

rate  $\text{NH}_3 = 6.29 \times 10^{-5} \text{ mol/L}\cdot\text{s}$

rate  $\text{N}_2$  consumed =  $(6.29 \times 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}}) \left( \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} \right) = \boxed{3.15 \times 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}}}$

rate  $\text{H}_2$  consumed =  $(6.29 \times 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}}) \left( \frac{3 \text{ mol H}_2}{2 \text{ mol NH}_3} \right) = \boxed{9.44 \times 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}}}$

11.18)

a) rate =  $\frac{10.4 \text{ mL}}{3.3 \text{ min}} = 3.2 \text{ mL/min}$

b) rate =  $\frac{17.3 \text{ mL}}{6.9 \text{ min}} = 2.5 \text{ mL/min}$

11.20) plot on next page.

a) rate<sub>0-10s</sub> =  $\frac{0.326 - 0 \frac{\text{mol}}{\text{L}}}{10\text{s} - 0\text{s}} = 0.0326 \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$

rate<sub>10-20s</sub> =  $\frac{0.572 - 0.326 \frac{\text{mol}}{\text{L}}}{20\text{s} - 10\text{s}} = 0.0246 \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$

rate<sub>20-30s</sub> =  $0.0178 \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$

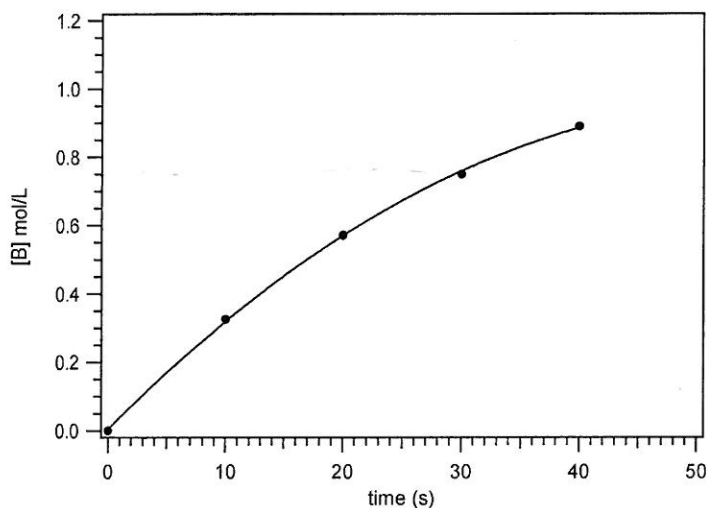
rate<sub>30-40s</sub> =  $0.0140 \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$

Rate decreases at each 10s interval b/c there are progressively fewer atoms/molecules to react as time progresses.

b) The  $[\text{A}]$  should decrease at  $\frac{1}{2}$  the rate of increase of B.  
c) use the plot to determine tangent at this point.

rate =  $0.015 \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$

11.20)



11.24)

$$a) 3.5 \times 10^{-14} \frac{\text{cm}^3}{\text{molecule} \cdot \text{s}} \left( \frac{1 \text{ mL}}{\text{cm}^3} \right) \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}} \right) = 2.1 \times 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

$$b) 4.3 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

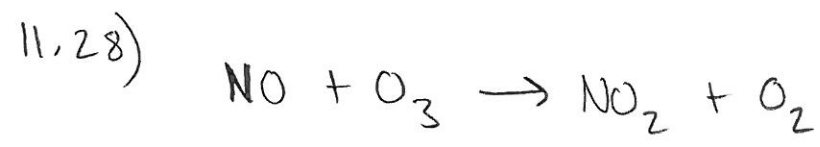
$$c) 3.7 \times 10^{-9} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

11.26)  $\text{CO(g)} + \text{NO}_2\text{(g)}$  2<sup>nd</sup>-order  $\text{NO}_2$ ; 0-order in CO

$$a) \text{rate} = k[\text{NO}_2]^2$$

$$b) \text{rate} = k\left(\frac{1}{2}\right)^2 = k\left(\frac{1}{4}\right) \Rightarrow \text{rate is } \frac{1}{4} \text{ the original value}$$

c) no change; Rate does not depend on concentration of CO.



$$\text{rate} = k[\text{NO}]^1[\text{O}_3]^1 \quad ; \quad k = 1.9 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

$$\text{rate} = 1.9 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} (1.2 \times 10^{-5} \text{ mol/L}) (2.0 \times 10^{-5} \text{ mol/L})$$

$$\text{rate} = 4.6 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

11.30)

$[\text{H}_2\text{O}_2]$  doubled,  $[\text{KI}]$  constant  $\Rightarrow$  Rate doubles

$\hookrightarrow$  Rate is 1<sup>st</sup>-order w.r.t.  $[\text{H}_2\text{O}_2]$

$[\text{H}_2\text{O}_2]$  constant;  $[\text{KI}]$  doubled  $\Rightarrow$  Rate doubles

$\hookrightarrow$  Rate is 1<sup>st</sup>-order w.r.t.  $[\text{KI}]$

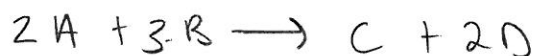
$$\text{rate} = k[\text{H}_2\text{O}_2]^1[\text{KI}]^1$$

$$k = \frac{\text{rate}}{[\text{H}_2\text{O}_2]^1[\text{KI}]^1} = \frac{(0.090 \frac{\text{mol}}{\text{min}}) (\frac{1\text{L}}{1000\text{mol}})}{(0.15)(0.033)}$$

$$k = 1.8 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$$

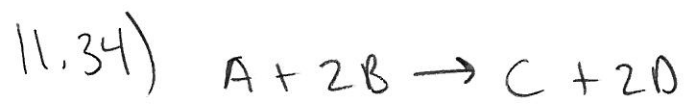
11.32) First-order in Both Reactants (like 11.30)

$$\text{rate} = k[\text{A}][\text{B}]$$

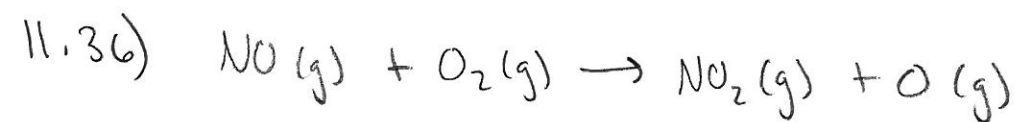


$$k = \frac{\text{rate}}{[\text{A}][\text{B}]} = \frac{0.132 \frac{\text{mol}}{\text{L} \cdot \text{s}}}{(0.127 \frac{\text{mol}}{\text{L}})(0.30 \frac{\text{mol}}{\text{L}})} = 3.5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

using data entry 2:

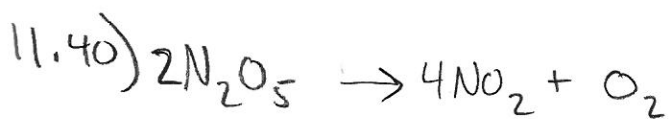


$$\text{rate} = k[A]$$



rate =  $k[NO][O_2]$  first-order w.r.t. both Reactants

$$k = \frac{\text{rate}}{[NO][O_2]} = \frac{1.6 \times 10^{-16} \frac{\text{mol}}{\text{L} \cdot \text{s}}}{(0.002 \frac{\text{mol}}{\text{L}})(0.010 \frac{\text{mol}}{\text{L}})} = 8.0 \times 10^{-12} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$



$k = 5.25 \times 10^{-4} \text{ s}^{-1}$  (First-order)

$[N_2O_5]_0 = 0.100 \text{ M}$

$[N_2O_5]_t = 0.100 \text{ M} (0.0100) = 0.0010 \text{ M}$

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

$$t = -k^{-1} \ln \frac{[N_2O_5]_0}{[N_2O_5]_t} = \left( \frac{-1}{5.25 \times 10^{-4} \text{ s}^{-1}} \right) \ln \left( \frac{0.001 \text{ M}}{0.100 \text{ M}} \right)$$

$$t = 8,770 \text{ s}$$

11.42) The implication is that amoxicillin is a compound that degrades w/ a lifetime such that two weeks is a sufficient period to decompose the sample. Refrigeration slows the rate of reaction, lengthening the usefulness of the drug.

11.44)  $k = 4.0 \times 10^{-8} \text{ s}^{-1} @ 25^\circ\text{C}$   $t_{1/2} = ?$

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{\ln(2)}{4.0 \times 10^{-8} \text{ s}^{-1}} = 1.73 \times 10^7 \text{ s} \left( \frac{1 \text{ year}}{3.15569 \times 10^7 \text{ s}} \right)$$

$$t_{1/2} = 0.548 \text{ years} = \boxed{0.55 \text{ years}}$$

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

say  $[A]_0 = 1 \text{ M}$

$[A]_t = 0.125 \text{ M}$  (12.5% of original)

$$\left( \frac{-1}{40 \text{ min}} \right) \ln \left( \frac{0.125 \text{ M}}{1 \text{ M}} \right) = k$$

$$k = 5.199 \times 10^{-2} \text{ min}^{-1}$$

$$t_{1/2} = \frac{\ln(2)}{5.199 \times 10^{-2} \text{ min}^{-1}} = \boxed{13.3 \text{ min}}$$

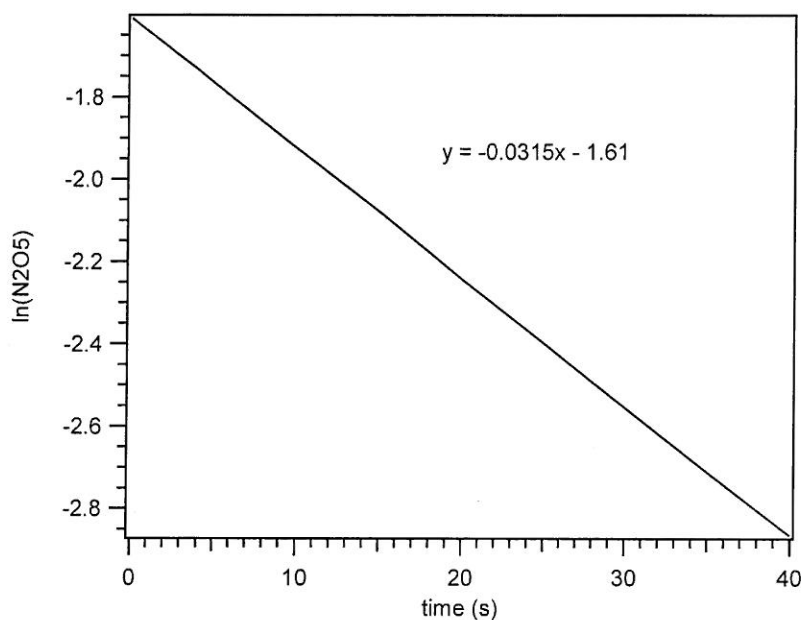
$$[A]_{2 \text{ hr}} = [A]_{120 \text{ min}} = [A]_0 e^{-kt} = (1 \text{ M}) e^{-(5.199 \times 10^{-2} \text{ min}^{-1})(120 \text{ min})}$$

$$[A]_{120} = 0.00195 (243 \text{ g}) = \boxed{0.474 \text{ g}}$$

or you could do Mass directly.

$$A_{2 \text{ hr}} = (243 \text{ g}) e^{-(5.199 \times 10^{-2} \text{ min}^{-1})(120)} = \boxed{0.474 \text{ g}}$$

11.48)



$$k = -(\text{slope})$$

$$k = 0.0315 \text{ min}^{-1}$$

$$t_{1/2} = \frac{\ln(2)}{k} = 22.0 \text{ min}$$

11.50) Need to take the difference between sets of time & pressure readings, then plot them in a spreadsheet and determine the order. The rxn order is zero.



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

$$[A]_0 = 8$$

$$[A]_{1\text{min}} = 4$$

$$[A]_{3\text{min}} = 2$$

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

$$k = (1\text{min})\left(\frac{1}{4}\right) - (1\text{min})\left(\frac{1}{8}\right) = 0.125 \text{ min}^{-1}$$

11.60)

a) Fastest @ 310 K?

Cis-2-butene

b) lowest activation energy?

Cis-2-butene

c) highest activation energy?

allene

11.62) An intermediate is a species formed in one elementary step of a reaction mechanism & consumed in another.

11.64)

a)  $\text{rate} = k[\text{Cl}][\text{ICl}]$

b)  $\text{rate} = k[\text{O}][\text{O}_3]$

c)  $\text{rate} = k[\text{NO}_2]^2$

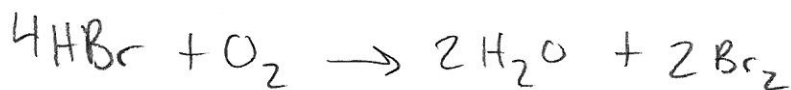
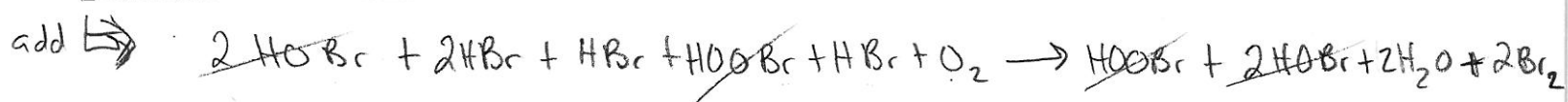
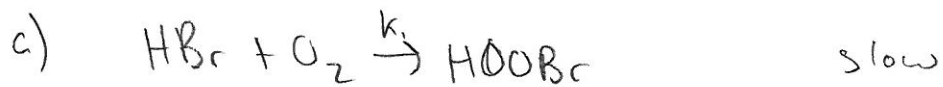
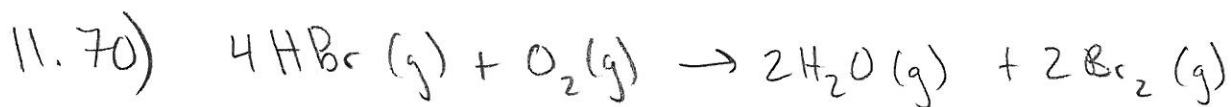
11.66) Reaction intermediates in Chapman cycle?

O atoms

11.68)

pg 8

Most likely the one dish washer is the rate-determining step.



b) Intermediates:  $\text{HOBr} + \text{HOB}$

c) Bimolecular

$$d) \quad \text{rate 1} = k_1 [\text{HBr}] [\text{O}_2]$$

$$\text{rate 2} = k_2 [\text{HOBr}] [\text{HBr}]$$

$$\text{rate 3} = k_3 [\text{HOB}] [\text{HBr}]$$

e) Rate-determining step?

↳ First step

11.72) NO. The catalyst increases the reaction rate by providing a pathway w/ a lower activation energy & is not consumed.



11.96)  $0.075 \text{ ppm}$

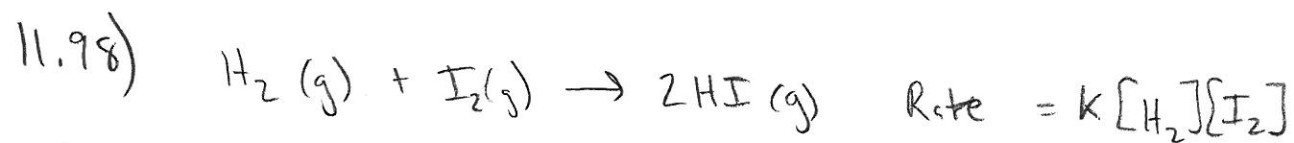
$$[O_3] = 1.5 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

Assuming the molar mass of air is  $29 \text{ g/mol}$

$$1.5 \times 10^{-3} \frac{\text{mol}}{\text{L}} \times \frac{48 \text{ g } O_3}{\text{mol } O_3} \times \frac{1000 \text{ mL}}{\text{L}} \times \left( \frac{1 \text{ L}}{1 \text{ mg}} \right) \text{ ppm}$$

$$[O_3] \Rightarrow 60,000 \text{ ppm}$$

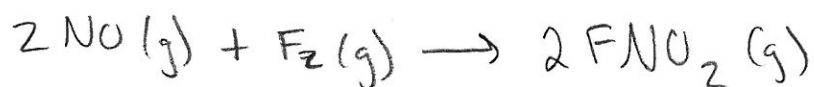
Which is significantly greater than  $0.0075 \text{ ppm}$



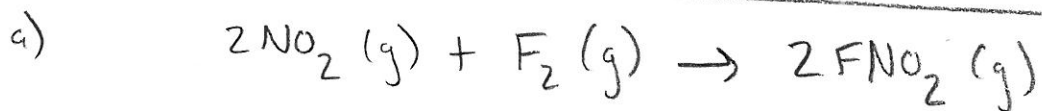
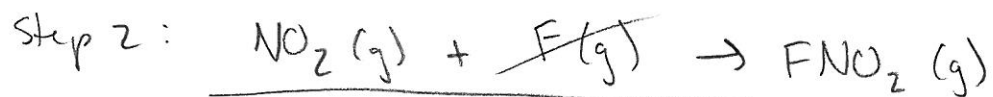
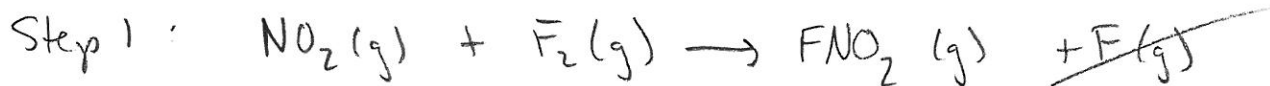
- a) False. This reaction may occur via a single-step reaction, but the word "must" is not appropriate w/o further information
- b) True
- c) False. Rise in Temp will cause the value of  $k$  to increase.
- d) False. raising the temp. increases the # of collisions & provides the energy needed to overcome the energy of activation barrier.
- e) False. doubling either reactant would double the Rate.  
Doubling both reactants would increase the Rate by a factor of 4.
- f) True.

11.100)

pg 10



$$\text{rate} = k[\text{NO}_2][\text{F}_2]$$



b) Step 1 is the rate-determining step