

Equilibrium Constants

A reversible reaction is at equilibrium when the forward and reverse processes occur at equal rates. Chemical equilibria are dynamic processes characterized by constant amounts of reactant and product species. The composition of a reaction mixture may be represented by a mathematical function known as the reaction quotient, Q . For a reaction at equilibrium, the composition is constant, and Q is called the equilibrium constant, K . A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases.

15.1 Chemical Equilibria

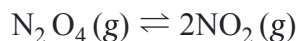
Learning Objectives

By the end of this section, you will be able to:

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

The convention for writing chemical equations involves placing reactant formulas on the left side of a reaction arrow and product formulas on the right side. By this convention, and the definitions of “reactant” and “product,” a chemical equation represents the reaction in question as proceeding from left to right. **Reversible reactions**, however, may proceed in both forward (left to right) and reverse (right to left) directions. When the rates of the forward and reverse reactions are equal, the concentrations of the reactant and product species remain constant over time and the system is at **equilibrium**. The relative concentrations of reactants and products in equilibrium systems vary greatly; some systems contain mostly products at equilibrium, some contain mostly reactants, and some contain appreciable amounts of both.

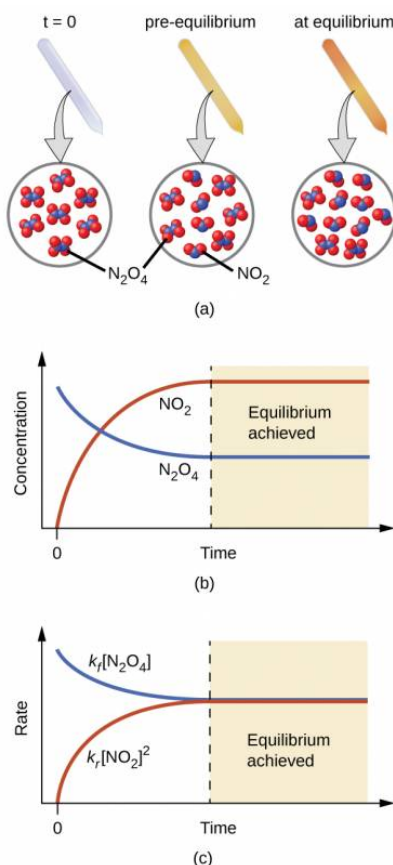
[Figure 15.1](#) illustrates fundamental equilibrium concepts using the reversible decomposition of colorless dinitrogen tetroxide to yield brown nitrogen dioxide, an elementary reaction described by the equation:



Note that a special double arrow is used to emphasize the reversible nature of the reaction.

Figure 15.1

(a) A sealed tube containing colorless N_2O_4 darkens as it decomposes to yield brown NO_2 . (b) Changes in concentration over time as the decomposition reaction achieves equilibrium. (c) At equilibrium, the forward and reverse reaction rates are equal.



For this elementary process, rate laws for the forward and reverse reactions may be derived directly from the reaction stoichiometry:

$$\text{rate}_f = k_f [\text{N}_2\text{O}_4]$$

$$\text{rate}_r = k_r [\text{NO}_2]^2$$

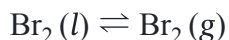
As the reaction begins ($t = 0$), the concentration of the N_2O_4 reactant is finite and that of the NO_2 product is zero, so the forward reaction proceeds at a finite rate while the reverse reaction rate is zero. As time passes, N_2O_4 is consumed and its concentration falls, while NO_2 is produced and its concentration increases (Figure 15.1b). The decreasing concentration of the reactant slows the forward reaction rate, and the increasing product concentration speeds the reverse reaction rate (Figure 15.1c). This process continues until the forward and reverse reaction rates become equal, at which time the reaction has reached equilibrium, as characterized by constant concentrations of its reactants and products (shaded areas of Figure 15.1b and Figure 15.1c). It's important to emphasize that chemical equilibria are dynamic; a reaction at equilibrium has not “stopped,” but is proceeding in the forward and reverse directions at the same rate. This dynamic nature is essential to understanding equilibrium behavior as discussed in this and subsequent chapters of the text.

Figure 15.2

A two-person juggling act illustrates the dynamic aspect of chemical equilibria. Each person is throwing and catching clubs at the same rate, and each holds a (approximately) constant number of clubs.



Physical changes, such as phase transitions, are also reversible and may establish equilibria. This concept was introduced in another chapter of this text through discussion of the vapor pressure of a condensed phase (liquid or solid). As one example, consider the vaporization of bromine:



When liquid bromine is added to an otherwise empty container and the container is sealed, the forward process depicted above (vaporization) will commence and continue at a roughly constant rate as long as the exposed surface area of the liquid and its temperature remain constant. As increasing amounts of gaseous bromine are produced, the rate of the reverse process (condensation) will increase until it equals the rate of vaporization and equilibrium is established. A photograph showing this phase transition equilibrium is provided in [Figure 15.3](#).

Figure 15.3

A sealed tube containing an equilibrium mixture of liquid and gaseous bromine. (credit: <http://images-of-elements.com/bromine.php>)



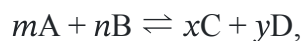
15.2 Equilibrium Constants

Learning Objectives

By the end of this section, you will be able to:

- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient** (Q). For a reversible reaction described by



the reaction quotient is derived directly from the stoichiometry of the balanced equation as

$$Q_c = \frac{[C]^x [D]^y}{[A]^m [B]^n},$$

where the subscript *c* denotes the use of molar concentrations in the expression. If the reactants and products are gaseous, a reaction quotient may be similarly derived using partial pressures:

$$Q_p = \frac{P_C^x P_D^y}{P_A^m P_B^n}$$

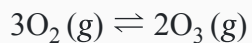
Note that the reaction quotient equations above are a simplification of more rigorous expressions that use *relative* values for concentrations and pressures rather than *absolute* values. These relative concentration and pressure values are dimensionless (they have no units); consequently, so are the reaction quotients. For purposes of this introductory text, it will suffice to use the simplified equations and to disregard units when computing *Q*. In most cases, this will introduce only modest errors in calculations involving reaction quotients.

EXAMPLE 15.2.1

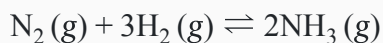
Writing Reaction Quotient Expressions

Write the concentration-based reaction quotient expression for each of the following reactions:

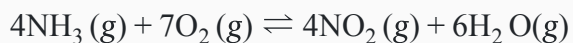
(a)



(b)



(c)



Solution

(a)

$$Q_c = \frac{[\text{O}_3]^2}{[\text{O}_2]^3}$$

(b)

$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

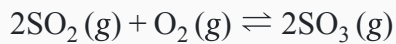
(c)

$$Q_c = \frac{[\text{NO}_2]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^7}$$

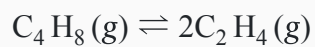
Check Your Learning

Write the concentration-based reaction quotient expression for each of the following reactions:

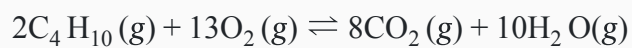
(a)



(b)



(c)



✓ Answer

(a)

$$Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]};$$

(b)

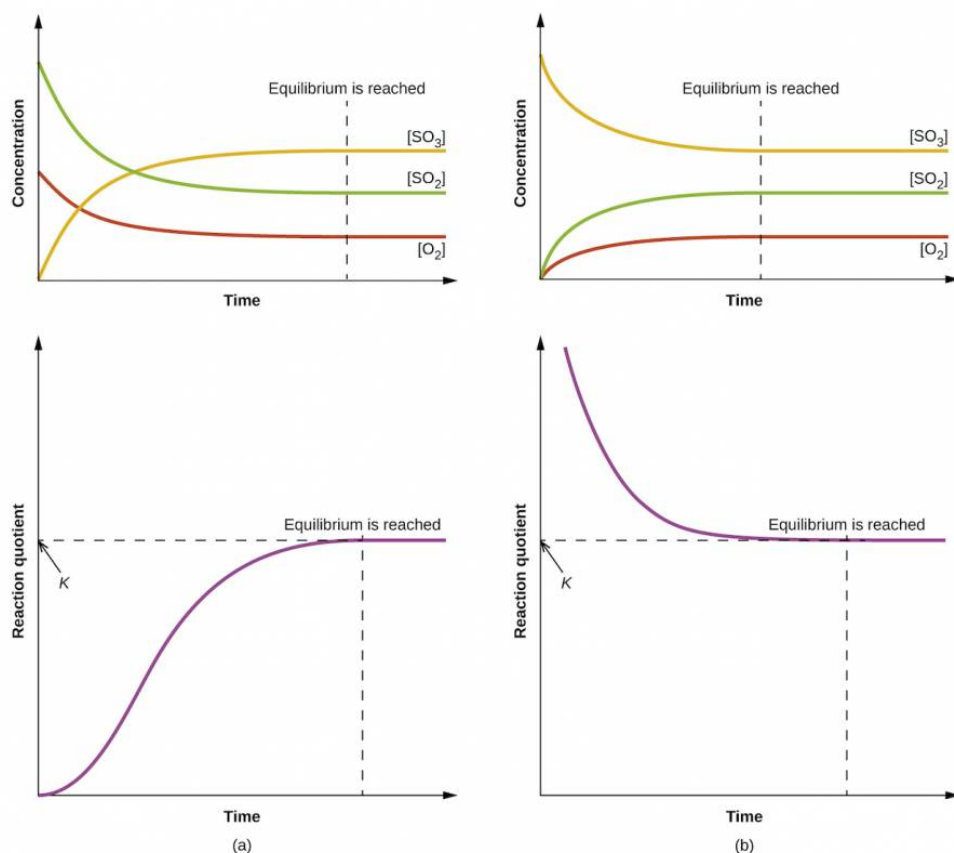
$$Q_c = \frac{[\text{C}_2\text{H}_4]^2}{[\text{C}_4\text{H}_8]};$$

(c)

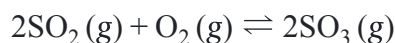
$$Q_c = \frac{[\text{CO}_2]^8[\text{H}_2\text{O}]^{10}}{[\text{C}_4\text{H}_{10}]^2[\text{O}_2]^{13}}$$

Figure 15.4

Changes in concentrations and Q_c for a chemical equilibrium achieved beginning with (a) a mixture of reactants only and (b) products only.



The numerical value of Q varies as a reaction proceeds towards equilibrium; therefore, it can serve as a useful indicator of the reaction's status. To illustrate this point, consider the oxidation of sulfur dioxide:



Two different experimental scenarios are depicted in [Figure 15.4](#), one in which this reaction is initiated with a mixture of reactants only, SO_2 and O_2 , and another that begins with only product, SO_3 . For the reaction that begins with a mixture of reactants only, Q is initially equal to zero:

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{0^2}{[SO_2]^2 [O_2]} = 0$$

As the reaction proceeds toward equilibrium in the forward direction, reactant concentrations decrease (as does the denominator of Q_c), product concentration increases (as does the numerator of Q_c), and the reaction quotient consequently increases. When equilibrium is achieved, the concentrations of reactants and product remain constant, as does the value of Q_c .

If the reaction begins with only product present, the value of Q_c is initially undefined (immeasurably large, or infinite):

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{[SO_3]^2}{0} \rightarrow \infty$$

In this case, the reaction proceeds toward equilibrium in the reverse direction. The product concentration and the numerator of Q_c decrease with time, the reactant concentrations and the denominator of Q_c increase, and the reaction quotient consequently decreases until it becomes constant at equilibrium.

The constant value of Q exhibited by a system at equilibrium is called the **equilibrium constant, K** :

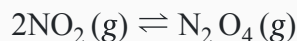
$$K \equiv Q \text{ at equilibrium}$$

Comparison of the data plots in [Figure 15.4](#) shows that both experimental scenarios resulted in the same value for the equilibrium constant. This is a general observation for all equilibrium systems, known as the **law of mass action**: At a given temperature, the reaction quotient for a system at equilibrium is constant.

EXAMPLE 15.2.2

Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:



When 0.10 mol NO_2 is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, $[\text{NO}_2] = 0.016 \text{ M}$ and $[\text{N}_2\text{O}_4] = 0.042 \text{ M}$.

(a) What is the value of the reaction quotient before any reaction occurs?

(b) What is the value of the equilibrium constant for the reaction?

Solution

As for all equilibrium calculations in this text, use the simplified equations for Q and K and disregard any concentration or pressure units, as noted previously in this section.

(a) Before any product is formed,

$$[\text{NO}_2] = \frac{0.10 \text{ mol}}{1.0 \text{ L}} = 0.10 \text{ M},$$

and $[\text{N}_2\text{O}_4] = 0 \text{ M}$. Thus,

$$Q_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{0}{0.10^2} = 0$$

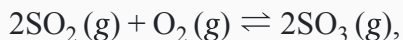
(b) At equilibrium,

$$K_c = Q_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$$

The equilibrium constant is 1.6×10^2 .

Check Your Learning

For the reaction



the concentrations at equilibrium are $[\text{SO}_2] = 0.90 \text{ M}$, $[\text{O}_2] = 0.35 \text{ M}$, and $[\text{SO}_3] = 1.1 \text{ M}$. What is the value of the equilibrium constant, K_c ?

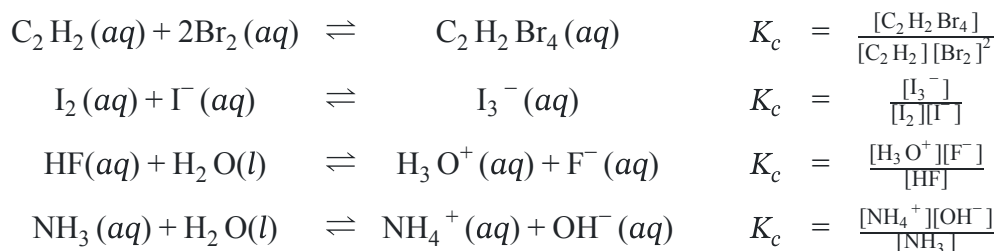
✓ Answer

$$K_c = 4.3$$

By its definition, the magnitude of an equilibrium constant explicitly reflects the composition of a reaction mixture at equilibrium, and it may be interpreted with regard to the extent of the forward reaction. A reaction exhibiting a large K will reach equilibrium when most of the reactant has been converted to product, whereas a small K indicates the reaction achieves equilibrium after very little reactant has been converted. It's important to keep in mind that the magnitude of K does *not* indicate how rapidly or slowly equilibrium will be reached. Some equilibria are established so quickly as to be nearly instantaneous, and others so slowly that no perceptible change is observed over the course of days, years, or longer.

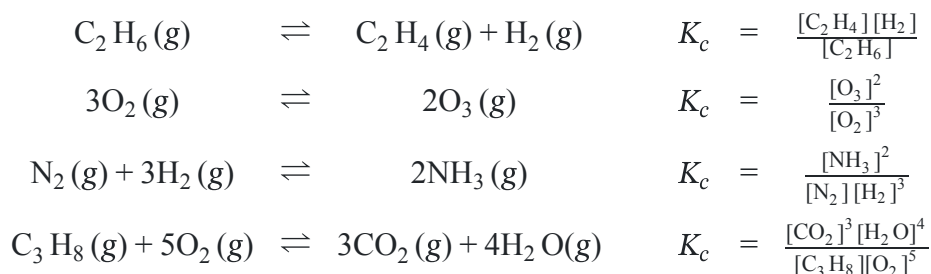
15.3 Homogeneous Equilibria

A homogeneous equilibrium is one in which all reactants and products (and any catalysts, if applicable) are present in the same phase. By this definition, homogeneous equilibria take place in *solutions*. These solutions are most commonly either liquid or gaseous phases, as shown by the examples below:



These examples all involve aqueous solutions, those in which water functions as the solvent. In the last two examples, water also functions as a reactant, but its concentration is *not* included in the reaction quotient. The reason for this omission is related to the more rigorous form of the Q (or K) expression mentioned previously in this chapter, in which *relative concentrations for liquids and solids are equal to 1 and needn't be included*. Consequently, reaction quotients include concentration or pressure terms only for gaseous and solute species.

The equilibria below all involve gas-phase solutions:



For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (K_c) or partial pressures (K_p) of the reactants and products. A relation between these two K values may be simply derived from the ideal gas equation and the definition of molarity:

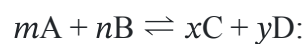
$$PV = nRT$$

$$P = \left(\frac{n}{V}\right)RT$$

$$= MRT$$

where P is partial pressure, V is volume, n is molar amount, R is the gas constant, T is temperature, and M is molar concentration.

For the gas-phase reaction



$$K_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n}$$

$$= \frac{([C] \times RT)^x ([D] \times RT)^y}{([A] \times RT)^m ([B] \times RT)^n}$$

$$= \frac{[C]^x [D]^y}{[A]^m [B]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}}$$

$$= K_c (RT)^{(x+y) - (m+n)}$$

$$= K_c (RT)^{\Delta n}$$

And so, the relationship between K_c and K_P is

$$K_P = K_c (RT)^{\Delta n}$$

where Δn is the difference in the molar amounts of product and reactant gases, in this case:

$$\Delta n = (x+y) - (m+n)$$

EXAMPLE 15.3.1

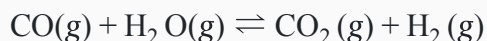
Calculation of K_P

Write the equations relating K_c to K_P for each of the following reactions:

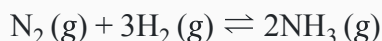
(a)



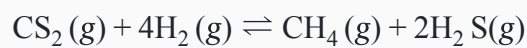
(b)



(c)



(d) K_c is equal to 0.28 for the following reaction at 900 °C:



What is K_P at this temperature?

Solution

$$(a) \Delta n = (2) - (1) = 1$$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^1 = K_c (RT)$$

$$(b) \Delta n = (2) - (2) = 0$$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^0 = K_c$$

$$(c) \Delta n = (2) - (1 + 3) = -2$$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^{-2} =$$

$$\frac{K_c}{(RT)^2}$$

$$(d) K_P = K_c (RT)^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0$$

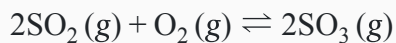
×

$$10^{-5}$$

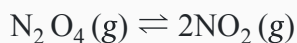
Check Your Learning

Write the equations relating K_c to K_P for each of the following reactions:

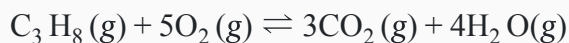
(a)



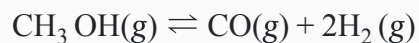
(b)



(c)



(d) At 227 °C, the following reaction has $K_c = 0.0952$:



What would be the value of K_P at this temperature?

✓ Answer

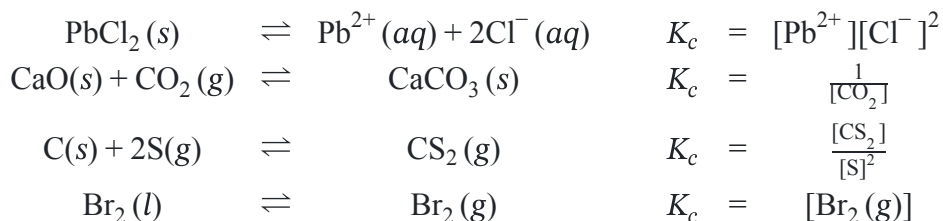
(a) $K_P = K_c (RT)^{-1}$; (b) $K_P = K_c (RT)$; (c) $K_P = K_c (RT)$; (d) 160 or 1.6

×

10^2

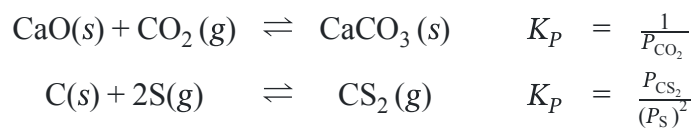
15.4 Heterogeneous Equilibria

A **heterogeneous equilibrium** involves reactants and products in two or more different phases, as illustrated by the following examples:



Again, note that concentration terms are only included for gaseous and solute species, as discussed previously.


Two of the above examples include terms for gaseous species only in their equilibrium constants, and so K_P expressions may also be written:



Keq Practice

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