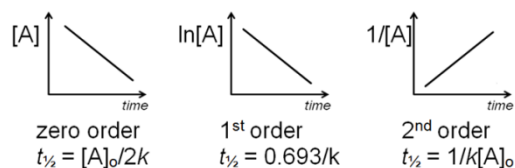


- rate laws, integrated rate laws, graphs and half-lives
- energy diagrams
- mechanisms



### PROBLEMS

- A reaction follows the rate law: rate =  $k[A]^2$ . Which of the following plots will give a straight line?
  - $1/[A]$  vs  $1/\text{time}$
  - $[A]^2$  vs time
  - $1/[A]$  vs time
  - $\ln[A]$  vs time
  - $[A]$  vs time
- For the following reaction:  $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}(\text{g})$ , the rate law is: rate =  $k[\text{NO}_2]^2$ . If a small amount of gaseous carbon monoxide (CO) is added to a reaction mixture that was 0.10 M in  $\text{NO}_2$  and 0.20 M in CO, which of the following statements is true?
  - Both k and the reaction rate remain the same
  - Both k and the reaction rate increase
  - Both k and the reaction rate decrease
  - Only k increases; the reaction rate remains the same
  - Only the reaction rate increases; k remains the same
- The specific rate constant, k, for radioactive beryllium-11 is  $0.049 \text{ s}^{-1}$ . What mass of a 0.500 mg sample of beryllium-11 remains after 28 seconds?
  - 0.250 mg
  - 0.125 mg
  - 0.0625 mg
  - 0.375 mg
  - 0.500 mg
- The slow rate of a particular chemical reaction might be attributed to which of the following?
  - a low activation energy
  - a high activation energy
  - the presence of a catalyst
  - the temperature is high
  - the concentration of the reactants are high
- The steps below represent a proposed mechanism for the catalyzed oxidation of CO by  $\text{O}_3$ .

Step 1:  $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$   
 Step 2:  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$   
 What are the overall products of the catalyzed reaction?

- $\text{CO}_2$  and  $\text{O}_2$
- $\text{NO}$  and  $\text{CO}_2$
- $\text{NO}_2$  and  $\text{O}_2$
- $\text{NO}$  and  $\text{O}_2$
- $\text{NO}_2$  and  $\text{CO}_2$

- The decomposition of ammonia to the elements is a first-order reaction with a half-life of 200 s at a certain temperature. How long will it take the partial pressure of ammonia to decrease from 0.100 atm to 0.00625 atm?
  - 200 s
  - 400 s
  - 800 s
  - 1000 s
  - 1200 s
- The energy difference between the reactants and the transition state is
  - the free energy
  - the heat of reaction
  - the activation energy
  - the kinetic energy
  - the reaction energy
- The purpose of striking a match against the side of a box to light the match is
  - to supply the free energy for the reaction
  - to supply the activation energy for the reaction
  - to supply the heat of reaction
  - to supply the kinetic energy for the reaction
  - to catalyze the reaction
- The table below gives the initial concentrations and rate for three experiments:

Exp	$[\text{CO}]_0$	$[\text{Cl}_2]$	Rate <sub>0</sub>
1	0.200	0.100	$3.9 \times 10^{-25}$
2	0.100	0.200	$3.9 \times 10^{-25}$
3	0.200	0.200	$7.8 \times 10^{-25}$

The reaction is  $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$ .  
What is the rate law?

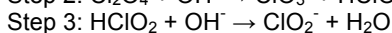
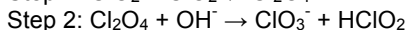
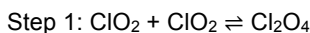
- Rate =  $k[\text{CO}]$
  - Rate =  $k[\text{CO}]^2[\text{Cl}_2]$
  - Rate =  $k[\text{Cl}_2]$
  - Rate =  $k[\text{CO}][\text{Cl}_2]^2$
  - Rate =  $k[\text{CO}][\text{Cl}_2]$
- The reaction  $(\text{CH}_3)_3\text{CBr}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow (\text{CH}_3)_3\text{COH}(\text{aq}) + \text{HBr}(\text{aq})$  follows the rate law: rate =  $k[(\text{CH}_3)_3\text{CBr}]$ . What will be the effect of decreasing the concentration of  $(\text{CH}_3)_3\text{CBr}$ ?
    - The rate of the reaction will increase.
    - More HBr will form.
    - The rate of the reaction will decrease.
    - The reaction will shift to the left.
    - The equilibrium constant will increase.
  - When the concentration of  $\text{H}^+(\text{aq})$  is doubled for the reaction  $\text{H}_2\text{O}_2(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{Fe}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{g})$ , there is no change in the reaction rate. This indicates that
    - the  $\text{H}^+$  is a spectator ion.
    - the rate-determining step does not involve  $\text{H}^+$ .
    - the reaction mechanism does not involve  $\text{H}^+$ .
    - the  $\text{H}^+$  is a catalyst.
    - the rate law is first order with respect to  $\text{H}^+$ .
  - The mechanism below has been proposed for the reaction of  $\text{CHCl}_3$  with  $\text{Cl}_2$ .
    - $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$  fast
    - $\text{Cl} + \text{CHCl}_3 \rightarrow \text{CCl}_3 + \text{HCl}$  slow
    - $\text{CCl}_3 + \text{Cl} \rightarrow \text{CCl}_4$  fast
 Which of the following rate laws is consistent with this mechanism?
    - rate =  $k[\text{Cl}_2]$
    - rate =  $k[\text{CHCl}_3][\text{Cl}_2]$
    - rate =  $k[\text{CHCl}_3]$
    - rate =  $k[\text{CHCl}_3]/[\text{Cl}_2]$
    - rate =  $k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$

**FREE-RESPONSE**

13. A set of experiments were conducted to study the reaction:  $2\text{ClO}_2(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{ClO}_3^-(\text{aq}) + \text{ClO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$ . The initial concentrations and rates are reported in the table below.

Exp	$[\text{OH}^-] \text{ (M)}$	$[\text{ClO}_2] \text{ (M)}$	Rate of formation of $\text{ClO}_3^- \text{ (M/min)}$
1	0.030	0.020	0.166
2	0.060	0.020	0.331
3	0.030	0.040	0.661

- Write the rate law of the reaction.
- Determine the value of the rate constant, including units.
- Calculate the initial rate of disappearance of  $\text{ClO}_2$  in experiment 1.
- The following mechanism has been proposed for this reaction:



Which step is the rate-determining step? Show that the mechanism is consistent with both the rate law for the reaction and with the overall stoichiometry.

- C
- A
- B
- B
- A
- C
- C
- B
- E
- C
- B
- E

13.

a.  $\text{rate} = k[\text{ClO}_2]^2[\text{OH}^-]$

b.  $1.4 \times 10^4 \text{ / M}^2\text{min}$

c.  $-0.332 \text{ mol/L} \cdot \text{min}$

d. Step 1:  $\text{rate} = k_f[\text{ClO}_2]^2 = k_r[\text{Cl}_2\text{O}_4]$

Step 2:  $\text{rate} = k[\text{Cl}_2\text{O}_4][\text{OH}^-] = k'[\text{ClO}_2]^2[\text{OH}^-]$  (by substituting  $[\text{Cl}_2\text{O}_4] \propto [\text{ClO}_2]^2$  from the fast equilibrium in step 1)

Step 3:  $\text{rate} = k''[\text{HClO}_2][\text{OH}^-]$

For Step 1, the ratio of  $[\text{Cl}_2\text{O}_4]$  to  $[\text{ClO}_2]$  is 1:2, based on the coefficients of the reaction in step 1. So the reaction in step 2 can be re-written as:  $2\text{ClO}_2 + \text{OH}^- \rightarrow \text{ClO}_3^- + \text{HClO}_2$  and the rate becomes  $\text{rate} = k[\text{ClO}_2]^2[\text{OH}^-]$ , which matches the rate law in part a. This must mean that Step 2 is the rate-determining step.