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CHANGES IN CONCENTRATION AND IN PARTIAL PRESSURE IN CHEMICAL EQUILIBRIA: STUDENTS' AND TEACHERS' MISUNDERSTANDINGS

Received 20 October 2003; revised 1 July 2004; accepted 4 November 2004

ABSTRACT: We discuss two questions that deal with changes in concentration or partial pressures of the gases involved in chemical equilibrium systems. This paper analyses the responses and reasons given by both high school and fourth-year university students as well as by both pre-service and in-service teachers. The sample was taken from the Spanish context, where Le Chatelier's principle is compulsory for Grade-12 chemistry students as well as for first year university students. It is reported that Le Chatelier's qualitative statements were the main and almost exclusively conceptual tools used to predict equilibrium shifts when changing pressure, volume or mass. In some cases, incorrect rules led students to state correct shift predictions. Changes in concentration caused by a variation in the volume of the equilibrium vessel were mainly associated with equilibrium shift mass changes. Equilibrium law was not used at all by students; a minor number of teachers did mention the equilibrium constant in their explanations. Thus, few correct answers were ascertained. Gas behaviour misunderstandings were one of the most important obstacles when coping with changes in partial pressure due to changes in both mass and volume. Many responses concentrated on physical behaviour of gases, instead of going beyond using the equilibrium law. Many teachers erroneously associated changes in partial pressure caused by a variation in the volume of the equilibrium vessel with equilibrium shift mass changes. Eventually, this paper presents evidence, both theoretical and empirical, to conclude that Le Chatelier's rules should be abandoned completely in chemical education. Thus, it suggests the teaching of these problems on the basis of the equilibrium law, and the focussing on the 'history' of the system under consideration. Obviously, such an approach will not solve all the problems one has with Le Chatelier's rules, but it is a promising approach. [*Chem. Educ. Res. Pract.*, 2004, 5, 281-300]

KEY WORDS: *chemical equilibrium prerequisites; changes in concentration; changes in partial pressure; Le Chatelier's principle; equilibrium law; teachers' and students' misunderstandings*

GENERAL AND COMMON FLAWS IN THE TEACHING AND LEARNING THE CHEMICAL EQUILIBRIUM TOPIC

There is a wide range of problematic areas of students' understanding of chemical equilibrium (Griffiths, 1994; Garnett, Garnett & Hackling, 1995; Quílez & Solaz, 1995; Van Driel & Gräber, 2002; Raviolo & Martínez, 2003). Teachers consider that chemical equilibrium is one of the most difficult chemistry concepts to teach (Finley et al. 1982), while students regard this topic as one of the most difficult to learn (Butts & Smith, 1987). One of the reasons that explains the aforementioned facts is that chemical equilibrium is an abstract

¹ Some of the results of this article were presented at the *VI International Conference on Enseñanza de las Ciencias* (Barcelona, 2001).

concept demanding the mastery of a large number of subordinate concepts. Therefore, research papers (Quílez & Solaz, 1995) suggest that dealing with this complex concept calls for an in-depth consideration of the prerequisites for learning it. Teachers should prevent their students from not having the previous knowledge required for solving chemical equilibrium problems. For example, if students find difficult to deal with the concentration concept (Gabel & Samuel, 1986), they will surely fail when trying to apply it to the domain of chemical equilibrium. Also, a basic knowledge of the physical behaviour of gases is required (Crosby, 1987; Lin & Cheng, 2000; Stavridou & Solomonidou, 2000). Students should be able to use properly the ideal-gas equation, as well as to understand the concept of partial pressure when dealing with the K_p equation in gaseous equilibria. The mole and stoichiometry are also important prerequisites to deal with chemical equilibrium (Hackling & Garnet, 1985; Kousathana & Tsapralis, 2002).

Another area that impedes students' understanding of chemical equilibrium goes beyond the problems students have handling the mathematical steps which are necessary to solve equilibrium calculations (Hudle & Pillay, 1996). Students usually apply formulas in an algorithmic way but without a proper understanding of the concepts involved (Bergquist & Heikkinen, 1990). Some of these difficulties might emerge because virtually all problem-solving activities in standard courses focus on problems for which an algorithmic solution has been taught (Camacho & Good, 1989). A similar view was supported by Crosby (1987), who ascertained that students' chemical equilibrium errors and misconceptions could be directly related to the instruction experienced by the students. Also, Quílez & Solaz (1995) reinforced that assumption reporting that teachers' methodology when solving chemical equilibrium problems may support some of the difficulties students hold. In addition, textbooks usually solve problems by one method only, applying directly a formula, and asking for mathematical results without reasons or justifications; hence, emphasising quantitative aspects of learning at the expense of qualitative reasoning. With this idea in mind, Gabel et al. (1984) warned that if students do not understand a chemical concept qualitatively, they are likely to conduct only mindless manipulations of mathematical equations.

Le Chatelier's principle as a key source of students' misunderstandings

As has been stated above, there are many problems associated with a proper understanding of chemical equilibrium. In a recent study (Quílez, 2004), we reported misconceptions associated with the introduction of the idea of chemical equilibrium, as well as with the understanding the nature of this concept. This study concentrates on another important source of students' and teachers' misunderstandings, which is the use and application of Le Chatelier's principle. The following is a summary of the main problematic areas related with this topic.

Language difficulties

One of the areas in which chemical-equilibrium educational research has identified numerous difficulties and misunderstandings is students' and teachers' use and application of Le Chatelier's rules (Bucat & Fensham, 1995; Quílez & Solaz, 1995; Quílez, 2002). We will refer in this paper to Le Chatelier's rules instead of Le Chatelier's principle because textbooks use many similar statements, which, in turn, may express divergent and even contradictory ideas. The words that are used in their qualitative formulations, as well as the ideas that are behind the diverse, vague and ambiguous statements may lead to wrong

predictions (Driscoll, 1960; Haydon, 1980; Treptow, 1980; Gold & Gold, 1984, 1985; Jordaan, 1993; Quílez & Sanjosé, 1996; Quílez, 1997a, 1998a). Furthermore, Piquette (2001), dealing with the origin of students' alternative conceptions in chemical equilibrium, reported that teachers were discouraged by the particular vocabulary that is traditionally used to teach Le Chatelier's principle, noticing that it was difficult to explain the precise meaning of the words used in its current qualitative statements. According to Pedrosa & Dias (2000), language used in textbooks may give rise or reinforce student alternative conceptions about chemical equilibrium (e.g. Le Chatelier's principle statements).

Limited character

There are many examples in the literature (de Heer, 1957; 1986; Wright, 1969; Bridgart & Kemp, 1985; Jordan, 1993; Solaz & Quílez, 1995, 1998; 2001; Voska & Heikkinen, 2000; Kousathana & Tsaparlis, 2002) in which it has been discussed that Le Chatelier (qualitative) principle cannot be of help to predict the evolution of a disturbed equilibrium system. Prigogine & Defay (1954) stated: 'Le Chatelier and Braun suffers from a number of important exceptions. Many workers have attempted to restate this principle in a completely general form; but this form, if it exists at all, is necessarily very complex'. The problems that have arisen due to the limited character of Le Chatelier's principle (Gold & Gold, 1984, 1985; Quílez, 1995) exceed the scope of this paper. However, we want to note that, historically, one of the main critical arguments that Le Chatelier had to face with is that in chemical equilibrium the changes in concentration do not always follow the changes in the mass of each of the chemicals involved in the reaction (Posthumus, 1933). With this regard, Knox (1985) has provided a useful analysis of the effect of an increase in pressure to the equilibrium of the reaction for the synthesis of ammonia. Moreover, Allsop & George (1984) warned that changes in the volume of an equilibrium system lead to changes in mass that do not parallel the variations occurred in concentration. Eventually, Solaz & Quílez (1997) gave a general discussion of changes in concentration to the cases involving the change in mass of the equilibrium system.

Ontological problem/foundation

We want to stress that when we refer to Le Chatelier's principle, we are posing an ontological problem. We have previously mentioned that under the title Le Chatelier's principle we can find many different textbook qualitative statements. Furthermore, Le Chatelier himself gave three different qualitative statements for his principle (Le Chatelier, 1884, 1888, 1933). But, thermodynamics gives a set of accurate and precise mathematical formulations that restrict its range of applicability (de Heer, 1957; 1986; Quílez, 1995).

On the other hand, students learn the taught rule (Le Chatelier's qualitative principle) by heart and they try to apply it without understanding, fixating on the pervasive set of reasoning rule-rote recalling algorithm. Despite these rules being sometimes helpful to answer questions correctly, in various empirical studies the conclusion was drawn that students as well as teachers often use and apply them erroneously (Bucat & Fensham, 1995), even when reporting the correct answer. For example, Voska & Heikkinen, (2000) found that some students answer Le Chatelier's questions correctly using erroneous reasoning.

The application of Le Chatelier's rules may have an ontological foundation based on an action/reaction chemical behaviour, *i.e.*, transferring an inappropriate understanding of Newton's third law (Brown & Clement, 1987) to disturbed chemical equilibria: firstly (*action*), a 'stress' is applied to a system, and, secondly (*reaction*), the system responds trying

to: a) relieve (oppose, counteract, cancel, minimise, reduce, compensate, adjust, etc.) the 'stress' (or, the *effect* of the 'stress'); or b) restore the initial conditions. Similarly, Níaz (1995, 1998) reported that some students conceptualise chemical equilibrium as a product of opposing forces. This idea can be traced back historically (Quílez, 1995, 2004) to the beginning of the first mathematical equilibrium equations, based on opposing chemical forces (Waage & Guldberg, 1962), to Le Chatelier himself (Le Chatelier, 1888), who also founded his principle on the behaviour of mechanical forces. Later, Nernst, in his popular textbook (Nernst, 1922), presented Le Chatelier's 1888 qualitative statement as the action/reaction principle. This mechanical foundation has fostered its recall and application, supporting the view that Le Chatelier's rules are easy-to-apply statements by means of a linear causal reasoning (Quílez, 1997a), in which students may find that the second part of the above action/reaction reasoning does not necessarily mean that a chemical reaction takes place (Hackling & Garnett, 1985). In a recent study (Quílez, 1998b), first-year university students were asked about the changes in the mass of both $\text{Cl}_2(\text{g})$ and $\text{COCl}_2(\text{g})$ when adding $\text{CO}(\text{g})$, at constant volume and temperature, to the following equilibrium: $\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g})$. It was found that a forward shift (increase in the amount of COCl_2) did not necessarily mean that the amount of Cl_2 would decrease (about one in three students stated that the mass of Cl_2 would remain unchanged).

Current educational approach

Despite the current approach of most general chemistry textbooks, in which they apply their own Le Chatelier's rule along with a discussion based on the mathematical meaning of the equilibrium constant (usually making use of the reaction quotient, Q), their effect on students performance has been minimal. Quílez & Solaz (1995), Quílez (1998b), and Tyson et al. (1999) studied how both secondary and university students as well as high school teachers solved questions about changes in chemical equilibria. They found that most of them, in general, displayed a great resistance to using and interpreting mathematical expressions in this context. Thus, they seldom used the equilibrium constant to predict a change in chemical equilibrium. Instead, they usually tried to interpret the problem in terms of Le Chatelier's rules, which then very often lead to wrong answers. This choice may be explained taking into account the epistemological background discussed by Níaz (1998), which is founded on Lakatos's philosophy. A teaching attempt to use a mathematical language, which has a great conceptual demand, would be eclipsed by rote recalling algorithms, based on hopefully infallible easy-to-apply rules. Thus, this way of reasoning would compete with other forms of a better rigorous foundation. Eventually, these rules would prove themselves very hard to remove, which would explain their persistence.

Metaphysical flavour

Another circumstance that has contributed to its persisting popularity is that it has obtained a metaphysical flavour, for it might be interpreted in terms of 'common sense' or 'everyday experience' (de Heer, 1996). For example, Feo et al. (1978) labelled it as 'the rebelliousness' principle. Thus, the tradition initiated by Brancroft (1911), which has been reinforced recently (Thomsen, 2000), fostered that some authors extended Le Chatelier's range of applicability beyond chemistry to economics, psychology, physics or biology (Quílez, 1995).

Educational suggestions

In order to avoid some of the problems that emerge when applying Le Châtelier's rules, many suggestions can be found in the literature (Van Driel & Gräber, 2002). Katz (1961), Allsop & George (1984), Solaz (1993), Solaz & Quílez (1995), and Quílez (2002) recommended the use of the equilibrium law because it helps to predict accurately the changes in an equilibrium system which are due to changes in pressure, volume or mass. Hondebrink (1981) suggested that this approach has merit for a better understanding of processes in general, and it provides a basis for an eventual confrontation with thermodynamics in university courses. Hence, and more specifically, the comparison between the values of the reaction quotient, Q , and that of the equilibrium constant, K , may serve, firstly, as a general criterion in order to decide if the equilibrium has been disturbed ($Q \neq K$), and, secondly, to predict the sense (forward or reverse) of the subsequent reaction till a new equilibrium is attained. Performing mathematical discussions explaining the chemical implications associated with the two possible non-equilibrium inequalities, *i.e.* $Q < K$ and $Q > K$, has the advantage that it can be justified later by thermodynamics within a more advanced level (Quílez & Solaz, 1996; Quílez, 2002). Another advantage is that the above proposal allows to trace the 'history of the equilibrium system' (Stravidou & Solomonidou, 2000) [*i.e.* to represent the successive steps that take place from the initial equilibrium position to the final one, which is attained due to a chemical reaction that takes place from an intermediate non-equilibrium position resulting from a disturbance (the physical change) made to the first equilibrium position].

**CHANGES IN CONCENTRATION OR IN PARTIAL PRESSURE
(GASEOUS MIXTURES) IN EQUILIBRIUM SYSTEMS**

Quílez & Solaz (1995) and Quílez (1998b) reported that Spanish high school teachers as well as first-year university students found that the effect of diluting a weak acid solution (*i.e.* its volume is increased) was a hard problem to deal with (*e.g.* a wide range of miscellaneous misunderstandings and incorrect reasons were present in their responses). Few teachers could predict accurately a forward shift, and in any of the responses was stated that although in the new equilibrium position the total amount of H_3O^+ ions was greater, the acidity, $[\text{H}_3\text{O}^+]$, of the solution was lower. Demerouti, Kousathana, and Tsaparlis (2004) also reported grade-12 students' difficulties and failure to apply La Chatelier's principle in predicting changes of the pH and the degree of ionization of solutions of weak acids and bases, caused upon dilution of the solutions.

Turning to chemical equilibria in gaseous mixtures, Kousathama & Tsaparlis (2002) reported that many students, when dealing with changes in pressure, used solely Boyle's law to set out the change in volume (ideal physical behaviour), without taking into account the changes in the total amount of the gases involved in the reaction (chemical behaviour).

Some misleading erroneous statements were found in a popular Spanish teachers' web site (SM, 2002), aimed for solving past official university chemistry exams for grade-12 students. In questions about gas equilibrium shifts due to changes in pressure, teachers quoted Boyle's law to reason their responses, as follows (literally): 'If it is increased the total pressure of the system, in order to keep $pV = \text{constant}$, the equilibrium shifts to where there is a less number of moles'; or 'A gas system must obey $pV = \text{constant}$, thus, a decrease in pressure leads to an increase in volume, that is, the equilibrium shifts in which there is more moles.' Although these statements have a (principal, explicit) physical rather than (implicit) chemical foundation (or, at least, a mixed confusing physical/chemical behaviour), students

(as well as teachers) might view them as helpful easy-to-apply statements in order to find the correct equilibrium shift. Moreover, those teaching claims lack a proper representation of the successive steps that take place from the initial equilibrium position to the final one. Thus, some of the difficulties reported by Stravridou & Solomonidou (2000) might have been originated or/and reinforced with the aid of such meaningless explanations.

Banerjee (1991), working on both prospective and in-service teachers in India, made use of the following chemical equilibrium: $\text{CO(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons \text{COCl}_2\text{(g)}$, and asked them for the change in the concentration of CO when the volume was halved by increasing the pressure. Only 23% of the teachers gave the correct answer; 33% of the responses agreed that the concentration of CO in the new equilibrium position will be less than in the first one; 17% of teachers thought that the concentration would remain unchanged; finally, 25% gave no answer. The same question was used by Quílez (1998b) (although this time the question dealt with the change in the concentration of Cl_2 due to an increase of the volume by a decrease in pressure). He administered it to both first-year and second-year university students and to both pre-service and in-service high school chemistry teachers. The worst score of correct answers (26 %) corresponded to in-service teachers (42% of them answered that the new concentration was greater than in the first equilibrium position), while 49% of pre-service teachers, 43% of second-year university students, and 53% of first-year university students correctly considered that the concentration of Cl_2 in the new equilibrium position would be less than in the first one. This question was part of a set of both multiple choice and open questions, dealing with changes in mass, volume, pressure and temperature in chemical equilibria. In the open questions, the responses were mainly based on Le Chatelier's rules. Therefore, it was concluded that in this specific multiple choice question (as well as in the others that were used in that study) there were similar implicit reasons. Hence, it was hypothesised that correct answers were due to erroneous reasoning. Note that only a minor percentage of each group had realised that both the volume and the amount of substance of Cl_2 were greater than in the first equilibrium position (22% of in-service teachers thought that data were insufficient for conclusion, while 10-12% of the rest of the groups agreed with this assumption). Almost any of the responses might had gone beyond this reasoning using the chemical equilibrium law.

PURPOSE AND METHOD

Banerjee (1991) and Quílez (1998b) papers were unable to explain both the conceptual tools and the based reasons used by both high school teachers and university students to deal with changes in concentration in gaseous equilibrium systems. In this work, we have tried to deal with this lack of explanation. Furthermore, keeping this previous aim in mind, we will attempt to extend the findings reported by Kousathama & Tsaparlis (2002), focussing on the explanations given to changes in partial pressures due to both a change in the volume of the vessel and in the mass of one of the gases involved in the equilibrium system.

We are going to discuss two questions that deal with changes in concentration or partial pressures of the gases involved in chemical equilibrium systems. Both questions have been selected from a collection of compulsory general chemistry exams aimed for grade-12 chemistry students that had successfully passed their last high school course. In Spain, those exams are yearly made by university teachers to test how grade-12 students cope with their high school chemistry syllabus. The two questions are as follows:

Question 1.- Consider the following equilibrium: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$.

Explain what the variation on the concentration of $\text{NO}_2(\text{g})$ will be when: a) the total pressure is increased, at constant temperature; b) the volume of the reacting system is increased, at constant temperature.

Question 2.- Consider the following chemical equilibrium: $\text{NH}_4\text{Br}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HBr}(\text{g})$.

Explain how the partial pressure of $\text{HBr}(\text{g})$ will change after each of the following modifications: a) addition of $\text{NH}_3(\text{g})$; b) the volume of the vessel is doubled.

Note. Emphasis has been added.

We will analyse the responses and reasons given by both high school and fourth-year university students as well as by both pre-service and in-service teachers. We will concentrate on determining which are the main difficulties when dealing with changes in concentration or in partial pressures in chemical equilibria. As chemical equilibrium knowledge is deeper for both university students and teachers than for freshman students, it is expected that both advanced groups will perform better than high school students. Thus, we will try to trace how the ascertained misunderstandings evolve or persist through years of learning, focussing on the existence of similar reasoning strategies that may impede a proper understanding of the related issues.

Content analysis of the two questions used in this study

Question 1

The first question deals with the following homogeneous equilibrium: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$. Despite the fact that the usual Le Chatelier's rules may predict the shift in the position of equilibrium when a pressure/volume change is made, the rules are unable to predict the resulting changes in the concentration of both gases. Instead, an argumentation based on the equilibrium constant will predict not only the chemical shift, but also the resulting changes in concentration. If the volume is increased, the initial position of equilibrium is broken up, for $Q_c < K_c$; therefore, the forward reaction proceeds in a greater extent till a new equilibrium position is attained ($Q_c = K_c$). We can surely predict that the new concentration of $\text{N}_2\text{O}_4(\text{g})$ is lower than the one corresponding to the first equilibrium because its mass has diminished and the volume has been increased. Thus, taking into account the mathematical equation of K_c , it is easy to reason that the concentration of NO_2 will change in the same way (but notice that both its mass and the volume have increased). Similarly, if the volume is diminished, the concentration of both gases will increase. As $\text{NO}_2(\text{g})$ is brown, and $\text{N}_2\text{O}_4(\text{g})$ is colourless, this change favours the colour of the system becoming darker. Conversely, the colour of system becomes lighter when the concentrations of both NO_2 and N_2O_4 diminish (the volume is increased). Thus, changes in colour parallel changes in the concentration of NO_2 , which are opposite to changes in its amount.

However, this chemical system has been traditionally considered as a good example to introduce the effect of change in pressure/volume on gaseous equilibria because it is claimed that equilibrium shifts can be connected with colour changes in the system. Yang (1993) reported that in some textbooks that connection was inappropriately stated. Thus, it was claimed that when pressure on the system is increased (*i.e.*, its volume is decreased), the net

reaction shifts by increasing the amount of N_2O_4 until a new equilibrium position is achieved, but assuming that the colour of the system becomes lighter, because the change in the colour of the gaseous mixture is thought to parallel the change in the amount of NO_2 . Conversely, it was also claimed that when the pressure on the system is decreased (*i.e.*, its volume is increased), the colour darkens, because the equilibrium has shifted by increasing the amount of NO_2 . Nowadays, those erroneous assumptions are still present in both high school and university chemistry textbooks (Atkins, 1992; Feltre, 1993; Oró et al. 1997; Ouahes & Dévallez, 1998; Petrucci & Harwood, 1999; Umland & Bellama, 1999; Lister & Renshaw, 2000; Vokins, 2000), and even in books aimed at answering official exams (Zubiaurre & Arsuaga, 2000, 2003; Foglino, 2002).

Question 2

The second question deals with the following heterogeneous equilibrium: $\text{NH}_4\text{Br}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HBr}(\text{g})$. It consists of two parts. The first one implies the addition of $\text{NH}_3(\text{g})$. However, notice that it is not stated how the disturbance is made (*i.e.* that isothermal addition can be made keeping constant pressure or the volume of the vessel). Some authors (*e.g.* Morcillo & Fernández, 1992) did not take care of it in order to explain their answer. This lack of a proper control of the variables involved has been reported elsewhere (Quílez, 2000).

Let us assume that this addition is made at constant volume and temperature to allow Le Chatelier's principle to make a backward reaction shift prediction. [The reader is reminded that if the pressure is kept constant, instead of the volume, and, in addition, if the molar fraction of the gas that is added is greater than 0.5, then the solid will decompose to a greater extent until a new equilibrium position is achieved (Quílez, 2002)]. An addition of $\text{NH}_3(\text{g})$ disturbs the equilibrium ($Q > K$); therefore, the reverse reaction proceeds in a greater extent till a new equilibrium position is achieved ($Q_c = K_c$). As the amount of $\text{HBr}(\text{g})$ has diminished and the volume has been kept constant, the partial pressure of $\text{HBr}(\text{g})$ has diminished too. Thus, in the new equilibrium position, the partial pressure of NH_3 is greater than in the first one, for the value of the equilibrium constant remains unchanged.

As in the first question, in the second part of this question, the usual Le Chatelier's rules may predict the shift in the position of the equilibrium when a pressure/volume change is made. But, in order to predict a possible change in the partial pressure of the gases involved, we must solely base our explanation on the mathematical equation of K_n . Let us state fully this last explanation. An increase in the volume of the vessel disturbs the initial equilibrium ($Q < K$); therefore, the forward reaction proceeds in a greater extent till a new equilibrium position is achieved ($Q_n = K_n$). The new equilibrium position has a greater amount of the two gases, but their partial pressures remain unchanged, for K_p does not change (*i.e.* in the equation of the partial pressure, $p_i = n_iRT/V$, the increased volume is eventually compensated by an increase in the amount of substance). But, this full mathematical reasoning is scarcely used. This fact is a source of incorrect predictions about the change in partial pressure in gaseous equilibrium mixtures. For example, Dauchot, Slosse & Wilmet (1993), dealing with the equilibrium $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, stated that a decrease in volume of the vessel would finally produce a decrease in the amount of PCl_3 , which would decrease its partial pressure.

The aforementioned equilibrium-law reasoning can be also extended to changes in concentration. However, we found that teachers did not use it (Zubiaurre & Arsuaga, 2000; SM, 2002). Instead, changes in mass were paralleled with changes in concentration. For example, a question asked about the change in the concentration of NH_3 due to an increase in

pressure in the following system: $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$. The explanation was as follows: ‘An increase in pressure makes the equilibrium to shift from the side with greater number of moles to the one with less number of moles. In this case, there will be a left shift, decreasing the concentration of ammonia.’

Sample

Two groups of grade-12 high school chemistry students participated in the study: Ss-1 ($n = 28$) and Ss-2 ($n = 30$). In addition, a group of fourth-year university chemistry students, Us ($n = 27$); a group of in-service chemistry teachers (T1 = 31); and a group of pre-service chemistry teachers, T2 ($n = 20$), were given the two questions.

In Spain, Le Chatelier’s principle is a compulsory topic for grade-12 chemistry students. There is also a mandated syllabus on this topic in 1st-year chemistry courses. At this level, Q - K inequalities are usually introduced. An advanced justification of equilibrium shifts is based on the second law of thermodynamics. Fourth-year university chemistry students are well acquainted with advanced thermodynamics.

Pre-service high school teachers were prepared as chemists during five years of study within a faculty of chemistry. After graduation, they were registered in a program for future chemistry teachers. Currently, this course consists of 60 hours of theoretical classes and is compulsory for teaching in a high school. In-service high school chemistry teachers had at least five years’ teaching experience in chemistry.

RESULTS AND DISCUSSION

Analyses of responses based on the two questions involved were conducted to find out if:

- both the equilibrium shift is correctly predicted and the explanations are properly founded;
- the correct change in concentration/partial pressure is accurately predicted.

Tables 1, 2, 3 and 4 summarise the main results corresponding to the type of answers given by each of the groups tested for Question 1. Tables 5, 6, 7 and 8 do the same for Question 2. Sometimes within the text, we add some extra data in order to report the heterogeneity of certain categories of responses, *e.g.* when making a distinction between various qualitatively different ways of applying Le Chatelier’s principle. Moreover, percentages of incorrect explanations as well as the ones corresponding to appropriate explanations enlarge the data given in the tables.

Question 1

In Question 1, references to equilibrium law explanations were seldom found. Equilibrium shift predictions were mainly based on Le Chatelier’s rules (Tables 1 and 3).

TABLE 1. Percentages of backward shift answers and main explanations given when pressure is increased, at constant temperature, in the equilibrium: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$.

	T-1	T-2	Ss-1	Ss-2	Us
backward shift	90	55	78 (LC-1: 54)	43	74
Le Chatelier	61	50	85	83 (LC-2: 50)	83
K	18	-	-	-	7

Although the majority (78%) of the students of Ss-1 group made correct predictions, many (54%) explanations were based on an improper application of Le Chatelier's qualitative statements (LC), using a causal linear reasoning, as follows (LC-1):

‘When pressure increases, *there is an increase in the total number of moles of the reaction*; it would go to the left, since according to Le Chatelier, when a factor, as pressure, disturbs the equilibrium, the system evolves in the way that counteracts the disturbance, thus the system shifts to the left because it is where there is the less number of moles.’

These students did not realise they were applying a rule that contradicts gas behaviour. They assumed that the final result of the left shift (‘less number of moles’) had to be the opposing consequence of an initial increase in ‘the total number of moles’. This full statement was not found in the Ss-2 group. However, we can find some similarities. 50 % of responses in Ss-2 group made right shift prediction (LC-2). Let us quote the most common right shift answer:

If $\uparrow P \rightarrow \downarrow V \xrightarrow{\text{Le Chatelier}} \uparrow V \rightarrow$ right shift (40%)

In 10 % of these type of responses, this reasoning was extended as follows:

If $\uparrow P \rightarrow \downarrow V = \downarrow \text{number of moles} \xrightarrow{\text{Le Chatelier}} \uparrow V = \uparrow \text{number of moles} \rightarrow$ right

Note that the core sequence of the aforementioned explanations are similar (*i.e.* looking for a counteracting equilibrium behaviour, which finally enables to predict the equilibrium shift). It seems that Grade-12 students find it difficult both to cope with what is to be counteracted (*i.e.* the ‘stress’ or the *effect* of the ‘stress’) and to understand what this counteracting action means. As chemistry teachers for Ss-1 and Ss-2 groups were different, a particular teaching approach might be behind the differences in reasoning between both student groups. Inability to recall or to apply Le Chatelier's principle was the main difficulty found among pre-service teachers (T2) and fourth-year university students (Us). 35% of T2 responses were unable to predict any shift, and in 10% a right shift was predicted. This last prediction was found in 19% of Us responses.

Let us now comment on the results of Table 2. High school students were unable to predict a change in the concentration of $\text{NO}_2(\text{g})$, for almost all of them only envisioned the equilibrium shift. Quílez & Solaz (1995) reported that first-year university students assumed that an increase in the amount of solids (heterogeneous equilibria) produced the same change in their concentration. Allsop & George (1984) suggested that although students appear to be under the impression that statements such as ‘the equilibrium shifts to the left’ mean more *reactants* and less *products*, they give no consideration at all to changes in concentrations. Therefore, in the present study, it may be hypothesised that high school students feel that those changes in concentration are obvious, for they parallel changes in mass. But, as has been discussed above, in the case of equilibrium systems it is not enough to recall the concept of molarity. We must stress that reasoning on the equilibrium law expression is the appropriate way to report accurate changes in concentration. However, in the rest of the groups, a change in $[\text{NO}_2(\text{g})]$ was mainly based on the variation in the mass of $\text{NO}_2(\text{g})$, which supports the previous hypothesis. Only in 6% of T1 responses was correctly stated that the concentration would increase, explaining it on the basis of the equilibrium law. Moreover, in 3% of T1 answers was suggested that it was not possible to know the change in the concentration of $\text{NO}_2(\text{g})$ because its amount had diminished, but the volume had diminished

TABLE 2. Percentages of change in $[\text{NO}_2(\text{g})]$ and explanations given when pressure is increased, at constant temperature, in the equilibrium: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$.

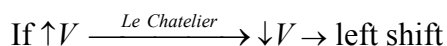
	T-1	T-2	Ss-1	Ss-2	Us
decrease	65	55	4	7	48
increase	6	10	-	17	15
only shift given	16	20	81	59	30
Explanation					
mass	58	65	4	24	63
K	9	-	-	-	-
Boyle's law	-	25	14	7	7

too. A surprising finding was the responses that mentioned only Boyle's law. In some of those responses it was suggested that if the volume had diminished, then an increase in the concentration would have taken place.

The overall discussion made for Tables 1 and 2 applies also to the data of Tables 3 and 4. The parallel misunderstandings and difficulties between Tables 1 and 3 can be seen by observing some key figures. Once again, among Ss-1 correct responses (53%), most of them (48 %) were based on an improper application of Le Chatelier's qualitative statements, as follows (LC-3):

'When the volume of the vessel is increased, then pressure diminishes, therefore, *there is a decrease in the total number of moles of the reaction*; it would go to the right, since according to Le Chatelier, when a factor disturbs the equilibrium, the system evolves in the way that counteracts the disturbance, thus the system shifts to the right because it is there where is the greater number of moles.'

57% of responses in Ss-2 group predicted a left shift. The most common left shift answer (LC-4) was symbolically as follows:



Now, 40% of T2 responses were unable to predict any shift. Left shift prediction was stated in 19% of Us responses.

Similarly, results of Table 4 are consistent with those of Table 2. Once more, high school students were unable to predict a change in the concentration of $\text{NO}_2(\text{g})$. In the rest of the groups, a change in $[\text{NO}_2(\text{g})]$ was mainly explained on the basis of the variation in the mass of $\text{NO}_2(\text{g})$. In 3% of T1 responses it was correctly stated that the concentration would decrease, explaining it on the basis of the equilibrium law. Moreover, in 3% of T1 answers it was supported that it was not possible to know the change in the concentration of $\text{NO}_2(\text{g})$ because its amount had increased, but the volume had increased too. There were also some responses which used only Boyle's law.

TABLE 3. Percentages of forward shift answers and explanations when volume is increased, at constant temperature, in the equilibrium: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$.

	T-1	T-2	Ss-1	Ss-2	Us
forward shift	81	50	53 (LC-3: 48)	17	70
Le Chatelier	51	40	84	74 (LC-4: 57)	78
K	32	10	-	-	11

TABLE 4. Percentages of change in $[NO_2(g)]$ and explanations when volume is increased, at constant temperature, in the equilibrium: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.

	T-1	T-2	Ss-1	Ss-2	Us
increase	61	45	4	4	48
decrease	3	5	-	20	11
only shift given	16	-	80	50	30
Explanation					
mass	58	35	4	20	59
K	13	5	-	-	-
Boyle's law	-	30	14	4	7

Question 2

The main results corresponding to the first part of Question 2 are summarised in Tables 5 and 6. It was expected that correct shift predictions would exceed the figures outlined in Table 5, for students find it easy to predict equilibrium shifts when a reactive is added to an equilibrium mixture (see, *e.g.*, Quílez, 1998b). However, most students extent incorrectly Le Chatelier's qualitative rules to cases in which the mass of a solid is changed in an heterogeneous equilibrium system. Now the first part of Question 2 asks for the change in the partial pressure of $HBr(g)$, rather than for the equilibrium shift. It seems that many students (about one in four) as well as some teachers concentrated on this change (physical behaviour of gases), without noticing that after the addition of $NH_3(g)$ (a non-equilibrium position) a chemical reaction takes place until a new equilibrium position is attained. Results shown in Table 6 support this assumption. But let us discuss the responses in detail.

As with Question 1, Le Chatelier's rules were mainly applied for predicting the equilibrium shift (Table 5). Few teachers' responses made use of the equilibrium law. Let us quote some students' statements. In the Ss-1 group two left-type shift statements were found:

'When introducing NH_3 the volume decreases and the pressure of $HBr(g)$ increases and then also the number of moles, and the equilibrium shifts to the side where there is less number of moles, that is, to $NH_4Br(s)$.'

'When introducing NH_3 into the vessel, let's suppose that the volume is the same, pressure increases, which implies a greater number of moles, the equilibrium shifts to the left in order to equal the equilibrium.'

In the first of the above statements, it seems that students assumed that 'the volume of $HBr(g)$ has been reduced' due to an addition of $NH_3(g)$. Once again, some students could not understand gas behaviour. These two statements reproduce the misunderstandings found in the case of Question 1. Moreover, the following incorrect reasoning led to an opposite shift prediction, as follows:

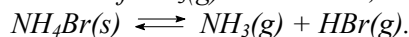
'When introducing NH_3 , the volume increases and pressure decreases, which implies a reduction in the number of moles; the system would go to the right, since according to Le Chatelier when a factor disturbs the equilibrium, the system evolves in the way that counteracts the disturbance, thus the system shifts to the right because it is where there is the greater number of moles.'

TABLE 5. Percentages of backward shift answers and main explanations when the amount of $\text{NH}_3(\text{g})$ is increased, at constant volume and temperature, in the equilibrium:

	T-1	T-2	Ss-1	Ss-2	Us
backward shift	71	50	25	60	44
Le Chatelier	58	55	36	60	48
K	13	15	-	-	-

In the responses of the other groups it was found that in most cases of application of Le Chatelier's rules it was predicted that the system would shifted to the left (reactant side) because a product was added to the equilibrium. But, only in 6% of T1 responses was mentioned that this statement is always true when the isothermal addition of NH_3 is made keeping constant the volume of the vessel (*i.e.* a proper control of the variables involved was made).

There are many subcategories behind the data of Table 6. We will only report the most representatives. A backward shift was the main explanation used to predict the decrease in the partial pressure of HBr (Table 6). But this was not the case for many responses, for a wide range of difficulties appeared when trying to cope with the change in the partial pressure of HBr. Among those that did not make any shift prediction, 6% of T1 responses, 10% T2 responses as well as 19% of Us responses said that an increase in the total number of moles would increase total pressure, thus, increasing partial pressure of $\text{HBr}(\text{g})$. Also, in 8% of Us responses it was stated that the partial pressure of $\text{HBr}(\text{g})$ would increase because 'its volume had been decreased' (or 'there was more volume for NH_3 '). Furthermore, high school students made use of the ideal-gas equation to arrive at an increase in the partial pressure of $\text{HBr}(\text{g})$: 23% Ss-2 responses as well as 21% of Ss-1 responses agreed with this assumption, stating that the addition of NH_3 had increased the total number of moles, and thus, the pressure of HBr. An additional 14% assumed that, as the volume had not changed, a greater amount in the total number of molecules had given less room for those of HBr, producing an increase in its pressure. All of the responses that assumed that the partial pressure of $\text{HBr}(\text{g})$ would remain unchanged predicted backward shift. This misunderstanding might be explained on the basis of previous similar findings (Hackling & Garnet; 1985; Quílez, 1998b).

TABLE 6. Percentages of change in the partial pressure of $\text{HBr}(\text{g})$ and main explanations when the amount of $\text{NH}_3(\text{g})$ is increased, at constant volume and temperature, in the equilibrium:

	T-1	T-2	Ss-1	Ss-2	Us
increase	16	20	-	13	26
decrease	71	50	-	10	37
unchanged	-	15	7	13	22
only shift given	4	-	36	60	30
Explanation					
mass	71	50	-	10	44
K	13	15	-	-	11
$pV=nRT$ or Boyle	6	10	35	23	27

The results corresponding to the second part of Question 2 are summarised in Tables 7 and 8. The figures in Table 7 highly contrast those of Table 3. In Question 1, most of the responses predicted a shift when changing the volume (Table 3), but in Question 2, when dealing with the same disturbance, most students as well as many teachers did not predict the equilibrium shift. Rather, responses concentrated on using Boyle's law (Table 8). 19% of T1 responses correctly reasoned that a forward shift did not mean an increase in the partial pressure of HBr, because it remained unchanged, taking into account the equilibrium law. However, this was not the case for the rest of responses that made a correct shift prediction (35%), stating that the partial pressure of HBr would increase. In 30% of T2 responses as well as in 15% of Us responses a parallel was drawn between the changes in both partial pressure and mass. 15% of T2 responses accurately based their answer on the equilibrium law. 6% of T1 responses reasoned on the equation $p_i = n_i RT/V$, stating that a change in p_i was not possible to predict because both n_i and V had increased. None of the students reported a correct answer. The misunderstandings mentioned above appeared again in this question. For example, Ss-1's idiosyncratic use of Le Chatelier's rules was consistent with that previously discussed.

TABLE 7. Percentages of forward shift answers and main explanations when the volume of the vessel is doubled, at constant temperature, in the equilibrium: $NH_4Br(s) \rightleftharpoons NH_3(g) + HBr(g)$.

	T-1	T-2	Ss-1	Ss-2	Us
forward shift	58	45	18	7	26
Le Chatelier	32	30	39	14	18
K	26	15	-	-	-

TABLE 8. Percentages of change in the partial pressure of HBr(g) and main explanations when the volume of the vessel is doubled, at constant temperature, in the equilibrium: $NH_4Br(s) \rightleftharpoons NH_3(g) + HBr(g)$.

	T-1	T-2	Ss-1	Ss-2	Us
increase	35	35	-	7	11
decrease	26	30	50	63	41
unchanged	19	20	-	-	11
Explanation					
mass	35	30	-	7	15
K	26	15	-	-	-
Boyle's law	26	30	50	63	48

CONCLUSIONS AND RECOMMENDATIONS

In spite of the current educational approach of modern general chemistry textbooks when dealing with the prediction of the evolution of a disturbed chemical equilibrium (*i.e.* a discussion based on Le Chatelier's rules is carried out along with the use of the equilibrium law), it is reported that Le Chatelier's rules were the main and almost exclusively conceptual tools used to predict equilibrium shifts when changing pressure, volume or mass. Moreover, as it has been reported in previous papers (Quílez & Solaz, 1995; Quílez, 1998b), a later deep exposition to thermodynamics seems to have little effect on an accurate use of the equilibrium law by both students and teachers. A small proportion of in-service high school teachers used the equilibrium law; these reasons were scarcely used by both university

students and pre-service teachers. Most of high school students made use of their own misapplied Le Chatelier's rules: *e.g.* some of these statements contradict gas behaviour. However, in some cases, those incorrect rules led students to make correct predictions. Characteristic erroneous explanations made by the high-school student groups might have originated from particular teaching approaches.

Changes in concentration caused by a variation in the volume of the equilibrium vessel were mainly associated with equilibrium shift mass changes. Moreover, an inability to reason in terms of the chemical equilibrium concept was noted, restricting gaseous-equilibrium systems to their physical behaviour. With the exception of in-service teachers, pre-service teachers and students used Boyle's law, relating changes in concentration with changes in volume. Few in-service teachers noticed changes in both volume and mass. Failure to keep in mind more than one variable was a common pattern in most of the explanations. The equilibrium law was not used at all by students, while only a small number of teachers did mention the equilibrium constant in their explanations. As a result, few correct answers were obtained.

Dealing with equilibrium systems involving gases was a difficult task for most of the students. Misunderstanding of gas behaviour was the most important obstacle when coping with changes in partial pressure due to changes in both mass and volume. Once again, many responses concentrated on the physical behaviour of the gases involved, instead of using the equilibrium law to report the chemical changes occurred. Surprisingly, not only did students use these explanations, but also teachers did. Moreover, responses that predicted a correct shift were unable to evaluate the associated changes in partial pressure. It seems that some pre-service teachers as well as some students did not understand that in an equilibrium shift reactants as well products change their mass (*i.e.* a chemical reaction is produced). Changes in partial pressure caused by a variation in the volume of the equilibrium vessel were mainly associated with equilibrium shift mass changes. Thus, the change in the volume was used to predict the equilibrium shift, but it was not considered in order to try to foresee a variation in the partial pressure. This is another case of reduction of the variables involved. Few responses discussed changes in partial pressure based on the equilibrium law.

Rote learning and algorithmic procedures may be behind some of the most important difficulties reported in this study. These findings reinforce previous research on problem solving in chemistry that reveal that a majority of students solve all problems by applying a memorised algorithm without understanding the concepts and principles involved (Herron, 1996). Le Chatelier's rules were widely misapplied by high school students when dealing with equilibrium shifts. Language usage impeded a proper use of these rules, which might have been presented to students using a causal linear reasoning. Such a teaching approach might have been reinforced by incorrect previous mechanical knowledge. Furthermore, these rules were applied by both teachers and university students beyond their limited scope. This work supports some previous findings according to which explanations based on the equilibrium law might have been eclipsed by qualitative simple rules. That is, students and many teachers prefer the explanation which they perceive as the one that requires the least expenditure of cognitive effort.

Turning to recommendations, we start by emphasising the need of teaching strategies that apply the equilibrium law. Such strategies may be more effective if they are designed keeping in mind a general pattern of conceptual change (Níaz, 1998). Those educators who still maintain that Le Chatelier's qualitative principle is a useful conceptual tool should keep in mind the limited character of Le Chatelier's principle, and that its vague and ambiguous formulations lead to a wide range of situations in which the principle is widely misapplied. Furthermore, this qualitative and supposed simple principle usually impedes using the more

formal, precise and accurate scientific reasoning that is based on the the Q - K inequalities. These problems call then for a teaching approach grounded solely on the equilibrium law, which promotes proportional reasoning. Although there are some promising attempts based on that research line (Quílez, 1997b), there is a long-term well-planned teaching task to be carried out. Obviously, such an approach will not solve all the problems arising from the use and (mis)application of Le Chatelier's qualitative rules, but it seems that it can be successful in helping students understand the concepts involved.

An advanced justification of equilibrium shifts takes in consideration the Q - K approach, although it is now justified on the basis of the second law of thermodynamics (Brenon-Audat, Busquet & Mesnil, 1993; Quílez & Solaz, 1996). As a matter of fact, a complete understanding of the underlying issues in chemical equilibrium will only be possible after students have studied thermodynamics. A more advanced thermodynamic treatment can be based on the changes in the extent of reaction in open equilibria (Solaz & Quílez, 2001). Finally, it should be added that although kinetic reasoning strategies can also be used to predict chemical equilibrium shifts (Tyson et al., 1999), it has been claimed (Bucat & Fenshan, 1995) that the Q - K approach may be easier for freshman students.

Although the thermodynamic treatment far exceeds the one that can be developed at the freshman level, it is important to emphasise that there is no reason to insist on teaching the Le Chatelier's rules. An evolutionary curricular perspective, grounded on the equilibrium law, should be kept in mind instead (Quílez, 2002). This means that it is not necessary to include all the cases of equilibrium disturbance in the high school chemistry syllabus. At this level, the study of isothermal equilibrium perturbations can be reduced to the following cases:

- i) change in the mass, at constant volume, of the chemicals (one or more) involved in the equilibrium system;
- ii) variation in the pressure/volume of the equilibrium mixture:
 - a) in the case of closed gaseous systems (the vessel has a mobile piston);
 - b) in the case of aqueous equilibrium solutions (the volume is changed adding or removing water).

By checking the Q - K inequalities, high school students may reason mathematically in order to find out if the equilibrium has been disturbed and, then, to predict the subsequent reaction that takes place until a new equilibrium position is attained.

The results of this study call also for a teaching methodology that enables students to trace the 'history of the equilibrium system'. However, this 'history' has some language problems associated with it (Quílez et al., 2003). Students should be aware of what means to *disturb* a chemical equilibrium, *i.e.* to recognise which are the physical changes that may disrupt an initial equilibrium position. This disturbance can be understood on the basis of the physical behaviour of the chemicals involved. A variation on the initial conditions of the equilibrium system (*i.e.* isothermal changes in pressure, volume or mass) should be viewed as a possible change in the concentration (or partial pressure in gaseous mixtures) of one or more of the chemicals involved. The equilibrium has been disturbed when the new values do not fit the equilibrium constant. Once a non-equilibrium position has been identified, students should be able to predict how the system will attain a new equilibrium position. A mathematical discussion based on the meaning of both the equation of the reaction quotient (Q) and its value, leads to the conclusion that in order to restore the value of the equilibrium constant (K), a chemical reaction takes place, thus changing the amounts of all reactants and products. Therefore, teaching the *evolution* from a non-equilibrium situation to a new

equilibrium position is another language problem to cope with in order to enhance students understanding. Eventually, the whole of this explanation enables students to realise one of the differences between physical and chemical equilibria (Tyson et al. 1999). Moreover, students should be cautioned about the range of applicability of the gas laws (e.g. Boyle's law) for predicting changes in concentration or in partial pressure. In conclusion, this issue of terminology and mathematical reasoning can be summarised in two mental steps: i) a physical change that disrupts the initial equilibrium position, causing a non-equilibrium state, and ii) followed by a chemical reaction until a new equilibrium position is achieved.

ACKNOWLEDGEMENTS: The author wish to thank Dr. Jan van Driel of the *University of Leiden* (The Netherlands) for his helpful comments on a draft version of this paper. Also, the author is grateful to the Editor for helping with the revision of the initial manuscript.

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