

14.6: Reaction Directions (Empirical Explanation)

Learning Objectives

- To predict in which direction a reaction will proceed.
- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

We previously saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a quantity called the Reaction Quotient (Q). The expression for the Reaction Quotient has precisely the same form as the equilibrium constant expression from the [Law of Mass Action](#), except that Q may be derived from a set of values measured at any time during the reaction of any mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:



the Reaction Quotient is defined as follows:

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (14.6.2)$$

To understand how information is obtained using a Reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,



For this reaction, $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \quad (14.6.4)$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Table 14.6.1: Three Conditions of the dissociation of dinitrogen tetroxide to nitrogen dioxide (Equation 14.6.1)

Experiment	$[\text{NO}_2] \text{ (M)}$	$[\text{N}_2\text{O}_4] \text{ (M)}$	$Q = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K .

Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q

approach K . If $Q = K$, for example, then the system is already at equilibrium, and no further change in the composition of the system will occur unless the conditions are changed. If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is less than the ratio at equilibrium. Therefore, the reaction will proceed to the right as written, forming products at the expense of reactants. Conversely, if $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is greater than at equilibrium, so the reaction will proceed to the left as written, forming reactants at the expense of products. These points are illustrated graphically in Figure 14.6.1.

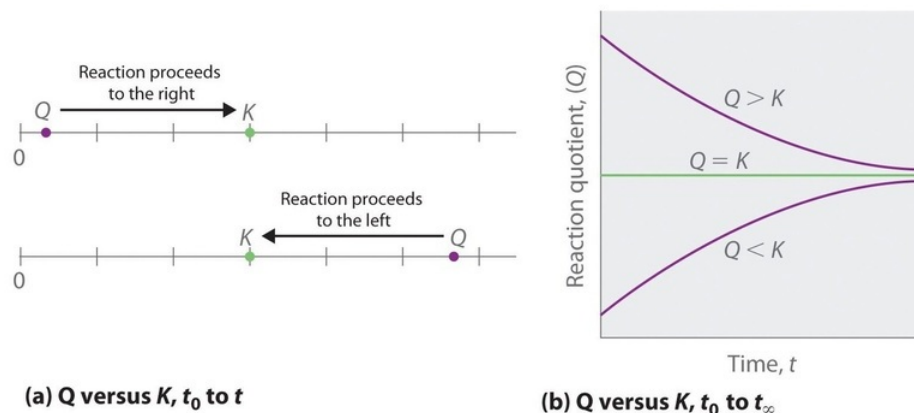
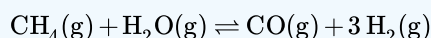


Figure 14.6.1: Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K . (a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K . (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.

If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.

✓ Example 14.6.1: steam-reforming

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a steam-reforming reaction:



$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4 , 8.0×10^{-3} mol of H_2O , 1.6×10^{-2} mol of CO , and 6.0×10^{-3} mol of H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O ?

Given: balanced chemical equation, K , amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

- Calculate the molar concentrations of the reactants and the products.
- Use Equation 14.6.2 to determine Q . Compare Q and K to determine in which direction the reaction will proceed.

Solution:

A: We must first find the initial concentrations of the substances present. For example, we have 1.2×10^{-2} mol of CH_4 in a 2.0 L container, so

$$\begin{aligned} [CH_4] &= \frac{1.2 \times 10^{-2} \text{ mol}}{2.0 \text{ L}} \\ &= 6.0 \times 10^{-3} \text{ M} \end{aligned}$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} M$,
- $[CO] = 8.0 \times 10^{-3} M$, and
- $[H_2] = 3.0 \times 10^{-3} M$.

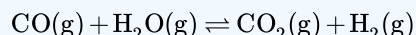
B: We now compute Q and compare it with K :

$$\begin{aligned} Q &= \frac{[CO][H_2]^3}{[CH_4][H_2O]} \\ &= \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} \\ &= 9.0 \times 10^{-6} \end{aligned}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4 .

? Exercise 14.6.1

In the water–gas shift reaction introduced in Example 14.6.1, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:



$K = 0.64$ at 900 K. If 0.010 mol of both CO and H_2O , 0.0080 mol of CO_2 , and 0.012 mol of H_2 are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer

$Q = 0.96$ ($Q > K$), so the reaction will proceed to the left, and CO and H_2O will form.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K , such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:



Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of CO_2 at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 14.6.2 which shows a plot of $[CO_2]$ versus the amount of $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to CO_2 because the amount of $PbCO_3$ is not sufficient to give a CO_2 concentration equal to K . Thus the left portion of the graph represents a system that is not at equilibrium because it contains only $CO_2(g)$ and $PbO(s)$. In contrast, when just enough $PbCO_3$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the CO_2 concentration: the graph is a horizontal line. Thus any CO_2 concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $PbCO_3$ and PbO are present. For example, the point labeled A in Figure 14.6.2 lies above the horizontal line, so it corresponds to a $[CO_2]$ that is greater than the equilibrium concentration of CO_2 ($Q > K$). To reach equilibrium, the system must decrease $[CO_2]$, which it can do only by reacting CO_2 with solid PbO to form solid $PbCO_3$. Thus the reaction in Equation 14.6.5 will proceed to the left as written, until $[CO_2] = K$. Conversely, the point labeled B in Figure 14.6.2 lies below the horizontal line, so it corresponds to a $[CO_2]$ that is less than the equilibrium concentration of CO_2 ($Q < K$). To reach equilibrium, the system must increase $[CO_2]$, which it can do only by decomposing solid $PbCO_3$ to form CO_2 and solid PbO . The reaction in Equation 14.6.5 will therefore proceed to the right as written, until $[CO_2] = K$.

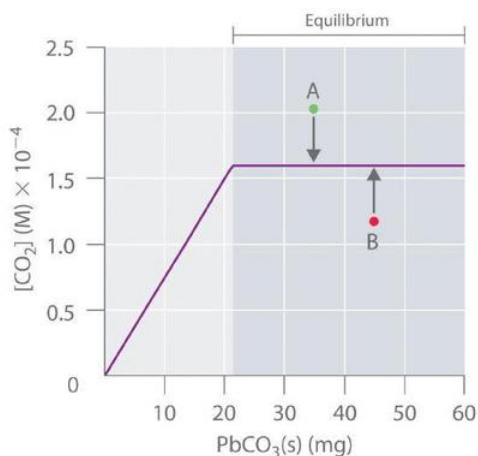


Figure 14.6.2: The Concentration of Gaseous CO_2 in a Closed System at Equilibrium as a Function of the Amount of Solid $PbCO_3$ Added. Initially the concentration of $CO_2(g)$ increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to $CO_2(g)$ and solid PbO . Once the CO_2 concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2]$, as long as the temperature remains constant.

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:



and the equilibrium constant K is $[H_2O]/[H_2]$. If $[H_2O]$ is doubled at equilibrium, then $[H_2]$ must also be doubled for the system to remain at equilibrium. A plot of $[H_2O]$ versus $[H_2]$ at equilibrium is a straight line with a slope of K (Figure 14.6.3). Again, only those pairs of concentrations of H_2O and H_2 that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 14.6.6 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point A in Figure 14.6.3 lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture ($Q < K$). Thus the reaction in Equation 14.6.6 will proceed to the right as written, consuming H_2 and producing H_2O , which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point B in Figure 14.6.3 lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture ($Q > K$). Thus the reaction in Equation 14.6.6 will proceed to the left as written, consuming H_2O and producing H_2 , which causes the concentration ratio to move down and to the right toward the equilibrium line.

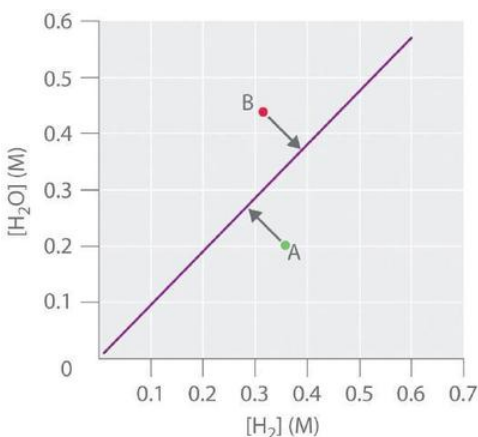
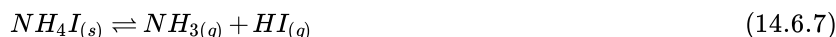


Figure 14.6.3: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO(s) + H_{2(g)} \rightleftharpoons Cd(s) + H_2O(g)$ System at Equilibrium. For any equilibrium concentration of $H_2O(g)$, there is only one equilibrium concentration of $H_2(g)$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K .

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:



For this system, K is equal to the product of the concentrations of the two products: $[NH_3][HI]$. If we double the concentration of NH_3 , the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 14.6.4. As a result, for a given concentration of either HI or NH_3 , only a single equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which $[NH_3] = [HI] = K^{1/2}$. Any point that lies below and to the left of the equilibrium curve (such as point A in Figure 14.6.4) corresponds to $Q < K$, and the reaction in Equation 14.6.7 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point B in Figure 14.6.4) corresponds to $Q > K$, and the reaction in Equation 14.6.7 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

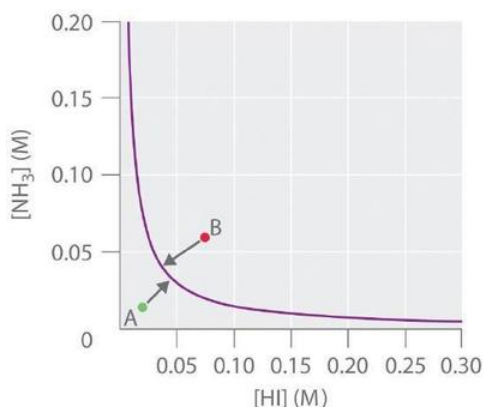


Figure 14.6.4: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for the $NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)}$ System at Equilibrium. Only one equilibrium concentration of $NH_{3(g)}$ is possible for any given equilibrium concentration of $HI_{(g)}$. In this case, the two are inversely proportional. Thus a large $[HI]$ at equilibrium requires a small $[NH_3]$ at equilibrium and vice versa.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_p). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.



Video 14.6.1: See www.youtube.com/watch?v=pnU7ogsgUW8 to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O₂, and NO₂ are at equilibrium:



The formation of additional amounts of NO₂ decreases the total number of molecules in the system because each time two molecules of NO₂ form, a total of three molecules of NO and O₂ are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO₂ into NO and O₂, which tends to restore the pressure.

Now consider this reaction:

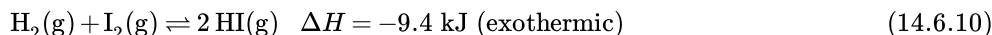


Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the Reaction Quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.



Because this reaction is exothermic, we can write it with heat as a product.



Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H₂ and I₂ and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H₂ and I₂ decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO₂ and N₂O₄ in this reaction



The positive ΔH value tells us that the reaction is endothermic and could be written



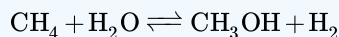
At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO₂ molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N₂O₄ increases, and the concentration of brown NO₂ decreases, causing the brown color to fade.

📌 Temperature is Neither a Reactant nor Product

It is not uncommon that textbooks and instructors to consider heat as a independent "species" in a reaction. While this is rigorously incorrect because one cannot "add or remove heat" to a reaction as with species, it serves as a convenient mechanism to predict the shift of reactions with changing temperature. For example, if heat is a "reactant" ($\Delta H > 0$), then the reaction favors the formation of products at elevated temperature. Similarly, if heat is a "product" ($\Delta H < 0$), then the reaction favors the formation of reactants. A more accurate, and hence preferred, description is discussed below.

✓ Example 14.6.2: Steam Reforming of Methane

The commercial production of hydrogen is carried out by treating natural gas with steam at high temperatures and in the presence of a catalyst ("steam reforming of methane"):



Given the following boiling points: CH_4 (methane) = -161°C , H_2O = 100°C , CH_3OH = 65° , H_2 = -253°C , predict the effects of an increase in the total pressure on this equilibrium at 50° , 75° and 120°C .

Solution

To identify the influence of changing pressure on the three reaction conditions, we need to identify the correct reaction including the phase of each reactant and product. Calculate the change in the moles of gas for each process:

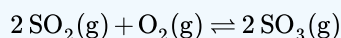
Temperature

Equation
Δn_g
shift

50°	$[\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{OH}(\text{l}) + \text{H}_2(\text{g})]$	0	none	75°	$[\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{OH}(\text{g}) + \text{H}_2(\text{g})]$	+1	to left	120°	$[\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g}) + \text{H}_2(\text{g})]$	0	none
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? Exercise 14.6.2

What will happen to the equilibrium when the volume of the system is decreased?



Answer

Decreasing the volume leads to an increase in pressure which will cause the equilibrium to shift towards the side with fewer moles. In this reaction, there are three moles on the reactant side and two moles on the product side, so the new equilibrium will shift towards the products (to the right).

Summary

The Reaction Quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction. Reaction Quotient:

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The Reaction Quotient (Q or Q_p) has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium.

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Footnotes

1. Herrlich, P. "The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?" *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

Contributors and Attributions

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