

# Chapter 1

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## Stoichiometric Coefficients and Reaction Progress Variables

### 1.0 INTRODUCTION

In the absence of chemical reactions, Earth would be a barren planet. No life of any sort would exist. Even if we were to exempt the fundamental reactions involved in life processes from our proscription on chemical reactions, our lives would be extremely different from what they are today. There would be no fire for warmth and cooking, no iron and steel with which to fashion even the crudest implements, no synthetic fibers for making clothing or bedding, no combustion engines to power our vehicles, and no pharmaceutical products to treat our health problems.

One feature that distinguishes the chemical engineer from other types of engineers is the ability to analyze systems in which chemical reactions are occurring and to apply the results of his or her analysis in a manner that benefits society. Consequently, chemical engineers must be well acquainted with the fundamentals of chemical reaction kinetics and the manner in which they are applied in reactor design. In this book we provide a systematic introduction to these subjects. Three fundamental types of equations are employed in the development of the subject: material balances, energy balances, and rate expressions.

*Chemical kinetics* is the branch of physical chemistry that deals with quantitative studies of the rates at which chemical processes occur, the factors on which these rates depend, and the molecular acts involved in reaction processes. A description of a reaction in terms of its constituent molecular acts is known as the *mechanism* of the reaction. Physical and organic chemists are interested in chemical kinetics primarily for the light that it sheds on molecular properties. From interpretations of macroscopic kinetic data in terms of molecular mechanisms, they can gain insight into the nature of reacting systems, the processes by which chemical bonds are made and broken, and the structure of the resulting product. Although chemical engineers find the concept of a reaction mechanism

useful in the correlation, interpolation, and extrapolation of rate data, they are more concerned with applications of chemical kinetics in the development of profitable manufacturing processes.

Chemical engineers have traditionally approached kinetics studies with the goal of describing the behavior of reacting systems in terms of macroscopically observable quantities such as temperature, pressure, composition, and Reynolds number. This empirical approach has been very fruitful in that it has permitted chemical reactor technology to develop to the point that it can be employed in the manufacture of an amazing array of products that enhance our quality of life.

The dynamic viewpoint of chemical kinetics focuses on variations in chemical composition with either time in a batch reactor or position in a continuous flow reactor. This situation may be contrasted with the essentially static perspective of thermodynamics. A *kinetic system* is a system in which there is unidirectional movement toward thermodynamic equilibrium. The chemical composition of a closed system in which a reaction is occurring evolves as time elapses. A system that is in thermodynamic equilibrium, on the other hand, undergoes no net change with time. The thermodynamicist is interested only in the initial and final states of the system and is not concerned with the time required for the transition or the molecular processes involved therein; the chemical kineticist is concerned primarily with these issues.

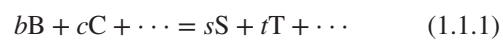
In principle, one can treat the thermodynamics of chemical reactions on a kinetic basis by recognizing that the equilibrium condition corresponds to the situation in which the rates of the forward and reverse reactions are identical. In this sense kinetics is the more fundamental science. Nonetheless, thermodynamics provides much vital information to the kineticist and to the reactor designer. In particular, the first step in determining the economic feasibility of producing a given material from a specified

feedstock should be a determination of the product yield at equilibrium at the conditions of the reactor outlet. Since this composition represents the goal toward which the kinetic process is moving, it places an upper limit on the product yield that may be obtained. Chemical engineers must also employ thermodynamics to determine heat transfer requirements for proposed reactor configurations.

## 1.1 BASIC STOICHIOMETRIC CONCEPTS

### 1.1.1 Stoichiometric Coefficients

An arbitrary chemical reaction may be written as



where  $b$ ,  $c$ ,  $s$ , and  $t$  are the stoichiometric coefficients of the species B, C, S, and T, respectively. We define generalized stoichiometric coefficients ( $\nu_i$ ) for reaction (1.1.1) by rewriting it in the following manner:

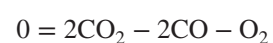
$$0 = \nu_B B + \nu_C C + \nu_S S + \nu_T T + \dots \quad (1.1.2)$$

where  $\nu_B = -b$ ,  $\nu_C = -c$ ,  $\nu_S = s$ , and  $\nu_T = t$ . The generalized stoichiometric coefficients are defined as positive quantities for the products of the reaction and as negative quantities for the reactants. The coefficients of species that are neither produced nor consumed by the indicated reaction are taken to be zero. Equation (1.1.2) has been written in transposed form with the zero first to emphasize the use of this sign convention, even though this transposition is rarely used in practice. One may further generalize equation (1.1.2) by rewriting it as

$$0 = \sum_i \nu_i A_i \quad (1.1.3)$$

where the sum is taken over all components  $A_i$  present in the system.

There are many equivalent ways of writing the stoichiometric equation for a reaction. For example, one could write the oxidation of carbon monoxide in our notation as

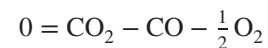


instead of the more conventional form, which has the reactants on the left side and the products on the right side:



This second form is preferred, provided that one keeps in mind the proper sign convention for the stoichiometric coefficients. For the example above,  $\nu_{\text{CO}} = -2$ ,  $\nu_{\text{O}_2} = -1$ , and  $\nu_{\text{CO}_2} = 2$ .

Alternatively, this reaction may be written as



The choice is a matter of personal convenience. The essential point is that the ratios of the stoichiometric coefficients are unique for a specific reaction. In terms of the two forms of the chemical equation above,

$$\frac{\nu_{\text{CO}}}{\nu_{\text{O}_2}} = \frac{-2}{-1} = \frac{-1}{-1/2} = 2$$

Because the reaction stoichiometry can be expressed in various ways, one must always write down a stoichiometric equation for the reaction under study during the initial stages of the analysis and base subsequent calculations on this reference equation. If a consistent set of stoichiometric coefficients is used throughout the calculations, the results can be readily understood and utilized by other workers in the field.

### 1.1.2 Reaction Progress Variables

To measure the progress of a reaction along a particular pathway, it is necessary to define a parameter that provides a measure of the degree of conversion of the reactants. For this purpose it is convenient to use the concept of the *extent* or degree of *advancement* of a reaction. This concept has its origins in the thermodynamic literature, dating back to the work of de Donder (1). Consider a *closed system*, one in which there is no exchange of matter between the system and its surroundings, where a single chemical reaction may occur according to equation (1.1.3). Initially, there are  $n_{i0}$  moles of constituent  $A_i$  present in the system. At some later time there are  $n_i$  moles of species  $A_i$  present. At this time the molar extent of reaction ( $\xi$ ) is defined as

$$\xi = \frac{n_i - n_{i0}}{\nu_i} \quad (1.1.4)$$

This equation is valid for all species  $A_i$ , a fact that is a consequence of the law of definite proportions. The molar extent of reaction  $\xi$  is a time-dependent extensive variable that is measured in moles. It is a useful measure of the progress of the reaction because it is not tied to any particular species  $A_i$ . Changes in the mole numbers of two species  $i$  and  $j$  can be related to one another by eliminating  $\xi$  between two expressions that may be derived using equation (1.1.4):

$$n_j = n_{j0} + \frac{\nu_j}{\nu_i}(n_i - n_{i0}) \quad (1.1.5)$$

If more than one chemical reaction is possible, an extent may be defined for each reaction. If  $\xi_k$  is the extent of the  $k$ th reaction, and  $\nu_{ki}$  is the stoichiometric coefficient

of species  $i$  in reaction  $k$ , the total change in the number of moles of species  $A_i$  as a consequence of  $r$  reactions is

$$n_i - n_{i0} = \sum_{k=1}^{k=r} \nu_{ki} \xi_k \quad (1.1.6)$$

Another advantage of using the concept of extent is that it permits a unique specification of the rate of a given reaction. This point is discussed in Section 3.0. The major drawbacks of the concept are that the extent is defined for a closed system and that it is an extensive variable. Consequently, the extent is proportional to the mass of the system being investigated.

The fraction conversion  $f$  is an intensive measure of the progress of a reaction. It is a variable that is simply related to the extent of reaction. The fraction conversion of a reactant  $A_i$  in a closed system in which only a single reaction is occurring is given by

$$f = \frac{n_{i0} - n_i}{n_{i0}} = 1 - \frac{n_i}{n_{i0}} \quad (1.1.7)$$

The variable  $f$  depends on the particular species chosen as a reference substance. In general, the initial mole numbers of the reactants do not constitute simple stoichiometric ratios, and the number of moles of product that may be formed is limited by the amount of one of the reactants present in the system. If the extent of reaction is not limited by thermodynamic equilibrium constraints, this limiting reagent is the one that determines the maximum possible value of the extent of reaction ( $\xi_{\max}$ ). We should refer our fractional conversions to this stoichiometrically limiting reactant if  $f$  is to lie between zero and unity. Consequently, the treatment used in subsequent chapters will *define fractional conversions in terms of the limiting reactant*. In analyzing conventional batch reactors in which only a single reaction is occurring, one may employ either the concept of fraction conversion or the concept of extent of reaction. A batch reactor is a closed system, a system for which there is no transport of matter across the boundaries between the system and its surroundings. When multiple reactions take place in a batch reactor, it is more convenient to employ the extent concept. However, for open systems such as continuous flow reactors, the fraction conversion of the limiting reagent is more useful in conducting the

analysis, sometimes in conjunction with the concept of reaction yield, as described in Chapter 9. An *open system* is one whose analysis requires consideration of the transport of matter across the boundaries between the system and its surroundings.

One can relate the extent of reaction to the fraction conversion by solving equations (1.1.4) and (1.1.7) for the number of moles of the limiting reagent  $n_{\text{lim}}$  and equating the resulting expressions:

$$n_{\text{lim}} = n_{\text{lim},0} + \nu_{\text{lim}} \xi = n_{\text{lim},0}(1 - f) \quad (1.1.8)$$

or

$$\xi = -\frac{f n_{\text{lim},0}}{\nu_{\text{lim}}} \quad (1.1.9)$$

The maximum extent of an irreversible reaction ( $\xi_{\max,\text{irr}}$ ) can be obtained by setting  $f$  in equation (1.1.9) equal to 1. However, for reversible reactions, the maximum extent of reaction is limited by the position of chemical equilibrium. For these situations, equation (1.1.9) becomes

$$\xi_e = -\frac{f_e n_{\text{lim},0}}{\nu_{\text{lim}}} \quad (1.1.10)$$

where  $f_e$  and  $\xi_e$  are the conversion and extent of reaction at equilibrium, respectively.  $\xi_e$  will always be less than  $\xi_{\max,\text{irr}}$ . However, in many cases  $\xi_e$  is approximately equal to  $\xi_{\max,\text{irr}}$ . In these cases the equilibrium for the reaction highly favors formation of the products, and only an *extremely small* quantity of the limiting reagent remains in the system at equilibrium. We classify these reactions as *irreversible*. When the extent of reaction at equilibrium differs measurably from  $\xi_{\max}$ , we classify the reaction involved as *reversible*. From a thermodynamic point of view, all reactions are reversible. However, to simplify the analysis, when one is analyzing a reacting system, it is often convenient to neglect the reverse reaction. For “irreversible” reactions, one then arrives at a result that is an extremely good approximation to the correct answer.

## LITERATURE CITATION

1. DE DONDER, T., *Leçons de thermodynamique et de chimie-physique*, Gauthier-Villars, Paris 1920.