#### **OpenStax: Integrated Rate Laws**

### Example 12.6

The rate constant for the first-order decomposition of cyclobutane, C<sub>4</sub>H<sub>8</sub> at 500 °C is  $9.2 \times 10^{-3} \text{ s}^{-1}$ :

### $C_4H_8 \longrightarrow 2C_2H_4$

How long will it take for 80.0% of a sample of C<sub>4</sub>H<sub>8</sub> to decompose?

Use the integrated form of the first-order rate law  $ln([A]_0/[A]) = kt$  to answer questions regarding time:

# $1.7 \text{ x } 10^2 \text{ s}$

# lodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer.

lodine-131 decays to xenon-131 according to the equation:

I-131  $\rightarrow$  Xe-131 + electron

The decay is first-order with a rate constant of 0.138 d<sup>-1</sup>. All radioactive decay is first order. How many days will it take for 90% of the iodine–131 in a 0.500 M solution of this substance to decay to Xe-131?

### 16.7 days

# Example 12.7

Show that the relationship between the  $In[H_2O_2]$  and time is linear by graphing.

Trial	Time, h	[H <sub>2</sub> O <sub>2</sub> ] (M)	In[H <sub>2</sub> O <sub>2</sub> ]
1	0	1.000	0.0
2	6.00	0.500	-0.693
3	12.00	0.250	-1.386
4	18.00	0.125	-2.079
5	24.00	0.0625	-2.772



Determine the rate constant from this data.

 $k = -slope = 1.155 \times 10^{-1} h^{-1}$ 

### Example 12.8

Trial	Time (s)	[A]	ln[A]	1/[A]
1	4.0	0.220	-1.514	4.545
2	8.0	0.144	-1.938	6.944
3	12.0	0.110	-2.207	9.091
4	16.0	0.088	-2.430	11.36
5	20.0	0.074	-2.603	13.51

a. Graph the following data to determine whether the reaction  $A \rightarrow B + C$  is first order.



The data represents a second order rate.  $k = 0.600 L^2 mol^{-2} s^{-1}$ 

#### b. Test these data to confirm that this dimerization reaction is second-order.

2 C <sub>4</sub> H <sub>6</sub> (g) ->	C <sub>8</sub> H <sub>12</sub> (g)
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Trial	Time (s)	[C <sub>4</sub> H <sub>6</sub> ] (M)	In[C₄H <sub>6</sub> ]	1/[C <sub>4</sub> H <sub>6</sub> ]
1	0	1.00 × 10 <sup>-2</sup>	-4.61	100
2	1600	5.04 × 10 <sup>-3</sup>	-5.29	198
3	3200	3.37 × 10⁻³	-5.69	297
4	4800	2.53 × 10⁻³	-5.98	395
5	6200	2.08 × 10 <sup>-3</sup>	-6.18	481



The data represents a second order rate. k = 0.06125 L<sup>2</sup> mol<sup>-2</sup> s<sup>-1</sup>

c. Does the following data fit a second-order rate law?

Trial	Time (s)	[A] (M)	In[A]	1/[A]
1	5	0.952	-0.0492	1.05
2	10	0.625	-0.470	1.60
3	15	0.465	-0.766	2.15
4	20	0.370	-0.994	2.70
5	25	0.308	-1.18	3.25
6	35	0.230	-1.47	4.35



The data represents a second order rate. k = 0.110

#### 4. A study of the rate of dimerization of $C_4H_6$ given the data shown in the table:

 $2C_4H_6 \rightarrow C_8H_{12}$ 

Time (s)	0	1600	3200	4800	6200
[C <sub>4</sub> H <sub>6</sub> ] (M)	1.00 × 10 <sup>-2</sup>	5.04 × 10 <sup>-3</sup>	3.37 × 10⁻³	2.53 × 10⁻³	2.08 × 10⁻³

(a) Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.

Rate<sub>12</sub> = -  $(5.04 \times 10^{-3} - 1.00 \times 10^{-2}) / (1600 - 0) = 4.96 \times 10^{-3} / 1600$ Rate<sub>12</sub> =  $3.10 \times 10^{-6} L^2$  mol<sup>-2</sup> s<sup>-1</sup>

Rate<sub>23</sub> = -  $(3.37 \times 10^{-3} - 5.04 \times 10^{-2}) / (3200 - 1600) = 1.67 \times 10^{-3} / 1600$ Rate<sub>23</sub> = 1.04 x 10<sup>-6</sup> L<sup>2</sup> mol<sup>-2</sup> s<sup>-1</sup>

(b) Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus [C<sub>4</sub>H<sub>6</sub>]. What are the units of this rate?

Rate<sub>3</sub> = - (2.53 x  $10^{-3}$  - 5.04 x  $10^{-2}$ ) / (4800-1600) = 2.51 x  $10^{-3}$  / 3200 Rate<sub>3</sub> = 7.84 x  $10^{-7}$  mol L<sup>-1</sup> s<sup>-1</sup>

(c) Determine the average rate of formation of  $C_8H_{12}$  at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

Rate<sub>2</sub> = - 0.5 \* (3.37 x 10<sup>-3</sup> – 1.00 x 10<sup>-3</sup>) / (3200 – 0) = 0.5 \* 6.63 x 10<sup>-3</sup> / 3200 Rate<sub>2</sub> = 1.04 x 10<sup>-6</sup> mol L<sup>-1</sup> s<sup>-1</sup> Rate<sub>3</sub> = - 0.5 \* (2.53 x 10<sup>-3</sup> – 5.04 x 10<sup>-3</sup>) / (4800 – 1600) = 0.5 \* 2.51 x 10<sup>-3</sup> / 3200 Rate<sub>3</sub> = 3.92 x 10<sup>-7</sup> mol L<sup>-1</sup> s<sup>-1</sup>

5. A study of the rate of the reaction represented as  $2A \rightarrow B$  gave the following data:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
[A] (M)	1.00	0.775	0.625	0.465	0.360	0.285	0.230

(a) Determine the average rate of disappearance of A between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.

Rate<sub>2</sub> = - (0.625 - 1.00) / (10.0 - 0.0) = 0.375 / 10.0Rate<sub>2</sub> = 3.75 x 10<sup>-2</sup> mol L<sup>-1</sup> s<sup>-1</sup>

(b) Estimate the instantaneous rate of disappearance of A at 15.0 s from a graph of time versus [A]. What are the units of this rate?

Rate<sub>4</sub> = - (0.0.360 - 0.625) / (20.0 - 10.0) = 0.265 / 10.0Rate<sub>4</sub> = 2.65 x 10<sup>-2</sup> mol L<sup>-1</sup> s<sup>-1</sup>

(c) Use the rates found in parts (a) and (b) to determine the average rate of formation of B between 0.00 s and 10.0 s, and the instantaneous rate of formation of B at 15.0 s.

Rate<sub>3</sub> =  $0.5 \times 3.75 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$ Rate<sub>3</sub> =  $1.875 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$ 

k4 = 0.5 \* 2.65 x 10<sup>-2</sup> mol L<sup>-1</sup> s<sup>-1</sup> k4 = 1.325 x 10<sup>-2</sup> mol L<sup>-1</sup> s<sup>-1</sup>

33. Use the data provided to graphically determine the order and rate constant of the following reaction:

 $SO_2CI_2 \rightarrow SO_2 + CI_2$ 

Time (s)	0	5.00 × 10 <sup>3</sup>	1.00 × 10 <sup>4</sup>	1.50 × 10 <sup>4</sup>	2.50 × 10 <sup>4</sup>	3.00 × 10 <sup>4</sup>	4.00 × 10 <sup>4</sup>
[SO <sub>2</sub> Cl <sub>2</sub> ] (M)	0.100	0.0896	0.0802	0.0719	0.0577	0.0517	0.0415
In[SO <sub>2</sub> Cl <sub>2</sub> ]	-2.30	-2.41	-2.52	-2.63	-2.85	-2.96	-3.18
1/[SO <sub>2</sub> Cl <sub>2</sub> ]	10.0	11.2	12.5	13.9	17.3	19.3	24.1



Order [SO<sub>2</sub>Cl<sub>2</sub>] = 1

# k = 2.20 x 10<sup>-5</sup> s<sup>-1</sup>

34. Use the data provided in a graphical method to determine the order and rate constant of the following reaction:

 $\rm 2P \rightarrow Q + W$ 

Time (s)	9.0	13.0	18.0	22.0	25.0
[P] (M)	1.077 × 10⁻³	1.068 x 10 <sup>-3</sup>	1.055 × 10⁻³	1.046 × 10⁻³	1.039 × 10⁻³
In[P]	-6.834	-6.842	-6.854	-6.863	-6.869
1/]P]	928.5	936.3	947.9	956	962.5



### Order P = 0, [P] at 0.0 s = 1.0986 x 10<sup>-3</sup> M

# k = 2.39 x 10<sup>-6</sup> mol L<sup>-1</sup> s<sup>-1</sup>

### 35. Pure ozone decomposes slowly to oxygen

 $2O_3(g) \rightarrow 3O_2(g).$ 

Use the data provided in a graphical method and determine the order and rate constant of the reaction.

Time (h)	0	2.0 × 10 <sup>3</sup>	7.6 × 10 <sup>3</sup>	1.00 × 10 <sup>4</sup>	1.23 × 10 <sup>4</sup>	1.43 × 10 <sup>4</sup>	1.70 × 10 <sup>4</sup>
[O <sub>3</sub> ] (M)	1.00 × 10⁻⁵	4.98 × 10 <sup>-6</sup>	2.07 × 10 <sup>-6</sup>	1.66 × 10⁻ <sup>6</sup>	1.39 × 10⁻ <sup>6</sup>	1.22 × 10⁻ <sup>6</sup>	1.22 × 10 <sup>-6</sup>
In[O₃]	-1.15	-1.22	-1.31	-1.33	-1.35	-1.36	-1.36
1/[O₃]	1.00 x 10⁵	2.01 x 10⁵	4.83 x 10⁵	6.02 x 10⁵	7.19 x 10⁵	8.20 x 10⁵	8.20 x 10 <sup>5</sup>





k = 42.4 L<sup>2</sup> mol<sup>-2</sup> h<sup>-1</sup>

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

 $2X \rightarrow Y + Z$ 

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
ln[X]	-2.31	-3.00	-3.41	-3.69	-3.91	-4.10	-4.25	-4.38
1/[X]	10.1	20.1	30.1	40.2	50.0	60.2	69.9	80.0





# k = 2.00 L<sup>2</sup> mol<sup>-2</sup> h<sup>-1</sup>

49. 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 <sub>3</sub> H <sub>5</sub> N <sub>3</sub> O <sub>9</sub> ] (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
k	7.80	5.53	3.57	2.78	1.94	1.44	1.05	6.17
	x 10 <sup>-3</sup>	x 10 <sup>-3</sup>	x 10 <sup>-3</sup>	x 10 <sup>-3</sup>	x 10 <sup>-2</sup>	x 10 <sup>-2</sup>	x 10 <sup>-2</sup>	x 10 <sup>-3</sup>

Order  $C_3H_5N_3O_9 = 1$  (half-life about the same regardless of starting concentration)

k = 2.5 x 10<sup>-3</sup> s<sup>-1</sup>

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