

Sections 15.3 and 15.4
Rate Laws and Concentration Changes over Time

Rate Laws and Concentration Changes over Time

In these sections...

- a. Format of a rate law
- b. Order of a reaction
- c. Determining a rate law using initial rates
- d. Using integrated rate laws
- e. Graphical determination of the rate law
- f. Half-life
- g. Radioactive decay

Rate Laws: Mathematically relating concentration and rates

Concentration Dependence

- It makes sense that as concentration increases, the number of collisions per second will increase
- Therefore, in general, as concentration increases, rate increases
- But, it depends on which collisions control the rate
- So, you *can't* predict concentration dependence: it must be measured experimentally

Rate Laws (also called Rate Equations)

For the reaction: $\text{NO}_2 \rightarrow \text{NO} + \frac{1}{2} \text{O}_2$

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

Rate Laws: Examples

first order reaction

For the reaction: $2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO} + \text{O}_2$

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

second order reaction

For the reaction: $\text{NO}_2 \rightarrow \text{NO} + \frac{1}{2} \text{O}_2$

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

first order in CO and in NO₂; second order overall

For the reaction: $\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$

$$\text{Rate} = k[\text{CO}][\text{NO}_2]$$

What is the overall order for a reaction with
rate = $k[\text{CO}_2]^2[\text{H}^+]$

Determining a Rate Law

Determining the rate law must be done by experiment; the reaction equation does **not** tell you the rate law

Two methods: Initial Rates and the Graphical Method

Method of Initial Rates

- Measure the rate of the reaction right at the start.
- Vary the starting concentrations
- Compare initial rates to initial concentrations

Determining a Rate Law: Initial Rate Method

- Isolation of variables: Vary only one concentration at a time and keep temperature constant
- If concentration doubles and:
 - Rate does not change, then zero order
 - Rate doubles, then first order
 - Rate quadruples, then second order
- General Rule:

$$\frac{\text{Rate in experiment 2}}{\text{Rate in experiment 1}} = \frac{[A_2]^n}{[A_1]^n} = \left(\frac{[A_2]}{[A_1]}\right)^n$$

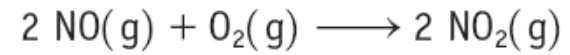
Initial Rate Method: Example 1



	$[\text{NH}_4\text{NCO}]_{\text{initial}}$	initial rate
Experiment 1	0.14 M	$2.2 \times 10^{-4} \text{ mol/L} \cdot \text{min}$
Experiment 2	0.28 M	$8.9 \times 10^{-4} \text{ mol/L} \cdot \text{min}$

What is the rate law?

Initial Rate Method: Multiple Reactants



Experiment	Initial Concentrations (mol/L)		Initial Rate (mol/L · s)
	[NO]	[O ₂]	
1	0.020	0.010	0.028
2	0.020	0.020	0.057
3	0.020	0.040	0.114
4	0.040	0.020	0.227
5	0.010	0.020	0.014

Concentration-Time Relationships: A = reactant

Reaction Order	Integrated Rate Law	Rearranged Rate Law	Straight-Line Plot
Zero order	$[A]_t = [A]_0 - kt$	$[A]_t = -kt + [A]_0$ $y = mx + b$	$y = [A]_t$ $x = t$ slope = $-k$
First order	$\ln \frac{[A]_t}{[A]_0} = -kt$ <hr/> $[A]_t = [A]_0 e^{-kt}$	$\ln[A]_t = -kt + \ln[A]_0$ $y = mx + b$	$y = \ln[A]_t$ $x = t$ slope = $-k$
Second order	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ $y = mx + b$	$y = 1/[A]_t$ $x = t$ slope = k

Graphical Method for Determining Rate Laws

How it works: $A = \text{reactant}$

1. Collect $[A]$ over an interval of times.
2. Make plots of

$[A]$ vs. time

$\ln[A]$ vs. time

$1/A$ vs. time

Only one will be linear. That tells you the reaction order.

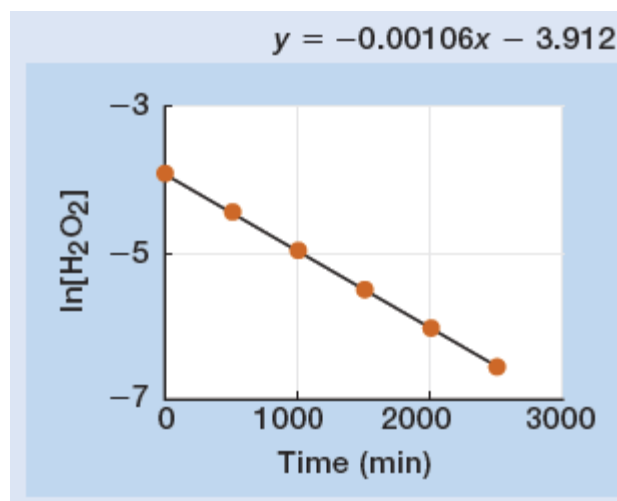
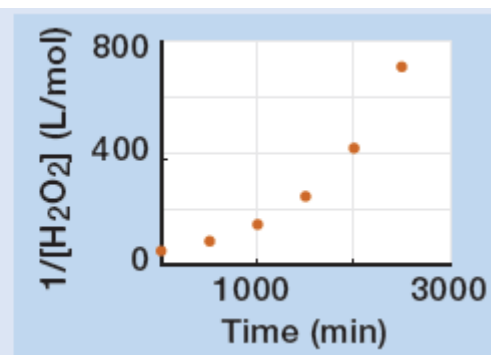
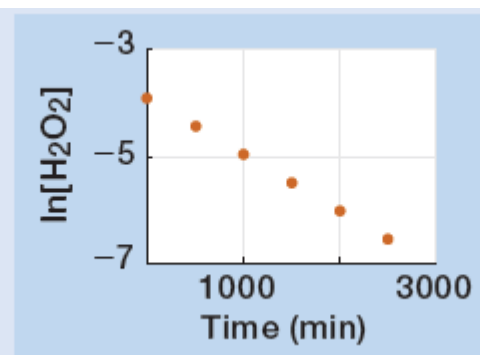
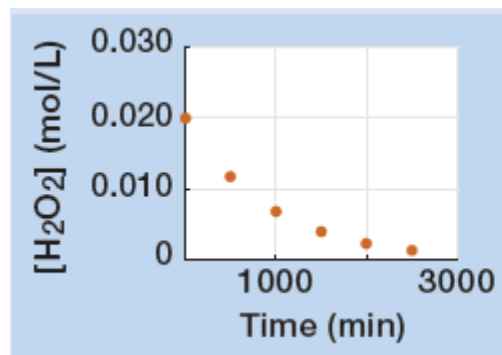
The slope of that linear plot is the rate constant (its absolute value).

Graphical Method for Determining Rate Laws

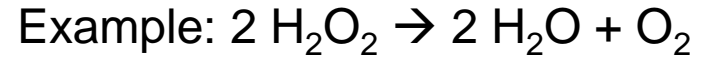
Concentration versus time data have been collected for the decomposition of H_2O_2 at 300 K.



$[\text{H}_2\text{O}_2]$ (mol/L)	Time (min)
0.0200	0
0.0118	500.
0.00693	1000.
0.00408	1500.
0.00240	2000.
0.00141	2500.

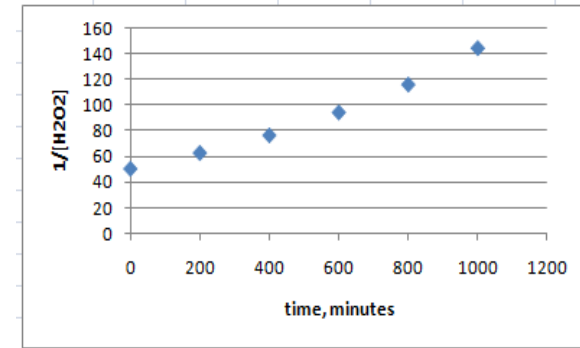
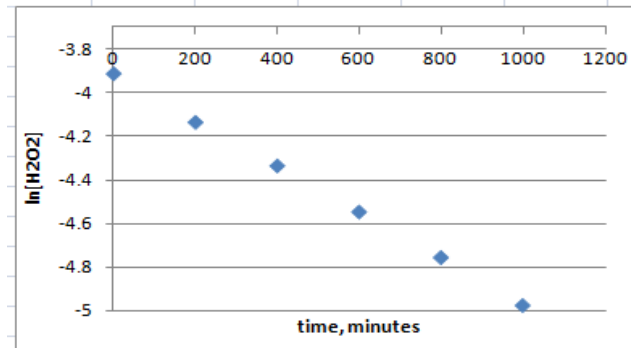
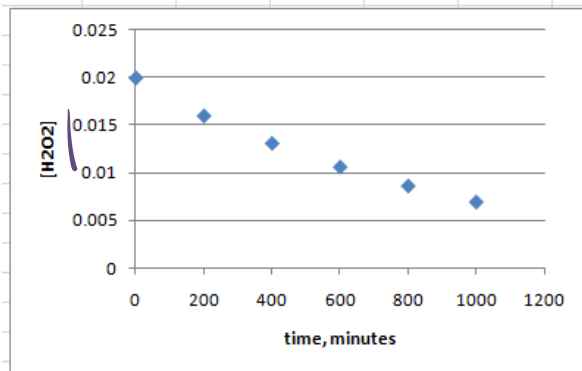


Graphical Method for Determining Rate Laws: Finding the Order

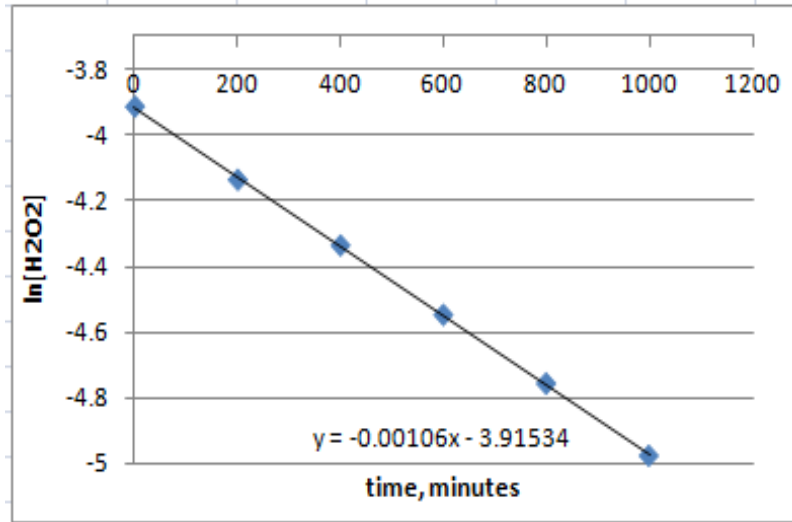


<u>Time(min)</u>	<u>[H₂O₂](mol/L)</u>
0	0.0200
200	0.0160
400	0.0131
600	0.0106
800	0.0086
1000	0.0069

Book1				
	A	B	C	D
1	time	[H2O2]	ln[H2O2]	1/[H2O2]
2	0	0.02	-3.91202	50
3	200	0.016	-4.13517	62.5
4	400	0.0131	-4.33514	76.33588
5	600	0.0106	-4.5469	94.33962
6	800	0.0086	-4.75599	116.2791
7	1000	0.0069	-4.97623	144.9275



Graphical Method for Determining Rate Laws: Finding k



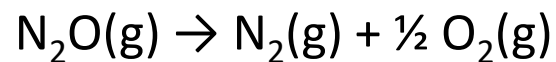
Using Concentration-Time Equations: General Idea

Table 14.4.1 Integrated Rate Laws for Reactions of Type $A \rightarrow \text{Products}$

Reaction Order	Rate Law	Integrated Rate Law
Zero order	$\text{rate} = k [A]^0 = k$	$[A]_t = [A]_0 - kt$ (14.1)
First order	$\text{rate} = k[A]$	$\ln \frac{[A]_t}{[A]_0} = -kt$ (14.2)
Second order	$\text{rate} = k[A]^2$	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$ (14.3)

Using Concentration-Time Equations: Example 1

The decomposition of nitrous oxide at 565 °C



is second order in N_2O with a rate constant of $1.10 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$.
If an experiment is performed where the initial concentration of N_2O is 0.108 M, what is the N_2O concentration after 1250 seconds?

Second order

$$\text{rate} = k[\text{A}]^2$$

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

Using Concentration-Time Equations: Example 2

The isomerization of methyl isonitrile to acetonitrile in the gas phase at 250 °C is first order ($k = 3.00 \times 10^{-3} \text{ s}^{-1}$).



How much time is required for the concentration of CH_3NC to drop to 0.0142 M if its initial concentration was 0.107 M?

First order

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

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

Using Concentration-Time Equations: Example 3

The isomerization of methyl isonitrile to acetonitrile in the gas phase at 250 °C is first order ($k = 3.00 \times 10^{-3} \text{ s}^{-1}$).



How much time is required for 90.0% of the CH_3NC initially present in a reaction flask to be converted to product at 250 °C?

First order

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

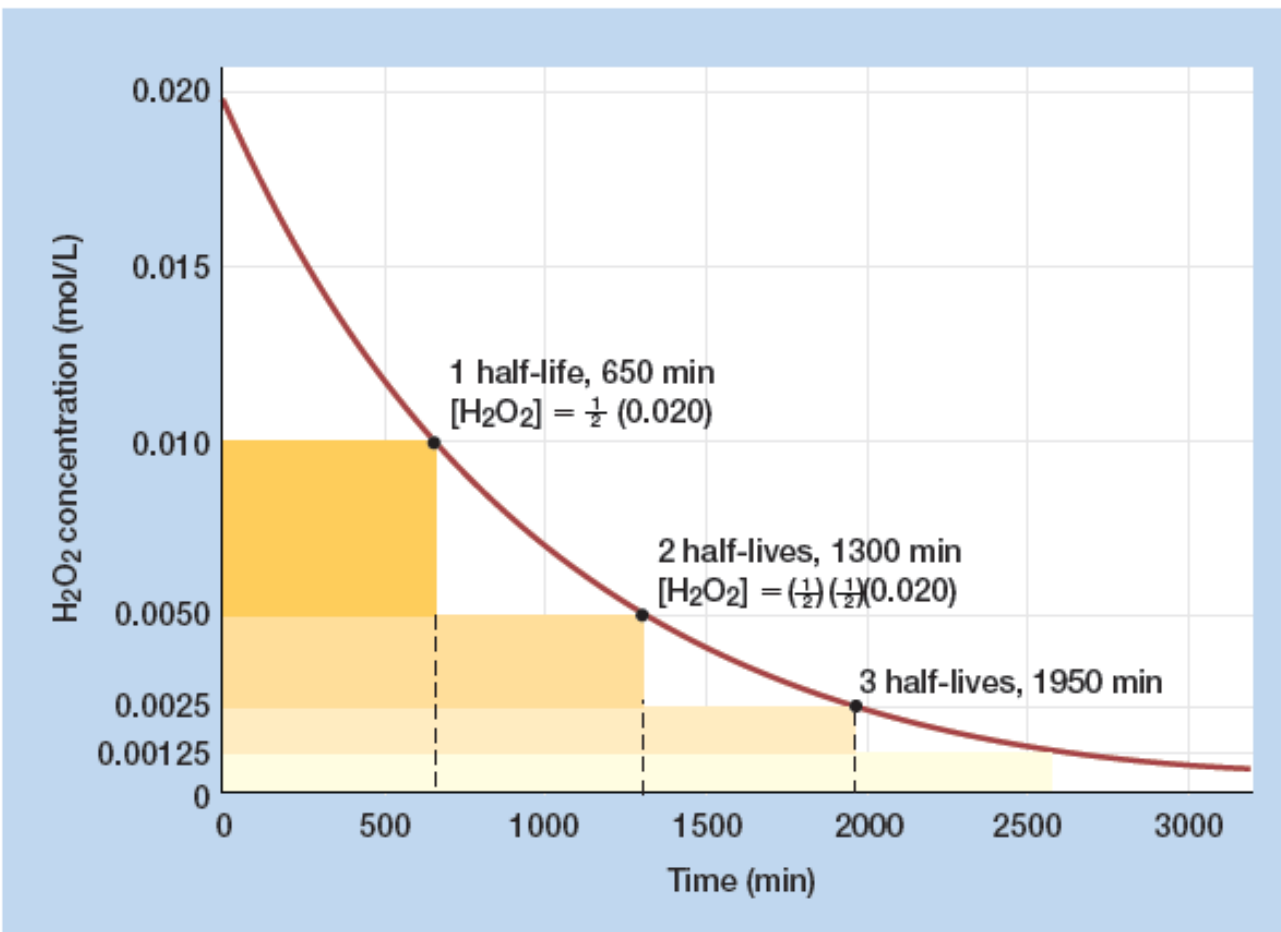
$$[A]_t = [A]_0 e^{-kt}$$

Half-Life

The time required for the reactant concentration to decrease to $\frac{1}{2}$ its original concentration.



Number of half-lives passed	1	2	3	4	x
Fraction of reactant remaining	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$(\frac{1}{2})^x$



Concentration–time data for the decomposition of H_2O_2

Half-Life Equations

Table 14.4.3 Half-Life Equations for Reactions of Type A → Products

Reaction Order	Integrated Rate Law	Substitute $t = t_{1/2}$ and $[A]_t = \frac{1}{2}[A]_0$	Half-Life Equation
Zero order	$[A]_t = [A]_0 - kt$	$\frac{1}{2}[A]_0 = [A]_0 - k(t_{1/2})$	$t_{1/2} = \frac{[A]_0}{2k}$ (14.4)
First order	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\ln(\frac{1}{2}[A]_0) = \ln[A]_0 - kt_{1/2}$	$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$ (14.5)
Second order	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$	$\frac{1}{(\frac{1}{2}[A]_0)} = \frac{1}{[A]_0} + k(t_{1/2})$	$t_{1/2} = \frac{1}{k[A]_0}$ (14.6)

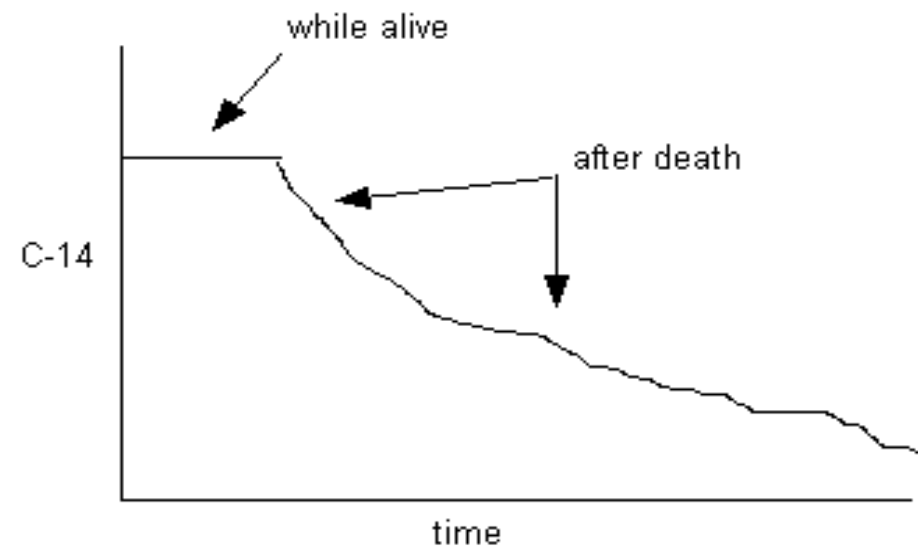
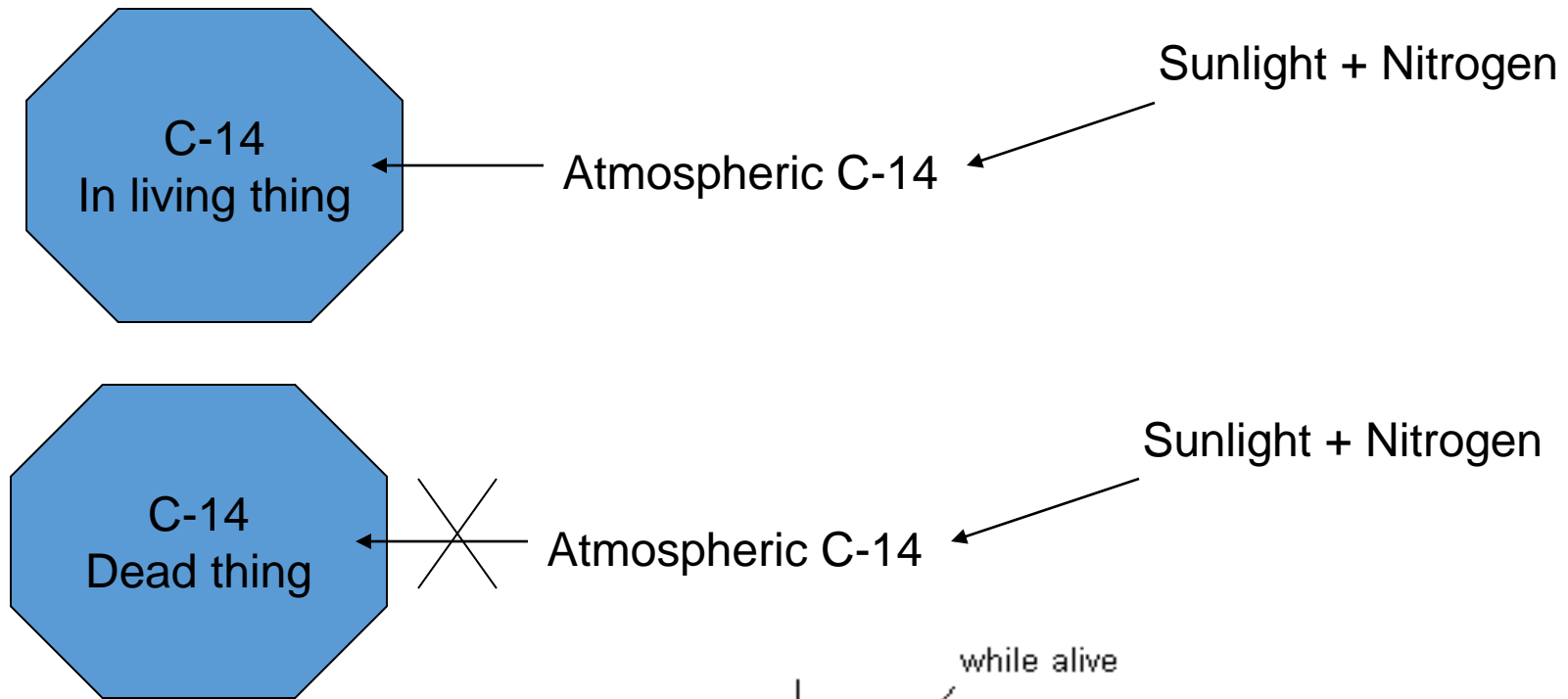
Radioactive Decay

All radioisotopes decay via first order reactions. Instead of concentrations, amounts are used.

$$\ln \frac{N_t}{N_o} = -kt \quad N_t = N_o e^{-kt}$$

Measured as radioactive activity, in counts per minute (cpm) using a detector.

Radioactive Decay: Carbon Dating



Isotopes of C:

^{12}C = 99% stable

^{13}C = ~1% stable

^{14}C = very small, unstable

Radioactive Carbon Dating: Example

The Carbon-14 activity of an artifact in a burial site is found to be 8.6 counts per minute per gram. Living material has an activity of 12.3 counts per minute per gram. How long ago did the artifact die? $t_{1/2} = 5730$ years

$$\ln \frac{N_t}{N_o} = -kt \quad N_t = N_o e^{-kt}$$