Section 79 – Integrated Rate Laws

79-1. Describe how graphical methods can be used to determine the order of a reaction and its rate constant from a series of data that includes the concentration of *A* at varying times.

Solution

Plot $[A]$, $\ln[A]$, and $\frac{1}{[A]}$ versus time, *t*. A linear plot of $[A]$ versus *t* indicates a zero-order reaction with slope = $-k$. A linear plot of ln[A] versus *t* indicates a first-order reaction with $k = -$slope. A linear plot of $\frac{1}{[A]}$ versus *t* indicates a second-order reaction with k = slope.

79-2. What is the half-life for the first-order decay of phosphorus–32? ($^{32}_{15}P \longrightarrow {}^{32}_{16}S + e^-$) The rate constant for the decay is 4.85×10^{-2} day^{-1}.

Solution

The half-life is $t_{1/2} = \frac{0.693}{k}$, where *k* is the rate constant:

$$k = \frac{0.693}{t_{1/2}} = 4.85 \times 10^{-2}\ d^{-1}$$

$$t_{1/2} = \frac{0.693}{4.85 \times 10^{-2}\ d^{-1}} = 14.3\ d$$

79-3. What is the half-life for the first-order decay of carbon–14? ($^{14}_{6}C \longrightarrow {}^{14}_{7}N + e^-$) The rate constant for the decay is 1.21×10^{-4} year^{-1}.

Solution

The half-life of a first-order reaction is $t_{1/2} = \frac{0.693}{k}$ is the rate constant:

$$t_{1/2} = \frac{1}{1.21 \times 10^{-4}\ y^{-1}} = 5.73 \times 10^{3}\ y$$

79-4. Some bacteria are resistant to the antibiotic penicillin because they produce penicillinase, an enzyme with a molecular weight of 3×10^4 g/mol that converts penicillin into inactive molecules. Although the kinetics of enzyme-catalyzed reactions can be complex, at low concentrations this reaction can be described by a rate law that is first order in the catalyst (penicillinase) and that also involves the concentration of penicillin. From the following data: 1.0 L of a solution containing 0.15 μg (0.15×10^{-6} g) of penicillinase, determine the order of the reaction with respect to penicillin and the value of the rate constant.

[Penicillin] (*M*)	Rate (mol L^{-1} min^{-1})

2.0×10^{-6}	1.0×10^{-10}
3.0×10^{-6}	1.5×10^{-10}
4.0×10^{-6}	2.0×10^{-10}

Solution

The reaction is first order with respect to penicillinase, and the rate doubles as [penicillin] doubles. Thus the rate equation is:

rate = k[penicillinase][penicillin]

Using the data in the first row,

$$k = \frac{1.0 \times 10^{-10} \text{ mol L}^{-1} \text{ min}^{-1}}{\left(\dfrac{0.15 \times 10^{-6} \text{ g L}^{-1}}{3.0 \times 10^{4} \text{ g mol}^{-1}}\right)(2.0 \times 10^{-6} \text{ mol L}^{-1})} = 1.0 \times 10^{7} \text{ L mol}^{-1} \text{ min}^{-1}$$

79-5. Both technetium–99 and thallium–201 are used to image heart muscle in patients with suspected heart problems. The half-lives are 6 h and 73 h, respectively. What percent of the radioactivity would remain for each of the isotopes after 2 days (48 h)?

Solution

The half-life of a first-order reaction is determined from the expression:

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

Tc, $k = \frac{0.693}{6 \text{ h}} = 0.116 \text{ h}^{-1}$

Tl, $k = \frac{0.693}{73 \text{ h}} = 0.00949 \text{ h}^{-1}$;

for a first-order reaction:

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

Let $[A_0]$ = unity, then

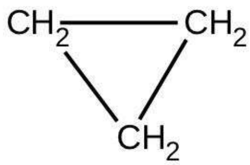
for Tc: $\ln \frac{1}{[A]} = 0.116 \text{ h}^{-1} \times 48 \text{ h} = 5.568$

Convert 5.568, a natural log, to the corresponding number by taking the *e*s of both sides:

$\frac{1}{[A]} = 261.9$; $[A] = 0.004$ or 0.4% after multiplying by 100%;

for Tl: $\ln \frac{1}{[A]} = 0.00949 \text{ h}^{-1} \times 48 \text{ h} = 0.4555$; convert 0.4555, a natural log, to the corresponding number by taking the *e*s of both sides: $\frac{1}{[A]} = 1.577$; $[A] = 0.63$ or 63% after multiplying by 100%.

79-6. There are two molecules with the formula C_3H_6. Propene, $CH_3CH = CH_2$, is the monomer of the polymer polypropylene, which is used for indoor-outdoor carpets. Cyclopropane is used as an anesthetic:



When heated to 499 °C, cyclopropane rearranges (isomerizes) and forms propene with a rate constant of $5.95 \times 10^{-4}\ s^{-1}$. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

Solution

The provided rate constant's unit is s^{-1}, indicating the reaction is first-order, and so

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.95 \times 10^{-4}\ s^{-1}} = 1.16 \times 10^{3}\ s$$

The fraction remaining after 0.75 h may be determined from the integrated rate law:

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

Rearranging this equation to isolate the fraction remaining yields

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

Converting the time to seconds and substituting values for k and t gives

$$\ln \frac{[A]_t}{[A]_0} = e^{-kt} = e^{-\left(5.95\times10^{-4}\ s^{-1}\right)(0.75\ h)\left(\frac{60\ m}{1\ hr}\right)\left(\frac{60\ s}{1\ min}\right)} = 0.20$$

And so, 20% of the reactant remains.

78-7. Suppose that the half-life of steroids taken by an athlete is 42 days. Assuming that the steroids biodegrade by a first-order process, how long would it take for $\frac{1}{64}$ of the initial dose to remain in the athlete's body?

Solution

This problem can be solved "on your fingers", by working out the half-lives to get to 1/64 of the original does (i.e., after one half-life there would be ½ left; after two half-lives there would be ½ x ½ = ¼ left; after three half-lives there would be ½ x 1/4 = 1/8 left; after four half-lives there would be ½ x 1/8 = 1/16 left; after five half-lives there would be ½ x 1/16 = 1/32 left; and after six half-lives there would be ½ x 1/32 = 1/64 left. The six half-lives = 6 x 42 days = 252 days. OR you can calculate the time as follows:

$\frac{1}{64} = \frac{1}{2^x}$ where x represents the number of half-life periods $x = 6$, so (6)(42) = 252 days.

78-8. In 2012, the skeleton of King Richard III was found under a parking lot in England. If tissue samples from the skeleton contain about 93.79% of the carbon-14 expected in living tissue, what year did King Richard III die? The half-life for carbon-14 is 5730 years.

Solution

Use the half-life equation for a first order process: $t_{1/2} = \frac{0.693}{k}$. $5730 = \frac{0.693}{k}$. So $k = 1.21 \times 10^{-4}$ y^{-1}. Next plug into the integrated rate law for a first order reaction: $\ln(0.9379) = -(1.21 \times 10^{-4})t + \ln(1.00)$ where 1.00 represents 100% of the carbon-14;
t = 530 years. 2015 – 530 = 1485, the year that King Richard III died.

78-9. Nitroglycerine is an extremely sensitive explosive. In a series of carefully controlled experiments, samples of the explosive were heated to 160 °C and their first-order decomposition studied. Determine the average rate constants for each experiment using the following data:

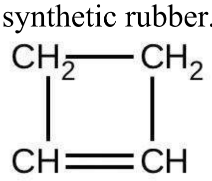
Initial $[C_3H_5N_3O_9]$ (M)	4.88	3.52	2.29	1.81	5.33	4.05	2.95	1.72
t (s)	300	300	300	300	180	180	180	180
% Decomposed	52.0	52.9	53.2	53.9	34.6	35.9	36.0	35.4

Solution

From the first-order rate law, calculate the value of $[A]$, $\ln\left(\frac{[A]_0}{[A]}\right)$, and k. The values are tabulated:

$[A]_0$ (M)	$[A]$ (M)	$\ln\left(\frac{[A]_0}{[A]}\right)$	t (s)	$k \times 10^3$ (s^{-1})
4.88	2.34	0.734	300	2.45
3.52	1.66	0.752	300	2.51
2.29	1.07	0.761	300	2.53
1.81	0.834	0.775	300	2.58
5.33	3.49	0.423	180	2.36
4.05	2.61	0.439	180	2.47
2.95	1.89	0.445	180	2.48
1.72	1.11	0.438	180	2.43

78-10. For the past 10 years, the unsaturated hydrocarbon 1,3-butadiene $(CH_2 = CH - CH = CH_2)$ has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. An isomer exists also as cyclobutene:



The isomerization of cyclobutene to butadiene is first-order and the rate constant has been measured as 2.0×10^{-4} s^{-1} at 150 °C in a 0.53-L flask. Determine the partial pressure of cyclobutene and its concentration after 30.0 minutes if an isomerization reaction is carried out at 150 °C with an initial pressure of 55 torr.

Solution

For a first-order reaction:

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

$$\ln\frac{[55 \text{ torr}]}{[P \text{ torr}]} = 2.0 \times 10^{-4} \text{ s}^{-1} \times 30.0 \text{ min} \times 60 \text{ s min}^{-1}$$

$$\ln 55 - \ln P = 0.36$$

$$\ln P = \ln 55 - 0.36 = 4.01 - 0.36 = 3.65$$

$$P = 38 \text{ torr}$$

As both reactants are gases, the pressure remains constant at 55 torr. The concentration of cyclobutene is found from the ideal gas law, $PV = nRT$:

$$n = \frac{PV}{RT} = \frac{\frac{38 \text{ torr}}{760 \text{ torr}} \times 0.53 \text{ L}}{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 423 \text{ K}}$$

$$n = 7.6 \times 10^{-4}$$

$$; \text{ molarity} = \frac{n}{0.53 \text{ L}} = 1.4 \times 10^{-3}\ M$$

79-11. What is the half-life for the decomposition of NOCl when the concentration of NOCl is 0.15 *M*? The rate constant for this second-order reaction is 8.0×10^{-8} L mol^{-1} s^{-1}.

Solution

In a second-order reaction, the rate is concentration-dependent, $t_{1/2} = \frac{1}{k[A]_0}$.

$$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{8.0 \times 10^{-8} \text{ L mol}^{-1} \text{ s}^{-1} [0.15\ M]} = 8.3 \times 10^{7} \text{ s}$$

79-12. What is the half-life for the decomposition of O_3 when the concentration of O_3 is 2.35×10^{-6} *M*? The rate constant for this second-order reaction is 50.4 L mol^{-1} h^{-1}.

Solution

In a second-order reaction, the rate is concentration-dependent, $t_{1/2} = \frac{1}{k[\text{A}]_0}$.

$$t_{1/2} = \frac{1}{k[\text{A}]_0} = \frac{1}{50.4 \text{ L mol}^{-1} \text{ h}^{-1}[2.35 \times 10^{-6}\ M]} = 8.44 \times 10^{3} \text{ h}$$

79-13. The reaction of compound *A* to give compounds *C* and *D* was found to be second-order in *A*. The rate constant for the reaction was determined to be 2.42 L mol^{-1} s^{-1}. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

Solution

For a second-order reaction, the half-life is concentration-dependent:

$$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{2.42 \text{ L mol}^{-1} \text{ s}^{-1} \times 0.500 \text{ mol L}^{-1}} = 0.826 \text{ s}$$

79-14. The half–life of a reaction of compound A to give compounds D and E is 8.50 min when the initial concentration of A is 0.150 M. How long will it take for the concentration to drop to 0.0300 M if the reaction is (a) first order with respect to A or (b) second order with respect to A?

Solution

(a) In a first-order reaction, the half-life is given by $t_{1/2} = 0.693/k$. Knowing $t_{1/2}$, the value of k can be determined:

$$k = \frac{0.693}{8.50 \text{ min}} = 0.0815 \text{ min}^{-1}$$

Then, from:

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

$$t = \ln\left[\frac{0.150 \cancel{\text{mol}} \cancel{\text{L}^{-1}}}{0.0300 \cancel{\text{mol}} \cancel{\text{L}^{-1}}}\right] \times \frac{1}{0.0815 \text{ min}^{-1}} = 1.60944 \times 12.27 \text{ min} = 19.7 \text{ min};$$

(b) In a second-order reaction, the rate is concentration-dependent:

$$t_{1/2} = \frac{1}{k[A]_0}$$

$$k = \frac{1}{t_{1/2}[A]_0} = \frac{1}{8.50 \text{ min } [0.150 \text{ mol L}^{-1}]} = 0.784 \text{ L mol}^{-1} \text{ min}^{-1}$$

Then substitution into:

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

Gives:

$$t = \frac{\frac{1}{0.0300 \text{ mol L}^{-1}} - \frac{1}{0.150 \text{ mol L}^{-1}}}{0.784 \text{ L mol}^{-1} \text{ min}^{-1}} = \frac{33.333 \cancel{\text{L}} \cancel{\text{mol}^{-1}} - 6.667 \cancel{\text{L}} \cancel{\text{mol}^{-1}}}{0.784 \cancel{\text{L}} \cancel{\text{mol}^{-1}} \text{ min}^{-1}} = 34.0 \text{ min}$$

79-15. From the given data, use a graphical method to determine the order and rate constant of the following reaction:

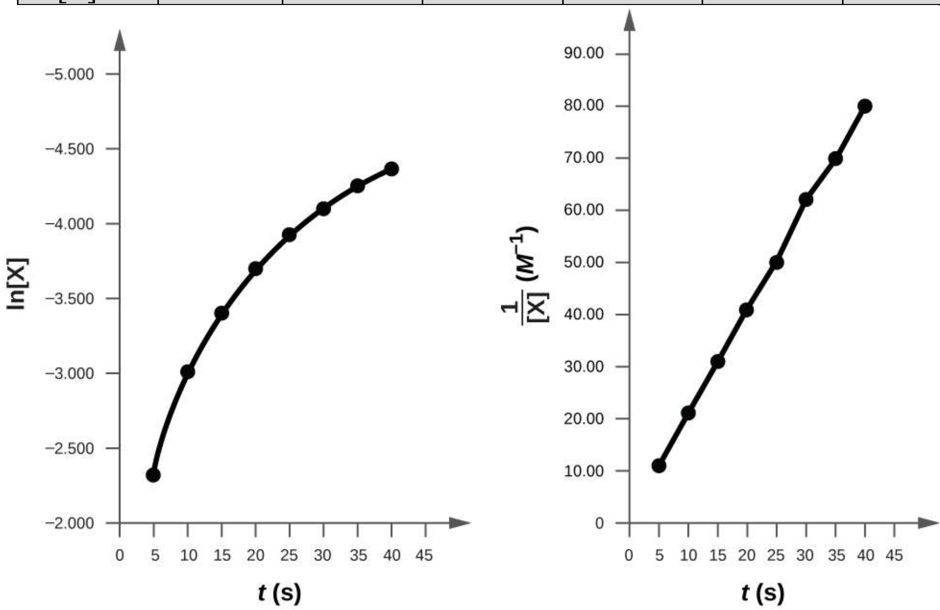
$$2X \longrightarrow Y + Z$$

Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
$[X]$ (M)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125

Solution

To distinguish a first-order reaction from the second-order reaction, we plot $\ln[X]$ against t and compare that plot with a plot of $\frac{1}{[X]}$ versus t. The necessary data are as follows:

Time (s)	5.0	10.0	15.00	20.00	25.00	30.00	35.00	40.00
$\frac{1}{[X]}$	10.10	20.12	30.12	40.16	50.00	60.24	69.93	80.00
ln[*X*]	−2.313	−3.002	−3.405	−3.693	−2.313	−4.098	−4.247	−4.382



(a) (b)

The plot shows that the reaction data are constant with second-order kinetics, as $\frac{1}{[X]}$ versus t is a straight line.