A Brief Review on the Contributions to the Knowledge of the Difficulties and Misconceptions in Understanding the Chemical Equilibrium

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ABSTRACT— *The existence and persistence of errors in the understanding of chemical equilibrium denotes student's difficulties in learning and also in teaching methodologies. The knowledge of these difficulties, in depth, can help teachers to try to overcome them. This work is a review together with new contributions on the chemical equilibrium misconceptions analyzed by a group of university and high school teachers. On the one hand, we pretend to collect some of most common difficulties that students, from high school and university, show in relation to chemical equilibrium and Le Chatelier's Principle application. On the other hand, we also intend to analyze the possible causes and even, occasionally, make suggestions of activities to help teachers to improve the topic. This work collects difficulties and misconceptions related with basic concepts of equilibrium (system type, forward and reverse reaction rates, stoichiometry, catalyst function, equilibrium constant and reaction quotient, changes of equilibrium constant with temperature and concentration…); as well as with the understanding and the prediction of the direction of change in the equilibrium position by changing different variables such us composition, volume, pressure or temperature. Finally, educational implications addressed to the teachers have been underlined in order to amend the observed mistakes by alerting students and changing methodologies. In order to not excessively lengthen the study, ionic equilibria have not been addressed. Moreover, the work makes special emphasis on the most common and significant conceptual errors but, obviously, is not an exhaustive revision of all the possible misconceptions.*

Keywords— misconceptions and errors, chemical equilibrium, learning and teaching methodologies.

1. INTRODUCTION

The experience demonstrates that the students' ideas associated with chemical equilibria are among the most difficult to teach and learn in pre-university chemistry levels even though it is supposed that students do not have preconceived ideas about the chemical equilibrium. In this sense, this topic has been one of the most debated issues in the teaching of chemistry, as shown by the great number of references dealing with in the last three decades (see all references).

The present work is a review together with new contributions on the chemical equilibrium misconceptions analysed by a group of university professors in conjunction with high school teachers. Two main goals are pretended, on the one hand, to collect some of the typical difficulties that both collectives of students (from high school and university) show in relation to chemical equilibrium and Le Chatelier's Principle (LCP). On the other hand, we also intend to analyse the possible causes and even, occasionally, make suggestions of activities addressed to help the teachers to overcome these difficulties.

2. DIFFICULTIES IN UNDERSTANDING BASIC ASPECTS OF CHEMICAL EQUILIBRIUM

Let us first consider some of the main difficulties detected in learning about chemical equilibrium basic concepts:

2.1. Need of Considering a Closed System

It has been observed that many students do not consider that one of the conditions required of a chemical system to reach equilibrium is that the system is closed (Furió & Ortíz, 1983), and others incorrectly assume that gaseous equilibria take place in open containers (van Driel & Gräber, 2003). The reason could be due to the fact that teachers do not make enough emphasis when explaining the equilibria conditions related to the kind of system, and students interpret that are equally applicable to a closed vial or a glass (Tyson et al., 1999).

Therefore, in order to help students to understand the importance of that equilibrium is reached in a closed system, an item commonly used at high school with satisfactory results, has been proposed by the authors in their lectures:

Item 1. If a closed container containing a certain amount of $CaCO_3(s)$ is heated to a certain temperature, the carbonate decomposes according to the reaction: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. Keeping the temperature constant, a moment arrives in which the quantities of solids remain constant indefinitely. What will happen to the quantities of solid if this process had been carried out in an open container? Explain your answer.

This item aims to show how the final state, depending on conditions, can be achieved before the reagent is depleted. Therefore, it should be clear from the beginning of the subject that systems in can achieve an equilibrium state only in closed systems. The results shown that a significant percentage of students answered correctly.

2.2. A "dynamic" equilibrium: forward and reverse reaction rates

Other condition for a reaction to be at equilibrium is that the rate of the forward and reverse reactions should be equal, leading then to a state of dynamic equilibrium. This situation is represented by a double arrow, which means that the reaction proceeds in both directions (so-called reversible reactions).

Among the most frequent and common difficulties regarding the reaction rates, it can be noted the following: i) consider that the forward reaction rate is greater than the reverse reaction rate; ii) incorrectly assume that the direct reaction has to be completed before the reverse starts (van Driel and Gräber, 2003); iii) when equilibrium is reached no reaction occurs (Gorodetsky & Gussarsky, 1986; Maskill & Cachapuz, 1989; Griffiths, 1994; Thomas & Schwenz, 1998); iv) think that the rate of the reverse reaction varies similarly to that of the forward reaction, so increasing one of them the other also increases and vice versa (Hackling & Garnett, 1985). The lack of knowledge that two opposite reactions are involved in an equilibrium process is probably due to the emphasis made by teachers in the initial/first lessons of chemistry where reactions become complete.

Regarding reversibility, when students access to the equilibrium lessons, they only have previously studied irreversible reactions (represented by an arrow) that finish when a reactant has been spent. Therefore is difficult for them to assume the existence of two simultaneous opposite reactions, which is a crucial concept to understand how the equilibrium is attained. In this sense, another students' idea is that the equilibrium state is conceived as two states, one attributed to the reactants and a different one to the products, that is, they have a compartmentalized view of the chemical equilibrium (Johnstone et al., 1977; Furió & Ortíz, 1983; Cachapuz & Maskill, 1989; Paiva & Gil, 2000; Chiu et al., 2002; Akkus et al., 2003). Several reasons can be argued to explain this interpretation. On the one hand students approach this topic with a concept of equilibrium that comes from their experiences with mechanics (static concept). On the other, the traditional teaching uses physical analogies that may contribute to create a static idea of the equilibria (Johnstone et al., 1977); or to identify the concept of reversibility with the physical movement and to achieve equilibrium when everything is equalled (Maskill & Cachapuz, 1989). Moreover, the way to represent equilibrium with the double arrow separating the two sides of the equation may induce students to interpret the balance as two separate systems that evolve from one to another.

In addition, from a macroscopic point of view, the chemical equilibrium is attained when the concentrations of substances involved always satisfy certain relation (K_c) and all mixtures give the same value of K_c at constant temperature, which helps to strengthen the idea of a static equilibrium. These ideas make difficult to admit that equilibrium is a dynamic concept necessary to understand the new composition obtained when the equilibrium state is modified. It is important to note that K_c defined in terms of concentrations is not strictly constant but vary within a range, typically, of about 10 %. Equilibrium constants are defined as a function of activities, however this matter is outside the scope of the contents for secondary school or first chemistry university levels.

In order to help in the understanding of the chemical equilibrium as a dynamic process, it is recommended to use a microscopic treatment based on collision model. This approach makes clear that whenever there is a reactant molecule,

the products can be formed leading to the existence of two opposite reactions with different initial rates that equal when the equilibrium is achieved. Furthermore, the microscopic model allows explaining that when changing one of the reaction rates, the system will evolve until reaching a new equilibrium state with different composition.

2.3. Mass versus concentration

One of the most common mistakes accounts with the association or identification of two concepts: mass and concentration. Some students believe that the amount of substance (in mole) is the concentration and even identify "solid concentration" with solid mass (Wheeler & Kass, 1978; Furió & Ortíz, 1983; Quílez & Solaz, 1995; van Driel & Gräber, 2003; Akkus et al., 2003; Quílez, 2004; Quílez, 2006). This difficulty could be originated in the historically discussion of establishing how the amount of substance affected the chemical equilibrium. Also, it is worthwhile to point out the difficulty of students in understanding that solids have constant concentration at equilibrium. In this sense, Furió et al. (1983) asked for different ways to increase the solid concentration in the following example: $NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g)$. Most students chosen the answer that shifted the reaction towards the formation of solid but they do not chosen the only correct answer that was "the question is absurd" since the term "solid concentration" is meaningless. Nevertheless, the most striking fact was that also a significant percentage of teachers responded incorrectly, which suggests that sometimes the error is not conceptual but rather methodological since a comprehensive reading of the statement has not been made.

2.4. Difficulties undertaking stoichiometry

Regarding the equilibrium concentrations, some students think that the concentrations of all the species involved in the system are equal at equilibrium (Tyson et al., 1999) or that concentrations of the reactants and the products were equal at equilibrium (Hackling & Garnett, 1985; Huddle & Pillay, 1996; Akkus et al., 2003; Stieff & Wilenski, 2003). This mistake can be attributed to the fact that students assume that equal stoichiometric coefficients should correspond to equal concentrations.

Other difficulties with stoichiometry also occur when the molar ratio of reactants is different from 1:1 and very often the students do not relate the reaction stoichiometry with the expression of the equilibrium constant (Piquette & Heikkinen, 2005). A good example that highlights the difficulties in managing stoichiometric calculations, proposed by our group, is the following:

Item 2. For the reaction $4NH_3(g) + 7O_2(g) \leftrightarrow 2N_2O_4(g) + 6H_2O(g)$, the initial concentrations are $[N_2O_4]_0 = [H_2O]_0 = 3.60$ mol.L^{-1} and the water concentration at equilibrium is $[H_2O]_e = 0.60$ mol.L^{-1}. Calculate the equilibrium concentration of $NH_3(g)$ in mol.L^{-1}. Answers:

a) 3.00   b) 2.00   c) 2.40   d) 0.90   e) the equilibrium constant for the calculation is needed

In solving the problem, some high school students made the following balance between initial and equilibrium moles:

	NH$_3$ (g)	O$_2$ (g)	N$_2$O$_4$ (g)	H$_2$O (g)
n_0	—	—	3.60	3.60
Δn	x	x	x	x
n_{eq}	x	x	3.60 – x	3.60 – x

As can be seen, they did not take into account the stoichiometry of the reaction, otherwise they should had written 4x, 7x, 3.60 – 2x and 3.60 – 6x respectively, for the equilibrium moles of all species. Most of the mistakes in stoichiometric calculations are associated with difficulties dealing with previous concepts such as atom, molecule, chemical reaction, balanced equation, mole, and the law of conservation of mass or mathematical calculations involving proportionality.

In other cases, they apply incorrectly the stoichiometry, for example, multiplying the initial quantities by the stoichiometric coefficient. Summarizing, difficulties in solving quantitative equilibria exercises have been analyzed by (Camacho & Good, 1989; Niaz, 1995; Tsaparlis & Kousathana, 1995; Tsaparlis et al. 1998; Niaz, 2001; Kousathana & Tsaparlis, 2002), among others.

2.5. Catalyst function

As it is well known, a catalyst acts increasing the reaction rate but does not alter the equilibrium position. In different assays related with this topic, a 21% of students answered that the catalyst only increases the rate of the forward reaction

(Voska & Heikkinen, 2000) whereas a significant percentage of students said that a catalyst affects in a different way the rates of the forward and reverse reactions at equilibrium (Hackling & Garnett, 1985; Griffiths, 1994). Some others also believe that the concentration of reactants or products changes with the addition of the catalyst (Griffiths, 1994) or that the catalyst can be used to drive the reaction in the side that we are interested in (Johnstone et al., 1977).

2.6. Equilibrium constant and reaction quotient

The equilibrium constant reports on the degree of transformation of a chemical system and can be expressed in terms of concentration (K_c) or pressure (K_p) of species when the equilibrium is attained. The reaction quotient, Q, refers to concentrations (Q_c) or pressures (Q_p) of the substances in a non-equilibrium situation.

The difficulties related to the equilibrium constant concept could be summarized and classified as follows:

1. Regarding temperature, T, the most usual misconceptions are: i) do not consider K_{eq} constant at a given T (Furió & Ortíz, 1983; Bergquist & Heikkinen, 1990); ii) think that the K_{eq} value does not depend on T (Voska & Heikkinen, 2000); iii) or when K_{eq} depends on T, it always does in a directly proportional way, that is, if temperature increases also the K_{eq} does (Voska & Heikkinen, 2000).

2. Regarding concentration: i) think that K_{eq} changes with the change of concentrations at constant T (Bergquist & Heikkinen, 1990; van Driel & Gräber, 2003); ii) the K_{eq} value increases as more products are added to the system at equilibrium at constant T (Hackling & Garnett, 1985). This suggests that the students focus/pay attention only to one specie, ignoring the concentration of the other species and their stoichiometric relationships. iv) identify Q with K_{eq} (Piquette & Heikkinen, 2005).

3. Regarding reaction rate: interpret the value of the constant equilibrium with the reaction rate, assuming that the higher the K_{eq} the faster the reaction proceeds (Banerjee, 1991).

Most of these highlighted difficulties may be due, in general, to do not make enough insistence in differencing between Q and K_{eq}.

3. DIFFICULTIES IN UNDERSTANDING AND PREDICTING THE DIRECTION OF CHANGE IN EQUILIBRIUM POSITION

A system in equilibrium can be disturbed by changes in different magnitudes: composition, pressure, volume and temperature. As a consequence, the chemical reaction will proceed in either of both directions until a new equilibrium state is achieved. To predict how a system evolves when its equilibrium state is disturbed, two approaches can be used: the Le Chatelier's Principle (LCP) for a qualitative prediction, and the equilibrium law for a quantitative analysis.

For simplicity, the LCP is widely used in the teaching of chemical equilibrium from a qualitative point of view, and therefore, difficulties related to understanding or misapplication is also profusely found in the literature (Banerjee, 1991; Quílez & Solaz, 1995; Tyson et al., 1999; Voska & Heikkinen, 2000; van Driel & Gräber, 2003; Kind, 2004; Quílez, 2006). In this regard, Quílez attributes the incorrect implementation of the LCP to three main reasons: i) problems derived from of inductive method of generating the scientific knowledge; ii) difficulties arising from use of scientific language; and iii) the conceptual demand required in the study of systems with different variables to be controlled.

Let us now, to discuss more in-depth the observed students difficulties.

3.1. Equilibrium position when changing composition

Specifically, the composition of the substances involved in the chemical equilibrium can be altered by changing the number of moles of the involved gaseous substances at constant volume and temperature or at constant pressure and temperature.

3.1.1. Adding or removing a reactive gas at constant P and T.

The misconceptions related to addition or removal of a reactive gas at constant pressure and temperature, have been studied by different researchers such as Katz (1961); Quílez & Solaz (1995); Solaz & Quílez (2001); Quílez (2006) and Cheung et al. (2009), among others.

In first place, we discuss the work of Katz focused on a general gas reaction aA(g) + bB(g) ↔ dD(g) + eE(g), for which the reaction quotient, in terms of mole numbers, is written as:

$$Q_p = \frac{x_D^d \, x_E^e}{x_A^a \, x_B^b} P^{\Delta n} = \frac{n_D^d \, n_E^e}{n_A^a \, n_B^b} \left(\frac{P}{n_T} \right)^{\Delta n} \qquad (1)$$

being n_i and x_i the mole number and mole fraction of the i specie, respectively; P the total pressure, n_T the total mole number, and Δn the difference in the number of gaseous moles of products and reactants. To evaluate the effect of the addition of a reactant or product (for example E) at constant pressure, the derivative of Q_p regarding n_E has to be calculated:

$$\left[\frac{\partial Qp}{\partial n_E} \right]_P = \frac{n_D^d \, e \, n_E^{e-1}}{n_A^a \, n_B^b} \left(\frac{P}{n_T} \right)^{\Delta n} + \frac{n_D^d \, n_E^e}{n_A^a \, n_B^b} P^{\Delta n} \left(\frac{-\Delta n}{n_T^{\Delta n+1}} \right) \qquad (2)$$

taking in mind that Q_x is expressed as:

$$Q_x = \left(n_D^d \, n_E^e \big/ n_A^a \, n_B^b \, n_T^{\Delta n} \right) \qquad (3)$$

and making some rearrangements, finally:

$$\left[\frac{\partial Qp}{\partial n_E} \right]_P = Q_x \frac{e \, P^{\Delta n}}{n_E} - Q_x P^{\Delta n} \left(\frac{\Delta n}{n_T} \right) = Q_x P^{\Delta n} \left(\frac{e}{n_E} - \frac{\Delta n}{n_T} \right) \qquad (4)$$

According to equation (4), the derivative is positive if $x_E \Delta n < e$ and is negative if $x_E \Delta n > e$. For simplicity, these general equations can be applied to the reaction $2NH_3(g) \leftrightarrow N_2(g) + 3H_2(g)$, for which the reaction quotient is expressed as (Katz, 1961):

$$Q_p = \frac{n_{N_2} \, n_{H_2}^3}{n_{NH_3}^2} \left(\frac{P}{n_T} \right)^2 \qquad (5)$$

Some conclusions can be derived depending on which specie is added or removed:

a) If a reactant, ammonia for example, is added at constant pressure, both n_{NH3} and n_T increase and then $Q_p < K_p$. In order to restore the equilibrium state, the reaction will be shifted to the products, in agreement with that predicted by the Le Chatelier's principle (LCP).

b) If a product, hydrogen for instance, is added at constant pressure, both n_{H2} and n_T increase but with an inverse effect. As the percentage of increase for n_{H2} is higher than for n_T, the reaction would shift to the reagents in order to counteract the disturbance, also in agreement with the LCP.

c) Finally, if nitrogen is added, the LCP predicts the shifting of the reaction to the reagents, as in the preceding case. However, let us consider this case from a quantitative point of view. The addition of nitrogen would increase the n_{N2} and n_T, affecting the numerator and the denominator of equation (5) but in a different way due to their exponents (1 and 2, respectively). Therefore, is not clear which is the effect on the equilibrium position and it is necessary to calculate the derivative of Q_p regarding n_{N2} at constant pressure:

$$\left[\frac{\partial Q_p}{\partial n_{N_2}} \right]_p = \frac{n_{H_2}^3 P^2}{n_{NH_3}^2} \left(1 - \frac{2 \, n_{N_2}}{n_T} \right) = \frac{n_{H_2}^3 P^2}{n_{NH_3}^2} \left(1 - 2 \, x_{N_2} \right) \qquad (6)$$

As seen from equation (6), the derivative is positive if $x_{N2} < \frac{1}{2}$. Then, Q_p increases with the nitrogen addition and the reaction goes toward reagents as the LCP predicts. However, if $x_{N2} > \frac{1}{2}$ the derivative would be negative, Q_p decreases and the reaction shifts toward products in contradiction with the LCP. The same behaviour has been found for the reaction of synthesis of ammonia by decomposition of ammonium bromide NH_4Br (s) $\leftrightarrow NH_3$ (g) + HBr (g) when ammonia, a reactive gas, is added (Quílez & Solaz, 1995; Quílez, 2006).

A similar question, was proposed by Cheung at a chinese teacher's group (Cheung et al. 2009):

Item 3. The $NH_4HS(s) \leftrightarrow NH_3(g) + H_2S(g)$ reaction is at equilibrium in a vessel fitted with a movable piston. The numbers of moles of NH_3 and H_2S in the equilibrium mixture are $1.10 \cdot 10^{-2}$ and $1.65 \cdot 10^{-2}$, respectively. The total volume of the gaseous mixture is 1.0 L. What will happen if $1.35 \cdot 10^{-2}$ moles of H_2S gas is suddenly added to the equilibrium system at constant temperature and pressure? Show the calculations.

A typical solution would be first calculate the equilibrium constant:

$$K_c = [NH_3][H_2S] = \frac{n_{NH_3}}{V}\frac{n_{H_2S}}{V} =$$

$$= \frac{1.65 \cdot 10^{-2}}{1.0}\frac{1.10 \cdot 10^{-2}}{1.0} = 1.82 \cdot 10^{-4}$$

(7)

Secondly, calculate the new volume (remember that there is a plunger) obtained after the H_2S addition by applying the gas perfect equation to the new gas total mole number ($1.10 \cdot 10^{-2} + 1.65 \cdot 10^{-2} + 1.35 \cdot 10^{-2} = 4.10 \cdot 10^{-2}$). Since P and T are constant, $V_i/n_{Ti} = V_f/n_{Tf}$, and $V_f = 1.49$ L.

Thirdly, calculate the value of the new Q_c and compare it with K_c:

$$Q_c = [NH_3]_0[H_2S]_0 = \frac{1.10 \cdot 10^{-2}}{1.49}\frac{3.00 \cdot 10^{-2}}{1.49} = 1.49 \cdot 10^{-4}$$

(8)

and, since $Q_c < K_c$ the equilibrium shifts towards products. Obviously, another way to solve the problem would be through K_p, as follows:

$$K_p = p_{NH_3}p_{H_2S} = x_{NH_3}x_{H_2S}P^2 =$$

$$= \frac{1.10 \cdot 10^{-2} \times 1.65 \cdot 10^{-2}}{(2.75 \cdot 10^{-2})^2} P^2 = 0.24\ P^2$$

(9)

the addition of H_2S leads to a Q_c value of:

$$Q_p = p'_{NH_3}p'_{H_2S} = x_{NH_3}x_{H_2S}P^2 =$$

$$= \frac{1.10 \cdot 10^{-2} \times 3.00 \cdot 10^{-2}}{(4.10 \cdot 10^{-2})^2} P^2 = 0.196\ P^2$$

(10)

The comparison between Q_p and K_p shows again that $Q_p < K_p$ and the reaction shifts towards products. The results shown that only 14 of the 50 participant teachers were able to correctly answer the problem, from which 13 make quantitative calculations through Q_c and K_c and 1 used the expressions of Q_p and K_p. Other 7 teachers failed in calculating Q_c since they did not consider the volume change (the most common misconception) and concluded that the equilibrium is shifted toward the reactants.

One possible reason is that in gaseous equilibrium systems, the equilibrium law is often expressed as K_p instead of K_c in many chemistry textbooks. The teacher may not have recognized that the concentrations of gas species can be expressed as moles per litre occupied. Another possible reason for this misconception is that the teacher did not recognize that the conditions under which the system is disturbed are very important (movable piston and addition of gas made at constant pressure and temperature). It was also striking that, although 14 teachers managed to correctly answer, none of them pointed out that the shift in the equilibrium position (displacement towards products) was inconsistent with that predicted by the LCP (displacement towards reagents).

Other results worthy to be considered were the obtained by Cheung in a study with secondary school chemistry teachers in Hong Kong (Cheung, 2009). The proposed question was:

Item 4. The reaction CS_2 (g) + $4H_2$ (g) ↔ CH_4 (g) + $2H_2S$ (g) is at equilibrium in a reactor fitted with a movable piston. If a small amount of CS_2 (g) is suddenly added to the equilibrium mixture at constant pressure and temperature, what will happen to the number of CH_4 (g) molecules when equilibrium is re-established? Give reasons for your answer.

Few of the 33 participant teachers applied the equilibrium law to quantitatively solve the problem, 28 predicted that the number of molecules of CH_4 will increase and 9 of them based their answer only on the basis of the Le Chatelier's principle. Therefore, if the LCP is applied, the equilibrium position must shift to the right in order to counteract the increase of CS_2 molecules. However, the addition of CS_2 gas will also increase the total volume of the system and will change the concentration of all species and the effect on the equilibrium position will depend on the relative composition. In this sense, only 3 teachers answered correctly by applying the expression for the equilibrium constant:

$$K_c = \frac{n_{CH_4}\, n_{H_2S}^2}{n_{CS_2}\, n_{H_2}^4} V^2$$

(11)

As seen, if a small amount of CS_2 gas is added at constant pressure and temperature, the new position of equilibrium will depend on the relationship V^2/n_{CS_2}. Thus, if this ratio is greater than K_c (or $Q_c > K_c$) the system will move to the reagents, and if the ratio is lower than K_c will shift to the products. Four teachers applied the equilibrium law

considering only the change in the of CS_2 concentration, without taking into account the change in the total volume and in the concentration of the other chemical species.

3.1.2. Adding or removing a reactive gas at constant V and T.

To evaluate this effect in the equilibrium position of an ideal gas reaction aA(g) + bB(g)↔ dD(g) + eE(g), one can use the expression of the equilibrium constant in terms of concentrations:

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b} = \left(\frac{n_D^d\, n_E^e}{n_A^a\, n_B^b}\right)\frac{1}{V^{\Delta n}} = \frac{Q_n}{V^{\Delta n}} \qquad (12)$$

As seen, the addition of a reagent at constant volume causes a decreasing on Q_n and the reaction will be shifted to products in order to restore the equilibrium, and the contrary will occur if a product is added. This fact is in agreement with the LCP predictions. However, if we asked for the effect on other variable, such as the partial pressure of a given specie, the LCP is not longer valid since is unable to predict correctly what happen (Solaz & Quílez, 2001). Let us explain it with the following example proposed and analysed in our lectures:

Item 5. The ammonium bromide is a crystalline solid which decomposes in an endothermic process according to: NH_4Br (s) ↔ NH_3 (g) + HBr (g). Explain how the HBr pressure and the amount of NH_4Br(s) change if NH_3 (g) is added to the reaction vessel at equilibrium.

In first place, the statement says nothing about temperature or container volume, so it is necessary to assume that temperature and volume are constant. Then, if NH_3(g) is added, the partial pressure of ammonia (p_{NH3}) will increase, and given that $K_p = p_{NH_3}p_{HBr}$ is constant, the HBr partial pressure (p_{HBr}) has to be reduced. As a consequence, part of NH_3 reacts with HBr to produce NH_4Br(s) which amount increases. In other words, since Q_p is greater than K_p, the system evolves toward the reactants until equilibrium is re-established. In this case, the LCP is able to correctly predict the direction of the reaction shifting, stating that the more product added more NH_4Br(s) is obtained. However, the LCP cannot say anything about the partial pressure of HBr(g) and, as said before, the reasoning must be based on the expression of the equilibrium constant K_p (Quílez, 2006).

3.2. Equilibrium position when changing the volume of the container at constant T

The changes in the total volume of the reaction vessel are associated to: i) a change of the total pressure at constant temperature and total mole number; ii) adding an inert gas at constant pressure and temperature; or iii) adding/removing a reactive gas at constant pressure and temperature (see section 3.1.1).

3.2.1. Effect of the variation of volume on the partial pressure.

Again, the limitations of the LCP can be illustrated through a variation of item 5 related to the change in total volume, also proposed in our classes:

Item 6. The ammonium bromide is a crystalline solid which decomposes in an endothermic process according to the reaction: NH_4Br (s) ↔ NH_3 (g) + HBr (g) in a vessel at equilibrium. Explain how the HBr (g) pressure and the amount of NH_4Br(s) change if the volume of the container is doubled at constant temperature.

In the light of the equilibrium law, and in order to keep $K_p = p_{NH_3}p_{HBr}$ constant, both partial pressures have to remain constant. However, as the volume is twice the number of moles of HBr and NH_3 must also be double and, in consequence, the solid NH_4Br must dissociate and its amount will decrease. Another valid way of reasoning would be: if the volume is doubled the partial pressures are halved and then $Q_p < K_p$. To reach a new equilibrium state and given that NH_3:HBr ratio is 1:1 and K_p is constant, the system shifts to form more amount of products until their partial pressures attained the same value as in the initial equilibrium.

As stated in the preceding section, LCP can properly predict the way of the reaction shift, but not the effect on the partial pressure of the HBr(g). The use of the state equation of gases, $p_iV = n_iRT$, does not allow to conclude anything about the partial pressure since both n_i and V increase. For this purpose, the reasoning must be based on the mathematical expression of the equilibrium constant as discussed above (Quílez, 2006).

3.2.2. Effect of the variation of volume on the concentration.

Next, we will illustrate the effect of a change of volume on the concentration of substances and the misapplication of the LCP in predicting the shifting of the equilibrium, through the following question (Quílez, 2004; Quílez, 2006; Cheung, 2009):

Item 7. The reaction N_2O_4 (g) $\leftrightarrow$ $2NO_2$ (g) is at equilibrium in a syringe. If the volume decreases at constant temperature by moving the plunger, will the concentration of NO_2 (g) be higher or lower than the original concentration when equilibrium is re-established? Give reasons for your answer.

The results showed that 14 of 33 participant teachers focused on the increasing of the total pressure and used the LCP to predict that the system moved to reagents in order to counteract this disturbance. Therefore, they concluded that the $[NO_2]$ concentration would be lower than the original value when the equilibrium is restored. As can be seen, all these teachers had not taken into account the change in volume, and then in the concentration of other species. Only 2 teachers answered correctly by using the equilibrium law and the expression of the corresponding equilibrium constant:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(n_{NO_2}/V)^2}{(n_{N_2O_4}/V)} = \frac{(n_{NO_2})^2}{n_{N_2O_4}V} \qquad (13)$$

As can be deduced from equation (13), if the volume decreases at constant temperature, Q_c would be higher than K_c and the system moves to the reagents, the amount of N_2O_4 increases and also the N_2O_4 concentration. Therefore, to keep K_C constant, the NO_2 concentration must also be higher than in the initial equilibrium. It is evidenced, again, that the LCP predicts well the direction of the equilibrium position but incorrectly states what happens with the NO_2 concentration.

3.2.3. Effect of the addition of an inert gas at constant P and T.

The addition of an inert gas at constant pressure and temperature is another clear way of changing the volume of the container (given that is not rigid). Let us analyse this effect through the following example proposed to our students:

Item 8. The reaction $2NO_2$ (g) $\leftrightarrow$ N_2O_4 (g) is at equilibrium in a syringe. What is observed in the system when argon is added at constant pressure and temperature?

The equilibrium constant K_c as a function of the total volume is written as:

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{(n_{N_2O_4}/V)}{(n_{NO_2}/V)^2} = \frac{n_{N_2O_4}V}{n_{NO_2}^2} \qquad (14)$$

As the total pressure is constant, the addition of gas argon implies that the volume should increase. Then, $Q_c > K_c$ and the system will shift to the reagents. One could also argue from another point of view, by using the equilibrium constant as a function of partial pressures, K_p:

$$K_P = \frac{p_{N_2O_4}}{p_{NO_2}^2} = \frac{x_{N_2O_4}}{x_{NO_2}^2}\frac{1}{P} = \frac{n_{N_2O_4}}{n_{NO_2}^2}\frac{n_T}{P} \qquad (15)$$

As it is easily deduced, at constant pressure, the addition of gas argon increases the total mole number and $Q_p > K_p$ and the system will shift to the reagents. Obviously for systems in which $\Delta n = 0$, the equilibrium position is not altered by adding an inert gas given that in these cases either equation (14) or (15) would not depend on total volume or total mole number.

The application of the LCP leads to the same conclusion: the addition of argon at constant pressure increases the volume and to counteract, the system moves to the side where the number of moles are higher, that is to the reactants, in order to reach a new equilibrium state.

However, in other studies the addition of an inert gas at constant pressure and temperature was erroneously analysed through the LCP. Specifically, in the survey carried out by Cheung (2009) with the reaction CO (g) + $2H_2$ (g) $\leftrightarrow$ CH_3OH (g), 22 of the 33 participant teachers predicted that the equilibrium state did not change at all. They indicated that the partial pressures of the substances involved in the reaction do not change (since they did not take into account the volume change) and so the system remains in equilibrium. Moreover, 12 of them explicitly cited the LCP in their reasoning saying that argon does not participate in the reaction.

3.3. Equilibrium position when changing the total pressure at constant T

The changes in the total pressure are associated to: i) adding/removing a reactive gas at constant volume and temperature (see section 3.1.2); ii) a change of the recipient volume at constant temperature and total mole number (see section 3.2.1); or iii) adding an inert gas at constant volume and temperature.

3.3.1. Effect of the addition of an inert gas at V y T constants

This last case will be illustrated through the following example, analysed at our classes:

Item 9. The reaction $2NO_2$ (g) ↔ N_2O_4 (g) is at equilibrium in an hermetic container. What is observed in the system when argon is added at constant volume and temperature?

As easily deduced from equations (14) and (15), since the total volume is constant, $Q_c = K_c$ and $Q_p = K_p$ given that the total mole number increases in the same proportion that the total pressure. In consequence, the equilibrium position is unchanged by addition of an inert gas at constant V and T. Moreover, the effect does not depend on the stoichiometry of the reaction at all.

The LCP prediction is in good agreement with the equilibrium law since the partial pressures of all species are not changed, as it can be demonstrated by taken into account that $n_T = n_{N_2O_4} + n_{NO_2} + n_{Ar}$ and $P = n_T RT/V$. The substitution of these expressions yields for the partial pressures to:

$$p_{N_2O_4} = x_{N_2O_4} P = \frac{n_{N_2O_4}}{n_T} \frac{n_T RT}{V} = n_{N_2O_4} \frac{RT}{V} \qquad (16a)$$

and

$$p_{NO_2} = x_{NO_2} P = \frac{n_{NO_2}}{n_T} \frac{n_T RT}{V} = n_{NO_2} \frac{RT}{V} \qquad (16b)$$

However, different studies have evidenced that not only students but also teachers and textbooks incorrectly solved the addition of an inert gas either at constant V and T when applying the LCP (Quílez, 2006; Paiva et al., 2008). Usually they argued that the addition of the inert gas increases the total pressure and causes the shifting of the equilibrium position to the side with lower mole number in order to diminish the pressure.

3.4. Equilibrium position when changing the temperature

The effect of a temperature change can be discussed at constant pressure or at constant volume, although the most common case at secondary school levels and many university courses are to keep the pressure constant.

3.4.1. Effect of changing temperature at P constant.

First of all it is necessary to know the sign of the reaction enthalpy, that is, we need to know if the process under study is exothermic or endothermic.

Let us consider first a general exothermic process, such as: $2A$ (g) ↔ B (g) with $\Delta_r H^o < 0$. From a qualitative viewpoint and according to LCP, if temperature is increased the system shifts in the direction of the endothermic reaction, that is to the reactants side. Conversely, if the temperature decreases the reaction moves toward the products. Obviously, the opposite behaviour it will be observed if the process was endothermic ($\Delta H^0 > 0$).

For a quantitative approach we need to apply the Van't Hoff equation (P = constant) given by (Gold & Gold, 1985):

$$\frac{d \ln K_P}{dT} = \frac{\Delta_r H^0}{RT^2} \qquad (17)$$

or its integrated form if it is assumed that ΔH^0 does not change with temperature:

$$\ln \left(\frac{K_{P2}}{K_{P1}} \right) = -\frac{\Delta_r H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad (18)$$

For an exothermic reaction ($\Delta_r H^o < 0$), an increase in temperature (dT > 0) provokes a negative variation of $d\ln K_p$ which means that $K_{p2} < K_{p1}$ and reaction shifts toward the reactants. Conversely, if the reaction is endothermic ($\Delta_r H^o > 0$) it will move toward the products. The opposite behaviour should be observed if the temperature is decreased. Therefore, it can be concluded that either LCP or the Van't Hoff equation are in agreement, and are able to correctly predict the changes in temperature at constant pressure.

3.4.2. Effect of changing temperature at V constant.

Although this case is not very common, it could be interesting to analyse it since an important contradiction can be outlined. For the general exothermic process depicted above and according to LCP, if temperature is increased the system shifts in the direction of the endothermic reaction, that is, to the reactants side. Conversely, if the temperature decreases the reaction moves toward the products. Obviously, the opposite behaviour it will be observed if the process

was endothermic. As seen, the qualitative prediction is the same independently of the process would take place at constant pressure or at constant volume.

Nevertheless, this reasoning is wrong since when temperature increases at constant volume, the total pressure also increases. Then, in order to reach a new equilibrium, the total mole number has to decrease and the system moves toward products, or in other words in the exothermic way, which is the contrary to the LCP prediction.

For a quantitative approach, the thermodynamic treatment must be based on the Van't Hoff equation at V constant (Katz, 1961; Gold & Gold, 1985; Solaz & Quílez, 1998):

$$\frac{d \ln K_c}{dT} = \frac{\Delta_r U^0}{RT^2} \qquad (19)$$

where $\Delta_r U^0$ is the change of the standard internal energy. Therefore, if $\Delta_r U^0 > 0$, as temperature increases the system moves towards the products, whereas if $\Delta_r U^0 < 0$, shifts to the reactants. Since teachers and students are more familiarized with reaction enthalpy, we can express $\Delta_r U^0$ as a function of $\Delta_r H^o$ through the relationship:

$$\Delta_r U^o = \Delta_r H^o - \Delta n RT \qquad (20)$$

and by substitution into equation (19):

$$\frac{d \ln K_c}{dT} = \frac{\Delta_r H^o}{RT^2} - \frac{\Delta n}{T} \qquad (21)$$

Thus, for a system in which $\frac{d \ln K_c}{dT} < 0$, as T increases the K_c decreases, whereas if $\frac{d \ln K_c}{dT} > 0$, as T increases the K_c also increases. Obviously, in this case, to properly predict the equilibrium direction when temperature varies at constant volume, both $\Delta_r H^o$ and Δn values must be known.

This behaviour is clearly seen in the following example:

Item 10. The reaction $2CO_2(g) + 4H_2(g) \leftrightarrow CH_3OH(l) + CO(g) + 2H_2O(l)$ takes place at constant volume. At 1 atm and 300K the enthalpy reaction is $\Delta_r H^o = -8,4$ kJ. Justify the shifting of the reaction when temperature is increased.

Attending only to the sign of enthalpy, most students said that reaction shifts towards reactants, that is, to the endothermic side of the reaction. However and given that is an isochoric process, the correct answer needs to calculate de $\Delta_r U^0$ value. As $\Delta n = -5$, equation (20) yields $\Delta_r U^0 = 4,07$ kJ. Therefore and according to equation (19), if temperature increases the system moves towards the products.

Finally, we would like to note that the strict thermodynamic way of addressing this situation should be by using the Helmholtz free energy, A, since is the thermodynamic potential defined at constant volume ($A = U - TS$) although its complexity is beyond the scope of the present work. A theoretical treatment of this topic can be seen in Solaz & Quílez (1998).

To emphasize that the analysis of the effects of temperature change on the chemical equilibrium is more complex than it seems, the following question was proposed to a select group of students who participated in the XXV National Chemistry Olympiad held in Spain:

Item 11. For a given reaction at equilibrium, $K_p = 1.0$ at 300 K and $K_p = 2.0$ at 600 K. Therefore, we can say that:

a) $K_p = 1.5$ at 450 K

b) Increasing the pressure in the system promotes the formation of products

c) The reaction is exothermic

d) K_p increases with increasing pressure

e) The reaction is endothermic

The results shown that a 27% of this select group of general chemistry students were not able to correctly answer the question. A possible explanation of this error could be due to the difficulty in relating enthalpy, temperature and equilibrium constant.

Summarizing, among the most common errors observed when changing the temperature of a system at equilibrium are the following:

a) A high percentage of students (65%) think the direction of an equilibrium shift can be predicted without knowing whether the reaction is endothermic or exothermic. In this regard, some of them believe that a decrease in temperature always decreases the value of the equilibrium constant (Voska & Heikkinen, 2000).

b) A 14% of students think that increasing the temperature of a gaseous equilibrium system at constant volume, will increases the pressure of the system. The resulting pressure will cause equilibrium shifts to the side of chemical equation with fewer moles of gas (Voska & Heikkinen, 2000).

c) Some also think that increasing the temperature of the system will increase the number of collisions favouring the formation of more products than reactants (Voska & Heikkinen, 2000).

d) Frequently, they associate temperature changes with speed changes (Hackling & Garnett, 1985; Banerjee, 1991). Most students believe that for an exothermic reaction, the rate of the direct reaction diminishes when increasing temperature. They try to interpret according to the LCP and, then, confuse the rate and the extent of the reaction.

4. OTHER EFFECTS

In addition to the classical effects described and analysed in the previous sections, educational research has also found the difficulties encountered when adding solids, pure liquids or solutions to equilibrium systems.

4.1. Adding solids to a system at equilibrium

It has been found that students, teachers and, even, some textbooks incorrectly apply the Le Chatelier's principle when a system in equilibrium involves solid species. In these cases, it is pointed out that the addition or removal of a small amount of solid it will shift the equilibrium position in the direction that counteract this effect (Tyson et al., 1999) or it will change the "solid concentration" (Quílez, 2006).

Moreover, students usually make use of an additional rule "solids do not affect the equilibrium" since are not included in the K_{eq} expression, which leads to the erroneous assumption that "the amount of solid in an equilibrium system can not be altered".

Our teaching experience is also in agreement with these authors, and it has been corroborated through the following item:

Item 12. Given the equilibrium system: $6\ CO(g) + 6\ H_2O(l) \leftrightarrow C_6H_{12}O_6(s) + 6\ O_2(g)$ with $\Delta_rH° = 2816$ kJ. Predict how the amount of glucose is modified as the temperature increases at constant pressure.

A significant percentage of students answer that the amount of glucose remains unchanged since the solids do not affect the equilibrium position, without taking into account that temperature has been changed.

4.2. Adding water to an equilibrium system

Some problems appeared when applying the LCP to a system at equilibrium if water is added. This case has been reported by Tyson et al. (1999), through the following question:

Item 13. Consider the reversible reaction that is in a state of equilibrium in a solution, which is blue in color:

$$Co(H_2O)_6^{2}(aq) + 4\ Cl^-(aq) \leftrightarrow CoCl_4^{2-}(ac) + 6\ H_2O(l)$$
$$\text{pink} \qquad\qquad\qquad \text{blue}$$
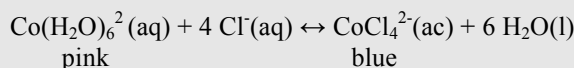
What will be observed if water is added to the system?
a) *the solution turns pink   b) the solution becomes more blue   c) the solution remains unchanged
Reasons:
1) to counter the increase in amount of water present the system will form more $Co(H_2O)_6^{2+}(aq)$
2) liquids are not included in the expression for K and hence the ratio of products to reactants will not be disturbed
3) *the ratio of concentration of products compared to reactants as expressed by Q will decrease and $Co(H_2O)_6^{2+}(aq)$ will form
4) the forward reaction has a higher mole ratio than the backward
5) *to counter the decreased concentration of $Cl^-(aq)$ the system will form more $Co(H_2O)_6^{2+}(aq)$
(*scientifically acceptable response)

The results obtained by these authors shown that a 75% of students correctly predict what will happen but many of them used a not scientifically correct reasoning. When asked why the equilibrium mixture turned pink, a typical response of students and teachers was "the system opposes the change trying to reduce the amount of water present", according to the LCP. The authors say that this explanation is not correct because it is not the extra water that disturbed the equilibrium. The real fact is that when adding water to the system in solution, the total volume increases and the concentrations of the aqueous species are reduced. In consequence, Q (reaction quotient) > K (equilibrium constant), and in order to reach a new equilibrium state the system evolves toward the reactants. Someone can argue that item 13 is not suitable to study the addition of water to an equilibrium system, since equilibria involving complex ions take place in several stages. However, we think that is a good and relevant example provided that this stage is considered the predominant in the reaction.

In conclusion, although the pure liquids are not included in the expression of K, one cannot ignore the fact that other variables can change, as the concentrations (in aqueous solutions) and then alter the equilibrium since $Q \neq K$. Therefore, the system will shift in the forward or backward direction depending on the stoichiometry to re-establish the value of the equilibrium constant.

The problem with solids and pure liquids disappear if a rigorous treatment based on activities rather than on concentrations was made. However this matter is outside the scope of the secondary school contents or first chemistry university levels.

4.3. Adding an amount of solution

Another interesting problem is the case of adding an amount of solution to a system at equilibrium, as shown in the following item (Tyson et al., 1999):

Item 14. It you have a 0.5 M solution of sodium dichromate ($Na_2Cr_2O_7$) in which the following equilibrium is established: $\qquad 2CrO_4^{2-}(ac) + 2 H^+(ac) \leftrightarrow Cr_2O_7^2 (ac) + H_2O(l)$
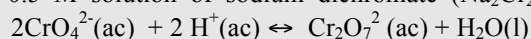
$\qquad\qquad\qquad\qquad$ yellow $\qquad\qquad\qquad\qquad$ orange

and you add 10 mL of 0.5 M solution of sodium to the original solution. What would be observed?
a) the solution becomes yellow
b) the solution becomes deeper orange
c) *the solution remains unchanged
Reasons:
1) to counteract the increased amount of $Cr_2O_7^{2-}(ac)$ the system will form more $CrO_4^{2-}(ac)$
2) there will be more collisions between particles of $Cr_2O_7^{2-}(ac)$ and $H_2O(l)$
3) because of increase in $Cr_2O_7^{2-}(ac)$, Q will be greater than K
4) *there is no change in concentration of any species
5) *the value of the ratio expresses by Q is unchanged
6) because of increased volume there will be fewer collisions between particles
(*scientifically acceptable response)

The results indicated that the question was incorrectly answered by a 98% of the first-year university students and an 85% of secondary school students surveyed. Most of students paid attention only to the added specie and selected the answer (a) and give the reason (1), according to LCP, without taking into account whether there was a change in concentration of one species relative to the other. Let us see what really happens to the concentration: the initial value is $[c]_o= 0.5$ M and the initial number of moles, $n_o = 0.5 \times V$. The number of added moles is 0.5×0.01, the final mole number is $0.5(V+0.01)$ and the final volume is $V+0.01$, and therefore, concentration after solution addition does not change.

These errors are very common among students and can be largely attributed to the methodology used in the teaching process. We think that there is no enough insistence on the analysis of the complete situation and in all the possible variables affected. Most times teachers use to apply rules that can respond as quickly as possible. These rules give good results often, but not always, in addition to not encourage the use of deeper reasoning in problem solving.

5. CONCLUSIONS AND IMPLICATIONS

From a educational point of view, one of the necessary requirements to develop a topic is to know the previous ideas that the students have about the same, the conceptual difficulties often found and even the possible errors and misconceptions that may be committed after the explanation of the topic.

Regarding to previous ideas on equilibria, the secondary high school students do not have any although they have some ideas that comes from their daily experience or from the physics lessons. In all cases, their previous view on the

chemical equilibrium refers to a static situation what is a great difficulty to understand that equilibrium is a dynamic process. In addition, they use to think that under a perturbation, the systems evolves to reach the same state of equilibrium than before instead of assume that a new and different equilibrium state is established. Other question really hard to understand for students is the fact that in the same system two simultaneous and opposite reactions account whose rates are equal at equilibrium.

To help students to understand these basic concepts, it is recommended to explain equilibrium not only from a macroscopic viewpoint but also with a microscopic interpretation of the situation. It has been observed that the macroscopic view leads to students to believe that the rate of the forward reaction decreases until it vanishes. At that moment, since there is no reaction, the amounts of all species are held constant. However, if a microscopic interpretation based on the collisions model is also explained, it will be more easy to understand that two simultaneous reactions are taking part. The rate of the forward reaction diminishes as the collisions probability also decreases resulting in a progressive increase of the backward reaction rate (for the same reason, an increase in collisions). In that way is easy to understand that the process is dynamic since while having reactant molecules collision probability will exist.

Educational research has also proved that a significative percentage of students show difficulties when solving exercises due to different misconceptions such us: attributing a concentration value to a pure solid; not considering the stoichiometry of the reaction; confusing the catalyst function by considering it as another reagent; etc… Teachers can correct these mistakes by taking notice and alerting students when these factors appear in questions or numerical exercises.

The second part of this work is mainly devoted to analyse the students' difficulties related with the consequences of perturbing the equilibrium state when different system variables are changed. From a qualitative point of view, the Le Chatelier principle (LCP) is frequently used to assess the reaction evolution. Quantitatively, the best way to do it is by comparing the value of Q (reaction quotient) with the value of K_{eq} (equilibrium constant). The mistakes that students commit –and also a percentage of teachers, as seen in some cited works–, are mainly due to the lack of a prior and in-depth analysis of the problem statement. Most times, the explicit change of one variable has implicitly associated the change of other variable that is not taken into account, then leading to an incorrect answer. For example, if a reactive specie is added at constant pressure to a gas equilibrium, necessarily have an increase of volume, although it is not specified. Similarly, if an aqueous reactive specie is added to an equilibrium in solution, necessarily the concentrations of all the species involved are modified due to the increase in the total volume. In both cases, it may happen that the two simultaneous changes cause an evolution of the system in the same direction or in opposite directions. Therefore, when both effects go in the same direction, a merely qualitative prediction according to the LCP will be sufficient and will give a correct result. On the contrary, if changes act as opposites, it will be necessary to perform a quantitative treatment.

In summary, from an educational point of view and in order to correctly predict the evolution of a system at equilibrium when it is disturbed, it would be advisable to follow these steps:

i) first, conduct a thorough analysis of the exercise's statement to determine precisely which variables have changed;

ii) second, apply the Le Chatelier principle –since is quick and easy– to the perturbance in two cases: if only one variable changes or whenever more than one variable change but producing the evolution of the system in the same direction; and

iii) third, if the variables affected act in opposite directions, a quantitative treatment should be performed by calculating the value of the reaction quotient, Q, and comparing it with that of the equilibrium constant, K_{eq}.

6. ACKNOWLEDGEMENTS

Appendix

This appendix is intended to quickly summarize and compile the main difficulties that students face when studying the chemical equilibrium:

section	concept	misconceptions/errors
Basic aspects of chemical equilibrium	1. Need of considering a closed system	• Think that gas equilibria can be achieved in open systems
	2. Forward and backward reaction rates	• Not assume that both reactions occur simultaneously • Conceive the equilibrium state as two different states, one for reactants and one for products • Believe that at equilibrium the reaction stops, or view the equilibrium as static
	3. Mass *vs.* concentration	• Identify solid mass with solid "concentration"
	4. Stoichiometry	• Not considering the stoichiometric coefficients in the expression of the quantities present at equilibrium • Do not link the reaction stoichiometry with the expression of the equilibrium constant
	5. Catalyst function	• Consider that the catalyst only increases the rate of the forward reaction • Consider that the catalyst affects differently to the forward and backward reaction rates • Believe that the concentration of the species change with the presence of the catalyst
	6. Reaction quotient and Equilibrium constant	• Confusing K with Q • Consider that K, instead of Q, changes when concentrations are modified at constant temperature • Identify a large value of the equilibrium constant with a high reaction rate • Do not consider that K_{eq} is constant at a given T • Believe that if temperature increase also the K_{eq} increases
Predicting the direction of change in equilibrium position	1. Change in the system variables (concentrations, pressure, volume,…) at constant temperature	• Do not consider that a change of any of equilibrium conditions implies the variation of other variable • Believe that the Le Chatelier principle (LCP) is always applicable, and therefore, apply it incorrectly when more than one variable changes • Do not perform a quantitative treatment when required due to the change of more than one variable with opposite effects • Say that the equilibrium constant changes
	2. Change of temperature	• Ignore the exo- or endothermic nature of the reaction • Believe that an increase in temperature always increases K_{eq} favoring the formation of products, independently of the exo-or endothermic process nature • Difficulty in knowing whether a reaction is exothermic or endothermic from K_{eq} values at different temperatures
	3. Adding a solid	• Believe that adding a solid increases its concentration and shifts the equilibrium • Consider that the amount of solid in a system in equilibrium can not be altered
	4. Adding water to an aqueous system when acts as reactant or product	• Analyze the evolution considering only the influence of water as a reactant or product but not consider that all concentrations wil be affected
	5. Adding an amount of solvent or solution	• Pay attention only to the specie added without analyzing that volume changes and also the concentrations of the other species present

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