

Joan Josep SOLAZ<sup>1</sup> and Juan QUÍLEZ<sup>2</sup>

<sup>1</sup> IES Camp de Túria. 46160 Lliria. Valencia

<sup>2</sup> IES 'José Ballester' Departamento de Física y Química, Valencia

## CHANGES OF EXTENT OF REACTION IN OPEN CHEMICAL EQUILIBRIA

*Received 9 April 2001; revised 26 September 2001; accepted 27 September 2001*

**ABSTRACT:** Many thermodynamics and physical chemistry textbooks provide a quantitative formulation of Le Chatelier's principle that restricts its applicability to conditions involving changes in  $T$  at  $P$  constant and changes in  $P$  at  $T$  constant. Both equations give the variation of the extent of reaction,  $\xi$ . However, most textbooks do not present a similar discussion about the change of  $\xi$  in an open equilibrium mixture. These possible disturbances are usually solved by using one of the many available qualitative statements of Le Chatelier's principle. But, these cases involve some situations in which Le Chatelier's principle is limited. Furthermore, all its qualitative statements are vague and ambiguous, and they are usually nonequivalent. Thus, both high school and college chemistry students, and also many chemistry teachers hold a wide range of misconceptions when they try to predict the possible evolution of a chemical equilibrium system that may have been perturbed by changing its mass. The aim of this paper is not to establish didactic guidelines for treating these problems, but to fill the gap resulting from the lack of a relevant advanced thermodynamic discussion, and to find the mathematical expressions of the variation of  $\xi$ , with the infinitesimal variation in the mass of a chemical equilibrium mixture. [*Chem. Educ. Res. Pract. Eur.*: 2001, 2, 303-312]

**KEY WORDS:** *Le Chatelier's principle; extent of reaction; change in the mass; chemical equilibrium condition; chemical equilibrium disturbance; chemical equilibrium shift*

### INTRODUCTION

Many thermodynamics and physical chemistry textbooks provide a quantitative formulation of Le Chatelier's principle that restricts its applicability to conditions involving changes in  $T$  at  $P$  constant and changes in  $P$  at  $T$  constant (Callen; 1960; Kirkwood and Oppenheim, 1961):

$$\left( \frac{\partial \xi_{eq}}{\partial T} \right)_P = \frac{\Delta_r H / T}{G''} \quad [1]$$

$$\left( \frac{\partial \xi_{eq}}{\partial P} \right)_T = -\frac{\Delta_r V}{G''} \quad [2]$$

where  $G''$  is defined as

$$G'' = \left( \frac{\partial(\Delta_r G)}{\partial \xi} \right)_{T,P} = \left( \frac{\partial^2 G}{\partial \xi^2} \right)_{T,P} > 0 \quad [3]$$

if the equilibrium considered is stable, and  $\xi$  is the extent of reaction, defined as

$$d\xi = \frac{dn_i}{\nu_i} \quad [4]$$

where  $dn_i$  represents the variation in the amount of substance of a component ( $i$ ) involved in a chemical change, and  $\nu_i$  is its stoichiometric coefficient. [The deduction of the equation of the variation of  $\xi$  with  $T$  at  $V$  constant was previously reported (Solaz and Quílez, 1998).]

However, most textbooks do not present a similar discussion about the change of  $\xi$  in an open equilibrium mixture. In an equilibrium mixture, this change may imply the following cases: a) change in the mass of a reactant or product; b) addition of an inert gas. These possible disturbances are usually solved by using one of the qualitative statements of Le Chatelier's principle. But, if this is the case, we must take into account that Le Chatelier himself (Le Chatelier, 1933) stated that his previous statements (Le Chatelier, 1884, 1888, 1908) were not equivalent. Furthermore, many authors have tried to find an easy general qualitative formulation for this principle, but this aim has ended up being an impossible task to achieve (Prigogine & Defay, 1954). As a result, the attempt of finding the correct answer in the prediction of the evolution of a disturbed chemical equilibrium system depends in most cases on the set of words used to formulate Le Chatelier's principle (Allsop & George, 1984; Driscoll, 1960, Gold & Gold, 1985; Haydon, 1980; de Heer, 1957, 1986; Jordaan, 1993; Quílez, 1997, 1998a). Moreover, some historical studies (Gold & Gold, 1984; Quílez, 1995; Quílez & Sanjosé, 1996) have argued that there are many nonequivalent Le Chatelier's rules, which convert Le Chatelier's principle into an ontological problem. Hence, both the limited character of Le Chatelier's rule (Bridgart & Kemp, 1985; Helfferich, 1985; Quílez & Solaz, 1994; Solaz & Quílez, 1995) and its vague and ambiguous formulation impede, in many cases, an accurate prediction about the evolution of a chemical equilibrium mixture that has been disturbed (Quílez & Solaz, 1995). Thus, both high school and college chemistry students, and also many chemistry teachers, hold a wide range of misconceptions when they try to predict the possible evolution of a chemical equilibrium system that may have been perturbed by changing its mass (see, Table 1; Quílez, 1998b; Quílez & Solaz, 1995). Many of these errors are originated because most of the students consider each one of Le Chatelier's qualitative statements as an easy rule that can infallibly be applied, whatever the case may be.

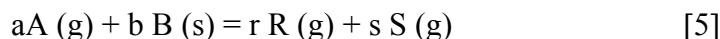
The aim of this paper is to fill the gap resulting from the lack of an advanced thermodynamic discussion in the prediction of a possible shift in cases that imply a change in the mass of a chemical equilibrium. Therefore, we have enlarged the quantitative treatment given in current textbooks by finding the mathematical expressions of the variation of the advancement of reaction,  $\xi$ , with the infinitesimal variation in the mass of a chemical equilibrium mixture.

### CHANGE IN THE MASS OF THE SYSTEM, AT CONSTANT PRESSURE AND TEMPERATURE

Let us consider the following chemical equilibrium system:

**TABLE 1.** *Change in mass and the misapplication of the Le Chatelier's principle.*

- a. Addition of one of the reactants, at constant pressure and temperature, to an equilibrium mixture *always* shifts the equilibrium to the product side.
- b. Addition of solids to heterogeneous equilibrium systems shifts the equilibrium. If the solid is a reactant, its addition shifts the equilibrium to the product side.
- c. Addition of an inert gas *never* disturbs the equilibrium because there is no reaction.
- d. Addition of an inert gas at constant volume and temperature increases the total pressure. This change will be minimized by the lower amount of molecule reaction proceeding to a greater extent than previously.
- e. Addition of an inert gas at constant pressure and temperature disturbs the equilibrium increasing the pressure. This change will be minimized (in order to achieve the initial value) by the lower amount of molecule reaction proceeding to a greater extent than previously.
- f. Addition of an inert gas at constant pressure and temperature does not disturb the equilibrium because: a) the pressure is kept constant; b) the volume increases, but this change does not disturb the equilibrium because the pressure is kept constant; c) the molar fractions of the gases involved in the equilibrium do not change.
- g. Addition of an inert gas at constant pressure and temperature in a reaction of this type  $A(g) \rightleftharpoons B(g) + C(g)$ , diminishes the partial pressure of  $A(g)$ . Therefore, this change shifts the equilibrium to the reactant side.



for which we define  $\Delta v = (r + s) - a$ .

### Change in the mass of one of the gases involved in the reaction

Let us take into account the chemical equilibrium mixture given in equation 5 and let us suppose the mass of  $R(g)$  has been changed, at constant  $P$  and  $T$ . In this open system the change in the amount of substance of component  $R(g)$  may be attributed to two causes: on the one hand, to the increment in the extent of reaction,  $d\xi$ , which causes a change in  $n_R$  of  $rd\xi$ ; and on the other, to an additional increment,  $d\alpha$ , caused by a transfer of matter to or from the surroundings. We thus have

$$dn_R = rd\xi + d\alpha \quad [6]$$

The following discussion will take into account the variation of  $\left(\frac{\partial G}{\partial \xi}\right)_{P,T,\alpha} = \Delta_r G$ ,

because now  $G = f(P, T, \xi, \alpha)$ . If we bear in mind that the thermodynamic equilibrium condition is  $d(\Delta_r G) = 0$ , the variation of  $\Delta_r G$ , due to the change  $dn_R$  under constant  $P$  and  $T$ , between the initial state of equilibrium and the final one will be

$$d(\Delta_r G) = \left(\frac{\partial \Delta_r G}{\partial n_R}\right)_{P,T,n_{i \neq R}} dn_R = 0 \quad [7]$$

Taking into account equation 6 we can write

$$d(\Delta_r G) = \left( \frac{\partial \Delta_r G}{\partial \alpha} \right)_{P,T,\xi} d\alpha + \left( \frac{\partial \Delta_r G}{\partial \xi} \right)_{P,T,\alpha} d\xi = 0 \quad [8]$$

Now, let's evaluate the value of  $\left( \frac{\partial \Delta_r G}{\partial \alpha} \right)_{P,T,\xi}$ . Therefore, we must bear in mind the van't Hoff equation (Brenon-Audat et al. 1993)

$$\Delta_r G = RT \ln \frac{Q^0}{K^0} \quad [9]$$

where  $Q^0$  is the reaction quotient, defined, for ideal gases, as

$$Q^0 = \prod_i \left( \frac{P_i}{P^0} \right)^{\nu_i} = \prod_i \frac{n_i^{\nu_i}}{n^{\Delta \nu}} \left( \frac{P}{P^0} \right)^{\Delta \nu} \quad (P^0 = 1 \text{ bar}) \quad [10]$$

and  $K^0$  is the equilibrium constant, defined, for ideal gases, as

$$K^0 = \prod_i \left( \frac{P_{i,eq}}{P^0} \right)^{\nu_i} \quad [11]$$

Thus, we can write the van't Hoff equation as follows

$$\Delta_r G = RT \left[ \ln \frac{n_R^r n_S^s}{n_A^a} \left( \frac{P}{P^0 n} \right)^{\Delta \nu} - \ln K^0 \right] \quad [12]$$

Therefore, we finally obtain for the reaction we have considered above

$$\left( \frac{\partial \Delta_r G}{\partial \alpha} \right)_{P,T,\xi} = RT \left( \frac{\partial \ln Q^0}{\partial \alpha} \right)_{P,T,\xi} = RT \left( \frac{r}{n_R} - \frac{\Delta \nu}{n} \right) \quad [13]$$

then, we can express equation 8 as follows

$$0 = RT \left( \frac{r}{n_R} - \frac{\Delta \nu}{n} \right) d\alpha + \left( \frac{\partial \Delta_r G}{\partial \xi} \right)_{P,T,\alpha} d\xi \quad [14]$$

which can finally be written

$$\frac{d\xi}{d\alpha} = \frac{RT}{G'} \left( \frac{\Delta \nu}{n} - \frac{r}{n_R} \right) \quad [15]$$

The case corresponding to an addition of R(g), at  $P$  and  $T$  constant, has two different possibilities of reaction. Let us explain these cases with the help of equation 15. Adding R(g) ( $d\alpha > 0$ ) can produce a shift which implies the reaction  $a A(g) + b B(s) \rightarrow r R(g) + s S(g)$ . This reaction means  $d\xi > 0$ . Therefore,  $\frac{\Delta v}{n} - \frac{r}{n_R} > 0$ , which obeys the condition  $X_R > \frac{r}{\Delta v}$ , where  $X_R$  is the molar fraction of R ( $n_R/n$ ). A similar discussion can be taken when  $X_R < \frac{r}{\Delta v}$ . In this case the addition of an infinitesimal amount of R(g),  $d\alpha$ , shifts the equilibrium position in a way that the following reaction takes place:  $r R(g) + s S(g) \rightarrow a A(g) + b B(s)$ .

A similar discussion can be carried out when  $d\alpha < 0$ . Again, two possibilities of chemical shift are obtained. If  $X_R > \frac{r}{\Delta v}$ , it means that  $d\xi < 0$ ; thus, removing an infinitesimal amount of R(g) shifts the equilibrium position in a way that the following reaction takes place:  $r R(g) + s S(g) \rightarrow a A(g) + b B(s)$ . And if  $X_R < \frac{r}{\Delta v}$ , it means that  $d\xi > 0$ ; thus, removing an infinitesimal amount of R(g) shifts the equilibrium position producing the following reaction:  $a A(g) + b B(s) \rightarrow r R(g) + s S(g)$ .

### Addition of an inert gas

In this open system the change in the infinitesimal variation in the total amount of gases,  $dn$ , may be attributed to two causes: on the one hand, to the increment in the extent of reaction,  $d\xi$ , which causes a change in each of the gases of reaction:  $dn_R = rd\xi$ ;  $dn_S = sd\xi$ ;  $dn_A = -ad\xi$ ; and, on the other, to an additional increment  $dn_I$ , caused by a transfer of the inert gas (I) from the surroundings. We thus have that  $dn$  is given by the following equation

$$dn = dn_I + rd\xi + sd\xi - ad\xi \quad [16]$$

which can be expressed as

$$dn = dn_I + \Delta v d\xi \quad [17]$$

The addition of  $dn_I$  mol of the inert gas may imply a change in  $\Delta_r G$ , which can be written as

$$d(\Delta_r G) = \left( \frac{\partial(\Delta_r G)}{\partial n} \right)_{T, P, n_i \neq I} dn \quad [18]$$

and taking into account that the variation of  $\Delta_r G$ , due to the change  $dn_I$  under constant  $P$  and  $T$ , is a function of the two variables  $n_I$  and  $\xi$ , we have

$$d(\Delta_r G) = \left( \frac{\partial(\Delta_r G)}{\partial n_I} \right)_{T, P, n_i \neq I} dn_I + \left( \frac{\partial(\Delta_r G)}{\partial \xi} \right)_{T, P, n_I} d\xi \quad [19]$$

The first term of the above equation can be easily evaluated starting from equation 12

$$\left( \frac{\partial(\Delta_r G)}{\partial n_1} \right)_{T,P,n_i \neq 1} = -\frac{RT \cdot \Delta v}{n} \quad [20]$$

Thus, we can express equation 19 as follows

$$d(\Delta_r G) = -\frac{RT\Delta v}{n} dn_1 + \left( \frac{\partial(\Delta_r G)}{\partial \xi} \right)_{T,P,n_1} d\xi \quad [21]$$

and bearing in mind that the variation of  $d(\Delta_r G)$  between the initial state of equilibrium and the final one is zero

$$-\frac{RT\Delta v}{n} dn_1 + \left( \frac{\partial(\Delta_r G)}{\partial \xi} \right)_{T,P,n_1} d\xi = 0 \quad [22]$$

we finally obtain

$$\frac{d\xi}{dn_1} = \frac{RT \cdot \Delta v}{nG''} \quad [23]$$

We already know that  $G'' > 0$ ; therefore, equation 23 means that the way in which the equilibrium shifts depends only on the sign of  $\Delta v$ . Thus, if we keep  $P$  and  $T$  constant, and  $\Delta v < 0$ , the addition of an inert gas ( $dn_1 > 0$ ) to the gaseous equilibrium mixture implies that  $d\xi < 0$ ; if  $\Delta v > 0$ , then  $d\xi > 0$ . There is no change if  $\Delta v = 0$ .

### CHANGE IN THE MASS OF THE SYSTEM, AT CONSTANT VOLUME AND TEMPERATURE

#### Change in the mass of one of the gases involved in the reaction

Let us take into account the chemical equilibrium mixture given in equation 5 and let us suppose the mass of R(g) has been changed, at constant  $V$  and  $T$ . In this open system the change in the amount of substance of component R(g) may be attributed to two causes: on the one hand, to the increment in the extent of reaction,  $d\xi$ , which causes a change in  $n_R$  of  $rd\xi$ ; and on the other, to an additional increment  $d\alpha$  caused by a transfer of matter to or from the surroundings. We thus have

$$dn_R = rd\xi + d\alpha \quad [6]$$

The following discussion will take into account the variation of the quantity (Brenon-Audat et al., 1993)

$$\left( \frac{\partial A}{\partial \xi} \right)_{T,V,\alpha} = \left( \frac{\partial G}{\partial \xi} \right)_{P,T,\alpha} = \Delta_r G \quad [24]$$

So, we can write the thermodynamic equilibrium condition as follows

$$d\left(\frac{\partial A}{\partial \xi}\right)_{T,V,\alpha} = 0 \quad [25]$$

and the variation of  $\left(\frac{\partial A}{\partial \xi}\right)_{T,V,\alpha}$ , due to the change  $dn_R$  under constant  $T$  and  $V$ , between the initial state of equilibrium and the final one is

$$d\left(\frac{\partial A}{\partial \xi}\right)_{T,V,\alpha} = \left[ \frac{\partial}{\partial \alpha} \left( \frac{\partial A}{\partial \xi} \right)_{V,T,\alpha} \right]_{V,T,n_{i \neq R}} dn_R = 0 \quad [26]$$

Therefore, taking into account equation 6

$$d\left(\frac{\partial A}{\partial \xi}\right)_{T,V,\alpha} = \left[ \frac{\partial}{\partial \alpha} \left( \frac{\partial A}{\partial \xi} \right)_{T,V,\alpha} \right]_{T,V,\xi} d\alpha + \left( \frac{\partial^2 A}{\partial \xi^2} \right)_{T,V,\alpha} d\xi = 0 \quad [27]$$

and bearing in mind the van't Hoff equation

$$\left( \frac{\partial A}{\partial \xi} \right)_{T,V,\alpha} = RT \ln \frac{Q^0}{K^0} \quad [28]$$

where

$$Q^0 = \prod_i n_i^{v_i} \left( \frac{P}{P^0 \cdot n} \right)^{\Delta v} = \prod_i n_i^{v_i} \left( \frac{RT}{P^0 V} \right)^{\Delta v} \quad [29]$$

and then, for equation 5 we have

$$\left( \frac{\partial A}{\partial \xi} \right)_{T,V,\alpha} = RT \left[ \ln \frac{n_R^r n_S^s}{n_A^a} \left( \frac{RT}{P^0 V} \right)^{\Delta v} - \ln K^0 \right] \quad [30]$$

we obtain the value for the first term of equation 27

$$\left[ \frac{\partial}{\partial \alpha} \left( \frac{\partial A}{\partial \xi} \right)_{T,V,\alpha} \right]_{T,V,\xi} = \frac{RT}{n_R} \quad [31]$$

Thus, from equation 27 we can write

$$\frac{RT}{n_R} d\alpha + \left( \frac{\partial^2 A}{\partial \xi^2} \right)_{T,V,\alpha} d\xi = 0 \quad [32]$$

Finally

$$\frac{d\xi}{d\alpha} = - \frac{RT}{n_R A'} \quad [33]$$

where

$$A'' = \left( \frac{\partial^2 A}{\partial \xi^2} \right)_{T,V,\alpha} > 0 \quad (\text{if the equilibrium considered is stable}) \quad [34]$$

Equation 33 means that if we keep  $T$  and  $V$  constant, the addition of one of the products,  $R(g)$  ( $d\alpha > 0$ ) will shift the equilibrium in the way of the formation of reactants ( $d\xi < 0$ ). On the contrary, if an amount of  $R(g)$  is extracted from the reaction vessel ( $d\alpha < 0$ ), the equilibrium will shift in the formation of products ( $d\xi > 0$ ).

In the case of heterogeneous equilibria, we must bear in mind that pure solids and pure liquids are not taken in the expression of  $K^\circ$  nor of  $Q^\circ$ . Therefore, if we consider the change in the mass of  $B(s)$  in the equation 5, and repeat all the previous steps, we finally obtain

$$\frac{d\xi}{d\alpha} = 0 \quad [35]$$

The change in the amount of pure solids or liquids in heterogeneous chemical equilibrium systems does not disturb the equilibrium.

### Addition of an inert gas

The starting point of this discussion is similar to the previous one, carried out for the addition of an inert gas, at constant pressure and temperature. We, therefore, can write equation 17

$$dn = dn_I + \Delta v d\xi \quad [17]$$

The variation of  $\left( \frac{\partial A}{\partial \xi} \right)_{T,V,n_I}$  between the initial state of equilibrium and the final one is

$$d \left( \frac{\partial A}{\partial \xi} \right)_{T,V,n_I} = \left[ \frac{\partial}{\partial n} \left( \frac{\partial A}{\partial \xi} \right)_{V,T,n_I} \right]_{V,T,n_{i \neq I}} dn = 0 \quad [36]$$

Taking into account that the variation of  $\left( \frac{\partial A}{\partial \xi} \right)_{T,V,n_I}$ , due to the change  $dn_I$  under constant  $V$  and  $T$ , is function of the two variables  $n_I$  and  $\xi$ , we can write

$$\left( \frac{\partial A}{\partial \xi} \right)_{T,V,n_I} = \left[ \frac{\partial}{\partial n_I} \left( \frac{\partial A}{\partial \xi} \right)_{T,V,n_I} \right]_{T,V,n_{i \neq I}} dn_I + \left( \frac{\partial^2 A}{\partial \xi^2} \right)_{T,V,n_I} d\xi = 0 \quad [37]$$

and bearing in mind the van't Hoff equation

$$\left( \frac{\partial A}{\partial \xi} \right)_{T,V,n_I} = RT \ln \frac{Q}{K^\circ} \quad [38]$$

where



$$\left(\frac{\partial A}{\partial \xi}\right)_{T,V,n_i} = RT \left[ \ln \frac{n_R^r n_S^s}{n_A^a} \left(\frac{RT}{P^0 V}\right)^{\Delta v} - \ln K^0 \right] \quad [39]$$

we obtain

$$\left[ \frac{\partial}{\partial n_i} \left(\frac{\partial A}{\partial \xi}\right)_{V,T,n_i} \right]_{V,T,n_{i \neq i}} = 0 \quad [40]$$

and finally

$$\frac{d\xi}{dn_i} = 0 \quad [41]$$

The addition of an inert gas, at constant volume and temperature, does not disturb the equilibrium.

### CONCLUSIONS

When considering the perturbations of chemical equilibria, current advanced approaches only consider the variation of  $\xi$  with  $P$ , at  $T$  constant, and the variation of  $\xi$  with  $T$ , at  $P$  constant. These equations are accurate mathematical formulations for Le Chatelier's principle. Therefore, they restrict the conditions in which Le Chatelier's principle can be applied. However, in most textbooks the cases that involve the variation of  $\xi$  with the mass of the equilibrium mixture are not deduced. So, we have enlarged on the usual thermodynamic treatment carried out for the variation of  $\xi$ . Our approach has focused on finding the variation of  $\xi$  in open systems.

The cases we have analysed are usually solved by using a wide range of qualitative rules that are considered general, valid and easy to apply statements. But, in spite of the broad attack launched by many authors about the limited character of these rules and their ambiguous and vague formulations, they have remained as the principal and almost exclusive tool to solve the related problems (Quílez, 1998b; Quílez, 2000; Quílez & Solaz, 1995). As a consequence, a great variety of misconceptions has been reported.

Although the main aim of this paper is not to establish didactic guidelines to treat those problems, we consider that a well-founded thermodynamic approach will help college students and future chemistry teachers to avoid current misconceptions.

**CORRESPONDENCE:** Juan QUÍLEZ, IES 'José Ballester' Departamento de Física y Química, C/Alemany, s/n, 46019 Valencia, Spain; fax: 963663563; e-mail: j.quilez@teleline.es

### REFERENCES

- Allsop, R.T. & George, N.H. (1984). Le Chatelier - A redundant principle? *Education in Chemistry*, 21, 54-56.
- Brenon-Audat, F., Busquet, C., & Mesnil, C. (1993). *Thermodynamique chimique*. Paris: Hachette.
- Bridgart, G.J. & Kemp, H.R. (1985). A limitation on the use of the Le Chatelier's principle. *The Australian Science Teachers' Journal*, 31, 60-62.
- Callen, H.B. (1960). *Thermodynamics*. New York: Wiley.
- De Heer, J. (1957). The principle of Le Chatelier and Braun. *Journal of Chemical Education*, 34, 375-380.

- De Heer, J. (1986). *Phenomenological thermodynamics with applications to chemistry*. New Jersey: Prentice Hall.
- Driscoll, D.R. (1960). The Le Chatelier principle. *The Australian Science Teachers' Journal*, 31, 60-62.
- Gold, J. & Gold, V. (1984). Neither Le Chatelier's nor a principle? *Chemistry in Britain*, 20, 802-804.
- Gold, J. & Gold, V. (1985). Le Chatelier's principle and the laws of van't Hoff. *Education in Chemistry*, 22, 82-85.
- Haydon, A.J. (1980). Le Chatelier -A statement of principle. *School Science Review*, 62, 318-321.
- Helfferich, F.G. (1985). Le Chatelier - right or wrong? Optimizing chemical reaction equilibria. *Journal of Chemical Education*, 62, 305-308.
- Jordaan, F. (1993). Disturbing Le Châtelier's principle. *Chemeda: The Australian Journal of Chemical Education*, 38, 175-181.
- Kirkwood, J.G. & Oppenheim, I. (1961). *Chemical thermodynamics*. New York: McGraw-Hill.
- Le Chatelier, H. L. (1884). Sur un énoncé général des lois des équilibres chimiques. *Comptes Rendus Académie des Sciences*, 99, 786-789.
- Le Chatelier, H. L. (1888). Recherches expérimentales et théoriques sur les équilibres chimiques. *Annales des Mines*, 13, 157-382.
- Le Chatelier, H. L. (1908). *Leçons sur le carbone, la combustion et les lois chimiques*. Paris: Dunod et Pinat Editeurs.
- Le Chatelier, H. L. (1933). Sur la loi du déplacement de l'équilibre chimique. *Comptes Rendus Académie des Sciences*, 196, 1557-1560.
- Prigogine, I. & Defay, R. (1954). *Chemical thermodynamics*. London: Longmans Green.
- Quílez, J. (1995). Una formulación para un principio: Análisis histórico del principio de Le Chatelier. *Revista Mexicana de Física*, 41, 586-598.
- Quílez, J. (1997). El principio de Le Chatelier como regla cualitativa: un obstáculo epistemológico en el aprendizaje del equilibrio químico. *Infancia y Aprendizaje*, 78, 73-86.
- Quílez, J. (1988a). Dificultades semánticas en el aprendizaje de la química: el principio de Le Chatelier como ejemplo paradigmático. *Alambique. Didáctica de las Ciencias Experimentales*, 17, 105-111.
- Quílez, J. (1998b). Persistencia de errores conceptuales relacionados con la incorrecta aplicación del principio de Le Chatelier. *Educación Química*, 9, 367-377.
- Quílez, J. (2000). Acerca de la resolución de problemas y la evaluación del equilibrio químico. *Educación Química*, 11, 395-403.
- Quílez, J. & Sanjosé V. (1996). El principio de Le Chatelier a través de la historia y su formulación didáctica en la enseñanza del equilibrio químico. *Enseñanza de las Ciencias*, 14, 381-390.
- Quílez, J. & Solaz, J.J. (1994). Análisis termodinámico de las insuficiencias del principio de Le Chatelier en el desplazamiento del equilibrio químico. *Afinidad*, 51(454), 435-438.
- Quílez, J. & Solaz, J.J. (1995). Students' and teachers' misapplication of the Le Chatelier's principle. Implications for the teaching of chemical equilibrium. *Journal of Research in Science Teaching*, 32, 939-957.
- Solaz, J.J. & Quílez, J. (1995). Thermodynamics and the Le Chatelier's principle. *Revista Mexicana de Física*, 41(1), 128-138.
- Solaz, J.J. & Quílez, J. (1998). Unequivocal prediction of chemical equilibrium shift when changing the temperature at constant volume. *Physics Education*, 15(1), 29-33.