Name: ______________________

AP Chemistry Big Idea Review

Background
The AP Chemistry curriculum is based on 6 Big Ideas and many Learning Objectives associated with each Big Idea. This review will cover all of the Big Ideas and Learning Objectives (LO).

Directions
Working as directed by your teacher, complete all of the questions in the packet. Be sure to write out your thinking and justifications for all of your answers to the questions in the packet. For all multiple choice questions, describe why the correct answer is correct and why the other answers are not correct. For the calculations, show all work and label all units.

When you are finished with the packet, identify which Big Ideas and Learning Objectives are your strengths and which are your weaknesses. This will help you focus your studies for the remainder of your review time before the exam. Good Luck.

Big Idea 6: Equilibrium

Any bond or intermolecular attraction that can be formed can be broken. These two processes are in dynamic competition, sensitive to initial conditions and external perturbation. When all else fails, equilibrium is products over reactants, raised to the coefficients for aqueous solutions and gases.

LO 6.1 The student is able to, given a set of experimental observations regarding physical, chemical, biological, or environmental processes that are reversible, construct an explanation that connects the observations to the reversibility of the underlying chemical reactions or processes.

Example:

According to the graph on the left, how many hours does it take for the reaction to reach equilibrium?
LO 6.2 The student can, given a manipulation of a chemical reaction or set of reactions (e.g., reversal of reaction or addition of two reactions), determine the effects of that manipulation on \( Q \) or \( K \).

Example:
At 1000K, \( K_p = 1.85 \) for the reaction:
\[
\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{SO}_3(g)
\]

a) What is the value of \( K_p \) for the reaction, \( \text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \)?

b) What is the value of \( K_p \) for the reaction, \( 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \)?

LO 6.3 The student can connect kinetics to equilibrium by using reasoning about equilibrium, such as LeChatelier's principle, to infer the relative rates of the forward and reverse reactions.

Example:

<table>
<thead>
<tr>
<th>A concentration–time graph for this system is shown below.</th>
<th>What event occurred at time ( t ) to cause the change in equilibrium concentrations?</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Graph" /></td>
<td>A. The pressure was decreased at a constant temperature.</td>
</tr>
<tr>
<td></td>
<td>B. The temperature was increased at a constant volume.</td>
</tr>
<tr>
<td></td>
<td>C. A catalyst was added at a constant temperature and volume.</td>
</tr>
<tr>
<td></td>
<td>D. Additional NO gas was added at a constant volume and temperature</td>
</tr>
</tbody>
</table>

LO 6.4 The student can, given a set of initial conditions (concentrations or partial pressures) and the equilibrium constant, \( K \), use the tendency of \( Q \) to approach \( K \) to predict and justify the prediction as to whether the reaction will proceed toward products or reactants as equilibrium is approached.

Example:
At 100\(^{\circ}\)C the equilibrium constant for the reaction \( \text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g) \) has the value \( K_c = 2.19 \times 10^{-10} \). Are the following mixtures of \( \text{COCl}_2, \text{CO}, \) and \( \text{Cl}_2 \) at 100\(^{\circ}\)C at equilibrium? If not, indicate the direction that the reaction must proceed in order to achieve equilibrium:

a) \([\text{COCl}_2] = 2.00 \times 10^{-3} \text{ M}, [\text{CO}] = 3.3 \times 10^{-6} \text{ M}, [\text{Cl}_2] = 6.62 \times 10^{-6} \text{ M}\)

b) \([\text{COCl}_2] = 4.50 \times 10^{-2} \text{ M}, [\text{CO}] = 1.1 \times 10^{-7} \text{ M}, [\text{Cl}_2] = 2.25 \times 10^{-6} \text{ M}\)

c) \([\text{COCl}_2] = 0.0100 \text{ M}, [\text{CO}] = 1.48 \times 10^{-6} \text{ M}, [\text{Cl}_2] = 1.48 \times 10^{-6} \text{ M}\)

LO 6.5 The student can, given data (tabular, graphical, etc.) from which the state of a system at equilibrium can be obtained, calculate the equilibrium constant, \( K \).

The equilibrium \( 2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g) \) is established at 500 K. An equilibrium mixture of the three gases has partial pressures of 0.095 atm, 0.171 atm, and 0.28 atm for NO, Cl\(_2\), and NOCl, respectively. Calculate the \( K_p \) for the reaction at 500 K.
LO 6.6 The student can, given a set of initial conditions (concentrations or partial pressures) and the equilibrium constant, \( K \), use stoichiometric relationships and the law of mass action (\( Q \) equals \( K \) at equilibrium) to determine qualitatively and/or quantitatively the conditions at equilibrium for a system involving a single reversible reaction.

Example:
For the equilibrium: \( \text{Br}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{BrCl}(g) \) at 400 K, \( K_c = 7.0 \). If 0.25 mol of \( \text{Br}_2 \) and 0.25 mol of \( \text{Cl}_2 \) are introduced into a 1.0-L container at 400 K, what will be the equilibrium concentrations of \( \text{Br}_2 \), \( \text{Cl}_2 \), and \( \text{BrCl} \)?

LO 6.7 The student is able, for a reversible reaction that has a large or small \( K \), to determine which chemical species will have very large versus very small concentrations at equilibrium.

Example:
\( \text{CoO}(s) + \text{CO}(g) \rightleftharpoons \text{Co}(s) + \text{CO}_2(g) \quad K_c = 490 \)
For the reaction listed above, if 1 mole of each reactant were placed in a reaction vessel and allowed to reach equilibrium, which gas would be in higher concentration, \( \text{CO}_2 \) or \( \text{CO} \)? Justify.

LO 6.8 The student is able to use LeChatelier’s principle to predict the direction of the shift resulting from various possible stresses on a system at chemical equilibrium.

Consider the following equilibrium, for which \( \Delta H < 0 \)
\[
2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)
\]
How will each of the following changes affect the equilibrium mixture of all three gases?

a) \( \text{O}_2(g) \) is added to the system
b) The reaction mixture is heated
c) \( \text{SO}_3(g) \) is removed

d) Products removed

e) Reactants removed

LO 6.9 The student is able to use LeChatelier’s principle to design a set of conditions that will optimize a desired outcome, such as product yield.

Consider \( 4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightleftharpoons 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g) \quad \Delta H = -904.4 \text{ kJ} \).

Design an experiment that would maximize the yield of \( \text{NO}(g) \). Be sure to include the amounts of products and reactants, the general temperature, and ways to exploit LeChatlier’s principle to maximize the yield.

LO 6.10 The student is able to connect LeChatelier’s principle to the comparison of \( Q \) to \( K \) by explaining the effects of the stress on \( Q \) and \( K \).

Example:

To the right, is a representation of a reaction at equilibrium. Describe how the following changes would affect the system and how equilibrium would shift to counter those changes:

a) Reactants added
b) Products added
c) Reactants removed
d) Products removed
LO 6.11 The student can generate or use a particulate representation of an acid (strong or weak or polyprotic) and a strong base to explain the species that will have large versus small concentrations at equilibrium.

In the boxes below, draw a representation of a strong acid (HX) dissolving in water on the left and a weak acid (HY) dissolving in water on the right. Be sure to include water molecules in your representation.

<table>
<thead>
<tr>
<th>HX = Strong acid</th>
<th>HY = Weak acid</th>
</tr>
</thead>
</table>

LO 6.12 The student can reason about the distinction between strong and weak acid solutions with similar values of pH, including the percent ionization of the acids, the concentrations needed to achieve the same pH, and the amount of base needed to reach the equivalence point in a titration.

Example:
You have 50 mL of a 0.010 M solution of HCl
Calculate the pH and the amount of 0.010 M NaOH that would be needed to titrate this acid to equivalence.

You also have 50 mL of a 1.0 M solution of HNO₂
Calculate the pH and the amount of 1.0 M NaOH that would be needed to titrate this acid to equivalence.

LO 6.13 The student can interpret titration data for monoprotic or polyprotic acids involving titration of a weak or strong acid by a strong base (or a weak or strong base by a strong acid) to determine the concentration of the titrant and the \( pK_a \) for a weak acid, or the \( pK_b \) for a weak base.

Example:
Using the titration data on the right, calculate the \( pK_a \) for the weak acid, knowing its pH at equivalence.
LO 6.14 The student can, based on the dependence of $K_w$ on temperature, reason that neutrality requires $[H^+]= [OH^-]$ as opposed to requiring pH = 7, including especially the applications to biological systems. Example: The dissociation of water is endothermic. When heat is added to water, what happens to the value of K? How does adding heat affect the pH of neutral water?

LO 6.15 The student can identify a given solution as containing a mixture of strong acids and/or bases and calculate or estimate the pH (and concentrations of all chemical species) in the resulting solution. Example: A sample of ammonia (NH$_3$) is titrated with a strong acid to the equivalence point. Write the net ionic equation for the reaction and describe whether the pH at the equivalence point is less than, greater than, or equal to 7.

LO 6.16 The student can identify a given solution as being the solution of a monoprotic weak acid or base (including salts in which one ion is a weak acid or base), calculate the pH and concentration of all species in the solution, and/or infer the relative strengths of the weak acids or bases from given equilibrium concentrations. Example: An unknown salt is either NaF, NaCl, NaOCl. When 0.050 mol of the salt dissolved in water to form 0.500 L of solution, the pH of the solution is 8.08. What is the identity of the salt?

LO 6.17 The student can, given an arbitrary mixture of weak and strong acids and bases (including polyprotic systems), determine which species will react strongly with one another (i.e., with $K > 1$) and what species will be present in large concentrations at equilibrium. Example: A beaker contains a mixture of 1 mol of nitric acid (HNO$_3$) and 1 mol of nitrous acid (HNO$_2$). Write the net ionic equation for the reaction when 0.5 mol of NaOH is added to the beaker. The Ka for nitrous acid is 7.2 x 10$^{-4}$.

LO 6.18 The student can design a buffer solution with a target pH and buffer capacity by selecting an appropriate conjugate acid-base pair and estimating the concentrations needed to achieve the desired capacity. Example: You need to prepare a buffer with a pH of 6.0 and you have access to the following acids and their sodium salts. Describe how you would prepare the buffer with the target pH.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Conjugate Base</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorous acid</td>
<td>HClO$_3$</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>HC$_2$H$_3$O$_2$</td>
<td>$1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Hydrocyanic acid</td>
<td>HCN</td>
<td>$6.2 \times 10^{-10}$</td>
</tr>
</tbody>
</table>
LO 6.19 The student can relate the predominant form of a chemical species involving a labile proton (i.e., protonated/deprotonated form of a weak acid) to the pH of a solution and the $pK_a$ associated with the labile proton.

Example:

A weak acid, acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$), is titrated with NaOH in the graph on the right. At 10mL of NaOH added to the acid, what is the chemical in highest concentration in the solution?

a) $\text{HC}_2\text{H}_3\text{O}_2$
b) $\text{NaOH}$
c) $\text{C}_2\text{H}_3\text{O}_2^-$
d) $\text{H}^+$

LO 6.20 The student can identify a solution as being a buffer solution and explain the buffer mechanism in terms of the reactions that would occur on addition of acid or base.

Example:

A solution is prepared with 1.0 M acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) and sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$).

a) Write the net ionic equation for the reaction when a drop of NaOH is added to the solution.
b) Write the net ionic equation for the reaction when a drop of HCl is added to the solution.

LO 6.21 The student can predict the solubility of a salt, or rank the solubility of salts, given the relevant $K_{sp}$ values.

Example:

Which of the salts on the right is most soluble in water?

<table>
<thead>
<tr>
<th>Salt</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgBr</td>
<td>$7.70 \times 10^{-13}$</td>
</tr>
<tr>
<td>BaSO$_4$</td>
<td>$1.08 \times 10^{-10}$</td>
</tr>
<tr>
<td>FeS</td>
<td>$3.70 \times 10^{-19}$</td>
</tr>
</tbody>
</table>

LO 6.22 The student can interpret data regarding solubility of salts to determine, or rank, the relevant $K_{sp}$ values.

A student measures the solubility of a set of salts in water. Salt A has a molar solubility of 0.15 mol/L and Salt B is $3.5 \times 10^{-3}$ mol/L. Which salt has a higher $K_{sp}$ value?
**LO 6.23** The student can interpret data regarding the relative solubility of salts in terms of factors (common ions, pH) that influence the solubility.

Example:
Would a sample of barium sulfate (BaSO₄, Ksp = 1.08 x 10⁻¹⁰) be more soluble in a solution of pure water or sulfuric acid? Justify your response.

**LO 6.24** The student can analyze the enthalpic and entropic changes associated with the dissolution of a salt, using particulate level interactions and representations.

Example:
Solubility of KNO₃ in water at various temperatures:

<table>
<thead>
<tr>
<th>Temperature°C</th>
<th>Solubility g</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>20</td>
<td>33</td>
</tr>
<tr>
<td>30</td>
<td>48</td>
</tr>
<tr>
<td>40</td>
<td>65</td>
</tr>
<tr>
<td>50</td>
<td>84</td>
</tr>
</tbody>
</table>

Based on the data above, is the dissolution of KNO₃ an exothermic or endothermic process? Justify your response.

**LO 6.25** The student is able to express the equilibrium constant in terms of ΔG° and RT and use this relationship to estimate the magnitude of K and, consequently, the thermodynamic favorability of the process.

Consider the following reaction:

\[ \text{NO}_2 (g) + \text{N}_2\text{O} (g) \rightarrow 3 \text{NO} (g) \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH°₁ (kJ)</th>
<th>ΔS° (J/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂ (g)</td>
<td>33.84</td>
<td>240.45</td>
</tr>
<tr>
<td>N₂O (g)</td>
<td>81.6</td>
<td>220.0</td>
</tr>
<tr>
<td>NO (g)</td>
<td>90.37</td>
<td>210.62</td>
</tr>
</tbody>
</table>

Calculate the value of ΔG° for the reaction
Calculate the value of K for the reaction
Which is favored in the reaction, reactants or products? Justify your response.