

7.9: Acid Solutions that Water Contributes pH

Unlike **strong** acids/bases, weak acids and weak bases do not completely dissociate (separate into ions) at equilibrium in water, so calculating the pH of these solutions requires consideration of a unique **ionization constant** and **equilibrium concentrations**. Although this is more difficult than calculating the pH of a strong acid or base solution, most biochemically important acids and bases are considered weak, and so it is very useful to understand how to calculate the pH of these substances. The same basic method can be used to determine the pH of aqueous solutions of many different weak acids and bases.

Introduction

An aqueous solution of a weak acid or base contains both the protonated and unprotonated forms of the compound, so an **ICE table** can be made and used to plug in concentrations into an **equilibrium constant expression**. The ionization constant for the acid (K_a) or base (K_b) is a measure of how readily the acid donates protons or how readily a base accepts protons. Because you are calculating pH, you must solve for the unknown concentration of **hydronium** ions in solution at equilibrium.

The first step in calculating the pH of an aqueous solution of any weak acid or base is to notice whether the initial concentration is high or low relative to 10^{-7} M (the concentration of hydronium and hydroxide ions in water due to the **autoionization** of water). If the concentration of the acid or base is very close to or less than 10^{-7} M, then the solution is considered dilute and additional steps must be taken to calculate pH.

Weak Acids and Bases

You must first be familiar with equilibrium constant expressions and how to write them for a chemical reaction. Then, by making an **ICE table**, you can find unknown concentration values that can be plugged into this equilibrium expression.

✓ Example 7.9.1: Vinegar as a Weak Acid

What is the pH of 1.5 L of a vinegar that is 3% acetic acid by mass? ($K_a = 1.8 \times 10^{-5}$)

Solution

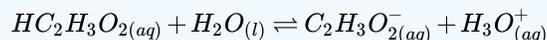
To start, you must find the initial concentration of acetic acid in the vinegar. Assume that the vinegar is really just a solution of acetic acid in water, and that density = 1 g/mL.

So if the vinegar is 3% acetic acid by mass and the molar mass of $\text{HC}_2\text{H}_3\text{O}_2 = 60.05$ g/mol, then

$$\frac{1.5\text{L, vinegar}}{1\text{L}} \times \frac{1000\text{mL}}{1\text{L}} \times \frac{1\text{g}}{1\text{mL}} \times \frac{3\text{g, acetic acid}}{100\text{g, vinegar}} \times \frac{1\text{mol, acetic acid}}{60.05\text{g, acetic acid}} = 0.75 \text{ mol } \text{HC}_2\text{H}_3\text{O}_2$$

Divide 0.75 mol by 1.5 L to get an initial concentration of 0.50 M.

Now make an ICE table, considering the ionization of acetic acid in water into acetate ion and hydronium ion. Because only solutes and gases are incorporated into the equilibrium expression, you can ignore the concentration of water (a pure liquid) in our calculations.



	$\text{HC}_2\text{H}_3\text{O}_2$	H_2O	$\text{C}_2\text{H}_3\text{O}_2^-$	H_3O^+
Initial	0.5	---	0	0
Change	-x	---	+x	+x
Equilibrium	0.5 - x	---	x	x

For every acetic acid molecule that dissociates, one acetate ion and one hydronium ion is produced. This can be represented by subtracting "x" from the original acetic acid concentration, and adding "x" to the original concentrations of the dissociated ions.

You can create a modified equilibrium constant expression

$$K_a = \frac{[C_2H_3O_2^-][H_3O^+]}{[HC_2H_3O_2]}$$

and then plug in the concentration values you found in the ICE table

$$1.8 \times 10^{-5} = \frac{x^2}{0.5 - x}$$

so

$$x^2 + (1.8 \times 10^{-5})x - (9 \times 10^{-6}) = 0$$

then use the quadratic formula to calculate

$$x = 0.0030 \text{ M} = [H_3O^+]$$

which can be plugged into the formula

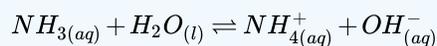
$$\begin{aligned} pH &= -\log[H_3O^+] \\ -\log(0.0030) &= pH = 2.5 \end{aligned}$$

The same thing can be done for calculating the pH of a weak base.

✓ Example 7.9.2: Ammonia as a Weak Base

What is the pH of a 7.0×10^{-3} M NH_3 solution? ($pK_b = 4.74$)

Solution



	NH_3	H_2O	NH_4^+	OH^-
I	7.0×10^{-3}	---	0	0
C	-x	---	+x	+x
E	$7.0 \times 10^{-3} - x$	---	x	x

Instead of K_b , you were given pK_b . So to get K_b

$$pK_b = -\log(K_b) = 4.74$$

$$K_b = 10^{-4.74} = 1.8 \times 10^{-5}$$

Plug these values into the equilibrium expression to get

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} = \frac{x^2}{7 \times 10^{-3} - x}$$

and use the quadratic formula to find that

$$x = 3.46 \times 10^{-4} \text{ M} = [OH^-]$$

so

$$pOH = -\log(3.46 \times 10^{-4}) = 3.46$$

and in water at 25 degrees

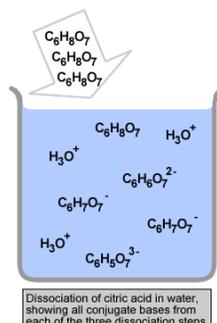
$$pH + pOH = 14$$

Hence:

$$14 - 3.46 = pH = 10.54$$

Weak Polyprotic Acids and Bases

Polyprotic acids have more than one proton to donate to water, and so they have more than one ionization constant (K_{a1} , K_{a2} , etc) that can be considered. Polyprotic bases take more than one proton from water, and also have more than one ionization constant (K_{b1} , K_{b2} , etc).



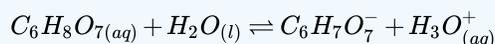
Most often the first proton exchange is the only one that considerably affects pH. This is discussed more at the end of the first example.

✓ Example 7.9.3: Citric Acid as a Polyprotic Acid

What is the pH of a grapefruit that contains 0.007 M citric acid solution ($C_6H_8O_7$)?
 ($K_{a1} = 7.5 \times 10^{-4}$, $K_{a2} = 1.7 \times 10^{-5}$, $K_{a3} = 4.0 \times 10^{-7}$)

Solution

Make an ICE table for the first dissociation



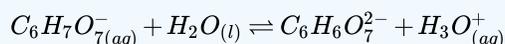
	$C_6H_8O_7$	H_2O	$C_6H_7O_7^-$	H_3O^+
I	0.007	---	0	0
C	-x	---	+x	+x
E	0.007 - x	---	x	x

$$K_{a1} = \frac{[C_6H_7O_7^-][H_3O^+]}{[C_6H_8O_7]} = 7.5 \times 10^{-4} = \frac{x^2}{0.007 - x}$$

and use the quadratic formula to find that

$$x = 0.00195 \text{ M} = [H_3O^+]$$

Then a second ICE table can be made for the second dissociation



	$C_6H_7O_7^-$	H_2O	$C_6H_6O_7^{2-}$	H_3O^+
I	0.00195	---	0	0.00195
C	-x	---	+x	+x
E	0.00195 - x	---	x	0.00195 + x

Remember that, for the first dissociation, $x = [H_3O^+] = [C_6H_7O_7^-]$, so you can plug in the first value of x in for the initial concentrations of $C_6H_7O_7^-$ and H_3O^+ .

$$K_{a2} = \frac{[C_6H_6O_7^{2-}][H_3O^+]}{[C_6H_7O_7^-]} = 1.7 \times 10^{-5} = \frac{(x)(0.00195 + x)}{0.00195 - x}$$

and use the quadratic formula to find that

$$x = 1.67 \times 10^{-5}$$

$$[H_3O^+] = 0.00195 + 1.67 \times 10^{-5} = 0.00197 \text{ M}$$

$$-\log(0.00197) = pH = 2.71$$

Note that if you ignored the addition of hydronium from the second dissociation, then $[H_3O^+] = 0.00195 \text{ M}$, and using this value to calculate pH still gives you the answer of 2.71.

So even though you made two ICE tables (you could even make a third table for K_{a3}), the protons donated in the second dissociation were negligible compared to the first dissociation. So you can see that it is really only the first dissociation that affects pH. Most often this is the case, and only one ICE table is necessary. It is up to you how certain you want to be and how many ICE tables you want to make when you calculate these problems.

✓ Example 7.9.4: Soda Ash as a Polyprotic Base

What is the pH of a saturated solution of sodium carbonate (Na_2CO_3)?

(solubility in water is 21.6 g/100mL at room temperature and for carbonic acid, H_2CO_3 , $K_{a1} = 4.5 \times 10^{-7}$, $K_{a2} = 4.7 \times 10^{-11}$)

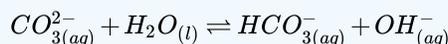
Solution

First, you have to find the initial concentration of CO_3^{2-} which can be found from

$$\frac{21.6 \text{ g } Na_2CO_3}{105.99 \text{ g}} \times \frac{1 \text{ mol}}{105.99 \text{ g}} = 0.204 \text{ mol } Na_2CO_3 = 0.204 \text{ mol } CO_3^{2-}$$

then divide 0.204 mol by 0.100 L to get 2.04 M CO_3^{2-}

Plug into an ICE table



	CO_3^{2-}	H_2O	HCO_3^-	OH^-
I	2.04	---	0	0
C	-x	---	+x	+x
E	2.04 - x	---	x	x

But notice that the equilibrium constants are for carbonic acid. If you were considering the dissociation of carbonic acid, you would write the following expressions

$$K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = 4.5 \times 10^{-7}$$

for



$$K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = 4.7 \times 10^{-11}$$

for



The second acid ionization constant corresponds to the first base ionization constant (because the base reactions go backwards). To convert the second acid ionization constant to the first base ionization constant, you use the equation

$$K_a \times K_b = K_w = 10^{-14}$$

so that

$$K_{a2} \times K_{b1} = 10^{-14}$$

$$K_{b1} = \frac{10^{-14}}{4.7 \times 10^{-11}} = 2.13 \times 10^{-4}$$

Use the same equation to convert the first acid ionization constant to the second base ionization constant

$$K_{a1} \times K_{b2} = 10^{-14}$$

$$K_{b2} = \frac{10^{-14}}{4.5 \times 10^{-7}} = 2.22 \times 10^{-8}$$

The expressions for the protonation of carbonate are now known to be

$$K_{b1} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 2.13 \times 10^{-4}$$

for

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$$K_{b2} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} = 2.22 \times 10^{-8}$$

for



Plug the ICE tables values into the first equilibrium expression

$$K_{b1} = \frac{x^2}{2.04 - x} = 2.13 \times 10^{-4}$$

and use the quadratic formula to solve

$$x = 0.0207 \text{ M} = [OH^-]$$

You can ignore the second base ionization constant because it removes a negligible amount of protons from water. If you want to test this by making an ICE table, you should get that the total hydroxide concentration is $0.0207000222 \text{ M} \approx 0.0207 \text{ M}$

$$\text{so pOH} = -\log(0.0207) = 1.68$$

$$\text{pH} + \text{pOH} = 14$$

$$14 - 1.68 = \text{pH} = \mathbf{12.32}$$

Dilute Weak Acids and Bases

'Dilute' refers to the concentration of the acid or base in water. If the concentration is close to or below 10^{-7} M , then you must consider the donation of hydronium ions from water as well as from your acid or base. This is done by making an ICE table to find the protonation of the acid or base, while also incorporating the [ion product of water](#).

✓ Example 7.9.5: Dilute Weak Acid

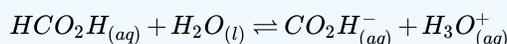
An average bee sting contains 5 micrograms of formic acid (HCO_2H). What is the pH of a 500 mL solution of formic acid? ($\text{p}K_a = 3.75$)

Solution

First calculate the number of moles of formic acid was excreted.

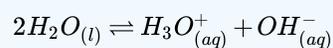
$$\frac{5.00 \mu\text{g}}{10^6 \mu\text{g}} \times \frac{1\text{g}}{46.03\text{g, HCO}_2\text{H}} = 1.09 \times 10^{-7} \text{ mol, HCO}_2\text{H}$$

$$\frac{1.09 \times 10^{-7} \text{ mol}}{0.500\text{L}} = 2.17 \times 10^{-7} \text{ M}$$



	HCO ₂ H	H ₂ O	CO ₂ H ⁻	H ₃ O ⁺
I	2.17 × 10 ⁻⁷	---	0	0
C	-x	---	+x	+x
E	2.17 × 10 ⁻⁷ - x	---	x	x

A second ICE table can be made for the autoionization of water



	2H ₂ O	H ₃ O ⁺	OH ⁻
I	---	0	0
C	---	+y	+y
E	---	y	y

Notice that total [H₃O⁺] = x + y

$$pK_a = 3.75$$

$$K_a = 10^{-3.75} = 1.78 \times 10^{-4}$$

So you can simultaneously solve both equations

$$K_a = \frac{[\text{CO}_2\text{H}^-][\text{H}_3\text{O}^+]}{[\text{HCO}_2\text{H}]} = \frac{x(x+y)}{2.17 \times 10^{-7} - x} = 1.78 \times 10^{-4}$$

and

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (x+y)(y) = 10^{-14}$$

These calculations can be tricky, and it is very easy to make mistakes. It is usually easier to use variables to solve these problems instead of handling awkward numbers.

For this problem use

- a = K_a = 1.78 × 10⁻⁴
- c = initial [HCO₂H] = 2.17 × 10⁻⁷
- w = K_w = 10⁻¹⁴

$$a = \frac{x(x+y)}{c-x}$$

and

$$(x+y)(y) = w$$

$$ac - ax = x^2 + xy$$

and

$$x = \frac{w}{y} - y$$

$$ac - a \left(\frac{w}{y} - y \right) = \left(\frac{w}{y} - y \right)^2 + \left(\frac{w}{y} - y \right) y$$

$$ac - \frac{aw}{y} + ay = \frac{w^2}{y^2} - \frac{2wy}{y} + y^2 + \frac{wy}{y} - y^2$$

$$ac - \frac{aw}{y} + ay = \frac{w^2}{y^2} - 2w + y^2 + w - y^2$$

$$ac - \frac{aw}{y} + ay = \frac{w^2}{y^2} - w$$

$$ac - \frac{aw}{y} + ay + w = \frac{w^2}{y^2}$$

$$acy^2 - awy + ay^3 + wy^2 = w^2$$

$$ay^3 + (ac + w)y^2 - awy - w^2 = 0$$

so when we plug back in the values

$$(1.78 \times 10^{-4})y^3 + ((1.78 \times 10^{-4})(2.17 \times 10^{-7}) + (10^{-14}))y^2 - (1.78 \times 10^{-4})(10^{-14})y - (10^{-14})^2 = 0$$

$$(1.78 \times 10^{-4})y^3 + (3.86 \times 10^{-11})y^2 - (1.78 \times 10^{-18})y - 10^{-28} = 0$$

and use a graphing calculator to find that

$$y = 3.91 \times 10^{-8}$$

and

$$x = \frac{w}{y} - y = \frac{10^{-14}}{3.91 \times 10^{-8}} - 3.91 \times 10^{-8} = 2.17 \times 10^{-7}$$

and total

$$[H_3O^+] = (x + y) = (2.17 \times 10^{-7} + 3.91 \times 10^{-8}) = 2.56 \times 10^{-7} \text{ M}$$

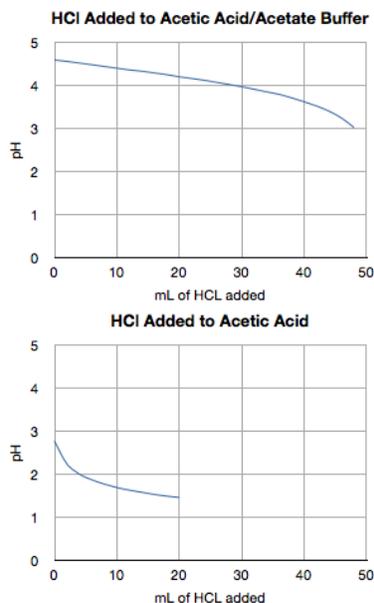
so

$$-\log[H_3O^+] = -\log(2.56 \times 10^{-7}) = pH = 6.59$$

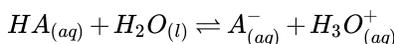
Compare this value to $pH = 6.66$, which is what would have been calculated if the autoprotionization of water was not considered.

Buffer Solutions

Buffer solutions resist pH change when more acid or base is added. They are made from a weak acid and its [conjugate](#) base or a weak base and its conjugate acid. The [Henderson-Hasselbalch approximation](#) can be used to find the pH of a buffer solution, and is derived from the acid equilibrium expression.



Almost 50 mL of HCl was required to decrease the pH of an acetic acid/acetate buffer solution by about 1.5, but only 20 mL of HCl to decrease a pure acetic acid solution by the same amount.



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

$$\log(K_a) = \log\left(\frac{[A^-][H_3O^+]}{[HA]}\right)$$

$$\log(K_a) = \log[H_3O^+] + \log\left(\frac{[A^-]}{[HA]}\right)$$

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

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

A similar equation can be used for bases

$$pOH = pK_b + \log\left(\frac{[HB^+]}{[B]}\right)$$

✓ Example 7.9.6: Blood

The pH of blood plasma is 7.40, and is maintained by a carbonic acid/hydrogen carbonate buffer system. What mass of sodium bicarbonate (NaHCO_3) should be added to a one liter solution of 0.250 M H_2CO_3 to maintain the solution at pH of 7.40? ($pK_a = 6.35$)

Solution

$$pH = pK_a + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$7.40 = 6.35 + \log\left(\frac{[HCO_3^-]}{[0.250]}\right)$$

$$1.05 = \log[HCO_3^-] - \log(0.250)$$

$$0.448 = \log[HCO_3^-]$$

$$[HCO_3^-] = 0.356 M$$

$$(0.356 M) \times (1 L \text{ solution}) = 0.356 \text{ mol } HCO_3^-$$

$$[0.356 \text{ mol } HCO_3^- \times \frac{1 \text{ mol } NaHCO_3}{1 \text{ mol } HCO_3^-} \times \frac{84.01 \text{ g}}{1 \text{ mol, } NaHCO_3}] = 29.9 \text{ g sodium bicarbonate}$$

It is also possible to use the Henderson-Hasselbalch equation to find pK_a , pH, or $[HA]$ if the other variables are given or calculated. Also notice that because $\frac{[A^-]}{[HA]}$ will cancel out the unit of volume, moles of HA and A^- can be used instead of molarity.

References

1. *CRC Handbook of Chemistry and Physics*, 91st ed.; CRC Press: Boca Raton, FL., 2010.
2. *Merck Index*, 12th ed.; Merck & Co.: Whitehouse Station, NJ., 1996.

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