

Calculations In Chemistry

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Module 27 – Kinetics: Rate Laws

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Module 27 — Kinetics: Rate Laws

Prerequisites: It will be helpful if you have completed Module 20 – Graphing before this module.

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Lesson 27A: Reaction Rates

Introduction to Reaction Rates

In most chemical reactions, for the reaction to take place, the reactant particles must collide.

As the *temperature* at which a reaction is run increases, the reaction nearly always occurs at a faster rate. Why? If reactant particles are at higher temperatures, they are traveling faster on average, and they have higher average kinetic energy on average. This means that when they collide, at higher temperatures they hit harder, and when they collide with higher energy they are more likely to react.

Reactions also proceed faster when the reactants are at higher concentrations in solvents or in gas mixtures. Why? When the particles are more concentrated, they collide more often.

Kinetics

Reaction kinetics includes the study of

- the speed (the rate) of chemical reactions;
- the mechanism of chemical reactions: the “intermediate” particles that form in the transition from reactants to products; and
- reaction energetics: how much energy is needed to form intermediates, and how reaction rates are affected by temperature.

Why is kinetics important? We would like to speed up certain reactions that are important to society, such as the

- burning of gasoline in internal combustion engines, so that incompletely burned combustion products do not escape into the environment; and
- converting graphite (pencil lead) into “industrial diamonds” for drills and cutting tools.

Other reactions, we would like to slow down, such as

- the conversion of the iron in steel to iron oxide (rust), and
- the decay of ozone (O₃) in earth’s upper atmosphere, which protects life forms from the harmful elements of solar radiation.

Kinetics helps in understanding, and potentially controlling, these processes.

Definitions

A **rate** is a *change* in a quantity per unit of *time*. A rate is a ratio that always has a *time* unit in the denominator.

- *Speed* (or velocity) is a measure of how fast an object is moving: the rate of change of position per unit of time, in units such as miles per *hour* or meters per *second*.
- An *interest rate* is the percentage of a loan amount you must pay, per *month* or per *annum* (per year), in addition to re-paying the principal.

The rate of a chemical reaction measures how fast the reactants are used up, and/or how fast the products are formed.

A **reaction mechanism** breaks down an overall chemical reaction into individual steps, identifying the *temporary* particles that form in the transition from reactants to products.

The rate of a reaction is determined by the *slowest step* in the mechanism: the **rate-determining step**. **Rate-law equations** measure the characteristics of the rate-determining step of a reaction.

Catalysts are substances that cause a reaction to go faster, but are not used up in the reaction.

- Metals such as platinum and palladium are used in a car's catalytic converter to help ensure that incompletely burned gasoline reacts with oxygen.
- **Enzymes** are biological catalysts: carbon-based molecules that regulate living processes.

Average and Instantaneous Reaction Rates

In chemical reactions, the rate at which one reactant is used up, or one product is formed, is defined as the **rate of change** of the **concentration** of the reactant or product.

$$\text{Rate} = \frac{\text{change in } [A]}{\text{change in time}}$$

For most reactions, a graph of the concentration of a reactant or product ($[A]$) versus time will produce a smooth **curve** (an exception is the zero-order reaction, discussed below, for which the graph is a line).

Two types of reaction rates are the **average rate** and the **instantaneous rate**.

- The **average** reaction rate between two times t_1 and t_2 is defined as

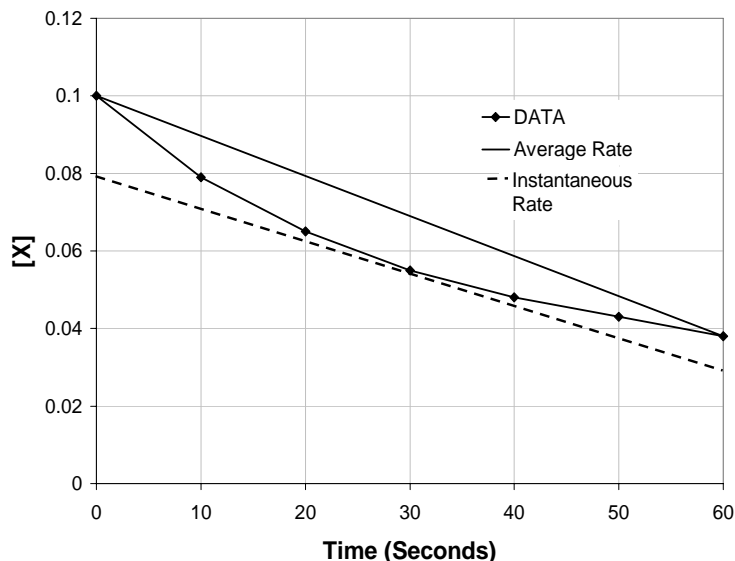
$\text{Average Rate} = \frac{\text{change in } [A]}{\text{change in time}} = \frac{\Delta[A]}{\Delta t} = \frac{[A]_2 - [A]_1}{t_2 - t_1}$

This equation must be memorized.

On a graph $[A]$ versus time, the average rate will be the **slope** of the line between the two points $(t_1, [A]_1)$ and $(t_2, [A]_2)$.

- The **instantaneous** rate is, in the notation of calculus, $d[A]/dt$, the rate at a specific time t . At a given time, the instantaneous rate can be calculated by graphing measurements for $[A]$ versus time, drawing a line tangent to the curve at the time, and calculating the slope of the tangent line.

For most reactions, the two slopes, representing the values for the average rate between two close points, and the instantaneous rate at a time half-way between the two points, will be close but not the same.



Average Rate Calculations

To calculate an average reaction rate from concentration versus time measurements:

- Select the two measurements of concentration versus time to be averaged.
- Assign the *lower* time to be t_1 , and
- Apply the average rate definition:

$$\text{Average Rate} = \frac{\text{change in } [A]}{\text{change in time}} = \frac{\Delta[A]}{\Delta t} = \frac{[A]_2 - [A]_1}{t_2 - t_1}$$

Use those steps on the following example.

- Q1.** For the data at the right, calculate the average rate of the reaction for the time between three and five minutes.

(When you come to a * * * * * line, *cover below* the line and answer the questions above the line in your notebook.)

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Assign t_1 to be the lower time: 3.0 min. $[A]_1$ is then 0.275 M.

Using the equation for average rate:

$$\text{Average Rate} = \frac{\Delta[A]}{\Delta t} = \frac{[A]_2 - [A]_1}{t_2 - t_1} = \frac{0.215 \text{ M} - 0.275 \text{ M}}{5.0 \text{ min.} - 3.0 \text{ min.}} = \boxed{-0.030 \frac{\text{mol}}{\text{L} \cdot \text{min.}}}$$

Time	[A]
0	0.500M
1.0 min.	0.395 M
2.0 min.	0.325 M
3.0 min.	0.275 M
4.0 min.	0.240 M
5.0 min.	0.215 M

Note about this result:

1. The negative sign for the rate reflects that [A] is decreasing with time.
2. The *units* can be written in several equivalent ways.

$$\frac{\text{M}}{\text{min.}} = \text{M} \cdot \text{min.}^{-1} = \frac{\text{mol}}{\text{L}} \cdot \frac{1}{\text{min.}} = \frac{\text{mol}}{\text{L} \cdot \text{min.}} = \text{mol} \cdot \text{L}^{-1} \cdot \text{min.}^{-1}$$

Follow the math from step to step between these equivalent forms.

3. Note the similarity between the equation for *average rate* between two times and the formula for the *slope* of a line on a graph:

$$\mathbf{m} = \text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$$

The equation for the average rate between two times matches the form of a slope formula in which the x values are always time values.

The *average rate* of a reaction is the *slope* of a line between two points on a graph that represent the concentrations plotted at y_1 and y_2 at times t_1 and t_2 plotted on the x -axis.

Practice A

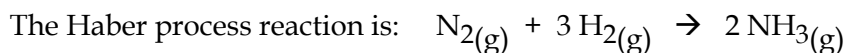
1. State two ways to speed up the rate of a reaction.
2. For the reaction $A + 2B \rightarrow 2C$, the average rate of reaction of A is $-1.50 \times 10^{-3} \text{ M} \cdot \text{s}^{-1}$ during the first 2.00 minutes of the reaction. If $[A] = 0.240 \text{ M}$ after 2.00 minutes, what was the initial $[A]$?

Rates of Disappearance versus Appearance

If the balanced equation for a reaction is known, and the rate at which any *one* of the reactants is used up or products form is known, *all* of the rates of disappearance of reactants and appearance of products can easily be calculated. The coefficients of a balanced equation supply the simple whole-number ratios needed for these calculations.

Try applying that rule to the following example.

- Q.** The Haber process uses nitrogen gas (isolated from air) and hydrogen gas (which can be produced from water) plus catalysts and energy to produce ammonia. Ammonia can be converted to fertilizers that improve food production.



At a time when the nitrogen gas is reacting at a rate of 0.060 M/s ,

- a. What is the rate of reaction of the hydrogen gas?
- b. What is the rate of ammonia formation?

Solve, then check your answer below.

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- a. For every one N_2 molecule used up, three H_2 must be used up, so the rate of change in hydrogen gas concentration is: $(-0.060 \text{ N}_2 \text{ M/s}) \times (3 \text{ H}_2/\text{N}_2) = -0.180 \text{ H}_2 \text{ M/s}$.

Note that though a rate of *disappearance* can be labeled as positive, what is measured rate equations is a rate of change in *concentration*, so that in calculations, a rate at which substances are *used up* must be assigned a negative sign.

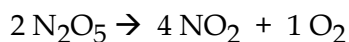
Try Part B.

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- b. For every one nitrogen molecule used up, two ammonia molecules must be formed. The rate of ammonia formation must be $0.060 \text{ M/s} \times 2 = +0.120 \text{ M/second}$.

Practice B: Check your answer after each part.

1. The gas dinitrogen pentoxide decomposes to form nitrogen dioxide gas and oxygen gas. The balanced equation is



Measurements of $[\text{N}_2\text{O}_5]$ are recorded at the right.

- a. Calculate the average rate of reaction of N_2O_5 during the first three minutes of the reaction.
- b. Calculate the average rate of oxygen gas formation during the first three minutes of the reaction.
- c. Calculate the average rate of NO_2 formation between 2.0 and 4.0 minutes.

Time	$[\text{N}_2\text{O}_5]$
0	0.200 M
1.0 min.	0.141 M
2.0 min.	0.100 M
3.0 min.	0.0707 M
4.0 min.	0.0500 M

ANSWERS

Practice A

1. Increase the temperature at which the reaction is run or increase the concentration of one or more of the reactants.
2. WANTED: Initial $[\text{A}]$, which in symbols is $[\text{A}]_0$, the concentration of A at time = 0.
The problem provides the average rate, and the average rate equation is the only one we know so far.

$$\text{Average Rate} = \frac{\Delta[\text{A}]}{\Delta t} = \frac{[\text{A}]_2 - [\text{A}]_1}{t_2 - t_1} = -1.50 \times 10^{-3} \text{ M} \cdot \text{s}^{-1}$$

DATA: $[\text{A}]_2 = 0.240 \text{ M}$ $[\text{A}]_1 = [\text{A}]_0 = ?$ $t_2 = 2.00 \text{ min.} = 120. \text{ seconds}$ $t_1 = 0 \text{ s}$

The rate constant uses seconds, but the data includes minutes. In equations, the units must be consistent. The easier conversion is to seconds. If needed, adjust your work and complete the calculation.

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SOLVING in symbols first: $?$ = $[A]_0 = [A]_1 = -\{ (-1.50 \times 10^{-3} \text{ M} \cdot \text{s}^{-1})(t_2 - t_1) - [A]_2 \} =$
 $= -\{ (-1.50 \times 10^{-3} \text{ M} \cdot \text{s}^{-1})(120 \text{ s}) - 0.240 \text{ M} \} = -(-0.180 \text{ M} - 0.240 \text{ M}) = \mathbf{0.420 \text{ M} = [A]_0}$

Practice B

1a. **Average Rate** = $\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{[\text{N}_2\text{O}_5]_2 - [\text{N}_2\text{O}_5]_1}{t_2 - t_1} = \frac{0.0707 \text{ M} - 0.200 \text{ M}}{3.0 \text{ min.} - 0 \text{ min.}} = \boxed{-0.043 \frac{\text{mol}}{\text{L} \cdot \text{min.}}}$

1b. For every two N_2O_5 used up, one is O_2 is formed.

Average Rate of O_2 formation = $-0.043 \text{ M/min.} \times 1/2 = \boxed{+ 0.022 \text{ M/min.}}$

1c. The only data available during that time period is for N_2O_5 being used up, but if we know that average rate, we can use coefficients to calculate rates for the other reactants and products.

Average Rate = $\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{[\text{N}_2\text{O}_5]_2 - [\text{N}_2\text{O}_5]_1}{t_2 - t_1} = \frac{0.0500 \text{ M} - 0.100 \text{ M}}{4.0 \text{ min.} - 2.0 \text{ min.}} = -0.025 \frac{\text{mol N}_2\text{O}_5}{\text{L} \cdot \text{min.}}$

In the balanced equation, NO_2 is being produced at double that rate. Substances being used up should be given a negative, and substances being formed a positive, rate of change in *concentration*.

$(-0.025 \text{ M/min N}_2\text{O}_5) \times 2 = \boxed{+ 0.050 \text{ M/min. NO}_2}$

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Lesson 27B: Rate Laws

A **rate law** (also called a *differential rate law*) expresses how the rate of a reaction depends on the *concentration* of reacting particles.

When studying the impact of a single reactant particle A on a reaction rate, the rate law equation is

$$\text{Rate} = \frac{\Delta[A]}{\Delta t} = k [A]^n$$

where **k** is the **rate constant** and **n** is an exponent that is termed the **order** of the reactant.

The rate constant **k** is a number with units that will always be the same when a given reaction is carried out at the *same temperature*. For most reactions, the rate constant will change significantly even with a small temperature change. Typically, an increase in temperature of 10°C will roughly double a reaction rate.

In a chemical reaction: $A + B + C \rightarrow D + E$, the rate of the forward reaction will be predicted by the rate law:

$$\text{Rate} = k [A]^n [B]^o [C]^p$$

where the exponents **n**, **o**, and **p** are the *order* of each reactant. If each exponent and the rate constant **k** can be calculated, a complete rate law for the reaction can be written.

To understand the mechanism of a chemical reaction, the first step is to “determine the **form** of the rate law” by determining the order (the exponent) for each [reactant] in the rate-law equation.

Zero Order Reactants

If the exponent in a rate equation is zero ($n = 0$) for a reactant, the reaction is termed *zero order* for that reactant, and the rate equation is: **rate = $k[A]^0 = k$** (anything to the zero power equals one).

If a reaction has only one reactant, and that reactant is zero order, the reaction proceeds at a *constant rate*: the rate does not depend on the concentration of the reactant. Reactions where the rate is determined by a catalyst are often zero order.

First Order Reactants

For a first-order reactant, **n = 1**, and **rate = $k[A]^1 = k[A]$** . The rate of the reaction is directly proportional to the concentration of A: if the reactant *concentration is doubled*, the reaction *rate is doubled*.

The decay of radioactive isotopes is one type of process with first-order kinetics.

Second Order Reactants

For a second-order reactant, **n = 2**, and **rate = $k[A]^2$** . If the [reactant] is *doubled*, the reaction *rate will be four times as fast*.

Summary: Commit this chart to memory.

Order	Zero	First	Second
Rate Law	rate = $k[A]^0 = k$	rate = $k[A]^1 = k[A]$	rate = $k[A]^2$
When [A] doubles:	rate stays same	rate doubles	rate quadruples

In a rate law, the value of the exponents is *not* determined by the coefficients of the balanced equation. The order (the exponent) for each reactant must be determined by experiment.

Three methods that can determine the order for a reactant are:

- Varying the reactant *concentration*, and analyzing the *initial rate* of the reaction;
- Arithmetic analysis of how the reactant *concentration* changes with *time*; and
- Graphical analysis of how reactant concentration changes with time.

Let's consider these one at a time.

Finding the Order: Concentration versus Initial Rate

When determining the order of a reactant by varying its concentration, the **initial rate** of the reaction is measured: the rate just after the reaction begins, when very few of the products have been formed.

Why measure the *initial rate*? In theory, all chemical reactions are **reversible**: a reaction that goes forward can go backward. In practice, *some* reactions go forward and backward easily; the reversible color change of an acid-base indicator is one example. Other reactions strongly tend to go only one direction: most "burning" goes strongly to completion.

Analysis of reaction-rate data can be difficult if a reaction is going both forward and backward, but for a reaction to go backward, the products must exist. After reactants are first mixed, when not much of the products have been formed, the reaction is going forward far more than it is going backward. This simplifies kinetics calculations.

Use the characteristics of zero-, first-, and second-order reactants to solve this question.

Q. For the reaction: $A \rightarrow B$, based on the data at the right,

- determine the *order* of A.
- Write the rate law.

* * * * *

Answer

- The data shows that in Experiment 2, [A] is doubled compared to Experiment 1, and the reaction rate doubled as well. Comparing Experiment 3 to Experiment 1, when [A] was tripled, the reaction rate tripled.

This reaction fits the definition of "*first order in A.*"

- The rate law is: **Rate = $k[A]$** , where the exponent of [A] is **one**.

Expt.	[A]	Initial Rate (mol/L·s)
1	0.20 M	1.3×10^{-4}
2	0.40 M	2.6×10^{-4}
3	0.60 M	3.9×10^{-4}

Try one more example.

- Q. For the reaction: $C \rightarrow D$, the data at the left is collected.
- Determine the order of C.
 - Write the rate law.
 - Using the results of Expt. 2 and the rate law, calculate a *value* for the rate constant (**k**).

Expt.	[C]	Initial Rate (mol / L • s)
1	0.10 M	1.0×10^{-4}
2	0.20 M	4.0×10^{-4}
3	0.40 M	16.0×10^{-4}

* * * * *

Answer

- In Experiment 2, the [C] is doubled compared to Expt. 1, and the reaction rate quadrupled. Comparing Expt. 3 to Expt. 1, when [C] is four times higher, the reaction rate is 16 times higher. This reaction is “second order in C.”
- This behavior fits the rate law: **rate = k[C]²**.

If needed, adjust your work and then try Part C.

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- Since **k** is a constant in the rate law equation, data from any one of the three experiments, substituted into the rate law, should give the same value for **k**.

Solve **Rate = k[C]²** for **k** in symbols first, then substitute data from Expt. 2 in the chart above.

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$$k = \frac{\text{Rate}}{[\text{C}]^2} = \frac{4.0 \times 10^{-4} \text{ (mol/L} \cdot \text{s)}}{[0.20 \text{ mol/L}]^2} = \frac{4.0 \times 10^{-4}}{0.040} \frac{\text{mol} \cdot \text{L}^2}{\text{L} \cdot \text{s} \cdot \text{mol}^2} = \boxed{1.0 \times 10^{-2} \frac{\text{L}}{\text{mol} \cdot \text{s}}}$$

Recall that in simplifying the units, when a fractional unit is in the denominator, it helps to separate the fractional unit into a reciprocal, then invert the reciprocal (see Lesson 17C).

The *units* of the answer above can be written in several equivalent ways, including

$$\frac{\text{L}}{\text{mol} \cdot \text{s}} = \frac{1}{\text{M} \cdot \text{s}} = \text{M}^{-1} \cdot \text{s}^{-1} = \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

Concentration versus Initial Rate for More Than One Reactant

In an overall chemical reaction: $A + B + C \rightarrow D + E$, the rate of the forward reaction will be predicted by the *rate law equation*:

$$\text{Rate} = k [\text{A}]^n [\text{B}]^o [\text{C}]^p$$

The **overall reaction order** for the reaction is the *sum* of the reactant *exponents*.

For a reaction with more than one reactant, it is relatively easy to determine the order of each reactant if, in a series of experiments, the concentration of each reactant is varied while the other reactant concentrations are held constant.

This is a key principle of experimental design: when multiple variables affect an outcome, vary one and measure the impact on the second while holding the others constant.

Try this problem.

Q. For the reaction $A + B \rightarrow C$, the data at the right is collected.

- Determine the order of A and B.
- Write the overall rate law.
- Find the overall reaction order.
- Using the rate law and Expt. 1 data, find a numeric value and units for **k**.

Expt.	[A]	[B]	Initial Rate (mol / L • s)
1	0.10 M	0.10 M	2.1×10^{-5}
2	0.20 M	0.10 M	8.0×10^{-5}
3	0.20 M	0.20 M	16.1×10^{-5}

* * * * *

Answers

- Comparing Experiment 2 to Experiment 1, [B] is held constant, while [A] doubles, and the reaction rate approximately quadruples. Allowing for experimental error, this indicates that the *power* of [A] is **2**, and A is therefore a *second-order* reactant.

Comparing Experiment 3 to Experiment 2, the [A] is held constant, while the [B] doubles, and the reaction rate approximately doubles. This fits the profile for B being a *first-order* reactant.

- What is the overall rate equation for this reaction? **Rate = $k[A]^2[B]^1 = k[A]^2[B]$** .
- The “**overall** reaction order” for the reaction is the sum of the exponents: $2 + 1 = 3$. The reaction is said to be “*third-order overall*.”
- Since **k** is constant in all of the experiments, you can use data from any one of the experiments to calculate **k**. Since **Rate = $k[A]^2[B]$** , if we use Expt. 1 data:

$$k = \frac{\text{Rate}}{[A]^2[B]} = \frac{2.1 \times 10^{-5} \text{ mol/L} \cdot \text{s}}{(0.10 \text{ mol/L})^2 (0.10 \text{ mol/L})} = \frac{2.1 \times 10^{-5} \text{ mol/L} \cdot \text{s}}{10^{-3} \text{ mol}^3/\text{L}^3}$$

$$= 2.1 \times 10^{-2} \frac{\text{mol}}{\text{L} \cdot \text{s}} \bullet \frac{\text{L}^3}{\text{mol}^3} = \boxed{2.1 \times 10^{-2} \frac{\text{L}^2}{\text{mol}^2 \cdot \text{s}}}$$

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Relationships to Memorize

- Average Rate** = $\frac{\text{change in [A]}}{\text{change in time}} = \frac{\Delta[A]}{\Delta t} = \frac{[A]_2 - [A]_1}{t_2 - t_1} = \text{slope}$ between points $(t_1, [A]_1)$ and $(t_2, [A]_2)$.

Order:	Zero	First	Second
Rate Law:	rate = $k[A]^0 = k$	rate = $k[A]^1 = k[A]$	rate = $k[A]^2$
If [A] doubles, the rate:	Stays the same	Doubles	Quadruples

- For reaction $A + B + C \rightarrow D + E$, the rate-law equation is: **Rate = $k[A]^n[B]^0[C]^p$**
- Overall reaction order = sum of the exponents in the rate law.

5. Knowing the rate of disappearance or appearance for any one of the reactants or products, coefficients will calculate the rates for the other reactants and products.

Practice A: Finding Order From Concentration versus Initial Rate

Answers are at the end of this lesson.

1. For the reaction $X + Y \rightarrow Z$, the data at the right is collected.
- Determine the order of X and Y.
 - Write the overall rate equation.
 - Find the overall order for the reaction.
 - Calculate a value for k.

Expt.	[X]	[Y]	Initial Rate (mol / L • s)
1	0.25 M	0.10 M	1.0×10^{-5}
2	0.25 M	0.20 M	4.0×10^{-5}
3	0.50 M	0.10 M	4.0×10^{-5}

2. For the reaction $A + B \rightarrow C$, the data at the right is collected.
- Determine the order of A and B.
 - Write the overall rate equation.
 - Find the overall order for the reaction.

Expt.	[A]	[B]	Initial Rate (mol / L • s)
1	0.20 M	0.50 M	3.5×10^{-5}
2	0.40 M	1.0 M	1.4×10^{-4}
3	0.40 M	0.50 M	1.4×10^{-4}

Finding the Order Using Rate, Time, and Half-Life

The **half-life** of a reactant measures how much *time* is required for *half* of the reactant to be used up.

In problems where the goal is simply to determine the *order* of a reactant from concentration versus time data, the order can often be determined by *half-life analysis*.

Half Lives and Order

If sufficient data is available, the order of a reactant can be determined by estimating the *percentage* of the original concentration *remaining* at a time equal to *double* the *first* half-life.

- For *zero-order* reactants: after the *first* half-life, half of the reactant is used up. At a time equal to *double* the first half-life, *all* of the reactant is used up. A zero-order reactant is used up at a constant rate.
- First-order reactants have a constant half-life: the time for the second half-life is the same as the first.

For *first-order* reactants: after the first half-life, half of the reactant is used up, and half remains. At a time equal to double the first half-life, half of that remaining $1/2$ is used up, and $1/4$ of the original amount remains. After *triple* the first half-life, $1/2$ of the $1/4$, = $1/8^{\text{th}}$ of the original amount remains.

- For *second-order* reactants: after the first half-life, half of the reactant remains. At a time equal to *double* the first half-life, **1/3** of the reactant remains. At a time equal to *triple* the first half-life, **1/4** of the original reactant remains.

For second-order reactants, the time to reduce 1/2 to 1/4 is twice as long as to reduce the original amount by half; the second half-life is twice as long as the first.

Summary: memorize these relationships.

1	Order →	Zero	First	Second
2	Rate Law	rate = $k[A]^0 = k$	rate = $k[A]^1 = k[A]$	rate = $k[A]^2$
3	If [A] doubles , the rate :	Stays the same	Doubles	Quadruples
4	At double the first half-life, [A] remaining is:	None	25%	33%

To Use the “Double the First Half-Life” Method to Determine Reaction Order

If sufficient data is available:

- Estimate the *first* half-life: the time required for one-half of the original [reactant] to be used up.
- Estimate what percentage of the original concentration is remaining at a time that is *double* the first half-life.
- Use the “double the first half-life” rules to determine the *order* of the reactant.

Let’s apply this method to a problem.

Q1. For the reaction: $C \rightarrow D$, time and [C] are measured as a reaction proceeds. Based on the rules above,

- estimate the first half-life of C in the reaction.
- Determine the order of reactant C in the rate law,

* * * * *

Answer

The original concentration is cut in half after 20. seconds, so the first half-life of C is 20 s.

Double the first half-life is 40 s. The [C] at 40 s is **1/4** (25%) of the original concentration.

This behavior fits: **rate = $k[C]^1 = k[C]$** . This reaction is *first* order in C.

Time	[C]
0	1.00 M
10. s	0.71 M
20. s	0.50 M
30. s	0.35 M
40. s	0.25 M
50. s	0.17 M

Try another example.

Q2. For the reaction: $R \rightarrow S$, [R] and time are measured.

- Estimate the first half-life of R in the reaction.
- Estimate the [R] after double the first half-life.
- Determine the order of reactant R,

* * * * *

Time	[R]
0	0.200 M
5.0 s	0.125 M
9.0 s	0.095 M
14 s	0.074 M
18 s	0.063M
22 s	0.054 M

Answer

- The original concentration is cut in half, to 0.100 M, after *about* 8 s.
- Double the first half-life is *about* 16 s. The [R] at *about* 16 s is *about* 0.069 M.

Is this zero, first, or second order?

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- Since $0.069 \text{ M}/0.200 \text{ M} = 0.345$; about 34% of the original concentration remains at double the first half-life, which is close to 33%. This approximately fits the profile for a second-order reactant: $\text{rate} = k[\text{R}]^2$.

In many problems, not enough data is provided to allow analysis at “double the first half-life,” and this method cannot be used. In those cases, however, the reaction order can often be determined by the graphical analysis methods that we will learn in the next lesson.

Practice B: Order From Concentration, Time, and Half-life

- For the reaction: $X \rightarrow Y$, [X] and time are measured as a reaction proceeds.

- Estimate the first half-life of X in the reaction.
- Determine the order in X.
- Write the rate equation.
- Calculate the average rate of the reaction during its first 100 seconds.
- Which of these can be written as an answer *unit* for part d? After each, write YES or NO.

Time	[X]
0	0.100 M
25 s	0.079 M
50. s	0.065 M
100. s	0.048 M
150. s	0.038 M
200. s	0.032 M

- 1) $\frac{\text{M}}{\text{s}}$ 2) $\text{M} \cdot \text{s}^{-1}$ 3) $\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ 4) $\frac{\text{mol}}{\text{L} \cdot \text{s}}$

- For the reaction: $D \rightarrow E$, [D] and time are measured at the right. Write the rate-law expression.

Time	[D]
0	0.050 M
25 s	0.044 M
50. s	0.038 M
100. s	0.025 M
200. s	0 M

- For the reaction: $A \rightarrow B$, [A] and time are measured. Write the rate equation.

Time	[A]
0	0.100 M
1.0 hour	0.095 M
2.0 hours	0.090 M
3.0 hours	0.085 M
4.0 hours	0.081 M

ANSWERS**Practice A: Order From Concentration versus Rate**

- 1 a. The rate of the forward reaction will be predicted by the rate equation:

$$\text{Rate} = k [\text{X}]^n [\text{Y}]^p$$

To find the order for **X**, choose two experiments where the other variable **[Y]** is held *constant* while **[X]** is changed. In experiments 1 and 3, **[Y]** is held constant.

Expt.	[X]	[Y]	Initial Rate (mol / L · s)
1	0.25 M	0.10 M	1.0×10^{-5}
2	0.25 M	0.20 M	4.0×10^{-5}
3	0.50 M	0.10 M	4.0×10^{-5}

Comparing experiments 1 and 3, **[X]** is doubled, and the rate goes up four times. This indicates that the reaction is “second order in X;” the exponent of **[X]** in the rate equation is **two**.

To find the order for **Y**, choose two experiments where the other variable **[X]** is held constant while **[Y]** is changed. In experiments **1 and 2**, **[X]** is constant.

Comparing experiments 1 and 2, **[Y]** is doubled, and the rate goes up four times. This indicates that the exponent for **[Y]** is 2, and the exponent of **[Y]** in the rate equation is **two**.

- b. The overall rate equation is: $\text{Rate} = k [\text{X}]^2 [\text{Y}]^2$
 c. The overall order for the reaction is the sum of the exponents: $2 + 2 = 4$.
 d. Since **k** is constant, you can use the rate law with data from any one of the experiments to calculate **k**. Solving $\text{Rate} = k [\text{X}]^2 [\text{Y}]^2$ for **k**, if we use data from Experiment 3:

$$k = \frac{\text{Rate}}{[\text{X}]^2 [\text{Y}]^2} = \frac{4.0 \times 10^{-5} \text{ mol / L} \cdot \text{s}}{(5 \times 10^{-1} \text{ mol / L})^2 (1 \times 10^{-1} \text{ mol / L})^2} = \frac{4.0 \times 10^{-5} \text{ mol / L} \cdot \text{s}}{25 \times 10^{-4} \text{ mol}^4 / \text{L}^4}$$

$$= 0.16 \times 10^{-1} \frac{\text{mol}}{\text{L} \cdot \text{s}} \cdot \frac{\text{L}^4}{\text{mol}^4} = 1.6 \times 10^{-2} \frac{\text{L}^3}{\text{mol}^3 \cdot \text{s}}$$

- 2 a. The rate of the forward reaction will be predicted by the rate equation: $\text{Rate} = k [\text{A}]^n [\text{B}]^p$

To find the order for **A**, choose two experiments where the other variable (**B**) is held **constant**: experiments **1 and 3**.

To compare the rates more easily, rewrite the values of the initial rates so that they all have the same exponential term. It is easiest if you give all of the values the same exponential term as the *smallest* exponential term in the series, and change the others (see Lesson 1B) to match the exponential of the smallest.

If you needed that hint, try the problem again.

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Expt.	[A]	[B]	Initial Rate (mol / L · s)
1	0.20 M	0.50 M	3.5×10^{-5}
2	0.40 M	1.0 M	1.4×10^{-4}
3	0.40 M	0.50 M	1.4×10^{-4}

For experiments 2 and 3, the rate becomes 14×10^{-5} .

Comparing experiments 1 and 3, [A] is doubled, and the rate goes up $14/3.5 = 4$; it quadruples. This indicates that the exponent of [A] in the rate equation is **two** (when the concentration goes up by a factor of 2, the rate goes up by a factor of 2 squared). The reaction is said to be “*second* order in A.”

To find the order for **B**, choose two experiments where the other variable (**A**) is held constant: experiments 2 and 3.

From experiment 3 to 2, [B] is doubled, but the rate stays the same. This indicates that the exponent for [B] is 0.

- b. The overall rate equation is: $\text{Rate} = k [A]^2 [B]^0 = k [A]^2$
 c. The overall order for the reaction is the sum of the exponents: $2 + 0 = 2$.

Practice B: Order From Concentration, Time, and Half-life

1. a. The initial concentration is reduced to one-half after about 95 seconds.
 b. Double the first half-life would be about 190 s. At that point, *about* **34%** of the initial concentration remains ($0.034/0.100$). After double the first half-life, 0% remains if zero order, 25% if first order, and **33%** if second order. The data fit **second** order in X.
 c. **Rate = k [X]²**
 d. Average rate = change in [X] per unit of time. Set t_1 as the lower t value ($t = 0$).

Time	[X]
0	0.100 M
25 s	0.079 M
50. s	0.065 M
100. s	0.048 M
150. s	0.038 M
200. s	0.032 M

$$\text{Average rate} = \frac{\Delta [X]}{\Delta t} = \frac{[X]_2 - [X]_1}{t_2 - t_1} = \frac{0.048 \text{ M} - 0.100 \text{ M}}{100 \text{ s} - 0 \text{ s}} = \frac{-0.052 \text{ M}}{100 \text{ s}} = \boxed{-5.2 \times 10^{-4} \frac{\text{M}}{\text{s}}}$$

- e. All are YES. All four forms are equivalent

2. a. The initial concentration has been cut in half after 100 seconds. Double the first half-life is 200 s. At 200 s, no D remains. This fits behavior that is “zero order in D.”

$$\text{Rate} = k [D]^0 = k$$

Zero order in D would also mean a constant rate of change for [D].

Check: do the [D] numbers drop by about the same amount every 50 seconds?

Time	[D]
0	0.050 M
25 s	0.044 M
50. s	0.038 M
100. s	0.025 M
200. s	0 M

3. Some problems will not offer enough data to get close to “double the first half-life.” This is an example. Though [A] seems to be falling at a constant rate, which would indicate zero order, zero and first order have similar rates initially. This problem does not provide enough data to use the “double the first half-life” method, and at this point the rate equation cannot be determined.

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Lesson 27C: The Integrated Rate Law – Zero Order

Prerequisites: Lessons 27A and 27B. In addition, you will need to know the rules for graphing in Graphing Module 20.

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Two Forms of the Rate Law

In a chemical reaction: $A + B + C \rightarrow D + E$, the rate of the forward reaction will be predicted by the rate equation:

$$\text{Rate} = k [A]^n [B]^0 [C]^p$$

In the previous lesson, the rate constant and the order of the reactants was determined by measurements of the concentration of each reactant versus

- the initial rate of the reaction, and
- the concentration at a time that is double the first half-life.

A third method of determining the rate law is to graphically analyze the measurements of concentration versus time.

The rate law above uses concentration and *rate* as variables. To calculate a rate law graphically, the rate laws are stated using concentration and *time* as variables.

To begin, commit the following chart to *memory*.

Rate Law Summary

1	Order →	Zero	First	Second
2	Differential Rate Law	rate = $k[A]^0 = k$	rate = $k[A]^1 = k[A]$	rate = $k[A]^2$
3	If [A] doubles, the rate:	Stays the same	Doubles	Quadruples
4	At double the first half-life, [A] remaining is:	None	25%	33%
5	Integrated Rate Law	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = +kt + \frac{1}{[A]_0}$

In the chart:

- The Row 2 equations are usually called the rate laws, but the more proper term, to distinguish them from Row 5, is the **differential rate laws**. In calculus, the instantaneous rate is defined in terms of the differential $d[A]/dt$.
- Row 5 is termed the **integrated rate laws** because those laws can be obtained by integrating (using calculus) the form of the rate law in Row 2.
- In the differential rate laws, concentration and *rate* are variables. In the integrated rate laws concentration and *time* are variables.
- The **ln** in the first-order integrated rate law represents the natural logarithm; and
- $[A]_0$ represents the *initial* concentration of a reactant, the concentration at *time* = 0.

The two rate equations in each *column* are mathematically equivalent: the differential and integrated rate laws for each order are the same relationship stated in two different ways.

Since the Row 2 equations are more simple, why bother with Row 5? Row 5 has one advantage: all three of the Row 5 equations are in the form $y = mx + b$, which is the general equation for a line.

(The zero- and first-order differential-rate laws can be matched to $y = mx + b$, but the second order rate law is in the form $y = mx^2$, which is algebraically quite different. The form $y = mx + b$ fits all three of the *integrated* rate laws.)

Let's briefly review the rules for the equation for a line.

Analyzing Linear Data

When values of x and y are graphed in Cartesian (x,y) coordinates, if the points fall on a straight line, the data will fit the equation $y = mx + b$. In this equation,

- y and x are *variables*, and m and b are *constants*.
- m is the slope of the line. A line has a *constant* slope; m will have the same value between all points on the line. If m is positive, the slope of the line is up (/); if m is negative the slope is down (\).
- To *calculate* m , memorize: $m = \text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$
- b is the y -intercept: the value of y when $x = 0$, which is the value of y when the line crosses the y -axis. b will be positive if a line crosses the y -axis above the origin of the graph and negative if the line crosses below the origin.
- Once the value of the slope is calculated, b can be calculated by substituting into $y = mx + b$ for any data point on the line.
- While m and b have constant values in the equation for a line, y and x can change. If a value is chosen for either y or x , and the values for the constants m and b are known, the equation $y = mx + b$ can be solved for the other variable.
- If the values for any three of the terms y , m , x , and b are known, the equation can be solved for an unknown fourth term.

Practice A: Answers are at the end of this lesson. If you are unsure about an answer, check after each part. If you need additional help with this topic, see Module 20.

1. If graphed data fits the equation: $y = mx + b$
 - a. What ratio will be constant between any two points?
 - b. What formula is used to calculate slope?

2. Using the data at the right, with °C values on the x -axis,
- Calculate the slope between any two points. Include units.
 - Calculate the slope between any *other* two points.
 - Are the slope results consistent with the equation $y = mx + b$? Why or why not?
 - Substituting the variable symbols in the data, write the equation for the line.
 - What is the numeric value and unit of m ?
 - Using the equation, the m value, and any x and y value in the data table, calculate the y -intercept.
 - Write the equation for the line, substituting both the symbols for the y - and x -axis variables and the numeric values and units for the two constants.
 - Test the equation. Pick a °C value from the table that you have not used in your calculations. Plug that °C value into your Step g equation and calculate a °F. Compare the calculated °F to the actual °F in the table at that °C.
 - Starting from the data table, what were you able to accomplish by the steps above?

°F	°C
-40.	-40.
32	0
68	20.
122	50.
212	100.

The Zero-Order Integrated Rate Law

Compare the *zero-order* integrated rate law: $[A]_t = -k t + [A]_0$

to the equation for a line: $y = m x + b$

The two equations have the same form:

- Like y and x , $[A]_t$ and t are variables: quantities that are varied to study the rate.
- $[A]_0$ is constant: the $[A]$ at the start of the experiment (when $t = 0$).
- $-k$ is a constant. Its value is minus the rate constant for the reaction.

If data for $[A]$ and t obey the zero-order rate law above, then

- A graph of $[A]_t$ versus t must be a straight line; and
- A value for k can be calculated from the slope of the graph of $[A]_t$ versus t .
- The *slope* of the line (a constant) must be equal to *minus* the rate constant k ;

Once k is known at the temperature conditions of the reaction, a complete rate law, including values for the constants, can be written. Whenever the reaction is run at that temperature, that rate law can then be used to predict $[A]$ at any stated t , or to predict the time when $[A]$ will reach a certain value.

This fulfills a central purpose of science: to develop equations that accurately predict results of a process under a variety of conditions.

Calculating the Slope to Find the Rate Constant

To practice using rate laws, let's go back to data from the previous lesson that we thought might be zero order and apply graphical analysis.

- Q. For the reaction: $D \rightarrow E$, measurements of $[D]$ and time are recorded at the right.

Time	$[D]$
0	0.050 M
25 s	0.044 M
50. s	0.038 M
100. s	0.025 M
150. s	0.013 M

Do the following steps.

- a. Assuming the reaction is zero order in D, write the differential and integrated forms of the rate law for this reactant.

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Differential Rate Law: $\text{rate} = k[D]^0 = k$

Integrated Rate Law: $[D]_t = -kt + [D]_0$

- b. Match the symbols in the zero-order integrated rate law to the symbols in the equation for a line.

$y =$

$m =$

$x =$

$b =$

* * * * *

The zero-order integrated rate law: $[D]_t = -k t + [D]_0$

The equation for a line: $y = m x + b$

$y = [D]_t$ = the variable concentration of D at a variable time t

$m = -k$ = a constant = minus the rate constant

$x = t$ = time, a variable

$b = [D]_0 = 0.050 \text{ M}$ = the concentration of D initially, at $t = 0$.

- c. What data plotted on y and x will result in a straight line with a slope = $-k$?

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When $y = mx+b$, a graph of y vs. x will be a straight line with a slope m .

For this data, plotting $[D]$ on y and t on x should result in a straight line with a slope = $m = -k$

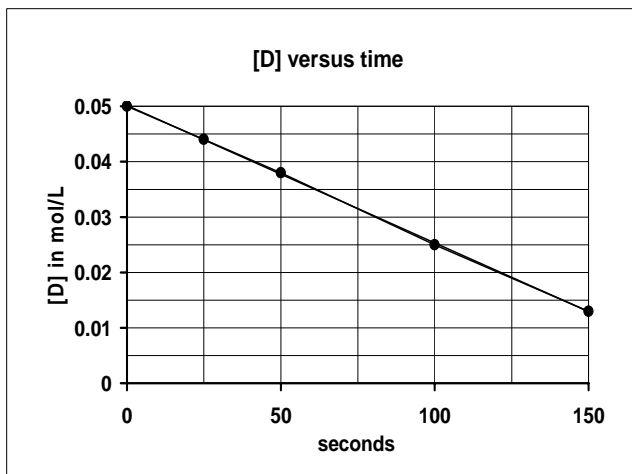
- d. Graph the data in the table above that should result in a straight line. Either use a graphing program or use your own graph paper and the "graphing by hand" rules in Module 20.

* * * * *

Your graph should look similar to the graph at the right.

The straight line means that the data fits the behavior expected for a *zero-order* reaction.

- e. Calculate the slope between two widely separated points on the line.



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The calculation below uses the two points at the left and right sides of the plot.

However, the value for the slope should be the same no matter which two points on the line are used to calculate the slope. On a straight line, the slope between any two points is the same: a constant.

Setting $x_1 = t_1 = 0$ s (the lower time), y_1 will then = 0.050 M.

$$\begin{aligned} m = \text{slope} &= \frac{\text{rise}}{\text{run}} = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{0.013 \text{ M} - 0.050 \text{ M}}{150 \text{ s} - 0 \text{ s}} = \frac{-0.037 \text{ M}}{150 \text{ s}} \\ &= \boxed{-2.5 \times 10^{-4} \text{ M/s}} \end{aligned}$$

- f. The graph is consistent with $[D]_t = -kt + [D]_0$; the integrated rate law equation for a zero order reactant.

If the values of the two constants $-k$ and $[D]_0$ are known, the integrated rate law can be used to make *predictions* about $[D]$ and t .

Find the *numeric value* and *units* of the rate constant in the integrated rate law that fits this data.

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The integrated rate law is: $[D]_t = -kt + [D]_0$

and the equation for a line is: $y = mx + b$

$$m = -k, \text{ so } \boxed{k = -m = +2.5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}}$$

- g. Write the *value* of $[D]_0$ that can be substituted into the integrated rate law for the data above.

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$[D]_0$ is the $[D]$ in the data at time = 0 seconds, so $[D]_0 = 0.050$ M

- h. Write the integrated rate law, substituting the numeric values of the two constants found above in place of the symbols for the two constants.

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$$[D]_t = -kt + [D]_0 ; \boxed{[D]_t = - (+ 2.5 \times 10^{-4} \text{ mol/L} \cdot \text{s})(t) + 0.050 \text{ M}}$$

- g. *Test* the equation: plug in data for a time in the data table that was not used to calculate the slope. See if the equation predicts the **[D]** in the data at that time.

To match the answer below, use **t** = 50 s.

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$$\text{Use } [D]_t = - (2.5 \times 10^{-4} \text{ mol/L} \cdot \text{s})(t) + 0.050 \text{ M} .$$

At **t** = 50 s,

$$\begin{aligned} &= - (2.5 \times 10^{-4} \text{ mol/L} \cdot \text{s})(\mathbf{50 \text{ s}}) + 0.050 \text{ M} = - (12.5 \times 10^{-3} \text{ mol/L}) + 0.050 \text{ M} \\ &= - (0.0125 \text{ mol/L}) + 0.050 \text{ M} = 0.0375 \text{ M} = \mathbf{0.038 \text{ M}} \end{aligned}$$

which agrees with the data in the table at **t** = 50. s. The integrated rate law, with its constants added, correctly predicts the experimental result.

* * * * *

Summary: Use these steps to *calculate the constants* for a **zero-order-rate** equation from experimental data.

1. Write the zero-order integrated rate law: $[A]_t = -k t + [A]_0$
and, under it, the equation for a line: $y = m x + b$
2. Graph the values of **y** and **x** in the data table for the experiment. If the data points fall close to a straight line, the data fit the prediction for a reactant that is zero order in A.
3. Calculate the slope for two widely separated points on the graph.
$$m = \Delta y / \Delta x = \Delta [A] / \Delta t$$
3. Write the equation that explains and predicts the data.
 - a. Use the slope (**m**) to write a value for **k**.
 - b. Write the zero-order integrated rate law substituting numeric **values** in place of the symbols for the two constants: **k** and **[A]₀**.
 - c. Test the rate law: pick an unused time from the data table, plug that time into the rate law, and see if the equation predicts the **[A]** that is in the data at that time **t**.
 - d. If yes, the data is consistent with a zero-order reactant.
If no, and if the graph was a line, check your values for **k** and **[A]₀**.

* * * * *

Practice B. Use the steps above for these calculations.

- For the data at the right,
 - Graph the data, putting the independent variable (see Lesson 19C if needed) on the x -axis.
 - Does the data fit the prediction for zero-order in A? Why or why not?
 - Calculate the slope between two widely spaced points of data.
 - Write a rate law that fits the data. Include values and units for the two constants in the rate law.
 - Test your rate law: see if it correctly predicts [A] at $t = 3.5$ min.
- If experimental data fits the linear equation $\ln[A] = -kt + \ln[A]_0$
 - What values would be plotted on the y -axis, and what on the x -axis, to produce the graph of a line?
 - What term in the equation above would be the y -intercept?
 - What ratio would be constant between any two points?
 - What is the relationship between k and the slope?

Time	[A]
0	0.500 M
1.0 min.	0.460 M
2.5 min.	0.400 M
3.5 min.	0.360 M
5.0 min.	0.300 M
7.0 min.	0.220 M

ANSWERS

Practice A

- 1a. If $y = mx + b$, constant ratio? **The slope: $\Delta y / \Delta x$**

$$m = \text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$$

$$m = \text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\Delta y}{\Delta x} = \frac{\Delta^\circ\text{F}}{\Delta^\circ\text{C}} = \frac{^\circ\text{F}_2 - ^\circ\text{F}_1}{^\circ\text{C}_2 - ^\circ\text{C}_1}$$

- 2 a. Using the 2nd and last points, setting x_1 as the lower x number,

$$m = \frac{^\circ\text{F}_2 - ^\circ\text{F}_1}{^\circ\text{C}_2 - ^\circ\text{C}_1} = \frac{(212 - 32)^\circ\text{F}}{(100 - 0)^\circ\text{C}} = \boxed{1.80^\circ\text{F}/^\circ\text{C} = m}$$

- All slopes should calculate to the same result.
- $y = mx + b$ is the equation for a line, and a line has a constant slope, so two equal slopes are consistent with the equation for a line.
- Equation for line: $^\circ\text{F} = (m)(^\circ\text{C}) + b$

$^\circ\text{F}$	$^\circ\text{C}$
-40.	-40.
32	0
68	20.
122	50.
212	100.

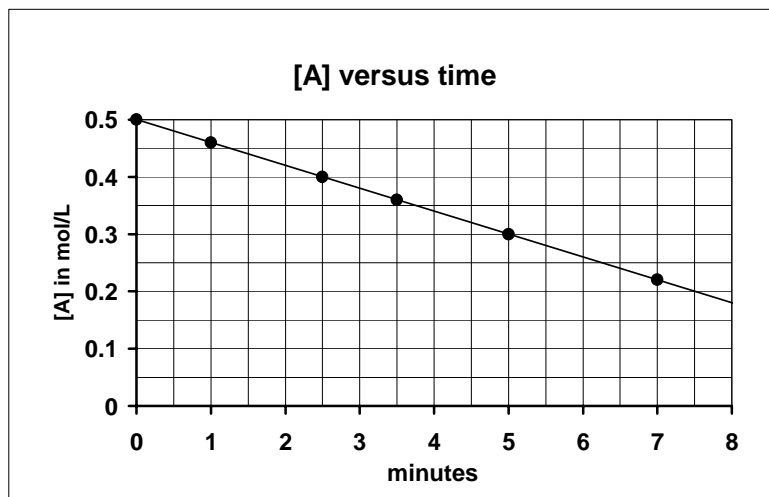
- e. See Part A answer: $m = 1.80 \text{ } ^\circ\text{F}/^\circ\text{C}$
- f. Since $y = mx + b$, if we choose the easy case, in which $x = ^\circ\text{C} = 0 \text{ } ^\circ\text{C}$, $y = ^\circ\text{F} = 32 \text{ } ^\circ\text{F}$,
Substituting into the rate law: $32 \text{ } ^\circ\text{F} = (m)(0) + b$, so $32 \text{ } ^\circ\text{F} = b$.
- g. $y = mx + b$, $^\circ\text{F} = (m)(^\circ\text{C}) + b$; $^\circ\text{F} = (1.80 \text{ } ^\circ\text{F}/^\circ\text{C}) ^\circ\text{C} + 32 \text{ } ^\circ\text{F}$
- h. If we choose $50 \text{ } ^\circ\text{C}$, $^\circ\text{F} = (1.80 \text{ } ^\circ\text{F}/^\circ\text{C})(50 \text{ } ^\circ\text{C}) + 32 \text{ } ^\circ\text{F} = 90^\circ\text{F} + 32 \text{ } ^\circ\text{F} = 122 \text{ } ^\circ\text{F}$
In the data table, $50^\circ\text{C} = 122^\circ\text{F}$. The equation correctly predicted the $^\circ\text{F}$ result.
- i. You were able to derive an equation which explains the numbers in the table and predicts results for measurements not in the table. In science, that's considered "cool."
The above relationship is generally remembered as $^\circ\text{F} = 9/5 (^\circ\text{C}) + 32$ which matches the equation for the DATA developed above.

Practice B

- 1a. The independent (more controlled) variable in this experiment is the *time* at which the measurements were taken.

Your results should be similar to the graph at the right. The points fall close to a straight line.

- 1b. If the points on a graph of $[A]$ versus time fall close to a straight line, the data fits zero order behavior.



- 1c. If you use any two widely spaced points, your answer should be close to the slope found below.

If the points chosen are at the left and right sides of the graph above,

At $x_1 = t_1 = 0$ minutes (the lower time), $y_1 = 0.500 \text{ M}$

Estimating that at $x_2 = t_2 = 8$ minutes, $y_2 \approx 0.18 \text{ M}$.

$$m = \frac{\text{rise}}{\text{run}} = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{0.18 \text{ M} - 0.500 \text{ M}}{(8.0 - 0) \text{ min.}} = \frac{-0.32 \text{ M}}{8.0 \text{ min.}} = 0.040 \text{ M/min.} = \boxed{-4.0 \times 10^{-2} \text{ M/min.}}$$

- 1d. Since the slope is constant,

- the data is consistent with the equation $y = mx + b$, and since $y = [A]$ and $x = \text{time}$ for the graph,
- the data is consistent with the zero-order rate law: $[A]_t = -kt + [A]_0$ where

k (the rate constant) = $-m$ = minus the slope; so $k = \boxed{+4.0 \times 10^{-2} \text{ M/min}}$,

and $[A]_0$ = the $[A]$ in the data at $t = 0$, which is 0.500 M . Since $[A]_t = -kt + [A]_0$;

the proposed specific rate law is $[A]_t = -(+4.0 \times 10^{-2} \text{ M/min})(t) + 0.500 \text{ M}$

$$\begin{aligned} 1e. \quad [A]_t &= -(+4.0 \times 10^{-2} \text{ M/min})(t) + 0.500 \text{ M} = \\ &= -(+4.0 \times 10^{-2} \text{ M/min})(3.5 \text{ min.}) + 0.500 \text{ M} = \\ &= -14 \times 10^{-2} \text{ M} + 0.500 \text{ M} = -0.14 \text{ M} + 0.500 \text{ M} = \boxed{0.36 \text{ M}} \end{aligned}$$

This calculated $[A]$ matches the data at $t = 3.5$ minutes. The proposed rate law works.

$$2a. \quad \text{This equation is linear:} \quad \ln[A]_t = -kt + \ln[A]_0$$

because it matches the form $y = mx + b$

For linear data, the plot of y versus x is a line, so for the specific equation above, $\ln[A]$ vs. t plots as a line.

$$2b. \quad \text{The } y\text{-intercept?} \quad b = \ln[A]_0$$

2c. Constant for a line, in general: $\Delta y / \Delta x$;

$$\text{For this specific equation: } m = \text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln[A]}{\Delta t} = \frac{\ln[A]_2 - \ln[A]_1}{t_2 - t_1}$$

$$2d. \quad k = -m \quad (\text{or } m = -k)$$

* * * * *

Lesson 27D: Base 10 Logarithms

Prerequisites: Lessons 1A to 1C only.

Timing: This lesson must be done before first-order-integrated rate law calculations, but it may be helpful at any time that base 10 logarithm calculations are encountered in science classes.

Pretest: If you think you know this topic, try the last 4 calculations in *Practice C* at the end of this lesson. If you can do those calculations, skip the lesson.

* * * * *

Logarithms

To solve first-order integrated rate law calculations, it will be necessary to

- Take the **natural log** of numbers, and
- Convert natural logs to numbers.

To do so, you will need to calculate using the **ln** function and the number e . Let's review the rules for powers and logarithms.

As always, on the problems below, **cover** the answers *below* the * * * * * line and write your answer the questions that are *above* the line.

I. Numbers, Bases, and Exponents

Any positive value that is written in fixed-decimal notation (as a regular number) can be expressed as a number (a base) to a power.

For example: Computer science often calculates in *base 2*,
such as $1,024 = 2^{10}$, and (fill in the blank) $2^4 = \underline{\hspace{2cm}}$.

* * * * *

$$2^4 = 2 \times 2 \times 2 \times 2 = 16.$$

However, values can be represented by any base to any power. Using your calculator, convert this base and power to a fixed-decimal number:

$$3.5^{2.7} = \underline{\hspace{2cm}} \quad (\text{Use the calculator that you will use for quizzes and tests.})$$

* * * * *

- A standard TI-type calculator might use: $3.5 \boxed{y^x} 2.7 \boxed{=}$
- On a graphing calculator (*if allowed*), try: $3.5 \boxed{\wedge} 2.7 \boxed{\text{enter}}$
- On a reverse Polish (RPN) calculator, try: $3.5 \boxed{\text{enter}} 2.7 \boxed{y^x}$

Write or circle a key sequence that gives a result of **29.4431...**

A primary goal of science is to discover relationships that explain how our universe works. Those relationships are often most simply expressed as equations that include *base e*. Calculations involving these relationships may be done in both base 10 and base *e*, but base 10 is more familiar, and the rules are parallel for all bases, so let's consider base 10 calculations first.

II. Powers of 10

Numeric values can be expressed by a variety of methods: as fixed-decimal numbers, as exponential notation, or as a number to a power. In scientific calculations, we often express numeric values as 10 to a power, where the power can be either an integer or a number with decimals.

For example:

$$10^2 = \text{the fixed-decimal number } 100 \quad \text{and} \quad 10^3 = \text{the number } \underline{\hspace{2cm}}.$$

$$\text{Without a calculator, } \textit{estimate} \text{ the value of this number: } 10^{2.5} = \underline{\hspace{2cm}}.$$

* * * * *

$100 = 10^2 < 10^{2.5} < 10^3 = 1,000$; half-way between 100 and 1000 is 550..., but the answer is sure to be "somewhere between 100 and 1,000."

Now, use a calculator to get an exact answer. $10^{2.5} = \text{what number? } \underline{\hspace{2cm}}$.

* * * * *

- On a standard TI-type calculator, you might try: $2.5 \boxed{10^x}$
and/or $10 \boxed{y^x} 2.5 \boxed{=}$ and/or $2.5 \boxed{2^{\text{nd}} \text{ or INV}} \boxed{\log}$. Try all three.
- On a graphing calculator, you might try: $10 \boxed{\wedge} 2.5 \boxed{\text{enter}}$
- On an RPN scientific calculator, try: $2.5 \boxed{\text{enter}} \boxed{10^x}$

Circle or write down a sequence that makes sense to you and gives this result: **316**

Compare 316 to your estimate. They should be close: maybe off by 2 or 3 times, but not off by a whole decimal place or power. Most errors in your operation of a calculator will be caught if you use the rule: "estimate, then calculate."

On sf/rounding: When converting between numbers and exponentials or logarithms, the statistical justification for significant figures breaks down. We will add a systematic rule when we study acid-base pH. Until then, we will use these rules:

- If an exponent is a whole number, assume math rules and exact numbers.
- If an exponent has a decimal, round answers to 3 significant figures.

Q. Use your calculator key sequence tested above to convert these powers of 10 to values in scientific notation.

If you are unsure about an answer, check it below before doing the next part.

a. $10^{23.7798} =$ (estimate): _____ (calculate): _____

b. $10^{-3.9} =$ (estimate): _____ (calculate): _____

★ ★ ★ ★ ★

Answers

a. $10^{23.7798} = 6.02 \times 10^{23}$

Note how your calculator *displayed* the exponent. You will need to translate the calculator display into scientific notation when writing answers.

b. $10^{-3.9} = 1.26 \times 10^{-4}$

To enter a *negative* number, usually a $\boxed{+/-}$ or $\boxed{(-)}$ key must be used.

- On a standard TI-type calculator, try: 3.9 $\boxed{+/-}$ $\boxed{10^x}$
- On an RPN calculator, try: 3.9 $\boxed{+/-}$ $\boxed{\text{enter}}$ $\boxed{10^x}$

Checking Powers of 10

One outcome of the estimation logic above is this rule that can be used to check values expressed as powers of 10:

When a value expressed as 10 to a power is compared to the same value written in scientific notation, the *exponents* of each 10 must be within ± 1 of each other.

Note how the rule applies to the answers to the two problems above.

Using your calculator, check that rule on these.

a. $10^{6.7} =$ (in scientific notation): _____ (exponents ± 1) _____

b. $10^{-9.7} =$ (in scientific notation): _____ (expos ± 1) _____

c. $10^{-13.2} =$ (in scientific notation): _____ (expos ± 1) _____

* * * * *

- a. $10^{6.7} = 5.01 \times 10^6$. (expos ± 1 ? 6.7 and 6 = ✓)
- b. $10^{-9.7} = 2.00 \times 10^{-10}$ (expos ± 1 ?) ✓
- c. $10^{-13.2} = 6.31 \times 10^{-14}$ (expos ± 1 ?) ✓

Practice A: Use the calculator that you will use on tests. Answers are at the end of this lesson.

1. $10^{+16.5} =$ _____ (expos ± 1 ?) ____
2. $10^{-16.5} =$ _____ (expos ± 1 ?) ____
3. $10^{2.2} =$ _____ (expos ± 1 ?) ____
4. $10^{-11.7} =$ _____ (expos ± 1 ?) ____
5. $10^{-0.7} =$ _____ (expos ± 1 ?) ____

III. Logarithm Definitions

In words, we will define a logarithm in two ways.

A logarithm is simply an exponent.

A logarithm answers the question: if a number is written as a base number to a power, what is the power?

A logarithm can be a power of any base.

Example Because $2^4 = 16$, the *base 2 log* of 16 can be written as: $\log_2 16 = 4$

In science, *base 10* and *base e* are the bases for logarithms that are used most often. The symbol for a **base 10** logarithm is simply **log**. If no base is specified, you should assume that *log* means a *base 10* log. The symbol for a *base e* log (a *natural log*) is **ln**.

IV. Base 10 Logs

- a. The **log** function on your calculator finds a *base 10* log.

The *log* function answers the question: if a number is written as 10 to a power, what is the power?

Using that rule, answer these *without* a calculator.

Write the log of 1) 10^2 2) 1000 3) 0.001

* * * * *

- 1) The log of 10^2 is **2**. 2) $\log 1000 = \log 10^3 = 3$ 3) $\log 0.001 = \log 10^{-3} = -3$
- b. The equation defining log is $\log 10^x \equiv x$. It must be memorized.

It may be helpful to remember this example: **the log of 100 is 2.**

- c. For a fixed-decimal number *greater* than one, its log value will be a positive number.

Positive numbers between 0 and 1 have a negative log, as in example 3) above.

- d. One way to check that you are doing calculator operation properly is to do a *simple* calculation, first in your head or on paper, then on the calculator. The two answers should agree. Let's try that method.

Without a calculator, write the log of 1) 100 2) 10,000 3) 0.01

Using a *calculator*, find the log of 1) 100 2) 10,000 3) 0.01

* * * * *

Without a calculator:: 1) The log of 100 = the log of $10^2 = 2$.

2) The log of 10,000 = $\log 10^4 = 4$ 3) The log of 0.01 = $\log 10^{-2} = -2$

For part 1) on a calculator,

- A standard TI-type calculator might use: 100 **log**
- On an RPN calculator, try: 100 **enter** **log**
- Some graphing calculators may not have a log button. You can learn a work around ($\log x = \ln x / 2.303$) or buy an inexpensive calculator with a **log** button.

Did the calculator answers agree with your mental arithmetic? They must.

- e. To check a conversion between a base 10 log and a number, apply this rule.

The log of a number and the *exponent* of the number written in *scientific* notation must agree within ± 1 .

Use your calculator to answer these, then apply the rule above to check your answer.

1) $\text{Log}(7.4 \times 10^6) =$ (on the calculator): _____ ($\pm 1 ?$ ___)

* * * * *

1) $\text{Log}(7.4 \times 10^6) =$ (on the calculator): **6.87** ($\pm 1 ?$ ✓)

Answer these using your calculator:

2) $\text{Log}(7.4 \times 10^{-6}) =$ _____ ($\pm 1 ?$ ___)

3) $\text{Log} 2,000 =$ _____ ($\pm 1 ?$ ___)

* * * * *

2) $\text{Log}(7.4 \times 10^{-6}) =$ **-5.13** ($\pm 1 ?$ ✓)

Keys: 7.4 $\boxed{\text{E or EE}}$ 6 $\boxed{+/-}$ $\boxed{\log}$ or if RPN: 7.4 $\boxed{\text{E or EE}}$ 6 $\boxed{+/-}$ $\boxed{\text{enter}}$ $\boxed{\log}$

3) $\text{Log } 2,000 = \log(2 \times 10^3) = 3.30$ ($\pm 1 ? \checkmark$)

Summary: Log Rules to Commit to Memory

1. A *logarithm* is simply an exponent: the power to which a base number is raised.
2. A logarithm answers the question: if a number is written as a base to a power, what is the power?
3. The equation defining a **log** is $\boxed{\log 10^x \equiv x}$; the *log* of 100 is 2 .
4. Calculator $\boxed{\log}$ buttons find the *power* of a value expressed as 10 to a power.
5. *Checking log results*: when a number is written in scientific notation, its power of 10 must agree with its base 10 logarithm within ± 1 .

Design flashcards or other memory devices and practice as needed so that you can apply these rules intuitively and fluently in calculations.

Practice B: Practice with the calculator you will use on tests.

1. $10^{-5.4} =$ (in scientific notation): _____ (expos $\pm 1 ?$) ____

2. $10^{-11.5} =$ _____ (expos $\pm 1 ?$) ____

3. $10^{-0.5} =$ (number): _____ (scientific notation): _____ (expos $\pm 1 ?$) ____

4. $\text{Log}(6.8 \times 10^{12}) =$ _____ ($\pm 1 ?$ __)

5. $\text{Log}(6.8 \times 10^{-12}) =$ _____ ($\pm 1 ?$ __)

6. $\text{Log } 4.6 =$ _____ ($\pm 1 ?$ __)

7. $\text{Log } 0.0020 =$ _____ ($\pm 1 ?$ __)

V. Converting From Logs to Numbers

- a. Knowing a log, we need to be able to write the fixed-decimal number. This is called *taking the antilog*, or taking the **inverse log**, but it is easier to remember what this means (and what buttons to press) if you remember what a log is.

A log is _____.

Note the same “is it reasonable?” quick check. The *log* and the *exponent* of the number in scientific notation should agree, ± 1 .

* * * * *

$$4) \text{ Log } x = 8.7, x = \boxed{501,00,000 \text{ or } 5.01 \times 10^8} \quad (\pm 1 ? \checkmark)$$

$$5) \text{ Log } x = -10.7, x = \boxed{2.00 \times 10^{-11}} \quad (\pm 1 ? \checkmark)$$

In cases like 4) and 5), your calculator may answer in exponential notation and display the exponent *far* to the right -- where you may miss it when looking for just the significant digits. That's another reason to check your answers.

Summary: Add these to your memorized log rule list.

6. Knowing the log of a number, to find the number, calculate the value for 10^{\log} . This is called “taking the antilog” or “finding the inverse log.”
7. $\boxed{10^{\log x} = x}$. Recite and repeat to remember: “10 to the log x equals x .”
8. On a calculator, to convert a log value to a number:
 - Input the log value, then press $\boxed{\text{INV}} \boxed{\text{LOG}}$; or $\boxed{2\text{nd}} \boxed{\text{LOG}}$; or
 - Input the log, then press $\boxed{10^x}$. or input 10, $\boxed{x^y}$, input the log, $\boxed{=}$.
9. When you encounter log calculations, it helps to write:
 - $\boxed{\log 10^x = x}$; the *log* of 100 is 2; and
 - $\boxed{10^{\log x} = x}$; “10 to the log x equals x .”

Practice C

1. $\text{Log } x = 12.4, x = \underline{\hspace{2cm}}$ ($\pm 1 ? \underline{\hspace{1cm}}$)
2. $\text{Log } A = -5.9, A = \underline{\hspace{2cm}}$ ($\pm 1 ? \underline{\hspace{1cm}}$)
3. $\text{Log } D = -0.25, D = \underline{\hspace{2cm}}$ ($\pm 1 ? \underline{\hspace{1cm}}$)
4. Antilog of 1.1 = $\underline{\hspace{2cm}}$ ($\pm 1 ? \underline{\hspace{1cm}}$)
5. $10^{-3.3} = \underline{\hspace{2cm}}$ (expos $\pm 1 ? \underline{\hspace{1cm}}$)
6. $\text{Log}(2.0 \times 10^{-9}) = \underline{\hspace{2cm}}$ ($\pm 1 ? \underline{\hspace{1cm}}$)
7. $\text{Log } 0.50 = \underline{\hspace{2cm}}$ ($\pm 1 ? \underline{\hspace{1cm}}$)

ANSWERS**Practice A**

- $10^{+16.5} = 3.16 \times 10^{16}$ (expos ± 1 ?) ✓
- $10^{-16.5} = 3.16 \times 10^{-17}$ (expos ± 1 ?) ✓
- $10^{2.2} = 1.58 \times 10^2$ (expos ± 1 ?) ✓
- $10^{-11.7} = 2.00 \times 10^{-12}$
- $10^{-0.7} = 2.00 \times 10^{-1}$

Practice B

- $10^{-5.4} = 3.98 \times 10^{-6}$ (± 1 ?) ✓
- $10^{-11.5} = 3.16 \times 10^{-12}$ (± 1 ?) ✓
- $10^{-0.5} =$ (number): **0.316** (std. notation): **3.16×10^{-1}** (± 1 ?) ✓
- $\text{Log}(6.8 \times 10^{12}) = 12.8$
- $\text{Log}(6.8 \times 10^{-12}) = -11.2$
- $\text{Log } 4.6 = 0.663$
- $\text{Log } 0.0020 = \text{Log}(2.0 \times 10^{-3}) = -2.70$

Practice C

- $\text{Log } x = 12.4, x = 2.51 \times 10^{12}$
- $\text{Log } x = -5.9, x = 1.26 \times 10^{-6}$
- $\text{Log } x = -0.25, x = 0.562 = 5.62 \times 10^{-1}$
- Antilog of 1.1 = $10^{1.1} = 12.6 = 1.26 \times 10^1$
- $10^{-3.3} = 5.01 \times 10^{-4}$
- $\text{Log}(2.0 \times 10^{-9}) = -8.70$
- $\text{Log } 0.50 = -0.301$

Lesson 27E: Natural Log Calculations

Prerequisites: Complete Lesson 27D on base 10 logs before this lesson.

Timing: This lesson must be done before first-order-integrated rate law calculations, but it may be helpful at any time that base e logarithm calculations are encountered in science classes.

Pretest: If you think you know this topic, try the last 4 calculations in the *Practice* at the end of this lesson. If you can do those calculations, skip the lesson.

* * * * *

I. Base e Calculations

a. The Symbol e

In mathematical and scientific equations, the lower-case e is an abbreviation for a number: **2.7182818...** For calculations, the value $e = 2.718$ must be memorized.

The number e has many interesting mathematical properties. In science, e is found in many equations that predict natural phenomena. In these equations, e is the base for values expressed in the form e^x , and e is termed the **natural exponential**.

Examples:

A process with a constant rate of growth will obey the equation

$$[A]_t = [A]_0 \cdot e^{kt} \quad \text{where } k \text{ is the rate constant and } t \text{ is the time since } t = 0.$$

For a constant rate of *decay*, this rate law can be written in two equivalent ways:

$$[A]_t = [A]_0 \cdot e^{-kt} \quad \text{or as} \quad \ln[A]_t = -kt + \ln[A]_0$$

To calculate first-order rate laws from time data, we will use both e and **ln**.

b. Calculating with natural exponentials

We know that e^1 equals what number? _____

* * * * *

2.718.... Now find a value for e^1 on your calculator, using 1 and the e^x function. Write the key sequence that produces the answer 2.718...

* * * * *

- A standard TI-type calculator might use: 1 e^x .
- On an RPN scientific calculator, try: 1 enter e^x .

Use *your* key sequence to calculate these, then check your answers below.

$$1) e^2 = \qquad 2) e^{2.5} = \qquad 3) e^{-1} = \qquad 4) e^{-2.5} =$$

(Because the statistical basis for significant figures does not apply to logarithmic calculations, in these lessons we will use this general rule: during e and **ln** calculations, round fixed-decimal numbers and significands in answers that are not integers to 3 significant figures.)

* * * * *

$$1) e^2 = 7.39 \qquad 2) e^{2.5} = 12.2$$

Recall that to enter a negative number, you usually use a $\boxed{+/-}$ key.

$$3) e^{-1} (= 1/e = 1/2.718..) = 0.368 \qquad 4) e^{-2.5} (= 1/e^{2.5}) = 0.0821$$

Note: Some calculators use an **E** at the right side of the answer screen to show the power of **10** for numbers in scientific notation. That **E** is *not* the same as the symbol *e* for the natural exponential.

II. Calculations Using ln

a. Natural Logs

The **ln** function (the **natural log**) answers this question: if a number is written as *e* to a power, what is the power?

Just as by definition, $\log 10^x \equiv x$, the natural log definition is $\boxed{\ln e^x \equiv x}$

Use the natural log definition to do these *without* a calculator.

$$1) \ln e^0 = \qquad 2) \ln e^1 = \qquad 3) \ln e^{-4} =$$

* * * * *

$$1) \ln e^0 = 0 \qquad 2.) \ln e^1 = 1 \qquad 3) \ln e^{-4} = -4$$

By definition, $\ln e = \underline{\hspace{2cm}}$.

* * * * *

$$\ln e = \ln e^1 = 1.$$

Try this one in your head: $\ln(2.718)$ should equal about $\underline{\hspace{2cm}}$.

* * * * *

$$\ln(2.718) \approx \ln e \approx \ln e^1 \approx 1.$$

Now do the same calculation on your calculator: $\ln(2.718) = \underline{\hspace{2cm}}$

* * * * *

Is the calculator answer close to the mental arithmetic answer? It must be.

Write down the key sequence that works for $\ln(2.718)$ above.

The same steps should take the natural log of any positive number. Try these

$$1) \text{ Using your calculator: } \ln(314) =$$

* * * * *

$$1) \ln 314 = 5.75$$

To *check* an answer, *after* writing it down, use the $\boxed{e^x}$ key and see if you *return* to the number you were taking the **ln** of. Try that as a check on these:

$$2) \ln 0.0050 = \underline{\hspace{2cm}} \quad (\text{after writing answer, use } \boxed{e^x} \text{). Check? } \underline{\hspace{2cm}}$$

$$3) \ln (6.02 \times 10^{23}) = \underline{\hspace{2cm}} \quad \text{Check? } \underline{\hspace{2cm}}$$

4) $\ln(19.29 \times 10^{-15}) =$ _____ Check? ____

* * * * *

2) $\ln 0.0050 = -5.30$ 3) $\ln(6.02 \times 10^{23}) = 54.8$ 4) $\ln(19.29 \times 10^{-15}) = -31.6$

Note in part 4), that a calculator does *not* require the input of *scientific* notation. However, if you use the e^x key to check your answer, it will likely return the original number *converted* to scientific notation.

Practice A: Use the calculator you will use on quizzes and tests to do these. Round fixed-decimals and significant figures in answers that are not integers to 3 significant figures.

1. $e^{2.0} =$

2. $e^{-4.7} =$

3. $e^{-11} =$

4. $\ln(42) =$

5. $\ln(0.0200) =$

6. $\ln(9 \times 10^5) =$

7. $\ln(5.00 \times 10^{-4}) =$

8. $\ln(10^{-4}) =$

b. **Converting ln Values to Numbers**

A base 10 definition: $10^{\log x} \equiv x$

A base e definition: $e^{\ln x} \equiv x$

Both of those definitions must be memorized. Noting their similarities will help.

Using the bottom equation, for some calculations involving **ln** and e you will not need a calculator. Try this:

$$e^{\ln(11)} =$$

* * * * *

$$e^{\ln(11)} = 11$$

The equation $e^{\ln x} \equiv x$ also means that if you know the **ln** value, to find the corresponding fixed-decimal *number*, make the **ln** value a power of e .

If $\ln(x) = 1$, the value for the number x (do in your head) is _____

* * * * *

$$\text{If } x = e^{\ln x} = e^1 = 2.718\dots$$

Knowing that answer, do the same **ln** to number conversion on your calculator by taking the antilog.

If $\ln(x) = 1$, the value of x obtained using the calculator is _____

* * * * *

Input the **ln** value, then press $\boxed{\text{INV or 2nd}} \boxed{\ln}$ or press $\boxed{e^x}$.

Write or circle the key sequence that converted $\ln(x) = 1$ to the number 2.718...

Use your key sequence to convert the following **ln** values to numbers. Write first write the number in terms of e , then the number, then the number in scientific notation.

1) If $\ln(X) = 6$, $X = e^{\quad} =$ (number): _____ = (sci. notation): _____

* * * * *

1) If $\ln(X) = 6$, $X = e^6 =$ (nbr): **403** = (sci. notation): **4.03×10^2**

Unlike base 10, in base e calculations there is no obvious correlation between the scientific notation exponent and the base e logarithm that helps in checking your answer. However, you can check by taking the **ln** of the number answer and see if it returns to the original **ln** value.

Try these.

2) If $\ln(X) = -4.5$; $X = e^{\quad} =$ (nbr): _____ = (sci. notation): _____

3) If $\ln(X) = 57.2$; $X =$ _____

4) If $\ln [A] = 0.0300$, $[A] = e^{\quad} =$ (nbr. and unit): _____

* * * * *

2) If $\ln(X) = -4.5$, $X = e^{-4.5} =$ **0.0111** = **1.11×10^{-2}**

3) $\ln(X) = 57.2$, $X = e^{57.2} =$ **6.94×10^{24}**

4) If $\ln [A] = 0.0300$, $[A] = e^{0.0300} =$ **1.03 M**

c. **Units and Logarithms**

Note that in 4) above, the unit expected for a concentration has been added. From a strict mathematical perspective, logarithms cannot be taken of values with units, and logarithm values do not have units. All precisely stated scientific relationships obey these rules.

However, some of these precise scientific equations can be very complex, or they can involve quantities that are difficult to measure. In those cases, the equations we write in chemistry are often “shortcuts” that simplify the complex relationships in order to speed problem solving.

When using these shortcut equations, the rules for dimensional homogeneity and unit cancellation may not apply, and special rules may be needed to assign units to answers. To make shortcut equations work, two of our rules will be

When taking the logarithm (using any base) of a value with units, write the result as a value without units.

If a WANTED unit to be calculated is based on a logarithm value, convert all of the units supplied in the problem to *consistent* units if needed, then *attach* the appropriate consistent unit to the answer.

The shortcut equations we will encounter frequently in upcoming lessons will involve taking a logarithm of a concentration in moles per liter. The rule will be: if a $[x]$ is wanted, attach the unit moles/liter (M) to the answer.

Apply that rule to the following problems. Write the answer as a fixed-decimal number *or* in scientific notation. When in doubt, check answers as you go.

5) $\ln[Z] = -12.5$, $[Z] =$ _____

* * * * *

5) $[Z] = e^{-12.5} = 3.73 \times 10^{-6} \text{ M}$ (attach the *unit* of concentration: mol/L)

6) $\ln[R] = -0.17$, $[R] =$ _____

7) $[D] = e^{-1.39}$, $[D] =$ _____

8) $\ln(0.250 \text{ M}) =$ _____

9) $\ln[A] = -2.63$, $[A] =$ _____

* * * * *

6) $[R] = e^{-0.17} = 0.844 \text{ M}$ (add M) 7) $[D] = 0.249 \text{ M}$

8) $\ln(0.250 \text{ M}) = -1.39$ (drop the unit) 9) $[A] = e^{-2.63} = 0.0721 \text{ M}$

d. Notes on Notation with e and \ln

Be careful to distinguish “taking the \ln ” from “the \ln value.”

$\ln(7.389) =$ _____. Try it. You should get close to 2.

But if $\ln = 7.389$, the number *with* that \ln is _____. Try it.

* * * * *

If $\ln = 7.389$, the number is $e^{7.389} = 1,620$

If you get lost on a natural log calculation, a good strategy is to do a similar and simple base 10 mental computation, and then apply the same logic to the natural log case. Simple base 10 calculations can be solved in your head, and the formulas and steps for base 10 and base e calculations are parallel.

e. Converting between base 10 and natural logs

A general rule for the logarithm of any base is $\log_b(x) = \ln(x)/\ln(b)$ where b is the base. For base 10 logs, this equation becomes

$$\text{Log}_{10}(x) = \ln(x)/\ln(10) = \text{Log}_{10}(x) = \ln(x)/2.303$$

This relationship is generally memorized as $\ln(x) = 2.303 \log(x)$ or as

“The *natural* log of a number is always 2.303 times higher than the base 10 log.”

Try using the above equation to solve this *without* a calculator:

Q1. $\ln(10) =$

* * * * *

$$A1. \ln(10) = 2.303 \log(10) = 2.303 \log(10^1) = 2.303(1) = \mathbf{2.303}$$

Check this answer by solving Q1 using your calculator.

Try the following without a calculator in a manner similar to A1.

$$Q2. \ln(100) =$$

$$Q3. \ln(1) =$$

$$Q3. \ln(0.10) =$$

* * * * *

$$A2. \ln(100) = 2.303 \log(100) = 2.303 \log(10^2) = 2.303(2) = \mathbf{4.606}$$

$$A3. \ln(1) = 2.303 \log(1) = 2.303 \log(10^0) = 2.303(0) = \mathbf{0}$$

$$A4. \ln(0.10) = 2.303 \log(0.10) = 2.303 \log(10^{-1}) = 2.303(-1) = \mathbf{-2.303}$$

Now check these answers by solving Q2-4 using your calculator.

Summary: Add these rules to your in-memory log-rule list from the prior lesson. Commit the log rules to memory. Design and use flashcards as needed.

10. The symbol e is an abbreviation for a number with special properties: $e = 2.718\dots$

11. The **ln (natural log)** function answers the question: if a number is written as e to a power, what is the power?

12. When you encounter **log** or **ln** calculations, it helps to write:

$$\log 10^x \equiv x \quad \text{and} \quad 10^{\log x} \equiv x. \quad \text{“The log of 10 to the } x \text{ is } x; \text{ 10 to the log } x \text{ is } x\text{.”}$$

$$\ln e^x \equiv x \quad \text{and} \quad e^{\ln x} \equiv x. \quad \text{Write the base 10 rules, then substitute } e \text{ and } \ln.$$

Note the patterns. Note the logic: A log is an exponent.

13. Knowing the **ln** value, to find the number, take the *antilog*. On a calculator,

- input the **ln** value, then press $\boxed{\text{INV}} \boxed{\ln}$; or
- Input the **ln** value, then press $\boxed{e^x}$. An ln is simply an exponent of e .

14. $\boxed{\ln(x) = 2.303 \log(x)}$

15. Write logs as a value without units. If a concentration is WANTED, attach the consistent concentration units to the answer.

Practice B: Try the odd-numbered problems first. Complete the even numbered problems for additional practice or pre-test review. Round fixed-decimal numbers and significant figures in answers that are not integers to 3 sf.

1. $e^{5.2} =$

2. $e^{-1.7} =$

3. $e^{-20.75} =$

4. $\ln 1066 =$ 5. $\ln 0.0050 =$ 6. $\ln(3 \times 10^8) =$
 7. $\ln(14.92 \times 10^{-6}) =$ 8. $\ln e^{6.20} =$ 9. $e^{\ln(42.6)} =$
 10. If $\ln(X) = -6.8$, $X = e^{\quad} =$ (number in sci. notation): _____
 11. If $\ln D = 7.4822$, $D =$ 12. If $\ln(x) = -12.5$, $x =$
 13. If $\log[A] = -9$, $[A] =$ 14. If $\log x = 13.7$, $x =$
 15. $\text{Log } A = -13.7$, $A =$ 16. $10^{-11.7} =$
 17. $\ln[B] = -13.7$, $[B] =$ 18. $e^{-11.7} =$
 19. $\ln(0.050 \text{ M}) =$ 20. $e^{-0.693} =$

Solve the problems below in your notebook.

21. If $\log(x) = 5.0$, $\ln(x) =$ 22. if $\ln(x) = 34.5$, $\log(x) =$
 23. If $\ln(x) = -(0.075 \text{ day}^{-1})(4.0 \text{ days})$; $x = ?$
 24. Given: $\ln[A] = (-0.0173 \text{ s}^{-1})(t) + 0.693$
 a. If $t = 20. \text{ s}$, $[A] = ?$ b. If $[A] = 0.710 \text{ M}$, $t = ?$
 25. Given: $\ln[A] = (-0.0241 \text{ yrs.}^{-1})(t) - 4.61$
 a. If $[A] = 0.0025 \text{ M}$, $t = ?$ b. If $t = 28.8 \text{ years}$, $[A] = ?$

ANSWERS

Practice A

1. $e^{2.0} = 7.39$ 2. $e^{-4.7} = 9.10 \times 10^{-3}$ 3. $e^{-11} = 1.67 \times 10^{-5}$ 4. $\ln 42 = 3.74$
 5. $\ln 0.020 = -3.91$ 6. $\ln(9 \times 10^5) = 13.7$ 7. $\ln(5.0 \times 10^{-4}) = -7.60$
 8. $\ln(10^{-4}) = \ln(1 \times 10^{-4}) = -9.21$

Practice B

1. $e^{5.2} = 181$ 2. $e^{-1.7} = 0.183$ 3. $e^{-20.75} = 9.74 \times 10^{-10}$
 4. $\ln 1066 = 6.97$ 5. $\ln 0.0050 = -5.30$ 6. $\ln(3 \times 10^8) = 19.5$
 7. $\ln(14.92 \times 10^{-6}) = -11.1$ 8. $\ln e^{6.2} = 6.20$ 9. $e^{\ln(42.6)} = 42.6$
 10. If $\ln X = -6.8$, $X = e^{-6.8} =$ (number in sci. notation): 1.11×10^{-3}
 11. If $\ln D = 7.4822$, $D = 1780$ 12. If $\ln(x) = -12.5$, $x = e^{-12.5} = 3.73 \times 10^{-6}$
 13. If $\log[A] = -9$, $[A] = 1.00 \times 10^{-9} \text{ M}$ (When finding a concentration, add the unit)

14. If $\log x = 13.7$, $x = 5.01 \times 10^{13}$
15. $\text{Log } A = -13.7$, $A = 2.00 \times 10^{-14}$
16. $10^{-11.7} = 2.00 \times 10^{-12}$
17. $\ln[B] = -13.7$, $[B] = 1.12 \times 10^{-6} \text{ M}$
18. $e^{-11.7} = 8.29 \times 10^{-6}$
19. $\ln(0.050 \text{ M}) = -3.00$ (When finding a log, drop the unit)
20. $e^{-0.693} = 0.500$
21. If $\log(x) = 5.00$, $\ln(x) = ?$ $\ln(x) = 2.303 \log(x)$; $\ln(x) = (2.303)(5.00) = 11.5$
22. If $\ln(x) = 34.5$, $\log(x) = ?$ $\ln(x) = 2.303 \log(x)$; ; $\log(x) = 34.5/2.303 = 15.0$
23. If $\ln(x) = -(0.075 \text{ day}^{-1})(4.0 \text{ days})$; $x = ?$

$$\ln(x) = -0.300 \text{ (day}^{-1}\text{)(days)} = -0.300 \text{ day}^0 = -0.300 (1) = -0.300$$

$$x = e^{\ln(x)} = e^{-0.300} = 0.741$$

24. Given that $\ln[A] = (-0.0173 \text{ s}^{-1})(t) + 0.693$

a. Strategy: to find $[A]$, first solve for $\ln[A]$

$$? = \ln[A] = (-0.0173 \text{ s}^{-1})(20.0 \text{ s}) + 0.693 = -0.346 + 0.693 = 0.347$$

WANTED is $[A]$ at 20 s. Known is: $\ln[A] = 0.347$ Solve for $[A]$.

* * * * *

$$[A] = e^{\ln[A]} = e^{0.347} = 1.41 \text{ M} \quad (\text{If a concentration is wanted, attach M as unit})$$

b. Strategy: Solve for t in symbols first.

* * * * *

$$\begin{aligned} t &= \frac{\ln[A] - 0.693}{-0.0173 \text{ s}^{-1}} = \frac{\ln[0.710 \text{ M}] - 0.693}{-0.0173 \text{ s}^{-1}} = \frac{-0.342 - 0.693}{-0.0173 \text{ s}^{-1}} = \\ &= \frac{-1.035}{-0.0173 \text{ s}^{-1}} = \boxed{59.9 \text{ s} = t} \quad (\text{answer unit math: } 1/\text{s}^{-1} = (\text{s}^{-1})^{-1} = \text{s}) \end{aligned}$$

25. Given that $\ln[A] = (-0.0241 \text{ /yr.})(t) - 4.61$

a. Strategy: Solve for t in symbols first.

$$\begin{aligned} t &= \frac{\ln[A] + 4.61}{-0.0241 \text{ /yr.}} = \frac{\ln[0.0025 \text{ M}] + 4.61}{-0.0241 \text{ yr}^{-1}} = \frac{-5.99 + 4.61}{-0.0241 \text{ yr}^{-1}} = \\ &= \frac{-1.38}{-0.0241 \text{ yr}^{-1}} = \boxed{57.3 \text{ years} = t} \end{aligned}$$

b. Strategy: to find $[A]$, first solve for $\ln[A]$

$$? = \ln[A] = (-0.0241 \text{ yr}^{-1})(28.8 \text{ yr.}) - 4.61 = -0.694 - 4.61 = -5.30$$

WANTED is $[A]$. Known is: $\ln[A] = -5.30$ Solve for $[A]$.

* * * * *

$$[A] = e^{\ln[A]} = e^{-5.30} = \boxed{0.00500 \text{ M}} \quad \text{If a } [] \text{ is wanted, attach M to answer.}$$

* * * * *

Lesson 27F: Integrated Rate Law – First Order

Prerequisites: Complete Lessons 27D and 27E before this lesson.

* * * * *

For first-order reactants, one form that is written for the integrated rate law is

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

The most commonly encountered reaction that is first order is the nuclear process of radioactive decay, which is always first-order. However, the steps of standard chemical reactions can also be first order as well.

The easiest way to learn to use this rate law is by example.

First-Order Calculations

In some rate law calculations, the order of a reactant is supplied, and the problem can be solved by simply writing and solving the appropriate rate law.

For the following problem, begin by listing and assigning symbols to the WANTED and DATA. Then decide what equation relates those symbols. Solve the equation in symbols before plugging in numbers. If you get stuck, read the answer until unstuck, then try again.

- Q.** Radon-222 is a noble gas nuclide that decays to form other elements. The rate for this radioactive decay is first order, with a rate constant of 0.181/day. If the original [Rn-222] in a sample is 2.5×10^{-4} M, what will be the [Rn-222] after two weeks?

* * * * *

WANTED: $[\text{Rn}]_{\text{after 2 weeks}} = [\text{Rn}]_t$

DATA: $0.181 / \text{day} = 0.181 \text{ day}^{-1} = k$ (for the unit: $1/x \equiv x^{-1}$)
 2 weeks = $t = 14 \text{ days}$ (convert to units *consistent* with the rate *constant*)

Initial concentration = $2.5 \times 10^{-4} \text{ M} = [\text{Rn}]_0$

The rate is first order. We know two equations for first-order rates:

Differential law: **Rate** = $k[A]$ and Integrated law: $\ln[A]_t = -kt + \ln[A]_0$

Which equation is the best match with the symbols in the data?

* * * * *

When the rate data includes time, the integrated law will usually be needed to solve.

Write the specific equation: $\ln [\text{Rn}]_t = -kt + \ln [\text{Rn}]_0$

See if you can solve for the WANTED amount.

* * * * *

Strategy: To find $[\text{Rn}]_t$, first solve the rate equation for $\ln[\text{Rn}]_t$, then use $[\text{Rn}] = e^{\ln [\text{Rn}]}$

* * * * *

$$\begin{aligned} \ln [Rn] &= -kt + \ln [Rn]_0 \\ &= -(0.181 \text{ day}^{-1})(14 \text{ days}) + \ln(2.5 \times 10^{-4} \text{ M}) \\ &= -2.53 - 8.29 = -10.82 = \ln [Rn]_{14 \text{ days}} \end{aligned}$$

(Math help? See Lesson 27E, section II.) If needed, finish solving for the WANTED unit.

* * * * *

$$\text{WANT: } [Rn]_{\text{after 14 days}} = e^{\ln [Rn]} = e^{(-10.82)} = \boxed{2.0 \times 10^{-5} \text{ M Rn}}$$

* * * * *

Units of Concentration

In rate-law calculations, the units for concentration may be either moles/liter *or* units *proportional* to moles per liter. The units must also be consistent: the same for all measures of concentration in a given problem.

Some of the “proportional to moles per liter” units found in rate problems are

- grams per unit of volume for a substance; such as g/cm³;
- atoms of a substance per unit of volume: e.g. atoms/liter;
- counts of radioactive decay/time
- atoms per unit proportional to volume for a given substance: such as “atoms/gram dried cotton;”
- pressure of a gas in any pressure units: kPa, torr, or other pressure units;
- partial pressure of a gas in any pressure units.

Why is gas pressure proportional to concentration? Since, for an ideal gas, $PV=nRT$, rearranging terms we can write

$$n/V = \text{moles/liter} = P/RT = P \times (\text{the constant } 1/RT \text{ at constant temperature}).$$

This equation can be re-written as: **[ideal gas] = (a constant) x P** which is one of the forms for a direct proportion (Lesson 18A). At a constant temperature (which is required for a rate constant to be constant), molar concentration is therefore directly proportional to pressure for a gas with ideal behavior.

Units of the First-Order Rate Constant

The units for first-order rate constants (**k**) are generally expressed as as “1/time” units, such as “sec⁻¹.” However, in solving first-order rate equations, solving for concentration may not produce a unit as part of the answer. This is because the form we use for the first-order rate equation is a “shortcut.” The terms $\ln[A]_t$ and $\ln[A]_0$ are easy to calculate values for, but taking a logarithm of a value with units is not legal and is one indication that our equation is a simplification of a more complex relationship.

To solve first-order rate calculations, our rule will be: when *1/time* units are used for **k**, you must *add units* to any *concentration* calculated in the problem, and those units must be *consistent* with the concentration unit (or the unit proportional to concentration) used elsewhere in the problem. If no unit for concentration is supplied, assume the unit is moles/liter.

Practice A

1. The earth's atmosphere has a small amount of carbon dioxide that contains ^{14}C (carbon-14), a radioactive isotope of carbon. While a plant is alive, C-14 is stored in its cells during photosynthesis. Living plants have a relatively constant and predictable concentration of radioactive carbon. After the plant is harvested and/or dies, the radioactive carbon is no longer replenished, and the concentration of C-14 in the non-living plant material falls as C-14 undergoes radioactive decay at a first-order rate.

By measuring the amount of C-14 in the remains of the plant, how long ago the plant was harvested can be determined. The rate constant for the decay of C-14 is $1.21 \times 10^{-4} \text{ year}^{-1}$. If the [C-14] in freshly harvested cotton fibers is 2.00×10^{10} atoms/gram, and the [C-14] in a cotton garment found in a burial tomb is found to be 1.12×10^{10} atoms/g, how many years ago was the cotton harvested?

2. Using the same k value for C-14 and the same [C-14] at harvest supplied in Problem One, calculate the atoms per gram that would be found in a sample after 10,000. years.
3. Using the same k value for C-14 and the same [C-14] at harvest supplied in Problem One, calculate the half-life of C-14: how many years are required for the [C-14] to be reduced to 1/2 of the concentration at harvest.

4. In an experiment, a first-order rate equation for a decay reaction is found to be

$$\ln [B] = - (0.200 \text{ year}^{-1})(t) - 3.22 \quad \text{What was the original [B]?$$

First-Order Reactions and Graphical Analysis

Some rate law calculations require that the order of a reactant be determined from experimental data *before* applying a rate law to solve. When the order of a reactant is not known, it can be determined by graphical analysis. Graphical analysis is also used to find the specific rate law equation that explains the data.

For the following question, cover below the * * * * * line, then answer the questions above the line.

- Q. For the reaction: $A \rightarrow B$, time and [A] are measured as a reaction proceeds. The data is recorded at the right.
- a. Use the "first half-life" method and [A] to determine the order of the reaction, and then check your answer below.

* * * * *

seconds	[A] in M	ln[A] in ln(M)
0	2.00	
20.0	1.41	
40.0	1.00	
60.0	0.710	
80.0	0.500	
100.	0.353	
120.	0.250	

The first half-life is 40. s. Double the first half-life is 80 s. At $t = 80$ sec., $[A] = 25\%$ of the original concentration. This fits the behavior of *first* order in A.

- b. Using a calculator, add values for $\ln[A]$ to the last column of the table above, then check your answers below.

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Sample: If $[A] = 2.00$ M,

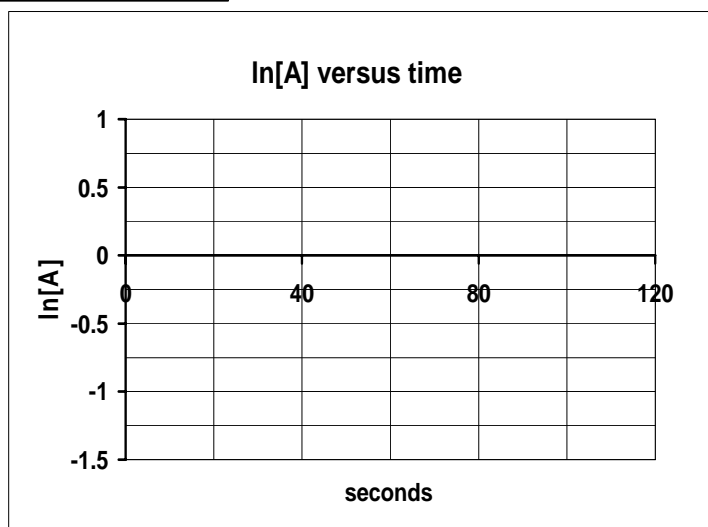
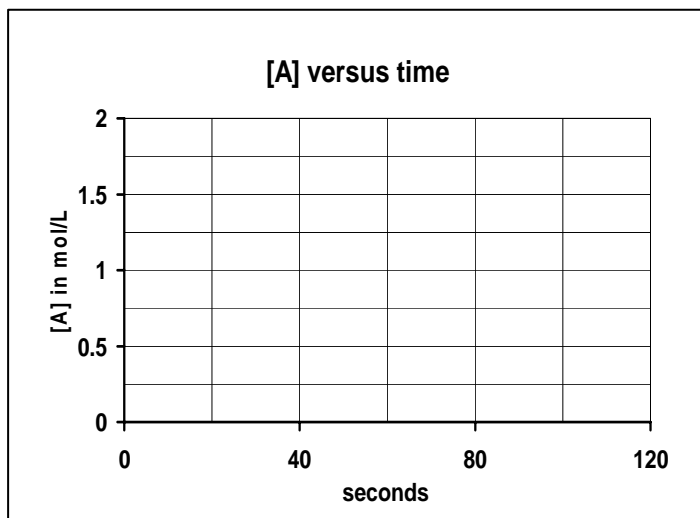
$$\ln[A] = \ln(2.00 \text{ M}) = 0.693 = 0.693$$

We will use the shortcut: if you take the **ln** of a unit, omit the unit in the answer.

Your values should match those at the right.

- c. On the two grids below, graph the data: first $[A]$ vs. time, then $\ln[A]$ vs. time.

seconds	$[A]$ in M	$\ln[A]$
0	2.00	0.693
20.0	1.41	0.344
40.0	1.00	0
60.0	0.710	-0.342
80.0	0.500	-0.693
100.	0.353	-1.04
120.	0.250	-1.39

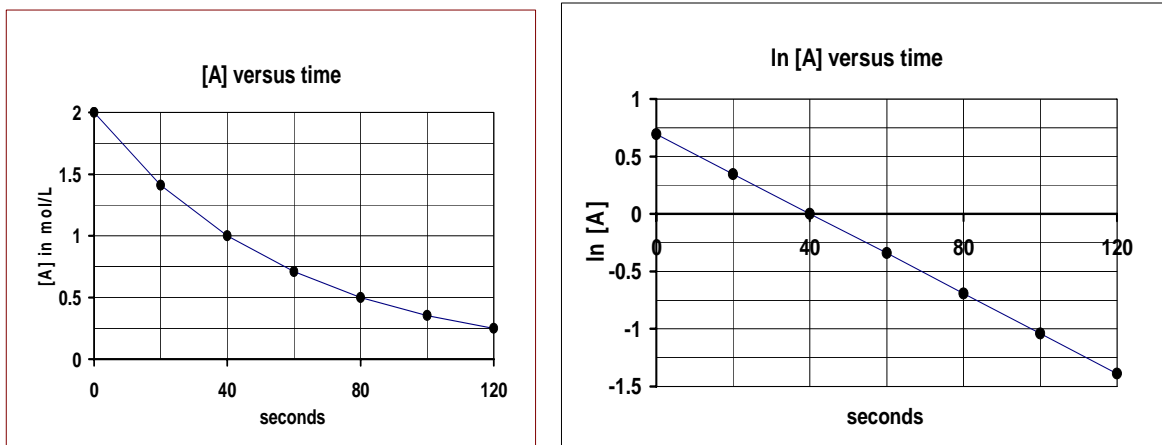


- d. For which graph does the data fit closer to linear behavior?
- e. For the graph that is linear, calculate the slope of the line.
- f. Based on the two graphs, does the data better fit the behavior of a reaction that is zero order in A, or first order in A?

Check your answers below.

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d. Your graphs should be similar to these.



The linear graph is the plot of $\ln[A]$ vs. time.

e. For the slope calculation, using the lowest and highest x values on the graph:

At $t_1 = \text{lowest time} = 0 \text{ s}$, $\ln[A] = 0.693$; at $t_2 = 120 \text{ s}$, $\ln[A] = -1.39$

$$m = \frac{\text{rise}}{\text{run}} = \frac{\Delta \ln[A]}{\Delta t} = \frac{\ln[A]_2 - \ln[A]_1}{t_2 - t_1} = \frac{(-1.39 - 0.693)}{(120 - 0) \text{ s}} = -0.0174 \text{ s}^{-1}$$

★ ★ ★ ★ ★

f. For this data,

- The slope of $[A]$ vs. **time**, which was constant for *zero-order* reactants, is *not* constant for this *first-order* reactant data.
- The slope of $\ln[A]$ vs. time is constant;

Let's analyze the first-order rate law to see why this is the case.

1. Write the two forms of the rate law for a reaction $A \rightarrow B$ that is first-order in A.

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Differential rate law: $\text{Rate} = k[A]$

Integrated rate law: $\ln[A]_t = -kt + \ln[A]_0$

2. Compare the first-order **integrated** rate law: $\ln[A]_t = -kt + \ln[A]_0$

to the equation for a line on a graph: $y = mx + b$

Write the symbols in the first-order integrated rate law next to the corresponding symbols in the equation for a line.

$y =$

$m =$

$x =$

$b =$

Then, for the data in the problem above, after the symbols for the two constants, add the *values* for the two *constants*. Include numbers and units.

* * * * *

$y = \ln[A]_t =$ a variable amount.

$m = -k =$ the constant slope = -0.0174 s^{-1} from Part (e) above.

$x = t =$ **time**, a variable.

$b = \ln [A]_0 = \ln ([A] \text{ initially, at } t = 0) = \ln(2.00 \text{ M}) = +0.693$

3. Write the value for k , with its units.

* * * * *

Since $m = -k$, $k = -m = -(\text{the slope}) = +0.0174 \text{ s}^{-1}$

4. Write the first-order integrated rate law,

a. as memorized; then

b. re-write the law, keeping the same *variable* symbols, but substituting for the two *constants* the values and units of the constants. This result is the calculated integrated rate law.

* * * * *

a. The rate law using symbols:

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

b. Substituting the constants:

$$\ln[A]_t = - (+ 0.0174 \text{ s}^{-1}) (t) + 0.693$$

5. *Test* your rate law: choose a *time* in the original data table that was *not* used to calculate the slope. Enter that time into the calculated integrated rate law and calculate $[A]$. Then compare that calculated $[A]$ to the actual $[A]$ in the data table. See if the law, with your calculated constants, predicts the $[A]$ in the data at that time.

(Use $t = 60.0 \text{ s}$ to match the answer below.)

* * * * *

Equation: $\ln[A]_t = - (+ 0.0174 \text{ s}^{-1}) (t) + 0.693$

DATA: (list the **symbols** for the *variables* in the equation, but don't re-write the known constants.)

$\ln[A]_t = ?$

$t = 60.0 \text{ s}$

WANTED: $[A]_t$ at $t = 60.0 \text{ s}$

Strategy: To find $[A]_t$, use the equation to find $\ln[A]_t$, then use $[A] = e^{\ln[A]}$

If you needed that hint, adjust your work and finish from there.

* * * * *

$$\begin{aligned}
 ? = \ln[A]_t &= -(+0.0174 \text{ s}^{-1})(t) + 0.693 \\
 &= -(+0.0174 \text{ s}^{-1})(60.0 \text{ s}) + 0.693 \quad \{ (\text{s}^{-1})(\text{s}^1) = \text{s}^0 = 1 \} \\
 &= -(1.044) + 0.693 = -0.351
 \end{aligned}$$

WANTED is $[A]$ at 60.0 s. Known is: $\ln[A]_{60 \text{ s}} = -0.351$

Solve for $[A]_{60 \text{ s}}$.

* * * * *

$$[A] = e^{\ln[A]} = e^{-0.351}$$

$$[A] = 0.704 \text{ M} \quad (\text{add the unit for concentration used in the problem: mol/L})$$

In the original data table at $t = 60. \text{ s}$, $[A] = 0.710 \text{ M}$

Allowing for rounding and experimental error, this calculated answer and the data in the original table agree. In predicting the experimental data, the **first-order** integrated rate law, with its calculated constants, worked.

* * * * *

6. Test your equation again: use the calculated rate law to find the *time* at which $[A]$ will equal 0.353 M.

* * * * *

$$\text{Rate Law: } \ln[A] = -(+0.0174 \text{ s}^{-1})(t) + 0.693$$

$$\text{DATA: } [A] = 0.353 \text{ M}$$

$$\ln[A] = \ln(0.353 \text{ M}) = -1.041$$

$$t = ?$$

Solve the equation in symbols for the wanted symbol.

* * * * *

$$t = \frac{\ln[A] - 0.693}{-0.0174 \text{ s}^{-1}} = \frac{-1.041 - 0.693}{-0.0174 \text{ s}^{-1}} = \frac{-1.734}{-0.0174 \text{ s}^{-1}}$$

$$t = \boxed{99.7 \text{ s}}$$

Compare this calculated time to the time in the original table at $[A] = 0.353 \text{ M}$.

The first-order integrated rate law, with its calculated constants added, explains and predicts, within experimental error, the results of the experiment.

Practice B. Answers are at the end of this lesson.

1. Write the integrated rate law for a

a. zero order reactant: _____

b. First-order reactant: _____

2. To get a straight line graph using [A] and time data,
 - a. For a zero-order reactant, plot _____ on the y-axis and _____ on the x-axis.
 - b. For a first-order reactant, plot _____ on the y-axis and _____ on the x-axis.
 3. What ratio that uses concentration and time must be constant for a
 - a. zero-order reactant: _____
 - b. First-order reactant: _____
 4. What will be the term for the *y*-intercept in an integrated rate law that is
 - a. Zero order: _____
 - b. First-order: _____
 5. If reactant A is first order, and [A] versus time data is collected,
 - a. Will a plot of [A] versus time have points on a line? _____
 - b. What plot will produce points on a line? _____
-

ANSWERS

Practice A

1. The WANTED and DATA include terms for both time and a first-order rate constant. What *equation* includes those terms?

The first-order integrated rate law: $\ln [A] = -kt + \ln [A]_0$

That equation will work for any units that are proportional to concentration. Assume that atoms/g is proportional to molar concentration for cotton.

$$\begin{aligned} \text{DATA: } \ln[A] &= \ln[\text{C-14}]_{\text{after decay}} \\ &= \ln(1.12 \times 10^{10} \text{ atoms/g}) = + 23.14 \end{aligned}$$

$$k = 1.21 \times 10^{-4} \text{ year}^{-1}$$

$$t = ?$$

$$\ln [A]_0 = \ln [\text{C-14}]_0 = \ln(2.00 \times 10^{10} \text{ atoms/g}) = + 23.72$$

Solving for the WANTED symbol in symbols first:

$$t = \frac{\ln [A] - \ln [A]_0}{-k} = \frac{(+ 23.14 - 23.72)}{- 1.21 \times 10^{-4} \text{ yr}^{-1}} = \frac{- 0.58}{- 1.21 \times 10^{-4}} \text{ yr.} = \boxed{4,800 \text{ yr.}}$$

2. For first-order decay, use the first-order integrated rate law: $\ln [A] = -kt + \ln [A]_0$

WANTED: $[C-14]_{\text{after } 10,000. \text{ years}}$, in atoms/gram

DATA: Use the equation symbols to make the data table.

$$\ln[A] = \ln[C-14]_{\text{after } 10,000. \text{ years}} = ?$$

$$k = 1.21 \times 10^{-4} \text{ year}^{-1}$$

$$t = 10,000. \text{ years}$$

$$\ln [A]_0 = \ln [C-14]_0 = \ln(2.00 \times 10^{10} \text{ atoms/g}) = + 23.72$$

Strategy: To find the $[C-14]_{\text{after decay}}$, use the rate law to find $\ln[C-14]_{\text{after decay}}$ first.

$$\text{Then use: } ? = [C-14] = e^{\ln [C-14]}$$

If you needed that hint, adjust your work and finish.

* * * * *

$$\begin{aligned} \ln[C-14]_{\text{after decay}} &= -(1.21 \times 10^{-4} \text{ year}^{-1})(10,000 \text{ yrs}) + 23.72 \\ &= -1.21 + 23.72 \\ &= + 22.51 \end{aligned}$$

WANTED is $[C-14]_{10,000 \text{ yrs}}$. Known is: $\ln[C-14]_{10,000 \text{ yrs}} = + 22.51$

Solve for $[C-14]$.

* * * * *

$$[C-14]_{10,000 \text{ yrs}} = e^{\ln[C-14]} = e^{+22.51} = 5.97 \times 10^9 \text{ atoms/g}$$

When solving for concentration, *add* the consistent concentration unit in the DATA.

3. For first-order decay, use the first-order integrated rate law: $\ln [A] = -kt + \ln [A]_0$

WANTED: Half-life of C-14

Strategy: Half-life is time it takes for initial concentration to be cut in half.

$$\text{Since } [C-14]_{\text{original}} = 2.00 \times 10^{10} \text{ atoms/g}$$

$$[C-14]_{\text{at half-life}} = 1.00 \times 10^{10} \text{ atoms/g} \quad (\text{half as much})$$

If you needed that hint, adjust and try the problem again.

* * * * *

$$\text{DATA: } \ln [C-14]_{\text{at half-life}} = \ln(1.00 \times 10^{10} \text{ atoms/g}) = 23.03$$

$$k = 1.21 \times 10^{-4} \text{ year}^{-1}$$

$$t = ? \text{ years}$$

$$\ln [A]_0 = \ln [C-14]_0 = \ln(2.00 \times 10^{10} \text{ atoms/g}) = + 23.72$$

Solve the rate equation for the WANTED symbol, in symbols first.

$$t = \frac{\ln [A] - \ln [A]_0}{-k} = \frac{(+23.03 - 23.72)}{-1.21 \times 10^{-4} \text{ yr}^{-1}} = \frac{0.69}{1.21 \times 10^{-4}} \text{ yr.} = 5,700 \text{ yr.}$$

Does this answer make sense? In problem one, a little *less* than half of the initial C-14 had decayed in 4,800 years, so 5,700 years for exactly half is in close agreement.

In problem 2, the 10,000 year time of decay was a little less than two 5,700 year half lives. After 2 half lives, 25% of the original amount should be remaining for first-order decay. In problem 2, 10,000 years is a little less than 2 half lives and $0.597 \times 10^{10} / 2.00 \times 10^{10} = 30\%$, or a bit more than 25% of the original, remains. This is about what would be expected by estimation.

These three answers are consistent.

4. WANTED: $[B]_0$ (Write the *symbol* for the WANTED *initial* concentration of B)

DATA: This is a first-order reaction. The first-order equation that includes $[B]_0$ is

$$\ln [B] = -kt + \ln [B]_0 \quad . \quad \text{Compare that to the form of the given equation:}$$

$$\ln [B] = -(0.200 \text{ year}^{-1})(t) - 3.22$$

$$\ln [B]_0 = -3.22 \quad (\text{Finish from here})$$

* * * * *

$$[B]_0 = e^{\ln[B]_0} = e^{-3.22} = 0.0400 \text{ M B}$$

If a concentration is wanted, add M as unit unless other units proportional to the molarity are used in the problem.

Practice B

- Zero order: $[A] = -kt + [A]_0$
 - First-order: $\ln [A] = -kt + \ln [A]_0$
- To get a straight line for a zero-order reactant, plot $[A]$ on the y -axis and t on the x -axis.
 - For a first-order reactant, plot $\ln [A]$ on the y -axis and t on the x -axis.
- Constant ratio for a zero-order reactant: $\Delta[A] / \Delta t$
 - First-order reactant: $\Delta \ln[A] / \Delta t$
- The y -intercept in an integrated rate law that is zero order: $[A]_0$
 - First order: $\ln [A]_0$
- Will a plot of first order $[A]$ vs. time have points on a line? **No**
 - What plot will? $\ln [A]$ vs. t

* * * * *

Lesson 27G: Reciprocal Math

Timing: This lesson should be done before calculations using the second-order integrated rate law.

Pretest: If you think you know this topic, try the last lettered *part* of each calculation in Practice B at the end of the lesson. If you can do those calculations, skip the lesson.

Prerequisites: Complete Lesson 17C (Complex Unit Cancellation) before this lesson.

* * * * *

Rules For Reciprocals

Second-order rate laws will require work with reciprocals of both numbers and units. Some rules for reciprocals are as follows.

1. The reciprocal of X is $1/X$. Three equivalent ways to write the **reciprocal of X** are:

$$\frac{1}{X} = 1/X = X^{-1} \quad \text{Also:} \quad \frac{1}{X^3} = 1/X^3 = X^{-3}$$

2. The reciprocal of $1/X$ is X . The *reciprocal* of the *reciprocal* of X is X .

In equation format:
$$\frac{1}{\frac{1}{X}} = 1/(1/X) = (X^{-1})^{-1} = X$$

3. On a calculator, to convert a reciprocal to a number, either

- a. divide the denominator into one,

Example: $1/8 = (1 \text{ divided by } 8) = 0.125$

- b. or, take the reciprocal of the denominator using the reciprocal $\boxed{1/x \text{ or } x^{-1}}$ key.

Example: to convert $1/8$ to a number, input $8 \boxed{1/x \text{ or } x^{-1}}$. Try it.

4. If you know the value of the reciprocal of a number, and you want the number, take the reciprocal of the reciprocal value.

Example: Since $1/(1/x) = x$ if $1/A = 0.25$, $A = 1/0.25 = 4$

Practice A. Learn the rules, then apply them below. If you are unsure of an answer, check at the end of the lesson before doing the next problem. Doing every other problem today, and the rest tomorrow, will help in remembering the rules.

1. Trying these without a calculator, convert these reciprocals to numbers.

a. $1/(3/4) =$ b. $1/(1/8.2) =$ c. $1/e^{-1} =$

2. Using a calculator as needed, convert these reciprocals to numbers.

a. $1/7.9 =$ b. $1/0.40 =$ c. $(2,000)^{-1} =$

d. $(0.75)^{-1} =$ e. $1/e^3 =$ f. $(1/6.2)^{-1} =$

- c. To simplify the fraction, *invert* any reciprocal *fractions*, cancel units that cancel, and multiply the terms.

Practice C. If you are unsure of an answer, check the answer at the end of the lesson before doing the next problem. Do the math for both the number and its units. Do every other part, and more if you need more practice.

1. Write the following without a denominator by using positive and negative exponents.

a. $\frac{\text{mol}}{\text{L} \cdot \text{sec.}}$

b. $1/(\text{mol} \cdot \text{s}^{-2}) =$

c. $(\text{meters}/\text{s}^2)^{-1} =$

d. $(\text{meters}/\text{s}^{-2})^{-1} =$

e. $\frac{1}{\frac{\text{mol}}{\text{L} \cdot \text{s}}} =$

f. $1/\text{s}^{-1} =$

2. Write these units as simple fractions, with a numerator and denominator, in which all of the exponents are *positive* (for additional review, see Lesson 17C).

b. $1/(\text{sec.}/\text{L})$

b. $\frac{1}{\frac{\text{mol}}{\text{L} \cdot \text{s}}}$

c. $\frac{\text{M}^{-1}}{\text{M}^{-1} \cdot \text{s}^{-1}}$

3. Convert **mol/L** to **M** for molarity, and then write these units without a denominator.

a. $1/(\text{mol}/\text{L})$

b. $\frac{1}{\frac{\text{mol}}{\text{L} \cdot \text{s}}}$

4. In these, convert **M** to **moles/liter**, then express the unit without a denominator by using positive and negative exponents.

a. $\text{M} \cdot \text{s}^{-1} =$

b. $1/(\text{M} \cdot \text{s}^{-1}) =$

c. $\frac{\text{M}^{-1}}{\text{s}} =$

d. $(\text{M}/\text{s}^{-1})^{-1} =$

5. Simplify: convert to a number and unit on one line, without a denominator.

a. $1/(8.00 \text{ mol})$

b. $1/(0.25 \text{ mol}/\text{L})$

c. $(0.450 \text{ M}^{-1} \cdot \text{s}^{-1})(25.0 \text{ s})$

d. $(0.500 \text{ M}^{-1} \cdot \text{s}^{-1})(15.0 \text{ s}) + 1.20 \text{ M}^{-1}$

6. Solve $1/[\text{A}] = +kt + 1/[\text{A}]_0$ for a. **k** b. **t** c. $1/[\text{A}]_0$ d. **[A]**

7. Given this equation: $1/[\text{A}] = (0.250 \text{ M}^{-1} \cdot \text{s}^{-1})(\text{t}) + 2.00 \text{ M}^{-1}$
and $\text{t} = 30.0 \text{ s}$, solve for **[A]**.

8. Given the same equation as in problem 7, if **[A]** = 0.174 M, solve for **t**.

ANSWERS**Practice A**

There are many ways to do these calculations. Use any legal methods that get the same answer.

- a. $1/(3/4) = 4/3 = 1.33$ b. $1/(1/8.2) = 8.2$ c. $1/e^{-1} = (e^{-1})^{-1} = e^1 = 2.718\dots$
- a. $1/7.9 = 0.13$ b. $1/0.40 = 2.5$ c. $(2,000)^{-1} = 0.0005$ or 5×10^{-4}
 d. $(0.75)^{-1} = 1.33$ e. $1/e^3 = 1/20.09 = 0.0498$ f. $(1/6.2)^{-1} = 1/(1/6.2) = 6.2$
- If $1/A = 0.0625$, $A = 1/(1/A) = 1/0.0625 = 16.0$ 4. If $1/D = 12.5$, $D = 1/12.5 = 0.0800$
- a. $1/(4.7 \times 10^3) = 2.1 \times 10^{-4}$ [keys might be: 4.7 [E or EE] 3 [1/x]]
 b. $1/(9.2 \times 10^{-11}) = 1.1 \times 10^{10}$ [keys might be: 9.2 [E or EE] 11 [+/-] [1/x]]
 c. $(2.5 \times 10^{-2})^{-1} = 40.$ [enter the number, then, to take a -1 power, use [1/x]]
 d. $(1/2.5 \times 10^{-2})^{-1} = [(2.5 \times 10^{-2})^{-1}]^{-1} = (2.5 \times 10^{-2})^{+1} = 2.5 \times 10^{-2}$

Practice B

- a. $1/10^2 = 10^{-2}$ b. $1/10^{-10} = 10^{+10}$ c. $1/\log(100) = 1/2 = 0.5$
 d. $(3^{-2})^{-1} = 3^2 = 9$ e. $1/(4^{-2}) = (4^{-2})^{-1} = 4^2 = 16$
- a. $1/(5.0 \times 10^5) = 1/5.0 \times 1/10^5 = 0.20 \times 10^{-5} = 2.0 \times 10^{-6}$
 b. $1/(5.0 \times 10^{-5}) = 1/5.0 \times 1/10^{-5} = 0.20 \times 10^5 = 2.0 \times 10^4$

Practice C

- a. $\frac{\text{mol}}{\text{L} \cdot \text{sec}} = \text{mol} \cdot \text{L}^{-1} \cdot \text{sec}^{-1}$ b. $1/(\text{mol} \cdot \text{s}^{-2}) = (\text{mol} \cdot \text{s}^{-2})^{-1} = \text{mol}^{-1} \cdot \text{s}^2$
 c. $(\text{meters}/\text{s}^2)^{-1} = (\text{meters} \cdot \text{s}^{-2})^{-1} = \text{meters}^{-1} \cdot \text{s}^2$
 d. $(\text{meters}/\text{s}^{-2})^{-1} = (\text{meters} \cdot \text{s}^2)^{-1} = \text{meters}^{-1} \cdot \text{s}^{-2}$
 e. $\frac{1}{\frac{\text{mol}}{\text{L} \cdot \text{s}}} = 1/(\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}) = \text{mol}^{-1} \cdot \text{L} \cdot \text{s}$ f. $1/\text{s}^{-1} = (\text{s}^{-1})^{-1} = \text{s}$
- One way to do these is to use the rule: to take the reciprocal of a fraction, invert the fraction.
 - $1/(\text{sec.}/\text{L}) = \frac{\text{L}}{\text{sec.}}$
 - $\frac{1}{\frac{\text{mol}}{\text{L} \cdot \text{s}}} = \frac{\text{L} \cdot \text{s}}{\text{mol}}$
 - $\frac{1}{\frac{\text{M}^{-1}}{\text{M}^{-1} \cdot \text{s}^{-1}}} = 1/\text{s}^{-1} = \text{s}$
- a. $1/(\text{mol}/\text{L}) = 1/\text{M} = \text{M}^{-1}$ b. $\frac{1}{\frac{\text{mol}}{\text{L} \cdot \text{s}}} = \frac{1}{\frac{\text{M}}{\text{s}}} = (\text{M} \cdot \text{s}^{-1})^{-1} = \text{M}^{-1} \cdot \text{s}$

4. a. $M \bullet s^{-1} = \frac{\text{mol}}{L} \bullet s^{-1} = \text{mol} \bullet L^{-1} \bullet s^{-1}$
 b. $1/(M \bullet s^{-1}) = (\text{mol} \bullet L^{-1} \bullet s^{-1})^{-1} = \text{mol}^{-1} \bullet L \bullet s$
 c. $\frac{M^{-1}}{s} = (\text{mol} \bullet L^{-1})^{-1} \bullet s^{-1} = \text{mol}^{-1} \bullet L \bullet s^{-1}$
 d. $(M/s^{-1})^{-1} = (\text{mol} \bullet L^{-1} \bullet s)^{-1} = \text{mol}^{-1} \bullet L \bullet s^{-1}$
5. a. $1/(8.00 \text{ mol}) = 0.125 \text{ mol}^{-1}$ b. $1/(0.25 \text{ mol/L}) = (1/0.25)(1/(\text{mol} \bullet L^{-1})) = 4.0 \text{ mol}^{-1} \bullet L$
 c. $(0.450 \text{ M}^{-1} \bullet \text{s}^{-1})(25.0 \text{ s}) = 11.2 \text{ M}^{-1}$
 d. $(0.500 \text{ M}^{-1} \bullet \text{s}^{-1})(15.0 \text{ s}) + 1.20 \text{ M}^{-1} = 7.50 \text{ M}^{-1} + 1.20 \text{ M}^{-1} = 8.70 \text{ M}^{-1}$
6. a. $k = \frac{1/[A] - 1/[A]_0}{t}$ b. $t = \frac{1/[A] - 1/[A]_0}{k}$
 c. $1/[A]_0 = [A]^{-1} - kt$ d. $[A] = (kt + 1/[A]_0)^{-1}$

7. Given $1/[A] = (0.250 \text{ M}^{-1} \bullet \text{sec}^{-1})(t) + 2.00 \text{ M}^{-1}$ and $t = 30.0 \text{ s}$, solve for $[A]$.

Strategy: Since the equation solves for $1/[A]$, first solve the equation for $1/[A]$, then take the reciprocal of $1/[A]$ to find $[A]$.

* * * * *

Equation: $1/[A] = (0.250 \text{ M}^{-1} \bullet \text{sec}^{-1})(t) + 2.00 \text{ M}^{-1}$

DATA: Use the equation's symbols for variables to make the data table.

$$1/[A] = ?$$

$$t = 30.0 \text{ s}$$

$$\begin{aligned} \text{Solve:} \quad ? &= 1/[A] = (0.250 \text{ M}^{-1} \bullet \text{s}^{-1})(30.0 \text{ s}) + 2.00 \text{ M}^{-1} = \\ &= 7.50 \text{ M}^{-1} + 2.00 \text{ M}^{-1} = \boxed{9.50 \text{ M}^{-1} = 1/[A]} \end{aligned}$$

$$[A] = 1/(1/[A]) = 1/(9.50 \text{ M}^{-1}) = \boxed{0.105 \text{ M} = [A]}$$

8. Given the same equation and $[A] = 0.174 \text{ M}$, solve for t .

Equation: $1/[A] = (0.250 \text{ M}^{-1} \bullet \text{s}^{-1})(t) + 2.00 \text{ M}^{-1}$

DATA: Use the equation's *variables* in the data table.

$$1/[A] = 1/(0.174 \text{ M}) = 5.75 \text{ M}^{-1}$$

$$t = ? \quad \text{Solve in symbols before substituting numbers.}$$

$$t = \frac{1/[A] - 2.00 \text{ M}^{-1}}{(0.250 \text{ M}^{-1} \bullet \text{s}^{-1})} = \frac{5.75 \text{ M}^{-1} - 2.00 \text{ M}^{-1}}{(0.250 \text{ M}^{-1} \bullet \text{s}^{-1})} = \frac{3.75 \text{ M}^{-1}}{(0.250 \text{ M}^{-1} \bullet \text{s}^{-1})} = 15.0 \text{ s}$$

* * * * *

Lesson 27H: Integrated Rate Law – Second Order

The following table summarizes the rate law equations used for zero-, first-, and second-order reactants. You need to be able to write these 9 rows from *memory*.

* * * * *

Summary: Rate Laws

1	Order →	Zero	First	Second
2	(Differential) Rate Law	rate = $k[A]^0 = k$	rate = $k[A]^1 = k[A]$	rate = $k[A]^2$
3	If [A] doubles, the rate:	Stays the same	Doubles	Quadruples
4	At double the first half-life, [A] remaining is:	None	25%	33%
5	Integrated Rate Law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = +kt + \frac{1}{[A]_0}$
6	To graph a line, plot:	[A] on y, t on x	$\ln[A]$ on y, t on x	$1/[A]$ on y, t on x
7	This slope is constant between any 2 points:	$\Delta[A] / \Delta t$	$\Delta \ln[A] / \Delta t$	$\Delta 1/[A] / \Delta t$
8	Rate constant (k) =	Minus the slope	Minus the slope	The slope
9	Half-life and k	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{-(\ln 1/2)}{k} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

To do the problems below, begin by memorizing the table's first 8 rows for *second-order* reactants. Practice until you can write those 8 rows from memory. Then, cover below the * * * * * lines below with a cover sheet and answer the questions above the line.

- Write two forms of the rate law for a reaction $A \rightarrow B$ that is *second-order* in A.

* * * * *

Second-order differential rate law: Rate = $k [A]^2$

Second-order integrated rate law: $1/[A] = +kt + 1/[A]_0$

- Compare the second-order integrated rate law: $1/[A] = +kt + 1/[A]_0$

to the equation for a line on a graph: $y = mx + b$

Write the symbols in the second-order integrated rate law next to the matching symbols in the equation for a line.

$y =$

$m =$

$x =$

$b =$

* * * * *

$$y = 1/[A]$$

$$m = +k$$

$$x = t$$

$$b = 1/[A]_0$$

3. Fill in the blanks on these. For a reaction that is second order in A,
- What ratio that uses [A] and time will be constant? _____
 - What will be the *y*-intercept term in the integrated rate law? _____
 - If [A] versus time data is collected,
 - Will a plot of [A] versus time have points on a line? _____
 - What plot will produce points on a line? _____

* * * * *

- a. $\Delta 1/[A]/\Delta t$ b. $1/[A]_0$ c. i. **No** ii. $1/[A]$ versus *t*

To learn the method for graphical analysis of second-order data, try this example.

Q. For the reaction: $D \rightarrow E$, [D] and time are measured.

- Based on the data at the right, estimate the first half-life of D in the reaction.
- Estimate [D] after double the first half-life;
- Determine the **order** of reactant D.
- Write the differential rate law.

Time	[D]	1/[D]
0	0.400 M	
10.0 s	0.250 M	
18.0 s	0.192 M	
28.0 s	0.149 M	
36.0 s	0.127 M	
44.0 s	0.110 M	

* * * * *

- The original concentration is cut in half, to 0.200 M, after *about* 16 s.
- Double the first half-life is *about* 32 s. [D] at *about* 32 s is *about* 0.130 M.
- Since $0.130 \text{ M}/0.400 \text{ M} = 0.32$; about 32% of the original concentration remains at double the first half-life, which is close to 33%. This fits the profile for a *second-order* reactant.
- rate = $k[D]^2$**
- If this data represents a second-order reactant, what ratio using [D] and *t* should be constant?

* * * * *

- The ratio $\Delta (1/[D])/\Delta t$, which is the slope component in the second-order integrated rate law, should be constant.
- Using a calculator, calculate values for $1/[D]$ in the table above. Enter the results in the last column, then check your answers below.

* * * * *

f. Sample calculations:

For $1/[D]$: If $[D] = 0.400 \text{ M}$,

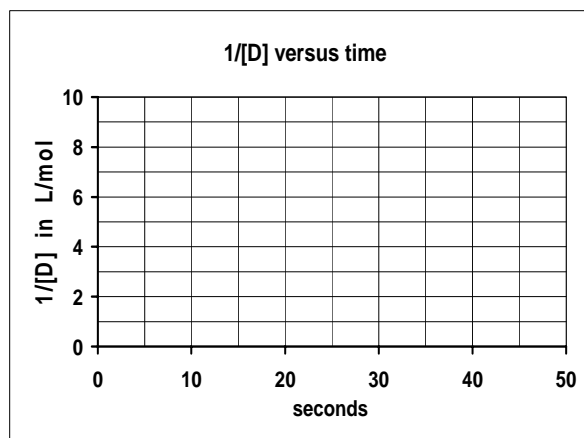
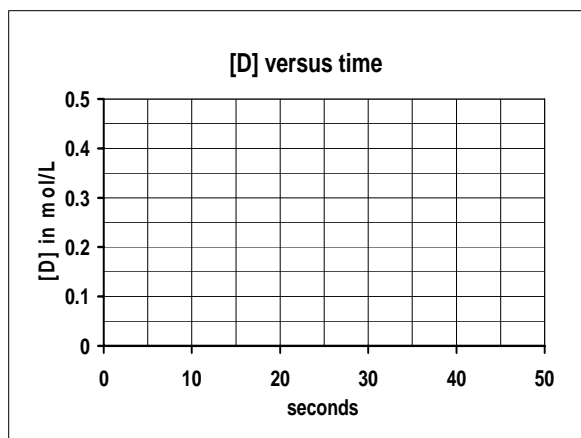
$$1/[D] = 1/0.400 \text{ M} = 2.50 \text{ M}^{-1}$$

★ ★ ★ ★ ★

Your values should match those at the right.

g. On the two grids below, graph the data: first $[D]$ vs. time, then $1/[D]$ vs. time.

Time	[D]	$1/[D]$
0	0.400 M	2.50 M^{-1}
10.0 s	0.250 M	4.00 M^{-1}
18.0 s	0.192 M	5.21 M^{-1}
28.0 s	0.149 M	6.70 M^{-1}
36.0 s	0.127 M	7.87 M^{-1}
44.0 s	0.110 M	9.10 M^{-1}



- h. For which graph is the data closer to linear behavior?
- i. For the graph that is linear, calculate the slope of the line between two widely spaced points.
- j. Based on the graph, does the data better fit the behavior of a reaction that is zero order in D, or second order in D?

Check your answers below.

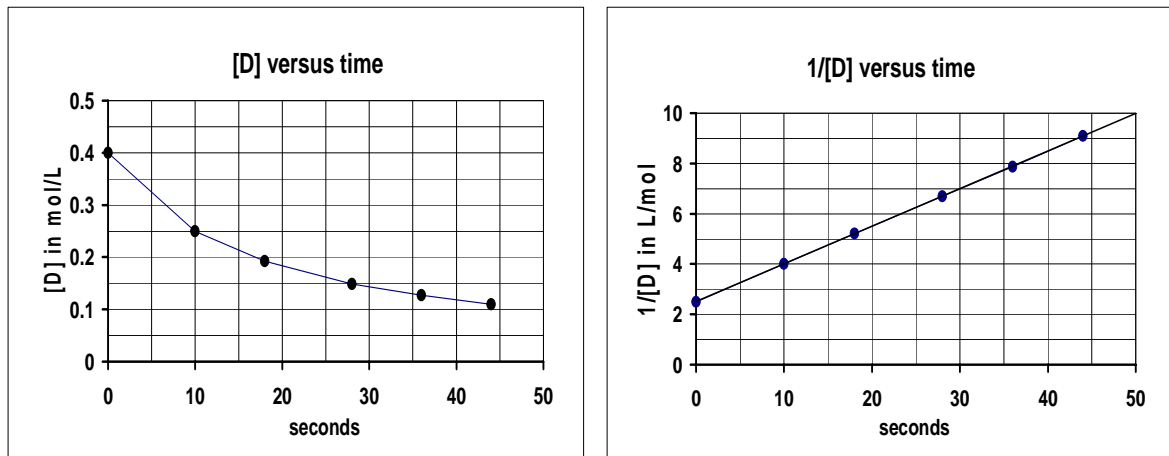
★ ★ ★ ★ ★

- h. The second graph should be very close to linear behavior (see next page).
- i. For slope between 0 and 50 s, at $t_1 =$ the lowest time = 0 s, $1/[D] = 2.50 \text{ M}^{-1}$

At $t_2 = 50 \text{ s}$, $1/[D] \approx 10.0 \text{ M}^{-1}$

$$m = \text{slope} = \frac{\Delta 1/[D]}{\Delta t} = \frac{1/[D]_2 - 1/[D]_1}{t_2 - t_1} = \frac{(10.0 - 2.50) \text{ M}^{-1}}{(50.0 - 0) \text{ s}} = \frac{0.150 \text{ M}^{-1}}{\text{s}}$$

For real experimental data, the slope between points will vary, and the slope of the “best line” among the points will be a judgment call with uncertainty.



- j. When a graph is linear, the equation for the line is

$$y\text{-axis variable} = (\text{constant slope})(x\text{-axis variable}) + y\text{-intercept}$$

Since the first graph above is not linear, but the second is, the data in the table fits the equation

$$1/[D] = (\text{constant slope})(\text{time}) + y\text{-intercept}$$

The value of the y -intercept is the value of y when time = 0, which is represented in symbols as $1/[D]_0$. The equation for the line above is therefore

$$1/[D] = (\text{constant slope})(\text{time}) + 1/[D]_0$$

which matches the form of the second-order integrated rate law:

$$1/[D] = +kt + 1/[D]_0$$

For data that is second-order in D, the slope ratio $\Delta(1/[D])/\Delta t$ should be constant. In the second graph above it is.

- k. For this experiment, the numeric values and units for the constants are:

$$k = \underline{\hspace{2cm}} \text{ and } 1/[D]_0 = \underline{\hspace{2cm}}$$

* * * * *

- k. For the above reaction, in symbols, the rate law is: $1/[D] = +kt + 1/[D]_0$

Since the rate law is in the form $\rightarrow y = mx + b$

for this data: $k = m = \text{the constant slope} = 0.150 \text{ M}^{-1} \cdot \text{s}^{-1}$ from part i,

and $1/[D]_0 = 1/[D] \text{ at } 0 \text{ s} = 1/0.400 \text{ M} = 2.50 \text{ M}^{-1}$

- l. Write the specific rate law for this data, keeping the same *variable* symbols but substituting the values and units of the two constants.

* * * * *

1. In symbols: $1/[D] = +kt + 1/[D]_0$

Substituting the constants, the rate law for this data is:

$$1/[D] = (0.150 \text{ M}^{-1}\cdot\text{s}^{-1}) (t) + 2.50 \text{ M}^{-1}$$

- m. Test the rate law: choose a *time* value in the original data table that you did *not* use to calculate a slope. Plug that time into the rate law. See if the law, with your calculated constants, accurately predicts the [D] in the data at that time.

(Use $t = 36.0 \text{ s}$ to match the answer below.)

* * * * *

m. Rate Law: $1/[D] = (0.150 \text{ M}^{-1}\cdot\text{s}^{-1}) (t) + 2.50 \text{ M}^{-1}$

DATA: $1/[D] = ?$

$t = 36.0 \text{ s}$

WANTED: $[D]$

Strategy: To find [D], use the rate law to find $1/[D]$, and then take the reciprocal to find [D].

If needed, adjust your work and finish.

* * * * *

$$? = 1/[D] = (0.150 \text{ M}^{-1}\cdot\text{s}^{-1})(36.0 \text{ s}) + 2.50 \text{ M}^{-1}$$

$$= 5.40 \text{ M}^{-1} + 2.50 \text{ M}^{-1} = \boxed{7.90 \text{ M}^{-1} = 1/[D]}$$

$$[D] = 1/(1/[D]) = 1/(7.90 \text{ M}^{-1}) = \boxed{0.127 \text{ M} = [D]}$$

Compare that answer to the original data table for $t = 36.0 \text{ s}$. Does the rate equation predict the experimental result?

- n. Test your equation again: use the equation to calculate the **time** at which [A] will equal 0.192 M .

* * * * *

n. Rate Law: $1/[D] = +kt + 1/[D]_0$

DATA: $[D] = 0.192 \text{ M}$

$$1/[D] = 1/(0.192 \text{ M}) = 5.21 \text{ M}^{-1}$$

$$k = (0.150 \text{ M}^{-1}\cdot\text{s}^{-1})$$

$$t = ?$$

$$1/[D]_0 = 1/0.400 \text{ M} = 2.50 \text{ M}^{-1}$$

Strategy: Solve the equation for t , first in symbols, then plug in values.

* * * * *

$$t = \frac{1/[D] - 1/[D]_0}{k} = \frac{5.21 \text{ M}^{-1} - 2.50 \text{ M}^{-1}}{0.150 \text{ M}^{-1}\cdot\text{s}^{-1}} = \frac{2.71 \text{ M}^{-1}}{0.150 \text{ M}^{-1}\cdot\text{s}^{-1}} = \boxed{18.1 \text{ s}}$$

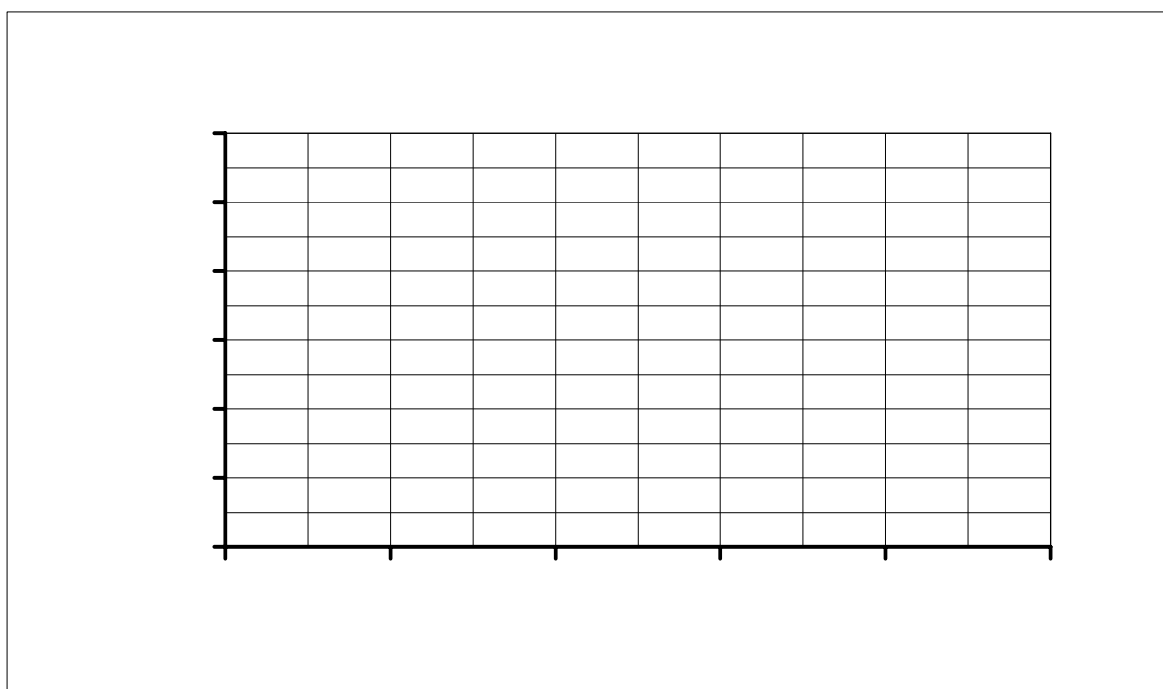
Compare this calculated time to the time in the original table at $[A] = 0.192 \text{ M}$.

The answers agree within one doubtful digit. Once an integrated rate law with its calculated constants is known, the concentration of the reactant at *any* time, and the time required to reach *any* concentration, can be calculated.

Practice: If you are unsure of the answer to any part, check it before doing the next part. Additional second-order calculations will be found in the next lesson.

1. In the reaction: $A \rightarrow B$, time and $[A]$ are measured as a reaction proceeds.
 - a. Using the “double the first half-life” method, determine the order of the reaction.
 - b. Write the differential and the integrated rate law that fits this data, in symbols.
 - c. What two variables will need to be plotted to produce a line with a constant slope?
 - d. Graph the data to determine the rate constant for the reaction. You may use the grid below, your own graph paper, or graphing software.
 - e. Write the integrated rate law with values for the two constants.
 - f. Calculate the predicted $[A]$ at $t = 1450 \text{ sec}$.
 - g. How long will it take for $[A]$ to equal 0.100 M ?

Time	[A]	
0	0.500 M	
60.0 s	0.444 M	
150. s	0.381 M	
225 s	0.340 M	
450. s	0.255 M	
900. s	0.174 M	



ANSWERS

- 1 a. The first half-life is about 460 s. Double the first half-life is about 920 s. At $t = 920$ s, $[A] \approx 0.170/0.500 =$ about 34% of the original concentration. This fits the behavior of second order in A.

- b. Second-order differential rate law: $\text{Rate} = k [A]^2$
 Second-order integrated rate law: $1/[A] = +kt + 1/[A]_0$

- c. Calculate values for $1/[A]$,
 (see values at right)
 then graph $1/[A]$ versus t .

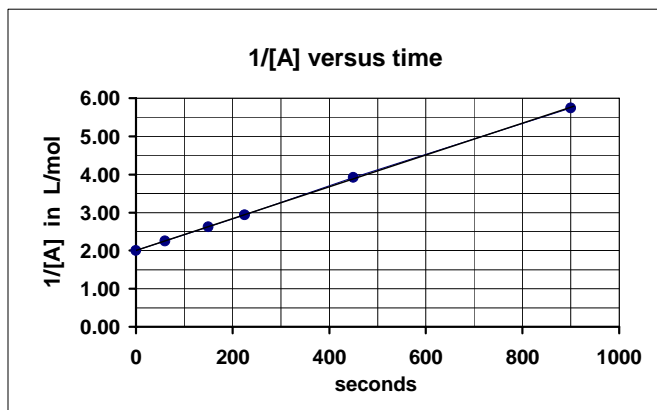
Time	[A]	$1/[A]$ in L/mol
0	0.500 M	2.00
60.0 s	0.444 M	2.25
150. s	0.381 M	2.62
225 s	0.340 M	2.94
450. s	0.255 M	3.92
900. s	0.174 M	5.75

- d. For second order reactions, the slope of the graph of $1/[A]$ versus t is the value of the rate constant.

To find the rate constant, calculate the slope of the line.

* * * * *

Using the second-order integrated rate law and the estimated data points from the graph at 0 s and 900 s, the rate constant is:



$$k = m = \frac{\Delta 1/[A]}{\Delta t} = \frac{1/[A]_2 - 1/[A]_1}{t_2 - t_1} = \frac{(1/0.174 - 1/0.500) \text{ M}^{-1}}{(900 - 0) \text{ s}} = \frac{5.75 - 2}{900} = \mathbf{0.00416 \frac{\text{M}^{-1}}{\text{s}}}$$

Your slope may differ slightly. Taking the slope of a line that is a “best fit” involves uncertainty.

- e. Integrated Rate Law: $1/[A] = (0.00416 \text{ M}^{-1} \cdot \text{s}^{-1}) (t) + 2.00 \text{ M}^{-1}$
 f. To find $[A]$, use the rate law to find $1/[A]$ and then take its reciprocal.

$$1/[A] = (0.00416 \text{ M}^{-1} \cdot \text{s}^{-1}) (1450 \text{ s}) + 2.00 \text{ M}^{-1} = \mathbf{8.04 \text{ M}^{-1}}$$

$$[A] = 1/(1/[A]) = 1/8.04 \text{ M}^{-1} = \mathbf{0.124 \text{ M}}$$

- g. Rate Law: $1/[A] = +kt + 1/[A]_0$

$$t = \frac{1/[A] - 1/[A]_0}{k} = \frac{(1/0.100 - 2.00) \text{ M}^{-1}}{k} = \frac{8.00 \text{ M}^{-1}}{0.00416 \text{ M}^{-1} \cdot \text{s}^{-1}} = \mathbf{1,920 \text{ s}}$$

* * * * *

Lesson 27I: Half-Life Calculations

Timing: IF you are asked to solve *half-life* calculations as part of your unit on kinetics, do this lesson now. You will also need to download and complete Lesson 39D as part of the following lesson.

If you are *not* asked to solve calculations that include half-lives at this point in your course, do not do this lesson.

IF you are asked to solve *only radioactive decay* half-life calculations at this point in your course, do not complete this lesson, but instead complete Lesson 39D.

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Half-Lives: Simple Multiple Cases

The half-life of a reactant (symbol $t_{1/2}$) is the time required for a [reactant] to reach 50% of its initial concentration. After one half life, half of a sample remains and half is used up. Recall that for a

- Zero-order reactant, at double the first half-life, all of the reactant is used up.
- First-order reactant (including radioactive isotopes), the half-life is constant.
 - At double the first half-life, 1/4 of the original concentration remains;
 - At triple the first half-life, 1/8 of the original concentration remains.
- Second-order reactant,
 - At double the first half-life, 1/3 of the original concentration remains;
 - At triple the first half-life, 1/4 of the original concentration remains.
 - Each successive half-life requires twice the time of the preceding half-life.

Though the rate laws and the above rules are stated in terms of concentration, they will also be true for any measure that is proportional to concentration. If the reacting particles are in a sample that has a constant volume (which should be assumed unless other conditions are stated), these rules will apply to particle counts as well as concentration.

For half-life calculations involving these easy multiples, problems can often be solved quickly using the rules above. These easy multiple rules can also be used to estimate answers as a check for problems that are not easy multiples.

Practice A

1. The nucleus of carbon-14 undergoes first-order radioactive decay with a half-life of 5,730 years. In a sample of constant volume containing C-14 ,
 - a. After how many years will 75% of the original C-14 nuclei decay?
 - b. After how many half-lives will the [C-14] be 1/16th of its original concentration?
 - c. What percentage of the C-14 will be present after 3 half lives?

2. For a second-order reactant, if the first half-life is 25 seconds,
 - a. How long is the second half-life?
 - b. After how much time the reactant have one-third of its original concentration?
 - c. What percentage of the original reactant concentration will remain after 175 s?
3. For zero-order reactants,
 - a. if the first half-life for a reactant is 15 seconds, how much remains after 30. s?
 - b. If all of a different reactant is used up after 80. seconds, what is its half-life?

Half-Life Calculations for Non-Simple Multiples

These equations relate half-life and rate constants.

1	Order →	Zero	First	Second
9	Half-life and k	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{-(\ln 1/2)}{k} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

These formulas can be derived by substituting $t_{1/2}$ for t and $1/2 [A]_0$ for $[A]_t$ in each integrated rate law, but it will likely speed your work to simply memorize them. It helps to note that all of these equations solve for $t_{1/2}$ and have k in the denominator.

If a half-life is known, these equations will find values for the rate constant k without calculating slopes.

First-Order Reactants

First-order reactants are a special case. Note that in the three half-life equations above, first-order reactants are the only type for which the half-life does not depend on the original concentration of the reactant.

The integrated rate law for first-order reactants is

$$\ln[A]_t = -kt + \ln[A]_0 \quad \text{which can be re-written as} \quad \ln[A]_t - \ln[A]_0 = -kt$$

Using the rule that “the log of a quotient is the subtraction of the logs,” the second equation above can be written as

$$\ln \left[\frac{[A]_t}{[A]_0} \right] = -kt \quad \text{which can be written} \quad \boxed{\ln(\text{fraction remaining}) = -kt}$$

The four equations above are equivalent ways to write the first-order integrated rate law. First order rate calculations often involve fractions or percentages, and in such cases the *fraction* form above will be the most convenient to use.

The above equations apply to any reactants that are first-order, but the decay of radioactive nuclei is the first-order process encountered most frequently.

One difference between chemical reactions that are first order and radioactive decay (a nuclear reaction) is that for chemical reactions, the rate constant for a reactant will vary with temperature, but in radioactive decay, at the range of temperatures encountered in the earth's atmosphere or interior, the rate constant remains constant: a characteristic of the particular isotope. However, other aspects of first order half-life calculations are the same for both chemical reactions and radioactive decay.

Because calculations involving the decay of radioactive isotopes are the type of first-order kinetics encountered most often, in these lessons we cover the math of first-order in Lesson 39D as part of Nuclear Chemistry. If you are assigned calculations involving either radioactive decay *or* first-order half-lives for chemical reactions at this time, during the study of kinetics in your course, you should complete Lesson 39D now, then return to this point in these lessons.

Zero- and Second-Order Reactants

Zero- and second-order half-life calculations apply the two half-life equations:

$$\text{Zero-order half-life: } t_{1/2} = [A]_0/2k \quad \text{Second-order half-life: } t_{1/2} = 1/(k[A]_0)$$

Try the following example in your notebook.

- Q.** For a second-order reactant D, at 25°C, 50% of the original 0.180 M D remains after 3.00 minutes. Calculate
- The rate constant for the reaction.
 - [D] after 9.0 minutes.
 - The time required for [D] to reach 0.025 M.

* * * * *

Answer

- a.** WANT: **k**

Part A may be done in several ways, but the quickest is to use the half-life equation. By definition, the first half-life is the time when 50% of the original reactant remains.

DATA: $t_{1/2} = 3.00 \text{ min.}$

The equation that relates **k** and $t_{1/2}$ for second-order reactants is

$$t_{1/2} = 1/(k[A]_0)$$

Solve in symbols for the WANTED **k** first, and then find a value for **k**.

* * * * *

$$k = \frac{1}{t_{1/2} ([A]_0)} = \frac{1}{(3.00 \text{ min}) (0.180 \text{ M})} = \boxed{1.85 \text{ M}^{-1} \cdot \text{min}^{-1}}$$

* * * * *

- b.** WANT: $[D]_{9.0 \text{ min}} = [D]_t$

DATA: $t = 9.0 \text{ min}$

The equation that uses t , k from Part a and $[A]_t$ for second-order reactants is the second-order integrated rate law.

$$1/[D]_t = +kt + 1/[D]_0$$

To find $[D]_t$, find $1/[D]_t$ and then take its reciprocal.

* * * * *

Substituting the constants: $1/[D]_t = (1.85 \text{ M}^{-1} \cdot \text{min}^{-1})(t) + (1/0.180) \text{ M}^{-1}$

Substituting t : $1/[D]_{9.0 \text{ min}} = (1.85 \text{ M}^{-1} \cdot \text{min}^{-1})(9.0 \text{ min}) + 5.56 \text{ M}^{-1}$

$$= 16.7 \text{ M}^{-1} + 5.56 \text{ M}^{-1} = 22.3 \text{ M}^{-1} = 1/[D]_{9.0 \text{ min}}$$

$$[D]_{9.0 \text{ min}} = ?$$

* * * * *

$$[D]_{9.0 \text{ min}} = ? = 1/(1/[D]_{9.0 \text{ min}}) = 1/(22.3 \text{ M}^{-1}) = \boxed{0.045 \text{ M}}$$

Is this answer reasonable? Use what you know about half-lives to *estimate* the result.

* * * * *

Note that 9.0 minutes is triple the first half-life. For second-order kinetics, after triple the first half-life, 25% of the [original] remains. For $[D]$, 25% of the original 0.180 M = **0.045 M**. The “double the first half-life” rules can be a check or an alternate way to solve Part b.

* * * * *

c. WANT: t

DATA: $0.025 \text{ M} = [D]_t$

The equation that uses $[D]$ and t for this second-order reactant is

In symbols: $1/[D]_t = +kt + 1/[D]_0$

With constants: $1/[D]_t = (1.85 \text{ M}^{-1} \cdot \text{min}^{-1})(t) + 5.56 \text{ M}^{-1}$

Solving for t :

$$t = \frac{1/[D] - 1/[D]_0}{k} = \frac{40.0 \text{ M}^{-1} - 5.56 \text{ M}^{-1}}{1.85 \text{ M}^{-1} \cdot \text{min}^{-1}} = \frac{34.4 \text{ M}^{-1}}{1.85 \text{ M}^{-1} \cdot \text{min}^{-1}} = \boxed{19 \text{ min.}}$$

Practice B: If you are unsure of the answer to a part, check it before doing the next part.

- For a reaction $A \rightarrow D$ that is second order in A, $k = 6.0 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.
 - If after 150. s, $[A] = 0.200 \text{ M}$, what was the original $[A]$?
 - Calculate the first half-life of A.

2. For a catalyzed reaction $D \rightarrow E$, a graph of $[D]$ versus time results in a straight line with a slope of $-8.0 \times 10^{-6} \text{ M/s}$.
- What is the order in D?
 - Write the differential and integrated rate laws for the reaction.
 - If the initial $[D] = 0.250 \text{ M}$, calculate the half-life for the reaction.
3. By definition, the half life $t_{1/2}$ is the time required to reach $1/2 [A]_0$. Substitute $t_{1/2}$ for t and $1/2 [A]_0$ for $[A]_t$, then solve for $t_{1/2}$ in the integrated rate laws for
- The zero order law
 - The first order law
 - The second order law
- Compare these answers to the equations in Row 9 of the Kinetics Rules chart.
-

ANSWERS

Practice A

- 1a. First-order half-life is constant. If 75% has decayed, 25% remains. Half remains after one half-life, half of that half (25%) remains after two half lives. Two half lives = $2 \times 5,730 \text{ years} = 11,460 \text{ years}$.
- 1b. Half remains after one half-life, 1/4th after two, 1/8th after three, 1/16th after **four** half-lives.
- 1c. Half remains after one half-life, 1/4th after two, 1/8th after three; $1/8 = 0.125 = 12.5\%$
- 2a. For second-order reactants, double the first: **50. sec.**
- 2b. One-third of the [original] remains after double the first half-life: **after 50 seconds of reaction.**
- 2c. For second-order reactants, each successive half-life is double the preceding. If half remains after the first 25 sec, 1/4th remains 50 seconds after that, and 1/8th remains 100 seconds after that. $25+50+100 =$ after 175 seconds, $1/8\text{th} = 0.125 = 12.5\% \text{ remains}$.
- 3a. **None.** 3b. **40 sec.**

Practice B

- 1a. WANT: $[A]_0$
 DATA $150. \text{ s} = t$
 $6.0 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} = k$
 $0.200 \text{ M} = [A]_t$
 The second-order law that uses t , k , $[A]_0$ and $[A]_t$ is: $1/[A]_t = +kt + 1/[A]_0$
 Solving for the term with the WANTED symbol: $1/[A]_0 = -kt + 1/[A]_t$
 Substituting: $1/[A]_0 = -(6.0 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})(150. \text{ s}) + (1/0.200) \text{ M}^{-1}$
 $= -0.90 \text{ M}^{-1} + 5.00 \text{ M}^{-1} = 4.10 \text{ M}^{-1} = 1/[A]_0$
 $[A]_0 = 1/(1/[A]_0) = 1/(4.1 \text{ M}^{-1}) = \boxed{0.244 \text{ M}}$

1b. WANTED: $t_{1/2}$ DATA: $k = 6.0 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ The second-order equation that includes $t_{1/2}$ and k is $t_{1/2} = 1/(k[A]_0)$. $[A]_0 = 0.244 \text{ M}$

$$t_{1/2} = 1/(k[A]_0) = 1/[(6.0 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})(0.244 \text{ mol/L})] = 1/(1.464 \times 10^{-3} \text{ s}^{-1}) = 683 \text{ s} = t_{1/2}$$

2a. If concentration vs. time is linear, the reaction is zero order. 4b. $\text{rate} = k$ and $[A]_t = -kt + [A]_0$ 2c. WANTED: $t_{1/2}$ DATA: For zero-order half-life: $t_{1/2} = [D]_0/2k$ $[D]_0 = 0.250 \text{ M}$ $k = \text{minus the slope of } [D] \text{ vs. } t = +8.0 \times 10^{-6} \text{ M/sec.}$

$$\text{SOLVE: } t_{1/2} = [D]_0/2k = \frac{0.250 \text{ M}}{16 \times 10^{-6} \text{ M/sec}} = 1.6 \times 10^4 \text{ s}$$

3a. $[A]_t = -kt + [A]_0$

$$1/2[A]_0 = -k t_{1/2} + [A]_0$$

$$-1/2[A]_0 = -k t_{1/2}$$

$$t_{1/2} = [A]_0/2k$$

3b. $\ln[A]_t = -kt + \ln[A]_0$

$$\ln(1/2[A]_0) = -k t_{1/2} + \ln[A]_0$$

$$k t_{1/2} = \ln[A]_0 - \ln(1/2[A]_0)$$

$$k t_{1/2} = \ln([A]_0/1/2[A]_0)$$

$$k t_{1/2} = \ln(2)$$

$$t_{1/2} = 0.693/k$$

3c. $1/[A]_t = +kt + 1/[A]_0$

$$1/[(1/2)[A]_0] = +k t_{1/2} + 1/[A]_0$$

$$2/[A]_0 = +k t_{1/2} + 1/[A]_0$$

$$2/[A]_0 - 1/[A]_0 = +k t_{1/2}$$

$$(2-1)/[A]_0 = +k t_{1/2}$$

$$t_{1/2} = 1/k/[A]_0$$

* * * * *

Summary: Kinetics

$$1. \text{ Average Reaction Rate} = \frac{\text{change in } [A]}{\text{change in time}} = \frac{\Delta[A]}{\Delta t} = \frac{[A]_2 - [A]_1}{t_2 - t_1}$$

2. If the rate of reaction of one component is known, the rates of appearance and disappearance of other reactants and products can be calculated from the coefficients.

3. The Rate Laws

1	Order →	Zero	First	Second
2	(Differential) Rate Law	rate = $k[A]^0 = k$	rate = $k[A]^1 = k[A]$	rate = $k[A]^2$
3	If $[A]$ doubles, the rate:	Stays the same	Doubles	Quadruples
4	At double the first half-life, $[A]$ remaining is:	None	25%	33%

5	Integrated Rate Law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$ or $\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$ or $\ln(\text{fraction}) = -kt$	$\frac{1}{[A]} = +kt + \frac{1}{[A]_0}$
6	To graph a line, plot:	[A] on y, t on x	$\ln[A]$ on y, t on x	$1/[A]$ on y, t on x
7	This slope is constant:	$\Delta[A] / \Delta t$	$\Delta \ln[A] / \Delta t$	$\Delta 1/[A] / \Delta t$
8	Rate constant (k) =	Minus the slope	Minus the slope	The slope
9	Half-life and k	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{-(\ln 1/2)}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Log Rules

1. A **logarithm** is an exponent: the power to which a base number is raised.
2. A logarithm answers the question: if a number is written as a base number to a power, what is the power?
3. On a **calculator**,
 - The $\boxed{\log}$ button calculates the power of a number written as 10 to a power.
 - $\boxed{10^x}$ or $\boxed{2^{\text{nd}}}$ or $\boxed{\text{INV}}$ $\boxed{\log}$ buttons convert from "10 to a power" to a number.
4. The definition of a **log** is $\boxed{\log 10^x = x}$; the **log of 100 is 2** .
5. Knowing the log of a number, to find the number, calculate the value for 10^{\log} . This is called "taking the antilog" or "finding the inverse log."
6. $\boxed{10^{\log x} = x}$. Recite and repeat to remember: "10 to the log x equals x."
7. Knowing the log, to find the number, take the antilog. On a calculator,
 - input the log value, then press $\boxed{\text{INV}}$ $\boxed{\text{LOG}}$; or $\boxed{2^{\text{nd}}}$ $\boxed{\text{LOG}}$; or
 - Input the log value, then press $\boxed{10^x}$. A log is simply an exponent.
8. **Checking log answers:** when a number is written in scientific notation, its power of 10 must agree with its base 10 **logarithm** within ± 1 .
9. The symbol e is an abbreviation for a number that has special properties: **2.718...**
10. The **ln (natural log)** function answers the question: if a number is written as e to a power, what is the power?
11. Knowing the **ln**, to find the number, take the antilog:
 - input the log, then press $\boxed{\text{INV}}$ $\boxed{\ln}$; or
 - Input the log, then press $\boxed{e^x}$. An ln is simply an exponent of e .
12. When you encounter log calculations, it helps to write:

$\log 10^x = x$ and $10^{\log x} = x$. "The log of 10 to the x is x; 10 to the log x is x."

$\ln e^x = x$ and $e^{\ln x} = x$. Write the base 10 rules, then substitute e and \ln .

13. $2.303 \log(x) = \ln(x)$

Reciprocal Rules

- Three equivalent ways of representing the **reciprocal of X** are: $\frac{1}{X} = 1/X = X^{-1}$
- The reciprocal of $1/X$ is X . The reciprocal of the reciprocal of X is X .
In equation format: $\frac{1}{\frac{1}{X}} = 1/(1/X) = (X^{-1})^{-1} = X$
- To convert a reciprocal to a number, using a calculator, either divide the number into one or use the reciprocal $\boxed{1/x \text{ or } x^{-1}}$ key.
- If you know the value of the reciprocal of a number, and you want the number, take the reciprocal of the reciprocal value.
- To take the reciprocal of a *unit* of measurement, change the sign of its exponent.
- To take the reciprocal of a number to a power, change the sign of the power.
- To multiply exponentials, add the exponents. To take an exponential to a power, multiply the exponents.
- To take the reciprocal of a fraction, invert the fraction.
- When a term has *two* fraction lines (either _____ or /), *separate* the terms that are *fractions*. To do so, apply these steps in this order.
 - If a term has a fraction in the *denominator*, separate the terms into a *reciprocal* of the fraction ($1/\text{fraction in the denominator}$) multiplied by the remaining terms.
 - If there is a fraction in the *numerator*, *separate* that fraction from the other terms in the numerator or denominator.
 - To simplify fractions, invert reciprocal *fractions*, cancel units, and multiply terms.

$$\frac{\frac{1}{\frac{B}{C}}}{C} = 1/(B/C) = (B \bullet C^{-1})^{-1} = B^{-1} \bullet C = C/B$$

#