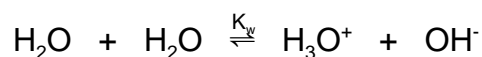# Chem 321 Lecture 10 - Acid-Base Equilibria (Review)
10/1/13

Student Learning Objectives

In any aqueous solution at equilibrium, the water self-ionization reaction is also at equilibrium. That is,

$$H_2O \ + \ H_2O \ \overset{K_w}{\rightleftharpoons} \ H_3O^+ \ + \ OH^-$$

and

(at 25°C) $K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$

If this self-ionization reaction is the only significant source of H_3O^+ and OH^-, then

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \ M$$

A solution where the hydronium ion concentration equals the hydroxide ion concentration is a neutral solution with a pH $\approx$ -log $[H_3O^+]$ $\approx$ 7. If an acid is added to water, the hydronium ion concentration increases, causing a corresponding decrease in the hydroxide ion concentration. If a base is present, the hydroxide ion concentration increases and the hydronium ion concentration decreases. In summary,

acidic solution $[H_3O^+] > [OH^-]$ pH < 7

neutral solution $[H_3O^+] = [OH^-]$ pH ~ 7

basic solution $[H_3O^+] < [OH^-]$ pH > 7

Guidelines for Solving Acid/Base Equilibrium Problems

The first step is to **IDENTIFY WHAT YOU HAVE IN SOLUTION**. Possible options include: strong acid, weak acid, strong base, weak base, buffer, or neutral solution. If the problem involves the mixing of a strong acid or strong base with another base or acid, consider any possible neutralization reaction <u>before</u> deciding what is present.
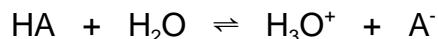
STRONG ACID (HA)

$[H_3O^+] \approx [HA]$ and pH $\approx$ -log $[H_3O^+]$

STRONG BASE (B)

$[OH^-] \approx n \, [B]$ where n is the number of OH^-/ formula unit of base
pOH $\approx$ -log $[OH^-]$ and pH $\approx$ 14 - pOH

WEAK ACID (HA)
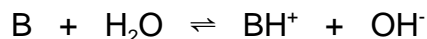
Write the equation for the weak acid dissociation and assign initial and equilibrium concentrations to the reactants and products.

$$HA \; + \; H_2O \; \rightleftharpoons \; H_3O^+ \; + \; A^-$$

Most problems can then be solved by setting the reaction quotient equal to the acid dissociation equilibrium constant (K_a).   **Table of Acid Dissociation Constants**

WEAK BASE (B)

Write the equation for the weak base hydrolysis reaction and assign initial and equilibrium concentrations to the reactants and products.

$$B \; + \; H_2O \; \rightleftharpoons \; BH^+ \; + \; OH^-$$

Most problems can then be solved by setting the reaction quotient equal to the base hydrolysis equilibrium constant (K_b).

BUFFER

Look for the presence of comparable amounts of a weak acid (HA) and its conjugate base (A^-). Write the equation for the weak acid dissociation and assign initial and equilibrium concentrations to the reactants and products.

$$HA \; + \; H_2O \; \rightleftharpoons \; H_3O^+ \; + \; A^-$$
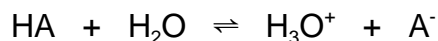
If $K_a < 10^{-3}$ and <u>both</u> $[HA]_{init}$ and $[A^-]_{init}$ are $> 10^{-3}$ M, then $[HA]_{eq} \approx [HA]_{init}$ and $[A^-]_{eq} \approx [A^-]_{init}$. When both of these criteria are met, then the Henderson-Hasselbalch equation is a convenient approach to solving the buffer problem.

$$pH \; = \; pK_a \; + \; \log \frac{[A^-]}{[HA]}$$

If these criteria are not met, most buffer problems can be solved by setting the reaction quotient equal to the acid dissociation equilibrium constant (K_a).
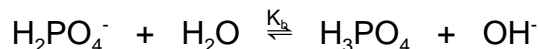
Example 7.1

Problem

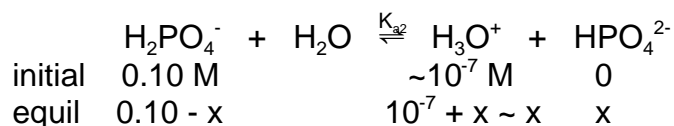Calculate the pH of a 0.10 M aqueous solution of KH_2PO_4.

Solution

First, decide what you have in solution. The K^+ will not react with water, but $H_2PO_4^-$ can. Since $H_2PO_4^-$ is an amphiprotic substance, you must determine whether base hydrolysis or acid dissociation is more important. This is done by comparing the equilibrium constants for these two reactions.

$$H_2PO_4^- \ + \ H_2O \ \overset{K_a}{\rightleftharpoons} \ H_3O^+ \ + \ HPO_4^{2-}$$

$$H_2PO_4^- \ + \ H_2O \ \overset{K_b}{\rightleftharpoons} \ H_3PO_4 \ + \ OH^-$$

Notice that K_a is the same as K_{a2} for H_3PO_4 and equals 6.3×10^{-8}. K_b must be calculated from K_a for the conjugate acid (H_3PO_4) [$K_b = 10^{-14}/7.1 \times 10^{-3} = 1.4 \times 10^{-12}$].

Since $K_a \gg K_b$ for $H_2PO_4^-$, the acid dissociation process is more important and we can treat this problem as a weak acid in solution. (Note: We will return to this problem and see that a significant error is introduced by ignoring the base hydrolysis reaction.)

Follow the guideline above for a weak acid in solution.

$$H_2PO_4^- \ + \ H_2O \ \overset{K_{a2}}{\rightleftharpoons} \ H_3O^+ \ + \ HPO_4^{2-}$$

	$H_2PO_4^-$		H_3O^+	HPO_4^{2-}
initial	0.10 M		$\sim 10^{-7}$ M	0
equil	0.10 - x		$10^{-7} + x \sim x$	x

where x equals the increase in the [HPO_4^{2-}]. The equilibrium concentration of H_3O^+ is also approximated by x. This assumes that $x \gg 10^{-7}$ M.

Example 7.1 (continued)

Solution

Thus,

$$K_a = 6.3 \times 10^{-8} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{(x)(x)}{0.10 - x} \simeq \frac{x^2}{0.10}$$

Note that the approximation made in the denominator assumes that $x \ll 0.10$ M.

Solving this gives $x = 7.9 \times 10^{-5}$ M. Thus, $[H_3O^+] = 7.9 \times 10^{-5}$ M and pH $\simeq 4.10$.

Both assumptions that were made, $x \gg 10^{-7}$ M and $x \ll 0.10$ M, are valid.

$H_2PO_4^-$ can be treated like a monoprotic acid. The dissociation of HPO_4^{2-} is not significant since its K_a is much smaller and its dissociation is further suppressed by the H_3O^+ produced in the dissociation of $H_2PO_4^-$.

        Suppose that you wanted to know the pH of a solution made from mixing 100. mL of 0.030 M KH_2PO_4 with 100. mL of 0.050 M K_2HPO_4. Notice that the two solutes, $H_2PO_4^-$ and HPO_4^{2-}, are a weak acid-base conjugate pair. Since the mixture will contain comparable amounts of a weak acid and its conjugate base a **buffer** solution will form. "Comparable amounts" generally means that the concentrations are within a factor of 10 of each other. To see why this is necessary, recall that the most important characteristic of a buffer is that it resists a change in pH when diluted or challenged with addition of acid or base. As the above guideline to solving buffer problems suggests, consider the buffer chemistry in terms of the weak acid dissociation reaction. (Note: There is one, rather rare, situation in which this approach does not work.)

$$HA + H_2O \overset{K_a}{\rightleftharpoons} H_3O^+ + A^-$$
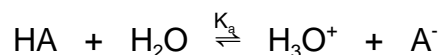
At equilibrium, the reaction quotient equals K_a.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Rearranging gives

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

and

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

These last two relationships indicates that the hydronium ion concentration and pH depend on the ratio of the weak and conjugate base concentrations. When a buffer is diluted, both concentrations decrease by the same factor, so their ratio along with the $[H_3O^+]$ and the pH don't change.

When a small amount of strong acid is added to a buffer, it will react with the weak base of the buffer.

$$H_3O^+ \ + \ A^- \ \overset{K}{\to} \ HA \ + \ H_2O$$
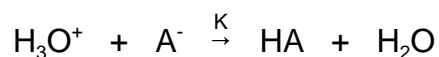
This reaction converts some of the buffer weak base (A⁻) to its conjugate acid (HA), hence altering their concentration ratio slightly. This results in only a slight change in the logarithm of the ratio and only a slight change in pH for the buffer. Note that the reaction between a strong acid and a weak base generally heavily favors the products; that is, K for this reaction is very large (a single arrow is used here). This neutralization reaction is the reverse of a weak acid dissociation process, so $K = 1/K_a$.

In a similar way, when a small amount of strong base is added to a buffer, it will react with the weak acid present.

$$OH^- \ + \ HA \ \overset{K}{\to} \ H_2O \ + \ A^-$$
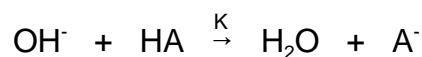
The net effect on the buffer is to convert some HA to A⁻ and alter the logarithm of their concentration ratio, and ultimately the pH, only slightly. Note that this reaction also heavily favors the products.

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Check for Understanding 7.1   **Solution**

1.   What is the relationship between K for the reaction of a strong base with a weak acid and K_a for the weak acid?

</div>

Thus, it is desirable and necessary to have both a weak acid and a weak base present in order to stabilize the buffer pH. The suggestion that there be no more than a factor of 10 difference between the conjugate pair concentrations is an arbitrary guideline to ensure that you have a significant amount of each present.

The **most effective buffer** is one in which the conjugate pairs have large and nearly identical concentrations.

most effective buffer: $[HA] \approx [A^-]$

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]} \approx K_a$$

$$pH \approx pK_a$$

If [HA] and [A$^-$] must be within a factor of 10 of each other, you can show that for a buffer

$$pH = pK_a \pm 1$$

Therefore, to select the appropriate weak acid-base conjugate pair to stabilize a given pH, look for a weak acid with a pK_a within one unit of the desired pH.

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Check for Understanding 7.2   **Solution**

1.   Use the posted information about acid dissociation constant values to determine which acid-base conjugate pair would be suitable to prepare a buffer at pH = 4 and at pH = 8.

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Now let us return to calculating the pH of the buffer solution formed by mixing solutions containing a weak acid and its conjugate base.

Example 7.2

Problem

Calculate the pH of a solution made from mixing 100. mL of 0.030 M KH_2PO_4 with 100. mL of 0.050 M K_2HPO_4.

Solution

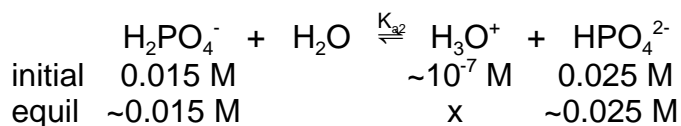In this buffer problem, the weak acid dissociation reaction is:

$$H_2PO_4^- \ + \ H_2O \ \overset{K_a}{\rightleftharpoons} \ H_3O^+ \ + \ HPO_4^{2-}$$

where K_a equals 6.3×10^{-8}.

To get the initial concentrations of the weak acid and conjugate base, notice that each solution is, in effect, being diluted by an equal volume of the other solution. Thus, the concentrations given need to be halved.

$$[H_2PO_4^-]_{init} = 0.015 \text{ M} \qquad\qquad [HPO_4^{2-}]_{init} = 0.025 \text{ M}$$

In the buffer problem guideline, the "10^{-3} rules" suggest that if $K_a < 10^{-3}$ and <u>both</u> $[HA]_{init}$ and $[A^-]_{init}$ are $> 10^{-3}$ M, then $[HA]_{eq} \approx [HA]_{init}$ and $[A^-]_{eq} \approx [A^-]_{init}$. Since both criteria are met, these simplifying assumptions can be made. The "concentration table" for this buffer then looks like this.

$$\begin{array}{lcccc}
& H_2PO_4^- \ + \ H_2O & \overset{K_{a2}}{\rightleftharpoons} & H_3O^+ & + \ HPO_4^{2-} \\
\text{initial} & 0.015 \text{ M} & & \sim 10^{-7} \text{ M} & 0.025 \text{ M} \\
\text{equil} & \sim 0.015 \text{ M} & & x & \sim 0.025 \text{ M}
\end{array}$$

Note that in this case x is defined as the equilibrium concentration of H_3O^+.

Example 7.2 (continued)

Solution

Substituting into the reaction quotient gives:

$$K_a = 6.3 \times 10^{-8} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{(x)(0.025)}{0.015}$$

Solving this gives x = 3.7_8 x 10^{-8} M. Thus, [H$_3$O$^+$] = 3.7_8 x 10^{-8} M and pH ≈ 7.42.

Since both of the "10^{-3} rules" were satisfied, the Henderson-Hasselbalch equation could also be used to get the pH. Note that the pK$_a$ of H$_2$PO$_4^-$ is 7.20.

$$pH = pK_a + \log\frac{[A^-]}{[HA]} = 7.20 + \log\frac{0.025}{0.015} = 7.42$$

Exercises for Acid-Base Equilibria