Le Chatelier's Principle

Imagine a tightrope walker balanced on a thin wire. The smallest gust of wind could cause the tightrope walker to lose her balance. Luckily, she is able to maintain her balance by adjusting the long pole she carries.

In a similar way, a chemical reaction at equilibrium can be disturbed and shifted away from equilibrium. Instead of a gust of wind, the factors that alter chemical equilibria are concentrations of reactants and products, pressure, and temperature.

The effects of changes in concentrations, pressure, and temperature can be predicted using Le Chatelier's principle.

Le Chatelier's principle states that if a chemical system at equilibrium is disturbed by a change in a property, the system adjusts in a way that opposes the change.

The application of Le Chatelier's principle involves an initial equilibrium state, a shifting "non-equilibrium" state, and a new equilibrium state.

Changes in Concentration

If more of a particular substance is added to a reaction at equilibrium, the concentration of that substance increases. The reaction will return to equilibrium by consuming some of the added substance.

- adding reactants to a system at equilibrium results in a shift to the right (reactants are consumed and products are produced)

- adding products to a system at equilibrium results in a shift to the left (reactants are produced and products are consumed)

Conversely, if a substance is removed, its concentration decreases. The reaction will return to equilibrium by producing more of the substance that was removed.

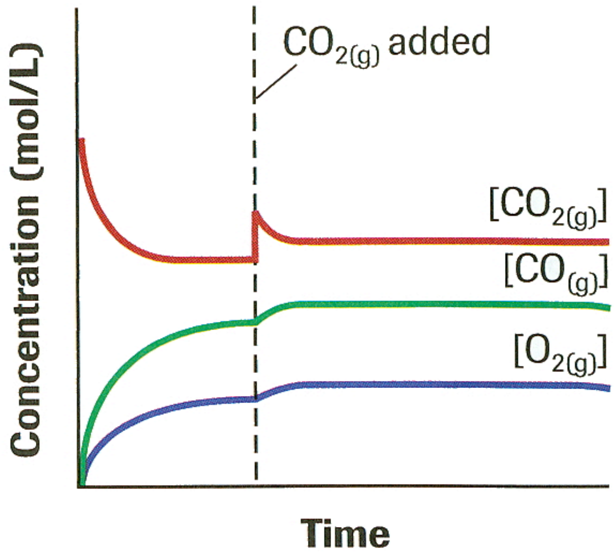
- removing reactants from a system at equilibrium results in a shift to the left (reactants are produced and products are consumed)

- removing products from a system at equilibrium results in a shift to the right (reactants are consumed and products are produced)

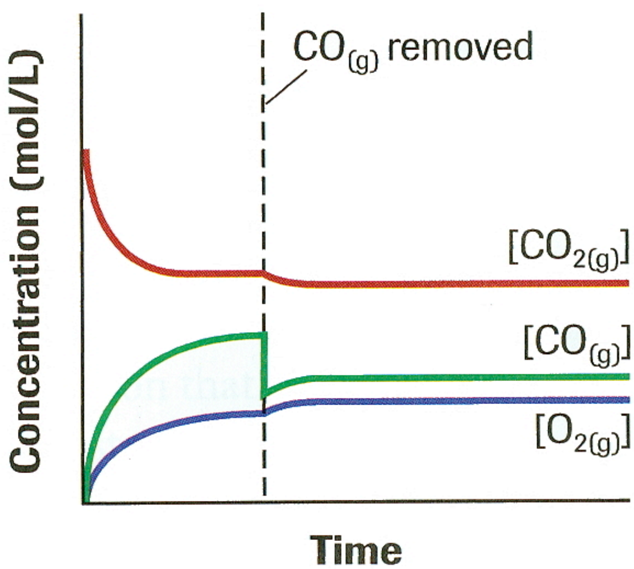
Consider the reaction below

$$2CO_2(g) \Leftrightarrow 2CO(g) + O_2(g)$$

If additional carbon dioxide is added to this system at equilibrium, the equilibrium will shift to remove some of the added carbon dioxide. In other words, the equilibrium will shift to the right (the forward reaction). Carbon dioxide will be consumed, while additional carbon monoxide and oxygen gas are produced. The concentration-time graph below illustrates this equilibrium shift.



The removal of a product will also shift the equilibrium forward, to the right. For example, if carbon monoxide was removed, the equilibrium would shift to the right to replace some of the removed carbon monoxide. The concentration-time graph below illustrates this equilibrium shift.



In chemical equilibrium shifts, the imposed concentration change is normally only partially counteracted. In other words, the concentrations of the reactants and products in the final equilibrium are usually different from the concentrations in the original equilibrium state.

It is important to note that, even though adding or removing a substance shifts the equilibrium position, it has no effect on the equilibrium constant.

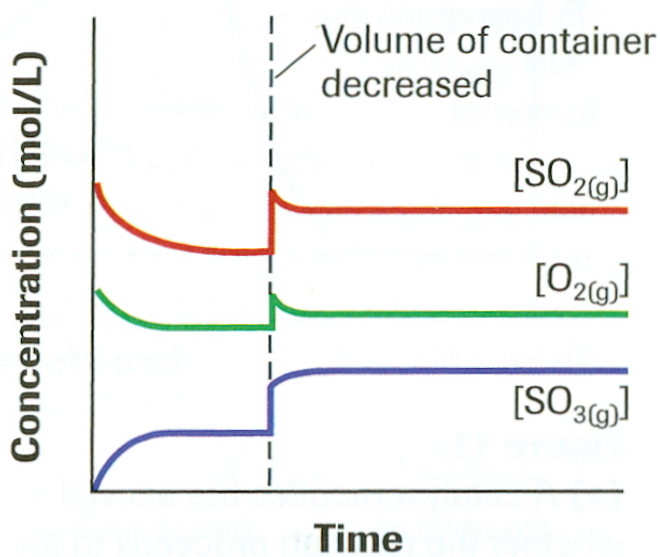
Changes in Pressure

If a system contains one or more gases, a change in volume causes a change in the pressure of the gas. Increasing the volume decreases the pressure. Decreasing the volume increases the pressure.

To predict whether a change in pressure will affect the equilibrium state, we must consider the total number of moles of gas reactants and the total number of moles of gas products. For example, consider the reaction below.

$$\underbrace{2SO_2(g)+O_2(g)}_{\substack{2\ mol+1\ mol \\ 3\ mol}} \Leftrightarrow \underbrace{2SO_3(g)}_{2\ mol}$$

If the volume of the vessel containing this reaction mixture is decreased, the overall pressure is increased. Le Chatelier's principle suggests that the system will react in a way that resists the change (i.e. in a way that reduces the pressure). In this case, the equilibrium will shift to the right, which decreases the number of gas molecules in the container and reduces the pressure (see graph below).



If the volume of the vessel is increased, the pressure is decreased, and the shift is in the opposite direction, to the left, which counteracts the change by producing more gas molecules.

A system with equal numbers of gas molecules on each side of the equation will not shift after a change in volume, since no shift can change the pressure in the vessel.

Systems involving only liquids or solids are not affected by changes in pressure. Substances in these condensed states are virtually incompressible, and so reactions involving them cannot counteract pressure changes.

Changes in Temperature

The energy in a chemical equilibrium equation can be treated as though it were a reactant or a product.

Endothermic reaction: $reactants + energy \Leftrightarrow products$

Exothermic reaction: $reactants \Leftrightarrow products + energy$

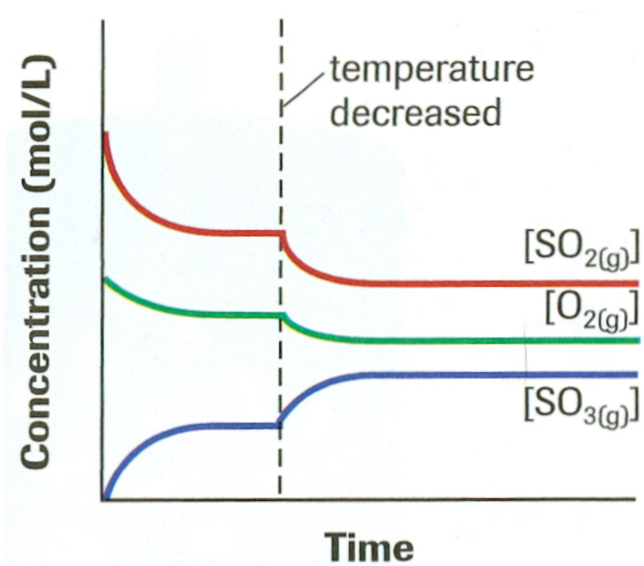
Energy can be added to or removed from a system by heating or cooling the container. In either situation, the equilibrium shifts to minimize the change.

If the container is cooled, the system tries to "warm" itself and the equilibrium shifts in the direction that produces heat (towards the side of the equation containing "energy"). If the container is heated, the equilibrium shifts in the direction that absorbs heat (away from the side of the equation containing "energy").

In the exothermic production of sulfur trioxide, as part of the contact process for making sulfuric acid, the product is favored if the temperature of the system is kept low.

$$2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g) + energy$$

Removing energy (cooling) causes the system to shift to the right. This shift yields more sulfur trioxide while at the same time partially replacing the energy that was removed. The graph below illustrates this equilibrium shift.



Changes That Don't Affect Equilibrium Position

We have looked at three changes that have an effect on the equilibrium of a chemical system—concentration changes, energy (temperature) changes, and pressure (volume) changes. There are other changes that have no effect on the equilibrium position of a chemical system.

Adding Catalysts

A catalyst decreases the time required to reach equilibrium, but does not affect the final position of equilibrium. The presence of a catalyst in a chemical reaction system lowers the activation energy of both the forward and reverse reactions by the same amount, so the equilibrium establishes much more quickly but at the same position as it would without the catalyst. Forward and reverse rates are increased equally.

Adding Inert Gases

The pressure of a gaseous system can be changed by adding a gas while keeping the volume constant. If the gas is inert in the system, for example, if it is a noble gas or if it cannot react with the entities in the system, the equilibrium position of the system will not change.

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WORKSHEET FOR LE CHATELIER'S PRINCIPLE

For each of the following equilibrium reactions an action or activity has taken place that will initially alter the equilibrium of the reactions. You are to read the action performed and predict its effect on the chemical reactions. State which reaction becomes "dominant". State if the shift on the equilibrium is to the right or to the left. State whether the reactant listed increases or decreases in concentration as a result of the initial action.

$$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)} + 92KJ$$

Action	Reaction Becoming dominant	Direction of shift	Effect on [N2]	Effect on [H2]	Effect on [NH3]	Effect on Temperature in vessel
Add N_2						
Remove NH_3						
Increase temp.						
Increase Pressure						
Remove H_2						

$$PBr_{5\ (g)} + 75\ KJ \leftrightarrow PBr_{3\ (g)} + Br_{2\ (g)}$$

Action	Reaction Becoming dominant	Direction of shift	Effect on $[PBr_5]$	Effect on $[PBr_3]$	Effect on $[Br_2]$	Effect on Temperature in vessel
AddBr_2						
Remove PBr_3						
Increase Temp.						
Increase Pressure						
Cool the Reaction						

$2SO_{3(g)}$ + 200KJ ⇔ $2SO_{2(g)}$ + $O_{2\,(g)}$

Action	Reaction Becoming dominant	Direction of shift	Effect on [SO3]	Effect on [SO2]	Effect on [O2]	Effect on Temperature in vessel
Remove SO_2						
Heat the reaction						
Lower Pressure						
Cool the reaction						
Increase O_2						

$SO_{2(g)}$ + $NO_{2(g)}$ ⇔ $SO_{3(g)}$ + $NO_{(g)}$ + 150 KJ

Action	Reaction Becoming dominant	Direction of shift	Effect on [SO2]	Effect on [NO2]	Effect on [SO3]	Effect on [NO]	Effect on Temperature in vessel
Remove NO_2							
Add NO_2							
Increase pressure							
Lower Temp.							
Add SO_3							

$UO_{2(g)}$ + $4HF_{(g)}$ + 450 Kj ⇔ $UF_{4(g)}$ + $2H_2O_{(g)}$

Action	Reaction Becoming dominant	Direction of shift	Effect on [UO2]	Effect on [HF]	Effect on [UF4]	Effect on [H2O]	Effect on Temperature in vessel
Add H_2O							
Increase temp.							
Lower pressure							
Remove UF_4							
Add HF							