

Reaction Quotients and Le Chatelier

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure. The system's response to these disturbances is described by Le Châtelier's principle: An equilibrium system subjected to a disturbance will shift in a way that counters the disturbance and re-establishes equilibrium. A catalyst will increase the rate of both the forward and reverse reactions of a reversible process, increasing the rate at which equilibrium is reached but not altering the equilibrium mixture's composition (K does not change).

16.1 Predicting the Direction of a Reaction

Learning Objectives

- Relate the magnitude of an equilibrium constant to properties of the chemical system

The equilibrium constant for a reaction can be used to predict the behavior of mixtures containing its reactants and/or products. As demonstrated by the sulfur dioxide oxidation process described above, a chemical reaction will proceed in whatever direction is necessary to achieve equilibrium. Comparing Q to K for an equilibrium system of interest allows prediction of what reaction (forward or reverse), if any, will occur.

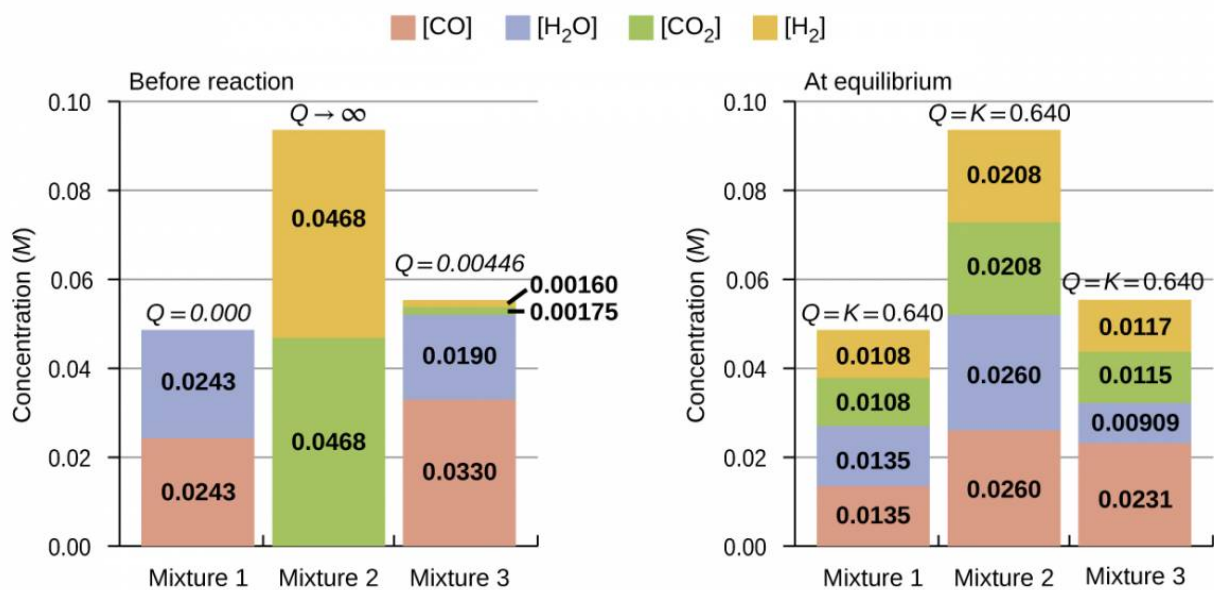
To further illustrate this important point, consider the reversible reaction shown below:



The bar charts in [Figure 17.1](#) represent changes in reactant and product concentrations for three different reaction mixtures. The reaction quotients for mixtures 1 and 3 are initially lesser than the reaction's equilibrium constant, so each of these mixtures will experience a net forward reaction to achieve equilibrium. The reaction quotient for mixture 2 is initially greater than the equilibrium constant, so this mixture will proceed in the reverse direction until equilibrium is established.

Figure 16.1

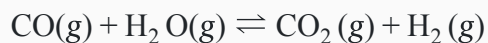
Compositions of three mixtures before ($Q_c \neq K_c$) and after ($Q_c = K_c$) equilibrium is established for the reaction $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$.



EXAMPLE 16.1.1

Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:



$$K_c = 0.64$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[\text{CO}]_i$	0.020 M	0.011 M	0.0094 M
$[\text{H}_2\text{O}]_i$	0.020 M	0.0011 M	0.0025 M
$[\text{CO}_2]_i$	0.0040 M	0.037 M	0.0015 M
$[\text{H}_2]_i$	0.0040 M	0.046 M	0.0076 M

Solution

Experiment 1:

$$Q_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.0040)(0.0040)}{(0.020)(0.020)} = 0.040.$$

$$Q_c < K_c (0.040 < 0.64)$$

The reaction will proceed in the forward direction.

Experiment 2:

$$Q_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$$Q_c > K_c (140 > 0.64)$$

The reaction will proceed in the reverse direction.

Experiment 3:

$$Q_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

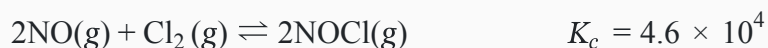
$$Q_c < K_c (0.48 < 0.64)$$

The reaction will proceed in the forward direction.

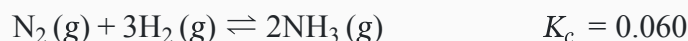
Check Your Learning

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

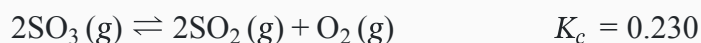
(a) A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl₂(g), and 0.500 mol of NOCl:



(b) A 5.0-L flask containing 17 g of NH₃, 14 g of N₂, and 12 g of H₂:



(c) A 2.00-L flask containing 230 g of SO₃(g):



✓ Answer

(a) $Q_c = 6.45 \times 10^3$, forward. (b) $Q_c = 0.23$, reverse. (c) $Q_c = 0$, forward.

16.2 Shifting Equilibria: Le Châtelier's principle

Learning Objectives

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

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Châtelier's principle

A system at equilibrium is in a state of dynamic balance, with forward and reverse reactions taking place at equal rates. If an equilibrium system is subjected to a change in conditions that affects these reaction rates differently (a *stress*), then the rates are no longer equal and the system is not at equilibrium. The system will subsequently experience a net reaction in the direction of greater rate (a *shift*) that will re-establish the equilibrium. This phenomenon is summarized by Le Châtelier's principle: *if an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium.*

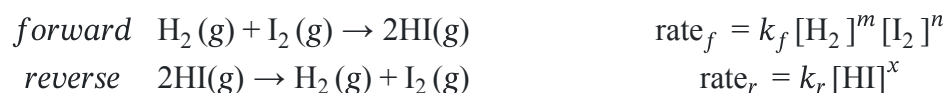
Reaction rates are affected primarily by concentrations, as described by the reaction's rate law, and temperature, as described by the Arrhenius equation. Consequently, changes in concentration and temperature are the two stresses that can shift an equilibrium.

16.3 Effect of a Change in Concentration

If an equilibrium system is subjected to a change in the concentration of a reactant or product species, the rate of either the forward or the reverse reaction will change. As an example, consider the equilibrium reaction



The rate laws for the forward and reverse reactions are



When this system is at equilibrium, the forward and reverse reaction rates are equal.

$$\text{rate}_f = \text{rate}_r$$

If the system is stressed by adding reactant, either H_2 or I_2 , the resulting increase in concentration causes the rate of the forward reaction to increase, exceeding that of the reverse reaction:

$$\text{rate}_f > \text{rate}_r$$

The system will experience a temporary net reaction in the forward direction to re-establish equilibrium (*the equilibrium will shift right*). This same shift will result if some product HI is removed from the system, which decreases the rate of the reverse reaction, again resulting in the same imbalance in rates.

The same logic can be used to explain the left shift that results from either removing reactant or adding product to an equilibrium system. These stresses both result in an increased rate for the reverse reaction

$$\text{rate}_f < \text{rate}_r$$

and a temporary net reaction in the reverse direction to re-establish equilibrium.

As an alternative to this kinetic interpretation, the effect of changes in concentration on equilibria can be rationalized in terms of reaction quotients. When the system is at equilibrium,

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = K_c$$

If reactant is added (increasing the denominator of the reaction quotient) or product is removed (decreasing the numerator), then $Q_c < K_c$ and the equilibrium will shift right. Note that the three different ways of inducing this stress result in three different changes in the composition of the equilibrium mixture. If H_2 is added, the right shift will

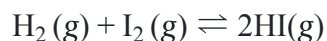
consume I_2 and produce HI as equilibrium is re-established, yielding a mixture with a greater concentrations of H_2 and HI and a lesser concentration of I_2 than was present before. If I_2 is added, the new equilibrium mixture will have greater concentrations of I_2 and HI and a lesser concentration of H_2 . Finally, if HI is removed, the new equilibrium mixture will have greater concentrations of H_2 and I_2 and a lesser concentration of HI. Despite these differences in composition, *the value of the equilibrium constant will be the same after the stress as it was before* (per the law of mass action). The same logic may be applied for stresses involving removing reactants or adding product, in which case $Q_c > K_c$ and the equilibrium will shift left.

For gas-phase equilibria such as this one, some additional perspectives on changing the concentrations of reactants and products are worthy of mention. The partial pressure P of an ideal gas is proportional to its molar concentration M ,

$$M = \frac{n}{V} = \frac{P}{RT}$$

and so changes in the partial pressures of any reactant or product are essentially changes in concentrations and thus yield the same effects on equilibria. Aside from adding or removing reactant or product, the pressures (concentrations) of species in a gas-phase equilibrium can also be changed by *changing the volume occupied by the system*. Since all species of a gas-phase equilibrium occupy the same volume, a given change in volume will cause the same change in concentration for both reactants and products. In order to discern what shift, if any, this type of stress will induce the stoichiometry of the reaction must be considered.

At equilibrium, the reaction



is described by the reaction quotient

$$Q_p = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} = K_p$$

If the volume occupied by an equilibrium mixture of these species is decreased by a factor of 3, the partial pressures of all three species will be increased by a factor of 3:

$$Q_p' = \frac{(3P_{HI})^2}{3P_{H_2} 3P_{I_2}} = \frac{9P_{HI}^2}{9P_{H_2} P_{I_2}} = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} = Q_p = K_p$$

$$Q_p' = Q_p = K_p$$

And so, changing the volume of this gas-phase equilibrium mixture does not result in a shift of the equilibrium.

A similar treatment of a different system,



however, yields a different result:

$$Q_p = \frac{P_{\text{NO}^2} P_{\text{O}^2}}{P_{(\text{NO}^2)^2}} = K_p$$

$$Q_p' = \frac{(3P_{\text{NO}})^2 3P_{\text{O}^2}}{(3P_{\text{NO}^2})^2} = \frac{9P_{\text{NO}^2} 3P_{\text{O}^2}}{9P_{(\text{NO}^2)^2}} = \frac{27P_{\text{NO}^2} P_{\text{O}^2}}{P_{(\text{NO}^2)^2}} = 3Q_p > K_p$$

$$Q_p' = 3Q_p > K_p$$

In this case, the change in volume results in a reaction quotient greater than the equilibrium constant, and so the equilibrium will shift left.

These results illustrate the relationship between the stoichiometry of a gas-phase equilibrium and the effect of a volume-induced pressure (concentration) change. If the total molar amounts of reactants and products are equal, as in the first example, a change in volume does not shift the equilibrium. If the molar amounts of reactants and products are different, a change in volume will shift the equilibrium in a direction that better “accommodates” the volume change. In the second example, two moles of reactant (NO_2) yield three moles of product ($2\text{NO} + \text{O}_2$), and so decreasing the system volume causes the equilibrium to shift left since the reverse reaction produces less gas (2 mol) than the forward reaction (3 mol). Conversely, increasing the volume of this equilibrium system would result in a shift towards products.

LINK TO LEARNING

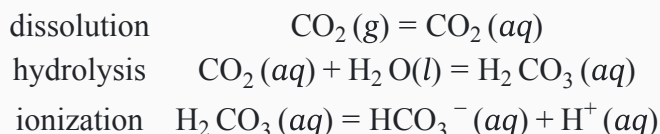
Check out this [link](#) to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

16.3.1 CHEMISTRY IN EVERYDAY LIFE

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804) developed a method of infusing water with carbon dioxide to make carbonated water. Priestly's approach involved production of carbon dioxide by reacting oil of vitriol (sulfuric acid) with chalk (calcium carbonate).

The carbon dioxide was then dissolved in water, reacting to produce hydrogen carbonate, a weak acid that subsequently ionized to yield bicarbonate and hydrogen ions:

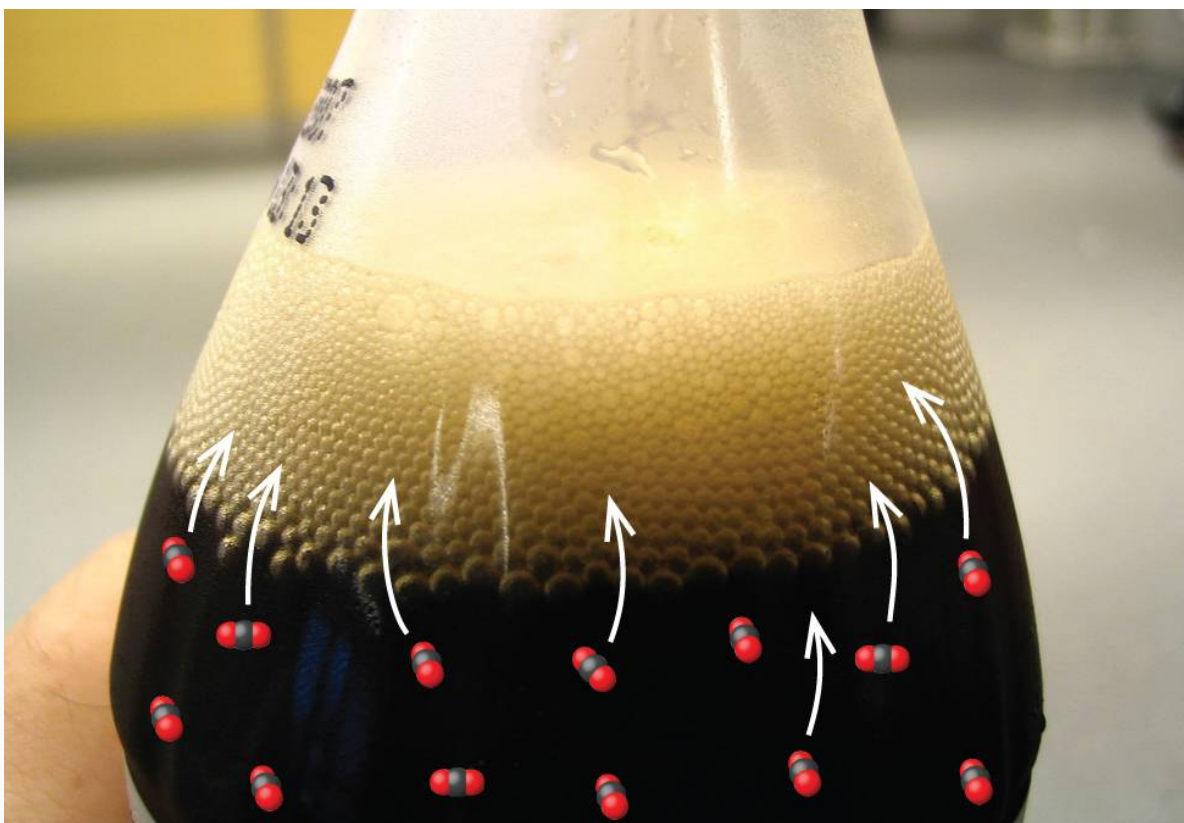


These same equilibrium reactions are the basis of today's soft-drink carbonation process. Beverages are exposed to a high pressure of gaseous carbon dioxide during the process to shift the first equilibrium above to the right, resulting in desirably high concentrations of dissolved carbon dioxide and, per similar shifts in the other two equilibria, its hydrolysis and ionization products. A bottle or can is then nearly filled with the carbonated beverage, leaving a relatively small volume of air in the container above the beverage surface (the *headspace*) before it is sealed. The pressure of carbon dioxide in the container headspace is very low immediately after sealing, but it rises as the dissolution equilibrium is re-established by shifting to the left. Since the volume of the beverage is significantly greater than the volume of the headspace, only a relatively small amount of dissolved carbon dioxide is lost to the headspace.

When a carbonated beverage container is opened, a hissing sound is heard as pressurized CO_2 escapes from the headspace. This causes the dissolution equilibrium to shift left, resulting in a decrease in the concentration of dissolved CO_2 and subsequent left-shifts of the hydrolysis and ionization equilibria. Fortunately for the consumer, the dissolution equilibrium is usually re-established slowly, and so the beverage may be enjoyed while its dissolved carbon dioxide concentration remains palatably high. Once the equilibria are re-established, the $\text{CO}_2(\text{aq})$ concentration will be significantly lowered, and the beverage acquires a characteristic taste referred to as "flat."

Figure 16.2

Opening a soft-drink bottle lowers the CO_2 pressure above the beverage, shifting the dissolution equilibrium and releasing dissolved CO_2 from the beverage. (credit: modification of work by "D Coetzee"/Flickr)



16.4 Effect of a Change in Temperature

Consistent with the law of mass action, an equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the equilibrium constant, K . When an equilibrium shifts in response to a temperature change, however, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.

To understand this phenomenon, consider the elementary reaction



Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation's stoichiometry:

$$\begin{aligned}\text{rate}_f &= k_f [A] \\ \text{rate}_r &= k_r [B]\end{aligned}$$

When the system is at equilibrium,

$$\text{rate}_r = \text{rate}_f$$

Substituting the rate laws into this equality and rearranging gives

$$k_f [A] = k_r [B]$$

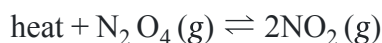
$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

The equilibrium constant is seen to be a mathematical function of the rate constants for the forward and reverse reactions. Since the rate constants vary with temperature as described by the Arrhenius equation, it stands to reason that the equilibrium constant will likewise vary with temperature (assuming the rate constants are affected to different extents by the temperature change). For more complex reactions involving multistep reaction mechanisms, a similar but more complex mathematical relation exists between the equilibrium constant and the rate constants of the steps in the mechanism. Regardless of how complex the reaction may be, the temperature-dependence of its equilibrium constant persists.

Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction. For example, the decomposition of dinitrogen tetroxide is an endothermic (heat-consuming) process:



For purposes of applying Le Chatelier's principle, heat (q) may be viewed as a reactant:



Raising the temperature of the system is akin to increasing the amount of a reactant, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left. For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed.

Files

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