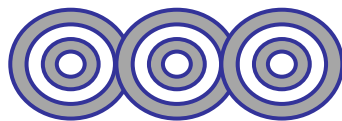




# Fundamentals of Analytical Chemistry



## Acid-Base Equilibria

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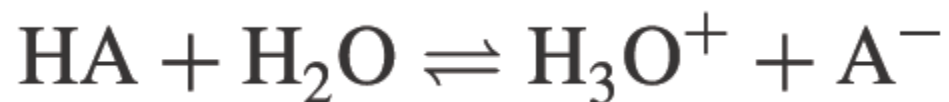
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# **Acid-Base Theories**

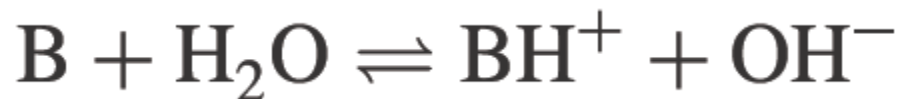
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# Arrhenius theory – H<sup>+</sup> & OH<sup>-</sup>

**Acid** is any substance that ionizes (partially or completely) in water to give hydrogen ions (which associate with the solvent to give hydronium ions, H<sub>3</sub>O<sup>+</sup>):



A **base** ionizes in water to give hydroxide ions. Weak (partially ionized) bases generally ionize as follows:



while strong bases such as metal hydroxides (e.g., NaOH) dissociate as



The Arrhenius theory is restricted to aqueous solutions (water as the solvent).

# Brønsted-Lowry theory – taking & giving protons

The theory of solvent systems is suitable for ionizable solvents, but it is not applicable to acid–base reactions in nonionizable solvents such as benzene or dioxane.

**Acid** is any substance that can donate a proton ( $\text{H}^+$ ), and a **base** is any substance that can accept a proton ( $\text{H}^+$ ).

**A Brønsted-Lowry acid**... must have a removable (acidic) proton

**A Brønsted-Lowry base**... must have a pair of nonbonding electrons

## Brønsted Acid–Base Reactions

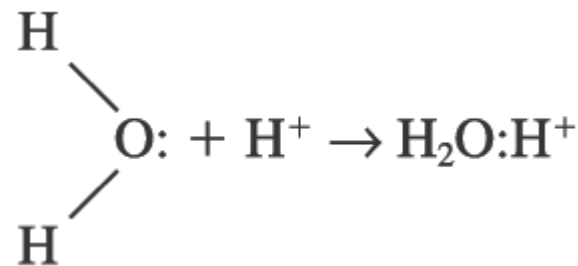
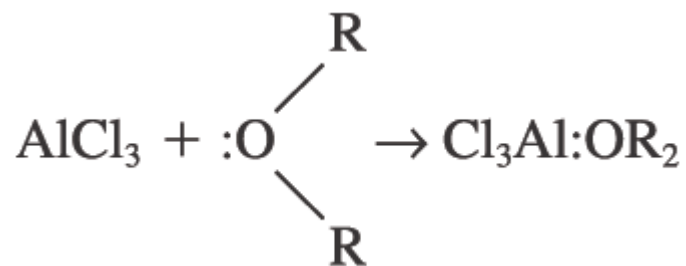
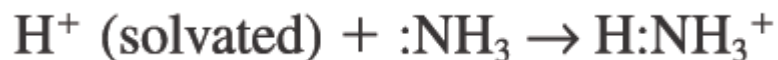
Solvent	Acid <sub>1</sub>	+	Base <sub>2</sub>	→	Acid <sub>2</sub>	+	Base <sub>1</sub>
$\text{NH}_3$ (liq.)	HOAc		$\text{NH}_3$		$\text{NH}_4^+$		$\text{OAc}^-$
$\text{H}_2\text{O}$	HCl		$\text{H}_2\text{O}$		$\text{H}_3\text{O}^+$		$\text{Cl}^-$
$\text{H}_2\text{O}$	$\text{NH}_4^+$		$\text{H}_2\text{O}$		$\text{H}_3\text{O}^+$		$\text{NH}_3$
$\text{H}_2\text{O}$	$\text{H}_2\text{O}$		$\text{OAc}^-$		HOAc		$\text{OH}^-$
$\text{H}_2\text{O}$	$\text{HCO}_3^-$		$\text{OH}^-$		$\text{H}_2\text{O}$		$\text{CO}_3^{2-}$
$\text{C}_2\text{H}_5\text{OH}$	$\text{NH}_4^+$		$\text{C}_2\text{H}_5\text{O}^-$		$\text{C}_2\text{H}_5\text{OH}$		$\text{NH}_3$
$\text{C}_6\text{H}_6$	H picrate		$\text{C}_6\text{H}_5\text{NH}_2$		$\text{C}_6\text{H}_5\text{NH}_3^+$		picrate <sup>-</sup>

Conjugate acid-base pairs are denoted in the same color.

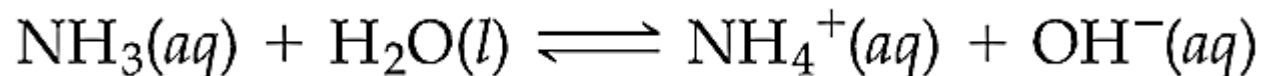
# Lewis theory – taking & giving electrons

An **acid** is a substance that can accept an electron pair and a **base** is a substance that can donate an electron pair. The latter frequently contains an oxygen or a nitrogen as the electron donor. Thus, nonhydrogen-containing substances are included as acids.

Examples of acid-base reactions in the Lewis theory are as follows:



Consider the following example that compares the relationship between the definitions of acids and bases – an aqueous solution of ammonia, in which the following equilibrium occurs:



-Ammonia is an Arrhenius base because adding it to water leads to an increase in the concentration of  $\text{OH}^-(aq)$ .

-Ammonia is a Brønsted-Lowry base because it accepts a proton from  $\text{H}_2\text{O}$ . The  $\text{H}_2\text{O}$  molecule in the equation acts as a Brønsted-Lowry acid because it donates a proton to the  $\text{NH}_3$  molecule.

-Ammonia is a Lewis base because it donates an electron pair.

***Note...***

An acid and a base always work together to transfer a proton. In other words, a substance can function as an acid only if another substance simultaneously behaves as a base.

Some substances can act as an acid in one reaction and as a base in another.

For example,  $\text{H}_2\text{O}$  is a Brønsted-Lowry base in its reaction with  $\text{HCl}$  and a Brønsted-Lowry acid in its reaction with  $\text{NH}_3$ .

A substance that is capable of acting as either an acid or a base is called **amphiprotic**.

An amphiprotic substance acts as a base when combined with something more strongly acidic than itself and an acid when combined with something more strongly basic than itself.

e.g.,  $\text{HCO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{H}_2\text{O}$

# Conjugate acids and bases



## In the forward reaction:

HX donates a proton to H<sub>2</sub>O. Therefore, HX is the Brønsted-Lowry acid, and H<sub>2</sub>O is the Brønsted-Lowry base.

## In the reverse reaction:

H<sub>3</sub>O<sup>+</sup> ion donates a proton to the X<sup>-</sup> ion, so H<sub>3</sub>O<sup>+</sup> is the acid and X<sup>-</sup> is the base.

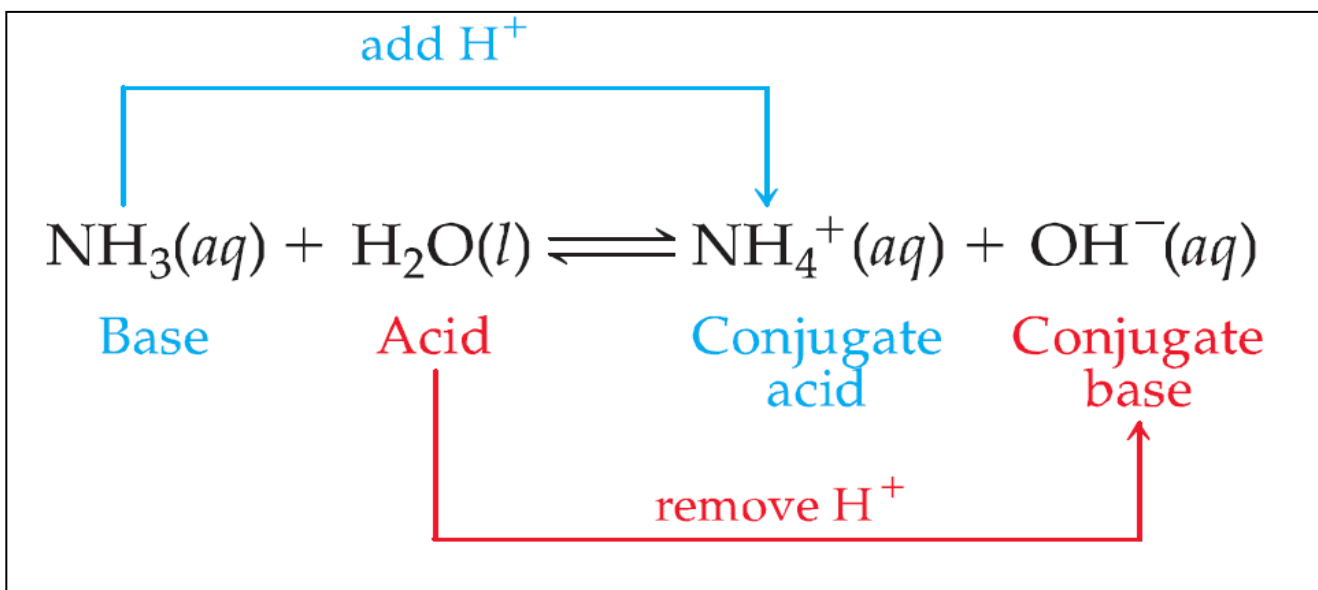
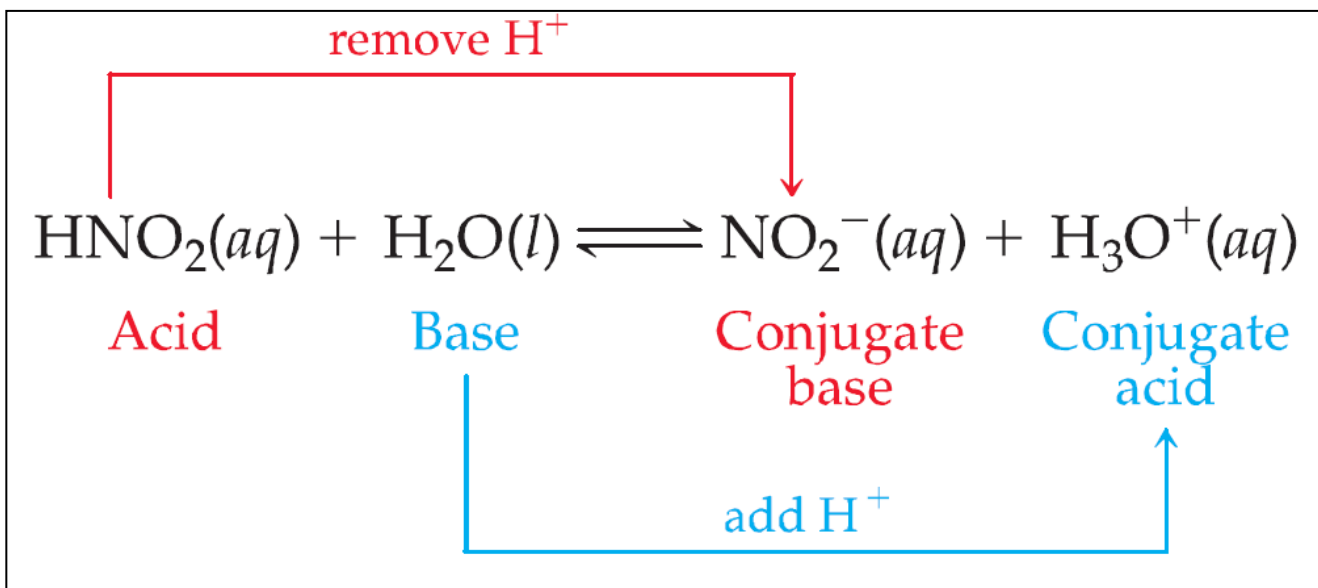
When the acid HX donates a proton, it leaves X<sup>-</sup> which can act as a base. Likewise, when H<sub>2</sub>O acts as a base, it generates H<sub>3</sub>O<sup>+</sup>, which can act as an acid.

An acid and a base such as HX and X<sup>-</sup> that differ only in the presence or absence of a proton are called a **conjugate acid-base pair**.

-Every acid has a conjugate base, formed by removing a proton from the acid, e.g., OH<sup>-</sup> is the conjugate base of H<sub>2</sub>O, and X<sup>-</sup> is the conjugate base of HX.

-Every base has a conjugate acid, formed by adding a proton to the base, e.g., H<sub>3</sub>O<sup>+</sup> is the conjugate acid of H<sub>2</sub>O, and HX is the conjugate acid of X<sup>-</sup>.





## Example

(a) What is the conjugate base of each of the following acids:

$\text{HClO}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{PH}_4^+$ ,  $\text{HCO}_3^-$ ?

(b) What is the conjugate acid of each of the following bases:

$\text{CN}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{O}$ ,  $\text{HCO}_3^-$ ?

## Solution

(a)  $\text{HClO}_4$  less one proton ( $\text{H}^+$ ) is  $\text{ClO}_4^-$ . The other conjugate bases are  $\text{HS}^-$ ,  $\text{PH}_3$ , and  $\text{CO}_3^{2-}$ .

(b)  $\text{CN}^-$  plus one proton ( $\text{H}^+$ ) is  $\text{HCN}$ . The other conjugate acids are  $\text{HSO}_4^-$ ,  $\text{H}_3\text{O}^+$ , and  $\text{H}_2\text{CO}_3$ .

## Practice Exercise

Write the formula for the conjugate acid of each of the following:

$\text{HSO}_3^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}$ .

**Answers:**  $\text{H}_2\text{SO}_3$ ,  $\text{HF}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{HCO}^+$

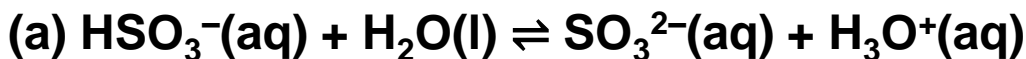
## Example

The hydrogen sulfite ion ( $\text{HSO}_3^-$ ) is amphiprotic.

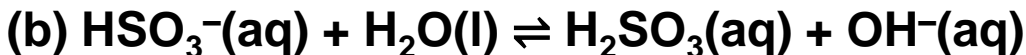
**(a)** Write an equation for the reaction of  $\text{HSO}_3^-$  with water, in which the ion acts as an acid.

**(b)** Write an equation for the reaction of  $\text{HSO}_3^-$  with water, in which the ion acts as a base. In both cases identify the conjugate acid–base pairs.

## Solution



The conjugate pairs in this equation are  $\text{HSO}_3^-$  (acid) and  $\text{SO}_3^{2-}$  (conjugate base); and  $\text{H}_2\text{O}$  (base) and  $\text{H}_3\text{O}^+$  (conjugate acid).



The conjugate pairs in this equation are  $\text{H}_2\text{O}$  (acid) and  $\text{OH}^-$  (conjugate base), and  $\text{HSO}_3^-$  (base) and  $\text{H}_2\text{SO}_3$  (conjugate acid).

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# **Acid-Base Equilibria**

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# Acid and base strength

	ACID	BASE		
100% ionized in H <sub>2</sub> O	Strong	HCl	Cl <sup>-</sup>	Negligible
		H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	
		HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	
		H <sub>3</sub> O <sup>+</sup> (aq)	H <sub>2</sub> O	
Acid strength increases ↑	Weak	HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Weak
		H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	
		HF	F <sup>-</sup>	
		HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
		H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>	
		H <sub>2</sub> S	HS <sup>-</sup>	
		H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>	
		NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	
		HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	
		HPO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	
			H <sub>2</sub> O	
Negligible		OH <sup>-</sup>	O <sup>2-</sup>	Strong
		H <sub>2</sub>	H <sup>-</sup>	
		CH <sub>4</sub>	CH <sub>3</sub> <sup>-</sup>	
				100% protonated in H <sub>2</sub> O

Base strength increases ↓

**Strong acids are completely dissociated in water.**

Their conjugate bases are quite weak.

**Weak acids only dissociate partially in water.**

Their conjugate bases are weak bases.

**Substances with negligible acidity do not dissociate in water.**

Their conjugate bases are exceedingly strong.

**Example:**

CH<sub>4</sub> contains hydrogen but does not demonstrate any acidic behavior in water. Its conjugate base (CH<sub>3</sub><sup>-</sup>) is a strong base.

The seven most common **strong acids** are:

HCl, HBr, HI, HNO<sub>3</sub>, HClO<sub>3</sub>, and HClO<sub>4</sub> (monoprotic)

H<sub>2</sub>SO<sub>4</sub> (diprotic).

These are, by definition, strong electrolytes and exist totally as ions in aqueous solution.

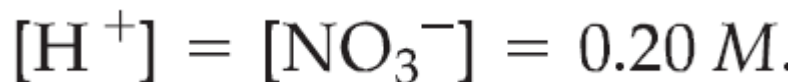
For the monoprotic strong acids,



Strong acids are strong electrolytes, existing in aqueous solution entirely as ions.

For example,

0.20 M solution of HNO<sub>3</sub>(aq)



**Strong bases** are the soluble hydroxides, which are the alkali metal (group 1A) hydroxides ( $\text{Na}^+$  and  $\text{K}^+$ ) and heavier alkaline earth metal (group 2A) hydroxides ( $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ ).

These substances dissociate completely in aqueous solution.

Strong bases are strong electrolytes, existing in aqueous solution entirely as ions.

For example,

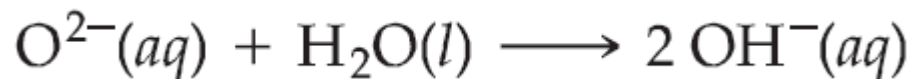
0.30 M NaOH consists of

0.30 M  $\text{Na}^+(\text{aq})$  and 0.30 M  $\text{OH}^-(\text{aq})$

hydrogen 1 H 1.0079		
lithium 3 Li 6.941	beryllium 4 Be 9.0122	
sodium 11 Na 22.990	magnesium 12 Mg 24.305	
potassium 19 K 39.098	calcium 20 Ca 40.078	
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	
caesium 55 Cs 132.91	barium 56 Ba 137.33	57- *
francium 87 Fr [223]	radium 88 Ra [226]	89-1 *

Although all the hydroxides of the alkali metals (group 1A) are strong electrolytes, LiOH, RbOH, and CsOH are not commonly encountered in the laboratory. The hydroxides of the heavier alkaline earth metals  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ , and  $\text{Ba}(\text{OH})_2$ , are also strong electrolytes. They have limited solubilities, however, so they are used only when high solubility is not critical.

Another strong bases include the **oxide ion**. **Ionic metal oxides**, especially  $\text{Na}_2\text{O}$  and  $\text{CaO}$ , are often used in industry when a strong base is needed. The  $\text{O}^{2-}$  reacts with water to form  $\text{OH}^-$ , leaving virtually no  $\text{O}^{2-}$  remaining in the solution:



Thus, a solution formed by dissolving 0.010 mol of  $\text{Na}_2\text{O}(\text{s})$  in enough water to form 1.0 L of solution will have  $[\text{OH}^-] = 0.020 \text{ M}$  and a pH of 12.30.



- The stronger an acid, the weaker is its conjugate base.
- The stronger a base, the weaker is its conjugate acid.

In any acid-base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base.



$\text{H}_2\text{O}$  is a much stronger base than  $\text{Cl}^-$ , so the equilibrium lies so far to the right that  $K$  is not measured ( $K \gg 1$ ).



Acetate  $\text{CH}_3\text{COO}^-$  is a stronger base than  $\text{H}_2\text{O}$ , so the equilibrium favors the left side ( $K < 1$ ).

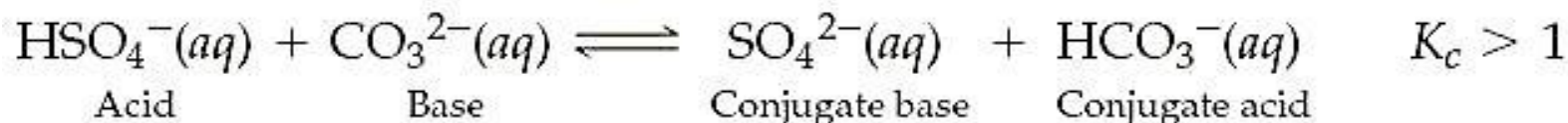
## Example

For the following proton-transfer reaction, use Acid-Base strength Figure to predict whether the equilibrium lies predominantly to the left (that is,  $K_c < 1$ ) or to the right ( $K_c > 1$ ):



## Solution

$\text{CO}_3^{2-}$  appears lower in the right-hand column in the Figure and is therefore a stronger base than  $\text{SO}_4^{2-}$ .  $\text{CO}_3^{2-}$ , therefore, will get the proton preferentially to become  $\text{HCO}_3^-$ , while  $\text{SO}_4^{2-}$  will remain mostly unprotonated. The resulting equilibrium will lie to the right, favoring products (that is,  $K_c > 1$ ).



# Acid-base equilibria in water

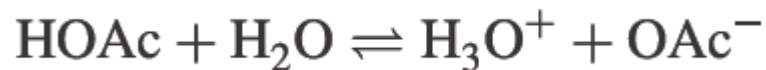
When an acid or base is dissolved in water, it will dissociate, or ionize, the amount of ionization being dependent on the strength of the acid or the base. A “strong” electrolyte is completely dissociated, while a “weak” electrolyte is partially dissociated.

Hydrochloric acid is a strong acid, and in water, its ionization is complete:



An equilibrium constant would have a value of infinity.

Acetic acid is a weak acid, which ionizes only partially in water (a few percent):



$$K_a = \frac{[\text{H}^+][\text{OAc}^-]}{[\text{HOAc}]}$$

Pure water ionizes slightly, or undergoes autoprotolysis



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



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

$K_w$  is the thermodynamic autoprotolysis, or self-ionization, constant.

$K_w$  is exactly  $1.00 \times 10^{-14}$  at  $24^\circ\text{C}$  and even at  $25^\circ\text{C}$ ,

$$[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

In pure water, then, the concentrations of these two species are equal since there are no other sources of  $\text{H}^+$  or  $\text{OH}^-$  except  $\text{H}_2\text{O}$  dissociation:

$$[\text{H}^+] = [\text{OH}^-]$$

Therefore,

$$[\text{H}^+][\text{OH}^-] = (x)(x) = 1.0 \times 10^{-14}$$

$$x^2 = 1.0 \times 10^{-14}$$

$$x = 1.0 \times 10^{-7} \text{ M} = [\text{H}^+] = [\text{OH}^-]$$

## Example

A  $1.0 \times 10^{-3} \text{ M}$  solution of hydrochloric acid is prepared. What is the hydroxide ion concentration?

## Solution

Since hydrochloric acid is a strong electrolyte and is completely ionized, the  $\text{H}^+$  concentration is  $1.0 \times 10^{-3} \text{ M}$ .

Thus,

$$(1.0 \times 10^{-3}) [\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{OH}^-] = 1.0 \times 10^{-11} \text{ M}$$

## Example

Calculate the concentration of  $\text{H}^+_{(aq)}$  in;

(a) a solution in which  $[\text{OH}^-]$  is  $0.010\text{ M}$ ,

(b) a solution in which  $[\text{OH}^-]$  is  $1.8 \times 10^{-9}\text{ M}$ .

*Note:* In this problem and all that follow, we assume, unless stated otherwise, that the temperature is  $25^\circ\text{C}$ .

## Solution

(a)  $[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$

$$[\text{H}^+] = \frac{(1.0 \times 10^{-14})}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12}\text{ M}$$

$[\text{OH}^-] > [\text{H}^+]$  This solution is **basic**

(b)  $[\text{H}^+] = \frac{(1.0 \times 10^{-14})}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-9}} = 5.6 \times 10^{-6}\text{ M}$

$[\text{H}^+] > [\text{OH}^-]$  This solution is **acidic**

# The pH scale

The concentration of  $\text{H}^+$  or  $\text{OH}^-$  in aqueous solution can vary over extremely wide ranges, from 1  $M$  or greater to  $10^{-14}$   $M$  or less. It is more convenient to compress the acidity scale by placing it on a logarithm basis.

The pH of a solution was defined as:

$$\text{pH} = -\log[\text{H}^+]$$

The minus sign is used because most of the concentrations encountered are less than 1  $M$ , and so this design at ion gives a positive number.

A similar definition is made for the hydroxide ion concentration:

$$\text{pOH} = -\log[\text{OH}^-]$$

The equation in logarithm form for a more direct calculation of pH or pOH is

$$-\log K_w = -\log[\text{H}^+][\text{OH}^-] = -\log[\text{H}^+] - \log [\text{OH}^-]$$

$$\text{p}K_w = \text{pH} + \text{pOH}$$

At 25°C,

$$14.00 = \text{pH} + \text{pOH}$$

- A 1 *M* HCl solution has a pH of 0 and pOH of 14.
- A 1 *M* NaOH solution has a pH of 14 and a pOH of 0.



## Example

Calculate the pH of a  $2.0 \times 10^{-3} \text{ M}$  solution of HCl.

## Solution

HCl is completely ionized, so

$$[\text{H}^+] = 2.0 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(2.0 \times 10^{-3}) = 3 - \log 2.0 = 3 - 0.30 = 2.70$$

## Example

Calculate the pOH and the pH of a  $5.0 \times 10^{-2} \text{ M}$  solution of NaOH at 25°C.

## Solution

$$\text{pOH} = -\log(5.0 \times 10^{-2}) = 2 - \log 5.0 = 2 - 0.70 = 1.30$$

$$\text{pH} + 1.30 = 14.00 \quad \text{pH} = 12.70$$

## Example

What is the pH of a 0.040 *M* solution of HClO<sub>4</sub>?

## Solution

$$\text{pH} = -\log(0.040) = 1.40$$

## Example

What is the pH of a 0.0011 *M* solution of Ca(OH)<sub>2</sub>?

## Solution

Ca(OH)<sub>2</sub> is a strong base that dissociates in water to give two OH<sup>-</sup> ions per formula unit. Thus, the concentration of OH<sup>-</sup>(aq) for the solution is  $2 \times (0.0011) = 0.0022$  *M*

*Method 1:*

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{0.0022} = 4.55 \times 10^{-12} \text{ M} \quad \text{pH} = -\log(4.55 \times 10^{-12}) = 11.34$$

*Method 2:*

$$\text{pOH} = -\log(0.0022) = 2.66 \quad \text{pH} = 14.00 - \text{pOH} = 11.34$$

### Example

The pH of a solution is 9.67. Calculate the hydrogen ion concentration in the solution.

### Solution

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

$$-\log[\text{H}^+] = 9.67$$

$$[\text{H}^+] = 10^{-9.67}$$

$$[\text{H}^+] = 2.1 \times 10^{-10} \text{ M}$$

### Example

Calculate the pH of a solution prepared by mixing 2.0 mL of a strong acid solution of pH 3.00 and 3.0 mL of a strong base of pH 10.00.

### Solution

$$[\text{H}^+] \text{ of acid solution} = 1.0 \times 10^{-3} \text{ M}$$

$$\text{mmol H}^+ = 1.0 \times 10^{-3} \text{ M} \times 2.0 \text{ mL} = 2.0 \times 10^{-3} \text{ mmol}$$

$$\text{pOH of base solution} = 14.00 - 10.00 = 4.00$$

$$[\text{OH}^-] = 1.0 \times 10^{-4} \text{ M}$$

$$\text{mmol OH}^- = 1.0 \times 10^{-4} \text{ M} \times 3.0 \text{ mL} = 3.0 \times 10^{-4} \text{ mmol}$$

$$\text{There is an excess of acid. mmol H}^+ = 0.0020 - 0.0003 = 0.0017 \text{ mmol}$$

$$\text{Total Volume} = (2.0 + 3.0) \text{ mL} = 5.0 \text{ mL}$$

$$[\text{H}^+] = 0.0017 \text{ mmol} / 5.0 \text{ mL} = 3.4 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log 3.4 \times 10^{-4} = 4 - 0.53 = 3.47$$

# Weak acids and bases

In **strong** acids and bases, the **ionization** is assumed to be **complete** and the concentration of  $\text{H}^+$  or  $\text{OH}^-$  is determined readily from the concentration of the acid or base, the calculations are straightforward.

**Weak** acids or bases are only **partially ionized**. We can use the equilibrium constant ( $K$ ) for the ionization reaction to express the extent to which a weak acid or base ionizes.

Comparing the behavior of 1  $M$   $\text{CH}_3\text{COOH}$  and 1  $M$   $\text{HCl}$ . When the  $\text{Mg}$  is dropped into the acid,  $\text{H}_2$  gas is formed. The rate of reaction and  $\text{H}_2$  formation is higher for  $\text{HCl}$  on the right. Eventually, the same amount of  $\text{H}_2$  forms in both cases. The 1  $M$   $\text{CH}_3\text{COOH}$  contains only 0.004  $M$   $\text{H}^+(\text{aq})$ , whereas the 1  $M$   $\text{HCl}$  solution contains 1  $M$   $\text{H}^+(\text{aq})$ .



- For a generalized **weak acid dissociation**,,



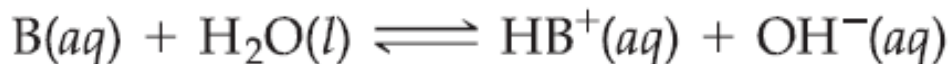
or



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

This equilibrium constant  $K_a$  is called the **acid-dissociation constant**.

- For a generalized **weak base dissociation**,,



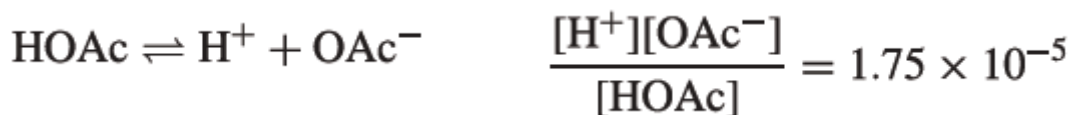
$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

This equilibrium constant  $K_b$  is called the **base-dissociation constant**.

## Example

Calculate the pH and pOH of a  $1.00 \times 10^{-3} M$  solution of acetic acid. The acidity constant for acetic acid at  $25^\circ\text{C}$  is  $1.75 \times 10^{-5}$ .

## Solution



	[HOAc]	[H <sup>+</sup> ]	[OAc <sup>-</sup> ]
Initial	$1.00 \times 10^{-3}$	0	0
Equilibrium	$1.00 \times 10^{-3} - x$	$x$	$x$

$$\frac{(x)(x)}{1.00 \times 10^{-3} - x} = 1.75 \times 10^{-5}$$

$$\frac{x^2}{1.00 \times 10^{-3}} = 1.75 \times 10^{-5}$$

$$x = 1.32 \times 10^{-4} M \equiv [\text{H}^+]$$

$$\text{pH} = -\log(1.32 \times 10^{-4}) = 4 - \log 1.32 = 4 - 0.12 = 3.88$$

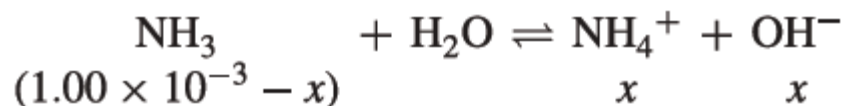
$$\text{pOH} = 14.00 - 3.88 = 10.12$$

If  $C_{\text{HA}} > 100 K_a$ ,  
 $x$  can be neglected compared to  $C_{\text{HA}}$

## Example

The basicity constant  $K_b$  for ammonia is  $1.75 \times 10^{-5}$  at  $25^\circ\text{C}$ . (It is only coincidental that this is equal to  $K_a$  for acetic acid). Calculate the pH and pOH for a  $1.00 \times 10^{-3} \text{ M}$  solution of ammonia.

## Solution



$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.75 \times 10^{-5}$$

$$\frac{(x)(x)}{1.00 \times 10^{-3}} = 1.75 \times 10^{-5}$$

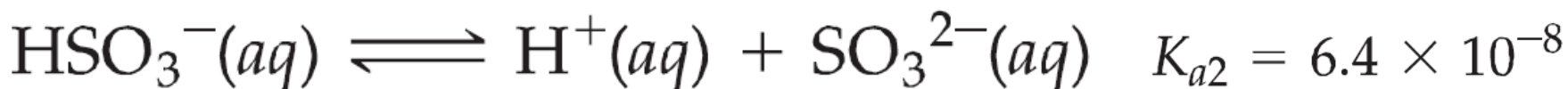
$$x = 1.32 \times 10^{-4} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log 1.32 \times 10^{-4} = 3.88$$

$$\text{pH} = 14.00 - 3.88 = 10.12$$

# Polyprotic acids

Polyprotic acids have more than one ionizable H atom



The acid dissociation constants for these equilibria are labeled  $K_{a1}$  and  $K_{a2}$ .

In the preceding example  $K_{a2}$  is much smaller than  $K_{a1}$ .

**It is always easier to remove the first proton from a polyprotic acid than to remove the second.**

Similarly, for an acid with three ionizable protons, it is easier to remove the second proton than the third. Thus, the  $K_a$  values become successively smaller as successive protons are removed.



## Acid-dissociation constants of some common polyprotic acids

Name	Formula	$K_{a1}$	$K_{a2}$	$K_{a3}$
Ascorbic	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	$8.0 \times 10^{-5}$	$1.6 \times 10^{-12}$	
Carbonic	$\text{H}_2\text{CO}_3$	$4.3 \times 10^{-7}$	$5.6 \times 10^{-11}$	
Citric	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	$7.4 \times 10^{-4}$	$1.7 \times 10^{-5}$	$4.0 \times 10^{-7}$
Oxalic	$\text{H}_2\text{C}_2\text{O}_4$	$5.9 \times 10^{-2}$	$6.4 \times 10^{-5}$	
Phosphoric	$\text{H}_3\text{PO}_4$	$7.5 \times 10^{-3}$	$6.2 \times 10^{-8}$	$4.2 \times 10^{-13}$
Sulfurous	$\text{H}_2\text{SO}_3$	$1.7 \times 10^{-2}$	$6.4 \times 10^{-8}$	
Sulfuric	$\text{H}_2\text{SO}_4$	Large	$1.2 \times 10^{-2}$	
Tartaric	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	$1.0 \times 10^{-3}$	$4.6 \times 10^{-5}$	

Sulfuric acid is strong acid with respect to the removal of the first proton. Thus, the reaction for the first ionization step lies completely to the right:



$\text{HSO}_4^-$ , on the other hand, is a weak acid for which  $K_{a2} = 1.2 \times 10^{-2}$ .

Because  $K_{a1}$  is so much larger than subsequent dissociation constants for these polyprotic acids, most of the  $\text{H}^+(aq)$  in the solution comes from the first ionization reaction. As long as successive  $K_a$  values differ by a factor of  $10^3$ .

If the difference between the  $K_{a1}$  for the first dissociation and subsequent  $K_{a2}$  values is  $10^3$  or more, the pH generally depends *only* on the first dissociation.

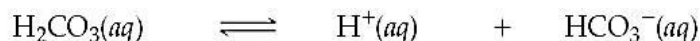
## Example

The solubility of  $\text{CO}_2$  in pure water at  $25^\circ\text{C}$  and  $0.1\text{ atm}$  pressure is  $0.0037\text{ M}$ . The common practice is to assume that all of the dissolved  $\text{CO}_2$  is in the form of carbonic acid  $\text{H}_2\text{CO}_3$ , which is produced by reaction between the  $\text{CO}_2$  and  $\text{H}_2\text{O}$ :

What is the pH of a  $0.0037\text{ M}$  solution of  $\text{H}_2\text{CO}_3$ ?



## Solution



Initial	$0.0037\text{ M}$	$0$	$0$
Change	$-x\text{ M}$	$+x\text{ M}$	$+x\text{ M}$
Equilibrium	$(0.0037 - x)\text{ M}$	$x\text{ M}$	$x\text{ M}$

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{(x)(x)}{0.0037 - x} = 4.3 \times 10^{-7}$$

$$x = 4.0 \times 10^{-5}\text{ M}$$

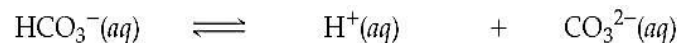
$$0.0037 - x \approx 0.0037$$

$$\frac{(x)(x)}{0.0037} = 4.3 \times 10^{-7}$$

$$x^2 = (0.0037)(4.3 \times 10^{-7}) = 1.6 \times 10^{-9}$$

$$x = [\text{H}^+] = [\text{HCO}_3^-] = \sqrt{1.6 \times 10^{-9}} = 4.0 \times 10^{-5}\text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(4.0 \times 10^{-5}) = 4.40$$



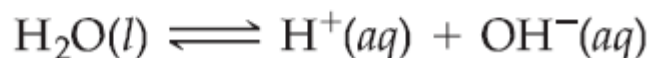
Initial	$4.0 \times 10^{-5}\text{ M}$	$4.0 \times 10^{-5}\text{ M}$	$0$
Change	$-y\text{ M}$	$+y\text{ M}$	$+y\text{ M}$
Equilibrium	$(4.0 \times 10^{-5} - y)\text{ M}$	$(4.0 \times 10^{-5} + y)\text{ M}$	$y\text{ M}$

$$K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{(4.0 \times 10^{-5})(y)}{4.0 \times 10^{-5}} = 5.6 \times 10^{-11}$$

$$y = 5.6 \times 10^{-11}\text{ M} = [\text{CO}_3^{2-}]$$

# Relationship between $K_a$ and $K_b$

To see if we can find a corresponding quantitative relationship, let's consider the  $\text{NH}_4^+$  and  $\text{NH}_3$  conjugate acid-base pair. Each of these species reacts with water:



$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$\begin{aligned} K_a \times K_b &= \left( \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \right) \left( \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \right) \\ &= [\text{H}^+][\text{OH}^-] = K_w \end{aligned}$$

$K_a$  and  $K_b$  are related in this way:

$$\mathbf{K_a \times K_b = K_w}$$

Therefore, if you know one of them, you can calculate the other.

This relationship is so important that it should receive special attention: The product of the acid-dissociation constant for an acid and the base-dissociation constant for its conjugate base equals the ion-product constant for water.

$$K_a \times K_b = K_w$$

As the strength of an acid increases (larger  $K_a$ ), the strength of its conjugate base must decrease (smaller  $K_b$ ) so that the product  $K_a \times K_b$  equals  $1.0 \times 10^{-14}$  at 25 °C.

This important relationship applies only to **conjugate acid-base pairs**.

Last Equation can be written in terms of  $pK_a$  and  $pK_b$  by taking the negative log of both sides:

$$pK_a + pK_b = pK_w = 14.00 \quad \text{at } 25 \text{ } ^\circ\text{C}$$

## Some conjugate acid-base pairs

Acid	$K_a$	Base	$K_b$
HNO <sub>3</sub>	(Strong acid)	NO <sub>3</sub> <sup>-</sup>	(Negligible basicity)
HF	$6.8 \times 10^{-4}$	F <sup>-</sup>	$1.5 \times 10^{-11}$
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	$1.8 \times 10^{-5}$	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	$5.6 \times 10^{-10}$
H <sub>2</sub> CO <sub>3</sub>	$4.3 \times 10^{-7}$	HCO <sub>3</sub> <sup>-</sup>	$2.3 \times 10^{-8}$
NH <sub>4</sub> <sup>+</sup>	$5.6 \times 10^{-10}$	NH <sub>3</sub>	$1.8 \times 10^{-5}$
HCO <sub>3</sub> <sup>-</sup>	$5.6 \times 10^{-11}$	CO <sub>3</sub> <sup>2-</sup>	$1.8 \times 10^{-4}$
OH <sup>-</sup>	(Negligible acidity)	O <sup>2-</sup>	(Strong base)

## Example

Calculate **(a)** the base-dissociation constant,  $K_b$ , for the fluoride ion ( $F^-$ ); **(b)** the acid-dissociation constant,  $K_a$ , for the ammonium ion ( $NH_4^+$ ).

- $K_a$  for the weak acid HF,  $K_a = 6.8 \times 10^{-4}$ .
- $K_b$  for weak base  $NH_3$ ,  $K_b = 1.8 \times 10^{-5}$ .

## Solution

**(a)**  $K_a$  for HF =  $6.8 \times 10^{-4}$ . We can calculate  $K_b$  for the conjugate base,  $F^-$ :

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

**(b)**  $K_b$  for  $NH_3 = 1.8 \times 10^{-5}$ . we can calculate  $K_a$  for the conjugate acid,  $NH_4^+$ :

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

# Acid-base properties of salt solutions

Ions can also exhibit acidic or basic properties.

**Salt** solutions can be acidic or basic.

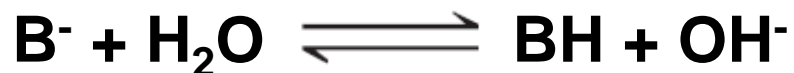
Because **nearly all salts are strong electrolytes**, we can assume that when salts dissolve in water, they are completely dissociated.

Consequently, the acid-base properties of salt solutions are due to the behavior of their constituent cations and anions.

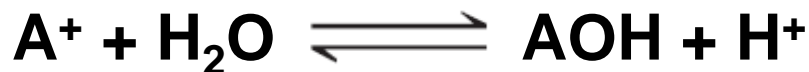
Many ions are able to react with water to generate  $\text{H}^+_{(\text{aq})}$  or  $\text{OH}^-_{(\text{aq})}$ . This type of reaction is often called **hydrolysis**. The pH of an aqueous salt solution can be predicted qualitatively by considering the ions of which the salt is composed.

# Effect of cation and anion in solution

1. An **anion** that is the conjugate base of a **strong acid** will not affect the pH.
2. An **anion** that is the conjugate base of a **weak acid** will increase the pH.



3. **Cations** of the **strong bases** will not affect the pH.
4. A **cation** that is the conjugate acid of a **weak base** will decrease the pH.



5. When a solution contains both the conjugate base of a weak acid and the conjugate acid of a weak base, the affect on pH depends on the  $K_a$  and  $K_b$  values:

- If  $K_a > K_b$ , the ion will cause the solution to be acidic.
- If  $K_b > K_a$ , the solution will be basic.





Salt solutions can be neutral, acidic, or basic. These three solutions contain the acid-base indicator bromthymol blue.

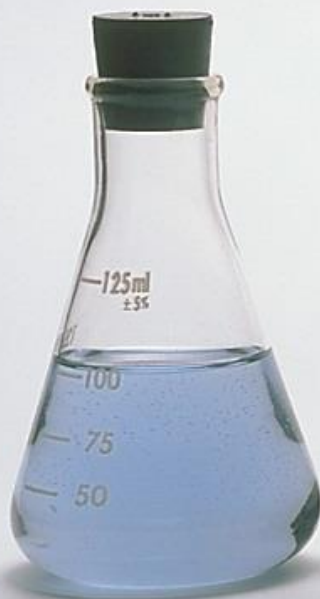
- (a) NaCl solution is neutral (pH = 7.0)**
- (b)  $\text{NH}_4\text{Cl}$  solution is acidic (pH = 3.5)**
- (c) NaClO solution is basic (pH = 9.5)**

This Figure demonstrates the influence of several salts on pH.

Salt:  
Indicator:  
Estimated pH:

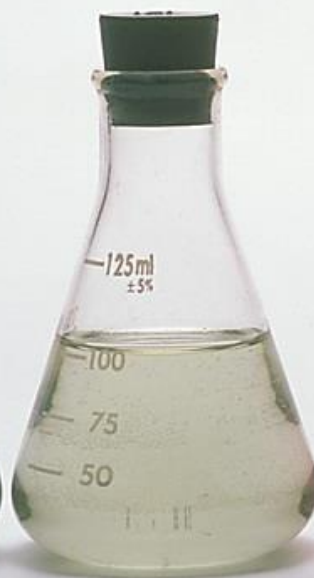
$\text{NaNO}_3$   
Bromthymol  
blue

7.0



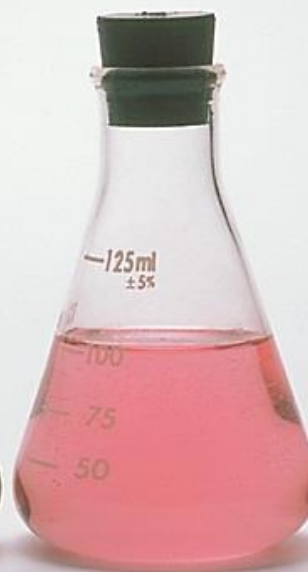
$\text{Ca}(\text{NO}_3)_2$   
Bromthymol  
blue

6.9



$\text{Zn}(\text{NO}_3)_2$   
Methyl  
red

5.5



$\text{Al}(\text{NO}_3)_3$   
Methyl  
orange

3.5



## Example

Determine whether aqueous solutions of each of the following salts will be acidic, basic, or neutral: (a)  $\text{Ba}(\text{CH}_3\text{COO})_2$ , (b)  $\text{NH}_4\text{Cl}$ , (c)  $\text{CH}_3\text{NH}_3\text{Br}$ , (d)  $\text{KNO}_3$ , (e)  $\text{Al}(\text{ClO}_4)_3$ .

## Solution

**(a)** This solution contains  $\text{Ba}^{2+}$  & acetate ions. The cation,  $\text{Ba}^{2+}$ , is an ion of one of the heavy alkaline earth metals and will therefore not affect the pH. The anion,  $\text{CH}_3\text{COO}^-$ , is the conjugate base of the weak acid  $\text{CH}_3\text{COOH}$  and will hydrolyze to produce  $\text{OH}^-$  ions, thereby making the solution **basic**.

**(b)** This solution contains  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions.  $\text{NH}_4^+$  is the conjugate acid of a weak base  $\text{NH}_3$  and is therefore acidic.  $\text{Cl}^-$  is the conjugate base of a strong acid  $\text{HCl}$  and therefore has no influence on the pH of the solution. Because the solution contains an ion that is acidic  $\text{NH}_4^+$  and one that has no influence on pH  $\text{Cl}^-$ , the solution of  $\text{NH}_4\text{Cl}$  will be **acidic**.

**(c)** This solution contains  $\text{CH}_3\text{NH}_3^+$  and  $\text{Br}^-$  ions.  $\text{CH}_3\text{NH}_3^+$  is the conjugate acid of a weak base  $\text{CH}_3\text{NH}_2$ , an amine and is therefore acidic.  $\text{Br}^-$  is the conjugate base of a strong acid  $\text{HBr}$  and is therefore pH-neutral. Because the solution contains one ion that is acidic and one that is neutral, the solution of  $\text{CH}_3\text{NH}_3\text{Br}$  will be **acidic**.

**(d)** This solution contains the  $\text{K}^+$  ion, which is a cation of group 1A, and the ion  $\text{NO}_3^-$ , which is the conjugate base of the strong acid  $\text{HNO}_3$ . Neither of the ions will react with water to any appreciable extent, making the solution **neutral**.

**(e)** This solution contains  $\text{Al}^{3+}$  and  $\text{ClO}_4^-$  ions. Cations, such as  $\text{Al}^{3+}$ , that are not in groups 1A or 2A are acidic. The  $\text{ClO}_4^-$  ion is the conjugate base of a strong acid  $\text{HClO}_4$  and therefore does not affect pH. Thus, the solution of  $\text{Al}(\text{ClO}_4)_3$  will be **acidic**.

# Buffer solutions

Buffers are solutions of a weak conjugate acid-base pair.

They are particularly resistant to pH changes, even when strong acid or base is added.

Solutions, which contain a weak conjugate acid-base pair, can resist drastic changes in pH upon the addition of small amounts of strong acid or base. These solutions are called **buffered solutions** (or merely buffers).



Human blood is slightly basic with a normal pH of 7.35 to 7.45. Death may result if the blood pH falls below 6.8 or rises above 7.8. when the pH falls below 7.35, the condition is called acidosis; when it rises above 7.45, the condition is called alkalosis.

The major buffer system that used to control the pH of blood is the **carbonic acid - bicarbonate** buffer system.



A scanning electromicrograph of a group red blood cells

The important equilibria in this buffer system are:





# Composition and action of buffered solutions

A buffer resists changes in pH because it contains both an acid to neutralize  $\text{OH}^-$  ions and a base to neutralize  $\text{H}^+$  ions.

The acid and base that make up the buffer, however, must not consume each other through a neutralization reaction. These requirements are fulfilled by a weak acid-base conjugate pair such as



Buffers are often prepared by mixing a weak acid or a weak base with a salt of that acid or base.

## Examples;

-The  $\text{CH}_3\text{COOH}-\text{CH}_3\text{COO}^-$  buffer can be prepared, by adding  $\text{CH}_3\text{COONa}$  to a solution of  $\text{CH}_3\text{COOH}$ .

-The  $\text{NH}_4^+-\text{NH}_3$  buffer can be prepared by adding  $\text{NH}_4\text{Cl}$  to a solution of  $\text{NH}_3$ .

To understand better how a buffer works, let's consider a buffer composed of a weak acid (HX) and one of its salt (MX, where  $M^+$  could be  $Na^+$ ,  $K^+$ , or another cation). The acid-dissociation equilibrium in this buffered solution involves both the acid and its conjugate base:



The corresponding acid-dissociation-constant expression is

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

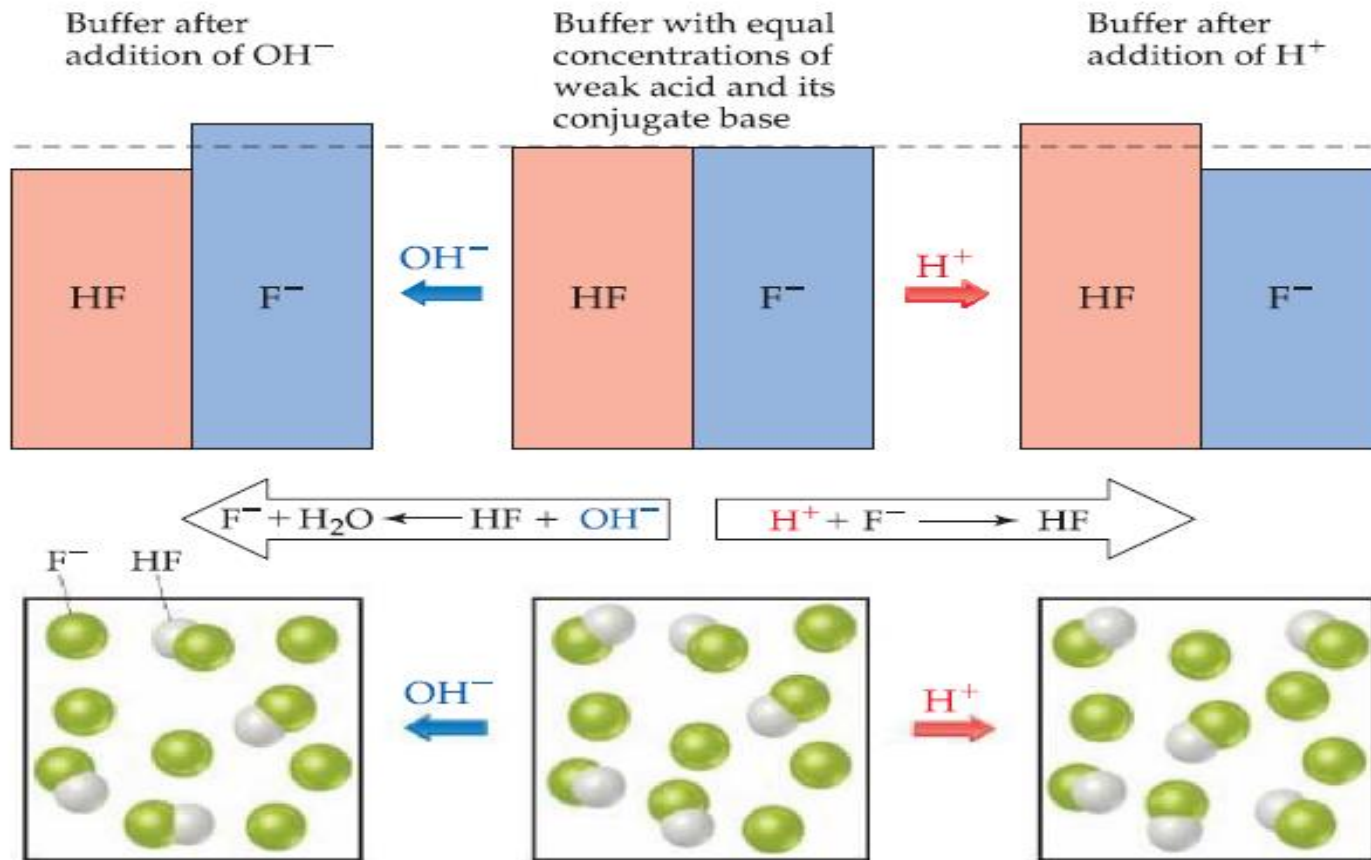
Solving this expression for  $[H^+]$ , we have

$$[H^+] = K_a \frac{[HX]}{[X^-]}$$

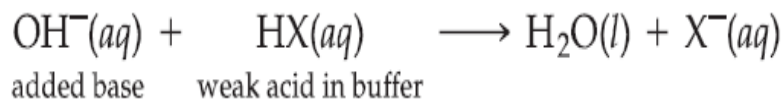
Thus, the  $[H^+]$ , and thus the pH, is determined by two factors:

- the value of  $K_a$  for the weak-acid component of the buffer, and
- the ratio of the concentrations of the conjugate acid-base pair,  $[HX] / [X^-]$ .

## Buffer action

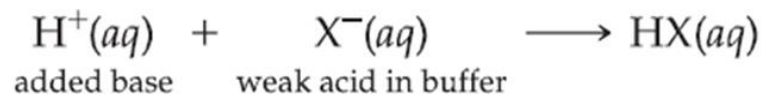


If  $\text{OH}^-$  ions are added to the buffered solution, they react with the acid component of the buffer to produce water and  $\text{X}^-$ :



This reaction causes  $[\text{HX}]$  to decrease and  $[\text{X}^-]$  to increase. As long as the amounts of  $\text{HX}$  and  $\text{X}^-$  in the buffer are large compared to the amount of  $\text{OH}^-$  added, however, the ratio  $[\text{HX}] / [\text{X}^-]$  does not change much, and thus the change in pH is small.

If  $\text{H}^+$  ions are added, they react with the base component of the buffer:



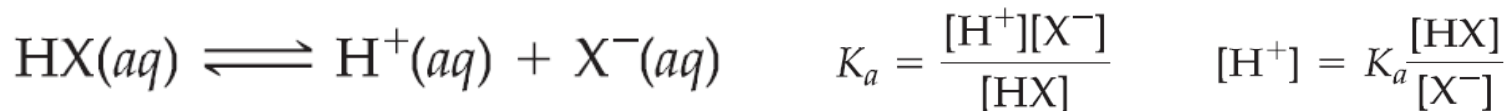
This reaction can also be represented using  $\text{H}_3\text{O}^+$ :



Using either equation, we see that the reaction causes  $[\text{X}^-]$  to decrease and  $[\text{HX}]$  to increase. As long as the change in the ratio  $[\text{HX}] / [\text{X}^-]$  is small, the change in pH will be small.



# Calculating the pH of a buffer



Taking -log of both sides of equation, we have

$$-\log[\text{H}^+] = -\log\left(K_a \frac{[\text{HX}]}{[\text{X}^-]}\right) = -\log K_a - \log \frac{[\text{HX}]}{[\text{X}^-]}$$

Because  $-\log[\text{H}^+] = \text{pH}$  and  $-\log K_a = \text{p}K_a$ , we have

$$\text{pH} = \text{p}K_a - \log \frac{[\text{HX}]}{[\text{X}^-]} = \text{p}K_a + \log \frac{[\text{X}^-]}{[\text{HX}]}$$

In general,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

Where [acid] and [base] refer to the equilibrium concentrations of the conjugate acid-base pair. Note that when [base] = [acid],  $\text{pH} = \text{p}K_a$ .

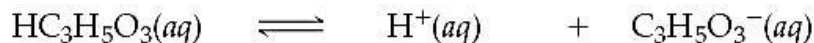
This Equation is known as the **Henderson-Hasselbalch equation**.

In doing equilibrium calculations, we have seen that we can normally neglect the amounts of the acid and base of the buffer that ionize (very small amount,  $K_a$  or  $K_b$  very small). Therefore, we can usually use the starting concentrations of the acid and base components of the buffer directly in the Henderson-Hasselbalch equation.

## Example

What is the pH of a buffer that is 0.12 *M* in lactic acid [CH<sub>3</sub>CH(OH)COOH, or HC<sub>3</sub>H<sub>5</sub>O<sub>3</sub>] and 0.10 *M* in sodium lactate [CH<sub>3</sub>CH(OH)COONa or NaC<sub>3</sub>H<sub>5</sub>O<sub>3</sub>]? For lactic acid,  $K_a = 1.4 \times 10^{-4}$ .

## Solution



Initial	0.12 <i>M</i>	0	0.10 <i>M</i>
Change	- <i>x M</i>	+ <i>x M</i>	+ <i>x M</i>
Equilibrium	(0.12 - <i>x</i> ) <i>M</i>	<i>x M</i>	(0.10 + <i>x</i> ) <i>M</i>

$$K_a = 1.4 \times 10^{-4} = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{x(0.10 + x)}{(0.12 - x)}$$

Because  $K_a$  is small and a common ion is present,  $x$  is small relative to either 0.12 or 0.10 *M*. Thus, the equation can be simplified to give

$$K_a = 1.4 \times 10^{-4} = \frac{x(0.10)}{0.12}$$

$$[\text{H}^+] = x = \left(\frac{0.12}{0.10}\right)(1.4 \times 10^{-4}) = 1.7 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(1.7 \times 10^{-4}) = 3.77$$

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 3.85 + \log\left(\frac{0.10}{0.12}\right) \\ &= 3.85 + (-0.08) = 3.77\end{aligned}$$

# Buffer capacity

**Buffer capacity** is the amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree. The buffer capacity depends on the amount of acid and base from which the buffer is made.

The pH of the buffer depends on the  $K_a$  for the acid and on the relative concentrations of the acid and base that comprise the buffer.

From equation below,  $[H^+]$  for a 1 L solution that is 1 M in  $CH_3COOH$  and 1 M in  $CH_3COONa$  will be the same as for a 1 L solution that is 0.1 M in  $CH_3COOH$  and 1.0 M in  $CH_3COONa$ . The first solution has a greater buffering capacity, however, because it contains more  $CH_3COOH$  and  $CH_3COO^-$ .

The greater the amounts of the conjugate acid-base pair, the more resistant is the ratio of their concentrations, and hence the pH, is to change.

$$[H^+] = K_a \frac{[HX]}{[X^-]}$$

# pH range

The **pH range** of any buffer is the pH range over which the buffer system works or acts effectively.

Buffers most effectively resist a change in pH in either direction when the concentrations of weak acid and conjugate base are about the same.

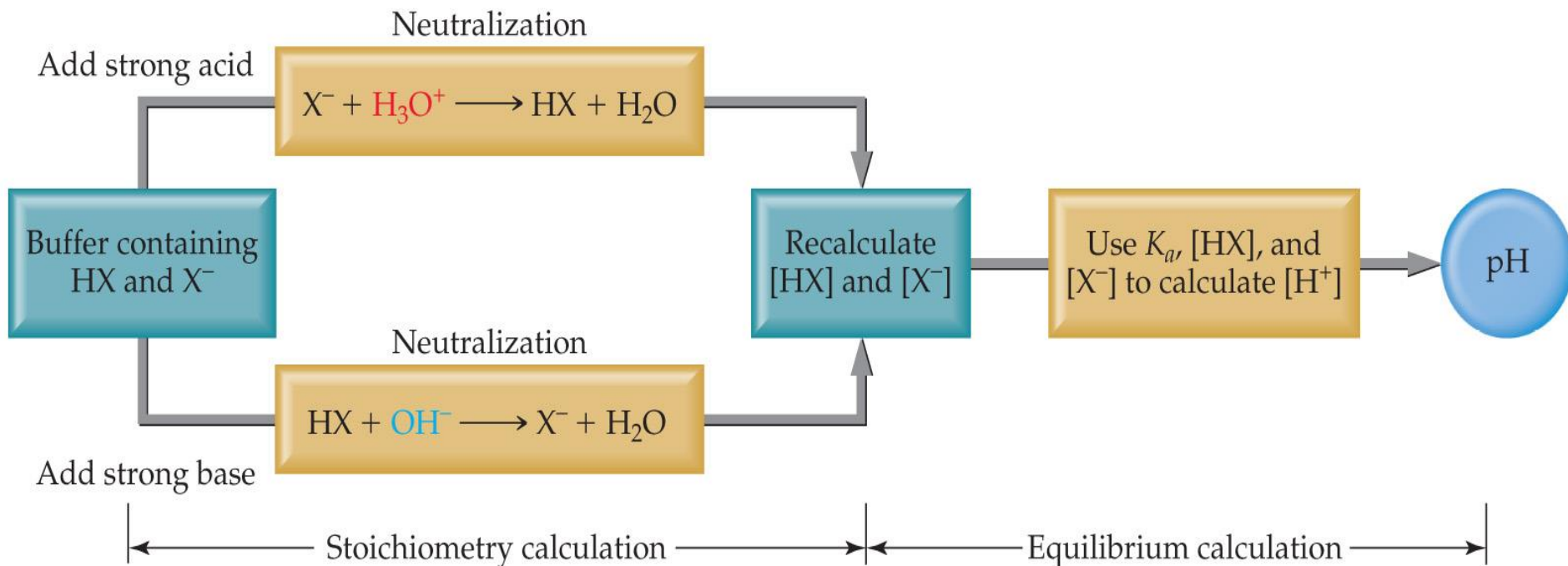
From equation below, when the concentrations of weak acid and conjugate base are equal,  $\text{pH} = \text{pK}_a$ . This relationship gives the optimal pH of any buffer. Thus, we usually try to select a buffer whose acid form has a  $\text{pK}_a$  close to the desired pH.

In practice, we find that if the concentration of one component of the buffer is more than 10 times the concentration of the other component, the buffering action is poor.

Because  $\log 10 = 1$ , buffers usually have a usable range within  $\pm 1$  pH unit of  $\text{pK}_a$  (that is, a range of  $\text{pH} = \text{pK}_a \pm 1$ )

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

# Addition of strong acids or bases to buffers



When a strong acid is added to the buffer, the added H<sup>+</sup> is consumed by X<sup>-</sup> to produce HX; thus, [HX] increases and [X<sup>-</sup>] decreases.

When a strong base is added to the buffer, the added OH<sup>-</sup> is consumed by HX to produce X<sup>-</sup>; thus, [HX] decreases and [X<sup>-</sup>] increases.

## Example

A buffer is made by adding 0.30 mol  $\text{CH}_3\text{COOH}$  and 0.30 mol  $\text{CH}_3\text{COONa}$  to enough water to make 1.0 L of solution. The pH of the buffer is 4.74. **(a)** Calculate the pH of this solution after 0.02 mol of NaOH is added. **(b)** For comparison, calculate the pH that would result if 0.02 mol of NaOH were added to 1.0 L of pure water (neglect any volume changes).

$$[\text{HA}] = [\text{A}^-], \text{ so.... } \text{p}K_a = \text{pH} = 4.74$$

## Solution

0.280 M  $\text{CH}_3\text{COOH}$   
0.320 M  $\text{CH}_3\text{COONa}$   
pH = 4.80

Buffer  
0.300 M  $\text{CH}_3\text{COOH}$   
0.300 M  $\text{CH}_3\text{COONa}$   
pH 4.74

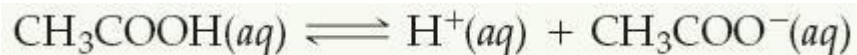
add 0.020 mol  $\text{OH}^-$

0.320 M  $\text{CH}_3\text{COOH}$   
0.280 M  $\text{CH}_3\text{COONa}$   
pH = 4.68

**(a)**



Buffer before addition	0.300 mol	0	—	0.300 mol
Addition	—	0.020 mol	—	—
Buffer after addition	0.280 mol	0	—	0.320 mol



$$\text{pH} = 4.74 + \log \frac{0.320 \text{ mol}/1.00 \text{ L}}{0.280 \text{ mol}/1.00 \text{ L}} = 4.80$$

**(b)** To determine the pH of a solution made by adding 0.02 mol of NaOH to 1.0 L of pure water, we can first determine pOH.

$$\text{pH} = 14 - (-\log 0.020) = 12.30$$

Note that although the small amount of NaOH changes the pH of water significantly, the pH of the buffer changes very little.

