

# Do the equilibrium constants have units? A discussion on how general chemistry textbooks calculate and report the equilibrium constants

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## Abstract

An analysis of the literature concerning the dimensionality of equilibrium constants reveals that this topic manifests as a controversial issue. Based on this previous examination, this work studies if general chemistry textbooks accurately define and calculate equilibrium constants. In order to evaluate those textbooks, in the first part of this study the experimental equilibrium constants,  $K_p$  and  $K_c$ , and the thermodynamic equilibrium constant,  $K^\circ$ , are defined. Also, the equations that relate each constant to the other two are given. In the specific presentation of these quantities, an example is discussed both performing their accurate calculation and reporting them using the proper units. In the second part of this study, it is examined the way both first-year university chemistry textbooks and pre-university chemistry textbooks determine equilibrium constants, concentrating on how they handle the units of these quantities. Many textbooks treat  $K_p$  and  $K_c$  as dimensionless quantities. This misleading assumption is caused by a problem in the terminology used as in many cases  $K_p$  (or  $K_c$ ) plays the role  $K^\circ$ . In order to avoid this misleading treatment of the equilibrium constants some suggestions are provided.

## Keywords

Equilibrium constants, General chemistry text books, Definition, Calculation and Units

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## Introduction

### *Purpose*

The equilibrium constant is a basic and important thermodynamic concept that is usually introduced in pre-university chemistry courses. This concept has revealed to be controversial as some authors (Abrantes & Nieto de Castro, 1985; Boggs, 1958; Centellas, 2008; Cox, Dixon, Morris & Roberts, 1979; Harris, 1978, 1982; Gil & Paiva, 1999; Gordus, 1991; Quintero, 1987; Ronneau, 1993; Rosenberg & Kotz, 1999; Tykodi, 1986) state that equilibrium constants are unitless quantities while other studies (Antonik, 1993; Delorme, 1985; Depovere & Weiler, 1993a, 1993b; Henry, 1967; Laidler, 1990; Mills, 1989, 1995; Molyneux, 1991; Pethybridge & Mills, 1979; Treptow, 1999; Vickerman, 1979; Wright, 1979) discuss that the experimental equilibrium constants, viz.  $K_p$  and  $K_c$ , must be expressed with units, whereas the thermodynamic equilibrium constant,  $K^\circ$ , is a dimensionless quantity. Thus, the existence of these two opposed views is not of

## State of the literature

- An important subject of science textbook research has been the detection of possible inconsistencies and erroneous treatments that may exist.
- Educational studies suggest that one of the sources of students' learning difficulties in physical chemistry lies in how textbooks and teachers deal with key chemistry concepts.
- The discussion concerning the dimensionality of equilibrium constants has revealed to be controversial.

## Contribution of this paper to the literature

- This work strives for clarifying how to properly calculate and report each of the equilibrium constants.
- This study reports the main misrepresentations and problematic issues concerning the treatment of equilibrium constants performed by general chemistry textbooks.
- Several suggestions are provided in order to avoid current textbook misrepresentations.

a minor importance as students are regularly requested by their teachers to be careful when reporting quantities as they must be expressed using their corresponding correct units. The clarification of this issue should be resolved in order to avoid confusion on students (Quílez, 2016; Quílez-Díaz & Quílez-Pardo-2015).

The aim of this study is to describe how chemistry textbooks report equilibrium constants. I hypothesized that the aforementioned controversy had permeated textbook presentation and calculation of equilibrium constants. Thus, I considered that many textbooks would be treating experimental equilibrium constants as unitless quantities.

The discussion that follows consists of two main parts. The first one is based on initial examinations dealing with the term standard in thermodynamics (Cox, 1982; Freeman, 1985; Treptow, 1999) and focuses on how to define and report the equilibrium constants. This analysis establishes that the aforementioned controversial subject matter is essentially a terminological problem. In order to avoid erroneous treatments, this work has tried to provide a clear presentation of each of the quantities involved and has exemplified how to report them. Taking into account this initial theoretical foundation, this educational research inspects in its second part how both pre-university chemistry textbooks and first-year university chemistry textbooks deal with equilibrium constants.

### *Equilibrium constants: definition, calculation and units*

The aim of this section is to present a clear differentiation on two related quantities: the thermodynamic equilibrium constant,  $K^\circ$ , and the experimental equilibrium constants,  $K_p$  and  $K_c$ . In this regard, this article tries to provide a proper level of understanding of the implications of how different units lead to different numerical values of the equilibrium constants for a particular reaction.

Following the IUPAC recommendation (Ewing, Lilley, Oloffson, Rätzsch & Somsen, 1994; Mills, Cvitas, Homann, Kallay & Kuchitsu, 1993) and the equilibrium constant expressions provided in

several educational papers (Borge, 2015; Quílez, 2012, 2016), in **Boxes 1** and **2** are summarized the equations that define each quantity, as well as their mathematical relationships. The equations reported in those boxes assume ideal equilibrium behaviour of the species involved.

**Box 1.** Glossary of equilibrium constant terms and their units for a given chemical equilibrium represented as:  $a A(g) + b B(g) \rightleftharpoons c C(g) + d D(g)$ .

Practical equilibrium constants,  $K_p$  and  $K_c$ :

$$K_p = \left\{ \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} \right\}_{eq}; \quad (1)$$

its units are (unit of pressure) $^{\Delta n(g)}$

$$K_c = \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)_{eq}; \quad (2)$$

its units are (unit of concentration) $^{\Delta n(g)}$

Mathematical equation relating  $K_p$  to  $K_c$ :

$$K_p = K_c (RT)^{\Delta n(g)} \quad (3)$$

Thermodynamic equilibrium constant,  $K^\circ$  (unitless quantity):

$$K^\circ = \left\{ \frac{(p_C / p^\circ)^c (p_D / p^\circ)^d}{(p_A / p^\circ)^a (p_B / p^\circ)^b} \right\}_{eq}; \quad (4)$$

$p^\circ = 1 \text{ bar}$

$$\Delta\mu^0 = \Delta_r G^0 = -RT \ln \left\{ \frac{(p_C / p^\circ)^c (p_D / p^\circ)^d}{(p_A / p^\circ)^a (p_B / p^\circ)^b} \right\}_{eq} = -RT \ln K^\circ \quad (5)$$

$$K^\circ = \exp[-\Delta_r G^0 / RT] \quad (6)$$

Mathematical equations relating  $K_p / K_c$  to  $K^\circ$ :

$$K_p = K^\circ (p^\circ)^{\Delta n(g)} \quad (7a)$$

$$K_c = K^\circ \left( \frac{p^\circ}{RT} \right)^{\Delta n(g)} \quad (7b)$$

$p^\circ = 1 \text{ bar}$

Units of  $K_p$ :

$$K_p = K^\circ (\text{bar})^{\Delta n(g)} = K^\circ \left( \frac{1}{1.01325} \text{ atm} \right)^{\Delta n(g)} = K^\circ (10^5 \text{ Pa})^{\Delta n(g)} \quad (8)$$

**Box 2.** Glossary of equilibrium constant terms and their units for a given chemical equilibrium represented as:  $a A(aq) + b B(aq) \rightleftharpoons c C(aq) + d D(aq)$ .

Practical equilibrium constant  $K_c$ :

$$K_c = \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)_{eq}; \quad (9)$$

its units are (unit of concentration) $^{\Delta n}$

Thermodynamic equilibrium constant,  $K^\circ$  (unitless quantity):

$$K^\circ = \left\{ \frac{(c_C / c^\circ)^c (c_D / c^\circ)^d}{(c_A / c^\circ)^a (c_B / c^\circ)^b} \right\}_{eq}; \quad (10)$$

$c^\circ = 1 \text{ mol L}^{-1}$

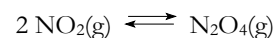
$$\Delta\mu^0 = \Delta_r G^0 = -RT \ln \left\{ \frac{(c_C / c^\circ)^c (c_D / c^\circ)^d}{(c_A / c^\circ)^a (c_B / c^\circ)^b} \right\}_{eq} = -RT \ln K^\circ \quad (11)$$

$$K^\circ = \exp[-\Delta_r G^0 / RT] \quad (12)$$

Mathematical equation relating  $K_c$  to  $K^\circ$ :

$$K_c = K^\circ (c^\circ)^{\Delta n}; c^\circ = 1 \text{ mol L}^{-1} \quad (13)$$

Practical gas phase equilibrium examples discussing equations grouped in **Box 1** may help students in the differentiation between both the experimental equilibrium constants,  $K_p$  and  $K_c$ , and the thermodynamic constant,  $K^\circ$ , which also may allow them to perform a sound treatment concerning their units. This analysis can be exemplified calculating the values of  $K^\circ$ ,  $K_p$  and  $K_c$  for chemical equilibrium systems (Quílez-Díaz & Quílez Pardo, 2015). In the discussion that follows, these calculations are performed for the following equilibrium (Quílez, 2016):



In this particular case,  $\Delta_r G^0 = -4,728.7 \text{ J mol}^{-1}$ . Then, from equation (6) we obtain:

$$K^\circ = \exp[-\Delta_r G^0 / RT] = 6.7364; T = 298.15 \text{ K.}$$

Thus, considering that  $p^\circ = 1 \text{ bar}$ ,  $K_p$  can be easily calculated by using equation (7a), as  $\Delta n(g) = -1$ ,  $K_p = K^\circ (p^\circ)^{-1} = 6.7364 \text{ bar}^{-1}$ . Moreover, as  $1 \text{ atm} = 1.01325 \text{ bar}$ , other values of  $K_p$  can be reported considering equation (8):  $K_p = 6.8257 \text{ atm}^{-1}$  and  $K_p = 6.7364 \times 10^{-5} \text{ Pa}^{-1}$ . Notice that the values of  $K^\circ$  and  $K_p$  are the same when  $K_p$  is expressed in bar units. Finally, using equation (3),

$$K_c = K_p (RT) = 166.99 (\text{mol L}^{-1})^{-1}; T = 298.15 \text{ K.}$$

But  $K_p$  can also be calculated employing equation (1), instead of equation (7a), which means to determine previously the corresponding equilibrium values of partial pressures. This case can be exemplified using the data ( $T = 298.15$  K) reported on a previous article (Raff, 2014):  $p(\text{NO}_2)_{\text{eq}} = 0.34987$  bar;  $p(\text{N}_2\text{O}_4)_{\text{eq}} = 0.82507$  bar. In the equilibrium we are exemplifying, we can express  $K_p$  as follows:

$$K_p = \left[ \frac{p(\text{N}_2\text{O}_4)}{p(\text{NO}_2)^2} \right]_{\text{eq}} \quad (14)$$

Then,  $K_p = [0.82507 \text{ bar} / (0.34987 \text{ bar})^2] = 6.7403 \text{ bar}^{-1}$  (it is stressed that units must be reported). Notice that this value is slightly different from the numerical quantity reported when using equation (7a). That is, the calculation of  $K_p$  from the thermodynamic equilibrium constant,  $K^\circ$ , produces a value that differs from the one obtained from equation (1), where experimental values of partial pressures are considered. Those unequal values for  $K_p$  calculated using distinct equations are due to deviations from the ideal behaviour of the gaseous equilibrium mixture.

**Box 3** summarises the expressions corresponding to each equilibrium constant and their corresponding values calculated for the equilibrium  $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ ;  $T = 298.15$  K.

**Box 3.** Equilibrium constant equations and their corresponding values for the equilibrium  $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ ;  $T = 298.15$  K.

$2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ ; $T = 298.15$ K			
$K^\circ = \exp[-\Delta_r G^\circ / RT]$ ( $p^\circ = 1$ bar)	$K_p = K^\circ (p^\circ)^{-1}$ (method A)	$K_c = K_p(RT)$	
	$K_p = \left[ \frac{p(\text{N}_2\text{O}_4)}{p(\text{NO}_2)^2} \right]_{\text{eq}}$ (method B)	$K_c = K^\circ \left( \frac{p^\circ}{RT} \right)^{-1}$	
6.7364	(A) 6.7364 bar <sup>-1</sup> (B) 6.7403 bar <sup>-1</sup>	(A) 6.8257 atm <sup>-1</sup> (A) 6.7364 × 10 <sup>-5</sup> Pa <sup>-1</sup>	(A) 166.99 (mol L <sup>-1</sup> ) <sup>-1</sup>

We have calculated one value for  $K^\circ$  ( $p^\circ = 1$  bar), which is dimensionless ( $K^\circ = 6.7364$ ). Using equations (7a) and (8), this value has allowed to calculate three different values for  $K_p$ , depending on the units of pressure used ( $K_p = 6.7364 \text{ bar}^{-1}$ ,  $K_p = 6.8257 \text{ atm}^{-1}$  and  $K_p = 6.7364 \times 10^{-5} \text{ Pa}^{-1}$ ). From equation (14), we have calculated a different bar unit value for this quantity:  $K_p = 6.7403 \text{ bar}^{-1}$ .

Analogous examples can be performed in cases involving aqueous solution equilibria. In these situations, we must employ the equations summarized in **Box 2**. Concerning equilibrium constants, an analogous discussion as the one performed in the case of a gas phase equilibrium can be carried out. That is, when applying equation (13), we must note that as we have taken  $c^\circ = 1 \text{ mol/L}$ , only if the units of  $K_c$  are  $(\text{mol/L})^{\Delta n}$ , does its value equal that of  $K^\circ$ . However, it must be stressed that although  $K_c$  and  $K^\circ$  may yield the same value, it does not mean that there is only one quantity. In this particular case, two identical calculated values correspond to two different

quantities.  $K^\circ$  is a unitless quantity and in this circumstance,  $K_c$  has the dimensions of mol/L raised to the power of  $\Delta n$ . But, if other concentration units are employed, a different value for  $K_c$  is obtained. For example, at 298.15 K, for acetic acid (Pethybridge & Mills, 1979):  $K^\circ = 1.751 \cdot 10^{-5}$  ( $c^\circ = 1 \text{ mol L}^{-1}$ );  $K_c = 1.751 \cdot 10^{-5} \text{ mol L}^{-1}$  and  $K_c = 1.756 \cdot 10^{-5} \text{ mol kg}^{-1}$ .

### Presentation and calculation of equilibrium constants in general chemistry textbooks

#### Sample

The sample of textbooks studied consists of two groups (Annex):

- Grade-12 chemistry textbooks (N = 45);
- first-year university chemistry textbooks (N = 39).

The sample of Grade-12 chemistry textbooks covers an ample collection of textbooks through a large span of time (more than thirty years, including the recent editions corresponding to the most important publishers of pre-university chemistry textbooks in the Spanish context). Moreover, two international textbooks are part of this sample as there is an increasing number of Spanish chemistry students that chose to study this subject in English. Also, several textbooks devoted to solving chemical equilibrium exercises have been taken into consideration.

On the other hand, the sample of university chemistry textbooks covers a wide range of books, which have been selected considering that they are well known by a great audience as most of them have been translated into different languages. Particularly, most of the books in the sample have been translated into Spanish and can be found in the libraries of Spanish universities. Also, in many cases, they have been subjected to several editions, which represents a signal of their approval by many chemistry teachers. The selected books correspond to editions made during the last thirty years. Eventually, they have been chosen for similar examinations in previous educational research papers. As in both samples the span of time covered for textbook editions is large, it may help to analyse if the terminological issue examined in this study is a long-standing problem.

#### Research issues

Considering that general chemistry textbooks may not define equilibrium constants properly and even may confuse these quantities, this study has focused on trying to find out if textbooks:

- 1) define each of the equilibrium constants (i.e.  $K_p$ ,  $K_c$  and  $K^\circ$ );
- 2) report  $K_p$  and  $K_c$  using the appropriate units;
- 3) calculate  $K^\circ$  as a unitless quantity;
- 4) present and use the mathematical equation relating  $K_p$  to  $K^\circ$ ;
- 5) assume that  $K_p$  plays the role of  $K^\circ$ .

That is, those items have been used to guide the examination on how chemistry textbooks define, calculate and report equilibrium constants. Particularly, this research aims to establish if there is confusion when naming and determining both  $K_p$  and  $K^\circ$ . In this regard, this work also studies if

units are used properly in each case and if textbooks differentiate those quantities, establishing the corresponding mathematical relationship between them.

## Results and discussion

Keeping in mind the aforementioned research issues, this analysis has concentrated on finding textbook inconsistencies and erroneous treatments concerning the definition and calculation of chemical equilibrium constants. The major results obtained in this examination are provided in **Table 1**.

As there are some differences in the results obtained for each of the two levels analysed, the discussion that follows firstly concentrates on the examination of Grade-12 chemistry textbooks and later on the particular cases for first-year chemistry textbooks are discussed.

In the analysis of each sample, the main features describing how textbooks deal with equilibrium constants will be presented. Several explicit references will be provided when some particular significant cases are worth to be mentioned.

### Grade-12 textbooks

Spanish Grade-12 chemistry textbooks introduce, without exception, the experimental equilibrium constants  $K_p$  and  $K_c$ , as in equations (1) and (2). They also present equation (3). In 56% of the sample those experimental constants are reported as dimensionless quantities in two situations: a) when determining their values after introducing experimental data in equations (1) and (2) and b) when using equation (3) for the calculation of one of the two constants, knowing the value of the other one.

In one textbook (Barrio, Sánchez, Bárcena & Caamaño, 2016)  $K_p$  is reported as a unitless quantity, but  $K_c$  does have units of  $(\text{mol L}^{-1})^{(\Delta n)}$ . Among these textbooks that do not report the value of  $K_p$  with units, there is not usually an explanation stating why they treat  $K_p$  as dimensionless quantity. In three textbooks (Cardona, Pozas, Martín & Ruíz, 2003; García & García-Serna, 2003; Morcillo, Fernández, Carrión, 1998) it is warned that in spite that pressure values must be reported in atm and concentration values in  $\text{mol L}^{-1}$ , both  $K_p$  and  $K_c$  are considered dimensionless quantities. A similar statement was found in a book (Climent, Domingo, Latre, Sanz, Silla, Soler, & Viché, 1989) aimed at instructing the essential chemistry topics to Grade-12 Spanish students in their preparation for the final official chemistry exam to access university. Additionally, in two textbooks (Carriedo, Fernández & García, 2016; Illana, Araque, Liébana & Teijón, 2016) it is mentioned that both  $K_p$  and  $K_c$  should have units but in ideal conditions both constants are expressed in terms of activities. Then, it is stated that as these quantities are dimensionless, thus both constants can be reported as unitless quantities. Consequently, those textbooks that treat  $K_p$  and  $K_c$  as unitless quantities do not care about the units of the  $RT$  product when using equation (3).

Several additional cases have been found where both  $K_p$  and  $K_c$  are treated as dimensionless quantities; particularly, five books of problems for Grade-12 chemistry students (Domingo & Silla,

1991; Fidalgo & Fernández, 2005; Goldberg, 2001; Guardia, Menéndez & de Prada, 2009; López, 2000) and even a doctoral dissertation (Moncaleano, 2008) aimed at the pedagogical study of chemical equilibrium. Furthermore, the same case can be found in a series of textbooks (Fernández, 2016; Morcillo & Fernández, 1991; Zubiaurre & Arsuaga, 2007) that for more than twenty-five years have been collecting and solving the problems and questions corresponding to the final official exams for Grade-12 Chemistry made by the Spanish universities. Thus, as official exams are key references for Chemistry teachers and their students, this last finding may have contributed to not overcoming the reported confusion concerning the units of the equilibrium constants.

When units are reported, the common units for  $K_c$  are  $(\text{mol/L})^{\Delta n}$ . The usual units for  $K_p$  are  $(\text{atm})^{\Delta n}$ ; only in four textbooks (9%) the units of  $K_p$  are also  $(\text{Pa})^{\Delta n}$ . There is no explicit discussion in any of the books in the sample on the units of  $K_c$  and  $K_p$ .

Concerning the thermodynamic equilibrium constant,  $K^\circ$ , this quantity is normally not defined (89 %). However, in one textbook (Brown & Ford, 2014) it is defined as  $K_c$ . Conversely,  $K^\circ$  is accurately introduced in only four textbooks (9 %) of the sample analysed. In three textbooks (Andrés, Antón, Barrio, de la Cruz & González, 2000; Caamaño & Obach, 2000; Caamaño, Obach & Servent, 1991) their authors state that the standard pressure is 1 atm and readers are explicitly warned that  $K^\circ$  is a unitless quantity. In their discussion, they state that as  $p^\circ = 1 \text{ atm}$ , the values of  $K^\circ$  and  $K_p$  are identical when partial pressures are measured in atm. Only one textbook (Simón, García-Serna, & Romero, 2016) was found where both  $K^\circ$  is defined and the given standard state for gases is  $p^\circ = 1 \text{ bar}$ .

Regarding the calculation of the thermodynamic equilibrium constant,  $K^\circ$ , in many cases (78 %) the following equation is introduced,

$$\Delta G^\circ = -RT \ln K_p, \quad (15)$$

assuming, consequently, that  $K_p$  is the thermodynamic equilibrium constant. The values textbooks report for  $K_p$  in this situation usually have no units, but they do not explain why the obtained figure is presented without units. Thus, in some textbooks  $K_p$  is firstly defined as an experimental quantity and then reported having units of pressure, but later on it is calculated as a unitless quantity when it is assumed to play the role of the thermodynamic equilibrium constant, as presented in equation (15). In one textbook (Pozas, Martín, Rodríguez, Ruiz & Vasco, 2016) their authors use in equation (15) the previous calculated value of  $K_p$ , having units of pressure (i.e.  $(\text{atm})^{\Delta n}$ ); that is, the experimental value obtained using equation (1) is now reported without units and then introduced in equation (15) in order to calculate  $\Delta G^\circ$ . However, in two textbooks (Barrio & Belmonte, 1992; Belmonte, 1999) the reported value for  $K_p$ , after calculating this quantity as  $K_p = \exp[-\Delta G^\circ/RT]$ , has atm units. This is also the case of two books of problems (García, Lozano & Teijón, 1991; Fernández & Pérez, 2004) aimed at preparing Grade-12 students for their official Chemistry exam for entering university.



**Table 1.** Main misrepresentations and problematic issues concerning the treatment of equilibrium constants performed by general chemistry textbooks.

Research issue	Grade-12 textbooks	First-year university textbooks
Definition of the equilibrium constants (i.e. $K_p$ , $K_c$ and $K^\circ$ ).	<ol style="list-style-type: none"> <li>1) <math>K_p</math> and <math>K_c</math> are defined (100 %)</li> <li>2) The thermodynamic equilibrium constant (i.e. <math>K^\circ</math>) is not explicitly defined (89 %).</li> </ol>	<ol style="list-style-type: none"> <li>1) <math>K_p</math> and <math>K_c</math> are defined (100 %).</li> <li>2) The thermodynamic equilibrium constant (i.e. <math>K^\circ</math>) is not explicitly defined (92 %).</li> </ol>
Appropriate units for $K_p$ and $K_c$ and $K^\circ$ as a unitless quantity.	<ol style="list-style-type: none"> <li>1) <math>K_p</math> and <math>K_c</math> are reported as unitless quantities (56 %). <ul style="list-style-type: none"> <li>• There is not a clarification explaining why the authors of textbooks have treated the experimental equilibrium constants (i.e. <math>K_p</math> and <math>K_c</math>) as dimensionless quantities (53 %).</li> <li>• When using equation <math>K_p = K_c (RT)^{\Delta n(g)}</math>, it is assumed unitless numbers for both <math>K_p</math> and <math>K_c</math> and, nothing is said about the units of the product <math>RT</math> (56 %).</li> </ul> </li> <li>2) When <math>K_p</math> is reported having units, authors usually employ atm for partial pressures, neglecting other pressure units such as bar or Pa (91 %).</li> <li>3) <math>K^\circ</math> is defined as a unitless quantity (9 %).</li> <li>4) Only one textbook refers to the current standard pressure value: <math>p^\circ = 1</math> bar.</li> </ol>	<ol style="list-style-type: none"> <li>1) The experimental equilibrium constants (i.e. <math>K_p</math> and <math>K_c</math>) are reported as unitless quantities (74 %): <ul style="list-style-type: none"> <li>• There is not clarification explaining why the authors of textbooks have treated the experimental equilibrium constants (i.e. <math>K_p</math> and <math>K_c</math>) as dimensionless quantities (18 %).</li> <li>• Both <math>K_p</math> and <math>K_c</math> are unitless because there are more rigorous methods for expressing those quantities (33 %).</li> <li>• It is customary to report those quantities without units (18 %).</li> <li>• <math>K_p</math> is defined in terms of activities (5 %).</li> <li>• When using equation <math>K_p = K_c (RT)^{\Delta n(g)}</math>, it is assumed unitless numbers for both <math>K_p</math> and <math>K_c</math> and, usually, nothing is said about the units of the product <math>RT</math> (74 %).</li> </ul> </li> <li>2) When <math>K_p</math> is reported having units, authors usually employ atm for partial pressures, neglecting other pressure units such as bar or Pa (92 %).</li> <li>3) <math>K^\circ</math> is defined as a unitless quantity (8 %).</li> <li>4) There is not reference to the current standard pressure value: <math>p^\circ = 1</math> bar (92 %).</li> </ol>
Presentation and use of the mathematical equation relating $K_p$ (or $K_c$ ) to $K^\circ$ .	They are not presented in any textbook.	Few textbooks present and use these equations (8 %).
Assumption that $K_p$ plays the role of $K^\circ$ .	<ol style="list-style-type: none"> <li>1) It is assumed that <math>K_p</math> plays the role of the thermodynamic equilibrium constant (<math>K^\circ</math>) (78 %).</li> <li>2) The following mathematical relationship is usually used <math>\Delta G^\circ = -RT \ln K_p</math> (78 %).</li> <li>3) There is not an exposition clarifying why when performing the calculation of <math>K_p</math> using the above equation, it must be reported as a unitless quantity (78 %).</li> </ol>	<ol style="list-style-type: none"> <li>1) There is not explicit distinction between the thermodynamic equilibrium constant, <math>K^\circ</math>, and the practical or experimental equilibrium constants, <math>K_p</math> and <math>K_c</math> (92 %).</li> <li>2) In many cases, it is explicitly stated that <math>K^\circ</math> means <math>K_p/K_c</math> (62 %).</li> <li>3) It is used the following mathematical relationship <math>\Delta G^\circ = -RT \ln K_p</math> or a similar one as it is assumed that the thermodynamic equilibrium constant is <math>K_p</math> (or <math>K_c</math>) (62 %).</li> </ol>

Finally, it is worthy to note that equation (15) contains two errors: a) it uses  $\Delta G^\circ$  instead of  $\Delta_r G^\circ$  and b) it is assumed that  $K_p = K^\circ$  (or  $K_c = K^\circ$ ). In this work, we have concentrated on the second inaccuracy. The correct expression is equation (5) (Borge, 2015; Quílez, 2012). This expression was found in only three Grade-12 textbooks (8 %) of the sample analysed. Also, it should be noted that in this logarithmic relationship the units of  $\Delta_r G^\circ$  are those of the product  $RT$  (i.e. J mol<sup>-1</sup>) as the other part of equation (5) (i.e.  $\ln K^\circ$ ) represents the Napierian logarithm of a number (i. e.  $K^\circ$  is unitless), instead of the logarithm of a dimensioned quantity (e. g.  $K_p$  or  $K_c$ ) (Boggs, 1958; Copley, 1958; Laidler, 1995) because dimensions are not carried at all in a logarithmic function (Matta, Massa, Gubskaya & Knoll, 2011).

The previous findings show that among the current Spanish Grade-12 Chemistry textbooks there is only one case (Simón, García-Serna, & Romero, 2016) that accurately both introduces and calculates the three equilibrium constants (i.e.  $K_p$ ,  $K_c$  and  $K^\circ$ ). Moreover, this study has shown that during the last thirty years, few textbooks have properly defined and calculated those quantities. In more than half of the sample analysed,  $K_p$  and  $K_c$  are treated as dimensionless quantities and it is usually assumed that  $K_p$  (or  $K_c$ ) plays the role of the thermodynamic equilibrium constant,  $K^\circ$ . Thus, the misleading way which Spanish Grade-12 Chemistry textbooks treat those quantities has revealed to be a long-standing problem when teaching chemical equilibrium to high school students. By the same token, complementary and referential material for the study of chemistry, such as books of problems and official chemistry exams to enter university, may have contributed to those inaccurate assumptions.

### First-year textbooks

The examination carried out on first-year chemistry textbooks reveals that a small percentage (26%) express  $K_p$  and  $K_c$  having units. These cases mean that  $K_p$  usually has (atm) <sup>$\Delta_n$</sup>  units; Freemantle (1991) express  $K_p$  in (Pa) <sup>$\Delta_n$</sup>  units and Burrows (2017) report several examples in which  $K_p$  is measured in (Pa) <sup>$\Delta_n$</sup> , (atm) <sup>$\Delta_n$</sup>  and (bar) <sup>$\Delta_n$</sup>  units.

Among the textbooks that consider these quantities as dimensionless (74%), there is more diversity than in the case of Grade-12 textbooks. In a first group of seven textbooks (18 %) there is no mention to why they have omitted units. However, in one of them (Spencer, Bodner & Rickard, 2008) their authors warn that in spite that  $K_p$  is a dimensionless quantity, any calculation involving it requires that partial pressures must be reported in atm units. In a second group, textbooks (18 %) give explanations that may surprise their readers. For example, in one textbook it is stated the following "...the units of equilibrium constant can always be figured out from the equilibrium constant expression. Therefore, it is customary to omit the units, and we shall follow that custom here" (Moore, Stanitski, Wood, Kotz & Joesten, 1998, p. 574). Additionally, Zumdahl and Zumdahl (2007, p. 583) state:

The reason for this is beyond the scope of this text, but it involves corrections for the nonideal behaviour of the substances taking part in the reaction. When these corrections are made, the units cancel out and the corrected  $K$  has no units. Thus, we will not use units for  $K$  in this text.

Finally, in a third group of textbooks (33 %), after presenting the general equations for both  $K_p$  and  $K_c$ , as in equations (1) and (2), and examples for the calculation of each of these two quantities, the reader is warned that the figures obtained are dimensionless as their authors make reference to a more rigorous treatment of the equilibrium constants in which these quantities are defined in terms of activities. They usually explain that each term in the equilibrium constant represents the ratio of the measured quantity of the substance (molar concentration or pressure) to the thermodynamic standard-state quantity of the substance, recalling that these standard states are mol L<sup>-1</sup> for a substance in solution and 1 atm for gases. Thus, they conclude that although they consider experimental values of partial pressures in atm or concentrations in mol L<sup>-1</sup>, as each term is understood to be a ratio of a concentration or partial pressure to a standard value, the units on each term cancel, which results in the value of  $K_p$  (or  $K_c$ ) having no units. Moreover, when using equation (3) ( $K_p = K_c (RT)^{\Delta n(g)}$ ), they assume unitless numbers for both  $K_p$  and  $K_c$  and, usually, nothing is said about the units of the product  $RT$ . However, in one textbook (Jespersen, Brady & Hyslop, 2012) the reader is advised that the following  $R = 0.0821$  L atm mol<sup>-1</sup>K<sup>-1</sup> is the only value of  $R$  that can be used in equation (3). Additionally, a similar framework is embodied in two textbooks (Petrucci, Harwood, Herring & Madura, 2006; Atkins & Jones, 2010) as their authors define only one equilibrium constant in terms of activities although they name it as  $K_p$ .

In an advanced thermodynamic section of the topic chemical equilibrium all the textbooks analysed introduce an equation that usually has this customary presentation,

$$\Delta G^\circ = -RT \ln K \quad (16)$$

The main textbook inaccuracy is that their authors assume explicitly (62 %) that the calculation of  $K$  in equation (16) means to calculate  $K_p$  (and also  $K_c$  and  $K_p$ ). That is, in several textbooks (21 %) it is understood that the equilibrium constant that appears in the above equation is actually  $K_p$ . This assumption prompts that in some textbooks (10%),  $K_p$  is written in the above equation (16)

$$\Delta G^\circ = -RT \ln \left\{ \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} \right\}_{eq} = -RT \ln K_p \quad (17)$$

Similarly, in another group of textbooks (26 %) their authors state that  $K = K_p$  in the case of gases ( $p^\circ = 1$  atm) and  $K = K_c$  in the case of aqueous diluted solutions ( $c^\circ = 1$  mol/L). Additionally, in several textbooks (8 %), equation (16) is used to calculate  $K_p$ .

Thus, the symbol  $K_p$  (and also  $K_c$  and  $K_p$ ) is misleadingly used to denote the thermodynamic equilibrium constant,  $K^\circ$ . Also, one may infer that the value of  $K_p$  introduced in equation (17) has units of pressure. Hence, equation (17) may lead to incorrect assumptions because it hides the fact that the argument of the logarithm is dimensionless. Similar to the above discussion on equation (15), equations (5) and (17) are not the same as  $K_p$  is a dimensioned quantity, but logarithmic quantities are unitless. Thus, one must remark that in order to explicitly make dimensionless the thermodynamic equilibrium constant,  $K^\circ$  (instead of  $K_p$ ), equation (17) must accurately be rewritten introducing the standard pressure on it (Borge, 2015), as has been done in equation (5).

This misleading assumption in which the thermodynamic equilibrium constant,  $K^\circ$ , is represented by the symbol  $K_p$  may derive from a careless neglect of the units in equation (5) as  $p^\circ = 1$  bar (1 atm for most textbooks) and then the  $p^\circ$  values may be considered unnecessary (because units cancel out) and thus the denominators are omitted (Zumdahl & DeCoste, 2017) which certainly may confuse our students as they may find (and use) mathematical expressions containing logarithms of quantities with units.

The previous examination shows that in few freshman textbooks (Burrows, Holman, Parsons, Pilling & Price, 2017; Oxtoby, Gillis & Campion, 2012; Petrucci, Herring, Madura & Bissonnette, 2017) the three equilibrium constants (i.e.  $K_p$ ,  $K_c$  and  $K^\circ$ ) are accurately defined. Concerning their units and the calculation of  $K_p$  (or  $K_c$ ) using equations (7a) and (13), in only two textbooks (Burrows, Holman, Parsons, Pilling & Price, 2017; Petrucci, Herring, Madura & Bissonnette, 2017) there is a clear discussion on this issue. Thus, in three quarters of the sample analysed,  $K_p$  and  $K_c$  are treated as dimensionless quantities and it is usually assumed that  $K_p$  (or  $K_c$ ) plays the role of the thermodynamic equilibrium constant,  $K^\circ$ . Hence, as in the case of pre-university textbooks, the misleading way which first-year textbooks treat those quantities has revealed to be a long-standing problem.

In the study that corresponds to the dimensionality of  $K^\circ$  in equation (16), all textbooks, except one case (Atkins, 1989), treat the thermodynamic equilibrium constant as a unitless quantity, although in a 15 % of the sample there is not any explanation stating why this quantity is dimensionless. In a textbook of chemistry problems of this university level (Adamson, 1975) there is another case in which  $K^\circ$  appears having units. Finally, only in three textbooks (8 %) their authors state that the standard value of pressure is  $p^\circ = 1$  bar; thus, the majority of textbooks take for this value  $p^\circ = 1$  atm.

As a final comment, an inspection of some advanced textbooks reveals that their treatment of the quantities analysed in this study is quite more accurate than in the case of first-year textbooks. However, confusing equation (17) was found in a higher-level textbook (Raff, 2001). Moreover, in some well-known physical chemistry textbooks (Chang, 2000; Engel & Reid, 2012; Levine, 2009; McQuarrie & Simon, 1997; Mortimer, 2000; Vemulapalli, 1993) the thermodynamic equilibrium constant is named using the  $K$  symbol keeping the subscript  $p$  on it, which may not help to overcome the confusion between these two different quantities,  $K^\circ$  and  $K_p$ . Conversely, this terminological association is not present in two textbooks of this type (Atkins & de Paula, 2010; Silbey, Alberty & Bawendi, 2005). Eventually, a clear presentation of each equilibrium constant can be found in two advanced thermodynamic textbooks (Brenon-Audat, Busquet & Mesnil, 1993; DeVoe, 2016).

### Concluding remarks, final comments and educational suggestions

The first part of this article has provided a brief summary concerning the definition and calculation of the different equilibrium constants (i.e.  $K_p$ ,  $K_c$  and  $K^\circ$ ). This analysis has also presented an example in order to aid in the discussion involving the calculation and proper units of those quantities. Particularly, the thermodynamic equilibrium constant,  $K^\circ$ , is a unitless quantity because

it is calculated in reference to specific standard states (e.g. 1 bar or 1 mol L<sup>-1</sup>) (i.e. equations (4) and (10)). These reference states should be specified as they have calculational effects depending on which is used. Conversely,  $K_p$  has units of pressure (e.g. bar, atm, Pa, etc.) and  $K_c$  has units of concentration (e.g. mol L<sup>-1</sup>, mol kg<sup>-1</sup>). The terminological examination of these three different quantities has served to base the study on how chemistry textbooks deal with equilibrium constants.

Concerning how chemistry textbooks define and report equilibrium constants, the main findings of this study are the following:

- 1) Many textbooks present  $K_c$  and  $K_p$  as dimensionless quantities.
  - a) Particularly, in more than half of the Grade-12 textbooks' sample and in three quarters of first-year textbooks their authors report experimental equilibrium constants without units.
  - b) In several cases, first-year textbooks refer to a more rigorous method (i.e. activities) when defining  $K_c$  and  $K_p$ , assuming that units cancel out. In other instances, an explanation stating why  $K_c$  and  $K_p$  are reported as unitless quantities is not given or simply it is asserted that it is customary to omit units.
  - c) Authors usually do not care about the units of the product  $RT$  when performing calculations using the equation  $K_p = K_c (RT)^{\Delta n(g)}$ .
- 2) When  $K_p$  is reported having units, authors usually employ atm as the unit for partial pressures, neglecting other pressure units such as bar or Pa.
- 3) The thermodynamic equilibrium constant,  $K^\circ$ , is normally not defined.
- 4) In most of the chemistry textbooks analysed there is not explicit distinction between both  $K^\circ$  and  $K_p$ ; thus, this quantity usually plays the role of  $K^\circ$ .
- 5) The mathematical relationship between  $K^\circ$  and  $K_p$  is normally not given; a similar case was found concerning  $K^\circ$  and  $K_c$ .
- 6) Most textbooks still refer to the value 1 atm as the standard state pressure, thus few of them use the current value,  $p^\circ = 1$  bar.
- 7) In the equation  $\Delta_r G^\circ = -RT \ln K^\circ$ , it is usually assumed that  $K^\circ$  is  $K_p$ ; in several cases, that equation is written as  $\Delta_r G^\circ = -RT \ln K_p$ , reinforcing the assumption that  $K_p$  plays the role of  $K^\circ$ .
- 8) In the introduction and discussion of the meaning of equation  $\Delta_r G^\circ = -RT \ln K^\circ$ , it is not normally explained why  $K^\circ$  is a dimensionless quantity.

The cases discussed in this article demonstrate how deep the terminological misrepresentations on the equilibrium constants are rooted both in pre-university chemistry textbooks and in those corresponding to first-year level. This confusion in terminology leads to report  $K_p$  and  $K_c$  as dimensionless quantities. As most educators usually follow what is stated in textbooks, this

misleading treatment of equilibrium constants may have also permeated the way how chemistry teachers deal with these quantities, which warns about the importance of possible re-education of teachers in order to guarantee that students learn these topics properly.

In order to avoid current misrepresentations, the thermodynamic equilibrium constant,  $K^\circ$ , should be defined as well as the practical equilibrium constants,  $K_p$  and  $K_c$ , stating the equations that relate both  $K^\circ$  to  $K_p$  and  $K^\circ$  to  $K_c$ . These equations may help in understanding why  $K^\circ$  is a unitless quantity whereas the experimental equilibrium constants, viz.  $K_p$  and  $K_c$ , must be expressed having units. In addition, this study has showed how different units lead to different numerical values for the practical equilibrium constants corresponding to a particular equilibrium equation. Also, it has discussed that although  $K^\circ$  and  $K_p$  (or  $K^\circ$  and  $K_c$ ) may yield the same value (i.e. gas pressure values measured in bar; concentrations in mol L<sup>-1</sup>), it does not mean that there is only one quantity, which first-year chemistry textbooks usually name  $K_p$  (or  $K_c$ ).

Selected examples, as the one performed in this study, may allow students to accurately deal with equilibrium constants' calculation and units. Still, it is suggested a progression in this presentation as the correct treatment of the thermodynamic equilibrium constant,  $K^\circ$ , would be beyond the scope of a pre-university level as students of these introductory chemistry courses may be unable to understand the formalities, concepts and equations that allow the calculation of  $K^\circ$  when connecting it with  $\Delta_r G^\circ$  using equation (6). Thus, Grade-12 chemistry textbooks should solely define both  $K_p$  and  $K_c$ , reporting them with their proper units. That is, when solving chemical equilibrium problems, the performance of ICE tables should allow students the introduction of the corresponding values (and their units) in the corresponding equilibrium constant expression (i.e. equations (1) and (2)), which eventually could lead them to report the calculated constant as a dimensioned quantity. This case also applies when using equation (3) in the study of gaseous equilibrium reactions. Hence, the complete treatment discussed in this study, which involves the definition and calculation of the thermodynamic constant,  $K^\circ$ , as well as its relationship to  $K_p$  and  $K_c$ , would be left to first-year university chemistry textbooks. That is, in this college level, after reminding students the dimensioned experimental equilibrium constants (i.e.  $K_p$  and  $K_c$ ), firstly introduced in their pre-university general chemistry course, the equilibrium constant,  $K^\circ$ , should be defined as a dimensionless quantity that can be calculated using equation (6). Additionally,  $K_p$  can be calculated from  $K^\circ$  employing equation (7a); similarly,  $K_c$  can be obtained from equation (7b) or equation (13), taking in mind that these expressions assume ideal behaviour of the species involved in the equilibrium mixture.

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## Appendix: List of General Chemistry textbooks examined

### A) Grade-12 Spanish Chemistry textbooks

- Guillén, J., Julia, S., Masana, J. & Pascual, A. (1978). *Química COU*. Madrid: Magisterio Español.
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- Guillem, C. (1979). *Química COU*. Alcoy: Marfil.
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- Oroz, J. (1989). *Química COU*. Madrid: SM.
- Alonso, P., Cebeira, R., García, M. J. & Ortega, E. (1990). *Química COU*. Madrid: McGraw Hill.
- Morcillo, J. & Fernández, M. (1990). *Química COU*. Madrid: Anaya.
- Caamaño, A., Obach, D. & Servent, A. (1991). *Química COU*. Barcelona: Teide.
- Latre, F. & Usó, J. (1991). *Química*. Vila-real: Miralles.
- Sauret, M. (1991). *Química COU*. Madrid: Bruño.
- Masjuan, M. D., Dou, J. M. & Pelegrín, J. (1991). *Química COU*. Barcelona: Casals.
- Arróspide, M. C. & Piñar, M. I. (1992). *Química COU*. Zaragoza: Luis Vives.
- Barrio, J. I. & Belmonte, M. (1992). *Química COU*. Reacción. Madrid: SM.
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- Oro, L. A., Andreu, J. L., Fernández, M. C. & Pérez-Torrente, J. J. (1999). *Química 2*. Madrid: Santillana.
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- Caamaño, A. & Obach, D. (2000). *Química 2*. Barcelona: Teide.
- Barrío, J. I. & Montejo, C. (2003). *Química 2*. Madrid: SM.
- Cardona, A. R., Pozas, A., Martín, R. & Ruíz, A. (2003). *Química 2*. Madrid: McGraw Hill.
- Fidalgo, J. A. & Fernández, M. R. (2003). *Química 2*. León: Everest.
- García, T. & García-Serna, J. R. (2003). *Química*. Barcelona: Edebé.
- Pérez, M. A., Pastor, E. & Ortiz, M. J. (2003). *Química 2*. Madrid: Santillana.
- Rodríguez, A., Pozas, A., Martín, R. & Ruíz, A. (2007). *Química*. Madrid: McGraw Hill.
- Barrio, J. I., Bárcena, A. I., Sánchez, A. & Caamaño, A. (2009). *Química 2*. Madrid: SM.
- Fontanet, À. (2009). *Química*. Barcelona: Vicens Vives.
- Zubiaurre, S., Arsuaga, J. M. & Garzón, B. (2009). *Química 2*. Madrid: Anaya.
- Guardia, C., Menéndez, A. I. & de Prada, F. (2009). *Química*. Madrid: Santillana.
- Brown, C. & Ford, M. (2014). *Higher Level Chemistry*, (2nd ed). Harlow: Pearson.
- Ryan, L. & Norris, R. (2014). *A Level Chemistry*, (2nd ed). Cambridge: Cambridge University Press.
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- Carriedo, G. A., Fernández, J. M. & García, M. J. (2016). *Química 2*. Madrid: Paraninfo.
- Guardia, C. & Menéndez, A. I. (2016). *Química 2*. Madrid: Santillana.
- Illana, J., Araque, J. A., Liébana, A. & Teijón, J. M. (2016). *Química 2*. Madrid: Anaya.
- Manuel, M. M. & Pizarro, F. (2016). *Química 2*. Zaragoza: Edelvives.

- Masjuan, M. D. & Pelegrín, J. (2016). *Química 2*. Barcelona: Casals.
- Pozas, A.; Martín, R.; Rodríguez, A.; Ruiz, A. & Vasco, A. J. (2016). *Química 2*. Madrid: McGraw Hill.
- Sauret, M. (2016). *Química 2*. Madrid: Bruño.
- Simón, B.; García-Serna, J. & Romero, J. J. (2016). *Química 2*. Barcelona: Edebé.
- Vidal, M. C.; Peña, J. (2016). *Química 2*. Madrid: Oxford.

### B) First-year university Chemistry textbooks

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- Atkins, P. W. (1989). *General Chemistry*. New York: Scientific American Books.
- Bailar, J. C., Moeller, T., Kleinberg, J., Guss, C. O., Castellion, M. E. & Metz, C. (1989). *Chemistry*. San Diego: Hartcourt.
- Bodner, G. M. & Pardue, H. L. (1989). *Chemistry: an Experimental Science*. New York: Wiley.
- Segal, B. G. (1989). *Chemistry. Experiment and Theory*. New York: Wiley.
- Freemantle, M. (1991). *Chemistry in Action*. London: MacMillan.
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- Brown, T. L., LeMay, H. E. & Bursten, B. E. (1997). *Chemistry: the Central Science*. New Jersey: Prentice Hall.
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- Moore, J. W., Stanitski, C. L., Wood, J. L., Kotz, J. C. & Joesten, M. D. (1998). *The Chemical World. Concepts and Applications*. Orlando: Saunders.
- Umland, J. B. & Bellama, J. M. (1999). *General Chemistry*. Pacific Grove: Brooks/Cole.
- Brady, J. E., Russell, J. W. & Holum, J. R. (2000). *Chemistry. Matter and its Changes*. New York: Wiley.
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- Hill, J. W. & Petrucci, R. H. (2002). *General Chemistry. An integrated approach*. New Jersey: Prentice Hall.
- Olmsted, J. & Williams, G. M. (2002). *Chemistry*. New York: Wiley.
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- Tro, N. J. (2003). *Introductory Chemistry*. New Jersey: Prentice Hall.
- Petrucci, R. H., Harwood, W. S., Herring, G. E. & Madura, J. (2006). *General Chemistry: Principles and Modern Applications*. New Jersey: Prentice-Hall.
- Zumdahl, S. S. & Zumdahl, S. S. (2007). *Chemistry*. Boston: Houghton Mifflin.
- Buthelezi, T., Dingrando, L., Hainen, N., Winstrom, C. & Zike, D. (2008). *Chemistry. Matter and change*. Columbus: McGraw-Hill.
- McMurry, J., & Fay. C. (2008). *Chemistry*. New Jersey: Prentice Hall.
- Spencer, J. N., Bodner, G. M. & Rickard, L. H. (2008). *Chemistry. Structure and Dynamics*. New York: Wiley.
- Silberberg, M. S. (2009). *Chemistry. The Molecular Nature of Matter and Change*. New York: McGraw-Hill.
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- Oxtoby, D. W., Gillis, H. P. & Campion, N. H. (2012). *Principles of Modern Chemistry*. Belmont: Brooks/Cole.

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