

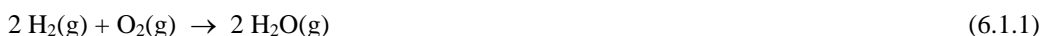
CHM 3400 – Fundamentals of Physical Chemistry
Chapter 6 - Supplementary Material

1. Basic concepts in chemical kinetics

One of the results of our application of thermodynamics to systems of interest to chemists was the development of a method for finding the equilibrium constant for a chemical reaction. This made it possible to predict, given the initial conditions in a system, the final concentrations of chemical substances present when equilibrium occurs.

We are also interested in the time it takes for a system to reach equilibrium. Chemical kinetics is the study of the rates at which chemical reactions occur, along with the mechanisms and other aspects of reactions.

To begin we will focus on irreversible chemical reactions, that is, reactions that only proceed to a significant extent in one direction. As an example, consider the combustion of hydrogen to form water.



Assuming that there is no significant concentration of reaction intermediates (species that form and then disappear as reactants are converted into products), the rate at which the above reaction occurs can be determined by either measuring the rate of disappearance of H_2 or O_2 , or the rate of appearance of H_2O . These can be written in terms of the change in concentration of these species as a function of time.

$$\text{disappearance of H}_2 \quad \text{d[H}_2\text{]}/\text{dt} \quad (6.1.2)$$

$$\text{disappearance of O}_2 \quad \text{d[O}_2\text{]}/\text{dt} \quad (6.1.3)$$

$$\text{appearance of H}_2\text{O} \quad \text{d[H}_2\text{O]}/\text{dt} \quad (6.1.4)$$

Note that other ways of expressing concentration, such as partial pressure (for gases) can also be used.

However, there is a problem with using the eq 6.1.2 – 6.1.4 to follow the rate of chemical reaction. For our example, hydrogen disappears from the system twice as fast as oxygen. In addition, concentrations of H_2 and O_2 decrease as the reaction proceeds, while concentration of H_2O increases. To avoid these problems and obtain the same value for the rate of a chemical reaction we do the following. First, we divide the observed change in concentration with respect to time by the stoichiometric coefficient used to balance the reaction. Second, we add a negative sign when examining the change in concentration of a reactant. For the reaction in eq 6.1.1, this rate of reaction is then

$$\text{Rate} = - (1/2) \text{d[H}_2\text{]}/\text{dt} = - \text{d[O}_2\text{]}/\text{dt} = + (1/2) \text{d[H}_2\text{O]}/\text{dt} \quad (6.1.5)$$

Using this method for expressing the rate of reaction leads to a value for the rate that is the same no matter which reactant or product concentration is monitored.

One goal of chemical kinetics is to find an equation, called a rate law, that predicts the rate of a chemical reaction as a function of the properties of the system, including temperature, concentrations of reactants, products, and other species present, and anything else that might affect how fast the reaction takes place. There is no reason to expect this will lead to a simple expression for the rate of reaction. However, it is often observed, particularly for simple reactions, that the rate law takes on the following form

$$\text{Rate} = k [\text{A}]^p [\text{B}]^q [\text{C}]^r \quad (6.1.6)$$

In eq 6.1.6 A, B, C, ... represent concentrations of chemical substances in the system that affect the rate at which the reaction takes place (these are usually reactants, though the rate of reaction can also depend on the concentration of a

product, or of a catalyst). The power p is called the order of reaction with respect to A, and similarly for q and r . The reaction orders are expected (based on the connection between rate laws and reaction mechanisms, discussed later) to be zero or small positive integers, although fractional reaction orders or negative values for reaction order are occasionally observed. An overall order of reaction is defined as the sum of the individual reaction orders. Finally, k , the rate constant, is a number whose value only depends on temperature. The units of k are different for different reactions, and can be found using dimensional analysis.

For some reactions, particularly those with complicated reaction mechanisms, expressions more complicated than 6.1.6 are needed. In fact, for many systems computer modeling is required to predict how reactant and product concentrations change with time. However, eq 6.1.6 is often seen to apply for simple reactions.

2. Initial rate method

To make use of eq 6.1.6 requires that the values for the reaction orders and rate constant be found. Several methods for doing this have been developed, the most common of which is the method of initial rates.

Consider a reaction whose rate law is given by eq 6.1.6. If we take the logarithm of both sides of this equation we get

$$\ln(\text{Rate}) = \ln(R) = \ln(k) + p \ln[A] + q \ln[B] + r \ln[C] \quad (6.2.1)$$

The observed rate of reaction will change as the reaction proceeds, as the concentrations of A, B, C...will change. However, if we measure the initial rate of reaction the concentrations will be their initial values, which can be found from knowing how the reaction system has been prepared. So

$$\ln(R_i) = \ln(k) + p \ln[A]_i + q \ln[B]_i + r \ln[C]_i \quad (6.2.2)$$

where we use “i” to indicate the initial rate and initial concentrations.

If we take the derivative of eq 6.2.2 with respect to $\ln[A]_i$, the logarithm of the initial concentration of A, for a series of experiments where the initial concentrations of B and C are held constant, and conducted at the same temperature, then

$$\left(\frac{\partial \ln(k)}{\partial \ln[A]_i}\right)_{[B]_i, [C]_i, T} = \left(\frac{\partial \ln[B]_i}{\partial \ln[A]_i}\right)_{[B]_i, [C]_i, T} = \left(\frac{\partial \ln[C]_i}{\partial \ln[A]_i}\right)_{[B]_i, [C]_i, T} = 0 \quad (6.2.3)$$

and so

$$\left(\frac{\partial \ln(R_i)}{\partial \ln[A]_i}\right)_{[B]_i, [C]_i, T} = p \quad (6.2.4)$$

Equation 6.2.4 tells us that if we plot $\ln(R_i)$ vs $\ln[A]_i$ for a series of experiments carried out at the same temperature and where the initial concentrations of B and C are kept constant, the slope will be equal to p , the order of reaction with respect to A. The other reaction orders can be found in a similar manner.

$$\left(\frac{\partial \ln(R_i)}{\partial \ln[B]_i}\right)_{[A]_i, [C]_i, T} = q \quad (6.2.5)$$

$$\left(\frac{\partial \ln(R_i)}{\partial \ln[C]_i}\right)_{[A]_i, [B]_i, T} = r \quad (6.2.6)$$

Once the reactions orders have been determined, the value for the rate constant can be found by solving eq 6.1.6 for k

$$k = \frac{R_i}{[A]_i^p [B]_i^q [C]_i^r} \quad (6.2.7)$$

Note that before eq 6.2.7 is used to find an experimental value for k, we should round off the values for the reaction orders p, q, r...to the nearest integer values, based on our expectations.

If we have experimental values for the initial rate of reaction for two experiments carried out at the same temperature and where all but the initial concentration of A have been held constant, eq 6.2.4 can be used to find the following result

$$\frac{\ln(R_{i,2}/R_{i,1})}{\ln([A]_{i,2}/[A]_{i,1})} = p \quad (6.2.8)$$

with similar expressions that can be used to find the values for q and r. Note, however, it is far better, when the data are available, to use eq 6.2.4, 6.2.5, and 6.2.6 to find the reaction orders rather than expressions such as eq 6.2.8. This is because plotting all of the data tends to average out errors in the individual experiments.

3. Integrated rate laws

There are several common rate laws that are observed for chemical reactions. These are labeled in terms of the overall order of reaction, and whether the rate law is homogeneous (depends on only one concentration) or heterogeneous (depends on several concentrations). These include the following

$$\text{Rate} = k \quad \text{zero order reaction} \quad (6.3.1)$$

$$\text{Rate} = k [A] \quad \text{first order, homogeneous} \quad (6.3.2)$$

$$\text{Rate} = k [A]^2 \quad \text{second order, homogeneous} \quad (6.3.3)$$

$$\text{Rate} = k [A] [B] \quad \text{second order, heterogeneous} \quad (6.3.4)$$

Note that there are several possible second order heterogeneous rate laws, with eq 6.3.4 being the one most commonly observed.