

# CHAPTER 14

## CHEMICAL KINETICS

### PRACTICE EXAMPLES

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- 1A (E)** The rate of consumption for a reactant is expressed as the negative of the change in molarity divided by the time interval. The rate of reaction is expressed as the rate of consumption of a reactant or production of a product divided by its stoichiometric coefficient.

$$\text{rate of consumption of A} = \frac{-\Delta[\text{A}]}{\Delta t} = \frac{-(0.3187 \text{ M} - 0.3629 \text{ M})}{8.25 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 8.93 \times 10^{-5} \text{ M s}^{-1}$$

$$\text{rate of reaction} = \text{rate of consumption of A} \div 2 = \frac{8.93 \times 10^{-5} \text{ M s}^{-1}}{2} = 4.46 \times 10^{-5} \text{ M s}^{-1}$$

- 1B (E)** We use the rate of reaction of A to determine the rate of formation of B, noting from the balanced equation that 3 moles of B form (+3 moles B) when 2 moles of A react (-2 moles A). (Recall that “M” means “moles per liter.”)

$$\text{rate of B formation} = \frac{0.5522 \text{ M A} - 0.5684 \text{ M A}}{2.50 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}}} \times \frac{+3 \text{ moles B}}{-2 \text{ moles A}} = 1.62 \times 10^{-4} \text{ M s}^{-1}$$

- 2A (M)**

- (a) The 2400-s tangent line intersects the 1200-s vertical line at 0.75 M and reaches 0 M at 3500 s. The slope of that tangent line is thus

$$\text{slope} = \frac{0 \text{ M} - 0.75 \text{ M}}{3500 \text{ s} - 1200 \text{ s}} = -3.3 \times 10^{-4} \text{ M s}^{-1} = - \text{instantaneous rate of reaction}$$

$$\text{The instantaneous rate of reaction} = 3.3 \times 10^{-4} \text{ M s}^{-1}.$$

- (b) At 2400 s,  $[\text{H}_2\text{O}_2] = 0.39 \text{ M}$ . At 2450 s,  $[\text{H}_2\text{O}_2] = 0.39 \text{ M} + \text{rate} \times \Delta t$   
At 2450 s,  $[\text{H}_2\text{O}_2] = 0.39 \text{ M} + [-3.3 \times 10^{-4} \text{ mol H}_2\text{O}_2 \text{ L}^{-1} \text{ s}^{-1} \times 50 \text{ s}]$   
 $= 0.39 \text{ M} - 0.017 \text{ M} = 0.37 \text{ M}$

- 2B (M)** With only the data of Table 14.2 we can use only the reaction rate during the first 400 s,  $-\Delta[\text{H}_2\text{O}_2]/\Delta t = 15.0 \times 10^{-4} \text{ M s}^{-1}$ , and the initial concentration,  $[\text{H}_2\text{O}_2]_0 = 2.32 \text{ M}$ .

We calculate the change in  $[\text{H}_2\text{O}_2]$  and add it to  $[\text{H}_2\text{O}_2]_0$  to determine  $[\text{H}_2\text{O}_2]_{100}$ .

$$\Delta[\text{H}_2\text{O}_2] = \text{rate of reaction of H}_2\text{O}_2 \times \Delta t = -15.0 \times 10^{-4} \text{ M s}^{-1} \times 100 \text{ s} = -0.15 \text{ M}$$

$$[\text{H}_2\text{O}_2]_{100} = [\text{H}_2\text{O}_2]_0 + \Delta[\text{H}_2\text{O}_2] = 2.32 \text{ M} + (-0.15 \text{ M}) = 2.17 \text{ M}$$

This value differs from the value of 2.15 M determined in *text* Example 14-2b because the *text* used the initial rate of reaction ( $17.1 \times 10^{-4} \text{ M s}^{-1}$ ), which is a bit faster than the average rate over the first 400 seconds.

**3A (M)** We write the equation for each rate, divide them into each other, and solve for  $n$ .

$$R_1 = k \times [\text{N}_2\text{O}_5]_1^n = 5.45 \times 10^{-5} \text{ M s}^{-1} = k(3.15 \text{ M})^n$$

$$R_2 = k \times [\text{N}_2\text{O}_5]_2^n = 1.35 \times 10^{-5} \text{ M s}^{-1} = k(0.78 \text{ M})^n$$

$$\frac{R_1}{R_2} = \frac{5.45 \times 10^{-5} \text{ M s}^{-1}}{1.35 \times 10^{-5} \text{ M s}^{-1}} = 4.04 = \frac{k \times [\text{N}_2\text{O}_5]_1^n}{k \times [\text{N}_2\text{O}_5]_2^n} = \frac{k(3.15 \text{ M})^n}{k(0.78 \text{ M})^n} = \left(\frac{3.15}{0.78}\right)^n = (4.04)^n$$

We kept an extra significant figure (4) to emphasize that the value of  $n = 1$ . Thus, the reaction is first-order in  $\text{N}_2\text{O}_5$ .

**3B (E)** For the reaction, we know that  $\text{rate} = k[\text{HgCl}_2]^1[\text{C}_2\text{O}_4^{2-}]^2$ . Here we will compare Expt. 4 to Expt. 1 to find the rate.

$$\frac{\text{rate}_4}{\text{rate}_1} = \frac{k[\text{HgCl}_2]^1[\text{C}_2\text{O}_4^{2-}]^2}{k[\text{HgCl}_2]^1[\text{C}_2\text{O}_4^{2-}]^2} = \frac{0.025 \text{ M} \times (0.045 \text{ M})^2}{0.105 \text{ M} \times (0.150 \text{ M})^2} = 0.0214 = \frac{\text{rate}_4}{1.8 \times 10^{-5} \text{ M min}^{-1}}$$

The desired rate is  $\text{rate}_4 = 0.0214 \times 1.8 \times 10^{-5} \text{ M min}^{-1} = 3.9 \times 10^{-7} \text{ M min}^{-1}$ .

**4A (E)** We place the initial concentrations and the initial rates into the rate law and solve for  $k$ .

$$\text{rate} = k[\text{A}]^2[\text{B}] = 4.78 \times 10^{-2} \text{ M s}^{-1} = k(1.12 \text{ M})^2(0.87 \text{ M})$$

$$k = \frac{4.78 \times 10^{-2} \text{ M s}^{-1}}{(1.12 \text{ M})^2(0.87 \text{ M})} = 4.4 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$$

**4B (E)** We know that  $\text{rate} = k[\text{HgCl}_2]^1[\text{C}_2\text{O}_4^{2-}]^2$  and  $k = 7.6 \times 10^{-3} \text{ M}^{-2} \text{ min}^{-1}$ .

Thus, insertion of the starting concentrations and the  $k$  value into the rate law yields:

$$\text{Rate} = 7.6 \times 10^{-3} \text{ M}^{-2} \text{ min}^{-1} (0.050 \text{ M})^1 (0.025 \text{ M})^2 = 2.4 \times 10^{-7} \text{ M min}^{-1}$$

**5A (E)** Here we substitute directly into the integrated rate law equation.

$$\ln [\text{A}]_t = -kt + \ln [\text{A}]_0 = -3.02 \times 10^{-3} \text{ s}^{-1} \times 325 \text{ s} + \ln (2.80) = -0.982 + 1.030 = 0.048$$

$$[\text{A}]_t = e^{0.048} = 1.0 \text{ M}$$

**5B (M)** This time we substitute the provided values into text Equation 14.13.

$$\ln \frac{[\text{H}_2\text{O}_2]_t}{[\text{H}_2\text{O}_2]_0} = -kt = -k \times 600 \text{ s} = \ln \frac{1.49 \text{ M}}{2.32 \text{ M}} = -0.443 \quad k = \frac{-0.443}{-600 \text{ s}} = 7.38 \times 10^{-4} \text{ s}^{-1}$$

$$\text{Now we choose } [\text{H}_2\text{O}_2]_0 = 1.49 \text{ M}, [\text{H}_2\text{O}_2]_t = 0.62, \quad t = 1800 \text{ s} - 600 \text{ s} = 1200 \text{ s}$$

$$\ln \frac{[\text{H}_2\text{O}_2]_t}{[\text{H}_2\text{O}_2]_0} = -kt = -k \times 1200 \text{ s} = \ln \frac{0.62 \text{ M}}{1.49 \text{ M}} = -0.88 \quad k = \frac{-0.88}{-1200 \text{ s}} = 7.3 \times 10^{-4} \text{ s}^{-1}$$

These two values agree within the limits of the experimental error and thus, the reaction is first-order in  $[\text{H}_2\text{O}_2]$ .

- 6A** (M) We can use the integrated rate equation to find the ratio of the final and initial concentrations. This ratio equals the fraction of the initial concentration that remains at time  $t$ .

$$\ln \frac{[A]_t}{[A]_0} = -kt = -2.95 \times 10^{-3} \text{ s}^{-1} \times 150 \text{ s} = -0.443$$

$$\frac{[A]_t}{[A]_0} = e^{-0.443} = 0.642; \quad 64.2\% \text{ of } [A]_0 \text{ remains.}$$

- 6B** (M) After two-thirds of the sample has decomposed, one-third of the sample remains.

Thus  $[H_2O_2]_t = [H_2O_2]_0 \div 3$ , and we have

$$\ln \frac{[H_2O_2]_t}{[H_2O_2]_0} = -kt = \ln \frac{[H_2O_2]_0 \div 3}{[H_2O_2]_0} = \ln(1/3) = -1.099 = -7.30 \times 10^{-4} \text{ s}^{-1} t$$

$$t = \frac{-1.099}{-7.30 \times 10^{-4} \text{ s}^{-1}} = 1.51 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 25.1 \text{ min}$$

- 7A** (M) At the end of one half-life the pressure of DTBP will have been halved, to 400 mmHg. At the end of another half-life, at 160 min, the pressure of DTBP will have halved again, to 200 mmHg. Thus, the pressure of DTBP at 125 min will be intermediate between the pressure at 80.0 min (400 mmHg) and that at 160 min (200 mmHg). To obtain an exact answer, first we determine the value of the rate constant from the half-life.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{80.0 \text{ min}} = 0.00866 \text{ min}^{-1}$$

$$\ln \frac{(P_{\text{DTBP}})_t}{(P_{\text{DTBP}})_0} = -kt = -0.00866 \text{ min}^{-1} \times 125 \text{ min} = -1.08$$

$$\frac{(P_{\text{DTBP}})_t}{(P_{\text{DTBP}})_0} = e^{-1.08} = 0.340$$

$$(P_{\text{DTBP}})_t = 0.340 \times (P_{\text{DTBP}})_0 = 0.340 \times 800 \text{ mmHg} = 272 \text{ mmHg}$$

- 7B** (M)

- (a) We use partial pressures in place of concentrations in the integrated first-order rate equation. Notice first that more than 30 half-lives have elapsed, and thus the ethylene oxide pressure has declined to at most  $(0.5)^{30} = 9 \times 10^{-10}$  of its initial value.

$$\ln \frac{P_{30}}{P_0} = -kt = -2.05 \times 10^{-4} \text{ s}^{-1} \times 30.0 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} = -22.1 \quad \frac{P_{30}}{P_0} = e^{-22.1} = 2.4 \times 10^{-10}$$

$$P_{30} = 2.4 \times 10^{-10} \times P_0 = 2.4 \times 10^{-10} \times 782 \text{ mmHg} = 1.9 \times 10^{-7} \text{ mmHg}$$

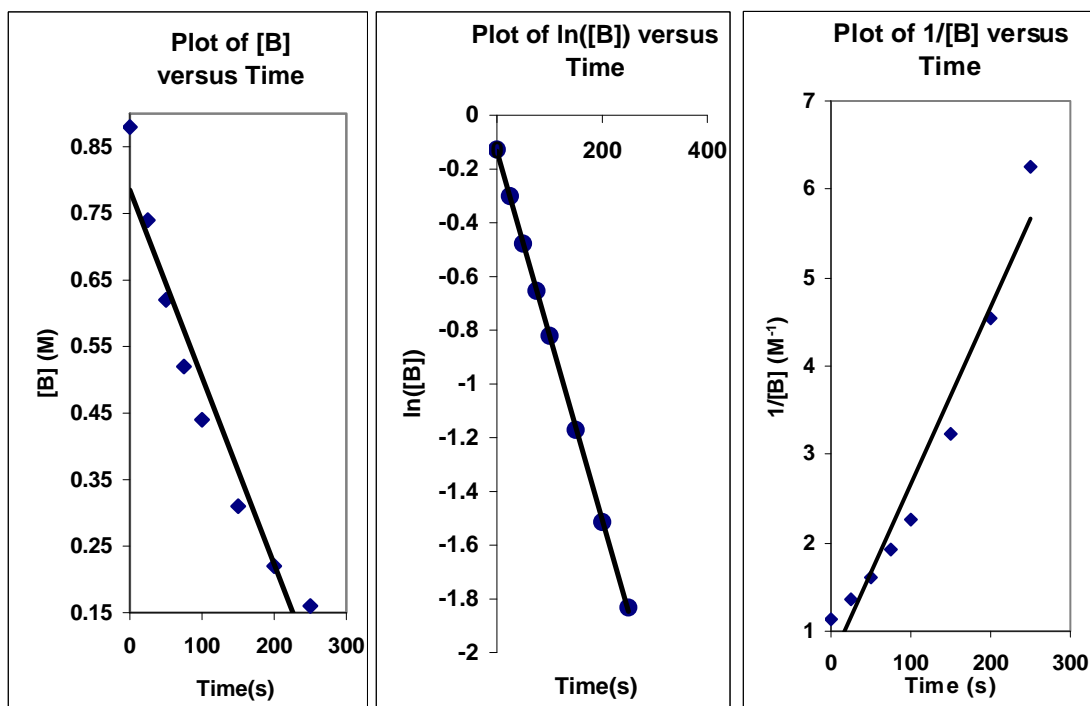
- (b)  $P_{\text{ethylene oxide}}$  initially 782 mmHg  $\rightarrow 1.9 \times 10^{-7}$  mmHg ( $\sim 0$ ). Essentially all of the ethylene oxide is converted to  $\text{CH}_4$  and  $\text{CO}$ . Since pressure is proportional to moles, the final pressure will be twice the initial pressure (1 mole gas  $\rightarrow$  2 moles gas; 782 mmHg  $\rightarrow$  1564 mmHg). The final pressure will be  $1.56 \times 10^3$  mmHg.

**8A (D)** We first begin by looking for a constant rate, indicative of a zero-order reaction. If the rate is constant, the concentration will decrease by the same quantity during the same time period. If we choose a 25-s time period, we note that the concentration decreases (0.88 M – 0.74 M =) 0.14 M during the first 25 s, (0.74 M – 0.62 M =) 0.12 M during the second 25 s, (0.62 M – 0.52 M =) 0.10 M during the third 25 s, and (0.52 M – 0.44 M =) 0.08 M during the fourth 25-s period. This is hardly a constant rate and we thus conclude that the reaction is not zero-order.

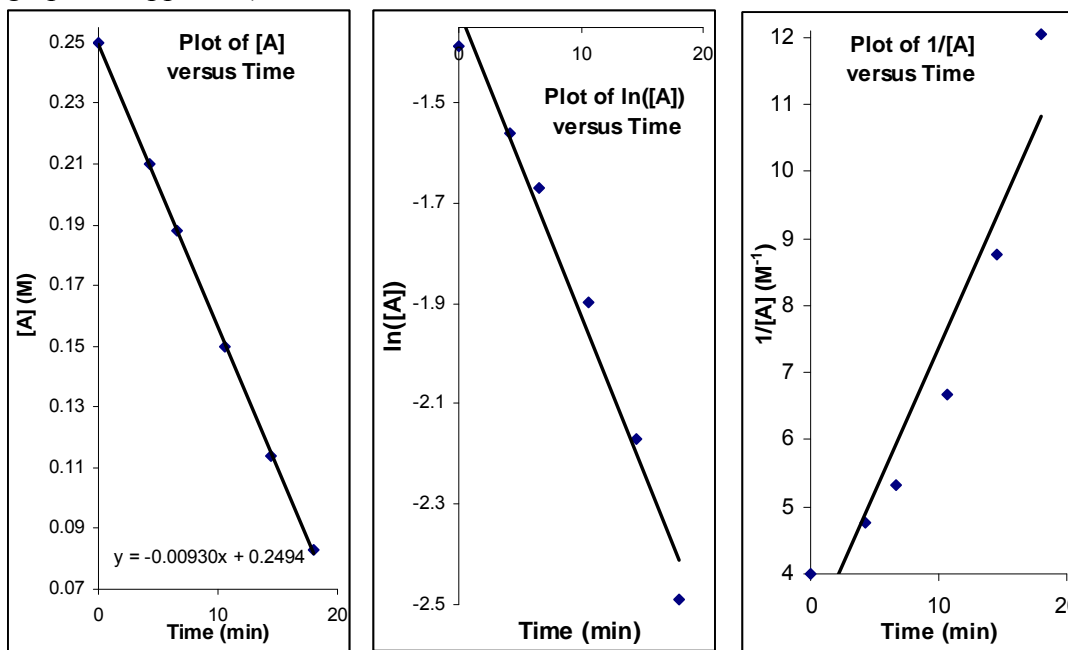
We next look for a constant half-life, indicative of a first-order reaction. The initial concentration of 0.88 M decreases to one half of that value, 0.44 M, during the first 100 s, indicating a 100-s half-life. The concentration halves again to 0.22 M in the second 100 s, another 100-s half-life. Finally, we note that the concentration halves also from 0.62 M at 50 s to 0.31 M at 150 s, yet another 100-s half-life. The rate is established as first-order. The rate constant is

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100 \text{ s}} = 6.93 \times 10^{-3} \text{ s}^{-1}.$$

That the reaction is first-order is made apparent by the fact that the  $\ln[\text{B}]$  vs time plot is a straight line with slope =  $-k$  ( $k = 6.85 \times 10^{-3} \text{ s}^{-1}$ ).



- 8B (D)** We plot the data in three ways to determine the order. (1) A plot of  $[A]$  vs. time is linear if the reaction is zero-order. (2) A plot of  $\ln [A]$  vs. time will be linear if the reaction is first-order. (3) A plot of  $1/[A]$  vs. time will be linear if the reaction is second-order. It is obvious from the plots below that the reaction is zero-order. The negative of the slope of the line equals  $k = -(0.083 \text{ M} - 0.250 \text{ M}) \div 18.00 \text{ min} = 9.28 \times 10^{-3} \text{ M/min}$  ( $k = 9.30 \times 10^{-3} \text{ M/min}$  using a graphical approach).



- 9A (M)** First we compute the value of the rate constant at  $75.0^\circ\text{C}$  with the Arrhenius equation. We know that the activation energy is  $E_a = 1.06 \times 10^5 \text{ J/mol}$ , and that  $k = 3.46 \times 10^{-5} \text{ s}^{-1}$  at  $298 \text{ K}$ . The temperature of  $75.0^\circ\text{C} = 348.2 \text{ K}$ .

$$\ln \frac{k_2}{k_1} = \ln \frac{k_2}{3.46 \times 10^{-5} \text{ s}^{-1}} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{1.06 \times 10^5 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{298.2 \text{ K}} - \frac{1}{348.2 \text{ K}} \right) = 6.14$$

$$k_2 = 3.46 \times 10^{-5} \text{ s}^{-1} \times e^{+6.14} = 3.46 \times 10^{-5} \text{ s}^{-1} \times 4.6 \times 10^2 = 0.016 \text{ s}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.016 \text{ s}^{-1}} = 43 \text{ s at } 75^\circ\text{C}$$

- 9B (M)** We use the integrated rate equation to determine the rate constant, realizing that one-third remains when two-thirds have decomposed.

$$\ln \frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_0} = \ln \frac{[\text{N}_2\text{O}_5]_0 \div 3}{[\text{N}_2\text{O}_5]_0} = \ln \frac{1}{3} = -kt = -k(1.50 \text{ h}) = -1.099$$

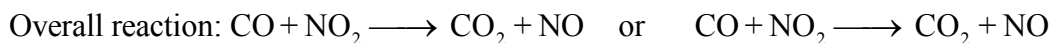
$$k = \frac{1.099}{1.50 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 2.03 \times 10^{-4} \text{ s}^{-1}$$

Now use the Arrhenius equation to determine the temperature at which the rate constant is  $2.04 \times 10^{-4} \text{ s}^{-1}$ .

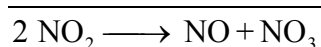
$$\ln \frac{k_2}{k_1} = \ln \frac{2.04 \times 10^{-4} \text{ s}^{-1}}{3.46 \times 10^{-5} \text{ s}^{-1}} = 1.77 = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{1.06 \times 10^5 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{298 \text{ K}} - \frac{1}{T_2} \right)$$

$$\frac{1}{T_2} = \frac{1}{298 \text{ K}} - \frac{1.77 \times 8.3145 \text{ K}^{-1}}{1.06 \times 10^5} = 3.22 \times 10^{-3} \text{ K}^{-1} \quad T_2 = 311 \text{ K}$$

**10A (M)** The two steps of the mechanism must add, in a Hess's law fashion, to produce the overall reaction.



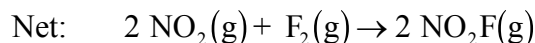
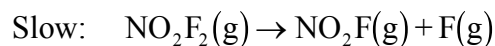
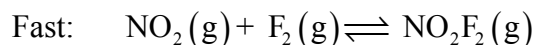
First step:



If the first step is the slow step, then it will be the rate-determining step, and the rate of that step will be the rate of the reaction, namely, rate of reaction =  $k_1 [\text{NO}_2]^2$ .

**10B (M)**

(1) The steps of the mechanism must add, in a Hess's law fashion, to produce the overall reaction. This is done below. The two intermediates,  $\text{NO}_2\text{F}_2(\text{g})$  and  $\text{F}(\text{g})$ , are each produced in one step and consumed in the next one.



(2) The proposed mechanism must agree with the rate law. We expect the rate-determining step to determine the reaction rate: Rate =  $k_3 [\text{NO}_2\text{F}_2]$ . To eliminate  $[\text{NO}_2\text{F}_2]$ , we recognize that the first elementary reaction is very fast and will have the same rate forward as reverse:  $R_f = k_1 [\text{NO}_2][\text{F}_2] = k_2 [\text{NO}_2\text{F}_2] = R_r$ . We solve for the concentration of intermediate:  $[\text{NO}_2\text{F}_2] = k_1 [\text{NO}_2][\text{F}_2]/k_2$ . We now substitute this expression for  $[\text{NO}_2\text{F}_2]$  into the rate equation: Rate =  $(k_1 k_3/k_2) [\text{NO}_2][\text{F}_2]$ . Thus the predicted rate law agrees with the experimental rate law.

## INTEGRATIVE EXAMPLE

**A. (M)**

- (a) The time required for the fixed ( $c$ ) process of souring is three times as long at 3 °C refrigerator temperature (276 K) as at 20 °C room temperature (293 K).

$$\ln \frac{c/t_2}{c/t_1} = \ln \frac{t_1}{t_2} = \ln \frac{64 \text{ h}}{3 \times 64 \text{ h}} = -1.10 = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{E_a}{R} \left( \frac{1}{293 \text{ K}} - \frac{1}{276 \text{ K}} \right) = \frac{E_a}{R} (-2.10 \times 10^{-4})$$

$$E_a = \frac{1.10 R}{2.10 \times 10^{-4} \text{ K}^{-1}} = \frac{1.10 \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}{2.10 \times 10^{-4} \text{ K}^{-1}} = 4.4 \times 10^4 \text{ J/mol} = 44 \text{ kJ/mol}$$

- (b) Use the  $E_a$  determined in part (a) to calculate the souring time at 40 °C = 313 K.

$$\ln \frac{t_1}{t_2} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{4.4 \times 10^4 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{313 \text{ K}} - \frac{1}{293 \text{ K}} \right) = -1.15 = \ln \frac{t_1}{64 \text{ h}}$$

$$\frac{t_1}{64 \text{ h}} = e^{-1.15} = 0.317 \quad t_1 = 0.317 \times 64 \text{ h} = 20. \text{ h}$$

**B. (M)** The species  $A^*$  is a reactive intermediate. Let's deal with this species by using a steady state approximation.

$$d[A^*]/dt = 0 = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*]. \text{ Solve for } [A^*]. \quad k_{-1}[A^*][A] + k_2[A^*] = k_1[A]^2$$

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2} \quad \text{The rate of reaction is: Rate} = k_2[A^*] = \frac{k_2 k_1[A]^2}{k_{-1}[A] + k_2}$$

At low pressures ( $[A] \sim 0$  and hence  $k_2 \gg k_{-1}[A]$ ), the denominator becomes  $\sim k_2$  and the rate law is

$$\text{Rate} = \frac{k_2 k_1[A]^2}{k_2} = k_1[A]^2 \quad \text{Second-order with respect to } [A]$$

At high pressures ( $[A]$  is large and  $k_{-1}[A] \gg k_2$ ), the denominator becomes  $\sim k_{-1}[A]$  and the rate law is

$$\text{Rate} = \frac{k_2 k_1[A]^2}{k_{-1}[A]} = \frac{k_2 k_1[A]}{k_{-1}} \quad \text{First-order with respect to } [A]$$

## EXERCISES

**Rates of Reactions**

**1. (M)**  $2A + B \rightarrow C + 3D \quad -\frac{\Delta[A]}{\Delta t} = 6.2 \times 10^{-4} \text{ M s}^{-1}$

(a)  $\text{Rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} = 1/2(6.2 \times 10^{-4} \text{ M s}^{-1}) = 3.1 \times 10^{-4} \text{ M s}^{-1}$

(b)  $\text{Rate of disappearance of B} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} = 1/2(6.2 \times 10^{-4} \text{ M s}^{-1}) = 3.1 \times 10^{-4} \text{ M s}^{-1}$

(c)  $\text{Rate of appearance of D} = -\frac{3}{2} \frac{\Delta[A]}{\Delta t} = 3(6.2 \times 10^{-4} \text{ M s}^{-1}) = 9.3 \times 10^{-4} \text{ M s}^{-1}$

2. (M) In each case, we draw the tangent line to the plotted curve.

(a) The slope of the line is  $\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{1.7 \text{ M} - 0.6 \text{ M}}{400 \text{ s} - 1600 \text{ s}} = -9.2 \times 10^{-4} \text{ M s}^{-1}$

$$\text{reaction rate} = -\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = 9.2 \times 10^{-4} \text{ M s}^{-1}$$

(b) Read the value where the horizontal line  $[\text{H}_2\text{O}_2] = 0.50 \text{ M}$  intersects the curve,  $\approx 2150 \text{ s}$  or  $\approx 36 \text{ minutes}$

3. (E)  $\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{(0.474 \text{ M} - 0.485 \text{ M})}{82.4 \text{ s} - 71.5 \text{ s}} = 1.0 \times 10^{-3} \text{ M s}^{-1}$

4. (M)

(a)  $\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.1498 \text{ M} - 0.1565 \text{ M}}{1.00 \text{ min} - 0.00 \text{ min}} = 0.0067 \text{ M min}^{-1}$

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.1433 \text{ M} - 0.1498 \text{ M}}{2.00 \text{ min} - 1.00 \text{ min}} = 0.0065 \text{ M min}^{-1}$$

(b) The rates are not equal because, in all except zero-order reactions, the rate depends on the concentration of reactant. And, of course, as the reaction proceeds, reactant is consumed and its concentration decreases, so the rate of the reaction decreases.

5. (M)

(a)  $[\text{A}] = [\text{A}]_i + \Delta[\text{A}] = 0.588 \text{ M} - 0.013 \text{ M} = 0.575 \text{ M}$

(b)  $\Delta[\text{A}] = 0.565 \text{ M} - 0.588 \text{ M} = -0.023 \text{ M}$

$$\Delta t = \Delta[\text{A}] \frac{\Delta t}{\Delta[\text{A}]} = \frac{-0.023 \text{ M}}{-2.2 \times 10^{-2} \text{ M/min}} = 1.0 \text{ min}$$

$$\text{time} = t + \Delta t = (4.40 + 1.0) \text{ min} = 5.4 \text{ min}$$

6. (M) Initial concentrations are  $[\text{HgCl}_2] = 0.105 \text{ M}$  and  $[\text{C}_2\text{O}_4^{2-}] = 0.300 \text{ M}$ .

The initial rate of the reaction is  $7.1 \times 10^{-5} \text{ M min}^{-1}$ . Recall that the reaction is:



The rate of reaction equals the rate of disappearance of  $\text{C}_2\text{O}_4^{2-}$ . Then, after 1 hour, assuming that the rate is the same as the initial rate,

(a)  $[\text{HgCl}_2] = 0.105 \text{ M} - \left( 7.1 \times 10^{-5} \frac{\text{mol C}_2\text{O}_4^{2-}}{\text{L} \cdot \text{s}} \times \frac{2 \text{ mol HgCl}_2}{1 \text{ mol C}_2\text{O}_4^{2-}} \times 1 \text{ h} \times \frac{60 \text{ min}}{1 \text{ h}} \right) = 0.096 \text{ M}$

(b)  $[\text{C}_2\text{O}_4^{2-}] = 0.300 \text{ M} - \left( 7.1 \times 10^{-5} \frac{\text{mol}}{\text{L} \cdot \text{min}} \times 1 \text{ h} \times \frac{60 \text{ min}}{1 \text{ h}} \right) = 0.296 \text{ M}$



**7.** (M)

$$(a) \text{ Rate} = \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[C]}{2\Delta t} = 1.76 \times 10^{-5} \text{ M s}^{-1}$$

$$\frac{\Delta[C]}{\Delta t} = 2 \times 1.76 \times 10^{-5} \text{ M s}^{-1} = 3.52 \times 10^{-5} \text{ M/s}$$

$$(b) \frac{\Delta[A]}{\Delta t} = -\frac{\Delta[C]}{2\Delta t} = -1.76 \times 10^{-5} \text{ M s}^{-1} \text{ Assume this rate is constant.}$$

$$[A] = 0.3580 \text{ M} + \left( -1.76 \times 10^{-5} \text{ M s}^{-1} \times 1.00 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \right) = 0.357 \text{ M}$$

$$(c) \frac{\Delta[A]}{\Delta t} = -1.76 \times 10^{-5} \text{ M s}^{-1}$$

$$\Delta t = \frac{\Delta[A]}{-1.76 \times 10^{-5} \text{ M/s}} = \frac{0.3500 \text{ M} - 0.3580 \text{ M}}{-1.76 \times 10^{-5} \text{ M/s}} = 4.5 \times 10^2 \text{ s}$$

**8.** (M)

$$(a) \frac{\Delta n[\text{O}_2]}{\Delta t} = 1.00 \text{ L soln} \times \frac{5.7 \times 10^{-4} \text{ mol H}_2\text{O}_2}{1 \text{ L soln} \cdot \text{s}} \times \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2\text{O}_2} = 2.9 \times 10^{-4} \text{ mol O}_2/\text{s}$$

$$(b) \frac{\Delta n[\text{O}_2]}{\Delta t} = 2.9 \times 10^{-4} \frac{\text{mol O}_2}{\text{s}} \times \frac{60 \text{ s}}{1 \text{ min}} = 1.7 \times 10^{-2} \text{ mol O}_2 / \text{min}$$

$$(c) \frac{\Delta V[\text{O}_2]}{\Delta t} = 1.7 \times 10^{-2} \frac{\text{mol O}_2}{\text{min}} \times \frac{22,414 \text{ mL O}_2 \text{ at STP}}{1 \text{ mol O}_2} = \frac{3.8 \times 10^2 \text{ mL O}_2 \text{ at STP}}{\text{min}}$$

**9.** (M) Notice that, for every 1000 mmHg drop in the pressure of A(g), there will be a corresponding 2000 mmHg rise in the pressure of B(g) plus a 1000 mmHg rise in the pressure of C(g).

(a) We set up the calculation with three lines of information below the balanced equation: (1) the initial conditions, (2) the changes that occur, which are related to each other by reaction stoichiometry, and (3) the final conditions, which simply are initial conditions + changes.

	A(g)	→	2B(g)	+	C(g)
Initial	1000. mmHg		0. mmHg		0. mmHg
Changes	-1000. mmHg		+2000. mmHg		+1000. mmHg
Final	0. mmHg		2000. MmHg		1000. mmHg

$$\text{Total final pressure} = 0. \text{ mmHg} + 2000. \text{ mmHg} + 1000. \text{ mmHg} = 3000. \text{ mmHg}$$

	A(g)	→	2B(g)	+	C(g)
Initial	1000. mmHg		0. mmHg		0. mmHg
Changes	-200. mmHg		+400. mmHg		+200. mmHg
Final	800 mmHg		400. mmHg		200. mmHg

$$\text{Total pressure} = 800. \text{ mmHg} + 400. \text{ mmHg} + 200. \text{ mmHg} = 1400. \text{ mmHg}$$

**10. (M)**

(a) We will use the ideal gas law to determine  $\text{N}_2\text{O}_5$  pressure

$$P\{\text{N}_2\text{O}_5\} = \frac{nRT}{V} = \frac{\left(1.00 \text{ g} \times \frac{1 \text{ mol N}_2\text{O}_5}{108.0 \text{ g}}\right) \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times (273 + 65) \text{ K}}{15 \text{ L}} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 13 \text{ mmHg}$$

(b) After 2.38 min, one half-life passes. The initial pressure of  $\text{N}_2\text{O}_5$  decreases by half to 6.5 mmHg.

(c) From the balanced chemical equation, the reaction of 2 mol  $\text{N}_2\text{O}_5(\text{g})$  produces 4 mol  $\text{NO}_2(\text{g})$  and 1 mol  $\text{O}_2(\text{g})$ . That is, the consumption of 2 mol of reactant gas produces 5 mol of product gas. When measured at the same temperature and confined to the same volume, pressures will behave as amounts: the reaction of 2 mmHg of reactant produces 5 mmHg of product.

$$\begin{aligned} P_{\text{total}} &= 13 \text{ mmHg N}_2\text{O}_5 \text{ (initially)} - 6.5 \text{ mmHg N}_2\text{O}_5 \text{ (reactant)} + \left(6.5 \text{ mmHg}_{\text{(reactant)}} \times \frac{5 \text{ mmHg}_{\text{(product)}}}{2 \text{ mmHg}_{\text{(reactant)}}}\right) \\ &= (13 - 6.5 + 16) \text{ mmHg} = 23 \text{ mmHg} \end{aligned}$$

**Method of Initial Rates****11. (M)**

(a) From Expt. 1 to Expt. 3, [A] is doubled, while [B] remains fixed. This causes the rate to increase by a factor of  $\frac{6.75 \times 10^{-4} \text{ M s}^{-1}}{3.35 \times 10^{-4} \text{ M s}^{-1}} = 2.01 \approx 2$ .

Thus, the reaction is first-order with respect to A.

From Expt. 1 to Expt. 2, [B] doubles, while [A] remains fixed. This causes the rate to increase by a factor of  $\frac{1.35 \times 10^{-3} \text{ M s}^{-1}}{3.35 \times 10^{-4} \text{ M s}^{-1}} = 4.03 \approx 4$ .

Thus, the reaction is second-order with respect to B.

(b) Overall reaction order = order with respect to A + order with respect to B = 1 + 2 = 3. The reaction is third-order overall.

(c) Rate =  $3.35 \times 10^{-4} \text{ M s}^{-1} = k(0.185 \text{ M})(0.133 \text{ M})^2$

$$k = \frac{3.35 \times 10^{-4} \text{ M s}^{-1}}{(0.185 \text{ M})(0.133 \text{ M})^2} = 0.102 \text{ M}^{-2} \text{ s}^{-1}$$

**12. (M)** From Expt. 1 and Expt. 2 we see that [B] remains fixed while [A] triples. As a result, the initial rate increases from  $4.2 \times 10^{-3} \text{ M/min}$  to  $1.3 \times 10^{-2} \text{ M/min}$ , that is, the initial reaction rate triples. Therefore, the reaction is first-order in [A]. Between Expt. 2 and Expt. 3, we see that [A] doubles, which would double the rate, and [B] doubles. As a consequence, the initial rate goes from  $1.3 \times 10^{-2} \text{ M/min}$  to  $5.2 \times 10^{-2} \text{ M/min}$ , that is, the rate quadruples. Since an additional doubling of the rate is due to the change in [B], the reaction is first-order in [B]. Now we determine the value of the rate constant.

$$\text{Rate} = k[\text{A}]^1[\text{B}]^1 \quad k = \frac{\text{Rate}}{[\text{A}][\text{B}]} = \frac{5.2 \times 10^{-2} \text{ M/min}}{3.00 \text{ M} \times 3.00 \text{ M}} = 5.8 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$$

The rate law is  $\text{Rate} = (5.8 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1})[\text{A}]^1[\text{B}]^1$ .

- 13. (M)** From Experiment 1 to 2,  $[\text{NO}]$  remains constant while  $[\text{Cl}_2]$  is doubled. At the same time the initial rate of reaction is found to double. Thus, the reaction is first-order with respect to  $[\text{Cl}_2]$ , since dividing reaction 2 by reaction 1 gives  $2 = 2^x$  when  $x = 1$ . From Experiment 1 to 3,  $[\text{Cl}_2]$  remains constant, while  $[\text{NO}]$  is doubled, resulting in a quadrupling of the initial rate of reaction. Thus, the reaction must be second-order in  $[\text{NO}]$ , since dividing reaction 3 by reaction 1 gives  $4 = 2^x$  when  $x = 2$ . Overall the reaction is third-order:  $\text{Rate} = k [\text{NO}]^2[\text{Cl}_2]$ . The rate constant may be calculated from any one of the experiments. Using data from Exp. 1,

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{Cl}_2]} = \frac{2.27 \times 10^{-5} \text{ M s}^{-1}}{(0.0125 \text{ M})^2(0.0255 \text{ M})} = 5.70 \text{ M}^{-2} \text{ s}^{-1}$$

- 14. (M)**

- (a) From Expt. 1 to Expt. 2,  $[\text{B}]$  remains constant at 1.40 M and  $[\text{C}]$  remains constant at 1.00 M, but  $[\text{A}]$  is halved ( $\times 0.50$ ). At the same time the rate is halved ( $\times 0.50$ ). Thus, the reaction is first-order with respect to A, since  $0.50^x = 0.50$  when  $x = 1$ . From Expt. 2 to Expt. 3,  $[\text{A}]$  remains constant at 0.70 M and  $[\text{C}]$  remains constant at 1.00 M, but  $[\text{B}]$  is halved ( $\times 0.50$ ), from 1.40 M to 0.70 M. At the same time, the rate is quartered ( $\times 0.25$ ). Thus, the reaction is second-order with respect to B, since  $0.50^y = 0.25$  when  $y = 2$ .

From Expt. 1 to Expt. 4,  $[\text{A}]$  remains constant at 1.40 M and  $[\text{B}]$  remains constant at 1.40 M, but  $[\text{C}]$  is halved ( $\times 0.50$ ), from 1.00 M to 0.50 M. At the same time, the rate is increased by a factor of 2.0.

$$\left[ \text{Rate}_4 = 16 \text{ Rate}_3 = 16 \times \frac{1}{4} \text{ Rate}_2 = 4 \text{ Rate}_2 = 4 \times \frac{1}{2} \text{ Rate}_1 = 2 \times \text{Rate}_1. \right]$$

Thus, the order of the reaction with respect to C is  $-1$ , since  $0.5^z = 2.0$  when  $z = -1$ .

$$\begin{aligned} \text{(b)} \quad \text{rate}_5 &= k(0.70 \text{ M})^1(0.70 \text{ M})^2(0.50 \text{ M})^{-1} = k\left(\frac{1.40 \text{ M}}{2}\right)^1\left(\frac{1.40 \text{ M}}{2}\right)^2\left(\frac{1.00 \text{ M}}{2}\right)^{-1} \\ &= k \frac{1}{2} (1.40 \text{ M})^1 \frac{1}{2} (1.40 \text{ M})^2 \frac{1}{2} (1.00 \text{ M})^{-1} = \text{rate}_1 \left(\frac{1}{2}\right)^{1+2-1} = \text{rate}_1 \left(\frac{1}{2}\right)^2 = \frac{1}{4} \text{rate}_1 \end{aligned}$$

This is based on  $\text{rate}_1 = k(1.40 \text{ M})^1(1.40 \text{ M})^2(1.00 \text{ M})^{-1}$

**First-Order Reactions**

- 15. (E)**
- (a) TRUE The rate of the reaction does decrease as more and more of B and C are formed, but not because more and more of B and C are formed. Rather, the rate decreases because the concentration of A must decrease to form more and more of B and C.
- (b) FALSE The time required for one half of substance A to react—the half-life—is independent of the quantity of A present.
- 16. (E)**
- (a) FALSE For first-order reactions, a plot of  $\ln [A]$  or  $\log [A]$  vs. time yields a straight line. A graph of  $[A]$  vs. time yields a curved line.
- (b) TRUE The rate of formation of C is related to the rate of disappearance of A by the stoichiometry of the reaction.
- 17. (M)**
- (a) Since the half-life is 180 s, after 900 s five half-lives have elapsed, and the original quantity of A has been cut in half five times.  
 final quantity of A =  $(0.5)^5 \times$  initial quantity of A =  $0.03125 \times$  initial quantity of A  
 About 3.13% of the original quantity of A remains unreacted after 900 s.  
 or  
 More generally, we would calculate the value of the rate constant, k, using  

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{180 \text{ s}} = 0.00385 \text{ s}^{-1}$$
 Now  $\ln(\% \text{ unreacted}) = -kt = -0.00385 \text{ s}^{-1} \times (900 \text{ s}) = -3.465$   
 $(\% \text{ unreacted}) = 0.0313 \times 100\% = 3.13\%$  of the original quantity.
- (b) Rate =  $k[A] = 0.00385 \text{ s}^{-1} \times 0.50 \text{ M} = 0.00193 \text{ M/s}$
- 18. (M)**
- (a) The reaction is first-order, thus  

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.100 \text{ M}}{0.800 \text{ M}} = -54 \text{ min}(k) \quad k = -\frac{-2.08}{54 \text{ min}} = 0.0385 \text{ min}^{-1}$$
 We may now determine the time required to achieve a concentration of 0.025 M  

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.025 \text{ M}}{0.800 \text{ M}} = -0.0385 \text{ min}^{-1}(t) \quad t = \frac{-3.47}{-0.0385 \text{ min}^{-1}} = 90. \text{ min}$$
- (b) Since we know the rate constant for this reaction (see above),  
 Rate =  $k[A]^1 = 0.0385 \text{ min}^{-1} \times 0.025 \text{ M} = 9.6 \times 10^{-4} \text{ M/min}$

**19. (M)**

(a) The mass of A has decreased to one fourth of its original value, from 1.60 g to 0.40 g. Since  $\frac{1}{4} = \frac{1}{2} \times \frac{1}{2}$ , we see that two half-lives have elapsed.

Thus,  $2 \times t_{1/2} = 38 \text{ min}$ , or  $t_{1/2} = 19 \text{ min}$ .

$$(b) \quad k = 0.693/t_{1/2} = \frac{0.693}{19 \text{ min}} = 0.036 \text{ min}^{-1} \quad \ln \frac{[A]_t}{[A]_0} = -kt = -0.036 \text{ min}^{-1} \times 60 \text{ min} = -2.2$$

$$\frac{[A]_t}{[A]_0} = e^{-2.2} = 0.11 \quad \text{or} \quad [A]_t = [A]_0 e^{-kt} = 1.60 \text{ g A} \times 0.11 = 0.18 \text{ g A}$$

**20. (M)**

$$(a) \quad \ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.632 \text{ M}}{0.816 \text{ M}} = -0.256 \quad k = \frac{-0.256}{16.0 \text{ min}} = 0.0160 \text{ min}^{-1}$$

$$(b) \quad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0160 \text{ min}^{-1}} = 43.3 \text{ min}$$

(c) We need to solve the integrated rate equation to find the elapsed time.

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.235 \text{ M}}{0.816 \text{ M}} = -1.245 = -0.0160 \text{ min}^{-1} \times t \quad t = \frac{-1.245}{-0.0160 \text{ min}^{-1}} = 77.8 \text{ min}$$

(d)  $\ln \frac{[A]_t}{[A]_0} = -kt$  becomes  $\frac{[A]_t}{[A]_0} = e^{-kt}$  which in turn becomes

$$[A] = [A]_0 e^{-kt} = 0.816 \text{ M} \exp\left(-0.0160 \text{ min}^{-1} \times 2.5 \text{ h} \times \frac{60 \text{ min}}{1 \text{ h}}\right) = 0.816 \times 0.0907 = 0.074 \text{ M}$$

**21. (M)** We determine the value of the first-order rate constant and from that we can calculate the half-life. If the reactant is 99% decomposed in 137 min, then only 1% (0.010) of the initial concentration remains.

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.010}{1.000} = -4.61 = -k \times 137 \text{ min} \quad k = \frac{-4.61}{-137 \text{ min}} = 0.0336 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0336 \text{ min}^{-1}} = 20.6 \text{ min}$$

- 22. (E)** If 99% of the radioactivity of  $^{32}\text{P}$  is lost, 1% (0.010) of that radioactivity remains. First we compute the value of the rate constant from the half-life.  $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.3 \text{ d}} = 0.0485 \text{ d}^{-1}$

Then we use the integrated rate equation to determine the elapsed time.

$$\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt \quad t = -\frac{1}{k} \ln \frac{[\text{A}]_t}{[\text{A}]_0} = -\frac{1}{0.0485 \text{ d}^{-1}} \ln \frac{0.010}{1.000} = 95 \text{ days}$$

- 23. (D)**

(a)  $\ln \left( \frac{\frac{35}{100} [\text{A}]_0}{[\text{A}]_0} \right) = \ln(0.35) = -kt = (-4.81 \times 10^{-3} \text{ min}^{-1})t \quad t = 218 \text{ min.}$

Note: We did not need to know the initial concentration of acetoacetic acid to answer the question.

- (b) Let's assume that the reaction takes place in a 1.00L container.

$$10.0 \text{ g acetoacetic acid} \times \frac{1 \text{ mol acetoacetic acid}}{102.090 \text{ g acetoacetic acid}} = 0.09795 \text{ mol acetoacetic acid.}$$

After 575 min. (~ 4 half lives, hence, we expect ~ 6.25% remains as a rough approximation), use integrated form of the rate law to find  $[\text{A}]_t = 575 \text{ min.}$

$$\ln \left( \frac{[\text{A}]_t}{[\text{A}]_0} \right) = -kt = (-4.81 \times 10^{-3} \text{ min}^{-1})(575 \text{ min}) = -2.766$$

$$\frac{[\text{A}]_t}{[\text{A}]_0} = e^{-2.766} = 0.06293 \text{ (~ 6.3\% remains)} \quad \frac{[\text{A}]_t}{0.09795 \text{ moles}} = 0.063 \quad [\text{A}]_t = 6.2 \times 10^{-3} \text{ moles.}$$

$[\text{A}]_{\text{reacted}} = [\text{A}]_0 - [\text{A}]_t = (0.098 - 6.2 \times 10^{-3}) \text{ moles} = 0.092 \text{ moles acetoacetic acid.}$  The stoichiometry is such that for every mole of acetoacetic acid consumed, one mole of  $\text{CO}_2$  forms. Hence, we need to determine the volume of 0.0918 moles  $\text{CO}_2$  at 24.5 °C (297.65 K) and 748 torr (0.984 atm) by using the Ideal Gas law.

$$V = \frac{nRT}{P} = \frac{0.0918 \text{ mol} \left( 0.08206 \frac{\text{L atm}}{\text{K mol}} \right) 297.65 \text{ K}}{0.984 \text{ atm}} = 2.3 \text{ L CO}_2$$

- 24. (M)**

(a)  $\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt = \ln \frac{2.5 \text{ g}}{80.0 \text{ g}} = -3.47 = -6.2 \times 10^{-4} \text{ s}^{-1}t$

$$t = \frac{3.47}{6.2 \times 10^{-4} \text{ s}^{-1}} = 5.6 \times 10^3 \text{ s} \approx 93 \text{ min}$$

We substituted masses for concentrations, because the same substance (with the same molar mass) is present initially at time  $t$ , and because it is a closed system.

$$(b) \text{ amount O}_2 = 77.5 \text{ g N}_2\text{O}_5 \times \frac{1 \text{ mol N}_2\text{O}_5}{108.0 \text{ g N}_2\text{O}_5} \times \frac{1 \text{ mol O}_2}{2 \text{ mol N}_2\text{O}_5} = 0.359 \text{ mol O}_2$$

$$V = \frac{nRT}{P} = \frac{0.359 \text{ mol O}_2 \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times (45 + 273) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 9.56 \text{ L O}_2$$

**25. (D)**

- (a) If the reaction is first-order, we will obtain the same value of the rate constant from several sets of data.

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.497 \text{ M}}{0.600 \text{ M}} = -k \times 100 \text{ s} = -0.188, \quad k = \frac{0.188}{100 \text{ s}} = 1.88 \times 10^{-3} \text{ s}^{-1}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.344 \text{ M}}{0.600 \text{ M}} = -k \times 300 \text{ s} = -0.556, \quad k = \frac{0.556}{300 \text{ s}} = 1.85 \times 10^{-3} \text{ s}^{-1}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.285 \text{ M}}{0.600 \text{ M}} = -k \times 400 \text{ s} = -0.744, \quad k = \frac{0.744}{400 \text{ s}} = 1.86 \times 10^{-3} \text{ s}^{-1}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.198 \text{ M}}{0.600 \text{ M}} = -k \times 600 \text{ s} = -1.109, \quad k = \frac{1.109}{600 \text{ s}} = 1.85 \times 10^{-3} \text{ s}^{-1}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.094 \text{ M}}{0.600 \text{ M}} = -k \times 1000 \text{ s} = -1.854, \quad k = \frac{1.854}{1000 \text{ s}} = 1.85 \times 10^{-3} \text{ s}^{-1}$$

The virtual constancy of the rate constant throughout the time of the reaction confirms that the reaction is first-order.

- (b) For this part, we assume that the rate constant equals the average of the values obtained in part (a).

$$k = \frac{1.88 + 1.85 + 1.86 + 1.85}{4} \times 10^{-3} \text{ s}^{-1} = 1.86 \times 10^{-3} \text{ s}^{-1}$$

- (c) We use the integrated first-order rate equation:

$$[A]_{750} = [A]_0 \exp(-kt) = 0.600 \text{ M} \exp(-1.86 \times 10^{-3} \text{ s}^{-1} \times 750 \text{ s})$$

$$[A]_{750} = 0.600 \text{ M} e^{-1.40} = 0.148 \text{ M}$$

**26. (D)**

- (a) If the reaction is first-order, we will obtain the same value of the rate constant from several sets of data.

$$\ln \frac{P_t}{P_0} = -kt = \ln \frac{264 \text{ mmHg}}{312 \text{ mmHg}} = -k \times 390 \text{ s} = -0.167, \quad k = \frac{0.167}{390 \text{ s}} = 4.28 \times 10^{-4} \text{ s}^{-1}$$

$$\ln \frac{P_t}{P_0} = -kt = \ln \frac{224 \text{ mmHg}}{312 \text{ mmHg}} = -k \times 777 \text{ s} = -0.331, \quad k = \frac{0.331}{777 \text{ s}} = 4.26 \times 10^{-4} \text{ s}^{-1}$$

$$\ln \frac{P_t}{P_0} = -kt = \ln \frac{187 \text{ mmHg}}{312 \text{ mmHg}} = -k \times 1195 \text{ s} = -0.512, \quad k = \frac{0.512}{1195 \text{ s}} = 4.28 \times 10^{-4} \text{ s}^{-1}$$

$$\ln \frac{P_t}{P_0} = -kt = \ln \frac{78.5 \text{ mmHg}}{312 \text{ mmHg}} = -k \times 3155 \text{ s} = -1.38, \quad k = \frac{1.38}{3155 \text{ s}} = 4.37 \times 10^{-4} \text{ s}^{-1}$$

The virtual constancy of the rate constant confirms that the reaction is first-order.

- (b) For this part we assume the rate constant is the average of the values in part (a):  $4.3 \times 10^{-4} \text{ s}^{-1}$ .
- (c) At 390 s, the pressure of dimethyl ether has dropped to 264 mmHg. Thus, an amount of dimethyl ether equivalent to a pressure of  $(312 \text{ mmHg} - 264 \text{ mmHg} =) 48 \text{ mmHg}$  has decomposed. For each 1 mmHg pressure of dimethyl ether that decomposes, 3 mmHg of pressure from the products is produced. Thus, the increase in the pressure of the products is  $3 \times 48 = 144 \text{ mmHg}$ . The total pressure at this point is  $264 \text{ mmHg} + 144 \text{ mmHg} = 408 \text{ mmHg}$ . Below, this calculation is done in a more systematic fashion:

	$(\text{CH}_3)_2\text{O}(\text{g})$	$\rightarrow$	$\text{CH}_4(\text{g})$	$+$	$\text{H}_2(\text{g})$	$+$	$\text{CO}(\text{g})$
Initial	312 mmHg		0 mmHg		0 mmHg		0 mmHg
Changes	- 48 mmHg		+ 48 mmHg		+ 48 mmHg		+ 48 mmHg
Final	264 mmHg		48 mmHg		48 mmHg		48 mmHg

$$P_{\text{total}} = P_{\text{DME}} + P_{\text{methane}} + P_{\text{hydrogen}} + P_{\text{CO}}$$

$$= 264 \text{ mmHg} + 48 \text{ mmHg} + 48 \text{ mmHg} + 48 \text{ mmHg} = 408 \text{ mmHg}$$

- (d) This question is solved in the same manner as part (c). The results are summarized below.

	$(\text{CH}_3)_2\text{O}(\text{g})$	$\rightarrow$	$\text{CH}_4(\text{g})$	$+$	$\text{H}_2(\text{g})$	$+$	$\text{CO}(\text{g})$
Initial	312 mmHg		0 mmHg		0 mmHg		0 mmHg
Changes	- 312 mmHg		+ 312 mmHg		+ 312 mmHg		+ 312 mmHg
Final	0 mmHg		312 mmHg		312 mmHg		312 mmHg

$$P_{\text{total}} = P_{\text{DME}} + P_{\text{methane}} + P_{\text{hydrogen}} + P_{\text{CO}}$$

$$= 0 \text{ mmHg} + 312 \text{ mmHg} + 312 \text{ mmHg} + 312 \text{ mmHg} = 936 \text{ mmHg}$$

- (e) We first determine  $P_{\text{DME}}$  at 1000 s.  $\ln \frac{P_{1000}}{P_0} = -kt = -4.3 \times 10^{-4} \text{ s}^{-1} \times 1000 \text{ s} = -0.43$

$$\frac{P_{1000}}{P_0} = e^{-0.43} = 0.65 \quad P_{1000} = 312 \text{ mmHg} \times 0.65 = 203 \text{ mmHg}$$

Then we use the same approach as was used for parts (c) and (d)

	$(\text{CH}_3)_2\text{O}(\text{g})$	$\rightarrow$	$\text{CH}_4(\text{g})$	$+$	$\text{H}_2(\text{g})$	$+$	$\text{CO}(\text{g})$
Initial	312 mmHg		0 mmHg		0 mmHg		0 mmHg
Changes	- 109 mmHg		+ 109 mmHg		+ 109 mmHg		+ 109 mmHg
Final	203 mmHg		109 mmHg		109 mmHg		109 mmHg

$$P_{\text{total}} = P_{\text{DME}} + P_{\text{methane}} + P_{\text{hydrogen}} + P_{\text{CO}}$$

$$= 203 \text{ mmHg} + 109 \text{ mmHg} + 109 \text{ mmHg} + 109 \text{ mmHg} = 530. \text{ mmHg}$$



## Reactions of Various Orders

### 27. (M)

(a) Set II is data from a zero-order reaction. We know this because the rate of set II is constant.  $0.25 \text{ M}/25 \text{ s} = 0.010 \text{ M s}^{-1}$ . Zero-order reactions have constant rates of reaction.

(b) A first-order reaction has a constant half-life. In set I, the first half-life is slightly less than 75 sec, since the concentration decreases by slightly more than half (from 1.00 M to 0.47 M) in 75 s. Again, from 75 s to 150 s the concentration decreases from 0.47 M to 0.22 M, again by slightly more than half, in a time of 75 s. Finally, two half-lives should see the concentration decrease to one-fourth of its initial value. This, in fact, is what we see. From 100 s to 250 s, 150 s of elapsed time, the concentration decreases from 0.37 M to 0.08 M, i.e., to slightly less than one-fourth of its initial value. Notice that we cannot make the same statement of constancy of half-life for set III. The first half-life is 100 s, but it takes more than 150 s (from 100 s to 250 s) for [A] to again decrease by half.

(c) For a second-order reaction,  $1/[A]_t - 1/[A]_0 = kt$ . For the initial 100 s in set III, we have

$$\frac{1}{0.50 \text{ M}} - \frac{1}{1.00 \text{ M}} = 1.0 \text{ L mol}^{-1} = k 100 \text{ s}, \quad k = 0.010 \text{ L mol}^{-1} \text{ s}^{-1}$$

For the initial 200 s, we have

$$\frac{1}{0.33 \text{ M}} - \frac{1}{1.00 \text{ M}} = 2.0 \text{ L mol}^{-1} = k 200 \text{ s}, \quad k = 0.010 \text{ L mol}^{-1} \text{ s}^{-1}$$

Since we obtain the same value of the rate constant using the equation for second-order kinetics, set III must be second-order.

28. (E) For a zero-order reaction (set II), the slope equals the rate constant:

$$k = -\Delta[A]/\Delta t = 1.00 \text{ M}/100 \text{ s} = 0.0100 \text{ M/s}$$

29. (M) Set I is the data for a first-order reaction; we can analyze those items of data to determine the half-life. In the first 75 s, the concentration decreases by a bit more than half. This implies a half-life slightly less than 75 s, perhaps 70 s. This is consistent with the other time periods noted in the answer to Review Question 18 (b) and also to the fact that in the 150-s interval from 50 s to 200 s, the concentration decreases from 0.61 M to 0.14 M, which is a bit more than a factor-of-four decrease. The factor-of-four decrease, to one-fourth of the initial value, is what we would expect for two successive half-lives. We can determine the half-life more accurately, by obtaining a value of  $k$  from the relation  $\ln([A]_t/[A]_0) = -kt$  followed by  $t_{1/2} = 0.693/k$ . For instance,

$$\ln(0.78/1.00) = -k(25 \text{ s});$$

$$k = 9.94 \times 10^{-3} \text{ s}^{-1}. \text{ Thus, } t_{1/2} = 0.693/9.94 \times 10^{-3} \text{ s}^{-1} = 70 \text{ s}.$$

30. (E) We can determine an approximate initial rate by using data from the first 25 s.

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{0.80 \text{ M} - 1.00 \text{ M}}{25 \text{ s} - 0 \text{ s}} = 0.0080 \text{ M s}^{-1}$$

**31. (M)** The approximate rate at 75 s can be taken as the rate over the time period from 50 s to 100 s.

$$(a) \quad \text{Rate}_{\text{II}} = -\frac{\Delta[A]}{\Delta t} = -\frac{0.00 \text{ M} - 0.50 \text{ M}}{100 \text{ s} - 50 \text{ s}} = 0.010 \text{ M s}^{-1}$$

$$(b) \quad \text{Rate}_{\text{I}} = -\frac{\Delta[A]}{\Delta t} = -\frac{0.37 \text{ M} - 0.61 \text{ M}}{100 \text{ s} - 50 \text{ s}} = 0.0048 \text{ M s}^{-1}$$

$$(c) \quad \text{Rate}_{\text{III}} = -\frac{\Delta[A]}{\Delta t} = -\frac{0.50 \text{ M} - 0.67 \text{ M}}{100 \text{ s} - 50 \text{ s}} = 0.0034 \text{ M s}^{-1}$$

Alternatively we can use  $[A]$  at 75 s (the values given in the table) in the relationship  $\text{Rate} = k[A]^m$ , where  $m = 0, 1$ , or  $2$ .

$$(a) \quad \text{Rate}_{\text{II}} = 0.010 \text{ M s}^{-1} \times (0.25 \text{ mol/L})^0 = 0.010 \text{ M s}^{-1}$$

$$(b) \quad \text{Since } t_{1/2} = 70 \text{ s}, \quad k = 0.693 / 70 \text{ s} = 0.0099 \text{ s}^{-1}$$

$$\text{Rate}_{\text{I}} = 0.0099 \text{ s}^{-1} \times (0.47 \text{ mol/L})^1 = 0.0047 \text{ M s}^{-1}$$

$$(c) \quad \text{Rate}_{\text{III}} = 0.010 \text{ L mol}^{-1} \text{ s}^{-1} \times (0.57 \text{ mol/L})^2 = 0.0032 \text{ M s}^{-1}$$

**32. (M)** We can combine the approximate rates from Exercise 31, with the fact that 10 s have elapsed, and the concentration at 100 s.

$$(a) \quad [A]_{\text{II}} = 0.00 \text{ M} \quad \text{There is no reactant left after 100 s.}$$

$$(b) \quad [A]_{\text{I}} = [A]_{100} - (10 \text{ s} \times \text{rate}) = 0.37 \text{ M} - (10 \text{ s} \times 0.0047 \text{ M s}^{-1}) = 0.32 \text{ M}$$

$$(c) \quad [A]_{\text{III}} = [A]_{100} - (10 \text{ s} \times \text{rate}) = 0.50 \text{ M} - (10 \text{ s} \times 0.0032 \text{ M s}^{-1}) = 0.47 \text{ M}$$

**33. (E)** Substitute the given values into the rate equation to obtain the rate of reaction.

$$\text{Rate} = k[A]^2[B]^0 = (0.0103 \text{ M}^{-1} \text{ min}^{-1})(0.116 \text{ M})^2 (3.83 \text{ M})^0 = 1.39 \times 10^{-4} \text{ M / min}$$

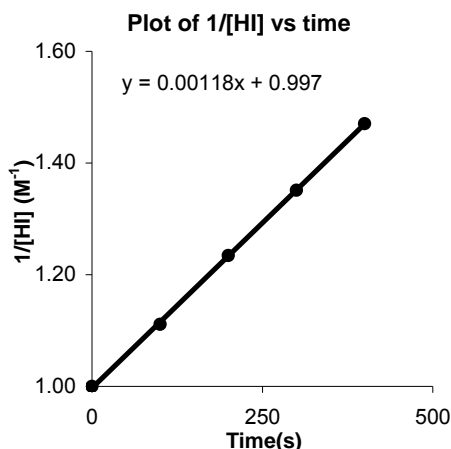
**34. (M)**

(a) A first-order reaction has a constant half-life. Thus, half of the initial concentration remains after 30.0 minutes, and at the end of another half-life—60.0 minutes total—half of the concentration present at 30.0 minutes will have reacted: the concentration has decreased to one-quarter of its initial value. Or, we could say that the reaction is 75% complete after two half-lives—60.0 minutes.

(b) A zero-order reaction proceeds at a constant rate. Thus, if the reaction is 50% complete in 30.0 minutes, in twice the time—60.0 minutes—the reaction will be 100% complete. (And in one-fifth the time—6.0 minutes—the reaction will be 10% complete. Alternatively, we can say that the rate of reaction is 10%/6.0 min.) Therefore, the time required for the reaction to be 75% complete =  $75\% \times \frac{60.0 \text{ min}}{100\%} = 45 \text{ min}$ .

35. (M) For reaction:  $\text{HI}(\text{g}) \rightarrow 1/2 \text{H}_2(\text{g}) + 1/2 \text{I}_2(\text{g})$  (700 K)

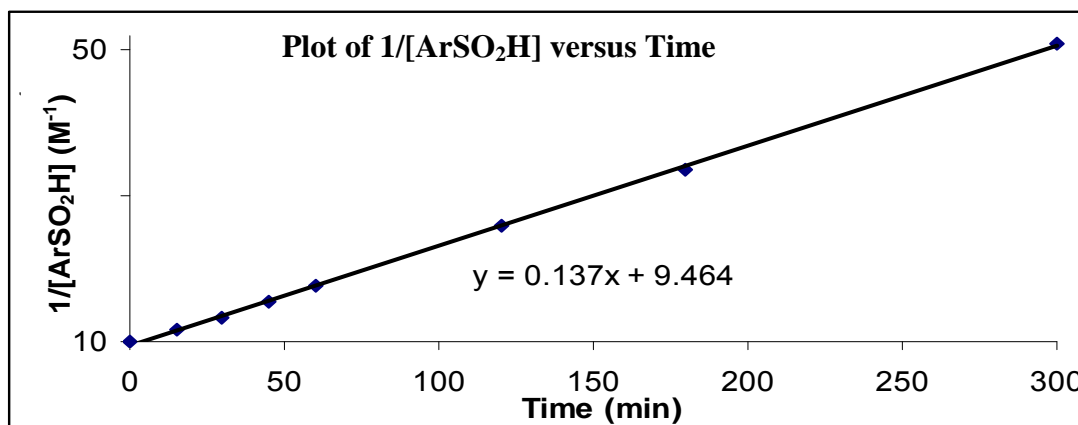
Time (s)	[HI] (M)	ln[HI]	1/[HI] ( $\text{M}^{-1}$ )
0	1.00	0	1.00
100	0.90	-0.105	1.11
200	0.81	-0.211	1.235
300	0.74	-0.301	1.35
400	0.68	-0.386	1.47



From data above, a plot of  $1/[\text{HI}]$  vs.  $t$  yields a straight line. The reaction is second-order in HI at 700 K. Rate =  $k[\text{HI}]^2$ . The slope of the line =  $k = 0.00118 \text{ M}^{-1}\text{s}^{-1}$

36. (D)

- (a) We can graph  $1/[\text{ArSO}_2\text{H}]$  vs. time and obtain a straight line. We can also graph  $[\text{ArSO}_2\text{H}]$  vs. time and  $\ln([\text{ArSO}_2\text{H}])$  vs. time to demonstrate that they do not yield a straight line. Only the plot of  $1/[\text{ArSO}_2\text{H}]$  versus time is shown.



The linearity of the line indicates that the reaction is second-order.

- (b) We solve the rearranged integrated second-order rate law for the rate constant, using the

longest time interval.  $\frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} = kt$   $\frac{1}{t} \left( \frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} \right) = k$

$$k = \frac{1}{300 \text{ min}} \left( \frac{1}{0.0196 \text{ M}} - \frac{1}{0.100 \text{ M}} \right) = 0.137 \text{ L mol}^{-1}\text{min}^{-1}$$

- (c) We use the same equation as in part (b), but solved for  $t$ , rather than  $k$ .

$$t = \frac{1}{k} \left( \frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} \right) = \frac{1}{0.137 \text{ L mol}^{-1}\text{min}^{-1}} \left( \frac{1}{0.0500 \text{ M}} - \frac{1}{0.100 \text{ M}} \right) = 73.0 \text{ min}$$

- (d) We use the same equation as in part (b), but solve for  $t$ , rather than  $k$ .

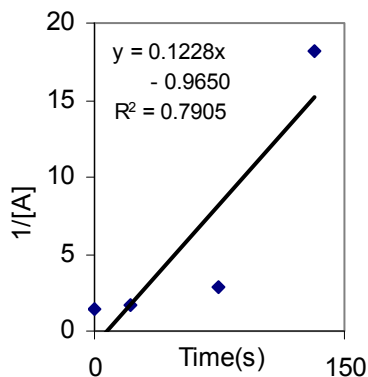
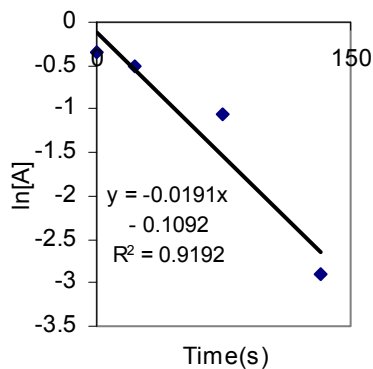
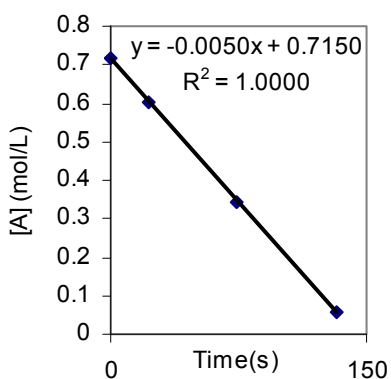
$$t = \frac{1}{k} \left( \frac{1}{[A]_t} - \frac{1}{[A]_0} \right) = \frac{1}{0.137 \text{ L mol}^{-1} \text{ min}^{-1}} \left( \frac{1}{0.0250 \text{ M}} - \frac{1}{0.100 \text{ M}} \right) = 219 \text{ min}$$

- (e) We use the same equation as in part (b), but solve for  $t$ , rather than  $k$ .

$$t = \frac{1}{k} \left( \frac{1}{[A]_t} - \frac{1}{[A]_0} \right) = \frac{1}{0.137 \text{ L mol}^{-1} \text{ min}^{-1}} \left( \frac{1}{0.0350 \text{ M}} - \frac{1}{0.100 \text{ M}} \right) = 136 \text{ min}$$

**37. (M)**

- (a) Plot  $[A]$  vs  $t$ ,  $\ln[A]$  vs  $t$ , and  $1/[A]$  vs  $t$  and see which yields a straight line.



Clearly we can see that the reaction is zero-order in reactant A with a rate constant of  $5.0 \times 10^{-3}$ .

- (b) The half-life of this reaction is the time needed for one half of the initial  $[A]$  to react.

$$\text{Thus, } \Delta[A] = 0.715 \text{ M} \div 2 = 0.358 \text{ M and } t_{1/2} = \frac{0.358 \text{ M}}{5.0 \times 10^{-3} \text{ M/s}} = 72 \text{ s.}$$

**38. (D)**

- (a) We can either graph  $1/[C_4H_6]$  vs. time and obtain a straight line, or we can determine the second-order rate constant from several data points. Then, if  $k$  indeed is a constant, the reaction is demonstrated to be second-order. We shall use the second technique in this case. First we do a bit of algebra.

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \qquad \frac{1}{t} \left( \frac{1}{[A]_t} - \frac{1}{[A]_0} \right) = k$$

$$k = \frac{1}{12.18 \text{ min}} \left( \frac{1}{0.0144 \text{ M}} - \frac{1}{0.0169 \text{ M}} \right) = 0.843 \text{ L mol}^{-1} \text{ min}^{-1}$$

$$k = \frac{1}{24.55 \text{ min}} \left( \frac{1}{0.0124 \text{ M}} - \frac{1}{0.0169 \text{ M}} \right) = 0.875 \text{ L mol}^{-1} \text{ min}^{-1}$$

$$k = \frac{1}{42.50 \text{ min}} \left( \frac{1}{0.0103 \text{ M}} - \frac{1}{0.0169 \text{ M}} \right) = 0.892 \text{ L mol}^{-1} \text{ min}^{-1}$$

$$k = \frac{1}{68.05 \text{ min}} \left( \frac{1}{0.00845 \text{ M}} - \frac{1}{0.0169 \text{ M}} \right) = 0.870 \text{ L mol}^{-1} \text{ min}^{-1}$$

The fact that each calculation generates similar values for the rate constant indicates that the reaction is second-order.

- (b) The rate constant is the average of the values obtained in part (a).

$$k = \frac{0.843 + 0.875 + 0.892 + 0.870}{4} \text{ L mol}^{-1} \text{ min}^{-1} = 0.87 \text{ L mol}^{-1} \text{ min}^{-1}$$

- (c) We use the same equation as in part (a), but solve for  $t$ , rather than  $k$ .

$$t = \frac{1}{k} \left( \frac{1}{[A]_t} - \frac{1}{[A]_0} \right) = \frac{1}{0.870 \text{ L mol}^{-1} \text{ min}^{-1}} \left( \frac{1}{0.00423 \text{ M}} - \frac{1}{0.0169 \text{ M}} \right) = 2.0 \times 10^2 \text{ min}$$

- (d) We use the same equation as in part (a), but solve for  $t$ , rather than  $k$ .

$$t = \frac{1}{k} \left( \frac{1}{[A]_t} - \frac{1}{[A]_0} \right) = \frac{1}{0.870 \text{ L mol}^{-1} \text{ min}^{-1}} \left( \frac{1}{0.0050 \text{ M}} - \frac{1}{0.0169 \text{ M}} \right) = 1.6 \times 10^2 \text{ min}$$

**39. (E)**

(a) initial rate =  $-\frac{\Delta[A]}{\Delta t} = -\frac{1.490 \text{ M} - 1.512 \text{ M}}{1.0 \text{ min} - 0.0 \text{ min}} = +0.022 \text{ M/min}$

initial rate =  $-\frac{\Delta[A]}{\Delta t} = -\frac{2.935 \text{ M} - 3.024 \text{ M}}{1.0 \text{ min} - 0.0 \text{ min}} = +0.089 \text{ M/min}$

- (b) When the initial concentration is doubled ( $\times 2.0$ ), from 1.512 M to 3.024 M, the initial rate quadruples ( $\times 4.0$ ). Thus, the reaction is second-order in A (since  $2.0^x = 4.0$  when  $x = 2$ ).

**40. (M)**

- (a) Let us assess the possibilities. If the reaction is zero-order, its rate will be constant. During the first 8 min, the rate is  $-(0.60 \text{ M} - 0.80 \text{ M})/8 \text{ min} = 0.03 \text{ M/min}$ . Then, during the first 24 min, the rate is  $-(0.35 \text{ M} - 0.80 \text{ M})/24 \text{ min} = 0.019 \text{ M/min}$ . Thus, the reaction is not zero-order. If the reaction is first-order, it will have a constant half-life that is consistent with its rate constant. The half-life can be assessed from the fact that 40 min elapse while the concentration drops from 0.80 M to 0.20 M, that is, to one-fourth of its initial value. Thus, 40 min equals two half-lives and  $t_{1/2} = 20 \text{ min}$ .

This gives  $k = 0.693/t_{1/2} = 0.693/20 \text{ min} = 0.035 \text{ min}^{-1}$ . Also

$$kt = -\ln \frac{[A]_t}{[A]_0} = -\ln \frac{0.35 \text{ M}}{0.80 \text{ M}} = 0.827 = k \times 24 \text{ min} \quad k = \frac{0.827}{24 \text{ min}} = 0.034 \text{ min}^{-1}$$

The constancy of the value of  $k$  indicates that the reaction is first-order.

- (b) The value of the rate constant is  $k = 0.034 \text{ min}^{-1}$ .

- (c) Reaction rate  $= \frac{1}{2}$  (rate of formation of B)  $= k[A]^1$  First we need [A] at  $t = 30 \text{ min}$

$$\ln \frac{[A]}{[A]_0} = -kt = -0.034 \text{ min}^{-1} \times 30 \text{ min} = -1.02 \quad \frac{[A]}{[A]_0} = e^{-1.02} = 0.36$$

$$[A] = 0.36 \times 0.80 \text{ M} = 0.29 \text{ M}$$

$$\text{rate of formation of B} = 2 \times 0.034 \text{ min}^{-1} \times 0.29 \text{ M} = 2.0 \times 10^{-2} \text{ M min}^{-1}$$

- 41. (M)** The half-life of the reaction depends on the concentration of A and, thus, this reaction cannot be first-order. For a second-order reaction, the half-life varies inversely with the reaction rate:  $t_{1/2} = 1/(k[A]_0)$  or  $k = 1/(t_{1/2}[A]_0)$ . Let us attempt to verify the second-order nature of this reaction by seeing if the rate constant is fixed.

$$k = \frac{1}{1.00 \text{ M} \times 50 \text{ min}} = 0.020 \text{ L mol}^{-1} \text{ min}^{-1}$$

$$k = \frac{1}{2.00 \text{ M} \times 25 \text{ min}} = 0.020 \text{ L mol}^{-1} \text{ min}^{-1}$$

$$k = \frac{1}{0.50 \text{ M} \times 100 \text{ min}} = 0.020 \text{ L mol}^{-1} \text{ min}^{-1}$$

The constancy of the rate constant demonstrates that this reaction indeed is second-order. The rate equation is  $\text{Rate} = k[A]^2$  and  $k = 0.020 \text{ L mol}^{-1} \text{ min}^{-1}$ .

42. (M)

- (a) The half-life depends on the initial  $[\text{NH}_3]$  and, thus, the reaction cannot be first-order. Let us attempt to verify second-order kinetics.

$$k = \frac{1}{[\text{NH}_3]_0 t_{1/2}} \text{ for a second-order reaction} \quad k = \frac{1}{0.0031 \text{ M} \times 7.6 \text{ min}} = 42 \text{ M}^{-1}\text{min}^{-1}$$

$$k = \frac{1}{0.0015 \text{ M} \times 3.7 \text{ min}} = 180 \text{ M}^{-1}\text{min}^{-1} \quad k = \frac{1}{0.00068 \text{ M} \times 1.7 \text{ min}} = 865 \text{ M}^{-1}\text{min}^{-1}$$

The reaction is not second-order. But, if the reaction is zero-order, its rate will be constant.

$$\text{Rate} = \frac{[\text{A}]_0 / 2}{t_{1/2}} = \frac{0.0031 \text{ M} \div 2}{7.6 \text{ min}} = 2.0 \times 10^{-4} \text{ M/min}$$

$$\text{Rate} = \frac{0.0015 \text{ M} \div 2}{3.7 \text{ min}} = 2.0 \times 10^{-4} \text{ M/min}$$

$$\text{Rate} = \frac{0.00068 \text{ M} \div 2}{1.7 \text{ min}} = 2.0 \times 10^{-4} \text{ M/min} \quad \text{Zero-order reaction}$$

- (b) The constancy of the rate indicates that the decomposition of ammonia under these conditions is zero-order, and the rate constant is  $k = 2.0 \times 10^{-4} \text{ M/min}$ .

43. (M) Zero-order:  $t_{1/2} = \frac{[\text{A}]_0}{2k}$       Second-order:  $t_{1/2} = \frac{1}{k[\text{A}]_0}$

A zero-order reaction has a half life that varies proportionally to  $[\text{A}]_0$ , therefore, increasing  $[\text{A}]_0$  increases the half-life for the reaction. A second-order reaction's half-life varies inversely proportional to  $[\text{A}]_0$ , that is, as  $[\text{A}]_0$  increases, the half-life decreases. The reason for the difference is that a zero-order reaction has a constant rate of reaction (independent of  $[\text{A}]_0$ ). The larger the value of  $[\text{A}]_0$ , the longer it will take to react. In a second-order reaction, the rate of reaction increases as the square of the  $[\text{A}]_0$ , hence, for high  $[\text{A}]_0$ , the rate of reaction is large and for very low  $[\text{A}]_0$ , the rate of reaction is very slow. If we consider a bimolecular elementary reaction, we can easily see that a reaction will not take place unless two molecules of reactants collide. This is more likely when the  $[\text{A}]_0$  is large than when it is small.

44. (M)

(a)  $\frac{[\text{A}]_0}{2k} = \frac{0.693}{k}$       Hence,  $\frac{[\text{A}]_0}{2} = 0.693$  or  $[\text{A}]_0 = 1.39 \text{ M}$

(b)  $\frac{[\text{A}]_0}{2k} = \frac{1}{k[\text{A}]_0}$ ,      Hence,  $\frac{[\text{A}]_0^2}{2} = 1$  or  $[\text{A}]_0^2 = 2.00 \text{ M}$        $[\text{A}]_0 = 1.414 \text{ M}$

(c)  $\frac{0.693}{k} = \frac{1}{k[\text{A}]_0}$ ,      Hence,  $0.693 = \frac{1}{[\text{A}]_0}$  or  $[\text{A}]_0 = 1.44 \text{ M}$

## Collision Theory; Activation Energy

**45. (M)**

- (a) The rate of a reaction depends on at least two factors other than the frequency of collisions. The first of these is whether each collision possesses sufficient energy to get over the energy barrier to products. This depends on the activation energy of the reaction; the higher it is, the smaller will be the fraction of successful collisions. The second factor is whether the molecules in a given collision are properly oriented for a successful reaction. The more complex the molecules are, or the more freedom of motion the molecules have, the smaller will be the fraction of collisions that are correctly oriented.
- (b) Although the collision frequency increases relatively slowly with temperature, the fraction of those collisions that have sufficient energy to overcome the activation energy increases much more rapidly. Therefore, the rate of reaction will increase dramatically with temperature.
- (c) The addition of a catalyst has the net effect of decreasing the activation energy of the overall reaction, by enabling an alternative mechanism. The lower activation energy of the alternative mechanism, (compared to the uncatalyzed mechanism), means that a larger fraction of molecules have sufficient energy to react. Thus the rate increases, even though the temperature does not.

**46. (M)**

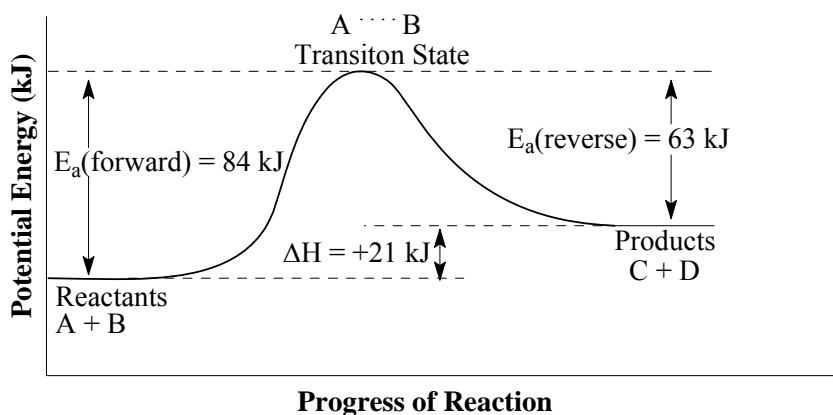
- (a) The activation energy for the reaction of hydrogen with oxygen is quite high, too high, in fact, to be supplied by the energy ordinarily available in a mixture of the two gases at ambient temperatures. However, the spark supplies a suitably concentrated form of energy to initiate the reaction of at least a few molecules. Since the reaction is highly exothermic, the reaction of these first few molecules supplies sufficient energy for yet other molecules to react and the reaction proceeds to completion or to the elimination of the limiting reactant.
- (b) A larger spark simply means that a larger number of molecules react initially. But the eventual course of the reaction remains the same, with the initial reaction producing enough energy to initiate still more molecules, and so on.

**47. (M)**

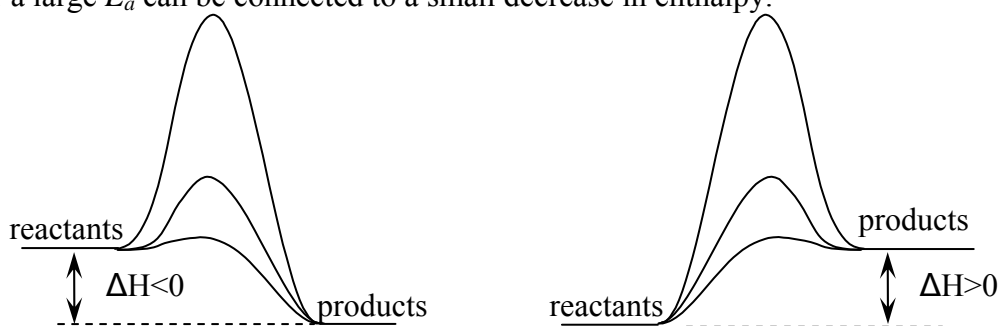
- (a) The products are 21 kJ/mol closer in energy to the energy activated complex than are the reactants. Thus, the activation energy for the reverse reaction is  $84 \text{ kJ/mol} - 21 \text{ kJ/mol} = 63 \text{ kJ/mol}$ .



(b) The reaction profile for the reaction in Figure 14-10 is sketched below.



48. (M) In an endothermic reaction (right),  $E_a$  must be larger than the  $\Delta H$  for the reaction. For an exothermic reaction (left), the magnitude of  $E_a$  may be either larger or smaller than that of  $\Delta H$ . In other words, a small activation energy can be associated with a large decrease in the enthalpy, or a large  $E_a$  can be connected to a small decrease in enthalpy.



49. (E)
- There are two intermediates (B and C).
  - There are three transition states (peaks/maxima) in the energy diagram.
  - The fastest step has the smallest  $E_a$ , hence, step 3 is the fastest step in the reaction with step 2 a close second.
  - Reactant A (step 1) has the highest  $E_a$ , and therefore the slowest smallest constant
  - Endothermic; energy is needed to go from A to B.
  - Exothermic; energy is released moving from A to D.

- 50. (E)**
- (a) There are two intermediates (B and C).
  - (b) There are three transition states (peaks/maxima) in the energy diagram.
  - (c) The fastest step has the smallest  $E_a$ , hence, step 2 is the fastest step in the reaction.
  - (d) Reactant A (step 1) has the highest  $E_a$ , and therefore the slowest smallest constant
  - (e) Endothermic; energy is needed to go from A to B.
  - (f) Endothermic, energy is needed to go from A to D.

### Effect of Temperature on Rates of Reaction

- 51. (M)**

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \ln \frac{5.4 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}}{2.8 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}} = \frac{E_a}{R} \left( \frac{1}{683 \text{ K}} - \frac{1}{599 \text{ K}} \right)$$

$$-3.95R = -E_a \times 2.05 \times 10^{-4}$$

$$E_a = \frac{3.95 R}{2.05 \times 10^{-4}} = 1.93 \times 10^4 \text{ K}^{-1} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} = 1.60 \times 10^5 \text{ J/mol} = 160 \text{ kJ/mol}$$

- 52. (M)**

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \ln \frac{5.0 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}}{2.8 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}} = \frac{1.60 \times 10^5 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{683 \text{ K}} - \frac{1}{T} \right)$$

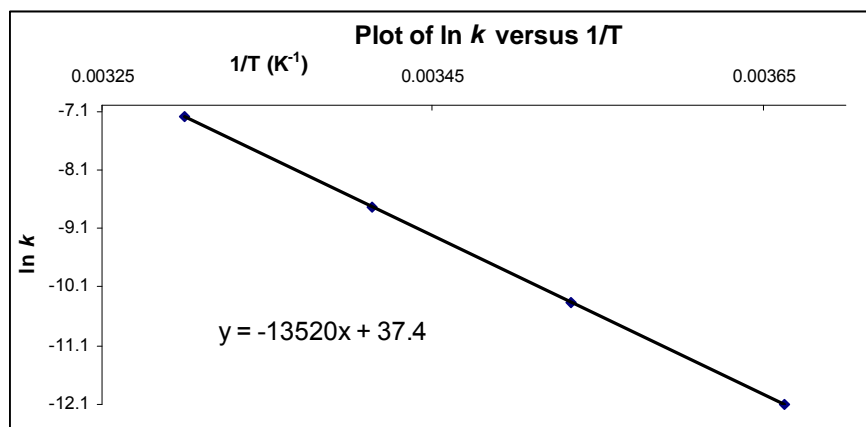
$$-1.72 = 1.92 \times 10^4 \left( \frac{1}{683 \text{ K}} - \frac{1}{T} \right) \quad \left( \frac{1}{683 \text{ K}} - \frac{1}{T} \right) = \frac{-1.72}{1.92 \times 10^4} = -8.96 \times 10^{-5}$$

$$\frac{1}{T} = 8.96 \times 10^{-5} + 1.46 \times 10^{-3} = 1.55 \times 10^{-3} \quad T = 645 \text{ K}$$

- 53. (D)**

- (a) First we need to compute values of  $\ln k$  and  $1/T$ . Then we plot the graph of  $\ln k$  versus  $1/T$ .

$T, ^\circ\text{C}$	0 °C	10 °C	20 °C	30 °C
$T, \text{K}$	273 K	283 K	293 K	303 K
$1/T, \text{K}^{-1}$	0.00366	0.00353	0.00341	0.00330
$k, \text{s}^{-1}$	$5.6 \times 10^{-6}$	$3.2 \times 10^{-5}$	$1.6 \times 10^{-4}$	$7.6 \times 10^{-4}$
$\ln k$	-12.09	-10.35	-8.74	-7.18



(b) The slope  $= -E_a / R$ .

$$E_a = -R \times \text{slope} = -8.3145 \frac{\text{J}}{\text{mol K}} \times -1.352 \times 10^4 \text{ K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 112 \frac{\text{kJ}}{\text{mol}}$$

(c) We apply the Arrhenius equation, with  $k = 5.6 \times 10^{-6} \text{ s}^{-1}$  at  $0^\circ\text{C}$  (273 K),  $k = ?$  at  $40^\circ\text{C}$  (313 K), and  $E_a = 113 \times 10^3 \text{ J/mol}$ .

$$\ln \frac{k}{5.6 \times 10^{-6} \text{ s}^{-1}} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{112 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{273 \text{ K}} - \frac{1}{313 \text{ K}} \right) = 6.306$$

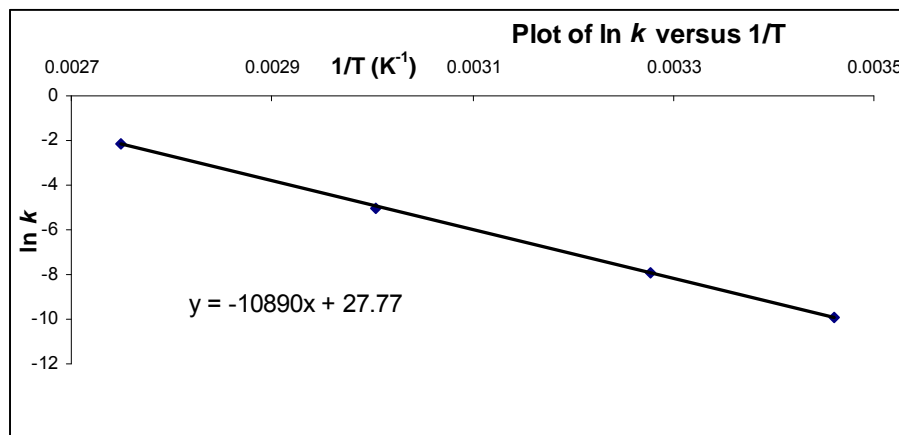
$$e^{6.306} = 548 = \frac{k}{5.6 \times 10^{-6} \text{ s}^{-1}} \quad k = 548 \times 5.6 \times 10^{-6} \text{ s}^{-1} = 3.07 \times 10^{-3} \text{ s}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3.07 \times 10^{-3} \text{ s}^{-1}} = 2.3 \times 10^2 \text{ s}$$

54. (D)

(a) Here we plot  $\ln k$  vs.  $1/T$ . The slope of the straight line equals  $-E_a / R$ . First we tabulate the data to plot. (the plot is shown below).

$T, ^\circ\text{C}$	15.83	32.02	59.75	90.61
$T, \text{K}$	288.98	305.17	332.90	363.76
$1/T, \text{K}^{-1}$	0.0034604	0.0032769	0.0030039	0.0027491
$k, \text{M}^{-1}\text{s}^{-1}$	$5.03 \times 10^{-5}$	$3.68 \times 10^{-4}$	$6.71 \times 10^{-3}$	0.119
$\ln k$	-9.898	-7.907	-5.004	-2.129



The slope of this graph =  $-1.09 \times 10^4 \text{ K} = E_a / R$

$$E_a = -(-1.089 \times 10^4 \text{ K}) \times 8.3145 \frac{\text{J}}{\text{mol K}} = 9.054 \times 10^4 \frac{\text{J}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 90.5 \frac{\text{kJ}}{\text{mol}}$$

- (b) We calculate the activation energy with the Arrhenius equation using the two extreme data points.

$$\begin{aligned} \ln \frac{k_2}{k_1} &= \ln \frac{0.119}{5.03 \times 10^{-5}} = +7.77 = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{E_a}{R} \left( \frac{1}{288.98 \text{ K}} - \frac{1}{363.76 \text{ K}} \right) \\ &= 7.1138 \times 10^{-4} \text{ K}^{-1} \frac{E_a}{R} \quad E_a = \frac{7.769 \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}{7.1138 \times 10^{-4} \text{ K}^{-1}} = 9.08 \times 10^4 \text{ J/mol} \end{aligned}$$

$E_a = 91 \text{ kJ/mol}$ . The two  $E_a$  values are in quite good agreement, within experimental limits.

- (c) We apply the Arrhenius equation, with  $E_a = 9.080 \times 10^4 \text{ J/mol}$ ,

$k = 5.03 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  at  $15.83 \text{ }^\circ\text{C}$  (288.98 K), and  $k = ?$  at  $100.0 \text{ }^\circ\text{C}$  (373.2 K).

$$\ln \frac{k}{5.03 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{90.80 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{288.98 \text{ K}} - \frac{1}{373.2 \text{ K}} \right)$$

$$\ln \frac{k}{5.03 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}} = 8.528 \quad e^{8.528} = 5.05 \times 10^3 = \frac{k}{5.03 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}}$$

$$k = 5.05 \times 10^3 \times 5.03 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1} = 0.254 \text{ M}^{-1} \text{ s}^{-1}$$

- 55.** (M) The half-life of a first-order reaction is inversely proportional to its rate constant:

$k = 0.693 / t_{1/2}$ . Thus we can apply a modified version of the Arrhenius equation to find  $E_a$ .

$$(a) \quad \ln \frac{k_2}{k_1} = \ln \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \ln \frac{46.2 \text{ min}}{2.6 \text{ min}} = \frac{E_a}{R} \left( \frac{1}{298 \text{ K}} - \frac{1}{(102 + 273) \text{ K}} \right)$$

$$2.88 = \frac{E_a}{R} 6.89 \times 10^{-4} \quad E_a = \frac{2.88 \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}{6.89 \times 10^{-4} \text{ K}^{-1}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 34.8 \text{ kJ/mol}$$

$$(b) \quad \ln \frac{10.0 \text{ min}}{46.2 \text{ min}} = \frac{34.8 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{T} - \frac{1}{298} \right) = -1.53 = 4.19 \times 10^3 \left( \frac{1}{T} - \frac{1}{298} \right)$$

$$\left( \frac{1}{T} - \frac{1}{298} \right) = \frac{-1.53}{4.19 \times 10^3} = -3.65 \times 10^{-4} \quad \frac{1}{T} = 2.99 \times 10^{-3} \quad T = 334 \text{ K} = 61 \text{ }^\circ\text{C}$$

- 56.** (M) The half-life of a first-order reaction is inversely proportional to its rate constant:  $k = 0.693 / t_{1/2}$ . Thus, we can apply a modified version of the Arrhenius equation.

$$(a) \quad \ln \frac{k_2}{k_1} = \ln \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \ln \frac{22.5 \text{ h}}{1.5 \text{ h}} = \frac{E_a}{R} \left( \frac{1}{293 \text{ K}} - \frac{1}{(40 + 273) \text{ K}} \right)$$

$$2.71 = \frac{E_a}{R} 2.18 \times 10^{-4}, \quad E_a = \frac{2.71 \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}{2.18 \times 10^{-4} \text{ K}^{-1}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 103 \text{ kJ/mol}$$

(b) The relationship is  $k = A \exp(-E_a / RT)$

$$k = 2.05 \times 10^{13} \text{ s}^{-1} \exp\left(\frac{-103 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times (273 + 30) \text{ K}}\right) = 2.05 \times 10^{13} \text{ s}^{-1} \times e^{-40.9} = 3.5 \times 10^{-5} \text{ s}^{-1}$$

**57. (M)**

(a) It is the change in the value of the rate constant that causes the reaction to go faster. Let  $k_1$  be the rate constant at room temperature, 20 °C (293 K). Then, ten degrees higher (30° C or 303 K), the rate constant  $k_2 = 2 \times k_1$ .

$$\ln \frac{k_2}{k_1} = \ln \frac{2 \times k_1}{k_1} = 0.693 = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{E_a}{R} \left( \frac{1}{293} - \frac{1}{303 \text{ K}} \right) = 1.13 \times 10^{-4} \text{ K}^{-1} \frac{E_a}{R}$$

$$E_a = \frac{0.693 \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}{1.13 \times 10^{-4} \text{ K}^{-1}} = 5.1 \times 10^4 \text{ J / mol} = 51 \text{ kJ / mol}$$

(b) Since the activation energy for the depicted reaction (i.e.,  $\text{N}_2\text{O} + \text{NO} \rightarrow \text{N}_2 + \text{NO}_2$ ) is 209 kJ/mol, we would not expect this reaction to follow the rule of thumb.

**58. (M)** Under a pressure of 2.00 atm, the boiling point of water is approximately 121 °C or 394 K. Under a pressure of 1 atm, the boiling point of water is 100° C or 373 K. We assume an activation energy of  $5.1 \times 10^4 \text{ J / mol}$  and compute the ratio of the two rates.

$$\ln \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{5.1 \times 10^4 \text{ J / mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{373} - \frac{1}{394 \text{ K}} \right) = 0.88$$

$\text{Rate}_2 = e^{0.88} \text{ Rate}_1 = 2.4 \text{ Rate}_1$ . Cooking will occur 2.4 times faster in the pressure cooker.

## Catalysis

**59. (E)**

(a) Although a catalyst is *recovered unchanged from the reaction mixture*, it does “take part in the reaction.” Some catalysts actually slow down the rate of a reaction. Usually, however, these negative catalysts are called inhibitors.

(b) The function of a catalyst is to *change the mechanism of a reaction*. The new mechanism is one that has a different (lower) activation energy (and frequently a different A value), than the original reaction.

**60. (M)** If the reaction is first-order, its half-life is 100 min, for in this time period [S] decreases from 1.00 M to 0.50 M, that is, by one half. This gives a rate constant of

$$k = 0.693 / t_{1/2} = 0.693 / 100 \text{ min} = 0.00693 \text{ min}^{-1}$$

The rate constant also can be determined from any two of the other sets of data.

$$kt = \ln \frac{[A]_0}{[A]_t} = \ln \frac{1.00 \text{ M}}{0.70 \text{ M}} = 0.357 = k \times 60 \text{ min} \quad k = \frac{0.357}{60 \text{ min}} = 0.00595 \text{ min}^{-1}$$

This is not a very good agreement between the two  $k$  values, so the reaction is probably not first-order in [A]. Let's try zero-order, where the rate should be constant.

$$\begin{aligned} \text{Rate} &= -\frac{0.90 \text{ M} - 1.00 \text{ M}}{20 \text{ min}} = 0.0050 \text{ M/min} & \text{Rate} &= -\frac{0.50 \text{ M} - 1.00 \text{ M}}{100 \text{ min}} = 0.0050 \text{ M/min} \\ \text{Rate} &= -\frac{0.20 \text{ M} - 0.90 \text{ M}}{160 \text{ min} - 20 \text{ min}} = 0.0050 \text{ M/min} & \text{Rate} &= -\frac{0.50 \text{ M} - 0.90 \text{ M}}{100 \text{ min} - 20 \text{ min}} = 0.0050 \text{ M/min} \end{aligned}$$

Thus, this reaction is zero-order with respect to [S].

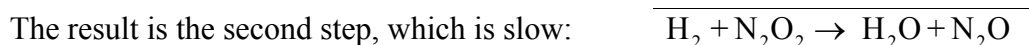
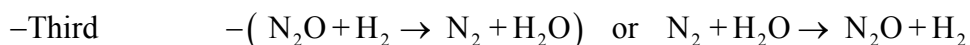
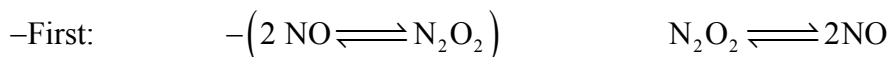
- 61.** (E) Both platinum and an enzyme have a metal center that acts as the active site. Generally speaking, platinum is not dissolved in the reaction solution (heterogeneous), whereas enzymes are generally soluble in the reaction media (homogeneous). The most important difference, however, is one of specificity. Platinum is rather nonspecific, catalyzing many different reactions. An enzyme, however, is quite specific, usually catalyzing only one reaction rather than all reactions of a given class.
- 62.** (E) In both the enzyme and the metal surface cases, the reaction occurs in a specialized location: either within the enzyme pocket or on the surface of the catalyst. At high concentrations of reactant, the limiting factor in determining the rate is not the concentration of reactant present but how rapidly active sites become available for reaction to occur. Thus, the rate of the reaction depends on either the quantity of enzyme present or the surface area of the catalyst, rather than on how much reactant is present (i.e., the reaction is zero-order). At low concentrations or gas pressures the reaction rate depends on how rapidly molecules can reach the available active sites. Thus, the rate depends on concentration or pressure of reactant and is first-order.
- 63.** (E) For the straight-line graph of Rate versus [Enzyme], an excess of substrate must be present.
- 64.** (E) For human enzymes, we would expect the maximum in the curve to appear around 37°C, i.e., normal body temperature (or possibly at slightly elevated temperatures to aid in the control of diseases (37 - 41 °C). At lower temperatures, the reaction rate of enzyme-activated reactions decreases with decreasing temperature, following the Arrhenius equation. However, at higher temperatures, these temperature sensitive biochemical processes become inhibited, probably by temperature-induced structural modifications to the enzyme or the substrate, which prevent formation of the enzyme-substrate complex.

## Reaction Mechanisms

- 65.** (E) The molecularity of an elementary process is the number of reactant molecules in the process. This molecularity is equal to the order of the overall reaction only if the elementary process in question is the slowest and, thus, the rate-determining step of the overall reaction. In addition, the elementary process in question should be the only elementary step that influences the rate of the reaction.
- 66.** (E) If the type of molecule that is expressed in the rate law as being first-order collides with other molecules that are present in much larger concentrations, the reaction will seem to depend only on the amount of those types of molecules present in smaller concentration, since the larger concentration will be essentially unchanged during the course of the reaction. Such a situation is quite common, and has been given the name pseudo first-order. It is also possible to have molecules which, do not participate directly in the reaction— including product molecules—

strike the reactant molecules and impart to them sufficient energy to react. Finally, collisions of the reactant molecules with the container walls may also impart adequate energy for reaction to occur.

- 67.** (M) The three elementary steps must sum to give the overall reaction. That is, the overall reaction is the sum of step 1 + step 2 + step 3. Hence, step 2 = overall reaction – step 1 – step 3. Note that all species in the equations below are gases.



The rate of this rate-determining step is:  $\text{Rate} = k_2 [\text{H}_2] [\text{N}_2\text{O}_2]$

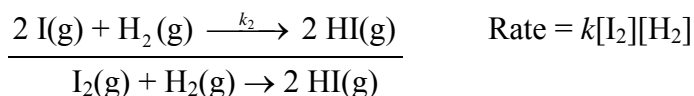
Since  $\text{N}_2\text{O}_2$  does not appear in the overall reaction, we need to replace its concentration with the concentrations of species that do appear in the overall reaction. To do this, recall that the first step is rapid, with the forward reaction occurring at the same rate as the reverse reaction.

$k_1 [\text{NO}]^2 = \text{forward rate} = \text{reverse rate} = k_{-1} [\text{N}_2\text{O}_2]$ . This expression is solved for  $[\text{N}_2\text{O}_2]$ , which then is substituted into the rate equation for the overall reaction.

$$[\text{N}_2\text{O}_2] = \frac{k_1 [\text{NO}]^2}{k_{-1}} \qquad \text{Rate} = \frac{k_2 k_1}{k_{-1}} [\text{H}_2] [\text{NO}]^2$$

The reaction is first-order in  $[\text{H}_2]$  and second-order in  $[\text{NO}]$ . This result conforms to the experimentally determined reaction order.

- 68.** (M) Proposed mechanism:  $\text{I}_2(\text{g}) \xrightleftharpoons[k_{-1}]{k_1} 2 \text{ I}(\text{g})$  Observed rate law:



The first step is a fast equilibrium reaction and step 2 is slow. Thus, the predicted rate law is  $\text{Rate} = k_2 [\text{I}]^2 [\text{H}_2]$ . In the first step, set the rate in the forward direction for the equilibrium equal to the rate in the reverse direction. Then solve for  $[\text{I}]^2$ .

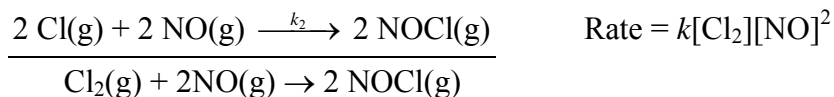
$$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}} \qquad \text{Use: } \text{Rate}_{\text{forward}} = k_1 [\text{I}_2] \text{ and } \text{Rate}_{\text{reverse}} = k_{-1} [\text{I}]^2$$

From this we see:  $k_1 [\text{I}_2] = k_{-1} [\text{I}]^2$ . Rearranging (solving for  $[\text{I}]^2$ )

$$[\text{I}]^2 = \frac{k_1 [\text{I}_2]}{k_{-1}} \qquad \text{Substitute into } \text{Rate} = k_2 [\text{I}]^2 [\text{H}_2] = k_2 \frac{k_1 [\text{I}_2]}{k_{-1}} [\text{H}_2] = k_{\text{obs}} [\text{I}_2] [\text{H}_2]$$

Since the predicted rate law is the same as the experimental rate law, this mechanism is plausible.

**69. (M)** Proposed mechanism:  $\text{Cl}_2(\text{g}) \xrightleftharpoons[k_{-1}]{k_1} 2\text{Cl}(\text{g})$  Observed rate law:



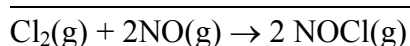
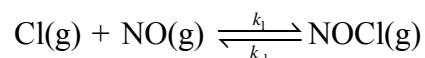
The first step is a fast equilibrium reaction and step 2 is slow. Thus, the predicted rate law is  $\text{Rate} = k_2[\text{Cl}]^2[\text{NO}]^2$ . In the first step, set the rate in the forward direction for the equilibrium equal to the rate in the reverse direction. Then express  $[\text{Cl}]^2$  in terms of  $k_1, k_{-1}$  and  $[\text{Cl}_2]$ . This mechanism is almost certainly not correct because it involves a tetra molecular second step.

$$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}} \quad \text{Use: } \text{Rate}_{\text{forward}} = k_1[\text{Cl}_2] \text{ and } \text{Rate}_{\text{reverse}} = k_{-1}[\text{Cl}]^2$$

From this we see:  $k_1[\text{Cl}_2] = k_{-1}[\text{Cl}]^2$ . Rearranging (solving for  $[\text{Cl}]^2$ )

$$[\text{Cl}]^2 = \frac{k_1[\text{Cl}_2]}{k_{-1}} \quad \text{Substitute into } \text{Rate} = k_2[\text{Cl}]^2[\text{NO}]^2 = k_2 \frac{k_1[\text{Cl}_2]}{k_{-1}} [\text{NO}]^2 = k_{\text{obs}}[\text{Cl}_2][\text{NO}]^2$$

There is another plausible mechanism.  $\text{Cl}_2(\text{g}) + \text{NO}(\text{g}) \xrightleftharpoons[k_{-1}]{k_1} \text{NOCl}(\text{g}) + \text{Cl}(\text{g})$



$$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}} \quad \text{Use: } \text{Rate}_{\text{forward}} = k_1[\text{Cl}_2][\text{NO}] \text{ and } \text{Rate}_{\text{reverse}} = k_{-1}[\text{Cl}][\text{NOCl}]$$

From this we see:  $k_1[\text{Cl}_2][\text{NO}] = k_{-1}[\text{Cl}][\text{NOCl}]$ . Rearranging (solving for  $[\text{Cl}]$ )

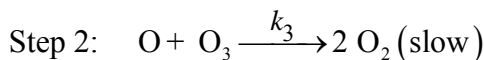
$$[\text{Cl}] = \frac{k_1[\text{Cl}_2][\text{NO}]}{k_{-1}[\text{NOCl}]} \quad \text{Substitute into } \text{Rate} = k_2[\text{Cl}][\text{NO}] = \frac{k_2 k_1 [\text{Cl}_2][\text{NO}]^2}{k_{-1}[\text{NOCl}]}$$

If  $[\text{NOCl}]$ , the product is assumed to be constant ( $\sim 0$  M using method of initial rates), then

$$\frac{k_2 k_1}{k_{-1}[\text{NOCl}]} = \text{constant} = k_{\text{obs}} \quad \text{Hence, the predicted rate law is } k_{\text{obs}}[\text{Cl}_2][\text{NO}]^2 \text{ which agrees with}$$

the experimental rate law. Since the predicted rate law agrees with the experimental rate law, both this and the previous mechanism are plausible, however, the first is dismissed as it has a tetramolecular elementary reaction (extremely unlikely to have four molecules simultaneously collide).

**70. (M)** A possible mechanism is: Step 1:  $\text{O}_3 \rightleftharpoons \text{O}_2 + \text{O}(\text{fast})$



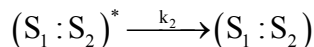
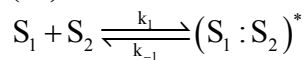
The overall rate is that of the slow step:  $\text{Rate} = k_3[\text{O}][\text{O}_3]$ . But O is a reaction intermediate, whose concentration is difficult to determine. An expression for [O] can be found by assuming that the forward and reverse “fast” steps proceed with equal speed.

$$\text{Rate}_1 = \text{Rate}_2 \quad k_1[\text{O}_3] = k_2[\text{O}_2][\text{O}] \quad [\text{O}] = \frac{k_1[\text{O}_3]}{k_2[\text{O}_2]} \quad \text{Rate} = k_3 \frac{k_1[\text{O}_3]}{k_2[\text{O}_2]} [\text{O}_3] = \frac{k_3 k_1}{k_2} \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

Then substitute this expression into the rate law for the reaction. This rate equation has the same form as the experimentally determined rate law and thus the proposed mechanism is plausible.



71. (M)



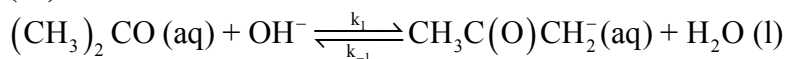
$$\frac{d(S_1 : S_2)^*}{dt} = k_1 [S_1][S_2] - k_{-1} (S_1 : S_2)^* - k_2 (S_1 : S_2)^*$$

$$k_1 [S_1][S_2] = (k_{-1} + k_2)(S_1 : S_2)^*$$

$$(S_1 : S_2)^* = \frac{k_1}{k_{-1} + k_2} [S_1][S_2]$$

$$\frac{d(S_1 : S_2)}{dt} = k_2 (S_1 : S_2)^* = \frac{k_2 \cdot k_1 [S_1][S_2]}{k_{-1} + k_2}$$

72. (M)



We note that  $\text{CH}_3\text{C}(\text{O})\text{CH}_2^-$  is an intermediate species. Using the steady state approximation, while its concentration is not known during the reaction, the rate of change of its concentration is zero, except for the very beginning and towards the end of the reaction. Therefore,

$$\frac{d[\text{CH}_3\text{C}(\text{O})\text{CH}_2^-]}{dt} = k_1 [(\text{CH}_3)_2\text{CO}][\text{OH}^-] - k_{-1} [\text{CH}_3\text{C}(\text{O})\text{CH}_2^-][\text{H}_2\text{O}]$$

$$-k_2 [\text{CH}_3\text{C}(\text{O})\text{CH}_2^-][(\text{CH}_3)_2\text{CO}] = 0$$

Rearranging the above expression to solve for  $\text{CH}_3\text{C}(\text{O})\text{CH}_2^-$  gives the following expression

$$[\text{CH}_3\text{C}(\text{O})\text{CH}_2^-] = \frac{k_1 [(\text{CH}_3)_2\text{CO}][\text{OH}^-]}{k_{-1}[\text{H}_2\text{O}] + k_2 [(\text{CH}_3)_2\text{CO}]}$$

The rate of formation of product, therefore, is:

$$\frac{d[\text{Pr od}]}{dt} = k_2 [\text{CH}_3\text{C}(\text{O})\text{CH}_2^-][(\text{CH}_3)_2\text{CO}]$$

$$= k_2 [(\text{CH}_3)_2\text{CO}] \cdot \frac{k_1 [(\text{CH}_3)_2\text{CO}][\text{OH}^-]}{k_{-1}[\text{H}_2\text{O}] + k_2 [(\text{CH}_3)_2\text{CO}]}$$

$$= \frac{k_2 k_1 [(\text{CH}_3)_2\text{CO}]^2 [\text{OH}^-]}{k_{-1}[\text{H}_2\text{O}] + k_2 [(\text{CH}_3)_2\text{CO}]}$$

## INTEGRATIVE AND ADVANCED EXERCISES

- 73. (M)** The data for the reaction starting with 1.00 M being first-order or second-order as well as that for the first-order reaction using 2.00 M is shown below

Time (min)	$[A]_0 = 1.00$ M (second order)	$[A]_0 = 1.00$ M (first order)	$[A]_0 = 2.00$ M (second order)	$[A]_0 = 2.00$ M (first order)
0	1.00	1.00	2.00	2.00
5	0.63	0.55	0.91	1.10
10	0.46	0.30	0.59	0.60
15	0.36	0.165	0.435	0.33
25	0.25	0.05	0.286	0.10

Clearly we can see that when  $[A]_0 = 1.00$  M, the first-order reaction concentrations will always be lower than that for the second-order case (assumes magnitude of the rate constant is the same). If, on the other hand, the concentration is above 1.00 M, the second-order reaction decreases faster than the first-order reaction (remember that the half-life shortens for a second-order reaction as the concentration increases, whereas for a first-order reaction, the half-life is constant).

From the data, it appears that the crossover occurs in the case where  $[A]_0 = 2.00$  M at just over 10 minutes.

$$\text{Second-order at 11 minutes: } \frac{1}{[A]} = \frac{1}{2} + \left( \frac{0.12}{\text{M min}} \right) \times (11 \text{ min}) \quad [A] = 0.549 \text{ M}$$

$$\text{First-order at 11 minutes: } \ln[A] = \ln(2) - \left( \frac{0.12}{\text{min}} \right) \times (11 \text{ min}) \quad [A] = 0.534 \text{ M}$$

A quick check at 10.5 minutes reveals,

$$\text{Second-order at 10.5 minutes: } \frac{1}{[A]} = \frac{1}{2} + \frac{0.12(10.5 \text{ min})}{\text{M min}} \quad [A] = 0.568 \text{ M}$$

$$\text{First-order at 10.5 minutes: } \ln[A] = \ln(2) - \frac{0.12(10.5 \text{ min})}{\text{M min}} \quad [A] = 0.567 \text{ M}$$

Hence, at approximately 10.5 minutes, these two plots will share a common point (point at which the concentration versus time curves overlap).

**74. (M)**

- (a) The concentration vs. time graph is not linear. Thus, the reaction is obviously not zero-order (the rate is not constant with time). A quick look at various half lives for this reaction shows the ~2.37 min (1.000 M to 0.5 M), ~2.32 min (0.800 M to 0.400 M), and ~2.38 min (0.400 M to 0.200 M). Since the half-life is constant, the reaction is probably first-order.

$$\text{(b) average } t_{1/2} = \frac{(2.37 + 2.32 + 2.38)}{3} = 2.36 \text{ min} \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.36 \text{ min}} = 0.294 \text{ min}^{-1}$$

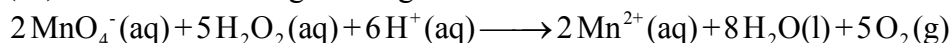
or perhaps better expressed as  $k = 0.29 \text{ min}^{-1}$  due to imprecision.

(c) When  $t = 3.5 \text{ min}$ ,  $[A] = 0.352 \text{ M}$ . Then,  $\text{rate} = k[A] = 0.294 \text{ min}^{-1} \times 0.352 \text{ M} = 0.103 \text{ M/min}$ .

$$(d) \text{ Slope} = \frac{\Delta[A]}{\Delta t} = -\text{Rate} = \frac{0.1480 \text{ M} - 0.339 \text{ M}}{6.00 \text{ min} - 3.00 \text{ min}} = -0.0637 \text{ M/min} \quad \text{Rate} = 0.064 \text{ M/min}$$

(e)  $\text{Rate} = k[A] = 0.294 \text{ min}^{-1} \times 1.000 \text{ M} = 0.294 \text{ M/min}$ .

**75. (M)** The reaction being investigated is:



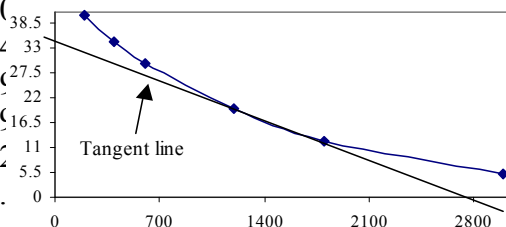
We use the stoichiometric coefficients in this balanced reaction to determine  $[\text{H}_2\text{O}_2]$ .

$$[\text{H}_2\text{O}_2] = \frac{37.1 \text{ mL titrant} \times \frac{0.1000 \text{ mmol MnO}_4^-}{1 \text{ mL titrant}} \times \frac{5 \text{ mmol H}_2\text{O}_2}{2 \text{ mmol MnO}_4^-}}{5.00 \text{ mL}} = 1.86 \text{ M}$$

**76. (D)** We assume in each case that 5.00 mL of reacting solution is titrated.

$$\begin{aligned} \text{volume MnO}_4^- &= 5.00 \text{ mL} \times \frac{2.32 \text{ mmol H}_2\text{O}_2}{1 \text{ mL}} \times \frac{2 \text{ mmol MnO}_4^-}{5 \text{ mmol H}_2\text{O}_2} \times \frac{1 \text{ mL titrant}}{0.1000 \text{ mmol MnO}_4^-} \\ &= 20.0 \times 2.32 \text{ M H}_2\text{O}_2 = 46.4 \text{ mL } 0.1000 \text{ M MnO}_4^- \text{ titrant at } 0 \text{ s} \end{aligned}$$

At 200 s	$V_{\text{titrant}} = 20.0 \times 2.01 \text{ M H}_2\text{O}_2 = 40.2 \text{ mL}$
At 400 s	$V_{\text{titrant}} = 20.0 \times 1.72 \text{ M H}_2\text{O}_2 = 34.4 \text{ mL}$
At 600 s	$V_{\text{titrant}} = 20.0 \times 1.49 \text{ M H}_2\text{O}_2 = 29.8 \text{ mL}$
At 1200 s	$V_{\text{titrant}} = 20.0 \times 0.98 \text{ M H}_2\text{O}_2 = 19.6 \text{ mL}$
At 1800 s	$V_{\text{titrant}} = 20.0 \times 0.62 \text{ M H}_2\text{O}_2 = 12.4 \text{ mL}$
At 3000 s	$V_{\text{titrant}} = 20.0 \times 0.25 \text{ M H}_2\text{O}_2 = 5.0 \text{ mL}$



The graph of volume of titrant vs. elapsed time is given above. This graph is of approximately the same shape as Figure 14-2, in which  $[\text{H}_2\text{O}_2]$  is plotted against time. In order to determine the rate, the tangent line at 1400 s has been drawn on the graph. The intercepts of the tangent line are at 34 mL of titrant and 2800 s. From this information we determine the rate of the reaction.

$$\text{Rate} = \frac{\frac{34 \text{ mL}}{2800 \text{ s}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.1000 \text{ mol MnO}_4^-}{1 \text{ L titrant}} \times \frac{5 \text{ mol H}_2\text{O}_2}{2 \text{ mol MnO}_4^-}}{0.00500 \text{ L sample}} = 6.1 \times 10^{-4} \text{ M/s}$$

This is the same as the value of  $6.1 \times 10^{-4}$  obtained in Figure 14-2 for 1400 s. The discrepancy is due, no doubt, to the coarse nature of our plot.

77. (M) First we compute the change in  $[\text{H}_2\text{O}_2]$ . This is then used to determine the amount, and ultimately the volume, of oxygen evolved from the given quantity of solution. Assume the  $\text{O}_2(\text{g})$  is dry.

$$\Delta[\text{H}_2\text{O}_2] = -\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} \Delta t = -\left(-1.7 \times 10^{-3} \text{ M/s} \times 1.00 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}}\right) = 0.102 \text{ M}$$

$$\text{amount O}_2 = 0.175 \text{ L soln} \times \frac{0.102 \text{ mol H}_2\text{O}_2}{1 \text{ L}} \times \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2\text{O}_2} = 0.00892 \text{ mol O}_2$$

$$\text{Volume O}_2 = \frac{nRT}{P} = \frac{0.00892 \text{ mol O}_2 \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 24) \text{ K}}{757 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 0.22 \text{ L O}_2$$

78. (M) We know that rate has the units of M/s, and also that concentration has the units of M. The generalized rate equation is  $\text{Rate} = k[\text{A}]_0$ . In terms of units, this becomes

$$\text{M/s} = \{\text{units of } k\} \text{M}_0. \text{ Therefore } \{\text{Units of } k\} = \frac{\text{M/s}}{\text{M}_0} = \text{M}_{1-0} \text{ s}^{-1}$$

79. (M)

(a) Comparing the third and the first lines of data,  $[\text{I}^-]$  and  $[\text{OH}^-]$  stay fixed, while  $[\text{OCl}^-]$  doubles. Also the rate for the third kinetics run is one half of the rate found for the first run. Thus, the reaction is first-order in  $[\text{OCl}^-]$ . Comparing the fourth and fifth lines,  $[\text{OCl}^-]$  and  $[\text{I}^-]$  stay fixed, while  $[\text{OH}^-]$  is halved. Also, the fifth run has a reaction rate that is twice that of the fourth run. Thus, the reaction is minus first-order in  $[\text{OH}^-]$ . Comparing the third and second lines of data,  $[\text{OCl}^-]$  and  $[\text{OH}^-]$  stay fixed, while the  $[\text{I}^-]$  doubles. Also, the second run has a reaction rate that is double that found for the third run. Thus, the reaction is first-order in  $[\text{I}^-]$ .

(b) The reaction is first-order in  $[\text{OCl}^-]$  and  $[\text{I}^-]$  and minus first-order in  $[\text{OH}^-]$ . Thus, the overall order =  $1 + 1 - 1 = 1$ . The reaction is first-order overall.

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

(c)

$$\text{using data from first run: } \frac{\text{Rate } [\text{OH}^-]}{[\text{OCl}^-][\text{I}^-]} = \frac{4.8 \times 10^{-4} \text{ M/s} \times 1.00 \text{ M}}{0.0040 \text{ M} \times 0.0020 \text{ M}} = 60. \text{ s}^{-1}$$

80. (M) We first determine the number of moles of  $\text{N}_2\text{O}$  produced. The partial pressure of  $\text{N}_2\text{O}(\text{g})$  in the “wet”  $\text{N}_2\text{O}$  is  $756 \text{ mmHg} - 12.8 \text{ mmHg} = 743 \text{ mmHg}$ .

$$\text{amount N}_2\text{O} = \frac{PV}{RT} = \frac{743 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \times 0.0500 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times (273 + 15) \text{ K}} = 0.00207 \text{ mol N}_2\text{O}$$

Now we determine the change in  $[\text{NH}_2\text{NO}_2]$ .

$$\Delta[\text{NH}_2\text{NO}_2] = \frac{0.00207 \text{ mol N}_2\text{O} \times \frac{1 \text{ mol NH}_2\text{NO}_2}{1 \text{ mol N}_2\text{O}}}{0.165 \text{ L soln}} = 0.0125 \text{ M}$$

$$[\text{NH}_2\text{NO}_2]_{\text{final}} = 0.105 \text{ M} - 0.0125 \text{ M} = 0.093 \text{ M} \quad k = \frac{0.693}{123 \text{ min}} = 0.00563 \text{ min}^{-1}$$

$$t = -\frac{1}{k} \ln \frac{[A]_t}{[A]_0} = -\frac{1}{0.00563 \text{ min}^{-1}} \ln \frac{0.093 \text{ M}}{0.105 \text{ M}} = 22 \text{ min} = \text{elapsed time}$$

- 81. (D)** We need to determine the partial pressure of ethylene oxide at each time in order to determine the order of the reaction. First, we need the initial pressure of ethylene oxide. The pressure at infinite time is the pressure that results when all of the ethylene oxide has decomposed. Because two moles of product gas are produced for every mole of reactant gas, this infinite pressure is twice the initial pressure of ethylene oxide.  $P_{\text{initial}} = 249.88 \text{ mmHg} \div 2 = 124.94 \text{ mmHg}$ . Now, at each time we have the following.  $(\text{CH}_2)_2\text{O}(\text{g}) \longrightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$

Initial: 124.94 mmHg    Changes:  $-x \text{ mmHg} +x \text{ mmHg} +x \text{ mmHg}$     Final:  $124.94 + x \text{ mmHg}$

Thus,  $x = P_{\text{tot}} - 124.94$  and  $P_{\text{EtO}} = 124.94 - x = 124.94 - (P_{\text{tot}} - 124.94) = 249.88 - P_{\text{tot}}$

Hence, we have, the following values for the partial pressure of ethylene oxide.

$t, \text{ min}$	0	10	20	40	60	100	200
$P_{\text{EtO}}, \text{ mmHg}$	124.94	110.74	98.21	77.23	60.73	37.54	11.22

For the reaction to be zero-order, its rate will be constant.

$$\text{The rate in the first 10 min is: Rate} = \frac{-(110.74 - 124.94) \text{ mmHg}}{10 \text{ min}} = 1.42 \text{ mmHg/min}$$

$$\text{The rate in the first 40 min is: Rate} = \frac{-(77.23 - 124.94) \text{ mmHg}}{40 \text{ min}} = 1.19 \text{ mmHg/min}$$

We conclude from the non-constant rate that the reaction is not zero-order. For the reaction to be first-order, its half-life must be constant. From 40 min to 100 min—a period of 60 min—the partial pressure of ethylene oxide is approximately halved, giving an approximate half-life of 60 min. And, in the first 60 min, the partial pressure of ethylene oxide is approximately halved. Thus, the reaction appears to be first-order. To verify this tentative conclusion, we use the integrated first-order rate equation to calculate some values of the rate constant.

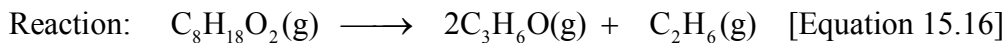
$$k = -\frac{1}{t} \ln \frac{P}{P_0} = -\frac{1}{10 \text{ min}} \ln \frac{110.74 \text{ mmHg}}{124.94 \text{ mmHg}} = 0.0121 \text{ min}^{-1}$$

$$k = -\frac{1}{100 \text{ min}} \ln \frac{37.54 \text{ mmHg}}{124.94 \text{ mmHg}} = 0.0120 \text{ min}^{-1} \quad k = -\frac{1}{60 \text{ min}} \ln \frac{60.73 \text{ mmHg}}{124.94 \text{ mmHg}} = 0.0120 \text{ min}^{-1}$$

The constancy of the first-order rate constant suggests that the reaction is first-order.

- 82. (M)** For this first-order reaction  $\ln \frac{P_t}{P_0} = -kt$  Elapsed time is computed as:  $t = -\frac{1}{k} \ln \frac{P_t}{P_0}$

We first determine the pressure of DTBP when the total pressure equals 2100 mmHg.



Initial: 800.0 mmHg

Changes:  $-x$  mmHg                       $+2x$  mmHg               $+x$  mmHg

Final: (800.0  $-x$ ) mmHg               $2x$  mmHg               $x$  mmHg

Total pressure =  $(800.0 - x) + 2x + x = 800.0 + 2x = 2100$ .

$x = 650$ . mmHg     $P\{\text{C}_8\text{H}_{18}\text{O}_2(\text{g})\} = 800$ . mmHg  $- 650$ . mmHg = 150. mmHg

$$t = -\frac{1}{k} \ln \frac{P_t}{P_0} = -\frac{1}{8.7 \times 10^{-3} \text{ min}^{-1}} \ln \frac{150. \text{ mmHg}}{800. \text{ mmHg}} = 19_2 \text{ min} = 1.9 \times 10^2 \text{ min}$$

- 83. (D)** If we compare Experiment 1 with Experiment 2, we notice that [B] has been halved, and also that the rate, expressed as  $\Delta[\text{A}]/\Delta t$ , has been halved. This is most evident for the times 5 min, 10 min, and 20 min. In Experiment 1, [A] decreases from  $1.000 \times 10^{-3}$  M to  $0.779 \times 10^{-3}$  M in 5 min, while in Experiment 2 this same decrease in [A] requires 10 min. Likewise in Experiment 1, [A] decreases from  $1.000 \times 10^{-3}$  M to  $0.607 \text{ M} \times 10^{-3}$  in 10 min, while in Experiment 2 the same decrease in [A] requires 20 min. This dependence of rate on the first power of concentration is characteristic of a first-order reaction. This reaction is first-order in [B]. We now turn to the order of the reaction with respect to [A]. A zero-order reaction will have a constant rate. Determine the rate

After over the first minute:               $\text{Rate} = \frac{-(0.951 - 1.000) \times 10^{-3} \text{ M}}{1 \text{ min}} = 4.9 \times 10^{-5} \text{ M/min}$

After over the first five minutes:               $\text{Rate} = \frac{-(0.779 - 1.000) \times 10^{-3} \text{ M}}{5 \text{ min}} = 4.4 \times 10^{-5} \text{ M/min}$

After over the first twenty minutes:               $\text{Rate} = \frac{-(0.368 - 1.000) \times 10^{-3} \text{ M}}{20 \text{ min}} = 3.2 \times 10^{-5} \text{ M/min}$

This is not a very constant rate; we conclude that the reaction is not zero-order. There are no clear half-lives in the data with which we could judge the reaction to be first-order. But we can determine the value of the first-order rate constant for a few data.

$$k = -\frac{1}{t} \ln \frac{[\text{A}]}{[\text{A}]_0} = -\frac{1}{1 \text{ min}} \ln \frac{0.951 \text{ mM}}{1.000 \text{ mM}} = 0.0502 \text{ min}^{-1}$$

$$k = -\frac{1}{10 \text{ min}} \ln \frac{0.607 \text{ mM}}{1.000 \text{ mM}} = 0.0499 \text{ min}^{-1} \qquad k = -\frac{1}{20 \text{ min}} \ln \frac{0.368 \text{ mM}}{1.000 \text{ mM}} = 0.0500 \text{ min}^{-1}$$

The constancy of the first-order rate constant indicates that the reaction indeed is first-order in [A]. (As a point of interest, notice that the concentrations chosen in this experiment are such that the reaction is pseudo-zero-order in [B]. Here, then it is not necessary to consider the variation of [B] with time as the reaction proceeds when determining the kinetic dependence on [A].)

84. (M) In Exercise 79 we established the rate law for the iodine-hypochlorite ion reaction:

Rate =  $k[\text{OCl}^-][\text{I}^-][\text{OH}^-]^{-1}$ . In the mechanism, the slow step gives the rate law;

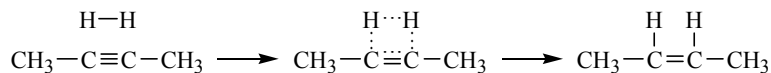
Rate =  $k_3[\text{I}^-][\text{HOCl}]$ . We use the initial fast equilibrium step to substitute for  $[\text{HOCl}]$  in this rate equation. We assume in this fast step that the forward rate equals the reverse rate.

$$k_1[\text{OCl}^-][\text{H}_2\text{O}] = k_{-1}[\text{HOCl}][\text{OH}^-] \quad [\text{HOCl}] = \frac{k_1[\text{OCl}^-][\text{H}_2\text{O}]}{k_{-1}[\text{OH}^-]}$$

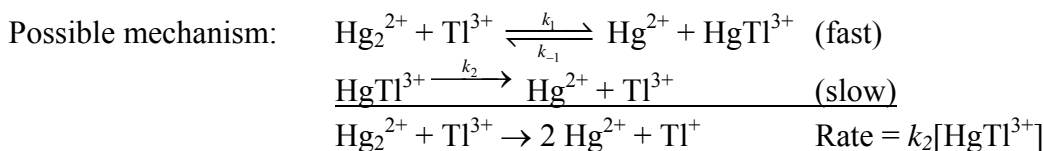
$$\text{Rate} = k_2[\text{I}^-] \frac{k_1[\text{OCl}^-][\text{H}_2\text{O}]}{k_{-1}[\text{OH}^-]} = \frac{k_2 k_1 [\text{H}_2\text{O}][\text{OCl}^-][\text{I}^-]}{k_{-1}[\text{OH}^-]} = k \frac{[\text{OCl}^-][\text{I}^-]}{[\text{OH}^-]}$$

This is the same rate law that we established in Exercise 79. We have incorporated  $[\text{H}_2\text{O}]$  in the rate constant for the reaction because, in an aqueous solution,  $[\text{H}_2\text{O}]$  remains effectively constant during the course of the reaction. (The final fast step simply involves the neutralization of the acid HOI by the base hydroxide ion,  $\text{OH}^-$ .)

85. (M) It is more likely that the *cis*-isomer, compound (I), would be formed than the *trans*-isomer, compound (II). The reason for this is that the reaction will involve the adsorption of both  $\text{CH}_3\text{—C}\equiv\text{C—CH}_3$  and  $\text{H}_2$  onto the surface of the catalyst. These two molecules will eventually be adjacent to each other. At some point, one of the  $\pi$  bonds in the  $\text{C}\equiv\text{C}$  bond will break, the  $\text{H—H}$  bond will break, and two  $\text{C—H}$  bonds will form. Since these two  $\text{C—H}$  bonds form on the same side of the carbon chain, compound (I) will be produced. In the sketches below, dotted lines (...) indicate bonds forming or breaking.



86. (D)  $\text{Hg}_2^{2+} + \text{Tl}^{3+} \rightarrow 2 \text{Hg}^{2+} + \text{Tl}^+$  Experimental rate law =  $k \frac{[\text{Hg}_2^{2+}][\text{Tl}^{3+}]}{[\text{Hg}^{2+}]}$



$$k_1[\text{Hg}_2^{2+}][\text{Tl}^{3+}] = k_{-1}[\text{Hg}^{2+}][\text{HgTl}^{3+}] \quad \text{—rearrange—} \rightarrow [\text{HgTl}^{3+}] = \frac{k_1[\text{Hg}_2^{2+}][\text{Tl}^{3+}]}{k_{-1}[\text{Hg}^{2+}]}$$

$$\text{Rate} = k_2[\text{HgTl}^{3+}] = \frac{k_2 k_1 [\text{Hg}_2^{2+}][\text{Tl}^{3+}]}{k_{-1}[\text{Hg}^{2+}]} = k_{\text{obs}} \frac{[\text{Hg}_2^{2+}][\text{Tl}^{3+}]}{[\text{Hg}^{2+}]}$$

**87. (M)**

$$\frac{\Delta \text{CCl}_3}{\Delta t} = \text{rate}_{\text{formation}} + \text{rate}_{\text{disappearance}} = 0 \quad \text{so } \text{rate}_{\text{formation}} = \text{rate}_{\text{decomposition}}$$

$$k_2[\text{Cl}(\text{g})][\text{CHCl}_3] = k_3[\text{CCl}_3][\text{Cl}(\text{g})] \quad \text{and, simplifying, } [\text{CCl}_3] = \frac{k_2}{k_3}[\text{CHCl}_3]$$

$$\text{since rate} = k_3[\text{CCl}_3][\text{Cl}(\text{g})] = k_3 \left( \frac{k_2}{k_3}[\text{CHCl}_3] \right) [\text{Cl}(\text{g})] = k_2[\text{CHCl}_3][\text{Cl}(\text{g})]$$

$$\text{We know: } [\text{Cl}(\text{g})] = \left( \frac{k_1}{k_{-1}}[\text{Cl}_2(\text{g})] \right)^{1/2} \quad \text{then } \text{rate}_{\text{overall}} = k_2[\text{CHCl}_3] \left( \frac{k_1}{k_{-1}}[\text{Cl}_2(\text{g})] \right)^{1/2}$$

$$\text{and the rate constant } k \text{ will be: } k = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} = (1.3 \times 10^{-2}) \left( \frac{4.8 \times 10^3}{3.6 \times 10^3} \right)^{1/2} = 0.015$$

**88. (D)**

$$\text{Rate} = k[\text{A}]^3 - \frac{d[\text{A}]}{dt} \quad \text{Rearrange: } -kt = \frac{d[\text{A}]}{[\text{A}]^3}$$

Integrate using the limits  $\rightarrow$  time (0 to  $t$ ) and concentration ( $[\text{A}]_0$  to  $[\text{A}]_t$ )

$$-k \int_0^t dt = \int_{[\text{A}]_0}^{[\text{A}]_t} \frac{d[\text{A}]}{[\text{A}]^3} \Rightarrow -kt - (-k(0)) = -\frac{1}{2} \frac{1}{[\text{A}]_t^2} - \left( -\frac{1}{2} \frac{1}{[\text{A}]_0^2} \right)$$

$$\text{Simplify: } -kt = -\frac{1}{2[\text{A}]_t^2} + \frac{1}{2[\text{A}]_0^2} \quad \text{Rearrange: } \frac{1}{2[\text{A}]_t^2} = kt + \frac{1}{2[\text{A}]_0^2}$$

$$\text{Multiply through by 2 to give the integrated rate law: } \frac{1}{[\text{A}]_t^2} = 2kt + \frac{1}{[\text{A}]_0^2}$$

To derive the half life ( $t_{1/2}$ ) substitute  $t = t_{1/2}$  and  $[\text{A}]_t = \frac{[\text{A}]_0}{2}$ 

$$\frac{1}{\left( \frac{[\text{A}]_0}{2} \right)^2} = 2kt_{1/2} + \frac{1}{[\text{A}]_0^2} = \frac{1}{\frac{[\text{A}]_0^2}{4}} = \frac{4}{[\text{A}]_0^2} \quad \text{Collect terms}$$

$$2kt_{1/2} = \frac{4}{[\text{A}]_0^2} - \frac{1}{[\text{A}]_0^2} = \frac{3}{[\text{A}]_0^2} \quad \text{Solve for } t_{1/2} \quad t_{1/2} = \frac{3}{2k[\text{A}]_0^2}$$

**89. (D)** Consider the reaction:  $\text{A} + \text{B} \rightarrow \text{products}$  (first-order in A, first-order in B). The initial concentration of each reactant can be defined as  $[\text{A}]_0$  and  $[\text{B}]_0$ . Since the stoichiometry is 1:1, we can define  $x$  as the concentration of reactant A and reactant B that is removed (a variable that changes with time).

$$\text{The } [\text{A}]_t = ([\text{A}]_0 - x) \quad \text{and} \quad [\text{B}]_t = ([\text{B}]_0 - x).$$

$$\text{Algebra note: } [\text{A}]_0 - x = -(x - [\text{A}]_0) \quad \text{and} \quad [\text{B}]_0 - x = -(x - [\text{B}]_0).$$



As well, the calculus requires that we use the absolute value of  $|x - [A]_0|$  and  $|x - [B]_0|$  when taking the integral of the reciprocal of  $|x - [A]_0|$  and  $|x - [B]_0|$

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{dx}{dt} = k[A]_t[B]_t = k([A]_0 - x)([B]_0 - x) \quad \text{or} \quad \frac{dx}{([A]_0 - x)([B]_0 - x)} = kdt$$

In order to solve this, partial fraction decomposition is required to further ease integration:

$$dx \left( \frac{1}{([B]_0 - [A]_0)} \right) \left( \frac{1}{([A]_0 - x)} - \frac{1}{([B]_0 - x)} \right) = kdt$$

Note: this is a constant

From the point of view of integration, a further rearrangement is desirable (See algebra note above).

$$dx \left( \frac{1}{([B]_0 - [A]_0)} \right) \left( \frac{-1}{|x - [A]_0|} - \frac{-1}{|x - [B]_0|} \right) = kdt$$

$$\text{Integrate both sides} \left( \frac{1}{([B]_0 - [A]_0)} \right) \left[ -\ln|x - [A]_0| - (-\ln|x - [B]_0|) \right] = kt + C$$

$$|x - [A]_0| = [A]_0 - x \quad \text{and} \quad |x - [B]_0| = [B]_0 - x \quad \text{Substitute and simplify}$$

$$\left( \frac{1}{([B]_0 - [A]_0)} \right) \ln \left( \frac{([B]_0 - x)}{[A]_0 - x} \right) = kt + C \quad \text{Determine C by setting } x = 0 \text{ at } t = 0$$

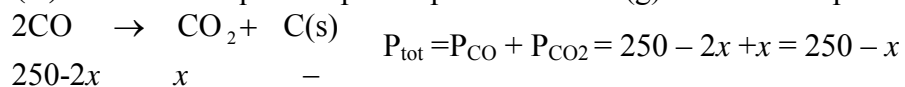
$$C = \left( \frac{1}{([B]_0 - [A]_0)} \right) \ln \frac{[B]_0}{[A]_0} \quad \text{Hence:} \left( \frac{1}{([B]_0 - [A]_0)} \right) \ln \left( \frac{([B]_0 - x)}{([A]_0 - x)} \right) = kt + \left( \frac{1}{([B]_0 - [A]_0)} \right) \ln \frac{[B]_0}{[A]_0}$$

$$\text{Multiply both sides by } ([B]_0 - [A]_0), \text{ hence, } \ln \left( \frac{([B]_0 - x)}{([A]_0 - x)} \right) = ([B]_0 - [A]_0) \times kt + \ln \frac{[B]_0}{[A]_0}$$

$$\ln \left( \frac{([B]_0 - x)}{([A]_0 - x)} \right) - \ln \frac{[B]_0}{[A]_0} = ([B]_0 - [A]_0) \times kt = \ln \frac{\left( \frac{([B]_0 - x)}{([A]_0 - x)} \right)}{\frac{[B]_0}{[A]_0}} = \ln \left( \frac{[A]_0 ([B]_0 - x)}{[B]_0 ([A]_0 - x)} \right)$$

$$\text{Set } ([A]_0 - x) = [A]_t \text{ and } ([B]_0 - x) = [B]_t \text{ to give } \ln \left( \frac{[A]_0 \times [B]_t}{[B]_0 \times [A]_t} \right) = ([B]_0 - [A]_0) \times kt$$

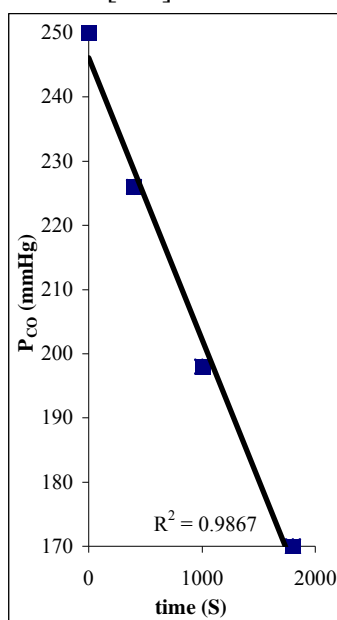
**90. (D)** Let  $250-2x$  equal the partial pressure of  $\text{CO}(\text{g})$  and  $x$  be the partial pressure of  $\text{CO}_2(\text{g})$ .



$P_{\text{tot}}$ [torr]	Time [sec]	$P_{\text{CO}_2}$	$P_{\text{CO}}$ [torr]
250	0	0	250
238	398	12	226
224	1002	26	198
210	1801	40	170

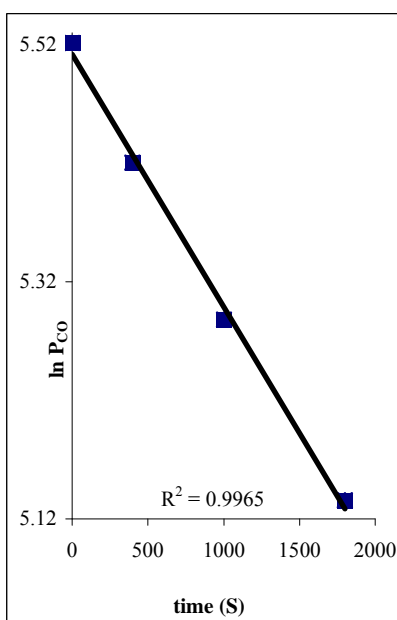
The plots that follow show that the reaction appears to obey a second-order rate law.

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



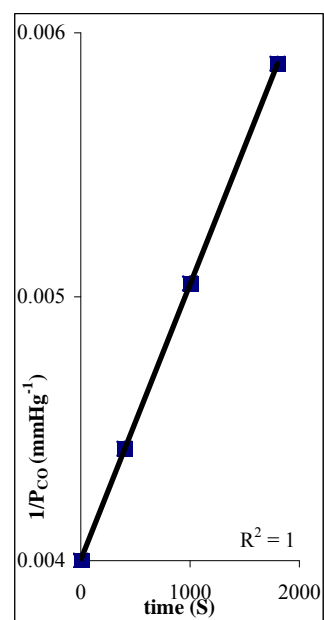
**ZERO ORDER PLOT**

T	$P_{\text{CO}}$
0	250
398	226
1002	198
1801	170



**1<sup>st</sup> ORDER PLOT**

T	$\ln P_{\text{CO}}$
0	5.521461
398	5.420535
1002	5.288267
1801	5.135798

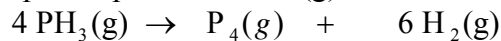


**2<sup>nd</sup> ORDER PLOT**

T	$1/\text{CO}$
0	0.004
398	0.004425
1002	0.005051
1801	0.005882

(Best correlation coefficient)

- 91. (D)** Let  $100-4x$  equal the partial pressure of  $\text{PH}_3(\text{g})$ ,  $x$  be the partial pressure of  $\text{P}_4(\text{g})$  and  $6x$  be the partial pressure of  $\text{H}_2(\text{g})$



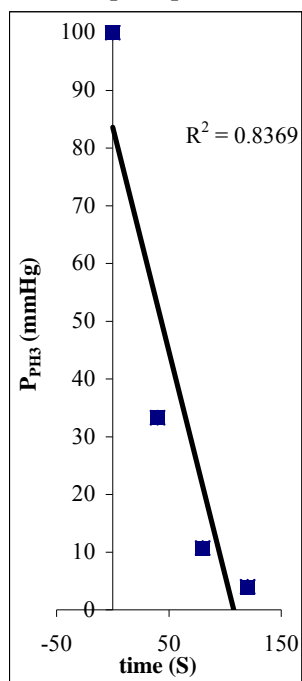
$$100 - 4x \quad x \quad 6x$$

$$P_{\text{tot}} = P_{\text{PH}_3} + P_{\text{P}_4} + P_{\text{H}_2} = 100 - 4x + x + 6x = 100 + 3x$$

$P_{\text{tot}}$ [torr]	Time [sec]	$P_{\text{P}_4}$ [torr]	$P_{\text{PH}_3}$ [torr]
100	0	0	100
150	40	50/3	100-(4)(50/3)
167	80	67/3	100-(4)(67/3)
172	120	72/3	100-(4)(72/3)

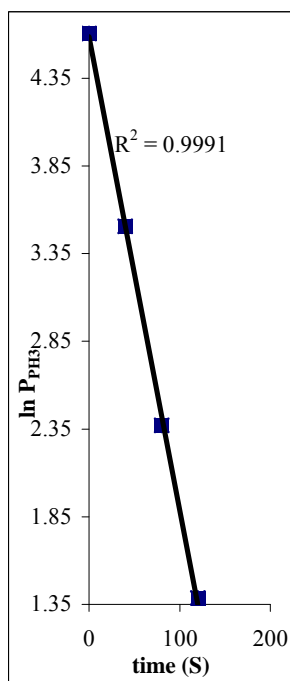
The plots to follow show that the reaction appears to obey a first-order rate law.

$$\text{Rate} = k[\text{PH}_3]$$



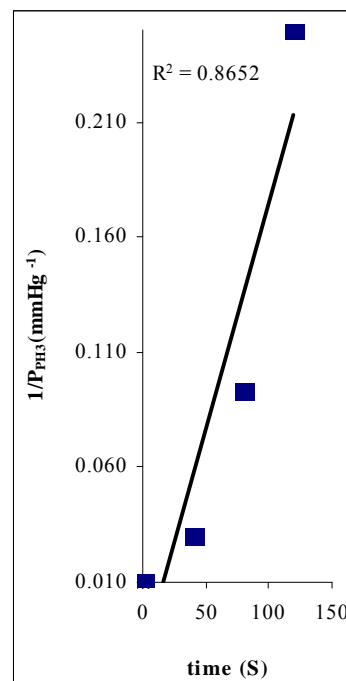
**ZERO ORDER PLOT**

T	$P_{\text{PH}_3}$
0	100
40	33.3
80	10.7
120	4



**1<sup>st</sup> ORDER PLOT**

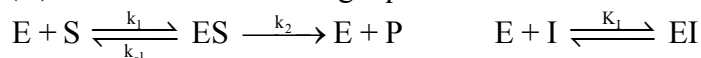
T	$\ln P_{\text{PH}_3}$
0	4.61
40	3.51
80	2.37
120	1.39



**2<sup>nd</sup> ORDER PLOT**

T	$1/P_{\text{PH}_3}$
0	0.010
40	0.030
80	0.093
120	0.250

92. (D) Consider the following equilibria.



Product production  $\frac{d[P]}{dt} = k_2[ES]$  Use the steady state approximation for [ES]

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = k_1[E][S] - [ES](k_{-1} + k_2) = 0$$

$$\text{solve for [ES]} \left( \text{Keep in mind } K_M = \frac{k_{-1} + k_2}{k_1} \right) \quad [ES] = \frac{k_1[E][S]}{k_{-1} + k_2} = \frac{[E][S]}{K_M}$$

$$\text{Formation of EI: } K_I = \frac{[E][I]}{[EI]} \quad [EI] = \frac{[E][I]}{K_I}$$

$$[E_o] = [E] + [ES] + [EI] = [E] + \frac{[E][S]}{K_M} + \frac{[E][I]}{K_I}$$

$$[E_o] = [E] \left( 1 + \frac{[S]}{K_M} + \frac{[I]}{K_I} \right) \quad \text{Solve for [E]} \quad [E] = \frac{[E_o]}{\left( 1 + \frac{[S]}{K_M} + \frac{[I]}{K_I} \right)}$$

$$\text{From above: } [ES] = \frac{[E][S]}{K_M} \quad [ES] = \frac{[E_o] \left( \frac{[S]}{K_M} \right)}{\left( 1 + \frac{[S]}{K_M} + \frac{[I]}{K_I} \right)} \quad \text{multiplication by } \frac{K_M}{K_M} \text{ affords}$$

$$[ES] = \frac{[E_o][S]}{\left( K_M + [S] + \frac{[I]K_M}{K_I} \right)} = \frac{[E_o][S]}{K_M \left( 1 + \frac{[I]}{K_I} \right) + [S]}$$

$$\text{Remember } \frac{d[P]}{dt} = k_2[ES] = \frac{k_2[E_o][S]}{K_M \left( 1 + \frac{[I]}{K_I} \right) + [S]}$$

$$\text{If we substitute } k_2[E_o] = V_{\max} \text{ then } \frac{d[P]}{dt} = \frac{V_{\max}[S]}{K_M \left( 1 + \frac{[I]}{K_I} \right) + [S]}$$

Thus, as [I] increases, the ratio  $\frac{V_{\max}[S]}{K_M \left( 1 + \frac{[I]}{K_I} \right) + [S]}$  decreases;

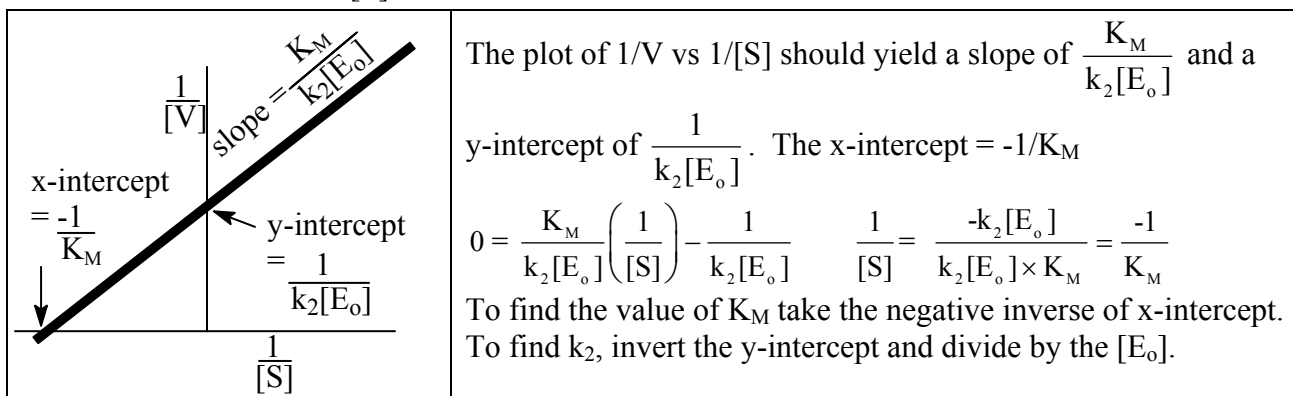
i.e., the rate of product formation decreases as [I] increases.

- 93. (D)** In order to determine a value for  $K_M$ , we need to rearrange the equation so that we may obtain a linear plot and extract parameters from the slope and intercepts.

$$V = \frac{k_2[E_o][S]}{K_M + [S]} \quad \frac{1}{V} = \frac{K_M + [S]}{k_2[E_o][S]} = \frac{K_M}{k_2[E_o][S]} + \frac{[S]}{k_2[E_o][S]}$$

$$\frac{1}{V} = \frac{K_M}{k_2[E_o][S]} + \frac{1}{k_2[E_o]} \quad \text{We need to have this in the form of } y = mx + b$$

Plot  $\frac{1}{V}$  on the y-axis and  $\frac{1}{[S]}$  on the x-axis. See result below:



**94. (M)**

- a) The first elementary step  $\text{HBr} + \text{O}_2 \xrightarrow{k_1} \text{HOBr}$  is rate-determining if the reaction obeys reaction rate =  $k [\text{HBr}][\text{O}_2]$  since the rate of this step is identical to that of the experimental rate law.
- b) No, mechanisms cannot be shown to be absolutely correct, only consistent with experimental observations.
- c) Yes; the sum of the elementary steps ( $3 \text{HBr} + \text{O}_2 \rightarrow \text{HOBr} + \text{Br}_2 + \text{H}_2\text{O}$ ) is not consistent with the overall stoichiometry (since HOBr is not detected as a product) of the reaction and therefore cannot be considered a valid mechanism.

**95. (M)**

- (a) Both reactions are first-order, because they involve the decomposition of one molecule.
- (b)  $k_2$  is the slow reaction.
- (c) To determine the concentration of the product,  $\text{N}_2$ , we must first determine how much reactant remains at the end of the given time period, from which we can calculate the amount of reactant consumed and therefore the amount of product produced. Since this is a first-order reaction, the concentration of the reactant,  $\text{N}_2\text{O}$  after time  $t$  is determined as follows:

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

$$[\text{N}_2\text{O}]_{0.1} = (2.0 \text{ M}) \cdot \exp\left(- (25.7 \text{ s}^{-1})(0.1 \text{ s})\right) = 0.153 \text{ M N}_2\text{O remaining}$$

The amount of  $\text{N}_2\text{O}$  consumed =  $2.0 \text{ M} - 0.153 \text{ M} = 1.847 \text{ M}$

$$[\text{N}_2] = 1.847 \text{ M NO} \times \frac{1 \text{ M N}_2}{2 \text{ M NO}} = 0.9235 \text{ M N}_2$$

(d) The process is identical to step (c).

$$[\text{N}_2\text{O}]_{0.1} = (4.0 \text{ M}) \cdot \exp\left(-\left(18.2 \text{ s}^{-1}\right)(0.025 \text{ s})\right) = 2.538 \text{ M N}_2\text{O remaining}$$

The amount of  $\text{N}_2\text{O}$  consumed =  $4.0 \text{ M} - 2.538 \text{ M} = 1.462 \text{ M}$

$$[\text{N}_2\text{O}] = 1.462 \text{ M NO} \times \frac{1 \text{ M N}_2\text{O}}{2 \text{ M NO}} = 0.731 \text{ M N}_2\text{O}$$

## FEATURE PROBLEMS

### 96. (D)

(a) To determine the order of the reaction, we need  $[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]$  at each time. To determine this value, note that  $58.3 \text{ mL N}_2(\text{g})$  evolved corresponds to total depletion of  $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ , to  $[\text{C}_6\text{H}_5\text{N}_2\text{Cl}] = 0.000 \text{ M}$ .

$$\text{Thus, at any point in time, } [\text{C}_6\text{H}_5\text{N}_2\text{Cl}] = 0.071 \text{ M} - \left( \text{volume N}_2(\text{g}) \times \frac{0.071 \text{ M C}_6\text{H}_5\text{N}_2\text{Cl}}{58.3 \text{ mL N}_2(\text{g})} \right)$$

$$\text{Consider 21 min: } [\text{C}_6\text{H}_5\text{N}_2\text{Cl}] = 0.071 \text{ M} - \left( 44.3 \text{ mL N}_2 \times \frac{0.071 \text{ M C}_6\text{H}_5\text{N}_2\text{Cl}}{58.3 \text{ mL N}_2(\text{g})} \right) = 0.017 \text{ M}$$

The numbers in the following table are determined with this method.

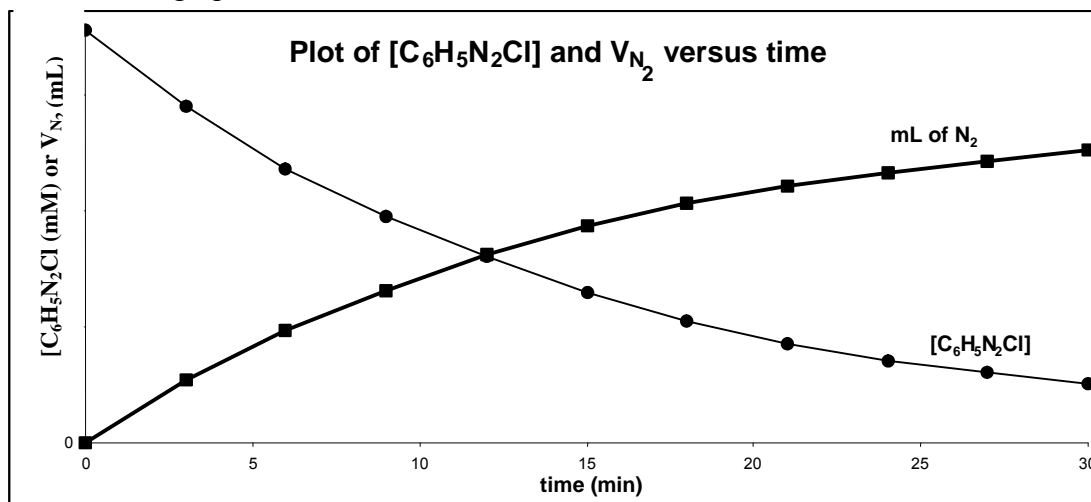
Time, min	0	3	6	9	12	15	18	21	24	27	30	$\infty$
$V_{\text{N}_2}$ , mL	0	10.8	19.3	26.3	32.4	37.3	41.3	44.3	46.5	48.4	50.4	58.3
$[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]$ , mM	71	58	47	39	32	26	21	17	14	12	10	0

[The concentration is given in thousandths of a mole per liter (mM).]

(b)

time(min)	0	3	6	9	12	15	18	21	24	27	30	$\infty$
$\Delta T(\text{min})$		3	3	3	3	3	3	3	3	3	3	
$[\text{C}_6\text{H}_5\text{N}_2\text{Cl}](\text{mM})$	71	58	47	39	32	26	21	17	14	12	10	$\infty$
$\Delta[\text{C}_6\text{H}_5\text{N}_2\text{Cl}](\text{mM})$		-13	-11	-8	-7	-6	-5	-4	-3	-2	-2	
Reaction Rate ( $\text{mM min}^{-1}$ )		4.3	3.7	2.7	2.3	2.0	1.7	1.3	1.0	0.7	0.7	

- (c) The two graphs are drawn on the same axes.



- (d) The rate of the reaction at  $t = 21$  min is the slope of the tangent line to the  $[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]$  curve. The tangent line intercepts the vertical axis at about  $[\text{C}_6\text{H}_5\text{N}_2\text{Cl}] = 39$  mM and the horizontal axis at about 37 min

$$\text{Reaction rate} = \frac{39 \times 10^{-3} \text{ M}}{37 \text{ min}} = 1.05 \times 10^{-3} \text{ M min}^{-1} = 1.1 \times 10^{-3} \text{ M min}^{-1}$$

The agreement with the reported value is very good.

- (e) The initial rate is the slope of the tangent line to the  $[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]$  curve at  $t = 0$ . The intercept with the vertical axis is 71 mM, of course. That with the horizontal axis is about 13 min.

$$\text{Rate} = \frac{71 \times 10^{-3} \text{ M}}{13 \text{ min}} = 5.5 \times 10^{-3} \text{ M min}^{-1}$$

- (f) The first-order rate law is  $\text{Rate} = k [\text{C}_6\text{H}_5\text{N}_2\text{Cl}]$ , which we solve for  $k$ :

$$k = \frac{\text{Rate}}{[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]} \quad k_0 = \frac{5.5 \times 10^{-3} \text{ M min}^{-1}}{71 \times 10^{-3} \text{ M}} = 0.077 \text{ min}^{-1}$$

$$k_{21} = \frac{1.1 \times 10^{-3} \text{ M min}^{-1}}{17 \times 10^{-3} \text{ M}} = 0.065 \text{ min}^{-1}$$

An average value would be a reasonable estimate:  $k_{\text{avg}} = 0.071 \text{ min}^{-1}$

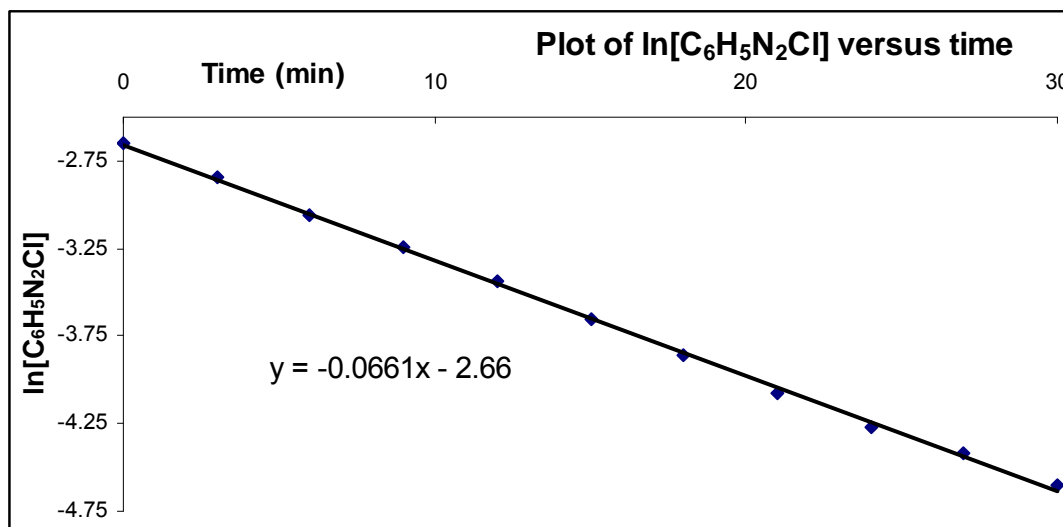
- (g) The estimated rate constant gives one value of the half-life:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.071 \text{ min}^{-1}} = 9.8 \text{ min}$$

The first half-life occurs when  $[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]$  drops from 0.071 M to 0.0355 M. This occurs at about 10.5 min.

- (h) The reaction should be three-fourths complete in two half-lives, or about 20 minutes.

- (i) The graph plots  $\ln[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]$  (in millimoles/L) vs. time in minutes.



The linearity of the graph demonstrates that the reaction is first-order.

- (j)  $k = -\text{slope} = -(-6.61 \times 10^{-2}) \text{ min}^{-1} = 0.0661 \text{ min}^{-1}$   
 $t_{1/2} = \frac{0.693}{0.0661 \text{ min}^{-1}} = 10.5 \text{ min}$ , in good agreement with our previously determined values.

**97. (D)**

- (a) In Experiments 1 & 2,  $[\text{KI}]$  is the same (0.20 M), while  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  is halved, from 0.20 M to 0.10 M. As a consequence, the time to produce a color change doubles (i.e., the rate is halved). This indicates that reaction (a) is first-order in  $\text{S}_2\text{O}_8^{2-}$ . Experiments 2 and 3 produce a similar conclusion. In Experiments 4 and 5,  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  is the same (0.20 M) while  $[\text{KI}]$  is halved, from 0.10 to 0.050 M. As a consequence, the time to produce a color change nearly doubles, that is, the rate is halved. This indicates that reaction (a) is also first-order in  $\text{I}^-$ . Reaction (a) is (1 + 1) second-order overall.

- (b) The blue color appears when all the  $\text{S}_2\text{O}_3^{2-}$  has been consumed, for only then does reaction (b) cease. The same amount of  $\text{S}_2\text{O}_3^{2-}$  is placed in each reaction mixture.

$$\text{amount } \text{S}_2\text{O}_3^{2-} = 10.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.010 \text{ mol Na}_2\text{S}_2\text{O}_3}{1 \text{ L}} \times \frac{1 \text{ mol S}_2\text{O}_3^{2-}}{1 \text{ mol Na}_2\text{S}_2\text{O}_3} = 1.0 \times 10^{-4} \text{ mol}$$

Through stoichiometry, we determine the amount of each reactant that reacts before this amount of  $\text{S}_2\text{O}_3^{2-}$  will be consumed.



$$\begin{aligned} \text{amount } \text{S}_2\text{O}_8^{2-} &= 1.0 \times 10^{-4} \text{ mol } \text{S}_2\text{O}_3^{2-} \times \frac{1 \text{ mol } \text{I}_3^-}{2 \text{ mol } \text{S}_2\text{O}_3^{2-}} \times \frac{1 \text{ mol } \text{S}_2\text{O}_8^{2-}}{1 \text{ mol } \text{I}_3^-} \\ &= 5.0 \times 10^{-5} \text{ mol } \text{S}_2\text{O}_8^{2-} \end{aligned}$$

$$\text{amount } \text{I}^- = 5.0 \times 10^{-5} \text{ mol } \text{S}_2\text{O}_8^{2-} \times \frac{2 \text{ mol } \text{I}^-}{1 \text{ mol } \text{S}_2\text{O}_8^{2-}} = 1.0 \times 10^{-4} \text{ mol } \text{I}^-$$

Note that we do not use “3 mol I<sup>-</sup>” from equation (a) since one mole has not been oxidized; it simply complexes with the product I<sub>2</sub>. The total volume of each solution is (25.0 mL + 25.0 mL + 10.0 mL + 5.0 mL =) 65.0 mL, or 0.0650 L.

The amount of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> that reacts in each case is 5.0 × 10<sup>-5</sup> mol and thus

$$\Delta[\text{S}_2\text{O}_8^{2-}] = \frac{-5.0 \times 10^{-5} \text{ mol}}{0.0650 \text{ L}} = -7.7 \times 10^{-4} \text{ M}$$

$$\text{Thus, Rate}_1 = \frac{-\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = \frac{+7.7 \times 10^{-4} \text{ M}}{21 \text{ s}} = 3.7 \times 10^{-5} \text{ M s}^{-1}$$

(c) For Experiment 2,  $\text{Rate}_2 = \frac{-\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = \frac{+7.7 \times 10^{-4} \text{ M}}{42 \text{ s}} = 1.8 \times 10^{-5} \text{ M s}^{-1}$

To determine the value of *k*, we need initial concentrations, as altered by dilution.

$$[\text{S}_2\text{O}_8^{2-}]_1 = 0.20 \text{ M} \times \frac{25.0 \text{ mL}}{65.0 \text{ mL total}} = 0.077 \text{ M} \quad [\text{I}^-]_1 = 0.20 \text{ M} \times \frac{25.0 \text{ mL}}{65.0 \text{ mL}} = 0.077 \text{ M}$$

$$\text{Rate}_1 = 3.7 \times 10^{-5} \text{ M s}^{-1} = k[\text{S}_2\text{O}_8^{2-}]^1[\text{I}^-]^1 = k(0.077 \text{ M})^1(0.077 \text{ M})^1$$

$$k = \frac{3.7 \times 10^{-5} \text{ M s}^{-1}}{0.077 \text{ M} \times 0.077 \text{ M}} = 6.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$[\text{S}_2\text{O}_8^{2-}]_2 = 0.10 \text{ M} \times \frac{25.0 \text{ mL}}{65.0 \text{ mL total}} = 0.038 \text{ M} \quad [\text{I}^-]_2 = 0.20 \text{ M} \times \frac{25.0 \text{ mL}}{65.0 \text{ mL}} = 0.077 \text{ M}$$

$$\text{Rate}_2 = 1.8 \times 10^{-5} \text{ M s}^{-1} = k[\text{S}_2\text{O}_8^{2-}]^1[\text{I}^-]^1 = k(0.038 \text{ M})^1(0.077 \text{ M})^1$$

$$k = \frac{1.8 \times 10^{-5} \text{ M s}^{-1}}{0.038 \text{ M} \times 0.077 \text{ M}} = 6.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

(d) First we determine concentrations for Experiment 4.

$$[\text{S}_2\text{O}_8^{2-}]_4 = 0.20 \text{ M} \times \frac{25.0 \text{ mL}}{65.0 \text{ mL total}} = 0.077 \text{ M} \quad [\text{I}^-]_4 = 0.10 \times \frac{25.0 \text{ mL}}{65.0 \text{ mL}} = 0.038 \text{ M}$$

We have two expressions for Rate; let us equate them and solve for the rate constant.

$$\text{Rate}_4 = \frac{-\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = \frac{+7.7 \times 10^{-4} \text{ M}}{\Delta t} = k[\text{S}_2\text{O}_8^{2-}]_4^1[\text{I}^-]_4^1 = k(0.077 \text{ M})(0.038 \text{ M})$$

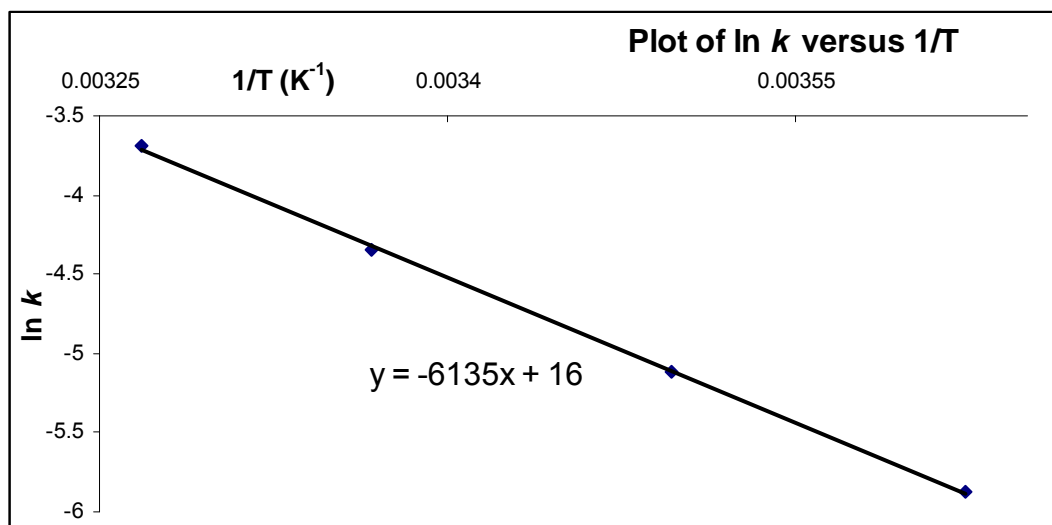
$$k = \frac{7.7 \times 10^{-4} \text{ M}}{\Delta t \times 0.077 \text{ M} \times 0.038 \text{ M}} = \frac{0.26 \text{ M}^{-1}}{\Delta t} \quad k_3 = \frac{0.26 \text{ M}^{-1}}{189 \text{ s}} = 0.0014 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{13} = \frac{0.26 \text{ M}^{-1}}{88 \text{ s}} = 0.0030 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{24} = \frac{0.26 \text{ M}^{-1}}{42 \text{ s}} = 0.0062 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{33} = \frac{0.26 \text{ M}^{-1}}{21 \text{ s}} = 0.012 \text{ M}^{-1} \text{ s}^{-1}$$

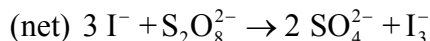
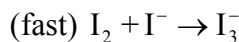
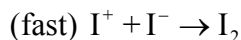
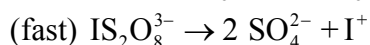
- (e) We plot  $\ln k$  vs.  $1/T$ . The slope of the line =  $-E_a / R$ .



$$E_a = +6135 \text{ K} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} = 51.0 \times 10^3 \text{ J/mol} = 51.0 \text{ kJ/mol}$$

The scatter of the data permits only a two significant figure result: 51 kJ/mol

- (f) For the mechanism to agree with the reaction stoichiometry, the steps of the mechanism must sum to the overall reaction, in the manner of Hess's law.



Each of the intermediates cancels:  $\text{IS}_2\text{O}_8^{3-}$  is produced in the first step and consumed in the second,  $\text{I}^+$  is produced in the second step and consumed in the third,  $\text{I}_2$  is produced in the third step and consumed in the fourth. The mechanism is consistent with the stoichiometry. The rate of the slow step of the mechanism is

$$\text{Rate}_1 = k_1 [\text{S}_2\text{O}_8^{2-}]^1 [\text{I}^-]^1$$

This is exactly the same as the experimental rate law. It is reasonable that the first step be slow since it involves two negatively charged species coming together. We know that like charges repel, and thus this should not be an easy or rapid process.

## SELF-ASSESSMENT EXERCISES

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- 98. (E)**
- (a)  $[A]_0$ : Initial concentration of reactant A
  - (b)  $k$ : Reaction rate constant, which is the proportionality constant between reaction rate and reactant concentration
  - (c)  $t_{1/2}$ : Half-life of the reaction, the amount of time that the concentration of a certain reactant is reduced by half
  - (d) Zero-order reaction: A reaction in which the rate is not dependent on the concentration of the reactant
  - (e) Catalyst: A substance which speeds up the reaction by lowering the activation energy, but it does not itself get consumed
- 99. (E)**
- (a) Method of initial rates: A study of the kinetics of the reaction by measuring the initial reaction rates, used to determine the reaction order
  - (b) Activated complex: Species that exist in a transitory state between the reactants and the products
  - (c) Reaction mechanism: Sequential elementary steps that show the conversion of reactant(s) to final product(s)
  - (d) Heterogeneous Catalyst: A catalyst which is in a different physical phase than the reaction medium
  - (e) Rate-determining step: A reaction which occurs more slowly than other reactions in a mechanism and therefore usually controls the overall rate of the reaction
- 100. (E)**
- (a) First-order and second-order reactions: In a first-order reaction, the rate of the reaction depends on the concentration of only one substrate and in a 1-to-1 manner (doubling the concentration of the reactant doubles the rate of the reaction). In a second-order reaction, the rate depends on two molecules reacting with each other at the elementary level.
  - (b) Rate law and integrated rate law: Rate law describes how the rate relates to the concentration of the reactants and the overall rate of a reaction, whereas the integrated rate law expresses the concentration of a reactant as a function of time
  - (c) Activation energy and enthalpy of reaction: Activation energy is the minimum energy required for a particular reaction to take place, whereas enthalpy of reaction is the amount of heat generated (or consumed) by a reaction when it happens
  - (d) Elementary process and overall reaction: Individual steps of a reaction mechanism, which describes any molecular event that significantly alters a molecule's energy or geometry or produces a new molecule
  - (e) Enzyme and substrate: An enzyme is a protein that acts as a catalyst for a biological reaction. A substrate is the reactant that is transformed in the reaction (in this context, by the enzyme).
- 101. (E)** The answer is (c). The rate constant  $k$  is only dependent on temperature, not on the concentration of the reactants

**102. (E)** The answers are (b) and (e). Because half-life is 75 seconds, the quantity of reactant left at two half-lives ( $75 + 75 = 150$ ) equals one-half of the level at 75 seconds. Also, if the initial concentration is doubled, after one half-life the remaining concentration would have to be twice as much as the original concentration.

**103. (E)** The answer is (a). Half-life  $t_{1/2} = 13.9$  min,  $k = \ln 2/t_{1/2} = 0.050 \text{ min}^{-1}$ . Rate of a first-order reaction is as follows:

$$\frac{d[A]}{dt} = k[A] = (0.050 \text{ min}^{-1})(0.40 \text{ M}) = 0.020 \text{ M min}^{-1}$$

**104. (E)** The answer is (d). A second-order reaction is expressed as follows:

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

If the rate of the reaction when  $[A] = 0.50$  is  $k(0.50)^2 = k(0.25)$ . If  $[A] = 0.25 \text{ M}$ , then the rate is  $k(0.0625)$ , which is  $1/4$  of the rate at  $[A] = 0.50$ .

**105. (M)** The answer is (b). Going to slightly higher temperatures broadens the molecular speed distribution, which in turn increases the fraction of molecules at the high kinetic energy range (which are those sufficiently energetic to make a reaction happen).

**106. (E)** The answer is (c). Since the reaction at hand is described as an elementary one, the rate of the reaction is  $k[A][B]$ .

**107. (E)** We note that from the given data, the half-life of the reaction is 100 seconds (at  $t = 0$ ,  $[A] = 0.88 \text{ M/s}$ , whereas at  $t = 100$ ,  $[A] = 0.44 \text{ M/s}$ ). Therefore, the rate constant  $k$  is:  
 $k = \ln 2/100 \text{ s} = 0.00693 \text{ s}^{-1}$ . We can now calculate instantaneous rate of the reaction:  
 $d[A]/dt = (0.00693 \text{ s}^{-1})(0.44 \text{ M}) = 3.0 \times 10^{-3} \text{ M} \cdot \text{s}^{-1}$

**108. (M)**

(a) For a first-order reaction,

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$t = \frac{\ln[A]_t - \ln[A]_0}{-k} = \frac{\ln(0.25) - 0}{-0.0231 \text{ min}^{-1}} = 60.0 \text{ min}$$

(b) For a zero-order reaction,

$$k = \frac{0.5}{t_{1/2}} = \frac{0.5}{30} = 0.0167 \text{ min}^{-1}$$

$$[A]_t - [A]_0 = -kt$$

$$t = \frac{[A]_t - [A]_0}{-k} = \frac{0.25 - 1.00}{-0.0167 \text{ min}^{-1}} = 45.0 \text{ min}$$

**109. (M)** The reaction is second-order, because the half-life doubles with each successive half-life period.

**110. (M)**

(a) The initial rate =  $\Delta M/\Delta t = (1.204 \text{ M} - 1.180 \text{ M})/(1.0 \text{ min}) = 0.024 \text{ M/min}$

(b) In experiment 2, the initial concentration is twice that of experiment A. For a second-order reaction:

$$\text{Rate} = k [A_{\text{exp } 2}]^2 = k [2 \times A_{\text{exp } 1}]^2 = 4 k [A_{\text{exp } 1}]^2$$

This means that if the reaction is second order, its initial rate of experiment 2 will be 4 times that of experiment 1 (that is, 4 times as many moles of A will be consumed in a given amount of time). The initial rate is  $4 \times 0.024 \text{ M/min} = 0.096 \text{ M/s}$ . Therefore, at 1 minute,  $[A] = 2.408 - 0.0960 = 2.312 \text{ M}$ .

(c) The half-life of the reaction, obtained from experiment 1, is 35 minutes. If the reaction is first-order, then  $k = \ln 2/35 \text{ min} = 0.0198 \text{ min}^{-1}$ .

For a first-order reaction,

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

$$[A]_{35\text{min}} = (2.408) \exp(-0.0198 \text{ min}^{-1} \cdot 30 \text{ min}) = 1.33 \text{ M}$$

**111. (D)** The overall stoichiometry of the reaction is determined by adding the two reactions with each other:  $A + 2B \rightleftharpoons C + D$

(a) Since I is made slowly but is used very quickly, its rate of formation is essentially zero. The amount of I at any given time during the reaction can be expressed as follows:

$$\frac{d[I]}{dt} = 0 = k_1 [A][B] - k_2 [B][I]$$

$$[I] = \frac{k_1}{k_2} [A]$$

Using the above expression for [I], we can now determine the overall reaction rate law:

$$\frac{d[C]}{dt} = k_2 [I][B] = k_2 \cdot \frac{k_1}{k_2} [A] \cdot [B] = k_1 [A][B]$$

(b) Adding the two reactions given, we still get the same overall stoichiometry as part (a). However, with the given proposed reaction mechanisms, the rate law for the product(s) is given as follows:

$$\frac{d[B_2]}{dt} = k_1[B]^2 - k_{-1}[B_2] - k_2[A][B] = 0$$

$$[B_2] = \frac{k_1[B]^2}{k_{-1} + k_2[A]}$$

Therefore,

$$\frac{d[C]}{dt} = k_2[A][B_2] = \frac{k_2 k_1 [A][B]^2}{k_{-1} + k_2[A]}$$

which does not agree with the observed reaction rate law.

- 112. (M)** The answer is (b), first-order, because only in a first-order reaction is the half-life independent of the concentration of the reacting species.
- 113. (E)** The answer is (a), zero-order, because in a zero-order reaction the relationship between concentration and time is:  $[A]_t = kt + [A]_0$
- 114. (M)** The answer is (d). The relationship between rate constant (and thus rate) between two reactions can be expressed as follows:

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

If  $T_2$  is twice  $T_1$ , the above expression gets modified as follows:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R} \left(\frac{1}{T_1} - \frac{1}{2T_1}\right)$$

$$\left(\frac{R}{E_a}\right) \ln\left(\frac{k_2}{k_1}\right) = \frac{T_1 - 1}{2T_1},$$

$$\ln\left(\frac{k_2}{k_1}\right)^{\frac{R}{E_a}} = \frac{T_1 - 1}{2T_1}$$

For reasonably high temperatures,

$$\ln\left(\frac{k_2}{k_1}\right)^{\frac{R}{E_a}} = \frac{T_1}{2T_1} = \frac{1}{2}$$

Therefore,

$$\left(\frac{k_2}{k_1}\right)^{\frac{R}{E_a}} = e^{1/2} = 1.64$$

- 115. (E)** The answer is (c), remain the same. This is because for a zero-order reaction,  $d[A]/dt = k[A]^0 = k$ . Therefore, the reaction rate is independent of the concentration of the reactant.
- 116. (M)** The overarching concept for this concept map is kinetics as a result of successful collision. The subtopics are collision theory, molecular transition theory. Molecular speed and orientation derive from collision theory. Transition complexes and partial bonds fall under the molecular transition theory heading. Deriving from the collision theory is another major topic, the Arrhenius relationship. The Arrhenius relationship encompasses the ideas of activation energy, Arrhenius collision factor, and exponential relationship between temperature and rate constant.