



# Chapter 16

## Acids and Bases

## Some Definitions

- **Arrhenius theory**: an acid forms  $\text{H}^+$  in water; and a base forms  $\text{OH}^-$  in water.
- But not all acid–base reactions involve water, and many bases ( $\text{NH}_3$ , carbonates) do not *contain* any  $\text{OH}^-$ .
- **Brønsted–Lowry theory** defines acids and bases in terms of proton ( $\text{H}^+$ ) transfer.
  - **an acid** is a **proton donor**.
  - **a base** is a **proton acceptor**.

# Limitation of Arrhenius Concept

According to the Arrhenius concept,

- Acids produce *hydrogen ion*, and bases produce *hydroxide ion* in *aqueous* solution.
- Only applies to “aqueous” solution.
- Only allows one kind of base, the *hydroxide ion*.

***A more general definition is required.***

# Brønsted-Lowry Acids and Bases

According to the Brønsted-Lowry theory,

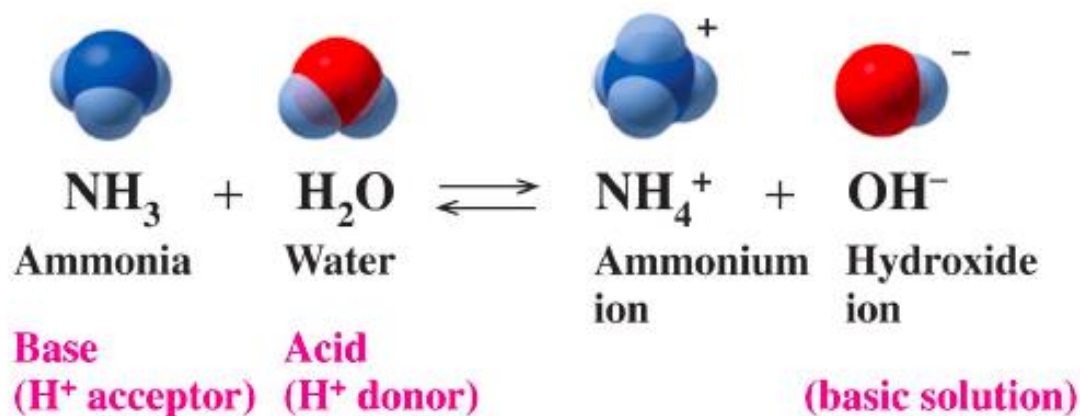
- Acids donate a proton ( $\text{H}^+$ ).
- Bases accept a proton ( $\text{H}^+$ ).



# NH<sub>3</sub>, A Brønsted-Lowry Base

In the reaction of ammonia and water,

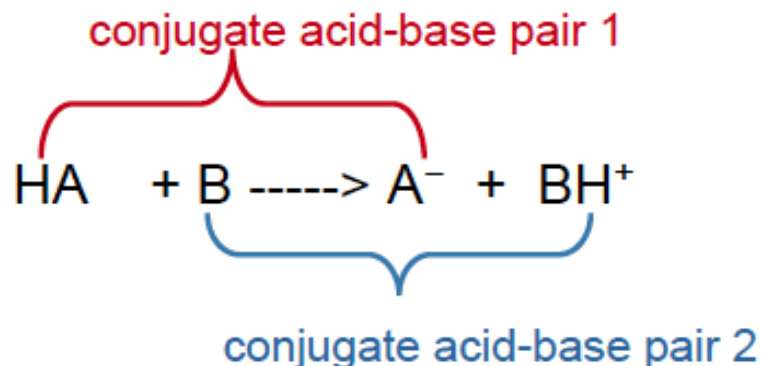
- NH<sub>3</sub> is the base that accept H<sup>+</sup>.
- H<sub>2</sub>O is the acid that donates H<sup>+</sup>.



# Conjugate Acid-Base Pairs

In any acid-base reaction, there are **two conjugate acid-base pairs**

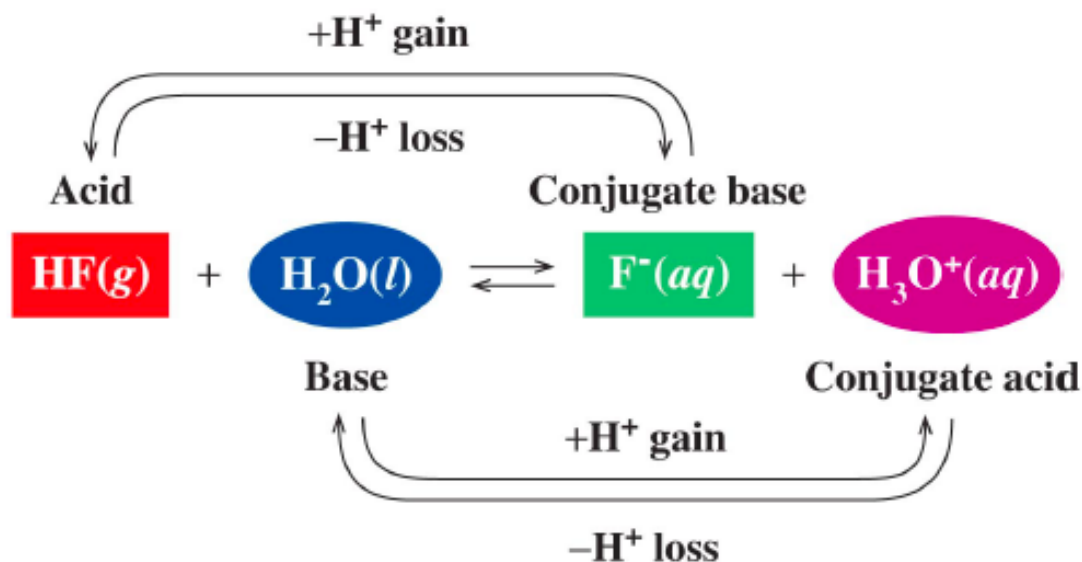
- Each related by the loss and gain of  $\text{H}^+$ .
- One occurs in the forward direction.
- One occurs in the reverse direction.



# Conjugate Acid-Base Pairs

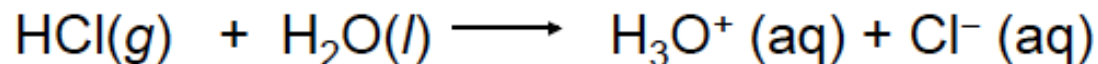
In the reaction of HF and H<sub>2</sub>O

- One conjugate acid-base pair is HF/F<sup>-</sup>.
- The other conjugate acid-base pair is H<sub>2</sub>O/H<sub>3</sub>O<sup>+</sup>.
- Each pair is related by a loss and gain of H<sup>+</sup>.

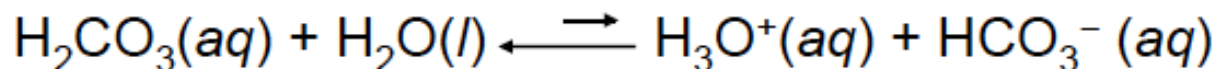


# Strengths of Acids

- **Strong acids** completely ionizes (100%) in aqueous solutions.



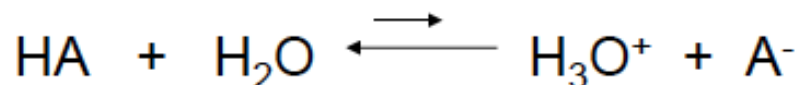
- **Weak acids** dissociate only slightly in water to form a solution of mostly molecules and a few ions.





# Acid Dissociation Constant

- In most cases, the rate of the dissociation of the acid is similar to the rate of the association.



- The equilibrium expression is

$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

- Because the concentration of  $\text{H}_2\text{O}$  is constant, the  $K_{\text{a}}$  expression for a weak acid is

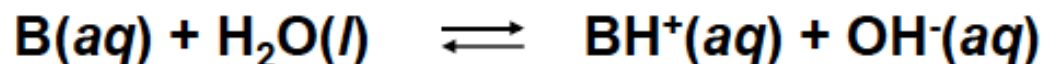
$$K_{\text{a}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

# Acid Characteristics and $K_a$

**Table 14.1 ► Various Ways to Describe Acid Strength**

Property	Strong Acid	Weak Acid
$K_a$ value	$K_a$ is large	$K_a$ is small
Position of the dissociation (ionization) equilibrium	Far to the right	Far to the left
Equilibrium concentration of $[H^+]$ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	$A^-$ much weaker base than $H_2O$	$A^-$ much stronger base than $H_2O$

# Base Dissociation Constant, $K_b$



base

conjugate acid

acid

conjugate base

- The equilibrium expression is

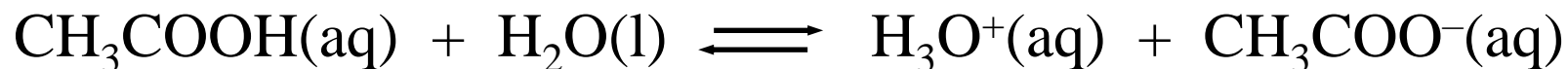
$$K_{\text{eq}} = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}][\text{H}_2\text{O}]}$$

- Because the concentration of  $\text{H}_2\text{O}$  is constant, the  $K_b$  expression for a weak acid is

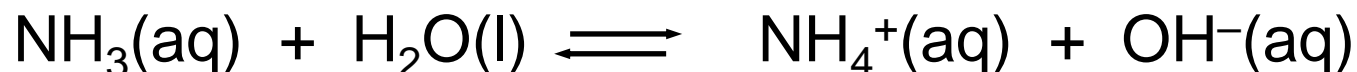
$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

# $K_a$ and $K_b$

The equilibrium constant for a Brønsted acid is represented by  $K_a$ , and that for a base is represented by  $K_b$ .



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$



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

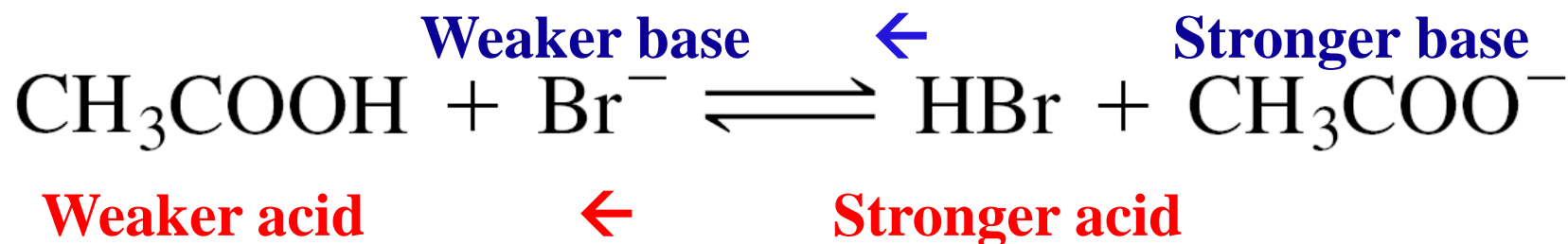
**Table 15.1 Relative Strengths of Some Brønsted–Lowry Acids and Their Conjugate Bases**

Acid	Conjugate Base
<p><b>The stronger the acid ...</b></p> <p>Increasing acid strength ↑</p> <p>... the weaker the conjugate acid.</p>	<p>... the weaker the conjugate base.</p> <p>↓ Increasing base strength</p> <p><b>And the stronger the base ...</b></p>
HI (hydroiodic acid)	I <sup>−</sup> (iodide ion)
HBr (hydrobromic acid)	Br <sup>−</sup> (bromide ion)
HCl (hydrochloric acid)	Cl <sup>−</sup> (chloride ion)
H <sub>2</sub> SO <sub>4</sub> (sulfuric acid)	HSO <sub>4</sub> <sup>−</sup> (hydrogen sulfate ion)
HNO <sub>3</sub> (nitric acid)	NO <sub>3</sub> <sup>−</sup> (nitrate ion)
H <sub>3</sub> O <sup>+</sup> (hydronium ion)	H <sub>2</sub> O (water)
HSO <sub>4</sub> <sup>−</sup> (hydrogen sulfate ion)	SO <sub>4</sub> <sup>2−</sup> (sulfate ion)
HNO <sub>2</sub> (nitrous acid)	NO <sub>2</sub> <sup>−</sup> (nitrite ion)
HF (hydrofluoric acid)	F <sup>−</sup> (fluoride ion)
CH <sub>3</sub> COOH (acetic acid)	CH <sub>3</sub> COO <sup>−</sup> (acetate ion)
H <sub>2</sub> CO <sub>3</sub> (carbonic acid)	HCO <sub>3</sub> <sup>−</sup> (hydrogen carbonate ion)
NH <sub>4</sub> <sup>+</sup> (ammonium ion)	NH <sub>3</sub> (ammonia)
HCO <sub>3</sub> <sup>−</sup> (hydrogen carbonate ion)	CO <sub>3</sub> <sup>2−</sup> (carbonate ion)
H <sub>2</sub> O (water)	OH <sup>−</sup> (hydroxide ion)
CH <sub>3</sub> OH (methanol)	CH <sub>3</sub> O <sup>−</sup> (methoxide ion)

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# Acid/Base Strength and Direction of Equilibrium

- Since HBr is a stronger acid than CH<sub>3</sub>COOH, the equilibrium for the reaction:

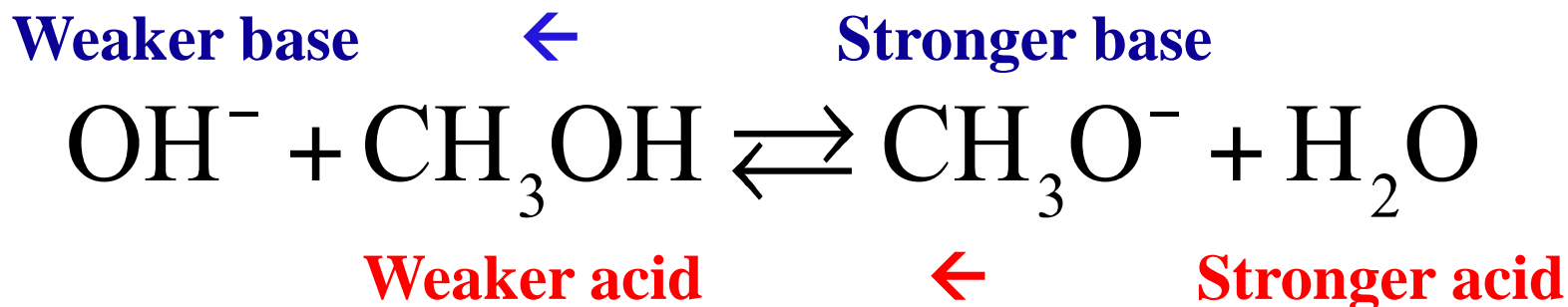


lies to the *left*.

- We reach the same conclusion by comparing the strengths of the *bases*.
- CH<sub>3</sub>COO<sup>-</sup> lies below Br<sup>-</sup> ; CH<sub>3</sub>COO<sup>-</sup> is the stronger base.

# Acid/Base Strength and Direction of Equilibrium

The equilibrium lies to

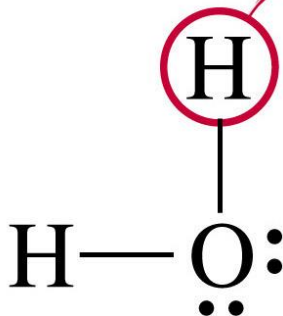


the *left*.

$\text{CH}_3\text{CH}_2-$  or  $\text{CH}_3-$  are typical electron donating groups!

# Water Is Amphiprotic

$\text{H}_2\text{O}$  acts as an acid when it *donates*  $\text{H}^+$ , forming the conjugate base  $\text{OH}^-$



$\text{H}_2\text{O}$  as an acid

$\text{H}_2\text{O}$  acts as a base when it *accepts*  $\text{H}^+$ , forming the conjugate acid  $\text{H}_3\text{O}^+$



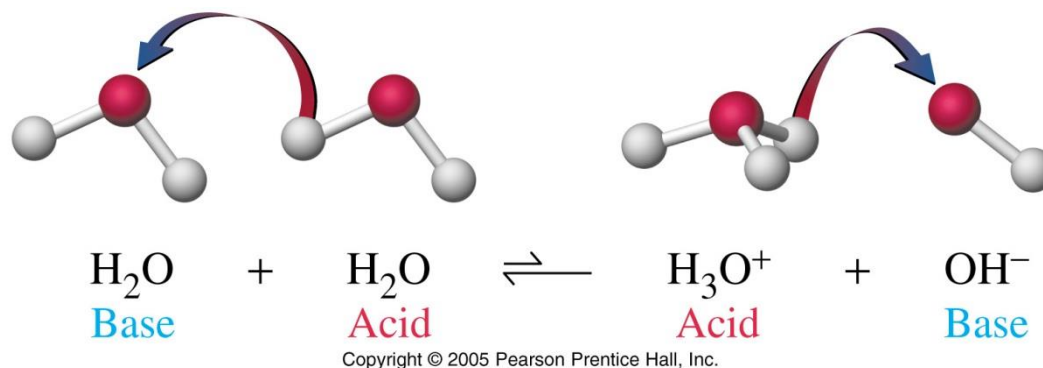
$\text{H}_2\text{O}$  as a base

**Amphiprotic: Can act as either an acid or as a base**



# Self-Ionization of Water

- Water conducts some electricity because water self-ionizes:



- The equilibrium constant for this process is called the *ion product of water* ( $K_w$ ).
- At 25°C,  $K_w = 1.0 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$

## Calculating $[\text{H}_3\text{O}^+]$

What is the  $[\text{H}_3\text{O}^+]$  of a solution if  $[\text{OH}^-]$  is  $5.0 \times 10^{-8} \text{ M}$ ?

**STEP 1** Write the  $K_w$  for water.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

**STEP 2** Rearrange the  $K_w$  expression.

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} / [\text{OH}^-]$$

**STEP 3** Substitute  $[\text{OH}^-]$ .

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} / 5.0 \times 10^{-8} = 2.0 \times 10^{-7} \text{ M}$$

# The pH Scale

- Concentration of  $\text{H}_3\text{O}^+$  can vary from about 10 M to  $10^{-14}$  M.
- A more convenient expression for  $\text{H}_3\text{O}^+$  is **pH**.

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

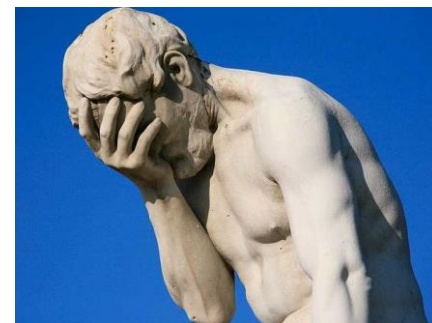
- The “negative logarithm” function of pH is so useful that it has been applied to other species and constants.

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

$$\text{p}K_w = -\log K_w = 14$$

at 298 K

PH  
Ph  
ph



# Calculating pH

Mathematically pH

- Is the negative log of the hydronium ion concentration,

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

- For a solution with  $[\text{H}_3\text{O}^+] = 1 \times 10^{-4}$

$$\text{pH} = -\log [1 \times 10^{-4}]$$

$$\text{pH} = -[-4.0]$$

$$\text{pH} = 4.0$$

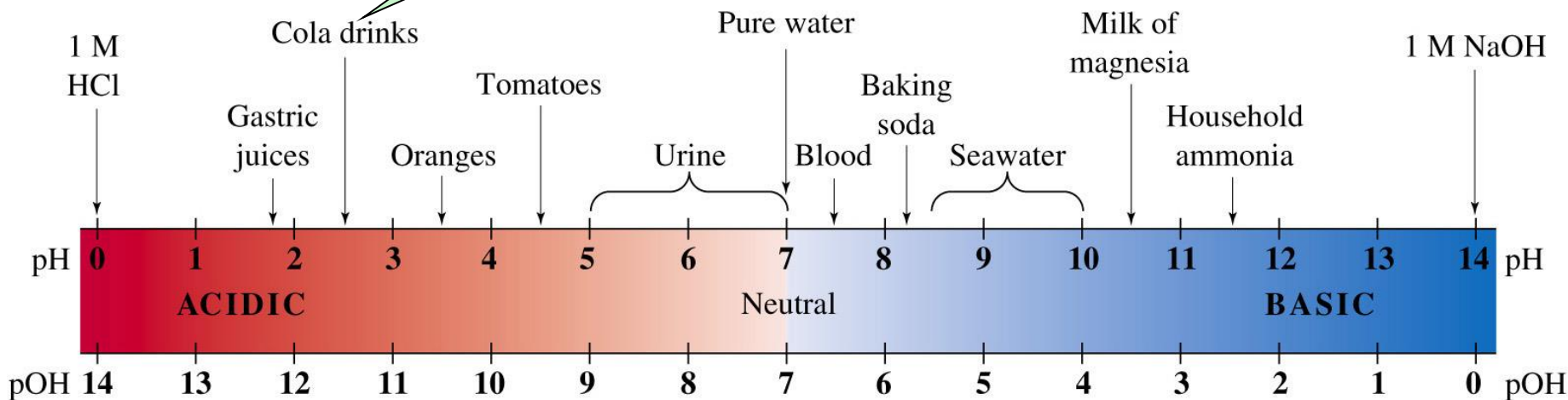
# Significant Figures in pH

When expressing log values, the number of decimal places in the pH is equal to the number of significant figures in the coefficient of  $[\text{H}_3\text{O}^+]$ .

	coefficient		decimal places
	↓		↓
$[\text{H}_3\text{O}^+] = 1 \times 10^{-4}$		pH = 4.0	
$[\text{H}_3\text{O}^+] = 8.0 \times 10^{-6}$		pH = 5.10	
$[\text{H}_3\text{O}^+] = 2.4 \times 10^{-8}$		pH = 7.62	

# The pH Scale

Cola drinks (pH about 2.5) are about \_\_\_\_\_ times as acidic as tomatoes (pH about 4.5)

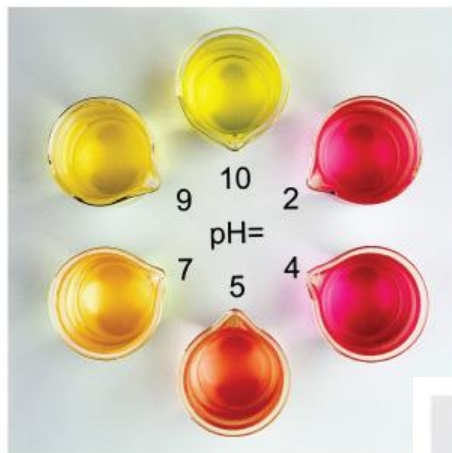


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# $K_w$ at Different Temperature

$T (^{\circ}\text{C})$	$K_w (\text{mol}^2 \text{ dm}^{-6})$	pH
0	$1.1 \times 10^{-15}$	7.47
10	$2.9 \times 10^{-15}$	7.27
20	$6.8 \times 10^{-15}$	7.08
25	$1.0 \times 10^{-14}$	7.00
30	$1.5 \times 10^{-14}$	6.92
40	$2.9 \times 10^{-14}$	6.77
50	$5.5 \times 10^{-14}$	6.63
100	$5.1 \times 10^{-13}$	6.14

# How Do We Measure pH?



Methyl red



Bromthymol blue



Phenolphthalein

- For less accurate measurements, one can use
  - Litmus paper
    - “Red” paper turns blue above pH ~ 8
    - “Blue” paper turns red below pH ~ 5
  - Or an indicator.



# How Do We Measure pH?

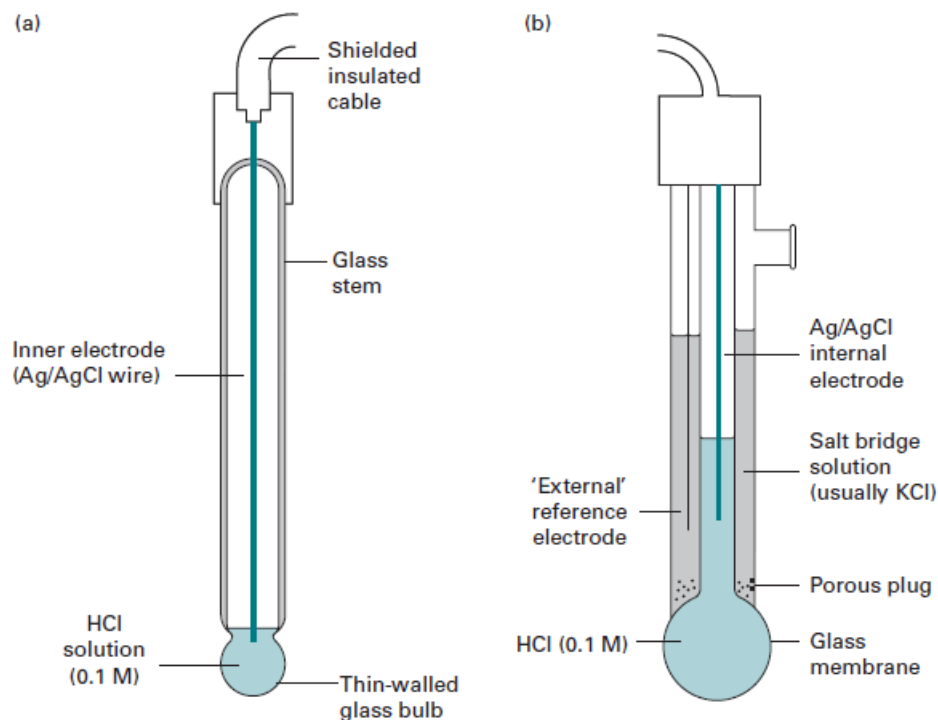




Fig. 1.1 Common pH electrodes: (a) glass electrode; (b) combination electrode.

pH meter: based on electromotive force change due to  $[H^+]$  difference – electrochemistry later

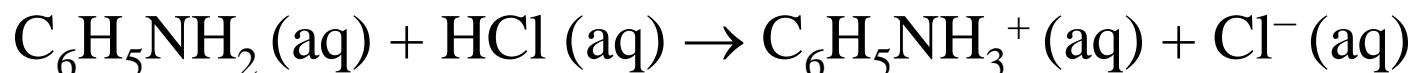
# Equilibrium in Solutions of Weak Acids and Weak Bases

**Table 15.2 Ionization Constants of Some Weak Acids and Weak Bases in Water at 25 °C**

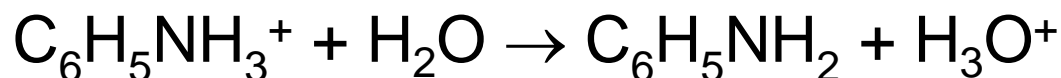
Ionization Equilibrium		Ionization Constant, $K$	p <i>K</i>
<b>Inorganic Acids</b>		$K_a =$	
Chlorous acid	$\text{HClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}_2^-$	$1.1 \times 10^{-2}$	1.96
Nitrous acid	$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$	$7.2 \times 10^{-4}$	3.14
Hydrofluoric acid	$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$	$6.6 \times 10^{-4}$	3.18
Hypochlorous acid	$\text{HOCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OCl}^-$	$2.9 \times 10^{-8}$	7.54
Hypobromous acid	$\text{HOBr} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OBr}^-$	$2.5 \times 10^{-9}$	8.60
Hydrocyanic acid	$\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-$	$6.2 \times 10^{-10}$	9.21
<b>Carboxylic Acids</b>		$K_a =$	
Chloroacetic acid	$\text{CH}_2\text{ClCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_2\text{ClCOO}^-$	$1.4 \times 10^{-3}$	2.85
Formic acid	$\text{HCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCOO}^-$	$1.8 \times 10^{-4}$	3.74
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{COO}^-$	$6.3 \times 10^{-5}$	4.20
Acetic acid	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$	$1.8 \times 10^{-5}$	4.74 
<b>Inorganic Bases</b>		$K_b =$	
Ammonia	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	$1.8 \times 10^{-5}$	4.74 
Hydrazine	$\text{H}_2\text{NNH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{NNH}_3^+ + \text{OH}^-$	$8.5 \times 10^{-7}$	6.07
Hydroxylamine	$\text{HONH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HONH}_3^+ + \text{OH}^-$	$9.1 \times 10^{-9}$	8.04
<b>Amines</b>		$K_b =$	
Dimethylamine	$(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$	$5.9 \times 10^{-4}$	3.23
Ethylamine	$\text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{NH}_3^+ + \text{OH}^-$	$4.3 \times 10^{-4}$	3.37
Methylamine	$\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$	$4.2 \times 10^{-4}$	3.38
Pyridine	$\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+ + \text{OH}^-$	$1.5 \times 10^{-9}$	8.82
Aniline	$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	$7.4 \times 10^{-10}$	9.13

# pH of Weak Acid Solutions

The organic base aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ) forms its conjugate acid, the anilinium ion, when treated with HCl.



If  $K_a$  for the anilinium ion is  $2.5 \times 10^{-5}$ , what is the pH of a 0.080 M solution of anilinium chloride?



$$0.08 - x$$

$$x$$

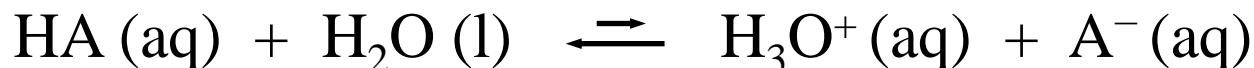
$$x$$

$$2.5 \times 10^{-5} = \frac{x^2}{0.08 - x} \quad \Rightarrow \quad 2.5 \times 10^{-5} = \frac{x^2}{0.08} \quad \Rightarrow \quad \begin{array}{l} x = 1.4 \times 10^{-3} \\ \text{pH} = 2.85 \end{array}$$

$$\frac{1.4 \times 10^{-3}}{0.08} = 1.75\% < 5\%$$

# Percent Dissociation

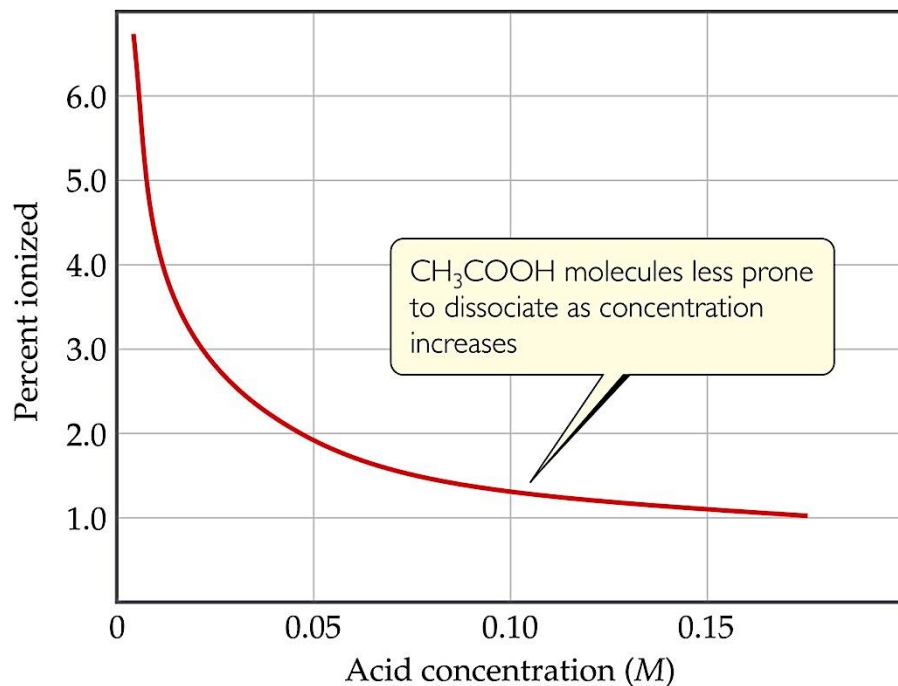
$$\text{Percent dissociation} = \frac{\text{Amount dissociated (mol/L)}}{\text{Initial concentration (mol/L)}} \times 100\%$$



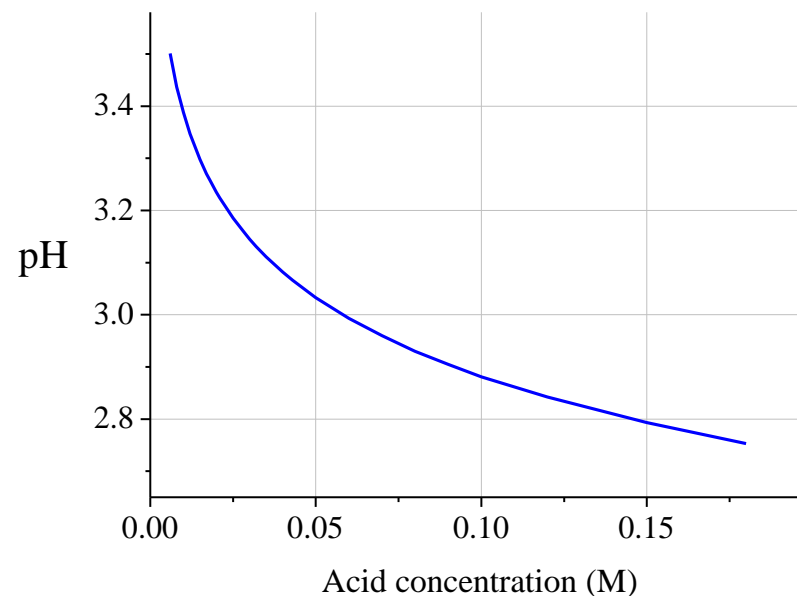
$$K_a = \frac{[\text{A}^-]^2}{[\text{HA}]}$$

$$[\text{A}^-] = \sqrt{K_a [\text{HA}]} \quad \longrightarrow \quad \frac{[\text{A}^-]}{[\text{HA}]_0} = \sqrt{\frac{K_a}{[\text{HA}]_0}}$$

# Acetic Acid



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$$\% \text{ dissociated} = \sqrt{\frac{K_a}{[\text{HA}]_0}}$$

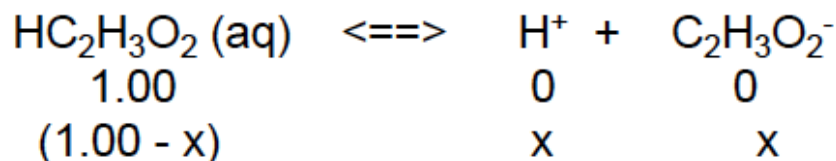
$$\text{pH} = \frac{1}{2}(\text{p}K_a - \log[\text{HA}])$$

# Percent Dissociation

Calculate the percent dissociation of acetic acid in the following solutions  
( $K_a = 1.8 \times 10^{-5}$ ).

(a) 1.00 M  $\text{HC}_2\text{H}_3\text{O}_2$

(b) 0.100 M  $\text{HC}_2\text{H}_3\text{O}_2$



$$K_a = ([\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]) / [\text{HC}_2\text{H}_3\text{O}_2] \approx x^2 / 1.00$$

$$x = 4.2 \times 10^{-3} \text{ M}$$

$$\text{p. d.} = 0.42 \%$$

$$K_a = ([\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]) / [\text{HC}_2\text{H}_3\text{O}_2] \approx x^2 / 0.100$$

$$x = 1.3 \times 10^{-3} \text{ M}$$

$$\text{p. d.} = 1.3 \%$$

The more dilute the weak acid solution, the greater is the percent dissociation.

# Polyprotic Acids

- A **monoprotic acid** has one ionizable H atom per molecule.
- A **polyprotic acid** has more than one ionizable H atom per molecule.
  - Sulfuric acid,  $\text{H}_2\text{SO}_4$       Diprotic
  - Carbonic acid,  $\text{H}_2\text{CO}_3$       Diprotic
  - Phosphoric acid,  $\text{H}_3\text{PO}_4$       Triprotic

**TABLE 7.4** Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	$K_{a1}$	$K_{a2}$	$K_{a3}$
Phosphoric acid	$\text{H}_3\text{PO}_4$	$7.5 \times 10^{-3}$	$6.2 \times 10^{-8}$	$4.8 \times 10^{-13}$
Arsenic acid	$\text{H}_3\text{AsO}_4$	$5 \times 10^{-3}$	$8 \times 10^{-8}$	$6 \times 10^{-10}$
Carbonic acid*	$\text{H}_2\text{CO}_3$	$4.3 \times 10^{-7}$	$4.8 \times 10^{-11}$	
Sulfuric acid	$\text{H}_2\text{SO}_4$	Large	$1.2 \times 10^{-2}$	
Sulfurous acid	$\text{H}_2\text{SO}_3$	$1.5 \times 10^{-2}$	$1.0 \times 10^{-7}$	
Hydrosulfuric acid†	$\text{H}_2\text{S}$	$1.0 \times 10^{-7}$	$\approx 10^{-19}$	
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	$6.5 \times 10^{-2}$	$6.1 \times 10^{-5}$	
Ascorbic acid (vitamin C)	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	$7.9 \times 10^{-5}$	$1.6 \times 10^{-12}$	

\*This is really  $\text{CO}_2(aq)$ .

†The  $K_{a2}$  value for  $\text{H}_2\text{S}$  is quite uncertain. Its small size makes it very difficult to measure.

$$K_{a1} \gg K_{a2} \gg K_{a3}$$

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In most cases, the pH of a polyprotic acid is determined by  $K_{a1}$ .  
But for dilute  $\text{H}_2\text{SO}_4$  solution,  $K_{a2}$  has to be considered.



# Phosphoric Acid

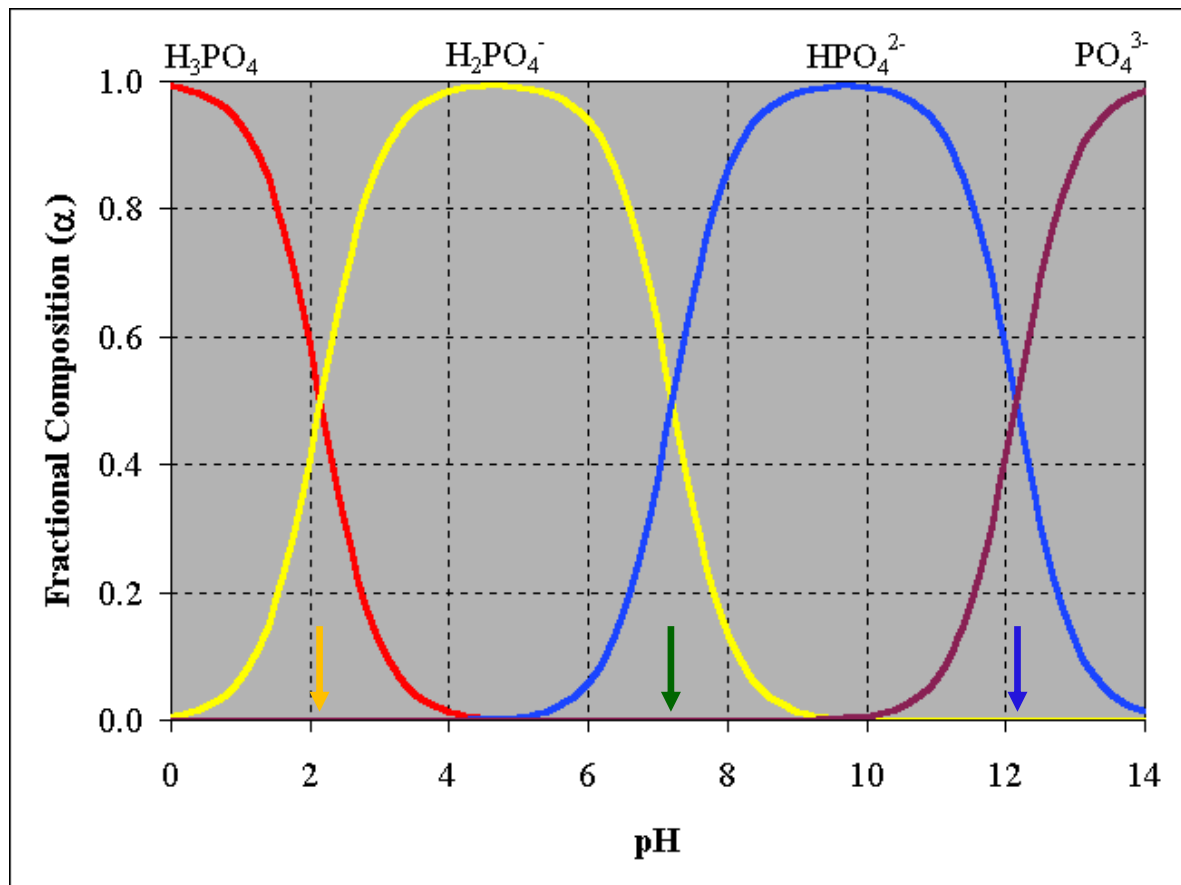


What is the mole fraction of  $\text{HPO}_4^{2-}$  at pH 9 ?

# Phosphoric Acid

$$\begin{aligned}
 f_{\text{HPO}_4^{2-}} &\equiv \frac{[\text{HPO}_4^{2-}]}{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]} \\
 &= \frac{1}{\frac{[\text{H}_3\text{PO}_4]}{[\text{HPO}_4^{2-}]} + \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} + 1 + \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}} \\
 &= \frac{1}{\frac{[\text{H}_3\text{PO}_4]}{[\text{H}_2\text{PO}_4^-]} \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} + \frac{[\text{H}^+]}{K_{\text{a}2}} + 1 + \frac{K_{\text{a}3}}{[\text{H}^+]}} \\
 &= \frac{1}{\frac{[\text{H}^+]^2}{K_{\text{a}1}K_{\text{a}2}} + \frac{[\text{H}^+]}{K_{\text{a}2}} + 1 + \frac{K_{\text{a}3}}{[\text{H}^+]}}
 \end{aligned}$$

# Phosphoric Acid

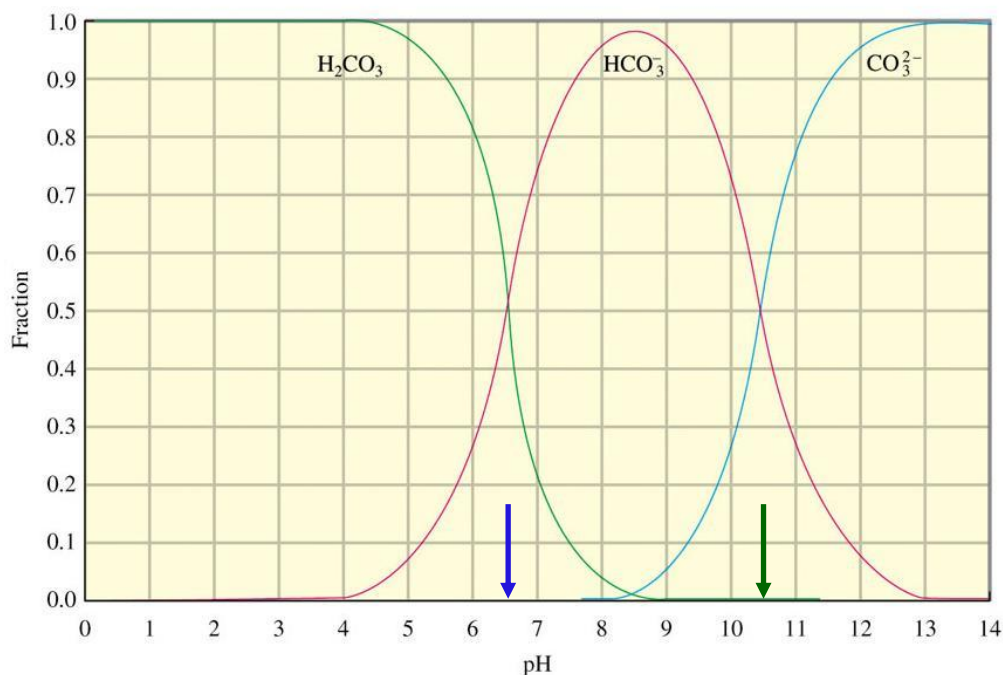
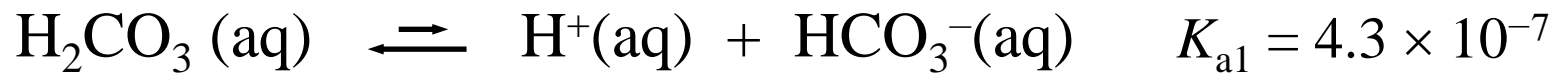


$$\text{pK}_{\text{a}1} = 2.12$$

$$\text{pK}_{\text{a}2} = 7.21$$

$$\text{pK}_{\text{a}3} = 12.32$$

# Carbonic Acid

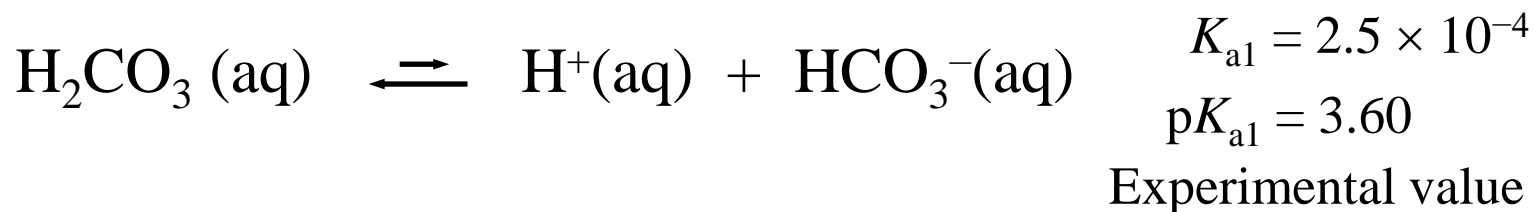


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$$\text{p}K_{a1} = 6.37$$

$$\text{p}K_{a2} = 10.32$$

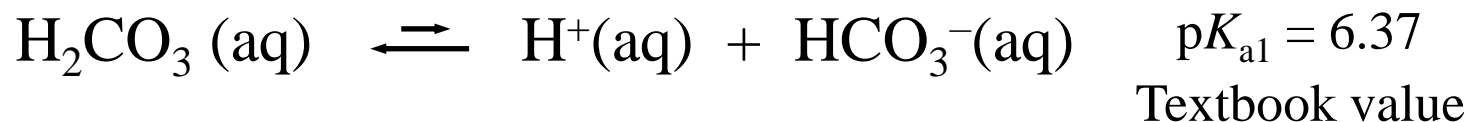
# Acidity of Carbonic Acid?



By convention,

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2] + [\text{H}_2\text{CO}_3]} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3] \left( \frac{1}{1.72 \times 10^{-3}} + 1 \right)} = 2.5 \times 10^{-4} \times \frac{1.72 \times 10^{-3}}{1 + 1.72 \times 10^{-3}}$$

$$= 4.3 \times 10^{-7}$$



# Acidity of Rain and Soft Drinks

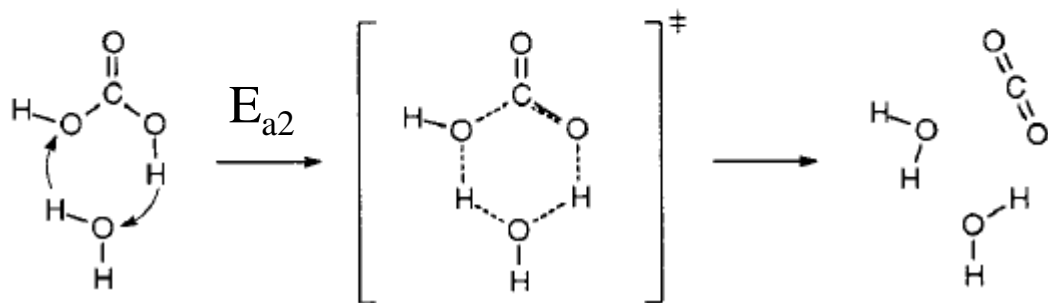
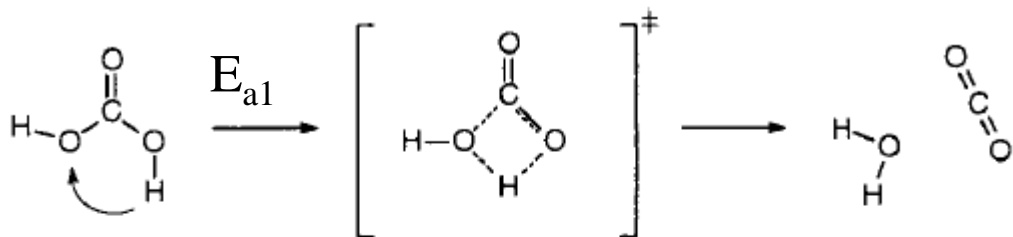
	$P_{\text{CO}_2}$ (atm)	pH	$[\text{CO}_2]$ (mol/L)	$[\text{H}_2\text{CO}_3]$ (mol/L)	$[\text{HCO}_3^-]$ (mol/L)	$[\text{CO}_3^{2-}]$ (mol/L)
A.	$3.5 \times 10^{-4}$	5.65	$1.2 \times 10^{-5}$	$2.0 \times 10^{-8}$	$2.2 \times 10^{-6}$	$5.6 \times 10^{-11}$
B.	2.5	3.72	$8.4 \times 10^{-2}$	$1.4 \times 10^{-4}$	$1.9 \times 10^{-4}$	$5.6 \times 10^{-11}$

- A. For normal atmospheric conditions, we get a slightly acid solution ( $pH = 5.7$ ) and the dissolved carbon is now essentially in the  $\text{CO}_2$  form.
- B. For a  $\text{CO}_2$  pressure typical of the one in soda drink bottles ( $\sim 2.5$  atm), we get a relatively acid medium ( $pH = 3.7$ ) with a high concentration of dissolved  $\text{CO}_2$ . These features contribute to the sour and sparkling taste of these drinks.

# Is Carbonic Acid very Unstable?



Transition states



Absolutely water-free carbonic acid is very stable. Liedl calculated a half-life of 180,000 years for it. However, carbonic acid decomposes immediately if it comes in contact with water. A single water molecule is enough to speed up the decomposition of a molecule of carbonic acid a billion times.

[Liedl K. and co-workers, *Angew. Chem. Int. Ed.* **2000**, 39(5), 891.]

# Calculating pH for Strong Acid

The pH of  $1.0 \times 10^{-10}$  M solution of HCl.

=> The major component is  $\text{H}_2\text{O}$

$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-10}) + (1.0 \times 10^{-7}) \approx 1.0 \times 10^{-7}$$

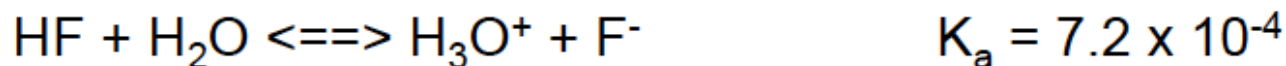
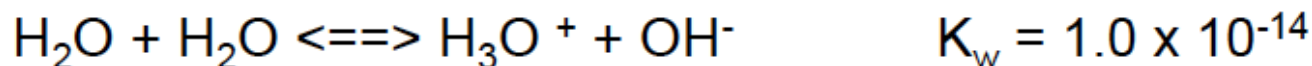
$$\text{pH} = 7.00$$



# Calculating pH for Weak Acid

The pH of 1.0 M solution of HF ( $K_a = 7.2 \times 10^{-4}$ ).

=> Major component in solution: HF,  $H_2O$



$$1.0 \quad \quad \quad 10^{-7} \approx 0 \quad 0$$

$$1.0 - x \quad \quad \quad x \quad x$$

$$K_a = [H_3O^+][F^-]/[HF] = 7.24 \times 10^{-4}$$

$$= (x)(x)/(1.0 - x) \approx (x)(x)/1.0$$

$$x = 2.7 \times 10^{-2}$$

$$pH = 1.57$$

**The 5% rule:**

$$[HA]_0 - x \approx [HA]_0$$

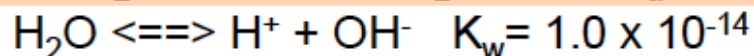
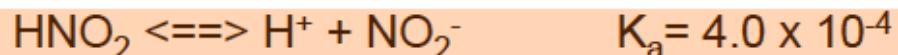
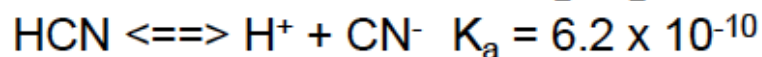
$$x / [HA]_0 \leq 5\%$$

$$(2.7 \times 10^{-2}) / 1.0 = 2.7\%$$

## pH of a Mixture of Weak Acids

Calculate the pH and  $[\text{CN}^-]$  of a solution that contains 1.00 M HCN ( $K_a = 6.2 \times 10^{-10}$ ) and 5.00 M  $\text{HNO}_2$  ( $K_a = 4.0 \times 10^{-4}$ ).

Major component: HCN,  $\text{HNO}_2$ ,  $\text{H}_2\text{O}$



$$\begin{aligned} K_a &= [\text{H}^+][\text{NO}_2^-]/[\text{HNO}_2] = (x)(x)/(5.00 - x) \approx x^2/5.00 \\ &= 4.0 \times 10^{-4} \end{aligned}$$

$$x = 4.50 \times 10^{-2}$$

Verify with the 5% rule:

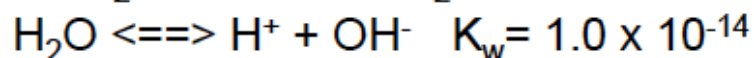
$$x / [\text{HNO}_2] = 4.50 \times 10^{-2} / 5.00 = 0.90\%$$

$$\text{pH} = -\log(4.50 \times 10^{-2}) = 1.347$$

## pH of a Mixture of Weak Acids

Calculate the pH and  $[\text{CN}^-]$  of a solution that contains 1.00 M HCN ( $K_a = 6.2 \times 10^{-10}$ ) and 5.00 M  $\text{HNO}_2$  ( $K_a = 4.0 \times 10^{-4}$ ).

Major component: HCN,  $\text{HNO}_2$ ,  $\text{H}_2\text{O}$



$$[\text{H}^+] = 4.5 \times 10^{-2}$$

$$K_a = [\text{H}^+][\text{CN}^-]/[\text{HCN}]$$

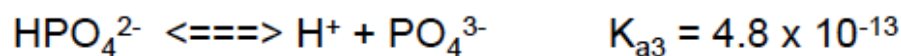
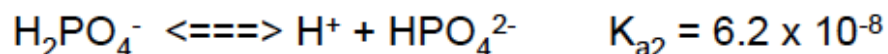
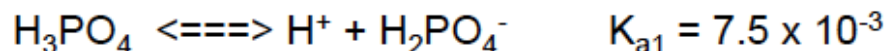
$$= (4.5 \times 10^{-2})[\text{CN}^-] / (1.00 - [\text{CN}^-]) \approx (4.5 \times 10^{-2})[\text{CN}^-] / 1.00$$

$$= 6.2 \times 10^{-10}$$

$$[\text{CN}^-] = 1.4 \times 10^{-8} \quad \{\text{verification: } 1.4 \times 10^{-8} / 1.00 = 0.0000014 \%\}$$

# The pH of a Polyprotic Acid

Calculate the pH of a 5.0 M  $\text{H}_3\text{PO}_4$  solution, and the equilibrium concentration of  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ .



$$K_{a1} = 7.5 \times 10^{-3} = [\text{H}^+][\text{H}_2\text{PO}_4^-]/[\text{H}_3\text{PO}_4] \approx x^2 / 5.0$$

$$x = 1.9 \times 10^{-1} \text{ M}$$

$$\text{pH} = 0.72$$

$$K_{a2} = 6.2 \times 10^{-8} = [\text{H}^+][\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] = (0.19)[\text{HPO}_4^{2-}] / (0.19)$$

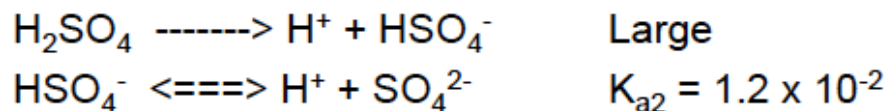
$$[\text{HPO}_4^{2-}] = 6.2 \times 10^{-8} \text{ M}$$

$$K_{a3} = 4.8 \times 10^{-13} = [\text{H}^+][\text{PO}_4^{3-}]/[\text{HPO}_4^{2-}] = (0.19)[\text{PO}_4^{3-}] / (6.2 \times 10^{-8})$$

$$[\text{PO}_4^{3-}] = 1.6 \times 10^{-19} \text{ M}$$

# The pH of a Polyprotic Acid

Calculate the pH of 1.0 M and 0.01 M  $\text{H}_2\text{SO}_4$  solution.



For 1.0 M solution

	$\text{HSO}_4^-$	$\text{H}^+$	$\text{SO}_4^{2-}$
Initial	1.0	1.0	0
Change	-x	+x	+x
Equilibrium	1.0-x	1.0+x	x

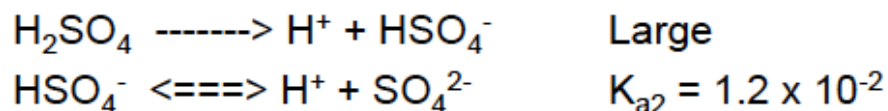
$$\begin{aligned}K_{a2} &= \frac{[1.0+x][x]}{[1.0-x]} \\ &\approx \frac{[1.0][x]}{[1.0]} \\ &= 1.2 \times 10^{-2} \\ x &= 1.2 \times 10^{-2}\end{aligned}$$

$$[\text{H}^+] = 1.0 + 1.2 \times 10^{-2} \approx 1.0$$

$$\text{pH} = -\log(1.0) = 0.00$$

# The pH of a Polyprotic Acid

Calculate the pH of 1.0 M and  $1.00 \times 10^{-2}$  M  $\text{H}_2\text{SO}_4$  solution.



For 0.01 M solution

	$\text{HSO}_4^-$	$\text{H}^+$	$\text{SO}_4^{2-}$
Initial	$1.00 \times 10^{-2}$	$1.00 \times 10^{-2}$	0
Change	-x	+x	+x
Equilibrium	$1.00 \times 10^{-2} - x$	$1.00 \times 10^{-2} + x$	x

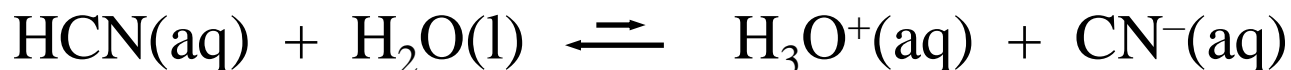
$$\begin{aligned} K_{a2} &= (1.00 \times 10^{-2} + x)(x) / (1.00 \times 10^{-2} - x) \\ &= 1.2 \times 10^{-2} \\ x &= 4.5 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} [\text{H}^+] &= 1.00 \times 10^{-2} + 4.5 \times 10^{-3} \\ &= 1.45 \times 10^{-2} \end{aligned}$$

$$\text{pH} = -\log(1.45 \times 10^{-2}) = 1.838$$


# Very Dilute Weak Acids

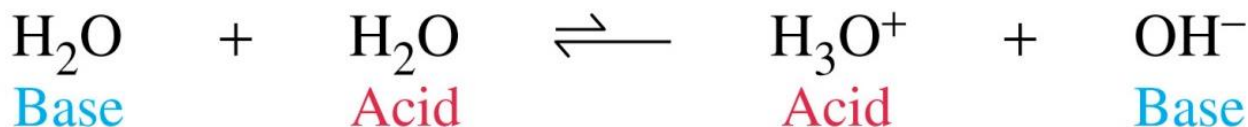
$$K_a = 6.2 \times 10^{-10}$$



$$1.0 \times 10^{-6} \text{ M}$$

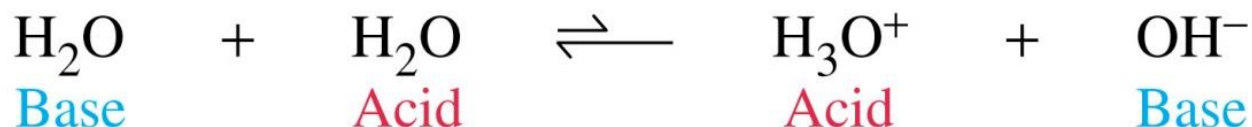
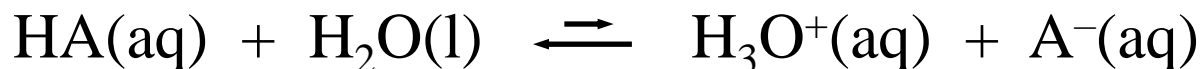
$$6.2 \times 10^{-10} = \frac{x^2}{1.0 \times 10^{-6} - x} \quad \Rightarrow \quad x = 2.5 \times 10^{-8}$$

pH = 7.60 



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# Very Dilute Weak Acids



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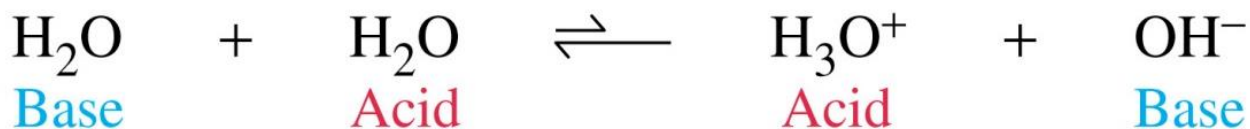
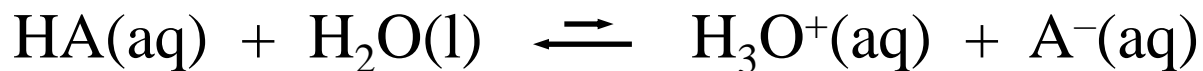
$$[\text{HA}]_0 = [\text{HA}] + [\text{A}^-] \quad \text{Material Balance}$$

$$[\text{H}^+] = [\text{A}^-] + [\text{OH}^-] \quad \text{Charge Balance}$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad K_w = [\text{H}^+][\text{OH}^-]$$



# Very Dilute Weak Acids



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$$K_a = \frac{[\text{H}^+]^2 - K_w}{[\text{HA}]_0 - \frac{[\text{H}^+]^2 - K_w}{[\text{H}^+]}}$$

$$[\text{HA}]_0 = [\text{HA}] + [\text{A}^-] \quad [\text{H}^+] = [\text{A}^-] + [\text{OH}^-]$$

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

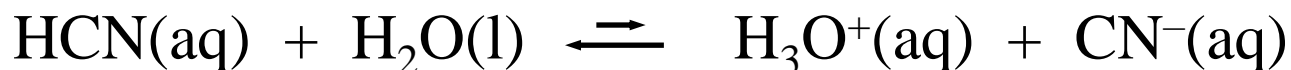
$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]_0 - [\text{A}^-]} = \frac{[\text{H}^+]([\text{H}^+] - [\text{OH}^-])}{[\text{HA}]_0 - ([\text{H}^+] - [\text{OH}^-])}$$

$$= \frac{[\text{H}^+] \left( [\text{H}^+] - \frac{K_w}{[\text{H}^+]} \right)}{[\text{HA}]_0 - \left( [\text{H}^+] - \frac{K_w}{[\text{H}^+]} \right)}$$

$$= \frac{[\text{H}^+]^2 - K_w}{[\text{HA}]_0 - \left( \frac{[\text{H}^+]^2 - K_w}{[\text{H}^+]} \right)}$$

# Very Dilute Weak Acids

$$K_a = 6.2 \times 10^{-10}$$

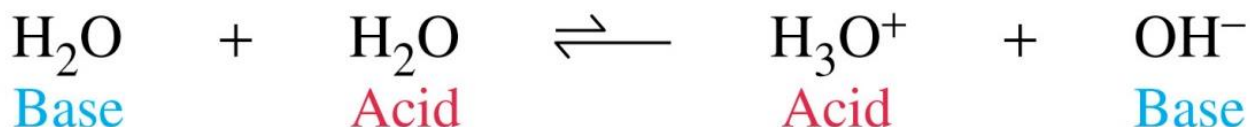
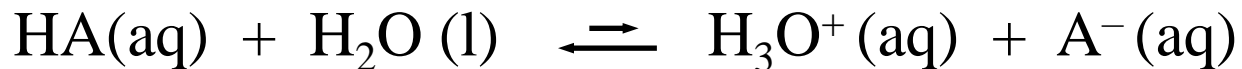


$$1.0 \times 10^{-6} \text{ M}$$

$$6.2 \times 10^{-10} = \frac{x^2}{1.0 \times 10^{-6} - x} \quad \Rightarrow \quad \begin{aligned} x &= 2.5 \times 10^{-8} \\ \text{pH} &= 7.60 \end{aligned}$$

$$K_a = \frac{[\text{H}^+]^2 - K_w}{[\text{HA}]_0 - \frac{[\text{H}^+]^2 - K_w}{[\text{H}^+]}} \quad \begin{aligned} x &= 1.034 \times 10^{-7} \\ \text{pH} &= 6.99 \end{aligned}$$

# Percentage Ionization Revisited



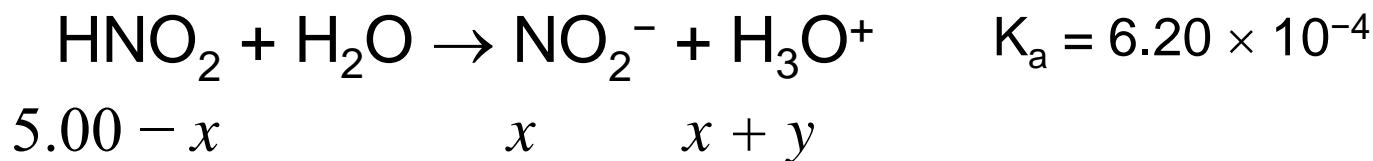
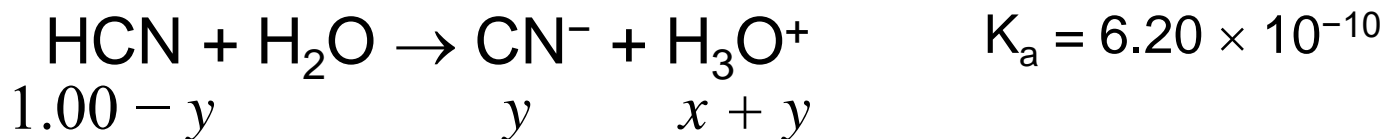
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$$\% \text{ Ionized} = \sqrt{\frac{K_a}{[\text{HA}]_0}}$$

$$\% \text{ Ionized} = \frac{[\text{A}^-]}{[\text{HA}]_0} = \frac{[\text{A}^-]}{[\text{HA}] + [\text{A}^-]} = \frac{1}{\frac{[\text{H}^+]}{K_a} + 1} \leq 100\%$$

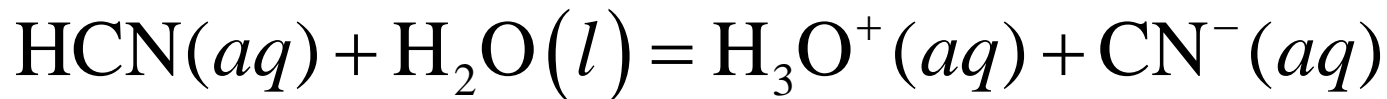
# pH of a Mixture of Weak Acids

Calculate the pH of a solution that contains 1.00 M HCN ( $K_a = 6.20 \times 10^{-10}$ ) and 5.00 M  $\text{HNO}_2$  ( $K_a = 6.20 \times 10^{-4}$ ). Also calculate the concentration of cyanide ion ( $\text{CN}^-$ ) in this solution at equilibrium.

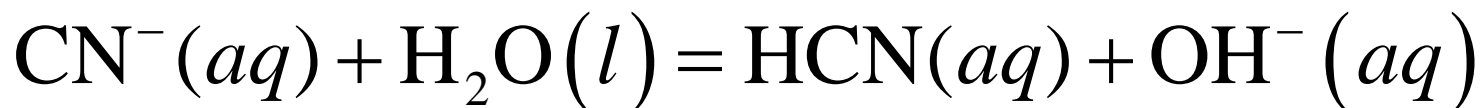


$$6.20 \times 10^{-4} = \frac{x^2}{5.00 - x} \quad \Rightarrow \quad x = 5.57 \times 10^{-2} \quad \text{pH} = 1.254$$
$$6.20 \times 10^{-10} = \frac{y \times 5.57 \times 10^{-2}}{1.00} \quad [\text{CN}^-] = 1.11 \times 10^{-8} \text{ M}$$

## Is $\text{CN}^-$ a Weak Base or Strong Base?



$$K_a = 6.2 \times 10^{-10}$$



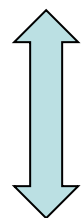
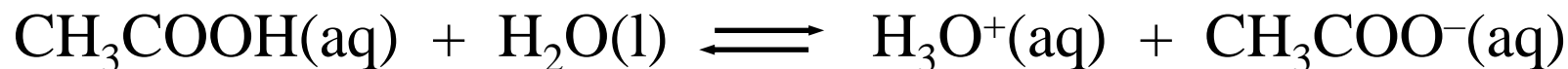
$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{[\text{HCN}]K_w}{[\text{CN}^-][\text{H}^+]} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$



# $K_a$ and $K_b$

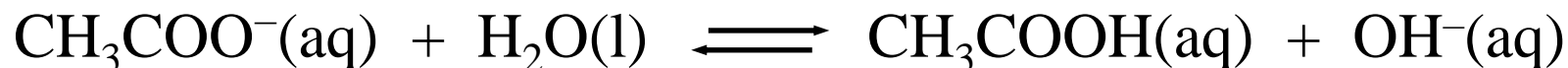
$K_a$  and  $K_b$  of a conjugate pair are related in this way:

$$K_a \times K_b = K_w$$



Conjugate pair

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$



$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

# $K_a$ and $K_b$

**TABLE 16.5 • 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)

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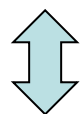
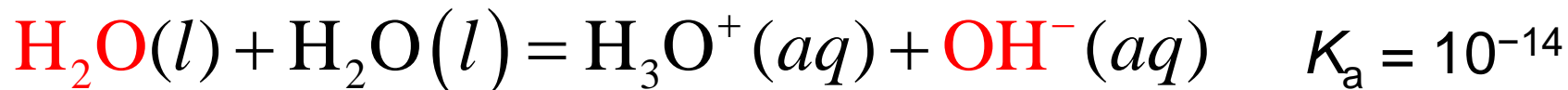
$$K_a \times K_b = K_w$$

$$\text{p}K_a + \text{p}K_b = 14 \quad \text{at } 298 \text{ K}$$

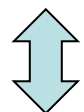
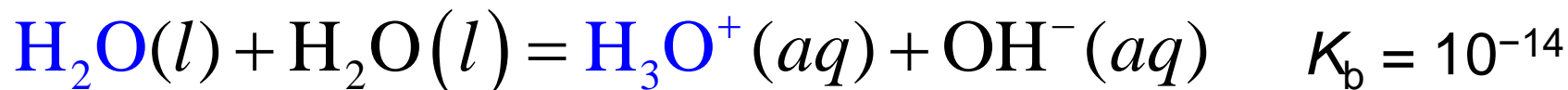
Therefore, if you know  $K_a$  of an acid, you can calculate the  $K_b$  of its conjugate base, and vice versa.



# $pK_a$ and $pK_b$ of Water



Conjugate pair

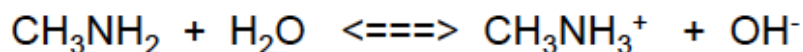


Conjugate pair



# pH of base solution

Calculate the pH of a 1.0 M methylamine solution ( $K_b = 4.38 \times 10^{-4}$ )



Initial	1.0	0	0
Change	-x	+x	+x
Equilibrium	(1.0-x)	x	x

$$K_b = \frac{x^2}{(1.0 - x)} \approx \frac{x^2}{1.0} = 4.38 \times 10^{-4}$$

$$x = [\text{OH}^-] = 2.1 \times 10^{-2}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = 4.8 \times 10^{-13}$$

$$\text{pH} = 12.32$$

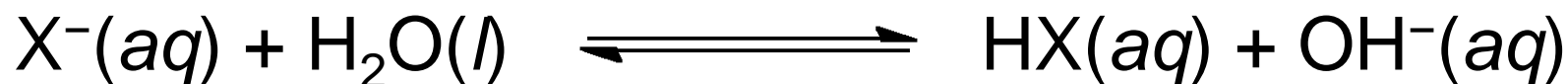
$$[\text{OH}^-] = 2.1 \times 10^{-2}$$

$$\text{pOH} = 1.68$$

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

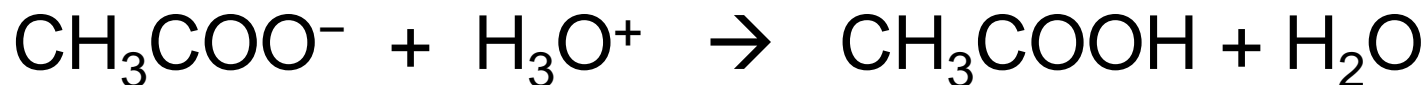
# Reactions of Anions with Water

- Anions are bases.
- As such, they can react with water in a **hydrolysis reaction** to form  $\text{OH}^-$  and the conjugate acid:



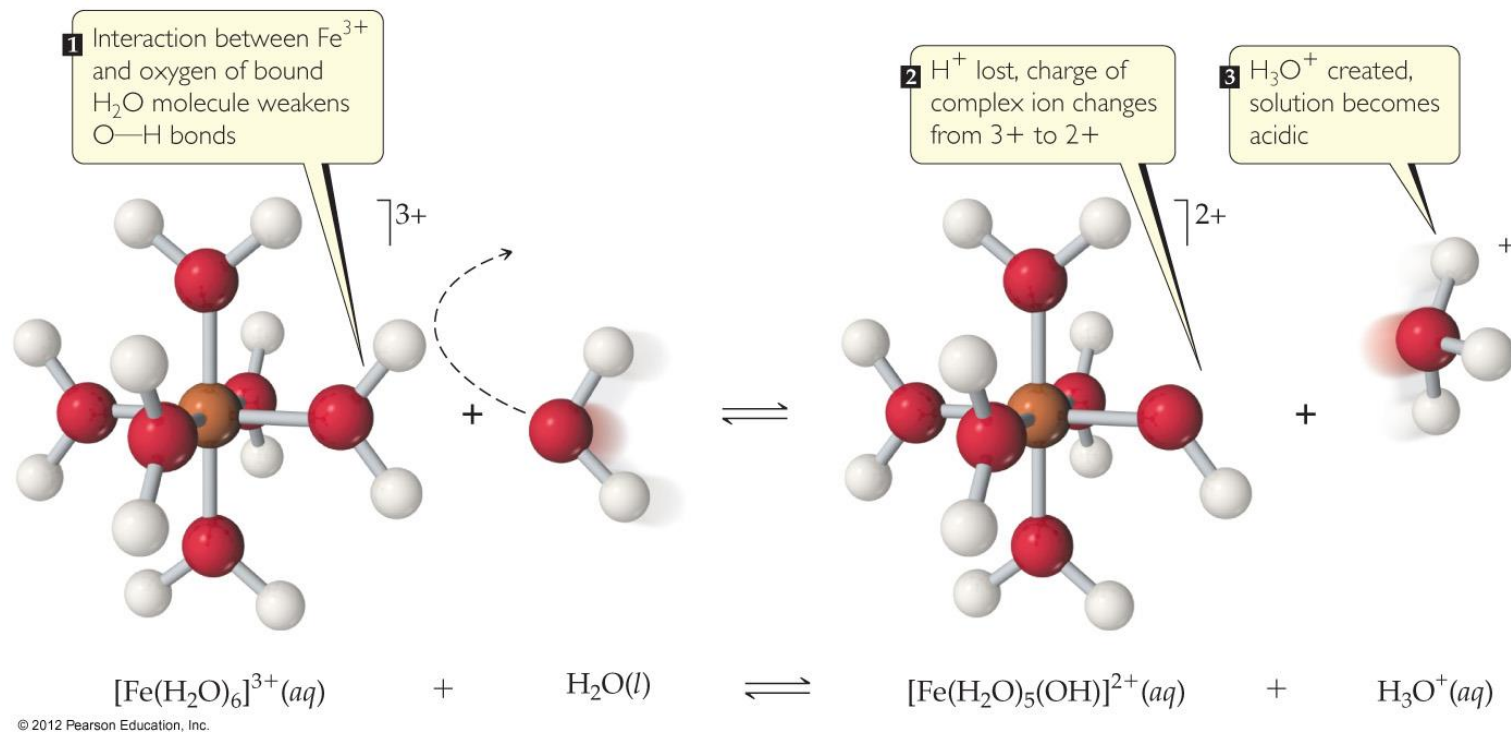
# Acid-Base Properties of Salts

- A solution of sodium acetate (which dissociates completely into sodium and acetate ions in water) is best described by



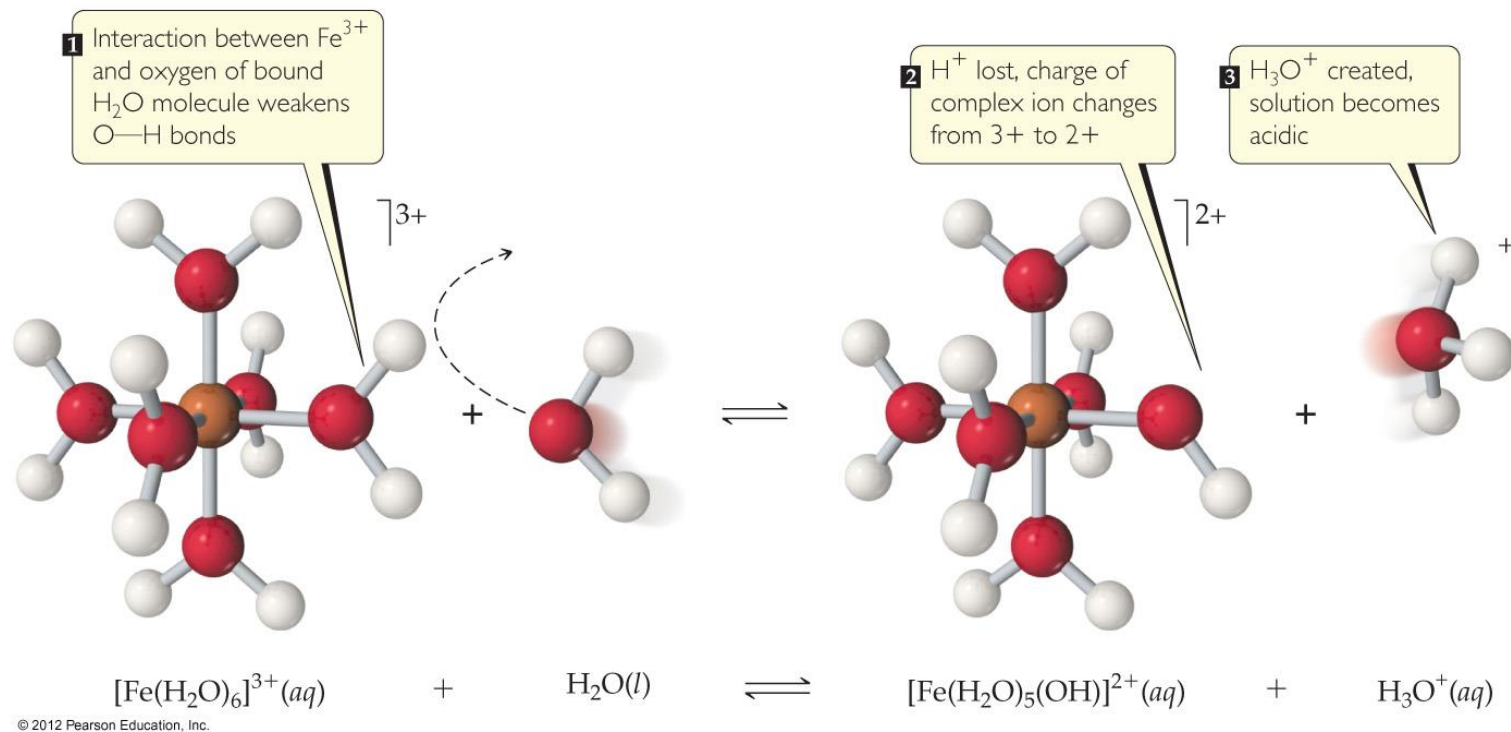
Because water is the solvent and is present in large amount!

# Reactions of Cations with Water



- Cations with acidic protons (like  $\text{NH}_4^+$ ) will lower the pH of a solution.
- Many metal cations that are hydrated in solution also lower the pH of the solution.

# Reactions of Cations with Water



- Attraction between nonbonding electrons on oxygen and the metal causes a shift of the electron density in water.
- This makes the O—H bond more polar and the water more acidic.

# Reactions of Cations with Water

**TABLE 16.6 • Acid-Dissociation Constants for Metal Cations in Aqueous Solution at 25 °C**

Cation	$K_a$	$\text{p}K_a$
$\text{Fe}^{2+}$	$3.2 \times 10^{-10}$	9.49
$\text{Zn}^{2+}$	$2.5 \times 10^{-10}$	9.60
$\text{Ni}^{2+}$	$2.5 \times 10^{-11}$	10.60
$\text{Fe}^{3+}$	$6.3 \times 10^{-3}$	2.20
$\text{Cr}^{3+}$	$1.6 \times 10^{-4}$	3.80
$\text{Al}^{3+}$	$1.4 \times 10^{-5}$	4.85

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- Greater charge and smaller size make a cation more acidic.

# Acid-Base Properties of Salts

- Salts of strong acids and strong bases form **neutral** solutions:  $\text{NaCl}$ ,  $\text{KNO}_3$
- Salts of weak acids and strong bases form **basic** solutions:  $\text{KNO}_2$ ,  $\text{NaClO}$
- Salts of strong acids and weak bases form **acidic** solutions:  $\text{NH}_4\text{NO}_3$
- Salts of weak acids and weak bases form solutions that may be acidic, neutral, or basic; it depends on the  $K_a$  and  $K_b$  values.



# Changes in pH for Salts in Water

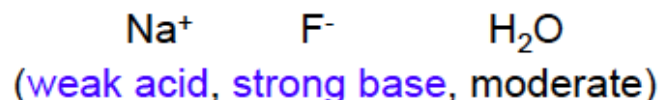
## Cations and Anions of Salts in Neutral, Basic, and Acidic Salt Solutions

Type of Solution	Cations	Anions	pH
<b>Neutral</b>	From strong bases Group 1A (1): $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ Group 2A (2): $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ (but not $\text{Be}^{2+}$ )	From strong acids $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{NO}_3^-$ , $\text{ClO}_4^-$	7.0
<b>Basic</b>	From strong bases Group 1A (1): $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ Group 2A (2): $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ (but not $\text{Be}^{2+}$ )	From weak acids $\text{F}^-$ , $\text{NO}_2^-$ , $\text{CN}^-$ , $\text{CO}_3^{2-}$ , $\text{SO}_4^{2-}$ , $\text{CH}_3\text{COO}^-$ , $\text{S}^{2-}$ , $\text{PO}_4^{3-}$	>7.0
<b>Acidic</b>	From weak bases $\text{NH}_4^+$ , $\text{Be}^{2+}$ , $\text{Al}^{3+}$ , $\text{Zn}^{2+}$ , $\text{Cr}^{3+}$ , $\text{Fe}^{3+}$ (small, highly charged metal ions)	From strong acids $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{NO}_3^-$ , $\text{ClO}_4^-$	<7.0

# The pH of Salts

Calculate the pH of 0.30 M NaF solution. (HF:  $K_a = 7.2 \times 10^{-4}$ )

Major component in solution:



	$\text{F}^-$	$+$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{HF}$	$+$	$\text{OH}^-$
Initial	0.30		0		0		0
Change	-x				+x		+x
Equilibrium	0.30-x				x		x

$$\left. \begin{array}{l} K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} \\ K_a = \frac{[\text{F}^-][\text{H}^+]}{[\text{HF}]} \end{array} \right\} \begin{array}{l} K_a \times K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} \times \frac{[\text{F}^-][\text{H}^+]}{[\text{HF}]} = [\text{H}^+][\text{OH}^-] = K_w \\ K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = K_w/K_a = 1.4 \times 10^{-11} = \frac{x^2}{0.30-x} \end{array}$$

$$x = 2.0 \times 10^{-6}$$

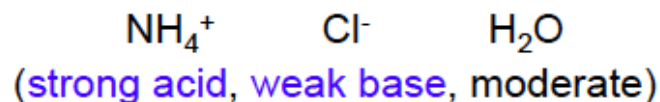
$$\text{pOH} = 5.69$$

$$\text{pH} = 14 - 5.69 = 8.31$$

# The pH of Salts

Calculate the pH of 0.10 M  $\text{NH}_4\text{Cl}$  solution. ( $\text{NH}_3$ :  $K_b = 1.8 \times 10^{-5}$ )

Major component in solution:



	$\text{NH}_4^+$	$\rightleftharpoons$	$\text{NH}_3$	+	$\text{H}^+$
Initial	0.10		0		0
Change	-x		+x		+x
Equilibrium	0.10-x		x		x

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

$$K_a = K_w/K_b = 5.6 \times 10^{-10} = \frac{x^2}{0.10-x}$$

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

$$x = 7.5 \times 10^{-6}$$

$$\text{pH} = 5.13$$

# Predict the pH of salts

The  $K_a$  value of cation

vs.

The  $K_b$  value of anion

(can be obtained from the  $K_a$  of its conjugate acid,  $K_w/K_b$ )

$K_a > K_b$	pH < 7 (acidic)
$K_b > K_a$	pH > 7 (basic)
$K_a = K_b$	pH = 7 (neutral)

Formula	Value of $K_a^*$
$\text{HSO}_4^-$	$1.2 \times 10^{-2}$
$\text{HClO}_2$	$1.2 \times 10^{-2}$
$\text{HC}_2\text{H}_2\text{ClO}_2$	$1.35 \times 10^{-3}$
$\text{HF}$	$7.2 \times 10^{-4}$
$\text{HNO}_2$	$4.0 \times 10^{-4}$
$\text{HC}_2\text{H}_3\text{O}_2$	$1.8 \times 10^{-5}$
$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	$1.4 \times 10^{-5}$
$\text{HOCl}$	$3.5 \times 10^{-8}$
$\text{HCN}$	$6.2 \times 10^{-10}$
$\text{NH}_4^+$	$5.6 \times 10^{-10}$
$\text{HOC}_6\text{H}_5$	$1.6 \times 10^{-10}$

$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  pH = 7

$$5.6 \times 10^{-10} \text{ vs. } (1 \times 10^{-14} / 1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$$

$\text{NH}_4\text{NO}_2$  pH < 7

$$5.6 \times 10^{-10} \text{ vs. } (1 \times 10^{-14} / 4.0 \times 10^{-4}) = 2.5 \times 10^{-11}$$

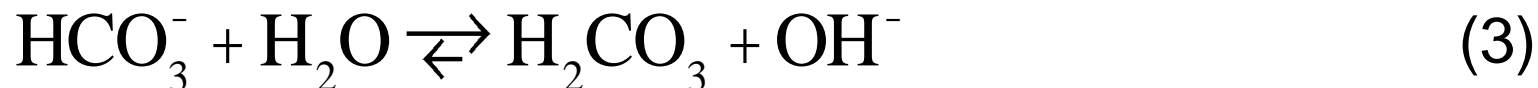
$\text{NH}_4\text{CN}$  pH > 7

$$5.6 \times 10^{-10} \text{ vs. } (1 \times 10^{-14} / 6.2 \times 10^{-10}) = 1.6 \times 10^{-5}$$

## Learning Check

Calculate the pH for the solution of 0.1 M aqueous solution of  $(\text{NH}_4)_2\text{CO}_3$ .

(For  $\text{H}_2\text{CO}_3$ ,  $\text{p}K_{\text{a}1} = 6.367$  and  $\text{p}K_{\text{a}2} = 10.329$ ;  $\text{NH}_3$ ,  $\text{p}K_{\text{b}} = 4.74$ )



From the material balance:

$$0.1 = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{H}_2\text{CO}_3] \quad (5)$$

$$0.2 = [\text{NH}_3] + [\text{NH}_4^+] \quad (6)$$

From the charge balance:

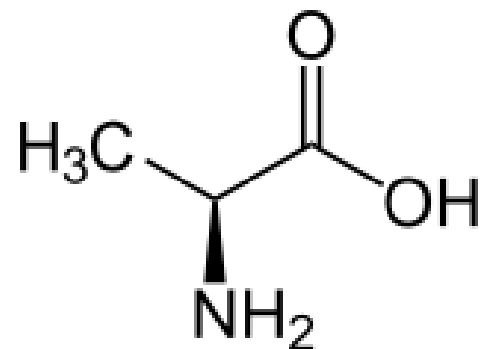
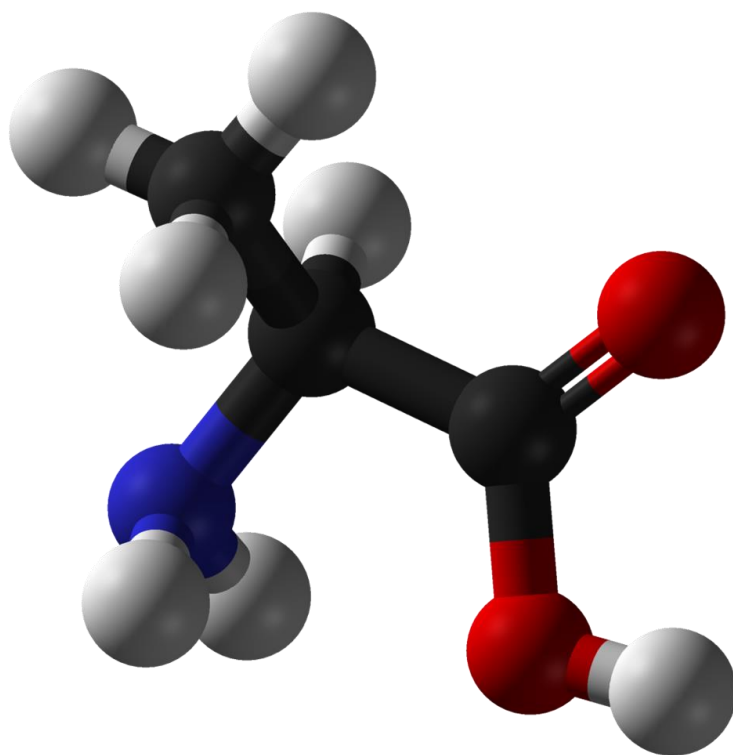
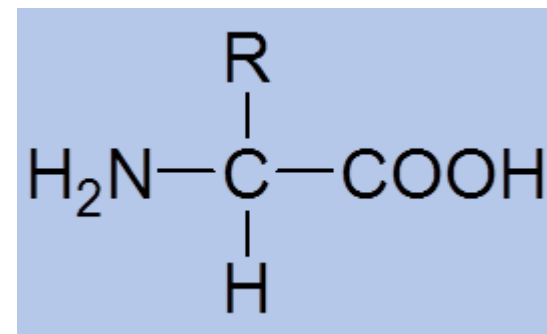
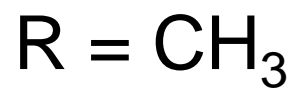
$$[\text{NH}_4^+] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (7)$$

$$\text{pH} = 9.229$$

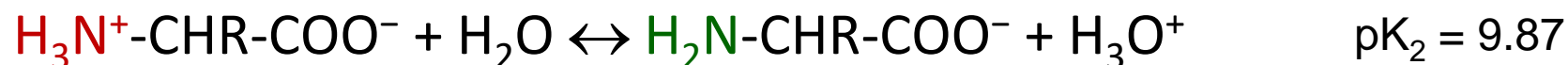
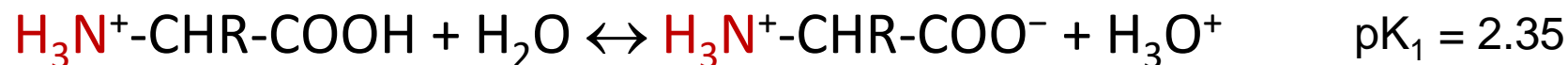
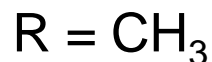
**CurTiPot**

# Amino Acids

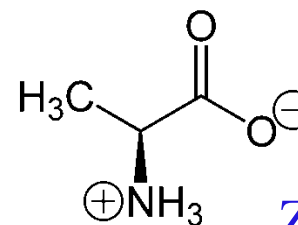
## Alanine



# Alanine



Roughly estimate  $K_c$  for



Zwitterionic form

We can imagine that the formation of a zwitterion occurs as a series of steps:



$$K_c = \frac{[{}^+\text{Ala}^-]}{[\text{Ala}]} = \frac{[\text{Ala}^-][\text{H}_3\text{O}^+]}{[\text{Ala}]} \frac{[{}^+\text{Ala}^-][\text{OH}^-]}{[\text{Ala}^-]} \times \frac{1}{K_w} \approx \frac{4.5 \times 10^{-3} \times 7.4 \times 10^{-5}}{10^{-14}} = 3.3 \times 10^7$$

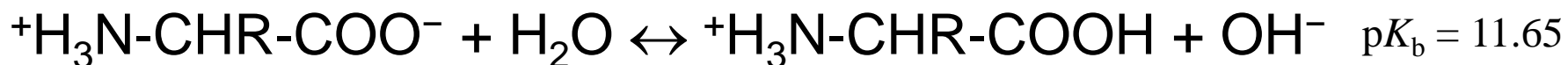
$\text{pK}_c \approx \text{pK}_1 - \text{pK}_2$



# Alanine

What is the pH of a 0.050 M aqueous solution of alanine?

Which of the following reaction we need to consider?



$$0.050 - x$$

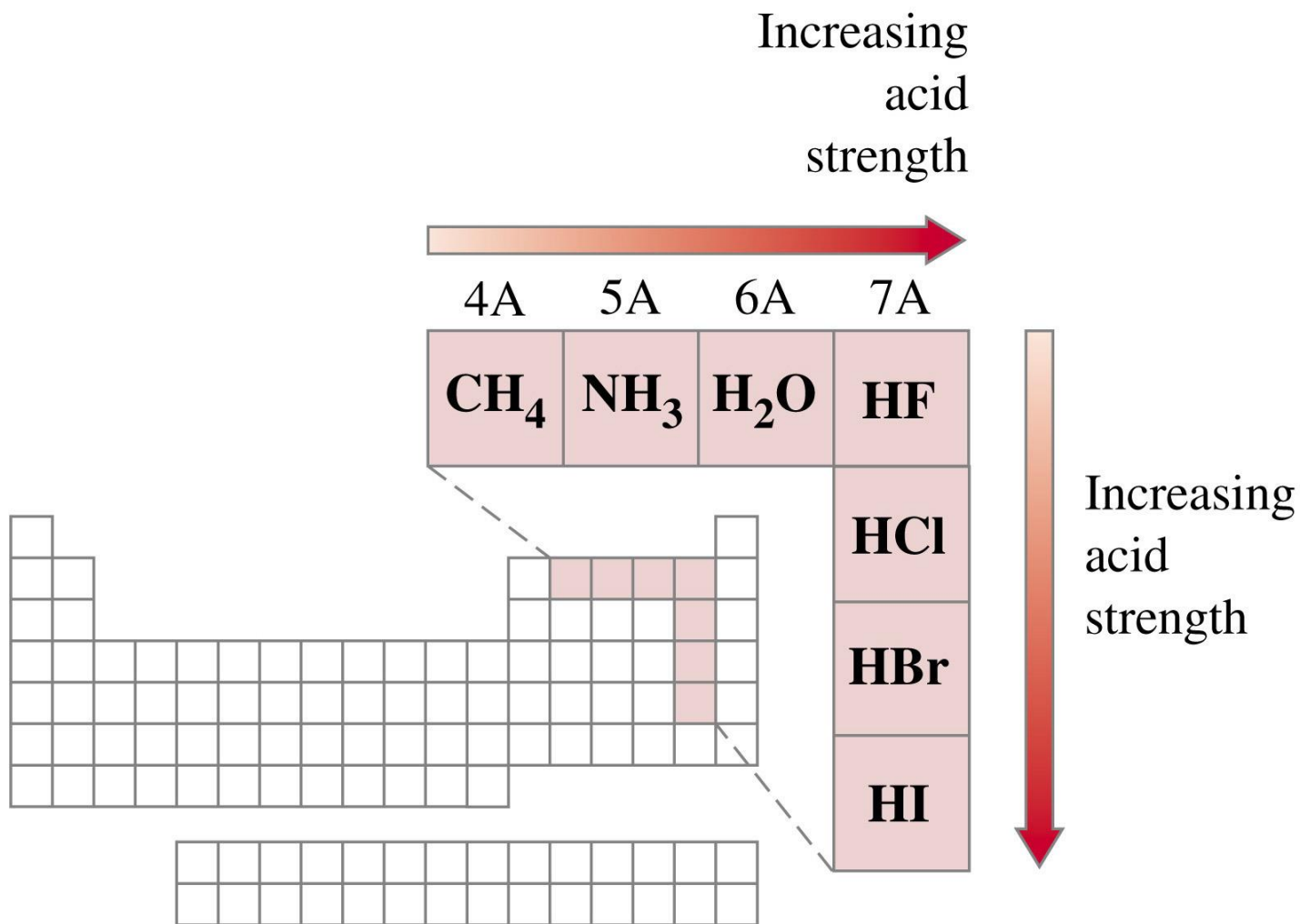
$$x$$

$$x$$

$$\Rightarrow 1.3 \times 10^{-10} = \frac{x^2}{0.05 - x}$$

$$\text{pH} = 5.50$$

# Periodic Trends in Acid Strength



# When does the H-X bond dissociate?

- For Brønsted-Lowry acid, X-H bond has to be dissociated.
- Two important structural factors
  - Bond Polarity (high is good)  
H-C vs. H-Cl  
neutral vs. strong acid
  - Bond Strength (low is good)  
H-F > HCl > HBr > HI  
Weak acid --> strong acid

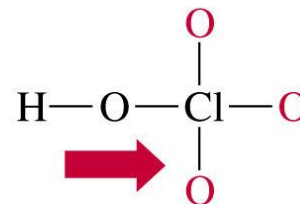
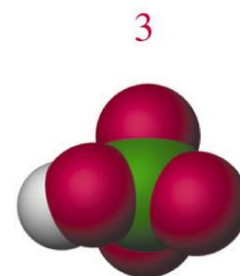
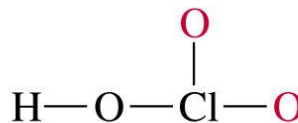
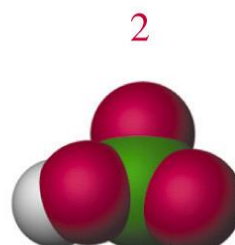
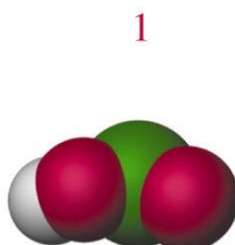
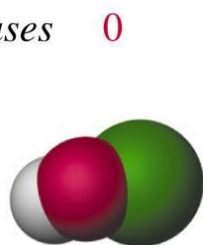
**Table 14.7 ▶ Bond Strengths and Acid Strengths for Hydrogen Halides**

H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

# Strength of Oxyacids

Acid strength ***increases*** with the electronegativity of the central atom, and with the *number* of terminal oxygen atoms.

Number of terminal O  
atoms (red) increases



Electron  
withdrawal

Acid strength  
increases

$$K_a = 2.9 \times 10^{-8} <$$

$$1.1 \times 10^{-2} <$$

$$\approx 1000 <$$

$$<$$

$$\approx 10^8$$

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# Oxyacids

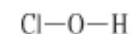
- Contains the group H-O-X.
- For a given series the **acid strength increases** with an increase in the **number of oxygen atoms** attached to the central atom.
- The greater the ability of X to draw electrons toward itself (**electronegative**), the **greater the acidity** of the molecule.

Table 14.8 ► Several Series of Oxyacids and Their  $K_a$  Values

Oxyacid	Structure	$K_a$ Value
HClO <sub>4</sub>		Large ( $\sim 10^7$ )
HClO <sub>3</sub>		$\sim 1$
HClO <sub>2</sub>		$1.2 \times 10^{-2}$
HClO		$3.5 \times 10^{-8}$

Table 14.9 ► Comparison of Electronegativity of X and  $K_a$  Value for a Series of Oxyacids

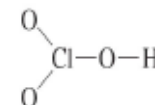
Acid	X	Electronegativity of X	$K_a$ for Acid
HOCl	Cl	3.0	$4 \times 10^{-8}$
HOBr	Br	2.8	$2 \times 10^{-9}$
HOI	I	2.5	$2 \times 10^{-11}$
HOCH <sub>3</sub>	CH <sub>3</sub>	2.3 (for carbon in CH <sub>3</sub> )	$\sim 10^{-15}$



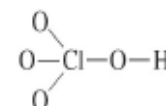
Electron density



Electron density



Electron density



Electron density

## Group Discussion

Select the stronger acid in each pair:

(a) nitrous acid,  $\text{HNO}_2$

nitric acid,  $\text{HNO}_3$

(b)  $\text{Cl}_3\text{CCOOH}$

$\text{BrCH}_2\text{COOH}$

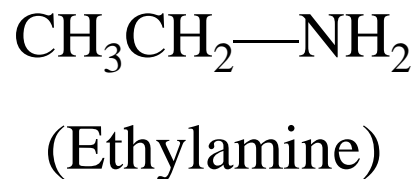
(c) Give a physical explanation of the keys that govern acid strengths?

If the O–H bond is more ionic, the proton is more acidic.

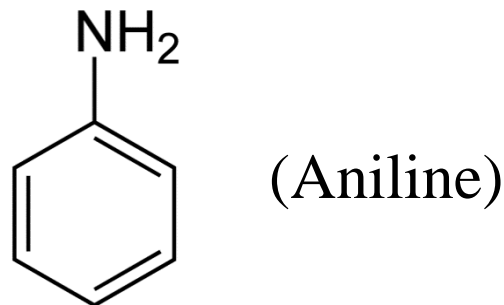
# Strengths of Amines as Bases

- **Aromatic** amines are much weaker bases than **aliphatic** amines.
- This is due in part to the fact that the  $\pi$  electrons in the benzene ring of an aromatic molecule are *delocalized* and can involve the nitrogen atom's lone-pair electrons in the resonance hybrid.
- As a result, the lone-pair electrons are much less likely to accept a proton.

## Aliphatic amine

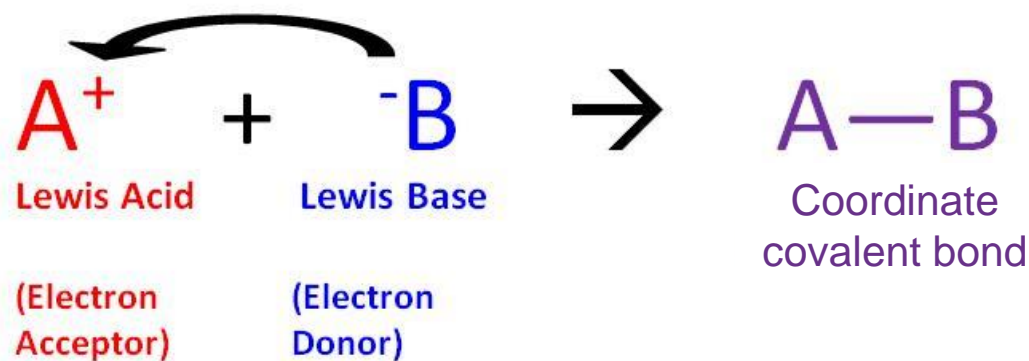


## Aromatic amine



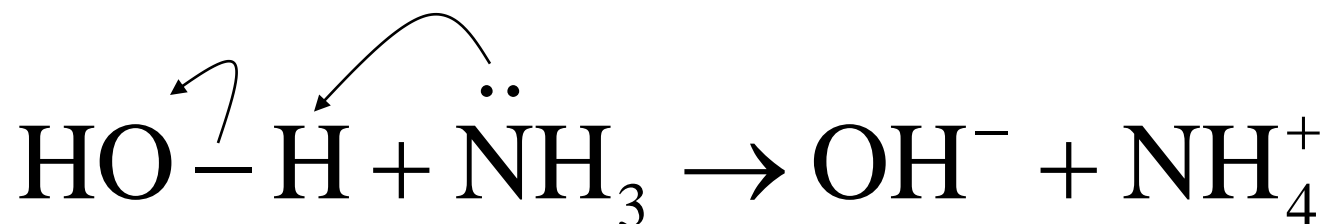
# Lewis Acids and Bases

- There are reactions in nonaqueous solvents, in the gaseous state, and even in the solid state that can be considered acid–base reactions which Brønsted–Lowry theory is not adequate to explain.
- A **Lewis acid** is a species that is an electron-pair acceptor and a **Lewis base** is a species that is an electron-pair donor.

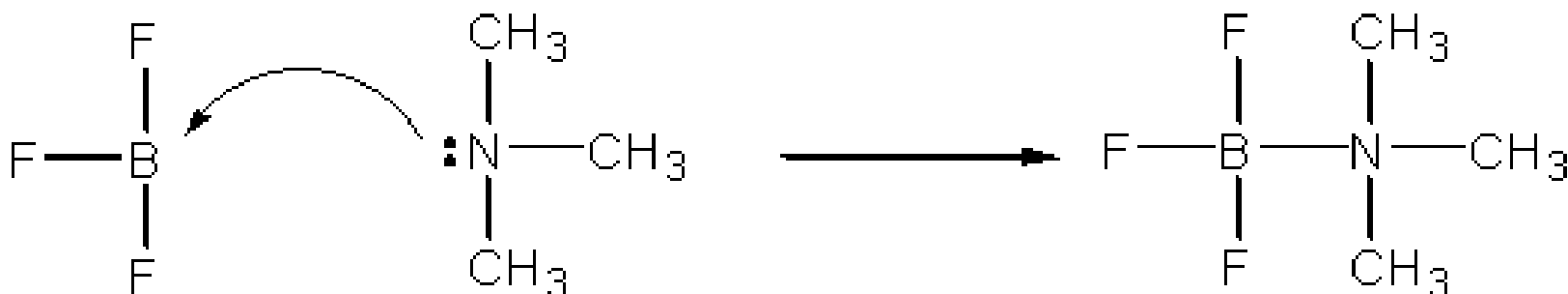




# From Proton Transfer to Electron Transfer



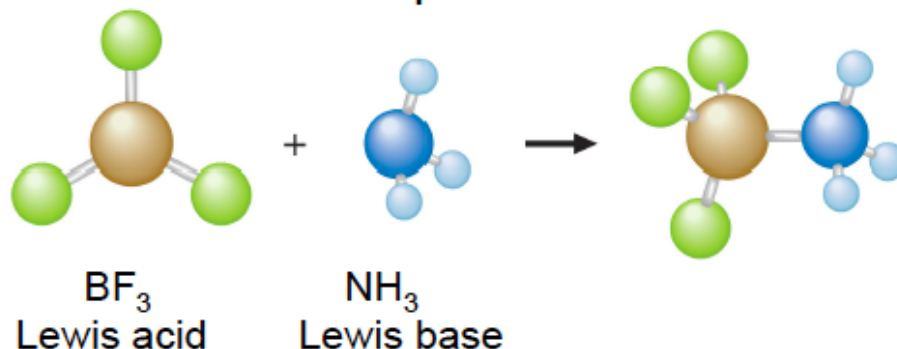
## Acid-Base Reaction without Proton Transfer



# The Lewis Acid-Base Model

Lewis acids and bases

- Lewis acid: electron pair *acceptor*
- Lewis base: electron pair *donor*

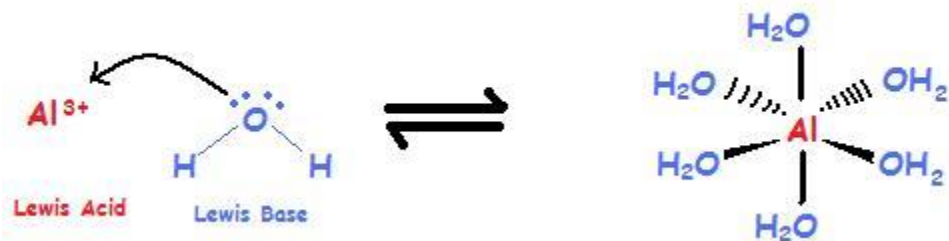


## ▶ Three Models for Acids and Bases

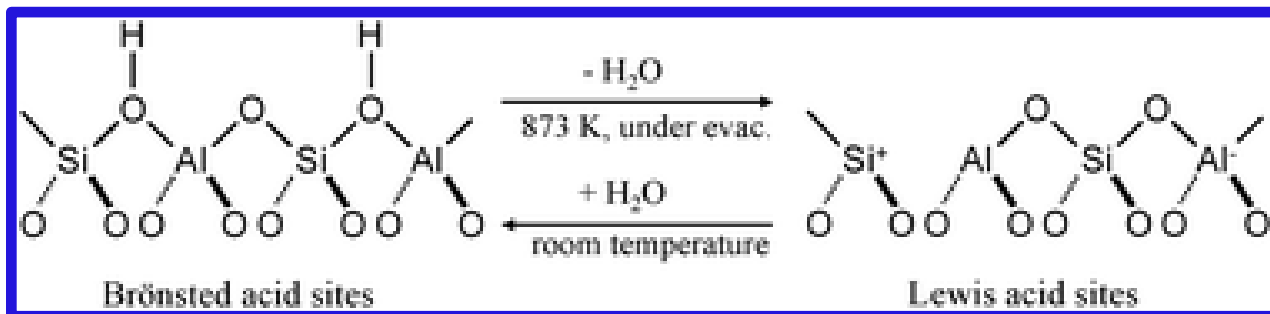
Model	Definition of Acid	Definition of Base
Arrhenius	H <sup>+</sup> producer	OH <sup>-</sup> producer
Brønsted–Lowry	H <sup>+</sup> donor	H <sup>+</sup> acceptor
Lewis	Electron-pair acceptor	Electron-pair donor

# Lewis Acids and Bases

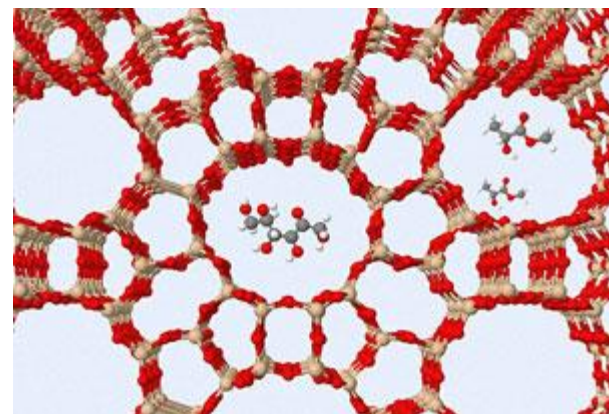
Lewis Acids	Lewis Bases	Reactions
$\text{BF}_3$	$\text{OMe}_2$	$\text{BF}_3 + \text{OMe}_2 \rightarrow \text{BF}_3\text{OMe}_2$
$\text{SiF}_4$	$\text{F}^-$	$\text{SiF}_4 + 2 \text{F}^- \rightarrow \text{SiF}_6^{2-}$
$\text{B}_2\text{H}_6$	$\text{H}^-$	$\text{B}_2\text{H}_6 + 2 \text{H}^- \rightarrow \text{B}_2\text{H}_8^- \rightarrow 2 \text{BH}_4^-$
$\text{AlCl}_3$	$\text{RCl}$	$\text{RCl} + \text{AlCl}_3 \rightarrow \text{R}^+ + \text{AlCl}_4^-$
$\text{SO}_2$	$\text{CaO}$	$\text{CaO(s)} + \text{SO}_2\text{(g)} \rightarrow \text{CaSO}_3\text{(s)}$
$\text{CO}_2$	$\text{H}_2\text{O}$	$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$



# Lewis Acids and Bases



- Common sugars such as glucose (center) can be broken down in the Lewis acid sites of zeotype catalysts into useful lactate esters (right)



M S Holm, S Saravanamurugan, E Taarning, *Science*, 2010, DOI: 10.1126/science.1183990

# Learning Check

Arrange the following 1.0 *M* solutions from lowest to highest pH.

HBr

NaOH

NH<sub>4</sub>Cl

NaCN

NH<sub>3</sub>

HCN

NaCl

HF

Justify your answer.