

Application of Integrated Rate Laws:

28. Zero-Order Reactions.

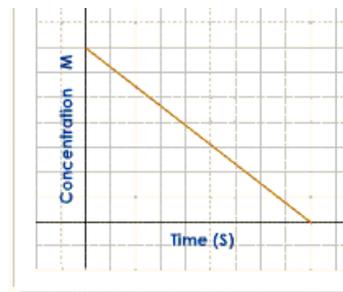
- a. Write a rate law equation for a zero-order reaction. Define each term in the equation.

Rate = $k [R]^0$ rate = rate constant x concentration of reactant to zero power so the $[R]^0 = 1$ and thus the rate is equal to the rate constant. The rate is independent of the concentration of the reactant.

- b. Write the integrated rate law equation for a zero-order reaction. Define each term in the equation. Since the rate is constant the graph already yields a straight line – no calculus necessary.

$[R]_t - [R]_0 = -kt$ If we graph reactant concentration as a function of time, the line will be straight. The slope of that line is the rate – a constant (straight line = constant slope)

- c. Sketch the graph that yields a linear relationship for a zero-order reaction. Label the axes.



- d. Describe how to determine whether a reaction is zero-order

Experiment – changing the initial concentration of reactant (independent variable) and measure the effect on rate (dependent variable). If the rate does not change, the reaction is zero order for that reactant. Example if double the concentration yields same rate – zero order.

You could also measure the concentration as a function of time as the reaction progress, if this relationship is linear, you would know that the reaction was zero order.

29. First-Order Reactions.

- a. Write a rate law equation for a first order reaction. Define each term in the equation.

Rate = $k [R]^1$ rate = rate constant x concentration of reactant to first power and thus the rate is equal to the rate constant times the concentration of reactants.

$$-\frac{d[A]}{dt} = k[A]$$

$$-\frac{d[A]}{[A]} = k dt$$

Integrate the left side from $[A] = [A]_0$ to $[A]$ and the right from $t = 0$ to t .

$$\int_{[A]_0}^{[A]} -\frac{d[A]}{[A]} = \int_0^t k dt$$

$$-\ln([A]) + \ln([A]_0) = k(t - 0)$$

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

- a. Write an equation that relates the concentration and time for a first order reaction. Define each term in the equation. (integrated rate law).

To the right you see the calculus to manipulate the differential rate law to yield the integrated rate. Integrated rate law allows us to relate time and concentration. You are only responsible for the integrated rate law and its application not its derivation.

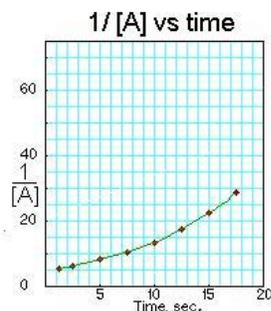
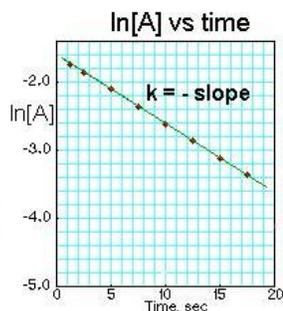
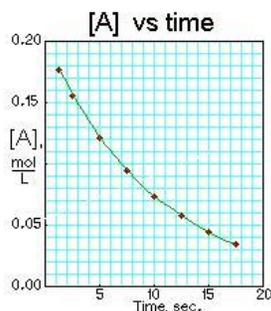
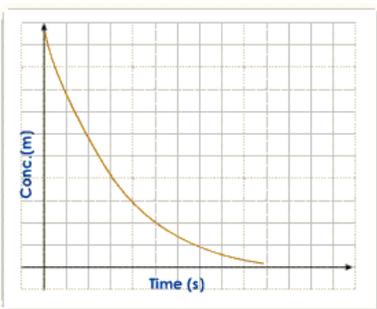
- c. Sketch the graph that yields a linear relationship for a first-order reaction. Label the axes.

When you rearrange the integrated rate law into the form of $y=mx+b$ you will note

$$\ln[R]_t = -k t + \ln[R]_0$$

$$y = m x + b$$

- d. Describe how to determine whether a reaction is first-order.



Experiment – changing the initial concentration of reactant (independent variable) and measure the effect on rate (dependent variable). If double the concentration, yields double the rate – the reaction is first order

for that reactant. Or if triple the concentration yields triple the rate – first order.

Another experiment would be to measure the reactant concentration as time goes by – graph this data as natural log of reactant concentration compared to time – if straight line first order.

30. Second-Order Reactions.

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^2$$

a. Write a rate law equation for a second-order reaction. Define each term in the equation.

$$\int_{[A]_0}^{[A]_t} -\frac{d[A]}{[A]^2} = \int_0^t k dt$$

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

Rate = k [R]² rate = rate constant x concentration of reactant to second power

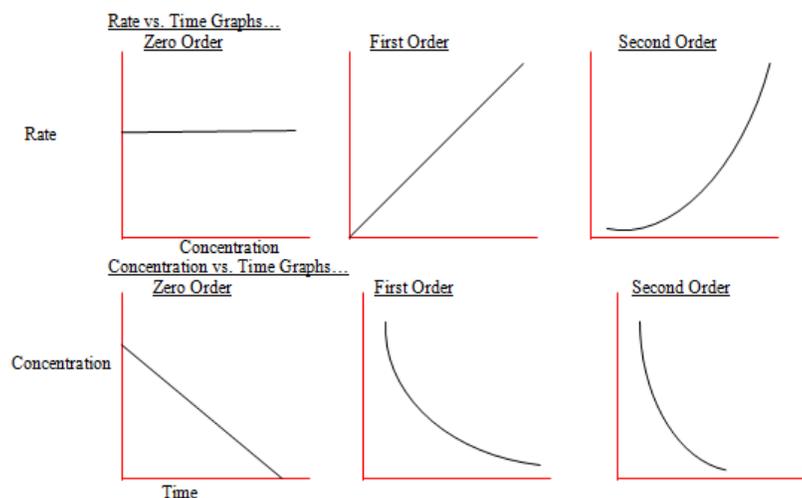
b. Write an equation that relates the concentration and time for a second-order reaction. Define each term in the equation. (integrated rate law).

The calculus is shown to the left. Once again you are only responsible for the final integrated equation and its application.

b. Sketch the graph that yields a linear relationship for a second-order reaction. Label the axes.

Once again rearrange the equation to y=mx+b. If you graph 1/[R] on the y-axis and time on the x-axis you will get a linear graph with the slope k.

e. Describe how to determine whether a reaction is second-order.



Experiment – changing the initial concentration of reactant (independent variable) and measure the effect on rate (dependent variable). If double the concentration, yields four times the rate – the reaction is second order for that reactant. Or if triple the concentration yields nine times the rate – second order.

Another experiment would be to measure the reactant concentration as time goes by – graph this data as natural log of reactant concentration compared to time – if straight line first order.

Application of Integrated Rate Law.

31. The following data were obtained for the reaction $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
(13.39 Jones and Atkins)

Time, s	0	4,000	8,000	12,000	16,000
[N ₂ O ₅], mol/L	2.15	1.88	1.64	1.43	1.25

ln [N ₂ O ₅]					
1/[N ₂ O ₅]					

- a. Plot the data on three different graphs to determine the rate law.
Graph each as a function of time – if linear with [N₂O₅] compared to time then zero order.
– if linear with ln [N₂O₅] compared to time then first order.
– if linear with 1/[N₂O₅] compared to time then second order.
- b. Write the rate law. Justify your answer using the graphs.
- b. From the graph determine the rate constant from the slope of the line.

32. The following data were obtained for the reaction $2 \text{HI}(\text{g}) \rightarrow 2 \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
(13.41 Jones and Atkins)

Time, s	0	1,000	2,000	3,000	4,000
[HI], mol/L	1,000	112	61	41	31

- a. Plot the data to confirm that the rate law is $\text{rate} = k[\text{HI}]^2$
Graph 1/[HI] on y axis and time on the x axis, a straight line shows second order
- b. From the graph determine the rate constant.
The slope of the line is the rate constant.

33. The following data were obtained for the reaction $\text{C}_2\text{H}_6(\text{g}) \rightarrow 2 \text{CH}_3(\text{g})$
(13.40 Jones and Atkins)

Time, s	0	1,000	2,000	3,000	4,000	5,000
[C ₂ H ₆], mol/L	1.59	0.92	0.53	0.31	0.18	0.10

- a. Plot the data to confirm that the reaction is first order.
Graph ln [C₂H₆] on y axis and time on the x axis, a straight line shows second order
- c. From the graph determine the rate constant.
The slope of the line is the opposite(negative) rate constant.

34. The rate law for the hydrolysis of sucrose to fructose and glucose is $-\text{[sucrose]}/\Delta t = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$.



After 2.57 hours at 27°C, the [sucrose] decreased from 0.0146 M to 0.0132 M. Find the rate constant.

First order so the integrated rate law is $\ln([R]_t/[R]_0) = -kt$ so plug in [R]_t – the concentration after some time 0.0132 M and the [R]₀ – the initial concentration 0.0146 M and the time is 2.57 hours. The solve for k.

first order integrated rate law

$$\ln([R]_t/[R]_0) = -kt$$

$$\ln(0.0132/0.0146) = k(2.57 \text{ hours}) \text{ so } k = 3.92 \times 10^{-2} \text{ hrs}^{-1}$$

and then add the appropriate units

35. The decomposition of SO₂Cl₂ is first order reaction: $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$
The rate constant is $2.8 \times 10^{-3} \text{ min}^{-1}$ at 600K. If the initial concentration of is $1.24 \times 10^{-3} \text{ mol/L}$, how long will it take for the concentration to drop to $0.31 \times 10^{-3} \text{ mol/L}$? (15.32)

first order integrated rate law

$$\ln([R]_t/[R]_0) = -kt$$

$$\ln(0.31 \times 10^{-3} \text{ mol/L} / 1.24 \times 10^{-3} \text{ mol/L}) = -2.8 \times 10^{-3} \text{ min}^{-1} t$$

$$t = 495 \text{ minutes}$$

36. Ammonium cyanate, NH₄NCO, rearranges in water to give urea, (NH₂)₂CO:



- a. The reaction is second order. Write the rate law. $\text{Rate} = k[\text{NH}_4\text{NCO}]^2$
 b. What are the units of k? L/mol s (when in doubt –go ahead and select seconds as the time unit)
 c. If the original concentration of NH_4NCO in solution is 0.229 mol/L , how long will it take for the concentration to decrease to 0.180 mol/L ?

second order integrated rate law

$$1/[\text{R}]_t - 1/[\text{R}]_0 = kt$$

$$1/.18 - 1/.229 = 0.0113 t$$

$$t = 105 \text{ seconds}$$

37. Hydrogen peroxide decomposes in to water and oxygen in a reaction that is first order with a rate constant of $1.06 \times 10^{-3} \text{ min}^{-1}$. $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\ell) + \text{O}_2(\text{g})$

first order integrated rate law

$$\ln([\text{R}]_t/[\text{R}]_0) = -kt$$

note: this fraction ($[\text{R}]_t/[\text{R}]_0$) is the fraction of reactant remaining

so replace the fraction ($[\text{R}]_t/[\text{R}]_0$) with fraction that represents the percent remaining

- a. How long will it take 15% of the sample to decompose?

$$\ln(0.15) = -1.06 \times 10^{-3} \text{ min}^{-1} t$$

$$t = 1.79 \times 10^{-3} \text{ min}$$

- b. How long will it take 85% to decompose?

$$\ln(0.85) = -1.06 \times 10^{-3} \text{ min}^{-1} t$$

$$t = 1.53 \times 10^{-2} \text{ min}$$

- c. How long will it take 50% to decompose- the half-life?

$$\ln(0.5) = -1.06 \times 10^{-3} \text{ min}^{-1} t$$

$$t = 6.54 \times 10^{-2} \text{ min}$$

38. The half-life of a radioisotope is found to be 4.55 minutes. If the decay follows first order kinetics, what percentage of isotope will remain after 2.00 hours?

Half life is the time it takes for half the reactants to react. $\ln(0.5) = -k t$

$$\ln(0.5) = -k 4.55 \text{ minutes} \text{ so } k = 0.152 \text{ minutes}^{-1}$$

Use this to find the k and then calculate the percent remaining in a second calculation.

$$\ln(x) = -0.152 \text{ min}^{-1} (120 \text{ minutes}) \text{ so fraction} = 1.2 \times 10^{-8} \text{ or } 1.2 \times 10^{-6} \%$$

Be careful of units – we were given minutes for calculation of k so units in minutes and then this second time was in hours.

39. The decomposition of SO_2Cl_2 is first order reaction: $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$
 The reaction has a half-life of 245 minutes at 600K. If you begin with 3.6×10^{-3} moles of $\text{SO}_2\text{Cl}_2(\text{g})$ in a 1.0L flask, how long will it take the quantity of SO_2Cl_2 to decrease to $2.0 \times 10^{-4} \text{ mol}$? (15.38)

40. Urea (a principle component of urine) can be formed by the rearrangement of ammonium cyanate by the following reaction:



$$\text{rate} = k[\text{NH}_4\text{NCO}]^2 \text{ where } k = 0.0113 \text{ L/mol}\cdot\text{min}$$

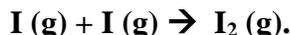
If the original concentration of ammonium cyanate is 0.229 M , how long (min.) will it take for the concentration to decrease to 0.180 M ?

$$\text{Second order rate law} \quad (1/[\text{R}]_t - 1/[\text{R}]_0) = kt$$

$$(1/0.18 - 1/0.229) = 0.0113 \text{ L/mol}\cdot\text{min } t$$

$$t = 10.5 \text{ min}$$

41. Iodine atoms can combine to form molecular iodine in the gas phase in the following reaction:



The reaction is second order and has a rate constant of $7.0 \times 10^9/\text{M s}$ at 23°C .

Calculate the half-life (in sec.) of the reaction if the initial concentration is 0.60 M .

42. From a set of kinetic data, a plot of the reciprocal of the concentration of a reactant as a function of time yielded a straight line with a positive slope. What is the order of the reaction?

Second order since the $1/[R]$ yields a straight line

43. From a set of kinetic data, a plot of the natural log of the concentration of a reactant as a function of time yielded a straight line with a negative slope. What is the order of the reaction?

First order since the $\ln[R]$ yields a straight line

44. Dinitrogen pentoxide, N_2O_5 , decomposes by first-order kinetics with a rate constant of $3.7 \times 10^{-5}/s$ at 298 K. (Jones and Atkins 13.31)

a. What is the half-life in hours for the decomposition of at 298 K?

$$\ln(0.5) = -k t$$

$$\ln(0.5) = -3.7 \times 10^{-5}/s \ t$$

$$t = 1.87 \times 10^4 \text{ s}$$

b. If $[N_2O_5] = 2.33 \times 10^{-2} \text{ mol/L}$, what will the concentration of N_2O_5 after 2.0 hours?

first order integrated rate law

$$\ln([R]_t/[R]_0) = -kt$$

$$\ln([R]_t/2.33 \times 10^{-2} \text{ mol/L}) = -3.7 \times 10^{-5}/s (2 \text{ hrs} \times 60 \text{ min/hr} \times 60 \text{ s/min})$$

$$\ln[R]_t - \ln 2.33 \times 10^{-2} \text{ mol/L} = -.2664$$

$$\ln[R]_t = -4.025$$

$$[R]_t = e^{-4.025}$$

$$[R]_t = 0.0179 \text{ mol/L}$$

c. How much time will have elapsed before the $[N_2O_5]$ decreases from 23.3 mmol/L to 17.6 mmol/L?

first order integrated rate law

$$\ln([R]_t/[R]_0) = -kt$$

$$\ln(17.6 \text{ mmol/L} / 23.3 \text{ mmol/L}) = -3.7 \times 10^{-5}/s \ t$$

$$t = 7.58 \times 10^3 \text{ s or } 2.11 \text{ hours}$$

45. Substance A forms substance B in the first order reaction $A \rightarrow 2B$, in which the concentration of A falls to 20% of its original concentration in 120 seconds. What is the rate constant for the reaction? Determine the time required for the concentration of A to fall to 10% of its original concentration? (Jones and Atkins 13.35)

first order integrated rate law

$$\ln([R]_t/[R]_0) = -kt$$

$$\ln(0.2) = -k \ 120 \text{ s}$$

$$k = 0.0134 \text{ s}^{-1}$$

first order integrated rate law

$$\ln([R]_t/[R]_0) = -kt$$

$$\ln(0.1) = -0.0134 \text{ s}^{-1} \ t$$

$$t = 172 \text{ seconds}$$