The Equilibrium Constant

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- Topic hierarchy

The equilibrium constant, K, expresses the relationship between products and reactants of a reaction at equilibrium with respect to a specific unit. There are two different types of equilibrium reactions: (1) heterogeneous and (2) homogeneous. This article illustrates the difference between the two, explains how to write equilibrium constants for both, and introduces the calculations involved with both the concentration and the partial pressure equilibrium constant.

Introduction

As mentioned above, there are two types of equilibrium reactions. It is important to understand the difference between the two, because their equilibrium constants are expressed differently.

Homogeneous

The simpler one, a homogeneous reaction, is one where the states of matter of the products and reactions are all the same (the word "homo" means "same"). In most cases, the solvent determines the state of matter for the overall reaction. For example, the synthesis of methanol from a carbon monoxide-hydrogen mixture is a *gaseous* **homogeneous** mixture, which contains two or more substances:

$$ CO (g)+ 2H_2 (g) \rightleftharpoons CH_3OH (g)$$

At equilibrium, the rate of the forward and reverse reaction are equal, which is demonstrated by the arrows. The equilibrium constant, however, gives the ratio of the units (pressure or concentration) of the products to the reactants when the reaction is at equilibrium.

The synthesis of ammonia is another example of a *gaseous* **homogeneous** mixture:

$$ N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) $$

Heterogeneous

A heterogeneous reaction is one where one or more states within the reaction differ (the Greek word "heteros" means "different"). For example, the formation of an aqueous solution of lead(II) iodide creates a **heterogeneous** mixture dealing with molecules in both the *solid* and *aqueous* states:

$$PbI_{2 (s)} \rightleftharpoons Pb^{+2}_{(aq)} + 2I^-_{(aq)}$$

The decomposition of sodium hydrogen carbonate (baking soda) at high elevations is another example of a **heterogeneous** mixture, this reaction deals with molecules in both the *solid* and *gaseous* states:

$$ 2NaHCO_{3 (s)} \rightleftharpoons Na_2CO_{3 (s)} + H_2O_{ (g)} + CO_{2 (g)} $$

$$ C_{(s)} + O_{2 (g)} \rightleftharpoons CO_{2 (g)} $$

Once again, this difference is emphasized so that students remember that equilibrium constant calculations are different from heterogeneous mixtures.

Writing Equilibrium Constants

An equilibrium constant is obtained by letting a single reaction proceed to equilibrium and then measuring the concentrations of each molecule involved in that reaction and creating a ratio of the product concentrations to reactant concentrations. Because the concentrations are measured at equilibrium, the equilibrium constant is remain the same for a given reaction independent of initial concentrations, which determine the rate (for an ideal reaction). This knowledge allowed scientists to derive a model expression that can serve as a "template" for any reaction. This basic "template" form of a homogeneous equilibrium constant is examined here.

This discussion makes use of the following hypothetical reaction:

$$aA (g) + bB (g) \rightleftharpoons gG (g) + hH (g)$$

*The lower case letters represent the number of moles of each molecule, the upper case letters represent the molecule itself, and the letters in the parenthesis always represents the state of matter of the molecule.

Equilibrium Constant of Concentration

The equilibrium constant of concentration gives the ratio of concentrations of products over reactants for a reaction that is at equilibrium. This is usually used when the state of matter for the reaction is (aq). The equilibrium constant expression is written as K_c, as in the expression below:

$$K_c = \dfrac{[G]^g[H]^h}{[A]^a[B]^b}$$

- If $K > 1$ then equilibrium favors products
- If $K < 1$ then equilibrium favors the reactants

Here, the letters inside the brackets represent the concentration of each molecule. Notice the mathematical product of the chemical products raised to the powers of their respective coefficients is the numerator of the ratio and the mathematical product of the reactants raised to the powers of their respective coefficients is the denominator. This is the case for every equilibrium constant. Keep in mind that this expression was obtained by a homogeneous equilibrium reaction. K represents an equilibrium constant and c represents concentration (e.g., K_c). This means that **every species** shows up in the expression, as long as it is a solution or a gas.

Equilibrium Constant of Pressure

Gaseous reaction equilibria are not expressed in terms of concentration, but instead in terms of partial pressures. The equilibrium constant of pressure gives the ratio of pressure of products over reactants for a reaction that is at equilibrium (again, the concentrations of all species are raised to the powers of their respective concentrations). The equilibrium constant is written as K_p, as shown below:

$$K_p= \dfrac{p^g_G \, p^h_H}{ p^a_A \,p^b_B}$$

- Where p can have units of pressure (e.g., atm or bar).

The procedure for this is the same as the procedure for the concentration constant above.

Conversion of K_c to K_p

To convert K_c to K_p, the following equation is used:

$$K_p = K_c(RT)^{\Delta{n_{gas}}}$$

where:

- $R=0.0820575\ \text{L atm mol}^{-1}\ \text{K}^{-1}$ or $8.31447\ \text{J mol}^{-1}\ \text{K}^{-1}$
- T= Temperature in Kelvin
- Δn_{gas}= Moles of gas (product) - Moles of Gas (Reactant)

Reaction Quotient

Another quantity of interest is the reaction quotient, Q_c, which is the same ratio constant at any point in the reaction at which the reaction is not at equilibrium. The reaction quotient is calculated the same way as is K_c, but is not necessarily equal to K_c. It is used to determine which way the reaction will proceed at any given point in time.

$$Q_c = \dfrac{[G]^g[H]^h}{[A]^a[B]^b}$$

- $Q_c > K_c$, then the reactions shifts to the left
- $Q_c < K_c$, then the reactions shifts to the right
- $Q_c = K_c$ then the reaction is still at equilibrium

The same process is employed when calculating Q_p.

Heterogeneous Mixture

The most important consideration for a heterogeneous mixture is that **solids and pure liquids are always excluded from the equilibrium constant**. In a mathematical perspective, the activities of solids and liquids each equal one, which does not affect the overall K value. Solvents also equal one. The molarity of solids, liquids, and solvents remain constant throughout the reaction, which means their value can be denoted as 1. This rule is extremely important to remember, especially in dealing with heterogeneous solutions.

Example 1

In a hypothetical reaction:

$$aA_{(s)} + bB_{(l)} \rightleftharpoons gG_{(aq)} + hH_{(aq)}$$

The equilibrium constant expression is written as follows:

$$K_c = \dfrac{[G]^g[H]^h}{1 \times 1} = [G]^g[H]^h$$

In this case, since solids and liquids do not affect the equilibrium constant expression, the expression is independent from the concentration of the reactants. Thus, A and B are omitted the final expression. When the product of the reaction is a solvent, the numerator equals one, which is illustrated in the following reaction:

$$H^+_{(aq)} + OH^–_{(aq)} \rightarrow H_2O_{ (l)}$$

The equilibrium constant expression would be:

$$K_c= \dfrac{1}{ [H^+][OH^-]}$$

which is the inverse of the autoionization constant of water (K_c)

$$K_c = \dfrac{1}{K_w}=1 \times 10^7$$

Manipulation of Constants

The equilibrium constant expression must be manipulated if a reaction is reversed or split into elementary steps. When the reaction is reversed, the equilibrium constant expression is inverted. The new expression would be written as:

$$K'= \dfrac{1}{\dfrac{[G]^g[H]^h}{[A]^a[B]^b}} = \dfrac{[A]^a[B]^b}{[G]^g[H]^h}$$

When there are multiple steps in the reaction, each with its own K (in a scenario similar to Hess's law problems), then the successive K values for each step are *multiplied* together to calculate the overall K.

Activities

Because the concentration of reactants and products are not dimensionless (i.e. they have units) in a reaction, the actual quantities used in an equilibrium constant expression are *activities*. *Activity* is expressed by the dimensionless ratio $\frac{[X]}{c^{\circ}}$ where $[X]$ signifies the molarity of the molecule and c is the chosen reference state:

$$a_b=\dfrac{[B]}{c^{\circ}}$$

For gases that do not follow the ideal gas laws, using activities will accurately determine the equilibrium constant that changes when concentration or pressure varies. Thus, the units are canceled and K becomes unitless.

Practice Problems

1. Write the equilibrium constant expression for each reaction.
    a. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
    b. $N_2O_{ (g)} + \dfrac{1}{2} O_{2(g)} \rightleftharpoons 2NO_{(g)}$
    c. $Cu_{(s)} + 2Ag^+_{(aq)} \rightleftharpoons Cu^{+2}_{(aq)} + 2Ag_{(s)}$
    d. $CaCO_{3 (g)} \rightleftharpoons CaCO_{(s)} + CO_{2 (g)}$

    e. $2NaHCO_{3 (s)} \rightleftharpoons Na_2CO_{3 (s)} + CO_{2 (g)} + H_2O_{ (g) }$

2. What is the K_c of the following reaction? $2SO_{2 (g)} + O_{2 (g)} \rightleftharpoons 2SO_{3 (g)}$ with concentration $SO_{2(g)} = 0.2 M O_{2 (g)} = 0.5 M SO_{3 (g)} = 0.7 \;M$ Also, What is the K_p of this reaction? At room temperature?
3. For the same reaction, the differing concentrations: $SO_{2 (g)} = 0.1\; M O_{2(g)} = 0.3\; M \;SO_{3 (g)} = 0.5\; M$ Would this go towards to product or reactant?
4. Write the Partial Pressure Equilibrium: $C_{(s)} + O_{2 (g)} \rightarrow CO_{2 (g)}$
5. Write the chemicl reaction for the following equilibrium constant: $K_p= \dfrac{P^2_{HI}}{P_{H_2} \times P_{I_2}}$

References

1. Petrucci, Ralph H. General Chemistry: Principles and Modern Applications 9th Ed. New Jersey: Pearson Education Inc. 2007.
2. http://dwb.unl.edu/Teacher/NSF/C14/C14Links/learn.chem.vt.edu/tutorials/equilibrium/eqexpression.html

Outside Links

- For more information on equilibrium constant expressions please visit the wikipedia site: http://en.wikipedia.org/wiki/Equilibrium_constant
- The image below can be found here: http://image.tutorvista.com/content/chemical-equilibrium/reaction-rate-time-graph.gif

Answers to Practice Problems

1. $K_c = \dfrac{ [SO_3]^2}{[O_2][SO_2]^2}$
2. $Kc = \dfrac{ [NO]^2}{[O_2]^{0.5}[N_2O]}$
3. $Kc = \dfrac{ [Cu^{+2}]}{[Ag^+]^2 }$
4. $Kc = \dfrac{ [CO_2]}{[CaCO_3]}$
5. $K_c = [H_2O][CO_2]$

What is K_c for the Reaction

1) Kc: 24.5

Kp: 1.002 Atm

2) Q_c= 83.33 > K_c therefore the reaction shifts to the left

1. $K_p= \dfrac{P_{CO_2}} {P_{O_2}}$
2. $H_2 (g)+ I_2 (g) \rightarrow 2HI(g)$

Contributors

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