A First Course on Kinetics and Reaction Engineering
Unit 1. Stoichiometry and Reaction Progress

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. This first unit reviews some basic concepts related to chemical reactions. Reaction stoichiometry is considered first, including the sign convention for stoichiometric coefficients that will be used throughout this course. The remainder of the unit reviews how stoichiometry can be used when calculating the composition of a reacting system as the reaction or reactions proceed. In doing so, some common reaction progress variables are introduced and defined. The concepts that are reviewed here will be utilized repeatedly throughout the remainder of the course, and therefore it is critically important to master them before proceeding to Parts II, III and IV.

Learning Objectives

Upon completion of this unit, you should be able to define, in words, the following terms:

- chemical reaction, reactant, product, irreversible reaction, reversible reaction, chemical reaction kinetics, rate expression (rate equation), environmental variables, chemical reaction engineering, chemical reactor, design equations, fermenter (chemostat), substrate, reaction progress variable, extensive variable, intensive variable, mathematically independent equations reactions, fractional conversion, limiting reactant, fraction of equilibrium conversion, selectivity, yield

Upon completion of this unit, you should be able to write the defining equation for the following quantities:

- extent of reaction (single reaction and multiple reactions), fractional conversion, fraction of equilibrium conversion

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:

- describe the relationship between kinetics and reaction engineering and use your understanding to distinguish kinetics problems from reaction engineering problems
- write a balanced chemical reaction and write the corresponding values (magnitude and sign) of the stoichiometric coefficients appearing in it (see Example 1.1)
- given a set of chemical reactions, determine whether they are mathematically independent and if they are not, eliminate reactions that are a linear combination of the other remaining reactions until a complete mathematically independent sub-set remains (see Supplemental Unit S1 and Example 1.4)
- distinguish between intensive and extensive variables in order to decide whether it is permissible to choose a basis for your calculations (see Example 1.2)
- given a reaction and a starting composition, identify the limiting reactant(s) (see Example 1.1)
- given the initial composition of a system and all of the reactions taking place within it

- calculate the composition at later times using known values of appropriate reaction progress variables (see Example 1.4) or final composition variables (see Example 1.2)
- write equations expressing any one composition or reaction progress variable in terms of others (see Example 1.3)

Information

This course is about modeling the rates of chemical reactions and modeling equipment where chemical reactions occur. A *chemical reaction* is a process that begins with one or more chemical species (atoms or molecules) known as the *reactants*. In the course of the chemical reaction, one or more chemical bonds among the atoms that make up the reactants are broken and/or formed. This results in the existence of a different set of chemical species known as the *products*. In a chemical reaction atoms are neither created nor destroyed; what changes is the bonding between the atoms. For this reason, a chemical reaction must be balanced. That is, for each element that participates in the reaction, the total number of atoms of that element present among the reactants must be the same as the total number of atoms of that element present among the products.

Conventionally a chemical reaction is written in a form similar to a mathematical equation. The reactants are listed on the left-hand side of the equation joined by plus (+) signs. Instead of an equals sign (=), an arrow is used in a chemical reaction. There are different conventions for the specific style of the arrow. Often a unidirectional arrow pointing from the reactants toward the products ($\rightarrow$) is used to signify an *irreversible reaction* (that is, a reaction where thermodynamic equilibrium permits essentially complete conversion of the reactants into the products). A bidirectional arrow ($\rightleftharpoons$) then indicates that the reaction is *reversible* (meaning that even after an infinite amount of time, some of the reactants will remain). The products are written on the right-hand side of the arrow, again separated by plus signs.

As already noted, atoms are not changed by chemical reactions, but the bonding amongst them is changed. As a consequence, chemical reactions must be balanced so that the exact same group of atoms appears on each side of the equation, but combined differently. For this reason, the number of molecules (or atoms) of one reactant participating in a reaction might not equal the number of molecules (or atoms) of other reactants or products. Instead, in a *balanced chemical reaction*, each chemical species is preceded by a number called its *stoichiometric coefficient*. The stoichiometric coefficients are chosen so that the overall reaction is balanced. If a stoichiometric coefficient is not explicitly written before a species in a reaction, then the magnitude of the stoichiometric coefficient is presumed to equal 1.

For a given reaction, stoichiometric coefficients are not unique. That is, there are more ways than one to write a balanced equation for a given reaction. However, in any pair of balanced equations for the same reaction, the ratio of the stoichiometric coefficients is constant. It is not necessary that stoichiometric coefficients be integers, except in special situations that will be discussed in future units. When writing a chemical reaction, the stoichiometric coefficients are all written as positive numbers, but when they are used as variables in other mathematical expressions, it becomes necessary to establish a sign convention for them. In this course, the symbol $v_{i,j}$ will be used in mathematical equations to denote the stoichiometric coefficient of species i in reaction j. If only one reaction is taking place, the subscript j

may be omitted. Additionally, if species i is a reactant in reaction j, then $v_{i,j}$ will be negative; if species i is a product of reaction j, $v_{i,j}$ will be positive, and if species i does not participate in reaction j as either reactant or product, $v_{i,j}$ will equal zero.

Now that we've defined a chemical reaction, two fields of study that are considered in this course can be described. *Chemical reaction kinetics* is the field of science concerned with understanding and modeling the rates of chemical reactions, i. e. how rapidly reactions occur. The resulting mathematical model for the reaction rate is called a *rate equation* or *rate expression*. It identifies which *environmental variables* (temperature, pressure and composition) affect the reaction rate and how the magnitude of the rate varies as the environmental variables change. Kinetics theories then explain why the rate is affected by the environmental variables.

The equipment in which a chemical reaction occurs is called a *chemical reactor* or simply a reactor. *Chemical reaction engineering* is the branch of chemical engineering concerned with the design, modeling, operation, and performance of chemical reactors. The models used in reaction engineering consist of mole, energy and momentum balances; collectively they are referred to as the design equations or the *reactor design equations*.

Chemical reaction kinetics and chemical reaction engineering are linked to each other in several ways. The design equations that form the basis of chemical reaction engineering include rate expressions that come from chemical reaction kinetics. Similarly, to measure the rate of a chemical reaction, one must use a reactor, and to analyze the resulting data, one must use the design equations. Put differently, kinetics and reaction engineering represent a model within a model: the model for the rate of a reaction (kinetics) is a part of the model for the reactor (reaction engineering) in which it occurs.

Chemical reaction thermodynamics are also important in both chemical kinetics and reaction engineering. Thermodynamic equilibrium limits how far a reaction is able to go at a given set of conditions (all the way to completion or part of the way to completion). Reaction kinetics add supplemental information describing how quickly a reaction can reach this thermodynamic limit. The methods of chemical thermodynamics are additionally used to determine the amount of energy that is released or absorbed as a chemical reaction takes place. The next two units in this course present a concise review of these aspects of chemical reaction thermodynamics.

At the most fundamental level, reactive biological processes are chemical reactions, but they often take place in tremendously complex environments (for example inside living cells) and they are often coupled with other physical processes (for example permeation through a cell membrane). As a result, the modeling of reactive biological processes can be very complicated. Nonetheless, there are some situations where biological reactions can be modeled in a manner that is essentially equivalent to the modeling of chemical reaction processes. This course will consider a few situations of the latter type.

Cell growth will be one of the types of biological systems that will be considered in this course. One might want to grow cells (or single cell organisms) because the cells themselves are valuable and useful. Alternatively, one might be more interested in the byproducts of cell growth. For example, certain organisms might take in sugar as a nutrient that allows them to grow. As they use the sugar to grow, the organisms might convert the sugar into alcohol which is then excreted from the cell. A biochemical

process might be constructed to facilitate this process, and while it might produce new cells or organisms, the product of interest is the alcohol. These types of biochemical processes rely on the cells or organisms to perform the biochemical transformations. The other type of biochemical process that will be considered in this course is one where a particular enzyme has been extracted from a cell and is being used independently of the cell to catalyze a reaction. This situation is much more similar to chemically reacting systems.

In studying reactive biological processes, it will be necessary to master a different nomenclature. While one speaks of reactants in a chemically reacting system, one might equivalently speak of *substrates* in a biologically reacting system. The reactor becomes the *fermentor* or *chemostat*, etc. Another big difference, in the study of cell growth processes, is that there is no fixed stoichiometry, and one must use average yields or adapt their modeling accordingly. Still, there are sufficient similarities and analogies between chemically reacting systems and simple biologically reacting systems that they can be considered simultaneously in an introductory course like this one.

In contrast, chemical reactions do have a fixed stoichiometry, and as a consequence, there are fixed relationships between the amounts of reactants that are consumed and the amounts of products that are produced. As a consequence, the initial and final compositions of a reacting system are related to each other through the stoichiometry of the reactions taking place. *Reaction progress variables* give some measure of how much reaction has taken place relative to a specified starting condition. When more than one reaction takes place simultaneously, reaction progress variables can also be defined to specify how much of one reaction has taken place relative to another reaction. Over time, several different variables have been used to characterize reaction progress. Reaction progress variables can be classified as extensive variables or intensive variables. An *extensive* variable is dependent upon, or imposes a value on, the size (or extent) of the system. For example, the number of moles is clearly an extensive variable. An *intensive* variable, not surprisingly, is independent of the size of the system under consideration. Mole fractions are examples of intensive variables.

The *extent of reaction* is a common <u>extensive</u> reaction progress variable. In a situation where there is only one reaction, j, taking place, the extent of that reaction, ξ_j, is defined by equation (1.1), wherein n_i^0 is the number of moles of species i initially present, n_i is the moles of species i in the system when the extent is equal to ξ_j and $v_{i,j}$ is the stoichiometric coefficient of species i in reaction j. The extent, as defined in equation (1.1), has units of moles. Equation (1.2) gives the corresponding definition that is used for flow systems. The molar flow rate of species i is denoted as $\dot{n}_i$ in equation (1.2) and $\dot{n}_i^0$ represents the inlet molar flow rate of species i. In equation (2.2) the extent of reaction, $\dot{\xi}_j$, has units of

moles per time. (Note: a convention used throughout this course is that a dot over the symbol for a quantity indicates a flow rate while the absence of a dot indicates an amount. Thus, as seen here, n_i denotes the moles of i while $\dot{n}_i$ denotes the molar flow rate of i.)

$$\xi_j = \frac{\left(n_i - n_i^0\right)}{\nu_{i,j}}$$ (1.1)

$$\dot{\xi}_j = \frac{\left(\dot{n}_i - \dot{n}_i^0\right)}{\nu_{i,j}}$$ (1.2)

It's important to be able to distinguish between intensive and extensive variables when solving problems. In some cases, every quantity that is given in a problem statement will be an intensive variable. When this happens, you will likely need to choose a basis for your calculations in order to be able to solve the problem. That means you will need to arbitrarily pick a value for one extensive quantity in the problem. In kinetics and reaction engineering problems, it's common to choose the total initial moles, total initial molar flow rate or the volume of the system, but you can choose a value for any one extensive variable. In problems where you do choose a basis, any extensive quantities that you calculate only apply for the chosen basis, but any intensive quantities that you calculate will apply no matter what basis is chosen. If one or more extensive quantities are specified in the problem statement, then you may not choose a basis when solving the problem.

When more than one reaction is taking place simultaneously, defining the extent of reaction becomes a little more complicated. To understand why, consider reactions (A), (B) and (C). If reactions (A) and (C) each occur once, the net effect is exactly the same as if reaction (B) had occurred once. If you started with some known mixture of CH_4, H_2O and CO_2, and then allowed the system to react, it wouldn't be possible to tell *which* reactions had occurred. The reason for this is that these three reactions are not mathematically independent. Reaction (B) is a linear combination of reactions (A) and (C) (in this case it is simply their sum). Even though you can't tell which reactions occurred, the final composition of the system is still related to the initial composition through the stoichiometry of the reactions.

$CH_4 + H_2O \rightarrow CO + 3\ H_2$ (A)

$CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2$ (B)

$CO_2 + H_2 \rightarrow CO + H_2O$ (C)
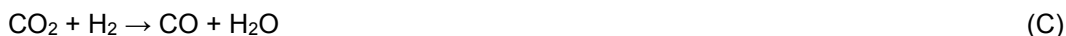
For this reason, the extent of reaction must be defined differently when dealing with multiple reactions. Before doing so, the set of reactions must be reduced to a complete mathematically independent sub-set by eliminating any reactions that are linear combinations of other reactions. For a given group of reactions, there can be several different sub-sets of complete mathematically independent reactions. Any one of the complete mathematically independent sub-sets can be used for the purpose of defining the extent of reaction. (Supplemental Unit S1 describes how to identify a complete mathematically independent sub-set of reactions or equations.) It is important to recognize that *even though all of the reactions are taking place, they are not all used to describe the composition of the system* as it reacts; to describe the composition of the system, only a complete mathematically independent sub-set is used.

Once all reactions that are linear combinations of other reactions have been eliminated, leaving a complete mathematically independent sub-set consisting of N_{ind} reactions, the extents of those N_{ind} reactions can be implicitly defined using equation (1.3). Note that in equation (1.3), the subscript j is limited to include only the N_{ind} mathematically independent reactions. Again, for flow systems, an equivalent definition can be used where the moles are replaced with molar flow rates and the extent has units of moles per time, equation (1.4).

$$n_i = n_i^0 + \sum_{j=1}^{N_{ind}} \nu_{i,j} \xi_j \qquad (1.3)$$

$$\dot{n}_i = \dot{n}_i^0 + \sum_{j=1}^{N_{ind}} \nu_{i,j} \dot{\xi}_j \qquad (1.4)$$

Two important attributes of the extent of reaction must be recognized. The first is that it uses one or more stoichiometric coefficients in its definition. Stoichiometric coefficients are not unique. For example, a reaction could be written as $2\,A \rightleftarrows B$ or as $A \rightleftarrows \frac{1}{2}\,B$. The reaction is the same in both cases, but the stoichiometric coefficients are different. As a result, the value computed for the extent of reaction will depend upon which set of stoichiometric coefficients is used. Consequently, *it is critical that in the course of any one analysis the same set of stoichiometric coefficients be used throughout that analysis*. A second point to recognize is that equation (1.1) will yield the same value for ξ_j no matter which species is used as i; this is also true for equation (1.2).

The *fractional conversion* (or the equivalent percent conversion) is probably the most common <u>intensive</u> reaction progress variable. The fractional conversion is only defined for reactants, and for a single reaction it is preferable (though not universally practiced) to define it in terms of the *limiting reactant*. If one starts with different amounts of each of the reactants, the limiting reactant is the one that will first become completely consumed. A quick way to identify the limiting reactant is to divide the starting amount of each reactant by the absolute value of its stoichiometric coefficient. The reactant for which this quotient has the smallest value is the limiting reactant. Equation (1.5) defines the fractional conversion of species k, f_k, for a batch system while equation (1.6) defines it for a flow system.

$$f_k = \frac{n_k^0 - n_k}{n_k^0} \qquad (1.5)$$

$$f_k = \frac{\dot{n}_k^0 - \dot{n}_k}{\dot{n}_k^0} \qquad (1.6)$$

Notice that the fractional conversion is dimensionless. In the case of a single <u>irreversible</u> reaction, the fractional conversion of the limiting reactant will lie between 0 and 1, while the maximum value of the fractional conversions of the other reactants will lie be less than or equal to 1. In the case of a single <u>reversible</u> reaction, even the fractional conversion of the limiting reagent will have a maximum value less

than 1, because thermodynamics will prevent the reaction from going to completion. For a single reversible reaction, the *fraction of equilibrium conversion* of species k, g_k, defined in equation (1.7) is sometimes used. The fraction of equilibrium conversion is just the actual conversion divided by the conversion if the system had gone to equilibrium. The principle advantage of the fraction of equilibrium conversion is that it must have a value between 0 and 1 when k is the limiting reagent. Equation (1.7) gives the definition in terms of a batch system and equation (1.8) in terms of a flow system.

$$g_k = \frac{f_k}{f_k\big|_{equil}} = \frac{\dfrac{n_k^0 - n_k}{n_k^0}}{\dfrac{n_k^0 - (n_k)\big|_{equil}}{n_k^0}} = \frac{n_k^0 - n_k}{n_k^0 - (n_k)\big|_{equil}} \tag{1.7}$$

$$g_k = \frac{\dot{n}_k^0 - \dot{n}_k}{\dot{n}_k^0 - (\dot{n}_k)\big|_{equil}} \tag{1.8}$$

When multiple reactions take place, there are several reaction progress variables that can be used to characterize how far one reaction has gone relative to another reaction. Unfortunately, some of these reaction progress variables for multiple reaction systems have acquired more than one definition over the years. Therefore whenever a value of a reaction progress variable is given, it is wise to ask how that variable was defined if there is any possibility of ambiguity. Generally the term *selectivity* refers to the ratio of the amount of one product or group of products to the amount of a second product or group of products. Similarly, the term *yield* generally refers to the ratio of the amount of one product or group of products relative to the amount of one particular reactant. One possible source of confusion with yields is that the amount of reactant can be either the amount consumed or the starting amount. Selectivities and yields both can be expressed using either moles or mass. Once again, whenever there is any possibility of ambiguity of the meaning of selectivity or yield, it is wise to ask for the definition being used.

A *mole table* can be very useful when performing calculations involving reacting systems. It shows how the amounts of the different species are related to each other through the stoichiometry of the reactions taking place. As shown below in Table 1.1, there are three columns in a mole table. The rows that make up the first column are used to identify every species present in the system. The very bottom row is used for all of the species combined. The corresponding, initial number of moles of the species are entered in the second column, and the third column contains the number of moles of the species expressed in terms of the extent(s) of reaction as in equation (1.3) above. If one is analyzing a flow system, a corresponding table can be constructed using the molar flow rates in place of the moles as in Table 1.2.

Table 1.1. An example of a mole table for a batch system.

Species	Initial Moles	Moles after Reaction
i	n_i^0	$n_i^0 + \sum_{j=1}^{N_{ind}} \nu_{i,j} \xi_j$
$\vdots$	$\vdots$	$\vdots$
All	$n_{total}^0 = \sum_{all\ i} n_i^0$	$n_{total}^0 + \sum_{all\ i} \sum_{j=1}^{N_{ind}} \nu_{i,j} \xi_j$

Table 1.2. An example of a mole table for a flow system.

Species	Initial Moles	Moles after Reaction
i	$\dot{n}_i^0$	$\dot{n}_i^0 + \sum_{j=1}^{N_{ind}} \nu_{i,j} \dot{\xi}_j$
$\vdots$	$\vdots$	$\vdots$
All	$\dot{n}_{total}^0 = \sum_{all\ i} \dot{n}_i^0$	$\dot{n}_{total}^0 + \sum_{all\ i} \sum_{j=1}^{N_{ind}} \nu_{i,j} \dot{\xi}_j$