

$$\Delta H^\circ = -484 \text{ kJ}$$

What does the values of ΔH° say about the chemical reaction?

***Thermodynamics** is not the whole story in chemistry. It only tells us where a reaction is going (that is the ratio of products to reactants when the reaction reaches equilibrium), it says nothing about **how long** it will take the reaction to get there. Not only do we have to know whether a reaction is thermodynamically favored, we also have to know whether the reaction can or will proceed at a finite rate. The study of the rate of reactions is called chemical kinetics

14.1-Reaction rates

Chemical Kinetics: The area of chemistry concerned with reaction rates and the sequence of steps by which reactions occur

Rate of reaction

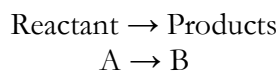
- measure of the speed at which a chemical reaction takes place

Average rate:

- The change in the concentration of a reactant or a product with time (M/s).

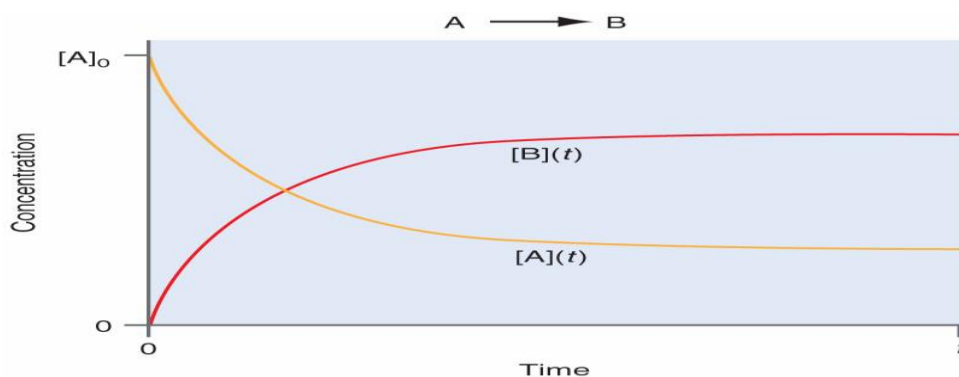
Rate expression

- mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time



$$\text{Average rate decomposition} = - \frac{\Delta [\text{reactants}]}{\Delta t} \qquad \text{Average rate formation} = \frac{\Delta [\text{products}]}{\Delta t}$$

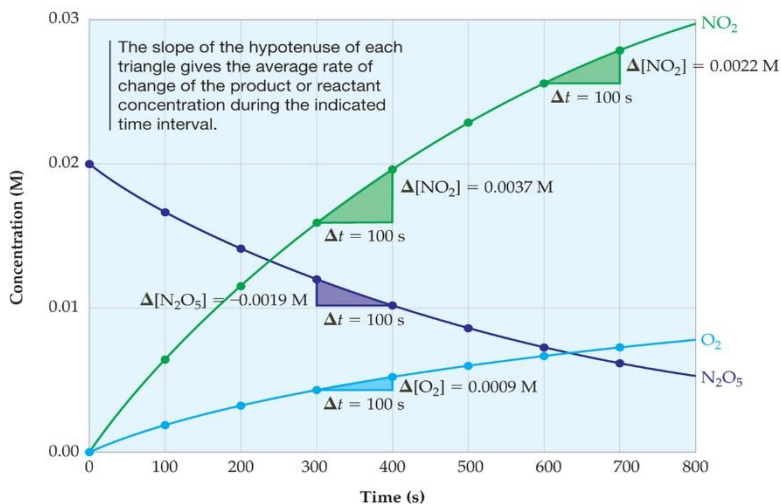
Is the reaction rate constant throughout the reaction? In what direction does it change?



Consider the decomposition of N_2O_5 to give NO_2 and O_2 :



The concentrations of O_2 and NO_2 increase as the concentration of N_2O_5 decreases.



The rate of **formation of O_2** is one-fourth the rate of **formation of NO_2** and one-half the rate of **decomposition of N_2O_5** .

From the graph looking at $t = 300$ to 400 s

$$\text{Rate } \text{N}_2\text{O}_5 = \frac{-0.0019 \text{ M}}{100 \text{ s}} = -1.9 \times 10^{-5} \text{ Ms}^{-1}$$

$$\text{Rate } \text{NO}_2 = \frac{0.0037 \text{ M}}{100 \text{ s}} = 3.7 \times 10^{-5} \text{ Ms}^{-1}$$

$$\text{Rate } \text{O}_2 = \frac{0.0009 \text{ M}}{100 \text{ s}} = 9 \times 10^{-6} \text{ Ms}^{-1}$$

Why do they differ?

The stoichiometric factors derived from this equation may be used to relate reaction rates in the same manner that they are used to relate reactant and product amounts. The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

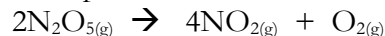
$$-\frac{\Delta \text{ mol } \text{N}_2\text{O}_5}{\Delta t \cdot (\text{L})} \times \frac{1 \text{ mol } \text{O}_2}{2 \text{ mol } \text{N}_2\text{O}_5} = \frac{\Delta \text{ mol } \text{O}_2}{\Delta t \cdot (\text{L})}$$

We can express this more simply without showing the stoichiometric factor's units:

$$-\frac{1}{2} \frac{\Delta \text{ mol } \text{N}_2\text{O}_5}{\Delta t \cdot \text{L}} = \frac{\Delta \text{ mol } \text{O}_2}{\Delta t \cdot \text{L}}$$

$$-\frac{1}{2} \text{ rate } \text{N}_2\text{O}_5 = \Delta \text{ rate } \text{O}_2$$

The mathematical relationship between the rates of reaction of N_2O_5 , NO_2 and O_2 can be expressed as



$$\text{Rate } \text{N}_2\text{O}_5 = \frac{1}{2} \times \frac{-0.0019 \text{ M}}{100 \text{ s}} = -9.5 \times 10^{-6} \text{ Ms}^{-1}$$

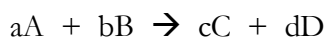
$$\text{Rate } \text{NO}_2 = \frac{1}{4} \times \frac{0.0037 \text{ M}}{100 \text{ s}} = 9.2 \times 10^{-6} \text{ Ms}^{-1}$$

$$\text{Rate } \text{O}_2 = \frac{1}{1} \times \frac{0.0009 \text{ M}}{100 \text{ s}} = 9 \times 10^{-6} \text{ Ms}^{-1}$$

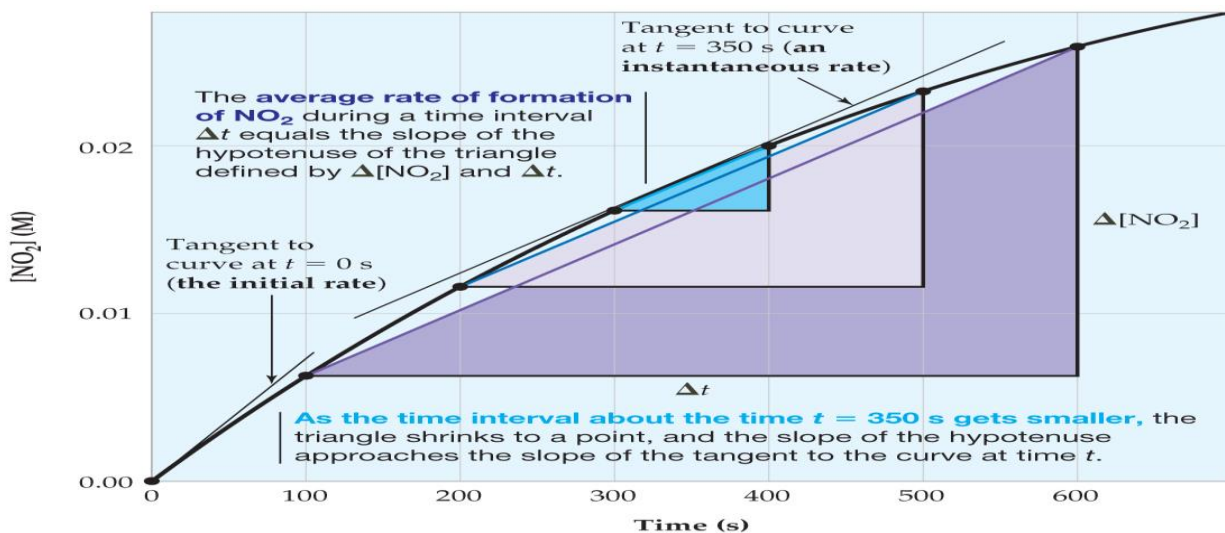
$$\boxed{} \frac{\Delta [\text{N}_2\text{O}_5]}{\Delta t} = \boxed{} \frac{\Delta [\text{NO}_2]}{\Delta t} = \boxed{} \frac{\Delta [\text{O}_2]}{\Delta t}$$

Dang2

To be consistent, the change in the concentration of each substance is multiplied by 1/coefficient.
 In general for the reaction at a given time:



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



The slope of the tangent at time t is defined as the instantaneous rate at that particular time. The initial rate is the slope of the tangent to the curve at $t = 0$.

Initial rate: the instantaneous rate at $t = 0$ (calculate as the slope of the tangent to the curve at $t = 0$)

- Rate at the start of reaction
- Equal to the negative slope of the curve reactant concentration versus $t=0$

Instantaneous rate: the rate that exists at a particular time t (calculated as the slope of the tangent to the curve at time t)

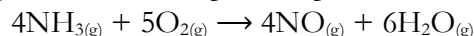
- Slope at one point of a curve
- The instantaneous rate is determined by taking the slope of a line tangent to the curve at that particular point.
- First derivative of the function (for all of you calculus fans)

Average rate: the average reaction rate that exists over a time period, Δt (calculated as the slope of the hypotenuses of the right triangles described in the above figure).

- Linear approximation of a curve

The larger the time interval, the more the average rate deviates from the instantaneous rate

Example: The first step in the production of nitric acid is the combustion of ammonia:



Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Example: Consider the chemical balanced equation:



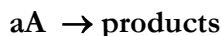
In the first 10.0 seconds of the reaction, the concentration of I^{-} dropped from 1.000 M to 0.868 M.

- Calculate the average rate of this experiment in this time interval

- Determine the rate of change in the concentration of H^{+} (that is, $\Delta[\text{H}^{+}]/\Delta t$) during this time interval

14.2 The rate law: The effect of Concentration on Reaction Rate

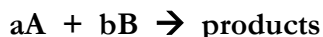
- Generally, the larger the concentration of reactant molecules, the faster the reaction.
 - This increases the frequency of reactant molecule contact.
 - Concentration of gases depends on the partial pressure of the gas.
 - Higher pressure = higher concentration
- Concentrations of solutions depend on the solute-to-solution ratio (molarity).
- The rate law of a reaction is the mathematical relationship between the rate of the reaction and the concentrations of the reactants and homogeneous catalysts as well.
- The rate law **must** be determined experimentally!
- The rate of a reaction is directly proportional to the concentration of each reactant raised to a power.
- For the reaction



The rate law would have the form given below.

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

For a reaction with multiple reactants

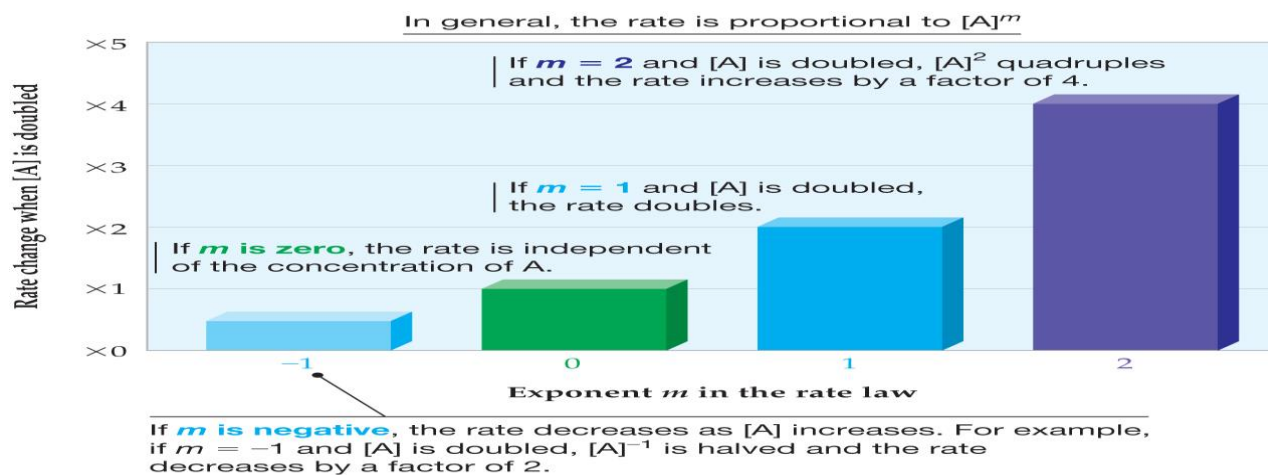


The complete form of rate law is written as

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

- x and y are called the **orders** for each reactant.
- k is called the **rate constant**.
- The rate constant, k , is only constant at constant temperature. Orders are generally not affected by a change in temperature
- The units of rate constant will change depending upon the overall order
- Only reactant concentrations are included in the rate law. (Rate laws are determined using “initial rate” where product concentrations are negligible.)
- Each concentration is expressed with an order (exponent). The orders have nothing to do with coefficients in the balanced chemical reaction and must be determined by experiment for a given reaction. It indicates to what extent the concentration of a species affects the rate of a reaction, as well as which species has the greatest effect.

- The orders can be positive or negative, whole numbers, fractions or zero. The orders that are most common are the following, which you should know by the indicated names: 1 (“first order”), 2 (“second order”), 3 (“third order”), $\frac{1}{2}$ (“half order”), 0 (“zero order”).
 - Zero-order in the reactant—there is no effect on the initial rate of reaction
 - First-order in the reactant—the initial rate of reaction doubles when the reactant is doubled
 - Second order in the reactant—the initial rate of the reaction quadruples when the reactant is doubled
- Third order in the reactant—the initial rate of reaction increases eightfold when the reactant is doubled



- The overall order for a reaction is the sum of the individual orders

- Rate ($M s^{-1}$) = $k [A][B]^2$

Overall order: $1 + 2 = 3$

- E.g Rate ($M s^{-1}$) = $k[A]$

Rate Law	Overall Reaction Order	Units for k
Rate = k	Zeroth order	M/s or $M s^{-1}$
Rate = $k[A]$	First order	$1/s$ or s^{-1}
Rate = $k[A][B]$	Second order	$1/(M \cdot s)$ or $M^{-1} s^{-1}$
Rate = $k[A][B]^2$	Third order	$1/(M^2 \cdot s)$ or $M^{-2} s^{-1}$

Determining units for rate constant, k

0th order

1st order

2nd order

14.3 Method of Initial Rates: Experimental Determination of a Rate Law

- * Experiments must be carried out to determine the orders of any reactants and the rate constant for any reaction.
- * The experimenter systematically varies the concentrations of reactants (at constant temperature) in a series of “runs” and measures the initial rate of reaction.
- * The experimenter could monitor the disappearance of any one of the reactants or the appearance of any one of the products, depending on the experimental convenience

Rules of logarithms

$$\begin{array}{ll} \log(1) = 0 & \ln(1) = 0 \\ \log(10) = 1 & \ln(e) = 1 \\ \log(100) = 2 & \ln(e^x) = x \\ \log(10^x) = x & \\ \log A^x = x \log A & \ln A^x = x \ln A \end{array}$$

Example: Consider the given data table for following reaction



Run	Initial [A] (M)	Initial rate (M/s)
1	0.15	0.008
2	0.30	0.016
3	0.60	0.032

- a. Write the generic rate law for this reaction, without showing any numerical values for the rate constant k or the order of A

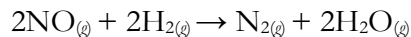
- b. Calculate the order of A ?

- c. What is the rate constant, k ? by plugging any one set (run) of data into the rate law that has been determined so far. Don't forget proper units!

- d. What is the overall order of this reaction?

- e. Write the rate law expression for this reaction?
- f. What is the initial rate A if the initial concentration of A was 0.053M?

Example: Consider the reaction of nitric oxide with hydrogen at 1280°C :



From the following data, determine rate law and rate constant

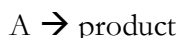
Run	Initial [NO] (M)	Initial [H ₂] (M)	Initial rate of formation N ₂ (M/min)
1	0.0100	0.0100	0.00600
2	0.0200	0.0300	0.144
3	0.0100	0.0200	0.0120

- To start, write an appropriate generic rate law, for which the rate constant and the orders are yet to be determine
- From the data table, compare any two runs where the concentration of H₂ is different but the concentration of NO remains constant. This will allow you to determine the effect of changing the concentration of H₂ on the rate of reaction, without any effect from NO.
- From the data table, compare any two runs where the concentration of NO is different but the concentration of H₂ remains constant. If there is none then use all concentration values and the calculated order of H₂ to determine the order of (power of) NO.

- 4) Determine the value of the rate constant, k , for the formation of $\text{N}_2(\text{g})$, by plugging any one set (run) of data into the rate law that has been determined so far. Don't forget proper units!
- 5) What is the overall order of this reaction ?
- 6) The full rate law for the formation of $\text{N}_2(\text{g})$ is
- 7) For the preceding reaction, what is the rate formation of $\text{N}_2(\text{g})$ when $[\text{NO}] = [\text{H}_2] = 2.50\text{M}$?
- 8) At what rate would H_2O be formed under the condition in question 6?
- 9) For the preceding reaction, by what factor will the rate of reaction change if you
- _____double $[\text{NO}]$
- _____double $[\text{H}_2]$

14.5 – Integrated Rate Law for a First Order Reaction

The rate law that we have been studying are often converted into an alternate mathematical form through integration (calculus). The resulting equation is referred to as the “integrated rate law”.



$$\text{Rate (Ms}^{-1}\text{)} = \frac{\Delta [A]}{\Delta t} = k [A] \quad \text{This is the "average rate"}$$

Using calculus, you get the following integrated rate law equation $\ln[A]_t = (-k)t + \ln[A]_0$

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

“Rate law” tells how a reaction rate depends on reactant concentrations, the “integrated law” tells how reactant concentration changes with time

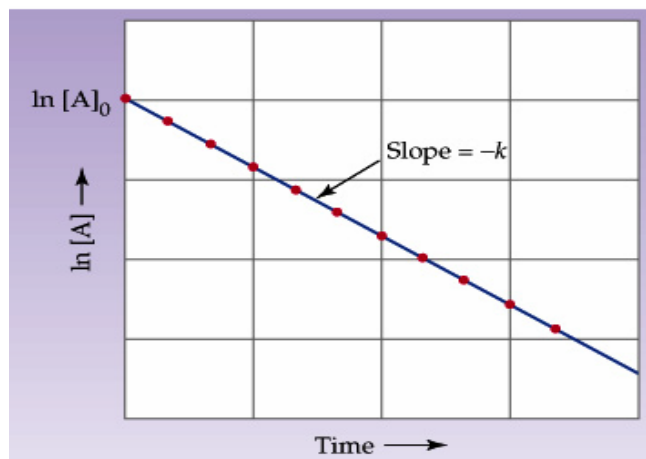
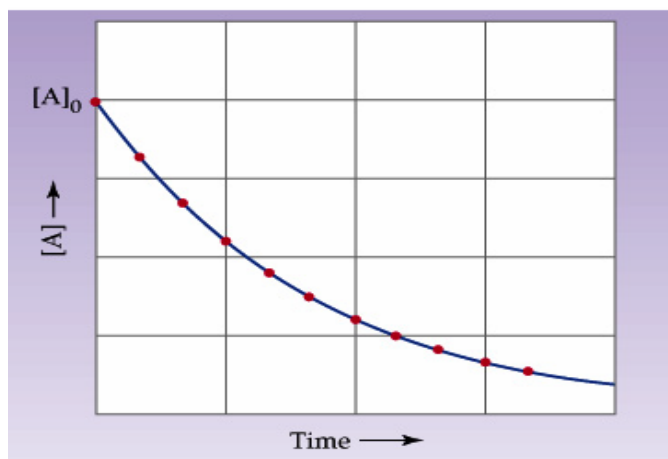
The integrated law can be used to determine:

1. *How Long Does it Take?*
2. *How Much Remains After a Given Time?*
3. *What Concentration Was Present Initially*

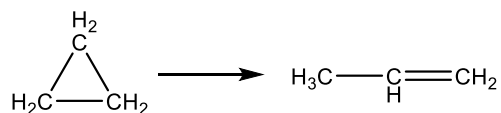
The above equation is only true for first order reactions. Different equations must be derived for other orders reaction such as zero order, second order, ect...

Graphical Method:

The integrated law shows the equation of a straight line. By plotting $\ln[A]$ versus time (t) is a straight line with slope ($m = -k$)



Example: Cyclopropane rearranges to form propene in the gas phase

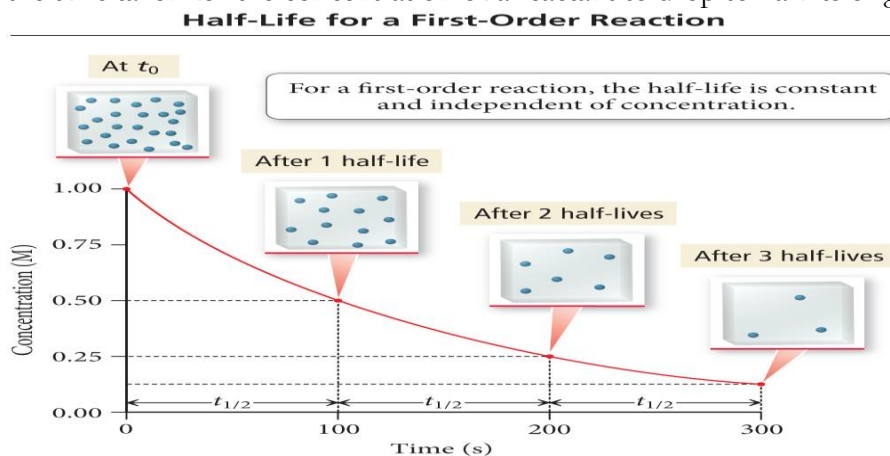


The reaction is first order in cyclopropane and has a measured rate constant of $3.36 \times 10^{-5} \text{ s}^{-1}$ at 720K. If the initial cyclopropane concentration is 0.0445M

- What will be the concentration of cyclopropane after 235 minutes?
- How long would (in minutes) it takes for the concentration of cyclopropane to decrease to 0.035M?

Half-Life of a First Order Reaction

Half-life ($t = 1/2$) is the time taken for the concentration of a reactant to drop to half its original value.



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

When $t = 1/2$, the fraction of A that remains, $[A]_t/[A]_0$, is 1/2. Therefore

$$\ln \frac{1}{2} = -k t_{1/2}$$

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

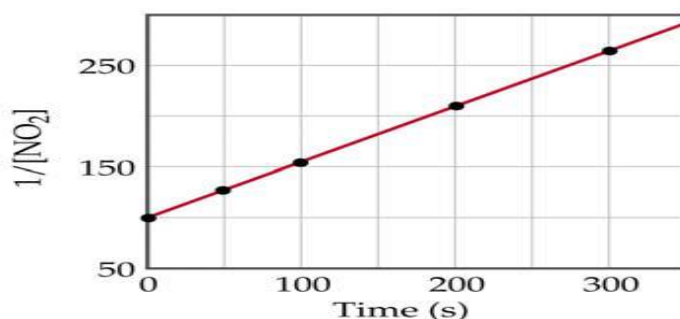
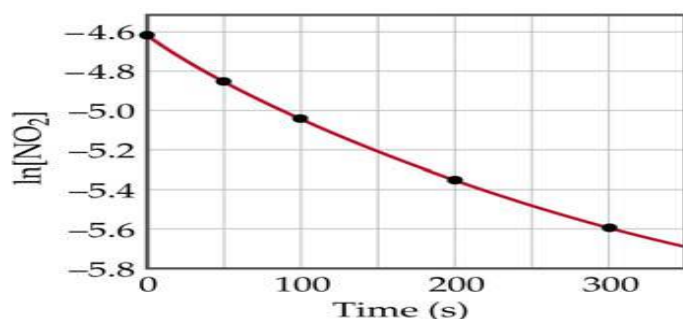
If you know “k” for the reaction, you also know $t_{1/2}$ and vice versa. The half-life is a useful, descriptive value.

b. How long (in hours) would it take for 75% of SO_2Cl_2 to decompose?

14.4 and 14.6 Integrates Law: Zeroth order and Second Order

Finding the Rate Law: Graphical Methods

For the reaction below, the same set of experiment data ($[A]$ and (t)) has been plotted in two different ways. Is the reaction 1st order?



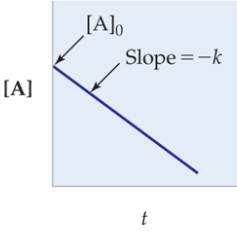
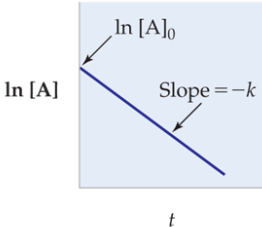
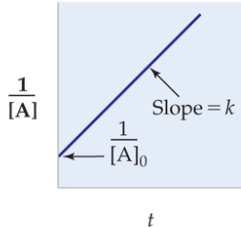
- The rate law **must** be determined experimentally.
- A graph of concentration of reactant versus time can be used to determine the effect of concentration on the rate of a reaction.
- This involves using calculus to determine the area under a curve, which is beyond the scope of this course.
- Later we will examine the results of this analysis so we can use graphs to determine rate laws for several simple cases

Graphical Determination of the Rate Law for $A \rightarrow \text{Product}$

In order to use integrated law method, lots of $[A]$ versus time, $\ln[A]$ versus time, and $1/[A]$ versus time allow determination of whether a reaction is zero, first, or second order. Whichever plot gives a straight line determines the order with respect to $[A]$.

- If linear is $[A]$ versus time, Rate = $k[A]^0$.
- If linear is $\ln[A]$ versus time, Rate = $k[A]^1$.
- If linear is $1/[A]$ versus time, Rate = $k[A]^2$

Table 14.4 Characteristics of Zeroth-, First-, and Second-order Reactions of the Type A → products

	Zeroth-Order	First-Order	Second-Order
Rate law	$-\frac{\Delta[A]}{\Delta t} = k$	$-\frac{\Delta[A]}{\Delta t} = k[A]$	$-\frac{\Delta[A]}{\Delta t} = k[A]^2$
Integrated Rate Law	$[A]_t = -kt + [A]_0$	$\ln [A]_t = -kt + \ln [A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
Linear graph	[A] versus t 	$\ln [A]$ versus t 	$\frac{1}{[A]}$ versus t 
Graphical determination of k	$k = -(\text{Slope})$	$k = -(\text{Slope})$	$k = \text{Slope}$
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$ (not constant)	$t_{1/2} = \frac{0.693}{k}$ (constant)	$t_{1/2} = \frac{1}{k[A]_0}$ (not constant)

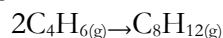
Example of Zeroth-Order

The rate constant for the decomposition of NH_3 on a platinum surface at 856°C is $1.50 \times 10^{-6} \text{ M/s}$.

a. What is the order of the reaction?

b. If the initial concentration of NH_3 is $1.50 \times 10^{-2} \text{ M}$, calculate the concentration of NH_3 after 30 mins

Example: The reaction of butadiene gas (C_4H_6) to yield C_8H_{12} gas is described by the equation:



This “dimerization” reaction is second order with a rate constant equal to $5.76 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}$ under certain conditions. If the initial concentration of butadiene is 0.200 M , what is the concentration after 10.0 min ?