

CHEM 116-Dr. Babb's Section
Answer Key to Exam I Lecture Problem Sheet

2. Strong electrolytes: strong acids, strong bases and soluble ionic compounds
 Weak electrolytes: weak acids and weak bases
 Non-electrolytes: soluble organic compounds that are not classified as weak acids or bases and other soluble molecular compounds.
3. AgNO₃, sol BaI₂, sol PbSO₄, insol Na₂CO₃, sol Sr(NO₃)₂, sol
 CaCl₂, sol AgOH, insol Pb(C₂H₃O₂)₂, sol (NH₄)₃PO₄, sol FeBr₃, sol
 Pb(ClO₄)₂, sol Hg₂Br₂, insol K₃PO₄, sol CaSO₄, insol MgCO₃, insol
 AgCl, insol BaSO₄, insol CuCl, sol CaS, sol Fe₂S₃, insol
 Fe(OH)₃, insol
- 4.
- A. FeBr₃ + 3 AgC₂H₃O₂ → Fe(C₂H₃O₂)₃ + 3 AgBr
 Net Ionic Eqn: Br⁻ + Ag⁺ → AgBr(s)
- B. (NH₄)₂SO₄ + BaCl₂ → BaSO₄ + 2 NH₄Cl
 Net Ionic Eqn: Ba⁺² + SO₄⁻² → BaSO₄(s)
- C. HNO₃ + CsC₂H₃O₂ → CsNO₃ + HC₂H₃O₂
 Net Ionic Eqn: H⁺ + C₂H₃O₂⁻ → HC₂H₃O₂(aq)
- D. HNO₂ + CsC₂H₃O₂ → CsNO₂ + HC₂H₃O₂
 Net Ionic Eqn: HNO₂(aq) + C₂H₃O₂⁻ → NO₂⁻ + HC₂H₃O₂(aq)
- E. 2 HClO₄ + Ba(OH)₂ → Ba(ClO₄)₂ + 2 H₂O
 Net Ionic Eqn: H⁺ + OH⁻ → H₂O
- F. 2 HClO + Ba(OH)₂ → Ba(ClO)₂ + 2 H₂O
 Net Ionic Eqn: HClO + OH⁻ → ClO⁻ + H₂O
- G. Na₂CO₃ + H₂SO₄ → Na₂SO₄ + CO₂ + H₂O
 Net Ionic Eqn: CO₃⁻² + 2 H⁺ → CO₂(g) + H₂O
- H. (NH₄)₂CO₃ + 2 NaOH → Na₂CO₃ + 2 NH₃ + 2 H₂O
 Net Ionic Eqn: NH₄⁺ + OH⁻ → NH₃(aq) + H₂O
- I. Fe(NO₃)₃ + 3 NH₃ + 3 H₂O → Fe(OH)₃ + 3 NH₄NO₃
 Net Ionic Eqn: Fe⁺³ + 3 NH₃(aq) + 3 H₂O → Fe(OH)₃(s) + 3 NH₄⁺
5. 0.25 M Ca⁺² and 0.50 M Cl⁻
6. 0.0600 mol C₂H₃O₂⁻
7. 17 g AlCl₃
8. 56 mL
9. 6.48 M Na⁺
10. 0.28 M Cl⁻
- 12.
- A. Seawater; solution of solid salt dissolved in liquid water
 B. Coca-Cola (soda water); solution of gaseous CO₂ dissolved in water
 C. Air; solution of many gases dispersed in gaseous N₂
 D. 14 karat gold (mixture of Au and Ag); solution of solid Au dissolved in solid Ag
 E. Brass (mixture of Zn and Cu); solution of solid Zn dissolved in solid Cu
 F. Milk; colloid of intermediate size, solid fat particles dispersed in liquid water.
 G. Paint; suspension of large solid TiO₂ particles dispersed in liquid water or oil
 H. Italian dressing; not a homogeneous mixture at all, really should be classified as a

heterogeneous mixture.

13. Polar substances dissolve more readily in water. Water is a polar substance and is held together in the condensed phases primarily by hydrogen bonding and dipole-dipole forces of attraction. Solutes that readily dissolve in water will have intermolecular forces of attraction similar to the water. Polar solutes and solutes which can hydrogen bond will readily dissolve in water. A short list of substances that readily dissolve in water is: NH_3 , HF , HCl , $\text{C}_2\text{H}_5\text{OH}$, CH_3OH , salts/ionic compounds, oxyacids, H_2O_2 . The general rule is "Like Dissolves Like". This means that polar solvents like to dissolve polar solutes; whereas, nonpolar solvents like to dissolve nonpolar solutes.
14. The solutes C_8H_{18} , wax ($\text{C}_{20}\text{H}_{42}$), and C_6H_6 are relatively non-polar and would be more soluble in the non-polar solvent hexane (C_6H_{14}) than in the polar solvent water.
16. The concentration unit of Molarity depends on temperature because the volume of a liquid is dependent somewhat on temperature.
17. Weight % $\text{CaCl}_2=3.85\%$; Weight % $\text{H}_2\text{O} = 96.15\%$
Mole fraction $\text{CaCl}_2=0.00645$; Mole fraction $\text{H}_2\text{O}=0.994$ (or 0.99257 if obtain by subtract.)
Molality $\text{CaCl}_2= 0.360 \text{ m}$
Molarity $\text{CaCl}_2=0.347 \text{ M}$
18. A. Molality $\text{C}_3\text{H}_8\text{O}_3=7.24 \text{ m}$
Molarity $\text{C}_3\text{H}_8\text{O}_3=4.78 \text{ M}$
Mole Fraction $\text{C}_3\text{H}_8\text{O}_3=0.115$; Mole Fraction $\text{H}_2\text{O}=0.885$
B. Mole Fraction $\text{NaCl}=0.083$
19. Molarity $\text{Ca}^{+2}=0.075 \text{ M}$
Molality $\text{Ca}^{+2}=0.075 \text{ m}$
ppm $\text{Ca}^{+2}=3.0 \times 10^3 \text{ ppm}$
20. Effect of T on solubility of solid solute in liquid solvent is variable dependent on ΔH for the dissolution process.
21. For many endothermic dissolution processes ($\Delta H_{\text{diss}}=+$): as T increases, Solubility increases.
22. For many exothermic dissolution processes ($\Delta H_{\text{diss}}=-$): as T increases, Solubility decreases.
23. Pressure has no effect on the solubility of a solid solute in a liquid solvent because volumes of liquids and solids are relatively independent of pressure.
24. As T increases, the solubility of a gaseous solute in liquid solvent decreases. At higher temperature more dissolved gas molecules have enough energy to escape the IMF's holding them dissolved in the liquid solvent resulting in a decreased solubility.
25. As P increases, solubility of a gaseous solute in liquid solvent increases. The gas above the liquid obeys the ideal gas law and as P increases, V_{gas} decreases. One way for the volume of the gas to decrease is for more of the gas to dissolve in the liquid solvent resulting in an increased solubility of the gas in the liquid. Henry's Law: $P = k \times C$ where C = solubility of gas in liquid in units of mol gas/L soln, k =Henry's Law constant in units of L-atm/mol and P=partial pressure of gas.

The Henry's Law constant for gaseous acetylene: $k=0.96 \text{ L-atm/mol}$

Solubility of acetylene in acetone at 12 atm is 12 mol/L

26. The value of a colligative property does not depend on the identity of the solute. The colligative properties only depend on the number of solute particles dissolved which itself depends on whether the solute is a strong, weak or nonelectrolyte when dissolved.

27. Pure water has a higher vapor pressure than a solution of sugar.
Raoult's Law: $P_{\text{soln}} = X_{\text{solvent}} P_{\text{solvent}}^*$ and $\Delta P = X_{\text{solute}} P_{\text{solvent}}^*$
28. A. $P_{\text{soln}} = 46.9$ torr and $\Delta P = 0.2$ torr
B. $P_{\text{soln}} = 44.9$ torr (HINT: CaCl_2 is a strong electrolyte)
29. $P_{\text{soln}} = X_1 P_1^* + X_2 P_2^*$
30. 51.8 mm Hg; This solution would display negative deviations to Raoult's law i.e. this solution would have a lower vapor pressure than Raoult's Law predicts.

31. Salt water has a higher boiling point than pure water.

$$\Delta T_B = m \times K_B$$

32. Pure water has a higher freezing point than salt water.

$$\Delta T_F = m \times K_F$$

33. K_B and K_F are properties of the solvent and have units of kg-C/mol.

34. A. 100.30 C

B. 100.60 C

35. 16 m

36. 328 g/mol

37. A. No, the freezing points will not be equivalent. The solution with the highest colligative molality will have the lowest freezing point. The solution with the lowest colligative molality will have the highest freezing point.

	<u>Molality</u>	<u>Colligative Molality</u>	<u>ΔT_F(C)</u>	<u>T_F(C)</u>
I.	0.50 m sugar	0.50 m	0.93	-0.93
II.	0.50 m NaCl	1.0 m	1.9	-1.9
III.	0.50 m AlCl_3	2.0 m	3.7	-3.7
IV.	0.50 m CaCl_2	1.5 m	2.8	-2.8

The 0.50 m sugar solution has the highest freezing point; while, the 0.50 m AlCl_3 solution has the lowest freezing point.

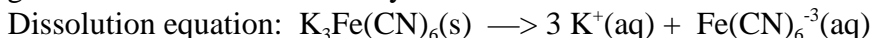
B. The solution with the highest colligative molality will have the highest boiling point. The solution with the lowest colligative molality will have the lowest boiling point.

	<u>Molality</u>	<u>Colligative Molality</u>
I.	0.40 m Na_2SO_4	1.2 m
II.	0.50 m KNO_3	1.0 m
III.	0.60 m $\text{C}_6\text{H}_{12}\text{O}_6$ (sugar)	0.60 m
IV.	0.35 m $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$	1.4 m
V.	0.60 m $\text{HC}_2\text{H}_3\text{O}_2$	slightly > 0.60 m because $\text{HC}_2\text{H}_3\text{O}_2$ is a weak electrolyte.

The 0.35 m $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$ has the highest boiling point; while, the 0.60 m $\text{C}_6\text{H}_{12}\text{O}_6$ (sugar) has the lowest boiling point.

38. 0.51 kg-C/mol

39. The $\text{K}_3\text{Fe}(\text{CN})_6$ dissociates into a total of four ions since the colligative molality is four times greater than the actual molality



40. -0.955 C

41. 1%

42. There will be a net flow of solvent from the pure solvent side to the solution side. The net flow of solvent from solvent to solution side will stop if the height of the liquid in the tube on the solution side exerts enough downward pressure. The downward pressure exerted by the height of solution in the tube that stops the net flow of solvent across the membrane is referred to as the osmotic pressure.
43. $\pi = MRT$ and/or $\pi V = nRT$
44. 0.00602 atm
45. 2.3×10^4 g/mol
46. Expected van't Hoff Factor = 4 (assuming complete ionization of the FeCl_3)
Observed van't Hoff Factor = 3.4 (as obtained from the equation $\pi = iMRT$)
47. If a pressure greater than the osmotic pressure is applied to the solution side, this will result in a net flow of solvent from the solution side to the pure solvent side. This process of reverse osmosis is one method of obtaining salt-free drinking water from seawater.
50. Not all reactions proceed at the same rate. There is no way to predict the reaction rate from the balanced equation. The only way to obtain the rate of a chemical reaction is from experiment.
51. Reaction rate has units of mol/L-sec or mol/L-min etc. To experimentally obtain reaction rate, measure variation in concentration of a reactant or product with time.
52. **Time Intervals:**
- | | 0-500 sec | 500-1000 sec | 1000-1500 sec |
|--|------------------|---------------------|----------------------|
| $-\Delta[\text{N}_2\text{O}_5]/\Delta t$ | 0.00296 M/sec | 0.00208 M/sec | 0.0015 M/sec |
| $\Delta[\text{NO}_2]/\Delta t$ | 0.00592 M/sec | 0.00416 M/sec | 0.0029 M/sec |
| $\Delta[\text{O}_2]/\Delta t$ | 0.00148 M/sec | 0.00104 M/sec | 0.00073 M/sec |
- Reaction rate is not constant and depends on amount of reactant such that (in general) as [Reactant] decreases, Rate of Rxn decreases.
- $-\Delta[\text{N}_2\text{O}_5]/\Delta t$ gives the average rate of disappearance of N_2O_5 over a long time interval.
 $-d[\text{N}_2\text{O}_5]/dt$ gives the instantaneous rate of disappearance of N_2O_5 at a specific time.
53. Rate of disappearance of $\text{O}_2 = 0.30$ M/sec
Rate of appearance of $\text{NO} = 0.24$ M/sec
Rate of appearance of $\text{H}_2\text{O} = 0.36$ M/sec
54. General Rate Law: $\text{Rate} = k[\text{A}]^m[\text{B}]^n$. The specific rate constant k depends only on temperature. The order of the reaction with respect to A is m th order; while, the order of the reaction with respect to B is n th order. The overall reaction order is $m + n$. The reaction orders can only be obtained from experiment and cannot be obtained from the coefficients in the net equation.
55. Reaction is second order in $[\text{NO}_2]$, zeroth order in $[\text{CO}]$ and second order overall. If $[\text{NO}_2]$ is doubled, the reaction rate will quadruple. If the $[\text{CO}]$ is halved, the reaction rate will remain unchanged. Units on k are $\text{M}^{-1}\text{sec}^{-1}$.
56. Reaction is second order in $[\text{NO}]$, first order in $[\text{O}_2]$ and third order overall. If $[\text{NO}]$ is tripled, the reaction rate will increase nine fold. If the $[\text{O}_2]$ is halved, the reaction rate will decrease by half. Units on k are $\text{M}^{-2}\text{sec}^{-1}$.
57. Reaction is first order in $[\text{SO}_2]$, $-1/2$ order in $[\text{SO}_3]$ and $1/2$ order overall. If $[\text{SO}_2]$ is doubled, the reaction rate will double. If $[\text{SO}_3]$ is doubled, the reaction rate will decrease to $(1/2)^{1/2}$ or 0.707 of its original value. Units on k are $\text{M}^{1/2}/\text{sec}$.
59. A. $\text{Rate} = k[\text{NOCl}]^2$
B. $k = 4.0 \times 10^{-8} \text{ M}^{-1}\text{sec}^{-1}$

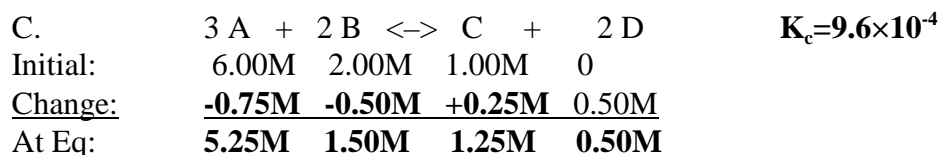
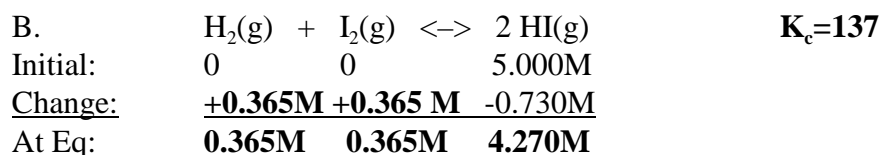
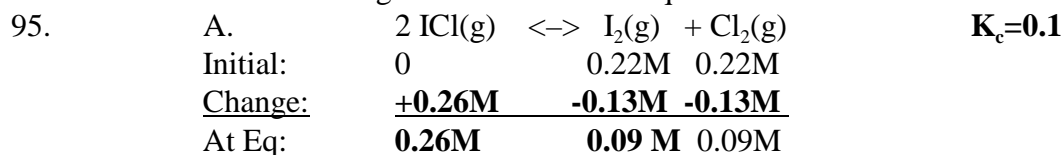
- C. Reaction rate will increase 16-fold.
60. A. Rate = $k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$
 B. $k=12 \text{ sec}^{-1}\text{M}^{-3}$
 C. 0.097 M/sec
62. A. [A] after 1 minute is 0.50 M; Half-life (τ)= 1.0×10^2 sec; it will take 2.0×10^2 sec for 75% of A to react; after three half-lives 0.094 M of A remains; the initial rate of the reaction is 0.0051 M/sec.
64. Reaction is second order in [HI] and Rate Law is: Rate = $k[\text{HI}]^2$; $k = 0.479 \text{ M}^{-1}\text{min}^{-1}$; $\tau=0.696$ min; it will take 2.8 min for 20% of the original amount of HI to remain.
66. Net Rxn: $2 \text{NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2$; Both steps are bimolecular; Rate = $k[\text{NO}_2][\text{O}_3]$; The NO_3 is an intermediate.
67. Net Rxn: $2 \text{O}_3 \rightarrow 3 \text{O}_2$; First elementary step is unimolecular while second is bimolecular; Rate = $k[\text{O}_3][\text{O}]$; The O is an intermediate.
68. Net Rxn: $2 \text{O}_3 \rightarrow 3 \text{O}_2$; First elementary step is unimolecular while second and third are bimolecular; the O and NO_2 are intermediates; the NO is a catalyst.
70. Activation Energy (E_A)= 1.66×10^5 J/mol; Pre-exponential factor (A) = $7.6\times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$; Specific rate constant (k) at 427 C = $0.031 \text{ M}^{-1}\text{sec}^{-1}$
71. Activation Energy (E_A)= 1.05×10^5 J/mol; Pre-exponential factor (A) = $8.49\times 10^{13} \text{ M}^{-1}\text{sec}^{-1}$; Specific rate constant (k) at 427 C = 0.17 sec^{-1}

CHEM 116-Dr. Babb's Sections

Answer Key to Exam II Lecture Problem Sheet

77. Numerical value of K depends only on T but does not depend on initial concentrations of reactants or products.
78. Since K_c for this reaction is less than 1 and $K_c = k_f/k_r$, then $k_r > k_f$. Since $K_c = [\text{Products}]/[\text{Reactants}]$ and for this reaction $K_c < 1$, then $[\text{Reactants}] > [\text{Products}]$.
79. Since K_c for this reaction is greater than 1 and $K_c = k_f/k_r$, then $k_f > k_r$. Since $K_c = [\text{Products}]/[\text{Reactants}]$ and for this reaction $K_c > 1$, then $[\text{Products}] > [\text{Reactants}]$.
80. When $K_c > 10^3$, then $[\text{Products}] \gg [\text{Reactants}]$ and reaction proceeds essentially 100% to completion.
When $K_c < 10^{-3}$, then $[\text{Reactants}] \gg [\text{Products}]$ and reaction proceeds hardly at all to completion.
When $10^{-3} < K_c < 10^3$, then $[\text{Products}] \sim [\text{Reactants}]$ and appreciable amounts (experimentally measurable quantities) of both reactants and products are present.
81. A. $K_c = [\text{NO}]^4[\text{H}_2\text{O}]^6/[\text{NH}_3]^4[\text{O}_2]^5$
B. $K_c = [\text{H}_2]^4/[\text{H}_2\text{O}]^4$
C. $K_c = [\text{CO}][\text{Cl}_2]/[\text{COCl}_2]$
D. $K_c = [\text{PCl}_5]/[\text{PCl}_3][\text{Cl}_2]$
E. $K_c = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3]$
F. $K_c = [\text{H}_2\text{O}]$
G. $K_c = [\text{CO}_2]$
82. Concentrations for pure solids, pure liquids and the solvent are not included in the equilibrium constant expression because these concentrations depend only on density and don't vary (i.e. are constant). These constant concentrations are already included into the numerical value of K.
83. A. 2.4×10^{-9}
B. 6.9×10^{25}
C. 2.0×10^4
D. 4.9×10^{-5}
85. A. $K_p = (p_{\text{SO}_3})^2/(p_{\text{SO}_2})^2(p_{\text{O}_2})$
B. $K_p = (p_{\text{NH}_3})^2/(p_{\text{H}_2})^3(p_{\text{N}_2})$
C. $K_p = (p_{\text{NO}})^4(p_{\text{H}_2\text{O}})^6/(p_{\text{NH}_3})^4(p_{\text{O}_2})^5$
86. 3.4
87. $K_p = K_c(\text{RT})^{\Delta n}$ or $K_c = K_p(\text{RT})^{-\Delta n}$
88. 4.03×10^{-4}
89. 0.58; Whenever $\Delta n_{\text{gas}} = 0$, then $K_c = K_p$.
90. Reaction quotient (Q_c) has same form as K_c except non-equilibrium or initial concentrations are used to calculate Q_c .
91. $Q_c = 6.25$ and $Q_c > K_c$. Thus this reaction is not at equilibrium and will proceed from right to left in order to reach equilibrium.
92. If $Q_c > K_c$, reaction proceeds from right to left in order to reach eq.
If $Q_c < K_c$, reaction proceeds from left to right in order to reach eq.
If $Q_c = K_c$, reaction is at equilibrium and will not react in a net way in either direction.
93. $Q_c = 0.202$ and $Q_c < K_c$. Thus this reaction is not at equilibrium and will proceed from left to right in order to reach equilibrium and more gaseous CO will be formed.

94. A. $Q_c=6.62 \times 10^{-4}$ and $Q_c > K_c$. Thus this reaction is not at equilibrium and will proceed from right to left in order to reach equilibrium.
 B. $Q_c=3.07 \times 10^{-4}$ and $Q_c = K_c$. Thus this reaction is at equilibrium and will not react in a net way in either direction.
 C. $Q_c=1.62 \times 10^{-5}$ and $Q_c < K_c$. Thus this reaction is not at equilibrium and will proceed from left to right in order to reach equilibrium.



96. $[\text{Cl}_2] = [\text{PCl}_3] = 0.22 \text{ M}$; $[\text{PCl}_5]=0.03 \text{ M}$

97. $1.12 \times 10^{-2} \text{ M}$

98. $p_{\text{NO}_2}=2.1 \text{ atm}$; $p_{\text{N}_2\text{O}_4}=18 \text{ atm}$

102. A. reaction proceeds from left to right in order to regain eq.
 B. reaction proceeds from right to left in order to regain eq.
 C. reaction proceeds from left to right in order to regain eq.
103. Addition of more solid BaSO_4 or BaO will have no effect on the eq. because concentrations of pure solids are not included in the eq. constant expression.
104. If total pressure is altered, the numerical value of K is not changed. The only factor influencing the value of K is temperature. However, a change in the total pressure does change the partial pressures of gaseous species and may remove the reaction from eq.
105. as P increases V decreases and reaction will proceed toward side of equation that occupies less volume. This means that reaction will proceed toward side of equation that has less moles of gas. In this instance, reaction will proceed toward the reactants in order to regain eq.
106. as P decreases due to V increase reaction will proceed toward side of equation that occupies more volume (i.e. toward side of equation with more moles of gas). However, in this case both sides of equation have same # moles of gas and thus occupy same volume. As a result, the eq. of this reaction is unaffected by changes in P due to V change.
107. as T increases, K_c decreases or as T decreases, K_c increases for an exothermic reaction.
108. as T increases, K_c increases or as T decreases, K_c decreases for an endothermic reaction.
109. as T increases, Heat increases so heat on the product side is increased and reaction will proceed from right to left in order to regain eq.
110. as T increases, Heat increases so heat on reactant side is increased and reaction will proceed from left to right in order to regain eq.

122. When $[\text{H}_3\text{O}^+] = 5. \times 10^{-2} \text{ M}$, then $[\text{OH}^-] = 2. \times 10^{-13} \text{ M}$. When $[\text{OH}^-] = 5. \times 10^{-5} \text{ M}$, then $[\text{H}_3\text{O}^+] = 2. \times 10^{-10} \text{ M}$.
123. $\text{pH} = -\log [\text{H}_3\text{O}^+]$; $\text{pOH} = -\log [\text{OH}^-]$; $\text{pK}_w = -\log K_w = -\log(1.0 \times 10^{-14}) = 14$;
 $\text{pH} + \text{pOH} = 14$
124. $\text{pH} > 7$ indicates a basic solution; $\text{pH} < 7$ indicates an acidic solution; $\text{pH} = 7$ indicates a neutral solution.
125. A. $\text{pH} = 5.17$ is an acidic solution;
 $\text{pOH} = 8.9$ has a solution $\text{pH} = 14 - 8.9 = 5.1$ and is an acidic solution.
 $\text{pH} = 7$ is a neutral solution.
- B. i. $\text{pH} = 6.5$ is an acidic solution.
 ii. $\text{pOH} = 5.5$ has a solution pH of 8.5 and is a basic solution.
 iii. $[\text{H}_3\text{O}^+] = 1 \times 10^{-9}$ is a basic solution since $[\text{H}_3\text{O}^+] < 1.0 \times 10^{-7} \text{ M}$ and $\text{pH} = 9.0$.
 iv. $[\text{OH}^-] = 1 \times 10^{-9}$ is an acidic solution since $[\text{OH}^-] < 1.0 \times 10^{-7} \text{ M}$ and $\text{pH} = 5.0$.
126. K_A = Acid Dissociation Constant; the higher the value of K_A , the stronger the acid; the lower the value of K_A , the weaker the acid.
 $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$ this eq. specified by K_A for HCl
 $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ this eq. specified by K_A for $\text{HC}_2\text{H}_3\text{O}_2$
127. K_B = Base Dissociation Constant; the higher the value of K_B , the stronger the base; the lower the value of K_B , the weaker the base.
 $\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ this eq. specified by K_B for NH_3
128. $[\text{H}_3\text{O}^+] = 0.25 \text{ M}$; $[\text{OH}^-] = 4.0 \times 10^{-14} \text{ M}$; $\text{pH} = 0.60$; $\text{pOH} = 13.40$
129. $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-12} \text{ M}$; $[\text{OH}^-] = 0.010 \text{ M}$; $\text{pH} = 12.00$; $\text{pOH} = 2.00$
130. $\text{pH} = 7.00$
131. $\text{pH} = 7.00$
132. $[\text{H}_3\text{O}^+] = 0.0030 \text{ M}$; $[\text{OH}^-] = 3.4 \times 10^{-12} \text{ M}$; $\text{pH} = 2.53$; $\text{pOH} = 11.47$;
 % Ionization HF = 12%
133. $K_A = 1.8 \times 10^{-4}$; % Dissociation of HCOOH = 2.4%
134. $[\text{H}_3\text{O}^+] = 2.7 \times 10^{-12} \text{ M}$; $[\text{OH}^-] = 0.0037 \text{ M}$; $\text{pH} = 11.57$; $\text{pOH} = 2.43$;
 % Ionization $\text{NH}_3 = 0.49\%$
135. A. $\text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ K_{A1}
 $\text{HSO}_3^-(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{SO}_3^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ K_{A2}
- B. $\text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ K_{A1}
 $\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ K_{A2}
 $\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{PO}_4^{3-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ K_{A3}
136. No, the pH of the resulting solution can be acidic, basic or neutral depending on the chemical identity of the salt.
137. The anion for the salt always comes from the acid; while, the cation for the salt always comes from the base.
138. NaCl is a neutral salt. NaCl is a strong electrolyte and dissolves and dissociates 100% as shown here: $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$. The Na^+ is a weak conjugate acid of the strong base NaOH. Therefore, Na^+ has no tendency to react with water (hydrolyze) to reform the original strong base. The Cl^- is the weak conjugate base of the strong acid HCl. Therefore, Cl^- has no tendency to react with water (hydrolyze) to reform the original strong acid. The pH of an aqueous solution of this type of salt (containing cation from strong base and anion from strong acid) will be the pH of pure water which is 7.

139. NH_4Cl is an acidic salt. NH_4Cl is a strong electrolyte and dissolves and dissociates 100% as shown here: $\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$. The Cl^- is the weak conjugate base of the strong acid HCl . Therefore, Cl^- has no tendency to react with water to reform the original strong acid. The NH_4^+ is the strong conjugate acid of the weak base NH_3 . Therefore, NH_4^+ has a tendency to react with water (hydrolyze) to reform the original weak base as shown here: $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$. During this reaction some H_3O^+ is produced resulting in a solution with an acidic pH ($\text{pH} < 7$).
140. KNO_2 is a basic salt. KNO_2 is a strong electrolyte and dissolves and dissociates 100% as shown here: $\text{KNO}_2(\text{s}) \rightarrow \text{K}^+(\text{aq}) + \text{NO}_2^-(\text{aq})$. The K^+ is a weak conjugate acid of the strong base KOH . Therefore, K^+ has no tendency to react with water (hydrolyze) to reform the original strong base. The NO_2^- is the strong conjugate base of the weak acid HNO_2 . Therefore, NO_2^- has a tendency to react with water (hydrolyze) to reform the original weak acid as shown here: $\text{NO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HNO}_2(\text{aq}) + \text{OH}^-(\text{aq})$. During this reaction some OH^- is produced resulting in a solution with a basic pH ($\text{pH} > 7$).
141. AlCl_3 is an acidic salt. AlCl_3 is a strong electrolyte and dissolves and dissociates 100% as shown here: $\text{AlCl}_3(\text{s}) \rightarrow \text{Al}^{+3}(\text{aq}) + 3 \text{Cl}^-(\text{aq})$. The Cl^- is the weak conjugate base of the strong acid HCl . Therefore, Cl^- has no tendency to react with water to reform the original strong acid. The Al^{+3} being a small, highly charged metal cation exists in solution as $\text{Al}(\text{H}_2\text{O})_6^{+3}(\text{aq})$. The association of the H_2O 's with the Al^{+3} tends to weaken the O-H bond in the H_2O 's making the waters surrounding the aluminum more acidic. Therefore, the $\text{Al}(\text{H}_2\text{O})_6^{+3}$ species has a tendency to react with water (hydrolyze) as an acid as shown here: $\text{Al}(\text{H}_2\text{O})_6^{+3}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Al}(\text{H}_2\text{O})_5\text{OH}^{+2}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$. During this reaction some H_3O^+ is produced resulting in a solutions with an acidic pH ($\text{pH} < 7$).
142. A. basic D. basic G. acidic
 B. acidic E. basic H. acidic
 C. neutral F. acidic
143. $K_A \times K_B = K_W$
144. NaF is a basic salt due to hydrolysis of F^- . $\text{pH} = 8.55$.
145. NH_4ClO_4 is an acidic salt due to hydrolysis of NH_4^+ . $\text{pH} = 4.69$.

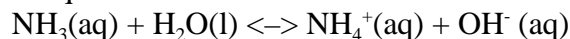
CHEM 116-Dr. Babb's Sections
Answer Key to Exam III Lecture Problem Sheet

146. In general, any factor that weakens the bond to hydrogen, makes the substance more acidic. For binary acids within the same group such as HCl, HF, HI, and HBr, the atom bonded to hydrogen (F, Cl, Br, I) becomes larger as proceed down the periodic table and this tends to weaken the bond to H. Thus, binary acids become more acidic as proceed from top to bottom with a column. Most acidic: $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$:Least acidic; Most acidic: $\text{H}_2\text{Te} > \text{H}_2\text{S} > \text{H}_2\text{O}$:Least acidic.
147. For binary acids within the same row such as CH_4 , NH_3 , H_2O , and HF, the atom the hydrogen is bonded to (C, N, O and F) becomes more electronegative as proceed across the row and this tends to weaken the bond to H. Thus these binary acids become more acidic as proceed from left to right within a row. Most acidic: $\text{HF} > \text{H}_2\text{O} > \text{NH}_3 > \text{CH}_4$:Least acidic.
148. In oxyacids, the H is always bonded to one of the oxygens. Any factor that weakens the O-H bond, makes the substance more acidic. Within an oxyacid series such as HClO, HClO_3 , HClO_2 and HClO_4 , as the number of oxygens bonded to the central atom increases, the oxidation number of the central atom increases causing a weakening of the O-H bond strength and an increase in the acidity. Most acidic: $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$.

For a series of oxyacids with the same number of oxygens but with different central atoms such as HOBr, HOCl, HOI, as the electronegativity of the central atom increases, the O-H bond strength weakens and the acidity increases. Most acidic: $\text{HOCl} > \text{HOBr} > \text{HOI}$:Least acidic.

149. Compare strengths of acids on reactant and product sides. The stronger acid has a greater tendency to give up its proton; therefore, the equilibrium will lie on the opposite side from the strongest acid.
- A. HBr is a stronger acid than HF. Eq lies on side opposite the HBr (i.e. on reactant side); thus, $[\text{Reactants}] > [\text{Products}]$ and $K < 1$.
- B. H_2O is a stronger acid than NH_3 . Eq lies on side opposite the H_2O (i.e. on product side); thus, $[\text{Products}] > [\text{Reactants}]$ and $K > 1$.
- C. HClO_2 is a stronger acid than HClO. Eq lies on side opposite the HClO_2 (i.e. on reactant side); thus, $[\text{Reactants}] > [\text{Products}]$ and $K < 1$.
- D. H_3O^+ is a stronger acid than H_2O . Eq. lies on side opposite the H_3O^+ (i.e. on the reactant side); thus, $[\text{Reactants}] > [\text{Products}]$ and $K < 1$.
- E. HBrO_3 is a stronger acid than HIO_3 . Eq. lies on side opposite the HBrO_3 (i.e. on the product side); thus, $[\text{Products}] > [\text{Reactants}]$ and $K > 1$.
154. As solid $\text{NaC}_2\text{H}_3\text{O}_2$ is added to 0.500 M $\text{HC}_2\text{H}_3\text{O}_2$, the $[\text{H}_3\text{O}^+]$ decreases and the pH increases. Why? Look at effect of addition of $\text{NaC}_2\text{H}_3\text{O}_2$, a strong electrolyte, on the acetic acid eq.
- $$\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$
- $$\text{NaC}_2\text{H}_3\text{O}_2(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$$
- As $\text{NaC}_2\text{H}_3\text{O}_2$ is added to an eq. mixture of 0.500 M $\text{HC}_2\text{H}_3\text{O}_2$, the common ion $\text{C}_2\text{H}_3\text{O}_2^-$ is added which shifts the acetic acid eq. to the left decreasing the $[\text{H}_3\text{O}^+]$ and increasing the pH.
- Addition of NaCl to an eq. mixture of 0.500 M $\text{HC}_2\text{H}_3\text{O}_2$ has no effect on the pH or acetic acid eq. because NaCl has no ion in common with the acetic acid eq.

155. As solid NH_4Cl is added to 0.500 M NH_3 , the $[\text{OH}^-]$ decreases, the $[\text{H}_3\text{O}^+]$ increases and the pH decreases. Why? Look at effect of addition of NH_4Cl , a strong electrolyte, on the ammonia eq.



As NH_4Cl is added to an eq. mixture of 0.500 M NH_3 , the common ion NH_4^+ is added which shifts the ammonia eq. to the left decreasing the $[\text{OH}^-]$ and decreasing the pH.

Addition of KNO_3 to an eq. mixture of 0.500 M NH_3 has no effect on the pH or ammonia eq. because KNO_3 has no ion in common with the ammonia eq.

156. For a 0.500 M $\text{HC}_2\text{H}_3\text{O}_2$ /0.250 M $\text{NaC}_2\text{H}_3\text{O}_2$: pH = 4.44 and % Ionization = 0.0072%.
For a 0.500 M $\text{HC}_2\text{H}_3\text{O}_2$: pH = 2.52 and % Ionization = 0.60%.
157. Buffer solution: A solution consisting of a weak acid and the conjugate base (or salt) of the weak acid. OR A solution consisting of a weak base and the conjugate acid (or salt) of the weak base.

Function of Buffer: Acts to maintain the pH of the solution at a relatively constant value even with the addition of strong base or strong acid.

If the following substances are mixed in equimolar amounts, will a buffer solution be formed?

- | | |
|---|---|
| A. HF and NaF; Yes | D. NH_3 and NH_4Cl ; Yes |
| B. $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2$; Yes | E. HCl and KCl; No |
| C. HCN and NaCN; Yes | F. NaOH and NaCl; No |
| | G. HF and NaOH; No |
| | H. NH_3 and HCl; No |

If equal volumes of the following solutions are mixed, will a buffer solution result?

- | | |
|--|--|
| A. 0.2 M HF and 0.1 M NaOH; Yes | |
| B. 0.2 M HF and 0.3 M NaOH; No | |
| C. 0.2 M HF and 0.2 M NaOH; No | |
| D. 0.2 M NaF and 0.1 M HCl; Yes | |
| E. 0.5 M NH_3 and 1.0 M HCl; No | |
| F. 0.2 M HCN and 0.2 M KOH; No | |
| G. 0.3 M HOCl and 0.15 M $\text{Ba}(\text{OH})_2$; No | |
| H. 0.3 M HOCl and 0.1 M $\text{Ba}(\text{OH})_2$; Yes | |
159. pH = 4.43
160. pH = 4.56
161. Henderson-Hasselbach equation: $\text{pH} = \text{pK}_A + \log[\text{base}]/[\text{acid}]$
162. When $[\text{Base}] = [\text{Acid}]$ then ratio $[\text{base}]/[\text{acid}] = 1$ and $\log(1) = 0$ so $\text{pH} = \text{pK}_A$. Thus, the pK_A is the midpoint of the buffer range.
163. pH = 3.13
164. If a buffer with a pH = 4.0 is needed in an experiment, then a buffer system with a pK_A value around 4.0 is needed.
- | | K_A | pK_A |
|---|-----------------------|---------------|
| A. $\text{HNO}_2/\text{NaNO}_2$ | 4.5×10^{-4} | 3.35 |
| B. $\text{HC}_2\text{H}_3\text{O}_2/\text{NaC}_2\text{H}_3\text{O}_2$ | 1.8×10^{-5} | 4.74 |
| C. $\text{HCOOH}/\text{NaCOOH}$ | 1.8×10^{-4} | 3.74 |
| D. $\text{C}_6\text{H}_5\text{COOH}/\text{NaC}_6\text{H}_5\text{COO}$ | 6.5×10^{-5} | 4.19 |
| E. HCN/NaCN | 4.9×10^{-10} | 9.31 |

F. $\text{NH}_3/\text{NH}_4\text{Cl}$ $K_B=1.8\times 10^{-5}$ 9.26

The best buffer system is that given in D because its pK_A value is closest to 4.0. To obtain a $\text{pH}=4.0$ using this buffer system, a concentration ratio of base:acid of 0.65 should be used. Therefore, if the $[\text{C}_6\text{H}_5\text{COOH}]$ is 1.0 M; the $[\text{NaC}_6\text{H}_5\text{COO}]$ should be 0.65 M.

165. $[\text{NH}_3]/[\text{NH}_4^+] = 1.7$
167. pH of original buffer solution = 5.04
 pH after addition of 0.0040 mol HCl = 4.80
 pH after addition of 0.0060 mol NaOH = 5.6
168. After addition of 0 mL of 0.25 M KOH : $\text{pH} = 0.30$
 After addition of 25 mL of 0.25 M KOH : $\text{pH}=0.9$ (prior to eq. pt.; excess strong acid present)
 After addition of 50 mL of 0.25 M KOH : $\text{pH} = 7$ (at eq. pt; only neutral salt present)
 After addition of 60 mL of 0.25 M KOH : $\text{pH} = 12.5$ (after eq. pt; excess strong base present)
 Volume of base needed to reach eq. pt = 50. mL
169. After addition of 0 mL of 0.20 M KOH : $\text{pH} = 2.23$
 After addition of 2.5 mL of 0.20 M KOH : $\text{pH} = 3.46$ ($1/2$ way to eq. pt; buffer present)
 After addition of 5.0 mL of 0.20 M KOH : $\text{pH} = 8.14$ (at eq. pt; only basic salt present)
 After addition of 6.0 mL of 0.20 M KOH : $\text{pH} = 12.1$ (after eq. pt; excess strong base present)
 Volume of base needed to reach eq. pt. = 5.0 mL
 pH $1/2$ way to eq. pt is equal to pK_A
170. After addition of 0 mL of 0.20 M HCl : $\text{pH} = 11.13$
 After addition of 5.0 mL of 0.20 M HCl : $\text{pH} = 9.26$ ($1/2$ way to eq. pt; buffer present)
 After addition of 10.0 mL of 0.20 M HCl : $\text{pH} = 5.22$ (at eq. pt; only acidic salt present)
 After addition of 15.0 mL of 0.20 M HCl : $\text{pH} = 1.54$ (after eq. pt; excess strong acid present)
 Volume of acid needed to reach eq. pt. = 10. mL
 pH $1/2$ way to eq. pt is equal to pK_A for NH_3
172. For phenolphthalein: color in acidic solution is colorless; color in basic solution is pink.
173. Phenolphthalein will change color around its $\text{pK}_{A,\text{In}}$ value which is 9.10. Phenolphthalein could be used in titration of strong acid with strong base since pH around eq. pt. changes from 4-10 with addition of 1 drop of base. Phenolphthalein could also be used in titration of weak acid with strong base since at eq. pt a basic salt with a basic pH is present. However, phenolphthalein could NOT be using in titration of a weak base with a strong acid since at eq. pt. an acidic salt with an acidic pH is present.
174. To answer find $\text{pK}_{A,\text{In}}$ for each indicator which gives pH around which indicator changes color. Phenolphthalein, $\text{pK}_A = 9.10$; methyl orange, $\text{pK}_A = 3.80$; bromothymol blue, $\text{pK}_A = 6.80$. Now decide the relative pH for each of the titrations in A-C.
- | | <u>Titration</u> | <u>Eq. Pt. Salt</u> | <u>pH at Eq. Pt.</u> | <u>Indicator</u> |
|----|------------------------------------|--------------------------|----------------------|--------------------|
| A. | HNO_3 with NH_3 | NH_4NO_3 | $\text{pH} < 7$ | methyl orange |
| B. | HNO_3 with KOH | KNO_3 | $\text{pH} = 7$ | bromothymol orange |
| C. | HClO_2 with NaOH | NaClO_2 | $\text{pH} > 7$ | phenolphthalein |
- NOTE: On the lecture problem sheet 174 C. should have had HClO_2 as the acid not HClO_3 .
177. $K_{\text{sp}} = 1.19\times 10^{-5}$
178. $K_{\text{sp}} = 2.11\times 10^{-33}$
179. Solubility: 7.3×10^{-7} M; 1.4×10^{-4} g/L
180. Solubility: 4.5×10^{-5} M; 1.6×10^{-2} g/L

181. $[\text{Ag}^+] = 2.9 \times 10^{-2} \text{ M}$; $[\text{SO}_4^{2-}] = 1.4 \times 10^{-2} \text{ M}$
182. Solubility in pure water: $3.6 \times 10^{-3} \text{ M}$
Solubility in 0.30 M KF: $2.0 \times 10^{-6} \text{ M}$
183. Both K_2SO_4 and BaCl_2 will decrease the solubility of BaSO_4 in water due to addition of common ion. Solubility in 0.10 M K_2SO_4 : $1.1 \times 10^{-9} \text{ M}$; Solubility in 0.25 M BaCl_2 : $4.4 \times 10^{-10} \text{ M}$; Solubility in pure water: $1.0 \times 10^{-5} \text{ M}$
184. Any salt that contains the conjugate base of a weak acid will have its solubility increased by addition of a strong acid (i.e. the salt will be more soluble at lower or acidic solution pH). Salts more soluble in acidic solution than in pure water are CaF_2 , MnS , and ZnCO_3 .
186. Any salt that is a metal hydroxide will have its solubility increased by addition of a strong acid (i.e. the salt will be more soluble at lower or acidic solution pH).
187. A. pH = 10.35
B. Solubility in pure water: $1.12 \times 10^{-4} \text{ M}$; Solubility in soln buffered at pH 8.00: 5.6 M.
188. Precipitate of MgCO_3 will form because $\text{IP} > \text{K}_{\text{sp}}$.
189. If $\text{IP} = \text{K}_{\text{sp}}$; no precipitate will form and the solution is saturated.
If $\text{IP} > \text{K}_{\text{sp}}$; a precipitate will form and the solution is supersaturated.
If $\text{IP} < \text{K}_{\text{sp}}$; a precipitate will not form and the solution is unsaturated.
190. Precipitate of Ag_2SO_4 will not form because $\text{IP} < \text{K}_{\text{sp}}$.
191. $[\text{Cl}^-] = 1.2 \times 10^{-7} \text{ M}$
192. To precipitate as much Hg_2^{+2} and Ag^+ as possible without precipitating Pb^{+2} need $[\text{Cl}^-] = 0.089 \text{ M}$. At this $[\text{Cl}^-]$, the $[\text{Hg}_2^{+2}]$ left in solution is $1.8 \times 10^{-16} \text{ M}$. Therefore, most of the Hg_2^{+2} has been precipitated.
193. A solution with a pH=0.52 will precipitate Pb^{+2} and Hg^{+2} .
A pH of slightly higher than 7.2 is needed to precipitate all of the Group III ions.
194. Yes, these two ions can be separated by adjusting the solution pH. To precipitate as much of the Cr^{+3} as possible without precipitating the Ni^{+2} the solution pH should be adjusted to 6.8.
195. Hg_2Br_2 (ppts. first): AgBr : CuBr : PbBr_2 (ppts. last)
196. Sn^{+2} will precipitate first.

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Answer Key to Exam IV Lecture Problem Sheet

199. First complex: $\text{Co}(\text{NH}_3)_6\text{Cl}_3 + 3 \text{AgNO}_3 \rightarrow \text{Co}(\text{NH}_3)_6^{+3} + 3 \text{AgCl}(\text{s})$; the three Cl^- are outside the coordination sphere since they act as any other ion in a precipitation reaction. The best way to designate the chemical formula of the first complex is as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$.
- Second complex: $\text{Co}(\text{NH}_3)_5\text{Cl}_3 + 2 \text{AgNO}_3 \rightarrow \text{Co}(\text{NH}_3)_5\text{Cl}^{+2} + 2 \text{AgCl}(\text{s})$; two of the three Cl^- are outside the coordination sphere since they act as any other ions in a precipitation reaction. The best way to designate the chemical formula of the second complex is as $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.
- Third complex: $\text{Co}(\text{NH}_3)_4\text{Cl}_3 + \text{AgNO}_3 \rightarrow \text{Co}(\text{NH}_3)_4\text{Cl}_2^+ + \text{AgCl}(\text{s})$; one of the three Cl^- is outside the coordination sphere since it acts as any other ion in a precipitation reaction. The best way to designate the chemical formula of the third complex is as $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$.
200. Complex IV would yield two moles of water/mol of complex when heated. Only in complex IV are two moles/molecules of water outside the coordination sphere and therefore weakly bound and easily lost during heating.
206. The best way to designate the first complex is $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$. This complex will yield two moles of AgCl /mol complex.
The best way to designate the second complex is $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$. This complex will yield two moles of AgBr /mol complex.
Ionization isomers are NOT possible for $\text{Na}[\text{Ag}(\text{CN})_2]$ because the ion outside the coordination sphere (the Na^+) can't act as a ligand and therefore, can't trade places with a ligand inside the coordination sphere.
207. For $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{+2}$, linkage isomers are possible since the monodentate ligand NO_2^- has two different donor ligand atoms, N and O. The ligand NO_2^- can either attach to the Co^{+3} through the N or through the O. The different colors of yellow and red for this complex are due to the NO_2^- attaching by N in one case and O in the other.
208. For $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, cis/trans geometric isomers are possible and the cis isomer is polar while the trans isomer is nonpolar. For $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$, fac/mer geometric isomers are possible and both isomers are polar. For $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2}$, geometric isomers are not possible.
209. For $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ (square planar), cis/trans geometric isomers are possible.
210. Geometric isomers are NOT possible when $\text{CN}=2$ and $\text{CN}=4$ (tetrahedral). Geometric isomers are only possible for $\text{CN}=6$ and $\text{CN}=4$ (square planar).
211. For $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{+3}$ cis/trans geometric isomers are possible. Optical isomers are possible for the cis form but not for the trans form.
212. For MX_3ABC , fac/mer geometric isomers are possible. Optical isomers are possible for the fac form but not for the mer form.
213. Optical isomers are only possible for tetrahedral complexes where all four species bonded to the central atom are different. Therefore, optical isomers are only possible for $[\text{MnClBrIF}]^{-2}$.
214. Bonding between ligand and metal cation is considered to be electrostatic, either ionic (if ligand is an anion) or ion-dipole (if ligand is neutral molecule).
215. Incoming ligands destabilize the metal cation d-orbitals causing the d-orbitals to increase in

energy. The d_{z^2} and $d_{x^2-y^2}$ (e_g) levels are destabilized more than the d_{xy} , d_{xz} and d_{yz} (t_{2g}) levels. The d_{z^2} and $d_{x^2-y^2}$ orbitals are destabilized the most since the incoming ligands are coming in pointing directly toward the lobes of these two orbitals.

218. Crystal field splitting in octahedral field (Δ_o) - difference in energy between e_g and t_{2g} levels.
 Weak field ligand - ligand that causes splitting between t_{2g} and e_g levels to be small.
 Strong field ligand - ligand that causes splitting between t_{2g} and e_g levels to be large.
 High spin complex - results when metal d-electrons singly occupy both t_{2g} and e_g levels before pairing; occurs when weak field ligands are present.
 Low spin complex - results when metal d-electrons singly occupy t_{2g} and then pair up in t_{2g} before singly occupying e_g levels; occurs when strong field ligands are present.

219. $CN^- > NO_2^- > en > NH_3 > OH^- > H_2O > F^- > Cl^- > Br^- > I^-$
 Strong field ligands result in low spin
 Weak field ligands result in high spin

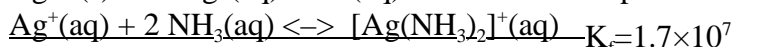
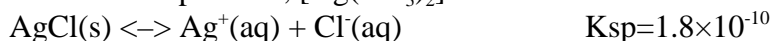
220.	<u>Complex</u>	<u>Metal cation</u>	<u>Ligand Type</u>	<u># unpaired e-</u>
A.	$[Cr(H_2O)_6]^{+3}$	$Cr^{+3} (d^3)$	weak field	three
B.	$[CoF_6]^{-3}$	$Co^{+3} (d^6)$	weak field	four
C.	$[Co(CN)_6]^{-3}$	$Co^{+3} (d^6)$	strong field	zero
D.	$[Ti(H_2O)_6]^{+3}$	$Ti^{+3} (d^1)$	weak field	one
E.	$[V(H_2O)_6]^{+3}$	$V^{+3} (d^2)$	weak field	two
F.	$[MnCl_6]^{-3}$	$Mn^{+3} (d^4)$	weak field	four
G.	$[FeF_6]^{-3}$	$Fe^{+3} (d^5)$	weak field	five
H.	$[Fe(CN)_6]^{-3}$	$Fe^{+3} (d^5)$	strong field	one
I.	$[Ni(NH_3)_6]^{+2}$	$Ni^{+2} (d^8)$	strong field	two
J.	$[Cr(CN)_6]^{-3}$	$Cr^{+3} (d^3)$	strong field	three
K.	$[Mn(CN)_6]^{-3}$	$Mn^{+3} (d^4)$	strong field	two
L.	$[Ni(H_2O)_6]^{+2}$	$Ni^{+2} (d^8)$	weak field	two

222. Colored compounds result when metal d-orbitals are partially filled with electrons.
 Colorless compounds result when metal d-orbitals are empty or totally filled with electrons.
- | | | |
|------------------------|----------------------------|---------------------------|
| NaBr colorless | $CuNO_3$ colorless | $Bi(NO_3)_3$ colorless |
| $AsCl_3$ colorless | $Cu(NO_3)_2$ colored | $Fe(C_2H_3O_2)_3$ colored |
| $HgCl_2$ colorless | KNO_3 colorless | $Pb(ClO_4)_2$ colorless |
| $Zn(NO_3)_2$ colorless | $[Ni(H_2O)_6]Cl_2$ colored | |
| $SbCl_3$ colorless | $Mn(NO_3)_3$ colored | |

223. Formation of a metal complex usually increases the solubility of a salt because K_f for formation of most metal complexes is $\gg 1$.

224. $Ag^+(aq) + 2 NH_3(aq) \leftrightarrow [Ag(NH_3)_2]^+(aq)$ $K_f = 1.7 \times 10^7$
 $Cu^{+2}(aq) + 4 NH_3(aq) \leftrightarrow [Cu(NH_3)_4]^{+2}(aq)$ $K_f = 1.1 \times 10^{13}$
 $Ag^+(aq) + 2 CN^-(aq) \leftrightarrow [Ag(CN)_2]^-(aq)$ $K_f = 1 \times 10^{21}$
 $Al^{+3}(aq) + 4 OH^-(aq) \leftrightarrow [Al(OH)_4]^-(aq)$ $K_f = 2.1 \times 10^{34}$
 $Cr^{+3}(aq) + 4 OH^-(aq) \leftrightarrow [Cr(OH)_4]^-(aq)$ $K_f = 8 \times 10^{29}$
 $Zn^{+2}(aq) + 4 OH^-(aq) \leftrightarrow [Zn(OH)_4]^{-2}(aq)$ $K_f = 2.8 \times 10^{15}$

225. $AgCl$ is more soluble in a solution of aqueous ammonia than in pure water due to formation of the very stable metal complex ion, $[Ag(NH_3)_2]^+$.



- Net Eq: $\text{AgCl}(s) + 2 \text{NH}_3(aq) \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+(aq) + \text{Cl}^-(aq) \quad K = K_{\text{sp}} \times K_f = 3.1 \times 10^{-3}$
226. Limited NH_3 : $\text{Cd}^{+2}(aq) + 2 \text{NH}_3(aq) + 2 \text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_2(s) + 2 \text{NH}_4^+(aq)$
 Excess NH_3 : $\text{Cd}(\text{OH})_2(s) + 4 \text{NH}_3(aq) \rightleftharpoons [\text{Cd}(\text{NH}_3)_4]^{+2}(aq) + 2 \text{OH}^-(aq)$
- Limited NH_3 : $\text{Zn}^{+2}(aq) + 2 \text{NH}_3(aq) + 2 \text{H}_2\text{O} \rightleftharpoons \text{Zn}(\text{OH})_2(s) + 2 \text{NH}_4^+(aq)$
 Excess NH_3 : $\text{Zn}(\text{OH})_2(s) + 4 \text{NH}_3(aq) \rightleftharpoons [\text{Zn}(\text{NH}_3)_4]^{+2}(aq) + 2 \text{OH}^-(aq)$
- Limited NH_3 : $\text{Cu}^{+2}(aq) + 2 \text{NH}_3(aq) + 2 \text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_2(s) + 2 \text{NH}_4^+(aq)$
 Excess NH_3 : $\text{Cu}(\text{OH})_2(s) + 4 \text{NH}_3(aq) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{+2}(aq) + 2 \text{OH}^-(aq)$
- Limited NH_3 : $\text{Ag}^+(aq) + \text{NH}_3(aq) + \text{H}_2\text{O} \rightleftharpoons \text{AgOH}(s) + \text{NH}_4^+(aq)$
 Excess NH_3 : $\text{AgOH}(s) + 2 \text{NH}_3(aq) \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+(aq) + \text{OH}^-(aq)$
- Limited NH_3 : $\text{Ni}^{+2}(aq) + 2 \text{NH}_3(aq) + 2 \text{H}_2\text{O} \rightleftharpoons \text{Ni}(\text{OH})_2(s) + 2 \text{NH}_4^+(aq)$
 Excess NH_3 : $\text{Ni}(\text{OH})_2(s) + 6 \text{NH}_3(aq) \rightleftharpoons [\text{Ni}(\text{NH}_3)_6]^{+2}(aq) + 2 \text{OH}^-(aq)$
227. Limited NaOH : $\text{Al}^{+3}(aq) + 3 \text{OH}^-(aq) \rightleftharpoons \text{Al}(\text{OH})_3(s)$
 Excess NaOH : $\text{Al}(\text{OH})_3(s) + \text{OH}^-(aq) \rightleftharpoons [\text{Al}(\text{OH})_4]^-(aq)$
- Limited NaOH : $\text{Zn}^{+2}(aq) + 2 \text{OH}^-(aq) \rightleftharpoons \text{Zn}(\text{OH})_2(s)$
 Excess NaOH : $\text{Zn}(\text{OH})_2(s) + 2 \text{OH}^-(aq) \rightleftharpoons [\text{Zn}(\text{OH})_4]^{-2}(aq)$
- Limited NaOH : $\text{Pb}^{+2}(aq) + 2 \text{OH}^-(aq) \rightleftharpoons \text{Pb}(\text{OH})_2(s)$
 Excess NaOH : $\text{Pb}(\text{OH})_2(s) + 2 \text{OH}^-(aq) \rightleftharpoons [\text{Pb}(\text{OH})_4]^{-2}(aq)$
- Limited NaOH : $\text{Cr}^{+3}(aq) + 3 \text{OH}^-(aq) \rightleftharpoons \text{Cr}(\text{OH})_3(s)$
 Excess NaOH : $\text{Cr}(\text{OH})_3(s) + \text{OH}^-(aq) \rightleftharpoons [\text{Cr}(\text{OH})_4]^-(aq)$
- Limited NaOH : $\text{Sn}^{+2}(aq) + 2 \text{OH}^-(aq) \rightleftharpoons \text{Sn}(\text{OH})_2(s)$
 Excess NaOH : $\text{Sn}(\text{OH})_2(s) + \text{OH}^-(aq) \rightleftharpoons [\text{Sn}(\text{OH})_3]^-(aq)$
228. Solubility of AgBr in $0.75 \text{ M NH}_3 = 2.3 \times 10^{-3} \text{ M}$.
 Solubility of AgBr in pure water $= 7.3 \times 10^{-7} \text{ M}$. Note that AgBr is 3200 times more soluble in 0.75 M NH_3 than in pure water due to formation of the very stable complex ion, $[\text{Ag}(\text{NH}_3)_2]^+$.
229. $[\text{Ni}^{+2}] = 7.6 \times 10^{-10} \text{ M}$; $[\text{NH}_3] = 0.70 \text{ M}$
230. Yes, AgCl will precipitate.
231. $\text{pH} = 10.1$
232. 1.2 M NH_3
234. $\Delta H = -$ (exothermic); this favors spontaneous process in forward direction but does not mean that overall the reaction is spontaneous.
 $\Delta H = +$ (endothermic); this favors nonspontaneous process in forward direction but does not mean that overall the reaction is nonspontaneous.
235. -904.56 kJ
236. Entropy = S = amount of randomness or disorder in a system. As amount of randomness/disorder increases, S increases. S does not have negative values but ΔS , which is the change in entropy during a process, can have negative values.

237. $\Delta S = +$; entropy is increasing and this favors spontaneous process in forward direction.
 $\Delta S = -$; entropy is decreasing and this favors nonspontaneous process in forward direction.

238. $S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$

- | | |
|-------------------|-------------------|
| A. $\Delta S = +$ | E. $\Delta S = -$ |
| B. $\Delta S = +$ | F. $\Delta S = +$ |
| C. $\Delta S = -$ | |
| D. $\Delta S = +$ | |

239. $4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 4 \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\text{g}); \Delta S = +$ because $n_{\text{gas}} = +1$
 $2 \text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g}) \rightarrow \text{N}_2\text{H}_4(\text{l}) + \text{O}_2(\text{g}); \Delta S = -$ because $n_{\text{gas}} = -2$

241. $+180.8 \text{ J/K}$

243. $\Delta G =$ Gibbs Free Energy; $\Delta G = \Delta H - T\Delta S$; $\Delta G = -$, spontaneous
 $\Delta G = +$, nonspontaneous

244. CASE#1: $\Delta H = +$; $\Delta S = +$; $\Delta G = \pm$, dependent on temperature

CASE#2: $\Delta H = +$; $\Delta S = -$ $\Delta G = +$, independent of temperature

CASE#3: $\Delta H = -$; $\Delta S = +$ $\Delta G = -$, independent of temperature

CASE#4: $\Delta H = -$; $\Delta S = -$ $\Delta G = \pm$, dependent on temperature

Crossover temperature: temperature at which reaction can be made to change spontaneity (i.e. spontaneous \rightarrow nonspontaneous or nonspontaneous \rightarrow spontaneous).

To calculate crossover temperature: $T = \Delta H / \Delta S$.

Crossover temperatures cannot be calculated for Cases #2 and #3 because these reactions are always either spontaneous or nonspontaneous at all temperatures.

245. $\Delta G^\circ(25 \text{ C}) = -1325.2 \text{ kJ}$; This reaction is spontaneous at 25 C. This reaction can be made nonspontaneous at any temperature above the crossover temperature of 9825 K.

246. A. -391.08 kJ ; spontaneous at 25 C

B. $+231.10 \text{ kJ}$; nonspontaneous at 25 C

247. $\Delta G^\circ =$ Gibbs free energy under standard conditions and at specified temperature.

Standard Conditions: all gases having partial pressure of 1 atm; all solutes having concentrations of 1 M; solids, liquids and gases in pure form.

$\Delta G =$ Gibbs free energy under nonstandard conditions and at specified temperature.

Equation relating ΔG° to ΔG : $\Delta G = \Delta G^\circ + RT \ln Q$

248. At 25 C: $\Delta G = +86.6 \text{ kJ}$; nonspontaneous

At 800 C: $\Delta G = -29.68 \text{ kJ}$; spontaneous

NOTE: To calculate ΔG at 25 C, ΔG° (at 25 C) could be calculated from standard Gibbs free energies of formation ΔG°_f since these are tabulated specifically at a temperature of 25 C. However to calculate ΔG at 800 C, ΔG° (at 800 C) had to be calculated from the equation $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$.

249. Derivation of equation relating ΔG° to K: $\Delta G = \Delta G^\circ + RT \ln Q$;

However at equilibrium the following conditions apply: 1. $\Delta G = 0$; 2. $Q = K$;

Therefore, the original equation becomes: $0 = \Delta G^\circ + RT \ln K$;

Rearranging for ΔG° : $\Delta G^\circ = -RT \ln K$;

Rearranging for K: $K = \exp(-\Delta G^\circ / RT)$

250. A. ΔG° (at 25 C) = -42 kJ/mol

B. Under the conditions given in Part B, the reaction is nonspontaneous in the forward direction. To determine this fact, either 1.) calculate $\Delta G = +5 \text{ kJ}$ under this set of nonstandard conditions OR 2.) calculate $Q = 2.0 \times 10^8$ and compare it to K.

251. $K(\text{at } 25\text{ C})=3.01\times 10^{-7}$; $K(\text{at } 200\text{ C})=0.15$
 NOTE: To calculate K at 200 C, ΔG° at 200 C must first be calculated from the equation $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$.
252. At 25 C, $\Delta G = -1388\text{ kJ}$; reaction is spontaneous
 At 750 C, $\Delta G = -1374\text{ kJ}$; reaction is spontaneous
253. A. At 25 C, $\Delta G^\circ = -407\text{ kJ}$ and $K = 2.2\times 10^{71}$; reaction is spontaneous under standard conditions.
 B. A temperature of 741 K (468 C) or above is needed to regenerate the P_4O_{10} . This temperature is the crossover temperature. At the crossover temperature the numerical value of K is 1.
 C. Yes, at 25 C the P_4O_{10} will spontaneously adsorb the water vapor. To determine this calculate $\Delta G = -351\text{ kJ}$ under this set of nonstandard conditions.
 NOTE: To calculate ΔG , Q must first be calculated. For this reaction, $Q = 1/(\text{p}_{\text{water}})^6$ where the p_{water} must be in units of atmospheres.
254. electrochemistry: study of interconversion between chemical and electrical energy
 electrochemical cell: cell that interconverts chemical and electrical energy
 galvanic cell: cell that converts chemical energy of a spontaneous chemical reaction to electrical energy (an electrical current is generated).
 electrolytic cell: cell that converts electrical energy to chemical energy (an electrical current is used to drive a non-spontaneous chemical reaction).
 Batteries are considered to be galvanic cells.
255. The solution turns blue indicating that Cu is oxidized to blue Cu(II) and at the same time Ag(I) is reduced to Ag(s).
 Net Ionic eqn: $\text{Cu}(\text{s}) + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}(\text{s})$.
 Oxidation Half-Rxn: $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}$
 Reduction Half-Rxn: $\text{Ag}^+ \rightarrow \text{Ag}(\text{s})$
256. No, a reaction between Ag(s) and Cu^{2+} would not occur. If the forward reaction between Cu(s) and Ag^+ is spontaneous; then, the reverse reaction between Ag(s) and Cu^{2+} is non-spontaneous.
257. A. electrode - conductor of electricity (usually made of metal)
 B. Anode - electrode at which oxidation occurs; Cathode - electrode at which reduction occurs.
 C. Electrons always flow from the anode to the cathode. By convention, the anode is given a (-) sign; while, the cathode is given a (+) sign.
 D. Salt bridge - used to keep the solutions in each half-cell electrically neutral. In anode compartment, as oxidation occurs positive ions are generated so negative ions flow out of salt bridge. In cathode compartment, as reduction occurs positive ions are lost so negative ions flow into the salt bridge.
258. $\text{Cu}(\text{s})|\text{Cu}^{2+}(1\text{ M})||\text{Ag}^+(1\text{ M})|\text{Ag}(\text{s})$
259. $\text{Pb}(\text{s})|\text{Pb}^{2+}(1\text{ M})|\text{F}_2(1\text{ atm})|\text{F}^-(1\text{ M})|\text{Pt}(\text{s})$
260. Net Cell Reaction: $\text{Sn}^{2+} + 2\text{Fe}^{3+} \rightarrow \text{Sn}^{4+} + 2\text{Fe}^{2+}$
 Pt on tin side is anode. Pt on iron side is cathode.
261. Net cell potential (E°_{cell}) is measured by placing a voltmeter in line and between the two half cells. $\Delta G^\circ = -nF E^\circ_{\text{cell}}$ where $n = \#$ mole of electrons transferred and $F = 96500\text{ C/mol e}^-$ (Faraday constant)