29. The rate of the reaction between hemoglobin (Hb) and carbon monoxide (CO) was studied at 20°C. The following data were collected with all concentration units in μmol/L. (A hemoglobin concentration of 2.21 μmol/L is equal to 2.21×10^{-6} mol/L.)

$[Hb]_0$ (μmol/L)	$[CO]_0$ (μmol/L)	Initial Rate (μmol/L · s)
2.21	1.00	0.619
4.42	1.00	1.24
4.42	3.00	3.71

a. Determine the orders of this reaction with respect to Hb and CO.
b. Determine the rate law.
c. Calculate the value of the rate constant.
d. What would be the initial rate for an experiment with $[Hb]_0 = 3.36$ μmol/L and $[CO]_0 = 2.40$ μmol/L?

30. The following data were obtained for the reaction

$$2ClO_2(aq) + 2OH^-(aq) \longrightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$$

where
$$\text{Rate} = -\frac{\Delta[ClO_2]}{\Delta t}$$

$[ClO_2]_0$ (mol/L)	$[OH^-]_0$ (mol/L)	Initial Rate (mol/L · s)
0.0500	0.100	5.75×10^{-2}
0.100	0.100	2.30×10^{-1}
0.100	0.0500	1.15×10^{-1}

a. Determine the rate law and the value of the rate constant.
b. What would be the initial rate for an experiment with $[ClO_2]_0$ 0.175 mol/L and $[OH^-]_0 = 0.0844$ mol/L?

43. A first-order reaction is 75.0% complete in 320. s.
a. What are the first and second half-lives for this reaction?
b. How long does it take for 90.0% completion?

46. The rate law for the reaction

$$2NOBr(g) \longrightarrow 2NO(g) + Br_2(g)$$

at some temperature is

$$\text{Rate} = -\frac{\Delta[NOBr]}{\Delta t} = k[NOBr]^2$$

a. If the half-life for this reaction is 2.00 s when $[NOBr]_0 = 0.900$ *M*, calculate the value of *k* for this reaction.
b. How much time is required for the concentration of NOBr to decrease to 0.100 *M*?

48. Consider the hypothetical reaction

$$A + B + 2C \longrightarrow 2D + 3E$$

where the rate law is

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A][B]^2$$

Pseudo-1st order rxn — 3rd order rxn

An experiment is carried out where $[A]_0 = 1.0 \times 10^{-2}$ *M*, $[B]_0 = 3.0$ *M*, and $[C]_0 = 2.0$ *M*. The reaction is started, and after 8.0 seconds, the concentration of A is 3.8×10^{-3} *M*.
a. Calculate *k* for this reaction.
b. Calculate the half-life for this experiment. 5.8 s
c. Calculate the concentration of A after 13.0 seconds.
d. Calculate the concentration of C after 13.0 seconds.

77. Consider the reaction

$$3A + B + C \rightarrow D + E$$

where the rate law is defined as

$$-\frac{\Delta[A]}{\Delta t} = k[A]^2[B][C]$$

An experiment is carried out where $[B]_0 = [C]_0 = 1.00$ *M* and $[A]_0 = 1.00 \times 10^{-4}$ *M*.
a. If after 3.00 min, $[A] = 3.26 \times 10^{-5}$ *M*, calculate the value of *k*.
b. Calculate the half-life for this experiment.
c. Calculate the concentration of B and the concentration of A after 10.0 min.

41. The reaction

$$A \longrightarrow B + C$$

is known to be zero order in A and to have a rate constant of 5.0×10^{-2} mol/L · s at 25°C. An experiment was run at 25°C where $[A]_0 = 1.0 \times 10^{-3}$ *M*.
a. Write the integrated rate law for this reaction.
b. Calculate the half-life for the reaction.
c. Calculate the concentration of B after 5.0×10^{-3} s has elapsed.

42. The radioactive isotope ^{32}P decays by first-order kinetics and has a half-life of 14.3 days. How long does it take for 95.0% of a sample of ^{32}P to decay?

29. $Hb + CO \rightarrow$ products

$\text{Rate} = k[Hb]^x[CO]^y$

a) • $X = 1$ Rxn is 1st order in Hb because when [CO] is constant and [Hb] is doubled, rxn rate doubles.

• $y = 1$ Rxn is 1st order in CO. When [Hb] is constant and [CO] is tripled, rxn rate triples.

b) $\text{Rate} = k[Hb][CO]$

c) $k = \dfrac{\text{Rate}}{[Hb][CO]} = \dfrac{.619 \frac{\mu mol}{L \cdot s}}{(2.21 \frac{\mu mol}{L})(1.00 \frac{\mu mol}{L})} = .280 \frac{L}{\mu mol \cdot s}$

$.280\ L\ \mu mol^{-1} s^{-1}$

d) $\text{Rate} = (.280\ L\ \mu mol^{-1} s^{-1})(3.36\ \mu mol\ L^{-1})(1.00\ \mu mol\ L^{-1})$

$= 2.26\ \mu mol\ L^{-1} s^{-1}$

The Rate Law

$\text{Rate} = k[ClO_2]^2[OH^-]$

30. a) $\text{Rate} = k[ClO_2]^x[OH^-]^y$

$X = 2 \rightarrow$ when $[ClO_2]$ is doubled and $[OH^-]$ is constant, Rate quadruples.

$y = 1 \rightarrow$ when $[OH^-]$ is doubled and $[ClO_2]$ is constant, Rate doubles.

$k = \dfrac{5.75 \times 10^{-2}\ mol/L \cdot s}{(.0500\ mol/L)^2\ (.100\ mol/L)} = 230\ L^2\ mol^{-2} s^{-1}$

41. a) $[A]_t - [A]_0 = -kt$

b) $\dfrac{(.5 \times 10^{-3} M) - (1.0 \times 10^{-3} M)}{-5.0 \times 10^{-2}\ mol/L \cdot s} = t_{1/2}$

$t_{1/2} = .010s$

c) $[A]_t - (1.0 \times 10^{-3} M) = (-5.0 \times 10^{-2} \frac{mol}{L \cdot s})(5.0 \times 10^{-3} s)$

$[A]_t = 7.5 \times 10^{-4} M$

A	$\rightarrow$ B	+ C
1.0×10^{-3}	0	0
-2.5×10^{-4}	$+2.5 \times 10^{-4}$	
7.5×10^{-4}	$2.5 \times 10^{-4} M$	

$[B]$ after 5×10^{-3} s

43. a) $\ln[25] - \ln[100] = -k(320\,s)$

or use this: $t_{1/2} = \frac{.693}{k}$

$k = .00433\,s^{-1}$

$\ln[.5] - \ln[1] = (-.00433\,s^{-1})(t_{1/2})$

There is no concentration dependence for 1st order ½ life

$t_{1/2} = 160\,s$

b) $\ln[10] - \ln[100] = (-.00433\,s^{-1})(t)$

$t = 532\,s$

46. a) $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$

Half-life for 2nd order reactions is dependend on concentration!

$\frac{1}{.450M} - \frac{1}{.900M} = k(2.00\,s)$

$k = .556\,M^{-1}s^{-1}$

b) $\frac{1}{.100M} - \frac{1}{.900M} = (.556\,M^{-1}s^{-1})(t)$

$t = 16.0\,s$

42. $t_{1/2} = \frac{.693}{k}$

$k = \frac{.693}{14.3\,days}$

$k = .0485\,days^{-1}$

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

$\ln[.05] - \ln[1] = (-.0485\,days^{-1})(t)$

$t = 62\,days$

48

(a) $\ln\frac{[A]_t}{[A]_0}$ $\ln[A]_t - \ln[A]_0 = -k't$

$$\frac{\ln 3.8\times10^{-3} - \ln 1.0\times10^{-2}}{8.0\,s} = \frac{(-k)(8.0\,s)}{8.0\,s}$$

$k' = .12\,s^{-1}$

$k' = k[B]^2$

3rd order k

$$k = \frac{k'}{[B]^2} = \frac{.12\,s^{-1}}{(3.0\,M)^2} = .013\,M^{-2}s^{-1}$$

b) $t_{1/2} = \frac{.693}{k'} = \frac{.693}{.12\,s^{-1}} = 5.8\,s$

$\ln[A]_t - \ln[A]_0 = -k't$

c) $\ln[A]_{13} - \ln(1.0\times10^{-2}\,M) = (-.12\,s^{-1})(13.0\,s)$

$[A]_{13} = .0021\,M$

d) $[A]_0 - [A]_{13} = \Delta[A]$

$1.0\times10^{-2} - .0021 = .0079\,M$

$A + B + 2C \longrightarrow$

2.0

$-.0079 \quad -.0158$

$1.98\,M$

$2.0\,M$

77. Pseudo 2nd order

a) $\frac{1}{[A]_t} - \frac{1}{[A]_0} = k't$

$\frac{1}{3.26 \times 10^{-5} M} - \frac{1}{1.00 \times 10^{-4} M} = k'(3.00 \text{ min})$

$k' = 6892$

$6890 \ M^{-1} \text{min}^{-1}$

$k' = k [B][C]$

$k = \frac{6890 \ M^{-1} \text{min}^{-1}}{(1.00 M)(1.00 M)} = 6890 \ M^{-3} \text{min}^{-1}$

b) $\frac{1}{.50 \times 10^{-4} M} - \frac{1}{1.00 \times 10^{-4} M} = \overbrace{(6890 M^{-3} \text{min}^{-1})}^{k'}(t)$

$t = 1.45 \text{ min}$

c) $\frac{1}{[A]_{10}} - \frac{1}{1.00 \times 10^{-4} M} = (6890 \ M^{-1} \text{min}^{-1})(10.0 \text{ min})$

$\frac{1}{[A]_{10}} = 78900 \ M^{-1}$

$[A]_{10} = 1.27 \times 10^{-5} M$

$3A + B + C \longrightarrow$

1.00×10^{-4} 1.00

$- 8.73 \times 10^{-5}$ $- 2.91 \times 10^{-5}$

1.27×10^{-5} $.999 M$

$\sim 1.00 M$