Chemistry 1B Homework
Chemistry: The Central Science, 14^{th} Edition

- Look over the Appendices to see what's there.
- Read pp. 1080-1085 in the back of the book. (This should be review for you, but you need to make sure you know it!)

Note: answers to the homework problems numbered in red are in the back of the book, on pages A-1 to A-30. Check your work using these answers, but do not ever copy the answers from the back of the book. If explanations are needed to answer the question, explain the answer **in your own words**. If a calculation is required, show your complete setup and work.

Any time a graph is needed as part of your homework, make sure to draw a full-page graph and follow the graphing guidelines. I recommend making graphs using a computer program, such as Microsoft Excel.

Homework assignments will cover one week’s worth of material and will be due on Thursdays. Each Thursday at the end of the lecture period, I will tell you how far to go on the homework assignment that will be due the following Thursday. (It can also be turned in the Monday after it’s officially due for full credit.)

Complete at least 80% of the problems on the homework assignment for full credit. Make note: it’s **not** a good idea to just skip the problems at the end of an assignment. These problems at the end are often very important! Make sure to practice all problem types so that you are prepared for anything on the quizzes and exams.

The first homework assignment will be assigned on Thursday, January 24 and will be due on Thursday, January 31. It will include some, but not all, of the problems from Chapter 14.

Problem numbers in parentheses are optional. Problem numbers that are underlined and any “additional problems” are especially important.

Chapter 14 Homework - Kinetics

These problems can be found on pp. 609-621 of the textbook.

Remember, any time a graph is needed as part of your homework, make sure to draw a **full-page graph** and follow the graphing guidelines.

2, 3, 6, 7, 8, 9, 11, 13, 15, 16, 17, <u>21</u>, 23bc, 25a, 27, 29, 31, 33, 35, 39, (41), 43, 45 (do this graphically), 47, 49, 51, (53), 55, 57, 59, 61, 63, 65, 67, 69, 71, 75, 95, 96, <u>110</u>, 112.

Chapter 15– Equilibrium

These problems can be found on pp. 656-663 of the textbook.
2, 13, 15, 17, 19, 21, 23, 25, 27, 31, 33, 35, 37, 41, 47, 51, 53, 55, 57, 59, 61, 63, 67, 74a, 79, 85, 90, 91.

Also, do:
"Gaseous Equilibrium Practice Problems" (handout)
"Practice Equilibrium Problems:" (handout)

Chapter 16– Acid-Base Equilibria

These problems can be found on pp. 708-715 of the textbook.
Problem numbers in parentheses are optional, but you should at least look at them and make sure you know how to do them.

1, 2, 15, (16), 17, 19, 21, 29ab, 30b, (31), (35 this one is tedious, but you should know how to do it), 41, 43abc, 45ab, (49), 51, 53, 57, 61, 63ac, 65 (calculate all ion concentrations), 69, 71, 73, 75bc, 77ab, 79a, 83, 85, 87, 89, 91, 95, 97, 12 (yes, #12, out of order but it makes more sense this way)

Additional problem:
Calculate the concentration of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, H_3O^+, and OH^- in a 0.0250 M solution of $H_3PO_{4\,(aq)}$. Determine the pH of the solution.

Chapter 17 part 1 - Buffers

These problems can be found on pp. 758 - 765 of the textbook.
Problems in parentheses are optional.

13, 15ab, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41b, (43), 45, 46, 47(a)b
3, 4, 5, 6, 7

Problems on handouts that are part of this HW assignment:

"Practice Problems: Acid-Base, Buffers" handout # 1, 2, 3, 4, 5, 6, 7, 8
"More Acid/Base Buffer Problems" handout #(2, 3, 4, 5), 6, (7) for extra practice

Chapter 17 Part 2 – Solubility

These problems can be found on pp. 758-765 of the textbook.
49, 51, 53, 55, 58, 59, 63, 65, 67, 69, 73, 75, 100, 8, 9, 12.

Additional Problems for Chapter 17 part 2: (see below for K_{sp}, K_a values to use)

1. Calculate the overall equilibrium constants for each of the following reactions and comment on the physical meaning of each of the results.

a. $Cu(OH)_{2\,(s)} + 2\ H_3O^+_{(aq)} \leftrightarrows Cu^{2+}_{(aq)} + 4\ H_2O_{(l)}$

b. $CaF_{2\,(s)} + 2\ H_3O^+_{(aq)} \leftrightarrows Ca^{2+}_{(aq)} + 2\ HF_{(aq)} + 2\ H_2O_{(l)}$

c. $Ba_3(PO_4)_{2\,(s)} + 6\ H_3O^+_{(aq)} \leftrightarrows 3\ Ba^{2+}_{(aq)} + 2\ H_3PO_{4\,(aq)} + 6\ H_2O_{(l)}$

2. If a solution contains 0.0020 M Al^{3+} and 0.0020 M Cd^{2+} and if OH^- is slowly added to the solution, the ions can be separated from each other.

a. If OH^- is slowly added to this solution, which compound will start to precipitate first? What is the $[OH^-]$ when the first compound starts to precipitate?

b. What is the concentration of the ion that precipitates first at the point at which the second ion starts to precipitate? What percent of the original ion remains in the solution? Would you consider this a complete separation?

3. If 20.0 mL of 0.10 M $Na_3PO_{4\,(aq)}$ is mixed with 40.0 mL of 0.10 M $Ba(NO_3)_{2\,(aq)}$, calculate the concentration of all ions once this system has reached equilibrium. K_{sp} of $Ba_3(PO_4)_{2\,(s)} = 3.4 \times 10^{-23}$.

4. a. Calculate the solubility (in g/L) of CuCl in 1.5 M $NaCN_{(aq)}$.
K_{sp} of CuCl = 1.9×10^{-7}, K_f of $Cu(CN)_2^-{}_{(aq)} = 1.0 \times 10^{16}$.

b. Calculate the solubility (in g/L) of CuCl in 1.5 M $NaCl_{(aq)}$.

5. When a light blue solution containing copper (II) ions is mixed with a solution of ammonia, a deep blue complex forms that has the formula $Cu(NH_3)_4^{2+}{}_{(aq)}$.

If 10.0 mL of 0.20 M $Cu(NO_3)_{2\,(aq)}$ is mixed with 80.0 mL of 2.0 M NH_3, calculate the concentration of Cu^{2+} remaining at equilibrium.

K_f of $Cu(NH_3)_4^{2+}{}_{(aq)}$ is 6.8×10^{12}.

6. Calculate the solubility (in g/L) of AgSCN in 2.5 M $NH_{3\,(aq)}$.

K_{sp} of AgSCN = 1.0×10^{-12}, K_f of $Ag(NH_3)_2^+{}_{(aq)} = 1.6 \times 10^7$

K_{sp} values:

$Cu(OH)_2$ 1.1×10^{-15}, CaF_2 3.45×10^{-11}, Ba_3PO_4 3.4×10^{-23},
$Al(OH)_3$ 4.6×10^{-33}, $Cd(OH)_2$ 7.2×10^{-15}

K_a values:

HF 6.3×10^{-4} H_3PO_4 $K_{a1} = 6.9 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, $K_{a3} = 4.8 \times 10^{-13}$

Answers:

1a. 1.1×10^{13}, 1b. 8.7×10^{-5}, 1c. 8.1×10^{20}, 2a. $Al(OH)_3$ when $[OH^-] = 1.3 \times 10^{-10}$ M, 2b. $[Al^{3+}] = 6.7 \times 10^{-16}$ M, 3.4×10^{-11} remains, complete. 3. $[Na^+] = 0.10$ M, $[NO_3^-] = 0.13$ M, $[Ba^{2+}] = 0.017$ M, $[PO_4^{3-}] = 2.7 \times 10^{-9}$M. 4a. 74 g/L, 4b. 1.3×10^{-5} g/L.
5. $[Cu^{2+}] = 4.0 \times 10^{-16}$ M. 6. 1.6 g/L

Chapter 19 – Thermodynamics

These problems can be found on pp. 838-847 of the textbook. Problems in parentheses are optional. Make sure to do the underlined problems.

4, 10, 16, 23, 31, 33, 35, 39, 41, 42, 43, 45, 47, 51ad, 55, 57c, 59a(c), 61, 63 (would each reaction be spontaneous at all temperatures, at no temperatures, at high temperatures, or at low temperatures? Explain.), 67, <u>69, 71,</u> (experimental bp of benzene is 80°C), 73, 75, 77, 79ab, 81, 83, (96a, 97).

Additional Problems for Chapter 19

(See below for thermodynamic values to use for these problems.)

1. a. The reaction: $CO_{2\,(g)} + H_{2\,(g)} \rightarrow CO_{(g)} + H_2O_{(g)}$
is nonspontaneous at room temperature but becomes spontaneous at a much higher temperature. What can you conclude from this about the signs of ΔH° and ΔS°? Explain your reasoning.
b. Using thermodynamic data, estimate the temperature at which this reaction becomes spontaneous under standard conditions. What are standard conditions for this reaction?
c. At 500°C, is this reaction spontaneous or nonspontaneous under standard conditions?
d. At 500°C, if $P_{CO_2} = P_{H_2} = P_{CO} = 2.0$ atm, what pressure of H_2O is needed to make this reaction spontaneous?

2. Use thermodynamic data to determine the solubility of:
a. $AgBr_{(s)}$ at 40.°C
b. $Na_2CO_{3\,(s)}$ at 75°C

3. a. Using thermodynamic data, estimate the normal boiling point of ethanol, C_2H_5OH. Hint: the normal boiling point is the bp at 1.00 atm pressure. A liquid will boil when its vapor pressure equals the atmospheric pressure (or the external pressure, if it is not open to the atmosphere).
b. The actual boiling point of ethanol is 78 °C. Compare this with your result in part a.

4. Estimate the vapor pressure of ethanol at 37 °C, using thermodynamic data. Express your result in mmHg.

5. Estimate the temperature at which the vapor presure of ethanol equals 500. mmHg. What is the approximate boiling point of ethanol at an external pressure of 500. mmHg?

6. The following reaction is nonspontaneous at room temperature.
$COCl_{2\,(g)} \rightarrow CO_{(g)} + Cl_{2\,(g)}$
To make it a spontaneous reaction, would you raise or lower the temperature? Explain, without doing a calculation. (Hint: what is the sign of ΔS?)

7. The normal melting point of benzene is 5.5°C. For the melting of benzene at 1 atm, what is the sign of:
a. $\Delta H°$? b. $\Delta S°$? c. $\Delta G°$ at 5.5°C? d. $\Delta G°$ at 0.0°C? e. $\Delta G°$ at 25.0°C?

8. Sodium carbonate, an important chemical used in the production of glass, is made from sodium hydrogen carbonate by the reaction:
$2\ NaHCO_{3\,(s)} \rightarrow Na_2CO_{3\,(s)} + CO_{2\,(g)} + H_2O_{(g)}$
At 30. °C, $K_P = 1.66 \times 10^{-5}$ and at 100 °C, $K_P = 0.231$.
Estimate $\Delta H°$ and $\Delta S°$ for the above reaction from this data.

Thermodynamic Properties of Substances at 25°C

Substance	$\Delta H°_f$, kJ/mol	$\Delta G°_f$, kJ/mol	S°, J/K•mol
$AgBr_{(s)}$	-100.4	-96.90	107
$Ag^+_{(aq)}$	105.6	77.11	72.68
$Br^-_{(aq)}$	-121.6	-104.0	82.4
$Na_2CO_{3\,(s)}$	-1131	-1044	135.0
$Na^+_{(aq)}$	-240.1	-261.9	59.0
$CO_3^{2-}{}_{(aq)}$	-677.1	-527.8	-56.9

Answers to additional problems, Ch. 19:

1. a. ΔH and ΔS must both be +
b. 695°C
c. nonspontaneous
d. 0.6 atm
2. a. 3×10^{-4} g/L (no sig figs)
b. 70 g/L (no sig figs)
3. a. 76°C
b. close
4. 100 mmHg
5. 66°C, 66°C
6. Raise temp
7. a. + b. + c. 0 d. + e. -
8. $\Delta H° = 128$ kJ/mol, $\Delta S° = 330$ J/mol•K

Chapter 20 - Electrochemistry

These problems can be found on pp. 890-899 of the textbook.
Problem numbers in parentheses are optional. Make sure to do the additional problems.
4, 13, 14, (15), ~~25, 29~~, (31), 33, ~~35, 37~~, 39, 41, 43, 44, 45, 47, 49, 51 (do one or two, not all three), 53, 55ac, 59, 61, 63, 65, 67, 69, 73, 81, 82, 84, 85, 89, 91, 93, 97 (do two, not all four parts), 98, 99ad
6, 7

Additional Problems for Chapter 20:

1. What is E_{cell} of the following voltaic cell?
$Cu_{(s)}$ | Cu^{2+} (0.10 M) || Ag_2CrO_4 (sat'd aq) | $Ag_{(s)}$
Hint: What is $[Ag^+]$ in saturated $Ag_2CrO_{4\ (aq)}$? $K_{sp} = 1.1 \times 10^{-12}$

2. What $[Cl^-]$ should be maintained in the anode half-cell if the following voltaic cell is to have E_{cell} = 0.100 V? K_{sp} AgCl = 1.8×10^{-10}
Ag, $AgCl_{(s)}$ | Cl^- (x M) || Cu^{2+} (0.25 M) | $Cu_{(s)}$

3. For the cell: $Ag_{(s)}$ | Ag^+ (aq, sat'd AgBr) || Ag^+ (aq, 0.100 M) | $Ag_{(s)}$
the measured value of E is 0.305 V.
a. What is $[Ag^+]$ in saturated AgBr?
b. What is the experimental value of K_{sp} for AgBr?
c. Sketch the cell.

4. Determine the potential for the following cell:
Pb | $PbSO_{4\ (s)}$, SO_4^{2-} (0.10 M) || H_3O^+ (1.0 M) | $H_{2\ (g)}$ (1.0 atm) | $Pt_{(s)}$
The anode is essentially a lead electrode, Pb|$Pb^{2+}_{(aq)}$. However, the anode solution is saturated with lead sulfate, so that the lead ion concentration is determined by the solubility product of $PbSO_4$ ($K_{sp} = 1.7 \times 10^{-8}$).

5. An electrode is prepared by dipping a silver strip into a solution saturated with silver thiocyanate ($AgSCN_{(s)}$) and containing 0.10 M SCN^-. The E_{cell} of the voltaic cell constructed by connecting this, as the cathode, to the standard hydrogen half-cell as the anode is 0.45 V. What is the solubility product of AgSCN?

Answers to additional problems for Chapter 20:

1. 0.257 V
2. 1 M Cl^-
3. a. 7.0×10^{-7} M, b. $K_{sp} = 5.0 \times 10^{-13}$
4. 0.326 V
5. $K_{sp} = 10^{-7}$

Chapter 21 – Nuclear Chemistry

These problems can be found on pp. 935-941 of the textbook.

1, 2, 6, 8, 9, 11, 13, 15, 19, 21, 23, 27, 29, 33, 34, 35, 36, 37, 39, 41, 42, 43, 45, 47, 49, 51, 53, 55, 56, 59, 60, 61, 62, 68, 72, 74, 76, 78, 85

For #78, you could approach it in two different ways. Try one!
a. Graph activity in dpm vs. time and estimate the half-life from the graph. (How long does it take for the activity to fall to ½ of its initial value?)
b. Graph the natural log (ln) of the activity vs. time. Since it's first order, this should be a straight line with a slope of –k. Calculate the slope, then get k, then calculate $t_{1/2}$.

Chapter 23– Transition Metals and Coordination Chemistry

These problems can be found on pp. 1022-1029 of the textbook.

15, 17, 22, 23, 24ab, 25, 27, 29, 31, 33, 35, 37, 39, (40), 41, 42, 43, 45, 47, 49, 51, 52, 53, 55, 56, 57, 59, 60, 61, 63, 65, 66, 70, 71, 76, 80, 82, 99.
Then: #2, 3, 4, 5, 8, 9, 10.

Chapter 24– Organic Chemistry

These problems can be found on pp. 1072-1079 of the textbook.

1, 2, 4, 7, 8, 9, 10, 15, 16, 17, 21, 22, 23 (draw the condensed structural formula for each), 27, 28, 29abde, 31, 32, 33, 43, 44, 45, 47, 48, 53, 57, 81, 83a, 85, 87.

Also - do the separate organic chemistry problem set (the green handout).