A First Course on Kinetics and Reaction Engineering
Unit 3. Reaction Equilibrium

Overview

This course is divided into four parts, I through IV. Part I reviews some topics related to chemical reactions that most students will have encountered in previous chemical engineering courses. Unit 3 examines chemical reaction equilibrium. More specifically, it shows how to calculate an equilibrium constant and how to use that equilibrium constant to calculate the equilibrium composition of a reacting system. The presentation here is abbreviated; for a more thorough discussion of this topic a textbook devoted to thermodynamics should be consulted (1-5). Equilibrium constants often appear in rate expressions, so the information presented here may be useful in future parts of the course. Whenever one embarks on a reaction engineering analysis of a reacting system, one of the first tasks should be an equilibrium analysis of that system, because it establishes the limiting conversion and selectivity of the reactions taking place.

Learning Objectives

Upon completion of this unit, you should be able to define, in words, the following terms:
  • chemical reaction equilibrium and equilibrium composition

Upon completion of this unit, you should be able to write the defining equation for the following quantities:
  • equilibrium constant at 298K in terms of the standard Gibbs free energy change at 298K, equilibrium constant at T in terms of the equilibrium constant at 298K and the temperature-dependent standard heat of reaction, equilibrium constant in terms of thermodynamic activities and thermodynamic activities in terms of composition variables

Upon completion of this unit, you should be able to perform the following specific tasks and be able to recognize when they are needed and apply them correctly in the course of a more complex analysis:
  • Generate an expression for the equilibrium constant for a reaction as a function of temperature (see Example 3.1)
  • Calculate the equilibrium composition of a reacting mixture given the temperature, pressure and initial composition (see Example 3.2)

Information

Starting with reactants in the proper stoichiometric proportions, some reactions cannot continue to the point where all the reactants are used up. Instead, the reaction stops, even though there are reactants still remaining. Reactions like this are called reversible reactions. The reason why the reaction stops is because it has reached *chemical reaction equilibrium*. Through thermodynamics, it is possible to calculate how much reaction will have taken place when the reaction reaches equilibrium. That is, one can calculate the equilibrium conversion of the reactants. The corresponding composition of the system is called the *equilibrium composition*. The first step is to calculate the equilibrium constant for the reaction. The equilibrium "constant" is not really a constant at all. It depends upon the temperature. The calculation

of an equilibrium constant for a reaction can be accomplished in three steps. First the standard Gibb's free energy change at 298 K is calculated for the reaction. Unit 2 explained how to do this. The resulting value is next used to calculation the equilibrium constant at 298 K, and finally the equilibrium constant at any other temperature T is calculated. This last step makes use of the standard heat of the reaction as a function of temperature, which was also considered in Unit 2.

The equilibrium constant for reaction j at 298 K, K_j(298 K), is found using equation (3.1). In equation (3.1), $\Delta G_j^0\left(298 \text{ K}\right)$ represents the standard change in the Gibb's free energy for reaction j at 298 K and R is the ideal gas constant. Equation (3.1) cannot be used directly to calculate the equilibrium constant at any temperature other than 298 K. The reason is that the standard change in the Gibb's free energy depends upon temperature. If the standard change in the Gibb's free energy for reaction j, $\Delta G_j^0\left(T\right)$, is known at some particular temperature T, then equation (3.2) can be used to find the equilibrium constant for reaction j, $K_j(T)$, at temperature T. More often, $\Delta G_j^0\left(T\right)$ is not known and equation (3.3) is used to find a value (or an expression) for the equilibrium constant at temperatures, T, other than 298 K.

$$K_j\left(298 \text{ K}\right) = \exp\left\{\frac{-\Delta G_j^0\left(298 \text{ K}\right)}{R\left(298K\right)}\right\} \tag{3.1}$$

$$K_j\left(T\right) = \exp\left\{\frac{-\Delta G_j^0\left(T\right)}{RT}\right\} \tag{3.2}$$

$$\frac{d\left(\ln\left(K_j\left(T\right)\right)\right)}{dT} = \frac{\Delta H_j^0\left(T\right)}{RT^2} \tag{3.3}$$

An expression for the equilibrium constant is found by separating the variables in equation (3.3) (giving equation (3.4)), integrating the result (giving equation (3.5)) and rearranging that result (giving equation (3.6)). In order to evaluate the integral in equation (3.6) an expression for the standard heat of reaction as a function of T is needed, and this can be found in the manner described in Unit 2.

$$d\left(\ln\left(K_j\left(T\right)\right)\right) = \frac{\Delta H_j^0\left(T\right)}{RT^2}dT \tag{3.4}$$

$$\int_{\ln\left(K_j\left(298 \text{ K}\right)\right)}^{\ln\left(K_j\left(T\right)\right)} d\left(\ln\left(K_j\left(T\right)\right)\right) = \int_{298K}^{T} \frac{\Delta H_j^0\left(T\right)}{RT^2}dT \tag{3.5}$$

$$K_j\left(T\right) = K_j\left(298 \text{ K}\right)\exp\left\{\int_{298 \text{ K}}^{T} \frac{\Delta H_j^0\left(T\right)}{RT^2}dT\right\} \tag{3.6}$$

The equilibrium constant, once its value in known, can be used to calculate the equilibrium composition of a reacting mixture. The initial composition of the mixture and the temperature and

pressure are needed to perform the calculation. Here one method for calculating equilibrium compositions is presented, but there are other approaches that can be used [1]. The first step in performing an equilibrium analysis is to identify a set of mathematically independent reactions from among all the reactions taking place (see Unit 1 and Supplemental Unit S1). Next, an equilibrium constant is calculated for each mathematically independent reaction at the temperature of interest, as described above.

Equation (3.7) relates the equilibrium constant to the thermodynamic activities, a_i, of the reactant and product species. In this equation, the symbol that looks like a large Greek letter pi signifies a continuous product. A continuous product is like a summation except the terms are multiplied together instead of added together. Recall that the stoichiometric coefficient of a reactant is negative and that of a product is positive in equation (3.7).

$$K_j(T) = \prod_{\substack{i=\text{all} \\ \text{species}}} a_i^{v_{i,j}} \tag{3.7}$$

The thermodynamic activity of species i is related to the fugacity of that species as it exists in the mixture, $\hat{f}_i$, and the fugacity of pure i in its standard state, $f_{i(ss)}$, as given in equation (3.8). For gases the standard state is usually taken to be an ideal gas at 1 atm. For this standard state, $f_{i(ss)}$ is equal to 1 atm. The fugacity of i as it exists in the mixture, $\hat{f}_i$, can be related to the composition. For a mixture of ideal gases equation (3.9) gives the relationship. Equation (3.10) is used when the gases are not ideal. In equation (3.9) and equation (3.10) y_i is the mole fraction of species i and φ_i is its fugacity coefficient.

$$a_i = \frac{\hat{f}_i}{f_{i(ss)}} \tag{3.8}$$

$$\hat{f}_i = y_i P \qquad \text{(ideal gases)} \tag{3.9}$$

$$\hat{f}_i = y_i \varphi_i P \qquad \text{(non-ideal gases)} \tag{3.10}$$

The fugacity coefficient, φ_i, can be calculated from the equation of state. For example, Smith and Van Ness [2] present plots of φ_i as a function of reduced pressure and temperature which result from using the law of corresponding states. Reid, Prausnitz and Sherwood [3] present equations for φ_i based upon other equations of state.

Combining equation (3.8) with either equation (3.9) or equation (3.10), and using the ideal gas at 1 atm as the standard state gives a relationship between thermodynamic activity and composition as expressed in equations (3.11) and (3.12).

$$a_i = \frac{y_i P}{1 \text{ atm}} \qquad \text{(ideal gases)} \tag{3.11}$$

$$a_i = \frac{y_i \varphi_i P}{1 \text{ atm}} \qquad \text{(non-ideal gases)} \tag{3.12}$$

For liquid solutions there are several ways to relate the thermodynamic activity to the composition. Equations (3.13) through (3.15) present three such relationships that are often used.

$$a_i = x_i \qquad \text{(ideal solutions)} \qquad (3.13)$$

$$a_i = h_i x_i \qquad \text{(non-ideal solutions where } i \text{ obeys Henry's law)} \qquad (3.14)$$

$$a_i = \gamma_i x_i \qquad \text{(non-ideal solutions in general)} \qquad (3.15)$$

In these equations x_i is the liquid phase mole fraction of species i, h_i is the Henry's Law constant for species i, and γ_i is the activity coefficient for species i. For a solid material, the standard state and the actual state are usually identical. Therefore, for a solid material the thermodynamic activity is usually equal to unity. The mole fractions (x denoting liquid phase and y denoting gas phase) in the preceding equations are defined in equation (3.16) where n_i represents the number of moles of species i and n_{total} represents the total number of moles in the associated phase.

$$y_i \text{ (or } x_i) = \frac{n_i}{n_{total}} \qquad (3.16)$$

The number of moles of each of the various species are related to each other through the initial composition and the stoichiometry of the reaction(s). That is, the number of moles of the species are expressed in terms of the initial number of moles and the extents of the independent reactions as described in Unit 1. After substitution into the equilibrium expressions for the independent reactions, this leads to a set of n equations (where n is the number of mathematically independent reactions) in n unknowns (the n independent extents of reaction). Once the extents of reaction have been determined, the equilibrium composition can be found through use of the definition of extent of reaction or through a mole table.

References Cited

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5. Bakzhizer, R.E., M.R. Samuels, and J.D. Ellaissen, Chemical Engineering Thermodynamics. 1972, Engelwood Cliffs, NJ: Prentice-Hall.