

# Recap

- $K_w$ ,  $K_a/K_b$
- Conjugate acid/base ( $pK_a + pK_b = 14$ )
- Strength of acid/base: empirical interpretation on molecular level

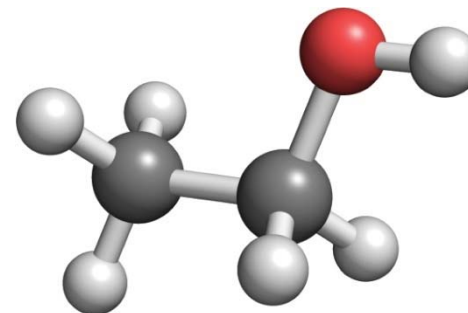
# Molecular Structure and Acid Strength: Resonances

Carboxylic acid, is a weak acid, though it is a **much stronger acid than alcohols** with the same number of carbon atoms.

In fact, **alcohols are usually not regarded as oxoacids**.

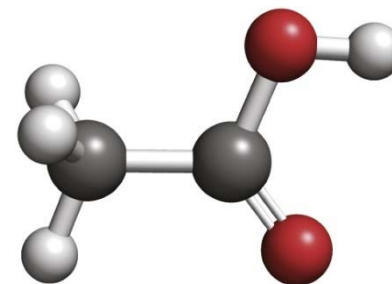
The second O atom in the carboxyl group, -COOH,

- increases the oxidation number of the carbon, polarizing the C-O-H bond, and
- helps stabilize the conjugate base by delocalizing electrons.



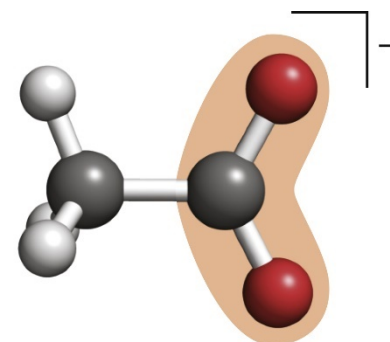
2 Ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$

Atkins, Chemical Principles: The Quest for Insight, 7e  
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3 Acetic acid,  $\text{CH}_3\text{COOH}$

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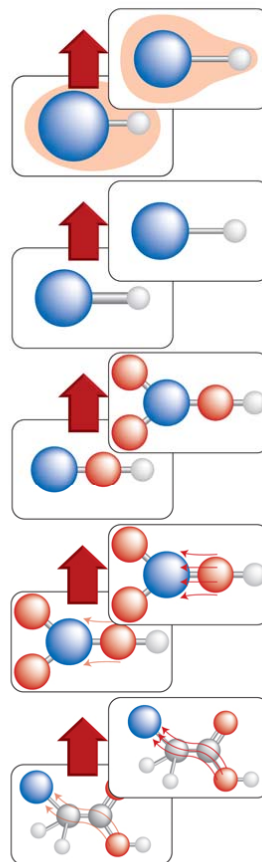
4 Acetate ion,  $\text{CH}_3\text{CO}_2^-$

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## Summary

1. Groups: bond strength
2. Periods: polarity
3. Oxidation number
4. Number of oxygen atoms: polarity
5. Resonances stabilized

TABLE 6C.7 Correlations of Molecular Structure and Acid Strength*	
Acid type	Trend
binary	The more polar the H—A bond, the stronger the acid. <i>This effect is dominant for acids of the same period.</i>
	The weaker the H—A bond, the stronger the acid. <i>This effect is dominant for acids of the same group.</i>
oxoacid	The greater the number of O atoms attached to the central atom (the greater the oxidation number of the central atom), the stronger the acid.
	For the same number of O atoms attached to the central atom, then the greater the electronegativity of the central atom, the stronger the acid.
carboxylic	The greater the electronegativities of the groups attached to the carboxyl group, the stronger the acid.



\*In each diagram, the arrows indicate the corresponding increase in acid strength.

*The greater the number of oxygen atoms and the more electronegative the atoms present in the molecules of an acid, the stronger is the acid. These trends are summarized in Table 6C.7.*

Table 6C.7

Atkins, *Chemical Principles: The Quest for Insight*, 7e

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Example 6C.2 Predict from their molecular structures which acid in each of the following pairs is the stronger one: (a)  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$ ; (b)  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_3$ ; (c)  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ .

(a)  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$ : When comparing in the same group we look for the larger, more polarized atom. Here Se is larger, more polarizable than S, so  $\text{H}_2\text{Se} > \text{H}_2\text{S}$ .

(b)  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_3$ : When comparing the same atom with a different number of oxygen atoms, the atom with the great number of oxygen atoms also has the greater oxidation number on the central atom. The sulfur in  $\text{H}_2\text{SO}_4$  has a +6 oxidation number and the sulfur in  $\text{H}_2\text{SO}_3$  has a +4, so  $\text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_3$ .

Example 6C.2 Predict from their molecular structures which acid in each of the following pairs is the stronger one: (a)  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$ ; (b)  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_3$ ; (c)  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ .

(c)  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ . We can only compare the oxidation numbers. The sulfur in  $\text{H}_2\text{SO}_4$  has a +6 oxidation number and the phosphorous in  $\text{H}_3\text{PO}_4$  has a +5, so  $\text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4$ .

## The pH of Solutions of Weak Acids and Bases

We will use **equilibrium tables** to calculate  $K_a$ s/ $K_b$ s and initial/final concentrations. One notable difference is we'll use **pH** as a way to find our final concentrations of our solutions.

Reminder (1 of 3): Equilibrium reactions have an (1) initial concentration, (2) change in concentration, and (3) a final concentration. These are easiest to calculate in a table.



	H <sub>2</sub>	I <sub>2</sub>	HI
initial			
change			
final			

In this and subsequent chapters we'll change the word **final** to **equilibrium** concentration just for convenience and consistency. These tables are often referred to as ICE tables.

	H <sub>2</sub>	I <sub>2</sub>	HI
initial			
change			
equilibrium			

## Reminder (2 of 3): percent ionization

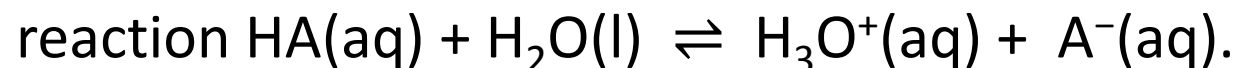
$$\% \text{ change} = \frac{\text{final concentration}}{\text{initial concentration}} \times 100$$

This was helpful when we wanted to simplify our calculations by **ignoring “x”** when the dissociation constant was very small, or when there was less than 5% decomposition or ionization change.

We'll continue using percent change, except in this chapter it is referred to as **percent deprotonation**, which has the same meaning,

$$\text{percent deprotonation} = \frac{\text{final concentration acid}}{\text{initial concentration acid}} \times 100 \text{ or}$$

$$\text{percent deprotonation} = \frac{[\text{H}_3\text{O}^+]}{[\text{HA}]} \times 100 \text{ for any generic weak acid}$$





Reminder (3 of 3): this is more of a note than a reminder.

The **autoprotolysis** of water  $\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$

where,  $K_w = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$ , and

$$K_w = [1.0 \times 10^{-7}][1.0 \times 10^{-7}] = 1.0 \times 10^{-14}$$

We note that  $1.0 \times 10^{-14}$  is so small that neither the  $[\text{H}_3\text{O}^+]$  nor  $[\text{OH}^-]$  concentrations are high enough to be considered a factor in our calculations; so these concentrations are very often ignored.

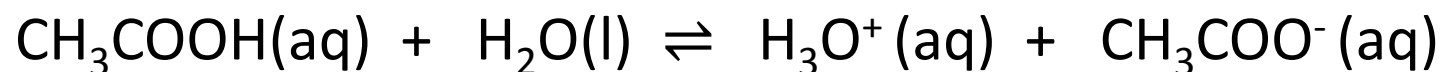
Final note—speeding up our ICE table calculations.

We can always use the quadratic equation for solving our ICE tables. However, quadratics are time consuming. It's better to make a guess before solving with a quadratic.

For instance if  $K = 7.6 \times 10^{-3}$  and a solution has an initial concentration of 0.10 M we could:

- 1) Solve using the 5% rule; like we learned in Focus 5, or
- 2) before doing any calculations we make a quick check by multiply  $K$  by 100. So for instance if  $K \times 100 < \underline{0.10 \text{ M}}$  (initial concentration), we can assume we won't need the quadratic. However always check percent deprotonation  $> 5\%$  at the end.

Example 6D.1 Calculate the pH and percentage deprotonation of 0.10 M  $\text{CH}_3\text{COOH}(\text{aq})$ , given that  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ .



Next we make an ICE table with known values.

	$\text{CH}_3\text{COOH}$	$\text{H}_3\text{O}^+$	$\text{CH}_3\text{COO}^-$
initial	0.10	0	0
change	-x	+x	+x
equilibrium	$0.10 - x$	x	x

Noting -x means the concentration is going away, and +x means appearing.

Example 6D.1 Calculate the pH and percentage deprotonation of 0.10 M  $\text{CH}_3\text{COOH}(\text{aq})$ , given that  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ .

	$\text{CH}_3\text{COOH}$	$\text{H}_3\text{O}^+$	$\text{CH}_3\text{COO}^-$
initial	0.10	0	0
change	-x	+x	+x
equilibrium	0.10 - x	x	x

Since  $K_a$  is  $1.8 \times 10^{-5}$  which is  $\ll 0.10$  we can ignore -x in  $0.10 - x$ .

$$\text{Solving } K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.10}, \quad x = \sqrt{1.8 \times 10^{-5} \times 0.10}$$

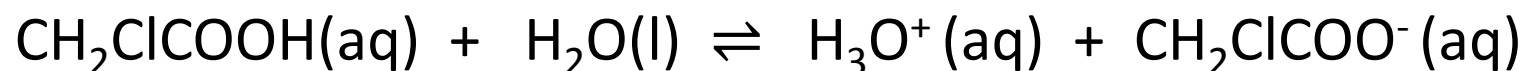
$$x = 1.3 \times 10^{-3} = [\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-], \text{ then using } \text{pH} = -\log [\text{H}_3\text{O}^+]$$

$\text{pH} = -\log [1.3 \times 10^{-3}] = 2.89$  (since this is less than a pH of 6, ignoring the autoprotolysis of water is valid)

$$\text{percentage deprotonation} = \frac{1.3 \times 10^{-3}}{0.10} \times 100 = 1.3\% \text{ (which is less than 5\% )}$$

Self-test 6D.1B Calculate the pH and percentage deprotonation of 0.22 M aqueous chloroacetic acid. Be sure to check any approximation to see whether it is valid. The  $K_a$  for chloroacetic acid is  $1.4 \times 10^{-3}$ .

$K_a$  is 100 times larger compared with the previous example



Next we make an ICE table.

	$\text{CH}_2\text{ClCOOH}$	$\text{H}_3\text{O}^+$	$\text{CH}_2\text{ClCOO}^-$
initial	0.22	0	0
change	-x	+x	+x
equilibrium	$0.22 - x$	x	x

We write in our known values.

Noting -x means the concentration is going away, and +x means appearing.

	CH <sub>2</sub> ClCOOH	H <sub>3</sub> O <sup>+</sup>	CH <sub>2</sub> ClCOO <sup>-</sup>
initial	0.22	0	0
change	-x	+x	+x
equilibrium	0.22 - x	x	x

A quick check  $1.4 \times 10^{-3} \times 100 > 0.22$  which means we'll probably have to use the quadratic, but let's check with the 5% rule first.

$$\text{Solving } K_a = 1.4 \times 10^{-3} = \frac{x^2}{0.22}, \quad x = \sqrt{1.4 \times 10^{-3} \times 0.22},$$

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

$$\text{check for \% change } \frac{1.8 \times 10^{-2}}{0.22} \times 100 = 8\%$$

which means we'll have to use the quadratic  $\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$1.4 \times 10^{-3} = \frac{x^2}{0.22-x}$ , this goes to  $x^2 + 1.4 \times 10^{-3}x - 3.1 \times 10^{-4}$ ,  
solving for  $x$  (using Microsoft's Mathematics, free)

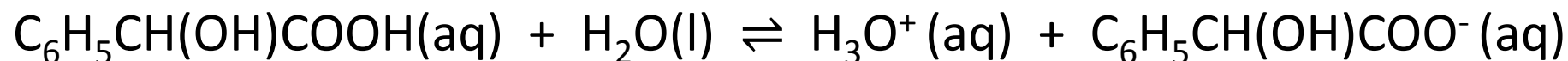
$x = 0.017$ ,  $0.22 - 0.017 = .020 = [\text{CH}_2\text{ClCOOH}]$ ,

$0.017 = [\text{H}_3\text{O}^+] = [\text{CH}_2\text{ClCOO}^-]$ ,

using  $\text{pH} = -\log [\text{H}_3\text{O}^+]$ ,  $\text{pH} = -\log [0.017] = 1.77$

percentage deprotonation =  $\frac{0.017}{0.22} \times 100 = 7.7\%$

Example 6D.2 (Find  $K$  given pH) The pH of a 0.010 M aqueous solution of mandelic acid,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$ , an antiseptic, is 2.95. What is the  $K_a$  of mandelic acid?



We've calculated  $K$ s like this in the previous chapter. Notice the pH is the concentration of the  $\text{H}_3\text{O}^+$  at equilibrium. Make an ICE table.

	$\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$	$\text{H}_3\text{O}^+$	$\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COO}^-$
initial	0.010	0	0
change	-0.0011	+ 0.0011	+ 0.0011
equilibrium	0.0089	0.0011	0.0011

We write in our known values. This time we know  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$  or  $10^{-2.95} = 0.0011$ .

We use this to find the changes.



Example 6D.2 The pH of a 0.010 M aqueous solution of mandelic acid,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$ , an antiseptic, is 2.95. What is the  $K_a$  of mandelic acid?

	$\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$	$\text{H}_3\text{O}^+$	$\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COO}^-$
initial	0.010	0	0
change	-0.0011	+ 0.0011	+ 0.0011
equilibrium	0.0089	0.0011	0.0011

We use these values to calculate our  $K_a$ .

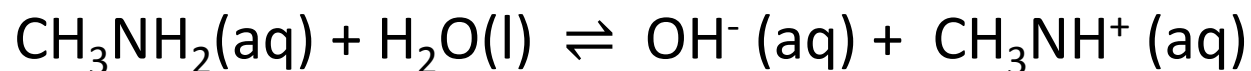
$$K_a = \frac{0.0011^2}{0.0089} = 1.4 \times 10^{-4}$$

## Solutions of Weak Bases

In the next section we examine weak base equilibrium. We treat these the same way we did with weak acids.

Example 6D.3 Calculate the pH and percentage protonation of a 0.20 M aqueous solution of methylamine,  $\text{CH}_3\text{NH}_2$ . The  $K_b$  for  $\text{CH}_3\text{NH}_2$  is  $3.6 \times 10^{-4}$ .

This is a base reaction in water



We start the ICE table

	$\text{CH}_3\text{NH}_2$	$\text{OH}^-$	$\text{CH}_3\text{NH}^+$
initial	0.20	0	0
change	-x	+x	+x
equilibrium	$0.20 - x$	x	x

We write in our known values.

We use “x” in our change.

	CH <sub>3</sub> NH <sub>2</sub>	OH <sup>-</sup>	CH <sub>3</sub> NH <sup>+</sup>
initial	0.20	0	0
change	-x	+x	+x
equilibrium	0.20 - x	x	x

Since  $K_b$  is  $3.6 \times 10^{-4}$  which is  $\ll 0.20$  we can ignore  $-x$  in  $0.20 - x$ .

$$\text{Solving } K_b = 3.6 \times 10^{-4} = \frac{x^2}{0.20}, \quad x = \sqrt{3.6 \times 10^{-4} \times 0.20}$$

$$x = 8.5 \times 10^{-3} = [\text{OH}^-] = [\text{CH}_3\text{NH}^+], \text{ using } \text{pOH} = -\log [\text{OH}^-]$$

$\text{pOH} = -\log [8.5 \times 10^{-3}] = 2.07$  (since this is greater than a pH of 8, autoprotolysis of water can be ignored),  $\text{pH} + \text{pOH} = 14$ ,  
 $\text{pH} = 14 - 2.07 = 11.9$

$$\text{percentage protonation} = \frac{8.5 \times 10^{-3}}{0.20} \times 100 = 4.3\% \text{ (which is less than 5\% \text{ \text{thumbs up}}))}$$

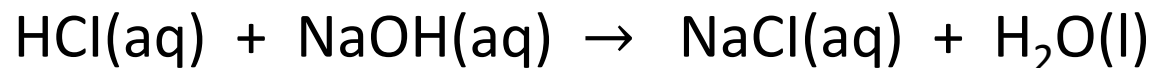
## The pH of Salt Solutions

In Fundamentals J we saw that a neutralization reaction between an acids and bases produced salt and water.

In general a strong acid and a metal hydroxide react accordingly.



An example of hydrochloric acid and sodium hydroxide reacting to produce table salt, sodium chloride, and water.



The pH of this solution will be 7, or neutral.

We are familiar with the meaning of a forward arrow,  $\rightarrow$ , implying the reaction never proceeds in the reverse direction.

## The pH of Salt Solutions

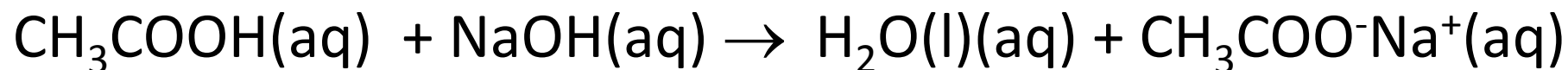
In another neutralization, a somewhat unexpected result appears.



Even though this is a neutralization reaction, **the measured pH is 9**.

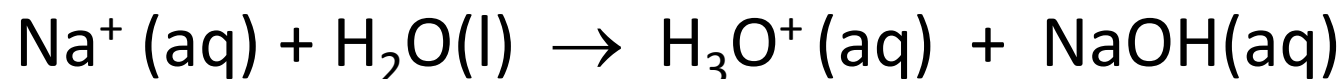
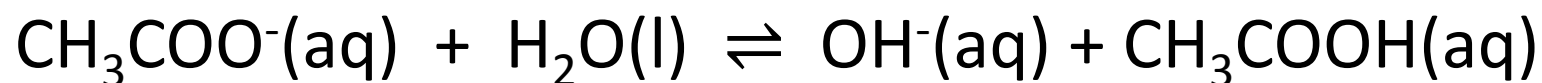
In Brønsted–Lowery theory the **conjugate acid** or **base** can be either **acidic** or **basic**.

## The pH of Salt Solutions



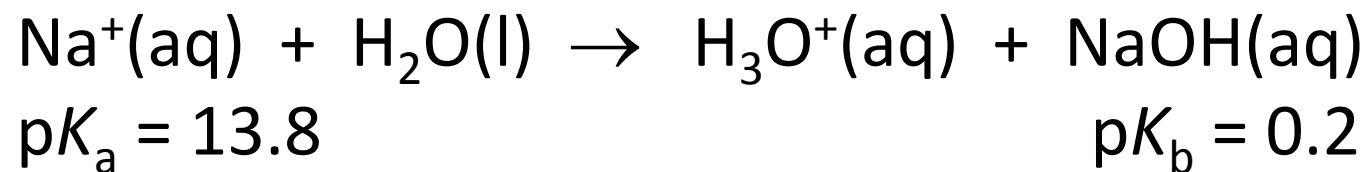
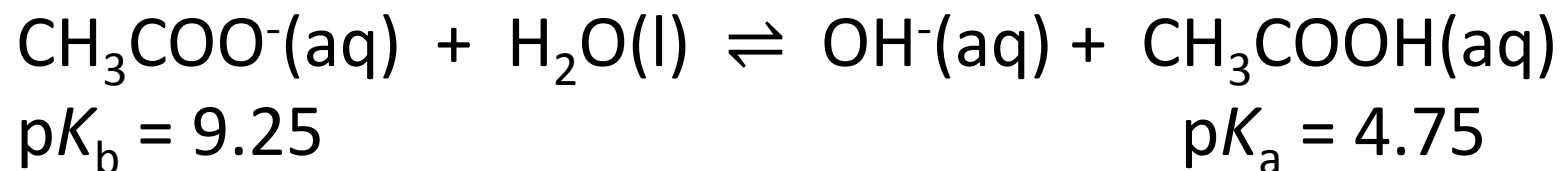
In the above example a weak acid reacts **completely** with a strong base.

The salt product  $\text{CH}_3\text{COO}^-\text{Na}^+$  is soluble in water and there are two possible reactions that this salt can still go through with water,



## The pH of Salt Solutions

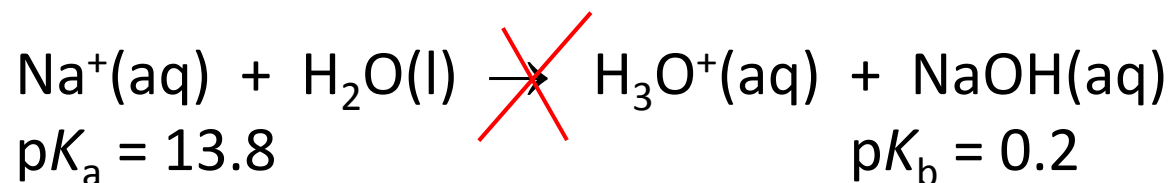
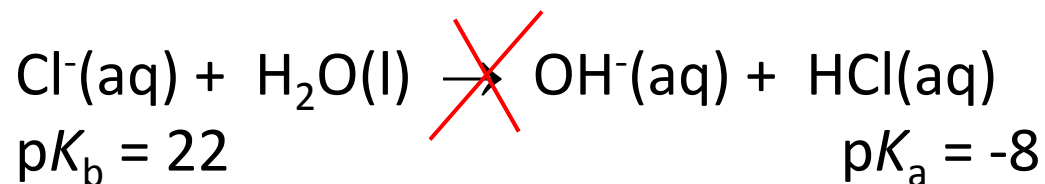
Comparing  $pK_a$ s and  $pK_b$ s we can make some observations.



NaOH is a strong base and  $\text{CH}_3\text{COOH}$  is a weak acid, so  
 $\text{NaCH}_3\text{COO}$  is basic



## The pH of Salt Solutions



Both  $\text{Cl}^-$  and  $\text{Na}^+$  are very weak (strong acid  $\downarrow$  pH 2, a strong base  $\uparrow$  pH 12) and  $\text{HCl}$  and  $\text{NaOH}$  are very strong, notice the  $pK$ s.

# The pH of Salt Solutions

**TABLE 6D.1** Acidic Character and  $K_a$  Values of Common Cations in Water\*

Character	Examples	$K_a$	$pK_a$
<b>Acidic</b>			
conjugate acids of weak bases	anilinium ion, $C_6H_5NH_3^+$	$2.3 \times 10^{-5}$	4.64
	pyridinium ion, $C_5H_5NH^+$	$5.6 \times 10^{-6}$	5.24
	ammonium ion, $NH_4^+$	$5.6 \times 10^{-10}$	9.25
	methylammonium ion, $CH_3NH_3^+$	$2.8 \times 10^{-11}$	10.56
small, highly charged metal cations	$Fe^{3+}$ as $Fe(H_2O)_6^{3+}$	$3.5 \times 10^{-3}$	2.46
	$Cr^{3+}$ as $Cr(H_2O)_6^{3+}$	$1.3 \times 10^{-4}$	3.89
	$Al^{3+}$ as $Al(H_2O)_6^{3+}$	$1.4 \times 10^{-5}$	4.85
	$Cu^{2+}$ as $Cu(H_2O)_6^{2+}$	$3.2 \times 10^{-8}$	7.49
	$Ni^{2+}$ as $Ni(H_2O)_6^{2+}$	$9.3 \times 10^{-10}$	9.03
	$Fe^{2+}$ as $Fe(H_2O)_6^{2+}$	$8 \times 10^{-11}$	10.1
<b>Neutral</b>			
Group 1 and 2 cations metal cations with charge +1	$Li^+$ , $Na^+$ , $K^+$ , $Mg^{2+}$ , $Ca^{2+}$ , $Ag^+$		
<b>Basic</b>			
	none		

Small, highly charged

Small, highly charged metal cations that can act as Lewis acids in water, such as  $Al^{3+}$  and  $Fe^{3+}$ , produce acidic solutions.



# The pH of Salt Solutions

**TABLE 6D.2** Acidic and Basic Character of Common Anions in Water

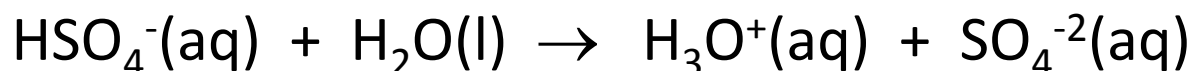
Character	Examples
<b>Acidic</b> very few	$\text{HSO}_4^-$ , $\text{H}_2\text{PO}_4^-$
<b>Neutral</b> conjugate bases of strong acids	$\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{NO}_3^-$ , $\text{ClO}_4^-$
<b>Basic</b> conjugate bases of weak acids	$\text{F}^-$ , $\text{O}^{2-}$ , $\text{OH}^-$ , $\text{S}^{2-}$ , $\text{HS}^-$ , $\text{CN}^-$ , $\text{CO}_3^{2-}$ , $\text{PO}_4^{3-}$ , $\text{NO}_2^-$ , $\text{CH}_3\text{CO}_2^-$ , other carboxylate ions

**Table 6D.2**

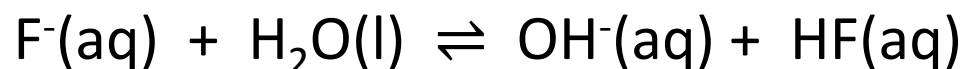
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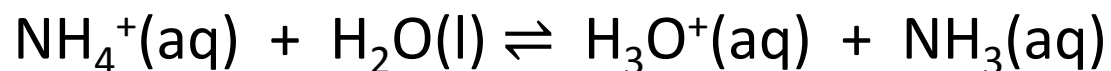
Hydrogen sulfates continue to react with water so it is considered strong acids.



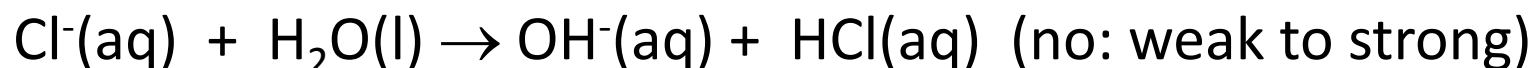
Basic solutions, here fluoride, react with water to make hydroxide, a base, and a weak acid HF and so make basic solutions.



Example 6D.4 Estimate the pH of 0.15 M  $\text{NH}_4\text{Cl}(\text{aq})$ ,  $K_b$  is  $1.8 \times 10^{-5}$ .



(yes: weak to weak will occur; also remember  $\text{NH}_4(\text{OH})$  is  $\text{NH}_3$ )



From  $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq})$  we can make an ICE table.

	$\text{NH}_4^+$	$\text{H}_3\text{O}^+$	$\text{NH}_3$
initial	0.15	0	0
change	-x	+x	+x
equilibrium	$0.15 - x$	x	x

Known values first.

Change values.

	$\text{NH}_4^+$	$\text{H}_3\text{O}^+$	$\text{NH}_3$
initial	0.15	0	0
change	-x	+x	+x
equilibrium	$0.15 - x$	x	x

Since  $K_b$  is  $1.8 \times 10^{-5}$  which is  $\lll 0.15$  we can ignore -x in  $0.15 - x$ .

Note: given the  $K_b$  the reaction is written as an acid, so we need the  $K_a$ .

$$K_a \times K_b = 1.0 \times 10^{-14}, \text{ so solving for } K_a, K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$\text{Solving } K_a = 5.6 \times 10^{-10} = \frac{x^2}{0.15}, \quad x = \sqrt{5.6 \times 10^{-10} \times 0.15}$$

$$x = 9.2 \times 10^{-6} = [\text{H}_3\text{O}^+] = [\text{NH}_3], \quad \text{using } \text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log [9.2 \times 10^{-6}] = 5.04,$$

$$\text{percentage deprotonation} = \frac{9.2 \times 10^{-6}}{0.15} \times 100 = 0.0061\% (< 5\% \text{ 👍})$$

## Polyprotic Acids and Bases

A polyprotic acid is a compound that can **donate more than one** proton.

Common polyprotic acids, include sulfuric acid,  $\text{H}_2\text{SO}_4$ , and carbonic acid,  $\text{H}_2\text{CO}_3$ , each of which can donate **two protons**, and phosphoric acid,  $\text{H}_3\text{PO}_4$ , which can donate **three protons**.

Polyprotic acids play a critical role in biological systems, because many enzymes can be regarded as polyprotic acids that carry out their vital functions.

## Polyprotic Acids and Bases

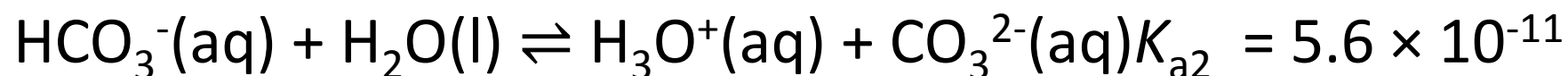
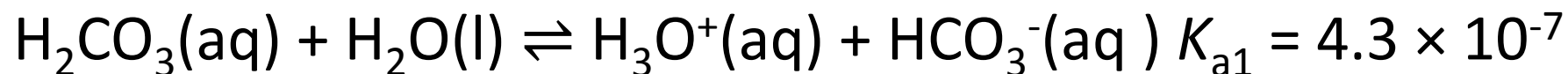
A polyprotic base is a species that can accept more than one proton.

Examples include the  $\text{CO}_3^{2-}$  and  $\text{SO}_3^{2-}$  anions, both of which can **accept two protons**, and the  $\text{PO}_4^{3-}$  anion, which can accept three protons.

The existence of each of these species is dependent on pH.

## The pH of Polyprotic Acids

Carbonic acid takes part in two successive proton transfer equilibria:



The conjugate base of  $\text{H}_2\text{CO}_3$  in the first equilibrium,  $\text{HCO}_3^-$ , acts as an acid in the second equilibrium. That ion produces in turn its own conjugate base,  $\text{CO}_3^{2-}$ .

We *notice* the acidity decreases significantly with each successive proton loss  $K_{a1} \gg K_{a2}$ .



# The pH of Polyprotic Acids

**TABLE 6E.1** Acidity Constants of Polyprotic Acids at 25 °C

Acid	$K_{a1}$	$pK_{a1}$	$K_{a2}$	$pK_{a2}$	$K_{a3}$	$pK_{a3}$
sulfuric acid, $H_2SO_4$	★ strong		$1.2 \times 10^{-2}$	1.92		
oxalic acid, $(COOH)_2$	$5.9 \times 10^{-2}$	1.23	$6.5 \times 10^{-5}$	4.19		
sulfurous acid, $H_2SO_3$	$1.5 \times 10^{-2}$	1.81	$1.2 \times 10^{-7}$	6.91		
phosphorous acid, $H_3PO_3$	$1.0 \times 10^{-2}$	2.00	$2.6 \times 10^{-7}$	6.59		
phosphoric acid, $H_3PO_4$	$7.6 \times 10^{-3}$	2.12	$6.2 \times 10^{-8}$	7.21	$2.1 \times 10^{-13}$	12.68
tartaric acid, $C_2H_4O_2(COOH)_2$	$6.0 \times 10^{-4}$	3.22	$1.5 \times 10^{-5}$	4.82		
carbonic acid, $H_2CO_3$	$4.3 \times 10^{-7}$	6.37	$5.6 \times 10^{-11}$	10.25		
hydrosulfuric acid, $H_2S$	$1.3 \times 10^{-7}$	6.89	$7.1 \times 10^{-15}$	14.15		

**Table 6E.1**

Atkins, *Chemical Principles: The Quest for Insight*, 7e

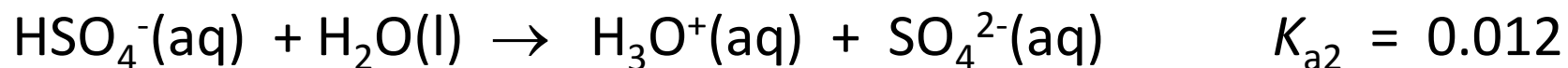
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

For all polyprotic acids or bases,  $K_{a1}$  is always the **greatest contributor** to **the overall pH** of the solution—except for  $H_2SO_4$ .

★ Only  $H_2SO_4$  has a large  $K_{a1}$  and  $K_{a2}$ .

Estimate the pH of 0.10 M  $\text{H}_2\text{SO}_4$ ,  $K_{a1}$  large,  $K_{a2} = .012$

The first proton loss is complete so,



$\text{H}_2\text{SO}_4(\text{aq})$  produces 0.10 M  $\text{H}_3\text{O}^+$ , therefore, we use  $K_{a2}$  for our ICE table

	$\text{HSO}_4^-$	$\text{H}_3\text{O}^+$	$\text{SO}_4^{2-}$
initial	0.10	0.10	0
change	$-x$	$+x$	$+x$
equilibrium	$0.10 - x$	$0.10 + x$	$x$

Known values first, note the initial  $\text{H}_3\text{O}^+$  concentration.

Change values.

Equilibrium values, note the  $\text{H}_3\text{O}^+$  concentration.

	$\text{HSO}_4^-$	$\text{H}_3\text{O}^+$	$\text{SO}_4^{2-}$
initial	0.10	0.10	0
change	$-x$	$+x$	$+x$
equilibrium	$0.10 - x$	$0.10 + x$	$x$

$K_{a2}$  0.012 is about the same as the initial 0.10 M so we'll have to use the quadratic  $\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$$0.012 = \frac{(0.10 + x)x}{0.10 - x} \quad \text{this goes to } x^2 + 0.11x - 0.0012, \text{ solving for } x$$

$$x = 0.010 = [\text{H}_3\text{O}^+] \quad \text{This value is combined with the 0.10 M } \text{H}_2\text{SO}_4$$

$$K_{a1} [\text{H}_3\text{O}^+] + K_{a2} [\text{H}_3\text{O}^+] = 0.10 \text{ M} + 0.010 \text{ M} = 0.11 \text{ M}$$

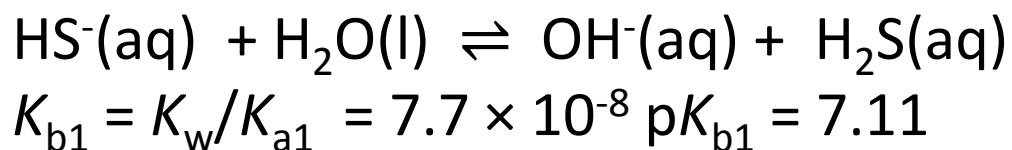
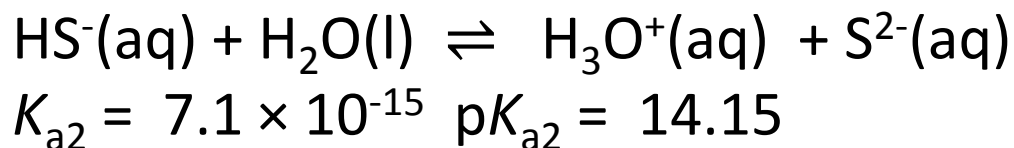
$$\text{using } \text{pH} = -\log [\text{H}_3\text{O}^+], \quad \text{pH} = -\log [0.11] = 0.95$$

**Reminder:** this is rare, and only happens with strong acids.

## Solutions of Salts of Polyprotic Acids

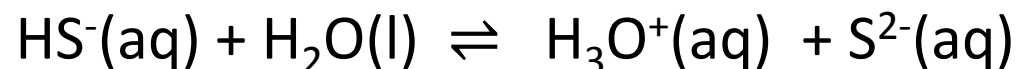
Conjugate bases of polyprotic acids are **amphiprotic**: they can act as either an acid or a base, donating or accepting a proton—this is a major topic in the next chapter.

For example, a hydrogen sulfide ion,  $\text{HS}^-$ , in water acts as both an acid and a base:

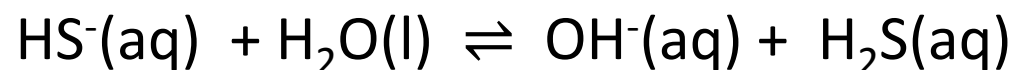


$\text{HS}^-$  is amphiprotic, so not immediately apparent whether NaHS is acidic or basic.

## Solutions of Salts of Polyprotic Acids



$$K_{a2} = 7.1 \times 10^{-15} \quad \text{p}K_{a2} = 14.15$$



$$K_{b1} = K_w/K_{a1} = 7.7 \times 10^{-8} \quad \text{p}K_{b1} = 7.11$$

However, we can use the  $\text{p}K_a$  and  $\text{p}K_b$  values of the  $\text{HS}^-$  ion to conclude that:

- $\text{HS}^-$  is a weak acid ( $K_{a2}$ ) and basic character of  $\text{S}^{2-}$  will dominate, and  $\text{pH} > 7$ .
- $\text{HS}^-$  is a weak base; again  $\text{pH} > 7$ .

A helpful equation is  $\text{pH} = \frac{1}{2} (\text{p}K_{a1} + \text{p}K_{a2})$  as long as initial concentration  $[X]_{\text{initial}} \gg \text{p}K_{a1}$ .

Example 6E.1 Estimate the pH of (a) 0.20 M  $\text{NaH}_2\text{PO}_4$  (aq); (b) 0.20 M  $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$ (aq), a salt of citric acid,  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ . For citric acid,  $\text{p}K_{\text{a}2} = 5.95$ , and  $\text{p}K_{\text{a}3} = 6.39$ .

(a) For  $\text{H}_3\text{PO}_4$   $K_{\text{a}1} = 7.6 \times 10^{-3}$ ,  $K_{\text{a}2} = 6.2 \times 10^{-8}$ ,  
 $\text{p}K_{\text{a}1} = 2.12$ ,  $\text{p}K_{\text{a}2} = 7.21$ .

Check if  $[X]_{\text{initial}} \gg \text{p}K_{\text{a}1}$ ,  $0.20 \gg 7.6 \times 10^{-3}$  which is true,

So  $\text{pH} = \frac{1}{2} (\text{p}K_{\text{a}1} + \text{p}K_{\text{a}2})$ ,  $\frac{1}{2} (2.12 + 7.21) = 4.66$

Example 6E.1 Estimate the pH of (a) 0.20 M  $\text{NaH}_2\text{PO}_4$  (aq); (b) 0.20 M  $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$  (aq), a salt of citric acid,  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ . For citric acid,  $\text{p}K_{\text{a}2} = 5.95$ , and  $\text{p}K_{\text{a}3} = 6.39$ .

(b) For citric acid,  $\text{p}K_{\text{a}2} = 5.95$ , and  $\text{p}K_{\text{a}3} = 6.39$ .

$$K_1 = 10^{-5.95} = 1.1 \times 10^{-6}$$

Check if  $[X]_{\text{initial}} \gg \text{p}K_{\text{a}2}$ ,  $0.20 \gg 1.1 \times 10^{-6}$  which is true,

$$\text{So pH} = \frac{1}{2} (\text{p}K_{\text{a}2} + \text{p}K_{\text{a}3}), \frac{1}{2} (5.95 + 6.39) = 6.17$$

## The Concentrations of Solute Species

**Environmental chemists** studying the **pollution** caused by fertilizers in runoff from fields or mineralogists studying the formation of sedimentary rocks as groundwater trickles through rock formations may need to know not only the **pH** but also the **concentrations** of each of the ions present in the solution.

We need to know the concentration of sulfite ion in a solution of sulfurous acid or the concentrations of phosphate and hydrogen phosphate ions in a solution of phosphoric acid.

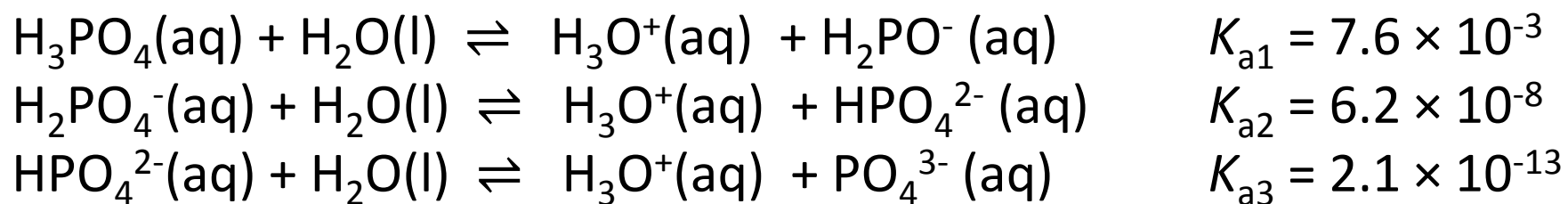


## The Concentrations of Solute Species

Next, **we learn to calculate the concentrations** of all the solute species in solution, from pH.

To **simplify the calculations**, species with a **greater amount** are not significantly affected by concentrations of species present in the **smaller amount**.

Example 6E.2 Calculate the concentrations of all solute species in 0.10 M  $\text{H}_3\text{PO}_4(\text{aq})$ .



- Setup an ICE table **for each  $K$** —there will be **3 ICE tables**.
- This will help us find the concentrations of  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{O}^+$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{OH}^-$ , and pH.

	$\text{H}_3\text{PO}_4$	$\text{H}_3\text{O}^+$	$\text{H}_2\text{PO}_4^-$
initial	0.10	0	0
change	-x	+x	+x
equilibrium	$0.10 - x$	x	x

Since  $K_a$  is  $7.6 \times 10^{-3}$  which is close to 0.10, we'll have to use the quadratic  $\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ , ( $K_a \times 100 > 0.10$ ).

$7.6 \times 10^{-3} = \frac{x^2}{0.10 - x}$  this goes to  $x^2 + 7.6 \times 10^{-3}x - 7.6 \times 10^{-4}$ ,  
solving for  $x$

$x = 0.024 = [\text{H}_3\text{O}^+] = [\text{H}_2\text{PO}_4^-]$  and  $[\text{H}_3\text{PO}_4] = 0.10 - 0.024 = 0.08 \text{ mol}\cdot\text{L}^{-1}$ .

Note,  $\text{H}_2\text{PO}_4^-$  is not a strong acid, so the  $\text{H}_3\text{O}^+$  comes from the first step or  $\text{H}_3\text{PO}_4$ .

	$\text{H}_3\text{PO}_4$	$\text{H}_3\text{O}^+$	$\text{H}_2\text{PO}_4^-$
initial	0.10	0	0
change	-x	+x	+x
equilibrium	$0.10 - 0.024 = 0.08$	0.024	0.024

These values go into our **next ICE table**.

	$\text{H}_3\text{PO}_4$	$\text{H}_3\text{O}^+$	$\text{H}_2\text{PO}_4^-$
initial	0.10	0	0
change	-x	+x	+x
equilibrium	$0.10 - 0.024 = 0.08$	0.024	0.024

For our next  $K$ ,  $K_{a2}$ , we find  $\text{HPO}_4^{2-}$ , noting  $[\text{H}_3\text{O}^+]$  and  $[\text{H}_2\text{PO}_4^-]$  come from our previous table, due to the strength of acid coming from the first step.

	$\text{H}_2\text{PO}_4^{2-}$	$\text{H}_3\text{O}^+$	$\text{HPO}_4^{2-}$
initial	0.024	0.024	0
change	-x	+x	+x
equilibrium	$0.024 - x$	$0.024 + x$	x

Solving for  $K_{a2}$  two things happen: (1) in both  $0.024 - x$ , and  $0.024 + x$ , “x” the amount dissociated,  $6.2 \times 10^{-8}$  is so small we ignore the “x’s”, and (2) our  $x = 6.2 \times 10^{-8} = [\text{HPO}_4^{2-}]$ .

$$K_{a2} = 6.2 \times 10^{-8} = \frac{(0.024)x}{0.024}$$

We carry the  $[\text{H}_3\text{O}^+]$  and  $[\text{HPO}_4^{2-}]$  to our next table.

	$\text{H}_3\text{PO}_4$	$\text{H}_3\text{O}^+$	$\text{H}_2\text{PO}_4^-$
initial	0.10	0	0
change	-x	+x	+x
equilibrium	$0.10 - 0.024 = 0.08$	0.024	0.024

	$\text{H}_2\text{PO}_4^{2-}$	$\text{H}_3\text{O}^+$	$\text{HPO}_4^{2-}$
initial	0.024	0.024	0
change	-x	+x	+x
equilibrium	$0.024 - x$	$0.024 + x$	x

	$\text{HPO}_4^{2-}$	$\text{H}_3\text{O}^+$	$\text{PO}_4^{3-}$
initial	$6.2 \times 10^{-8}$	0.024	0
change	-x	+x	+x
equilibrium	$6.2 \times 10^{-8} - x$	$0.024 + x$	x

Using similar assumptions for x, we solve for

$$K_{a3} = 2.1 \times 10^{-13} = \frac{(0.024)x}{6.2 \times 10^{-8}}, \quad x = 5.4 \times 10^{-19} = [\text{PO}_4^{3-}]$$

All  
concentrations:

$$[\text{H}_3\text{PO}_4] = 0.080 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 0.024 \text{ M}, \quad [\text{OH}^-] = 4.2 \times 10^{-13} \text{ M}$$

$$[\text{H}_2\text{PO}_4^-] = 0.024 \text{ M}$$

$$[\text{HPO}_4^{2-}] = 6.2 \times 10^{-8} \text{ M}$$

$$[\text{PO}_4^{3-}] = 5.4 \times 10^{-19} \text{ M}$$

$$\text{pH} = -\log [0.024] = 1.62$$

## Composition and pH

Sometimes we need to know how the concentrations of the ions present in a solution of a polyprotic acid vary with pH.

In rainwater, the amount of carbonic acid at low pH (when hydronium ions are abundant), should be dominant so we expect to see the fully protonated species  $\text{H}_2\text{CO}_3$ .

At high pH (when hydroxide ions are abundant), we expect the fully deprotonated species ( $\text{CO}_3^{2-}$ ) to be dominant.

At intermediate pH, we expect the intermediate species  $\text{HCO}_3^-$  to dominate.

## Composition and pH

Concentrations of solute species are all pH dependent.

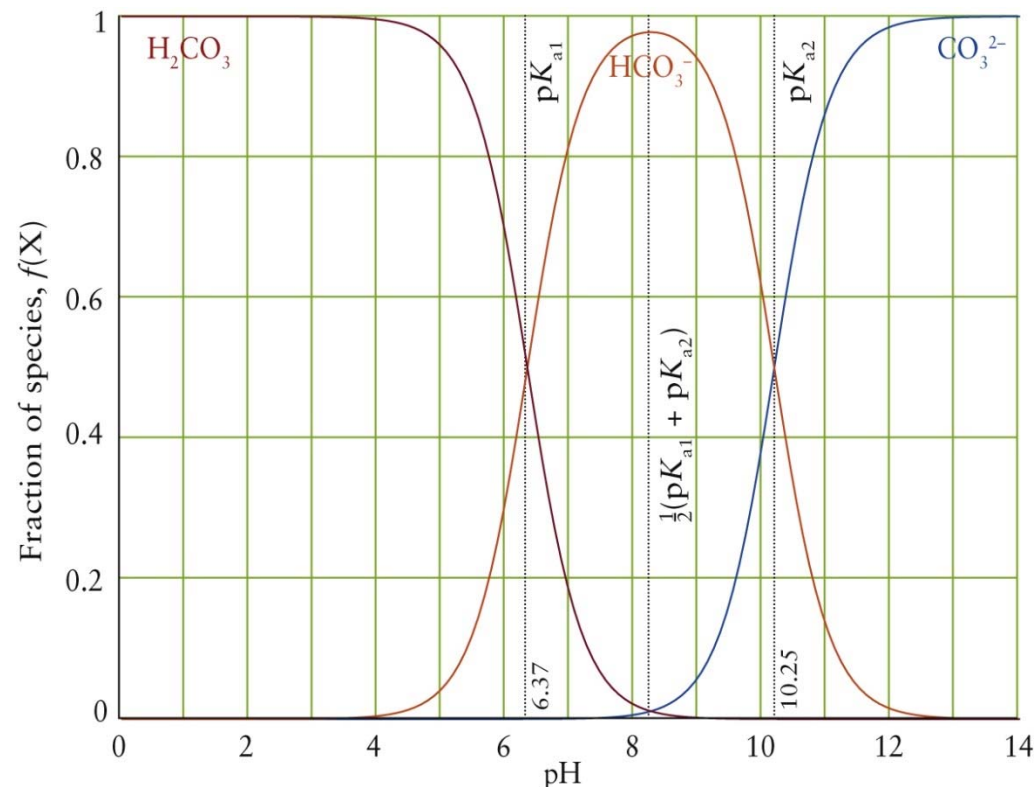


Figure 6E.1  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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$$H = [H_3O^+]^2 + [H_3O^+]K_{a1} + K_{a1}K_{a2}$$

We have found expressions for the fractions,  $f$ , of species in a solution of carbonic acid. They are easily generalized to any diprotic acid  $H_2A$ ,  $HA^-$ ,  $A^{2-}$ :

$$f(H_2A) = \frac{[H_3O^+]^2}{H}; \quad f(HA^-) = \frac{[H_3O^+]K_{a1}}{H}; \quad f(A^{2-}) = \frac{K_{a1}K_{a2}}{H};$$

## Autoprotolysis and pH

Asked to estimate the pH of  $1.0 \times 10^{-8} \text{ M HCl(aq)}$  we might say  
 $\text{pH} = 8.00$ .

That is **absurd**, because pH of 8.00 is basic, whereas HCl is an acid!

Two sources of error occur with hydronium ions:

(1) At very low acid concentrations, the supply of hydronium ions from the **autoprotolysis of water** is close to the **original source of acid**, here very low concentration of HCl, and (2) both sources must be taken into account.

We discuss this in the next two sections first taking into account autoprotolysis for strong acids and bases and then for weak ones.



## Very Dilute Solutions of Strong Acids and Bases

We have to include the contribution of autoprotolysis to pH only when the concentration of strong acid or base is **less than about  $10^{-6} \text{ mol}\cdot\text{L}^{-1}$** .

We need to consider **all** species in solution.

HCl, a strong acid would have, other than water,  $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$ , and  $\text{Cl}^-$ . We need **three equations** to find all their concentrations.

The first equation takes charge balance into account for an electrically neutral solution. There is only one type of cation,  $\text{H}_3\text{O}^+$ , then  $[\text{H}_3\text{O}^+] = [\text{Cl}^-] + [\text{OH}^-]$  (for a diprotic acid multiply by 2).

$[\text{OH}^-] = [\text{H}_3\text{O}^+] - [\text{Cl}^-]$  charge-balance relation

## Very Dilute Solutions of Strong Acids and Bases

The second equation takes material balance into account; all the added solute must be accounted for. Because HCl is a strong acid, the concentration of  $\text{Cl}^-$  ions in the solution is equal to the concentration of HCl,

$$[\text{Cl}^-] = [\text{HCl}]_{\text{initial}}$$

$$[\text{OH}^-] = [\text{H}_3\text{O}^+] - [\text{HCl}]_{\text{initial}} \quad \text{material balance}$$

The third is the  $K_w$ ,  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

## Very Dilute Solutions of Strong Acids and Bases

$[\text{OH}^-] = [\text{H}_3\text{O}^+] - [\text{Cl}^-]$  charge-balance relation

$[\text{OH}^-] = [\text{H}_3\text{O}^+] - [\text{HCl}]_{\text{initial}}$  material balance

The third is the  $K_w$ ,  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

Substituting the first two into the third we have,

$K_w = [\text{H}_3\text{O}^+] ([\text{H}_3\text{O}^+] - [\text{HCl}]_{\text{initial}})$  in quadratic form,

$[\text{H}_3\text{O}^+]^2 - [\text{HCl}]_{\text{initial}} [\text{H}_3\text{O}^+] - K_w = 0$  for any acid around pH 6.

For a base, we use NaOH and arrive at a similar formula:

$[\text{H}_3\text{O}^+]^2 - [\text{NaOH}]_{\text{initial}} [\text{H}_3\text{O}^+] - K_w = 0$  for any base around pH 8.

Example 6F.1 What is the pH of  $8.0 \times 10^{-8}$  M HCl(aq) solution?

For any acid we use  $[\text{H}_3\text{O}^+]^2 - [\text{HCl}]_{\text{initial}} [\text{H}_3\text{O}^+] - K_w = 0$ .

This goes to  $x^2 - (8.0 \times 10^{-8})x - 1.0 \times 10^{-14} = 0$ .

Solving with the quadratic equation we have  $x = 1.5 \times 10^{-7}$ .

Using  $\text{pH} = -\log (\text{H}_3\text{O}^+)$ ,  $-\log (1.5 \times 10^{-7}) = 6.82$ .

## Very Dilute Solutions of Weak Acids

Often for weak acids autoprotolysis of water is the greatest contributing factor to pH.

Four unknowns exist for a weak acid HA,  $A^-$ ,  $H_3O^+$ , and  $OH^-$ .

Both  $K_w = [H_3O^+][OH^-]$  and  $K_a = \frac{[H_3O^+][A^-]}{[HA]}$  are used to arrive at the following cubic equation (derivation is shown in your text).

$$[H_3O^+]^3 + K_a[H_3O^+]^2 - (K_w + K_a[HA]_{\text{initial}})[H_3O^+] - K_aK_w = 0$$

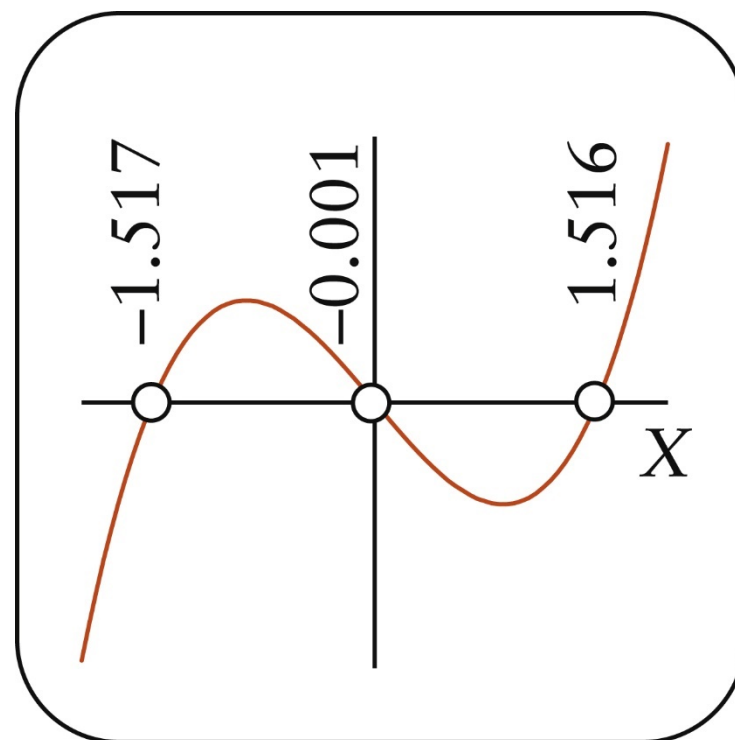
Example 6F.2 estimate the pH of a  $1.0 \times 10^{-4}$  M aqueous phenol solution. The  $K_a = 1.3 \times 10^{-10}$ .

$$[\text{H}_3\text{O}^+]^3 + K_a[\text{H}_3\text{O}^+]^2 - (K_w + K_a[\text{HA}]_{\text{initial}})[\text{H}_3\text{O}^+] - K_aK_w = 0$$

$$x^3 + (1.3 \times 10^{-10})x^2 - (2.3 \times 10^{-14})x - 1.3 \times 10^{-24} = 0$$

Solving for  $x$ ,  $x = 1.5 \times 10^{-7}$

$$\text{pH} = -\log(1.5 \times 10^{-7}) = 6.82$$



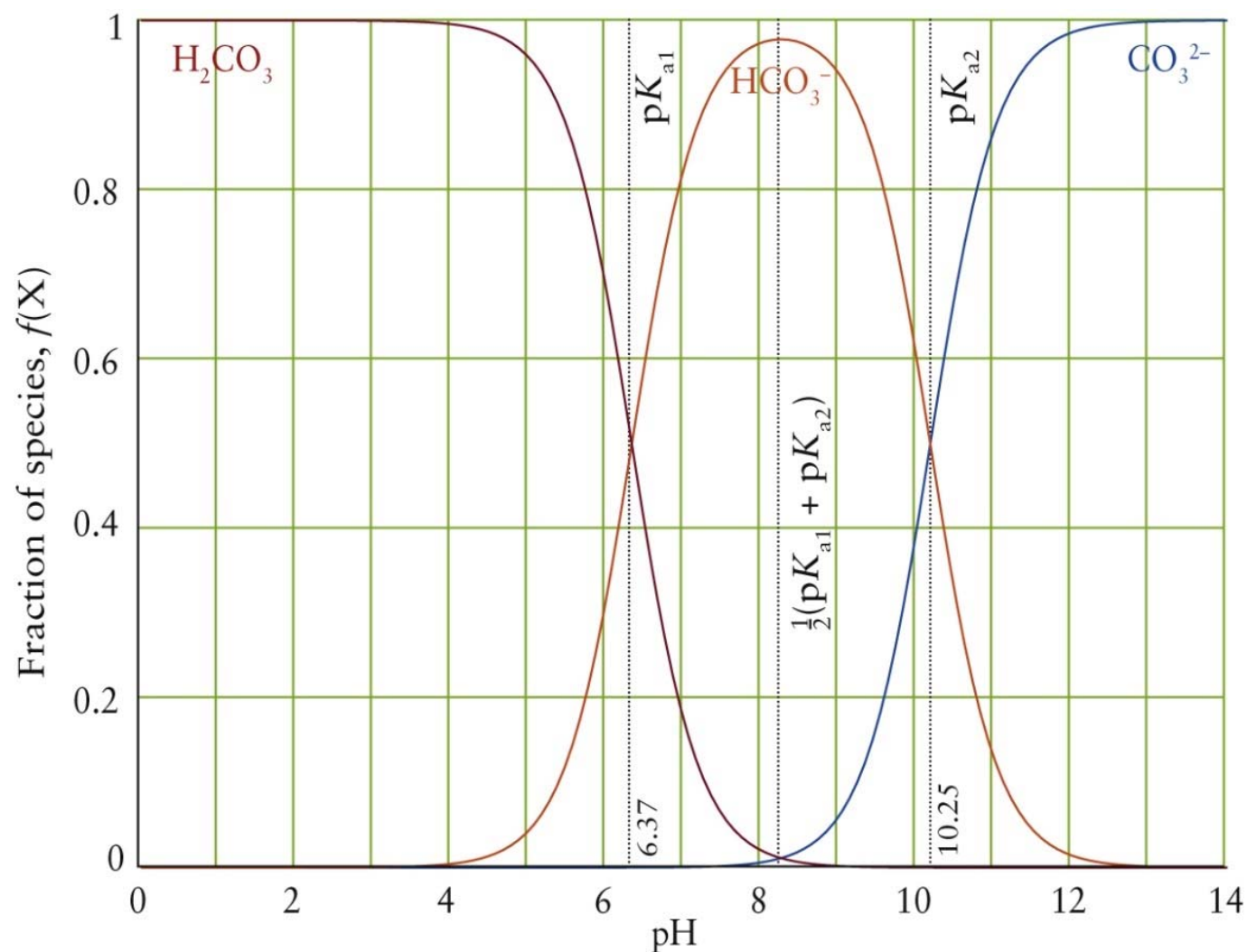
# Aqueous Solution Equilibrium

# In this section

- We define and design buffers;
- We investigate the pH change during a acid/base titration process;
- We investigate solubility products.



pH variation can cause significant changes to the concentrations of other solutes



**Figure 6E.1**

Atkins, *Chemical Principles: The Quest for Insight*, 7e

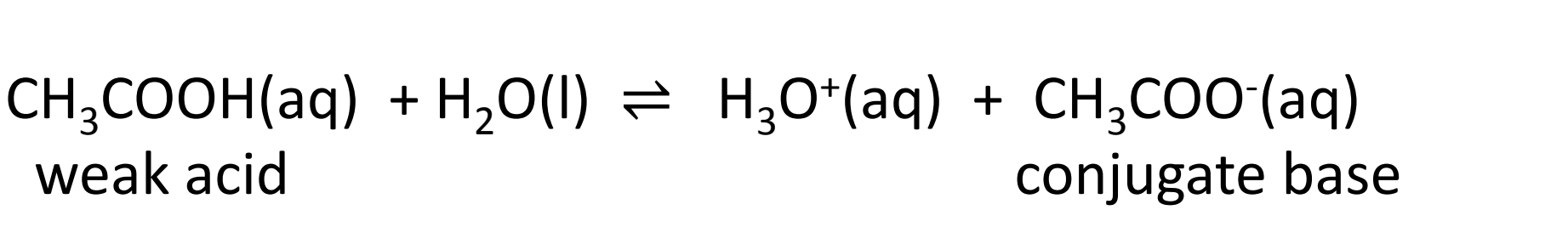
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## Buffer Action

A buffer is a solution that **resists a change in pH** when small amounts of strong acids or bases are added.

We see buffers in intravenous solutions to patients; blood plasma is buffered to a pH of 7.4 ( $\pm 0.2$ ); the ocean is buffered to a pH of 8.

A buffer is a **weak acid** with its **conjugate base** or a **weak base** with its **conjugate acid**.



## Buffer Action

For example, 1.0 L of water, would have a pH of 7.0.

Adding 1 mL of 1.0 M HCl solution, using our dilution formula ( $M_1V_1 = M_2V_2$ ), and assuming 1 mL would not change the volume of 1.0 L significantly, 0.001L,

$$M_2 = \frac{M_1V_1}{V_2}, \quad \frac{1.0 \text{ M} \times 0.001 \text{ L}}{1.0 \text{ L}} = 0.001 \text{ M H}_3\text{O}^+, \text{ pH} = -\log(0.001) = 3.0$$

That means the  $\Delta\text{pH} = 7 - 3$  or 4.

So the effect of 1 mL of a strong acid on 1 L of pure water (1 part per 1000) can increase water's ion concentration  $[\text{H}_3\text{O}^+]$  by 10,000!

## Buffer Action

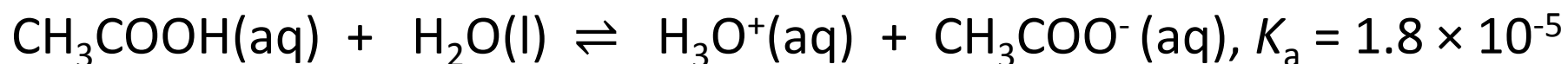
Our **definition of a buffer** is the ability to **resist a change in pH**.

Our previous example of  $\Delta\text{pH} = 7 - 3 = 4$  is not much resistance.

Next, we look at how to design a buffer.

We will calculate our **initial buffer pH** (an acid and its conjugate base).

Example 6G.1 Suppose we culture bacteria, something close to a pH = 4. We prepare a buffer solution that is 0.040 M  $\text{NaCH}_3\text{CO}_2(\text{aq})$  and 0.080 M  $\text{CH}_3\text{COOH}(\text{aq})$  at 25°C. What is the pH of the buffer solution?



We can make an ICE table, with our known values first,

	$\text{CH}_3\text{COOH}$	$\text{H}_3\text{O}^+$	$\text{CH}_3\text{COO}^-$
initial	0.080	0	0.040
change	-x	+x	+x
equilibrium	$0.080 - x$	x	$0.040 + x$

For a quick approximation  $K_a \times 100 < 0.040$  (0.040 is the smallest of the two starting concentrations), so we ignore -x, and +x, and we'll still check +x at the end for 5% ionization to make sure.

	CH <sub>3</sub> COOH	H <sub>3</sub> O <sup>+</sup>	CH <sub>3</sub> COO <sup>-</sup>
initial	0.080	0	0.040
change	-x	+x	+x
equilibrium	0.080	x	0.040

$$\text{Solving } K_a = 1.8 \times 10^{-5} = \frac{(0.040)x}{0.080}$$

$$x = \frac{(1.8 \times 10^{-5}) 0.080}{0.040}$$

$$x = 3.6 \times 10^{-5} = [\text{H}_3\text{O}^+], \text{ using } \text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log [3.6 \times 10^{-5}] = 4.44$$

$$\text{percentage deprotonation} = \frac{3.6 \times 10^{-5}}{0.040} \times 100 = 0.09\% \text{ (which is less than 5\% 👍)}$$

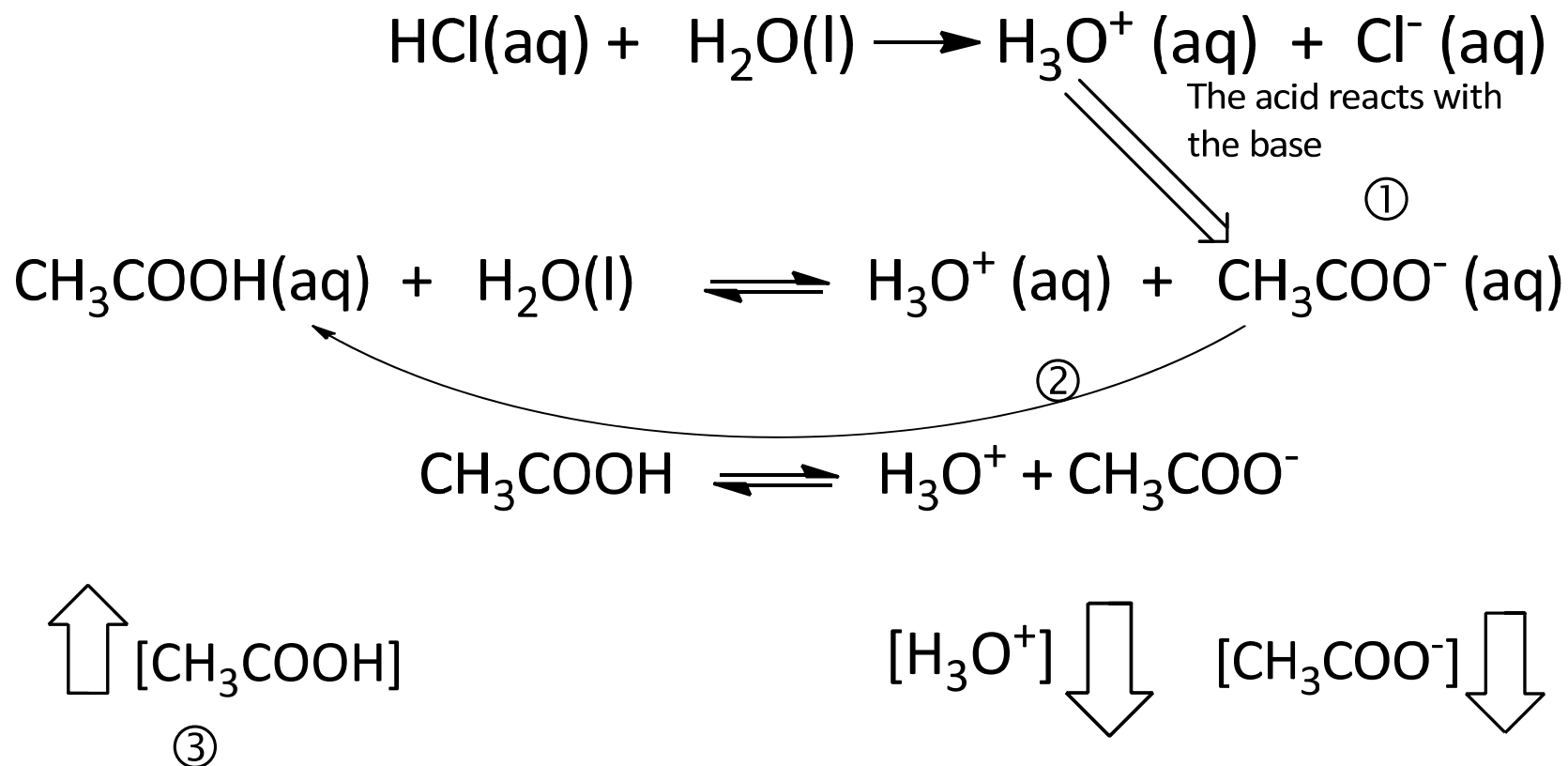
## A Buffer in Action

Adding 1 mL of 1.0 M HCl solution to 1.0 L of pure water produced a pH of 3.0, a change in the water's ion concentration  $[\text{H}_3\text{O}^+]$  of 10,000.

Now let's buffer the 1.0 L of pure water with our previous buffer acetic acid and conjugate acetate ion solution,  
 $\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$   
 $K_a = 1.8 \times 10^{-5}$ .

First we'll see the **descriptive** analysis followed by a **quantitative** interpretation of what happens when 1 mL of HCl is added to a buffer,  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$  solution.

Buffers are an acid conjugate base pairs (and visa versa).



HCl is removed, and replaced with CH<sub>3</sub>COOH!

1. The H<sub>3</sub>O<sup>+</sup> from the HCl reacts with the CH<sub>3</sub>COO<sup>-</sup>;
2. This produces more acid, CH<sub>3</sub>COOH;
3. The effect is a **strong acid is removed, replaced with a weak acid.**



Remember that a **strong acid** reacts completely with a **weak base**.

Adding 1 mL of 1.0 M HCl solution to a 1.0 L buffer solution of 0.040 M NaCH<sub>3</sub>CO<sub>2</sub> (aq) and 0.080 M CH<sub>3</sub>COOH(aq)



H<sub>3</sub>O<sup>+</sup> + CH<sub>3</sub>COO<sup>-</sup> ⇌ CH<sub>3</sub>COOH reacts first.

The ICE table shows the reaction between the strong acid and weak base—these must be in **moles** since we're showing a reaction.

$$\frac{1.0 \text{ mol HCl}}{1 \text{ L}} \times \frac{0.001 \text{ L}}{1} = 0.001 \text{ mol HCl}$$

$$\frac{0.040 \text{ mol acetate}}{1 \text{ L}} \times \frac{1 \text{ L}}{1} = 0.040 \text{ mol acetate}$$

	CH <sub>3</sub> COO <sup>-</sup>	H <sub>3</sub> O <sup>+</sup>	CH <sub>3</sub> COOH
initial	0.040 mol	0.001 mol	0.080 mol
change	-0.001 mol	-0.001 mol	+0.001 mol
equilibrium	0.039 mol	0	0.081 mol

	CH <sub>3</sub> COO <sup>-</sup>	H <sub>3</sub> O <sup>+</sup>	CH <sub>3</sub> COOH	
initial	0.040 mol	0.001 mol	0.080 mol	0.039 mol in 1 L = 0.039 mol·L <sup>-1</sup>
change	-0.001 mol	-0.001 mol	+0.001 mol	
equilibrium	0.039 mol	0	0.081 mol	0.081 mol in 1 L = 0.081 mol·L <sup>-1</sup>

We use these new values to calculate the pH of the buffer, after the HCl was added.

	CH <sub>3</sub> COOH	H <sub>3</sub> O <sup>+</sup>	CH <sub>3</sub> COO <sup>-</sup>
initial	0.081	0	0.039
change	-x	+x	+x
equilibrium	0.081	x	0.039

$$\text{Solving } K_a = 1.8 \times 10^{-5} = \frac{(0.039)x}{0.081}, \quad x = 3.7 \times 10^{-5} = [\text{H}_3\text{O}^+]$$

using  $\text{pH} = -\log [\text{H}_3\text{O}^+]$ ,  $\text{pH} = -\log [3.7 \times 10^{-5}] = 4.43$

$\Delta\text{pH} = 4.44 - 4.43 = 0.01$ , that is a much **less dramatic** increase than the 10,000 times increase without a buffer in pure water. **Also**, the Strong Acid is **gone**, replaced with a Weak Acid.