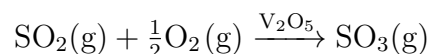


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Problem 18.6. In the presence of vanadium oxide, $\text{SO}_2(\text{g})$ reacts with an excess of oxygen to give $\text{SO}_3(\text{g})$:



This reaction is an important step in the manufacture of sulfuric acid. It is observed that tripling the SO_2 concentration increases the rate by a factor of 3, but tripling the SO_3 concentration decreases the rate by a factor of $1.7 \approx \sqrt{3}$. The rate is insensitive to the O_2 concentration as long as an excess of oxygen is present.

- (a) Write the rate expression for this reaction, and give the units of the rate constant k .
- (b) If $[\text{SO}_2]$ is multiplied by 2 and $[\text{SO}_3]$ by 4 but all other conditions are unchanged, what change in the rate will be observed?

Solution:

- (a) The rate expression for this reaction is

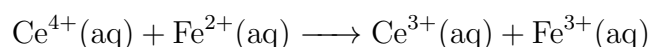
$$\text{rate} = k[\text{SO}_2][\text{SO}_3]^{-\frac{1}{2}}$$

The units of the rate constant k are $\text{mol L}^{-\frac{1}{2}} \text{s}^{-1}$.

- (b) The rate will not change.

□

Problem 18.8. The rate for the oxidation of iron(II) by cerium(IV)



is measured at several different initial concentrations of the two reactants:

$[\text{Ce}^{4+}](\text{mol L}^{-1})$	$[\text{Fe}^{2+}](\text{mol L}^{-1})$	Rate($\text{mol L}^{-1} \text{s}^{-1}$)
1.1×10^{-5}	1.8×10^{-5}	2.0×10^{-7}
1.1×10^{-5}	2.8×10^{-5}	3.1×10^{-7}
3.4×10^{-5}	2.8×10^{-5}	9.5×10^{-7}

- (a) Write the rate expression for this reaction.
- (b) Calculate the rate constant k and give its units.
- (c) Predict the initial reaction rate for a solution in which $[\text{Ce}^{4+}]$ is $2.6 \times 10^{-5} \text{ M}$ and $[\text{Fe}^{2+}]$ is $1.3 \times 10^{-5} \text{ M}$.

Solution:

- (a) Suppose the rate expression for this reaction is

$$\text{rate} = k[\text{Ce}^{4+}]^{n_1}[\text{Fe}^{2+}]^{n_2}$$

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$$\begin{aligned}\frac{\text{rate}_2}{\text{rate}_1} &= \left(\frac{[Fe^{2+}]_2}{[Fe^{2+}]_1} \right)^{n_2} \Rightarrow \frac{3.1 \times 10^{-7}}{2.0 \times 10^{-7}} = \frac{2.8 \times 10^{-5}}{1.8 \times 10^{-5}} \\ &\Rightarrow n_2 = 1 \\ \frac{\text{rate}_3}{\text{rate}_2} &= \left(\frac{[Ce^{4+}]_3}{[Ce^{4+}]_2} \right)^{n_1} \Rightarrow \frac{9.5 \times 10^{-7}}{3.1 \times 10^{-7}} = \left(\frac{3.4 \times 10^{-5}}{1.1 \times 10^{-5}} \right) \\ &\Rightarrow n_1 = 1\end{aligned}$$

Therefore, the rate expression for this reaction is

$$\text{rate} = k[Ce^{4+}][Fe^{2+}]$$

(b)

$$\begin{aligned}\text{rate}_1 &= k[Ce^{4+}]_1[Fe^{2+}]_1 \Rightarrow 2.0 \times 10^{-7} = k \times 1.1 \times 10^{-5} \text{ mol L}^{-1} \times 1.8 \times 10^{-5} \text{ mol L}^{-1} \\ &\Rightarrow k = 1.0 \times 10^3 \text{ mol}^{-1} \text{ L s}^{-1}\end{aligned}$$

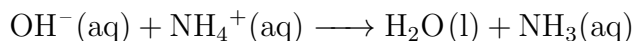
Therefore, the rate constant k is 1.0×10^3 , and its units are $\text{mol}^{-1} \text{ L s}^{-1}$.

(c) The initial rate is

$$\text{rate} = k[Ce^{4+}][Fe^{2+}] = 1.0 \times 10^3 \times 2.6 \times 10^{-5} \times 1.3 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1} = \underline{3.4 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}}$$

□

Problem 18.17. The rate for the reaction



is first order in both OH^- and NH_4^+ concentrations, and the rate constant k at 20°C is $3.4 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$. Suppose 1.00 L of a 0.0010 M NaOH solution is rapidly mixed with the same volume of 0.0010 M NH_4Cl solution. Calculate the time (in seconds) required for the OH^- concentration to decrease to a value of $1.0 \times 10^{-5} \text{ M}$.

Solution: The initial volume of OH^- and NH_4^+ is

$$[\text{OH}^-]_0 = [\text{NH}_4^+]_0 = \frac{0.0010 \text{ mol L}^{-1} \times 1.00 \text{ L}}{1.00 \text{ L} + 1.00 \text{ L}} = 0.00050 \text{ mol L}^{-1}$$

The rate for reaction can be written as

$$\begin{aligned}\text{rate} &= -\frac{d[\text{OH}^-]}{dt} = k[\text{OH}^-][\text{NH}_4^+] = k[\text{OH}^-]^2 \\ \Rightarrow \frac{1}{[\text{OH}^-]} - \frac{1}{[\text{OH}^-]_0} &= kt \Rightarrow t = \frac{\frac{1}{[\text{OH}^-]} - \frac{1}{[\text{OH}^-]_0}}{k} = \frac{\frac{1}{1.0 \times 10^{-5}} - \frac{1}{0.00050}}{3.4 \times 10^{10}} \text{ s} = \underline{2.9 \times 10^{-6} \text{ s}}\end{aligned}$$

□

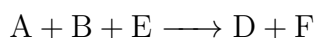
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Problem 18.25. Write the overall reaction and rate laws that correspond to the following reaction mechanisms. Be sure to eliminate intermediates from the answers.



Solution:

(a) The overall reaction is



The equilibrium constant of the first reaction is

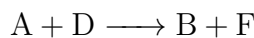
$$\frac{[C][D]}{[A][B]} = K = \frac{k_1}{k_{-1}}$$

$$\implies [C] = \frac{k_1[A][B]}{k_{-1}[D]}$$

The rate law is

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

(b) The overall reaction is



The equilibrium constant of the first and the second reaction is

$$\frac{[B][C]}{[A]} = K_1 = \frac{k_1}{k_{-1}} \implies [C] = \frac{k_1[A]}{k_{-1}[B]}$$

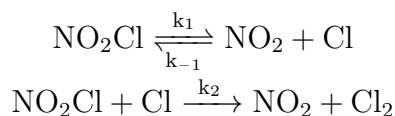
$$\frac{[E]}{[C][D]} = K_2 = \frac{k_2}{k_{-2}} \implies [E] = \frac{k_2}{k_{-2}}[C][D] = \frac{k_1 k_2 [A][D]}{k_{-1} k_{-2} [B]}$$

The rate law is

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

□

Problem 18.33. The mechanism for the decomposition of NO_2Cl is



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By making a steadystate approximation for $[Cl]$, express the rate of appearance of Cl_2 in terms of the concentrations of NO_2Cl and NO_2 .

Solution: The net rate of change of $[Cl]$ is

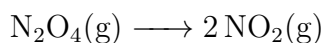
$$\begin{aligned}\frac{d[Cl]}{dt} &= k_1[NO_2Cl] - k_{-1}[NO_2][Cl] - k_3[NO_2Cl][Cl] = 0 \\ \implies [Cl] &= \frac{k_1[NO_2Cl]}{k_{-1}[NO_2] + k_2[NO_2Cl]}\end{aligned}$$

The rate of the overall reaction $2 NO_2Cl \longrightarrow 2 NO_2 + Cl_2$ is

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

□

Problem 18.38. Dinitrogen tetraoxide (N_2O_4) decomposes spontaneously at room temperature in the gas phase:



The rate law governing the disappearance of N_2O_4 with time is

$$-\frac{d[N_2O_4]}{dt} = k[N_2O_4]$$

At $30^\circ C$, $k = 5.1 \times 10^6 s^{-1}$ and the activation energy for the reaction is $54.0 kJ mol^{-1}$.

(a) Calculate the time (in seconds) required for the partial pressure of $N_2O_4(g)$ to decrease from 0.10 atm to 0.010 atm at $30^\circ C$. (b) Repeat the calculation of part (a) at $300^\circ C$.

Solution: Integrate the reaction rate equation to get

$$\begin{aligned}\ln[N_2O_4] - \ln[N_2O_4]_0 &= -kt \implies \ln 0.010 - \ln 0.10 = -5.1 \times 10^6 s^{-1} t \\ \implies t &= \underline{4.5 \times 10^7 s}\end{aligned}$$

(b) The rate constant at 300° is

$$\begin{aligned}k' &= \frac{k}{e^{-\frac{E_a}{RT}}} e^{-\frac{E_a}{RT'}} \\ &= \frac{5.1 \times 10^6 s^{-1}}{e^{-\frac{54.0 \times 10^3 J mol^{-1}}{8.31 J mol^{-1} K^{-1} \times (30+273.15) K}}} e^{-\frac{54.0 \times 10^3 J mol^{-1}}{8.31 J mol^{-1} K^{-1} \times (300+273.15) K}} \\ &= 1.2 \times 10^{11} s^{-1}\end{aligned}$$

Therefore,

$$\begin{aligned}\ln[N_2O_4] - \ln[N_2O_4]_0 &= -k't \implies \ln 0.010 - \ln 0.10 = -1.2 \times 10^{11} s^{-1} t \\ \implies t &= \underline{1.9 \times 10^{-11} s}\end{aligned}$$

□

Problem 18.47. Certain bacteria use the enzyme penicillinase to decompose penicillin and render it inactive. The Michaelis–Menten constants for this enzyme and substrate are $K_m = 5 \times 10^{-5} \text{ mol L}^{-1}$ and $k_2 = 2 \times 10^3 s^{-1}$.

(a) What is the maximum rate of decomposition of penicillin if the enzyme concentration is $6 \times 10^{-7} \text{ M}$?

(b) At what substrate concentration will the rate of decomposition be half that calculated in part (a)?

Solution:

(a) The maximum rate of decomposition of penicillin is

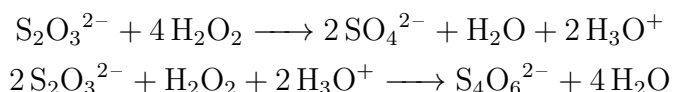
$$V_m = k_2[E_T] = 2 \times 10^3 s^{-1} \times 6 \times 10^{-7} \text{ mol L}^{-1} = \underline{1.2 \times 10^{-3} \text{ mol L}^{-1} s^{-1}}$$

(b) When the rate of decomposition is half that calculated in part (a)

$$\begin{aligned}\frac{V_{\max}[S]}{K_m + [S]} &= \frac{1}{2} V_{\max} \implies \frac{[S]}{5 \times 10^{-5} \text{ mol L}^{-1} + [S]} = \frac{1}{2} \\ \implies [S] &= \underline{5 \times 10^{-5} \text{ mol L}^{-1}}\end{aligned}$$

□

Problem 18.50. Suppose 1.00 L of $9.95 \times 10^{-3} \text{ M S}_2\text{O}_3^{2-}$ is mixed with 1.00 L of $2.52 \times 10^{-3} \text{ M H}_2\text{O}_2$ at a pH of 7.0 and a temperature of 25°C. These species react by two competing pathways, represented by the balanced equations.



At the instant of mixing, the thiosulfate ion ($\text{S}_2\text{O}_3^{2-}$) is observed to be disappearing at the rate of $7.9 \times 10^{-7} \text{ mol L}^{-1} s^{-1}$. At the same moment, the H_2O_2 is disappearing at the rate of $8.8 \times 10^{-7} \text{ mol L}^{-1} s^{-1}$.

(a) Compute the percentage of the $\text{S}_2\text{O}_3^{2-}$ that is, at that moment, reacting according to

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the first equation.

(b) It is observed that the hydronium ion concentration drops. Use the data and answer from part (a) to compute how many milliliters per minute of 0.100 M H_3O^+ must be added to keep the pH equal to 7.0.

Solution:

(a) Suppose the percentage of the $\text{S}_2\text{O}_3^{2-}$ that is reacting according to the first equation is α

$$\begin{aligned} 4 \text{ rate}_1 + \text{rate}_2 &= -\frac{d[\text{H}_2\text{O}_2]}{dt} \\ \implies 4 \times 7.9 \times 10^{-7} \text{ mol L}^{-1} \alpha + \frac{1}{2} \times 7.9 \times 10^{-7} \text{ mol L}^{-1} (1 - \alpha) &= 8.8 \times 10^{-7} \text{ mol L}^{-1} \\ \implies \alpha &= \underline{18\%} \end{aligned}$$

(b) The rate of the two reaction are

$$\begin{aligned} \text{rate}_1 &= 7.9 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} \alpha = 1.4 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} \\ \text{rate}_2 &= \frac{1}{2} 7.9 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} (1 - \alpha) = 3.2 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

The rate of hydronium ion concentration dropping is

$$\frac{d[\text{H}_3\text{O}^+]}{dt} = 2 \text{ rate}_1 - 2 \text{ rate}_2 = -3.6 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$$

The number of moles of consumed hydronium in 1 min is

$$\Delta n(\text{H}_3\text{O}^+) = -\frac{d[\text{H}_3\text{O}^+]}{dt} \times 60 \text{ s} \times (1.00 \text{ L} + 1.00 \text{ L}) = 4.32 \times 10^{-5} \text{ mol}$$

The volume needed to add in 1 min to keep the pH equal to 7.0 is

$$V = \frac{\Delta n(\text{H}_3\text{O}^+)}{c_0[\text{H}_3\text{O}^+]} = \frac{4.32 \times 10^{-5} \text{ mol}}{0.100 \text{ mol L}^{-1}} = 4.32 \times 10^{-4} \text{ L} = \underline{0.432 \text{ mL}}$$

□