The Concept of Equilibrium

There are two kinds of chemical reactions; those proceeding in only one direction that are known as **irreversible reactions**, and those proceeding in both directions that are known as **reversible reactions**. Irreversible reactions always proceed from reactants to products and go to completion when the reactants are exhausted. This situation is usually indicated by a single arrow going from reactants to products as shown below:

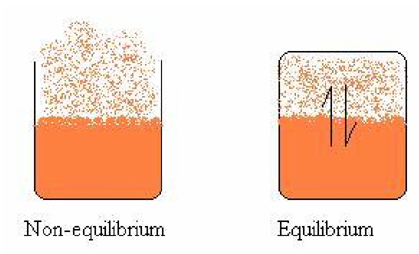
$$aA + bB + ... \longrightarrow cC + dD + ...$$

On the other hand, reversible reactions, at the start of the reaction, behave like irreversible reactions but some point in time, products begins to transform back into reactants. Eventually, the rate of the forward reaction becomes equal to the rate of reverse or backward reaction. When this happens, we say the **chemical equilibrium** has established or the chemical reaction has attained the equilibrium. This situation is usually indicated by double arrows going in opposite directions ($\rightleftarrows$) or two half-arrows ($\rightleftharpoons$) going in opposite directions:

$$aA + bB + ... \rightleftharpoons cC + dD + ...$$

When the chemical equilibrium is established, the concentrations of reactants and products do not change any more. That does not mean that concentrations of reactants are equal to the concentrations of products.

In order to understand the chemical equilibrium, let us consider the following two experiments. In the first beaker a pure solvent, such as, water is heated to the boiling point. At this point, water begins to boil. As a result, the liquid starts converting into gas that escapes into the surrounding. If we keep on heating the beaker, all the liquid eventually disappears into the surrounding in the form of gas. This is known as a non-equilibrium system(irreversible). In the second beaker, we have slightly altered the experiment by closing the mouth of the beaker. When the beaker is heated to the billing point, the liquid begins to boil and converts into the gas. This continue until all the empty space is



occupied by the gaseous molecules. Upon further heating, more gaseous molecules are produced but they cannot escape to the surrounding as in the first experiment. As a result, the same number of molecules returns to the liquid surface. Eventually, the number of molecules leaving the liquid surface becomes equal to the number of molecules returning to the liquid surface making the rate of going up into the gaseous phase equal to rate of coming down to the liquid surface thereby establishing the equilibrium, which is shown by double half-arrows in the second beaker. This equilibrium involves two phases of the same substance; it is refer to as physical rather than chemical equilibrium. **The term chemical equilibrium refers to the equilibrium in chemical reactions where different substances as reactants and products are involved.** If the above experiment refers to water, the number of H_2O molecules leaving the liquid phase is equal to the number of H_2O molecules returning to the liquids phase, which is expressed as

$$H_2O(l) \rightleftharpoons H_2O(g)$$

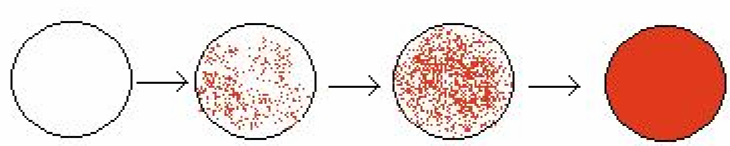
How Do We Know When the Equilibrium is Established?

In order to monitor this visually, it is critical that the reactant(s) and product(s) must have different visual display qualities, such as, different colors. When the equilibrium is attained, both colors are mixed and the resultant color will emerge that should also have visual display quality. This is best illustrated by equilibrium between dinitrogen tetroxide (N_2O_4) and nitrogen dioxide (NO_2) :

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

colorless *dark brown*

Suppose we started the reaction by placing some quantity of N_2O_4 (colorless) gas in an evacuated flask. Some brown color appears immediately indicating the formation of some NO_2 gas. The color becomes more intensified as more NO_2 gas is formed by the dissociation N_2O_4 gas. The color intensification continues until the equilibrium is reached. No further change in color takes place beyond the equilibrium.



N_2O_4 (g) equilibrium

The Equilibrium Constant Expression

To understand how to set up an equilibrium constant expression, let us consider the following general chemical reaction:

$$aA + bB \rightleftharpoons cC + dD$$

Where *a,b,c,* and *d* are the stoichiometric coefficients for A, B, C, and D. The equilibrium constant expression for the above reaction at a particular temperature is written as

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

where [ ] used to mean equilibrium molar concentration (mol/l or M). The K is known as an **equilibrium constant**, which relates the equilibrium concentrations of reactants to the concentrations of products. It is important to note the way the expression is written; it is the ratio of product of concentrations of products raised to the power of their respective coefficients (number of moles) to the product of concentrations of reactants raised to the power of their respective coefficients(number of moles). Writing the above mathematical expression for K is known as *law of mass action*.

Chemical reactions, whether reversible or non-reversible, follow the chemical kinetics. Thus we can gain better understanding of the equilibrium constant K by using the concept of chemical kinetics. Let k_f be the rate of forward reaction and k_r be the rate of reverse reaction as shown below.

$$aA + bB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

Then the forward rate is given by

$$\text{rate}_f = k_f\,[A]^a\,[B]^b$$

and the reverse rate by

$$\text{rate}_r = k_r\,[C]^c\,[D]^d$$

At equilibrium, the forward rate becomes equal to reverse rate as a result of no net change in concentrations of either reactants or products. Thus

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

or $$k_f[A]^a\,[B]^b = k_r\,[C]^c\,[D]^d$$

After rearranging the above equation, it takes the following form:

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

Since both k_f and k_r are constants at a given temperature, their ratio is also a constant that is equal to the equilibrium constant K.

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

The equilibrium constant K is a constant at a particular temperature regardless of equilibrium concentrations of the species involved because of quotient k_f / k_r.

The magnitude of the equilibrium constant K is useful in assessing the status of the equilibrium:

If $K = 1$, $[C]^c [D]^d = [A]^a [B]^b$, the reaction is in equilibrium

If $K >> 1$, $[C]^c [D]^d >> [A]^a [B]^b$, the equilibrium lies to the right of the reaction and favors the products

If $K << 1$, $[C]^c [D]^d << [A]^a [B]^b$, the equilibrium lies to the left of the reaction and favors the reactants