

Factors That Affect Chemical Equilibrium

Chemical equilibrium is a very delicate system that represents a perfect balance between forward and reverse reaction. A small disturb in the equilibrium may shift the equilibrium position either to right forming more products or to left forming more reactants. This reaction by the system is of course temporary and eventually the system will come back to equilibrium. This phenomenon can be expressed in the form of Le Chatelier's Principle.

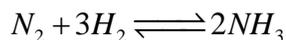
Le Chatelier's Principle

An important and very interesting qualitative principle governing the equilibrium is the principle of Le Chatelier. This principle, which is named after the French chemist Henry Louis Le Chatelier (1850-1936), may be stated as follows: *if an external stress is applied to a system at equilibrium, the system will tend to react in such way as to relieve the applied stress and tries to reestablish the equilibrium.* In chemical reaction terminology, the "stress" means change in concentration, pressure, volume or temperature.

Le Chatelier's principle can be understood either qualitatively or quantitatively doing some problems. However, we restrict ourselves only to qualitative explanation.

Change in Concentration

Consider the following equilibrium reaction



- (a). What happens if we increase the concentration of N_2 by adding more N_2 ?
- (b). What happens if we increase the concentration of H_2 by adding more H_2 ?
- (c). What happens if we increase the concentration of NH_3 by adding more NH_3 ?

- (d). What happens if we decrease the concentration of N_2 by removing some N_2 ?
- (e). What happens if we decrease the concentration of H_2 by removing some H_2 ?
- (f). What happens if we decrease the concentration of NH_3 by removing some NH_3 ?

Answer

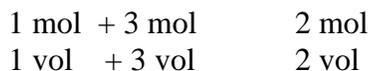
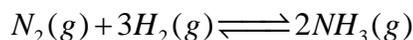
- (a) and (b). The answers to question (a) and (b) are the same. If we add either N_2 or H_2 , we increase the collisions between N_2 and H_2 thereby forming more product NH_3 . This is how the equilibrium counteracts the applied stress; **we say the equilibrium shifts from left to right.**
- (c) If we add more NH_3 , we increase the concentration of NH_3 . As a result, some NH_3 decomposes and forms more reactants. **We say the equilibrium shifts from right to left.**

- (d) and (e). The answers to question (d) and (e) are the same. If we remove either N_2 or H_2 , now there is less concentration of N_2 and H_2 . To offset the applied stress, the **equilibrium shifts from right to left**.
- (f) If we remove some NH_3 , **the equilibrium shifts from left to right** to counteract the applied stress.

Changes in Pressure and Volume

Pressure does not have any effect on concentrations of species that are present in solid, liquid or solution form. On the other hand, the change in pressure affects the concentrations of gases. According to ideal gas law, pressure and volume are inversely proportional to each other; the greater the pressure, the smaller the volume, and vice versa. Thus, it is just enough to understand the affect of change in pressure on the equilibrium system.

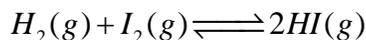
Let us consider the following equilibrium reaction:



What will happen if we increase the pressure (decrease the volume) on the system at constant temperature?

In order to understand the affect of pressure, it is very important to understand the total volume of reactants and products. According to Avogadro's law, the number of moles is directly proportional to the volume of the gas. Think that one mole is one volume. Therefore, there are 4 volumes (1 vol + 3 vol) on the reactant side and 2 volumes on the product side. The increase in pressure always affects the side that has more volume. Hence, increase in pressure **shifts the equilibrium from left to right**.

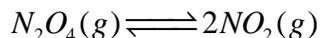
The pressure has no effect if the total volume of reactants is equal to the total volume of the products as in the following example.



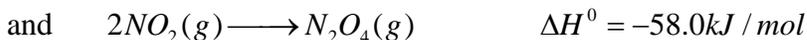
Changes in Temperature

A change in concentration, pressure or volume alters the position of the equilibrium but not the magnitude (value) of the equilibrium constant. However, the change in temperature changes the value of the equilibrium constant. To understand the effect of temperature, we must know whether the reaction is endothermic (absorption of heat) or

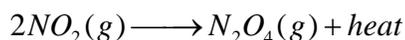
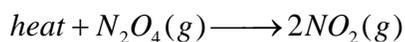
exothermic (release of heat). Let us consider the equilibrium reaction between dinitrogen tetroxide and nitrogen dioxide:



This reaction is endothermic in the forward direction and exothermic in the reverse direction:



To understand the effect of temperature (heat), let us re-write the above equations treating the heat as chemical reagent. Thus



Therefore, increase in temperature favors the endothermic reaction (forward reaction, i.e. left to right) while decrease in temperature favors the exothermic reaction (reverse reaction, i.e., right to left). What does it mean? It means that the value of the equilibrium constant increases when the heat is added (increase in temperature) and decreases when the heat is removed (cooling the system) that can be explained by the following equilibrium constant expression:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

I let your imagination chase this explanation!

The Effect of a Catalyst

The function of a catalyst is to speed up the reaction by lowering the activation energy. The catalyst lowers the activation energy of the forward reaction and reverse reaction to the same extent. Due to this, there is no shift in equilibrium or the change in the value of the equilibrium constant. Therefore, we conclude that the **catalyst has no effect on the equilibrium system.**