

# First-year university chemistry textbooks' misrepresentation of equilibrium constants

## La incorrecta representación de las constantes de equilibrio en los libros de primer curso universitario de química

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### Abstract

This paper analyses the misrepresentation of equilibrium constants. We report the way first-year university chemistry textbooks handle the units of equilibrium constants. In this case we have found out a problem of terminology. Many textbooks confuse  $K_p$  with  $K^\circ$ . One problem is proposed and solved in order to exemplify a correct treatment of the quantities involved, which help in the discussion and clarification of the misleading assumptions reported in this study.

**Key words:** general chemistry, thermodynamics; physical chemistry; equilibrium constants, textbook

### Resumen

Este trabajo analiza la representación incorrecta de las constantes de equilibrio. Se informa la forma en la que los libros de primer curso universitario de química utilizan las unidades de las constantes de equilibrio. Muchos libros confunden  $K_p$  con  $K^\circ$ . Se propone un problema y se resuelve para ejemplificar el correcto tratamiento de las magnitudes implicadas, lo que puede ayudar en la discusión y clarificación de los errores considerados en este estudio.

**Palabras clave:** química universitaria, termodinámica, química física, constante de equilibrio, libros de texto.

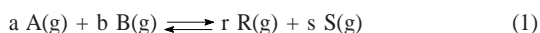
### INTRODUCTION

The aim of this paper is to review the terminology associated with the equilibrium constants. We will trace back the discussion carried out by different authors dealing with the units of the equilibrium constants as well as how they are presented in first-year university chemistry textbooks. Following IUPAC recommendations, we will present a pedagogical example in order to help in the clarification of the concepts involved.

### Equilibrium constant units: textbooks' misrepresentations

There has been a great number of articles dealing with the units of the equilibrium constant. In some of them it is stated that the equilibrium constant is dimensionless (BOGGS, 1958; COX *et al.* 1979; HARRIS, 1982; ABRANTES & NIETO, 1985; TYKODI, 1986; QUINTERO, 1987; GORDUS, 1991; RONNEAU, 1993; GIL & PAIVA, 1999; ROSENBERG & KOTZ, 1999), but in others, authors advocate that practical (or experimental) equilibrium constants, viz.  $K_p$  and  $K_c$ , do have units (HENRY, 1967; PETHYBRIDGE & MILLS, 1979; VICKERMAN, 1979; WRIGHT, 1979; DELORME, 1985; MILLS, 1989; MILLS, 1995; LAIDLER, 1990; MOLYNEUX, 1991; ANTONIK, 1993; DEPOVERE & WEILER, 1993a,b; TREPTOW, 1999). If we pay attention to this long discussion, it seems that the issue is essentially a terminological problem. Thus, our aim is to help in the teaching of this problematic topic. We consider that this is a very important issue because pre-college general chemistry textbooks assign units to the equilibrium constant. But, as we will discuss later, this situation changes in first-year university chemistry courses, for many general chemistry textbooks present equilibrium constants as dimensionless quantities.

Equilibrium constants  $K_p$  and  $K_c$  are usually defined before thermodynamics is taught. For example, in the case of the following equilibrium



$K_p$  is defined as an experimental quantity as follows

$$K_p = \left( \frac{p_R^r p_S^s}{p_A^a p_B^b} \right)_{eq} \quad (2)$$

where  $p_i$  is the partial pressure of each of the gases involved. They are usually measured in atmospheres (atm).

Similarly,  $K_c$  is defined as follows

$$K_c = \left( \frac{[R]^r [S]^s}{[A]^a [B]^b} \right)_{eq} \quad (3)$$

where the concentrations are usually measured in mol/L.

Thus, it seems that the units of  $K_p$  must be  $(\text{atm})^{\Delta v}$ , whereas those of  $K_c$  must be  $(\text{mol/L})^{\Delta v}$ , where,  $\Delta v = (r + s) - (a + b)$ . A few first-year university chemistry textbooks agree with those assumptions (YODER, SNYDAM & SNAVELY, 1980; ATKINS, 1989; SEGAL, 1989; GILLESPIE *et al.*, 1989). But, many authors state that both  $K_p$  and  $K_c$  are dimensionless. This statement may confuse students because they are always required to pay great attention to units elsewhere. This may be the case when some authors (MASTERTON, SLOWINSKI & STANITSKI, 1983; KOTZ & PURCELL, 1987; BODNER & PARDUE, 1989; BRADY, RUSSELL & HOLM, 2000; KOTZ & TREICHEL, 2003) do not explain why they omit units when reporting the calculation of experimental equilibrium constants. However, the reasons given in some textbooks may come as a surprise to students. MOORE *et al.* (1998) claim that

'the units of equilibrium constant can always be figured out from the equilibrium constant expression. Therefore, it is customary to omit units, and we shall follow that custom here'.

BROWN *et al.* (1997) give a similar statement. In other cases, the authors make reference to a better rigorous thermodynamic foundation for the equilibrium constant. UMLAND and BELLAMA (1999) state

'Units are not usually given for equilibrium constants because the more accurate ways of treating equilibrium constants used in thermodynamics and physical chemistry define equilibrium constants in terms of activities, not molarities. Activities, which are numerically equal to effective concentrations corrected for non ideal behaviour, are dimensionless numbers; that is, they have no units'.

Similar statements can be found in other textbooks (WHITTEN, GAILEY & DAVIS, 1997; PETRUCCI & HARWOOD, 1997; OLMSTED & WILLIAMS, 2002). WHITTEN *et al.* (1997), after defining  $K_c$  as an experimental quantity, add that the thermodynamic definition of the equilibrium constant make use of activities, instead of concentrations. Thus, they conclude that the equilibrium constant is dimensionless, because the values used for  $K_c$  are identical to those of concentrations, but dimensionless; that is, they have no units. And OLMSTED and WILLIAMS (2002) explain

'Although not stated explicitly, each concentration in a reaction quotient and in an equilibrium constant expression has been divided by standard concentration (1 atm for gases, 1 M for solutes) to make the equilibrium constant dimensionless. For example,

$$(p_{N_2O_4})_{eq} = \frac{(p_{N_2O_4})_{eq}}{1 \text{ atm}} \quad (4)$$

At somewhat later stage, textbooks present the thermodynamic foundation for the equilibrium constant. Eventually, they usually state the following equation

$$\Delta G^\circ = -RT \ln K^\circ \quad (5)$$

However, once again textbooks give different interpretations to  $K^\circ$  (which is usually named  $K$ ). MASTERTON *et al.* (1983), UMLAND and

BELLAMA (1999), and KOTZ and TREICHEL (2003) claim that  $K$  means  $K_p$ . ADAMSON (1975), GILLESPIE *et al.* (1989), ATKINS (1989) and BRADY *et al.* (2000) explicitly write  $\Delta G^\circ = -RT \ln K_p$ . MOREOVER, ADAMSON (1975) and ATKINS (1989) report the equilibrium constant with units when it is calculated from  $\Delta G^\circ$  values. OLMSTED and WILLIAMS (2002) do not make distinction between each of the mathematical expressions corresponding to  $K_p$  and  $K_c$ , for they call both of them  $K_{eq}$ . Later, in the thermodynamics section, they name also the equilibrium constant  $K_{eq}$ . Becker and Wentworth (1977) do not define experimental equilibrium constants. Instead, they present two equations. The first one corresponds to aqueous equilibria

$$\Delta G^\circ = -RT \ln K, \quad (6)$$

where

$$K = \frac{(a_c)^c}{(a_b)^b} = \frac{(\gamma_c)^c [C]}{(\gamma_b)^b [B]} \quad (7)$$

being  $a_i$  the activities of each of the chemicals involved, and  $\gamma_i$  the corresponding activity coefficients, in the equilibrium



In ideal solutions

$$K = \frac{[C]^c}{[B]^b} \quad (9)$$

The second equation presented by these authors corresponds to gaseous equilibria

$$\Delta G^\circ = -RT \ln K_p \quad (10)$$

where

$$K_p = \frac{(p_c)^c}{(p_b)^b} \quad (11)$$

Also, Petrucci and Harwood [37] conclude that in gaseous chemical equilibria  $K_{eq} = K_p$ .

It seems, therefore, that the authors have in mind a sound (thermodynamic) foundation for the presentation of the equilibrium constant(s). They advance some thermodynamic hints, leaving their justification for a more advanced level because the derivation of the equation  $\Delta_r G^\circ = -RT \ln K^\circ$  (the reader is reminded that  $\Delta_r G^\circ$  is the standard reaction Gibbs energy, an intensive quantity (Mills *et al.* 1993), which should not be confused with  $\Delta G^\circ$ , an extensive quantity) is usually beyond the scope of first-year university chemistry syllabus. The multiple formats in which textbooks provide the information concerned with this topic embody an array of names for the thermodynamic equilibrium constant (*e.g.*,  $K$ ,  $K^\circ$ ,  $K_p$ ,  $K_{eq}$ ,  $K_{th}$ ). Thus, authors seem to be concerned with an accurate thermodynamic presentation, neglecting or not paying attention to practical equilibrium constants ( $K_p$  and  $K_c$ ). Consequently, textbooks often do not explicitly distinguish between thermodynamic and

practical equilibrium constants. A summary of the above discussion is given in Table 1.

However, the IUPAC (MILLS *et al.* 1993) allows the use of  $K_p$  and  $K_c$ , having units, and a thermodynamic  $K^\circ$ , which is dimensionless. Knowing the value of one of them, it is easy to find out the corresponding values of the other two. The thermodynamic equilibrium constant is defined as follows (ideal behaviour)

$$K^\circ = \frac{\left(\frac{p(R)_{eq}}{p^\circ}\right)^r \left(\frac{p(S)_{eq}}{p^\circ}\right)^s}{\left(\frac{p(A)_{eq}}{p^\circ}\right)^a \left(\frac{p(B)_{eq}}{p^\circ}\right)^b} \quad (12)$$

Then, we are able to find the following relationship

$$K_p = K^\circ (p^\circ)^{\Delta \nu} \quad (13)$$

As  $p^\circ = 1$  bar, if the units of  $K_p$  are (bar) $\Delta \nu$ , its value equals that of  $K^\circ$ . But, as (atm) $\Delta \nu$  are usually the units of  $K_p$ , then the values of both constants are different.

Other relationships are

$$K_p = K_c (RT)^{\Delta \nu} \quad (14)$$

$$K^\circ = K_c \left(\frac{RT}{p^\circ}\right)^{\Delta \nu} \quad (15)$$

In *example 1* we outline the calculation of  $K^\circ$ ,  $K_p$  and  $K_c$ .

### Example 1

Calculate  $K^\circ$ ,  $K_p$  and  $K_c$  at 298.15 K for the ammonia synthesis equilibrium:



Thermodynamic data at 298.15 K ( $p^\circ = 1$  bar):  $\Delta H_f^\circ[NH_3(g)] = -46.11$  kJ/mol;  $S^\circ[N_2(g)] = 191.61$  J/K mol;  $S^\circ[H_2(g)] = 130.684$  J/K mol;  $S^\circ[NH_3(g)] = 192.45$  J/K mol;

### SOLUTION

$$\Delta_r H^\circ = -46.11 \text{ kJ/mol}$$

$$\Delta_r S^\circ = S^\circ[NH_3(g)] - \frac{1}{2} S^\circ[N_2(g)] - \frac{3}{2} S^\circ[H_2(g)] = -99.381 \text{ J/K mol}$$

Table 1

### Summary of general chemistry textbooks' misrepresentation of the equilibrium constants

- 1) Some textbooks do not explain why they omit units when reporting the calculus of experimental equilibrium constants (*i.e.*,  $K_c$  and  $K_p$ ).
- 2) Textbooks often do not explicitly distinguish between thermodynamic and practical equilibrium constants.
- 3)  $K_c$  and  $K_p$  are dimensionless.
  - Sometimes, it is explained that units are not given for equilibrium constants because there are more accurate ways of treating equilibrium constants.
  - In a few cases, it is stated that it is customary to omit the units of the equilibrium constant.
  - It is often usual to refer to activities after defining  $K_c$ , stating that the equilibrium constant has no units because the values used for  $K_c$  are identical to those of concentrations, but dimensionless.
- 4)  $K^\circ$  is identical to  $K_p$ .
- 5)  $\Delta G^\circ = -RT \ln K_p$ . Moreover, the different ways in which textbooks give the information concerned with this topic embody an array of names for the thermodynamic equilibrium constant (*eg.*  $K$ ,  $K^\circ$ ,  $K_p$ ,  $K_{eq}$ ,  $K_{th}$ ).
- 6) Some textbooks report the equilibrium constant with units (*i.e.*,  $K_p$  or  $K_c$ ) when it is calculated from equation  $K = e^{-\Delta G^\circ / RT}$ .

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0 = -16479.55 \text{ J/mol};$$

$$\Delta_r G^0 = -RT \ln K^0; \quad K^0 = e^{-\Delta_r G^0 / RT} = 771.35$$

$$K_p = K^0 (p^0)^{\Delta\nu} = 771.35 \text{ bar}^{-1}; \text{ as } 1 \text{ atm} = 1.01325 \text{ bar}, K_p = 781.57 \text{ atm}^{-1}$$

$$K_c = \frac{K_p}{(RT)^{\Delta\nu}} = 1.91 \cdot 10^4 (\text{mol/L})^{-1}$$

The value of  $K^0$  depends not only on the stoichiometry of the chemical equation that represents the equilibrium, but also on the standard pressure used to define the standard state (TYKODY, 86; TREPTOW, 1999). In *example 1*, we have calculated that  $K^0 = 771.35$  ( $p^0 = 1 \text{ bar}$ ); but, if  $p^0 = 1 \text{ atm}$  (as it used to be), then  $K^0 = 781.57$ . Thus, it used to be that  $K_p = K^0 (\text{atm})^{\Delta\nu}$ . This fact may be one of the sources of some of the textbooks' erroneous assumptions summarised in table 1.

The change in standard-state pressure does not affect the value of  $K_p$  (ANTONIK, 1993). The value of  $K_p$  depends on the units of pressure chosen. Moreover, experimental values of  $K_p$  may differ slightly from the ones outlined using thermodynamic data (TYKODY, 1986).

Finally, notice that if we refer our calculation to the current standard pressure ( $p^0 = 1 \text{ bar}$ ), the value of  $K^0$  differs from that of  $K_p$  when its units are not bar. That is, the equation  $\Delta_r G^0 = -RT \ln K^0$  enables one to find the numerically correct value of  $K_p$ , when  $p_i$  is measured in bar:  $K_p = K^0 (\text{bar})^{\Delta\nu}$ . Conversely, if it is not that case, we find that, as far as numerical values are concerned,  $K_p \neq K^0$ .

## CONCLUSIONS

Although there is only one thermodynamically correct definition of the equilibrium constant ( $K^0$ ), practical equilibrium constants ( $K_p$  and  $K_c$ ) are useful at first-year level. Usually, general chemistry textbooks introduce  $K_p$  and  $K_c$ , and, later, in the thermodynamics section, they eventually present the thermodynamic equilibrium constant, which is calculated taking into account its relationship with  $\Delta_r G^0$ . But, we have found that in many textbooks what comes out of the  $\Delta_r G^0$  calculation is  $K_p$  (that is,  $\Delta_r G^0 = -RT \ln K_p$ ). This confusion perhaps explains why in some general chemistry textbooks it is stated that  $K_p$  is a dimensionless quantity. Moreover, as  $K_p$  is usually measured in  $(\text{atm})^{\Delta\nu}$  units, and since  $p^0 = 1 \text{ bar}$ , it can be easily realised that, as far as numerical values are concerned,  $K^0 \neq K_p$ . Thus, in order to avoid those confusions it would be useful to follow the IUPAC recommendations (MILLS, 1989; MILLS *et al.*, 1993).

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