

# A First Course on Kinetics and Reaction Engineering

## Unit 7. The Steady State Approximation

### Overview

This course is divided into four parts, I through IV. Part II is focused upon modeling the rates of chemical reactions, that is, rate expressions. A mathematical expression for the rate of a non-elementary reaction can be generated using kinetic theories if the mechanism of the reaction is known. The resulting expression for the rate of the apparent, macroscopically observed non-elementary reaction is of limited utility because it contains concentrations (or partial pressures) of reactive intermediates. Those concentrations are very small and difficult to measure, Unit 7 introduces the Bodenstein steady state approximation and shows how it can be used to eliminate the concentrations of reactive intermediates from mechanistic rate expressions. It also presents a few common ways of simplifying those rate expressions, when applicable.

### Learning Objectives

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

- steady state
- kinetically insignificant reaction

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 assumption that a step is kinetically insignificant and apply it to simplify the rate expression derived from a reaction mechanism
- Describe the assumption that a step is effectively irreversible and apply it to simplify the rate expression derived from a reaction mechanism
- Describe the Bodenstein steady-state approximation and apply it to eliminate concentrations of reactive intermediates from the rate expression derived from a reaction mechanism

### Information

If its mechanism is known, the rate of a macroscopically observed, non-elementary reaction,  $j$ , can be determined from the rates of the elementary steps,  $s$ , in that mechanism using equation (7.1), as noted in Unit 6. Generally this leads to a rate expression that is not very useful for engineering purposes. The resulting rate expression will contain several terms, and it will include concentrations of reactive intermediates. The latter are present in a real system in very small concentrations. These concentrations are typically unknown, and they are very difficult to measure accurately. For these reasons, it is desirable to simplify the rate expression that results from the application of equation (7.1).

$$r_{i,j} = \sum_{\substack{s=\text{all} \\ \text{steps}}} \nu_{i,s} \left( k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} [m]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} [n]^{\nu_{n,s}} \right) \quad (7.1)$$

The simplification of the rate expression is accomplished by making different assumptions. Of course, the simplified rate expression that results from making an assumption will only be valid if the assumption is valid and if the mechanism being used is valid. That said, it is sometimes observed that the rate of one particular mechanistic step has virtually no effect upon the apparent rate of the macroscopically observed reaction. Thus *it is sometimes possible to assume that the rate of one or more steps is kinetically insignificant and to set the rates of those steps equal to zero*, equation (7.2). Similarly, it is sometimes observed that the rate in the reverse direction of a particular step is very small compared to its forward rate or that the step is thermodynamically able to go essentially to completion. Consequently, *it is sometimes possible to assume that a mechanistic step is irreversible and thus to drop the term corresponding to its rate in the reverse direction*, equation (7.3).

$$r_s = 0 \quad s = \text{kinetically insignificant step} \quad (7.2)$$

$$r_s = k_{s,f} \prod_{\substack{i=\text{all} \\ \text{reactants}}} [i]^{-\nu_{i,s}} \quad s = \text{irreversible step} \quad (7.3)$$

In 1907, Bodenstein [1] suggested an assumption related to reactive intermediates appearing in a reaction mechanism. As noted in Unit 6, reactive intermediates will be present at very low concentrations. This is a consequence of their high reactivity. As the reaction begins, the concentration of these species increases, but because they are so reactive, those intermediates formed undergo subsequent reaction very rapidly. In this way a steady state is quickly established whereby the rate at which reactive intermediates are being formed equals the rate at which they are undergoing subsequent reaction. Hence their concentration becomes constant and the overall rate of generation of the reactive intermediates becomes equal to zero. When the concentration of a species does not change over time, that concentration is said to be at *steady state*. One can assume that this steady state condition always exists, ignoring the brief time required for the concentrations of the reactive intermediates to build up to their steady state values. This is known as the *Bodenstein steady state approximation*. To apply the steady state approximation, the expression for the overall rate of generation of each reactive intermediate is extracted from the reaction mechanism and set equal to zero, equation (7.4).

$$0 = \sum_{\substack{s=\text{all} \\ \text{steps}}} \nu_{i,s} \left( k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} [m]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} [n]^{\nu_{n,s}} \right) \quad i = \text{reactive intermediate} \quad (7.4)$$

If there are  $N$  reactive intermediates, then equation (7.4) can be used once for each intermediate. This results in a set of  $N$  algebraic equations. This set of  $N$  equations can be solved for the concentrations of the  $N$  reactive intermediates (in terms of the rate coefficients in the mechanism and the concentrations of stable species such as the reactants and products of the macroscopically observed reaction). The resulting expressions for the concentrations of the reactive intermediates can be substituted back into the expression for the macroscopically observed, non-elementary reaction, equation (7.1). In this way the resulting rate expression for the macroscopically observed, non-elementary reaction

will no longer contain concentrations of reactive intermediates, and it will be much more useful for engineering purposes.

**References Cited**

1. Bodenstein, M. and S.C. Lind, Z. Physik. Chem., 1906. **57**: p. 168.