

3.1: Day 18- Reaction Rate

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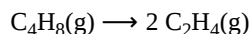
Day 18: Reaction Rate

D18.1 Reaction Rate

The **rate of a chemical reaction** is usually defined as *the change in concentration of a reactant or a product per unit time*. Rates can be determined by measuring the concentration of a reactant or product at each of a series of times after the reaction is started.

Often, it is easier to measure some property related to a substance's concentration instead. For example, for a reaction involving a colored reactant, light absorption can be measured at different times after the start of the reaction. Then the reactant's concentration at a given time can be calculated from the proportionality between light absorption and concentration.

Consider the decomposition reaction of cyclobutane to ethene in the gas phase:



The rate at which cyclobutane decomposes can be expressed in terms of the rate of change of its concentration:

$$\begin{aligned} \text{rate of decomposition of } \text{C}_4\text{H}_8 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[\text{C}_4\text{H}_8]_{t_2} - [\text{C}_4\text{H}_8]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[\text{C}_4\text{H}_8]}{\Delta t} \end{aligned}$$

In this equation, square brackets represent concentration in mol/L (M), so $\Delta[\text{C}_4\text{H}_8]$ represents the change in concentration of cyclobutane during the time interval Δt (that is, $t_2 - t_1$). The minus sign in front of the fraction is there because *reaction rate is defined to be positive*. The reactant concentration decreases as the reaction proceeds, making $\Delta[\text{C}_4\text{H}_8]$ a negative quantity, so a negative sign is needed to make the calculated rate positive.

Table 1 provides an example of data collected during the decomposition of C_4H_8 .

Table 1. concentrations of cyclobutane measured at 40 °C

Time (s)	$[\text{C}_4\text{H}_8]$ (M)	$\Delta[\text{C}_4\text{H}_8]$ (M)	Δt (s)	Rate of decomposition (M/s)
0.0	0.240			
20.0	0.120	-0.120	20.0	0.00600
40.0	0.060	-0.060	20.0	0.0030
60.0	0.030	-0.030	20.0	0.0015
80.0	0.015	-0.015	20.0	0.00075

Notice that the reaction rate varies with time, decreasing as the reaction proceeds and $[\text{C}_4\text{H}_8]$ decreases. An **average rate** over a given time period can be calculated using the concentrations at the beginning and end of the period. For example, the average rate for the first and last 20-second period are:

$$\begin{aligned} \text{rate} &= \frac{-\Delta[\text{C}_4\text{H}_8]}{\Delta t} = \frac{-(0.120 \text{ M} - 0.240 \text{ M})}{(20.0 \text{ s} - 0.00 \text{ s})} = 0.00600 \frac{\text{M}}{\text{s}} \\ \text{rate} &= \frac{-\Delta[\text{C}_4\text{H}_8]}{\Delta t} = \frac{-(0.015 \text{ M} - 0.030 \text{ M})}{(80.0 \text{ s} - 60.0 \text{ s})} = 0.00075 \frac{\text{M}}{\text{s}} \end{aligned}$$

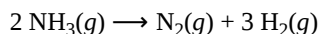
The *rate of reaction at any specific time* is known as the **instantaneous rate**. The *instantaneous rate when the reaction starts (at t_0)*, is the **initial rate**. The instantaneous rate of a reaction may be determined one of two ways:

- If concentration changes can be measured over very short time intervals, then average rates over these very short time intervals provide reasonably good approximations of instantaneous rates.
- If we plot concentration vs. time, the instantaneous rate at any time t is given by the negative of the slope of a straight line that is tangent to the curve at that time (Figure 1).

Figure 1. Graph of $[C_4H_8]$ versus time. The reaction rate at any instant is equal to the negative of the slope of a line tangent to this curve at that time. Tangents are shown at $t = 0$ s (magenta; initial rate) and at $t = 40$ s (orange); click on “+” signs for more information.

D18.2 Relative Rates of Reaction

The reaction rate can be expressed in terms of the change in concentration of any reactant or product, and therefore depends on the stoichiometry of the reaction. Let's use the ammonia decomposition reaction as an example:



From the balanced reaction, we can see that one N_2 molecule is produced for every two NH_3 molecules that have reacted. Therefore, the formation of N_2 is half as fast as disappearance of ammonia:

$$\text{rate} = -\frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t}$$

The negative sign accounts for the fact that NH_3 (reactant) concentration is decreasing while N_2 (product) concentration is increasing. The fraction $\frac{1}{2}$ accounts for the stoichiometry.

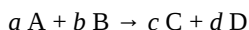
Similarly, because 3 mol H_2 forms during the time required for formation of 1 mol N_2 :

$$\text{rate} = \frac{\Delta[\text{N}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t}$$

Figure 2 plots concentrations vs. time for this reaction. At any time, the instantaneous rates for reactants and products are related by the reaction stoichiometry. For example, at 500 s the rate of H_2 production is three times greater than that for N_2 production.

Figure 2. Concentrations of reactants and products during the reaction $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$ as a function of time at 1100 °C. The rates of change of the three concentrations are related by the reciprocals of their stoichiometric coefficients. An example of this is shown by the different slopes (click on the “+” signs) of the tangents at $t = 500$ s.

The rate of a reaction is therefore defined by taking the change in concentration per unit time of a reactant or product and multiplying by the reciprocal of the stoichiometric coefficient for that reactant or product. The reaction rate determined this way is the same regardless of which reactant or product is measured during an experiment. For a generic reaction:



where lower-case letters are stoichiometric coefficients and upper-case letters represent chemical formulas, the rate of the reaction is:

$$\text{rate} = -\frac{1}{a} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b} \frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c} \frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d} \frac{\Delta[\text{D}]}{\Delta t}$$

D18.3 Factors Affecting Reaction Rates

During a chemical reaction, reactant molecules are changed into product molecules. This involves changes in bonding (i.e. bonds broken and bonds formed), and typically this requires molecules to come into close contact; that is, atomic-scale particles must collide to react. Anything that affects the number and/or effectiveness of those collisions will affect the rate of reaction.

Chemical Nature of the Reacting Substances

Some substances react faster than others. For example, potassium and calcium, which are next to each other in the fourth row of the periodic table, both react with water to form H_2 gas and a basic solution. Yet calcium reacts at a moderate rate, whereas potassium reacts so rapidly that the reaction is almost explosive. One factor affecting these different rates is that the reactions involve loss of electrons from potassium or calcium atoms, and potassium has a smaller first ionization energy, making loss of an electron easier.

https://mediaspace.wisc.edu/id/1_jkttq85m

Video 1. Different substances react at different rates. Left: reaction of potassium with water. Right: reaction of calcium with water. The reaction of potassium with water is faster. At the end of the video the calcium reaction is enlarged so that bubbles of $H_2(g)$ can be seen more easily.

Temperature

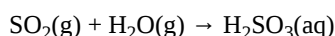
Chemical reactions typically occur faster at higher temperatures. At higher temperatures atomic-scale particles move faster, so they collide harder and more often, both of which increase the probability that they will react. For example, methane (CH_4) does not react rapidly with air at room temperature, but strike a match and POP!

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Video 2. Temperature affects the rate of a chemical reaction. Natural gas coming out of a burner does not combust rapidly until its temperature is raised by a burning match.

Concentrations

Reaction rates usually increase when the concentration of one or more of the reactants increases. In some cases, rates depend on the concentrations of products as well. For example, calcium carbonate ($CaCO_3$) deteriorates as a result of its reaction with the pollutant sulfur dioxide (SO_2). Specifically, sulfur dioxide reacts with water vapor to produce sulfurous acid:



Sulfurous acid then reacts with calcium carbonate:



The rate of the overall reaction depends on the concentration of sulfur dioxide in the air. In a more polluted atmosphere where the concentration of sulfur dioxide is higher, calcium carbonate deteriorates more rapidly (Figure 3).



Figure 3. Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water as well as thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. (credit: James P Fisher III)

In another example, a cigarette burns slowly in air, which contains about 21% oxygen by volume, but burns much more rapidly in pure oxygen, as shown in the video below.

https://mediaspace.wisc.edu/id/0_obzl113a

Video 3. Higher concentration usually increases reaction rate. The flask contains pure oxygen, which reacts with paper and tobacco in the cigarette. The cigarette burns much faster in pure oxygen than in air, which contains about one-fifth the oxygen concentration.

Presence and Concentration of a Catalyst

A **catalyst** is a substance that increases the rate of a chemical reaction by providing an alternative reaction pathway but is not consumed by the reaction. The greater the concentration of a catalyst the more the catalyst can speed up a reaction. How catalysts work will be discussed in detail later on in this course. Watch the video below to see how a catalyst can speed up the decomposition of hydrogen peroxide to oxygen and water.

https://mediaspace.wisc.edu/id/0_8ps7n4sa

Video 4. Effect of a catalyst. Manganese dioxide catalyzes decomposition of aqueous hydrogen peroxide, forming water and oxygen. Until the MnO_2 is added there is no perceptible reaction. A rapid reaction occurs as soon as the MnO_2 is added to the aqueous solution of H_2O_2 . The reaction is exothermic so the temperature goes up. The white cloud is water droplets that condense when heated water vapor cools after escaping from the soda bottle.

Surface Area

The factors discussed so far apply to **homogeneous reactions**, *reactions that occur in a single phase* (solid, liquid, or gas). If a reaction occurs at a surface, an increase in surface area of the intersection of two phases (such as the surface of a solid in contact with a gas) can increase the rate. *Reactions that take place at a surface* are called **heterogeneous reactions**. A finely divided solid (like a powder) has more surface area available for reaction than one large solid piece of the same substance. For example, large pieces of wood smolder, smaller pieces burn rapidly, and sawdust burns explosively. The video below shows how large pieces of iron can be held in a burner flame for a long time and hardly react, whereas iron powder blown into the flame sparkles as the tiny particles burn.

https://mediaspace.wisc.edu/id/0_r05fie4

Video 5. Surface area affects the rate of a heterogeneous reaction. A bar of iron held in a flame does not oxidize perceptibly, but when the iron is powdered and blown into the flame from a plastic bottle, a rapid reaction with oxygen occurs.

D18.4 Effect of Concentration: Rate Laws

Rate laws or **rate equations** are *mathematical expressions that relate the rate of a chemical reaction to the concentrations of reactants* (and sometimes products or catalysts). Often the rate of reaction is proportional to the concentration, or to a power of the concentration, of a substance involved in the reaction:

$$\text{rate} = k[A]^m[B]^n[C]^p \dots$$

Here, k is the **rate constant**, a *proportionality constant independent of reactant concentrations that is specific for a particular reaction at a particular temperature*.

Each exponent, m , n , or p , defines the **order of a reaction** with respect to each reactant, A, B, or C. It is *the power to which a concentration must be raised to correctly calculate the rate*. For example, if $m = 1$, the reaction is *first-order* with respect to A; if $n = 2$, the reaction is *second-order* with respect to B; if $p = 0$, the reaction is *zeroth-order* with respect to C, which means that the rate of the reaction is not affected by the concentration of C, because $[C]^0 = 1$. The **overall reaction order** is the sum of the individual orders, $m + n + p + \dots$. Reaction orders are usually positive integers, although they can be fractions or negative numbers.

Activity 1: Order of a Reaction and Rate Law

D18.5 Method of Initial Rates

The rate constant and the reaction orders must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. One way to do this is the **method of initial rates**. To use this method, *select two sets of rate data where all concentrations but one are the same and set up a ratio of the two rates and the two rate laws*. This will yield an equation that contains only one unknown: the reaction order of the substance whose concentration varies.

Activity 2: Rate Law from Initial Rates

Activity 3: Rate Law from Initial Rates, Mathematical Approach

D18.6 Reaction Order and Rate Constant Units

It is often true that, as in the last activity, the reaction orders in the rate law are different from the coefficients in the chemical equation for the reaction. It is important to note that *rate laws must be determined by experiment and are not reliably predicted by reaction stoichiometry*.

Reaction orders play a role in determining the units for the rate constant—the units for k are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate.

The units for the rate constant for common reaction orders are summarized below.

Overall Reaction Order ($m+n+\dots$)	Units of k ($M^{1-(m+n+\dots)}s^{-1}$)
zeroth	M/s or $M s^{-1}$
first	1/s or s^{-1}

Overall Reaction Order (m+n+...)	Units of k ($M^{1-(m+n+...)}s^{-1}$)
second	$1/M\ s$ or $M^{-1}\ s^{-1}$
third	$1/M^2\ s$ or $M^{-2}\ s^{-1}$

Day 18 Pre-class Podia Problem: Determining a Rate Law

This Podia problem is based on *today's pre-class* material; working through that material will help you solve the problem.

Consider these data for the hydrolysis of benzene sulfonyl chloride (abbreviated BSC) in aqueous solution containing fluoride ions at 15 °C. The concentration of BSC was $2 \times 10^{-4}\ M$ in all trials and from other experiments where no fluoride ions were present the reaction is known to be first order in BSC. Determine the rate law for the overall reaction. Also determine numeric values for all rate constants and express them in appropriate units.

Trial	$[F^-]$ (M)	Initial Rate (M/s)
1	0	2.4×10^{-7}
2	0.5×10^{-2}	5.4×10^{-7}
3	2.0×10^{-2}	13.9×10^{-7}
4	5.0×10^{-2}	32.0×10^{-7}

Two days before the next whole-class session, this Podia question will become live on [Podia](#), where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use [this link](#) to report them. A similar link will be included in each day's material. We appreciate your comments.

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