

Factors Affecting Chemical Equilibrium: Le Chatelier's Principle

Le Chatelier's Principle is useful in predicting how a system at equilibrium will respond when certain changes are imposed. Le Chatelier's Principle does NOT explain why the system changes, and is not an acceptable explanation for the change. It merely allows you to determine quickly how the system will change when a disturbance is imposed.

There are three common ways a stress may be applied to a chemical system at equilibrium:

1. changing the concentration (or partial pressure) of a reactant or product.
2. changing the temperature.
3. changing the volume of the container (which changes partial pressure of all gases in the reaction).

You should be aware that adding a gaseous substance that is not involved in the reaction changes the total pressure in the system but does not change the partial pressure of any of the reactants or products and therefore does not affect the equilibrium.

Le Chatelier's Principle states when a system at equilibrium is disturbed, the equilibrium shifts so as to partially undo (counteract) the effect of the disturbance.

Changes in Concentration or Partial Pressure

If a system at equilibrium is disturbed by adding a reactant or removing a product, Le Chatelier's Principle predicts that the equilibrium will shift forward, thus using up some of the added reactant or producing more of the removed product. In this way, the equilibrium shift partially counteracts the disturbance. Similarly, if the disturbance is the removal of a reactant or the addition of a product, the equilibrium will shift backward, thus producing more of the removed reactant or using up some of the added product. Once again, the shift tends to "undo" the disturbance. It should be noted that when the disturbance is an increase or decrease of concentration of reactant or product, the equilibrium shift tends to partially return the concentration to its former value but it never gets all the way back to the former value.

The equilibrium constant value, K_e is not changed by the addition or removal of reactants or products. Since the concentration of solids are constant, they do not appear in the equilibrium constant expression and their concentrations do not change when disturbances cause equilibrium shifts, however, the amount of the solid present most certainly does change. The amount of solid can increase or decrease but the concentration does not change.

Changes in Temperature

Increasing the temperature of a system at equilibrium increases both forward and reverse reaction rate, but it increases the endothermic reaction more than the exothermic. Therefore, in an exothermic reaction, the reverse reaction is endothermic and so increasing the temperature will increase the reverse reaction more than the forward reaction, and the equilibrium will shift backwards. Since the forward reaction produces heat and the reverse reaction consumes heat, Le Chatelier's Principle predicts that when heat is added, the equilibrium will shift backward, consuming heat, and thus partially countering the disturbance. Cooling an exothermic reaction slows both reactions but it slows the reverse

more than the forward, hence the equilibrium will shift forward producing more heat, thus partially undoing the stress.

For an endothermic reaction, all the same logic is involved except that the forward reaction is endothermic and the reverse reaction is exothermic. Therefore, heating an endothermic reaction causes the equilibrium to shift forward, and cooling an endothermic reaction causes the equilibrium to shift backward.

When an equilibrium shifts due to a temperature change all the substances on one side of the equation move in the same direction, that is, they all increase or they all decrease. Therefore, the equilibrium constant value will also change when the temperature is changed.

Changes in Volume

When the volume of a reaction vessel is decreased, the partial pressure (and concentration) of all gases in the container increase. The total pressure in the vessel will also increase. Le Chatelier's Principle predicts that the equilibrium will shift in a direction that tends to counteract the disturbance. Therefore, the equilibrium will shift to produce fewer moles of gaseous substances so that the pressure will decrease. Thus, decreasing the volume will cause the equilibrium to shift toward the side with fewer moles of gaseous substances. The reverse is true if the volume of the vessel is increased. The partial pressure of all gases will decrease, and the total pressure will decrease, so the equilibrium shift will be toward the side that contains more moles of gas, thus increasing pressure and partially counteracting the change.

The Addition of a Catalyst

The addition of a catalyst will increase both forward and reverse reaction rates. In the case of a catalyst, both reaction rates are increased by the same amount and therefore there will be no equilibrium shift.