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Equilibrium Constant Units Revisited

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Abstract: The problem of the units associated with equilibrium constants is revisited. A brief survey of the arguments for and against using units with equilibrium constants is presented and the compromise solution that we have adopted in our teaching, both at the university and school level, is presented and justified.

Introduction

Some of the most recent general chemistry and A-level type chemistry books used throughout the world assign units to equilibrium constants, whereas others present equilibrium constants as dimensionless quantities. This is a clear sign that there is an unresolved controversy concerning the teaching of chemical equilibrium at the introductory level. There have been numerous articles published on the subject as well (see, e.g., [1–9]). It is also of interest that the IUPAC publication "Quantities, Units and Symbols in Physical Chemistry" [10] has two entries for equilibrium constants.

One, often referred to as a "thermodynamic equilibrium constant," is unitless, and the other, a nonthermodynamic equilibrium constant, has units.

In this paper we will first summarise the opposing arguments and, then, present the compromise solution that we have adopted for our classes both at the school and university level.

Arguments for Equilibrium Constants with Units

1. Equilibrium constants are usually needed before thermodynamics is taught, making use of molarities or partial pressures of gases, well before the more sophisticated concepts of activity and fugacity associated with the consideration of reference states can be introduced. For example, we write

$$K_c = \frac{\left[\mathrm{Cr_2O_7^{2-}}\right]_\mathrm{e}}{\left[\mathrm{CrO_4^{2-}}\right]_\mathrm{e}^2 \left[\mathrm{H_3O^+}\right]_\mathrm{e}^2} = 3\times10^{14}\ \mathrm{mol^{-3}\ dm^9} \qquad (1)$$

for the equilibrium (at 25 °C)

$$2\mathrm{CrO_4^{2-}}(aq) + 2\mathrm{H_3O^+}(aq) \rightleftharpoons \mathrm{Cr_2O_7^{2-}}(aq) + 3\mathrm{H_2O}(l) \qquad (2)$$

instead of

$$K_c = \frac{\dfrac{\left[\mathrm{Cr_2O_7^{2-}}\right]_\mathrm{e}}{1\ \mathrm{mol\ dm^{-3}}}}{\left(\dfrac{\left[\mathrm{CrO_4^{2-}}\right]_\mathrm{e}}{1\ \mathrm{mol\ dm^{-3}}}\right)^2 \left(\dfrac{\left[\mathrm{H_3O^+}\right]_\mathrm{e}}{1\ \mathrm{mol\ dm^{-3}}}\right)^2} = 3\times10^{14} \qquad (3)$$

and

$$K_p = \frac{\left(P_{\mathrm{NH_3}}\right)_\mathrm{e}^2}{\left(P_{\mathrm{N_2}}\right)_\mathrm{e}\left(P_{\mathrm{H_2}}\right)_\mathrm{e}^3} = 6\times10^5\ \mathrm{atm^{-2}} \qquad (4)$$

for

$$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g) \qquad (5)$$

instead of

$$K_p = \frac{\left(\dfrac{\left(P_{\mathrm{NH_3}}\right)_\mathrm{e}}{1\ \mathrm{atm}}\right)^2}{\left(\dfrac{\left(P_{\mathrm{N_2}}\right)_\mathrm{e}}{1\ \mathrm{atm}}\right)\left(\dfrac{\left(P_{\mathrm{H_2}}\right)_\mathrm{e}}{1\ \mathrm{atm}}\right)^3} = 6\times10^5 \qquad (6)$$

It is inconsistent to use molarities or partial pressures in expressions like (1) and (4) but express *K* without units. In fact, this may surely confuse students who have been required to pay great attention to units elsewhere.

2. In general, the units associated with equilibrium constants indirectly reflect the set of stoichiometric coefficients in the chemical equation, for example (at 25 °C)

$$2\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{SO_3}(g) \quad K_p = 4\times10^{24}\,\mathrm{atm^{-1}} \qquad (7)$$

$$\mathrm{SO_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \rightleftharpoons 2\mathrm{SO_3}(g) \quad K_p = 2\times10^{12}\,\mathrm{atm^{-1/2}} \qquad (8)$$

whereas a unitless *K* requires an explicit reference to the equation being considered. Also, the use of units for *K* makes it clear which units are being considered, whereas a unitless *K* requires providing that information or the previous establishment of a convention. For example, the acidity constant of acetic acid at 25 ºC is either 1.751×10^{-5} mol dm^{-3} or 1.756×10^{-5} mol kg^{-1}, depending on whether molarities or molalities are used [2]. The problem becomes more apparent when mixed $K_{c,p}$ values are used, for example

$$\mathrm{Pb}(s) + 2\mathrm{H_3O^+}(aq) \rightleftharpoons \mathrm{Pb^{2+}}(aq) + \mathrm{H_2}(g) + 2\mathrm{H_2O}(l) \qquad (9)$$

$$K_{c,p} = \frac{\left[\mathrm{Pb}^{2+}\right]_\mathrm{e}\left(P_{\mathrm{H}_2}\right)_\mathrm{e}}{\left[\mathrm{H_3O^+}\right]_\mathrm{e}^2} \tag{10}$$

3. The consistency of the relationship between K_c and K_p for a gaseous system (equation 11)

$$K_p = K_c\left(RT\right)^{\Delta n_g} \tag{11}$$

(where Δn_g is the difference between the number of molecules of gaseous products and the number of molecules of gaseous reactants in the stoichiometric equation) requires that the equilibrium constants have units.

4. The rationalization of the form for the expression of equilibrium constants for elementary processes in terms of the microscopic rate constants for the forward ($\vec{k}$) and reverse ($\overleftarrow{k}$) reactions at equilibrium (equation 12), implies units.

$$K = \frac{\overrightarrow{k}}{\overleftarrow{k}} \tag{12}$$

In general, the units of $\vec{k}$ and $\overleftarrow{k}$ do not cancel each other.

5. As a consequence of introducing units for equilibrium constants two approaches are possible regarding unit consistency after the study of thermodynamics (or statistical mechanics).

a) The thermodynamic equilibrium constant K can be taken as the numerical value of K_c or K_p [8]. Then, expressions like

$$\Delta G^\circ = RT \ \ln K \tag{13}$$

are consistent unitwise.

b) Instead of writing (13), one can write for example

$$\Delta G^\circ = RT \ \ln \frac{K_p}{\mathrm{atm}^{\Delta n_g}} \tag{14}$$

for a gaseous equilibrium [2].

Arguments Against Equilibrium Constants with Units

1. Authors and teachers who present equilibrium constants as unitless are consistent with the fundamental thermodynamic (or statistical mechanical) interpretation of chemical equilibrium. From a practical point of view, they avoid an overemphasis on units that is largely not useful later. Instead of considering the thermodynamic equilibrium constant as the numerical part of K_c or K_p, these are defined in terms of the numerical values of concentrations or partial pressures. By using these numerical values a bridge to the topic of activities and fugacities of ideal systems is created.

2. It may also be argued that the process of discovering a quantity common to all equilibrium states for a given reaction) from experimental data is essentially numerical. For instance, for the reaction 15 (provided the temperature is the same), the units are of secondary importance

$$\mathrm{A+B+...} \rightleftharpoons \mathrm{C+D+...} \tag{15}$$

when comparisons like 16–18, below, are made for various equilibrium states.

$$([\mathrm{C}]_\mathrm{e} + [\mathrm{D}]_\mathrm{e} + ...) - ([\mathrm{A}]_\mathrm{e} + [\mathrm{B}]_\mathrm{e} + ...) \tag{16}$$

$$([\mathrm{C}]_\mathrm{e} + [\mathrm{D}]_\mathrm{e} + ...) \,/\, ([\mathrm{A}]_\mathrm{e} + [\mathrm{B}]_\mathrm{e} + ...) \tag{17}$$

$$([\mathrm{C}]_\mathrm{e} \times [\mathrm{D}]_\mathrm{e} \times ...) \,/\, ([\mathrm{A}]_\mathrm{e} \times [\mathrm{B}]_\mathrm{e} \times ...) \tag{18}$$

3. The use of unitless equilibrium constants requires a previous convention to be established: for K_c the values of the concentrations correspond to mol dm^{-3} (molarities) and for K_p the values of the partial pressures are in atm. (However, this would also be necessary for equilibrium constants with units in cases where the sum of the appropriate stoichiometric coefficients is the same for products and reactants.)

4. The relationship between chemical equilibrium and kinetics cannot be used as proof that equilibrium constants do, in general, have units. In fact, the rationalization of the form for the equilibrium constant expression in terms of the microscopic rate constants (for one-step reactions) for the forward and reverse transformations at equilibrium in terms of equation 12 is, in essence, of numerical nature. In any case, the relationship between chemical equilibrium and rates of reactions should be used with care to avoid misconceptions by the student, for example that the kinetic laws (at least at equilibrium) for the forward and reverse transformations of any reaction must reflect the stoichiometric coefficients.

5. The equilibrium constant is considered essentially as a numerical parameter, which, besides being common to the various equilibrium states (for a constant temperature), also appropriately measures the extent to which the composition of an equilibrium state differs from a state where all concentrations or partial pressures are unity (Q = 1). The idea of a numerical parameter is present in the use of pK values for acids and bases and, it is clearly the case for pH, which is defined at an introductory level as the symmetric logarithm of the numerical value of the H_3O^+ concentration.

6. The question of the relationship (11) between K_p and K_c for a gaseous system that requires units for both equilibrium constants deserves more attention. In particular, it should be realized that such a relationship implies two different standard states: 1 atm for K_p, equivalent to about 0.004 mol dm^{-3} at 298 K, and 1 mol dm^{-3} for K_c. If this is considered, then the temperature dependence of K_p and K_c are different when Δn_g is not zero. In fact, it is possible for K_c not to vary at all with temperature or to be lower at higher temperature while K_p increases with T. Should the standard states be the same, then K_p = K_c, even if $\Delta n_g \neq 0$, both constants being necessarily unitless and changing equally with temperature.

A Compromise

By proper consideration of the arguments for and against the use of units with equilibrium constants, we have adopted the following solution to this dilemma. We chose to use unitless values without involving activities/fugacities and without creating the problem of a learning inconsistency regarding unit analysis. We use the numerical values of the molarities or partial pressures (when expressed in atm) and represent them differently from the way we represent concentration or pressure. We use the symbol $|A|_e$, in place of $[A]_e$ (when expressed in mol dm^{-3}), for the numerical value of the concentration of A at equilibrium and we use $|p_B|_e$ for the numerical value of the partial pressure of B at equilibrium (when expressed in atm). For example, for the reaction in equation 2 instead of expressions 1 or 3, we have

$$K_c = \frac{\left|Cr_2O_7^{2-}\right|_e}{\left|CrO_4^{2-}\right|_e^2 \left|H_3O^+\right|_e^2} \qquad (19)$$

The same is done for the expression of the reaction quotient, Q.

For pH calculations for acid-base equilibria, the numerical value $|H_3O^+|_e$ is used directly to obtain the pH:

$$pH = -\log |H_3O^+|_e \qquad (20)$$

In some calculations, however, it may be necessary to add units to the numerical quantity obtained. For example, to express the solubility of AgCl in water, $[Ag^+]_e$, not $|Ag^+|_e$ must be used.

By stressing the fact that for each reaction (at a given temperature) there is a numerical parameter that, to a first approximation, is common to all equilibrium states, we address the central point and prepare the student for future study. There is no need to unlearn anything presented before or to make the initial formulization unduly complicated. In particular, the later need to consider reference states is, in part, introduced by: (1) the implicit consideration of reference states when the numerical values of concentrations or partial pressures are used and (2) by interpreting the extent of reaction in terms of the global change observed when reactants and products have equal opportunities by having unitary concentrations (or partial pressures) ($Q = 1$).

References

1. Cox, G. A.; Dixon, D.; Morris, R.; Roberts, J. P. *Educ. Chem.* **1979**, *16*, 101.
2. Pethybridge, A. D.; Mills, I. M. *Educ. Chem.* **1979**, *16*, 191.
3. Vickerman C. *Educ. Chem.* **1979**, *16*, 191.
4. Wright, P. G. *Educ. Chem.*, **1979**, *16*, 192.
5. Miekey, C. D. *J. Chem. Educ.* **1980**, *57*, 801.
6. Helfferich, F. G *J. Chem. Educ.* **1987**, *64*, 1069.
7. Quintero, G. B. *J. Chem. Educ.* **1987**, *64*, 1069.
8. Laidler, K. J. *J. Chem. Educ.* **1990**, *67*, 88.
9. Gordus, A. A. *J. Chem. Educ.* **1991**, *68*, 138.
10. International Union of Pure and Applied Chemistry. *Quantities, Units and Symbols in Physical Chemistry*; Blackwell Science: Oxford, 1993.

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