

# A First Course on Kinetics and Reaction Engineering

## Unit 4. Reaction Rates and Temperature Effects

### Overview

This course is divided into four parts, I through IV. Part II is focused upon modeling the rates of chemical reactions. Unit 4 is the first unit in Part II, and accordingly it begins by offering two commonly used definitions for a reaction rate. It then introduces rate expressions and discusses the variables that are expected to affect reaction rates and essential mathematical behavior that all rate expressions should exhibit. The sources for rate expressions are considered, and the unit presents the methodology used to generate one. Finally, Unit 4 examines the most common ways that temperature appears in a rate expression, with emphasis on the Arrhenius expression for temperature dependence of rate coefficients. The information in this unit is ubiquitous within “A First Course on Kinetics and Reaction Engineering,” so it should be mastered before proceeding to the next unit.

### Learning Objectives

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

- normalization factor
- catalyst
- heterogeneous catalyst
- homogeneous catalyst
- rate expression

Upon completion of this unit, you should be able to write the defining equation for the following quantities:

- rate of reaction  $j$  with respect to species  $i$
- generalized rate of reaction  $j$
- cell growth rate
- specific cell growth rate
- Arrhenius rate coefficient

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 differences between a chemical reaction rate and a cell growth rate
- List the steps for generating and validating a rate expression
- Realize that the mathematical form of a rate expression generally is not related to the stoichiometry of the reaction (see Example 4.1)
- Convert between generalized reaction rates and rates with respect to different participant species (see Examples 4.1 and 4.2)
- Select appropriate normalization factors for different kinds of reacting systems (see Example 4.1)
- Convert rates from one normalization factor to another (see Example 4.2)
- Describe the mathematical restrictions upon the functions used as rate expressions, and use them to determine whether a given function is suitable as a rate expression (see Example 4.3)

- Explain what is meant by “fit the design equations(s) to the experimental data” (see Example 4.6)
- Identify the pre-exponential factor and the activation energy in the Arrhenius expression for a rate coefficient (see Example 4.5)
- Find values for the pre-exponential factor, the activation energy or a rate coefficient at any temperature, given appropriate data (see Examples 4.5 and 4.6)

### Information

In this course, chemical reaction rates will be defined in two, related ways. The first is *the net rate of reaction  $j$  with respect to species  $i$* , symbolized by  $r_{i,j}$ . Consider a small volume element where a chemical reaction is taking place, and throughout which the composition, temperature and pressure are uniform. Letting  $V$  denote the volume of this element and  $\Delta n_{i,j}$  denote the net change in the number of moles of species  $i$  due to reaction  $j$  that occurs over an interval of time,  $\Delta t$ , the rate of reaction  $j$  with respect to species  $i$  can then be defined as shown in equation (4.1)

$$r_{i,j} = \frac{1}{V} \lim_{\Delta t \rightarrow 0} \frac{\Delta n_{i,j}}{\Delta t} = \frac{1}{V} \frac{dn_{i,j}}{dt} \quad (4.1)$$

In this case the rate is said to be normalized using the volume,  $V$ , of the system. Some reactions only take place on surfaces. In those cases, the best normalization factor for chemical reaction rates is the area of the surface on which the reaction occurs. The *normalization factor* is important because it makes the rate of reaction an intensive quantity. This is desirable since it permits measuring the rate of reaction in one location (say a small laboratory reactor) and then using that rate to describe the same reaction taking place somewhere else (say in a chemical plant). *The most appropriate normalization factor to use is the actual location where the reaction takes place.* Sometimes other normalization factors are used, and if care is not taken, this can lead to serious errors.

Heterogeneous catalytic reactions are one example of surface reactions. A *catalyst* is a material that, when added to a reaction environment, causes the rate of one or more reactions to increase, while the catalyst, itself, is neither produced nor consumed in the reaction. It is called a *heterogeneous* catalyst if the catalyst represents a different phase from the reacting mixture (e. g. a solid catalyst that catalyzes the reaction of gas phase reactants). Thus, an appropriate normalization factor for a reaction that is catalyzed by a heterogeneous catalyst would be the surface area of that catalyst. Alternatively it is called a *homogeneous* catalyst if the catalyst is in the same phase as the reactants and products (for example an acid dissolved in a solution that catalyzes the reaction between other solutes present in the solution).

The rate was defined in equation (4.1) above with respect to one particular species participating in the reaction. It is also possible to define a generalized rate of reaction. The *generalized net rate of reaction  $j$* ,  $r_j$ , defined in equation (4.2) below, is not tied to any one chemical species, but it does depend upon how the chemical reaction is written. (In particular, it depends upon which set of stoichiometric coefficients is used when writing the reaction.)

$$r_j = \frac{r_{i,j}}{\nu_{i,j}} = \frac{1}{V} \frac{d\xi_j}{dt} \quad (4.2)$$

The generalized rate of reaction is always positive, and it is useful for relating the rate with respect to one species to the rate (of the same reaction) with respect to a different species as shown in equation (4.3).

$$r_j = \frac{r_{i,j}}{\nu_{i,j}} = \frac{r_{k,j}}{\nu_{k,j}} \quad (4.3)$$

Biological cell growth often uses a slightly different definition for the rate. Recall that in cell growth there is no exact stoichiometry. It is very common to use both a cell growth rate and a specific growth rate. The *cell growth rate*,  $r_g$ , is defined in equation (4.4). It is analogous to the chemical reaction rate with respect to a particular species as defined above in equation (4.1), except instead of using the change in the number of moles, it uses the change in the mass of cells,  $m_{cells}$ .

$$r_g = \frac{1}{V} \lim_{\Delta t \rightarrow 0} \frac{\Delta m_{cells}}{\Delta t} = \frac{1}{V} \frac{dm_{cells}}{dt} \quad (4.4)$$

Letting  $C_{cells}$  denote the mass concentration of cells (for example, in units of  $\text{g cm}^{-3}$ ), the *specific cell growth rate*,  $\mu$ , is then defined as in equation (4.5).

$$\mu = \frac{r_g}{C_{cells}} \quad (4.5)$$

A *rate expression* is a mathematical equation expressing the functional dependence of a reaction rate upon the environmental variables (temperature, pressure and composition). That is, if  $\underline{x}$  is used to denote some set of composition variables, the rate expression is of the form given in equation (4.6). The function  $f$  in a rate expression should meet two criteria. First, the function  $f$  should be single-valued (if you substitute realistic values for  $T$ ,  $P$ , and  $\underline{x}$ , it should yield a single real root). Additionally, the function  $f$  should evaluate to zero if a temperature, pressure and composition that correspond to thermodynamic equilibrium are substituted into it.

$$r_j = f(T, P, \underline{x}) \quad (4.6)$$

The reason for the first criterion, that the rate expression be single valued, should be obvious. In a real chemically reacting system, setting the local temperature, pressure and composition fixes the local rate of reaction, and for any one temperature, pressure and composition, the rate is always the same. This criterion stipulates that the rate expression must yield that rate. The second criterion is a result of our definition of the rate as being the **net** change in the moles over time. Once thermodynamic equilibrium has been reached, there is no further change in the composition, and so the **net** rate becomes equal to

zero. At the molecular level, the reaction will still be taking place, but each occurrence in the forward direction is offset by an occurrence in the reverse direction.

In general, there is no way to know the mathematical form of a rate expression for a reaction. In thermodynamics, the equilibrium expression can be written as long as the reaction stoichiometry is known, but this is not true for rate expressions. The HBr synthesis reaction is given in equation (4.7). The rate expression for this reaction, equation (4.8) below, can't be simply generated from the stoichiometry, and if someone was shown the reaction, it's unlikely that they would guess the correct rate expression.



$$r_{4.7} = \frac{k_A P_{\text{H}_2}}{K_B + \frac{P_{\text{Br}_2}}{P_{\text{HBr}}}} \quad (4.8)$$

Unless someone else has already found an acceptable rate expression for a reaction, the rate expression must be generated by trial and error. Experimental data are needed for the trial and error process, so before the rate expression can be generated, it is necessary to perform experiments. Such experiments will be considered in detail in later units. For present purposes, the process of generating a rate expression can be summarized in the following trial and error procedure:

1. Choose a reactor for the experiments
  - a. Generate design equations for that reactor
  - b. Validate the design equations
2. Gather experimental data
  - a. Use the widest possible range of environmental variables
  - b. At the minimum, span the range of environmental variables in which the rate expression is expected to be used
3. Pick a mathematical function to be tested as a rate expression either
  - a. Empirically or
  - b. Based on theory
4. Substitute the rate expression selected in step 3 into the design equation(s) from step 1 and fit the resulting equation(s) to the data from step 2 by
  - a. Calculating its average value if there is only one parameter in the rate expression or
  - b. Least-squares fitting if there are multiple parameters
5. Decide whether the fit of the design equation to the data is acceptable based upon
  - a. Correlation coefficient
  - b. Confidence intervals or standard deviation of the parameter(s)
  - c. Rectifying (parity) plot
  - d. Residuals plots
6. If the accuracy of the fit is not acceptable, go back to step 3 and repeat the process using a different mathematical function.
7. The mathematical function that yielded an acceptable fit may be used as the rate expression within the range of the experimental data used in the fitting
  - a. There may be other mathematical functions that are just as accurate

- b. The rate expression may fail if extrapolated to values of the environmental variables outside the range used in the fitting

Subsequent units will consider each of the steps in this procedure in detail, but a few points are particularly important and worth mentioning briefly here. The first is the validation of the design equation(s). Kinetics experiments typically involve setting a reactor's temperature, pressure and initial or inlet composition and then measuring its final or outlet composition. The rate is not measured directly, but instead it is extracted from an analysis of the reactor. For this reason, it is particularly important to ensure that an accurate model is being used for the reactor. Each assumption that is made about the reactor should be tested and validated before the data are used (or better, before the data are even collected).

The second point involves the rate expressions and the parameters they contain. The mathematical expressions that are selected for testing as rate expressions will always contain one or more unknown parameters. For example, the values of rate coefficients, such as the  $k_A$  that appears in rate expression (4.8), are normally unknown before experimental studies are initiated. The "best" value for such parameters is selected as being the value that minimizes differences between the experimentally measured data and the corresponding data predicted by the rate expression/design equation. This is what is meant by the term "fit" in step 4 above, selecting the values for the parameters that minimize errors between what was measured experimentally and what the design equation (which contains the rate expression) predicts.

In the process for generating and validating a rate expression, one needs to select a rate expression to be tested (see step 3 above). Recall that the rate expression is a mathematical equation for the rate of a chemical reaction in terms of the environmental variables, that is, in terms of the temperature, pressure and composition. Temperature most commonly appears in a rate expression in three ways: in certain composition variables for gas phase species, embedded in equilibrium constants and embedded in rate coefficients.

For gas phase species, the partial pressure and the concentration depend upon temperature. For example, if species  $i$  is an ideal gas, then the partial pressure of species  $i$  depends upon the temperature according to equation (4.9), and similarly the concentration of species  $i$  depends upon the temperature according to equation (4.10). Thus, if a rate expression for a reaction involving gases is written using either the partial pressure or the concentration to represent the composition, then these quantities, in turn will depend upon the temperature.

$$P_i = \frac{n_i RT}{V} \quad (4.9)$$

$$C_i = \frac{n_i}{V} = \frac{P_i}{RT} \quad (4.10)$$

We will see that the equilibrium constant for a reaction may appear in a rate expression. The equilibrium constant depends exponentially upon the temperature, as was seen in Unit 3. For example, approximating the entropy and enthalpy of the reaction as constants, the equilibrium constant for a

reaction,  $j$ , is given by equation (4.11). Even though  $\Delta S_j$  and  $\Delta H_j$  are also functions of temperature, equation (4.11) often provides a good representation of the temperature dependence of the equilibrium constant, particularly if it is only used over a restricted range of temperatures.

$$K_j = \exp\left\{\frac{-\Delta G_j}{RT}\right\} = \exp\left\{\frac{\Delta S_j}{R}\right\} \exp\left\{\frac{-\Delta H_j}{RT}\right\} = K_{0,j} \exp\left\{\frac{-\Delta H_j}{RT}\right\} \quad (4.11)$$

The final way that temperature commonly appears in a rate expression is within the rate coefficient. Way back in 1889, Svante Arrhenius [1] used thermodynamic arguments and proposed that rate coefficients should depend upon the temperature according to equation (4.12). This expression has come to be known as the Arrhenius expression. It is the most common way to express the temperature dependence of a rate coefficient. The quantity  $k_{0,j}$  in equation (4.12) is often referred to as the pre-exponential factor and the quantity  $E_j$  is called the activation energy. While  $k_{0,j}$  has been used here to represent the pre-exponential factor, it is also very common to denote it as  $A_j$ . In general, the pre-exponential factor and the activation energy are taken to be constants, and their values are determined using experimental data. The well-known Arrhenius plot involves plotting the log (base  $e$ ) of the rate coefficient versus the reciprocal of the temperature. It can be seen from equation (4.13) that such a plot is expected to be linear with a slope equal to the negative of the activation energy divided by the gas constant and an intercept equal to the log (base  $e$ ) of the pre-exponential factor.

$$k_j = k_{0,j} \exp\left(\frac{-E_j}{RT}\right) \quad (4.12)$$

$$\ln k_j = \left(\frac{-E_j}{R}\right) \frac{1}{T} + \ln k_{0,j} \quad (4.13)$$

While the Arrhenius expression is very widely used to represent the temperature dependence of rate coefficients, there are other equations that are also used. These will not be explicitly presented here, but they might appear occasionally in examples or problems in other units in this course.

If you compare the temperature dependence of an equilibrium constant, as given in equation (4.11) to the Arrhenius expression, equation (4.13), you will see that they have an identical mathematical form. There is one notable difference between the two expressions, however. In the case of an equilibrium constant, the heat of the reaction appears in the numerator of the exponential term. We already know that the heat of reaction can be either positive or negative. In the case of a rate coefficient, the activation energy appears in the numerator of the exponential term, and the activation energy must always be positive in value. As such, a rate coefficient will always increase as the temperature increases whereas an equilibrium constant may either increase or decrease as the temperature increases, depending upon whether the reaction is exothermic or endothermic. You should convince yourself that an equilibrium constant for an exothermic reaction will decrease as the temperature increases; an equilibrium constant for an endothermic reaction increases with increasing temperature.

**References Cited**

1. S. Arrhenius, "Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren," Z. Physik. Chem. 4, 226 (1889).