

CHEM 116 - Dr. Babb's Sections
Lecture Problem Sheets

Acids, Bases, Electrolytes, Net Ionic Equations, Solubility, and Molarity of Ions in Soln.

1. Define the following terms: strong acid, strong base, weak acid, weak base, strong electrolyte, weak electrolyte, non-electrolyte, soluble, insoluble, and solubility. List the seven strong acids. Define the following types of solutions: saturated, unsaturated and supersaturated.
2. What types of substances can be classified as strong electrolytes? weak electrolytes? non-electrolytes?
3. List the solubility rules and use them to determine whether the substances listed below are soluble or insoluble in water.

AgNO ₃	BaI ₂	PbSO ₄	Na ₂ CO ₃	Sr(NO ₃) ₂	Fe(OH) ₃
CaCl ₂	AgOH	Pb(C ₂ H ₃ O ₂) ₂	(NH ₄) ₃ PO ₄	FeBr ₃	
Pb(ClO ₄) ₂	Hg ₂ Br ₂	K ₃ PO ₄	CaSO ₄	MgCO ₃	
AgCl	BaSO ₄	CuCl	CaS	Fe ₂ S ₃	

4. What are the three types of equations that can be written for any chemical reaction? Predict products and write Net Ionic Equations for the following aqueous reactions:
 - A. FeBr₃ + AgC₂H₃O₂
 - B. (NH₄)₂SO₄ + BaCl₂
 - C. HNO₃ + CsC₂H₃O₂
 - D. HNO₂ + CsC₂H₃O₂
 - E. HClO₄ + Ba(OH)₂
 - F. HClO + Ba(OH)₂
 - G. Na₂CO₃ + H₂SO₄
 - H. (NH₄)₂CO₃ + NaOH
 - I. Fe(NO₃)₃ + NH₃ + H₂O
5. What is the concentration of each ion in a 0.25 M CaCl₂ solution?
6. How many moles of acetate ion are present in 300.mL of 0.100 M Pb(C₂H₃O₂)₂?
7. How many grams of AlCl₃ are needed to prepare 500.mL of a solution that is 0.75M in the chloride ion?
8. What volume (in mL) of 0.15 M Na₃PO₄ will provide 0.025 mol Na⁺?
9. If 10.0g NaCl is added to 30.0 mL of 0.26 M Na₃PO₄, what is the molarity of Na⁺ in the resulting solution?
10. When 250.mL of 0.20 M BaCl₂ is mixed with 350. mL of 0.20 M NaCl, what is the molarity of chloride ion in the final solution?

Properties of Solutions and Concentration Units

11. Define the following terms: homogeneous mixture, heterogeneous mixture, solution, colloid, and suspension.
12. Are the following mixtures solutions? Identify the solute and solvent and the physical state of each.
 - A. Seawater
 - B. Coca-Cola (soda water)
 - C. Air
 - D. 14 karat gold (mixture of Au and Ag)
 - E. Brass (mixture of Zn and Cu)
 - F. Milk
 - G. Paint
 - H. Italian dressing
13. What types of substances dissolve in water more readily, nonpolar or polar substances? Why?
14. Which of the following would be more soluble in hexane (C₆H₁₄) than in water?

C ₈ H ₁₈	CH ₃ OH	CaBr ₂	Wax (C ₂₀ H ₄₂)
NH ₃	HCl	C ₆ H ₆	HC ₂ H ₃ O ₂
15. Write the equations used to calculate the following concentration units for solutions:
 - A. Molarity (M)
 - C. Mole Fraction (X_i)

- B. Weight Percent (Wt %)
 1. Part per billion (ppb)
 2. Part per million (ppm)
- D. Molality (m)
 E. Normality
16. The values of which of the concentration units depend on temperature?
 17. A solution is made by dissolving 20.0 g of CaCl_2 in 500. g of water. Calculate the weight percent, mole fraction, molality and molarity of the solution. (Assume that the density of the solution is the same as the density of pure water.)
 18. A. A glycerol-water solution is 40.0% (w/w) glycerol ($\text{C}_3\text{H}_8\text{O}_3$) and has a density of 1.101 g/mL. Calculate the molality, molarity and mole fraction of glycerol in this solution.
 B. A solution is 5.0 m NaCl. What is the mole fraction of NaCl in the solution?
 19. A sample of hard water has 1.5 g Ca^{+2} in every 500. ml of water. Calculate the molarity, molality and ppm of Ca^{+2} in the hard water.
 20. What effect does temperature have on the solubility of a solid in liquid?
 21. The dissolution of CuSO_4 in water is endothermic. Will the solubility of CuSO_4 increase or decrease as temperature is increased?
 22. The dissolution of SrSO_4 in water is exothermic. Will the solubility of SrSO_4 increase or decrease as temperature is decreased?
 23. What effect does pressure have on the solubility of a solid in a liquid? Why?
 24. What effect does temperature have on the solubility of a gas in a liquid?
 25. What effect does pressure have on the solubility of a gas in a liquid?
 State Henry's Law. What is the value of the Henry's law constant if 54 g of gaseous acetylene will dissolve in 1.0 L of liquid acetone at a pressure of 2.0 atm? What is the solubility of acetylene in acetone at 12 atm?

Colligative Properties

26. List the four colligative properties. Does the value of a colligative property depend on the identity of the solute? What does the value of the colligative property depend on?
27. Which has a higher vapor pressure, pure water or a sugar solution?
 State the form of Raoult's Law used to calculate the vapor pressure of a solution.
 State the form of Raoult's Law used to calculate the vapor pressure lowering of a solution.
28. A. Calculate the vapor pressure and the vapor pressure lowering of a solution made by dissolving 20.0g of solid glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in 500.0 g of water. The vapor pressure of pure water at 37 C is 47.1 torr.
 B. Calculate the vapor pressure of a solution made by dissolving 5.0 g CaCl_2 in 50.0 g water at 37 C.
29. If both the solute and solvent are volatile then both will contribute to the vapor pressure of the solution. What form of Raoult's law must be used to calculate the vapor pressure of the solution?
30. In a solution of ethanol and water, the mole fraction of water is 0.25. If the vapor pressure of water and ethanol at 25 C are 23.8 mm Hg and 61.2 mm Hg respectively, what is the vapor pressure of the solution? Would you expect this ethanol/water solution to display negative or positive deviations from Raoult's law?
31. Which has the higher boiling point, pure water or salt water?
 State the equation used to calculate the change in the boiling point of a solution.
32. Which has the higher freezing point, pure water or salt water?
 State the equation used to calculate the change in the freezing point of a solution.
33. The molal boiling point elevation constant and the molal freezing point depression constant are properties of which substance, solution, solute or solvent? What are the units of K_b and

- K_f ?
34. A. What is the boiling point of a 0.575 m sugar solution? ($K_b(\text{water})=0.52 \text{ kg} \cdot \text{C}/\text{mol}$)
 B. What is the boiling point of a 0.575 m hydrochloric acid solution?
 C. A solution is made by dissolving 6.72 g sodium chloride in 200. g water. Calculate both the freezing points and boiling points of this solution. How does the liquid range of this solution compare to that of pure water?
 35. Antifreeze (primarily ethylene glycol, $\text{C}_2\text{H}_6\text{O}_2$) is added to car radiators to prevent freezing. In 1994, the lowest winter temperature in Morgantown, WV was -20. F. What molality of ethylene glycol should have been present in car radiators to prevent freezing? (It is interesting to note that use of pure ethylene glycol would not have been sufficient since the freezing point of pure ethylene glycol is -17.4 C)
 36. A 0.100 g sample of PCB (polychlorinated biphenyl-a known carcinogen) was dissolved in 10.0 g camphor. The freezing point of the resulting solution was 178.28 C. Calculate the molecular weight of the PCB. ($\text{FP}(\text{pure camphor})=179.50 \text{ C}$; $K_f(\text{camphor})=40.0 \text{ kg} \cdot \text{C}/\text{mol}$)
 37. A. Will the freezing points of the following aqueous solutions be equivalent? If not, which will have the highest and which the lowest freezing point? Calculate the freezing point of each solution. ($K_f(\text{water})=1.86 \text{ kg} \cdot \text{C}/\text{mol}$)

i. 0.50 m sugar	iii. 0.50 m AlCl_3	v. 0.50 m HF
ii. 0.50 m NaCl	iv. 0.50 m CaCl_2	
 - B. Which of the following aqueous solutions will have the highest boiling point? Which will have the lowest boiling point?

i. 0.40 m Na_2SO_4	iv. 0.35 m $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$
ii. 0.50 m KNO_3	v. 0.60 m $\text{HC}_2\text{H}_3\text{O}_2$
iii. 0.60 m $\text{C}_6\text{H}_{12}\text{O}_6$ (sugar)	
 38. When 0.750 mol of sugar and 0.700 mol of NaCl are dissolved in $5.0 \times 10^3 \text{ g}$ of a solvent, the boiling point is elevated by 0.22 C. Calculate the molal boiling point elevation constant, K_b , of the solvent.
 39. A 4.94 g sample of $\text{K}_3\text{Fe}(\text{CN})_6$ was dissolved in 100. g of water and the freezing point of the resulting solution was -1.1 C. How many ions result from the dissolution of $\text{K}_3\text{Fe}(\text{CN})_6$ in water? Write the dissolution equation.
 40. What is the freezing point of a 0.500 m HF solution? HF is a weak electrolyte and the percent dissociation of HF is 2.65%.
 41. Calculate the percent dissociation of formic acid HCO_2H if a 0.60 m solution of HCO_2H freezes at -1.13 C. (This is problem 14-20 in the Problem Book.)
 42. A solution of salt water is separated from pure water by a semipermeable membrane (permeable to the solvent but not the solute). In which direction will the solvent flow? What causes solvent to stop flowing from the pure solvent side to the solution side?
 43. Write the equation that relates the solution molarity to the osmotic pressure.
 44. The formula for a low molecular weight starch is $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ where n is 200 on average. If 0.798 g of this starch is dissolved in 100.0 mL of water, what is the osmotic pressure of the solution at 25 C?
 45. A 2.00 g sample of a protein is dissolved in 0.100 L of water. The osmotic pressure of the resulting solution is 16 mm Hg at 25 C. Calculate the molar mass of the protein.
 46. A 0.0500 M FeCl_3 solution exerts an osmotic pressure of 4.16 atm at 25 C. Calculate the expected and observed van't Hoff Factors for this solution.
 47. A quantity of seawater is separated from a quantity of pure water by a semipermeable membrane. A piston applies pressure to the seawater side such that the applied pressure is greater than the osmotic pressure. What happens? (Note: This process is called Reverse

Osmosis)

48. If marooned at sea you should not drink seawater as this causes dehydration to occur more rapidly. From your knowledge of osmosis, explain.

Kinetics: Rate Law, Reaction Order and Determination of Rate Law

49. Define the following terms: chemical kinetics and reaction rate.
50. Do all reactions proceed at the same rate? Can the reaction rate be predicted from the chemical equation?
51. What are the units of the reaction rate? How would you measure the reaction rate?
52. Consider the following equation: $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$. From the following experimental data calculate the rate of disappearance of N_2O_5 , and the rates of appearances of NO_2 and O_2 , over the time intervals: 0-500 sec, 500-1000 sec, and 1000-1500 sec.

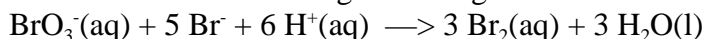
<u>time(sec)</u>	<u>[N₂O₅]</u>
0	5.00
500	3.52
1000	2.48
1500	1.75

Is the reaction rate constant? If not, what does it depend on?

What is the difference between $-\Delta[\text{N}_2\text{O}_5]/\Delta t$ and $-d[\text{N}_2\text{O}_5]/dt$?

53. Consider the following reaction: $4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 4 \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$
If the rate of disappearance of NH_3 is 0.24 M/sec, what is the rate of disappearance of O_2 and rate of appearance of H_2O and NO ?
54. What is the rate law for the general reaction: $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$? What does the specific rate constant, k , depend on? What is the order of a reaction? Can the order of the reaction with respect to each reactant be obtained from the net reaction?
55. The rate law for the reaction below is $\text{Rate} = k[\text{NO}_2]^2[\text{CO}]^0$. What is the order of the reaction with respect to each substance and what is the overall reaction order? What will happen to the reaction rate if $[\text{NO}_2]$ is doubled? if $[\text{CO}]$ is halved? What are the units on k ?
- $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{NO}(\text{g})$ at 200 C
56. The rate law for the reaction below is $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$. What is the order of the reaction with respect to each substance and what is the overall reaction order? What will happen to the reaction rate if $[\text{NO}]$ is tripled? if $[\text{O}_2]$ is halved? What are the units on k ?
- $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$
57. The rate law for the reaction below is $\text{Rate} = k[\text{SO}_2]/[\text{SO}_3]^{1/2}$. What is the order of the reaction with respect to each substance and what is the overall reaction order? What will happen to the reaction rate if $[\text{SO}_2]$ is doubled? if $[\text{SO}_3]$ is doubled? What are the units on k ?
- $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$ (using a Pt catalyst)
58. What four factors affect the rate of a reaction? How does the temperature affect the reaction rate? What is a catalyst and does it undergo any net change?
59. A. Use the method of initial rates to find the rate law for the following reaction:
- $2 \text{NOCl}(\text{g}) \rightarrow 2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g})$ at 27 C.
- | <u>[NOCl]</u> | <u>Initial Rate of Formation of NO</u> |
|---------------|--|
| 0.30M | 3.60×10^{-9} M/s |
| 0.60M | 1.44×10^{-8} M/s |
| 0.90M | 3.24×10^{-8} M/s |
- B. Calculate the value for the specific rate constant.
- C. How much will the reaction rate increase if the initial concentration of NOCl is increased from 0.30M to 1.2M?

60. A. Find the rate law for the following reaction given the initial rate data below.



Exp #	$[\text{BrO}_3^-]$	$[\text{Br}^-]$	$[\text{H}^+]$	$-\text{d}[\text{BrO}_3^-]/\text{dt}$
1	0.10 M	0.10 M	0.10 M	0.0012 M/s
2	0.20 M	0.10 M	0.10 M	0.0024 M/s
3	0.10 M	0.30 M	0.10 M	0.0035 M/s
4	0.20 M	0.10 M	0.15 M	0.0054 M/s
5	0.30 M	0.30 M	0.30 M	?

- B. What is the numerical value of the specific rate constant? What are the units of k?
 C. Calculate the initial rate of disappearance of BrO_3^- for Exp #5.

Kinetics: Integrated Form of Rate Law

61. Give the integrated form of a zeroth order reaction. Define the half-life and find the half-life for a general zeroth order reaction. Is the half life constant? For a zeroth order reaction, what type of plot will yield a straight line?
62. Give the integrated form of a first order reaction. Find the half-life for a general first order reaction. Is the half-life constant? For a first order reaction, what type of plot will yield a straight line?
- A. A certain first order reaction has the rate law $\text{Rate} = k[\text{A}]$ with $k = 0.0068 \text{ sec}^{-1}$. If the initial concentration of A is 0.75 M, what will be the concentration of A after 1 minute? What is the half-life for this reaction? How much time will it take for 75% of A to react? How much A will be left after the passage of three half-lives? What is the initial rate of the reaction?
63. Give the integrated form of a second order reaction. Find the half-life for a general second order reaction. Is the half-life constant? For a second order reaction, what type of plot will yield a straight line?
64. The following data were collected for the reaction: $2 \text{HI}(\text{g}) \longrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ at 580K.

Time (min)	$[\text{HI}]$
0	3.00M
16.7	0.120M
33.3	0.061M
50.0	0.041M
66.7	0.031M

Determine the reaction order and form of the rate law. (HINT: Plot $[\text{HI}]$ vs. t , $\ln[\text{HI}]$ vs. t and $1/[\text{HI}]$ vs. t .) Calculate the numerical values of the specific rate constant and the half-life of the reaction. After how much time will only 20% of the original amount of HI remain?

Kinetics: Elementary Reactions, Mechanisms, Catalysis and Arrhenius Equation

65. Define the terms: elementary step and reaction mechanism. Can the rate law be written directly for an elementary reaction?
66. A reaction mechanism that occurs in polluted air is the following:
- $$\text{NO}_2 + \text{O}_3 \longrightarrow \text{NO}_3 + \text{O}_2 \quad \text{SLOW}$$
- $$\text{NO}_3 + \text{NO}_2 \longrightarrow \text{N}_2\text{O}_5 \quad \text{FAST}$$
- Write the net reaction for this process, define the molecularity of each elementary step and write the rate law for this process. What is happening to the NO_3 ?
67. A reaction mechanism for the destruction of ozone, O_3 , in the stratosphere is:
- $$\text{O}_3 \longrightarrow \text{O}_2 + \text{O} \quad \text{FAST}$$
- $$\text{O}_3 + \text{O} \longrightarrow 2 \text{O}_2 \quad \text{SLOW}$$

Write the net reaction, define the molecularity of each elementary step and write the rate law for this process. Identify the intermediate.

68. A reaction mechanism for the destruction of ozone by high flying aircraft is the following:
- $$\text{O}_3 \longrightarrow \text{O}_2 + \text{O}$$
- $$\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$$
- $$\text{NO}_2 + \text{O} \longrightarrow \text{NO} + \text{O}_2$$

Write the net reaction and define the molecularity of each elementary step. Identify any reaction intermediates and catalysts.

69. Define the following terms: transition state and activation energy. On a molecular level, how does an increase in temperature lead to an increase in reaction rate? Give the Arrhenius equation. Show how the Arrhenius equation can be used to calculate the activation energy and pre-exponential factor.
70. The specific rate constant for the formation of HI was measured at two different temperatures. Calculate the numerical values of the activation energy and pre-exponential factor. Calculate the value of the specific rate constant at 427 C.

$\text{H}_2 + \text{I}_2 \longrightarrow 2 \text{HI}$	
<u>k (1/M-s)</u>	<u>Temp (K)</u>
2.7×10^{-4}	600
3.5×10^{-3}	650

71. The following rate constants were found for the decomposition of N_2O_5 at four different temperatures.

<u>k (1/s)</u>	<u>Temp (C)</u>
4.8×10^{-4}	45.0
8.8×10^{-4}	50.0
1.6×10^{-3}	55.0
2.8×10^{-3}	60.0

Make a plot of $\ln(k)$ vs. $1/T$. Calculate the activation energy and pre-exponential factor from the plot.

What is the value of the specific rate constant at 100.0 C?

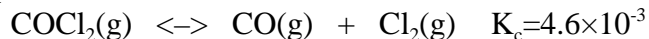
72. How does a catalyst increase the rate of a reaction? Is the reaction mechanism the same in the presence of a catalyst?

Chemical Equilibrium: Introduction to K_p and K_c

73. Define the following terms: equilibrium, equilibrium constant expression, and equilibrium constant.
74. Do all reactions go 100 % to completion (such that all reactants react to form products)? Are the concentrations of reactants and products changing at equilibrium? In a chemical reaction, once equilibrium is established it is referred to as a dynamic equilibrium. What does this mean?
75. At equilibrium, how are the rates of the forward and reverse reactions related?
76. For the general elementary reaction below, write the rate law for the forward reaction (Forward Rate=?) and the rate law for the reverse reaction (Reverse Rate=?). Derive the equilibrium constant (K) and equilibrium constant expression (K=?) by setting the Forward Rate = Reverse Rate.

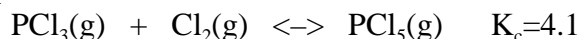


77. Does the numerical value of the equilibrium constant K depend on temperature?
78. Consider the equation below. What does the value of K_c tell you about the relative values of k_f and k_r ? What does the value of K_c tell you about the concentrations of products and reactants at equilibrium?



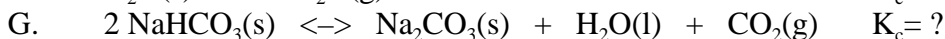
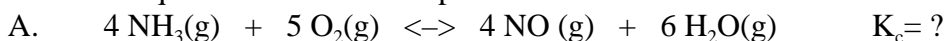
79. Consider the equation below. What does the value of K_c tell you about the relative values

of k_f and k_r ? What does the value of K_c tell you about the concentrations of products and reactants at equilibrium?



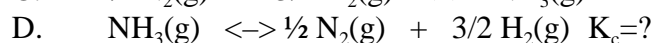
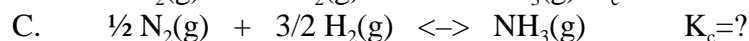
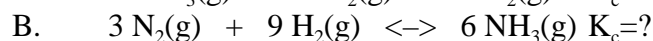
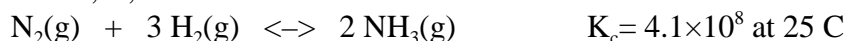
80. When K_c is large ($K > 10^{+3}$), how do the concentrations of reactants and products compare? When K_c is small ($K < 10^{-3}$), how do the concentrations of reactants and products compare? When K_c is intermediate ($10^{-3} < K < 10^{+3}$), how do the concentrations of reactants and products compare?

81. Write the equilibrium constant expressions for the chemical reactions below.

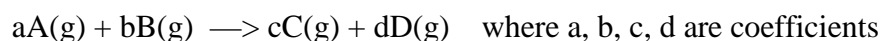


82. Are pure solids, pure liquids and solvents included in the equilibrium constant expression? Why not?

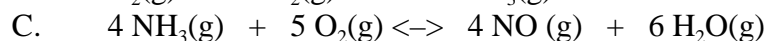
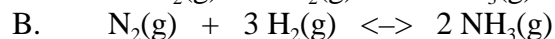
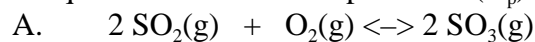
83. Given the chemical reaction below, calculate the numerical value of the equilibrium constant for the reactions in A, B, C and D.



84. Write the equilibrium constant expression (K_p) in terms of partial pressures for the general reaction:



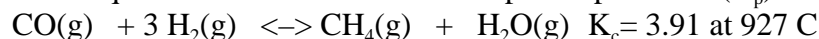
85. Write the equilibrium constant expressions (K_p) for the reactions below:



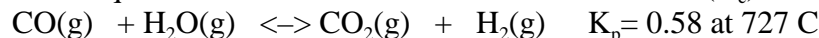
86. For the reaction in 85A, $K_c = 2.8 \times 10^2$ at a temperature of 727 C. What is the numerical value of K_p ?

87. What is the general mathematical equation that can be used to calculate K_c from K_p ? K_c from K_p ?

88. Calculate the equilibrium constant in terms of partial pressures (K_p) for the reaction below:



89. Calculate the equilibrium constant in terms of concentrations (K_c) for the reaction below:

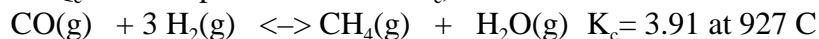


Under what conditions will K_c and K_p be equal (have the same value)?

Chemical Equilibrium: Reaction Quotient and Concentration Problems

90. What is the form of the reaction quotient Q_c ? What concentrations are used to calculate the numerical value of the reaction quotient?

91. Consider the reaction below with the given initial concentrations of products and reactants. Is the reaction already at equilibrium? If not, which way will it proceed to attain equilibrium? (HINT: Calculate Q_c and compare its value to K_c)



100. Why does the addition of a catalyst to an equilibrium mixture not change the equilibrium? Why does an increase of pressure due to addition of an inert gas not change the equilibrium concentrations of reactants and products?

101. If the temperature is changed, does the value of K_c change? Why?

102. Consider the reaction below



At Eq: 0.26M 0.09M 0.09M

What will happen (in which direction will the reaction proceed) if the following changes occur?

- A. 0.74 M ICl is added
- B. 0.74 M I_2 is added
- C. All of the Cl_2 is removed

103. Consider the reaction below which is at equilibrium



What will happen if more solid BaSO_4 is added? more solid BaO is added?

104. For a reaction at equilibrium, the pressure is increased by decreasing the volume. Will the equilibrium concentrations of species be altered? Is the numerical value of K_c or K_p changed?

105. Consider the reaction below which has already attained equilibrium



Which way will the reaction proceed to reach equilibrium if the pressure is increased by decreasing the volume?

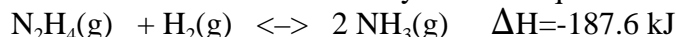
106. For the reaction $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$

Will a decrease in pressure by increasing volume alter the equilibrium concentrations of all species?

107. A certain reaction is exothermic ($\Delta H =$ negative). What happens to the numerical value of K_c if the temperature is increased? if the temperature is decreased?

108. A certain reaction is endothermic ($\Delta H =$ positive). What happens to the numerical value of K_c if the temperature is increased? if the temperature is decreased?

109. Consider the reaction below which has already attained equilibrium



In which direction will the reaction proceed if the temperature is increased?

110. Consider the reaction below which has already attained equilibrium



In which direction will the reaction proceed if the temperature is increased?

Acid/Base Theories and Conjugate Acid-Base Pairs

111. Define the following terms: Arrhenius acid, Arrhenius base, Lewis acid, Lewis base, Bronsted-Lowry acid and Bronsted-Lowry base.

112. Identify the Lewis acids and bases in the following reactions.

- A. $\text{BCl}_3 + \text{NH}_3 \rightleftharpoons \text{Cl}_3\text{B-NH}_3$
- B. $\text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+$
- C. $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$
- D. $\text{Ag}^+ + 2 \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$

113. Identify the Bronsted-Lowry acids and bases in the following reactions.

- A. $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^-$
- B. $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}$
- C. $\text{HPO}_4^{2-} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{PO}_4^{3-} + \text{H}_3\text{PO}_4$
- D. $\text{HCO}_3^- + \text{NaOH} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O} + \text{Na}^+$

114. Does H^+ exist alone in solution? How is H^+ usually written in acid/base equilibrium?
115. What is a conjugate acid/base pair? How does an acid differ from its conjugate base? How does a base differ from its conjugate acid?
116. For the reaction below, identify the conjugate acid/base pairs.

$$HC_2H_3O_2(aq) + H_2O \rightleftharpoons C_2H_3O_2^-(aq) + H_3O^+(aq)$$
117. Give the conjugate acid and conjugate base of each of the following species: NH_3 , HSO_4^- , CO_3^{2-} , and H_2O .
118. Does a strong acid have a strong or weak conjugate base? Does a weak acid have a strong or weak conjugate base? Does a strong base have a strong or weak conjugate acid? Does a weak base have a strong or weak conjugate acid?
119. In an acid/base reaction, to tell which way the equilibrium lies we look at the relative strengths of the two bases involved. Which base gets the H^+ , the stronger or the weaker base? Which way does the equilibrium lie for the following two reactions?
- A. $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$
- B. $HC_2H_3O_2(aq) + H_2O \rightleftharpoons C_2H_3O_2^-(aq) + H_3O^+(aq)$

K_w , pH, pOH, K_A and K_B , Calculation of pH for Strong and Weak Acids and Bases

120. Write the reaction for the dissociation of water. Write the form for the ion product constant of water, K_w . What does the value of K_w depend on? What are the equilibrium concentrations of H_3O^+ and OH^- in pure water?
121. Define an acidic, basic and neutral solution in terms of the concentrations of H_3O^+ and OH^- .
122. If $[H_3O^+] = 5 \times 10^{-2} M$, what is the $[OH^-]$? If $[OH^-] = 5 \times 10^{-5} M$, what is the $[H_3O^+]$?
123. Write the equations used to calculate pH, pOH and pK_w . Write the equation that relates pH, pOH, and pK_w .
124. A $pH > 7$ indicates what type of solution, acidic, basic or neutral? A $pH < 7$ indicates what type of solution, acidic, basic or neutral? A $pH = 7$ indicates what type of solution?
125. A. A $pH = 5.17$ indicates what type of solution, acidic, basic or neutral? A $pOH = 8.9$ indicates what type of solution, acidic, basic or neutral? A $pH = 7$ indicates what type of solution?
- B. Which of the solutions shown below is basic? A solution with.....
- | | |
|-----------------|------------------------------------|
| i. $pH = 6.5$ | iii. $[H_3O^+] = 1 \times 10^{-9}$ |
| ii. $pOH = 5.5$ | iv. $[OH^-] = 1 \times 10^{-9}$ |
126. What is K_A ? Write the equation that goes along with K_A for HCl and $HC_2H_3O_2$. What does K_A tell us about the strength of an acid? If K_A is small (10^{-3}) is the acid weak or strong?
127. What is K_B ? Write the equation that goes along with K_B for NH_3 . What does K_B tell us about the strength of a base? If K_B is small (10^{-3}) is the base weak or strong?
128. Calculate the $[H_3O^+]$, $[OH^-]$, pH and pOH for a 0.25 M $HClO_4$ solution.
129. Calculate the $[H_3O^+]$, $[OH^-]$, pH and pOH for a 0.0050 M $Ba(OH)_2$ solution.
130. Calculate the pH of a $1.0 \times 10^{-9} M$ HCl solution.
131. Calculate the pH of a $5.0 \times 10^{-10} M$ $Ca(OH)_2$ solution.
132. Calculate the $[H_3O^+]$, $[OH^-]$, pH, pOH and percent ionization for a 0.025 M HF solution. ($K_A(HF) = 3.5 \times 10^{-4}$)
133. The weak acid formic acid $HCOOH$ has a pH of 2.14 when the concentration of $HCOOH$ is 0.30 M. What is the value for the acid-dissociation constant K_A and what is the percent dissociation of the $HCOOH$?
134. Calculate the $[H_3O^+]$, $[OH^-]$, pH, pOH and percent ionization for a 0.75 M NH_3 solution. ($K_B(NH_3) = 1.8 \times 10^{-5}$)
135. A. Write all of the equilibrium equations established in a solution of 0.25 M H_2SO_3 and calculate the pH of the solution. ($K_{A1} = 1.5 \times 10^{-2}$; $K_{A2} = 6.3 \times 10^{-8}$)

- B. Write all of the equilibrium equations established in a solution of 0.25 M H_3PO_4 and calculate the pH of the solution. ($K_{A1}=7.5\times 10^{-3}$; $K_{A2}=6.2\times 10^{-8}$; $K_{A3}=4.8\times 10^{-13}$)

Hydrolysis of Salts

136. When a salt is dissolved in water (this process is called hydrolysis of the salt) is the pH of the resulting solution always neutral?
137. The general formula for formation of the salt is $\text{ACID} + \text{BASE} \rightarrow \text{SALT} + \text{H}_2\text{O}$. Where does the anion of the salt come from, the acid or the base? Where does the cation of the salt come from, the acid or the base?
138. A salt that contains the cation from a strong base and the anion from a strong acid will dissolve in water to give a neutral solution. Explain why using NaCl.
139. A salt that contains the cation of a weak base and the anion from a strong acid will dissolve in water to give an acidic solution. Explain why using chemical equations for NH_4Cl .
140. A salt that contains the cation of a strong base and the anion from a weak acid will dissolve in water to give a basic solution. Explain why using chemical equations for KNO_2 .
141. A salt that contains a small, highly charged metal cation and the anion from a strong acid will dissolve in water to give an acidic solution. Explain why using chemical equations for AlCl_3 .
142. When the following salts are dissolved in water, will the resulting solutions be acidic, basic or neutral.
- | | | | | | |
|----|-----------------------------------|----|-------------------------|----|----------------------------|
| A. | $\text{KC}_2\text{H}_3\text{O}_2$ | D. | NaF | G. | $\text{Zn}(\text{NO}_3)_2$ |
| B. | NH_4Br | E. | K_2CO_3 | H. | FeCl_2 |
| C. | KClO_4 | F. | AlBr_3 | | |
143. To do problem 144, K_B of F^- (the conjugate base of HF) is needed. Show how K_A for HF and K_B for F^- can be related by K_w .
144. Calculate the pH of a 0.45 M NaF solution. $K_A(\text{HF})=3.5\times 10^{-4}$
HINT: First predict whether this solution should be acidic, basic or neutral. Second write the equations for dissociation of the salt and any equilibrium established. Third calculate either K_A or K_B for the equilibrium.
145. Calculate the pH of 0.75 M NH_4ClO_4 . $K_B(\text{NH}_3)=1.8\times 10^{-5}$
HINT: First predict whether this solution should be acidic, basic or neutral. Second, write the equations for dissociation of the salt and any equilibrium established. Third, calculate either K_A or K_B for the equilibrium.

Strength of Acids

146. How does the strength of binary acids (consisting of H and some other nonmetal element) vary within a group? Why? Arrange the following in order of increasing acid strength: HCl, HF, HI, and HBr. Arrange the following in order of increasing acid strength: H_2S , H_2Te , and H_2O .
147. How does the strength of binary acids vary within a row? Why? Arrange the following in order of increasing acid strength: HF, H_2O , NH_3 , and CH_4 .
148. How does the strength of oxyacids (consisting of H, O and some other element) vary within a series? Arrange the following in order of increasing acid strength: HClO, HClO_3 , HClO_2 , and HClO_4 . How does the strength of an oxyacid vary with the electronegativity of the central atom? Arrange the following in order of increasing acid strength: HOBr, HOCl, and HOI.
149. Which of the following equilibria lie mostly on the product side (ie. in an equilibrium mixture which one has product concentrations > reactant concentrations)
- | | | | |
|----|---|----|---|
| A. | $\text{HF} + \text{Br}^- \rightleftharpoons \text{HBr} + \text{F}^-$ | D. | $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_3\text{O}^+$ |
| B. | $\text{NH}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{OH}^-$ | E. | $\text{HBrO}_3 + \text{IO}_3^- \rightleftharpoons \text{BrO}_3^- + \text{HIO}_3$ |
| C. | $\text{HClO} + \text{ClO}_2^- \rightleftharpoons \text{ClO}^- + \text{HClO}_2$ | | |

Neutralization, Common Ion Effect and Buffers

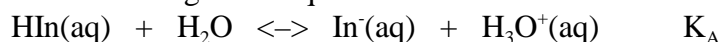
150. When a strong acid is neutralized by a strong base is the neutralization complete? Write the neutralization reaction for HNO_3 and KOH . What is the value of K_n (equilibrium constant for neutralization)? If stoichiometric amounts of acid and base are reacted will the resulting solution be acidic, basic or neutral?
151. When a weak acid is neutralized by a strong base is the neutralization complete? Write the neutralization reaction for HF and KOH . What is the value of K_n (equilibrium constant for neutralization)? ($K_A(\text{HF})=3.5 \times 10^{-4}$) If stoichiometric amounts of acid and base are reacted will the resulting solution be acidic, basic or neutral?
152. When a strong acid is neutralized by a weak base is the neutralization complete? Write the neutralization reaction for HClO_4 and NH_3 . What is the value of K_n (equilibrium constant for neutralization)? ($K_B(\text{NH}_3)=1.8 \times 10^{-5}$) If stoichiometric amounts of acid and base are reacted will the resulting solution be acidic, basic or neutral?
153. When a weak acid is neutralized by a weak base is the neutralization complete? Write the neutralization reaction for HF and NH_3 . What is the value of K_n (equilibrium constant for neutralization)? ($K_A(\text{HF})=3.5 \times 10^{-4}$; $K_B(\text{NH}_3)=1.8 \times 10^{-5}$) If stoichiometric amounts of acid and base are reacted will the resulting solution be acidic, basic or neutral?
154. What happens to the pH of a solution of 0.500 M $\text{HC}_2\text{H}_3\text{O}_2$ if a strong electrolyte like $\text{NaC}_2\text{H}_3\text{O}_2$ is added. NOTE: Addition of $\text{NaC}_2\text{H}_3\text{O}_2$ adds a common ion. Use Le'Chatelier's principle to predict the direction of the reaction. What will happen to the pH of 0.500 M $\text{HC}_2\text{H}_3\text{O}_2$ if NaCl is added?
155. What happens to the pH of a solution of 0.500 M NH_3 if a strong electrolyte like NH_4Cl is added. NOTE: Addition of NH_4Cl adds a common ion. Use Le'Chatelier's principle to predict the direction of the reaction. What will happen to the pH of 0.500 M NH_3 if KNO_3 is added?
156. Calculate the pH and % ionization of a solution which is 0.500 M $\text{HC}_2\text{H}_3\text{O}_2$ and 0.250 M $\text{NaC}_2\text{H}_3\text{O}_2$. How does the pH of this solution compare to that of 0.500 M $\text{HC}_2\text{H}_3\text{O}_2$? ($K_A(\text{HC}_2\text{H}_3\text{O}_2)=1.8 \times 10^{-5}$)
157. What is a buffer solution and what is its function? If the following substances are mixed in equimolar amounts, will a buffer solution be formed?
- | | | |
|---|---|--------------------------|
| A. HF and NaF | D. NH_3 and NH_4Cl | G. HF and NaOH |
| B. $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2$ | E. HCl and KCl | H. NH_3 and HCl |
| C. HCN and NaCN | F. NaOH and NaCl | |
- If equal volumes of the following solutions are mixed, will a buffer solution result?
- | | |
|----------------------------|---|
| A. 0.2 M HF and 0.1 M NaOH | E. 0.5 M NH_3 and 1.0 M HCl |
| B. 0.2 M HF and 0.3 M NaOH | F. 0.2 M HCN and 0.2 M KOH |
| C. 0.2 M HF and 0.2 M NaOH | G. 0.3 M HOCl and 0.15 M $\text{Ba}(\text{OH})_2$ |
| D. 0.2 M NaF and 0.1 M HCl | H. 0.3 M HOCl and 0.1 M $\text{Ba}(\text{OH})_2$ |
158. Explain using the $\text{HC}_2\text{H}_3\text{O}_2/\text{NaC}_2\text{H}_3\text{O}_2$ buffer system how a buffer maintains a relatively constant pH when small quantity of acid (HCl) or base (NaOH) is added.
159. A buffer solution consists of 0.500 M $\text{HC}_2\text{H}_3\text{O}_2$ and 0.250 M $\text{NaC}_2\text{H}_3\text{O}_2$. Calculate the pH of the resulting solution if 2.5×10^{-3} mol HClO_4 is added to 500. mL of the buffer. The pH of the buffer solution before addition of the HClO_4 was 4.44.
160. A buffer solution consists of 0.500 M $\text{HC}_2\text{H}_3\text{O}_2$ and 0.250 M $\text{NaC}_2\text{H}_3\text{O}_2$. Calculate the pH of the resulting solution if 0.025 mol NaOH is added to 500. mL of the buffer. The pH of the buffer solution before addition of the NaOH was 4.44.
161. Derive the Henderson-Hasselbach equation for a buffer solution consisting of weak acid/conjugate base (HF/NaF) and for a buffer solution consisting of weak base/conjugate

- acid ($\text{NH}_3/\text{NH}_4^+$).
162. If the concentrations of acid and conjugate base are equal what is the pH of the buffer solution equal to?
163. A buffer solution is 0.25 M HNO_2 and 0.15 M NaNO_2 . What is the pH of the buffer?
 $K_A(\text{HNO}_2)=4.5\times 10^{-4}$
164. A buffer solution with a pH of 4.0 is needed in an experiment. Which of the following buffer systems should be used? For the chosen buffer system, what concentration ratio of conjugate base:acid should be used to attain pH=4.0?
- | | | |
|----|--|--------------------------|
| A. | $\text{HNO}_2/\text{NaNO}_2$ | $K_A=4.5\times 10^{-4}$ |
| B. | $\text{HC}_2\text{H}_3\text{O}_2/\text{NaC}_2\text{H}_3\text{O}_2$ | $K_A=1.8\times 10^{-5}$ |
| C. | $\text{HCOOH}/\text{NaCOOH}$ | $K_A=1.8\times 10^{-4}$ |
| D. | $\text{C}_6\text{H}_5\text{COOH}/\text{NaC}_6\text{H}_5\text{COO}$ | $K_A=6.5\times 10^{-5}$ |
| E. | HCN/NaCN | $K_A=4.9\times 10^{-10}$ |
| F. | $\text{NH}_3/\text{NH}_4\text{Cl}$ | $K_B=1.8\times 10^{-5}$ |
165. A buffer with a pH of 9.5 is to be prepared from NH_3 and NH_4Cl . What ratio of base to salt would you use? $K_B(\text{NH}_3)=1.8\times 10^{-5}$
166. Explain why dilution of a buffer solution does not change the pH. Does a buffer work best when it's solution is dilute or concentrated (i.e. Which has a better buffer capacity a dilute or concentrated solution)? What concentration ratio of acid/salt or base/salt works best for buffers?
167. A buffer solution is 0.10 M $\text{HC}_2\text{H}_3\text{O}_2$ and 0.20 M $\text{NaC}_2\text{H}_3\text{O}_2$. What is the pH of this buffer solution? Calculate the pH after the addition of 0.0040 mol HCl to 100 ml of the buffer. Calculate the pH after the addition of 0.0060 mol NaOH to the buffer.

Titration, Titration Curves and Indicators

168. What is the shape of the titration curve (plot of pH vs. mL of added base) for titration of a strong acid by a strong base? In a titration, 25 mL of 0.50 M HNO_3 was titrated with 0.25 M KOH. Calculate the pH of the resulting solution after the addition of the following volumes of base: 0 mL, 25 mL, 50 mL, and 60 mL. What volume of base is needed to reach the equivalence point? What species is present at the equivalence point and what is the pH at the equivalence point?
169. What is the shape of the titration curve (plot of pH vs. mL of added base) for titration of a weak acid by a strong base? In a titration, 10 mL of 0.10 M HF was titrated with 0.20 M KOH. Calculate the pH of the resulting solution after the addition of the following volumes of base: 0 mL, 2.5 mL, 5.0 mL, and 6.0 mL. What volume of base is needed to reach the equivalence point? What species is present at the equivalence point and what is the pH at the equivalence point? When enough base has been added to neutralize half of the weak acid, what type of system is present? What is the pH half-way to the equivalence point?
 $(K_A(\text{HF})=3.5\times 10^{-4})$
170. What is the shape of the titration curve (plot of pH vs. mL of added acid) for titration of a weak base by a strong acid? In a titration, 20 mL of 0.10 M NH_3 was titrated with 0.20 M HCl. Calculate the pH of the resulting solution after the addition of the following volumes of acid: 0 mL, 5.0 mL, 10.0 mL, and 15.0 mL. What volume of acid is needed to reach the equivalence point? What species is present at the equivalence point and what is the pH at the equivalence point? When enough acid has been added to neutralize half of the weak base, what type of system is present? What is the pH half-way to the equivalence point?
 $(K_B(\text{NH}_3)=1.8\times 10^{-5})$
171. What is the difference between the equivalence point and the end point in a titration?
172. An indicator itself is a weak acid or base that has one color in acidic solution and a different

color in basic solution. The general equilibria for an indicator can be written as follows:



For phenolphthalein, HIn is colorless whereas In⁻ is pink. What is the color of the indicator in basic solution? In acidic solution?

173. For phenolphthalein, $K_A=7.9 \times 10^{-10}$. Around what pH will phenolphthalein change color? Could phenolphthalein be used as an indicator during the titration of a strong acid with a strong base (eg. HCl with NaOH)? strong base with a weak acid (eg. NaOH with $\text{HC}_2\text{H}_3\text{O}_2$)? strong acid with a weak base (eg. HBr with NH_3)?
174. Three titrations were to be carried out with the acids and bases indicated below. Choose the best indicator for each titration from the following: phenolphthalein $K_A=7.9 \times 10^{-10}$, methyl orange $K_A=1.6 \times 10^{-4}$, and bromothymol blue $K_A=1.6 \times 10^{-7}$.
- A. HNO_3 with NH_3
B. HNO_3 with KOH
C. HClO_3 with NaOH

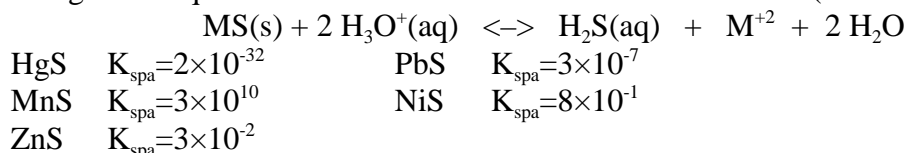
Solubility Product, Factors Affecting Solubility and Ion Product

175. What is K_{sp} ? Write the chemical equation for dissolution of $\text{Ca}_3(\text{PO}_4)_2$. Write the solubility product constant expression for this equation.
176. How is the numerical value of K_{sp} determined? What does its value depend on?
177. A sample of PbCl_2 was dissolved in water until a saturated solution was obtained (until some solid PbCl_2 was present). The concentration of Pb^{+2} in the solution was found to be $1.44 \times 10^{-2} \text{M}$. Calculate the numerical value of K_{sp} .
178. A saturated solution of $\text{Ca}_3(\text{PO}_4)_2$ was prepared and the concentration of Ca^{+2} was found to be $3.43 \times 10^{-7} \text{M}$. Calculate the numerical value of K_{sp} .
179. Calculate the solubility (in g/L and in mol/L) of AgBr in water. $K_{sp}(\text{AgBr})=5.4 \times 10^{-13}$.
180. Calculate the solubility (in g/L and in mol/L) of $\text{Mg}_3(\text{AsO}_4)_2$ in water. $K_{sp}(\text{Mg}_3(\text{AsO}_4)_2)=2.1 \times 10^{-20}$.
181. If Ag_2SO_4 is mixed with water to obtain a saturated solution, what is the concentration of each ion in the resulting solution? $K_{sp}(\text{Ag}_2\text{SO}_4)=1.2 \times 10^{-5}$.
182. Calculate the solubility of BaF_2 in pure water and in 0.30 M KF.
NOTE: KF adds a common ion.
183. BaSO_4 is only sparingly soluble with $K_{sp}=1.1 \times 10^{-10}$. Will addition of K_2SO_4 or BaCl_2 change the solubility of BaSO_4 ? If so, how? Calculate the solubility of BaSO_4 in 0.10 M K_2SO_4 and in 0.25 M BaCl_2 .
184. Will addition of an acid or a decrease in pH change the solubility of the following salts? How and why?
- | | |
|-------------------|-----------------------------|
| A. CaF_2 | D. Hg_2Br_2 |
| B. AgCl | E. MnS |
| C. PbI_2 | F. ZnCO_3 |
185. Show using equations how addition of an acid increases the solubility of ZnCO_3 .
Show using equations how addition of an acid increases the solubility of MnS .
186. Will addition of an acid (like HCl) or a decrease in pH change the solubility of $\text{Fe}(\text{OH})_3$, AgOH , $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$? Show using equations how addition of an acid increases the solubility of $\text{Mg}(\text{OH})_2$.
187. A. Calculate the pH of a solution saturated with $\text{Mg}(\text{OH})_2$. $K_{sp}(\text{Mg}(\text{OH})_2)=5.6 \times 10^{-12}$
B. Calculate the molar solubility of $\text{Mg}(\text{OH})_2$ in pure water and in water buffered at a pH of 8.00.
188. Will a precipitate form if 100. mL of 0.075 M $\text{Mg}(\text{NO}_3)_2$ is mixed with 200. mL of 0.010 M Na_2CO_3 ? $K_{sp}(\text{MgCO}_3)=6.8 \times 10^{-6}$ HINT: Calculate the ion product or reaction quotient (IP

- or Q_{sp}) and compare to K_{sp} .
189. If $IP(Q_{sp})=K_{sp}$ will a precipitate form and what type of solution is present (saturated, unsaturated or supersaturated)? If $IP(Q_{sp})>K_{sp}$ will a precipitate form and what type of solution is present? If $IP(Q_{sp})<K_{sp}$ will a precipitate form and what type of solution is present?
190. Will a precipitate form if 500. mL of 0.050 M $Ag_2C_2H_3O_2$ is mixed with 300. mL of 0.010M K_2SO_4 ? $K_{sp}(Ag_2SO_4)=1.2\times 10^{-5}$

Separations via Precipitation and Qualitative Analysis

191. A solution is 0.0015 M in each of the cations Ag^+ , Pb^{+2} , and Hg_2^{+2} . What concentration of chloride ion must be present to precipitate as much of the Hg_2^{+2} (as Hg_2Cl_2) as possible without precipitating the chlorides of Ag^+ and Pb^{+2} ? ($K_{sp}(Hg_2Cl_2)=1.4\times 10^{-18}$, $K_{sp}(PbCl_2)=1.2\times 10^{-5}$, $K_{sp}(AgCl)=1.8\times 10^{-10}$)
192. Consider question 191. What concentration of Cl^- is needed to precipitate all of the ions but Pb^{+2} ? What is the concentration of Hg_2^{+2} ions in the solution at this concentration of Cl^- ?
193. A solution with a pH of 0.52 is 0.0010 M in each of the cations Pb^{+2} , Hg^{+2} , Mn^{+2} , Ni^{+2} , and Zn^{+2} and 0.10 M in H_2S . Which of the cations will precipitate as the sulfide? The general equilibrium established for divalent metal cations (+2 charge) is:



- What pH is needed to precipitate all of the Group III cations as the sulfide?
194. A solution is 0.500 M in each of the ions Ni^{+2} and Cr^{+3} and has a pH of 4.00. Solid NaOH is added to precipitate the hydroxides. Can these two ions be separated from each other by adjusting the pH of the solution? What pH is needed to precipitate as much of the Cr^{+3} as possible without precipitating the Ni^{+2} ?
- | | |
|---------------------|-----------------------------|
| Ni(OH) ₂ | $K_{sp}=2\times 10^{-15}$ |
| Cr(OH) ₃ | $K_{sp}=6.3\times 10^{-31}$ |
195. A solution is 1.0×10^{-3} M in each of the metal cations Cu^+ , Pb^{+2} , Hg_2^{+2} and Ag^+ . Solid NaBr is added to this solution. In what order will the bromides precipitate?
- | | | | |
|---------------------------------|-----------------------------|------|-----------------------------|
| CuBr | $K_{sp}=6.3\times 10^{-9}$ | AgBr | $K_{sp}=5.4\times 10^{-13}$ |
| PbBr ₂ | $K_{sp}=6.6\times 10^{-6}$ | | |
| Hg ₂ Br ₂ | $K_{sp}=6.4\times 10^{-23}$ | | |

196. A solution is 0.0050M in Sn^{+2} and Al^{+3} and has a pH=1.00. Solid NaOH is added to make the solution more basic. Which of these metal cations will precipitate first?
- | | |
|---------------------|-----------------------------|
| Sn(OH) ₂ | $K_{sp}=3\times 10^{-27}$ |
| Al(OH) ₃ | $K_{sp}=2.0\times 10^{-32}$ |

Metal Complexes and Isomerism

197. What is a coordination compound (also called a metal complex)? What type of bonds are present between the ligands and the metal cation? The ligand acts as a Lewis Base toward the metal cation so what must be present on the ligand?
198. For the following metal complex salts identify the ions or molecules within the coordination sphere of the metal cation (those bonded with a coordinate covalent bond) and those bonded ionically to the complex. Calculate the charge on the complex ion and on the metal cation.
- | | | |
|--|--|---|
| [Ag(NH ₃) ₂]Cl | [Co(NH ₃) ₆]Cl ₃ | K ₂ [Ni(CN) ₄] |
| Na[Ag(CN) ₂] | [Co(NH ₃) ₅ Cl]Cl ₂ | [Cr(H ₂ O) ₆]SO ₄ |
| | [Co(NH ₃) ₄ Cl ₂]Cl | |
199. Three different metal complexes consisting of Co^{+3} , Cl^- and NH_3 with the chemical formulas

- cation in metal complexes. What type of attractions are present between the ligand and metal cation?
215. For a metal complex with CN=6, how do the incoming ligands affect the energy of the metal cation d-orbitals? Is the energy of all of the d-orbitals affected to the same extent? Which d-orbitals are destabilized the most by the presence of the ligands? Why?
216. For a metal complex with CN=4 (tetrahedral), how do the incoming ligands affect the energy of the metal cation d-orbitals? Is the energy of all of the d-orbitals affected to the same extent? Which d-orbitals are destabilized the most by the presence of the ligands? Why?
217. For a metal complex with CN=4 (square planar), how do the incoming ligands affect the energy of the metal cation d-orbitals? Is the energy of all of the d-orbitals affected to the same extent? Which d-orbitals are destabilized the most by the presence of the ligands? Why?
218. Define the crystal field splitting (Δ_o) for an octahedral complex. What is meant by the following terms: Weak field ligand, strong field ligand, high spin complex and low spin complex.
219. Give the spectrochemical series and identify weak field (high spin) and strong field (low spin) ligands.
220. Draw a crystal field energy level diagram and predict the number of unpaired electrons for the following complexes:
- | | | | |
|----|--|----|--|
| A. | $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$ | G. | $[\text{FeF}_6]^{-3}$ |
| B. | $[\text{CoF}_6]^{-3}$ | H. | $[\text{Fe}(\text{CN})_6]^{-3}$ |
| C. | $[\text{Co}(\text{CN})_6]^{-3}$ | I. | $[\text{Ni}(\text{NH}_3)_6]^{+2}$ |
| D. | $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ | J. | $[\text{Cr}(\text{CN})_6]^{-3}$ |
| E. | $[\text{V}(\text{H}_2\text{O})_6]^{+3}$ | K. | $[\text{Mn}(\text{CN})_6]^{-3}$ |
| F. | $[\text{MnCl}_6]^{-3}$ | L. | $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$ |
221. Show that for the systems d^1 , d^2 , d^3 , d^8 , d^9 and d^{10} two different spin states (high spin and low spin) are not possible. Show that for the systems d^4 - d^7 two different spin states are possible dependent on the field strength of the ligand.
222. What type of electronic configurations for metal cations always leads to colorless compounds? For transition metal complexes to be colored how many electrons must occupy the d-orbitals? Predict whether or not a solution of the following compounds would be colored?
- | | | |
|----------------------------|--|---|
| NaBr | CuNO_3 | $\text{Bi}(\text{NO}_3)_3$ |
| AsCl_3 | $\text{Cu}(\text{NO}_3)_2$ | $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$ |
| HgCl_2 | KNO_3 | $\text{Pb}(\text{ClO}_4)_2$ |
| $\text{Zn}(\text{NO}_3)_2$ | $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ | |
| SbCl_3 | $\text{Mn}(\text{NO}_3)_3$ | |

Amphoterism, Ammonia Complexes and Calculations Involving Complex Formation

223. Does formation of a metal complex usually increase or decrease the solubility of a salt?
224. Write the equations for the formation of the following metal complexes.
- | | | | |
|-----------------------------------|--------------------------|---------------------------------|--------------------------|
| $[\text{Ag}(\text{NH}_3)_2]^+$ | $K_f=1.7 \times 10^7$ | $[\text{Al}(\text{OH})_4]^-$ | $K_f=2.1 \times 10^{34}$ |
| $[\text{Cu}(\text{NH}_3)_4]^{+2}$ | $K_f=1.1 \times 10^{13}$ | $[\text{Cr}(\text{OH})_4]^-$ | $K_f=8 \times 10^{29}$ |
| $[\text{Ag}(\text{CN})_2]^-$ | $K_f=1 \times 10^{21}$ | $[\text{Zn}(\text{OH})_4]^{2-}$ | $K_f=2.8 \times 10^{15}$ |
225. Is AgCl more soluble in pure water or a solution of aqueous ammonia? Why? Write the NET equation that shows how solid AgCl can be dissolved by aqueous ammonia to form an ammonia complex. Calculate the value of the equilibrium constant for this equation. $K_{sp}(\text{AgCl})=1.8 \times 10^{-10}$; $K_f([\text{Ag}(\text{NH}_3)_2]^+)=1.7 \times 10^7$
226. The metal cations, Cd^{+2} , Zn^{+2} , Cu^{+2} , Ag^+ and Ni^{+2} form soluble ammonia complexes of

- $[\text{Cd}(\text{NH}_3)_4]^{+2}$, $[\text{Zn}(\text{NH}_3)_4]^{+2}$, $[\text{Cu}(\text{NH}_3)_4]^{+2}$, $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Ni}(\text{NH}_3)_6]^{+2}$. The test for formation of an ammonia complex is to add a limited amount of ammonia and then to add an excess of ammonia to a solution containing one of these ions. Give equations for the reaction that occurs with each of these metal cations in limited and excess ammonia.
227. Amphoteric hydroxides are soluble in both acidic and basic solutions but insoluble in neutral solutions. The metal cations Al^{+3} , Zn^{+2} , Pb^{+2} , Cr^{+3} and Sn^{+2} are amphoteric and form soluble complexes of $[\text{Al}(\text{OH})_4]^-$, $[\text{Zn}(\text{OH})_4]^{+2}$, $[\text{Pb}(\text{OH})_4]^{+2}$, $[\text{Cr}(\text{OH})_4]^-$ and $[\text{Sn}(\text{OH})_3]^-$ at high pH ($\text{pH} > 10$). The test for amphoteric nature is to add a limited amount of NaOH and then to add an excess of NaOH to a solution containing one of these ions. Give equations for the reaction that occurs for each of these ions in limited and excess NaOH.
228. Calculate the solubility of AgBr ($K_{\text{sp}} = 5.4 \times 10^{-13}$) in 0.75 M NH_3 . Compare the solubility of AgBr in pure water and in 0.75 M NH_3 .
 $K_{\text{f}}([\text{Ag}(\text{NH}_3)_2]^+) = 1.7 \times 10^7$
229. A solution is 0.60 M in $[\text{Cu}(\text{NH}_3)_4]^{+2}$ ($K_{\text{f}} = 1.1 \times 10^{13}$). Calculate the concentration of free Cu^{+2} and NH_3 in this solution.
230. Calculate the solubility of $\text{Cu}(\text{OH})_2$ in a solution of 1.2 M NH_3 .
 $K_{\text{sp}}(\text{Cu}(\text{OH})_2) = 1.6 \times 10^{-19}$; $K_{\text{f}}([\text{Cu}(\text{NH}_3)_4]^{+2}) = 1.1 \times 10^{13}$
231. Calculate the equilibrium concentrations of Ni^{+2} and NH_3 in the solution when 0.050 mol $\text{Ni}(\text{NO}_3)_2$ is added to 1000. mL of 1.0 M NH_3 . $K_{\text{f}}([\text{Ni}(\text{NH}_3)_6]^{+2}) = 5.6 \times 10^8$
232. The complex ion $[\text{Ag}(\text{NH}_3)_2]^+$ ($K_{\text{f}} = 1.7 \times 10^7$) is formed from a solution that is 0.10 M Ag^+ and 1.0 M NH_3 . After the complex is formed, the solution is made 0.030 M in NaCl. Will any AgCl precipitate? $K_{\text{sp}}(\text{AgCl}) = 1.8 \times 10^{-10}$

Spontaneity, Enthalpy, Entropy and Gibbs Free Energy

233. Define the following terms: spontaneous process and nonspontaneous process.
234. If a reaction is exothermic does that automatically mean that it is spontaneous in the forward direction? If a reaction is endothermic, does that automatically mean that it is nonspontaneous in the forward direction?
235. Given the standard heats of formation below, calculate the standard enthalpy of the reaction:

$$4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \longrightarrow 4 \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$$
 $\Delta H_{\text{f}}^\circ(\text{NO}(\text{g})) = +90.37 \text{ kJ/mol}$; $\Delta H_{\text{f}}^\circ(\text{H}_2\text{O}(\text{g})) = -241.8 \text{ kJ/mol}$; $\Delta H_{\text{f}}^\circ(\text{NH}_3(\text{g})) = -46.19 \text{ kJ/mol}$
236. Define entropy, S. Can S have a negative value? Can ΔS have a negative value?
237. If ΔS is positive during a reaction or process, is entropy increasing or decreasing during the process? If ΔS is negative during a reaction or process, is entropy increasing or decreasing during the process?
238. Arrange the phases liquid, solid and gas according to decreasing entropy. Predict the sign of ΔS (the change in entropy) for the following processes
- $\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{l})$
 - $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g})$
 - $\text{H}_2\text{O}(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{s})$
 - $\text{NaCl}(\text{s}) \longrightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
 - $\text{FeSO}_4(\text{s}) \longrightarrow \text{Fe}^{+2}(\text{aq}) + \text{SO}_4^{-2}(\text{aq})$
 - $\text{I}_2(\text{s}) \longrightarrow \text{I}_2(\text{aq})$
239. For the reaction given in question 235, predict the sign for the entropy change (ΔS). For the reaction $2 \text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g}) \longrightarrow \text{N}_2\text{H}_4(\text{l}) + \text{O}_2(\text{g})$, predict the sign for the entropy change (ΔS).
240. Show how the entropy of a substance depends on temperature. What is the entropy of a perfectly ordered crystalline solid at absolute zero? State the third law of thermodynamics.
241. Calculate the change in entropy from tabulated values of the standard molar entropies for the

reaction given in Question 235.

$$S^\circ(\text{NH}_3(\text{g}))=192.3 \text{ J/K-mol}$$

$$S^\circ(\text{NO}(\text{g}))=210.7 \text{ J/K-mol}$$

$$S^\circ(\text{O}_2(\text{g}))=205.0 \text{ J/K-mol}$$

$$S^\circ(\text{H}_2\text{O}(\text{g}))=188.7 \text{ J/K-mol}$$

242. State the second law of thermodynamics. Show how the expression for Gibbs Free Energy is obtained from the second law of thermodynamics. If during a reaction, the total entropy of the system and surroundings (ΔS_{total}) is increasing what is the sign of ΔG and is the reaction spontaneous in the forward direction?
243. Give the equation used to calculate the Gibbs Free Energy change (ΔG) for a reaction or process. What values of ΔG lead to spontaneous processes? nonspontaneous processes?
244. For the following signs of ΔH and ΔS predict the sign of ΔG and decide whether or not the sign of ΔG will depend on temperature.

CASE#1: $\Delta H= +; \Delta S= +$

CASE#2: $\Delta H= +; \Delta S= -$

CASE#3: $\Delta H= -; \Delta S= +$

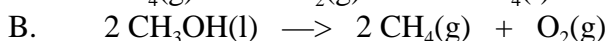
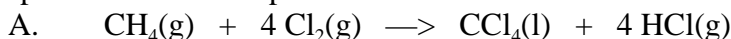
CASE#4: $\Delta H= -; \Delta S= -$

What is the crossover temperature and how is it calculated? Can a crossover temperature be calculated for CASE #2 and CASE #3? Why or why not?

245. For the reaction $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{l})$ Calculate the standard Gibbs free energy change. Decide whether the reaction is spontaneous in the forward direction. Calculate at what temperature the reaction will change in behavior from spontaneous to nonspontaneous or from nonspontaneous to spontaneous (ie. calculate the crossover temperature).

	$\Delta H_f^\circ(\text{kJ/mol})$	$S^\circ(\text{J/K-mol})$
$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.7	161
$\text{O}_2(\text{g})$		205.0
$\text{CO}_2(\text{g})$	-393.5	213.6
$\text{H}_2\text{O}(\text{l})$	-285.8	69.9

246. Calculate the standard Gibbs Free energy (ΔG°) from tabulated values of the standard Gibbs Free energy of formation (ΔG_f°) for the reactions below and decide whether the reaction is spontaneous or nonspontaneous in the forward direction.

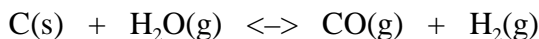


	$\Delta G_f^\circ(\text{kJ/mol})$	$\Delta H_f^\circ(\text{kJ/mol})$	$S^\circ(\text{J/K-mol})$
$\text{CH}_4(\text{g})$	-50.75		
$\text{CCl}_4(\text{l})$	-60.63		
$\text{HCl}(\text{g})$	-95.30		
$\text{CH}_3\text{OH}(\text{l})$	-166.3		
$\text{CO}(\text{g})$	-137.2	-110.5	197.6
$\text{H}_2\text{O}(\text{g})$	-228.6	-241.8	188.7
$\text{H}_2(\text{g})$	0	0	130.6
$\text{C}(\text{s,gr})$	0	0	5.7

Gibbs Free Energy and Equilibrium

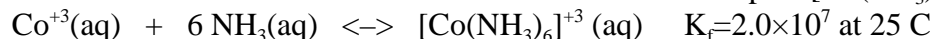
247. ΔG is the Gibbs Free Energy under nonstandard conditions. How is ΔG different from ΔG° ? Give the equation used to calculate ΔG from ΔG° and Q (the reaction quotient). NOTE: If a reaction consists of primarily gas phase reactants and products Q_p should be used. If a reaction consists of primarily solution phase reactant and products Q_c should be used.
248. Consider the reaction below. Initially a vessel contained 0.500 atm $\text{CO}(\text{g})$, 0.150 atm $\text{H}_2\text{O}(\text{g})$ and 4.25×10^{-2} atm $\text{H}_2(\text{g})$. Is the reaction spontaneous in the forward direction at

25 C? at 800 C? HINT: Calculate the value of ΔG . Values of ΔG_f° are given in question 246.



249. Use the facts that *i.* when a reaction is at equilibrium $\Delta G=0$ and *ii.* when a reaction is at equilibrium $Q=K$ to derive the relationship between ΔG° and K .

250. Consider the reaction for the formation of the cobalt ammonia complex $[\text{Co}(\text{NH}_3)_6]^{+3}$ below.



A. Calculate the Gibbs Free Energy under standard conditions for this reaction.

B. If $[\text{Co}^{+3}] = 0.00500 \text{ M}$, $[\text{NH}_3] = 0.10 \text{ M}$ and $[\text{Co}(\text{NH}_3)_6^{+3}] = 1.00 \text{ M}$ initially, is the reaction spontaneous in the forward direction?

251. For the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \quad \Delta G^\circ = +37.2 \text{ kJ}$

Calculate the equilibrium constant at 25 C. Calculate the equilibrium constant at 200 C.

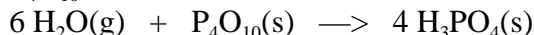
	ΔH_f° (kJ/mol)	S° (J/K-mol)
$\text{PCl}_5(\text{g})$	-374.9	364.6
$\text{PCl}_3(\text{g})$	-287.0	311.8
$\text{Cl}_2(\text{g})$		223.0

252. For the reaction $\text{C}_2\text{H}_4(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O(g)} \quad \Delta H^\circ = -1323 \text{ kJ}$

Decide whether or not the reaction is spontaneous in the forward direction under the following conditions: $p(\text{C}_2\text{H}_4) = 20 \text{ atm}$; $p(\text{O}_2) = 0.020 \text{ atm}$; $p(\text{CO}_2) = 0.010 \text{ atm}$; and $p(\text{H}_2\text{O}) = 0.010 \text{ atm}$ at 25 C. Under the same conditions, is the reaction spontaneous in the forward direction at 750 C?

	S° (J/K-mol)
$\text{CO}_2(\text{g})$	213.6
$\text{H}_2\text{O(g)}$	188.7
$\text{C}_2\text{H}_4(\text{g})$	219.6
$\text{O}_2(\text{g})$	205.0

253. The substance $\text{P}_4\text{O}_{10}(\text{s})$ is often used to adsorb water vapor in dry boxes by the following reaction:



A. Calculate ΔG° and K at 25 C and decide whether the reaction is spontaneous in the forward direction.

	ΔH_f° (kJ/mol)	S° (J/K-mol)
$\text{H}_3\text{PO}_4(\text{s})$	-1279	110.5
$\text{P}_4\text{O}_{10}(\text{s})$	-2984	228.9
$\text{H}_2\text{O(g)}$	-241.8	188.7

B. The P_4O_{10} is regenerated by heating the H_3PO_4 and removing the water. To what temperature should the H_3PO_4 be heated (i.e. at what temperature does the reaction become spontaneous in the reverse direction)? What is the value of K at this temperature?

C. The vapor pressure of water at 25 C is 17.5 mm Hg. Will the P_4O_{10} spontaneously adsorb the water vapor at 25 C?

Electrochemistry, Galvanic Cells and Standard Reduction Potentials

254. Define the following terms: electrochemistry, electrochemical cell, galvanic cell and electrolytic cell. Are batteries considered to be galvanic or electrolytic cells?

255. When a copper wire is placed in an aqueous solution of AgNO_3 what happens? Write the Net Ionic equation for this redox reaction and decide which of the substances are being oxidized and which reduced. Write the half-reactions for this redox reaction.

256. If a silver wire were placed in an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ would a reaction occur? Why or why not?