AVOIDING GENERAL CHEMISTRY TEXTBOOKS' MISREPRESENTATIONS OF CHEMICAL EQUILIBRIUM CONSTANTS

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ABSTRACT

This paper summarizes the misrepresentation of the the equilibrium constants in general chemistry textbooks. It is reported that there is a terminology problem as many authors state that practical equilibrium constants, viz. K_p and $K_{c,}$ are unit-less quantities. Also, in many chemistry textbooks K_p plays the role of the thermodynamic equilibrium constant, K^o. Thus, after reviewing the proper definition of each of the terms analyzed, one problem is presented in order to exemplify the correct treatment of the quantities involved, which may help in the discussion and clarification of the misleading conventions and assumptions reported in this study. *[African Journal of Chemical Education—AJCE 5(2), July 2015]*

INTRODUCTION

The equilibrium constants are fundamental quantities in the treatment of chemical equilibrium reactions. This paper aims to exemplify the correct treatment of these quantities in order to avoid current first-year university chemistry textbooks' misrepresentations.

Equilibrium constants

Discussion concerning the terminology of equilibrium constants has received great attention in different science education journals where contributions of authors from several countries can be found. This issue might seem controversial as in some articles it is stated that the equilibrium constant is dimensionless [1-11], but in others, authors advocate that practical (or experimental) equilibrium constants, viz. K_p and K_c, do have units [12-24]. But as it is discussed below, this debate is essentially a terminological problem and can be easily solved from a sound didactic approach.

Textbook misrepresentations

The above referred arguments may have confused general chemistry textbook authors when dealing with those quantities, as many of them state that practical equilibrium constants, K_p and K_c, are dimensionless and very often do not explicitly distinguish between the thermodynamic constant, K^o, and practical equilibrium constants. Moreover, the different ways in which textbooks give information concerned with this topic embody an array of names for the thermodynamic equilibrium constant (*e.g.*, K, K^o, K_p, K_{eq}, K_{th}). Thus, authors seem to be concerned with an accurate thermodynamic presentation, neglecting the proper introduction of practical equilibrium constants (K_p and K_c). The statements found in first-year university chemistry textbooks do confuse students because they are always required to pay great attention to units elsewhere and must know and differentiate the proper meaning of these basic terms. A qualitative list of general chemistry textbooks' misrepresentations of the equilibrium constants is the following:

1) Some textbooks do not explain why they omit units when reporting the calculation 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.
    - It is frequently stated that units are not given for equilibrium constants because there are more accurate ways of treating these quantities.
    - In a few cases, it is expressed that it is customary to omit the units of the equilibrium constant.
    - It is often usual to refer to activities after defining K_p/K_c, stating that the equilibrium constant has no units because the values used for K_p/K_c are identical to those of partial pressures/concentrations, but dimensionless.
4) There is usually no explicit distinction between both K^o and K_p, and K^o and K_c.
5) The mathematical relationships between both K^o and K_p, and K^o and K_c are normally not given.
6) K^o often means K_p.
7) $\Delta_r G^o = -RT \ln K^o$ is commonly writen as $\Delta G^o = -RT \ln K_p$. In this case, some authors do not report why K_p in this equation must be dimensionless. Moreover, the different ways in which textbooks give the information concerned with this equation embody an array of names for the thermodynamic equilibrium constant (*eg.* K, K^o, K_p, K_{eq}, K_{th}).
8) Some textbooks report the equilibrium constant with units when it is calculated from the equation $K = e^{-\Delta G^o / RT}$.
9) Most of the textbooks still refer to the value 1 atm as the standard state pressure, thus few of them use the current value, p^o = 1 bar.

An initial study on the way equilibrium constants are misrepresented in those textbooks was reported in a previous article [25]. A recent paper has provided a detailed discussion on this topic as it has augmented and updated the initial sample and also has included in its analysis a large sample of Grade-12 chemistry textbooks [26]. First-year chemistry textbooks consisted of 26 well-known textbooks that have gone through several editions, thereby showing their acceptance by chemistry teachers. Moreover, various studies published in science education journals have included those textbooks. It included textbooks whose authors are mainly from USA and Great Britain, covering textbook editions from 1989 to 2011. Grade-12 chemistry textbooks consisted of 35 textbooks edited throughout the last 30 years.

Most of the misrepresentations found in first-year university chemistry textbooks were also present in this pre-university level. Thus, in 60 % of first-year chemistry textbooks K_p and K_c are calculated as unit-less quantities, but in many of the cases analyzed, any explanation is given. Similar results were obtained in the case of Grade-12 chemistry textbooks. Moreover, in 91 % of first-year textbooks K_p was presented as the thermodynamic equilibrium constant. In addition, 96 % of these textbooks still refer to the value 1 atm as the standard state pressure. Similar values concerning those misrepresentations were obtained in the analysis of pre-university textbooks.

As stated above, the main conclusion from those two previous studies [25, 26] was that the quantities K^{o} and K_p are confused or represented by the same symbol. Thus, the aim of this article is to both differentiate these quantities and establish their relationships. This analysis will be mainly focused on their units.

Gas-phase equilibrium

As there is a great confusion in the terminology used by textbooks, it is necessary to review briefly the definition for each term.

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

$$\mathrm{a\,A(g) + b\,B(g) \rightleftharpoons r\,R(g) + s\,S(g)} \qquad (1)$$

K_p is defined as an experimental quantity as follows

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

where p_i is the partial pressure of each of the gases involved. They are usually measured in atm. Still, a few textbooks have recently changed this case reporting partial pressures of gases in bar [25, 26].

Similarly, K_c is defined as follows

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

where the concentrations are usually measured in mol L^{-1}.

That is, it seems that the units of K_p must be $(\mathrm{atm})^{\Delta n(\mathrm{g})}$, whereas those of K_c must be $(\mathrm{mol\ L^{-1}})^{\Delta n(\mathrm{g})}$, where, $\Delta n(\mathrm{g}) = (\mathrm{r} + \mathrm{s}) - (\mathrm{a} + \mathrm{b})$. Indeed, the IUPAC [27] allows the use of K_p and K_c having units. As it has been stated before, it was found [25, 26] that 40% of first-year university chemistry textbooks agreed with those conventions. Consequently, many authors treated both K_p and K_c as dimensionless quantities (60 %). Thus, students may get surprised when a great number of authors leave units when reporting the calculation of experimental equilibrium constants. For example, in some textbooks (27%), authors simply omit units in the calculation of K_p/K_c, without explaining why they do this.

In other cases, the explanations provided in some textbooks really may amaze students. For example, three textbook authors [28-30] just claimed that the units of the equilibrium constant can always be figured out from the equilibrium constant expression. In addition, some authors [31-33] stated that it is customary to omit units in expressing the equilibrium constant as there is a more rigorous thermodynamic foundation for the equilibrium constant. Thus, they explained that each partial pressure/concentration in an equilibrium constant expression has been divided by the standard value of pressure/concentration (1 atm for gases, 1 mol L^{-1} for solutes) to make K_p/K_c dimensionless.

Indeed, the IUPAC [27] defines a third equilibrium contant term: the thermodynamic constant, K^o, which is dimensionless. The thermodynamic equilibrium constant is defined as follows (ideal behaviour)

$$K^o = \frac{\left(\frac{p(R)_{eq}}{p^o}\right)^r \left(\frac{p(S)_{eq}}{p^o}\right)^s}{\left(\frac{p(A)_{eq}}{p^o}\right)^a \left(\frac{p(B)_{eq}}{p^o}\right)^b} \qquad (4)$$

Knowing the value of one of these three constants, it is easy to find out the corresponding values of the other two. Then, we are able to state the following relationship

$$K_p = K^o (p^o)^{\Delta n(g)} \qquad (5)$$

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

Other relationships are

$$K_p = K_c (RT)^{\Delta n(g)} \qquad (6)$$

$$K^o = K_c \left(\frac{RT}{p^o}\right)^{\Delta n(g)} \qquad (7)$$

The reader is reminded that the above equations are only valid for homogeneous gas-phase reactions where K^o contains dimensionless ratios of pressure/standard pressure for gaseous species. Rather, the thermodynamic equilibrium constant contains dimensionless ratios of concentration/standard concentration for aqueous species (as it will be examined in a subsequent section). Those mathematical relationships may help students in the differentiation between the practical equilibrium constants and the thermodynamic constant. However, the aforementioned recent study [26] has reported that equations (5) and (7) are usually not discussed in first-year chemistry textbooks.

A glossary of chemical equilibrium constants is given in Table 1.

Table 1. *Glossary of equilibrium constant terms for a given chemical equilibrium represented as:* a A(g) + b B(g) $\rightleftharpoons$ r R(g) + s S(g).

Practical equilibrium constants, K_p and K_c:

$$K_p = \left(\frac{\mathrm{p}_\mathrm{R}^\mathrm{r} \mathrm{p}_\mathrm{S}^\mathrm{s}}{\mathrm{p}_\mathrm{A}^\mathrm{a} \mathrm{p}_\mathrm{B}^\mathrm{b}} \right)_\mathrm{eq}$$; its units are (unit of pressure)$^{\Delta n(\mathrm{g})}$

$$K_c = \left(\frac{[\mathrm{R}]^\mathrm{r} [\mathrm{S}]^\mathrm{s}}{[\mathrm{A}]^\mathrm{a} [\mathrm{B}]^\mathrm{b}} \right)_{eq}$$; its units are (unit of concentration)$^{\Delta n(\mathrm{g})}$

Thermodynamic equilibrium constant, K^o (unitless quantity):

$$K^\mathrm{o} = \frac{\left(\frac{\mathrm{p(R)}_\mathrm{eq}}{\mathrm{p^o}} \right)^\mathrm{r} \left(\frac{\mathrm{p(S)}_\mathrm{eq}}{\mathrm{p^o}} \right)^\mathrm{s}}{\left(\frac{\mathrm{p(A)}_\mathrm{eq}}{\mathrm{p^o}} \right)^\mathrm{a} \left(\frac{\mathrm{p(B)}_\mathrm{eq}}{\mathrm{p^o}} \right)^\mathrm{b}}$$; $\mathrm{p^o}$ = 1 bar

Mathematical equation relating K_p and K^o :

$$K_p = K^\mathrm{o} (p^\mathrm{o})^{\Delta n(g)}$$

In *Example 1* we outline the calculation of K^o, K_p and K_c corresponding to a gas-phase equilibrium at a given temperature. In this problem, we calculate the equilibrium constant, K^o, with the help of the following equation

$$\Delta_r G^\mathrm{o} = -RT \ln K^\mathrm{o} \tag{8}$$

where $\Delta_r G^o$ is the standard free energy of reaction [34]. Equation (8) can be written for our purpose as follows

$$K^0 = e^{-\Delta_r G^\mathrm{o}/RT} \tag{9}$$

It must be stressed that K^o is dimensionless. However, two university textbooks[35,36] presented the equilibrium constant with units when it was calculated from the above equation. This finding was also reported concerning some current Grade-12 chemistry textbooks [26]. Other related misrepresentations arise when some authors assume that $K^o = K_p$ [25, 26], and thus they write equation (8) as follows

$$\Delta G^o = -RT \ln K_p \qquad (10)$$

Specifically, 80% of first-year chemistry textbooks presented the above equation and among those Grade-12 chemistry textbooks that treated this topic, in 80% of them equation (10) was also introduced. But it must be emphasized that equation (10) embodies two terminological misrepresentations: i) it is assumed that K_p plays the role of K^o; ii) ΔG^o is stated instead of $\Delta_r G^o$. This last confusion has been reported in two recent articles [34-37]. However, although one of these last papers [37] correctly states that in equation (10) the units on ΔG^o are not the same as the units on RT because ΔG^o is an extensive quantity with units of energy, whereas RT is intensive with units of energy mol^{-1}, it still commits the first aforementioned terminological misrepresentation keeping K_p, instead of using K^o. This case exemplifies how deep the confusion on the equilibrium constant terminology is rooted as not only does it broadly appear in first-year chemistry textbooks, but also it is present in an educational article dealing specifically with the incorrrect use and units of thermodynamic related quantities.

Note that K^o is dimensionless, but K_p has the dimensions of pressure raised to the power of Δn(g). In *Example 1* we have reported one value for K^o (p^o = 1 bar), but three different values for K_p, depending on the units of pressure used. The value of K_p equals that of K^o only when the partial pressures are reported in bar units. That is, $K^o = 771$ (p^o = 1 bar) and $K_p = 771$ bar^{-1}; $K_p = 781$ atm^{-1}; $K_p = 7.71 \times 10^{-3}$ Pa^{-1}. At this point it is worthily to note that before 1982 it used to be that p^o = 1 atm, and thus both values of K^o and K_p were the same when partial pressures were measured in atm units (in our example, K^o = 781 before 1982, and thus the value of K_p was equal to that of K^o when the units of pressure were atm; that is, it used to be that $K_p = K^o\ (\mathrm{atm})^{\Delta n(\mathrm{g})}$). That year, the IUPAC Commission on Thermodynamics recommended use of 1 bar, rather than the traditional 1 atm, as the standard-state pressure for tabulating themodynamic data [38].The effect of this modification had a slight variation in the values of thermodynamic equilibrium constants, K^o [5, 24, 39]. This change did not affect the values of K_p as they depend on the units of pressure used [21], as it has been exemplified in *Example 1*.

While these last two statements are true, it is also true that equilibrium calculations are almost never more accurate than about 5% because of deviations from ideal behavior, so the difference in the values of K_p is not important in practical terms when the units are atm instead of bar. However, this is not the case when other pressure units are used as Pa. Finally, in *Example 1* we have also reported the value of K_c. It should be noted that this quantity has the dimensions of concentration raised to the power of $\Delta n(\mathrm{g})$.

Example 1

Calculate K^o, K_p and K_c at 298.15 K for the ammonia synthesis equilibrium:

$$\tfrac{1}{2}\,N_2(g) + 3/2\,H_2(g) \rightleftharpoons NH_3(g)$$

Thermodynamic data at 298.15 K (p^o = 1 bar): $\Delta_f H^0[NH_3(g)] = -46.1$kJ/mol;

$S^o[N_2(g)] = 191.6$ J K^{-1}mol^{-1}; $S^o[H_2(g)] = 130.7$ J K^{-1}mol^{-1}; $S^o[NH_3(g)] = 192.5$ J K^{-1}mol^{-1};

SOLUTION

K^o can be calculated using the following equation $K^0 = e^{-\Delta_r G^o/RT}$. So, the value of $\Delta_r G^o$ is needed. It can be obtained from the equation $\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$.

$$\Delta_r H^0 = -46.1\text{kJ mol}^{-1}$$

$$\Delta_r S^0 = S^o[NH_3(g)] - \frac{1}{2}S^o[N_2(g)] - \frac{3}{2}S^o[H_2(g)] = -99.4 \text{ J K}^{-1}\text{mol}^{-1}$$

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0 = -16.5 \text{ kJ mol}^{-1};$$

$$K^0 = e^{-\Delta_r G^o/RT} = 771.$$

K_p and K_c are calculated as follows,

$K_p = K^o(p^o)^{\Delta n(g)} = 771$ bar^{-1}; as 1 atm = 1.01325 bar, it should be noticed that K_p = 781 atm^{-1}; also, as 1 bar = 10^5 Pa, K_p = 7.71 × 10^{-3} Pa^{-1}.

$$K_c = \frac{K_p}{(RT)^{\Delta n(g)}} = \frac{(781\ atm^{-1})}{(0.08206\ atm\ L\ mol^{-1}K^{-1} \times 298.15\ K)^{-1}} = 1.91\times10^4\,(\text{mol/L})^{-1}$$

Summary:

K^o (p^o = 1 bar)	K_p			K_c
771	771 bar^{-1}	781 atm^{-1}	7.71×10^{-3} Pa^{-1}	1.91×10^4 (mol/L)$^{-1}$

Hence, we must remark that only when the values of pressure are measured in bar does $K_p = K^o\,(\text{bar})^{\Delta n(g)}$. Conversely, if it is not that case, we find that, as far as numerical values are concerned, $K_p \neq K^o$. That is, the thermodynamic equilibrium constant has only one value (of course, the standard state must be stated as each standard state has its corresponding thermodynamic equilibrium constant value; in our example, p^o = 1 bar, which corresponds to the IUPAC recommendation), but K_p has many, depending in each case on the pressure units used to measure the partial pressures of the species involved in the gaseous mixture. These facts are usually not examined in general chemistry textbooks [26].

Aqueous equilibrium solutions

Although this paper deals mainly with equilibria involving gaseous mixtures, it may be necessary to make a brief discussion on aqueous equilibrium solutions. In these cases the thermodynamic equilibrium constant is defined analogously, but now the standard-state of an aqueous substance may be either $c^o = 1$ mol L^{-1} or $c^o = 1$ mol kg^{-1} [27]. For example, in a weak acid solution, HA(aq),

$$HA(aq) + H_2O(l) \rightleftarrows A^- (aq) + H_3O^+(aq) \qquad (11)$$

the thermodynamic equilibrium constant is as follows

$$K^o = \frac{\left(\frac{[A^-]_{eq}}{c^0}\right)\left(\frac{[H_3O^+]_{eq}}{c^0}\right)}{\left(\frac{[HA]_{eq}}{c^0}\right)} \qquad (12)$$

Once again, K^o is a dimensionless quantity, and its value depends on the standard state used. Thus, in aqueous equilibria the standard state must be given when the value of the equilibrium constant is reported.

For equation (11) K_c is expressed as

$$K_c = \frac{[A^-]_{eq}[H_3O^+]_{eq}}{[HA]_{eq}} \qquad (13)$$

and its value must be reported using concentration units. Notice that in aqueous solutions K^o and K_c are different quantities although they may have the same values. In our example, $K_c = K^o c^o$. That is, the values of K^o and K_c are the same when there is coincidence in the units of both the concentrations of the substances involved and the concentration standard-state used.

Thus, if $c^o = 1$ mol L^{-1} and the values of concentration, c_i, are expressed in mol L^{-1} units, the values of K_c and K^o are the same. But, if there is not such coincidence in the concentration units, then those quantities have different values. For example, at 25 ºC, if we use $c^o = 1$ mol L^{-1}, we have for the acetic acid: $K_c = 1{,}751 \times 10^{-5}$ mol L^{-1} and $K^o = 1{,}751 \times 10^{-5}$, but if the units of concentration used are mol kg^{-1}, then $K_c = 1{,}756 \times 10^{-5}$ mol kg^{-1} [13]. Similarly, when $c^o = 1$ mol kg^{-1}, the values of K_c and K^o are the same if the values of c_i are expressed in mol kg^{-1} units. This discussion may help to avoid current misrepresentations as in aqueous equilibrium solutions it is normally assumed that K_c plays the role of K^o [26]. Once again (analogously to the case of gas-phase equilibrium reactions), this confusion is also present in a recent article [37] dealing with the correct use and units of related quantities, which reinforces the view that terminological misrepresentations of the equilibrium constants are firmly anchored in current educational approaches associated to this topic.

CONCLUSIONS

When reporting the value of the thermodynamic equilibrium constant, K^o, the standard state must be specified. For gaseous reactions the IUPAC recommends $p^o = 1$ bar; in addition, for aqueous solution reactions $c^o = 1$ mol L^{-1} or $c^o = 1$ mol kg^{-1}. For each standard state there is only one value of K^o. Conversely, K_p and K_c have many values depending on the units of pressure/concentration chosen. That is, K^o is a unitless quantity; on the contrary, K_p has units of pressure (*eg*. bar, atm, Pa, etc.) and K_c has units of concentration (*eg*. mol L^{-1}, mol kg^{-1}).

Many first-year university chemistry textbooks assume that $K^o = K_p$ (and also $K^o = K_c$) and confusion on units is also widespread. These misrepresetations are also broadly present in pre-university chemistry textbooks.

The analysis of the example outlined in this article has helped in discussing the differentiation of practical equilibrium constants (ie. K_p and K_c) and the thermodynamic constant,

K^o. Thus, the treatment performed in this study may be useful for both textbook authors and their users (ie. general chemistry teachers and students) in order to avoid current misrepresentations [25, 26]. That is, this examination may help textbook authors when dealing with the proper definition of both the practical equilibrium constants and the thermodynamic equilibrium contant as well as when both performing their calculation and reporting their relationships. Still, given the discussion of the confusion among K^o, K_p, and K_c, some teachers would argue to define K^o only, which might pose a challenging didactic issue. As this suggestion might seem appropriate, for it would give rise to less confusion, since then K^o would be the only relevant parameter, it would need the use of activities of reactant and product species. However, we could presume this concept too difficult as it is both unnecessary and undesirable for an introductory course. Hence, the introduction of concepts such as activities would mean to advance what has traditionally been carefully treated in later years of the undergraduate curriculum and thus to add needless strains to beginners. This argument does also apply to pre-university chemistry textbooks as it seems neither essential nor beneficial to introduce the thermodynamic equilibrium constant at this level. Still, practical equilibrium constants should be defined properly and reported with the corresponding units.

Hence, similar problems to the example discussed in this study can be presented to students when dealing with equilibrium constants in first-year chemistry courses. This examination allows to apply the different equations provided in table 1, which may help in avoiding current terminological misrepresentations. That is, authors must always warn their readers that focusing on reporting quantities with the correct units is a basic activity that should not be overlooked. In addition, each term should be properly defined, allowing students to establish the mathematical relationships among them.

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