Skills to Develop

• Define a weak acid or base.
• Calculate pH and pOH of a weak acid or base solution using simple formula, quadratic equation, and including autoionization of water.
• Calculate the pH or pOH quickly.

Weak acids and bases are only partially ionized in their solutions, whereas strong acids and bases are completely ionized when dissolved in water. Some common weak acids and bases are given here. Furthermore, weak acids and bases are very common, and we encounter them often both in the academic problems and in everyday life. The ionization of weak acids and bases is a chemical equilibrium phenomenon. The equilibrium principles are essential for the understanding of equilibria of weak acids and weak bases. In this connection, you probably realize that conjugate acids of weak bases are weak acids and conjugate bases of weak acids are weak bases.

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<th>Common Weak Acids</th>
<th>Common Weak Bases</th>
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<td>Formula</td>
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<td>Formic</td>
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<tr>
<td>Acetic</td>
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</tr>
<tr>
<td>Trichloroacetic</td>
<td>(\text{CCl}_3\text{COOH})</td>
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<tr>
<td>Hydrofluoric</td>
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<tr>
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<td>Conjugate acids of weak bases</td>
<td>(\text{NH}_4^+)</td>
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Ionization of Weak Acids

Acetic acid, \(\text{CH}_3\text{COOH}\), is a typical weak acid, and it is the ingredient of vinegar. It is partially ionized in its solution.

\[
\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+ 
\]

The structure of the acetate ion, \(\text{CH}_3\text{COO}^-\), is shown below.
Example 1

In a solution of acetic acid, the equilibrium concentrations are found to be $[CH_3COOH] = 1.000$; $[CH_3COO^-] = 0.0042$). Evaluate the pH of this solution and the equilibrium constant of ionization of acetic acid.

**SOLUTION**

From the ionization of acetic acid,

\[
\begin{align*}
&\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+ \\
&0.100 \quad 0.0042 \quad 0.0042
\end{align*}
\]

we conclude that

\[
\begin{align*}
\text{[H}^+] &= \text{[CH}_3\text{COO}^-] \\
&= 0.0042
\end{align*}
\]

Thus, $\text{pH} = -\log 0.0042 = 2.376$.

The equilibrium constant of ionization,

\[
[K = \frac{(0.0042)^2}{1.000} = 1.78 \times 10^{-5}]
\]

**DISCUSSION**

The equilibrium constant of an acid is represented by $K_a$; and similar to the pH scale, a $pK_a$ scale is defined by

\[
[pK_a = -\log K_a]
\]

and for acetic acid, $pK_a = 4.75$. Note that $K_a = 10^{-pK_a}$.
The pH and pK\textsubscript{a} of Weak Acid

There are many weak acids, which do not completely dissociate in aqueous solution. As a general discussion of weak acids, let $\ce{HA}$ represent a typical weak acid. Then its ionization can be written as:

$$\ce{HA \rightleftharpoons H^+ + A^-}$$

In a solution whose label concentration is $C = \ce{[HA]} + \ce{[A^-]}$, let us assume that $x$ is the concentration that has undergone ionization. Thus, at equilibrium, the concentrations are

$$\ce{[HA]} = C - x$$

$$\ce{[H^+]} = \ce{[A^-]} = x$$

Make sure you understand why they are so, because you will have to set up these relationships in your problem solving. In summary, we formulate them as

| $\begin{array}{cccccl}
\ce{HA &\rightleftharpoons &H+ &+ &A- &} \\
C & & & & &\leftarrow \text{ initial concentration, assume } \textit{x} \text{ M ionized} \\
C-x & &x & &x &\leftarrow \text{ equilibrium concentration}
\end{array}$ |

$$K_{\text{a}} = \dfrac{x^2}{C - x}$$

$$\mathrm{pK_{a} = - \log K_{a}}$$

$$\mathrm{K_{a} = 10^{-pK_{a}}}$$

The $pK_{a}$ values of many weak acids are listed in table form in handbooks, and some of these values are given in Table E1.

Example 2

The $pK_{a}$ of acetic acid is 4.75. Find the pH of acetic acid solutions of labeled concentrations of 1.0 M, 0.010 M, and 0.00010 M.

**SOLUTION**

Assume the label concentration as $C$ and $x$ mole ionized, then the ionization and the equilibrium concentrations can be represented by the **ICE table** below.

| ICE | $\ce{[CH3COOH]}| \rightleftharpoons | \ce{CH3COO^-} | \ce{H^+}$ |
|-----|-----------------|----------------|---------|
| Initial | $C$ | 0 | 0 |
| Change | $-x$ | $+x$ | $+x$ |
ICE
\(\ce{CH3COOH}\) \(\rightleftharpoons\) \(\ce{CH_3COO^-}\) \(\ce{H+}\)

| Equilibrium | C - x | x | x |

with

\(\langle K_{\text{ac}} \rangle = \frac{x^2}{C - x}\)

The equation is then

\(\langle x^2 + K_{\text{ac}} \rangle x = C K_{\text{ac}} = 0\)

The solution of \(x\) is then

\(x = \frac{- K_{\text{ac}} + \sqrt{K_{\text{ac}}^2 + 4 C K_{\text{ac}}}}{2}\)

Recall that \(K_{\text{a}} = 1.78e-5\), the values of \(x\) for various \(C\) are given below:

| \(C\) | 1.0 | 0.010 | 0.00010 M |
| \(x\) | 0.0042 | 0.00041 | 0.0000342 M |

| pH | 2.38 | 3.39 | 4.47 |

**DISCUSSION**

In the above calculations, the following cases may be considered:

1. If \(x\) is small (< 1% of) compared to \(C\), then \((C-x \approx C)\). Thus,

\(\langle x = \sqrt{K_{\text{ac}} \times C} \rangle\)

Note that you are comparing \(x\) with \(C\) here. If \(C > 100^*K_{\text{a}}\), the above method gives satisfactory results.

2. If \(x\) is not small by comparison with \(C\), or \(C\) is not large in comparison to \(K_{\text{a}}\), then the equation takes this form:

\(\langle x^2 + K_{\text{ac}} \rangle x - C K_{\text{ac}} = 0\)

and the solution for \(x\), which must not be negative, has been given above.

3. Both cases 1 and 2 neglect the contribution of \(\langle \ce{[H+]} \rangle\) from the ionization of water. However, if the pH calculated from cases 1 and 2 falls in the range between 6 and 7, the concentration from self-ionization of water cannot be neglected. When the contribution of pH due to self-ionization of water cannot be neglected, there are two equilibria to be considered.

\(\langle \begin{array}{cccccl}
\ce{HA} &\rightleftharpoons &\ce{H+} &+ &\ce{A-} \\
C-x & &x & &x &\\n\ce{H2O} &\rightleftharpoons &\ce{H+} &+ &\ce{OH^-} &\rightarrow (\ce{[H2O]} = 55.6)
\end{array} \rangle\)
Thus,

\[
\begin{align}
\text{\ce{[H+]}} &= (x+y), \\
\text{\ce{[A-]}} &= x, \\
\text{\ce{[OH-]}} &= y,
\end{align}
\]

and the two equilibria are

\[
[K_\text{\ce{a}} = \dfrac{(x+y) x}{C - x}]
\]

and

\[
K_\text{\ce{w}} = (x+y) y, \quad (K_\text{\ce{w}} = 1 \times 10^{-14})
\]

There are two unknown quantities, \(x\) and \(y\) in two equations, and (1) may be rearranged to give

\[
x^2 + (y + K_\text{\ce{a}}) x - C K_\text{\ce{a}} = 0
\]

\[
x = \dfrac{-(y+K_\text{\ce{a}}) + ((y+K_\text{\ce{a}})^2 + 4 C K_\text{\ce{a}})^{1/2}}{2}
\]

One of the many methods to find a suitable solution for this problem is to use iterations, or successive approximations.

1. Assume that \(y = 1 \times 10^{-7}\)

2. Calculate an \(x\) value using the quadratic form

\[
x = \dfrac{-(y+K_\text{\ce{a}}) + ((y+K_\text{\ce{a}})^2 + 4 C K_\text{\ce{a}})^{1/2}}{2}
\]

3. Calculate a new \(y\) value (\(y_n\)) from the \(x\) just obtained using

\[
y_n = \dfrac{1 \times 10^{-14}}{x+y}
\]

4. Replace \(y\) in step (2) by \(y_n\), and recalculate \(x\).

5. Repeat steps (2) and (3) until the new values and the old values differ insignificantly.

The above procedure is actually a general method that always gives a satisfactory solution. This technique has to be used to calculate the pH of dilute weak acid solutions. Further discussion is given in the Exact Calculation of pH.

**Calculate pOH of Basic Solutions**

The discussion on weak acids provides a paradigm for the discussion of weak bases. For weak base \(\text{\ce{B}}\), the ionization is
\[
\ce{B- + H2O \rightleftharpoons HB + OH-}\]

and

\[
K_b = \dfrac{[HB][OH^-]}{[B-]}
\]

The pOH can be calculated for a basic solution if \(K_b\) is given. In this case, the discussion is similar and parallel to that given above for the calculation of pH of weak acids when \(K_a\) is known.

Questions

1. A weak acid is a compound that
   a. is completely ionized in solution,
   b. is not completely ionized in solution,
   c. gives a high pH in a solution,
   d. gives a low pH in its solution.
2. The acidity constant, \(K_a\), for a strong acid is
   a. infinity,
   b. very large,
   c. very small,
   d. zero.
3. Household vinegar is usually 5% acetic acid by volume. Calculate the molarity of this solution. Assume density of solution to be 1 g/mL. The formula weight of \(\ce{CH3COOH}\) is 60.
4. Acetic acid is a typical and familiar compound that provides a good example for numerical problems. Its acidity constant \(K_a\) is \(1.85 \times 10^{-5}\). What is the pH of a concentrated vinegar, which is a 1.0 M acetic acid solution?
5. If you dilute the vinegar 100 times in a soup that you are cooking, the concentration of your soup is 0.010 M in acetic acid.
6. Other ingredients are ignored. What is the pH of this solution?
7. What is the pH of a 0.010 M \(\ce{HCl}\) solution?
8. What is the pH of a \(1.0 \times 10^{-4}\) M acetic acid solution (\(K_a = 1.85 \times 10^{-5}\))?  
9. What is the pH of a \(1.0 \times 10^{-3}\) M chloroacetic acid solution (\(K_a = 1.4 \times 10^{-3}\))? This is an interesting numerical problem. Make a good effort to solve it.
10. What is the pH of a \(1.0 \times 10^{-6}\) M chloroacetic acid solution (\(K_a = 1.4 \times 10^{-3}\))?  
11. What is the pH of a \(1.0 \times 10^{-7}\) M chloroacetic acid solution (\(K_a = 1.4 \times 10^{-3}\))?
12. You have done a number of numerical problems involving various concentrations of some weak acids. These problems are inter-related. If you do not yet have the complete picture, you should review all these questions. Better yet, review the module. What is the pH of a \(1.0 \times 10^{-9}\) M solution of chloroacetic acid, \(K_a = 1.4 \times 10^{-3}\)?
Solutions

1. **Answer b**
   **Consider...**
   The pH of a solution depends on both the concentration and the degree of ionization, (or using $K_a$ as an indicator). In contrast, a strong acid is completely ionized in solution.

2. **Answer b**
   **Consider...**
   Infinity is a concept, it does not represent a definite value. Derive your answer from the definition of equilibrium constant. A strong acid is "completely" ionized in its solution, but the concentration of the conjugate acid is not zero. Thus, a very large $K_a$ is more realistic than infinity.

3. **Answer 0.8 M**
   **Consider...**
   Assume 1 L solution. You have 50 mL acetic acid in 1 L vinegar. The density is 1 g/mL, thus, you have 50 g acetic acid. There is 50 mL vinegar in 1.0 L of vinegar, $(\text{g} / 60 \times \text{per mol}) = 0.8 \text{ mol/L})$

4. **Answer 4.3e-3**
   **Consider...**
   Use the approximation of $[H+] = \sqrt{K_a \times C}$. The approximation is justified because 0.0043/1.0 = 0.4%. Note that most textbooks give $K_a = 1.75e-5$, but we assume a slightly different value in this and the following problems.

5. **Answer 3.4**
   **Consider...**
   Use the approximation of $[H+] = \sqrt{K_a \times C}$. The concentration of $[H+]$ goes from 3.3E-3 in a 1 M solution down to 4.3E-4 M in a 0.01 M solution. The concentration of $[H+]$ decreases 10 times when the concentration of the acid decreases 100 times.

6. **Answer 2**
   **Consider...**
   $[H+] = \text{0.010 M})$. The concentration of $[H+]$ is from $\text{HCl}$, which is a strong acid. The pH of a 0.01 M $\text{HCl}$ solution is lower than that of a 1 M acetic acid solution; compare with the previous problem.

7. **Answer 4.4**
   **Hint...**
   Note that $[H+] = \text{4.3E-5 \ times K_\text{ice a}}$ is 4% of $[\text{HA}]$ ($= 1.0E-4$). Use the formula
   \[x = \frac{-K_a + \sqrt{K_a^2 + 4 C K_a}}{2}\]
   and see what you get. You should use the quadratic formula to calculate $[H+]$. The value using the quadratic formula is 4.5 rather than 4.4 from $\sqrt{C \times K_{\text{ice a}}}$.

8. **Answer 3.2**
**Hint...**
Even a strong acid with concentration of 1.0E-3 M gives a pH of 3. When C and \( K_a \) are comparable, you have to use the quadratic formula.

9. **Answer 6.0**
   **Consider...**
   At this concentration, the acid is almost completely ionized.

10. **Answer 6.7**
    **Consider...**
    From the previous question, you know that the chloroacetic acid should have been completely ionized. Thus, \( [H+] \) is about 2e-7; half of that is contributed by the self-ionization of water. This corresponds to a pH of 6.7.

11. **Answer 7**
    **Consider...**
    Critical judgment is required. The pH is entirely due to the self-ionization of water at this concentration.

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