

Chemical Kinetics: Rates and Rate Laws

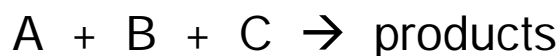
A. Rates

- *Chemical kinetics* is the study of how quickly chemical reactions proceed and the factors that affect the rate:
 - Nature and concentration of the reactants
 - Temperature
 - Presence of a catalyst
- Rates of chemical reactions are usually defined by comparing the change in reactant or product concentration over time.
- Consider the reaction $\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$
- We could measure the rate at which N_2 and H_2 are consumed and the rate at which NH_3 is produced.
- Due to the stoichiometry of the reaction, the rate of N_2 use will be $1/3$ the rate of H_2 use, and $1/2$ the rate of NH_3 production.
- Thus, the rate can be defined as

$$\text{Rate} = -\left(\frac{\Delta[\text{N}_2]}{\Delta t}\right) = -\frac{1}{3}\left(\frac{\Delta[\text{H}_2]}{\Delta t}\right) = +\frac{1}{2}\left(\frac{\Delta[\text{NH}_3]}{\Delta t}\right)$$

B. Concentration Effects: Rate Laws

- The effect of concentration is described using **rate laws**, which are mathematical expressions that link the rate of a reaction with reactant concentration.
- Consider the reaction

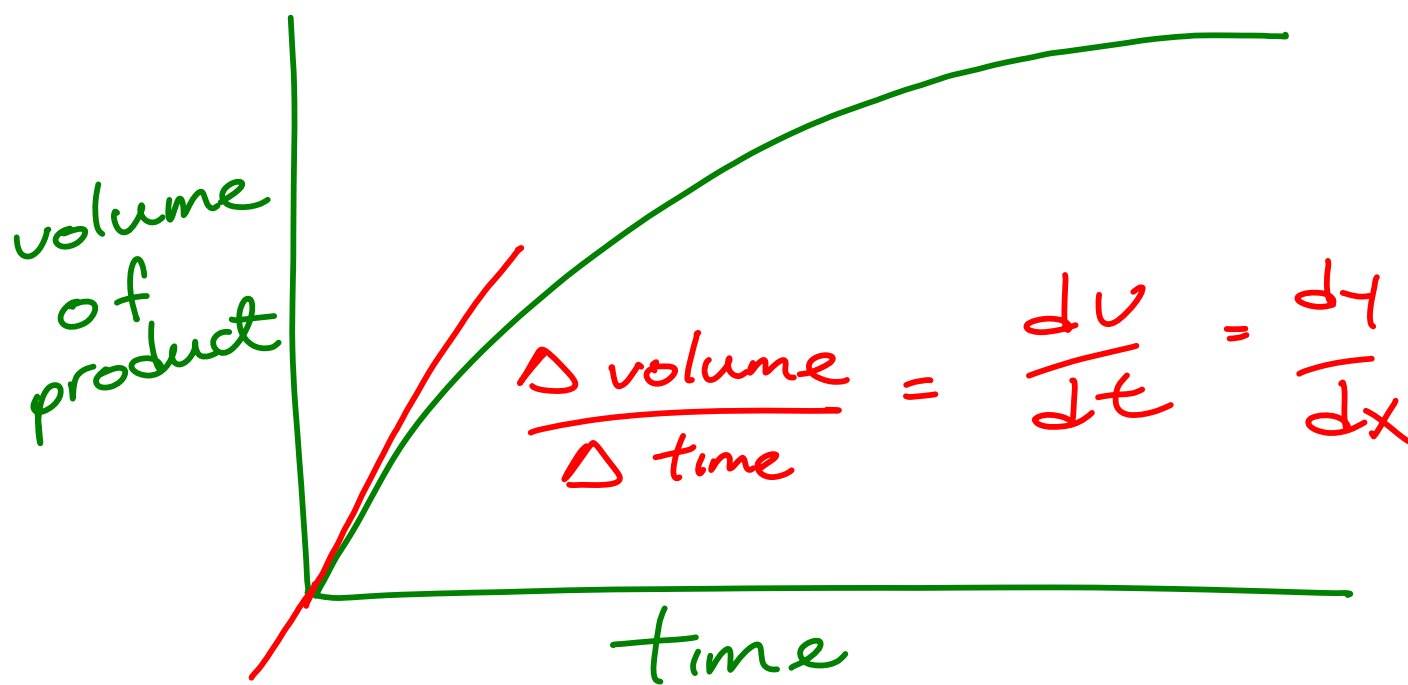


- The rate of the reaction is given by the equation below, where

$$\text{Rate} = k [A]^x [B]^y [C]^z$$

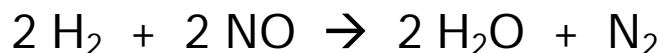
- concentrations are in molarity
 - k is the *rate constant* for the reaction *at a given temp*
 - and the exponents can only be found *experimentally*
- The exponential values determine the *order* of the reaction. They are usually whole numbers (but not always).
 - 2 = Second order
 - 1 = First order
 - 0 = Zero order (rate of the reaction is independent of the concentration of that reagent)
 - Remember, the exponents are experimentally measured and DO NOT correlate to the coefficients in the reaction equation.

- How do we experimentally determine the exponents? We usually use an experimental method that allows us to monitor the changes in a reactant or product. $A \rightarrow \text{products}$
- Suppose we have a reaction where a gas is evolved. We can measure the volume of gas produced as a function of time. The initial rate of gas evolution will be the slope at time zero.



- Usually, when we measure rates, we measure *initial rates*, which are the rates observed immediately after the reactants are mixed. As time passes, the reactants run out and the reaction ceases.

- Suppose we have the following reaction



$$\text{Rate} = k [\text{H}_2]^x [\text{NO}]^y$$

- The strategy is to:
 - vary one concentration at a time and monitor the rate
 - evaluate the exponents separately
 - combine the exponents into a rate law
 - substitute one data set to find k
- Collecting experimental data, we have initial rates

Expt #	[H ₂] (mol L ⁻¹)	[NO] (mol L ⁻¹)	Rate
i	0.1	0.2	5
ii	0.2	0.2	10
iii	0.1	0.4	20

- The exponents can be evaluated by logically thinking about the data (the preferred way), or by doing some math.
 - Comparing i and ii, doubling H₂ while keeping NO the same doubles the rate, so $x = 1$

$$\frac{\text{Rate}_{ii}}{\text{Rate}_i} = \frac{10}{5} = \frac{k [0.2]^x [0.2]^y}{k [0.1]^x [0.2]^y}$$

$$2 = \frac{(0.2)^x}{(0.1)^x} = \left(\frac{0.2}{0.1}\right)^x$$

- Comparing i and iii, doubling NO while keeping H₂ the same quadruples the rate, so $y = 2$

$$y = 2$$

$$\frac{\text{Rate}_{iii}}{\text{Rate}_i}$$

- Our rate law is therefore $\text{Rate} = k [\text{H}_2] [\text{NO}]^2$
- Substitute one set of values to calculate the rate constant

eg. $\text{Rate} = k [\text{H}_2] [\text{NO}]^2$

$$20 = k (0.1)(0.4)^2$$

$$k = 1250$$

$$\text{Rate} = k [A]^x$$

- Example: For the reaction $A \rightarrow \text{products}$ the data below was collected. Calculate the reaction and the rate constant k . (This one is harder to determine without doing some math)

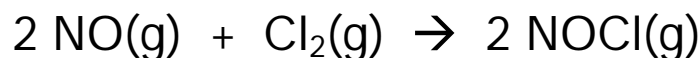
Expt #	[A] (mol L ⁻¹)	Rate
i	1.78×10^{-2}	6.00×10^{-5}
ii	2.85×10^{-2}	7.59×10^{-5}

$$\frac{\text{Rate}_{ii}}{\text{Rate}_i} = \frac{7.59}{6.00} = \frac{k [2.85]^x}{k [1.78]^x}$$

$$\frac{7.59}{6.00} = \left(\frac{2.85}{1.78} \right)^x$$

$$x = 0.5$$

- Example: The reaction below is second-order for NO and first-order for Cl₂. Which one of the following changes would cause the largest increase in the rate of reaction?



- o Making [Cl₂] three times higher $3x$
- o Making [NO] three times higher while halving [Cl₂] $9x \cdot \frac{1}{2}x = 4.5x$
- o Doubling both [NO] and [Cl₂] $8x$
- o Doubling [Cl₂] $2x$
- o Doubling [NO] $4x$

$$\text{Rate} = k [\text{NO}]^2 [\text{Cl}_2]$$

- It is also possible to determine the order of a reaction by doing only one single experiment. This involves monitoring the amount reactant or product at time intervals. The type of plot that gives a straight line tells us the reaction order.

1. First-order reactions

- Suppose the process $A \rightarrow \text{products}$ is first-order.

$$\text{Rate} = -\left(\frac{\Delta[A]}{\Delta t}\right) = k[A]$$

$-\frac{dA}{dt} = k[A]$
 $\frac{dA}{[A]} = -k \cdot dt$

- As the reaction proceeds, $[A]$ decreases. Thus, we can integrate this with respect to time to obtain the **integrated first-order rate law**.

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

OR

$$[A]_t = [A]_0 e^{-kt}$$

$$\ln[A] = -kt + C$$

\uparrow
 $\ln[A]_0$

- $[A]_t$ = concentration of A after time t has elapsed
- At $t = 0$ (start of the reaction), $[A]_t = [A]_0$

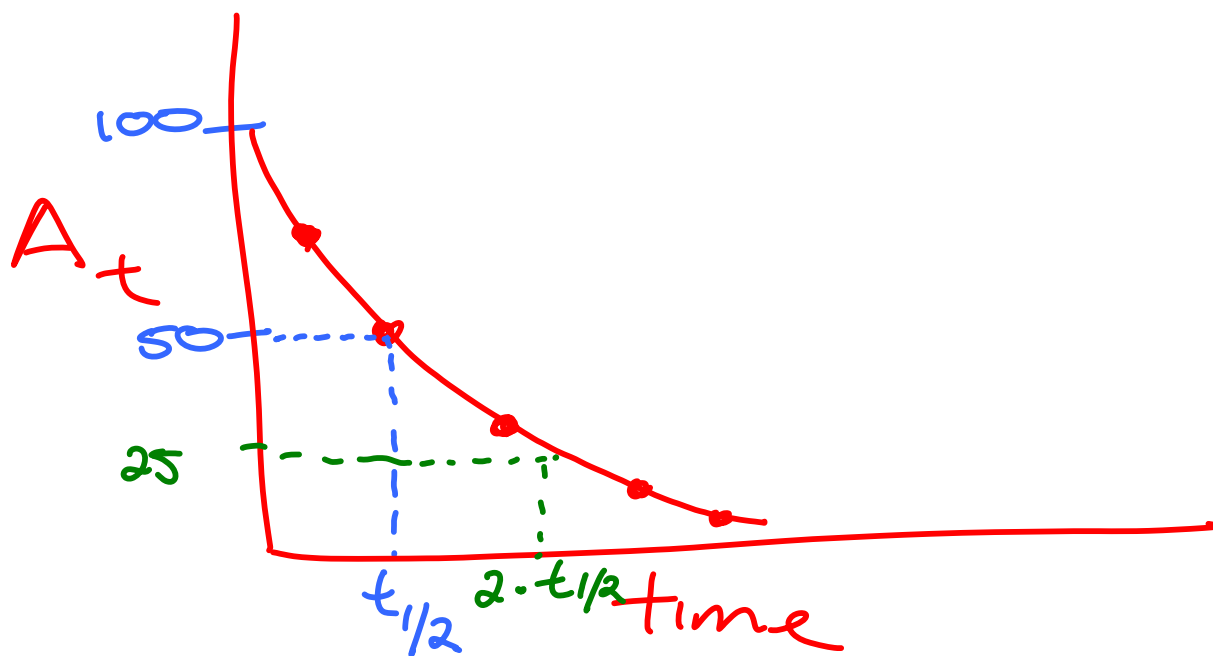
- This can be rearranged into an equation for a straight line.

$$\ln[A]_t - \ln[A]_0 = -kt \quad \rightarrow \quad \ln[A]_t = -kt + \ln[A]_0$$

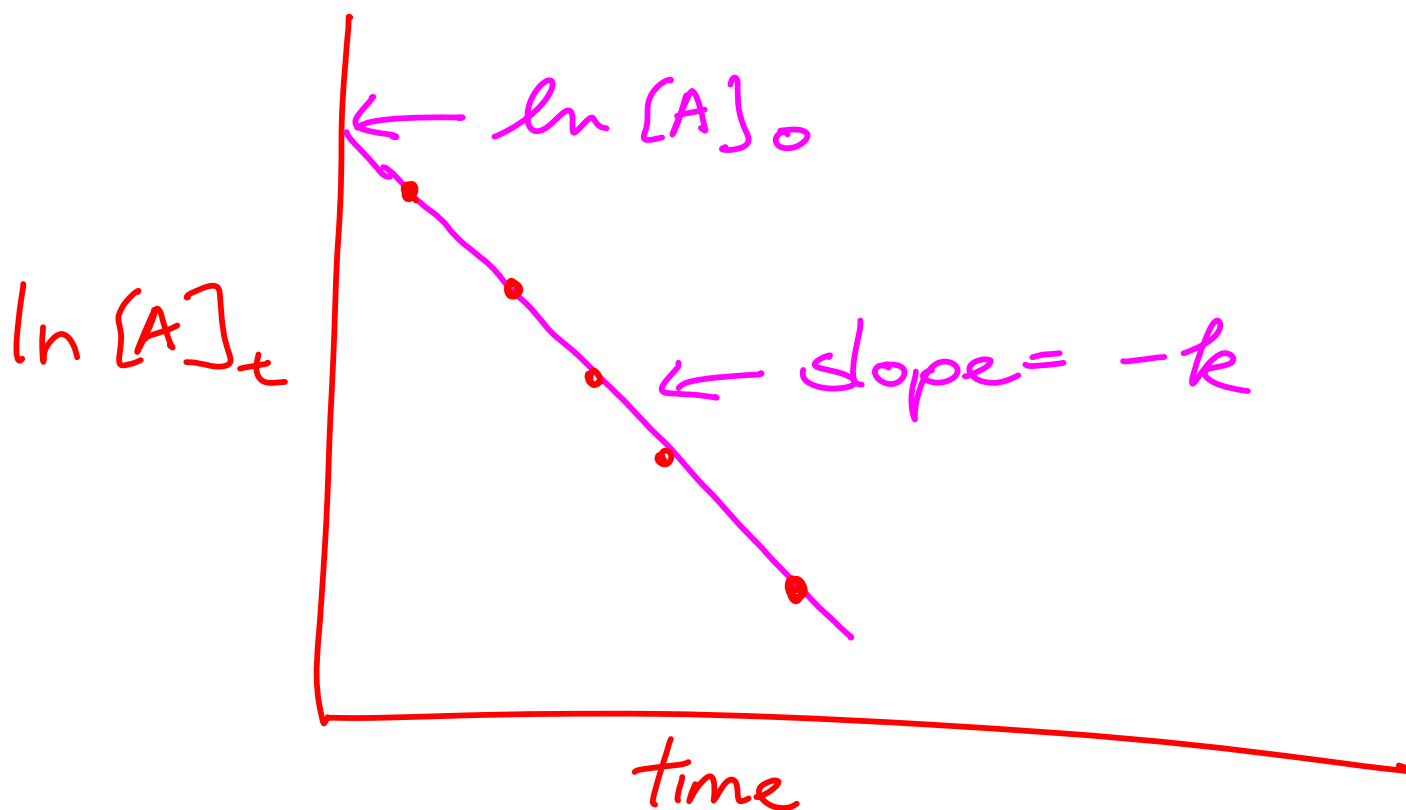
$y = mx + b$

- Thus, if a reaction is first-order, a plot of $\ln[A]_t$ as a function of time should yield a straight line. This is useful to "test" if a reaction is indeed first-order or not.

- Plot of $[A]$ as a function of time. The reaction slows down as A is consumed (exponential decay). $A \rightarrow \text{prod.}$



- Plot of $\ln[A]$ as a function of time



1st-order

- Example: For the decomposition $B \rightarrow \text{products}$ a plot of $\ln[B]$ versus time yielded a straight line with slope -0.35 min^{-1} .

$$k = +0.35 \text{ min}^{-1}$$

- ① If the starting $[B] = 0.160 \text{ M}$, find the $[B]$ after 4 minutes
- ② Find the time required for $[B]$ to drop to 0.100 M
- ③ Find the time required for half of B to decompose

$$\textcircled{1} [B]_t = [B]_0 e^{(-k)t}$$

$$= 0.039 \text{ M}$$

$$\textcircled{2} \ln [B]_t = -kt + \ln [B]_0$$

$$0.10 = (-.35)(t) + 0.16$$

$$\text{time} = 1.34 \text{ min}$$

$$\textcircled{3} \ln(0.08) = (-.35)(t) + \ln(0.16)$$

$$\text{time} = 1.98 \text{ min}$$

- The last calculation illustrates the concept of a **half life ($t_{1/2}$)**, the amount of time to use half of the reactants.
- $t_{1/2}$ is related to the rate constant k as follows


$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

$$\ln\left(\frac{50\%}{100\%}\right) = -kt_{1/2}$$

$$\ln(0.5) = -kt_{1/2}$$

$$-0.693 = -kt_{1/2}$$

$$t_{1/2} = \frac{0.693}{k} \quad \text{OR} \quad t_{1/2} = \frac{\ln 2}{k}$$

-  Realize that half-life is NOT dependent on the concentration of starting material. After one half-life, half remains. After two half-lives, a quarter remains. After three, an eighth remains.

$$\text{Fraction remaining} = (0.5)^{(\# \text{ of elapsed half-lives})}$$

- Example: a first-order reaction has a half-life of 11 minutes. What fraction of the reactant remains after 60 minutes?

$$\frac{60}{11} = 5.45 \text{ half-lives}$$

$$\text{frac left} = (0.5)^{5.45} = 0.023 \text{ (2.3\%)}$$

- Radioactive decay always proceeds according to first-order kinetics, so the rate constant for radioactive decay is often expressed in the form of a half-life.
- Example: Radioactive ^{218}Ra has a half-life of 0.030 s. What fraction of a sample of ^{218}Ra would remain after one second?

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- When doing such questions, be alert and see if it's asking how much is left or how much has been used
- Either use the fractional approach or calculate k .

$$\begin{aligned} \textcircled{1} \text{ frac left } t &= (.5)^{\# \text{ half-lives}} \\ &= (.5)^{33.3} \\ &= 9.3 \times 10^{-11} \end{aligned}$$

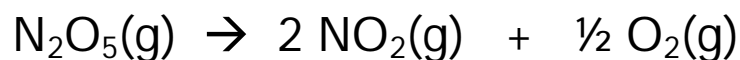
$$\textcircled{2} \quad t_{1/2} = \frac{\ln 2}{k} \quad k = 23.1 \text{ s}^{-1}$$

$$\begin{aligned} \ln A_t &= -kt + \ln A_0 \\ &= -(23.1)(1) + \ln(1) \\ &= -23.1 \end{aligned}$$

$$A_t = 9.29 \times 10^{-11}$$

$$t_{1/2} = 120\text{s}$$

- Example: The reaction below has a half-life of 120 seconds. If the initial concentration of N_2O_5 is 0.850 M, calculate the concentration of NO_2 after five minutes.



$$\frac{300\text{s}}{120\text{s}} = 2.5 \quad \frac{1}{2}\text{-lives}$$

$$\text{frac left} = (.5)^{2.5} = .177$$

$$.177 \times .850\text{M} = 0.150\text{M}$$

N_2O_5 left

$$1.4\text{M } \text{NO}_2$$

2. Zero-order reactions

- Suppose the process $A \rightarrow \text{products}$ is zero-order. That is, the speed of the reaction does not depend on $[A]$, only on k .

$$\text{Rate} = -\left(\frac{\Delta[A]}{\Delta t}\right) = k[A]^0 = k$$

- From this we can obtain the **integrated zero-order rate law**. (don't worry about how to integrate!)

$$[A]_t = -kt + [A]_0$$

y mx + b

- Note that there are no logarithmic functions.

- A plot of $[A]$ as a function of time yields a straight line.



3. Second-order reactions

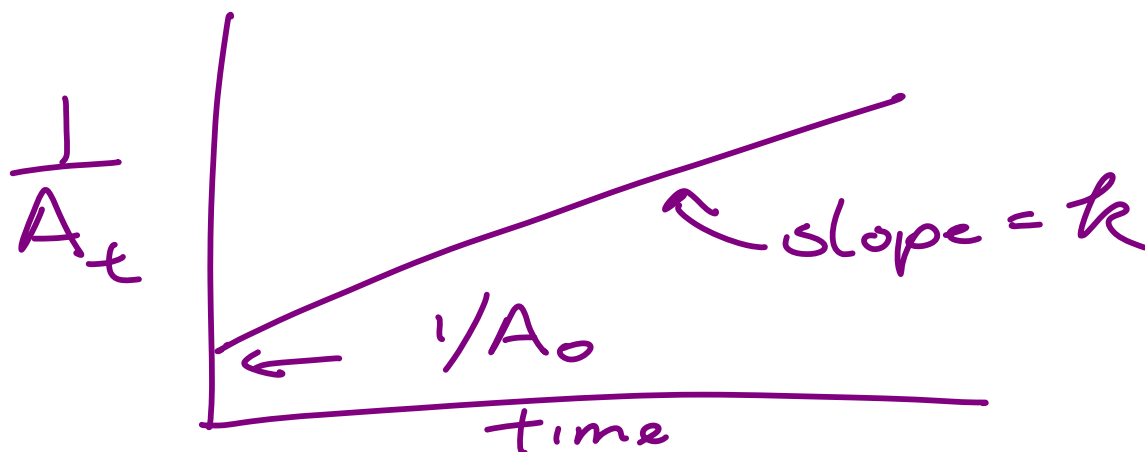
- Suppose the process $A \rightarrow \text{products}$ is second-order. The rate depends on k and the square of $[A]$.

$$\text{Rate} = -\left(\frac{\Delta[A]}{\Delta t}\right) = k[A]^2 \quad \frac{d[A]}{[A]^2} = -k dt$$

- From this we can obtain the **integrated second-order rate law**.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

- Again, no logarithmic functions.
- The slope is positive, not negative.
- A plot of $\frac{1}{[A]}$ as a function of time yields a straight line.



- Remember, to determine if a reaction is zero-, first-, or second-order, respectively plot $[A]$, $\ln[A]$, and $1/[A]$ as a function of time and see which one gives a straight line.

$$\text{Rate} = k[Z]^1$$

- Example: For reaction $Z \rightarrow \text{products}$, a plot of $\ln[Z]$ vs time (seconds) yields a straight line with slope -0.165 . What is the rate of the reaction ($\text{mol L}^{-1} \text{s}^{-1}$) when $[Z] = 0.750 \text{ M}$?

$$k = 0.165 \text{ s}^{-1}$$

$$\begin{aligned} \text{Rate} &= k[Z]^1 \\ &= (0.165)(0.75) \\ &= 1.24 \end{aligned}$$