1. Consider this reaction at equilibrium:

\[
\text{CO(g)} + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)
\]

Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance:

a) \(\text{COCl}_2\) is added to the reaction mixture.
b) \(\text{Cl}_2\) is added to the reaction mixture.
c) \(\text{COCl}_2\) is removed from the reaction mixture.

Le-Chatelier’s principle states that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium. If a chemical reaction is at equilibrium and experiences a change in pressure, temperature, or concentration of products or reactants, the equilibrium shifts in the opposite direction to offset the change.

a) \(\text{COCl}_2\) is added to the reaction mixture ---» back ward reaction (towards left)
b) \(\text{Cl}_2\) is added to the reaction mixture —» forward reaction (towards right)
c) \(\text{COCl}_2\) is removed from the reaction mixture ---» forward reaction (towards right)

2. Calculate the pH of the following:

a) 0.0030 M solution of HCl

\[
\text{pH} = -\log (\text{H}^+) = -\log (0.0030) = 2.52
\]

b) 0.30 M solution of HCN (Hint: use attached table!)

HCN is a weak acid = do an ICE chart.

<table>
<thead>
<tr>
<th></th>
<th>HCN</th>
<th>H⁺</th>
<th>CN⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.30 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[\text{Ka} = 6.17 \times 10^{-10} \Rightarrow \text{Ka is very small} \Rightarrow \text{use "x is small approximation" but check to see if it’s valid in the end.}\]

\[
x^2 / (0.30 - x) = \text{Ka}
\]

\[
x^2 / (0.30) = \text{Ka}
\]

\[
x^2 / (0.30) = 6.2 \times 10^{-10}
\]

\[
x = 1.36 \times 10^{-5}
\]

\[
[H^+] = 1.36 \times 10^{-5}
\]

\[
\text{pH} = -\log(1.36 \times 10^{-5}) = 4.87
\]

Check to see if approximation is valid:

\[
\text{% ionization} = ((\text{H}_3\text{O}^+) / [\text{HCN}]) \times 100% = (1.36 \times 10^{-5} \text{ M} / 0.30) \times 100% = 4.5 \times 10^{-3} \% < 5.0\%
\]
3. What is the concentration of OH\(^-\) ions in an aqueous solution whose hydrogen ion (H\(^+\)) concentration is 0.5 M?

\[
[\text{OH}^-][\text{H}^+] = 1.0 \times 10^{-14}
\]

\[
[\text{OH}^-] = 1.0 \times 10^{-14}
\]

\[
[\text{OH}^-] = 2.0 \times 10^{-14} \text{ M}
\]

4. The OH\(^-\) ion concentration of a blood sample is 3.0 \times 10^{-7} M. What is the pH of the blood?

\[
\text{pOH} = -\log [\text{OH}^-] = -\log (3.0 \times 10^{-7}) = 6.52
\]

\[
\text{pH} = 14 - \text{pOH} = 7.45
\]

5. What is the pH of a 1.4 \times 10^{-2} M Ba(OH)\(_2\) solution (strong base)?

\[
\text{Ba(OH)}_2 \rightarrow \text{Ba}^{2+} + 2\text{OH}^-;
\]

When you have a 1.4 \times 10^{-2} M solution of Ba(OH)\(_2\), \([\text{OH}^-] = (2)(1.4 \times 10^{-2} \text{ M}) = 0.028 \text{ M}

\[
\text{pOH} = -\log(0.028) = 1.55
\]

\[
\text{pH} = 14 - 1.55 = 12.45
\]

6. Buffers comprise weak acids and weak bases. They can be prepared in several ways. Which of the following mixtures are likely to be buffer solutions when mixed?

a) 0.1M KNO\(_3\) and 0.1M HNO\(_3\) (strong acid + conj base)

b) 0.2M HCl and 0.1M NH\(_3\) (strong acid + weak acid)

c) 0.1M NaNO\(_2\) and 0.1M HNO\(_2\) (weak acid + conj base)

d) 0.1M HCl and 0.2M NH\(_3\) (strong acid weak base and 0.2M is enough to dissolve 0.1M)

e) 0.1M HCl and 0.1M NH\(_3\) (strong acid weak base but 0.1 is not enough to dissolve 0.1M)

7. If a small amount of a strong acid is added to a buffer made up of a weak acid (HA) and the sodium salt of its conjugate base (NaA), the pH of the buffer solution does not change applicably because:

a) The strong acid reacts with A\(^-\) to give H\(_2\)A\(^+\)

b) The strong acid reacts with HA to give H\(_2\)A\(^+\)

c) The strong acid reacts with A\(^-\) to give HA

d) The Ka of HA is increased

e) no reaction occurs!
8. You want to prepare a buffer solution of formic acid (HCOOH) and sodium formate.

a) If you have 0.150 M formic acid, what concentration of sodium formate (NaHCOO\(^{-}\)) do you need to make a pH = 4.00 buffer?

\[
pH = pK_a + \log \left( \frac{[HCOO^{-}]}{[HCOOH]} \right)
\]

\[
4.00 = 3.75 + \log \left( \frac{x}{0.150} \right)
\]

\[
x = 0.267 \text{ M} \text{ NaHCOO}
\]

b) HCl (0.0050 mol) is added to 1.0 L of the buffer from (a) without changing the volume. What is the new pH?

HCOO\(^{-}\) (aq) + HCl (aq) ⇌ HCOOH (aq) + Cl\(^{-}\) (aq)

<table>
<thead>
<tr>
<th></th>
<th>HCOO(^{-})</th>
<th>HCl</th>
<th>HCOOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Addition</td>
<td>0.267</td>
<td>0</td>
<td>0.150</td>
</tr>
<tr>
<td>Addition</td>
<td>0.267 - 0.0050</td>
<td>+ 0.0050</td>
<td>0.150 + 0.0050</td>
</tr>
<tr>
<td>After Addition</td>
<td>0.262</td>
<td>0</td>
<td>0.155</td>
</tr>
</tbody>
</table>

\[
pH = pK_a + \log \left( \frac{\text{base}}{\text{acid}} \right)
\]

\[
pH = 3.75 + \log \left( \frac{0.262}{0.155} \right) = 3.98
\]

c) 10 mL of 0.0050 KOH is added to 1.0 L of the buffer from (a). What is the new pH?

HCOOH (aq) + KOH (aq) ⇌ HCOO\(^{-}\) (aq) + H\(_2\)O (l)

<table>
<thead>
<tr>
<th></th>
<th>HCOOH</th>
<th>KOH</th>
<th>HCOO(^{-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Addition</td>
<td>0.150</td>
<td>0</td>
<td>0.267</td>
</tr>
<tr>
<td>Addition</td>
<td>0.150 - (5.0 \times 10^{-5})</td>
<td>+ 5.0 \times 10^{-5}</td>
<td>0.150 + (5.0 \times 10^{-5})</td>
</tr>
<tr>
<td>After Addition</td>
<td>0.14995</td>
<td>0</td>
<td>0.26705</td>
</tr>
</tbody>
</table>

\[
[HCOOH] = \text{mol / L} = 0.14995 \text{ mol / 1.01 L} = 0.2644 \text{ M}
\]

\[
[HCOO^{-}] = \text{mol / L} = 0.26705 \text{ mol / 1.01 L} = 0.1485 \text{ M}
\]

\[
pH = 3.75 + \log \left( \frac{0.2644}{0.1485} \right) = 4.00
\]
9. A buffer contains equal amounts of weak acid and its conjugate base and has a pH of 5.25. Which is a reasonable value of buffer pH after the addition of a small amount of acid?
   a) 4.15
   b) 5.15
   c) 5.35
   d) 6.35

10. For the titration of 25.0 mL of 0.150 LiOH with 0.200M HNO₃, calculate the following
   a. initial pH
   b. the pH at 9.38 mL added acid
   c. the pH at 18.75 mL added acid
   d. the pH at 25.0 mL added acid
11. Calculate the pH of a buffer solution that is 0.060 M in methanoic acid (HCO$_2$H) and 0.180 M in sodium methanoate (NaCO$_2$H). For methanoic acid, the Ka is $1.8 \times 10^{-4}$.

**Use Henderson-Hasselbalch Approach:**

$$\text{pH} = \text{p}K_a + \log \left( \frac{\text{base}}{\text{acid}} \right)$$

**NaCO$_2$H = base, HCO$_2$H = acid**

$$\text{pH} = -\log (1.8 \times 10^{-4}) + \log \left( \frac{0.180}{0.060} \right)$$

$$\text{pH} = 3.74 + 0.477 = 4.22$$

12. What is the molar solubility of Mg(OH)$_2$?

a. in pure water

**in pure water**

$$\text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq)$$

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$1.2 \times 10^{-11} = (s)(2s)^2$$

$$1.2 \times 10^{-11} = 4s^2$$

$$s = \sqrt[4]{\frac{1.2 \times 10^{-11}}{4}}$$

$$s = 1.4 \times 10^{-4.5}$$
b) in a solution containing 0.364 M NaOH?

\[ \text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^- \]

\[ \text{Ksp} = [\text{Mg}^{2+}] [\text{OH}^-]^2 \]

\[ \text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^- \]

\[ \text{Ksp} = 5.0 \times 10^{-12} \] (5 is small)

\[ S = \frac{\text{Ksp}}{0.1329} = \frac{5.0 \times 10^{-12}}{0.1329} = 3.76 \times 10^{-11} \text{ M} \]

The calculated value of S is indeed small compared to 0.364 M, so the S is small approximation is valid.

13. If 2.00 mL of 0.200M NaOH are added to 1.00L of 0.100 M CaCl2 will precipitation occur?

The ions present in solution are Na+, OH-, Ca2+, Cl-. NaCl (Ca(OH)2)

The only possible precipitate is Ca(OH)2 (solubility rules)

\[ Q = \frac{[\text{Ca}^{2+}] [\text{OH}^-]^2}{\text{Ksp}} \]

\[ [\text{OH}^-] = 0.001 \text{ mol} / 1.002 \text{ L} = 3.99 \times 10^{-4} \text{ M} \]

\[ [\text{Ca}^{2+}] = 0.1 \text{ mol} / 1.002 \text{ L} = 0.098 \times 10^{-3} \text{ M} \]

\[ Q = \frac{(0.001)^2 (3.99 \times 10^{-4})^2}{5.0 \times 10^{-12}} = 1.589 \times 10^{-8} \]

Since \( Q < \text{Ksp} \), no precipitation will occur.

14. You mix a 150.0 mL sample of a solution that is \( 4.7 \times 10^{-4} \) M in Cu(NO3)2 with a 286.0 mL sample of a solution that is 0.40 M in NH3. After the solution reaches equilibrium,
14. You mix a 150.0 mL sample of a solution that is $4.7 \times 10^{-4}$ M in Cu(NO$_3$)$_2$ with a 286.0 mL sample of a solution that is 0.40 M in NH$_3$. After the solution reaches equilibrium, what concentration of Cu$^{2+}$(aq) remains?
15. Consider the following redox reaction:
\[ \text{Cd(s)} + 2\text{AgCl(s)} \rightarrow \text{CdCl}_2(\text{aq}) + 2\text{Ag(s)} \]

a. What is the oxidizing agent? AgCl
b. What substance is being oxidized? Cd

16. Balance the following reaction equations, identify the oxidizing and reducing agents, and identify substances that are oxidized and reduced.

a) \[ \text{Cu (s)} + \text{NO}_3^- (\text{aq}) \rightarrow \text{Cu}^{2+} (\text{aq}) + \text{NO} (\text{g}) \] (in acidic solution)

b) \[ \text{CN}^- (\text{aq}) + \text{MnO}_4^- (\text{aq}) \rightarrow \text{CNO}^- (\text{aq}) + \text{MnO}_2 (\text{s}) \] (in basic solution)