6,7} Furthermore, students believe that forward and reverse reactions alternate and exist as distinctly separate events when equilibrium is attained (compartmentalized view of equilibrium)^{8,9} or even that they are carried out in “distinct compartments”.^{10,11} In previous work,¹² we have presented and discussed a sequence of activities that try to solve these problems. In addition, the scientific literature on teaching research indicates that many students believe that the equilibrium concentrations of reactants and products are equal or proportional to the stoichiometric coefficients or fail in predicting the direction of reaction, to adapt to changes imposed from outside.^{3,13–15} In this work, we report and discuss a sequence of teaching activities designed to face these learning difficulties.

The teaching of chemical equilibrium in secondary schools usually starts from a kinetic qualitative approach.¹⁶ Several authors suggest that such an approach may lead students to develop some misconceptions,¹⁷ for example, a compartmental vision of chemical systems in the state of equilibrium. However, by organizing the educational activities in an appropriate

manner, the concept of reaction rate can be conveniently used to attain the concept of chemical equilibrium, thus facilitating student learning. It is the dynamic aspect to characterize the state of chemical equilibrium; hence, we believe that there is no convincing way to introduce it unless by starting from the concept of reaction rate. To prevent students from forming a static view of chemical equilibrium, it is necessary to conceptualize that at equilibrium, there are two opposite reactions occurring with the same rate. This is essential to explain the constancy of reactants and products concentrations at equilibrium.

All of these considerations have been tackled in a previous work,¹² where we have introduced a novel teaching sequence for learning the concept of chemical equilibrium applied to students of secondary school. The whole sequence is composed by the following 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.

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. While in the previous paper we have discussed in detail the results of the first three sections (a), (b), and (c) of the sequence,¹² here we report on the results of sections (d) and (e): from the idea of dynamic chemical equilibrium to the concept of equilibrium law. The next paper, which is ongoing, will be concerned with the last section (f) of the teaching sequence.

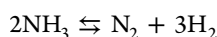
Reaction Rate and Number of Particles

The introduction of chemical equilibrium without the use of the reaction rate concept may generate particularly serious conceptual problems. In fact, in the course of our research, we have found that several students characterized the dynamic equilibrium with expressions such as “at the state of equilibrium, in a given time, the same number of particles that is transformed from reactants to products is transformed from products to reactants”, “at equilibrium, the same number of particles is transformed from products to reactants and vice versa”, and “at the state of equilibrium, an equal number of reagents is transformed into products, and an equal number of products becomes reagents”.

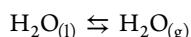
Similar expressions show that talking about the dynamism of the system in terms of the number of particles, without any explicit reference to the rate of reaction, can lead to significant conceptual errors. If we reflect on the following reaction scheme



on the basis of the above statements, if 100 molecules of PCl_5 decompose at equilibrium, we could hypothesize that at the same time, a total of 100 molecules of both PCl_3 and Cl_2 react with each other. If this occurs, the concentrations of reactants and products do not keep constant. Indeed, considering the stoichiometry of the reaction, by decomposition of 100 molecules of PCl_5 , 100 molecules of PCl_3 and 100 molecules of Cl_2 will form, but from a total of 100 molecules of products that react to each other, for simplicity we assume 50 of PCl_3 and 50 of Cl_2 , only 50 molecules of PCl_5 will form. This would result in a decrease of phosphorus pentachloride in the system and thus to a change in its concentration. This eventuality is not compatible with the state of chemical equilibrium. To circumvent the obstacle, it can be hypothesized with the use of an expression such as “the same number of particles” as referred to each of the species present at equilibrium. That is, in the previous case, it should be clear that 100 molecules of PCl_3 reacting with 100 molecules of Cl_2 will get 100 molecules of PCl_5 . However, if we apply the same reasoning to the following reaction scheme, it becomes immediately clear that this approach is still not adequate:



If we consider the case of water evaporation in a closed container, we can represent the situation of equilibrium as follows:



and assert that “at the same time, the same number of molecules of water passes from the liquid phase to the gaseous

phase and vice versa”. In this example of physical equilibrium, the statement is correct because there is only one species to the left and one to the right of the double arrow, and their ratio is 1:1. However, most of the reaction schemes contain more than one reagent or more than one product, and the stoichiometric ratios can be quite different. Therefore, we believe that the use of physical equilibria to introduce the chemical equilibrium requires caution.

Chemical Transformation and Chemical Reaction

The specificity of the chemical view of reality is given by the continuous shifting between microscopic and macroscopic levels, which characterizes the interpretation of chemical phenomena.^{18,19} To improve the understanding of the concept of chemical equilibrium, it would be important to distinguish the concept of chemical transformation from that of chemical reaction.^{20,21} In fact, a chemical transformation can be described and interpreted through both macroscopic and microscopic models as well as represented in a symbolic way. If it is stated that a chemical transformation involves changing the identity of substances, and the concept of *substance* belongs to the macroscopic level, in turn the use of the concept of substance involves the use of a *macroscopic model*. The model can be expressed as follows: “in a chemical change, the system evolves from the initial substances (reactants) to the final substances (products). The initial substances interact to each other giving rise to new substances”.¹⁹ However, chemical transformations can also be interpreted by using the concepts of atom and molecule, which are related to the *microscopic level*. Therefore, a description of chemical transformations at the microscopic level is through the model of chemical reaction, which can be expressed as follows: “in a chemical reaction, the particles of reagents interact with each other, and this leads to the formation of the particles of products”. All this implies is that to distinguish between *chemical transformation* (the phenomenon) and *chemical reaction* (the model through which the phenomenon is interpreted), a symbolic representation named *reaction scheme* can be applied.^{19–21} The benefits arising from the distinction between chemical transformation and chemical reaction are particularly important when dealing with the study of systems in chemical equilibrium. Since for constant values of temperature and pressure, there is no modification within time of the amount of substances that constitute the system, it is obviously required to assert that the chemical transformation is *ended* and *incomplete*.¹¹ However, the state of equilibrium is not static but dynamic and can be modeled with a direct reaction and an opposite one. By imagining two reactions, opposite to each other, that occur simultaneously and at the same rate, it allows us to understand why there is no more evolution of the system even if all the chemical species are susceptible to interact.²⁰

Although the distinction between chemical transformation and chemical reaction is very little practiced, it does not mean that it is not appropriate to take it into account in teaching. In fact, it can allow students to conceptualize two reactions, one opposite the other, taking place simultaneously at the same rate, and helps them to justify why there are no macroscopic changes in the system, although all chemical species continue to be reactive.

We also believe that it is appropriate to use the terms *direct reaction* and *opposite reaction* instead of “reaction that takes place in both directions”. It is difficult to conceive a single process that can occur simultaneously in one direction and the

Table 1. Proposed Systems in WS1

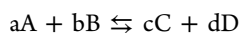
System 1					
	(mol/dm ³)	Increase	Decrease	No Change	I Do Not Know
PhOH _(aq)	1.50				
NH _{3(aq)}	1.80				
PhO ⁻ _(aq)	0				
NH ₄ ⁺ _(aq)	0				
System 2					
	(mol/dm ³)	Increase	Decrease	No Change	I Do Not Know
PhOH _(aq)	0				
NH _{3(aq)}	0				
PhO ⁻ _(aq)	0.98				
NH ₄ ⁺ _(aq)	3.50				

other without incurring in the risk of encouraging a pendulum-like concept of direct and opposite reactions. By contrast, talking about two separate processes, this difficulty can be easily overcome. In summary, in a system at the chemical equilibrium:

- (1) at the macroscopic level, the chemical transformation has ended and is incomplete;
- (2) at the microscopic level, two chemical reactions occur simultaneously, are opposite to each other, and occur at the same rate.

Reasons for a Different Approach to the Equilibrium Constant Expression

Concerning the teaching of the equilibrium law, it has been suggested that its kinetic derivation leads to incorrect conclusions.²² In fact, for a generic reaction scheme



equalizing the rate of the forward (V_f) and reverse (V_r) reactions

$$V_f = V_r$$

$$K_f \times [A]^m \times [B]^n = k_r \times [C]^x \times [D]^y$$

K_{eq} can be obtained from the ratio between the two rate constants (k_f/k_r):

$$[C]^x \times [D]^y / [A]^m \times [B]^n = k_f/k_r = K_{eq}$$

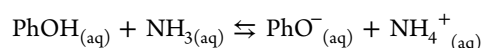
However, this procedure is not correct because the exponents m , n , x , and y , except for elementary reactions, do not coincide with the stoichiometric coefficients and must be determined experimentally. Therefore, such an approach to the equilibrium law is not acceptable.

Another approach to the equilibrium law requires its thermodynamics derivation; however, this road seems hardly feasible in a high school. In fact, it is necessary that students know concepts particularly insidious such as enthalpy and entropy. In our teaching activity, for the introduction of the equilibrium constant, we started from the need to find a criterion to predict the evolution of a system from an any initial state of equilibrium to a final one. The criterion that is meant to teach the students is that of the comparison between the value of the equilibrium constant, K_{eq} , and that of the reaction quotient, Q_r .

For the explanation of the educational model adopted and the manner in which the trial was carried out in sequence learning in the classroom, refer to our previous work cited.¹²

FROM A STATE OF NONEQUILIBRIUM TO A STATE OF EQUILIBRIUM

During a chemical transformation, a system may evolve from a state of nonequilibrium to a state of equilibrium. For students, this awareness must be the necessary premise to the second type of conceptual evolution of the systems, namely that in which beginning from a state of equilibrium, it comes to a different state of equilibrium. The distinction is conceptually significant because the starting points of the two situations described in the following activities are different, and thus also the problematic situations posed to the students must be different. In some cases, in the activities, it will be possible to hypothesize the outcome of the evolution of systems starting only by the reaction scheme and the amount of chemical substances involved (WS1, WS2, WS3), while in other cases, this is not possible (WS4). In fact, it is necessary to have a predictive and quantitative criterion that implies the comparison between the values of the equilibrium constant and the reaction quotient. The next section will lead to the concepts of the equilibrium constant and reaction quotient. Four activities are presented and carried out by the students in the classroom to aid in their understanding. No lab activity is required in this section; students are only asked to predict, justifying properly, the evolution of chemical systems on the basis of different starting situations. All such activities are related to different situation-issues based on the following reaction scheme:



The meaning of PhOH (phenol) and PhO⁻ (phenate ion) was, of course, previously explained to students.

Activity 1

The initial compositions of two different systems are proposed (Table 1), and students are asked to predict, justifying properly, the evolution. While the first system provides only the presence of the reagents, the second system involves only the presence of the products (WS1, Supporting Information).

All students indicated that in system 1, the concentrations of reactants decrease, while the concentrations of products increase. Conversely, in system 2, the concentrations of reactants increase, and those of products decrease. Together with acceptable answers ("The reagents are consumed, and therefore their concentration decreases in favor of that of products"; "In the course of the reaction, the concentration of reactants decreases because products are forming, whose concentration then increases"), there are some offering teleological explanations: "There are forming products, and

Table 2. Proposed Systems in WS2

System 1					
	(mol/dm ³)	Increase	Decrease	No Change	I Do Not Know
PhOH _(aq)	0.18				
NH _{3(aq)}	0.78				
PhO ⁻ _(aq)	0.09				
NH ₄ ⁺ _(aq)	0				
System 2					
	(mol/dm ³)	Increase	Decrease	No Change	I Do Not Know
PhOH _(aq)	0				
NH _{3(aq)}	1.00				
PhO ⁻ _(aq)	0.45				
NH ₄ ⁺ _(aq)	5.80				

Table 3. Proposed Systems in WS3

System 1					
	(mol/dm ³)	Increase	Decrease	No Change	I Do Not Know
PhOH _(aq)	0.65				
NH _{3(aq)}	0				
PhO ⁻ _(aq)	0.78				
NH ₄ ⁺ _(aq)	0				
System 2					
	(mol/dm ³)	Increase	Decrease	No Change	I Do Not Know
PhOH _(aq)	0				
NH _{3(aq)}	1.25				
PhO ⁻ _(aq)	0				
NH ₄ ⁺ _(aq)	2.70				

they must achieve equilibrium”; “The reagents are consumed to obtain the products”. Language problems of the students’ responses do not depend on translation. We have endeavored to translate the phrases of the students so that they do not lose the meaning of their responses.

During the discussion, the teacher clarifies the difference between proper scientific explanations and teleological explanations. The conclusion proposed by the teacher was: “in the first system, where only reagents are present, the chemical transformation takes place toward the right; in the second system, where only products are present, the chemical transformation takes place toward the left”.

Activity 2

The initial compositions of two new systems are proposed (Table 2) where the first system envisages the presence of reagents and only one product, while the second system implies the presence of the products and only one reagent (WS2, Supporting Information). For both systems, 89% of students identified the correct answer, and 11% proposed not acceptable forecasts. Examples of acceptable answers for one or the other system are “The PhO⁻_(aq) has no ammonium to react”, “Even if one of the products is already present in a certain amount, the reaction takes place toward the right and, as soon as NH₄⁺ will be produced, the reaction will also occur toward the left”, “Products become reagents of opposite reaction”.

For system 1, a student proposed that while reactants’ concentration decreases, that of ammonium ion increases; while for phenate ion, the student did not know, trying to explain that “it depends on the yield of reaction; however, the reagents’ concentration decreases because they have to form NH₄⁺”. As noted in the analysis of previous activity, even in this case, the

explanation seems teleological, and the teacher reiterated the difference between scientific and teleological explanations. Furthermore, the teacher invited students to reflect that if the concentration of reactants decreases, it means that a chemical transformation is expected to occur toward the right, hence the concentration of the products must necessarily increase. The student confirmed to have understood what didn’t work in this justification. The conclusions proposed by the teacher were:

- (1) In the first system, a chemical transformation is expected to occur toward the right, resulting in decreased concentrations of reactants, while those of the products increase. The initial absence of a product does not allow us to hypothesize a chemical transformation to the left.
- (2) In the second system, a chemical transformation is expected to occur towards the left, with a consequent decrease in the concentration of products and an increase of that of reactants. The initial absence of a reagent does not allow us to hypothesize a chemical transformation to the right.
- (3) In both systems, given the presence of the double arrow in the reaction scheme, chemical transformations are assumed concluded and incomplete, and consequently also the achievement of a state of dynamic chemical equilibrium.

Activity 3

In this activity, two different systems are proposed (Table 3), both involving the presence of a single reagent and a single product (WS3, Supporting Information).

For the first system, 83% of the predictions were correct, 11% were not acceptable, and 6% did not indicate any choice. For the second system, 82% of the predictions were correct,

Table 4. Proposed Systems in WS4

System 1					
	(mol/dm ³)	Increase	Decrease	No Change	I Do Not Know
PhOH _(aq)	0.15				
NH _{3(aq)}	0.15				
PhO [−] _(aq)	0.15				
NH ₄ ⁺ _(aq)	0.15				
System 2					
	(mol/dm ³)	Increase	Decrease	No Change	I Do Not Know
PhOH _(aq)	0.25				
NH _{3(aq)}	0.45				
PhO [−] _(aq)	0.25				
NH ₄ ⁺ _(aq)	0.45				

11% were not acceptable, and 7% did not indicate any choice. Examples of acceptable responses for one or the other system are “The chemical transformation does not happen because there are no reagents for the opposite transformations”; “we do not have a reagent, so the transformation cannot occur”; “a reaction cannot occur between two reagents if one of them is not present”. Examples of justifications for not acceptable forecasts are “State of dynamic chemical equilibrium” and “Reagents and products with lesser concentrations increase”. In other cases, students did not offer any justification. In the case of the first justification, the student said that they did not reflected sufficiently and therefore the response was the result of poor implementation. At the end of the discussion, which also involved the second not acceptable answer, the teacher proposed the following conclusion: “given a reaction scheme, if in a system one of the two reactants is absent, then the chemical transformation does not take place”. Although this conclusion may seem obvious (as well as useless can be considered the relevant request), in reality it is not so given the percentage of incorrect answers. These activities are necessary to bring to light and to solve the greatest number of misconceptions.

Activity 4

In the two systems proposed here (Table 4), the first involves all reagents and products at the same concentration, while the second is based on the presence of all the reagents and products in different concentrations (WS4, Supporting Information).

For the first system, 40% of the answers were correct. Students stated that they cannot make predictions: “It is not possible to determine anything because we do not know the yield of the reaction”; “Everything depends on the yield of the reaction, that is, the ratio between reagents and products, when the reaction is ended”. This kind of assertion, discussed also with the other students, indicates that some students believe they can use the concept of yield to have an indication of the prevalence of the reactants compared to the products or vice versa. Other examples of justifications are “I do not think we have enough data” and “I do not have enough information”. In this type of justification, we can see how students recognize they do not have a suitable predictive criterion. This is exactly what the worksheet aims to achieve. Forty-seven percent of the responses indicate that concentration does not change, and justifications are “The concentrations of reactants and products are equal, and therefore if the system is in equilibrium, the amount of reactants and products does not change”; “In this case, we have the right proportions for the two opposite

reactions to occur, and since they occur simultaneously, the concentration does not change”; “I cannot explain why, by intuition it seems to me fair to say that the concentrations do not change, because they are all identical, and the reactions take place in one way or another”. This kind of answer is in perfect agreement with the results of previous educational research;^{23–25} in fact, an idea emerges that the concentrations of reactants and products are equal at equilibrium. Four percent of the predictions are composite, that is, students indicate that the concentration of certain substances increases, the other decreases, and other still does not change; an example of a response is “The concentration of reactants decreases, while that of the products increases”. The statement is not a justification because it merely repeats what has been indicated in Table 2 for system 1. Finally, 9% of the students did not give any justification.

For the second system, 51% of the answers were correct and the justifications acceptable: “We do not know in which way the transformation takes place”; “We do not know whether, to get the equilibrium situation, the direct transformation or the opposite occurs”. Twenty-eight percent of the answers indicate that the concentration does not change, and the justification is that the system is at the state of equilibrium. Six percent of the predictions are composite, that is, students indicate that the concentration of certain substances increases, the other decreases, and other still does not change; an example of a response is “The first two concentrations decrease because they are reagents; PhO[−]_(aq) increases, but I do not know if NH₄⁺ increases or not because I do not know if it is at equilibrium”. The second statement reveals that the student has not yet fully understood that in a state of dynamic chemical equilibrium, the opposite reactions occur in the same system; thus, the concentrations of reactants and products are interdependent. In addition, the student was distracted by the fact that the ammonium ion is more concentrated than phenate ion; therefore, this student manifested doubts on its additional increase. Finally, stating that they did not know if the system is at equilibrium, the student partially improved its justification because they realized that the available data were not sufficient. Fifteen percent of students did not report any justification.

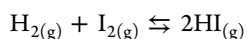
During the discussion, the prevailing hypothesis was that the available data were not sufficient to make a prediction, it would have been useful to have the yield of transformation, and it was therefore necessary to have a predictive criterion. The conclusion proposed by the teacher was: “to predict the evolution of a system from whatever initial state, it is necessary to have a predictive criterion”.

THE EQUILIBRIUM CONSTANT

As previously mentioned, the pretext for the introduction of the equilibrium constant is given by the need to find a general criterion to predict the evolution of a system from an initial state to any final state of equilibrium. The criterion that is meant to teach the students is that of the comparison between the value of the equilibrium constant, K_c , and that of the reaction quotient, Q_c . It is necessary that students realize how the value of the equilibrium constant provides an indication about the extent of a reaction toward the formation of products and that no chemical transformation is, in absolute terms, complete. In fact, the state of dynamic chemical equilibrium is established always. In such situations, the value of the equilibrium constant is very high but is not infinite, and the concentrations of the reagents are very low. The logic behind the equilibrium constant is that the equilibrium concentrations of reactants and products are constants; hence, it is reasonable to find a way to combine concentrations to attain a constant numerical value independently from the specific state of equilibrium. This is why we organize the subsequent activities. Four activities are presented and carried out by the students to aid in their understanding.

Activity 5

To have a quantitative criterion that allows us to predict the evolution of a system (from an initial state to any final state of equilibrium), it is necessary to quantitatively characterize the state of dynamic equilibrium. If at equilibrium the concentrations of reactants and products are constant and different from zero, then it is conceivable that a mathematical relationship between the concentrations of reactants and products has a constant value. On the basis of the above considerations and given the following reaction scheme



the composition at equilibrium of six different systems is proposed (Table 5), and students are asked to compose, on the

Table 5. Proposed Systems in WS5

System	Composition of the System at Equilibrium (mol/dm ³)			Values Obtained with the Proposed Relationship		
	H _{2(G)}	I _{2(G)}	HI _(G)	1° Attempt	2° Attempt	3° Attempt
1	1.14	0.12	2.52			
2	0.92	0.20	2.96			
3	0.77	0.31	3.34			
4	0.92	0.22	3.08			
5	0.345	0.345	2.35			
6	0.86	0.86	5.86			

basis of the above, a mathematical relationship that has constant value and to provide an indication of how much is favored the formation of products (WS5, Supporting Information).

To guide students to the correct formulation of the equilibrium constant, the time for three attempts was given where students were asked to indicate the proposed equation and the appropriate justification.

Twelve percent of the students were able to find the expression of equilibrium constant within the third attempt. Except in one case, which will be discussed later, the answers indicate that students do not follow a particular logic in achieving the mathematic expression. It is interesting to note that a student, who was asked to explain how they got their

outcome, has derived the equilibrium constant following a reasoning similar to that of Guldberg and Waage and van't Hoff. By explaining that this reasoning is applicable only in the case of elementary reactions, this student wrote that

$$k_1 \times [\text{H}_2]^a \times [\text{I}_2]^b = k_2 \times [\text{HI}]^c$$

where $a = 1$; $b = 1$; and $c = 2$

$$\frac{k_1}{k_2} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \text{ and } \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \text{constant (because } k_1 \text{ and } k_2 \text{ are constant)}$$

The student clearly expressed to know that this derivation was acceptable only if we consider elemental reactions, and this allowed the teacher to show the limits of what is written in the textbooks. Such a hydrogen–iodine system has been chosen because it is a typical example of not elementary process, for which a kinetic derivation of the equilibrium constant cannot be used.²⁶ In fact, almost all textbooks propose the kinetic derivation of the constant of equilibrium. Since students inevitably will learn such derivation, it is preferable to discuss it in advance, in such a way they are immunized. Eighty-eight percent of students were not able to find the expression of the equilibrium constant within the third attempt.

At the end of discussion, the teacher provided the general formulation of the equilibrium constant with its general reaction scheme ($a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$).

Activity 6

In this activity, students are asked to reconsider the reaction scheme, data, and problematic situation of system 1 in Activity 4. Knowing that the value of the equilibrium constant of the system is equal to $K_c = 0.20$ at 20 °C, they are asked to identify a criterion that allows them to predict the evolution of the system (WS6, Supporting Information).

Thirty percent of students used the data of initial composition to calculate the equilibrium constant and obtained it as a numerical value. They showed that the value obtained was greater than the given value of the constant and stated: “We are not in equilibrium because the constant is 1, not 0.20. So, according to the formula, in order to have a constant equal to 0.20, the concentrations of the products must decrease”; “By calculating the constant with the data in the table, you get 1. This means that, to obtain 0.20 for the equilibrium constant, the value of the denominator must decrease, that is, the concentration of products must decrease, which also influences the denominator to increase, thus contributing to decrease the value of the constant”; “Using the formula in the initial equilibrium constant, I got $K_c = 1$. If K_c must become 0.20, then the denominator (corresponding to the reactants) must increase and the numerator (corresponding to the products) decrease; therefore, the reaction is from the right to the left”. Twenty-eight percent of students failed the attempt to find a predictive criterion, and 42% did not propose any strategy.

At the end of the discussion, the teacher explained how to use the criterion of comparison: K_c (equilibrium constant)/ Q_c (reaction quotient). In addition, students were asked to reconsider reaction schemes, data and problematic situations of worksheets 1, 2, and 3, and to identify which of the systems described makes no sense to apply the criterion of comparison between Q_c and K_c . During the discussion, the teacher showed that, in the case of systems 1 and 2 of Worksheet 3, it does not make sense to apply the criterion of comparing K_c/Q_c . In fact,

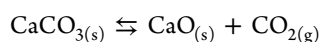
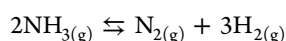
Table 6. Proposed System in WS8

		System			
	(mol/dm ³)	Increase	Decrease	No Change	I Do Not Know
Fe ³⁺ _(aq)	7.32 × 10 ⁻²				
Ag _(s)	0				
Ag ⁺ _(aq)	1.00 × 10 ⁻¹				
Fe ²⁺ _(aq)	1.50 × 10 ⁻¹				

in those cases, no chemical transformation can occur. To avoid mythization of the results of scientific research and develop the critical thinking of students, it is absolutely necessary to show them when a predictive criterion should not be applied.

Activity 7

Here, students are asked to consider the two reaction schemes below, one of which displayed a reactant and a product in solid state, and to write the corresponding equilibrium constants:



Then students are asked to explain how to calculate the concentration of a species in the solid state (WS7, Supporting Information).

The discussion should enable students to understand that the calculation of the concentration of a substance in the solid or liquid state (systems in which the state of equilibrium is established between different phases, “heterogeneous equilibrium”) does not make sense. In fact, the value obtained is always constant, regardless the amount considered. If the concentration of a solid, or a liquid, is constant, then it does not influence the value of the equilibrium constant and therefore does not have to be taken into account. Of course, in a thermodynamic perspective, the activities of solids and liquids each equal one, which does not affect the overall K value, but at the secondary school level, it is sufficient to reason in terms of concentrations: the molarity of solids and liquids remain constant throughout the transformation.

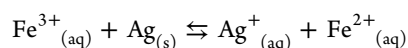
Concerning the first question, 83% of the students reported that a difference between the first and the second reaction scheme is given by the different physical state of the substances involved. Examples of responses are: “The reactions include substances in different states”; “In the first (reaction scheme, they) are gaseous and are solid in the second one”; “In the first (reaction), there are only gaseous substances; in the second one, there are also solid substances”. Three percent of students focused their attention on other differences such as different values of stoichiometric coefficients. Fourteen percent did not answer.

Concerning the second question, 63% correctly wrote the expression of the equilibrium constant for both the reaction schemes, while not yet neglecting, as it might be expected, the solids. Seventeen percent of students made mistakes in writing the equilibrium constants (they forgot an exponent to which elevate a concentration, used the plus sign instead of the multiplication sign, or swapped the position of concentration of the reactants with that of the products), and the remaining 20% did not write anything. The questions raised in this worksheet have a three-fold purpose: (a) to allow students to practice in writing the equilibrium constant, (b) to show that solids concentration should be omitted from the equilibrium constant,

and (c) to explain that in the case of gases, the constant can be written in terms of partial pressures.

Activity 8

On the basis of considerations at the end of the previous activity, now we can consider and discuss the limits of the criterion of comparison K_c/Q_r . The initial situation proposed to students involves ions in solutions and solid silver:



At 20 °C, the system reaches a state of chemical equilibrium characterized by $K_c = 0.313$. Starting from an initial composition in which solid silver is not present (Table 6), students are asked to predict the evolution of the system (WS8, Supporting Information).

Several studies²⁰ highlight the difficulties that many students encounter in making the correct prediction. In fact, in this case, if they calculate the value of Q_r and compare it with K_c , it can be seen that Q_r is less than K_c , so they are led to believe that the chemical transformation should occur to the right, allowing the system to reach a state of chemical equilibrium. However, given the absence of silver, the chemical transformation cannot occur, and this problematic situation allows us to assess how students mechanically apply the criterion of comparing K_c/Q_r and to highlight the limits of applicability of the criterion itself.

Another problematic situation that can be proposed, in which the criterion does not allow us to advance a correct prediction, is one in which a chemical species, either solid or liquid, is present in insufficient quantities so that Q_r can equal K_c . In light of this, it appears clear the importance of Worksheets 1, 2, 3, and 4.

Forty-six percent of students thought that it must be a chemical change. Examples of students' answers are: “a reaction can only take place from the right to the left, as there is no solid silver”; “The reaction takes place to the left”; “ $Q_r < K_c$; therefore, the transformation takes place toward the right”. Ten percent of students correctly pointed out that, even if the comparison between Q_r and K_c let them suppose that the direct transformation should occur, in reality, by missing one of the two reactants, the forecast is meaningless. Forty-four percent of students did not answer. Most of the students' answers, combined with the high percentage of students who did not answer, show that they have many difficulties in correctly predicting the evolution of the systems. Therefore, activities of this kind are essential to help them to face difficulties and to develop a critical thinking. The conclusion proposed by the teacher was: “the criterion of comparison between K_c/Q_r has limits. Therefore, before accepting, forecasts must be evaluated in light of the actual state of the system”.

CONCLUSIONS

The part of teaching sequence here described was tested on 54 students. The participation of students and their answers reveal that the activity may promote active learning. In fact, students

are asked to seek solutions to the problems proposed; they were not confined to the role of passive receivers of knowledge. The choice of the questions and their sequence serves to deal with learning difficulties in a gradual manner. The questions serve to reveal misconceptions students may have. The discussions are used to address these difficulties and to solve them. This is the central point of our learning strategy. Often students have unscientific ideas. If these are not traced and discussed, they remain for a long time. Many studies also highlighted the conceptual difficulties of teachers.²⁷ We think that this may depend on the type of teaching adopted. As indicated in the previous work,¹² the didactical sequence here described is intended to be used in a specific school context. In different situations, students may show difficulties we have not foreseen and that require much attention, so further adaptations may be necessary. We think that this kind of activity can contribute to the learning of chemistry.

■ ASSOCIATED CONTENT

§ Supporting Information

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

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Notes

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