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K_P DOES NOT PLAY THE ROLE OF THE THERMODYNAMIC EQUILIBRIUM CONSTANT, K^0: A DISCUSSED EXAMPLE ON GENERAL CHEMISTRY TEXTBOOKS' MISREPRESENTATIONS

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Abstract. Equilibrium constants are important quantities when dealing with chemical equilibrium. Many first-year chemistry textbook authors do not define these terms accurately and confusion arises when reporting them. On this regard, this research discusses a common erroneous treatment performed on the teaching equilibrium constants as many textbook authors assume that the practical equilibrium constant K_p plays the role of the thermodynamic equilibrium constant, K^o. Thus, many authors also state that K_p is a unitless quantity. Hence, after documenting a particular case that exemplifies some widespread terminological misrepresentations related to the handling of the equilibrium constants, which prompts to reviewing the proper definition of each of the terms analysed, one example is presented in order to illustrate the correct treatment of the quantities involved. This analysis may help in the discussion and clarification of the misleading conventions and assumptions reported in this study.

Keywords: equilibrium, misrepresentations, textbooks, thermodynamics

Introduction

Several research articles have discussed chemistry textbook misrepresentations of chemical concepts. We can find studies dealing with misleading presentations concerning electrochemistry (Sanger & Greenbowe, 1999), acid and base theories (Furió-Mas et al., 2005), chemical kinetics (Justi & Gilbert, 1999, chemical bonding (Bergqvist et al., 2013), Lewis structures (Suidan et al., 1995), atomic models (Niaz & Cardellini, 2011) or the amount of substance concept (Pekdag & Azizoglu, 2013). Particular examples can also be found in the field of thermodynamics. Cases that exemplify situations where textbooks confuse thermodynamic terms correspond to articles concerning entropy (Weber, 1996) and Gibbs energy (Quílez, 2012). A recent paper (Raff, 2014) both reviews the fundamental concepts and equations that determine spontaneity and equilibrium and discusses common teaching errors concerning those topics.

Purpose

The aim of this study is to perform a clear differentiation on two related quantities, the thermodynamic equilibrium constant, K^o, and the experimental equilibrium constant referred to partial pressures, K_p. 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 given reaction.

The aforementioned paper (Raff, 2014) has been chosen in the discussion that follows. In order to carry out its examination, the simple gas-phase reaction $2NO_2(g) \rightarrow N_2O_4(g)$ is used as an example. This case is reexamined in the ensuing discussion concerning equilibrium constants, as it allows the illustration of some current textbook misrepresentations concerning the terminology they usually use to denote these quantities as well as how they report their units.

Equilibrium constants' misrepresentations

Several research articles (Quílez, 2008; Quílez-Díaz & Quílez-Pardo, 2014) reviewed the controversial issues concerning the terminological problems arising when naming and calculating the equilibrium constants and also analysed how general chemistry textbooks dealt with these quantities. They reported that many first-year chemistry textbooks: (a) state that K_c and K_p are dimensionless quantities and thus report these quantities without units; (b) assume that K_p means the thermodynamic equilibrium constant, K^o; (c) make calculations using the following equation $\Delta G^o = -RT \ln K_p$, instead of $\Delta_r G^o = -RT \ln K^o$; (d) do not make explicit reference to the current pressure standard-state, $p^o = 1$ bar.

Discussion of a case exemplifying textbook equilibrium constants' misrepresentations

The aforementioned incorrect presentations are going to be analysed discussing the equilibrium constant terminology employed in a recent article (Raff, 2014). Although its presentation is accurate in discerning the different meanings and units of the main quantities involved and particularly its rather singular derivation of the thermodynamic equilibrium constant is formally correct, there is a terminological problem as its author assumes that K_p plays the role of K^o. Equations 18 and 19 of that paper are the following

$$dA = \frac{dn_C}{c}\left[\Delta\mu^0 + RT\ln\{\frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b}\}\right] \tag{1}$$

$$\Delta\mu^0 = -RT\ln\{\frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b}\}_{eq} = -RT\ln K_p \tag{2}$$

Later on, equation 18 (Eq (2) in this paper) is modified as equation 39 (Eq (3) in this paper)

$$\text{chemical force} = \text{- (slope of the thermodynamic potential, } G \text{ or } A) = \\ = -RT[\ln Q - \ln K_p] \quad (3)$$

where Q is defined as the usual ratio of partial pressures at a given point at which we wish to predict spontaneity or equilibrium. That is,

$$Q = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} \quad (4)$$

and thus, according to this treatment, the thermodynamic equilibrium constant is defined as follows

$$K_p = \left\{ \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} \right\}_{eq} \quad (5)$$

Hence, both Q and K_p seem to have units of pressure, although in the referred paper its author notes that each p_{i} appearing in the corresponding equations is the magnitude only. Thus, in agreement with this assertion, both Q and K_p must be unitless quantities. This last statement is rather confusing for anyone that is presented to Eqs (4) and (5), such as they are, as it holds a misleading terminological problem when defining the thermodynamic equilibrium constant. Consequently, Eqs (1) and (2) may lead to incorrect assumptions because they hide the fact that the argument of the logarithm in both cases is dimensionless. As logarithmic quantities are unitless (Boggs, 1958; Mills, 1995), the definition of the thermodynamic equilibrium constant cannot be equation 5. Thus, in order to explicitly make dimensionless the thermodymanic equilibrium constant, K^o (instead of K_p), Eqs (1) and (2) must accurately be rewritten intoducing the standard pressure on them (Borge, 2015). Their corresponding expressions are

$$dA = \frac{dn_C}{c}\left[\Delta\mu^0 + RT\ln\{\frac{(p_C/p^{\mathrm{o}})^c (p_D/p^{\mathrm{o}})^d}{(p_A/p^{\mathrm{o}})^a (p_B/p^{\mathrm{o}})^b}\}\right] \quad (6)$$

$$\Delta\mu^0 = -RT\ln\{\frac{(p_C/p^{\mathrm{o}})^c (p_D/p^{\mathrm{o}})^d}{(p_A/p^{\mathrm{o}})^a (p_B/p^{\mathrm{o}})^b}\}_{eq} = -RT\ln K^{\mathrm{o}} \quad (7)$$

where $p^o = 1$ bar is the standard pressure.

Eq (7) can also be written as follows (Quílez, 2012; Borge, 2015)

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

Notice that we have written K^o, instead of K_p, in Eqs (7) and (8) to denote the thermodynamic equilibrium constant.

In the aforementioned article (Raff, 2014) it is explicitly assumed that K_p is the thermodynamic equilibrium constant. That is, the thermodynamic equilibrium constant, K^{o}, and K_p are confused or represented by the same symbol. This misleading assumption may derive from a careless neglect of the units in Eqs (6) and (7) as $p^o = 1$ bar and then the p^o values may be considered unnecessary and thus the denominators are omitted, which certainly may confuse our students as they may find (and use) mathematical expressions containing logarithms of quantities with units.

A quite similar treatment to the case examined above can be found in an advanced chemistry textbook (Raff, 2001). Fortunately, this confusing approach is not present in some other well-known physical chemistry textbooks (Vemulapalli, 1993; McQuarrie & Simon, 1997; Chang, 2000; Mortimer, 2000; Levine, 2009; Engel & Reid, 2012; Silbey et al., 2005; Atkins & de Paula, 2010), although in many of them the thermodynamic equilibrium constant is named using the K symbol keeping the subscript p on it (Vemulapalli, 1993; McQuarrie & Simon, 1997; Chang, 2000; Mortimer, 2000; Levine, 2009; Engel & Reid, 2012), which may not help to overcome the confusion between these two different quantities, K^o and K_p.

In order to clarify the terminology concerning the equilibrium constants and thus to avoid both the discussed misrepresentation and the related erroneous assumptions stated in many first-year chemisty textbooks, it is essential that the different quantities be named differently. That is, the thermodynamic equilibrium constant, K^o, as well as the practical (or experimental) equilibrium constants, ie., K_p and K_c, should accurately be defined, mathematically related to each other and calculated (Quílez-Díaz & Quílez-Pardo, 2015). Eventually, this presentation may properly allow that students be able to establish their different meanings, values and units.

Practical or experimental 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

$$\mathrm{a\,A(g) + b\,B(g) \rightleftharpoons r\,R(g) + s\,S(g)} \tag{9}$$

K_p is defined as an experimental quantity as follows

$$K_p = \left[\frac{(p_R)^r (p_S)^s}{(p_A)^a (p_B)^b}\right]_{\mathrm{eq}} \tag{10}$$

where p_i is the partial pressure of each of the gases involved. They have been traditionally measured in atm (Quílez-Díaz & Quílez-Pardo, 2014).

Similarly, K_c is defined as follows

$$K_c = \left(\frac{[\mathrm{R}]^r [\mathrm{S}]^s}{[\mathrm{A}]^\mathrm{a} [\mathrm{B}]^\mathrm{b}} \right)_\mathrm{eq} \tag{11}$$

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

That is, it seems that the units of K_p must be $(\mathrm{atm})^{\Delta n(\mathrm{g})}$ (or $(\mathrm{bar})^{\Delta n(\mathrm{g})}$), whereas those of K_c must be $(\mathrm{mol\ L^{-1}})^{\Delta n(\mathrm{g})}$, where $\Delta n(\mathrm{g})$ is the change in the amount of gases, $\Delta n(\mathrm{g}) = (\mathrm{r} + \mathrm{s}) - (\mathrm{a} + \mathrm{b})$. Indeed, the IUPAC (Mills et al., 1993) allows the use of K_p and K_c having units. However, many general chemistry authors treat these quantities as dimensionless.

The IUPAC (Mills et al., 1993) defines a third equilibrium constant term: the thermodynamic constant, K^o. This quantity is defined as follows (ideal behaviour of the gaseous mixture)

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

It must be stressed that K^o is a dimensionless quantity and is a function of temperature only.

Thus, we have defined three different equilibrium constants: K^o is unitless, but K_p has the dimensions of pressure raised to the power of $\Delta n(\mathrm{g})$ and, analogously, K_c has the dimensions of concentration raised to the power of $\Delta n(\mathrm{g})$.

Knowing the value of one of these three constants (of course, the value of the fixed temperature must be specified), it is easy to find out the corresponding values of the other two. Then, we are able to state the following relationship

$$K_p = K^\mathrm{o} (p^\mathrm{o})^{\Delta n(g)} \tag{13}$$

As $p^\mathrm{o} = 1$ bar, if the units of K_p are $(\mathrm{bar})^{\Delta n(\mathrm{g})}$, its value equals that of K^o. Maybe, as in this case both values are the same, many authors might have assumed that K_p plays the role of the thermodynamic equilibrium constant, K^o. It must be stressed that although K^o and K_p yield the same value, it does not mean that there is only one quantity, which first-year chemistry textbooks usually name K_p. In this case, two identical calculated values correspond to two different quantities. K^o is a unitless quantity and in this circumstance K_p has the dimensions of bar raised to the power of $\Delta n(\mathrm{g})$. But, if $(\mathrm{atm})^{\Delta n(\mathrm{g})}$ are the units of K_p, then the values of both constants are different. These facts are usually not mentioned in general chemistry textbooks as equation 13 is normally absent and thus not discussed in those books (Quilez-Díaz & Quílez-Pardo, 2014).

A common relationship between K_p and K_c, usually presented in introductory chemistry textbooks, is the following

$$K_p = K_c (RT)^{\Delta n(g)} \tag{14}$$

Practical examples discussing Eqs (13) and (14) may help students in the differentiation between both the practical equilibrium constants, K_p and K_c, and the thermodynamic constant, K^o, which also may allow them to perform a sound treatment concerning their units. This analysis is exemplified for the following equilibrium system

$$2\ \mathrm{NO_2(g)} \rightleftharpoons \mathrm{N_2O_4(g)}$$

where $\Delta_f G^o[\mathrm{N_2O_4(g)}]$ = 97,786.7 J mol^{-1}; $\Delta_f G^o[\mathrm{NO_2(g)}]$ = 51,257.7 J mol^{-1}. Thus, $\Delta_r G^o$ = (97,786.7 J mol^{-1}) – 2(51,257.7 J mol^{-1}) = - 4,728.7 J mol^{-1}. Then, $K^o = \exp[-\Delta_r G^o/RT]$ = 6.7364; T = 298.15 K.

Assuming that p^o=1 bar, and as Δn(g)=-1, the value of K_p can be easily calculated, $K_p = K^o(p^o)^{-1}$=6.7364 bar^{-1}. Moreover, as 1 atm=1.01325 bar, K_p=6.8257 atm^{-1}. Also, as 1 bar = 10^5 Pa, K_p= 6.7364 × 10^{-5} Pa^{-1}. Finally, $K_c = K_p(RT)$ = 166.99 (mol L^{-1})$^{-1}$.

Summary,

$2\ \mathrm{NO_2(g)} \rightleftharpoons \mathrm{N_2O_4(g)}$; T = 298.15 K				
K° (p° = 1 bar)	K_p			K_c
6.7364	6.7364 bar^{-1}	6.8257 atm^{-1}	6.7364 x 10-5 Pa^{-1}	166.99 (mol L^{-1})$^{-1}$

Thus, we have calculated one value for K^o (p^o = 1 bar), but three different values for K_p, depending on the units of pressure used. Fig. 1 provides a general relationship between K^o and K_p concerning units.

$$K^o = \exp[-\Delta_r G^o/RT] \text{ (unitless)}$$

$$K_p = K^o (\mathrm{bar})^{\Delta n(\mathrm{g})} = K^o \left(\frac{1}{1.01325}\mathrm{atm}\right)^{\Delta n(\mathrm{g})} = K^o (10^5\ \mathrm{Pa})^{\Delta n(\mathrm{g})}$$

$$(p^o = 1 \text{ bar}; T)$$

Fig. 1. General relationship between K^o and K_p concerning units

The value of K_p equals that of K^o only when the partial pressures are reported in bar units. Hence, we must remark that only when the values of pressure are measured in bar does $K_p = K^o (\mathrm{bar})^{\Delta n(\mathrm{g})}$. 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, K^o, has only one value (of course, both the fixed temperature and the standard state must be stated as K^o varies with the temperature and each standard state has its corresponding thermodynamic equilibrium constant value; in our example, $T = 298.15$ K and $p^o = 1$ 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.

At this point it is worth noting 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. That year, the IUPAC Comission on Thermodynamics recommended use of 1 bar, rather than the traditional 1 atm, as the standard-state pressure for tabulating themodynamic data (Cox, 1982). The effect of this modification had a slight variation in the values of thermodynamic equilibrium constants, K^o (Freeman, 1985; Treptow, 1999). In our example, before 1982, it used to be $K^o = 6.8257$ ($p^o = 1$ atm; $T = 298.15$ K). But this change did not affect the values of K_p as they depend on the units of pressure used, as has been exemplified in the above example. Nevertheless, 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.

Still, assuming $p^o = 1$ bar and K_p measured in $(\text{bar})^{\Delta n(\text{g})}$ units, the numerical values of K^o and K_p are equal only when K_p is calculated utilizing the value of K^o, which involves to use Eqs (8) and (13), as has been performed in the previuos example. But if K_p is calculated using Eq (10), which means to determine the corresponding values of partial pressures in bar, then a different value is obtained (Tykodi, 1986). This case can be exemplified employing the equilibrium values (T=298.15 K) reported on the article that it is being analysed, $p(NO_2)_{eq} = 0.34987$ bar; $p(N_2O_4)_{eq} = 0.82507$ bar. Thus, we find that $K_p = (0.82507 \text{ bar}/(0.34987 \text{ bar})^2) = 6.7403 \text{ bar}^{-1}$ (similar K_p values can be found elsewhere (Yu & Gao, 1997); also, units must be reported, contrarily to the case of many general chemistry textbooks and the particular situation that is being discussed in this paper (Raff, 2014), as they report K_p as a unitless quantity). Eventually, one should notice that this method of calculation of K_p does not produce a value that equals that of the thermodynamic equilibrium constant ($K^o = 6.7364$), contradicting what is stated on the article examined. That is, equation 10 does not yield the value corresponding to the thermodynamic equilibrium constant. Those different values are due to deviations from the ideal behavior of the gases involved.

Summarizing ($T = 298.15$ K), Eq (10) produces $K_p = 6.7403 \text{ bar}^{-1}$.

Equation $K^o = \exp[-\Delta_r G^o/RT]$ and Eq (13) yield $K_p = 6.7364 \text{ bar}^{-1}$.

In Table 1 are summarised all the equilibrium constant definitions and their corresponding values calculated for the equilibrium 2 NO_2(g) $\rightleftharpoons$ N_2O_4 (g); T = 298.15 K.

Table 1. Equilibrium constant equations and their corresponding values for the equilibrium

2 NO_2(g) $\rightleftharpoons$ N_2O_4 (g); T = 298.15 K.

<table>
<tr><td colspan="5">2 NO_2(g) $\rightleftharpoons$ N_2O_4 (g); T = 298.15 K</td></tr>
<tr><td>K^o = exp[-DrG^o/RT] (p^o = 1 bar)</td><td colspan="3">$K_p = K^o(p^o)^{-1}$ (1)
$K_p = \left[\frac{p(N_2O_4)}{p(NO_2)^2}\right]_{eq}$ (2)</td><td>$K_c = K_p(RT)$</td></tr>
<tr><td>6.7364</td><td>(1) 6.7364 bar-^{1}
(2) 6.7403 bar-^{1}</td><td>(1) 6.8257 atm-^{1}</td><td>(1) 6.7364 ´ 10-5 Pa-^{1}</td><td>(1) 166.99 (mol L-1)-^{1}</td></tr>
</table>

Conclusions

The previous discussion has tried to give a clear presentation of the various different equilibrium constants that are used to solve problems in general chemistry textbooks. This treatment may help to overcome some of the current misrepresentations related to this topic.

K_p does not play the role of the themodynamic equilibrium constant, K^o. Indeed, they are different quantities. However, many first-year university chemistry textbooks assume that $K_p = K^o$ (or $K_c = K^o$) and confusion on units is also widespread. The cases discussed in this article exemplify how deep the terminological misrepresentations on the equilibrium constants are rooted as not only do they broadly appear in first-year chemistry textbooks, but also they are present in an educational article (Raff, 2014) dealing specifically with the incorrrect use and units of thermodynamic related quantities. Still, it must be credited that several general chemistry authors may know the difference between K_p and K^o, but their desire to make these concepts easier to their students might have oversimplified their presentations, which would have contributed to the terminological confusions examined in this study.

When reporting the value of the thermodynamic equilibrium constant, K^o, the standard state must be specified. For each standard state there is only one value of K^o. That is, if the standard state is 1 bar, K^o is the thermodynamic equilibrium constant that is calculated using the equation $K^o = \exp[-\Delta_r G^o/RT]$, in which $\Delta_r G^o$ has been obtained from thermodynamic tables with a standard state pressure of 1 bar. Conversely, K_p and K_c have many values depending on the units of partial pressures/concentrations chosen for their calculation. Furthermore, one should know to properly report these quantities. 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}). Nevertheless, the reader must be accounted for the fact that even at a specified temperature, the values of K_p and K_c in a particular unit of measurement are different in different situations, such as systems at equilibrium at different pressures/concentrations due to deviations from ideality in the gases involved.

In order to avoid current misrepresentations, the thermodynamic equilibrium constant, K^o, should be defined as well as the practical equilibrium constants, K_p and K_c, establishing their relationships with the help of selected examples, which may allow students to accurately deal with both their calculation and units. Moreover, one should realize that there are two common first-year ways for calculating K_p and K_c that produce in each case slight differences in the values obtained for the same quantity. If K_p (or K_c) is calculated using the thermodynamic equilibrium constant, K^o, one must not be surprised of the existence of a minor difference compared to the value directly calculated using the equilibrium data of partial pressures or concentrations. But, although quite similar values might be obtained, by no means does this second method (which is usually introduced in introductory chemistry courses) allow to calculate directly the thermodynamic equilibrium constant, assuming that the experimental value obtained corresponds to K^o. Yet, this assumption is present in the paper that has been discussed in this article, which may add more confusion to chemistry textbook authors and eventually to students.

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