

Section 13.1 The Equilibrium Condition

Equilibrium is not static, but is a highly dynamic state. At the macro level everything appears to have stopped but at the molecular level, there is frantic activity. The concentration of products builds as the reaction proceeds. There will come a time, in some reactions, where the products will collide and thus react and reform the reactants. When both the forward and reverse reaction occur at the same rate there is no change in concentration reactants and products and the reaction is said to be at equilibrium.

A double arrow ($\rightleftharpoons$) is used to show that a reaction can occur in either direction.

Section 13.2 The Equilibrium Constant

Let us use the following equation:



where A, B, C, and D represent chemical species and j , k , m , and n are their coefficients in the balanced equation.

Since the concentration of the products and reactants remains constant at equilibrium, we can set up a mass action expression: Which is the concentration of the products (raised to the power of their coefficients) divided by the concentration of the reactants (raised to the power of their coefficients).

$$K_c = \frac{[C]^m [D]^n}{[A]^j [B]^k}$$

This mass action expression can then be used to find a constant for the reaction at a given temperature. This constant is known as the equilibrium expression (K_c or K_{eq}). To change this into an equilibrium expression, set it equal to K_c .

$$K_c = \frac{[C]^m [D]^n}{[A]^j [B]^k}$$

Three conclusions about the equilibrium expression:

1. The equilibrium expression for a reaction is the reciprocal of that for the reaction written in reverse.
2. When the balanced equation for a reaction is multiplied by a factor n , the equilibrium expression for the new reaction is the original expression raised to the n th power. Thus $K_{new} = (K_{original})^n$.
3. The units for K are determined by the powers of the various concentration terms. The units for K therefore depend on the reaction being considered. [See p. 608](#)

Equilibrium position - set of equilibrium concentrations. There is only one equilibrium constant for a particular system at a particular temperature, but there are an infinite number of equilibrium positions. This can tell us in what direction the reaction will proceed (very important later on in this chapter).

Section 13.3 Equilibrium Expressions Involving Pressures

How is pressure related to concentration?

A couple of chapters ago we rearranged the ideal gas law to include molarity (except this time we are going to use C for concentration) -

$$PV = nRT \quad \text{or} \quad P = \left(\frac{n}{V} \right) RT = CRT$$

where C equals n/V , or the number of moles n of gas per unit volume V . Thus C represents the molar concentration of the gas.

****Notes have been derived from Zumdahl 4th ed. - All page and table references are made to this edition.**

If we examine this in terms of the Haber process:



we see that the equilibrium expression would look like -

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{C_{\text{NH}_3}^2}{(C_{\text{N}_2})(C_{\text{H}_2}^3)}$$

or in terms of the equilibrium partial pressures of the gases -

$$K_p = \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)}$$

Since we learned there is a relationship which exists between concentration and pressure, so there must be a relationship between K and K_p

$$K_p = K(RT)^{\Delta n}$$

where " Δn " is the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants. (you can see a derivation of this [equation on p. 611](#))

Section 13.4 Heterogeneous Equilibria

Homogeneous equilibria - where all reactants and products are all the same phase (ex. all gaseous).

Heterogeneous equilibria - where all reactants and products are not in the same phase. These equilibria do not depend on the amounts of pure solids or liquids present (ie. pure solids and liquids are not included in the equilibrium expression).

Section 13.5 Applications of the Equilibrium Constant

(lengthy discussion on p. 615 - p. 617)

Reaction Quotient (Q) - obtained by applying the law of mass action using initial concentrations instead of equilibrium concentrations. This will help us to determine which direction the reaction will proceed in to reach equilibrium.

Let's again examine this in terms of the Haber process :



The expression for the reaction quotient would then be:

$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3}$$

From this equation, 3 conditions may occur

1. Q is equal to K. The system is at equilibrium ; no shift will occur.
2. Q is greater than K. In this case, the ratio of initial concentrations of products to initial concentrations of reactants is too large. To reach equilibrium, a net change of products to reactants must occur. The system shifts to the left, consuming products and forming reactants, until equilibrium is achieved.
3. Q is less than K. In this case, the ratio of initial concentrations of products to initial concentrations of reactants is too small. The system must shift to the right, consuming reactants and forming products, to attain equilibrium.

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Section 13.6 Solving Equilibrium Problems

Here are a series of steps to help aid you in the solving of equilibrium problems:

- Step 1: Write the balanced equation for the reaction.
- Step 2: Write the equilibrium expression using the law of mass action.
- Step 3: List the initial concentrations.
- Step 4: Calculate Q , and determine the direction of the shift to equilibrium.
- Step 5: Define the change needed to reach equilibrium, and define the equilibrium concentrations by applying the change to the initial concentrations.
- Step 6: Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown.
- Step 7: Check your calculated equilibrium concentrations by making sure they give the correct value of K .

Small values of K and the resulting small shift to the right to reach equilibrium allow for simplification. This is okay as long as the resulting change in value is less than 5% of the original value. If not, then you must use the quadratic formula.

Section 13.7 Le Châtelier's Principle

Le Chatelier's Principle - if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change (or in other words, it will shift in the direction to alleviate the stress applied to the system).

Effect of change in concentration

If a reactant or product is added to a system at equilibrium, the system will shift away from the added component, to decrease the amount of the added component. If a reactant or product is removed the system will shift toward the removed component, to make more of the removed component.

Effect of a change in pressure

- (1) The addition of an inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants or products.
- (2) When the volume of the container holding a gaseous system is reduced, the system responds by reducing its own volume. This is done by decreasing the total number of gaseous molecules in the system, so the reaction will shift in the direction which has the least number of molecules.
- (3) Add or remove a gas product or reactant (see concentration change).

Effect of a change in temperature

It is important to realize that although the changes we have discussed so far may alter the equilibrium position, they do not alter the equilibrium constant. The value of K is altered with a change in temperature. If energy is added to an exothermic system at equilibrium by heating it, the shift will occur in the direction which will consume energy, that is, to the left. Opposite would be true for an endothermic equation (ie. the reaction will act like concentration - if heat is added it will shift away from the added energy).