

# A First Course on Kinetics and Reaction Engineering

## Unit 6. Reaction Mechanisms

### 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. The mathematical form of a rate expression for an elementary reaction is related to the stoichiometry of the elementary reaction, as discussed in Unit 5. Most of the time, however, the balanced equation for a chemical reaction does not reveal the actual process that takes place at the molecular level. Instead, it simply conveys the net effect of a set of different elementary reactions that actually occur at the molecular level. This group of elementary reactions is collectively referred to as the reaction mechanism. If the reaction mechanism is known, it often is possible to generate a rate expression for the single reaction that appears to be taking place, even though it never actually occurs at the molecular level. Unit 6 describes how to do this.

### Learning Objectives

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

- reaction mechanism
- reactive intermediate
- stoichiometric number
- initiation step
- termination step
- propagation step
- chain branching step
- chain transfer 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:

- Explain the difference between an elementary reaction and a macroscopically observed, non-elementary reaction
- Distinguish between an activated complex and a reactive intermediate
- State the rules that must be obeyed by reaction mechanisms
- Write an expression for the rate of a macroscopically observed, non-elementary reaction with respect to a particular participant species, given a mechanism for the overall reaction.
- Distinguish between a closed (chain) reaction mechanism and an open reaction mechanism
- Identify the initiation/termination, propagation, chain branching and chain transfer steps in a chain reaction mechanism

### Information

Rate expressions for elementary reactions can be generated from the theories presented in Unit 5, provided one knows that the reaction in question is elementary. If a reaction is not elementary (most are

not), then the theories can't be applied to it. However, if a reaction is not elementary, then at the molecular level there are different events occurring; what is observed at the macroscopic level is the net result of these other molecular events. The set of elementary reaction events that actually takes place at the molecular level is known as the *reaction mechanism*. Since each step in a reaction mechanism is, by definition, an elementary reaction step; the rate expressions for each of the mechanistic steps can be generated from the kinetic theories.

In most cases, reaction mechanisms are not studied solely for the purpose of finding a suitable rate expression for some macroscopically observed reactive process. They are studied to gain understanding of how a reaction takes place, often with the intention of using that knowledge to modify the reactive process. For example, a given reagent may simultaneously undergo two reactions, one producing a desired product and one producing an undesired product. Understanding the mechanism of the process might, for example, provide insight that permits the selection of a solvent in which the desired reaction is more favored. The study of reaction mechanisms typically involves a number of different kinds of experiments: spectroscopic, magnetic or other characterizations to identify intermediate species, quantum chemical calculations to estimate activation barriers, isotopic labeling studies to probe breakage of specific bonds and others, in addition to steady state kinetics experiments.

Over the course of the next several units, we will see how a rate expression for a macroscopically observed, non-elementary reaction can be generated from a knowledge of the underlying reaction mechanism. In the past, and still sometimes at present, this was one of the approaches used in the study of reaction mechanisms. The spectroscopic and other studies mentioned in the previous paragraph were used to postulate a reaction mechanism that was consistent with the results of those experiments. The postulated mechanism was then used to generate a rate expression for the overall, macroscopically observed reaction (even though it never occurs at the microscopic level). The resulting rate expression was then fit to experimental kinetics data as described in Unit 4. Clearly, if the rate expression did not fit the experimental data well, then the postulated mechanism was not correct. At the same time, if the rate expression did fit the experimental data well, that does not prove that the mechanism is correct. Recall, it is quite possible that multiple mathematical functions will fit a set of rate data equally well, so there could be a different reaction mechanism that yields an equally-acceptable rate expression.

This approach is becoming less common in the study of reaction mechanisms. It is now a routine matter to write rate expressions for every step in a reaction mechanism and then to solve the resulting set of equations using a computer. As such, it really isn't necessary to generate a single rate expression for the macroscopically observed, non-elementary reaction in order to fit it to the experimental data. Instead, one can use the rates of the mechanistic steps directly to see whether the proposed reaction mechanism is consistent with experimental kinetics data.

Nonetheless, the remainder of Section A of this part of the course will examine how a single rate expression for a non-elementary, macroscopically observed reaction can be generated from a mechanism that is proposed to underly that non-elementary reaction. The reasons for doing this are three-fold. First, this is quite common in earlier kinetics publications, so if one wants to be able to read that literature, one must understand the process. Second, we will see that rate expressions generated from reaction

mechanisms can have mathematical forms that are very different from the empirical power-law rate expressions and theoretical elementary step reaction mechanisms considered so far. As such, they may be capable of explaining behavior that cannot be explained by power-law rate expressions. Thus, even if one does not need to know the molecular details underlying a non-elementary reaction, they still may need a rate expression with the proper mathematical form in order to model that non-elementary reaction. Finally, if some day one is going to study reaction mechanisms, the knowledge gained in remainder of this section of the course will provide a good basis to build upon.

Returning to our consideration of rate expressions, suppose that we are considering what appears from macroscopic observation to be a single reaction and that we need a rate expression for this (apparent) single reaction. We've seen that rate expressions are generated by guessing a rate expression and then testing to see whether the guessed rate expression is capable of describing the performance of experimental reactors running the reaction in under consideration. We have three options in terms of guessing a rate expression for testing. One option is to use an empirical approach where we guess functions that are convenient to use, but that have no theoretical underpinnings. The second option is to guess that the reaction under consideration is elementary. In that case, the rate expression would be given by either equation (6.1) or equation (6.2). These equivalent equations are the theoretical rate expressions for elementary reactions that were derived in Unit 5. The rate coefficients may be assumed to obey the Arrhenius expression and the square brackets can represent either concentrations or partial pressures.

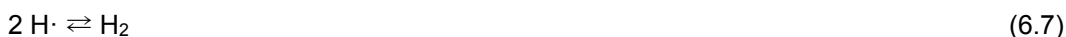
$$r_j = k_{j,f} \prod_{\substack{i=\text{all} \\ \text{reactants}}} [i]^{-\nu_{i,j}} - k_{j,r} \prod_{\substack{i=\text{all} \\ \text{products}}} [i]^{\nu_{i,j}} \quad (6.1)$$

$$r_j = k_{j,f} \left( \prod_{\substack{i=\text{all} \\ \text{reactants}}} [i]^{-\nu_{i,j}} \right) \left( 1 - \frac{\prod_{\substack{i=\text{all} \\ \text{species}}} [i]^{\nu_{i,j}}}{K_{j,eq}} \right) \quad (6.2)$$

If the reaction is not elementary, the third option is to recognize that while the macroscopically observed, non-elementary reaction does not actually occur, we can still describe the observed apparent reaction in terms of the underlying reaction mechanism. In this case, it is often possible to make assumptions about the steps in the reaction mechanism that allow a rate expression for the macroscopically observed, non-elementary reaction to be generated. Put differently, the third approach is to pretend that the macroscopically observed reaction actually does take place and to use the reaction mechanism to derive a rate expression for it from the reaction mechanism.

A classic example of a macroscopically observed, non-elementary reaction is the synthesis of HBr, equation (6.3). If it were possible to examine a reacting system of hydrogen and bromine at the molecular level, one would not observe a process wherein a hydrogen molecule and a bromine molecule collided yielding two hydrogen bromide molecules. Instead, one would see several different molecular events, as

given in equations (6.4) through (6.7). These four steps are called the reaction mechanism for HBr synthesis. By definition, each step in a reaction mechanism is an elementary reaction step. Consequently, reactions (6.4) through (6.7) are each elementary, and hence, they are reversible and their individual rate expressions are given by either equation (6.1) or (6.2).



There are a few rules that must be obeyed by a reaction mechanism:

1. There must be some linear combination of the mechanistic steps that exactly equals the apparent (non-elementary, macroscopically observed) overall reaction.
2. Each step in a reaction mechanism must be reversible. This is because the steps are elementary reactions and the *principle of microscopic reversibility* requires elementary steps to be reversible. That is the reason why double arrows were used in equations (6.4) through (6.7).
3. The mechanistic steps must be consistent with all available experimental data including kinetics of reaction, isotopic effects upon kinetics, isotope distributions in products, spectroscopic measurements, etc.

The last point is particularly important. A reaction mechanism should represent actual molecular events, and as such, experimental studies should be performed to ensure to the best extent possible that the proposed mechanistic steps actually take place. Quantum chemistry has now advanced to the point that it is quite useful in this regard. Using quantum chemical calculations it is possible to estimate the pre-exponential factor and the activation energy for elementary reaction steps, and this provides a good, additional check on the validity of a proposed reaction mechanism.

There are species which appear in the reaction mechanism that are not present in sufficient quantity to be observed macroscopically and which therefore do not appear in the overall (macroscopically observed, or apparent) reaction. Specifically, for the present example,  $\text{H}\cdot$  and  $\text{Br}\cdot$  appear in the reaction mechanism, but not in the overall, macroscopically observed reaction. Species which appear in the mechanism, but not in the overall reaction, are called *reactive intermediates*. (These should not be confused with the activated complex of transition state theory. Reactive intermediates are thermodynamically stable species that have very long lifetimes compared to activated complexes, but very short lifetimes compared to the reactants and products of the overall reaction.) Reactive intermediates are present in very small concentration when compared to reactants and products of the overall reaction. Reactive intermediates do not have to be free radicals as in the present example. Reactive intermediates can be neutral complexes, ions (free or solvated), surface complexes, etc. As the name implies, these species are highly reactive, and as a consequence, they never build up to

appreciable concentrations. (If they did, they would be observed at the macroscopic level, and that, in turn, would lead to one or more different macroscopically observed, non-elementary reactions.)

The first rule above is a necessary, but not sufficient, criterion to ensure that no reactive intermediate accumulates to the point of its concentration becoming macroscopically observable. An alternative way of stating the first rule above is that the macroscopically observed, non-elementary reaction is *not* mathematically independent from the reactions that constitute the mechanism. As such, it is easy to check that this rule is satisfied. One simply determines the number of mathematically independent reactions in the reaction mechanism (see Supplemental Unit S1). One then adds the apparent, macroscopically observed reaction to the set and re-determines the number of mathematically independent reactions. If the number of mathematically independent reactions does not change, that means the added reaction is not mathematically independent, and that means that the rule is satisfied.

There are two general types of reaction mechanism, wherein the steps of the mechanism either form an open sequence or a closed sequence of steps. Mechanisms with a closed sequence of steps are commonly referred to as chain reaction mechanisms. The distinguishing feature of a chain reaction (or closed sequence) mechanism is that it includes a set of elementary steps known as propagation steps. A *propagation step* is a step wherein one reactive intermediate participates as a reactant and another reactive intermediate is formed as a product within that single elementary step. The set of propagation steps forms a *closed sequence* where each reactive intermediate is produced in one propagation step and consumed in a different propagation step. In a chain reaction mechanism, the overall, macroscopically observed (non-elementary) reaction is, in fact, a linear combination of the propagation steps. As a consequence, propagation steps occur many, many more times than the other steps in the mechanism.

The HBr synthesis mechanism is an example of a chain reaction mechanism. Notice that reaction (6.5) consumes a Br· reactive intermediate and generates an H· reactive intermediate. Then reaction (6.6) consumes an H· reactive intermediate and generates a Br· reactive intermediate. If you add just these two propagation steps together, you get the overall reaction (6.3). Nonetheless, while this linear combination of the propagation steps equals the overall, macroscopically observed (non-elementary) reaction, the other steps are still needed. This can be seen by noting that if neither reaction (6.4) nor reaction (6.7) ever occurred, then there would not be any reactive intermediates present, and that would mean that the propagation steps could not occur. In theory, either reaction (6.4), in the forward direction, or reaction (6.7), in the reverse direction, would need to occur at least one time in order to get the propagation sequence going. Then at the end of the reaction, reaction (6.4), in the reverse direction, or (6.7), in the forward direction, would need to occur one time to use up the reactive intermediates. This shows why propagation steps occur many more times than the other steps.

Reactions (6.4) and (6.7) are examples of two additional kinds of steps found in chain reaction mechanisms. These kinds of steps are known as *initiation steps* and *termination steps*. An elementary initiation step does not have a reactive intermediate as a reactant, but it generates one or more reactive intermediates as products. Similarly, termination steps consume reactive intermediates without producing any new ones. As noted above, even though initiation and termination steps only need to occur a small

number of times compared to the propagation steps they are still a necessary kind of elementary reaction step for a chain reaction mechanism.

It has already been noted that every elementary step must be reversible. As such, the definitions just given for initiation and termination steps don't make much sense because the reverse of any initiation step will be a termination step by definition, and similarly, the reverse of any termination step will be an initiation step. It is perhaps better to refer to them as initiation/termination steps. Usually, when one says that a step is an initiation step, what they mean is that the step in the forward direction, as written, is an initiation step. Commonly, the mechanistic steps corresponding to an overall macroscopically observed reaction will be written so that the reactants in the initiation step are also reactants in the overall macroscopically observed reaction.

Chain transfer steps can also appear in chain reaction mechanisms. These steps are common in free radical polymerization mechanisms. In free radical polymerization, a very long hydrocarbon molecule (chain) has a free radical at one end. Monomer molecules react with the free radical end of the growing polymer chain, with the net result that the monomer unit adds to the end of the growing chain, and the free radical moves to the new end of that chain. In a *chain transfer step*, a monomer adds to the end of a growing polymer chain, but the free radical transfers to a different molecule. That is, a chain transfer step terminates one growing chain and starts a new one.

Yet another type of step in chain reactions is known as a chain branching step. Chain branching steps must be kept under control; if they are not controlled, they can lead to explosions. In an elementary *chain branching step*, one reactive intermediate is consumed, but two new reactive intermediates are generated. Clearly if these steps get out of control, the number of reactive intermediates will increase geometrically. This, coupled with the fact that reactive intermediates are so highly reactive, is why explosions can result from uncontrolled chain branching steps.

If it is not possible to identify propagation steps in a reaction mechanism, then the mechanism consists of an open sequence of reaction steps. Open sequences are a little less common than closed sequences. The reason has to do with the energy required for a reaction to take place. If, for example, in a chain reaction mechanism, the initiation step requires a significant energy input, but the propagation steps do not, the overall, macroscopically observed reaction is able to proceed with relative ease because the initiation step only needs to occur a small number of times. In contrast, if one step in an open sequence of steps requires a significant energy input, that amount of energy will be required every time the overall, macroscopically observed reaction takes place.

Returning to the rule that requires there to be a linear combination of the steps in the mechanism that equals the overall, macroscopically observed reaction, this means that when each step,  $s$ , is multiplied its own constant coefficient,  $b_s$ , and the results are added together, the overall, macroscopically observed reaction results. In some cases, there may not be unique values of  $b_s$  for every step in the reaction mechanism, but when the steps do have a unique value, the constant  $b_s$  is called the *stoichiometric number* of step  $s$ , which should not be confused with *stoichiometric coefficients* of species within the steps. The stoichiometric number corresponding to step  $s$ , namely  $b_s$ , is the number of times

step  $s$  must occur during a single occurrence of the overall, macroscopically-observed, non-elementary reaction.

Once a proposed mechanism has been checked to make sure it obeys the rules given earlier, it can be used to generate a rate expression for the corresponding non-elementary, macroscopically observed reaction, here denoted as reaction  $j$ . Specifically, the net rate of generation of species  $i$  in the overall macroscopically observed reaction,  $j$ , will be the sum of its rate of generation in each of the mechanistic steps. Thus, the rate of the overall macroscopically observed reaction,  $j$ , with respect to species  $i$  will be given by equation (6.8), where  $i$  denotes a reactant or product of the macroscopically observed overall (non-elementary) reaction,  $j$  denotes the macroscopically observed overall (non-elementary) reaction,  $s$  denotes a mechanistic step,  $v_{i,s}$  denotes the stoichiometric coefficient of species  $i$  in mechanistic step  $s$ ,  $r_{i,j}$  denotes the rate of the overall reaction  $j$  with respect to species  $i$  and  $r_s$  denotes the generalized rate of step  $s$ . By definition, the mechanistic steps are elementary reactions, and consequently their rate expressions are given by equation (6.1) or (6.2). Substitution of equation (6.1) into equation (6.8) gives equation (6.9) as the rate expression for the macroscopically observed reaction  $j$  with respect to species  $i$ .

$$r_{i,j} = \sum_{\substack{s=\text{all} \\ \text{steps}}} v_{i,s} r_s \quad (6.8)$$

$$r_{i,j} = \sum_{\substack{s=\text{all} \\ \text{steps}}} v_{i,s} \left( k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} [m]^{-v_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} [n]^{v_{n,s}} \right) \quad (6.9)$$