1. Consider consecutive elementary reactions:

   A + B ←→ C with forward rate constand k_{+1} and reverse constant k_{-1}

   C + D ←→ P + B with forward rate constant k_{+2} and reverse constant k_{-2}

   1. Write the overall reaction.
   2. Is the net reaction elementary or complex?
   3. Are the component reactions elementary or complex?
   4. What is B called?
   5. What is C called?
   6. Write the equilibrium constant for the net rxn in terms of rate constants k_1,k_{-1}, k_2,k_{-2}; it may be helpful to first write the equilibrium constants for the component rxns.
   7. Write the rate expression (diff.eqn) for [P]
   8. What is the order of the reaction for [B]? for [C]?

SOLUTION:

1 a. Overall rxn $A + D \rightarrow P$ (1)

b. Complex

c. Don't know

d. Catalyst

e. Intermediate

f. $K_1 = k_{+1}/k_{-1}$, $K_2 = k_{+2}/k_{-2}$

$$K_{net} = K_1 K_2 = \frac{k_{+1}k_{+2}}{k_{-1}k_{-2}}$$

g. $$\frac{d[P]}{dt} = k_{+2}[C][D] - k_{-2}[P][B]$$

h. $$\frac{d[B]}{dt} = -k_{+1}[A][B] + k_{-1}[C] + k_{+2}[C][D] - k_{-2}[P][B]$$

not ndd.

h. 1rst wrt B

1rst wrt C

2. How long would it take for 90% of the benzene from a crude oil spill to be degraded, given that the initial concentration in the ground water was 10^{-4} M and the benzene is cometabolized at a rate of 0.15 µmole L^{-1} d^{-1}?

a. What is the reaction?

b. What order is the reaction?

c. What is the integrated form of the rate law?

d. What time is required?

SOLUTION:

2. $C_0 = 10^{-4}$ M (2)

$k = 0.15 \times 10^{-6} \frac{M}{L d}$

a) $B \rightarrow CO_2 + H_2O$

b) Zero

c) $C = C_0 - kt$

d) $t = \frac{C_0 - C}{k} = \frac{10^{-4} - 0.1 \cdot 10^{-4}}{0.15 \times 10^{-6}} = 600 d$

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3. The accident at the Chernobyl nuclear reactor resulted in a large release of radionuclides to the atmosphere. These radionuclides then were removed from the atmosphere by both wet and dry deposition; this scenario generally results in high concentrations near the reactor and concentrations that decrease exponentially with increasing distance away from the reactor. One of the radionuclides that was released was ^{134}Cs. Cesium is taken up rapidly by vegetation, especially by blueberries. If the halflife for this isotope is 2.06 years, and the soils in the southern Swiss Alps were contaminated to a concentration five times higher than background concentrations, how long will it be before the concentrations in the soil drop to a level of twice background (a level at which it is considered safe to pick and eat blueberries)?

a. What is the reaction?

b. What is the order of the reaction?

c. What is the integrated form of the rate law?

d. How long will be required?

SOLUTION:

3. $\tau_{\frac{1}{2}} = 2.06\,yr$

$C_0 = 5 \cdot C_b$

$C = 2C_b$

a) ${}^{134}Cs \rightarrow prod$

b) 1st

c) $C = C_0 e^{-kt}$

d) $\tau_{\frac{1}{2}} = \frac{0.69}{k} \Rightarrow k = \frac{0.69}{2.06} = 0.33\,yr^{-1}$

e) $-\frac{1}{k}\ln\left(\frac{2C_b}{5C_b}\right) = t = -\frac{1}{0.33}\ln\left(\frac{2}{5}\right) = 2.78\,yr$

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4. Acid rain continues to be a problem because we have not yet decreased the emissions of nitrogen and sulfur oxides sufficiently. Between the emission of SO_x (or NO_x) and the acidification of rain, the SO_x has to be oxidized to sulfuric acid (H_2SO_4). There are two pathways for this reaction. Some of the SO_x dissolves into cloud droplets where it is oxidized primarily by H_2O_2 (peroxide), and some of the SO_x is oxidized in the gas phase by hydroxyl radical ($OH\cdot$). The gas phase reaction is:

$SO_{2(g)} + OH\cdot_{(g)} + O_{2(g)} \Rightarrow SO_{3(g)} + HO_2\cdot_{(g)}$ (1)

The SO_3 then dissolves in cloud or rain water to yield sulfuric acid:

$SO_3 + H_2O \Leftrightarrow H_2SO_4$ (2)

The concentration of hydroxyl radical is not greatly affected by reaction #1 because OH· concentration is buffered by other concentrations. The rate law for the first reaction is:

Rate = $k[SO_2][OH\cdot]$ (3)

a. If the rate constant for reaction #1 is 5.3×10^{6} m^3 $mole^{-1}$ s^{-1} (T = 25°C, P = 1 atm) and the concentration of OH· is buffered at 8.3×10^{-12} mole m^{-3}, how long would it take for reaction #1 to reduce the $SO_{2(g)}$ concentration by 50%?
b. What is the half-life for this reaction?

SOLUTION:

4. $k = 5.3\times10^{6} \frac{m^3}{mol \cdot s}$ (3)

$[OH\cdot] = 8.3\times10^{-12} \frac{mole}{m^3}$

$\tau_{\frac{1}{2}} = ?$

$\tilde{k} = 5.3\times10^{6} \cdot 8.3\times10^{-12} = 4.4\times10^{-9}\ s^{-1}$

$\tilde{\tau}_{\frac{1}{2}} = \frac{0.69}{\tilde{k}} = 156855\ s = 261\ min = 4.36\ hr$

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5. Recall the situation in Silbersee in Nürnberg. This lake experiences extremely high concentrations of hydrogen sulfide (H_2S) because of leachate from a nearby landfill containing gypsum. The city council accepted a plan by an engineering firm to install aerators in the lake. The aerators were thought to be a good investment because they would combat the problem in three ways. First, (as discussed in class) the air bubbles would strip the H_2S from the lake into the air. Second, the air should inhibit the sulfate-reducing bacteria because they require anaerobic conditions to live. Finally, the oxygen in the air can oxidize the hydrogen sulfide to sulfate which is not toxic. Let us determine if the kinetics of this last reaction would support the engineers' claim that the aeration system should work. The chemical reaction is:

$H_2S_{(aq)} + 2O_{2(aq)} \Longrightarrow SO_4^{2-} + 2H^+$

The engineers design the system such that oxygen will be supplied as fast as it is used such that the concentration of dissolved oxygen will remain constant. The rate law for the reaction is:

$$\frac{-d[H_2S]}{dt} = k[H_2S][O_2]$$

The value of the rate constant is determined experimentally to be 10^3 L $mole^{-1}$ d^{-1}.

a. What is the overall order of the reaction?
b. If oxygen is pumped at a rate that will maintain a concentration of 2 mg/L, how long will it take to this reaction to reduce the hydrogen sulfide from 500 μM to 1 μM?
c. Could this mechanism by itself be used to purify the lake?

SOLUTION:

5. $k = 10^3 \frac{L}{mole \cdot d}$

a) 2^{nd}

b) $\frac{C}{C_0} = \frac{1}{500}$

$$k' = \left(2\frac{\cancel{mg}}{\cancel{L}}\right)\left(\frac{10^{-3}\cancel{mole}}{32\cancel{mg}}\right)\left(10^3\frac{\cancel{L}}{\cancel{mole}\cdot d}\right)$$

$$k' = 0.0625\ d^{-1}$$

$$-\frac{1}{k}\ln\frac{C}{C_0} = -\frac{1}{0.0625}\ln\frac{1}{500} = 99\ d$$

c) 3 mo, things change
