

CH #12 HOMEWORK SOLUTIONS

16/18: All of these choices ^{would affect} the rate of the reaction, but b and c affect the rate by affecting the value of rate const.

Q. 22/24 (a) Rate: $k[I^-]^x[S_2O_8^{2-}]^y$; $\frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{k(0.080)^x(0.040)^y}{k(0.040)^x(0.040)^y}$

$$\frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{k(0.080)^x(0.040)^y}{k(0.080)^x(0.020)^y} = 2.0 = 2.0^x, \boxed{x=1}$$

$$2.0 = 2.0^y = \boxed{y=2}$$

(b) For the first experiment:

$$\frac{12.5 \times 10^{-6} \text{ mol}}{\text{L s}} = k \left(\frac{0.080 \text{ mol}}{\text{L}} \right) \left(\frac{0.040 \text{ mol}}{\text{L}} \right), \boxed{k = 3.9 \times 10^{-3} \text{ L/mol.s}}$$

Q. 28/30 (a) plot $\ln[A]$ vs time \rightarrow straight line \rightarrow First order
 $\text{Rate} = k[A]$; $\ln[A] = -kt + \ln[A]_0$; $k = 2.97 \times 10^{-2} \text{ min}^{-1}$
 Slope = $-k$

(b) Half life for first-order is

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k}$$

$$t_{1/2} = \frac{0.6931}{2.97 \times 10^{-2} \text{ min}^{-1}} = \boxed{23.3 \text{ min}}$$

(c) $\ln \left[\frac{[A]}{[A]_0} \right] = -kt$; $\ln \left(\frac{2.50 \times 10^{-3} \text{ M}}{2.00 \times 10^{-2} \text{ M}} \right) = (2.97 \times 10^{-2} \text{ min}^{-1})t$

$$t = \frac{\ln(0.125)}{-2.97 \times 10^{-2} \text{ min}^{-1}} = \boxed{70.0 \text{ min}}$$

Or. How much % Complet 87.5%, How much left $\boxed{12.5\%}$

$$100 \xrightarrow{t_{1/2}} 50.0\% \xrightarrow{t_{1/2}} 25.0\% \xrightarrow{t_{1/2}} \boxed{12.5\%} \quad \left\{ \begin{array}{l} 3 \text{ half life} \\ 3 \times 23.3 \text{ min} \\ = 69.9 \text{ min} \end{array} \right.$$

Q. 48: Since rate of slowest step equal to the rate of a reaction, then: Rate = rate of step 1
 The sum of all steps in a plausible must give the overall balanced reaction:
 $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$
 $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$
 $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$

Q.56 For two conditions: $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ $\Rightarrow T \neq$ independent

$$\ln\left(\frac{8.1 \times 10^{-2} \text{ s}^{-1}}{4.6 \times 10^{-2} \text{ s}^{-1}}\right) = \frac{E_a}{8.3145 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{273 \text{ K}} - \frac{1}{293 \text{ K}}\right)$$

$$0.57 = \frac{E_a}{8.3145} (2.5 \times 10^{-4}), \quad E_a = 1.9 \times 10^4 \text{ J/mol} = 19 \text{ kJ/mol}$$