Chemistry 132 NT

If trees could scream, would we be so cavalier about cutting them down? We might, if they screamed all the time, for no good reason.

Jack Handey

Chem 132 NT

Acid-Base Equilibria

Module 3

Solutions of a Weak Acid or Base and Another Solute

- **The Common-Ion Effect**
- **Buffers**

Reaction of zinc metal with hydrochloric acid.

Review

- Calculating the concentration of a species in a weak base solution using K_b
- Predicting whether a salt solution is acidic, basic, or neutral
- Obtaining the K_b for a basic anion from the K_a of its conjugate acid (hydrolysis).
- Obtaining the K_a for an acidic cation from the K_b of of its conjugate base (hydrolysis).
- Calculating concentrations of species and the pH in a solution of an ionic salt undergoing hydrolysis.

The Common Ion Effect

- The **common-ion effect** is the shift in an ionic equilibrium caused by the addition of a solute that provides an ion common to the equilibrium.

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

  - Consider a solution of acetic acid ($HC_2H_3O_2$), in which you have the equilibrium above.

The Common Ion Effect

- The **common-ion effect** is the shift in an ionic equilibrium caused by the addition of a solute that provides an ion common to the equilibrium.

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + \boxed{C_2H_3O_2^-(aq)}$$

  - If we were to add $NaC_2H_3O_2$ to this solution, it would provide $C_2H_3O_2^-$ ions which are present on the right side of the equilibrium.

The Common Ion Effect

- The **common-ion effect** is the shift in an ionic equilibrium caused by the addition of a solute that provides an ion common to the equilibrium.

$$HC_2H_3O_2(aq) \overset{\longleftarrow}{\rightleftharpoons} H^+(aq) + C_2H_3O_2^-(aq)$$

  - The equilibrium composition would shift to the left and the degree of ionization of the acetic acid is decreased.

The Common Ion Effect

- The **common-ion effect** is the shift in an ionic equilibrium caused by the addition of a solute that provides an ion common to the equilibrium.

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

  - This repression of the ionization of acetic acid by sodium acetate is an example of the **common-ion effect**.

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, HCH_2O and 0.018 M in sodium formate, $NaCH_2O$. What is the pH of the solution. The K_a for formic acid is 1.7×10^{-4}.
  - Consider the equilibrium below.

$$HCH_2O(aq) \rightleftharpoons H^+(aq) + CH_2O^-(aq)$$

Starting	0.025	0	0.018
Change	-x	+x	+x
Equilibrium	0.025-x	x	0.018+x

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, HCH_2O and 0.018 M in sodium formate, $NaCH_2O$. What is the pH of the solution. The K_a for formic acid is 1.7×10^{-4}.
  - The equilibrium constant expression is:

$$\frac{[H^+][CH_2O^-]}{[HCH_2O]} = K_a$$

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, HCH_2O and 0.018 M in sodium formate, $NaCH_2O$. What is the pH of the solution. The K_a for formic acid is 1.7×10^{-4}.
  - Substituting into this equation gives:

$$\frac{x(0.018 + x)}{(0.025 - x)} = 1.7 \times 10^{-4}$$

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, HCH_2O and 0.018 M in sodium formate, $NaCH_2O$. What is the pH of the solution. The K_a for formic acid is 1.7×10^{-4}.
  - Assume that x is small compared with 0.018 and 0.025. Then

$$(0.018 + x) \approx 0.018$$
$$(0.025 - x) \approx 0.025$$

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, HCH_2O and 0.018 M in sodium formate, $NaCH_2O$. What is the pH of the solution. The K_a for formic acid is 1.7×10^{-4}.
  - The equilibrium equation becomes

$$\frac{x(0.018)}{(0.025)} \approx 1.7 \times 10^{-4}$$

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, HCH_2O and 0.018 M in sodium formate, $NaCH_2O$. What is the pH of the solution. The K_a for formic acid is 1.7×10^{-4}.
  - Hence,

$$x \approx (1.7 \times 10^{-4}) \times \frac{0.025}{0.018} = 2.4 \times 10^{-4}$$

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, HCH_2O and 0.018 M in sodium formate, $NaCH_2O$. What is the pH of the solution. The K_a for formic acid is 1.7×10^{-4}.
  - Note that x <u>was</u> much smaller than 0.018 or 0.025.

$$pH = -\log(2.4 \times 10^{-4}) = 3.63$$

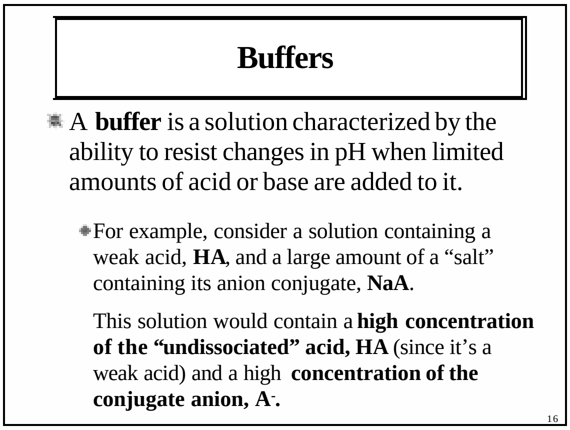
  - For comparison, the pH of 0.025 M formic acid alone (without the sodium formate) is 2.69.

Buffers

- A **buffer** is a solution characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it.
  - Buffers contain either a **weak acid and a salt containing its conjugate base anion**

    or

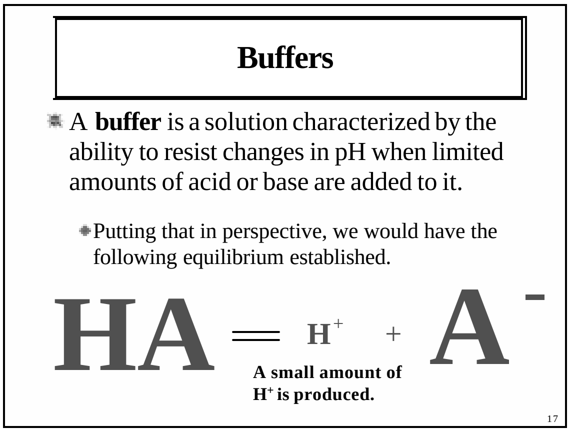
    a **weak base and a salt containing its conjugate acid cation**.
  - Thus, a buffer contains <u>both an acid species and a base species</u> in equilibrium.



Buffers

- A **buffer** is a solution characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it.
  - For example, consider a solution containing a weak acid, **HA**, and a large amount of a “salt” containing its anion conjugate, **NaA**.

    This solution would contain a **high concentration of the “undissociated” acid, HA** (since it’s a weak acid) and a high **concentration of the conjugate anion, A^-.**

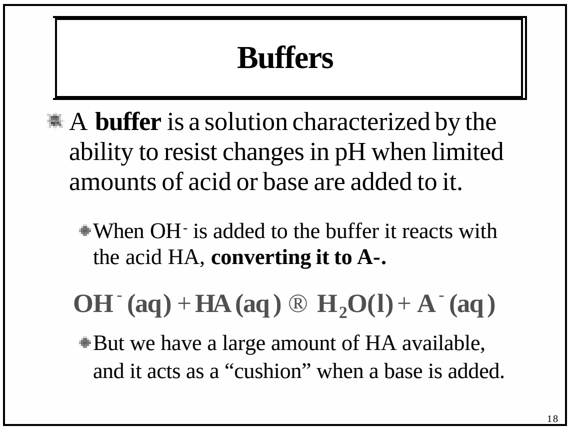


Buffers

- A **buffer** is a solution characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it.
  - Putting that in perspective, we would have the following equilibrium established.

$$HA \rightleftharpoons H^+ + A^-$$

A small amount of H^+ is produced.



Buffers

- A **buffer** is a solution characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it.
  - When OH^- is added to the buffer it reacts with the acid HA, **converting it to A-.**

$$OH^-(aq) + HA(aq) \rightarrow H_2O(l) + A^-(aq)$$

  - But we have a large amount of HA available, and it acts as a “cushion” when a base is added.

Buffers

- A **buffer** is a solution characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it.
  - When H_3O^+ is added to the buffer it reacts with the base A^-**, converting it to HA**.

$$H_3O^+(aq) + A^-(aq) ® HA(aq) + H_2O(l)$$

  - But we have a large amount of A^- available, and it acts as a “cushion” when an acid is added.

Buffers

- A **buffer** is a solution characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it.
  - Two important characteristics of a buffer are its **buffer capacity** and its **pH**.
  - Buffer capacity depends on the **amount** of acid and conjugate base present in the solution.
  - The next example illustrates how to calculate the pH of a buffer.

The pH of a Buffer

- The solution described in the following example is a **buffer**, because it is composed of a **weak acid** (0.10 M acetic acid) and **its conjugate base** (0.20 M acetate ion). Let’s calculate the pH.
  - As always, let’s set up a table of “starting” and “equilibrium” concentrations.

The pH of a Buffer

- The solution described in the following example is a **buffer**, because it is composed of a **weak acid** (0.10 M acetic acid) and **its conjugate base** (0.20 M acetate ion). Let’s calculate the pH.
  - The equilibrium reaction is:

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

Starting	0.10	0	0.20
Change	-x	+x	+x
Equilibrium	0.10-x	x	0.20+x

The pH of a Buffer

- The solution described in the following example is a **buffer**, because it is composed of a **weak acid** (0.10 M acetic acid) and **its conjugate base** (0.20 M acetate ion). Let’s calculate the pH.
  - The equilibrium constant expression is:

$$\frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_a$$

  - The K_a for acetic acid is given as 1.7×10^{-5}

The pH of a Buffer

- The solution described in the following example is a **buffer**, because it is composed of a **weak acid** (0.10 M acetic acid) and **its conjugate base** (0.20 M acetate ion). Let’s calculate the pH.
  - Substituting the value for the K_a and our equilibrium concentration expressions, we get:

$$\frac{(x)(0.20 + x)}{(0.10 - x)} = 1.7 \times 10^{-5}$$

The pH of a Buffer

- The solution described in the following example is a **buffer**, because it is composed of a **weak acid** (0.10 M acetic acid) and **its conjugate base** (0.20 M acetate ion). Let’s calculate the pH.
  - But we can use our simplifying assumption, since “x” is negligible compared to 0.10 or 0.20.

$$\frac{(x)(0.20)}{(0.10)} \approx 1.7 \times 10^{-5}$$

The pH of a Buffer

- The solution described in the following example is a **buffer**, because it is composed of a **weak acid** (0.10 M acetic acid) and **its conjugate base** (0.20 M acetate ion). Let’s calculate the pH.
  - Solving for x, we obtain:

$$x \approx 8.5 \times 10^{-6} = [H^+]$$

  - So, the pH of this buffer is:

$$pH = -\log(8.5 \times 10^{-6}) = 5.07$$

Adding Acid or Base to a Buffer

- The previous example described a buffer composed of acetic acid and sodium acetate. This buffer controls the equilibrium below.

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

  - As mentioned earlier, adding a strong acid to this buffer would convert some of the $C_2H_3O_2^-$ (a base) back into $HC_2H_3O_2$.
  - And a strong base to this buffer would convert more $HC_2H_3O_2$ (an acid) into $C_2H_3O_2^-$ (its conjugate base)

Adding Acid or Base to a Buffer

- The previous example described a buffer composed of acetic acid and sodium acetate. This buffer controls the equilibrium below.

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

  - Let’s try an example where we add a strong acid to this buffer.

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - When the hydrogen ion (from the HCl) is added to the buffer, it reacts **completely** with the acetate ion.

$$H^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq)$$

  - This initial reaction goes to completion until all of the H^+ (from HCl) has been used up.

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - We must first calculate the amounts of hydrogen ion, acetate ion and acetic acid present in the solution before reaction.

$$(0.010\ \mathrm{L\ HCl}) \times \frac{0.10\ \mathrm{mol\ HCl}}{1\mathrm{L\ HCl}} = 0.0010\ \mathrm{mol\ HCl}$$
$$= 0.0010\ \mathrm{mol}\ H^+$$

since HCl is a strong acid.

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - We must first calculate the amounts of hydrogen ion, acetate ion and acetic acid present in the solution before reaction.

$$(0.075\ \text{L soln}) \times \frac{0.20\ \text{mol}\ C_2H_3O_2^-}{1\ \text{L HCl}} = 0.015\ \text{mol}\ C_2H_3O_2^-$$

$$(0.075\ \text{L soln}) \times \frac{0.10\ \text{mol}\ HC_2H_3O_2}{1\ \text{L HCl}} = 0.0075\ \text{mol}\ HC_2H_3O_2$$

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A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - You can now assume that all of the hydrogen ion added (0.0010 mol) reacts with acetate ion.
  - Therefore, 0.0010 mol of acetate ion is used up and 0.0010 mol of acetic acid is produced.

$$\begin{aligned}\text{mol}\ C_2H_3O_2^- &= (0.015 - 0.0010)\ \text{mol}\ C_2H_3O_2^- \\ &= 0.014\ \text{mol}\ C_2H_3O_2^-\end{aligned}$$

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A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - You can now assume that all of the hydrogen ion added (0.0010 mol) reacts with acetate ion.
  - Therefore, 0.0010 mol of acetate ion is used up and 0.0010 mol of acetic acid is produced.

$$\begin{aligned}\text{mol}\ HC_2H_3O_2 &= (0.0075 + 0.0010)\ \text{mol}\ HC_2H_3O_2 \\ &= 0.0085\ \text{mol}\ HC_2H_3O_2\end{aligned}$$

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A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - Now that we know the amounts of acetic acid and acetate ion remaining after the addition of the HCl, we can solve the equilibrium calculation.
  - Note that the total volume of solution (the buffer and the HCl) is 75 mL + 10 mL, or **85 mL** (0.085 L).

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - Hence, the concentrations after the acid addition are:

$$[HC_2H_3O_2] = \frac{0.0085\,\text{mol}}{0.085\,\text{L}} = 0.10\,\text{M}$$

$$[C_2H_3O_2^-] = \frac{0.014\,\text{mol}}{0.085\,\text{L}} = 0.16\,\text{M}$$

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - Now we can construct the following table.

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

Starting	0.10	~0	0.16
Change	-x	+x	+x
Equilibrium	0.10-x	x	0.16+x

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - The equilibrium constant expression is:

$$\frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_a$$

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - Substituting, you get:

$$\frac{x(0.16+x)}{(0.10-x)} = 1.7 \times 10^{-5}$$

If we assume x is small, then:

$$(0.16+x) \approx 0.16 \quad \text{and} \quad (0.10-x) \approx 0.10$$

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - And simplifying, we get

$$\frac{x(0.16)}{(0.10)} \approx 1.7 \times 10^{-5}$$

or

$$x = (1.7 \times 10^{-5}) \times \frac{0.10}{0.16} = \boxed{1.1 \times 10^{-5}}$$

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - The H^+ concentration is 1.1 x 10^{-5}, so the pH is

$$pH = -\log[H^+] = -\log(1.1 \times 10^{-5}) = 4.96$$

  - The pH of the original buffer in our previous example was **5.07**.

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - The H^+ concentration is 1.1 x 10^{-5}, so the pH is

$$pH = -\log[H^+] = -\log(1.1 \times 10^{-5}) = 4.96$$

  - The addition of strong acid to the buffer dropped its pH by **only 0.11 pH units**.

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - The H^+ concentration is 1.1 x 10^{-5}, so the pH is

$$pH = -\log[H^+] = -\log(1.1 \times 10^{-5}) = 4.96$$

  - This illustrates the stability of the buffer.

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - The H^+ concentration is 1.1×10^{-5}, so the pH is

$$pH = -\log[H^+] = -\log(1.1 \times 10^{-5}) = 4.96$$

  - Adding the same amount of acid to 75 mL of pure water results in a **pH of 1.96.**

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - Had we added a like amount of base to this buffer, we would simply have converted a small amount of $HC_2H_3O_2$ into $C_2H_3O_2^-$.
  - This would have resulted in a pH of approximately **5.15**….again, only a slight change in pH from the original 5.07.

A Problem To Consider

- Calculate the **pH** of 75 mL of the buffer described in our previous example (0.10 M $HC_2H_3O_2$ and 0.20 M $NaC_2H_3O_2$) to which **10.0 mL of 0.10 M HCl is added**.
  - So the large excess “cushion” of undissociated $HC_2H_3O_2$ can absorb a large “shock” of base.
  - And the large excess “cushion” of the conjugate base, $C_2H_3O_2^-$, can absorb a large “shock” of acid.

Buffers

- The previous example illustrated the "mechanics" of how a buffer system maintains a constant pH.
  - Let's try an example of calculating the pH of a buffer composed of a weak base and its conjugate acidic cation.

A Problem To Consider

- Instructions for making up a buffer say to mix 60.0 mL of 0.100 M NH_3 with 40.0 mL of 0.100 M NH_4Cl. **What is the pH** of this buffer?
  - This buffer contains a base (NH_3) and its conjugate acid (NH_4^+) in equilibrium.

$$\mathbf{NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)}$$

  - To do this, we must calculate the moles of NH_3 and NH_4Cl present and divide by the total volume of the solution.

A Problem To Consider

- Instructions for making up a buffer say to mix 60.0 mL of 0.100 M NH_3 with 40.0 mL of 0.100 M NH_4Cl. **What is the pH** of this buffer?
  - Note that the instructions say to add 60.0 mL (0.0600 L) of 0.100 M NH_3, so…

$$\mathbf{moles\ NH_3 = molarity\ NH_3 \times liters\ NH_3\ soln.}$$
$$\mathbf{= 0.100\ \tfrac{mol}{L} \times 0.0600\ L}$$
$$\mathbf{= 0.00600\ mol\ NH_3}$$

  - In the same way, we find we have added **0.00400 mol NH_4^+** (from NH_4Cl).

A Problem To Consider

- Instructions for making up a buffer say to mix 60.0 mL of 0.100 M NH_3 with 40.0 mL of 0.100 M NH_4Cl. **What is the pH** of this buffer?
  - Total volume of buffer =

    60.0 mL + 40.0 mL = 100.0 mL (0.100 L)
  - Therefore, the concentration of base and conjugate acid are:

$$[NH_3] = \frac{0.00600\,\text{mol}}{0.100\,\text{L}} = 0.0600\,\text{M}$$

$$[NH_4^+] = \frac{0.00400\,\text{mol}}{0.100\,\text{L}} = 0.0400\,\text{M}$$

A Problem To Consider

- Instructions for making up a buffer say to mix 60.0 mL of 0.100 M NH_3 with 40.0 mL of 0.100 M NH_4Cl. **What is the pH** of this buffer?
  - Fill in the concentration table for the acid-base equilibrium (base ionization of NH_3).

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Starting	0.060	0.040	0
Change	-x	+x	+x
Equilibrium	0.060-x	0.040+x	x

A Problem To Consider

- Instructions for making up a buffer say to mix 60.0 mL of 0.100 M NH_3 with 40.0 mL of 0.100 M NH_4Cl. **What is the pH** of this buffer?
  - The equilibrium constant expression is:

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = K_b$$

  - The K_b for NH_3 is given as 1.8×10^{-5}.

A Problem To Consider

- Instructions for making up a buffer say to mix 60.0 mL of 0.100 M NH_3 with 40.0 mL of 0.100 M NH_4Cl. **What is the pH** of this buffer?
  - Substituting into this equation gives:

$$\frac{(0.040 + x)(x)}{(0.060 - x)} = 1.8 \times 10^{-5}$$

A Problem To Consider

- Instructions for making up a buffer say to mix 60.0 mL of 0.100 M NH_3 with 40.0 mL of 0.100 M NH_4Cl. **What is the pH** of this buffer?
  - Assuming that x is very small compared to 0.040 and 0.060, we can simplify

$$\frac{(0.040)(x)}{(0.060)} \approx 1.8 \times 10^{-5}$$

A Problem To Consider

- Instructions for making up a buffer say to mix 60.0 mL of 0.100 M NH_3 with 40.0 mL of 0.100 M NH_4Cl. **What is the pH** of this buffer?
  - Therefore,

$$x = \left({}^{0.060}/_{0.040}\right) \times (1.8 \times 10^{-5}) = 2.7 \times 10^{-5}$$

  - Thus, the hydroxide concentration is 2.7 x 10^{-5}. The pH of the buffer is:

$$pH = 14.00 - pOH = 14.00 + \log(2.7 \times 10^{-5}) = \boxed{9.43}$$

Operational Skills

- Calculating the common-ion effect on acid ionization.
- Calculating the pH of a buffer from given volumes of solution.

Time for a few review questions