A First Course on Kinetics and Reaction Engineering

Example 5.3

Problem Purpose

This example illustrates the analysis of a chemical reaction to determine whether it _could_ be elementary. _In doing so, it expands upon the information presented in the informational reading, introducing the concept of a unimolecular reaction._

Problem Statement

The hydrogenation of ethylene to ethane is given by reaction (1)

$$C_2H_4 + H_2 \rightleftarrows C_2H_6 \quad (1)$$

a. Could this reaction be elementary?
b. If the answer to part (a) was yes, what could be said about reaction (1).

Problem Analysis

We've already learned that you can't tell whether a reaction ***is elementary*** just by looking at the equation for it. However, knowing that an elementary reaction must be an exact description of what occurs in a singular molecular event, it is often possible to determine that a reaction ***is not elementary***. That is the approach we will take here.

Problem Solution

(a) At first glance, it might seem that reaction (1) could be elementary. If it were, the principle of microscopic reversibility would require it to occur in both the forward and reverse directions. In the forward direction there are two reactants involved, that is, the reaction is bimolecular in the forward direction. In the reverse direction, however, the reaction involves only one reactant. That is, the reverse reaction is unimolecular.

More advanced treatments of reaction kinetics typically include a section that is devoted to unimolecular reactions. It turns out that _a unimolecular reaction can't be elementary_. The single reactant molecule is a stable species. In order for it to react, it must acquire some energy. If that weren't the case, the reactant would not be a stable molecule to begin with. At normal temperatures and pressures, the reactant in a unimolecular reaction must collide with another species in order to gain sufficient energy to react. If the reactant must collide with a second species, that means the reaction must be bimolecular.

Another way to explain this is to note that if reaction (1) occurred in a single molecular event, then by conservation of energy, the product ethane molecule would contain sufficient energy to break apart and re-form the reactants. The only way that the product ethane molecule can be stabilized is if another molecule collides with it and some of its energy is transferred to that other molecule. At that point, the ethane would no longer contain sufficient energy to break apart and re-form the reactants. Thus, whether one views the forward reaction or the reverse reaction, one comes to the conclusion that the single product molecule must collide with another molecule. If that is the case, then reaction (1) is not an exact description of a reactive process that takes place in a single molecular event; it requires two molecular events.

In fact, there are theories that have been developed to explain the kinetics of unimolecular reactions. These theories are not presented here in “A First Course on Kinetics and Reaction Engineering.” Those who are interested in learning more about the theories for unimolecular reactions are referred to more advanced kinetics textbooks such as “Chemical Kinetics and Dynamics,” 2nd Ed., by Steinfeld, Francisco and Hase (Prentice Hall, 1999).

(b) If reaction (1) had been an elementary reaction, then we would know that it must be reversible and that its rate expression would have the form given in equation (2). In this case, however, reaction (1) is not elementary and consequently we have no idea what is the mathematical form of its rate expression.

$$r_1 = k_{1,f} C_{C_2H_4} C_{H_2} - k_{1,r} C_{C_2H_6} \tag{2}$$