# Chemical Kinetics and Rate Constants
ONEXYS Read-ahead

Introduction

Chemistry is all around us, from the rusting of iron to the cooking of food to the use of batteries and electricity to power our daily necessities. Chemical reactions are the means by which we sense the world around us, whether through odorants activating the olfactory systems of our brains or through light waves activating photoreceptor cells in our retina. An MIT study estimated that within a human cell over 100 chemical reactions can take place in a single second. Two of the most important questions that chemists consider are how fast these reactions occur, and how can their rates be controlled. *Chemical kinetics* is the area of chemistry specifically concerned with the rate of chemical reactions.

The general equation for any reaction is given by

$$\text{Reactants} \longrightarrow \text{Products}.$$
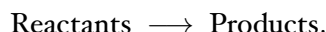
As an example of what happens to the number of molecules of reactants (A) and products (B) in such a reaction, Figure 1 shows the progress of a reaction $A \longrightarrow B$ over time.
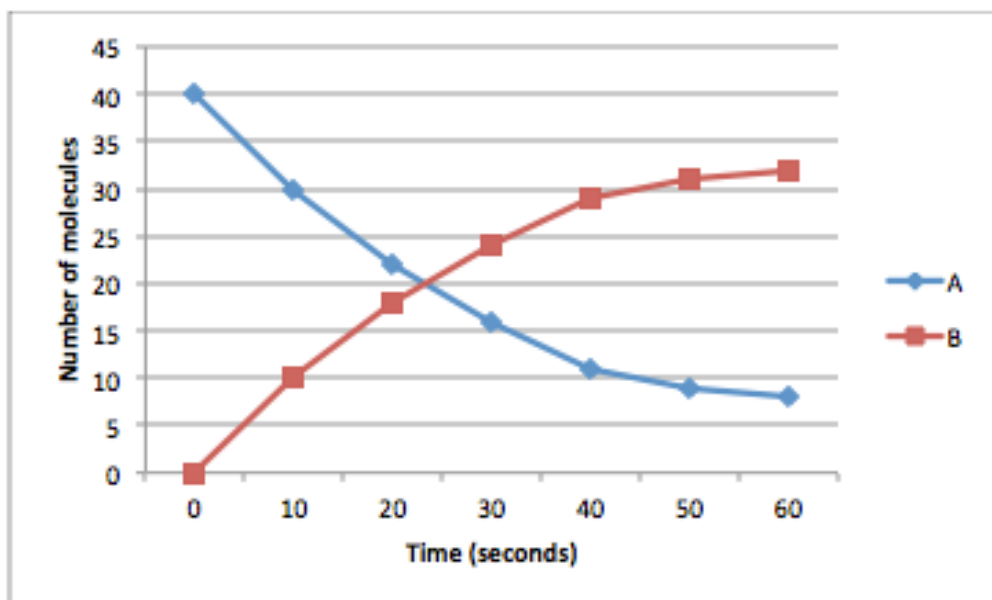

Figure 1: The progress of a chemical reaction over time.

The rate (or "velocity") of this reaction can be calculated by examining the change of the number of molecules over time. Assuming each reactant molecule lost becomes one product molecule gained the rate v can be approximated by the average rate over a small time interval, i.e.,

$$v \approx -\frac{\Delta A}{\Delta t} = \frac{\Delta B}{\Delta t},$$

where Δt is a (small) interval of time, $\Delta A = A_{\text{end}} - A_{\text{start}}$ is the change in the number of molecules of reactant in this time interval, and ΔB is the change in the number of molecules of product.

The simplest possible assumption is that the rate of a chemical equation is proportional to the concentrations of each of the reactants. The proportionality constant (k) is called the *rate constant*. k depends on many factors, including temperature, and must be determined experimentally. For example, for a reversible reaction with a forward rate constant of k_f and a backward rate constant of k_r, denoted by

$$A + B \xrightarrow{k_f} C$$
$$A + B \xleftarrow{k_r} C,$$
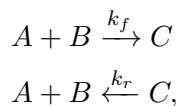
the net rate of C production equals $v = k_f[A][B] - k_r[C]$, where $[A]$ is the concentration of A, $[B]$ the concentration of B, and $[C]$ the concentration of C. At some point, the rate of production of C will saturate such that there is a complete balance between the forward reaction and the backward reaction. This is called *steady state*. In steady state $v = 0$, and there is no change in the concentration of C with time.

Instructions

After reading through the *Chemical Kinetics and Rate Constants* context and questions below, you should complete the application reflection in Canvas. Note: *you will have a chance to talk further with your coach before answering the questions below in detail*. The point of the pre-read is to "prime the pump" for further conversations with your coaches.

Chemical Kinetics and Rate Constants

Going back to the simple chemical equation we examined in the introduction, we will now take a closer look at 1) how to determine the rate constant, and 2) what this rate constant really represents.

While it can easily be identified how many molecules of A must react with a certain number of molecules of B to produce one molecule of C, the dependence of the rate of a reaction on the concentrations $[A]$ and $[B]$ of reactants must be determined empirically. The rate of the reaction can be proportional to the concentration of a reactant, the square of the concentration of the reactant and so on. In the introduction we assumed that the reaction rates are directly proportional to the concentrations of the reactants. In general, the rate for an irreversible $A + B \longrightarrow C$ reaction can be written as $v = k[A]^x[B]^y$, where x is the *order* of the reaction with respect to A and y is the order of the reaction with respect to B.

Questions

1. For an irreversible reaction $A + B \longrightarrow C$, write the equation for the reaction rate v if it is proportional to the square root of $[A]$ and to the square of $[B]$.
2. Suppose you perform a series of experiments with different concentrations of reactants A and B and measure the reaction rate. (Assume the reaction is irreversible.) From the data given below, determine x, y and k for the reaction rate $v = k[A]^x[B]^y$.

Experiment	Concentration of A (Molar)	Concentration of B (Molar)	Rate (Molar/s)
1	0.100	0.100	$3.00 * 10^{-6}$
2	0.200	0.100	$1.20 * 10^{-5}$
3	0.400	0.100	$4.80 * 10^{-5}$
4	0.100	0.300	$9.00 * 10^{-6}$
5	0.100	0.600	$1.80 * 10^{-5}$

Chemistry experiments are usually done under certain conditions. For example, you may remember from a high school chemistry course the term "STP" or standard temperature and pressure (Temperature = 273 K and Pressure = 1 atm). Chemical reactions occur at different rates at different temperatures. At higher temperatures, molecules have increased thermal energy and move faster. The increased energy and speed of molecules allows them to come into contact with other molecules more readily and thus allow for more rapid reactions.

The rate of a reaction can be thought to be proportional to the rate of molecule collisions. As molecules are colliding their energy must surpass an energetic barrier called the *activation energy* in order to initiate a reaction. The activation energy is defined as the minimum amount of energy needed for a reaction to occur. The activation energy of a reaction is like an energetic hill that needs to be climbed over in order to produce reaction products.

The dependence of the rate constant on temperature was studied in the late 19th century by the Swedish scientist Svante Arrhenius, who empirically described this relationship and coined the equation after himself. The Arrhenius equation is

$$k = Ae^{-E_a/RT},$$

where A is a constant, E_a is the activation energy (in Joules/mole), R is the ideal gas constant (8.314 Joules/ (Kelvin * mole)), and T is the temperature (in degrees Kelvin).

3. Suppose that for a reaction with activation energy $E_a = 5.0 \times 10^4$ Joules/mole, the rate constant was determined to be 3.4×10^{-2} s^{-1} at 25 degrees Celsius. What is the rate constant at 75 degrees Celsius?

4. (Graded for completeness only.) Under what condition does $k = A$? Under what condition does $k \approx A$?

5. Suppose you perform an experiment and measure the reaction rate constant at four different temperatures, as shown in the table below. Determine the activation energy of this reaction (E_a) and the value of the constant A in the Arrhenius equation.

Rate constant k	Temperature (Kelvin)
5.63936×10^{-10}	700
2.36099×10^{-9}	750
8.26464×10^{-9}	800
2.49654×10^{-8}	850

6. The Arrhenius equation can be *linearized* by taking the natural log of both sides. This gives $y = \ln(k)$ as a linear function of $x = 1/T$. For the data given in the table above, plot $\ln(k)$ as a function of $1/T$, and estimate the slope and y-intercept of the resulting line.

7. More generally, if you plot of $\ln(k)$ on the y-axis and $1/T$ on the x-axis, what are the slope and the y-intercept, in terms of A, E_a, and R?

8. You are supplied data from a colleague. You quickly notice that your colleague accidentally provided you with the rate constant data using $\log_{10}$ instead of the natural log (ln). Make the appropriate corrections and determine the activation energy (E_a) of this reaction and the value of the constant A.

$\log_{10}(k)$	Temperature (Kelvin)
-18.6290583	500
-16.9194993	550
-15.4948667	600
-11.5771272	800

Instructions, part deux

After reading and reflecting on these questions, complete the application reflection on Canvas. This will give your coach some insight on your thinking in order to best help you before you are required to formally answer these questions.