Name ______________________________________ AP Chemistry
Chapter 14 Chemical Kinetics

In this chapter we will examine chemical kinetics, a term that describes the rate of a chemical reaction. We will look at the factors that determine how fast a reaction occurs. More specifically, we will examine:

14.1 Reaction Rates

The speed at which a chemical reaction occurs is called the reaction rate. Several things have the capacity to affect the rate of a reaction, including reactant concentrations, temperature, presence of a catalyst, and surface area of reactants or catalysts.

14.2 The Dependence of Rate on Concentration

In this section the terms *rate constant* and *rate law* are introduced. You will learn how the units of the rate constant depend on the overall *order* of a reaction. You will also see the dependence of reaction rate on concentration of reactants, and a simulation in this section will explore this relationship.

14.3 The Change of Concentration with Time

Chemical reactions typically slow down as they progress. In this section you will encounter equations that show how the concentration of a reactant varies as a function of time. The term *half-life* is introduced, and you will learn to calculate the half-life of a process. The terms *first order*, and *second order* are presented, and equations are derived for solving problems of each type. You will use a simulation again in this section to explore the time-concentration connection..

14.4 Temperature and Rate

Reactions occur faster at higher temperatures. In this section the quantitative relationship between rate and temperature is presented. You will learn the term *activation energy*, and a simulation will illustrate the relationships that are derived.

14.5 Reaction Mechanisms

Some reactions occur in a single step, but many occur in a *series* of steps called *elementary processes*. In this section you will watch an animation of a *bimolecular* process, and you will learn how to tell whether a proposed reaction mechanism is plausible.

14.6 Catalysis

A catalyst increases the rate of a reaction by providing a different mechanism with a lower activation energy. You will learn about homogeneous and heterogeneous catalysis, and you'll see an animation of a catalyzed reaction on the atomic level.

Section 14.1 Reaction Rates

Chemical kinetics is the study of how rapidly chemical reactions occur. The **reaction rate** is defined in terms of the rate of appearance of a product or the rate of disappearance of a reactant. Reaction rates depend on

1. *The concentrations of the reactants:* Most chemical reactions proceed faster if the concentration of one or more of the reactants is increased. For example, steel wool burns with difficulty in air, which contains 20 percent O_2, but bursts into a brilliant white flame in pure oxygen.
2. *The temperature at which the reaction occurs:* The rates of chemical reactions increase as the temperature increases. It is for this reason that we refrigerate perishable foods such as milk. The bacterial reactions that lead to the spoiling of milk proceed much more rapidly at room temperature than they do at the lower temperatures of a refrigerator.
3. *The presence of a catalyst:* The rates of many reactions can be increased by adding a substance known as a *catalyst*. We will see that a catalyst increases the rate of a reaction, yet the catalyst is not consumed in the reaction. The physiology of most living species depends crucially on enzymes, protein molecules that act as catalysts, which increase the rates of selected biochemical reactions.
4. *The surface area of solid or liquid reactants of catalysts:* Reactions that involve solids often proceed faster as the surface area of the solid is increased. For example, a medicine in the form of a tablet will dissolve in the stomach and enter the bloodstream more slowly than the same medicine in the form of a fine powder.

Average and instantaneous Rates of Reaction

We can define the *average* rate of reaction as the change in moles of B (or A) per unit time. For the time interval between 0 and 20 minutes, the average rate is

We can also express this average rate in terms of the disappearance of A. Because the number of moles of A decreases, it is necessary to introduce a minus sign into the formula in order for rate to be expressed as a positive quantity.

The rate of appearance of B is equal to the rate of disappearance of A because they have a one-to-one stoichiometric relationship. Table 14.1 gives the average rate for each ten-second interval for the reaction A→ B.

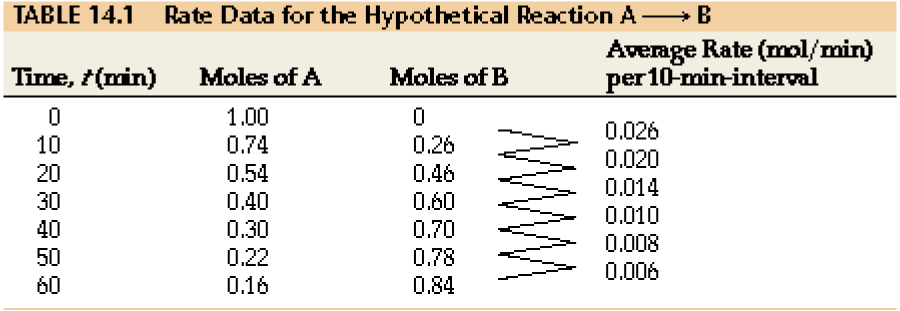


TABLE 14.1 Rate Data for the Hypothetical Reaction A ⟶ B

Time, *t* (min)	Moles of A	Moles of B	Average Rate (mol/min) per 10-min-interval
0	1.00	0	0.026
10	0.74	0.26	0.020
20	0.54	0.46	0.014
30	0.40	0.60	0.010
40	0.30	0.70	0.008
50	0.22	0.78	0.006
60	0.16	0.84	

Most often, reaction rates are expressed in units of concentration, usually *M*/s (Ms^{-1}), rather than moles. Consider the reaction

We start with a 0.1000 *M* aqueous solution of C_4H_9Cl and monitor the concentration as the reaction proceeds over the course of 15 minutes. We can express the average rate of reaction in terms of the change in concentration. (Square brackets are used to denote concentration.)

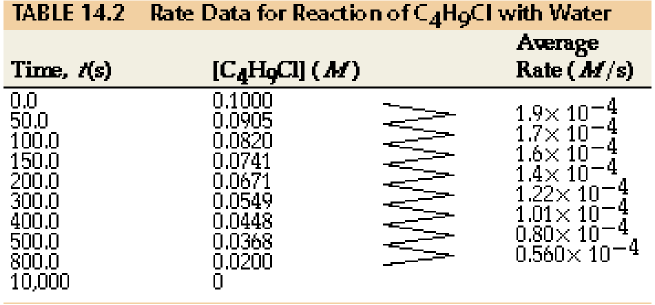


TABLE 14.2 Rate Data for Reaction of C_4H_9Cl with Water

Time, *t* (s)	$[C_4H_9Cl]$ (*M*)	Average Rate (*M*/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

Figure 14.5 shows the plot of $[C_4H_9Cl]$ versus time. Although we can calculate the average rate, it is usually desirable to know the **instantaneous rate** of a reaction at a particular time. The instantaneous rate is equal to the slope of the tangent to the curve at any given time.

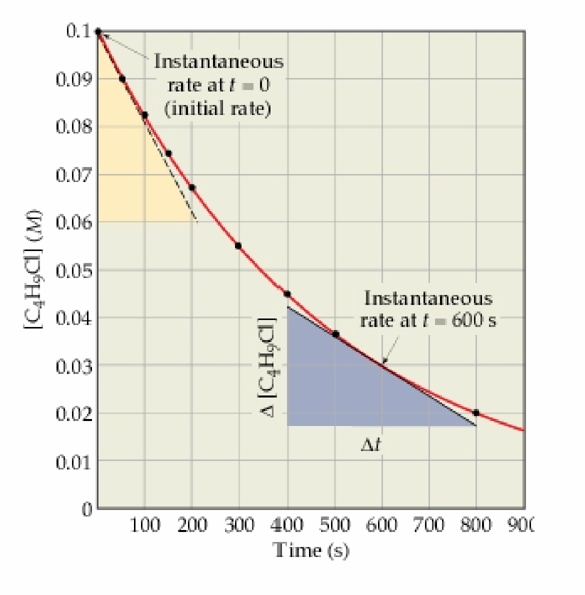


Figure 14. 5. Concentration of butyl chloride, C_4H_9Cl, as a function of time. The dots represent the experimental data from the first two columns of Table 14.2, and the red curve is drawn to smoothly connect these data points. Lines are drawn that are tangent to the curve at *t* = 0 and *t* = 600 s. Point at the tangent line at 600 s to see how the instantaneous reaction rate is calculated.

Section 14.1 practice problems

1. Using the data in Table 14.2, calculate the average rate of disappearance of C_4H_9Cl over the time interval from 50 to 150 seconds.

(b) Using Figure 14.5 estimate the instantaneous rate of disappearance of C_4H_9Cl at t = 0 (the initial state)

2. Using Figure 14.5, estimate the instantaneous rate of disappearance of C_4H_9Cl at t = 300 seconds.

3. How is the rate of disappearance of ozone related to the rate of appearance of oxygen in the following equation: $2O_3(g) \rightarrow 3O_2(g)$?

(b) If the rate of appearance of O_2, $\Delta[O_2] / \Delta t$, is 6.0×10^{-5} M/s at a particular instant, what is the value of the rate of disappearance of O_3, $-\Delta[O_3] / \Delta t$ at this same time?

4. The decomposition of N_2O_5 proceeds according to the following reaction: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

If the rate of disappearance of N_2O_5 at a particular instant in a reaction vessel is 4.2×10^{-7}M/s, what is the rate of appearance of

(a) NO_2

(b) O_2

Section 14.2 the Dependence of Rate on Concentration

Most chemical reactions slow down as they progress. This is due to the dependence of the reaction rate on reactant concentration. To study the effect that concentration has on the rate of a reaction, we vary the concentrations of reactants and measure the initial rate of reaction at each concentration. Table 14.3 contains data collected for the reaction

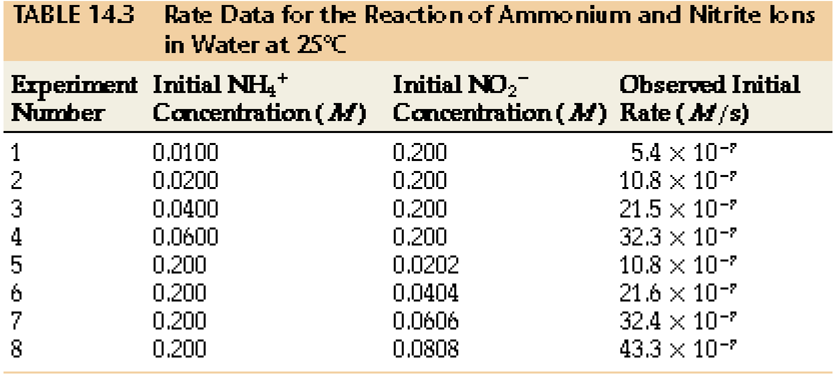


TABLE 14.3 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C

Experiment Number	Initial NH_4^+ Concentration (*M*)	Initial NO_2^- Concentration (*M*)	Observed Initial Rate (*M*/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

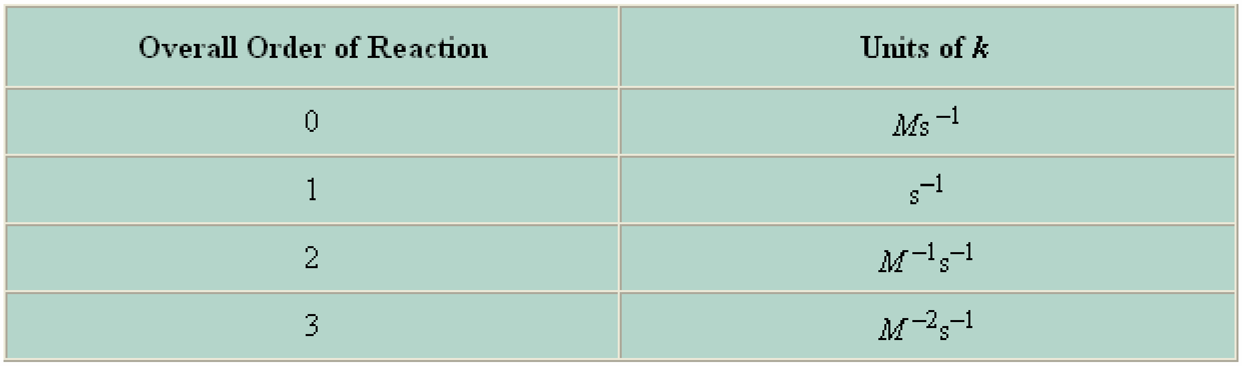
The data in the table indicate that the rate of this reaction does depend on the concentrations of both reactants. In fact, the rate appears to be proportional to each of the concentrations. If it is proportional to each reactant's concentration, then it is proportional to the *product* of their concentrations.

The constant *k* is the **rate constant**. The equation relating rate to reactant concentrations is called the **rate law**. Using any of the experiments listed in the table, we can determine the value of the rate constant. Using the data from experiment 2,

In general, reactions have the rate law

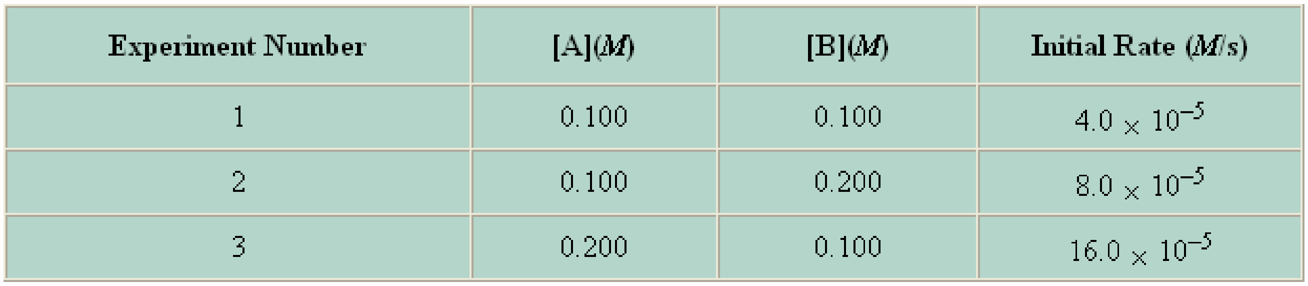
The exponents *m* and *n* must be determined experimentally. The exponent to which a reactant's concentration is raised in the rate law is referred to as the **reaction order** with respect to that reactant. In the ammonium ion and nitrite ion example, the exponents in the rate law were both 1. We would say that the reaction is *first order in ammonium ion* and *first order in nitrite ion.* The **overall reaction order** is the sum of the exponents in the rate law. We would then say that the ammonium and nitrite reaction is *second order overall*.

Units of the rate constant depend on the overall order of the reaction. In the ammonium and nitrite example the units of *k* are $M^{-1}s^{-1}$. These are the units necessary to cancel properly and give the rate in units of Ms^{-1}.



Overall Order of Reaction	Units of k
0	Ms^{-1}
1	s^{-1}
2	$M^{-1}s^{-1}$
3	$M^{-2}s^{-1}$

The rate law for a reaction can be determined using the method of initial rates. (Table 14.3 gave the initial rates for a series of experiments in which the reactant concentrations were varied.) For the reaction A + B $\rightarrow$ C, the following data were collected.



Experiment Number	[A](*M*)	[B](*M*)	Initial Rate (*M*/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	8.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

The rate law for this reaction is rate = $k[A]^m[B]^n$. We will use the experimental data to determine the values of *m*, *n*, and *k*.

To evaluate the effect of *one* reactant's concentration, we compare two experiments in which the *other* reactant concentration does not change. Note that when the concentration of A remains constant and the concentration of B is doubled, the rate doubles. This tells us that the reaction is first order in B.

When the concentration of B remains constant and the concentration of A is doubled, the rate increases by a factor of four. This tells us that the reaction is second order in A.

Reaction rate =

The reaction is ___________________________________

Practice Using Initial Rates to Determine Rate Laws

1. A particular reaction was found to depend on the concentration of the hydrogen ion, $[H^+]$. The initial rates varied as a function of $[H^+]$ as follows.

$[H^+]$ (M)	0.500	0.100	0.200
initial rate (M/s)	6.4×10^{-7}	3.2×10^{-7}	1.6×10^{-7}

(a) What is the order of the reaction in $[H^+]$?

(b) Predict the initial reaction rate when $[H^+] = 0.400$ M.

2. Consider the following reaction: $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

(a) The rate law for this reaction is first order in H_2 and second order in NO. Write the rate law.

(b) If the rate constant for the reaction at 1000K is $6.0 \times 10^4\ M^{-2} \cdot s^{-1}$, what is the reaction rate when $[NO] = 0.050$ M and $[H_2] = 0.010$ M?

(c) What is the reaction rate at 1000K when the concentration of NO is doubled, to 0.10 M, while the concentration of H_2 is 0.010 M?