Acids and Bases
8.7 pH and pK_a
8.8 Properties of Buffers
8.9 Henderson-Hasselbalch Equation
8.10 Buffer Capacity
Worksheet Key

1) After 20.0g of Na_2SO_4 are added to a 0.5 L saturated solution of $CaSO_4$, does the concentration of Ca^{2+} increase, decrease, or stay the same? Justify your answer. Assume that the overall volume of the solution does not change.

$$CaSO_{4(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$
$$Na_2SO_{4(s)} \rightarrow Na^{+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

$Na_2SO_{4(s)}$ will dissolve completely. The addition of excess SO_4^{2-} will shift the equilibrium of the first reaction to the left, according to Le Chatelier's principle. Excess SO_4^{2-} will combine with Ca^{2+} to form the precipitate $CaSO_{4(s)}$ until the product of $[Ca^{2+}][SO_4^{2-}]$ equals K_{sp} once again. This will **decreases** the concentration of Ca^{2+} in the solution.

2) After 31.0g of NaCl are added to a 1.0 L saturated solution of $PbCl_2$, does the concentration of Pb^{2+} increase, decrease, or stay the same? Justify your answer. Assume that the overall volume of the solution does not change.

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + 2\ Cl^{-}{}_{(aq)}$$
$$NaCl_{(s)} \rightarrow Na^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}$$

$NaCl_{(s)}$ will dissolve completely. The addition of Cl^- will shift the equilibrium of the first reaction to the left, according to Le Chatelier's principle. Excess Cl^- will combine with Pb^{2+} to form the precipitate $PbCl_{2(s)}$ until the product of $[Pb^{2+}][Cl^-]^2$ equals K_{sp} once again. This will **decreases** the concentration of Pb^{2+} in the solution.

3) Is $CaSO_4$ more soluble in 1.0 L of 0.25 *M* Li_2SO_4 or 1.0 L of 0.25 *M* $Al_2(SO_4)_3$? Explain.

$CaSO_4$ is more soluble in 0.25 *M* Li_2SO_4. The concentration of SO_4^- ions in the Li_2SO_4 solution is 0.25 *M*, whereas the concentration of SO_4^{2-} ions in the $Al_2(SO_4)_3$ solution is 0.75 *M*. Increasing the concentration of sulfate ions pushes the equilibrium below further to the left according to Le Chatelier's principle.

$$CaSO_{4(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

Thus, more $CaSO_4$ will dissolve in Li_2SO_4, because it has a lower sulfate ion concentration.

Use the table below to answer questions 4 through 8.

Acid	K_a at 25°C
HCN	6.2×10^{-10}
HOCl	3.5×10^{-8}
CH_3COOH	1.8×10^{-5}
HF	7.2×10^{-4}

4) Find the pK_a values for the weak acids in the above table.

$$\begin{aligned} pK_a &= -\log_{10}(K_a) \\ pK_{a(\mathrm{HCN})} &= -\log_{10}(6.2\times10^{-10}) = 9.21 \\ pK_{a(\mathrm{HOCl})} &= -\log_{10}(3.5\times10^{-8}) = 7.46 \\ pK_{a(\mathrm{CH_3COOH})} &= -\log_{10}(1.8\times10^{-5}) = 4.74 \\ pK_{a(\mathrm{HF})} &= -\log_{10}(7.2\times10^{-4}) = 3.14 \end{aligned}$$

5) Suppose you are required to create a buffer solution where the acid and its salt have very similar concentrations. Use your answers from question 4 to select the weak acid and its salt that would be used to create a buffered solution with a pH of about 7.50. Justify your choices.

The weak acid would be HOCl. This acid was chosen as its pK_a value is 7.46 and the desired pH is 7.50. Since we want fairly equal concentrations of a weak acid and its salt, it is necessary to choose an acid where p$K_a \simeq$ pH. The following equation demonstrates how pK_a = pH when the concentrations are equal, as log(1) = 0.

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

NaOCl or another soluble salt containing the OCl^- ion would be used to prepare this buffer.

6) Suppose you are required to create buffer solution where the acid and its salt have very similar concentrations. Use your answers from question 4 to select the weak acid and its salt that would be used to create a buffered solution with a pH of about 9.30. Justify your choices.

The weak acid would be HCN. This acid was chosen as its pK_a value is 9.21 and the desired pH is 9.30. Since we want fairly equal concentrations of a weak acid and its salt, it is necessary to choose an acid where p$K_a \simeq$ pH. The following equation demonstrates how pK_a = pH when the concentrations are equal, as log(1) = 0.

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

NaCN or another soluble salt containing the CN^- ion would be used to prepare this buffer.

7) Suppose you are required to create a buffer solution where the acid and its salt have very similar concentrations. Use your answers from question 4 to select the weak acid and its salt that would be used to create a buffered solution with a pH of about 3.25. Justify your choices.

The weak acid would be HF. This acid was chosen as its pK_a value is 3.14 and the desired pH is 3.25. Since we want fairly equal concentrations of a weak acid and its salt, it is necessary to choose an acid where pK_a $\simeq$ pH. The following equation demonstrates how pK_a = pH when the concentrations are equal, as log(1) = 0.

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

NaF or another soluble salt containing the F^- ion would be used to prepare this buffer.

8) Suppose you are required to create a buffered solution where the acid and its salt have very similar concentrations. Use your answers from question 4 to select the weak acid and its salt that would be used to create a buffered solution with a pH of about 4.70. Justify your choices.

The weak acid would be CH_3COOH. This acid was chosen as its pK_a value is 4.74 and the desired pH is 4.70. Since we want fairly equal concentrations of a weak acid and its salt, it is necessary to choose an acid where pK_a $\simeq$ pH. The following equation demonstrates how pK_a = pH when the concentrations are equal, as log(1) = 0.

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

$NaCH_3CO_2$ or another soluble salt containing the $CH_3CO_2^-$ ion would be used to prepare this buffer.

9) Two different 1.2 L buffered solutions were prepared using HOBr and LiOBr. Both buffered solutions had a pH of 5.2 at 25°C. After 0.17 moles of HI were added to each of the solutions, it was found that the pH of one solution had dropped to 4.9 and the pH of the other had dropped to 3.1.

a. What is the balanced net ionic equation for the reaction that occurred when HI was added to these buffered solutions?

$$OBr^-_{(aq)} + H^+_{(aq)} \rightarrow HOBr_{(aq)}$$

or

$$OBr^-_{(aq)} + H_3O^+_{(aq)} \rightarrow HOBr_{(aq)} + H_2O_{(l)}$$

b. What trend must be true when comparing the concentrations of HOBr and OBr^- in the two solutions if they shared the same pH before the HI was added? Justify your answer. (Hint: The concentrations of acid in the solutions are not the same.)

In order for the two buffered solutions to share the same pH, they needed to share the same [H^+]. They also have the same K_a value, as they are both at the same temperature. The equilibrium expression for both solutions can be rearranged as follows:

$$\text{HOBr} \rightarrow \text{OBr}^- + \text{H}^+$$

$$K_a = \frac{[\text{OBr}^-][\text{H}^+]}{[\text{HOBr}]}$$

$$\frac{K_a}{[\text{H}^+]} = \frac{[\text{OBr}^-]}{[\text{HOBr}]}$$

Since K_a:[H^+] is the same for both when they share the same pH, the ratio of concentrations of acid to conjugate base must also be the same.

c. Explain why the pH of the two solutions ended up being different after the same amount of HI was added to each.

After equal amounts of HI were added to both solutions, the ratios of K_a:[H^+] changed by a greater degree in the solution that ended up with a pH of 3.1 than it did in the solution that ended up with a pH of 4.9. The solution that ended up with a pH of 3.1 obtained a higher concentration of H^+. For this to happen, it must have had a lower concentration of OBr^- than did the solution that ended up with the higher pH.
Since the ratios were originally the same, the solution that ended up with a pH of 3.1 also had a lower concentration of HOBr when they shared the same pH.

10) The concentration of HF is 1.2 *M* and the concentration of NaF is 0.90 *M* in a buffer solution. What is the pH of the solution at 25°C? $pK_a = 3.14$ for HF at 25°C.

$$\text{pH} = \text{p}K_a + \log\frac{[\text{F}^-]}{[\text{HF}]}$$

$$\text{pH} = 3.14 + \log\frac{[0.90M]}{[1.2M]}$$

$$\text{pH} = 3.14 - 0.12$$

$$\text{pH} = 3.02$$

11) The concentration of lactic acid, $HC_3H_5O_3$, is 1.70 *M* and the concentration of $KC_3H_5O_3$ is 1.90 *M* in a buffer solution. What is the pH of the solution at 25°C? $K_a = 1.38 \times 10^{-4}$ at 25°C.

$$\text{pH} = \text{p}K_a + \log\frac{[\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]}$$

$$\text{pH} = -\log(1.38\times10^{-4}) + \log\frac{[1.90M]}{[1.70M]}$$

$$\text{pH} = 3.908$$

12) The concentration of benzoic acid, $HC_7H_5O_2$, is 2.10 *M* and the concentration of $NaC_7H_5O_2$ is 2.00 *M* in a buffer solution. What is the pH of the solution at 25°C? $K_a = 6.4 \times 10^{-5}$ at 25°C.

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{C_7H_5O_2}^-]}{[\mathrm{HC_7H_5O_2}]}$$

$$\mathrm{pH} = -\log(6.4\times10^{-5}) + \log\frac{[2.00M]}{[2.10M]}$$

$$\mathrm{pH} = 4.17$$

13) The concentration of HOCl is 1.1 *M* and the concentration of NaOCl is 1.1 *M* in a buffer solution. What is the pH of the solution at 25°C? $\mathrm{p}K_\mathrm{a} = 7.46$ at 25°C.

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{OCl}^-]}{[\mathrm{HOCl}]}$$

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a}$$

$$\mathrm{pH} = 7.46$$

14) A buffered solution was created by mixing solutions of NH_4Cl and NH_3 at 25°C. The final pH was measured to be 9.35, and K_a is 5.6×10^{-10} at 25°C. Which species, NH_4^+ or NH_3, has the highest concentration in this buffered solution? Justify your answer.

$$\mathrm{p}K_\mathrm{a} = -\log_{10}(K_\mathrm{a})$$

$$\mathrm{p}K_\mathrm{a} = -\log_{10}(5.6\times10^{-10}) = 9.25$$

$$\mathrm{pH} > \mathrm{p}K_\mathrm{a},\ \text{so}\ [\mathrm{NH_4}^+] < [\mathrm{NH_3}]$$

$$\text{When}\ \frac{[\mathrm{A}^-]}{[\mathrm{HA}]} > 1,\ \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} > 0,\ \text{and}\ \mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

15) A buffered solution was created by mixing solutions of HCN and KCN at 25°C. The final pH was measured to be 9.10 and K_a is 6.2×10^{-10} at 25°C. Which species, HCN or CN^-, has the highest concentration in this buffered solution? Justify your answer.

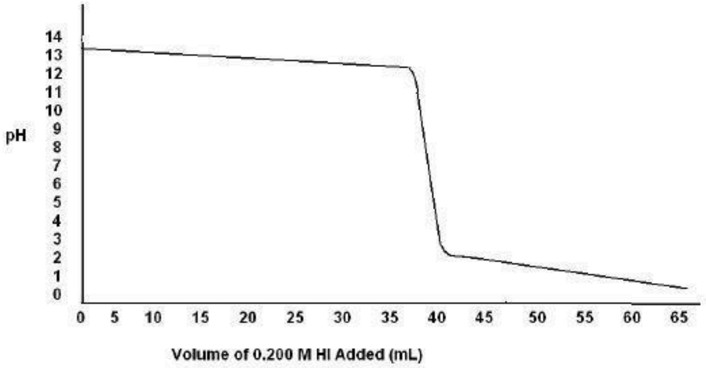
$$\mathrm{p}K_\mathrm{a} = -\log_{10}(K_\mathrm{a})$$

$$\mathrm{p}K_\mathrm{a} = -\log_{10}(6.2\times10^{-10}) = 9.21$$

$$\mathrm{pH} < \mathrm{p}K_\mathrm{a},\ \text{so}\ [\mathrm{HCN}] > [\mathrm{CN}^-]$$

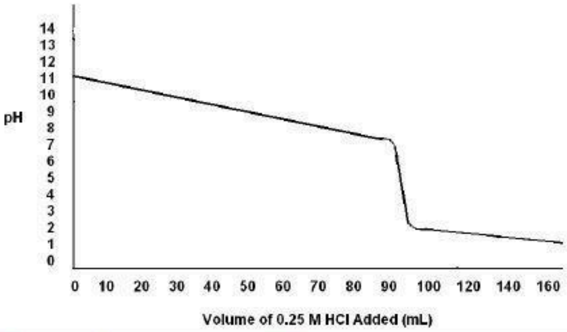
$$\text{When}\ 0 < \frac{[\mathrm{A}^-]}{[\mathrm{HA}]} < 1,\ \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} < 0,\ \text{and}\ \mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

16) A solution of KOH was titrated with HCl and the following curve was plotted. Which of the following indicators should be used to signal the endpoint of this titration: methyl red ($pK_a = 5.5$), litimus ($pK_a = 7.0$), or phenolphthalein ($pK_a = 8.7$)? Explain.



Litimus should be used, as $pK_{a(\text{litimus})}$ is the same as the pH of the solution at the equivalence point.

17) A 65 mL sample of 0.35 M NH_3 is titrated with 0.25 M HCl at 25°C and the following curve was plotted. Which of the following indicators should be used to signal the endpoint of this titration: methyl red ($pK_a = 5.5$), litimus ($pK_a = 7.0$), or phenolphthalein ($pK_a = 8.7$)? Justify your answer.



Methyl red would be the best indicator, as $pK_{a(\text{methyl red})}$ is very close to the pH of the solution at its equivalence point.

18) The pH of an HOCl solution is 3.9 at 25°C. $pK_a = 7.46$ at 25°C. Is the concentration of HOCl greater than, less than, or equal to the concentration of OCl^-? Justify your answer.

As we can see from the Henderson-Hasselbalch equation, when the pH is less than the pK_a, $\log([OCl^-]/[HOCl])$ must be a negative number. That only occurs when $[HOCl] > [OCl^-]$.

$$\text{pH} = \text{p}K_a + \log\frac{[OCl^-]}{[HOCl]}$$