

**Homework #1**  
**Chapter 15**  
*Chemical Kinetics*

8. Arrhenius Equation

$$k = Ae^{E_a/RT}$$

Therefore, k depends only on temperature.

The rate of the reaction depends on all of these items (a-d).

14. a)  $\frac{\text{mol}}{\text{L}\cdot\text{s}}$       b)  $\frac{\text{mol}}{\text{L}\cdot\text{s}}$       c)  $\frac{1}{\text{s}}$   
d)  $\frac{\text{L}}{\text{mol}\cdot\text{s}}$       e)  $\frac{\text{L}^2}{\text{mol}^2\cdot\text{s}}$

15. Rate has units of  $\frac{\text{mol}}{\text{L}\cdot\text{s}}$  therefore, the units of the rate constant must compensate for any missing/additional units.

$$\frac{\text{L}^{1/2}}{\text{mol}^{1/2}\cdot\text{s}}$$

18. a) General Rate Law

$$\text{Rate} = k[\text{NO}]^x[\text{Cl}_2]^y$$

Experiment	[NO] <sub>0</sub> (M)	[Cl <sub>2</sub> ] <sub>0</sub> (M)	Initial Rate ( $\frac{\text{mol}}{\text{L}\cdot\text{min}}$ )
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.20	1.45

From experiments 1 and 2 ([NO]<sub>0</sub> is kept constant) as the initial concentration of Cl<sub>2</sub> is doubled, the initial rate of the reaction doubles ( $\frac{0.36}{0.18}=2.0$ ); therefore, the reaction is first order with respect to Cl<sub>2</sub>.

From experiments 2 and 3 ([Cl<sub>2</sub>]<sub>0</sub> is kept constant) as the initial concentration of NO is doubled, the initial rate of the reaction quadruples ( $\frac{1.45}{0.36}=4.0$ ); therefore, the reaction is second order with respect to NO.

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

- b)  $\text{Rate} = k[\text{NO}]^2[\text{Cl}_2]$   
 $0.18 \frac{\text{mol}}{\text{L}\cdot\text{min}} = k(0.10 \text{ M})^2(0.10 \text{ M})$   
 $k = 180 \frac{\text{L}^2}{\text{mol}^2\cdot\text{min}}$

19. a) General Rate Law

$$\text{Rate} = k[\text{I}^-]^x[\text{OCl}^-]^y$$

Experiment	[I <sup>-</sup> ] <sub>0</sub> (M)	[OCl <sup>-</sup> ] <sub>0</sub> (M)	Initial Rate ( $\frac{\text{mol}}{\text{L}\cdot\text{s}}$ )
1	0.12	0.18	$7.91 \times 10^{-2}$
2	0.060	0.18	$3.95 \times 10^{-2}$
3	0.030	0.090	$9.88 \times 10^{-2}$
4	0.24	0.090	$7.91 \times 10^{-2}$

From experiments 1 and 2 ([OCl<sup>-</sup>]<sub>0</sub> is kept constant) as the initial concentration of I<sup>-</sup> is doubled, the initial rate of the reaction doubles ( $\frac{7.91 \times 10^{-2}}{3.95 \times 10^{-2}}=2.0$ ); therefore, the reaction is first order with respect to I<sup>-</sup>.

$$\text{Rate} = k[\text{I}^-][\text{OCl}^-]^y$$

You must find the order of  $\text{OCl}^-$  the long way.

Divide the 2 equations (in which the  $[\text{OCl}^-]$  changes) by each other.

$$\frac{7.91 \times 10^{-2} \frac{\text{mol}}{\text{L}\cdot\text{s}}}{9.88 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}}} = \frac{k(0.12)(0.18 \text{ M})^y}{k(0.030)(0.090 \text{ M})^y}$$

$$2.0 = 2.0^y$$

$$y = 1$$

$$\text{Rate} = k[\text{I}^-][\text{OCl}^-]$$

b)  $\text{Rate} = k[\text{I}^-][\text{OCl}^-]$

$$7.91 \times 10^{-2} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k(0.12 \text{ M})(0.18 \text{ M})$$

$$k = 3.7 \frac{\text{L}}{\text{mol}\cdot\text{s}}$$

c)  $\text{Rate} = k[\text{I}^-][\text{OCl}^-] = (3.7 \frac{\text{L}}{\text{mol}\cdot\text{s}})(0.15 \text{ M})(0.15 \text{ M}) = 0.082 \frac{\text{mol}}{\text{L}\cdot\text{s}}$

20. General Rate Law

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

Experiment	$[\text{N}_2\text{O}_5]_0$ (M)	Initial Rate ( $\frac{\text{mol}}{\text{L}\cdot\text{s}}$ )
1	0.0750	$8.90 \times 10^{-4}$
2	0.190	$2.26 \times 10^{-3}$
3	0.275	$3.26 \times 10^{-3}$
4	0.410	$4.85 \times 10^{-3}$

You must solve this problem the long way.

$$8.90 \times 10^{-4} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k(0.0750 \text{ M})^x$$

$$2.26 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k(0.190 \text{ M})^x$$

Divide the 2 equations by each other.

$$\frac{8.90 \times 10^{-4} \frac{\text{mol}}{\text{L}\cdot\text{s}}}{2.26 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}}} = \frac{k(0.0750 \text{ M})^x}{k(0.190 \text{ M})^x}$$

$$0.394 = 0.395^x$$

$$x = 1$$

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

$$8.90 \times 10^{-4} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k(0.0750 \text{ M})$$

$$k = 0.0119 \frac{1}{\text{s}}$$

21. a) General Rate Law

$$\text{Rate} = k[\text{NOCl}]^x$$

Experiment	$[\text{NOCl}]_0$ ( $\frac{\text{molecules}}{\text{cm}^3}$ )	Initial Rate ( $\frac{\text{molecules}}{\text{cm}^3\cdot\text{s}}$ )
1	$3.0 \times 10^{16}$	$5.98 \times 10^4$
2	$2.0 \times 10^{16}$	$2.66 \times 10^4$
3	$1.0 \times 10^{16}$	$6.64 \times 10^3$
4	$4.0 \times 10^{16}$	$1.06 \times 10^5$

From experiments 2 and 3, as the initial concentration of  $\text{NOCl}$  is doubled, the initial rate of the reaction quadruples ( $\frac{2.66 \times 10^4}{6.64 \times 10^3} = 4.0$ ); therefore, the reaction is second order with respect to  $\text{NOCl}$ .

$$\text{Rate} = k[\text{NOCl}]^2$$

b)  $5.98 \times 10^4 \frac{\text{molecules}}{\text{cm}^3\cdot\text{s}} = k(3.0 \times 10^{16} \frac{\text{molecules}}{\text{cm}^3})^2$

$$k = 6.6 \times 10^{-29} \frac{\text{cm}^3}{\text{molecules}\cdot\text{s}}$$

$$c) \quad k = 6.6 \times 10^{-29} \frac{\text{cm}^3}{\text{molecules}\cdot\text{s}} \left( \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}} \right) \left( \frac{1 \text{ L}}{10^3 \text{ cm}^3} \right) = 4.0 \times 10^{-8} \frac{\text{L}}{\text{mol}\cdot\text{s}}$$

22. a) General Rate Law

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

Experiment	[Hb] <sub>0</sub> ( $\frac{\mu\text{mol}}{\text{L}}$ )	[CO] <sub>0</sub> ( $\frac{\mu\text{mol}}{\text{L}}$ )	Initial Rate ( $\frac{\mu\text{mol}}{\text{L}\cdot\text{s}}$ )
1	2.21	1.00	0.619
2	4.42	1.00	1.24
3	4.42	3.00	3.71

From experiments 1 and 2 ([CO]<sub>0</sub> is kept constant) as the initial concentration of Hb is doubled, the initial rate of the reaction doubles ( $\frac{1.24}{0.619} = 2.00$ ); therefore, the reaction is first order with respect to Hb.

You cannot use the shortcut to calculate the order with respect to [CO]

Find 2 equations where the concentration of Hb is constant

$$1.24 \frac{\mu\text{mol}}{\text{L}\cdot\text{s}} = k \left( 4.42 \frac{\mu\text{mol}}{\text{L}} \right) \left( 1.00 \frac{\mu\text{mol}}{\text{L}} \right)^y$$

$$3.71 \frac{\mu\text{mol}}{\text{L}\cdot\text{s}} = k \left( 4.42 \frac{\mu\text{mol}}{\text{L}} \right) \left( 3.00 \frac{\mu\text{mol}}{\text{L}} \right)^y$$

Divide the 2 equations by each other.

$$\frac{1.24 \frac{\mu\text{mol}}{\text{L}\cdot\text{s}}}{3.71 \frac{\mu\text{mol}}{\text{L}\cdot\text{s}}} = \frac{k \left( 4.42 \frac{\mu\text{mol}}{\text{L}} \right) \left( 1.00 \frac{\mu\text{mol}}{\text{L}} \right)^y}{k \left( 4.42 \frac{\mu\text{mol}}{\text{L}} \right) \left( 3.00 \frac{\mu\text{mol}}{\text{L}} \right)^y}$$

$$0.33 = \frac{\left( 1.00 \frac{\mu\text{mol}}{\text{L}} \right)^y}{\left( 3.00 \frac{\mu\text{mol}}{\text{L}} \right)^y} = (0.33)^y$$

$$y = 1$$

The reaction is 1<sup>st</sup> order with respect to CO

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

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

$$0.619 \frac{\mu\text{mol}}{\text{L}\cdot\text{s}} = k \left( 2.21 \frac{\mu\text{mol}}{\text{L}} \right) \left( 1.00 \frac{\mu\text{mol}}{\text{L}} \right)$$

$$k = 0.280 \frac{\text{L}}{\mu\text{mol}\cdot\text{s}}$$

$$d) \quad \text{Rate} = 0.280 \frac{\text{L}}{\mu\text{mol}\cdot\text{s}} [\text{Hb}][\text{CO}] = \left( 0.280 \frac{\text{L}}{\mu\text{mol}\cdot\text{s}} \right) \left( 3.36 \frac{\mu\text{mol}}{\text{L}} \right) \left( 2.40 \frac{\mu\text{mol}}{\text{L}} \right) = 2.26 \frac{\mu\text{mol}}{\text{L}\cdot\text{s}}$$

23. a) General

$$\text{Rate} = k[\text{ClO}_2]^x[\text{OH}^-]^y$$

Experiment	[ClO <sub>2</sub> ] <sub>0</sub> (M)	[OH <sup>-</sup> ] <sub>0</sub> (M)	Initial Rate ( $\frac{\text{mol}}{\text{L}\cdot\text{s}}$ )
1	0.0500	0.100	$5.75 \times 10^{-2}$
2	0.100	0.100	$2.30 \times 10^{-1}$
3	0.100	0.0500	$1.15 \times 10^{-1}$

From experiments 1 and 2 ([OH<sup>-</sup>]<sub>0</sub> is kept constant) as the initial concentration of ClO<sub>2</sub> is doubled, the initial rate of the reaction quadruples ( $\frac{2.30 \times 10^{-1}}{5.75 \times 10^{-2}} = 4.00$ ); therefore, the reaction is second order with respect to ClO<sub>2</sub>.

From experiments 2 and 3 ([ClO<sub>2</sub>]<sub>0</sub> is kept constant) as the initial concentration of OH<sup>-</sup> is doubled, the initial rate of the reaction doubles ( $\frac{2.30 \times 10^{-1}}{1.15 \times 10^{-1}} = 2.00$ ); therefore, the reaction is first order with respect to OH<sup>-</sup>.

$$\text{Rate} = k[\text{ClO}_2]^2[\text{OH}^-]$$

Find k

$$5.75 \times 10^{-2} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k(0.0500 \text{ M})^2(0.100 \text{ M})$$

$$k = 230. \frac{\text{L}^2}{\text{mol}^2\cdot\text{s}}$$

$$\text{Rate} = 230. \frac{\text{L}^2}{\text{mol}^2\cdot\text{s}} [\text{ClO}_2]^2 [\text{OH}^-]$$

b)  $\text{Rate} = 230. \frac{\text{L}^2}{\text{mol}^2\cdot\text{s}} (0.175 \text{ M})^2 (0.0844 \text{ M}) = 0.594 \frac{\text{mol}}{\text{L}\cdot\text{s}}$

30. a) Because the plot of  $\frac{1}{[A]}$  versus time was linear the rate law is a second order rate law.

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

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

$$\frac{1}{[A]^2} d[A] = -k dt$$

$$\int_{[A]_0}^{[A]} \frac{1}{[A]^2} d[A] = \int_0^t -k dt$$

$$-\frac{1}{[A]} + \frac{1}{[A]_0} = -kt + 0$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \text{ (integrated rate law)}$$

The rate constant is the slope of the line  $k = 3.60 \times 10^{-2} \frac{\text{L}}{\text{mol}\cdot\text{s}}$

$$\text{Rate} = 3.60 \times 10^{-2} \frac{\text{L}}{\text{mol}\cdot\text{s}} [A]^2 \text{ (rate law)}$$

b) The half-life is the amount of time it takes for  $\frac{1}{2}$  of the original concentration to react.

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

$$\frac{1}{0.5(2.80 \times 10^{-3} \text{ M})} = \left(3.60 \times 10^{-2} \frac{\text{L}}{\text{mol}\cdot\text{s}}\right)t + \frac{1}{2.80 \times 10^{-3} \text{ M}}$$

$$t = 9920 \text{ s}$$

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

$$\frac{1}{7.00 \times 10^{-4} \text{ M}} = \left(3.60 \times 10^{-2} \frac{\text{L}}{\text{mol}\cdot\text{s}}\right)t + \frac{1}{2.80 \times 10^{-3} \text{ M}}$$

$$t = 29,800 \text{ s}$$

31. a) Because the plot of  $\ln[A]$  versus  $t$  is linear, this is a 1<sup>st</sup> order rate law.

$$\text{Rate} = k[A]$$

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

$$\frac{1}{[A]} d[A] = -k dt$$

$$\int_{[A]_0}^{[A]} \frac{1}{[A]} d[A] = - \int_0^t k dt$$

$$\ln[A] - \ln[A]_0 = -kt + 0$$

$$\ln[A] = -kt + \ln[A]_0 \text{ (integrated rate law)}$$

The rate constant is the negative slope of the line  $k = 2.97 \times 10^{-2} \frac{1}{\text{min}}$

$$\text{Rate} = 2.97 \times 10^{-2} \frac{1}{\text{min}} [A] \text{ (rate law)}$$

b)  $\ln[A] = -kt + \ln[A]_0$

$$\ln\left(\frac{1}{2}(2.00 \times 10^{-2} M)\right) = -\left(2.97 \times 10^{-2} \frac{1}{\text{min}}\right)t + \ln(2.00 \times 10^{-2} M)$$

$$t = 23.3 \text{ min}$$

c)  $\ln[A] = -kt + \ln[A]_0$

$$\ln(2.50 \times 10^{-3} M) = -\left(2.97 \times 10^{-2} \frac{1}{\text{min}}\right)t + \ln(2.00 \times 10^{-2} M)$$

$$t = 70.0 \text{ min}$$

32. a) Because the plot of  $[C_2H_5OH]$  versus  $t$  is linear, this is a 0<sup>th</sup> order rate law

$$\text{Rate} = k$$

$$-\frac{d[C_2H_5OH]}{dt} = k$$

$$d[C_2H_5OH] = -kdt$$

$$\int_{[C_2H_5OH]_0}^{[C_2H_5OH]} d[C_2H_5OH] = -\int_0^t kdt$$

$$[C_2H_5OH] - [C_2H_5OH]_0 = -kt + 0$$

$$[C_2H_5OH] = -kt + [C_2H_5OH]_0 \text{ (integrated rate law)}$$

The rate constant equals the negative slope of the line;  $k = 4.00 \times 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}}$

$$\text{Rate} = 4.00 \times 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}} \text{ (rate law)}$$

b)  $[C_2H_5OH] = -kt + [C_2H_5OH]_0$

$$\frac{1}{2}(1.25 \times 10^{-2} M) = -\left(4.00 \times 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}}\right)t + (1.25 \times 10^{-2} M)$$

$$t = 156 \text{ s}$$

c) Since this is a 0<sup>th</sup> order rate law (which means that the rate is independent of concentration), the amount of time that it takes to decompose the total amount of  $C_2H_5OH$  is just double the half-life.

$$t = 2(156 \text{ s}) = 312 \text{ s}$$

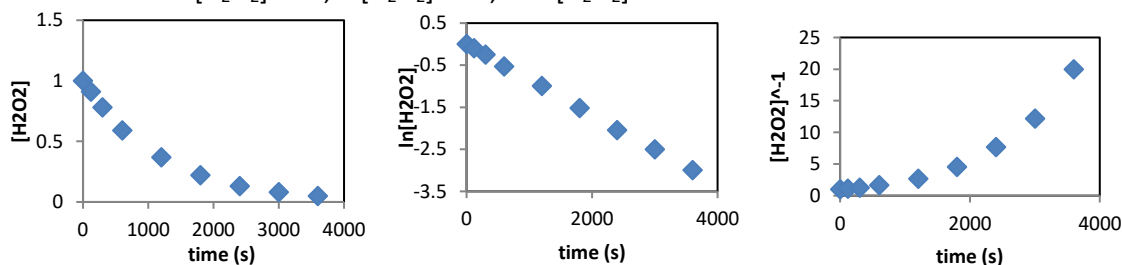
Or

$$0 = -\left(4.00 \times 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}}\right)t + (1.25 \times 10^{-2} M)$$

$$t = 312 \text{ s}$$

33. Plot

$[H_2O_2]$  vs.  $t$ ,  $\ln[H_2O_2]$  vs.  $t$ , and  $[H_2O_2]^{-1}$  vs.  $t$



Since the plot of  $\ln[H_2O_2]$  vs.  $t$  results in a linear relationship, the reaction is 1<sup>st</sup> order.

If you do not have a graphing calculator look at the spacing between the evenly spaced times to determine the order.

Time (s)	[H <sub>2</sub> O <sub>2</sub> ]	Difference between points	ln[H <sub>2</sub> O <sub>2</sub> ]	Difference between points	[H <sub>2</sub> O <sub>2</sub> ] <sup>-1</sup>	Difference between points
0	1.00	0.59-1.00=-0.41	0.00	-0.53-0.00=-0.53	1.00	1.7-1.00=0.7
600	0.59	-0.22	-0.53	-0.46	1.7	1.0
1200	0.37	-0.15	-0.99	-0.5	2.7	1.8
1800	0.22	-0.09	-1.5	-0.5	4.5	3.3
2400	0.13	-0.05	-2.0	-0.5	7.7	4.3
3000	0.082		-2.5		12	

Since the all the differences between ln[H<sub>2</sub>O<sub>2</sub>] are all approximately -0.5 this will be a straight line and the reaction is 1<sup>st</sup> order.

Differential Rate Law

$$Rate = k[H_2O_2]$$

Integrated Rate Law

$$\ln[H_2O_2] = -kt + \ln[H_2O_2]_0$$

The slope of the line will equal -k.

$$slope = \frac{rise}{run} = \frac{\ln(0.050 M) - \ln(1.00 M)}{3,600 s - 0 s} = -8.3 \times 10^{-4} \frac{1}{s} = -k$$

$$k = 8.3 \times 10^{-4} \frac{1}{s}$$

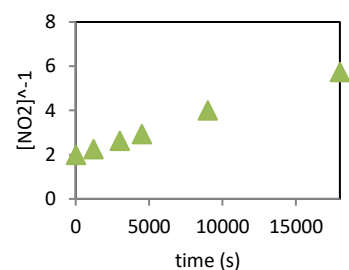
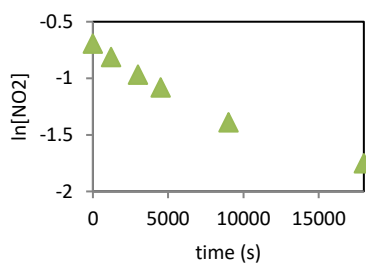
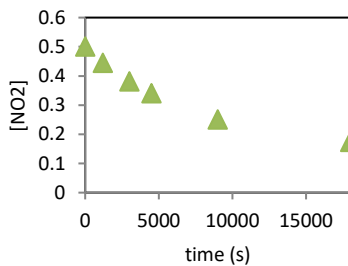
Calculate the concentration of H<sub>2</sub>O<sub>2</sub> after 4000. s.

$$\ln[H_2O_2] = -\left(8.3 \times 10^{-4} \frac{1}{s}\right)(4,000 s) + \ln(1.00 M)$$

$$[H_2O_2] = 0.036 M$$

### 35. Plot

[A] vs. t, ln[A] vs. t, and [A]<sup>-1</sup> vs. t



Since the plot of [A]<sup>-1</sup> vs. t is linear, this is a 2<sup>nd</sup> order rate law

If you do not have a graphing calculator look at the spacing between the evenly spaced times to determine the order. You must have at least 3 points.

Time (s)	[NO <sub>2</sub> ]	Difference between points	ln[NO <sub>2</sub> ]	Difference between points	[NO <sub>2</sub> ] <sup>-1</sup>	Difference between points
0	0.500	0.25-0.50=-0.25	-0.693	-1.39-0.693=-0.69	2.00	4.00-2.00=2.00
9.00×10 <sup>3</sup>	0.250	-0.076	-1.39	-0.36	4.00	1.75
1.80×10 <sup>4</sup>	0.174		-1.75		5.75	

This problem it is a little hard to determine. (I will not give you something this hard on an exam.)

The difference between the difference between the [NO<sub>2</sub>] points is 0.17 over a concentration range of 0.326 making the difference between differences 52%  $\left(\frac{0.17}{0.326} 100\% = 52\%\right)$  of the

range. The difference between the difference between the  $\ln[\text{NO}_2]$  is 0.33 over a  $\ln[\text{NO}_2]$  range of -1.06 making the difference between differences 31%  $\left(\frac{0.33}{1.06} 100\% = 33\%\right)$  of the range. The difference between the difference between  $[\text{NO}_2]^{-1}$  is 0.25 over a range of 3.75 making the difference between differences 6%  $\left(\frac{0.25}{3.75} 100\% = 6\%\right)$  of the range. The graph  $[\text{NO}_2]^{-1}$  has the smallest difference between differences, when you take the size of the range into account, the order is 2<sup>nd</sup> order.

Differential Rate Law

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

Integrated Rate Law

$$\frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0}$$

The slope of the line is the rate constant

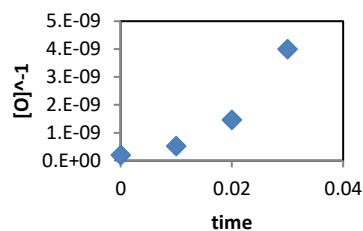
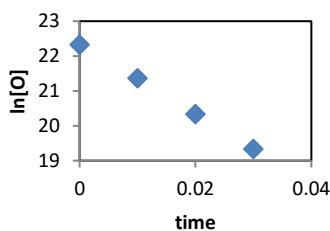
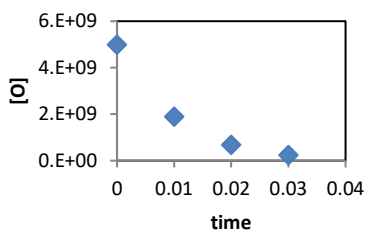
$$\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\frac{1}{0.174\text{ M}} - \frac{1}{0.500\text{ M}}}{1.80 \times 10^4\text{ s} - 0\text{ s}} = 2.08 \times 10^{-4} \frac{\text{L}}{\text{mol}\cdot\text{s}} = k$$

$$\frac{1}{[\text{NO}_2]} = \left(2.08 \times 10^{-4} \frac{\text{L}}{\text{mol}\cdot\text{s}}\right)t + \frac{1}{[\text{NO}_2]_0}$$

$$\frac{1}{[\text{NO}_2]} = \left(2.08 \times 10^{-4} \frac{\text{L}}{\text{mol}\cdot\text{s}}\right)(2.70 \times 10^4\text{ s}) + \frac{1}{0.500\text{ M}} = 7.62 \frac{\text{L}}{\text{mol}}$$

$$[\text{NO}_2] = 0.131\text{ M}$$

36. a) Plot  
[O] vs. t,  $\ln[\text{O}]$  vs. t, and  $[\text{O}]^{-1}$  vs. t



Since  $\ln[\text{O}]$  vs. t is linear, the rate expression is 1<sup>st</sup> order with respect to O.

If you do not have a graphing calculator look at the spacing between the evenly spaced times to determine the order.

Time (s)	[O]	Difference between points	$\ln[\text{O}]$	Difference between points	$[\text{O}]^{-1}$	Difference between points
0	$5.0 \times 10^9$	$1.9 \times 10^9 - 5.0 \times 10^9 = -3.1 \times 10^9$	22	$21 - 22 = -1.0$	$2.0 \times 10^{-10}$	$5.2 \times 10^{-10} - 2.0 \times 10^{-10} = 3.2 \times 10^{-10}$
0.010	$1.9 \times 10^9$	$-1.2 \times 10^9$	21	-1.0	$5.2 \times 10^{-10}$	$9.8 \times 10^{-10}$
0.020	$6.8 \times 10^8$	$-4.3 \times 10^8$	20	-1.0	$1.5 \times 10^{-9}$	$2.5 \times 10^{-9}$
0.030	$2.5 \times 10^8$		19		$4.0 \times 10^{-9}$	

Since all the differences between  $\ln[\text{H}_2\text{O}_2]$  are all approximately -1.0 this will be a straight line and the reaction is 1<sup>st</sup> order.

Differential Rate Law

- b) Overall Rate Law

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

Because the concentration of  $[\text{NO}_2] \gg [\text{O}]$  this can be turned into a pseudo rate law

$$\text{Rate} = k'[\text{O}]$$

$$k' = k[NO_2]$$

Determine  $k'$  using the 1<sup>st</sup> order integrated rate law

$$\ln[O] = -k't + \ln[O]_0$$

Therefore, the slope of the line is  $-k'$

$$slope = \frac{rise}{run} = \frac{\ln(2.5 \times 10^8 \frac{atoms}{cm^3}) - \ln(5.0 \times 10^9 \frac{atoms}{cm^3})}{3.0 \times 10^{-2} s - 0 s} = -1.0 \times 10^2 \frac{1}{s} = -k'$$

$$k' = 1.0 \times 10^2 \frac{1}{s}$$

Find  $k$

$$k' = k[NO_2]$$

$$(1.0 \times 10^2 \frac{1}{s}) = k[NO_2]$$

$$k = 1.0 \times 10^{-11} \frac{cm^3}{molecules \cdot s}$$

38. a) The order of the reaction with respect to A is 2<sup>nd</sup> order because the plot of  $[A]^{-1}$  vs.  $t$  is linear.

The integrated rate law is.

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

Therefore, the  $[A]_0^{-1}$  is the y intercept.  $[A]_0^{-1} = 10 \frac{L}{mol}$  and  $[A]_0 = 0.1 M$

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

$$k = slope = \frac{rise}{run} = \frac{70 \frac{L}{mol} - 20 \frac{L}{mol}}{6 s - 0 s} = 10 \frac{L}{mol \cdot s}$$

$$\frac{1}{[A]} = (10 \frac{L}{mol \cdot s})(9 s) + 10 \frac{L}{mol} = 100 \frac{L}{mol}$$

$$[A] = 0.01 M$$

- c) Calculate the time for the 1<sup>st</sup> half-life ( $[A] 0.1 \rightarrow 0.05$ )

$$\frac{1}{0.05 M} = (10 \frac{L}{mol \cdot s})t + \frac{1}{0.1 M}$$

$$t = 1 s$$

Calculate the time for the 2<sup>nd</sup> half-life

$$\frac{1}{0.025 M} = (10 \frac{L}{mol \cdot s})t + \frac{1}{0.05 M}$$

$$t = 2 s$$

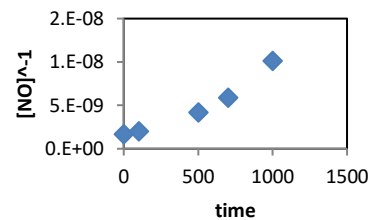
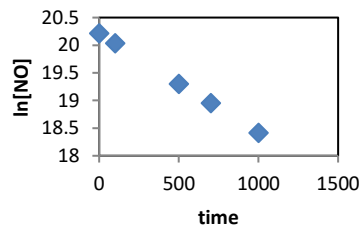
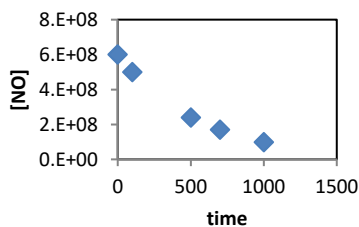
Calculate the time for the 3<sup>rd</sup> half-life

$$\frac{1}{0.0125 M} = (10 \frac{L}{mol \cdot s})t + \frac{1}{0.025 M}$$

$$t = 4 s$$

39. a) Plot

$[NO]$  vs.  $t$ ,  $\ln[NO]$  vs.  $t$ , and,  $[NO]^{-1}$  vs.  $t$



Since the plot of  $\ln[NO]$  vs.  $t$  is linear, the rate law is 1<sup>st</sup> order with respect to NO.



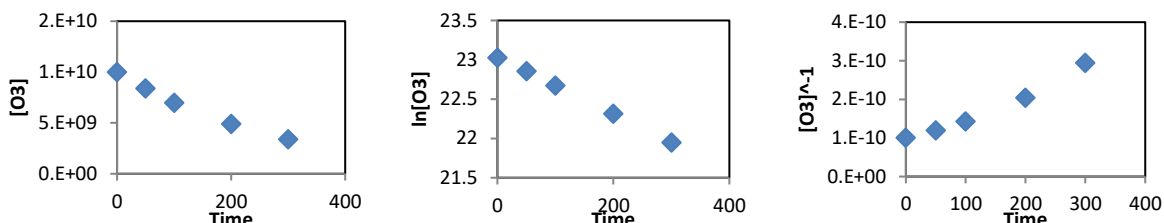
If you do not have a graphing calculator look at the spacing between the evenly spaced times to determine the order.

Time (s)	[NO]	Difference between points	ln[NO]	Difference between points	[NO] <sup>-1</sup>	Difference between points
0	6.0×10 <sup>8</sup>	2.4×10 <sup>8</sup> -6.0×10 <sup>8</sup> =-3.6×10 <sup>8</sup>	20	19-20=-1.0	1.7×10 <sup>-9</sup>	4.2×10 <sup>-9</sup> -1.7×10 <sup>-9</sup> = 2.5×10 <sup>-9</sup>
500	2.4×10 <sup>8</sup>	-1.4×10 <sup>8</sup>	19	-1.0	4.2×10 <sup>-9</sup>	5.8×10 <sup>-9</sup>
1000	9.9×10 <sup>7</sup>		18		1.0×10 <sup>-8</sup>	

Since the all the differences between ln[NO] are all approximately -1.0 this will be a straight line and the reaction is 1<sup>st</sup> order.

Plot

[O<sub>3</sub>] vs. t, ln[O<sub>3</sub>] vs. t, and [O<sub>3</sub>]<sup>-1</sup> vs. t



Since plot of ln[O<sub>3</sub>] vs. t is linear, the rate law is 1<sup>st</sup> order with respect to O<sub>3</sub>

If you do not have a graphing calculator look at the spacing between the evenly spaced times to determine the order.

Time (s)	[O <sub>3</sub> ]	Difference between points	ln[O <sub>3</sub> ]	Difference between points	[O <sub>3</sub> ] <sup>-1</sup>	Difference between points
0	1.0×10 <sup>10</sup>	7.0×10 <sup>9</sup> -1.0×10 <sup>10</sup> =-3.0×10 <sup>9</sup>	23.0	22.7-23.0=-0.3	1.0×10 <sup>-10</sup>	1.4×10 <sup>-10</sup> -1.0×10 <sup>-10</sup> = 4.0×10 <sup>-11</sup>
100	7.0×10 <sup>9</sup>	-2.1×10 <sup>9</sup>	22.7	-0.4	1.4×10 <sup>-10</sup>	6.0×10 <sup>-11</sup>
200	4.9×10 <sup>9</sup>	-1.5×10 <sup>9</sup>	22.3	-0.4	2.0×10 <sup>-10</sup>	9.0×10 <sup>-11</sup>
300	3.4×10 <sup>9</sup>		21.9		2.9×10 <sup>-10</sup>	

Since the all the differences between ln[O<sub>3</sub>] are all approximately -0.4 this will be a straight line and the reaction is 1<sup>st</sup> order.

b) Rate Law

$$Rate = k[NO][O_3]$$

c) When the [NO] data was taken the concentration of [O<sub>3</sub>]<sup>>></sup>[NO]. Therefore, a pseudo rate law can be written.

$$Rate = k'[NO]$$

$$k' = k[O_3]$$

Since the reaction was first order with respect to [NO] the slope of the line equals -k'

$$k' = -slope = -\frac{rise}{run} = -\frac{\ln\left(9.9 \times 10^7 \frac{molecules}{cm^3}\right) - \ln\left(6.0 \times 10^8 \frac{molecules}{cm^3}\right)}{1000.ms - 0.ms} = 0.0018 \frac{1}{ms}$$

When the [O<sub>3</sub>] data was taken the concentration of [NO]<sup>>></sup>[O<sub>3</sub>]. Therefore, a pseudo rate law can be written.

$$Rate = k''[O_3]$$

$$k'' = k[NO]$$

Since the reaction was first order with respect to [O<sub>3</sub>] the slope of the line equals -k''

$$k'' = -\text{slope} = -\frac{\text{rise}}{\text{run}} = -\frac{\ln\left(3.4 \times 10^9 \frac{\text{molecules}}{\text{cm}^3}\right) - \ln\left(1.0 \times 10^{10} \frac{\text{molecules}}{\text{cm}^3}\right)}{300. \text{ms} - 0 \text{ms}}$$

$$= 0.0036 \frac{1}{\text{ms}}$$

- d) You can solve this using either of the two data sets. In both data sets the reactions are pseudo 1<sup>st</sup> order system. Overall rate = pseudo 1<sup>st</sup> order rate

Using data set 1 [O<sub>3</sub>] held constant

$$k[\text{NO}][\text{O}_3] = k'[\text{NO}]$$

$$k = \frac{k'}{[\text{O}_3]} = \frac{0.0018 \frac{1}{\text{ms}}}{1.0 \times 10^{14} \frac{\text{molecules}}{\text{cm}^3}} = 1.8 \times 10^{-17} \frac{\text{cm}^3}{\text{molecules}\cdot\text{ms}}$$

Using data set 2 [NO] held constant

$$k[\text{NO}][\text{O}_3] = k''[\text{O}_3]$$

$$k = \frac{k''}{[\text{NO}]} = \frac{0.0036 \frac{1}{\text{ms}}}{2.0 \times 10^{14} \frac{\text{molecules}}{\text{cm}^3}} = 1.8 \times 10^{-17} \frac{\text{cm}^3}{\text{molecules}\cdot\text{ms}}$$

43.  $\ln[\text{PH}_3] = -kt + \ln[\text{PH}_3]_o$   
 $\ln(0.250 \text{ M}) = -k(120. \text{s}) + \ln(1.00 \text{ M})$   
 $k = 0.0116 \frac{1}{\text{s}}$   
 $\ln[\text{PH}_3] = -\left(0.0116 \frac{1}{\text{s}}\right)t + \ln[\text{PH}_3]_o$   
 $\ln(0.350 \text{ M}) = -\left(0.0116 \frac{1}{\text{s}}\right)t + \ln(2.00 \text{ M})$   
 $t = 151 \text{ s}$

47. a) Calculate k  
 $\ln[A] = -kt + \ln[A]_o$   
 $\ln(0.250[A]_o) = -k(320. \text{s}) + \ln[A]_o$   
 $\ln\left(\frac{0.250[A]_o}{[A]_o}\right) = -k(320. \text{s})$   
 $k = 0.00433 \frac{1}{\text{s}}$

Calculate time for 1<sup>st</sup> half life

$$\ln\left(\frac{1}{2}[A]_o\right) = -\left(0.00433 \frac{1}{\text{s}}\right)t + \ln[A]_o$$

$$\ln\left(\frac{\frac{1}{2}[A]_o}{[A]_o}\right) = -\left(0.00433 \frac{1}{\text{s}}\right)t$$

$$t = 159 \text{ s}$$

Calculate time for the 2<sup>nd</sup> half life

$$\ln\left(\frac{1}{4}[A]_o\right) = -\left(0.00433 \frac{1}{\text{s}}\right)t + \ln\left(\frac{1}{2}[A]_o\right)$$

$$\ln\left(\frac{\frac{1}{4}[A]_o}{\frac{1}{2}[A]_o}\right) = -\left(0.00433 \frac{1}{\text{s}}\right)t$$

$$t = 159 \text{ s}$$

- b)  $\ln(0.100[A]_o) = -\left(0.00433 \frac{1}{\text{s}}\right)t + \ln[A]_o$   
 $\ln\left(\frac{0.100[A]_o}{[A]_o}\right) = -\left(0.00433 \frac{1}{\text{s}}\right)t$   
 $t = 532 \text{ s}$

48. Since the time of the half-life doubles every successive half-life, the reaction is a 2<sup>nd</sup> order reaction

$$\begin{aligned} \text{a) } \frac{1}{[A]} &= kt + \frac{1}{[A]_o} \\ \frac{1}{0.05 M} &= k(10.0 \text{ min}) + \frac{1}{0.10 M} \\ k &= 1.0 \frac{L}{\text{mol}\cdot\text{min}} \\ \frac{1}{[A]} &= \left(1.0 \frac{L}{\text{mol}\cdot\text{min}}\right)(80.0 \text{ min}) + \frac{1}{0.10 M} = 90. \frac{L}{\text{mol}} \\ [A] &= 0.011 M \\ \text{b) } \frac{1}{[A]} &= \left(1.0 \frac{L}{\text{mol}\cdot\text{min}}\right)(30.0 \text{ min}) + \frac{1}{0.10 M} = 40. \frac{L}{\text{mol}} \\ [A] &= 0.025 M \end{aligned}$$

52. The problem wants you to find the time when  $[A] = 4.00[B]$ .

Known

$$k_A = 4.50 \times 10^{-4} \frac{1}{s}$$

$$k_B = 3.70 \times 10^{-3} \frac{1}{s}$$

Both 1<sup>st</sup> order reactions

Initially

$$[A]_o = [B]_o$$

$$\ln[A] = -kt + \ln[A]_o$$

$$\ln[B] = -kt + \ln[B]_o$$

Plug in  $[B]_o$  for  $[A]_o$  and  $[A] = 4.00[B]$  for  $[A]$  and solve for  $[B]$

$$\ln(4.00[B]) = -k_A t + \ln[B]_o$$

$$4.00[B] = e^{-k_A t + \ln[B]_o}$$

$$[B] = \frac{e^{-k_A t + \ln[B]_o}}{4.00}$$

Plug into equation for  $[B]$  and solve for  $t$

$$\ln[B] = -k_B t + \ln[B]_o$$

$$\ln\left(\frac{e^{-k_A t + \ln[B]_o}}{4.00}\right) = -k_B t + \ln[B]_o$$

$$\ln(e^{-k_A t + \ln[B]_o}) - \ln(4.00) = -k_B t + \ln[B]_o$$

$$-k_A t + \ln[B]_o - \ln(4.00) = -k_B t + \ln[B]_o$$

$$-k_A t - \ln(4.00) = -k_B t$$

$$-\ln(4.00) = (-k_B + k_A)t$$

$$t = \frac{-\ln(4.00)}{-k_B + k_A} = \frac{-\ln(4.00)}{-3.70 \times 10^{-3} \frac{1}{s} + 4.50 \times 10^{-4} \frac{1}{s}} = 427 \text{ s}$$

54. The concentrations of B and C are so much larger than A, therefore, during the course of the reaction they do not effectively change making this a pseudo 1<sup>st</sup> order reaction. The rate of the pseudo 1<sup>st</sup> order reaction is equal to the rate of the overall reaction times  $[B]^2$ .

$$\begin{aligned} \text{a) } \text{rate} &= k[A][B]^2 = k'[A] \\ k' &= k[B]^2 \\ \ln[A] &= -k't + \ln[A]_o \\ \ln(3.8 \times 10^{-3} M) &= -k'(8.0 \text{ s}) + \ln(1.0 \times 10^{-2} M) \\ k' &= 0.12 \frac{1}{s} \end{aligned}$$

$$k' = k[B]^2$$

$$k = \frac{k'}{[B]^2} = \frac{0.12 \frac{1}{s}}{(3.0 M)^2} = 0.013 \frac{L^2}{mol^2 \cdot s}$$

b)  $\ln[A] = -(0.12 \frac{1}{s})t + \ln[A]_o$

$$\ln(0.0050 M) = -(0.12 \frac{1}{s})t + \ln(1.0 \times 10^{-2} M)$$

$$t = 5.8 s$$

c)  $\ln[A] = -(0.12 \frac{1}{s})t + \ln[A]_o$

$$\ln[A] = -(0.12 \frac{1}{s})(13.0 s) + \ln(1.0 \times 10^{-2} M)$$

$$[A] = 0.0021 M$$

d) The concentration of C is the  $[C]_o - 2\Delta[A]$

$$\Delta[A] = 1.0 \times 10^{-2} M - 0.0021 M = 0.008 M$$

$$[C] = [C]_o - 2\Delta[A] = 2.0 M - 2(0.008 M) = 2.0 M$$

This should not be a surprising answer because in order to have a pseudo 1<sup>st</sup> order reaction with respect to A, the concentration of C must be essentially constant.

56. a) Elementary Step: An individual reaction in a proposed reaction mechanism. The rate law can be written from the coefficients in the balanced equation
- b) Molecularity: The number of reactant molecules (or free atoms) taking part in an elementary reaction. This is also the number of species that must collide in order to produce the reaction represented by an elementary reaction.
- c) Reaction Mechanism: The pathway that is proposed for an overall reaction and accounts for the experimental rate law.
- d) Intermediate: A species that is produced and consumed during a reaction but does not appear in the overall chemical equation.
- e) Rate Determining Step: The elementary reaction that governs the rate of the overall reaction. This is the slowest elementary reaction that occurs in a mechanism.

59. For elementary reactions the rate is just equal to the rate constant times the concentration of the reactants.

a)  $Rate = k[CH_3NC]$

b)  $Rate = k[O_3][NO]$

c)  $Rate = k[O_3]$

d)  $Rate = k[O_3][O]$

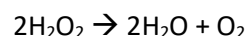
e)  $Rate = k[^{14}_6C]$

60. The rate law found in problem 33 was

$$Rate = k[H_2O_2]$$

In order for this to be the rate, the first step would have to be the rate determining step.

Overall Reaction

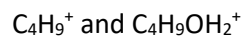


61.  $Rate = k[C_4H_9Br]$

Overall Reaction



Intermediates



63. The rate of a reaction is dependent on the slowest step.

a)  $Rate = k[NO][O_2]$  The mechanism is not consistent with rate law.

b)  $Rate = k_2[NO_3][NO]$

$NO_3$  is an intermediate, therefore, it needs to be eliminated from the rate equation. Use equilibrium to eliminate

$$k_1[NO][O_2] = k_{-1}[NO_3]$$

$$[NO_3] = \frac{k_1[NO][O_2]}{k_{-1}}$$

$$Rate = k_2[NO_3][NO] = k_2[NO] \frac{k_1[NO][O_2]}{k_{-1}} = \frac{k_2k_1[NO]^2[O_2]}{k_{-1}} = k[NO]^2[O_2]$$

The mechanism is consistent with rate law.

c)  $Rate = k[NO]^2$  The mechanism is not consistent with rate law.

d) In order for a mechanism to be plausible the elementary reactions must add up to the overall reaction. These elementary reactions do not add up to the overall reaction. In fact the middle reaction is not even balanced.

65.  $Rate = k_3[Br^-][H_2BrO_3^+]$

$H_2BrO_3^+$  is an intermediate therefore, needs to be eliminated from the rate law. Use equilibrium to eliminate the intermediate.

$$k_2[HBrO_3][H^+] = k_{-2}[H_2BrO_3^+]$$

$$[H_2BrO_3^+] = \frac{k_2[HBrO_3][H^+]}{k_{-2}}$$

$$Rate = k_3[Br^-][H_2BrO_3^+] = \frac{k_2k_3[Br^-][HBrO_3][H^+]}{k_{-2}}$$

$HBrO_3$  is an intermediate therefore, needs to be eliminated from the rate law. Use equilibrium to eliminate the intermediate.

$$k_1[BrO_3^-][H^+] = k_{-1}[HBrO_3]$$

$$[HBrO_3] = \frac{k_1[BrO_3^-][H^+]}{k_{-1}}$$

$$Rate = \frac{k_2k_3[Br^-][HBrO_3][H^+]}{k_{-2}} = \frac{k_1k_2k_3[Br^-][BrO_3^-][H^+]^2}{k_{-1}k_{-2}} = k[Br^-][BrO_3^-][H^+]^2$$

68. a)  $Rate = k_3[COCl][Cl_2]$

$COCl$  is an intermediate, therefore, it needs to be eliminated from the rate law. Use equilibrium to eliminate the intermediate.

$$k_2[CO][Cl] = k_{-2}[COCl]$$

$$[COCl] = \frac{k_2[CO][Cl]}{k_{-2}}$$

$$Rate = k_3[COCl][Cl_2] = \frac{k_3k_2[CO][Cl][Cl_2]}{k_{-2}}$$

Cl is an intermediate, therefore, it needs to be eliminated from the rate law. Use equilibrium to eliminate the intermediate.

$$k_1[Cl_2] = k_{-1}[Cl]^2$$

$$[Cl] = \frac{k_1^{1/2}[Cl_2]^{1/2}}{k_{-1}^{1/2}}$$

$$Rate = \frac{k_3 k_2 [CO][Cl][Cl_2]}{k_{-2}} = \frac{k_3 k_2 [CO][Cl_2] k_1^{1/2} [Cl_2]^{1/2}}{k_{-2} k_{-1}^{1/2}} = \frac{k_3 k_2 k_1^{1/2} [CO][Cl_2]^{3/2}}{k_{-2} k_{-1}^{1/2}}$$

$$Rate = k[CO][Cl_2]^{3/2}$$

b) COCl and Cl are intermediates

69. a) MoCl<sub>5</sub><sup>-</sup> is an intermediate

b)  $\frac{d[NO_2^-]}{dt} = k_2[NO_3^-][MoCl_5^-]$

Use the steady state approximation to eliminate the intermediate, rate of formation = rate of consumption

$$k_1[MoCl_6^{2-}] = k_{-1}[MoCl_5^-][Cl^-] + k_2[NO_3^-][MoCl_5^-]$$

$$[MoCl_5^-] = \frac{k_1[MoCl_6^{2-}]}{k_{-1}[Cl^-] + k_2[NO_3^-]}$$

$$\frac{d[NO_2^-]}{dt} = k_2[NO_3^-][MoCl_5^-] = \frac{k_1 k_2 [NO_3^-][MoCl_6^{2-}]}{k_{-1}[Cl^-] + k_2[NO_3^-]}$$

70. Need to calculate the rate of decomposition of O<sub>3</sub>

$$-\frac{d[O_3]}{dt} = k_1[M][O_3] + k_2[O][O_3] - k_{-1}[O_2][O][M]$$

Note: Rate of decomposition = ways O<sub>3</sub> used up – ways O<sub>3</sub> forms

O is an intermediate therefore need to remove it from the rate law.

Use the same steady state approximation to solve for [O]

$$k_1[M][O_3] = k_{-1}[O_2][O][M] + k_2[O][O_3]$$

$$[O] = \frac{k_1[M][O_3]}{k_{-1}[O_2][M] + k_2[O_3]}$$

$$-\frac{d[O_3]}{dt} = k_1[M][O_3] + k_2[O][O_3] - k_{-1}[O_2][O][M]$$

$$-\frac{d[O_3]}{dt} = k_1[M][O_3] + \frac{k_1 k_2 [M][O_3]^2}{k_{-1}[O_2][M] + k_2[O_3]} - \frac{k_1 k_{-1} [O_2][M]^2 [O_3]}{k_{-1}[O_2][M] + k_2[O_3]}$$

$$-\frac{d[O_3]}{dt} = \frac{k_1[M][O_3](k_{-1}[O_2][M] + k_2[O_3]) + k_1 k_2 [M][O_3]^2 - k_1 k_{-1} [O_2][M]^2 [O_3]}{k_{-1}[O_2][M] + k_2[O_3]}$$

$$-\frac{d[O_3]}{dt} = \frac{k_1 k_{-1} [O_2][M]^2 [O_3] + k_1 k_2 [M][O_3]^2 + k_1 k_2 [M][O_3]^2 - k_1 k_{-1} [O_2][M]^2 [O_3]}{k_{-1}[O_2][M] + k_2[O_3]}$$

$$-\frac{d[O_3]}{dt} = \frac{2k_1 k_2 [M][O_3]^2}{k_{-1}[O_2][M] + k_2[O_3]}$$

72. a) As the activation energy decreases the rate of the reaction goes up.

b) As the temperature increases the molecules/atoms move faster and more collisions occur, therefore, the faster the rate of the reaction.

c) As the frequency of collisions increases the rate of the reaction goes up.

d) As the orientation of collisions is more specific the rate of the reaction goes down.

$$79. \quad \ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{k_1}{3.52 \times 10^{-7} \frac{L}{mol \cdot s}}\right) = \frac{186 \frac{kJ}{mol}}{0.0083145 \frac{kJ}{mol \cdot K}} \left(\frac{1}{555 K} - \frac{1}{645 K}\right)$$

$$k_1 = 9.75 \times 10^{-5} \frac{L}{mol \cdot s}$$

$$80. \quad \ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{7.2 \times 10^{-4} \frac{1}{s}}{1.7 \times 10^{-2} \frac{1}{s}}\right) = \frac{E_a}{8.3145 \frac{J}{mol \cdot K}} \left(\frac{1}{720. K} - \frac{1}{660. K}\right)$$

$$E_a = 210,000 \frac{J}{mol}$$

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{k_1}{1.7 \times 10^{-2} \frac{L}{mol \cdot s}}\right) = \frac{210,000 \frac{J}{mol}}{8.3145 \frac{J}{mol \cdot K}} \left(\frac{1}{720. K} - \frac{1}{598 K}\right)$$

$$k_1 = 1.3 \times 10^{-5} \frac{1}{s}$$

After each half-life the number of moles of iodoethane is halved. Therefore after 3 half-lives there is  $\frac{1}{8}$  the number of moles of iodoethane that there was initially. For a gas,  $PV=nRT$ , therefore, since the volume, gas constant, and temperature are constant

$$\frac{P_1}{n_1} = \frac{P_2}{n_2}$$

$$\frac{894 \text{ torr}}{x} = \frac{P_2}{\frac{1}{8}x}$$

$$P_2 = 112 \text{ torr}$$

$$81. \quad \ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{7x}{x}\right) = \frac{5.40 \times 10^4 \frac{J}{mol}}{8.3145 \frac{J}{mol \cdot K}} \left(\frac{1}{295 K} - \frac{1}{T_1}\right)$$

$$T_1 = 324 K = 51^\circ C$$

$$83. \quad a) \quad \ln(k) = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln(A)$$

Therefore, when the  $\ln(k)$  is plotted vs.  $\frac{1}{T}$  the slope of the line equals  $-\frac{E_a}{R}$

$$-\frac{E_a}{R} = -\frac{E_a}{8.3145 \frac{J}{mol \cdot K}} = -1.10 \times 10^4 K$$

$$E_a = 9.15 \times 10^4 \frac{J}{mol} = 91.5 \frac{kJ}{mol}$$

b) When the  $\ln(k)$  is plotted vs.  $\frac{1}{T}$  the y intercept of the line equals  $\ln(A)$

$$\ln(A) = 33.5$$

$$A = 3.54 \times 10^{14} \frac{1}{s}$$

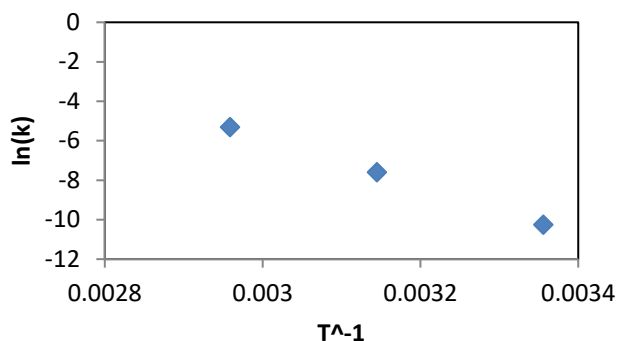
c)  $\ln(k) = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln(A)$

$$\ln(k) = -\frac{91,50 \frac{J}{mol}}{8.3145 \frac{J}{mol \cdot K}} \left( \frac{1}{298 K} \right) + \ln \left( 3.54 \times 10^{14} \frac{1}{s} \right) = -3.43$$

$$k = 0.0324 \frac{1}{s}$$

84.  $\ln(k) = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln(A)$

Therefore, if you plot the  $\ln(k)$  vs.  $\frac{1}{T}$  the slope of the line will be  $-\frac{E_a}{R}$

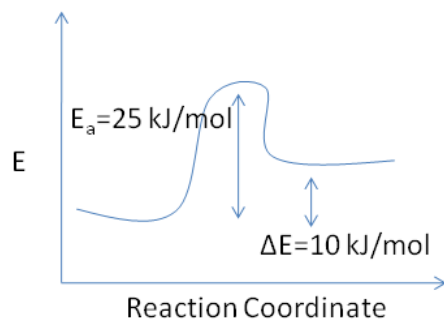


$$\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\ln(3.5 \times 10^{-5} \frac{1}{s}) - \ln(4.9 \times 10^{-3} \frac{1}{s})}{\frac{1}{298 K} - \frac{1}{338 K}} = -12,400 K$$

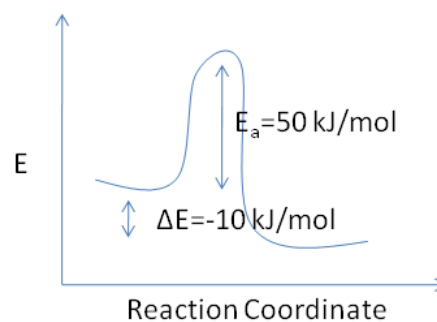
$$-12,400 K = \frac{E_a}{R} = \frac{E_a}{0.0083145 \frac{kJ}{mol \cdot K}}$$

$$E_a = 103 \frac{kJ}{mol}$$

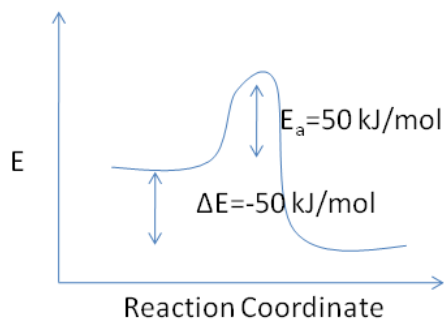
86. a)



b)



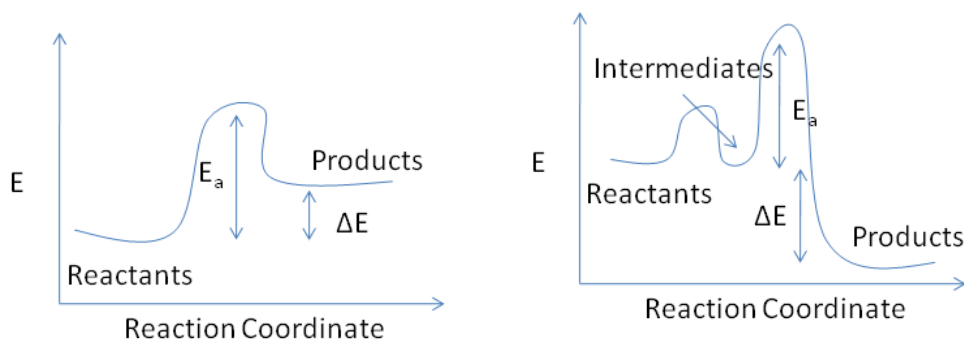
c)



The smaller the activation energy the greater the reaction rate. Therefore, reaction a will have the greatest rate.

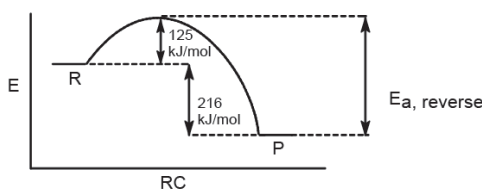


87.



The second graph is a two-step problem. 1<sup>st</sup>: reactants → intermediates 2<sup>nd</sup>: intermediates → products. Since the second reaction has the greater activation energy it will be the slower reaction and will determine the rate of the reaction. Therefore, we label the activation energy of the 2<sup>nd</sup> step.

88.



The activation energy for the reverse reaction is the  $-\Delta E + E_a$ .

$$-(-216 \frac{\text{kJ}}{\text{mol}}) + 125 \frac{\text{kJ}}{\text{mol}} = 341 \frac{\text{kJ}}{\text{mol}}$$

90. A catalyst increases the reaction rate because it provides another pathway with a lower activation energy for the reaction to proceed by. Homogeneous catalysts are present in the same phase as the reactants and heterogeneous catalyst are present in a different phase from the reactants. The uncatalyzed and catalyzed reactions most likely will have different rate laws because they have different pathways that they occur by.

94. a) The catalyst is the species that is initially added to the reaction but not used in the overall reaction. Therefore, NO is the catalyst.  
 b) An intermediate is a species that is formed in one of the steps of the reaction but not one of the reactants or products. Therefore, NO<sub>2</sub> is an intermediate.

c)  $\ln(k) = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln(A)$

$$\ln(k_{\text{cat}}) - \ln(k_{\text{uncat}}) = -\frac{E_a(\text{cat})}{R} \left(\frac{1}{T}\right) + \ln(A) - \left(-\frac{E_a(\text{uncat})}{R} \left(\frac{1}{T}\right) + \ln(A)\right)$$

$$\ln\left(\frac{k_{\text{cat}}}{k_{\text{uncat}}}\right) = \frac{1}{RT} (-E_a(\text{cat}) + E_a(\text{uncat}))$$

$$\ln\left(\frac{k_{\text{cat}}}{k_{\text{uncat}}}\right) = \frac{1}{(8.3145 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298 \text{ K})} (-11,900 \text{ J} + 14,000 \text{ J}) = 0.848$$

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = 2.3$$