A First Course on Kinetics and Reaction Engineering
Unit 8. Rate-Determining Step

Overview

This course is divided into four parts; 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 from its mechanism. Unit 8 introduces the concept of a rate-determining step and shows how to generate a mechanistic rate expression for cases where the mechanism includes a rate-determining step.

Learning Objectives

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

- rate-determining step
- quasi-equilibrated step

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 consequences of the existence of a rate-determining step upon the overall rate and upon the other reactions in the mechanism
- simplify the rate expression for a mechanism that involves a rate-limiting step so that the final rate expression does not contain concentrations or partial pressures of reactive intermediates

Information

Units 6 and 7 showed how to generate a mechanistic rate expression from a reaction mechanism and simplify it so that the concentrations of reactive intermediates do not appear in it. Sometimes one step in the mechanism is much more difficult or demanding than any of the other steps. This step introduces a bottleneck in the reaction kinetics; if the rate of this one step were somehow increased, the net rates of all the other steps and the observed overall rate would increase proportionally. This kind of step is referred to as a *rate-determining step* (rds) or the rate-limiting step. In situations where there is a rate-determining step, the rate expression can often be simplified considerably by making the assumption that the macroscopically observed rate of the apparent overall reaction is equal to the rate of the rate-determining step. This is expressed in equation (8.1) where j denotes the macroscopically observed (non-elementary) reaction and rds denotes the rate-determining step in the mechanism. Note that r_j in equation (8.1) is the generalized rate of the overall (non-elementary) reaction and not its rate with respect to any species. Further note that not all mechanisms have a rate-determining step.

$$r_j = r_{rds} \tag{8.1}$$

It is often stated that the rate determining step is the slowest step in the mechanism, but this is not an accurate statement. When the steps all have the same stoichiometric number (see Unit 6), then every step in the mechanism proceeds at the same net rate. If the rate determining step was much slower than

the steps before it, then the concentrations of the reactants of the rate-determining step would continually build up. Eventually, the concentrations of the reactants of the rate-determining step would become sufficiently large to be observed macroscopically. In that case, a macroscopic observation would no longer give the appearance that a single, non-elementary reaction was taking place. Thus, it is more accurate to say that the rate-determining step is the kinetic bottleneck or that it is the most demanding step, than to incorrectly state that it is the slowest step.

The concept of one step being more difficult or demanding can be put in more scientific terms. Recall that there must be some linear combination of the mechanistic steps that is equal to the macroscopically observed, non-elementary reaction. There is a free energy change associated with the overall macroscopically observed reaction, and there are free energy changes associated with each of the mechanistic steps. Since free energy is a state function, the free energy change for the overall, non-elementary reaction also is equal to the same linear combination of the free energy changes for the individual steps, as expressed in equation (8.2) where b_j represents the coefficient of step j in the linear combination that is equal to the macroscopically observed reaction. If there is one mechanistic step wherein essentially all of the overall free energy change takes place, that one step is the *rate-determining step*, equation (8.3). Since essentially all of the free energy change occurs in the rate-determining step, the free energy change for the other steps is essentially zero, equation (8.4). Note, again, that there does not have to be a rate-determining step in a reaction mechanism.

$$\Delta G_j = b_1 \Delta G_1 + b_2 \Delta G_2 + \cdots b_{rds} \Delta G_{rds} + \cdots \tag{8.2}$$

$$\Delta G_j \approx b_{rds} \Delta G_{rds} \tag{8.3}$$

$$\Delta G_k \approx 0 \qquad\qquad k \neq rds \tag{8.4}$$

If a rate-determining step exists for a particular reaction mechanism, there are two consequences. First, the rate-determining step, itself, may be assumed to be irreversible. That is, the reverse rate of the rate-determining step may be assumed to be negligible, leading to equation (8.5) where the coefficient b_{rds} has been incorporated into the rate coefficient, k_{rds}, and j corresponds to the macroscopically observed reaction. The second consequence is that since the free energy changes for all steps other than the rate-determining step are essentially zero, it may be assumed that all steps <u>other than the rate-determining step</u> reach a state of quasi-equilibrium. (Recall from thermodynamics that by definition the free energy change for a process at thermodynamic equilibrium is equal to zero.) This is expressed in equation (8.6) where $K_{eq,s}$ is the appropriate form of the equilibrium constant for step s.

$$r_j = r_{rds} = k_{rds,f} \left(\prod_{\substack{m=\text{all} \\ \text{reactants}}} \left[m \right]^{-\nu_{m,rds}} \right) \tag{8.5}$$

$$K_{eq,s} = \prod_{\substack{i = \text{all} \\ \text{species}}} \left[i \right]^{\nu_{i,s}} \qquad\qquad s \neq rds \tag{8.6}$$

Note that the rate expression that results from the application of equation (8.5) is likely to include the concentration of one or more reactive intermediates, and if it does, it is not suitable for many engineering purposes. In those cases, however, the quasi-equilibration assumption (equation (8.6)) can be applied to all other steps. The resulting equilibrium expressions can be solved for the concentrations of the reactive intermediates in terms of the concentrations of the reactants, products and the equilibrium constants for the steps other than the rate-determining step. Upon substitution into equation (8.5), a rate expression more suitable for engineering purposes results.

Rate expressions that are derived with the assumption of a rate-determining step will only apply for environmental conditions that are far from equilibrium. This is easily seen through examination of equation (8.5). If the overall, macroscopically observed reaction is reversible, then when the reaction reaches equilibrium, some amount of the reactants will remain. That is, the equilibrium concentrations of the reactants will be non-zero. If those non-zero equilibrium concentrations are inserted into equation (8.5), the rate that is calculated will also be non-zero, but at equilibrium the rate should equal zero. Recall that the free energy change due to the rate-determining step is equal to the overall free energy change. However, as the system approaches thermodynamic equilibrium the overall free energy change approaches zero (by definition) and the free energy change for every step approaches zero (according to the principle of microscopic reversibility). Thus, as the system approaches thermodynamic equilibrium it is no longer possible to identify a rate-determining step, and as a consequence, rate expressions that are derived with the assumption of a rate-determining step will only apply for environmental conditions that are far from equilibrium.