

15.9: A Deeper Look - Exact Treatment of Acid-Base Equilibria

Learning Objectives

- Calculate the pH when two weak acids are present in a solution.
- Calculate the pH when the concentration of the acid is very dilute.
- Calculate the pH by including the autoionization of water.

A common paradigm in solving for pHs in weak acids and bases is that the equilibria of solutions containing one weak acid or one weak base. In most cases, the amount of H^+ from the autoionization of water is negligible. For very dilute solutions, the amount of H^+ ions from the autoionization of water must also be taken into account. Thus, a strategy is given here to deal with these systems.

When two or more acids are present in a solution, the concentration of H^+ (or pH) of the solution depends on the concentrations of the acids and their acidic constants K_a . The hydrogen ion is produced by the ionization of all acids, but the ionizations of the acids are governed by their equilibrium constants, K_a 's. Similarly, the concentration of OH^- ions in a solution containing two or more weak bases depends on the concentrations and K_b values of the bases. For simplicity, we consider two acids in this module, but the strategies used to discuss equilibria of two acids apply equally well to that of two bases.

Dissociation of Acids and Bases in Water Couple Two Equilibria with a Common Ion H^+

If the pH is between 6 and 8, the contribution due to autoionization of water to $[\text{H}^+]$ should also be considered. When autoionization of water is considered, the method is called the **exact pH calculation** or the **exact treatment**. This method is illustrated below. When the contribution of pH due to self-ionization of water cannot be neglected, there are two coupled equilibria to consider:



ICE Table	HA	H^+	A^-
Initial	C	0	0
Change	$-x$	x	x
Equilibrium	$C - x$	x	x

and



ICE Table	H_2O	H^+	OH^-
Equilibrium	-	y	y

Thus,

$$[\text{H}^+] = (x + y) \quad (15.9.3)$$

$$[\text{A}^-] = x \quad (15.9.4)$$

$$[\text{OH}^-] = y \quad (15.9.5)$$

and the two equilibrium constants are

$$K_a = \frac{(x + y)x}{C - x} \quad (15.9.6)$$

and

$$K_w = (x + y)y \quad (15.9.7)$$

Although you may use the method of successive approximation, the formula to calculate the pH can be derived directly from Equations 15.9.6 and 15.9.7. Solving for x from Equation 15.9.7 gives

$$x = \frac{K_w}{y} - y \quad (15.9.8)$$

and substituting this expression into 15.9.6 results in

$$K_a = \frac{(x+y) \left(\frac{K_w}{y} - y \right)}{C - \frac{K_w}{y} + y} \quad (15.9.9)$$

Rearrange this equation to give:

$$[H^+] = (x+y) \quad (15.9.10)$$

$$= \frac{C - \frac{K_w}{y} + y}{\frac{K_w}{y} - y} K_a \quad (15.9.11)$$

Note that

$$\frac{K_w}{y} = [H^+] \quad (15.9.12)$$

so

$$y = \frac{K_w}{[H^+]}. \quad (15.9.13)$$

Thus, we get:

$$[H^+] = \frac{C - [H^+] + \frac{K_w}{[H^+]}}{[H^+] - \frac{K_w}{[H^+]}} K_a \quad (15.9.14)$$

As written, Equation 15.9.14 is complicated, but can be put into a polynomial form

$$[H^+]^3 + K_a[H^+]^2 - (K_w + CK_a)[H^+] - K_wK_a = 0 \quad (15.9.15)$$

Solving for the exact hydronium concentration requires solving a third-order polynomial. While this is [analytically feasible](#), it is an awkward equation to handle. Instead, we often consider two approximations to Equation 15.9.15 that can be made under limiting conditions.

Case 1: High Concentration Approximation

If $[H^+] > 1 \times 10^{-6}$, then

$$\frac{K_w}{[H^+]} < 1 \times 10^{-8}. \quad (15.9.16)$$

This is small indeed compared to $[H^+]$ and C in Equation 15.9.14. Thus,

$$[H^+] \approx \frac{C - [H^+]}{[H^+]} K_a \quad (15.9.17)$$

$$[H^+]^2 + K_a[H^+] - CK_a \approx 0 \quad (15.9.18)$$

Equation 15.9.18 is a quadratic equation with two solutions. However, only one will be positive and real:

$$[H^+] \approx \frac{-K_a + \sqrt{K_a^2 + 4CK_a}}{2} \quad (15.9.19)$$

Case 2: Low Concentration Approximation

If $[H^+] \ll C$, then

$$C - [H^+] \approx C \quad (15.9.20)$$

Equation 15.9.14 can be simplified

$$[H^+] \approx \frac{C}{[H^+]} K_a \quad (15.9.21)$$

$$[H^+] \approx \sqrt{CK_a} \quad (15.9.22)$$

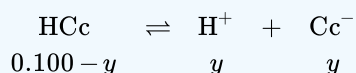
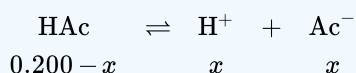
The treatment presented in deriving Equation 15.9.14 is more general, and may be applied to problems involving two or more weak acids in one solution.

✓ Example 15.9.1

Calculate the $[H^+]$, $[Ac^-]$, and $[Cc^-]$ when the solution contains 0.200 M HAc ($K_a = 1.8 \times 10^{-5}$), and 0.100 M HCc (the acidity constant $K_c = 1.4 \times 10^{-3}$). (HAc is acetic acid whereas HCc is chloroacetic acid).

Solution

Assume x and y to be the concentrations of Ac^- and Cc^- , respectively, and write the concentrations below the equations:



$$[H^+] = (x + y)$$

Thus, you have

$$\frac{(x + y)x}{0.200 - x} = 1.8 \times 10^{-5} \quad (15.9.23)$$

$$\frac{(x + y)y}{0.100 - y} = 1.4 \times 10^{-3} \quad (15.9.24)$$

Solving for x and y from Equations 15.9.23 and 15.9.24 may seem difficult, but you can often make some assumptions to simplify the solution procedure. Since HAc is a weaker acid than is HCc, you expect $x \ll y$. Further, $y \ll 0.100$. Therefore, $x + y \approx y$ and $0.100 - y \approx 0.100$. Equation 15.9.24 becomes:

$$\frac{(y)y}{0.100} = 1.4 \times 10^{-3} \quad (15.9.25)$$

which leads to

$$\begin{aligned} y &= (1.4 \times 10^{-3} \times 0.100)^{1/2} \\ &= 0.012 \end{aligned}$$

Substituting y in Equation 15.9.23 results in

$$\frac{(x + 0.012)x}{0.200 - x} = 1.8 \times 10^{-5} \quad (15.9.26)$$

This equation is easily solved, but you may further assume that $0.200 - x \approx 0.200$, since $x \ll 0.200$. Thus,

$$\begin{aligned} x &= \frac{-0.012 + (1.44 \times 10^{-4} + 1.44 \times 10^{-5})^{1/2}}{2} \\ &= 2.9 \times 10^{-4} \quad \leftarrow \text{Small indeed compared to } 0.200 \end{aligned}$$

You had a value of 0.012 for y by neglecting the value of x in Equation 15.9.24. You can now recalculate the value for y by substituting values for x and y in Equation 15.9.24

$$\frac{(2.9 \times 10^{-4} + y)y}{0.100 - 0.012} = 1.4 \times 10^{-3} \quad (15.9.27)$$

Solving for y in the above equation gives

$$y = 0.011$$

You have improved the y value from 0.012 to 0.011. Substituting the new value for y in a successive approximation to recalculate the value for x improves its value from 2.9×10^{-4} to a new value of 3.2×10^{-4} . Use your calculator to obtain these values. Further refinement does not lead to any significant changes for x or y .

Discussion

You should write down these calculations on your note pad, since reading alone does not lead to thorough understanding.

✓ Example 15.9.2

A weak acid HA has a K_a value of 4.0×10^{-11} . What are the pH and the equilibrium concentration of A^- in a solution of 0.0010 M HA?

Solution

For the solution of this problem, two methods are given here. If you like the x and y representation, you may use method (a).

Method (a)

The two equilibrium equations are:



$$[\text{H}^+] = (x + y) \quad (15.9.29)$$

$$\frac{(x + y)x}{0.0010 - x} = 4.0 \times 10^{-11} \quad (15.9.30)$$

$$(15.9.31)$$

$$(x + y)y = 1 \times 10^{-14} \quad (15.9.32)$$

Assume $y \ll x$, and $x \ll 0.0010$, then you have

$$\frac{(x)x}{0.0010} = 4.0 \times 10^{-11} \quad (15.9.33)$$

$$x = (0.0010 \times 4.0e^{-11})^{1/2} \quad (15.9.34)$$

$$= 2.0 \times 10^{-7} \quad (15.9.35)$$

Substituting 2.0×10^{-7} for x in 4 and solving the quadratic equation for y gives,

$$(2.0 \times 10^{-7} + y)y = 1 \times 10^{-14}$$

$$y = 4.1 \times 10^{-8}$$

Substituting 4.1×10^{-8} in Equation 15.9.30 but still approximating $0.0010 - x$ by 0.0010:

$$\frac{(x + 4.1 \times 10^{-8})x}{0.0010} = 4.0 \times 10^{-11} \quad (15.9.36)$$

Solving this quadratic equation for a positive root results in

$$x = 1.8 \times 10^{-7} \text{ M} \leftarrow \text{Recall } x = [\text{A}^-]$$

$$\begin{aligned} [\text{H}^+] &= x + y \\ &= (1.8 + 0.41) \times 10^{-7} \\ &= 2.2 \times 10^{-7} \\ \text{pH} &= 6.65 \end{aligned}$$

The next method uses the formula derived earlier.

Method (b)

Using the formula from the exact treatment, and using 2×10^{-7} for all the $[\text{H}^+]$ values on the right hand side, you obtain a new value of $[\text{H}^+]$ on the left hand side,

$$\begin{aligned} [\text{H}^+] &= \frac{C - [\text{H}^+] + \frac{K_w}{[\text{H}^+]}}{[\text{H}^+] - \frac{K_w}{[\text{H}^+]}} K_a \\ &= 2.24 \times 10^{-7} \\ \text{pH} &= 6.65 \end{aligned}$$

The new $[\text{H}^+]$ enables you to recalculate $[\text{A}^-]$ from the formula:

$$\begin{aligned} (2.24 \times 10^{-7})[\text{A}^-] &= C K_a \\ [\text{A}^-] &= \frac{(0.0010)(4.0 \times 10^{-11})}{2.24 \times 10^{-7}} \\ &= 1.8 \times 10^{-7} \end{aligned}$$

DISCUSSION

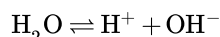
You may have attempted to use the approximation method:

$$\begin{aligned} x &= (C K_a)^{1/2} \\ &= 2.0 \times 10^{-7} \text{ M } \text{A}^-, \text{ or } \text{H}^+; \text{ pH} = 6.70 \end{aligned}$$

and obtained a pH of 6.70, which is greater than 6.65 by less than 1%. However, when an approximation is made, you have no confidence in the calculated pH of 6.70.

Summary

Water is both an acid and a base due to the autoionization,



However, the amount of H^+ ions from water may be very small compared to the amount from an acid if the concentration of the acid is high. When calculating $[\text{H}^+]$ in an acidic solution, approximation method or using the quadratic formula has been discussed in the modules on weak acids.

Contributors and Attributions

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