Answers to HW 9#

18.6   **a)** The rate equation is

$$\text{rate} = k[SO_2]\,[SO_3]^{-1/2} = k\,\frac{[SO_2]}{[SO_3]^{1/2}}$$

The reaction is one-half order overall so the units of k are $\text{mol}^{1/2}\ \text{L}^{-1/2}\ \text{s}^{-1}$.

b) The accelerating effect of the larger concentration of SO_2 is exactly offset by the decelerating effect of the larger concentration of SO_3. The rate does not change.

18.8   **a)** Increasing the concentration of Fe^{2+} by a factor of 1.6 between the first and second experiments (while the concentration of Ce^{4+} is constant) increases the rate by a factor of 1.6; the reaction is first-order in Fe^{2+}. Increasing the concentration of Ce^{4+} by a factor of 3.1 between the second and third experiments (while the concentration of Fe^{2+} stays constant) increases the rate by a factor of 3.1; the reaction is first-order in Ce^{4+}. The rate law is rate $= k[Fe^{2+}][Ce^{4+}]$.

b) Substitute one of the three sets of data into the rate law. The first set gives:

$$2.0 \times 10^{-7}\ \text{mol L}^{-1}\text{s}^{-1} = k\,(1.8 \times 10^{-5}\ \text{mol L}^{-1})(1.1 \times 10^{-5}\ \text{mol L}^{-1})$$

From this, $k = 1.0 \times 10^3\ \text{L mol}^{-1}\text{s}^{-1}$. The other two sets of data give the same k (to two significant figures).

c) Substitute the given concentrations and the k from part **b)** into the rate law. The initial rate should be $3.4 \times 10^{-7}\ \text{mol L}^{-1}\text{s}^{-1}$.

18.17

The reaction is the neutralization of $OH^-(aq)$ with $NH_4^+(aq)$. Aqueous acid-base reactions are generally fast. This reaction is no exception, as shown by the huge room-temperature rate constant of $k = 3.4 \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$. The answer will be a very short time. If 1.00 L of 0.0010 M NaOH and 1.00 L of 0.0010 M NH₄Cl are mixed, then *after* the mixing, but *before* the reaction can start each reactant has a concentration of 5.0×10^{-4} M. The kinetics are second-order overall

$$\text{rate} = \frac{-d[OH^-]}{dt} = k[OH^-][NH_4^+]$$

Throughout the reaction $[OH^-] = [NH_4^+]$. Let this concentration be represented by c. Then

$$\frac{-dc}{dt} = kc^2$$

Integrating this equation and inserting the initial condition gives

$$\frac{1}{c} = \frac{1}{c_0} + kt$$

This equation does not include the factor of 2 that appears in text equation 18.4 because the stoichiometry of the reaction lacks that factor. For c equal to 1.0×10^{-5} M and k equal to 3.4×10^{10} $\text{M}^{-1}\text{s}^{-1}$, the equation becomes

$$\frac{1}{1.0 \times 10^{-5} \text{ M}} = \frac{1}{5.0 \times 10^{-4} \text{ M}} + \left(3.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}\right)t$$

$$9.8 \times 10^4 \text{ M}^{-1} = \left(3.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}\right)t$$

$$t = \boxed{2.9 \times 10^{-6} \text{ s}}$$

18.25 **a)** The rate-limiting elementary step in a mechanism determines the overall reaction rate. In this case, the slow step is $C + E \longrightarrow F$. A preliminary version of the rate law is

$$\text{rate} = k_2[C][E]$$

Unfortunately, the expression involves the concentration of C, an intermediate. This is unacceptable. To eliminate [C] in the rate law, consider how C is formed. It arises in the first step of the mechanism, a fast equilibrium. For that first step

$$k_1[A][B] = k_{-1}[C][D] \quad \text{which is equivalent to} \quad \frac{k_1}{k_{-1}} = \frac{[C][D]}{[A][B]}$$

Solve either of these equations for the concentration of C and substitute into the preliminary rate law

$$\boxed{\text{rate} = \frac{k_1 k_2}{k_{-1}} \frac{[A][B][E]}{[D]}}$$

The overall reaction is the sum of the two steps $\boxed{A + B + E \longrightarrow D + F}$.

b) The overall reaction in this case is $\boxed{A + D \longrightarrow B + F}$. For the two fast equilibria these relationships hold

$$k_1[A] = k_{-1}[B][C] \qquad \text{and} \qquad k_2[C][D] = k_{-2}[E]$$

The last, slow step is the rate-determining step

$$\text{rate} = k_3[E]$$

But E is an intermediate and its concentration may not appear in the final rate expression. To eliminate [E], solve the second of the preceding pair of equations for [E] and substitute

$$\text{rate} = \frac{k_2 k_3}{k_{-2}}[C][D]$$

This expression *still* contains the concentration of an intermediate (C now). Eliminate [C] by solving the first of the pair for [C] and substituting

$$\boxed{\text{rate} = \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} \frac{[A][D]}{[B]}} = k_{\text{expt}} \frac{[A][D]}{[B]}$$

where the experimental k is the algebraic composite of the several step-wise rate constants. The reaction is first order in both A and D, is -1 order in B and first order overall.

18.33 The reaction is the decomposition of nitryl chloride $2\,\text{NO}_2\text{Cl} \longrightarrow 2\,\text{NO}_2 + \text{Cl}_2$. The mechanism involves an equilibrium breakdown of the reactant to NO_2 plus Cl followed by reaction of the

atomic chlorine with a second molecule of NO_2Cl to generate the products. The change in the concentration of Cl with time is

$$\frac{d[Cl]}{dt} = k_1[NO_2Cl] - k_{-1}[Cl][NO_2] - k_2[Cl][NO_2Cl]$$

because the rate of change of the concentration of Cl equals the rate of its production minus the rate of its consumption. The steady-state approximation is that $d[Cl]/dt = 0$. If so, then

$$k_1[NO_2Cl] - k_{-1}[Cl][NO_2] - k_2[Cl][NO_2Cl] = 0$$

and

$$[Cl] = \frac{k_1[NO_2Cl]}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$

The rate of the overall reaction equals the rate of the final elementary step, which generates the two products

$$\text{rate} = \frac{d[Cl_2]}{dt} = k_2[NO_2Cl][Cl]$$

Substitute the expression for the concentration of the Cl into this equation:

$$\boxed{\text{rate} = \frac{d[Cl_2]}{dt} = \frac{k_1 k_2[NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]}}$$

18.38   **a)** Let x represent the partial pressure of N_2O_4. The reaction is first order in x, hence

$$-\ln\frac{x}{x_0} = kt \quad \text{from which} \quad -\ln\frac{0.010 \text{ atm}}{0.10 \text{ atm}} = (5.1 \times 10^6 \text{s}^{-1})\,t \quad \text{and} \quad t = 4.5 \times 10^{-7}\text{ s}$$

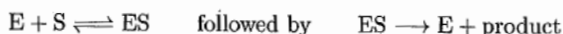**b)** Figure the rate constant k at 573.15 K using the Arrhenius equation

$$\ln\frac{k_{573}}{5.1 \times 10^6 \text{ s}^{-1}} = \frac{-54.0 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1}\text{ K}^{-1}}\left[\frac{1}{573.15 \text{ K}} - \frac{1}{303.15 \text{ K}}\right]$$

$$k_{573} = 1.2 \times 10^{11}\text{ s}^{-1}$$

Repeat the calculation of part **a)** using this bigger k

$$-\ln\frac{0.010 \text{ atm}}{0.10 \text{ atm}} = (1.2 \times 10^{11}\text{s}^{-1})\,t \quad \text{and} \quad t = 1.9 \times 10^{-11}\text{ s}$$

18.47   **a)** In the two-step reaction

$$E + S \rightleftharpoons ES \qquad \text{followed by} \qquad ES \longrightarrow E + \text{product}$$

S is penicillin, the substrate, and E is penicillinase,[3] the enzyme that accelerates its destruction. Write the Michaelis-Menten equation (text equation 18.15) and insert the constants K_m and k_2 that are given in the problem

$$\text{rate} = \frac{k_2[E]_0[S]}{[S] + K_m} = \frac{(2 \times 10^3 \text{ s}^{-1})(6 \times 10^{-7} \text{ mol L}^{-1})[S]}{[S] + 5 \times 10^{-5} \text{ mol L}^{-1}}$$

The rate of the reaction increases as $[S]$, the concentration of penicillin, increases. The maximum rate will be reached when $[S]$ is large compared to 5×10^{-5} mol L^{-1}. At this point, the denominator of the fraction essentially equals $[S]$ and cancels out the $[S]$ in the numerator

$$(\text{rate})_{max} = \frac{(2 \times 10^3 \text{ s}^{-1})(6 \times 10^{-7} \text{ mol L}^{-1})}{1} = \boxed{1 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}}$$

b) Rewrite the Michaelis-Menten equation inserting the desired rate (which equals half the maximum rate), the given concentration of enzyme, and the two constants

$$\text{rate} = \frac{(\text{rate})_{max}}{2} = \frac{1.2 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}}{2} = \frac{(2 \times 10^3 \text{ s}^{-1})(6 \times 10^{-7} \text{ mol L}^{-1})[S]}{[S] + 5 \times 10^{-5} \text{ mol L}^{-1}}$$

Solving for $[S]$ gives the concentration of penicillin required: $\boxed{5 \times 10^{-5} \text{ mol L}^{-1}}$.

18.50

This problem treats an instance of competing reactions reported in the literature (Inorg. Chem. **26** 948 (1987)).

a) The thiosulfate ion and hydrogen peroxide interact in two different ways. Let x be the initial rate of disappearance of $S_2O_3^{2-}$ by the first reaction and let $2y$ be the initial rate of disappearance of $S_2O_3^{2-}$ by the second reaction. Then $4x$ is the rate of disappearance

of H_2O_2 by the first reaction and y is the rate of disappearance of H_2O_2 by the second reaction. These relationships follow from the stoichiometry. It is now possible to write:

$$x + 2y = 7.9 \times 10^{-7} \text{ mol L}^{-1}\text{s}^{-1} \quad \text{and} \quad 4x + y = 8.8 \times 10^{-7} \text{ mol L}^{-1}\text{s}^{-1}$$

because the total rates of disappearance of the reactants are the sums of the rates via the different routes. Solving gives

$$x = 1.386 \times 10^{-7} \text{ mol L}^{-1}\text{s}^{-1} \quad \text{and} \quad y = 3.257 \times 10^{-7} \text{ mol L}^{-1}\text{s}^{-1}$$

The percentage of $S_2O_3^{2-}$ reacting at the first moment according to the first equation is the rate x divided by total rate of disappearance of $S_2O_3^{2-}$ times 100%. It is 18%.

b) The first reaction generates H_3O^+ at the initial rate $2x$, but the second reaction consumes H_3O^+ at the initial rate $2y$. The net rate of consumption of H_3O^+ is

$$2y - 2x = 3.742 \times 10^{-7} \text{ mol L}^{-1}\text{s}^{-1}$$

This rate is also the initial rate at which replacement H_3O^+ has to be added to keep the pH at 7.0. The volume of the solution to which it is added is 2.00 L, so 7.484×10^{-7} mol s^{-1} of H_3O^+ has to be added. In 60 s, this amounts to 4.49×10^{-5} mol. This much H_3O^+ is contained in 0.45 mL of 0.100 M H_3O^+.