

Kinetics and Integrated Rate Laws

Skill Builder -- KEY

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

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

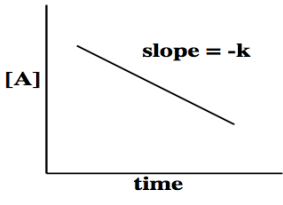
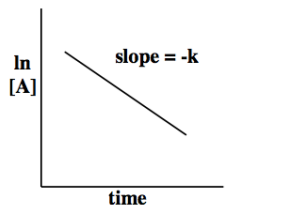
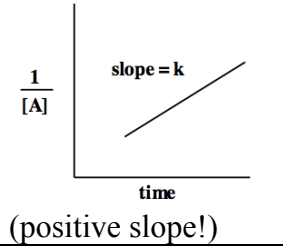
$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

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

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	$[A] = -kt + [A]_0$ $y = mx + b$	$\ln[A] = -kt + \ln[A]_0$ $y = mx + b$	$1/[A] = kt + 1/[A]_0$ $y = mx + b$
Graph			
*Memorization Tip	C	L	R
Half life Equations	$t_{1/2} = [A]_0/2k$	$t_{1/2} = 0.693/k$ (no $[A]_0$ in formula!)	$t_{1/2} = 1/k[A]_0$

* Graphing integrated rate laws should be **CLR** 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.

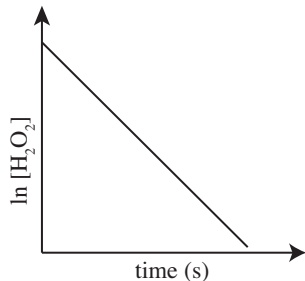
Problem Solving Tips

- 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

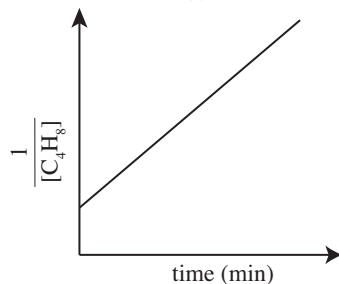
For each of the graphs below, (a) determine the order, (b) write the corresponding rate law expression and (c) units of k .

(1)



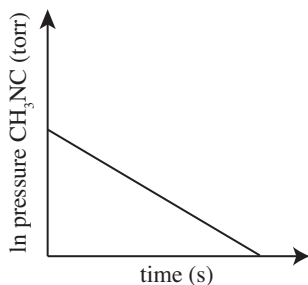
- a) 1st order
- b) $\ln[\text{H}_2\text{O}_2] - \ln[\text{H}_2\text{O}_2]_0 = -kt$
- c) 1 s^{-1}

(2)



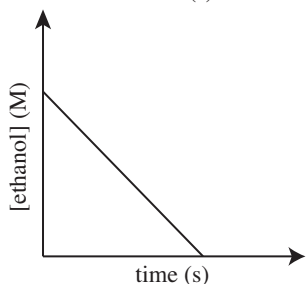
- a) 2nd order
- b) $1/[\text{C}_4\text{H}_8] - 1/[\text{C}_4\text{H}_8]_0 = kt$
- c) $1 \text{ min}^{-1} \text{ M}^{-1}$

(3)



- a) 1st order
 b) $\ln(P_{\text{CH}_3\text{NC}}) - \ln(P_{\text{CH}_3\text{NC}})_0 = -kt$
 c) s^{-1}

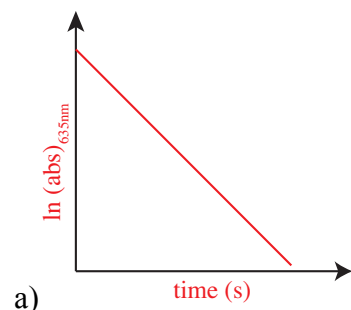
(4)



- a) Zero order
 b) $[\text{ethanol}] - [\text{ethanol}]_0 = -kt$
 c) M/s

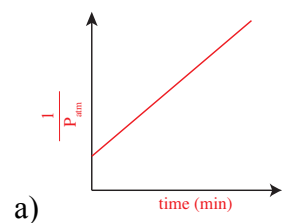
From the experiment description, (a) label the axes and sketch the line, (b) write the rate law expression, and (c) the integrated rate equation

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



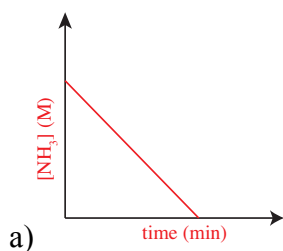
- b) $\text{rate} = k (\text{abs})^1$
 c) $\ln[\text{abs}] - \ln[\text{abs}]_0 = -kt$

(6) A pressure sensor is used to measure the production of $\text{NO}_2(\text{g})$ during a second order reaction. Pressure readings are collected every 5 minutes.



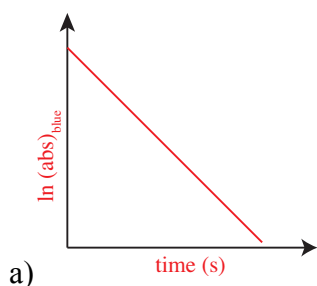
- b) $\text{rate} = k (P_{\text{atm}})^2$
 c) $1/(P_{\text{atm}}) - 1/(P_{\text{atm}})_0 = kt$

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



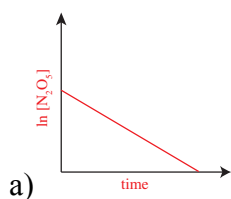
b) $\text{Rate} = k [\text{NH}_3]_0$
 c) $[\text{NH}_3] - [\text{NH}_3]_0 = -kt$

- (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.



b) $\text{Rate} = k (\text{abs})^1$
 c) $\ln(\text{abs}) - \ln(\text{abs})_0 = -kt$

- (9) The reaction $2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2$ is first order with respect to N_2O_5 . Using the axes, sketch the graph that represents the change in $[\text{N}_2\text{O}_5]$ over time as the reaction proceeds.



b) $\text{Rate} = k [\text{N}_2\text{O}_5]^1$
 c) $\ln[\text{N}_2\text{O}_5] - \ln[\text{N}_2\text{O}_5]_0 = -kt$

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.

$$1/[A]-1/[A]_0 = kt$$

$$1/[0.0981]-1/[0.657]_0 = k(17.0s)$$

$$k = 0.510 \text{ 1/M s}$$

- (11)
$$\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$$

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 $[\text{H}_2\text{O}_2]$ after 10 minutes if $[\text{H}_2\text{O}_2]_0$ is 0.200 M.

$$\ln[\text{H}_2\text{O}_2] - \ln[\text{H}_2\text{O}_2]_0 = -kt$$

$$\ln[\text{H}_2\text{O}_2] - \ln[0.200]_0 = (-0.0410 \text{ min}^{-1})(10 \text{ min})$$

$$[\text{H}_2\text{O}_2] = 0.132 \text{ M}$$

- (12) The rate constant for a second order reaction is $0.13 \text{ M}^{-1}\text{s}^{-1}$. 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?

$$1/[A]-1/[A]_0 = kt$$

$$1/[0.13]-1/[0.26]_0 = (0.13 \text{ M}^{-1}\text{s}^{-1}) t$$

$$t = 30. \text{ seconds}$$

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 $[A]_0$ 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.

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

$$225\text{s} = 0.693/k$$

$$k = 0.00308 \text{ s}^{-1}$$

- (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?

First find k .

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

$$13 \text{ min} = 0.693/k$$

$$k = 0.0533 \text{ min}^{-1}$$

Then find time using the integrated rate law.

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

$$\ln[0.055] - \ln[0.085]_0 = -0.0533t$$

$$t = 8.17 \text{ min}$$

- (15) The reaction given is first order: $2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$ 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?

Find k using provided info.

$$\ln[\text{H}_2\text{O}_2] - \ln[\text{H}_2\text{O}_2]_0 = -kt$$

$$\ln(0.075) - \ln(0.600) = -k(54 \text{ min})$$

$$k = 0.0385 \text{ min}^{-1}$$

Use k to find half-life:

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

$$t_{1/2} = 0.693/0.0385 \text{ min}^{-1}$$

$$t_{1/2} = 18.0 \text{ min}$$

- (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?

The half-life is 5 seconds. Five seconds pass every time the concentration of A is cut in half.

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

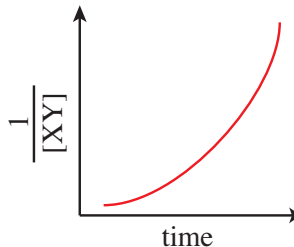
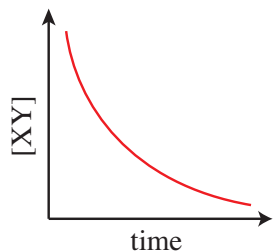
A constant half-life is indicative of 1st order reaction.

REFLECTION QUESTIONS

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

The rate law expression is a general equation that allows us to relate concentration and *rate* data. Once the order and value of k have been determined it allows us to calculate the initial rate of the reaction at various concentrations. The integrated rate law equation relates concentration and *time* data. It allows us to determine the concentration after an amount of time has passed, or the time required for the concentration to change by a certain amount.

- (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?

From Beer's law we know that absorbance is directly proportional to concentration
($A=abc$)

Pressure is proportional to molarity, as can be seen by the rearrangement of the ideal gas law.

$$PV=nRT$$

$$P = (n/V) RT$$

Pressure \approx Molarity

- (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."

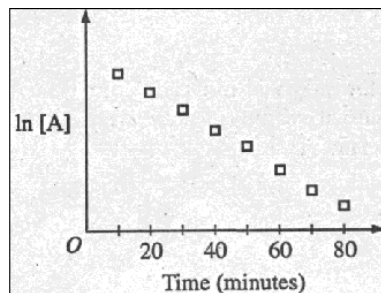
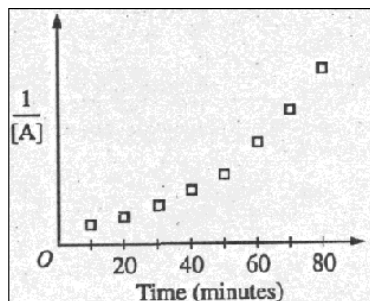
Time (h)	[H ₂ O ₂]
0	1.0 M
54	0.83 M
200	0.50 M
320	0.33 M
400	0.25 M
567	0.14 M

There are two instances in the table where the concentration decreases by half (from 1 M to 0.5 M and from 0.5 M to 0.25 M) and both those instances take 200 hours or occur. A consistent half-life is indicative of a 1st order reaction.

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.

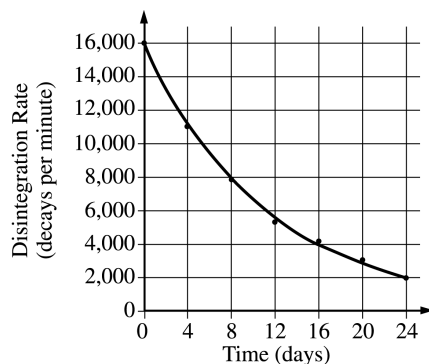
<p>Rate = $k[A]^1$. Since the graph of $\ln [A]$ vs. time is linear, it must be a first order reaction.</p>	<p>1 point for the equation with justification</p>
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(b) Describe how to determine the value of the rate constant for the reaction.

<p> $\ln[A] = -kt + \ln[A]_0$ $y = mx + b$ The linearized version of the rate law shows that the slope of the line is equal to $-k$. So, find the slope of the line and then change its sign. </p>	<p>1 point for indicating that it is the positive value of the slope of the line</p>
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2003B #8

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

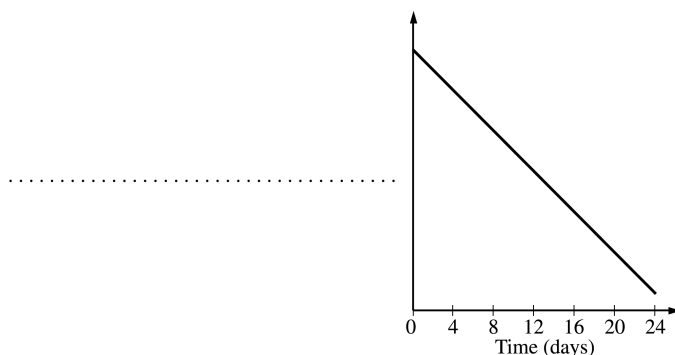


- (a) Determine the half-life, $t_{1/2}$, of I-131 using the graph above.

This graph shows a half-life of 8 days. That is the time required for the disintegration rate to fall from 16,000 to one half of its initial value 8,000.

1 point for half-life

- (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.

The label on the y- axis should be $\ln [I-131]$

1 point for correct label on y-axis

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

From the graph the units on the rate constant are days^{-1}

1 point for correct units

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

The slope of the line is $-k$. The slope is negative, so k is a positive number. The half-life can then be calculated using the relationship $t_{1/2} = 0.693/k$.

1 point for indicating slope is k

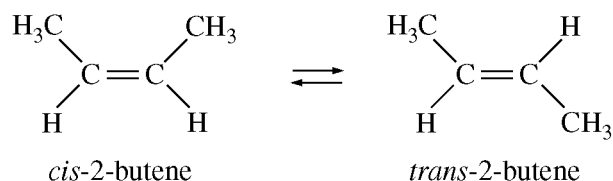
1 point for half-life equation

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

The half-life will be the same at the different temperatures. The half-life of a nuclear decay process is independent of temperature.

1 point

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 $P_{\text{cis-2-butene}}$	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.

For a first-order reaction, the half-life is independent of reactant concentration (or pressure) at constant T, as shown in trials 1, 2, and 3.

1 point is earned for a correct explanation.

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

$$\begin{aligned}
 t_{1/2} &= 0.693/k \\
 100 \text{ s} &= 0.693/k \\
 k &= 0.00693 \text{ s}^{-1}
 \end{aligned}$$

1 point is earned for correct numerical answer with units.

- (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.

The initial rate in trial 1 is less than that in trial 2 because $\text{rate} = k [\text{cis-2-butene}]$ or $\text{rate} = k P_{\text{cis-2-butene}}$ (with reference to values from both trials).

OR

because the initial concentration of *cis*-2-butene in trial 1 is less than that in trial 2 and k is constant

1 point is earned for the correct answer with justification.

- (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.

The temperature is higher in trial 4, meaning that the KE_{avg} of the molecules is greater. Consequently, in this trial a greater fraction of collisions has sufficient energy to overcome the activation energy barrier, thus the rate is greater.	1 point is earned for a correct answer with justification.
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