

# Buffering with Limestone

Mixtures of weak acids and their conjugate bases form buffer solutions. These resist large changes in pH when acids or bases are added to them. We've seen that calcium carbonate, limestone, is poorly soluble in water. It is the conjugate base of the bicarbonate ion. Mixtures of carbonate and bicarbonate ions buffer natural waters and prevent damage due to acid rain.

## Outline

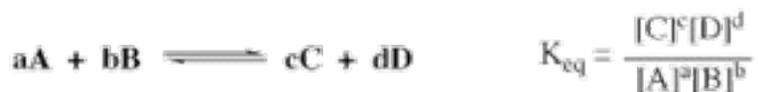
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# Equilibrium

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Consider a chemical system of reactants A and B going to products C and D. At equilibrium, the ratio of the concentration of products raised to the powers of their coefficients and the concentration of reactants raised to the power of their coefficients is constant.

Adding more A will cause the reaction system to adjust in the forward direction to find the equilibrium position. Addition of C will cause the reaction system to adjust in the reverse direction to find the equilibrium position.



*Add a quantity of A to the solution:*

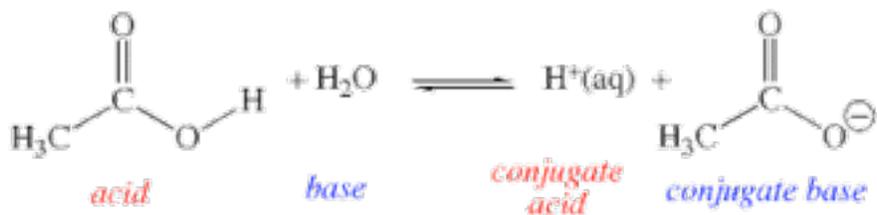


*Add a quantity of C to the solution:*



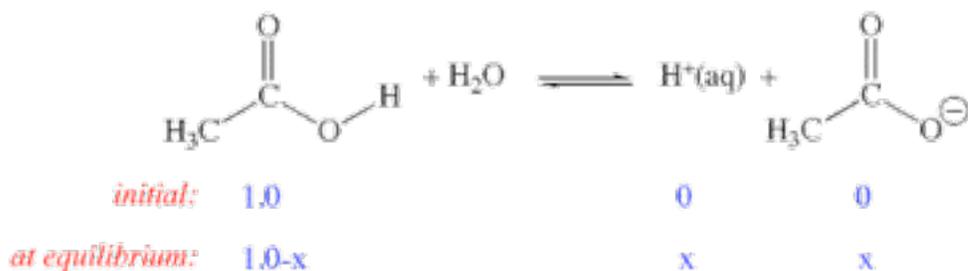
The system will adjust until the equilibrium condition is met:  $K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

The weak acid equilibrium is just like other systems in equilibrium.



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = 10^{-4.8}$$

Consider a solution of 1.0 moles of acetic acid in 1.0 L of water. The solution comes to equilibrium:



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(x)(x)}{(1.0-x)} = 10^{-4.8}$$

In weak acids, the extent of dissociation is small so (1.0-x) is approximately 1.

$$10^{-4.8} = x^2/1$$

$$10^{-4.8} = x^2$$

$$10^{-2.4} = x$$

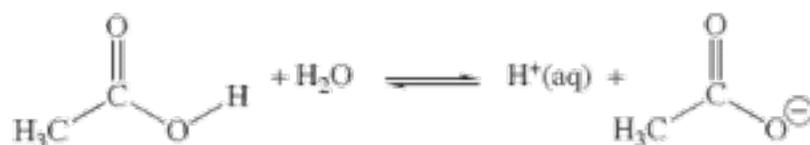
$$[\text{H}^+] = 0.004 \text{ M}$$

$$[\text{CH}_3\text{CO}_2^-] = 0.004 \text{ M}$$

$$[\text{CH}_3\text{CO}_2\text{H}] = (1.0 - 0.004) \text{ M} = 1.0 \text{ M}$$

If we add more reactant (acetic acid), the reaction should shift to the right. If we add more product (acetate ion) the reaction should shift to the left.

**Add 0.5 M acetic acid**



*initial:*      1.0 + 0.5                                      0.004              0.004

*at equilibrium:*      1.5-x                                      0.004+x              0.004+x

Because x will be small, (1.5+x) = 1.5

Let 0.004+x = y

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{y^2}{1.5} = 10^{-4.8}$$

$$10^{-4.8} = y^2 / (10^{0.2})$$

$$10^{-4.6} = y^2$$

$$10^{-2.3} = y$$

**[H<sup>+</sup>] = 0.005 M**

**[CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>] = 0.005 M**

**[CH<sub>3</sub>CO<sub>2</sub>H] = 1.5 M**

**Add 0.5 M acetate:**



*initial:*      1.0                                      0.004              (0.004 + 0.5)

*at equilibrium:*      1.0 + x                                      0.004-x              0.504-x

Because x will be small, (1.0+x) = 1.0 and (0.504-x) = 0.5

Let 0.004-x = y

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(0.5)y}{(1.0)} = 10^{-4.8}$$

$$10^{-4.8} = y / (10^{0.3})$$

$$10^{-4.5} = y$$

**[H<sup>+</sup>] = 0.00003 M**

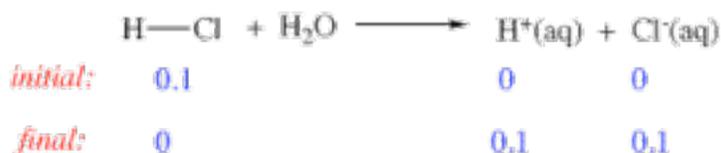
**[CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>] = 0.5 M**

**[CH<sub>3</sub>CO<sub>2</sub>H] = 1.0 M**

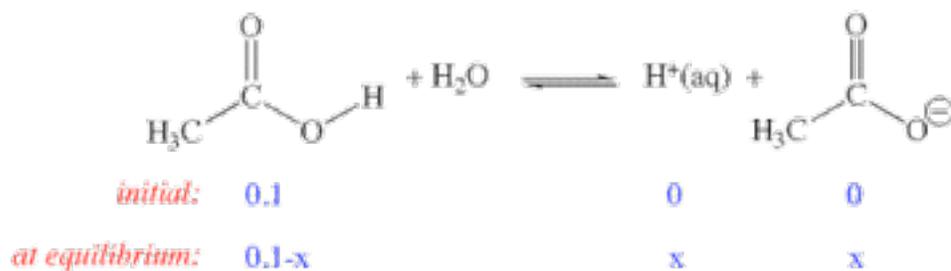
## pH of Acid Solutions

Let's look at solutions of two acids. Hydrochloric acid, HCl, is one of the strong acids and is completely dissociated in water.

Add 0.1 mol of the acid to 1.0 L of water:



$$\text{pH} = -\log[\text{H}^+] = -\log(10^{-1}) = 1.0$$



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(x)(x)}{(0.1-x)} = 10^{-4.8}$$

In weak acids, the extent of dissociation is small so (0.1-x) is approximately 0.1

$$10^{-4.8} = x^2/0.1$$

$$10^{-5.8} = x^2$$

$$10^{-2.9} = x$$

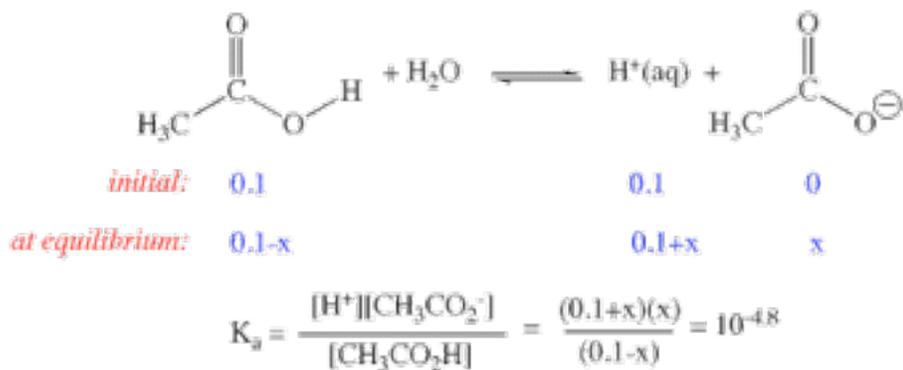
$$\text{pH} = -\log[\text{H}^+] = -\log(10^{-2.9}) = 2.9$$

In both cases, the solution is acidic with a pH much lower than the 7.0 value of pure water. The solution of the strong acid has a much lower pH than a solution of the same concentration of a weaker acid. The concentration of hydrogen ions in the solution made from HCl is 0.1 M while in the solution made from CH<sub>3</sub>CO<sub>2</sub>H it is 0.001 M.

## Addition of Strong Acids to Weak Acids

Now let's consider a solution made from 0.1 mol HCl and 0.1 mol CH<sub>3</sub>CO<sub>2</sub>H in 1.0 L of water.

The HCl is completely dissociated. The H<sup>+</sup>(aq) is one of the products of the CH<sub>3</sub>CO<sub>2</sub>H dissociation equilibrium. The relatively large concentration of one of the products suppresses the dissociation.



Because the dissociation is very small,  $(0.1-x) \approx 0.1$  and  $(0.1+x) \approx 0.1$

$$\begin{aligned}
 \frac{(0.1)(x)}{(0.1)} &= 10^{-4.8} \\
 x &= 10^{-4.8}
 \end{aligned}$$

$$\begin{aligned}
 [\text{H}^+] &= 0.1 \text{ M} \\
 [\text{CH}_3\text{CO}_2^-] &= 0.00002 \text{ M} \\
 [\text{CH}_3\text{CO}_2\text{H}] &= 0.1 \text{ M}
 \end{aligned}$$

*This comes from the HCl dissociation!*

*Essentially no dissociation of the weak acid!*

## Buffers

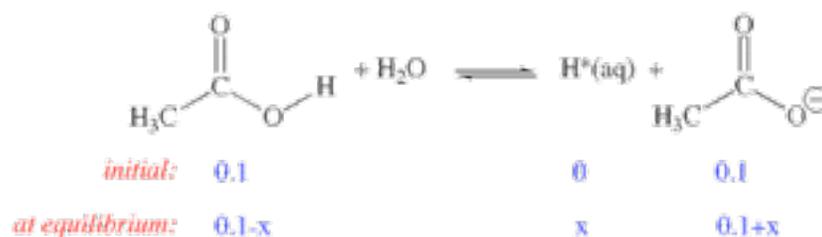
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### Weak Acid/Conjugate Base Solution

We saw that adding another source of protons (a product) decreases the dissociation of a weak acid. That is, when adding a product to a reaction system in equilibrium, the reaction tends to move to the left (decreasing product formation) until the ratio of products and reactants again equals the equilibrium constant.

We should expect to see the same thing when some amount of the conjugate base is added to a weak acid in equilibrium with water.

Add 0.1 mole of  $[\text{Na}][\text{CH}_3\text{CO}_2]$  to 1.0 L of the 0.1 M solution of  $\text{CH}_3\text{CO}_2\text{H}$ :



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(0.1+x)(x)}{(0.1-x)} = 10^{-4.8}$$

Because the dissociation is very small,  $(0.1-x) = 0.1$  and  $(0.1+x) = 0.1$

$$\frac{(0.1)(x)}{(0.1)} = 10^{-4.8}$$

$$x = 10^{-4.8}$$

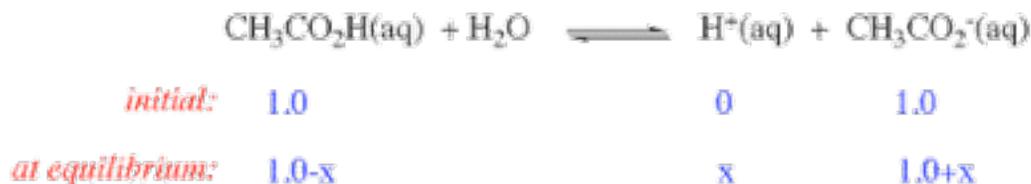
$$\text{pH} = 4.8$$

$$\begin{array}{l}
 [\text{H}^+] = 0.00002 \text{ M} \\
 [\text{CH}_3\text{CO}_2^-] = 0.1 \text{ M} \\
 [\text{CH}_3\text{CO}_2\text{H}] = 0.1 \text{ M}
 \end{array}$$

*This comes from the  $[\text{Na}][\text{CH}_3\text{CO}_2]$*

*Essentially no dissociation of the weak acid!*

What would happen if we combine 1.0 mol acetic acid and 1.0 mol acetate anion in 1.0 L of water?



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(1+x)(x)}{(1-x)} = 10^{-4.8}$$

Because the dissociation is very small,  $(1-x) = 1$  and  $(1+x) = 1$

$$\frac{(1)(x)}{(1)} = 10^{-4.8} \qquad x = 10^{-4.8} \qquad \text{pH} = 4.8 \qquad \begin{array}{l} [\text{H}^+] = 0.00002 \text{ M} \\ [\text{CH}_3\text{CO}_2^-] = 1.0 \text{ M} \\ [\text{CH}_3\text{CO}_2\text{H}] = 1.0 \text{ M} \end{array}$$

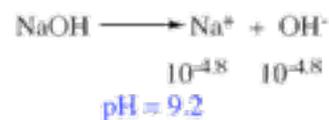
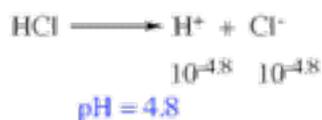
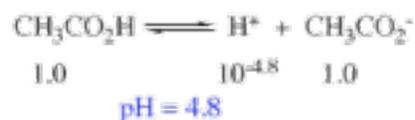
The concentration of both the acid and its conjugate base has increased 10 fold but the pH hasn't changed at all!

In any solution of a weak acid and its conjugate base, the pH depends on the ratio of the the two rather than the specific concentration of either. A 1:1 solution of the weak acid and its conjugate base will have a pH equal to the  $\text{pK}_a$  value for the acid.

## Adding Acid

A mixture of a weak acid and its conjugate base is a buffer. Its pH doesn't change very much when either acid or base is added.

Let's examine the 1.0 M buffer solution and compare it to an HCl (of pH= 4.8) and a NaOH solution (of pOH = 4.8).



*add 0.1 mol/L HCl*



$$\begin{array}{l} [\text{CH}_3\text{CO}_2^-] = 1.0 - 0.1 + x = 0.9 \\ [\text{H}^+] = x \\ [\text{CH}_3\text{CO}_2\text{H}] = 1.0 + 0.1 - x = 1.1 \end{array}$$

$$\begin{array}{l} 10^{-4.8} = (0.9/1.1)x \\ x = 10^{-4.7} \quad \text{pH} = 4.7 \quad \Delta\text{pH} = -0.1 \end{array}$$

$$\begin{array}{l} [\text{H}^+] = 10^{-4.8} + 10^{-1} \\ [\text{H}^+] = 10^{-1} \\ \text{pH} = 1 \quad \Delta\text{pH} = -3.8 \end{array}$$



$$\begin{array}{l} [\text{H}^+] = 10^{-1} - 10^{-4.8} \\ [\text{H}^+] = 10^{-1} \\ \text{pH} = 1 \quad \Delta\text{pH} = -8.2 \end{array}$$

*add 0.5 mol/L HCl*



$$\begin{array}{l} [\text{CH}_3\text{CO}_2^-] = 1.0 - 0.5 + x = 0.5 \\ [\text{H}^+] = x \\ [\text{CH}_3\text{CO}_2\text{H}] = 1.0 + 0.5 - x = 1.5 \end{array}$$

$$\begin{array}{l} 10^{-4.8} = (0.5/1.5)x \\ x = 10^{-4.3} \quad \text{pH} = 4.3 \quad \Delta\text{pH} = -0.5 \end{array}$$

$$\begin{array}{l} [\text{H}^+] = 10^{-4.8} + 10^{-0.3} \\ [\text{H}^+] = 10^{-0.3} \\ \text{pH} = 0.3 \quad \Delta\text{pH} = -4.5 \end{array}$$



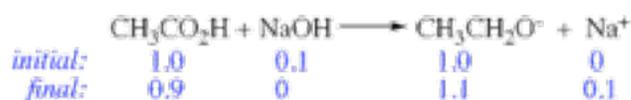
$$\begin{array}{l} [\text{H}^+] = 10^{-0.3} - 10^{-4.8} \\ [\text{H}^+] = 10^{-0.3} \\ \text{pH} = 0.3 \quad \Delta\text{pH} = -8.9 \end{array}$$

The pH of the buffer solution is more stable to the addition of excess acid. It changes much less than the solutions of either the strong acid or the strong base.

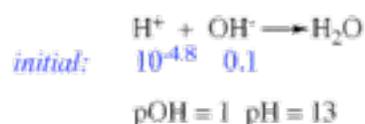
## Adding Base

We see the same thing when we add base to the buffer solution.

Add 0.1 mol/L NaOH to the 1.0 M buffer



Add 0.1 mol/L NaOH to the HCl (pH = 4.8)



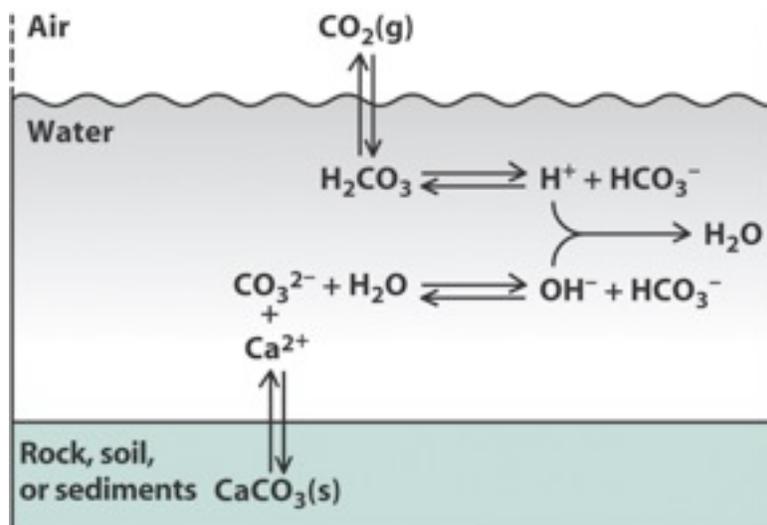
$$10^{-4.8} = (1.1/0.9)x$$

$$x = 10^{-4.9} \quad \text{pH} = 4.9 \quad \Delta\text{pH} = 0.1$$

## Limestone and Acid Rain

### Carbon Dioxide-Bicarbonate-Carbonate Equilibrium

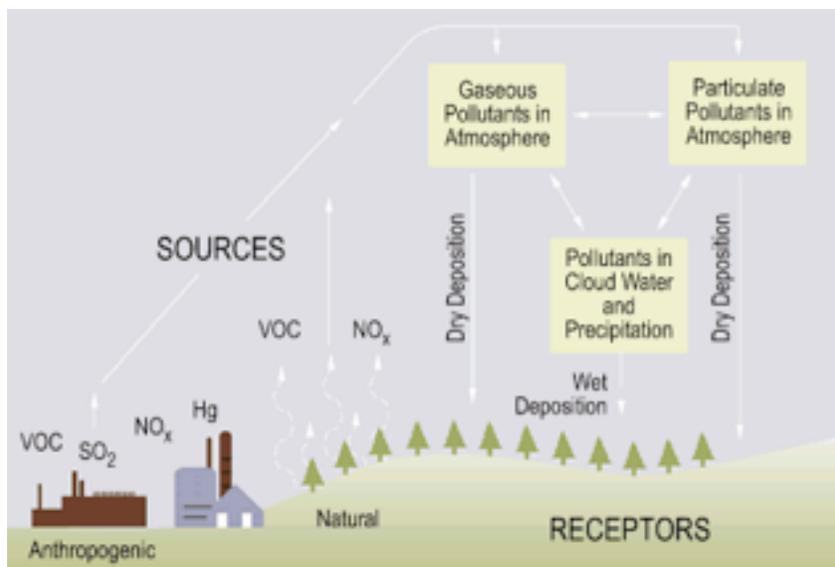
One important buffer in surface waters is the carbon dioxide/bicarbonate/carbonate buffer. When water is in equilibrium with both CO<sub>2</sub> from the atmosphere and carbonate containing rock, the pH of the water is buffered to a pH of 8.3, close to the pK<sub>a</sub> of the weak acid bicarbonate HCO<sub>3</sub><sup>-</sup> (pK<sub>a</sub> = 8.4).



The buffered water resists changes to pH from additional acid or base. Why is this important?

### Acid Rain

Acid rain is caused by the formation of nitric and sulfuric acids in our atmosphere. These compounds are strong acids and they are highly soluble in water and they dissolve in the water droplets within clouds.

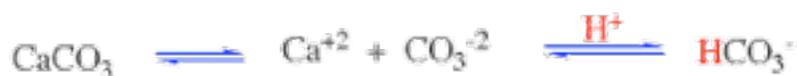


Most of the nitrogen and sulfur oxides result from human activities. The major sources of sulfur dioxide emissions are electric utilities (60 %), industrial combustion (17 %), and industrial processes (8 %). Transportation, with internal combustion engines, produced more than 50 % of all NO<sub>x</sub> with additional emissions from electric utilities (26 %) and industrial combustion (14 %). Agricultural activities, in particular manure handling, are the largest source of ammonia emissions but some ammonia is also given off by industry and by the transportation sector.

Acid rain causes acidification of lakes and streams and contributes to the damage of trees at high elevations and sensitive forest soils.

### Effect of Limestone

Calcium carbonate, [Ca][CO<sub>3</sub>] is a very common mineral. Limestone is one familiar form of calcium carbonate. Acids in acid rain promote the dissolution of calcium carbonate by reacting with the carbonate anion.



This produces a solution of bicarbonate. Because surface waters are in equilibrium with atmospheric carbon dioxide there is a constant concentration of carbonic acid, H<sub>2</sub>CO<sub>3</sub>, in the water.

The presence of limestone and other calcium carbonate rock in lakes and streams helps to maintain a constant pH because the minerals react with the excess acid. However, acid rain eventually can overcome the buffering capacity of the surface water.