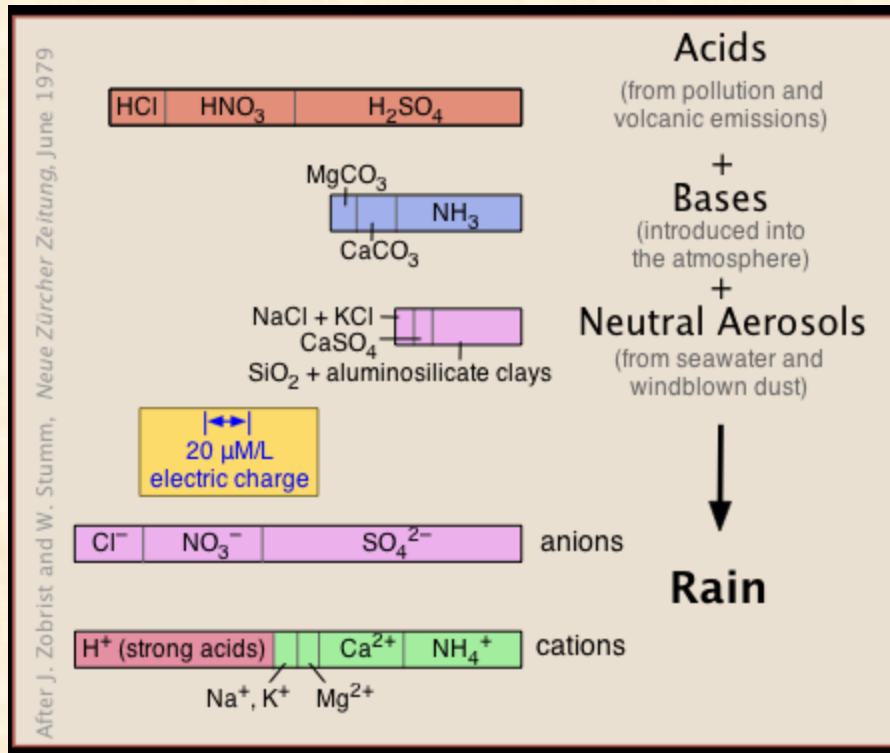
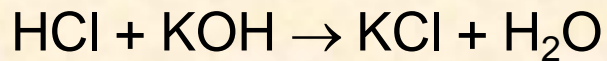


# Chapter 3 - Acid – Base Equilibria



	pH 6.5	pH 6.0	pH 5.5	pH 5.0	pH 4.5	pH 4.0
Trout	✓					
Bass	✓	✓	✓			
Perch	✓	✓	✓	✓		
Frogs	✓	✓	✓	✓	✓	
Salamanders	✓	✓	✓	✓	✓	✓
Clams	✓	✓	✓	✓	✓	✓
Crayfish	✓	✓	✓	✓	✓	✓
Snails	✓	✓	✓	✓	✓	✓
Mayfly	✓	✓	✓	✓	✓	✓



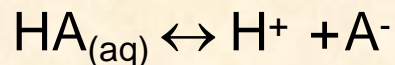
acid + base → salt + water

# What is an acid?

**The Arrhenius concept** proposed that acids are substances that produce hydrogen ions (H<sup>+</sup>) in aqueous solutions.



or



is the general form of the acid reaction. We can calculate an equilibrium constant ( $K_a$ ) for the reaction.  $K_a$  is called the acid dissociation constant.

$$K_a = [\text{H}^{+}][\text{A}^{-}] / [\text{HA}].$$

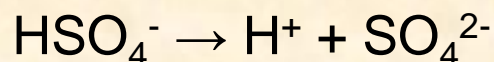
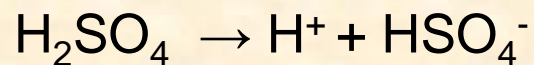
A strong acid is one that undergoes significant dissociation and has a very large  $K_a$ . A weak acid only partially dissociates and has a relatively small  $K_a$ .

$$\text{p}K_a = -\log K_a$$

**Table 3-1** Dissociation Constants for Acids at 25°C

Acid	Formula	pK <sub>a1</sub>	pK <sub>a2</sub>	pK <sub>a3</sub>
Hydrochloric	HCl	~-3		
Sulfuric	H <sub>2</sub> SO <sub>4</sub>	~-3	1.99	
Nitric	HNO <sub>3</sub>	0		
Oxalic	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	1.2	4.2	
Phosphoric	H <sub>3</sub> PO <sub>4</sub>	2.15	7.2	12.35
Hydrofluoric	HF	3.18		
Formic	HCOOH	3.75		
Acetic	CH <sub>3</sub> COOH	4.76		
Carbonic	H <sub>2</sub> CO <sub>3</sub>	6.35	10.33	
Hydrosulfuric	H <sub>2</sub> S	7.03	>14	
Boric	H <sub>3</sub> BO <sub>3</sub>	9.27	>14	
Silicic	H <sub>4</sub> SiO <sub>4</sub>	9.83	13.17	

As you noticed from the previous slide (Table 3-1), acids can contain more than one acidic proton.



Polyprotic acids have more than one  $\text{pK}_a$

Acids that undergo significant dissociation have a negative  $\text{pK}_a$ , and acids that only partially dissociate have a positive  $\text{pK}_a$ .

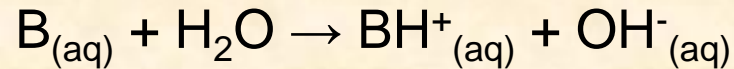


**Table 3-1** Dissociation Constants for Acids at 25°C

Acid	Formula	pK <sub>a1</sub>	pK <sub>a2</sub>	pK <sub>a3</sub>
Hydrochloric	HCl	~-3		
Sulfuric	H <sub>2</sub> SO <sub>4</sub>	~-3	1.99	
Nitric	HNO <sub>3</sub>	0		
Oxalic	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	1.2	4.2	
Phosphoric	H <sub>3</sub> PO <sub>4</sub>	2.15	7.2	12.35
Hydrofluoric	HF	3.18		
Formic	HCOOH	3.75		
Acetic	CH <sub>3</sub> COOH	4.76		
Carbonic	H <sub>2</sub> CO <sub>3</sub>	6.35	10.33	
Hydrosulfuric	H <sub>2</sub> S	7.03	>14	
Boric	H <sub>3</sub> BO <sub>3</sub>	9.27	>14	
Silicic	H <sub>4</sub> SiO <sub>4</sub>	9.83	13.17	

# What is a base?

**The Arrhenius concept** proposed that a base is a substance that produces OH<sup>-</sup> ions in aqueous solution.



is the general form of the base reaction. We can calculate an equilibrium constant ( $K_b$ ) for the reaction.  $K_b$  is called the base dissociation constant.

$$K_b = [BH^+][OH^-] / [B]$$

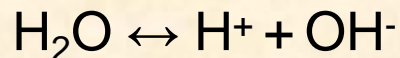
A strong base is one that undergoes essentially complete dissociation and has a large  $K_b$ . A weak base only partially dissociates and has a relatively small  $K_b$ .

$$pK_b = -\log K_b$$

Base (Hydroxide)	Formula	pK <sub>b1</sub>	pK <sub>b2</sub>	pK <sub>b3</sub>
Methylamine	CH <sub>3</sub> NH <sub>2</sub>	3.36		
Ammonium	NH <sub>4</sub> (OH)	4.7		
Magnesium	Mg(OH) <sub>2</sub>	8.6	2.6	
Pyridine	C <sub>5</sub> H <sub>5</sub> N	8.8		
Manganese	Mn(OH) <sub>2</sub>	9.4	3.4	
Ferrous	Fe(OH) <sub>2</sub>	10.6	4.5	
Al, amorphous	Al(OH) <sub>3</sub>	12.3	10.3	9.0
Al, gibbsite	Al(OH) <sub>3</sub>	14.8	10.3	9.0
Ferric, amorphous	Fe(OH) <sub>3</sub>	16.5	10.5	11.8

\*As it was with acids, bases may also require more than one step to completely dissociate. You may also notice the absence of NaOH. For our purposes, you may assume this base completely dissociates.

The dissociation of water and pH



and

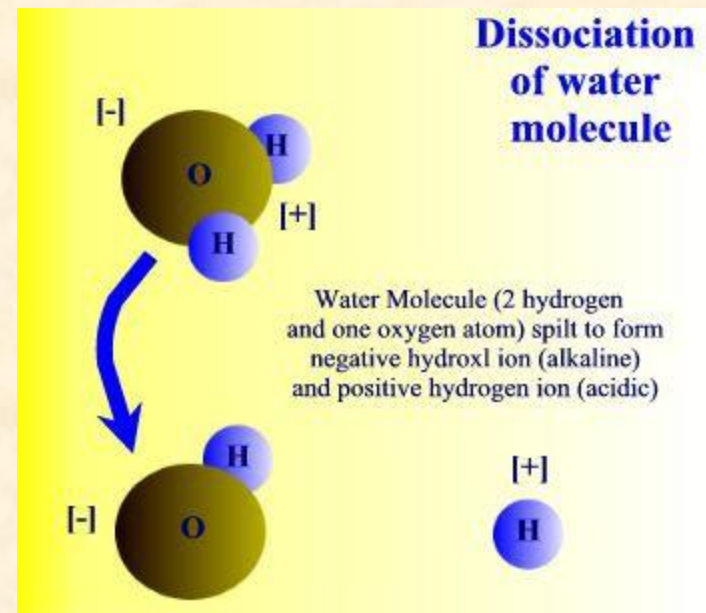
$$K_w = [\text{H}^+][\text{OH}^-] / [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

Where  $K_w$  is the equilibrium constant for water.

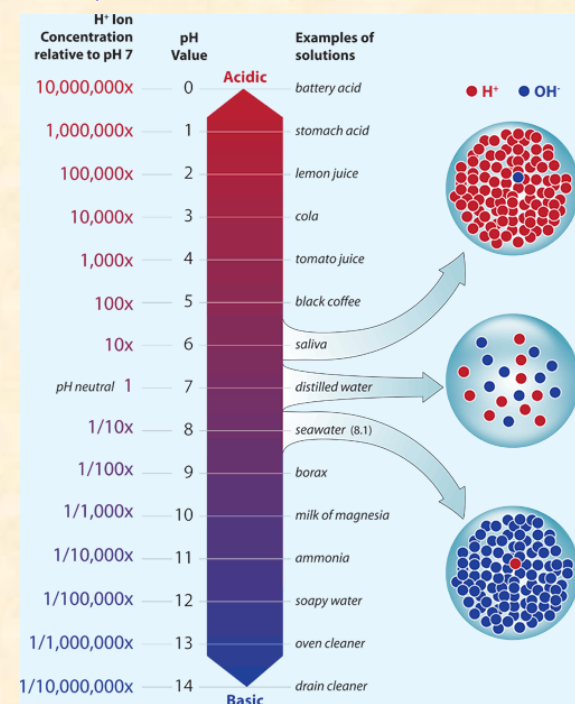
**$K_w$  varies as a function of temperature. (See table 3-3.)**

$$K_w(25^\circ\text{C}) = 10^{-14} = [\text{H}^+][\text{OH}^-]$$

*\*Remember that  $K_w$  is a constant, therefore if you know the  $K_w$  and the concentration of either  $\text{H}^+$  or  $\text{OH}^-$ , you can find the remaining unknown concentration.*



<http://www.fishdoc.co.uk/water/cocktail04.html>



<http://www.whoi.edu/oceanus/viewArticle.do?archives=true&id=65266>



Table 3-3 Dissociation Constants ( $K_w$ ) for Water as a Function of Temperature\*

T (°C)	-log $K_{eq}$		T (°C)	-log $K_{eq}$
0	14.938		30	13.836
5	14.727		35	13.685
10	14.528		40	13.542
15	14.340		45	13.405
20	14.163		50	13.275
24	14.000		55	13.152
25	13.9995		60	13.034

\*Data from CRC Handbook of Chemistry and Physics (2000).

If  $[H^+]$  for a solution is  $10^{-3}$ , what is  $[OH^-]$  in that solution?

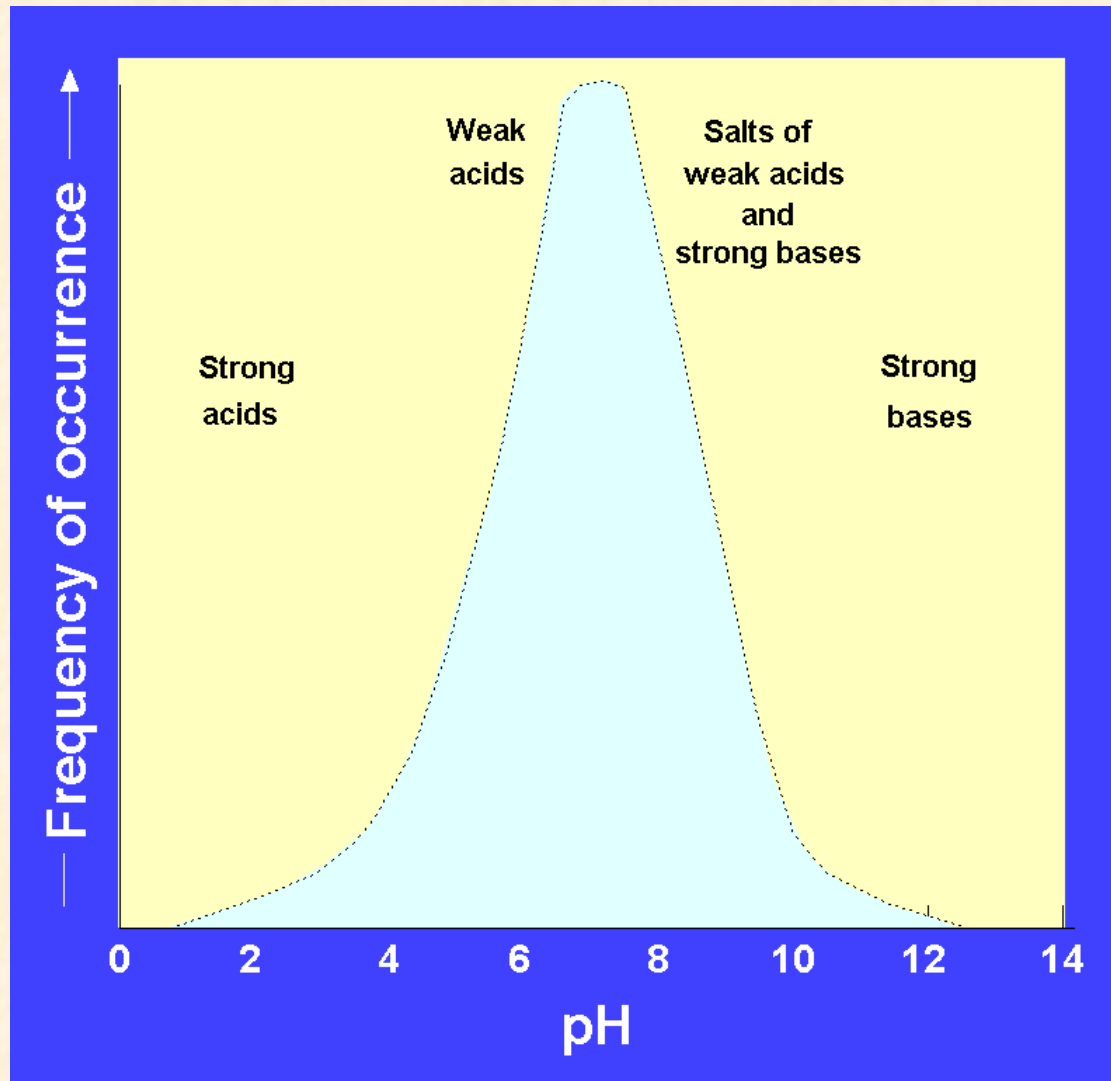
$$[OH^-] = 10^{-11}$$

The pH scale was designed to simplify the description of the acidity of a solution. The pH is often called the hydrogen ion exponent.

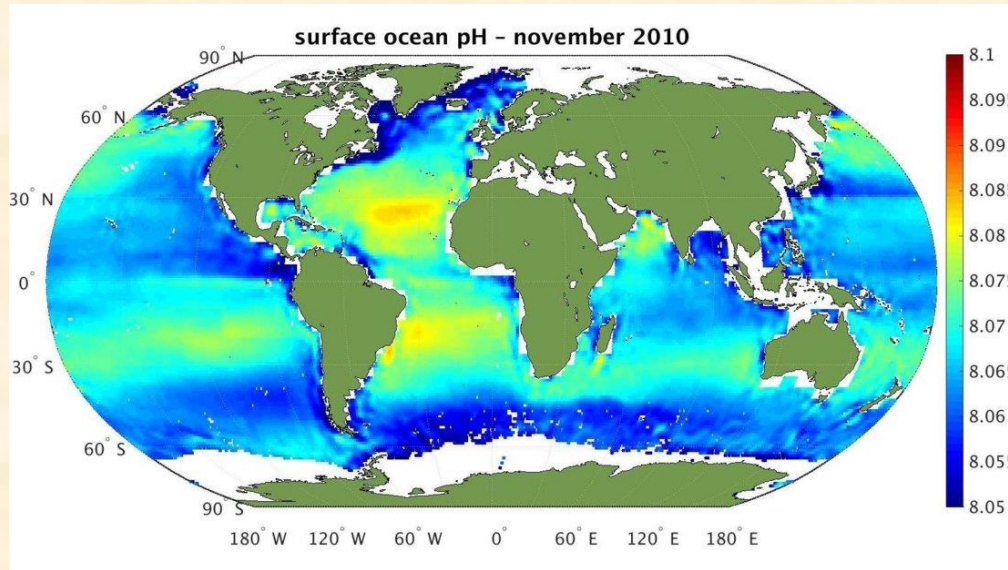
$$pH = -\log[H^+]$$

Therefore, if, for example  $[H^+] = 10^{-3}$ , then the  $pH = 3$ . Pure water at  $25^\circ\text{C}$  has a pH of 7. This means that the number of  $H^+$  ions and the number of  $OH^-$  ions are equal at  $10^{-7}$  each.

# Frequency of pH values in natural waters



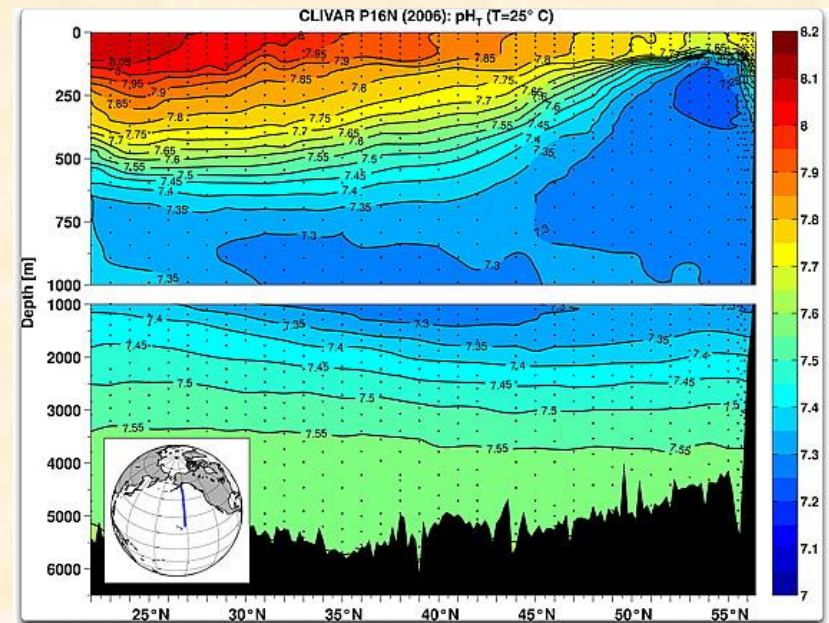
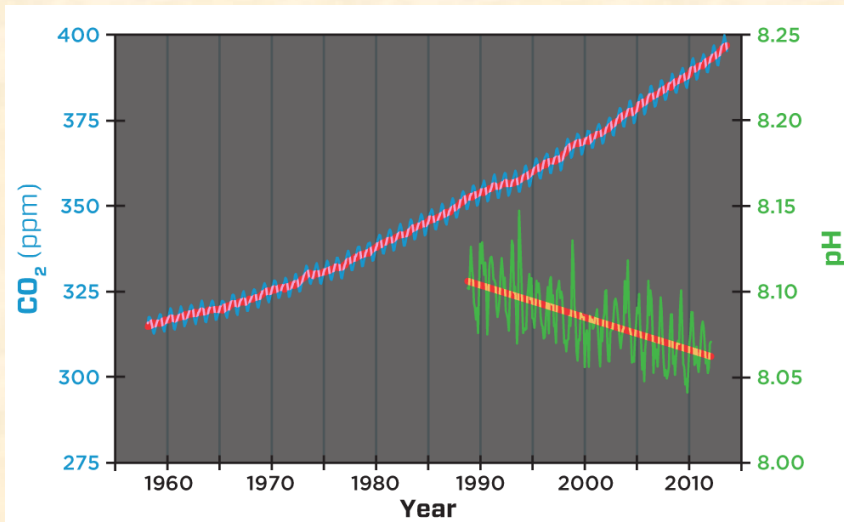
# pH of Ocean Water



Ocean surface water is slightly more basic at 30° N and S latitude, and least basic at high latitudes. Why?

Deeper ocean waters are less basic than surface waters. Why?

Seawater pH decreasing with time. Why?



Determine the pH of a solution with a  $[\text{OH}^-]$  of  $3 \times 10^{-5}$ .

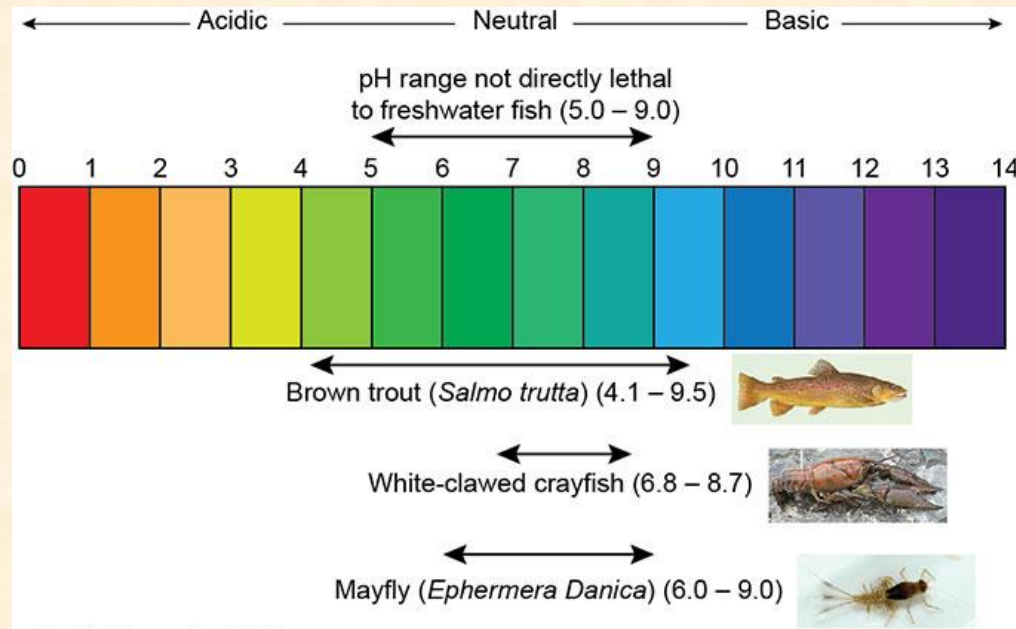
Recall:  $K_{w(25^\circ\text{C})} = 10^{-14} = [\text{H}^+][\text{OH}^-]$

$$10^{-14} / 3 \times 10^{-5} = [\text{H}^+]$$

$$[\text{H}^+] = 3.33 \times 10^{-9}. \Rightarrow \text{pH} = -\log(3.33 \times 10^{-9}) = 8.48$$

Is this solution acidic or basic?

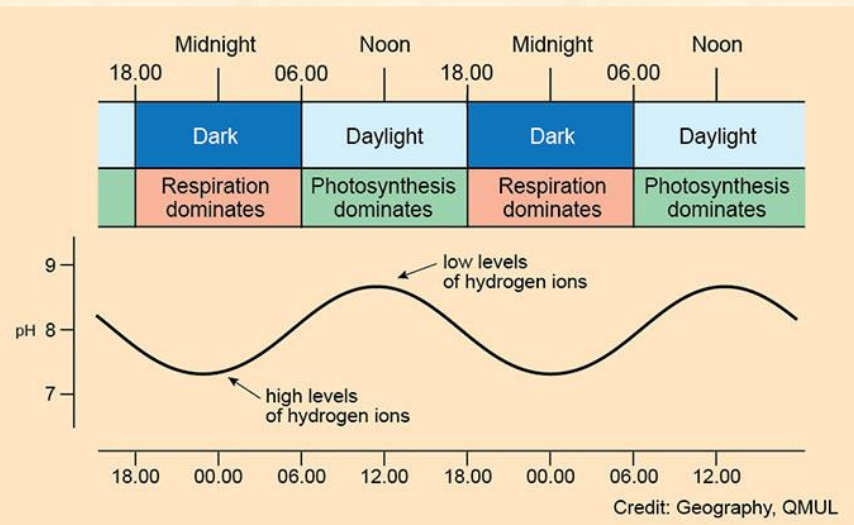
# pH of river systems



Credit: Geography, QMUL

pH range for healthy biotic environments

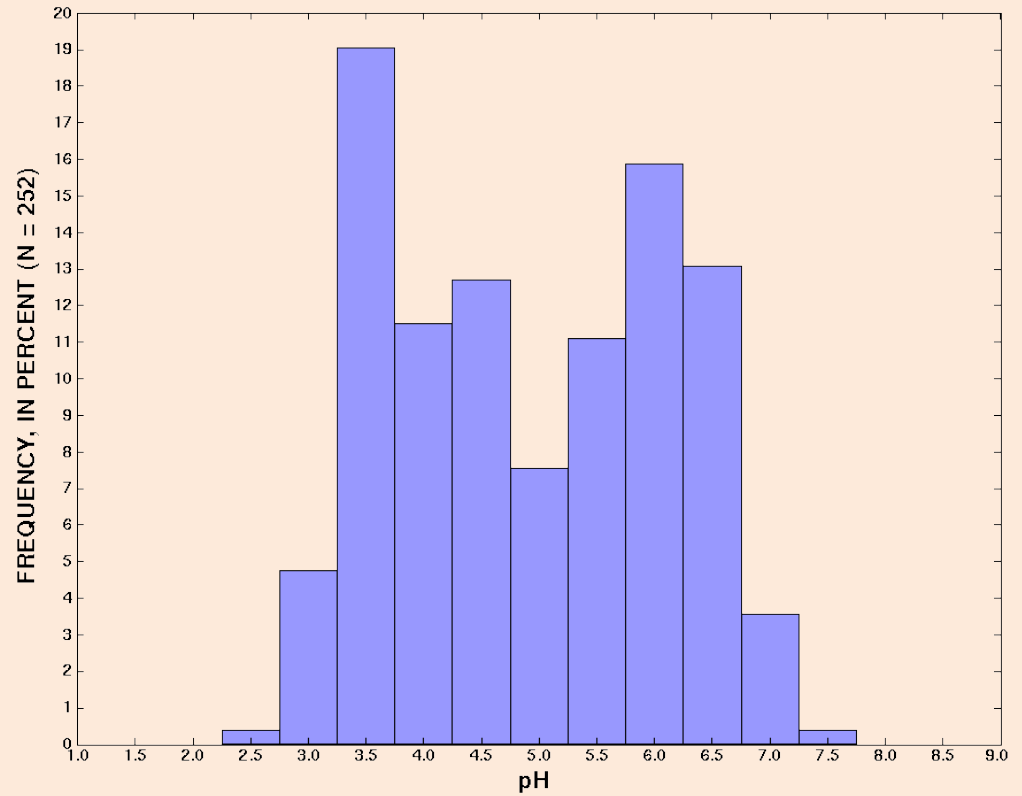
Why is there a daily cycle in river water (or lake) pH?



# Acid mine drainage

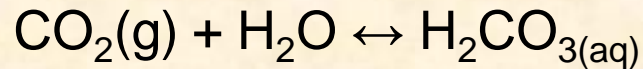
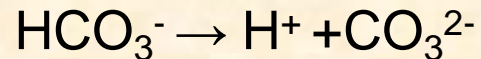
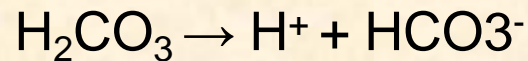
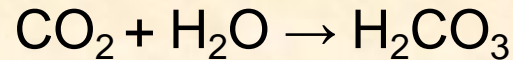


ANTHRACITE COAL-MINE DISCHARGES IN PENNSYLVANIA



# The Carbonic Acid System

The formation and dissociation of carbonic acid can be described by the following three equations.



$$[\text{H}_2\text{CO}_{3(\text{aq})}] = K_{\text{CO}_2} P_{\text{CO}_2}$$

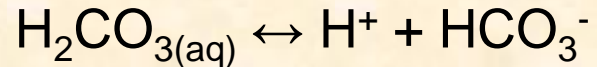
$K_{\text{CO}_2}$  = Henry's Law constant

$P_{\text{CO}_2}$  = partial pressure in atmospheres



The dissociation of  $\text{H}_2\text{CO}_{3(\text{aq})}$  is a two step process

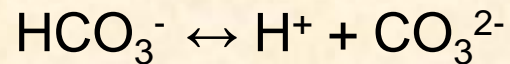
First dissociation



$$K_{a1} = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_{3(\text{aq})}]$$

$$\text{by definition } [\text{H}_2\text{CO}_{3(\text{aq})}] = 1$$

Second dissociation



$$K_{a2} = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]$$

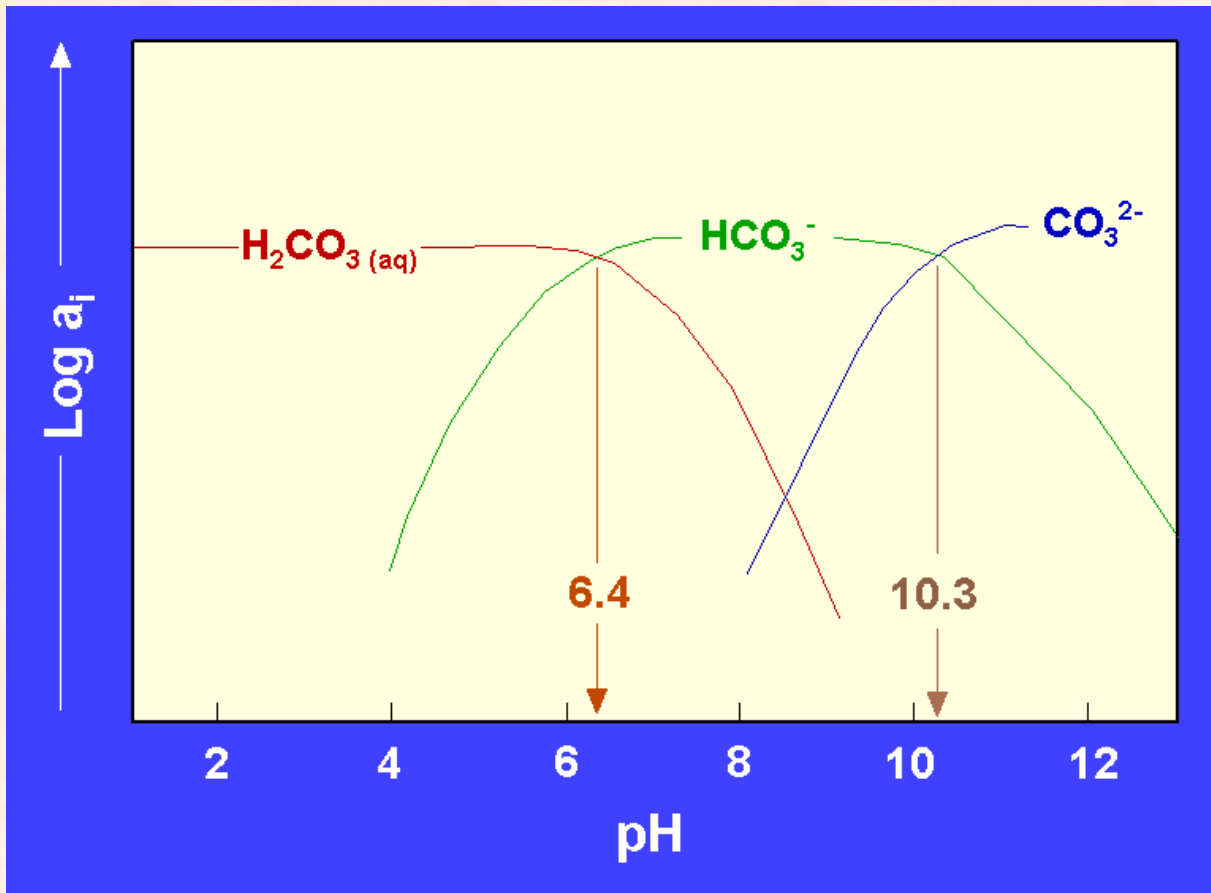
**Table 3–4** Equilibrium Constants for the Carbonate System\*

$T$ (°C)	Dissociation constants		Solubility products	
	$pK_{a_1}$	$pK_{a_2}$	$pK_{cal}$	$pK_{arg}$
0	6.58	10.63	8.38	8.22
5	6.52	10.55	8.39	8.24
10	6.46	10.49	8.41	8.26
15	6.42	10.43	8.43	8.28
20	6.38	10.38	8.45	8.31
25	6.35	10.33	8.48	8.34
30	6.33	10.29	8.51	8.37
45	6.29	10.20	8.62	8.49
60	6.29	10.14	8.76	8.64

At 25°C

$$[\text{H}_2\text{CO}_{3(\text{aq})}]/[\text{HCO}_3^-] = [\text{H}^+]/K_{a1} = [\text{H}^+]/10^{-6.35}$$

$$[\text{HCO}_3^-]/[\text{CO}_3^{2-}] = [\text{H}^+]/K_{a2} = [\text{H}^+]/10^{-10.33}$$



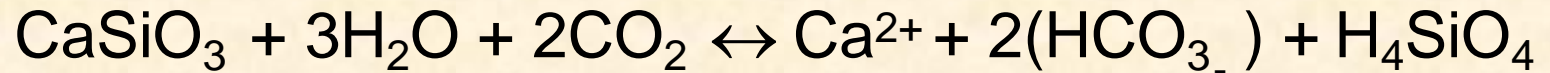
# What other factors can change the pH of natural waters?

**Table 3 -5. Examples of processes that control the CO<sub>2</sub> content & pH of surface and groundwaters**


Process	Reaction	pH
Temperature change	Increase T, decrease solubility of CO <sub>2</sub> (g)	Increases
	Decrease T, increase solubility of CO <sub>2</sub> (g)	Decreases
Photosynthesis	$6\text{CO}_{2(g)} + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_{2(g)}$	Increases
Respiration	$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_{2(g)} \rightarrow 6\text{CO}_{2(g)} + 6\text{H}_2\text{O}$	Decreases
Anaerobic decay	$2\text{CH}_2\text{O} \rightarrow \text{CH}_4(g) + \text{CO}_2(g)$	Decreases
Denitrification	$5\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+ \rightarrow 5\text{CO}_2(g) + 2\text{N}_2(g) + 7\text{H}_2\text{O}$	Increases
Dissolution of carbonate	$\text{CaCO}_3_{\text{calcite}} + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2(g)$	Increases
Precipitation of carbonate	$\text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2(g) \rightarrow \text{CaCO}_3_{\text{calcite}} + 2\text{H}^+$	Decreases
Weathering of Al-silicate minerals	$2\text{KAISi}_3\text{O}_8_{\text{feldspar}} + 2\text{CO}_2(g) + 11\text{H}_2\text{O} \rightarrow$	Increases
	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4_{\text{kaolinite}} + 2\text{K}^+ + 2\text{HCO}_3^- + 4\text{H}_4\text{SiO}_4(\text{aq})$	

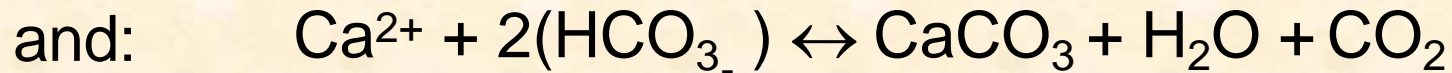
How does the weathering of calcium, silica and carbonate species change the atmospheric concentration of carbon dioxide?





wollastonite + water + carbon dioxide  $\leftrightarrow$  calcium + bicarbonate + silicic acid

  
From pore spaces  
&/or atmosphere



calcite + quartz  $\leftrightarrow$  wollastonite + carbon dioxide

For the CO<sub>2</sub> - H<sub>2</sub>O system there are two end-member cases:

An **open system**: in equilibrium with atmospheric CO<sub>2</sub>.

A **closed system**: isolated from atmospheric CO<sub>2</sub>.

We will first consider an open system, which is in equilibrium with atmospheric CO<sub>2</sub>. We need four equations to solve this problem: (1) equation 3–7, which relates the partial pressure of CO<sub>2</sub> to the concentration of H<sub>2</sub>CO<sub>3(aq)</sub>; (2) equation 3–8, which describes the dissociation of H<sub>2</sub>CO<sub>3(aq)</sub>; (3) equation 3–9, which describes the dissociation of HCO<sub>3</sub><sup>-</sup>; and (4) a charge balance equation. A basic constraint of solution chemistry is that the positive and negative charges of the species in solution must be equal. This is an important concept and is used repeatedly in solving water-chemistry problems. For the system CO<sub>2</sub>–H<sub>2</sub>O, the charge balance equation is written

$$m_{\text{H}^+} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-}$$

where *m* is the molar concentration of each species. We will make the assumption that measured molar concentrations are equal to activity. This is approximately true in very dilute solutions. For more precise calculations, activity coefficients can be calculated as described in Chapter 2 and the molar concentrations adjusted to take into account activity.

### Example 3-3 (Open system)

Calculate the pH of rainwater in equilibrium with atmospheric CO<sub>2</sub>.

*This book was first published in 2004, thus the data is more than 10 years old. What are the atmospheric CO<sub>2</sub> levels today?*

For the present day atmosphere = (400ppm)  $\Rightarrow P_{\text{CO}_2} = 10^{-3.40}\text{atm}$ .

$$[\text{H}_2\text{CO}_3] = K_{\text{CO}_2} P_{\text{CO}_2} = (10^{-1.47})(10^{-3.40}) = 10^{-4.87}.$$

$$K_a = [\text{H}^+][\text{HCO}_3^-] / [\text{H}_2\text{CO}_3] \therefore [\text{H}^+][\text{HCO}_3^-] = K_a[\text{H}_2\text{CO}_3] = (10^{-6.35})(10^{-4.87})$$

$$= [10^{-11.22}] \text{ If you assume that } [\text{H}^+] = [\text{HCO}_3^-] \text{ then } [\text{H}^+] = (10^{-11.22})^{0.5} \\ = 10^{-5.61} \text{ this means that the pH of "acid rain" is less than 5.61.}$$

It is important to note that the book suggest acid rain has a pH of 5.66. What does this imply if the atmospheric CO<sub>2</sub> concentrations approach 500ppm? Remember this is a logarithmic scale..... ***The pH would be 5.56.***



### Example 3-4 (Closed system)

A groundwater sample has a measured pH of 6.84 and  $\text{HCO}_3^-$  of  $460\text{mg L}^{-1}$ . We will assume that activity equals concentration. At  $25^\circ\text{C}$ , calculate the  $P_{\text{CO}_2}$  for this groundwater sample.

We must first convert the measured concentration of  $\text{HCO}_3^-$  to moles per liter. The atomic weight of  $\text{HCO}_3^- = 61.0\text{g}$

$$[\text{HCO}_3^-] = 460 \times 10^{-3} \text{ g L}^{-1} / 61\text{g/mol} = 7.54 \times 10^{-3} \text{ mol L}^{-1}$$

The using equation 3-15:  $\log P_{\text{CO}_2} = -\text{pH} + \log([\text{HCO}_3^-]/K_{a1}K_{\text{CO}_2})$

$$\log P_{\text{CO}_2} = -6.84 + \log([7.54 \times 10^{-3}] / 10^{-6.35}10^{-1.47}) = -1.14$$

$$P_{\text{CO}_2} = 10^{-1.14}$$

How does this compare with atmospheric concentrations? What does this imply about the groundwater? Is it close to a pollution source, anaerobic or aerobic decay or in supersaturated in  $\text{CaCO}_3$ ?

### Example 3-5

Calculate the concentration of each carbonate species in a solution at 25°C when  $C_T = 1 \times 10^{-3} \text{ mol L}^{-1}$  and  $\text{pH} = 5.7$ . Which species do you expect to be dominate?

$$\alpha_H = 1 + K_{a1}/[\text{H}^+] + K_{a1}K_{a2}/[\text{H}^+]^2 = 1 + (10^{-6.35})/(10^{-5.7}) + (10^{-6.35})(10^{-10.33})/(10^{-5.7})^2 = 1.224$$

$$[\text{H}_2\text{CO}_3] = C_T/\alpha_H = 1 \times 10^{-3} \text{ mol L}^{-1}/1.224 = 8.17 \times 10^{-4} \text{ mol L}^{-1}$$

$$[\text{HCO}_3^-] = C_T K_{a1}/[\text{H}^+] \alpha_H = (1 \times 10^{-3})(10^{-6.35})/(10^{-5.7})(1.224) = 1.83 \times 10^{-4} \text{ mol L}^{-1}$$

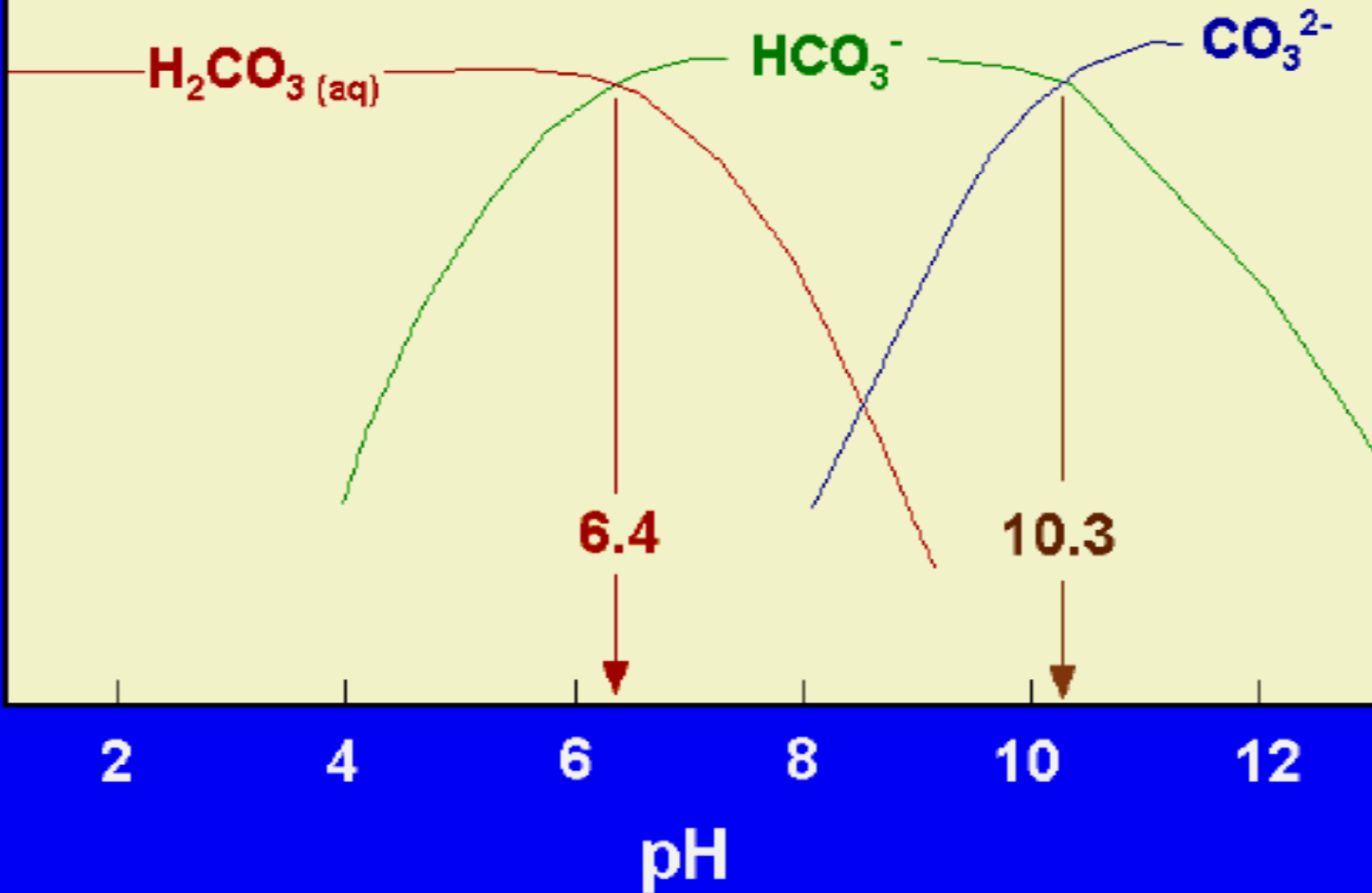
$$[\text{CO}_3^{2-}] = C_T K_{a1} K_{a2}/[\text{H}^+]^2 \alpha_H$$

$$= (1 \times 10^{-3})(10^{-6.35})(10^{-10.33})/(10^{-5.7})^2(1.224) = 4.29 \times 10^{-9} \text{ mol L}^{-1}$$

Do these concentrations make sense given a pH of 5.7

pH = 5.7:  $[H_2CO_3] = 8.17 \times 10^{-4}$ ,  $[HCO_3^-] = 1.83 \times 10^{-4}$ ,  $[CO_3^{2-}] = 4.29 \times 10^{-9}$

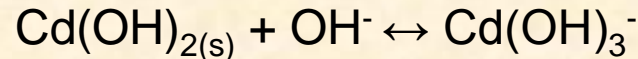
Log  $a_i$



## Amphoteric Hydroxides

**Amphoteric hydroxides** are hydroxides that can behave as either an acid or a base. This behavior varies as a function of pH.

Consider the following reaction, which represents the dissolution of  $\text{Cd}(\text{OH})_{2(s)}$  when a hydroxyl ion is added:



The equilibrium equation for this reaction is

$$K_A = [\text{Cd}(\text{OH})_3^-]/[\text{OH}^-]$$

where  $K_A$  is the equilibrium constant for the amphoteric reaction.

In a basic solution the reaction will move to the right forming  $\text{Cd}(\text{OH})_3^-$ . This will cause an increase in the  $\text{H}^+$  ions in solution (remember that  $K_w$  is a constant) and the hydroxide acts as an acid. In an acid solution, the reaction will move to the left releasing  $\text{OH}^-$  ions causing a decrease in  $\text{H}^+$  ions and the hydroxide acts as a base.

# Acidity and Alkalinity

**Acidity** is the capacity of water to donate protons. Also described as the ability of a solution to neutralize bases.

**Alkalinity** is the capacity of water to accept protons. Also described as the ability of a solution to neutralize acids.

**Nonconservative species:** species whose abundances vary as a function of pH or some other intensive variable (i.e. P & T).

**Conservative species:** species whose abundances do not vary as a function of pH or some other intensive variable (i.e. P & T).

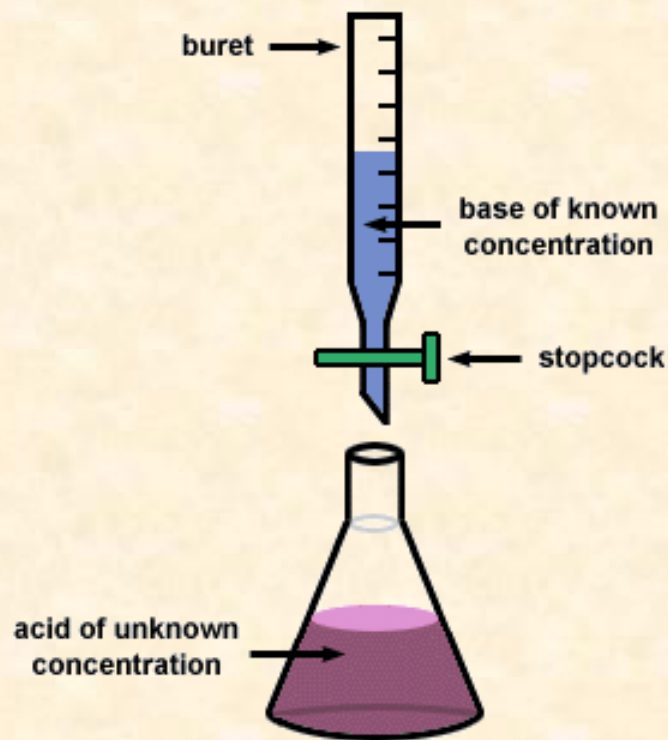
What is the easiest way to determine the concentration of either  $H^+$  or  $OH^-$ ?

## Titration

$$C_t \times V_t = C_s \times V_s$$

Where  $C_t$  is the concentration of the titrant,  $V_t$  is the volume of the titrant,  $C_s$  is the concentration (acidity or alkalinity) of the unknown solution and  $V_s$  is the volume of the unknown solution.

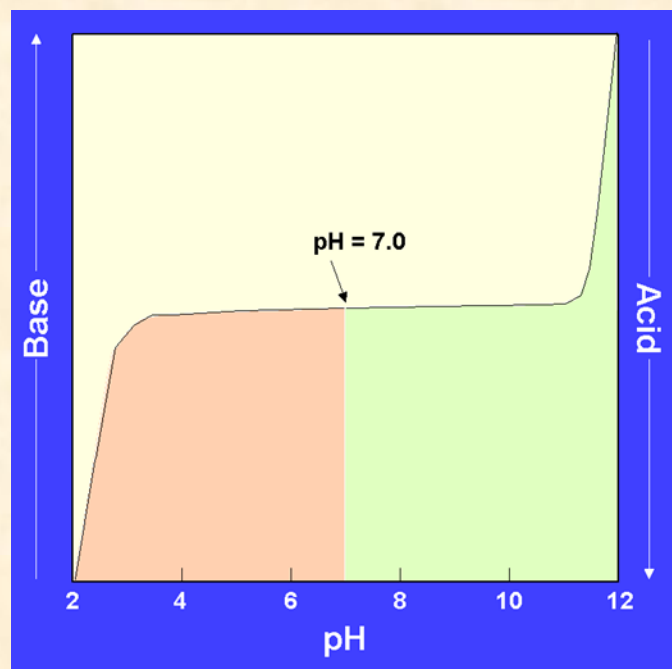
For strong acids and bases, acidity  $C_A = H^+$  and alkalinity  $C_B = OH^-$



For an acidity determination the titrant is a base. For an alkalinity determination the titrant is an acid.

### Example 3-11

100mL of an acidic solution is titrated with a 100 meq L<sup>-1</sup> NaOH solution. Neutrality (pH = 7) is achieved after 50mL of titrant have been added to the acid solution. Calculate the acidity of the solution.



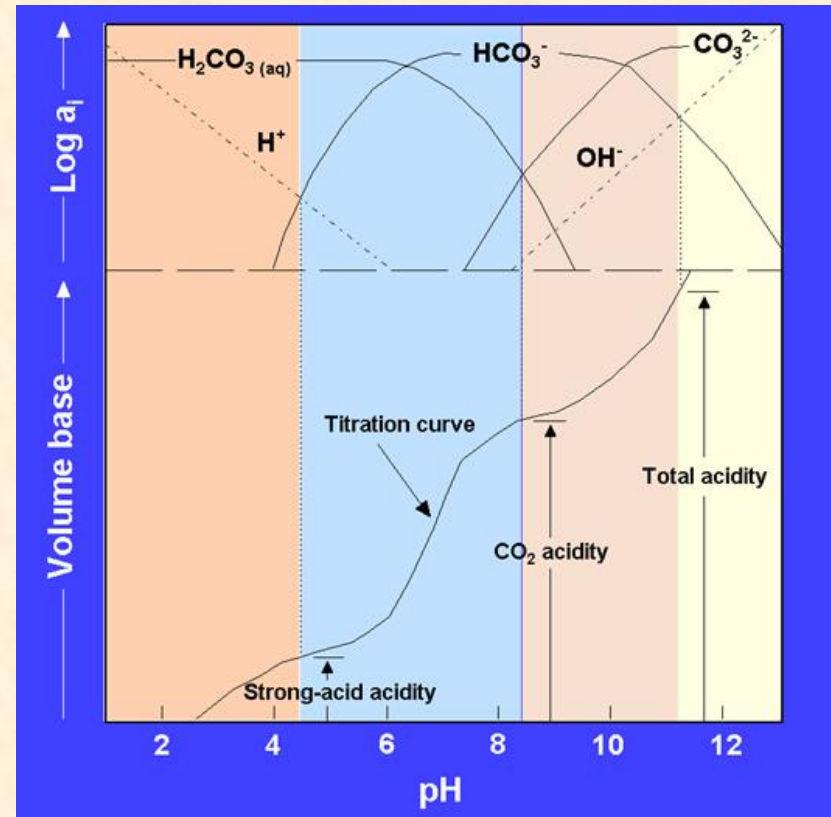
$$C_s = (C_t \times V_t) / V_s = ((100 \text{ meq L}^{-1})(50 \times 10^{-3} \text{ L})) / 100 \times 10^{-3} \text{ L}$$
$$= 50 \text{ meq L}^{-1} = \text{total acidity of the unknown}$$

If both strong and weak acids are present the titration curve is more complex. For example if a strong acid and carbonic acid are both present

$$C_A = 2H_2CO_{3(aq)} + HCO_3^- + H^+ - OH^-$$

The first inflection point,  $pH \approx 4.5$ , corresponds to the *strong-acid acidity*. The second inflection point at  $pH \approx 8.5$  corresponds to the *CO<sub>2</sub> acidity*, and the third inflection point at  $pH \approx 11.5$  corresponds to the *total acidity*.

For a solution that contains a strong base and a weak acid, we would titrate with a strong acid. The inflection points, with decreasing pH, would represent *caustic alkalinity*, *carbonate alkalinity*, and *total alkalinity*.





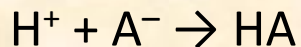
# Buffers

**Buffer:** A weak acid and its salt (or a weak base and its salt) form what is known as a *buffer*.

A ***buffered solution*** is a solution that resists changes in pH when either hydrogen or hydroxyl ions are added to the solution.

## ***Henderson–Hasselbalch equation***

Consider the following reaction:



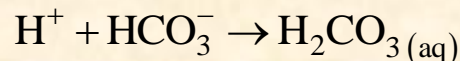
In this reaction, a  $\text{H}^+$  ion has combined with the salt of a weak acid (a conjugate base) to form a weak acid. The Henderson–Hasselbalch equation as for this generalized reaction is

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

where  $K_a$  is the equilibrium constant for the reaction.

**EXAMPLE 3–13** Let us suppose that we have 1 L of pure water with pH = 7.0. If we add  $10^{-4}$  mol of  $H^+$  ions to the pure water, the pH will drop to 4 ( $10^{-7}$  mol +  $10^{-4}$  mol =  $10^{-4}$  mol  $L^{-1}$  of  $H^+$ ). If carbonic acid is present in the solution, what will be the change in pH when the  $H^+$  ions are added? At pH = 7 and  $T = 25^\circ C$ , assume that  $[HCO_3^-] = 10^{-3}$  mol  $L^{-1}$ .

From equation 3–8 we get  $[H_2CO_{3(aq)}] = 10^{-3.65}$  mol  $L^{-1}$ . When we add  $H^+$  ions to the solution, the following reaction occurs:



an example of LeChâtelier's principle. According to this reaction, the added  $H^+$  ions combine with the  $HCO_3^-$  to form  $H_2CO_{3(aq)}$ . Thus, the activity of  $HCO_3^-$  decreases by  $10^{-4}$  mol  $L^{-1}$  and the activity of  $H_2CO_{3(aq)}$  increases by  $10^{-4}$  mol  $L^{-1}$ . Solving equation 3–40 for pH gives

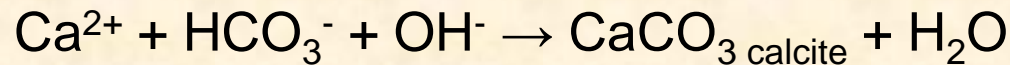
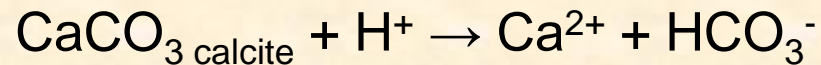
$$\begin{aligned} \text{pH} &= -\log K_{a_1} + \log \left( \frac{[HCO_3^-]}{[H_2CO_{3(aq)}]} \right) \\ &= 6.35 + \log \left( \frac{[10^{-3.0} - 10^{-4.0}]}{[10^{-3.65} + 10^{-4.0}]} \right) = 6.35 + 0.44 = 6.79 \end{aligned}$$

Due to the presence of carbonic acid, the pH only decreases by 0.21 units rather than 3.0 units.

## Types of reactions that can control pH

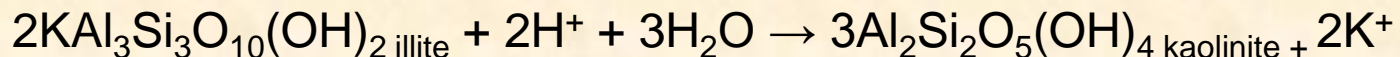
- Reactions that involve dissolved species in water (for example the carbonic acid – bicarbonate ion reaction)
- Reactions that require interactions between water and mineral species

For example the carbonic acid – calcite system



or

The reaction between the clay minerals illite and kaolinite



The **buffering capacity** is a measure of the amount of  $H^+$  or  $OH^-$  ions a solution can absorb without a significant change in pH. The capacity of a buffered solution is determined by the amount of [HA] and  $[A^-]$  in the solution. For an acidity titration, the buffering index,  $B$ , is defined as

$$B = \frac{dC_B}{dpH} \quad (3-42)$$

where  $dC_B$  is the increment of strong base added in eq  $L^{-1}$  (or meq  $L^{-1}$ ) and  $dpH$  is the corresponding change in solution pH. For an alkalinity titration, the buffering index is written

$$B = \frac{dC_A}{dpH} \quad (3-43)$$

where  $dC_A$  is the incremental amount of strong acid added.

The ability of a particular system to buffer changes in pH varies as a function of pH. For weak acids and bases, the maximum buffering capacity occurs at pH values that equal the dissociation constants,  $pK_a$  or  $pK_b$ , of the weak acid or base. At  $pH = pK_a$  (or  $pK_b$ ), the ratio  $[A^-]/[HA] = 1$  and is most resistant to change. The following example will illustrate this point.

**EXAMPLE 3–14** We will return to Example 3–13, the carbonate buffer. In this case, the initial pH is 6.35, equivalent to the first dissociation constant for carbonic acid. The total carbonate content is  $2 \times 10^{-3}$  mol  $L^{-1}$ . At pH = 6.35,  $H_2CO_{3(aq)}$  and  $HCO_3^-$  will be present in equal abundance. The activity of the  $CO_3^{2-}$  ion is negligible.

Hence, we can write

$$pH = -\log K_{a_1} + \log \left( \frac{[HCO_3^-]}{[H_2CO_{3(aq)}]} \right) = 6.35 + \log \left( \frac{[10^{-3.0}]}{[10^{-3.0}]} \right) = 6.35 + 0.0 = 6.35$$

We now add  $10^{-5}$  mol of  $H^+$  ions to 1 L of solution. After the addition we recalculate the pH:

$$\begin{aligned} pH &= -\log K_{a_1} + \log \left( \frac{[HCO_3^-]}{[H_2CO_{3(aq)}]} \right) \\ &= 6.35 + \log \left( \frac{[10^{-3.0} - 10^{-5.0}]}{[10^{-3.0} + 10^{-5.0}]} \right) = 6.35 + (-0.009) = 6.34 \end{aligned}$$

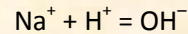
Because of the buffering capacity of the system, the pH has only changed by  $-0.01$  units. Let us continue to add acid until the pH of the solution is reduced to 5.35. At this pH,  $H_2CO_{3(aq)}$  is 10 times more abundant in the solution than  $HCO_3^{2-}$ . Under these conditions, what is the effect of a  $10^{-5}$  mol addition of  $H^+$ ?

$$\begin{aligned} pH &= -\log K_{a_1} + \log \left( \frac{[HCO_3^-]}{[H_2CO_{3(aq)}]} \right) \\ &= 6.35 + \log \left( \frac{[1.818 \times 10^{-4.0} - 10^{-5.0}]}{[1.818 \times 10^{-3.0} + 10^{-5.0}]} \right) = 6.35 + (-1.03) = 5.32 \end{aligned}$$

In this case, the pH has changed by  $-0.03$  pH units. Although not a large difference from the previous calculation, we can see that there has been a decrease in the buffering capacity of the solution. Repeating the calculation when pH = 4.35, with the same addition of acid, gives pH = 4.04, a change of  $-0.31$  pH units, clearly showing the declining effectiveness of the buffer.

## Buffering Index for H<sub>2</sub>O

We start with pure water, which we titrate with a NaOH solution; i.e., we are determining the total acidity of water. In this example, and all the following examples, we will assume that activity equals concentration. The charge balance equation is



and  $C_B = \text{Na}^+$ , which represents the total amount of base added to the solution. Substituting into the charge balance equation we can write

$$C_B = \text{OH}^- - \text{H}^+ = \frac{K_w}{\text{H}^+} - \text{H}^+ \quad (3-44)$$

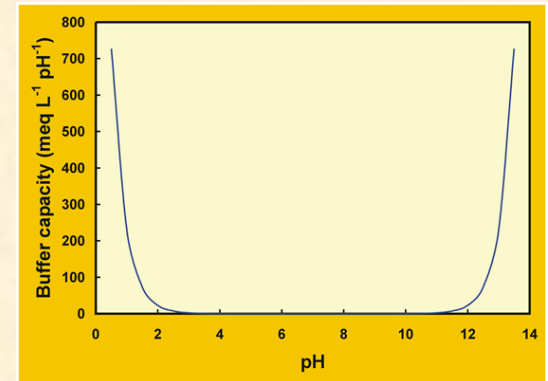
Taking the derivative of both sides gives

$$dC_B = \left[ -\frac{K_w}{(\text{H}^+)^2} - 1 \right] d\text{H}^+ \quad (3-45)$$

$\text{pH} = -\ln(\text{H}^+)/2.3$ , so  $d\text{H}^+ = d\text{pH}[-2.3(\text{H}^+)]$ . Substituting for  $d\text{H}^+$  gives the final form of the equation:

$$B_{\text{H}_2\text{O}} = \frac{dC_B}{d\text{pH}} = 2.3 \left[ \frac{K_w}{\text{H}^+} + \text{H}^+ \right] \quad (3-46)$$

Equation 3-46 is easily solved on a spreadsheet for a range of pH values, and the result of such a computation is shown graphically in Figure 3-5. The buffering capacity of water is greatest at very low and very high pHs and quickly declines to essentially zero at intermediate pH values. Hence, in most natural waters, H<sub>2</sub>O is not an important pH buffer.

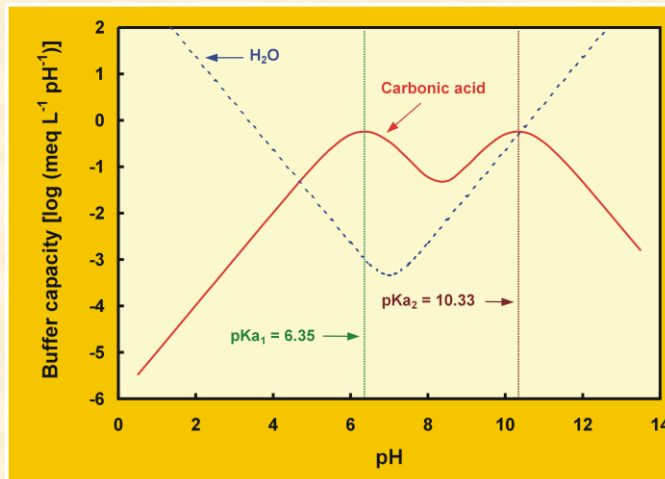


### Buffering Index for Weak Polyprotic Acids

As long as the dissociation constants differ by a factor of 20 or more, the solution for the buffering index of polyprotic acids is analogous to equation 3–52. Additional terms are added to represent the additional dissociation steps. Equation (3–53) is for a diprotic acid. Note that there are now two terms at the beginning of the equation that describe the first and second dissociation for the diprotic acid.

$$B = \frac{dC_B}{dpH^+} = 2.3 \left[ \frac{K_{a_1} C_A (H^+)}{(K_{a_1} + H^+)^2} + \frac{K_{a_2} C_A (H^+)}{(K_{a_2} + H^+)^2} + \frac{K_w}{H^+} + H^+ \right] \quad (3-53)$$

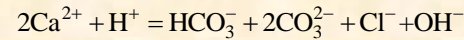
As previously mentioned, carbonic acid is one of the most important acids in the natural waters. Because carbonic acid is a diprotic acid, it will have two pH regions in which it acts as a buffer. The equation for carbonic acid is plotted in Figure 3–7 for  $C_A = 1 \times 10^{-3} \text{ mol L}^{-1}$ . Note the two regions of highest buffering capacity corresponding to  $pK_{a_1} = 6.35$  and  $pK_{a_2} = 10.33$ , the first and second dissociation constants, respectively, of carbonic acid. At pH values less than 4.7 and greater than 10.4, the buffering capacity of water is greater than that of carbonic acid.



**Figure 3–7** Variations in buffering capacity as a function of pH for the system carbonic acid–water when  $C_A = 1 \times 10^{-3} \text{ mol L}^{-1}$ .

### Buffering Index for the Calcite–Carbonic Acid System

As has been noted, this important system controls the long-term pH of the ocean. It also exerts a significant influence on the pH of fresh waters in contact with limestone or in soils containing carbonate minerals. The full derivation will not be done here (it can be found in Langmuir, 1997). This calculation is for a calcite-saturated solution with fixed total carbonate. The solution is titrated with HCl; therefore,  $C_A = Cl^-$ . The charge balance equation is



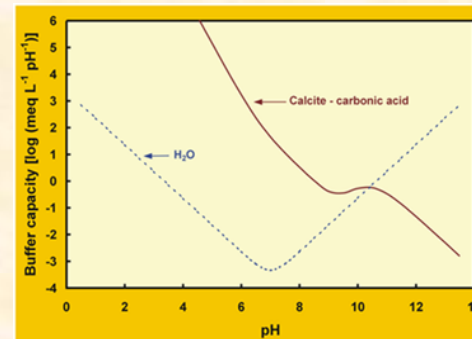
Substituting  $C_A$  for  $Cl^-$  and rearranging the charge balance equation in terms of  $C_A$  gives

$$C_A = H^+ - OH^- + 2Ca^{2+} - HCO_3^- - 2CO_3^{2-}$$

As we have done in the previous cases, we now carry out a set of substitutions so that the equation is written in terms of the  $H^+$  ion and then differentiate the resulting equation. After completion of these operations, the equation becomes

$$B = 2.3 \left[ (H^+) + \frac{K_w}{(H^+)} \right] + 2.3 \left[ \frac{C_T K_{a_2}^{-1} (H^+) \left[ K_{a_1}^{-1} K_{a_2}^{-1} (H^+)^2 + 4K_{a_2}^{-1} (H^+) + 1 \right]}{\left[ K_{a_1}^{-1} K_{a_2}^{-1} (H^+)^2 + K_{a_2}^{-1} (H^+) + 1 \right]^2} \right] + 2.3 \left[ \frac{(H^+)}{K_{cal} C_T} \left[ 2(H^+) + K_{a_1} \right] \right] \quad (3-54)$$

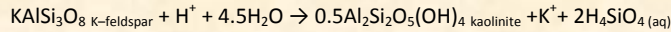
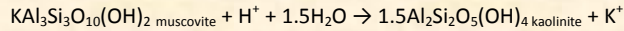
where  $C_T$  is the total carbonate concentration,  $K_{a_1}$  and  $K_{a_2}$  are the first and second dissociation constants for carbonic acid, and  $K_{cal}$  is the solubility constant for calcite. If we wanted to solve this equation for aragonite, we would use the aragonite solubility constant,  $K_{arag}$ . The equation has been written in three parts to illustrate the various components of the calculation. The first part represents the buffering capacity of water, the second the buffering capacity of carbonic acid, and the third the buffering capacity due to the dissolution of calcite. This system reacts relatively rapidly to changes in pH because calcite readily dissolves in acidic waters. Note that the dissolution of calcite tends to offset pH decreases. The precipitation of calcite is more difficult, so this system would not be as effective in mitigating pH increases. The buffering curve for the system calcite–carbonic acid, at 25°C and  $C_T = 1 \times 10^{-3} \text{ mol L}^{-1}$ , is shown in the figure.





### Buffering Index for Water–Silicate Mineral Systems

Consider the following reactions:



In the first reaction, hydrogen ions are consumed in the conversion of muscovite to the clay mineral kaolinite. In the second reaction, a common weathering reaction in humid temperate climates, hydrogen ions are consumed when K-feldspar is weathered to kaolinite. Both reactions are essentially irreversible, so they will only buffer hydrogen ion additions, i.e., pH decreases. We start by calculating the equilibrium constants (at 25°C) for both reactions. In each case,

$$K_{\text{eq}} = \frac{[\text{K}^+]}{[\text{H}^+]}$$

because activity = 1 for the other species in both equations. The free energies for the reactions are for the muscovite–kaolinite reaction,  $\Delta G_{\text{R}}^0 = -25.25 \text{ kJ mol}^{-1}$  and  $\log K_{\text{eq}} = 4.42$  and for the K-feldspar–kaolinite reaction,  $\Delta G_{\text{R}}^0 = -11.05 \text{ kJ mol}^{-1}$  and  $\log K_{\text{eq}} = -1.94$ .

The buffering index will have the same form for both mineral pairs. Here we will derive the buffering index equation for the muscovite–kaolinite pair. We start by assuming that we are titrating a water–mineral mixture with HCl ( $C_{\text{A}} = \text{Cl}^-$ ). The charge balance equation is

$$\text{H}^+ + \text{K}^+ = \text{OH}^- + \text{Cl}^-$$

The total acidity equation is

$$C_{\text{A}} = \text{H}^+ + \text{K}^+ - \text{OH}^-$$

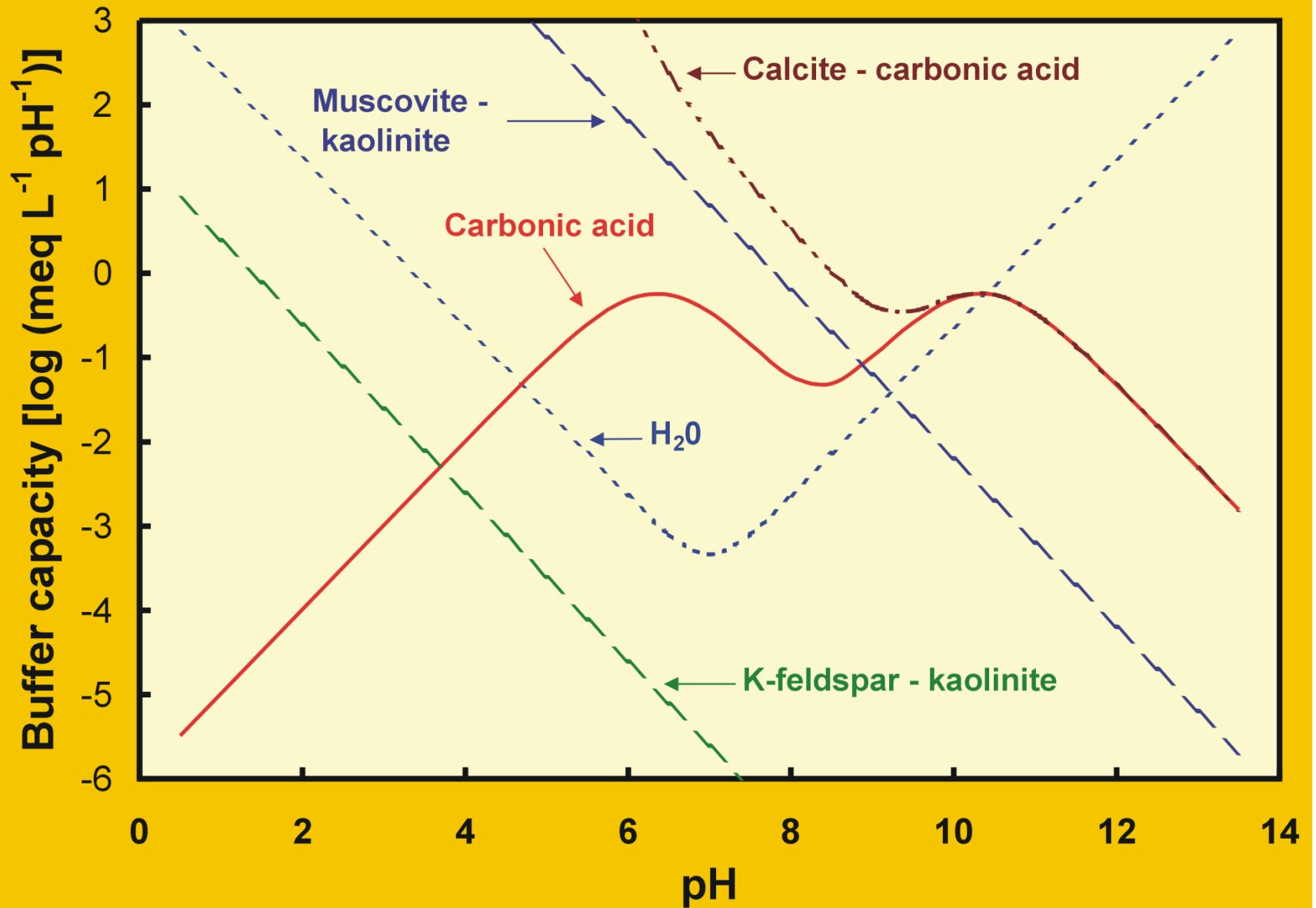
Because  $[\text{K}^+] = K_{\text{eq}}[\text{H}^+]$ , substitution into the total acidity equation for  $\text{K}^+$  and  $\text{OH}^-$  gives

$$C_{\text{A}} = K_{\text{eq}}[\text{H}^+] + [\text{H}^+] - \frac{K_{\text{w}}}{\text{H}^+} \quad (3-55)$$

Taking the derivative and substituting for  $d\text{H}^+$ , as in previous examples, gives

$$B = 2.3 \left[ (\text{H}^+) + \frac{K_{\text{w}}}{(\text{H}^+)^2} + K_{\text{eq}} (\text{H}^+) \right] = 2.3 \left[ (\text{H}^+) + \frac{10^{-14}}{(\text{H}^+)^2} + 10^{4.42} (\text{H}^+) \right] \quad (3-56)$$

For the K-feldspar–kaolinite reaction, we have a similar equation—the only difference is the value for the equilibrium constant. Silicic acid is not included in the buffer calculation because only at very basic pH values would there be any significant dissociation to  $\text{H}_3\text{SiO}_4^-$  (first dissociation constant =  $10^{-9.9}$ ). The buffering index equation for the K-feldspar–kaolinite pair is



## Mineral Reactivity

A final factor to consider is the rate at which buffering reactions will occur. Carbonate minerals are generally considered to be highly reactive, particularly when present as minute grains. Using the reactivity of carbonate minerals as a reference point, Table 3–7 lists the relative reactivity, at pH = 5, for a number of common minerals. What is meant by relative reactivity is, under the given set of conditions, compared to calcite, how readily the mineral will react with the fluid. For minerals with low relative reactivity, there is little interaction between the fluid and the mineral. Even if these minerals were effective buffers, we would not expect them to have a significant effect on pH.

**Table 3–7** Relative Reactivity of Common Minerals at pH = 5\*

Mineral group	Typical minerals	Relative reactivity at pH 5
Dissolving	Calcite, aragonite, dolomite, magnesite, brucite	1.00
Fast weathering	Anorthite, nepheline, forsterite, olivine, garnet, jadeite, leucite, spodumene, diopside, wollastonite	0.40
Slow weathering	Plagioclase feldspars (albite, oligoclase, labradorite), clays (vermiculite, montmorillonite)	0.01
Very slow weathering	K-feldspars (orthoclase, microcline), muscovite	0.01
Inert	Quartz, rutile, zircon	0.004

\*From Lawrence and Scheske (1997).