1. What would be the pH of a solution prepared by dissolving 120.1 g of CH₃COOH and 82 g of NaCH₃COO in 1 L of water? Acetic acid has a $K_a$ of $1.8 \times 10^{-5}$.

   1. 5.05
   2. 4.78
   3. 4.12
   4. 4.44  Correct

   Explanation:

   $120.1 \text{ g CH}_3\text{COOH} \times \frac{1 \text{ mol}}{60.05 \text{ g}} = 2 \text{ mol CH}_3\text{COOH}$

   $82 \text{ g of NaCH}_3\text{COO} \times \frac{1 \text{ mol}}{82.03 \text{ g}} = 1 \text{ mol NaCH}_3\text{COO}$

   For a buffer composed of a weak acid and its conjugate base,

   $[H^+] = K_a (C_a/C_b) = 1.8 \times 10^{-5} (2/1) = 3.6 \times 10^{-5}$

   pH = 4.44

   Note, it is adequate to use the moles of HA and A⁻ in place of their final concentrations.

2. Which of the following pairs of solutions would not result in a buffer upon mixing?

   1. 100 mL of 10 mM NaOH & 80 mL of 20 mM NH₄Cl
   2. 20 mL of 0.3 M NaF & 12 mL of 0.4 M HCl
   3. 0.4 L of 10 mM HClO₃ & 0.5 L of 8 mM C₆H₅NH₂  Correct
   4. 2 L of 1.35 M Ba(OH)₂ & 3 L of 2 M CHOOH

   Explanation: A buffer prepared by a neutralization reaction requires a weak acid mixed with less strong base or a weak base mixed with less strong acid. The only pair of solutions which fails to satisfy this constraint is 0.4 L of 10 mM HClO₃ and 0.5 L of 8 mM C₆H₅NH₂.

3. Consider the following acids and their provided $pK_a$s. Rank them in terms of increasing strength of their conjugate bases.

   CH₃COOH  $pK_a = 4.75$
   CH₃CHOHCOOH  $pK_a = 3.85$
   CHOOH  $pK_a = 3.74$
   CH₃CH₂COOH  $pK_a = 4.88$

   1. CHOOH < CH₃CHOHCOOH < CH₃COOH < CH₃CH₂COOH  Correct
   2. CH₃CH₂COOH < CHOOH < CH₃CHOHCOOH < CH₃COOH
   3. CH₃COOH < CH₃CH₂COOH < CHOOH < CH₃CHOHCOOH
   4. CH₃CHOHCOOH < CH₃COOH < CH₃CH₂COOH < CHOOH

   Explanation: The strength of an acid's conjugate base is directly proportional to the $pK_a$ of the acid.

4. Which of the following buffers could absorb the greatest amount of strong base before being exhausted?

   1. 45 mL of 2 mM N₂H₅Cl, 4 mM N₂H₄
   2. 3.2 L of 0.4 M HClO, 0.5 NaClO  Correct
   3. 2 L of 9 mM HF, 7 mM NaF
   4. 0.3 L of 0.4 M NH₄Cl, 0.6 M NH₃
   5. 20 mL of 5 M CHOOH, 4 M NaCHOO

   Explanation: Any strong base added to a buffer will react with and be neutralized by the weak acid species that is present. The buffer with the greatest amount of weak acid is 3.2 L of 0.4 M HClO, 0.5 NaClO.

5. If one added 200 mL of 6 M HCl to 1 L of a buffer composed 4.2 M CH₃COOH and 6.6 M NaCH₃COO, what would be the resulting pH? The $K_a$ of CH₃COOH is $1.8 \times 10^{-5}$.

   1. 5.3
2. 4.9
3. 5.1
4. 4.7  Correct
Explanation: The general reaction that takes place is $A^- + H^+ \rightarrow HA$. Initial amounts of each reactant are 6.6, 1.2 and 4.2 moles respectively. After the reaction goes to completion, the equilibrium concentrations are 5.4, 0 and 5.4 respectively. There is no need to calculate the final concentrations. For a buffer composed of a weak acid and its conjugate base, 

$$[H^+] = K_a(C_a/C_b) = 1.8 \times 10^{-5}(5.4/5.4) = 1.8 \times 10^{-5}$$

$pH = 4.7$

6. How many buffer regions and equivalence points would be visible on the titration curve of a weak tetraprotic acid?

1. 3, 1
2. 3, 4
3. 1, 4
4. 4, 1  
5. 4, 4  Correct
Explanation: Each ionizable proton will produce one buffer region and one equivalence point.

7. A 100 mL sample of 0.1 M $H_3PO_4$ is titrated with 0.2 M NaOH. What is the pH of the solution after 100 mL of NaOH has been added? Phosphoric acid has $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$ and $K_{a3} = 2.1 \times 10^{-13}$.

1. 4.10
2. 8.51
3. 4.67
4. 7.40
5. 9.94  Correct
Explanation: $0.1 \text{ M } H_3PO_4 \times 100 \text{ mL} = 0.01 \text{ moles } H_3PO_4$
$0.2 \text{ M } NaOH \times 100 \text{ mL} = 0.02 \text{ moles } OH^-$

Two equivalents of OH$^-$ have been added, and the solution will be at the second equivalence point, composed primarily of the amphoteric species $HPO_4^{2-}$.

$$[H^+] = (K_{ax} \cdot K_{ay})^{1/2} = (6.2 \times 10^{-8} \cdot 2.1 \times 10^{-13})^{1/2} = 1.14 \times 10^{-10}$$

$pH = 9.94$

8. What will be the pH at the first equivalence point of a titration of 0.2 M $H_2SO_4$ with 0.2 M NaOH? The $K_a$ for $HSO_4^-$ is $2 \times 10^{-2}$.

1. 1.45  Correct
2. 1.35
3. 7.00
4. not enough information
Explanation: At its first equivalence point, the predominant species of this titration will be $HSO_4^-$. Because the analyte and titrant are equimolar, the $[HSO_4^-]$ will be half of $C_a$, or 0.1 M. This is not an amphoteric solution because $HSO_4^-$ cannot function as a base. Because the $K_a$ of $HSO_4^-$ is so large, a full solution is required.

<table>
<thead>
<tr>
<th>R</th>
<th>$HSO_4^-$</th>
<th>$H^+$</th>
<th>$SO_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>- x</td>
<td>+ x</td>
<td>+ x</td>
</tr>
<tr>
<td>E</td>
<td>0.1 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

$$K_a = 2 \times 10^{-2} = (x)(x)/(0.1 - x)$$

$$x^2 + 2 \times 10^{-2}x - 2 \times 10^{-3} = 0$$
9. All of the salts below have the same approximate molar solubility except for one. Which is it?
   1. TlBr \( K_{sp} = 4.00 \times 10^{-6} \)
   2. PbI₂ \( K_{sp} = 7.47 \times 10^{-9} \)
   3. AgSCN \( K_{sp} = 1.16 \times 10^{-12} \) Correct
   4. CsIO₄ \( K_{sp} = 5.16 \times 10^{-6} \)

Explanation: Silver thiocyanate is a salt composed of one cation and one anion and thus its molar solubility is approximately equal to the square root of its \( K_{sp} \). The best approximation is therefore \((10^{-12})^{1/2} = 10^{-6}\).

10. The \( K_{sp} \) of MgNH₄PO₄ at 25 °C is \( 2.5 \times 10^{-13} \). What is its molar solubility at this temperature? (Hint: do the RICE diagram for this one.)
   1. \( 3.2 \times 10^{-4} \)
   2. \( 4.0 \times 10^{-5} \)
   3. \( 6.3 \times 10^{-5} \) Correct
   4. \( 1.2 \times 10^{-3} \)

Explanation: MgNH₄PO₄ will dissolve into Mg²⁺, NH₄⁺, and PO₄³⁻. Each will be produced in equal proportions and so \( K_{sp} = x^3 = 2.5 \times 10^{-13} \).

11. What would be the molar solubility of Sn(OH)₂ (\( K_{sp} = 10^{-26} \)) in pH 13 NaOH solution?
   1. \( 1 \times 10^{-24} \) Correct
   2. \( 4 \times 10^{-24} \)
   3. \( 1 \times 10^{-28} \)
   4. \( 4 \times 10^{-28} \)
   5. not enough information

Explanation: [OH⁻] = 0.1 M
molar solubility = \( (K_{sp}/[OH^-]^2) = [10^{-26}/(10^{-1})^2] = 10^{-24} \)

12. Consider the table below. Which anion would be the best for separating Pb²⁺ from Ca²⁺? Which would be the worst?

<table>
<thead>
<tr>
<th>( K_{sp} ) values</th>
<th>( C_2O_4^{2-} )</th>
<th>( CO_3^{2-} )</th>
<th>( SO_4^{2-} )</th>
<th>( IO_3^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb²⁺</td>
<td>2.74 × 10⁻¹¹</td>
<td>3.3 × 10⁻¹⁴</td>
<td>1.6 × 10⁻⁸</td>
<td>1.2 × 10⁻¹³</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2.57 × 10⁻⁹</td>
<td>8.7 × 10⁻⁹</td>
<td>4.93 × 10⁻⁵</td>
<td>6.44 × 10⁻⁷</td>
</tr>
</tbody>
</table>

1. \( C_2O_4^{2-} \) & \( SO_4^{2-} \)
2. \( IO_3^- \) & \( SO_4^{2-} \)
3. \( CO_3^{2-} \) & \( IO_3^- \)
4. \( IO_3^- \) & \( C_2O_4^- \) Correct
5. \( CO_3^{2-} \) & \( C_2O_4^- \)

Explanation: The \( K_{sp} \) values for \( IO_3^- \) are farthest apart and the values for \( C_2O_4^- \) are closest together.

13. A student used the equation \([H^+] = (K_a \cdot C_a)^{1/2}\) to calculate \([H^+]\) and got a value of 0.4 M. The actual value was determined experimentally to be 0.35 M. Which of the following are possible explanations for this discrepancy?
   I. \( K_a \) was too small
   II. \( K_a \) was too large
   III. \( C_a \) was too small
   1. I only
   2. II only Correct
3. III only
4. I & II
5. I & III
6. II & III
7. none

Explanation: If $K_a$ had been too small, the equation $[H^+] = (K_a \cdot C_a)^{1/2}$ would result in a small number for the proton concentration. Likewise, if $C_a$ has been too small. If $K_a$ was too large, however, our assumption that percent ionization is small is false and we will overestimate the proton concentration - just as the student did.

14. For a solution of $H_3PO_4$, addition of $Na_2HPO_4$ will increase the concentration of which of the following species?
   I. $H_3PO_4$
   II. $H_2PO_4^-$
   III. $PO_4^{3-}$

1. I only
2. II only
3. III only
4. I & II
5. I & III
6. II & III
7. I, II and III  Correct

Explanation: Because all of the variously protonated species of $H_3PO_4$ are in equilibrium with each other, addition of any species will increase the concentration of all species.

15. Determine the pH of a 5 M solution of $Na_2HPO_4$. Assume $H_3PO_4$ has a $pK_{a1}$ of 2.1, a $pK_{a2}$ of 7.2 and a $pK_{a3}$ of 12.7.

1. 9.95  Correct
2. 4.65
3. 7.4
4. not enough information

Explanation: $H_2PO_4^-$ is amphiprotic, and the pH is consequently the average of the $pK_a$ values according to the equation $pH = 0.5(pK_{ax} + pK_{ay})$.

16. Write a mass balance for carbon for a solution that initially contains $H_2CO_3$.

1. $C_{H_2CO_3} = [HCO_3^-] + [CO_3^{2-}]$
2. $C_{H_2CO_3} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$
3. $C_{H_2CO_3} = [CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$  Correct
4. $C_{H_2CO_3} = [CO_2] + [H_2CO_3]$

Explanation: $H_2CO_3$ is in equilibrium with its deprotonated species $HCO_3^-$ and $CO_3^{2-}$ and with its decomposition product $CO_2$.

17. How many equation are necessary to define a system initially composed of $MgNH_4PO_4$?

1. 9  Correct
2. 8
3. 7
4. 5

Explanation: Species that will have an unknown concentration are $[H^+]$, $[OH^-]$, $[PO_4^{3-}]$, $[HPO_4^{2-}]$, $[H_2PO_4^-]$, $[H_3PO_4]$, $[NH_4^+]$, $[NH_3]$ and $[Mg^{2+}]$.

18. Which of the following would be equal to $K_{a1}$ times $K_{a2}$ for orthocarbonic acid, $H_4CO_4$?

1. $[H_2CO_4^{2-}][H^+]/[H_4CO_4]$
2. $[H_3CO_4^-][H^+]/[H_4CO_4]$
3. \[ \frac{[H_2CO_4^2\text{-}][H^+]}{[H_3CO_4^-]} \]

4. \[ \frac{[H_2CO_4^2\text{-}][H^+][H_3CO_4^-]}{[H_4CO_4]} \]

5. \[ \frac{[H_2CO_4^2\text{-}][H^+]^2}{[H_4CO_4]} \]  \text{Correct}

Explanation: \( K_{a_1} = \frac{[H_3CO_4^-][H^+]}{[H_4CO_4]} \)

\( K_{a_2} = \frac{[H_2CO_4^2\text{-}][H^+]}{[H_3CO_4^-]} \)

\( K_{a_1} \cdot K_{a_2} = \frac{[H_2CO_4^2\text{-}][H^+]^2}{[H_4CO_4]} \)

19. What would be the pH of a 2 \( \times \) 10\(^{-8} \) M solution of Ba(OH)\(_2\)?

1. 7.009  \text{Correct}

2. 7.019

3. 7.013

4. 7.004

Explanation: For a dilute strong base, 
\[ [OH^-]^2 - C_b[OH^-] - Kw = 0 \]

\[ [OH^-] = x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

\( pOH = 6.991 \)

Alternatively, one could reason that the very low concentration of Ba(OH)\(_2\), 2 \( \times \) 10\(^{-9} \) M, should result in a pH very close to, but still more than 7.

20. What would be the [H\(^+\)], [HSO\(_4^-\)] and [SO\(_4^{2-}\)] in a 1 M solution of H\(_2\)SO\(_4\)?

1. 1.02, 0.98, 0.02 M, respectively  \text{Correct}

2. 0.00, 2.00, 1.00 M, respectively

3. 1.14, 0.86, 0.14 M, respectively

4. 0.14, 1.00, 0.14 M, respectively

Explanation: Because H\(_2\)SO\(_4\) is a strong acid, the reaction H\(_2\)SO\(_4\) \rightarrow H^+ + HSO\(_4^-\) goes to completion. In this case, producing a [H\(^+\)] of 1 M. Because HSO\(_4^-\) is a weak acid we must solve for the proton concentration it contributes to the total.

<table>
<thead>
<tr>
<th>R</th>
<th>HSO(_4^-)</th>
<th>H(^+)</th>
<th>SO(_4^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>E</td>
<td>1-x</td>
<td>1+x</td>
<td>x</td>
</tr>
</tbody>
</table>

\( K_a = 2 \times 10^{-2} = (1 + x)(x)/(1 - x) \)

\[ x^2 + 1.02x - 0.02 = 0 \]

\( x = 0.01924 \)

\( [H^+] = 1.01924 \) M

\( [HSO_4^-] = 0.98076 \)

\( [SO_4^{2-}] = 0.01924 \)

21. What would be the pH of a 4 mM M Na\(_3\)C\(_6\)H\(_5\)O\(_7\) solution (trisodium citrate)? Citric acid has \( K_{a_1} = 7.1 \times 10^{-4}, \) \( K_{a_2} = 1.7 \times 10^{-5} \) and \( K_{a_3} = 4.0 \times 10^{-7} \).

1. 6.62

2. 5.00

3. 9.00  \text{Correct}

4. 7.38

5. 7.00

Explanation: Na\(^+\) is a spectator, and C\(_6\)H\(_5\)O\(_7\)^{3-} (citrate) is a weak base.

40 mM = 0.004 M

\( K_{b_3} = Kw/K_{a_3} = 10^{-14}/4.0 \times 10^{-7} = 2.5 \times 10^{-8} \)
[OH⁻] = (K_b·C_b)^{1/2} = (2.5 \times 10^{-8} \cdot 0.004)^{1/2} = 10^{-5}
pH = 9

22. Fully balance the reaction below in acid. How many protons are needed? How many water molecules? (Hint: this one is tricky - the water molecules and protons go on the same side.)

\[ \text{N}_2(g) \quad \text{2 NH}_4\text{OH}(aq) \]

1. 3, 1  
2. 6, 2  \text{ Correct}  
3. 2, 2  
4. 8, 2  
5. 8, 1

Explanation: \( \text{N}_2(g) + 2 \text{H}_2\text{O} + 6\text{H}^+ + 6 \text{e}^- \rightarrow 2 \text{NH}_4\text{OH}(aq) \)

23. Fully Balance the reaction below in acid. What is the sum of the coefficients?

\[ \text{Zn}(s) + \text{MnO}_2(s) + \text{NH}_4\text{Cl}(aq) \rightarrow \text{ZnCl}_2(s) + \text{Mn}_2\text{O}_3(s) + \text{NH}_3(aq) \]

1. 7  
2. 12  
3. 6  
4. 10  \text{ Correct}  
5. 9

Explanation:
\[ \text{Zn}(s) + 2 \text{MnO}_2(s) + 2 \text{NH}_4\text{Cl}(aq) \rightarrow \text{ZnCl}_2(s) + \text{Mn}_2\text{O}_3(s) + 2 \text{NH}_3(aq) + \text{H}_2\text{O}(l) \]

24. Which of the following statements is untrue concerning ranking the strength/weakness of oxidizing/reducing agents.

1. A reactant with a high reduction potential is a good reducing reagent. \text{ Correct}  
2. A product with a low reduction potential is a good reducing reagent.  
3. A reactant with a low reduction potential is a poor oxidizing reagent.  
4. A product with a high reduction potential is a poor reducing agent.

Explanation: A reactant which is easily reduced is a good oxidizing agent.

25. If the two half reactions below were used to make a battery, what species would be consumed at the anode?

\[
\begin{align*}
\text{Pb}^{2+}(aq) + 2 \text{e}^- &\rightarrow \text{Pb}(s) \quad \text{E}^\circ = -0.13 \\
\text{Zn}^{2+}(aq) + 2 \text{e}^- &\rightarrow \text{Zn}(s) \quad \text{E}^\circ = -0.76 \\
\end{align*}
\]

1. Zn(s) \text{ Correct}  
2. Zn^{2+}(aq)  
3. Pb(s)  
4. Pb^{2+}(aq)

Explanation: A battery must have a positive standard cell potential and therefore the anodic reaction must consume Zn(s).

26. For a discharging battery, which of the following must be negative?

I. \text{E}^\circ_{\text{cell}}  
II. anode  
III. cathode  
1. I only  
2. II only \text{ Correct}  
3. III only  
4. I & II  
5. I & III  
6. II & III  
7. none must be negative

Explanation: By definition and by convention, in an electrolytic cell the anode is attributed a negative sign.

27. What would be the \text{E}^\circ_{\text{cell}} of an electrolytic cell made from the following two half reactions?
\[ \text{Pb}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Pb}(s) \quad E^\circ = -0.13 \]
\[ \text{Zn}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Zn}(s) \quad E^\circ = -0.76 \]
1. -0.89
2. 0.89
3. 0.63 \textbf{Correct}
4. -0.63

Explanation: \( E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.13 - (-0.76) = +0.63 \)

28. What is K for the reaction below at room temperature?
\[ \text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{OH}^-(aq) \quad E^\circ = 0.40 \text{ V} \]
1. \( 1.72 \times 10^-7 \)
2. \( 5.82 \times 10^6 \)
3. \( 8.70 \times 10^-28 \)
4. \( 1.15 \times 10^{27} \textbf{Correct} \)

Explanation: \( K = e^{nF/RT} = e^{[4(96,485)(0.40)]/(8.314)(298)} = 1.15 \times 10^{27} \)

29. How many grams of solid silver (Ag) could be produce by electrolysis a solution of Ag+ for 10 hours at a current of 0.02 amperes?
1. 0.80 g \textbf{Correct}
2. 2.24 \times 10^{-5} g
3. 1.34 \times 10^{-3} g
4. 0.016 g

Explanation: This is a 1 electron process.
10 hours \times (3,600 \text{ s} / \text{hr}) = 36,000 \text{ seconds}
\[ n_{\text{product}} = \frac{I \cdot t}{N_e \cdot F} = \frac{0.02 \cdot 36,000}{1 \cdot 96,485} = 0.0074623 \text{ moles Ag.} \]
0.0074623 moles Ag \times (107.8682 \text{ g/ 1 mol}) = 0.80 g

30. What [\text{Pb}^{2+}] and [\text{Sn}^{2+}] would be present at equilibrium in a battery built from the two half reactions below?
\[ \text{Pb}^{2+} \rightarrow \text{Pb} \quad E^\circ = -0.13 \]
\[ \text{Sn}^{2+} \rightarrow \text{Sn} \quad E^\circ = -0.14 \]
1. 0.629 M, 1.371 M \textbf{Correct}
2. 1.371 M, 0.629 M
3. 0.808 M, 1.192 M
4. 1.192 M, 0.808 M

Explanation: \( \text{Pb}^{2+} + \text{Sn} \rightarrow \text{Pb} + \text{Sn}^{2+} \quad E^\circ_{\text{cell}} = +0.01 \)

\[ E_{\text{cell}} = E^\circ_{\text{cell}} - (0.05916/N_e) \log Q \]
\[ 0 = 0.01 - (0.05916/2) \log([\text{Sn}^{2+}]/[\text{Pb}^{2+}]) \]
\[ \log(1+x/1-x) = 0.338 \]
\[ 1 + x = 2.178 - 2.178x \]
\[ 3.178x = 1.178 \]
\[ x = 0.371 \]