6.5: Heterogeneous Equilibria

The equilibrium constant, K, expresses the relationship between products and reactants of a reaction at equilibrium with respect to a specific unit.This article explains how to write equilibrium constant expressions, and introduces the calculations involved with both the concentration and the partial pressure equilibrium constant.

Homogeneous Reactions

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:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \tag{6.5.1}$$

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:

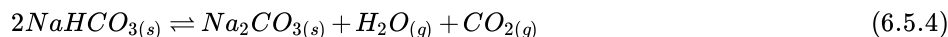$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \tag{6.5.2}$$

Heterogeneous Reactions

A heterogeneous reaction is one in which 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 particles in both the *solid* and *aqueous* states:

$$PbI_{2(s)} \rightleftharpoons Pb^{+2}_{(aq)} + 2I^-_{(aq)} \tag{6.5.3}$$

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:

$$2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)} \tag{6.5.4}$$

$$C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)} \tag{6.5.5}$$

This difference between homogeneous and heterogeneous reactions is emphasized so that students remember that solids, pure liquids, and solvents are treated differently than gases and solutes when approximating the activities of the substances in equilibrium constant expressions.

Writing Equilibrium Constant Expressions

The numerical value of an equilibrium constant is obtained by letting a single reaction proceed to equilibrium and then measuring the concentrations of each substance involved in that reaction. The ratio of the product concentrations to reactant concentrations is calculated. Because the concentrations are measured at equilibrium, the equilibrium constant remains the same for a given reaction independent of initial concentrations. This knowledge allowed scientists to derive a model expression that can serve as a "template" for any reaction. This basic "template" form of an equilibrium constant expression is examined here.

Equilibrium Constant of Activities

The thermodynamically correct equilibrium constant expression relates the activities of **<u>all</u>** of the species present in the reaction. Although the concept of activity is too advanced for a typical General Chemistry course, it is essential that the explanation of the derivation of the equilibrium constant expression starts with activities so that no misconceptions occur. For the hypothetical reaction:

$$bB + cC \rightleftharpoons dD + eE \tag{6.5.6}$$

the equilibrium constant expression is written as

$$K = \frac{a_D^d \cdot a_E^e}{a_B^b \cdot a_C^c} \tag{6.5.7}$$

*The lower case letters in the balanced equation represent the number of moles of each substance, the upper case letters represent the substance itself.

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

Equilibrium Constant of Concentration

To avoid the use of activities, and to simplify experimental measurements, the equilibrium constant of concentration approximates the activities of solutes and gases in dilute solutions with their respective molarities. However, the activities of solids, pure liquids, and solvents are **not** approximated with their molarities. Instead these activities are defined to have a value equal to 1 (one).The equilibrium constant expression is written as K_c, as in the expression for the reaction:

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)} \tag{6.5.8}$$

$$K_c = \frac{a_{H_3O^+} \cdot a_{F^-}}{a_{HF} \cdot a_{H_2O}} \approx \frac{[H_3O^+][F^-]}{[HF](1)} = \frac{[H_3O^+][F^-]}{[HF]} \tag{6.5.9}$$

Here, the letters inside the brackets represent the concentration (in molarity) of each substance. 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. A ratio of molarities of products over reactants is usually used when most of the species involved are dissolved in water. A ratio of concentrations can also be used for reactions involving gases if the volume of the container is known.
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Equilibrium Constant of Pressure

Gaseous reaction equilibria are often expressed 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 pressures of all species are raised to the powers of their respective coefficients). The equilibrium constant is written as K_p, as shown for the reaction:

$$aA_{(g)} + bB_{(g)} \rightleftharpoons gG_{(g)} + hH_{(g)} \tag{6.5.10}$$

$$K_p = \frac{p_G^g \, p_H^h}{p_A^a \, p_B^b} \tag{6.5.11}$$

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

Conversion of K_c to K_p

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

$$K_p = K_c(RT)^{\Delta n_{gas}} \tag{6.5.12}$$

where:

- R=0.0820575 L atm mol^{-1} K^{-1} or 8.31447 J mol^{-1} 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, which is the numerical value of the ratio of products to reactants at any point in the reaction. The reaction quotient is calculated the same way as is K, but is not necessarily equal to K. It is used to determine which way the reaction will proceed at any given point in time.

$$Q = \frac{[G]^g[H]^h}{[A]^a[B]^b} \tag{6.5.13}$$

- If $Q > K$, then the reactions shifts to the left to reach equilibrium
- If $Q < K$, then the reactions shifts to the right to reach equilibrium
- If $Q = K$ then the reaction is at equilibrium

The same process is employed whether calculating Q_c or Q_p.

Heterogeneous Mixture

The most important consideration for a heterogeneous mixture is that **solids and pure liquids and solvents have an activity that has a fixed value of 1**. From a mathematical perspective, with the activities of solids and liquids and solvents equal one, these substances do not affect the overall K or Q value. This convention is extremely important to remember, especially in dealing with heterogeneous solutions.

> ### ✔ Example 6.5.1
>
> In a hypothetical reaction:
>
> $$aA_{(s)} + bB_{(l)} \rightleftharpoons gG_{(aq)} + hH_{(aq)} \tag{6.5.14}$$
>
> The equilibrium constant expression is written as follows:
>
> $$K_c = \frac{[G]^g[H]^h}{1 \times 1} = [G]^g[H]^h \tag{6.5.15}$$
>
> In this case, since solids and liquids have a fixed value of 1, the numerical value of the expression is independent of the amounts of A and B. If the product of the reaction is a solvent, the numerator equals one, which is illustrated in the following reaction:
>
> $$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \tag{6.5.16}$$
>
> The equilibrium constant expression would be:
>
> $$K_c = \frac{1}{[H^+][OH^-]} \tag{6.5.17}$$
>
> which is the reciprocal of the autoionization constant of water (K_w)
>
> $$K_c = \frac{1}{K_w} = 1 \times 10^{14} \tag{6.5.18}$$

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:

$$K' = \frac{1}{\frac{[G]^g[H]^h}{[A]^a[B]^b}} = \frac{[A]^a[B]^b}{[G]^g[H]^h} \tag{6.5.19}$$

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.
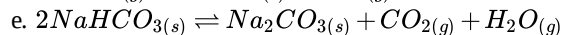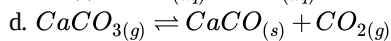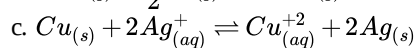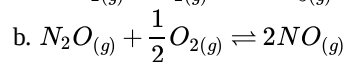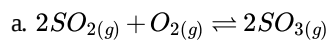
> ### 📌 Activities
>
> Because the concentration of reactants and products are not dimensionless (i.e. they have units) in a reaction, the actual quantities used in an equilibrium constant expression are *activities*. *Activity* is expressed by the dimensionless ratio $\frac{[X]}{c^\circ}$ where $[X]$ signifies the molarity of the molecule and c is the chosen reference state:
>
> $$a_b = \frac{[B]}{c^\circ} \tag{6.5.20}$$
>
> 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
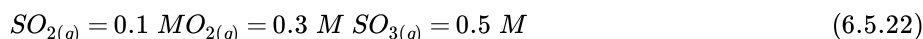
1. Write the equilibrium constant expression for each reaction.

    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?

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \tag{6.5.21}$$

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:

$$SO_{2(g)} = 0.1\ M O_{2(g)} = 0.3\ M\ SO_{3(g)} = 0.5\ M \tag{6.5.22}$$

Would this go towards to product or reactant?

4. Write the Partial Pressure Equilibrium:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{6.5.23}$$

5. Write the chemicl reaction for the following equilibrium constant:

$$K_p = \dfrac{P^2_{HI}}{P_{H_2} \times P_{I_2}} \tag{6.5.24}$$

References

1. Petrucci, Ralph H. <u>General Chemistry: Principles and Modern Applications 9th Ed.</u> New Jersey: Pearson Education Inc. 2007.

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: 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. $Kc = \dfrac{[Cu^{+2}]}{[Ag^+]^2}$

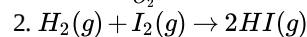4. $Kc = \dfrac{[CO_2]}{[CaCO_3]}$

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 and Attributions

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