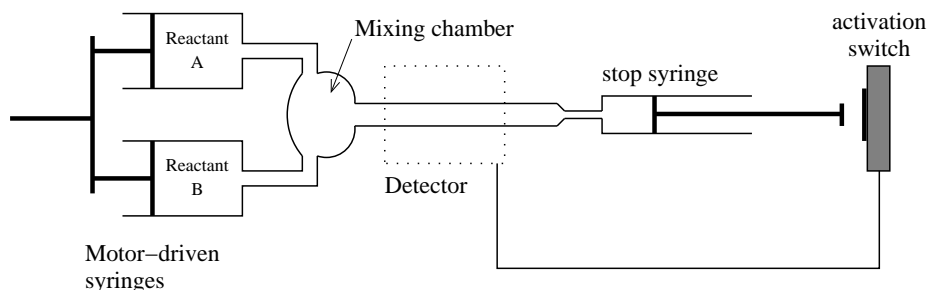


Chemistry 2740 Spring 2008 Practice Test 3 Solutions

1. (a) This is almost certainly not elementary. Three bonds have to be broken and three bonds made. That's a bit too much to happen in one step.
 - (b) This one could be elementary as it only involves the transfer of an oxygen radical anion (O^-) to NO.
- 2.



The reactants are injected into the mixing chamber by the motor-driven syringes, filling the sample cell (inside the detector) and eventually the stop syringe. Once the stop syringe makes contact with the activation switch, two things happen: (1) the syringe motor is turned off, and (2) the detector starts recording data. Because the detector is fixed, a wide variety of instruments of high sensitivity can be used so that the mixing chamber, sample cell and stop syringe can all be relatively small. A small apparatus can be filled quickly which, along with the activation of the detector by an electrical circuit, contributes to our ability to obtain data rapidly.

3. (a) If the reaction is elementary, then according to the law of mass action, it should obey second-order kinetics. The simplest way to show that it does is to draw a graph of $1/[C_2F_4]$ vs t . See figure 1. The data fit a line beautifully, confirming the second-order relationship. The rate constant is the slope of the line, which we find by linear regression:

$$k = 8.01 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}.$$

- (b) The amount of C_2F_4 used is twice the amount of dimer produced, so to make 0.1 mol of dimer we would use 0.2 mol of C_2F_4 , leaving us with 0.05 of the original 0.25 mol. The initial and final concentrations of C_2F_4 would be

$$\begin{aligned} [C_2F_4]_0 &= \frac{0.25 \text{ mol}}{0.60 \text{ L}} = 0.42 \text{ mol/L} \\ [C_2F_4] &= \frac{0.05 \text{ mol}}{0.60 \text{ L}} = 0.08 \text{ mol/L} \end{aligned}$$

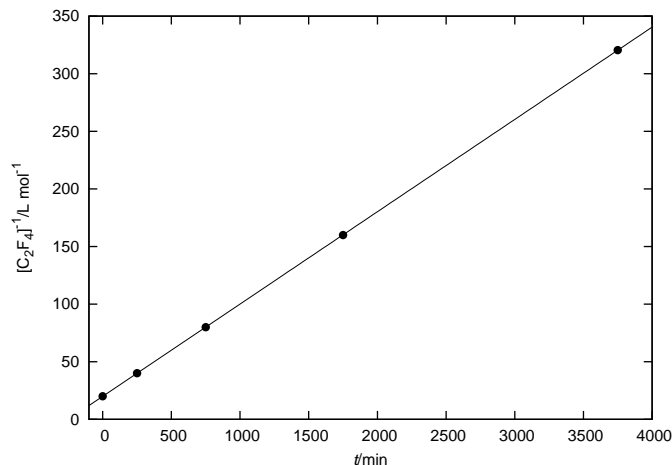


Figure 1: Second-order plot for question 3.

$$\begin{aligned}
 \frac{1}{[\text{C}_2\text{F}_4]} &= \frac{1}{[\text{C}_2\text{F}_4]_0} + kt \\
 \therefore t &= \frac{1}{k} \left(\frac{1}{[\text{C}_2\text{F}_4]} - \frac{1}{[\text{C}_2\text{F}_4]_0} \right) \\
 &= \frac{1}{8.01 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}} \left(\frac{1}{0.08 \text{ mol/L}} - \frac{1}{0.42 \text{ mol/L}} \right) \\
 &= 120 \text{ min.}
 \end{aligned}$$

(c)

$$\begin{aligned}
 k_+ &= \frac{8.01 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}}{60 \text{ s/min}} = 1.34 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}. \\
 K &= \frac{k_+}{k_-} = \frac{1.34 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}}{9.6 \times 10^{-13} \text{ s}^{-1}} = 1.4 \times 10^9 \text{ L/mol.}
 \end{aligned}$$

4. (a) The equilibrium approximation can be applied to the first step:

$$\begin{aligned}
 k_1[\text{Hg}_2^{2+}] &\approx k_{-1}[\text{Hg}^{2+}][\text{Hg}]. \\
 \therefore [\text{Hg}] &\approx \frac{k_1[\text{Hg}_2^{2+}]}{k_{-1}[\text{Hg}^{2+}]}.
 \end{aligned}$$

The rate of reaction is

$$\begin{aligned}
 v &= k_2[\text{Hg}][\text{Tl}^{3+}] \\
 &\approx \frac{k_1 k_2 [\text{Hg}_2^{2+}][\text{Tl}^{3+}]}{k_{-1}[\text{Hg}^{2+}]}.
 \end{aligned}$$

- (b) According to our rate law, doubling the mercury (II) ion concentration cuts the rate in half.