

18

REACTION RATES AND EQUILIBRIUM

Practice Problems

In your notebook, solve the following problems.

SECTION 18.1 RATES OF REACTION

- List three ways that reaction rates can generally be increased.
- Ethyl acetate ($C_4H_8O_2$) reacts with a solution of sodium hydroxide (NaOH) in water to form sodium acetate ($C_2H_3O_2Na$) and ethyl alcohol (C_2H_6O). Suppose at $25^\circ C$ two moles of ethyl acetate react completely in four hours. How would you express the rate of reaction?
- How would the following actions likely change the rate of the reaction in problem 2?
 - the temperature is lowered to $4^\circ C$.
 - the concentration of sodium hydroxide in water is increased.
- Ethyl acetate and water are not miscible; thus, the reaction in problem 2 only occurs at the interface of the two liquids. What would be the effect on the reaction rate of adding a solvent to make the reaction homogeneous?

SECTION 18.2 REVERSIBLE REACTIONS AND EQUILIBRIUM

- Write the expression for the equilibrium constant for this reaction:

$$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$$
- Calculate the equilibrium constant for the reaction in problem 1 if the equilibrium concentrations are $[N_2O_5] = 0.50 \text{ mol/L}$, $[NO_2] = 0.80 \text{ mol/L}$, $[O_2] = 0.20 \text{ mol/L}$.
- How would the equilibrium position for the equation in problem 1 be affected by
 - an addition of O_2 to the reaction vessel?
 - a decrease in the pressure?

- The equilibrium constant for the reaction of nitrogen dioxide to form dinitrogen tetroxide is 5.6.

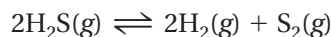
$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

In a one-liter container, the amount of N_2O_4 , at equilibrium, is 0.66 mol. What is the equilibrium concentration of NO_2 ?

- Write the equilibrium constant expression for each of the following reactions.

<ol style="list-style-type: none"> $4NO(g) + 2O_2(g) \rightleftharpoons 2N_2O_4(g)$ $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$ 	<ol style="list-style-type: none"> $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
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- What effect would an increase in pressure have on the equilibrium position of each reaction in problem 5?

7. Which value of K_{eq} indicates most favorably for product formation, $K_{\text{eq}} = 1 \times 10^{12}$, $K_{\text{eq}} = 1.5$, or $K_{\text{eq}} = 5.6 \times 10^{-4}$?
8. Hydrogen sulfide gas decomposes into its elements and establishes an equilibrium at 1400 °C.



A liter of this gas mixture at equilibrium contains 0.18 mol H_2S , 0.014 mol H_2 , and 0.035 mol S_2 . Calculate the equilibrium constant, K_{eq} , for this reaction.

SECTION 18.3 SOLUBILITY EQUILIBRIUM

- Write the solubility product expression for **a.** $\text{Ca}(\text{OH})_2$ and **b.** Ag_2CO_3 .
- What is the concentration of silver ions in a saturated solution of silver carbonate? The K_{sp} of Ag_2CO_3 is 8.1×10^{-12} .
- The equilibrium concentration of hydroxide ions in a saturated solution of iron(II) hydroxide is $1.2 \times 10^{-5} \text{M}$ at a certain temperature. Calculate the K_{sp} of $\text{Fe}(\text{OH})_2$ at this temperature.
- Strontium carbonate has a $K_{\text{sp}} = 9.3 \times 10^{-10}$ at 25°C. What is the concentration of strontium ions in a saturated solution of SrCO_3 ?
- What is the equilibrium concentration of silver ions at 25°C in a 1.0-L saturated solution of silver carbonate to which 0.20 mol of Na_2CO_3 has been added? The K_{sp} of Ag_2CO_3 is 8.1×10^{-12} at 25°C.
- Will a precipitate of PbSO_4 form when 400.0 mL of 0.0050M MgSO_4 is mixed with 600.0 mL of 0.0020M $\text{Pb}(\text{NO}_3)_2$? The K_{sp} of $\text{PbSO}_4 = 6.3 \times 10^{-7}$.
- Will precipitation of CaCO_3 occur when 500.0 mL of $4.2 \times 10^{-3} \text{M}$ CaCl_2 is mixed with 500.0 mL of $2.6 \times 10^{-3} \text{M}$ Na_2CO_3 ? The K_{sp} of CaCO_3 is 4.5×10^{-9} .
- Which of these compounds would not decrease the solubility of $\text{Mg}(\text{OH})_2$ when added to a saturated solution of the compound?

NaOH , MgCl_2 , NaCl , KOH

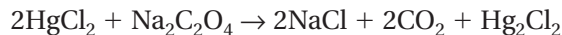
SECTION 18.4 ENTROPY AND FREE ENERGY

- When gently warmed, the element iodine will sublime:

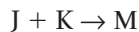
$$\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$$
 Is this process accompanied by an increase or decrease in entropy?
- Does entropy increase or decrease when air is cooled and liquefied (changed from a gas to a liquid)?
- Is the degree of disorder increasing or decreasing in these reactions?
 - $\text{H}_2(\text{g}) + \text{Br}_2(\text{l}) \rightarrow 2\text{HBr}(\text{g})$
 - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightarrow \text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{g})$
 - $2\text{XeO}_3(\text{s}) \rightarrow 2\text{Xe}(\text{g}) + 3\text{O}_2(\text{g})$
- Classify each of these systems as always spontaneous (A), never spontaneous (N), or depends on the relative magnitude of the heat and entropy changes (D).
 - entropy decreases, heat is released
 - entropy decreases, heat is absorbed
 - entropy increases, heat is absorbed
 - entropy increases, heat is released

SECTION 18.5 THE PROGRESS OF CHEMICAL REACTIONS

1. A first-order reaction has an initial reaction rate of $2.4 \text{ mol}/(\text{L}\cdot\text{s})$. What is the rate when one eighth the starting materials remain?
2. It has been experimentally determined that the rate law for the reaction between mercury(II) chloride and sodium oxalate is third-order overall and first-order with respect to HgCl_2 . Write the rate law for this reaction.



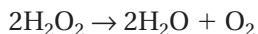
3. A combination reaction gave the following data. What is the rate law for this reaction?



Initial Concentration (mol/L)		Initial Rate (mol/L·s)
[J]	[K]	
0.30	0.50	0.080
0.60	0.50	0.160
0.60	0.25	0.080

4. Iodide ion catalyzes the decomposition of hydrogen peroxide. The reaction is first-order in H_2O_2 . What is the value of the rate constant, k , if the initial rate is $0.00842 \text{ mol}/(\text{L}\cdot\text{s})$?

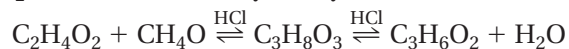
The initial concentration of H_2O_2 is 0.500 mol/L .



5. A proposed reaction mechanism has two intermediates. How many elementary reactions are in this mechanism?
6. The reaction $\text{A} + \text{B} \rightarrow \text{C}$ is first-order in A and B, second-order overall. Complete the following table:

Initial Concentration (mol/L)		Initial Rate (mol/L·s)
[A]	[B]	
0.50	0.50	0.020
0.50		0.040
0.25	1.0	

7. The condensation of acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) with methanol (CH_4O) to form methyl acetate ($\text{C}_3\text{H}_6\text{O}_2$) and water is catalyzed by HCl.



- a. How many elementary reactions are there in this condensation?
- b. Write the formula for the reaction intermediate(s).
- c. Write the rate law for this condensation.