

CHE152
Chapter 16 -Chemical Kinetics Additional Problems
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16.1 The conversion of CO to CO₂ in a catalytic converter is shown to be zero order with respect to CO. If the initial concentration of CO is 25.0 g/L, what will be its final concentration after 30.0 minutes? k for this reaction is 0.725 g/L-min.

16.2. How many minutes will it take to reduce the concentration of CO from 15.00 g/L to 0.010 g/L in a catalytic converter?

16.3 Given the data below determine the rate for the process A → products.

time, s	[A], M
0	3.500
100	3.210
200	3.050
300	2.810
400	2.490
500	2.190
600	1.980
700	1.720

- (a) How long will it take the concentration of A to decrease from 0.9950 M to 0.0350 M?
- (b) If the concentration of A is 2.280 M after 900 s, what was the initial concentration A?
- (c) Starting with [A] = 5.25 M, what is [A] after 1200.0 s?

16.4 B → products is a first order process. If after 80.0 s the concentration of B is 0.7500 M, what was the initial concentration of B? $k = 6.85 \times 10^{-3} \text{ s}^{-1}$.

16.5 Given the data below determine the rate for the process $B \rightarrow$ products.

time, min	[B], M
0	2.500
10.0	2.437
30.0	2.315
90.0	1.984
270.0	1.250
810.0	0.312
2430.0	0.00487
3000.0	0.00113

- (a) How long will it take the concentration of B to decrease from 0.9950 M to 0.0350 M?
(b) If the concentration of B is 2.280 M after 900.0 min, what was the initial concentration B?
(c) Starting with $[B] = 5.25$ M, what is $[B]$ after 1200.0 min?

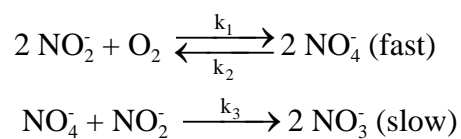
16.6 $C \rightarrow$ products is a second order process. If the initial concentration of C is 0.3750 M, what will be the concentration of C after 1500.0 seconds? $k = 0.00125 \text{ L mol}^{-1} \text{ s}^{-1}$.

16.7 Given the data below determine the rate for the process $C \rightarrow$ products.

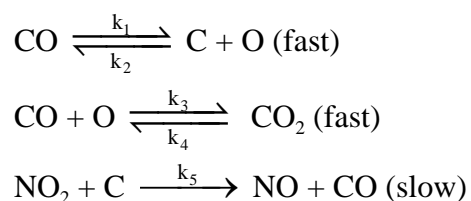
time, h	[C], M
0	0.9500
0.50	0.9113
1.50	0.8425
5.50	0.6473
8.50	0.5515
12.50	0.4605
15.50	0.4099
25.50	0.2999

- (a) How long will it take the concentration of A to decrease from 0.9950 M to 0.0350 M?
(b) If the concentration of A is 0.002280 M after 900.0 h, what was the initial concentration A?
(c) Starting with $[A] = 5.25$ M, what is $[A]$ after 1200.0 h?

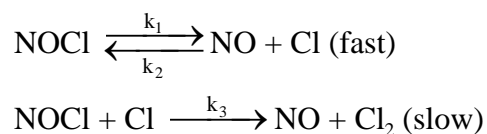
16.8 Determine the rate law for $2 \text{NO}_2 + \text{O}_2 \rightarrow 2 \text{NO}_3$ given the following two step mechanism:



16.9 Determine the rate law for $\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$ given the following mechanism:



16.10 Determine the rate law for $2 \text{NOCl} \rightarrow 2 \text{NO} + \text{Cl}_2$ given the following mechanism:



16.11 Calculate k_2 given the following, $k_1 = 0.00258 \text{ s}^{-1}$, $T_1 = 325.62 \text{ K}$, $T_2 = 568.91 \text{ K}$ and $E_a = 3.251 \times 10^5 \text{ J mol}^{-1}$.

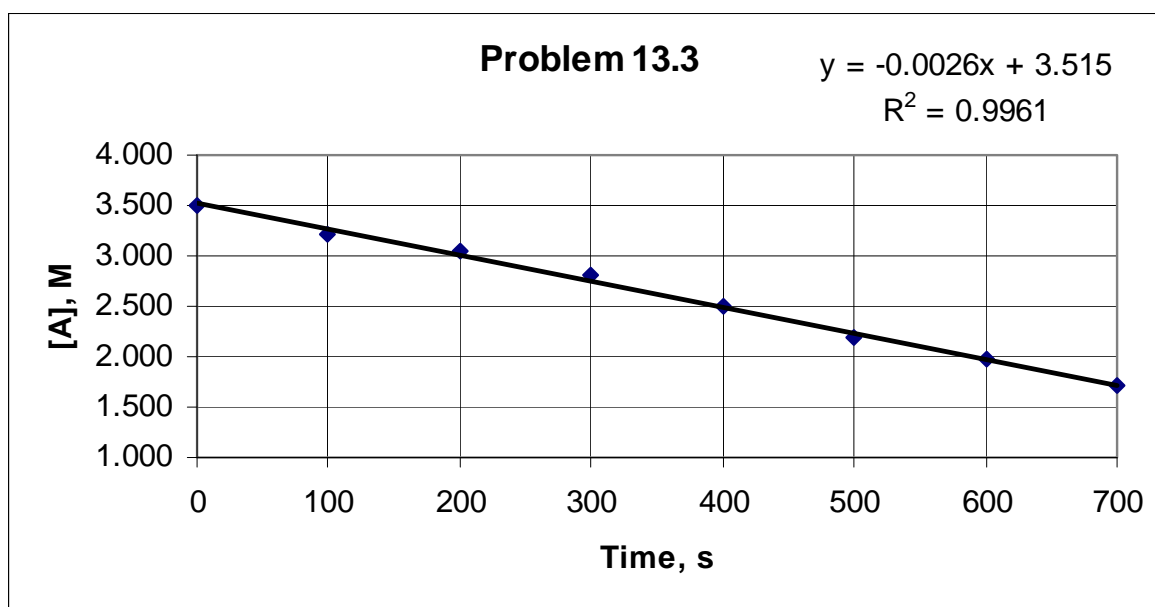
16.12 Calculate T_2 given the following: $k_1 = 0.000186 \text{ s}^{-1}$, $T_1 = 278.96 \text{ K}$, $k_2 = 0.00325 \text{ s}^{-1}$ and $E_a = 8.654 \times 10^4 \text{ J mol}^{-1}$.

$$16.1 [\text{CO}]_{30.0} = \frac{-0.725 \text{ g}}{\text{L min}} \times 30.0 \text{ min} + \frac{25.0 \text{ g}}{\text{L}} = \frac{3.25 \text{ g}}{\text{L}}$$

$$16.2 \frac{0.010 \text{ g}}{\text{L}} = \frac{-0.725 \text{ g}}{\text{L min}} \times t + \frac{15.00 \text{ g}}{\text{L}}$$

$$\frac{-14.99 \text{ g}}{\text{L}} = \frac{-0.725 \text{ g}}{\text{L min}} \times t; t = 20.7 \text{ min}$$

16.3 Since a plot of [A] v. time yields a straight line, the reaction is zero order.



$$[\text{A}]_t = -0.0026 \text{ mol L}^{-1} \text{ s}^{-1} \times t + 3.515 \text{ mol L}^{-1}$$

$$(a) 0.0350 \text{ M} = -\frac{0.0026 \text{ mol}}{\text{L s}} \times t + 0.9950 \text{ M}; t = 3.7 \times 10^2 \text{ s}$$

$$(b) 2.280 \text{ M} = -\frac{0.0026 \text{ mol}}{\text{L s}} \times 900 \text{ s} + [\text{A}]; [\text{A}] = 4.62 \text{ M}$$

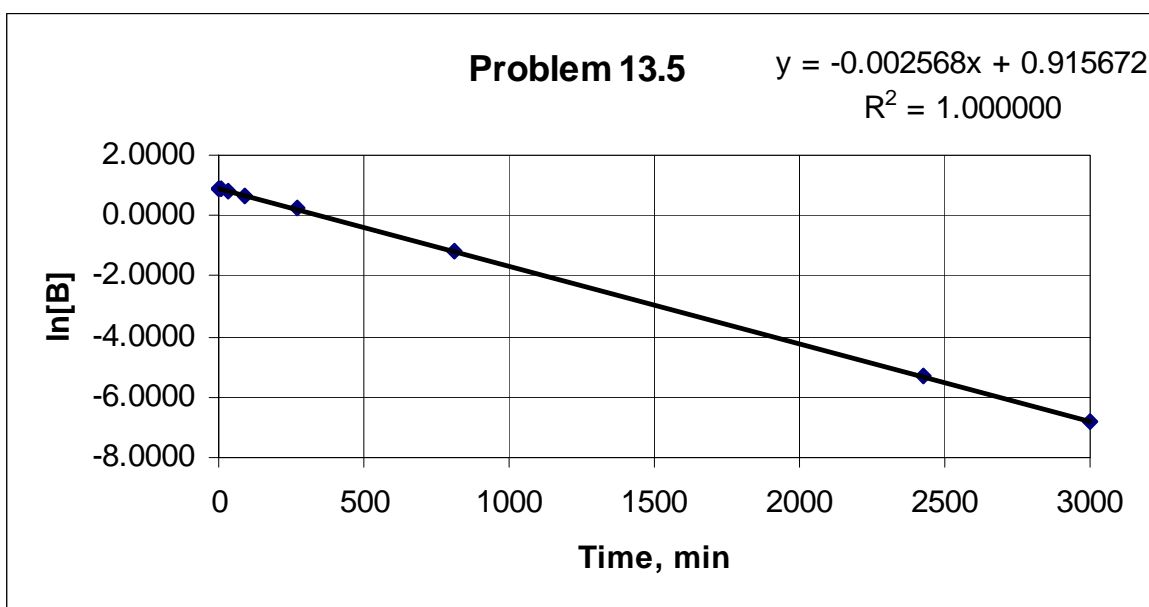
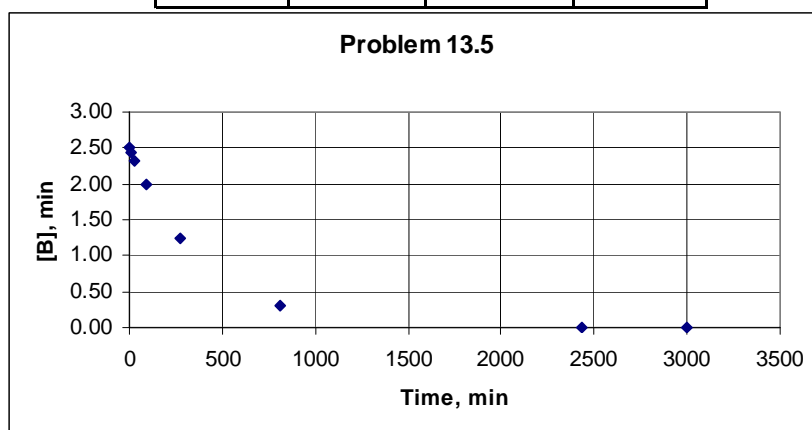
$$(c) [\text{A}]_{1200} = -\frac{0.0026 \text{ mol}}{\text{L s}} \times 1200.0 \text{ s} + 5.25 \text{ M} = 2.13 \text{ M}$$

$$16.4 \ln(0.7500) = \frac{-6.85 \times 10^{-3}}{s} \times 80.0s + \ln[B]_0$$

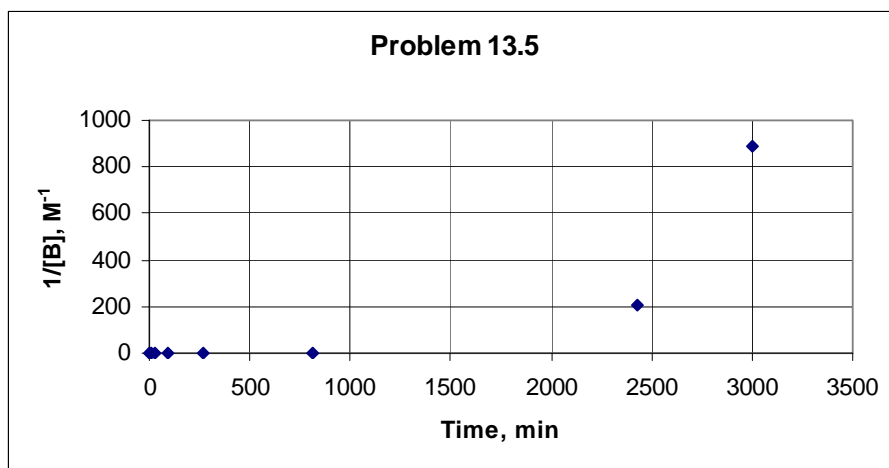
$$\ln[B]_0 = 0.260; [B]_0 = 1.30M$$

16.5 Since the plot of $\ln[B]$ vs. time yielded a straight line, the reaction is first order.

time, min	[B], M	$\ln[B]$	$1/[B]$
0	2.500	0.916	0.400
10	2.437	0.891	0.410
30	2.315	0.839	0.432
90	1.984	0.685	0.504
270	1.245	0.219	0.803
810	0.312	-1.164	3.202
2430	4.873E-03	-5.324	205.212
3000	1.128E-03	-6.787	886.525



$$\ln[B]_t = -0.00257 \text{ min}^{-1} \times t + 0.9157$$



$$(a) \ln(0.0350) = \frac{-0.00257}{\text{min}} \times t + \ln(0.9950); t = 1.30 \times 10^3 \text{ min}$$

$$(b) \ln(2.280) = \frac{-0.00257}{\text{min}} \times 900.0 \text{ min} + \ln[B]; \ln[B] = 3.14; [B] = 23.0 \text{ M}$$

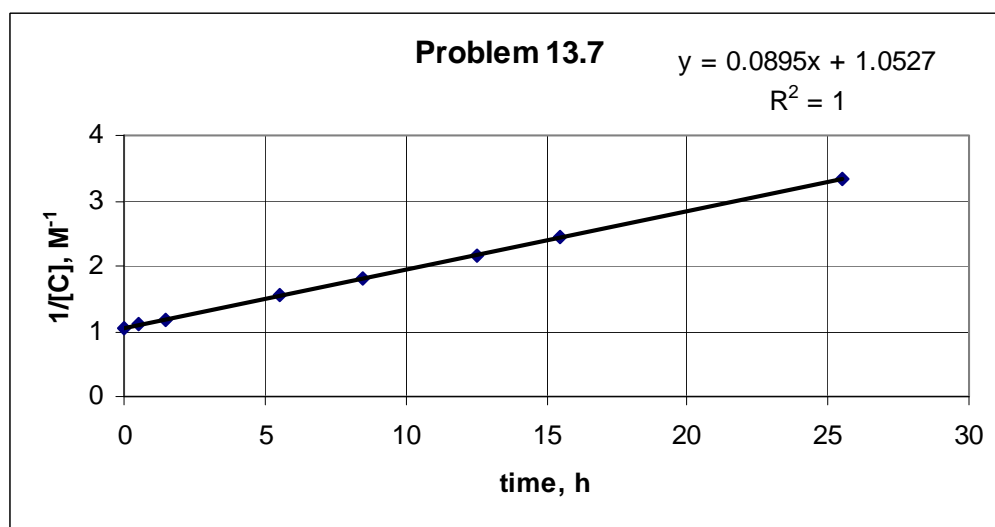
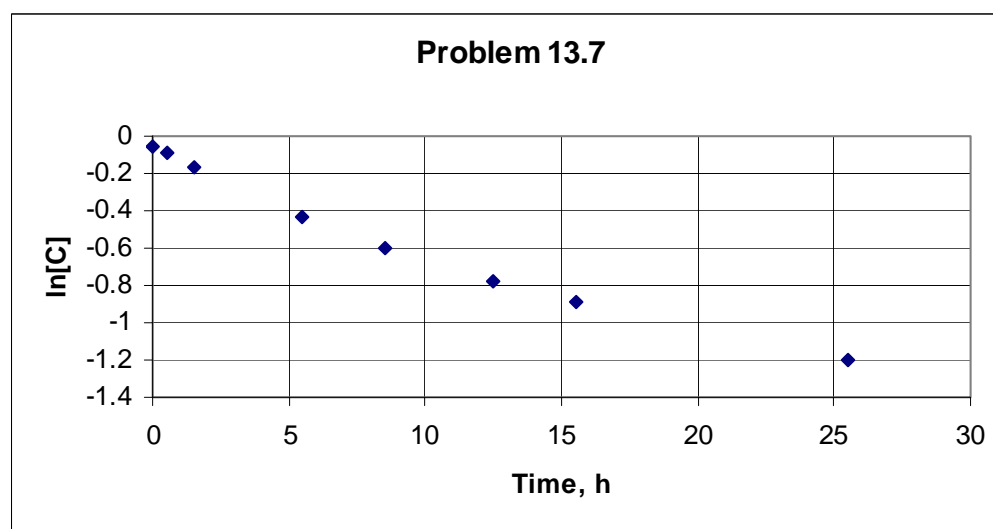
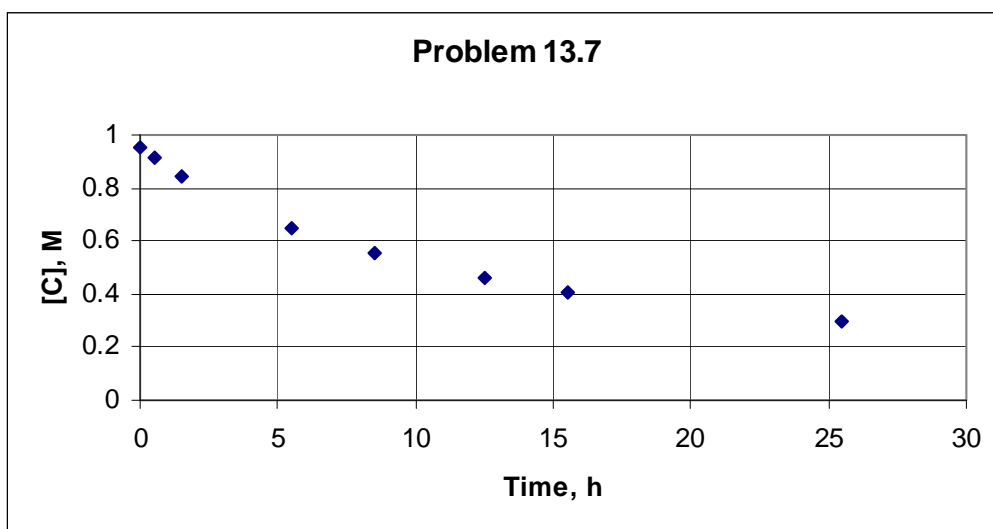
$$(c) \ln[B]_{1200} = \frac{-0.00257}{\text{min}} \times 1200 \text{ min} + \ln(5.25) = -1.43; [B] = 0.24 \text{ M}$$

$$16.6 \frac{1}{[C]_{1500}} = \frac{0.00125 \text{ L}}{\text{mol s}} \times 1500.0 \text{ s} + \frac{1}{0.3750 \text{ M}}; \frac{1}{[C]_{1500}} = 4.54 \text{ M}^{-1}$$

$$[C] = 0.220 \text{ M}$$

16.7 Since a plot of $1/[C]$ vs. time yielded a straight line, the reaction is second order.

time, h	[C]	ln[C]	1/[C]
0.00	0.9500	-0.05129	1.053
0.50	0.9113	-0.09288	1.097
1.50	0.8425	-0.17138	1.187
5.50	0.6473	-0.43495	1.545
8.50	0.5515	-0.59511	1.813
12.50	0.4605	-0.77544	2.172
15.50	0.4099	-0.89184	2.440
25.50	0.2999	-1.20431	3.334



$$\frac{1}{[C]}_t = 0.0895 \text{ L mol}^{-1}\text{h}^{-1} + 1.053 \text{ M}^{-1}$$

$$(a) \frac{1}{[0.0350 \text{ M}]} = \frac{0.0895 \text{ L}}{\text{mol h}} \times t + \frac{1}{[0.9950 \text{ M}]}; t = 308 \text{ h}$$

$$(b) \frac{1}{[0.00280 \text{ M}]} = \frac{0.0895 \text{ L}}{\text{mol h}} \times 900.0 \text{ h} + \frac{1}{[C]_0}; \frac{1}{[C]_0} = 276 \text{ M}^{-1}; [C]_0 = 0.00362 \text{ M}$$

$$(c) \frac{1}{[C]_{1200}} = \frac{0.0895 \text{ L}}{\text{mol h}} \times 1200.0 \text{ h} + \frac{1}{5.25 \text{ M}}; \frac{1}{[C]_{1200}} = 108 \text{ M}^{-1}$$

$$[C]_{1200} = 0.00930 \text{ M}$$

16.8 The slow step determines the rate law:

$$\text{rate} = k_3 [\text{NO}_4][\text{NO}_2]$$

Problem: NO_4 is not in our original (overall) reaction.

To get rid of NO_4 we use the fast step and solve for NO_4 :

$$k_1[\text{NO}_2^-]^2[\text{O}_2] = k_2[\text{NO}_4^-]^2$$

$$[\text{NO}_4^-]^2 = \frac{k_1}{k_2}[\text{NO}_2^-]^2[\text{O}_2]; [\text{NO}_4^-] = \sqrt{\frac{k_1}{k_2}}[\text{NO}_2^-]\sqrt{[\text{O}_2]}$$

substitute this for $[\text{NO}_4^-]$ in the rate law :

$$\text{rate} = \sqrt{\frac{k_1}{k_2}}[\text{NO}_2^-]\sqrt{[\text{O}_2]}k_3[\text{NO}_2^-] = k[\text{NO}_2^-]^2\sqrt{[\text{O}_2]}$$

rate = $k[\text{NO}_2^-]^2\sqrt{[\text{O}_2]}$; if this agrees with experimental rate, then the mechanism is plausible.

16.9 The slow step determines the rate law:

$$\text{rate} = k_5[\text{NO}_2][\text{C}]$$

Problem: C is not in our original (overall) reaction.

To get rid of C we use the fast step containing C and solve for [C]:

rate = $k_5[\text{NO}_2][\text{C}]$; problem : C is not in original (overall) reaction; we will use
the reaction that contains C to solve for [C]:

$$k_1[\text{CO}] = k_2[\text{C}][\text{O}]; [\text{C}] = \frac{k_1[\text{CO}]}{k_2[\text{O}]}; \text{substituting :}$$

rate = $k_5[\text{NO}_2] \frac{k_1[\text{CO}]}{k_2[\text{O}]}$; problem : O is not in original (overall) reaction; we will use
the reaction that contains O to solve for [O]:

$$k_3[\text{CO}][\text{O}] = k_4[\text{CO}_2]; [\text{O}] = \frac{k_4[\text{CO}_2]}{k_3[\text{CO}]}; \text{substituting :}$$

$$\text{rate} = k_5[\text{NO}_2] \frac{k_1[\text{CO}]}{k_2 \frac{k_4[\text{CO}_2]}{k_3[\text{CO}]}} = k \frac{[\text{CO}]^2}{[\text{CO}_2]}$$

rate = $k \frac{[\text{NO}_2][\text{CO}]^2}{[\text{CO}_2]}$; if this agrees with the experimental rate law, then the mechanism
is plausible.

16.10 The slow step determines the rate law:

$$\text{rate} = k_3[\text{NOCl}][\text{Cl}]$$

Problem: Cl is not in our original (overall) reaction.

To get rid of Cl we use the fast step containing Cl and solve for [Cl]:

$$k_1[\text{NOCl}] = k_2[\text{NO}][\text{Cl}]; [\text{Cl}] = \frac{k_1[\text{NOCl}]}{k_2[\text{NO}]}; \text{substituting into the rate law :}$$

$$\text{rate} = k_3[\text{NOCl}] \frac{k_1[\text{NOCl}]}{k_2[\text{NO}]} = k \frac{[\text{NOCl}]^2}{[\text{NO}]}$$

rate = $k \frac{[\text{NOCl}]^2}{[\text{NO}]}$; if this agrees with the experimental rate law, then the

mechanism is plausible.

16.11 There are three ways to solve this type of problem.

$$\text{Equation \#1: } k = Ae^{-E_a/RT}$$

$$0.00258 = Ae^{-3.251 \times 10^5 / 8.314472 \times 325.62}; 0.00258 = Ae^{-120.1}; 0.00258 = A(7.077 \times 10^{-53})$$

$$A = 3.65 \times 10^{49}; k_2 = 3.65 \times 10^{49} e^{-3.251 \times 10^5 / 8.314472 \times 568.91} = e^{-68.73} = 3.65 \times 10^{49}$$

$$k_2 = 3.65 \times 10^{49} (1.4 \times 10^{-30}) = 5.2 \times 10^{19} \text{ s}^{-1}$$

$$\text{Equation \#2: } \ln(k) = -\frac{E_a}{R} \times \frac{1}{T} + \ln(A)$$

$$\ln(k_2) = -\frac{3.251 \times 10^5 \text{ J/mol}}{8.314472 \text{ J/mol K}} \times \frac{1}{568.91 \text{ K}} + \ln(3.45 \times 10^{49})$$

$$\ln(k_2) = -68.72_{879} + 1.14065 \times 10^2 = 4.4533621 \times 10^1$$

$$k_2 = e^{4.4533621 \times 10^1} = 4.9 \times 10^{19} \text{ s}^{-1}$$

$$\text{Equation \#3: } \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{k_2}{0.00258}\right) = \frac{3.251 \times 10^5 \text{ J/mol}}{8.314472 \text{ J/mol K}} \left(\frac{1}{325.62 \text{ K}} - \frac{1}{568.91 \text{ K}}\right)$$

$$\ln\left(\frac{k_2}{0.00258}\right) = 3.910 \times 10^4 \text{ K} (0.0030711 \text{ K}^{-1} - 0.0017577 \text{ K}^{-1})$$

$$\ln\left(\frac{k_2}{0.00258}\right) = 3.910 \times 10^4 \text{ K} (0.0013134 \text{ K}^{-1})$$

$$\ln\left(\frac{k_2}{0.00258}\right) = 51.35_{2549}; \left(\frac{k_2}{0.00258}\right) = e^{51.35_{2549}}; \left(\frac{k_2}{0.00258}\right) = 2.0_{05066} \times 10^{22}$$

$$k_2 = 5.2 \times 10^{19} \text{ s}^{-1}$$

16.12 There are three ways to solve this type of problem.

$$\text{Equation \#1: } k = Ae^{-E_a/RT}$$

$$0.00186 = Ae^{-8.654 \times 10^4 / 8.314472 \times 278.96}; 0.00186 = Ae^{-37.31}; 0.00186 = A(62.5046 \times 10^{-17})$$

$$A = 2.9_{7578} \times 10^{13}; k_2 = 2.9_{7578} \times 10^{13} e^{-3.251 \times 10^5 / 8.314472 \times 568.91} = e^{-68.73} = 3.65 \times 10^{49}$$

$$0.00325 = 2.9_{7578} \times 10^{13} (e^{-8.654 \times 10^4 / 8.314472 \times T})$$

$$\ln(0.00325) = \ln(2.9_{7578} \times 10^{13}) + \ln(e^{-8.654 \times 10^4 / 8.314472 \times T})$$

$$-5.729 = 31.0241 + \frac{-8.654 \times 10^4}{8.314472 \times T}; -36.7531 = \frac{-8.654 \times 10^4}{8.314472 \times T}$$

$$0.0035_{311154} = \frac{1}{T}; T = 2.8_{320} \times 10^2 \text{ K}$$

$$\text{Equation \#2: } \ln(k) = -\frac{E_a}{R} \times \frac{1}{T} + \ln(A)$$

$$\ln(0.00325) = -\frac{8.654 \times 10^4 \text{ J/mol}}{8.314472 \text{ J/mol K}} \times \frac{1}{T} + \ln(2.9_{7578} \times 10^{13})$$

$$-5.72_{91} = -1.040_{8358} \times 10^4 \text{ K} \times \frac{1}{T} + 31.02_{4112}$$

$$-36.75 = -1.040_{8358} \times 10^4 \text{ K} \times \frac{1}{T}; \frac{1}{T} = 0.0035_{31125} \text{ K}^{-1}$$

$$T = 2.8_{319} \times 10^2 \text{ K}$$

$$\text{Equation \#3: } \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{0.00325}{0.000186}\right) = \frac{8.654 \times 10^4 \text{ J/mol}}{8.314472 \text{ J/mol K}} \left(\frac{1}{278.96 \text{ K}} - \frac{1}{T_2}\right)$$

$$2.861 = 1.040 \times 10^4 \text{ K} \left(0.0035847 \text{ K}^{-1} - \frac{1}{T_2}\right)$$

$$0.0002751 \text{ K}^{-1} = 0.0035847 \text{ K}^{-1} - \frac{1}{T_2}; -0.003310 \text{ K}^{-1} = 0.0035847 \text{ K}^{-1} = \frac{1}{T_2}$$

$$T_2 = 302 \text{ K}$$