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Rate law for a first order reaction

A first-order reaction is a reaction that proceeds at a rate that depends linearly on only one reactant concentration. Differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, whereas integrated rate laws are used for determining the reaction order and the value of the rate constant from experimental measurements. The differential equation describing first-order kinetics is given below: $\text{Rate} = -\frac{d[A]}{dt} = k[A]^1 = k[A]$ The "rate" is the reaction rate (in units of molar/time) and k is the reaction rate coefficient (in units of 1/time). However, the units of k vary for non-first-order reactions. These differential equations are separable, which simplifies the solutions as demonstrated below. First, write the differential form of the rate law. $\text{Rate} = -\frac{d[A]}{dt} = k[A]$ Rearrange to give: $\frac{d[A]}{[A]} = -k dt$ Second, integrate both sides of the equation. $\int \frac{1}{[A]} d[A] = -\int k dt$ $\ln[A] = -kt + \ln[A]_0$ Rearrange to solve for $[A]$ to obtain one form of the rate law: $[A] = [A]_0 e^{-kt}$ This can be rearranged to $\ln[A] = -kt + \ln[A]_0$ This can further be arranged into $y=mx+b$ form: $\ln[A] = -kt + \ln[A]_0$ The equation is a straight line with slope $m = (-k)$ and y -intercept $b = \ln[A]_0$ Now, recall from the laws of logarithms that $\ln\left(\frac{1}{[A]}\right) = -\ln[A]$ where $[A]$ is the concentration at time t and $[A]_0$ is the concentration at time 0, and k is the first-order rate constant. Figure 1: Decay profiles for first-order reactions with large and small rate constants. (CC BY; Stephen Lower) Because the logarithms of numbers do not have any units, the product $(-kt)$ also lacks units. This concludes that unit of k in a first order of reaction must be time^{-1} . Examples of time^{-1} include s^{-1} or min^{-1} . Thus, the equation of a straight line is applicable: $\ln[A] = -kt + \ln[A]_0$ To test if the reaction is a first-order reaction, plot the natural logarithm of a reactant concentration versus time and see whether the graph is linear. If the graph is linear and has a negative slope, the reaction must be a first-order reaction. To create another form of the rate law, raise each side of the previous equation to the exponent, e : $e^{\ln[A]} = e^{-kt + \ln[A]_0}$ Simplifying gives the second form of the rate law: $[A] = [A]_0 e^{-kt}$ The integrated forms of the rate law can be used to find the population of reactant at any time after the start of the reaction. Plotting $\ln[A]$ with respect to time for a first-order reaction gives a straight line with the slope of the line equal to $(-k)$. More information can be found in the article on rate laws. This general relationship, in which a quantity changes at a rate that depends on its instantaneous value, is said to follow an exponential law. Exponential relations are widespread in science and in many other fields. Consumption of a chemical reactant or the decay of a radioactive isotope follow the exponential decay law. Its inverse, the law of exponential growth, describes the manner in which the money in a continuously-compounding bank account grows with time, or the population growth of a colony of reproducing organisms. The reason that the exponential function ($y=e^x$) so efficiently describes such changes is that $dy/dx = e^x$; that is, e^x is its own derivative, making the rate of change of (y) identical to its value at any point. The following graphs represents concentration of reactants versus time for a first-order reaction. Plotting $\ln[A]$ with respect to time for a first-order reaction gives a straight line with the slope of the line equal to $(-k)$. The half-life ($t_{1/2}$) is a timescale on which the initial population is decreased by half of its original value, represented by the following equation. $\ln[A] = -\frac{1}{2}k t_{1/2} + \ln[A]_0$ After a period of one half-life, $(t = t_{1/2})$ and we can write $\ln\left(\frac{[A]_{1/2}}{[A]_0}\right) = -\frac{1}{2}k t_{1/2} = -\frac{1}{2}k t_{1/2} = -\frac{1}{2}k t_{1/2}$ Taking logarithms of both sides (remember that $\ln(e^x) = x$) yields $\ln\left(\frac{[A]_{1/2}}{[A]_0}\right) = -\frac{1}{2}k t_{1/2}$ Solving for the half-life, we obtain the simple relation $t_{1/2} = \frac{\ln 2}{k}$ $\approx 0.693/k$ This indicates that the half-life of a first-order reaction is a constant. Figure 2: Half lives graphically demonstrated for first-order reaction. Notice the half-life is independent of initial concentration. This is not the case with other reaction orders. (CC BY; Stephen Lower) Example 1: Estimated Rate Constants The half-life of a first-order reaction was found to be 10 min at a certain temperature. What is its rate constant? Solution Use Equation 20 that relates half life to rate constant for first order reactions: $k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{10 \text{ min}} = 0.0693 \text{ min}^{-1}$ As a check, dimensional analysis can be used to confirm that this calculation generates the correct units of inverse time. Notice that, for first-order reactions, the half-life is independent of the initial concentration of reactant, which is a unique aspect to first-order reactions. The practical implication of this is that it takes as much time for $[A]$ to decrease from 1 M to 0.5 M as it takes for $[A]$ to decrease from 0.1 M to 0.05 M. In addition, the rate constant and the half life of a first-order process are inversely related. Example 3: Determining Half Life If 3.0 g of substance A decomposes for 36 minutes the mass of unreacted A remaining is found to be 0.375 g. What is the half life of this reaction if it follows first-order kinetics? Solution There are two ways to approach this problem: The "simple inspection approach" and the "brute force approach" Approach #1: "The simple inspection approach" This approach is used when one can recognize that the final concentration of A is $\frac{1}{8}$ of the initial concentration and hence three half lives $\left(\left(\frac{1}{2}\right)^3 = \frac{1}{8}\right)$ have elapsed during this reaction. $t_{1/2} = \frac{36 \text{ min}}{3} = 12 \text{ min}$ This approach works only when the final concentration is $\left(\left(\frac{1}{2}\right)^n\right)$ that of the initial concentration, then (n) is the number of half lives that have elapsed. If this is not the case, then approach #2 can be used. Approach #2: "The brute force approach" This approach involves solving for k from the integral rate law (Equation 17) and then relating k to the $(t_{1/2})$ via Equation 20. $\ln\left(\frac{[A]_{1/2}}{[A]_0}\right) = -\frac{1}{2}k t_{1/2}$ $\ln\left(\frac{0.375 \text{ g}}{3 \text{ g}}\right) = -\frac{1}{2}k (36 \text{ min})$ Therefore, via Equation 20 $t_{1/2} = \frac{36 \text{ min}}{\ln 2} = \frac{36 \text{ min}}{0.693} = 51.9 \text{ min}$ The first approach is considerably faster (if the number of half lives evolved is apparent). Exercise 1 (PageIndex{2a}) Calculate the half-life of the reactions below: If 4.00 g A are allowed to decompose for 40 min, the mass of A remaining undecomposed is found to be 0.80 g. If 8.00 g A are allowed to decompose for 34 min, the mass of A remaining undecomposed is found to be 0.70 g. If 9.00 g A are allowed to decompose for 24 min, the mass of A remaining undecomposed is found to be 0.50 g. Answer Use the half life reaction that contains initial concentration and final concentration. Plug in the appropriate variables and solve to obtain: 17.2 min 9.67 min 5.75 min Exercise 2 Determine the percent H_2O_2 that decomposes in the time using $k = 6.40 \times 10^{-5} \text{ s}^{-1}$ The time for the concentration to decompose is 600.0 s after the reaction begins. The time for the concentration to decompose is 450 s after the reaction begins. Answer Rearranging Eq. 17 to solve for the $t_{1/2}$ $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{6.40 \times 10^{-5} \text{ s}^{-1}} = 10826.5 \text{ s} = 3.01 \text{ h}$ This is a simple plug and play application once you have identified this equation. $\ln\left(\frac{[H_2O_2]_{450}}{[H_2O_2]_0}\right) = -\frac{1}{2}k t_{1/2}$ $\ln\left(\frac{0.100 \text{ M}}{1.00 \text{ M}}\right) = -\frac{1}{2}(6.40 \times 10^{-5} \text{ s}^{-1})t_{1/2}$ $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{6.40 \times 10^{-5} \text{ s}^{-1}} = 10826.5 \text{ s} = 3.01 \text{ h}$ This is a simple plug and play application once you have identified this equation. $\ln\left(\frac{[H_2O_2]_{450}}{[H_2O_2]_0}\right) = -\frac{1}{2}k t_{1/2}$ $\ln\left(\frac{0.100 \text{ M}}{1.00 \text{ M}}\right) = -\frac{1}{2}(6.40 \times 10^{-5} \text{ s}^{-1})t_{1/2}$ $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{6.40 \times 10^{-5} \text{ s}^{-1}} = 10826.5 \text{ s} = 3.01 \text{ h}$ References Petrucci, Ralph H. General Chemistry: Principles and Modern Applications 9th Ed. New Jersey: Pearson Education Inc. 2007. Contributors and Attributions Jessie A. Key To gain an understanding of graphical methods used to determine rate laws. To gain an understanding of half-life with respect to first-order reactions. An alternate way to determine a rate law is to monitor the concentration of reactants or products in a single trial over a period of time and compare that to what is expected mathematically for a first-, second-, or zero-order reaction. First-Order Reactions We have seen earlier that the rate law of a generic first-order reaction where $A \rightarrow B$ can be expressed in terms of the reactant concentration: Rate of reaction = $-\frac{d[A]}{dt} = k[A]$ This form of the rate law is sometimes referred to as the differential rate law. We can perform a mathematical procedure known as an integration to transform the rate law to another useful form known as the integrated rate law: $\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$ where "ln" is the natural logarithm, $[A]_0$ is the initial concentration of A, and $[A]_t$ is the concentration of A at another time. The process of integration is beyond the scope of this textbook, but is covered in most calculus textbooks and courses. The most useful aspect of the integrated rate law is that it can be rearranged to have the general form of a straight line ($y = mx + b$). $\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$ Therefore, if we were to graph the natural logarithm of the concentration of a reactant (\ln) versus time, a reaction that has a first-order rate law will yield a straight line, while a reaction with any other order will not yield a straight line (Figure 17.7 "Concentration vs. Time, First-Order Reaction"). The slope of the straight line corresponds to the negative rate constant, $-k$, and the y -intercept corresponds to the natural logarithm of the initial concentration. Figure 17.7. Concentration vs. Time, First-Order Reaction This graph shows the plot of the natural logarithm of concentration versus time for a first-order reaction. Example 4 The decomposition of a pollutant in water at 15oC occurs with a rate constant of 2.39 y⁻¹, following first-order kinetics. If a local factory spills 6,500 moles of this pollutant into a lake with a volume of 2,500 L, what will the concentration of pollutant be after two years, assuming the lake temperature remains constant at 15oC? Solution We are given the rate constant and time and can determine an initial concentration from the number of moles and volume given. $[P]_0 = \frac{6500 \text{ mol}}{2500 \text{ L}} = 2.6 \text{ M}$ We can substitute this data into the integrated rate law of a first-order equation and solve for the concentration after 2.0 years: $\ln\left(\frac{[P]_t}{[P]_0}\right) = -kt$ $\ln\left(\frac{[P]_t}{2.6 \text{ M}}\right) = -(2.39 \text{ y}^{-1})(2.0 \text{ y})$ $\ln\left(\frac{[P]_t}{2.6 \text{ M}}\right) = -4.78$ $\frac{[P]_t}{2.6 \text{ M}} = e^{-4.78} = 0.0082$ $[P]_t = 0.021 \text{ M}$ Second-Order Reactions The rate for second-order reactions depends either on two reactants raised to the first power or a single reactant raised to the second power. We will examine a reaction that is the latter type: $C \rightarrow D$. The differential rate law can be written: Rate of reaction = $-\frac{d[C]}{dt} = k[C]^2$ The integrated rate law can be written in the form of a straight line as: $\frac{1}{[C]_t} = \frac{1}{[C]_0} + kt$ Therefore, if the reaction is zero order, a plot of $[E]$ versus t will produce a straight line with a slope that corresponds to the negative of the product of the rate constant and time, $-kt$, and a y -intercept that corresponds to the initial concentration, $[E]_0$ (Figure 17.9. "Concentration vs. Time, Zero-Order Reaction"). Figure 17.9. Concentration vs. Time, Zero-Order Reaction The graph shows the plot of concentration versus time for a zero-order reaction. Graphical Methods for Determining Reaction Order–A Summary We have just seen that first-, second-, and zero-order reactions all have unique, integrated rate-law equations that allow us to plot them as a straight line ($y = mx + b$) (Table 17.1 "Integrated Rate Law Summary"). When presented with experimental concentration–time data, we can determine the order by simply plotting the data in different ways to obtain a straight line. Table 17.1 Integrated Rate Law Summary Example 5 The following data were obtained for the reaction $3A \rightarrow 2B$: Time, s 0 5 10 15 20 $[A]$, M 0.200 0.0282 0.0156 0.0106 0.008 Determine the order of the reaction. Solution We can plot the characteristic kinetic plots of zero-, first-, and second-order reactions to determine which will give a straight line. Time, s $\ln[A]$, mol L⁻¹ $\ln\left(\frac{1}{[A]}\right)$, L mol⁻¹ 0 0.200 0.0282 0.0156 0.0106 0.008 4.55 94.3 20 0.008 4.83 125 Example Kinetics Plots The reaction is second order since $1/[A]$ versus t gives a straight line. Half-Life The half-life of a reaction, $t_{1/2}$, is the duration of time required for the concentration of a reactant to drop to one-half of its initial concentration. $\ln\left(\frac{[A]_{1/2}}{[A]_0}\right) = -kt$ Half-life is typically used to describe first-order reactions and serves as a metric to discuss the relative speeds of reactions. A slower reaction will have a longer half-life, while a faster reaction will have a shorter half-life. To determine the half-life of a first-order reaction, we can manipulate the integrated rate law by substituting $t_{1/2}$ for t and $[A]_{1/2} = \frac{1}{2}[A]_0$ for $[A]_t$, then solve for $t_{1/2}$: $\ln\left(\frac{[A]_{1/2}}{[A]_0}\right) = -kt$ $\ln\left(\frac{1/2[A]_0}{[A]_0}\right) = -k t_{1/2}$ $\ln\left(\frac{1}{2}\right) = -k t_{1/2}$ $t_{1/2} = \frac{\ln 2}{k}$ $\approx \frac{0.693}{k}$ Since the half-life equation of a first-order reaction does not include a reactant concentration term, it does not rely on the concentration of reactant present. In other words, a half-life is independent of concentration and remains constant throughout the duration of the reaction. Consequently, plots of kinetic data for first-order reactions exhibit a series of regularly spaced $t_{1/2}$ intervals (Figure 17.10 "Generic First-Order Reaction Kinetics Plot"). Figure 17.10. Generic First-Order Reaction Kinetics Plot This graph shows repeating half-lives on a kinetics plot of a generic first-order reaction. Example 6 A reaction having a first-order rate has a rate constant of $4.00 \times 10^{-3} \text{ s}^{-1}$. 1. Determine the half-life. 2. How long will it take for a sample of reactant at 1.0 M to decrease to 0.25 M? 3. What concentration of the 1.0 M sample of reactant would you expect to be present after it has reacted for 500 s? Solution 1. $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{4.00 \times 10^{-3} \text{ s}^{-1}} = 173 \text{ s}$ 2. A simple way to calculate this is to determine how many half-lives it will take to go from 1.00 M to 0.250 M and use the half-life calculated in part 1. 1 half-life = 0.500 M 2 half-lives = 0.250 M Therefore, it will take $2 \times 173 \text{ s} = 346 \text{ s}$. 3. We can use the rate-constant value in the integrated rate law to determine the concentration remaining. $\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$ $\ln\left(\frac{[A]_t}{1.0 \text{ M}}\right) = -(4.00 \times 10^{-3} \text{ s}^{-1})(500 \text{ s})$ $\ln\left(\frac{[A]_t}{1.0 \text{ M}}\right) = -2.0$ $\frac{[A]_t}{1.0 \text{ M}} = e^{-2.0} = 0.135$ $[A]_t = 0.14 \text{ M}$ The reaction rate may be determined by monitoring the concentration of reactants or products in a single trial over a period of time and comparing it to what is expected mathematically for a first-, second-, or zero-order reaction. The half-life of a reaction is the duration of time required for the concentration of a reactant to drop to one-half of its initial concentration. which of the following represents the integrated rate law for a first-order reaction. using an integrated rate law for a first-order reaction, write the rate law for a first order reaction. integrated rate law for a first order reaction. derive the integrated rate law for a first order reaction. derive the rate law for a first order reaction. represents the integrated rate law for a first-order reaction, which of the following is a rate law for a reaction that is first order with respect to oxygen

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