# Kinetics and Integrated Rate Laws

## Skill Builder

Here is an excerpt from the AP Equations and Constants Sheet. The boxes shaded in the table below reflect these 3 equations. You will only encounter zero, first and second order situations on the AP Exam.

**KINETICS**

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

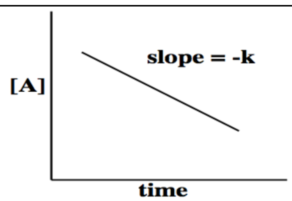
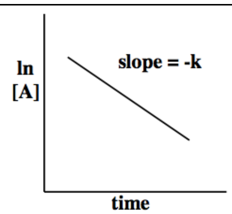
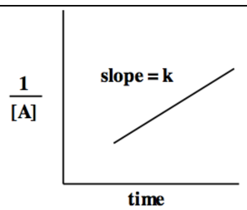
$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

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

$k$ = rate constant

$t$ = time

$t_{1/2}$ = half-life

| Summary Table | | | |
|---|---|---|---|
| | Zero Order | First Order | Second Order |
| Rate Law Expression | Rate = k $[A]^0$ | Rate = k $[A]^1$ | Rate = k $[A]^2$ |
| Integrated rate law | $[A]-[A]_0 = -kt$ | $\ln[A]-\ln[A]_0 = -kt$ | $1/[A]-1/[A]_0 = kt$ |
| Linearized integrated rate law | $[A] = -kt + [A]_0$<br>y = mx + b | $\ln[A] = -kt + \ln[A]_0$<br>y = mx + b | $1/[A] = kt + 1/[A]_0$<br>y = mx + b |
| Graph |  |  | <br>(positive slope!) |
| *Memorization Tip | **C** | **L** | **R** |
| Half life Equations | $t_{1/2} = [A]_0/2k$ | $t_{1/2} = 0.693/k$<br>(no $[A]_0$ in formula!) | $t_{1/2} = 1/k[A]_0$ |

* Graphing integrated rate laws should be **<u>CLR</u>** to you now! **C** (concentration vs time), **L** (ln of concentrations vs time), and **R** (reciprocal of concentration vs time)

**Type 1: Analyzing Graphs**

Be prepared to deal with graphs in one of these ways:

(1) Choosing between different graphs to determine order.
(2) Given the order, indicate what the axis must be labeled.
(3) Given the order of the reaction, sketch the graph.

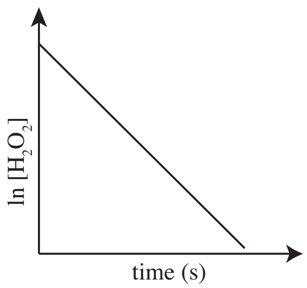
*Problem Solving Tips*

- Use the clues given on the axis of straight lines or clues of the graph itself, such as a positive or negative slope, to figure out the order of the reaction.
- When given different graphs with different y-axes, the one with the straightest line represents the appropriate relationship. Look at the y-axis and remember CLR!
- The rate constant, *k*, is always positive and is the absolute value of the slope of the straight line. The units are based on the order and the specific time unit described.

**PRACTICE**

For each of the graphs below, (a) determine the order, (b) write the corresponding rate law expression and (c) units of *k*.

1.

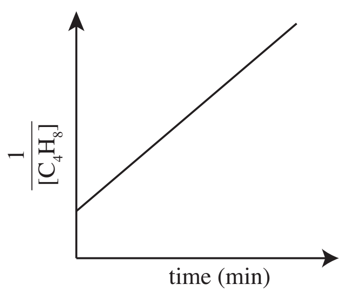



a)

b)

c)

2.



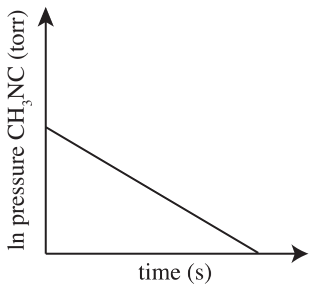

a)

b)

c)

3.

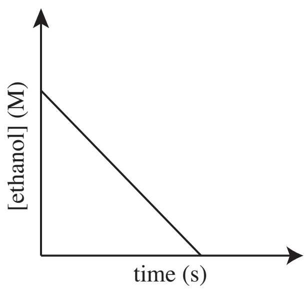



a)

b)

c)

4.




a)

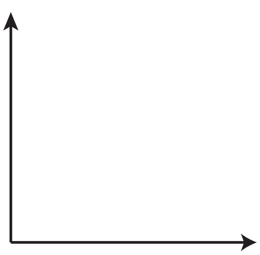
b)

c)

From the experiment description, (a) label the axes and sketch the line, (b) write the rate law expression, and (c) the integrated rate equation

5. The absorbance at 635 nm was measured every 10 seconds for a first order reaction.

a)

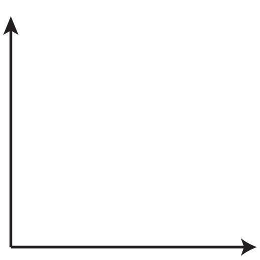


b)

c)

6. A pressure sensor is used to measure the production of $NO_2(g)$ during a second order reaction. Pressure readings are collected every 5 minutes.

a)

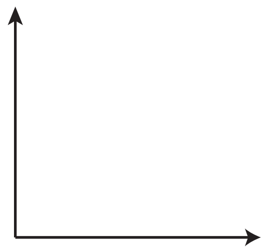


b)

c)

7. The decomposition of ammonia is a zero order reaction. Concentrations of ammonia are recorded every 10 minutes.

a)

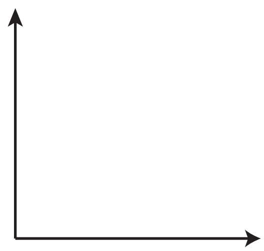


b)

c)

8. Crystal violet, a purple compound, turns colorless with hydroxide ion in a first order reaction. The absorbance of blue light was measured every 5 seconds.

a)

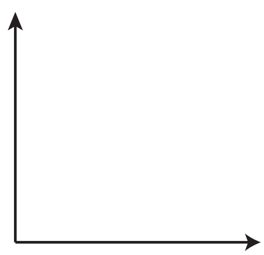


b)

c)

9. The reaction $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$ is first order with respect to $N_2O_5$. Using the axes, sketch the graph that represents the change in $[N_2O_5]$ over time as the reaction proceeds.

a)



b)

c)

**Type 2: Calculations Using Integrated Rate Laws**

Integrated rate laws can be used to solve for a variety of variables such as reaction time, initial concentration, concentration remaining after a particular amount of time passes, and rate constant, *k*.

*Problem Solving Tips*

- Scan the problem for the stated reaction order, then select the appropriate integrated equation found on the AP equation sheet.
- Watch for units of time. They might be hidden in a table heading or in the units of *k*.

10. What is the value of the rate constant for a second order reaction if the reactant concentration drops from 0.657 *M* to 0.0981 M in 17.0 s ? Include appropriate units.

11. $$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

The decomposition of $H_2O_2$ to water and oxygen follows first order kinetics with a rate constant of 0.0410 $min^{-1}$. Calculate the $[H_2O_2]$ after 10 minutes if $[H_2O_2]_0$ is 0.200 *M*.

12. The rate constant for a second order reaction is 0.13 $M^{-1}s^{-1}$. If the initial concentration of reactant is 0.26 mol/L, how long will it take for the concentration to decrease to 0.13 mol/L?

**Type 3: Half Lives**

Half-life is the time it takes for a reaction to use up half of its reactant concentration. Recognize that first order reactions have a **constant half-life**; regardless of the initial concentration of reactant, the time to reduce by half is the same. The same cannot be said for zero and second order; notice the inclusion of $[A]_O$ in their half-life equations.

*Problem Solving Tips*

- The first order half-life equation, $t_{1/2} = 0.693/k$, will commonly be used to solve for the rate constant, $k$. Then, that $k$ can then be used to solve other integrated rate law problems.
- If presented with a time and concentration data table, before you graph the data to determine order, look for a consistent half-life; that's indicative of a first order reaction and will save you graphing time.

13. Determine the rate constant of a first order process that has a half-life of 225 s.

14. The half-life of a first order reaction is 13 min. If the initial concentration of reactant is 0.085 *M*, how long does it take for the concentration to drop to 0.055 *M*?

15. The reaction given is first order: $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$ A solution originally at 0.600 *M* $H_2O_2$ is found to be 0.075 *M* after 54 min. What is the half-life of the reaction?

16. The reaction $A \rightarrow B$ is run over 20.0 seconds with the changes in concentration data provided in the table below.

| Time(s) | [A](M) |
|---|---|
| 0.00 | 1.60 |
| 5.0 | 0.80 |
| 10.0 | 0.40 |
| 15.0 | 0.20 |
| 20.0 | 0.10 |

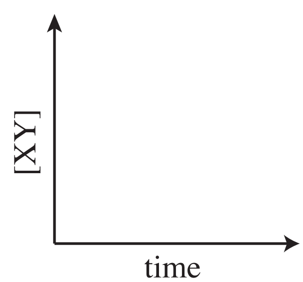
a) What is the half life of the given reaction?

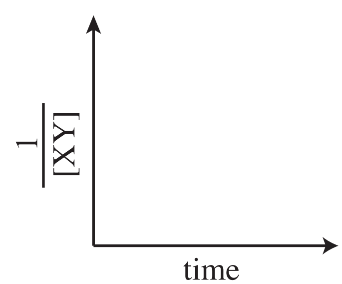
b) Based on the half-life, what can be assumed about the order of the given reaction?

## REFLECTION QUESTIONS

17. Explain the difference between a rate law expression and an integrated rate law equation. What variables are related in each?

18. If a plot of ln [XY] vs. time is linear, sketch the shapes of the graphs that would be expected for:



19. Why is it acceptable to plot absorbance or pressure values on the y-axis instead of concentration when solving these types of problems?

20. The data below are for the first order decomposition of hydrogen peroxide. Use the data to show what is meant by "first order reactions have a constant half-life."

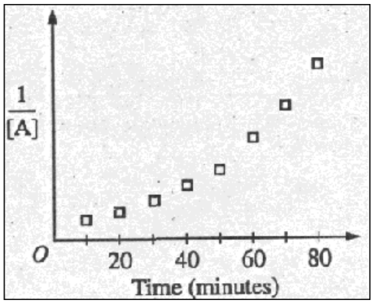
| **Time (h)** | **[$H_2O_2$]** |
|---|---|
| 0 | 1.0 M |
| 54 | 0.83 M |
| 200 | 0.50 M |
| 320 | 0.33 M |
| 400 | 0.25 M |
| 567 | 0.14 M |

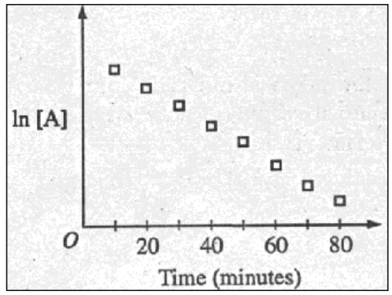
 

# AP Questions

**1998**

Data for the chemical reaction $2A \rightarrow B + C$ were collected by measuring the concentration of A at 10-minute intervals for 80 minutes. The following graphs were generated from analysis of data.



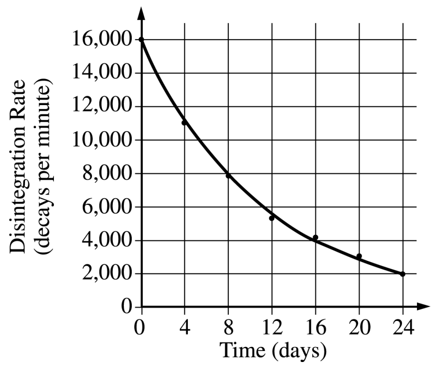

Use the information in the graphs above to answer the following.

(a) Write the rate-law expression for the reaction. Justify your answer.

(b) Describe how to determine the value of the rate constant for the reaction.

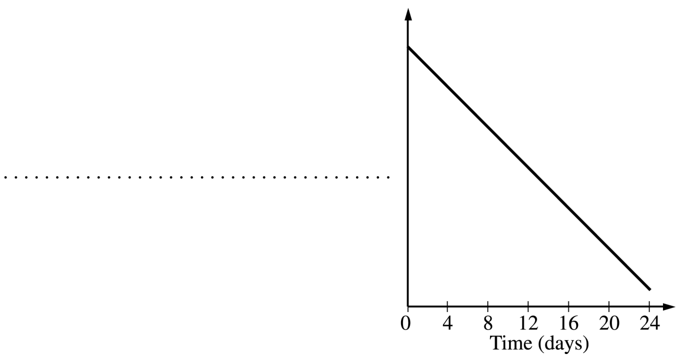
**2003B #8**

The radioactivity of a sample of I-131 was measured. The data collected are plotted on the graph below.




(a) Determine the half-life, $t_{1/2}$ , of I-131 using the graph above.

(b) The data can be used to show that the decay of I-131 is a first-order reaction, as indicated on the graph below.




(i) Label the vertical axis of the graph above.

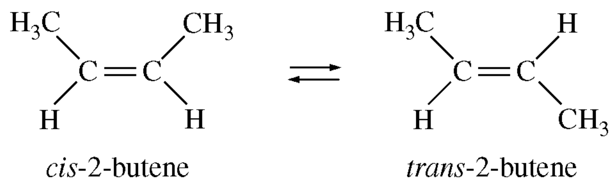
(ii) What are the units of the rate constant, $k$, for the decay reaction?

(iii) Explain how the half-life of I-131 can be calculated using the slope of the line plotted on the graph.

(c) Compare the value of the half-life of I-131 at 25°C to its value at 50°C.

**2014 #7**



The half-life ($t_{1/2}$) of the catalyzed isomerization of *cis*-2-butene gas to produce *trans*-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

| Trial | Initial $P_{cis\text{-2-butene}}$ | $V$ (L) | $T$ (K) | $t_{1/2}$ (s) |
|---|---|---|---|---|
| 1 | 300. | 2.00 | 350. | 100. |
| 2 | 600. | 2.00 | 350. | 100. |
| 3 | 300. | 4.00 | 350. | 100. |
| 4 | 300. | 2.00 | 365 | 50. |

(a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

(b) Calculate the rate constant, $k$, for the reaction at 350. K. Include appropriate units with your answer.

(c) Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.

(d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.