

Table 16.1 Some Common Acids and Bases and their Household Uses.

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Substance

Use

Acids

Acetic acid, CH_3COOH

Flavoring, preservative

Citric acid, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$

Flavoring

Ascorbic acid, $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$

Vitamin C; nutritional supplement

Aluminum salts, $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

In baking powder, with sodium hydrogen carbonate



Bases

Sodium hydroxide (lye), NaOH

Oven and drain cleaners

Ammonia, NH_3

Household cleaner

Sodium carbonate, Na_2CO_3

Water softener, grease remover

Sodium hydrogen carbonate, NaHCO_3

Fire extinguisher, rising agent in cake mixes (baking soda), mild antacid

Sodium phosphate, Na_3PO_4

Cleaner for surfaces before painting or wallpapering



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16.1

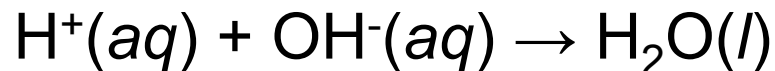
Arrhenius Acid-Base Definition

This is the earliest acid-base definition, which classifies these substances in terms of their behavior in **water**.

An **acid** is a substance with H in its formula that dissociates to yield H_3O^+ .

A **base** is a substance with OH in its formula that dissociates to yield OH^- .

When an acid reacts with a base, they undergo neutralization:



Brønsted-Lowry Acid-Base Definition

An acid is a ***proton donor***, any species that donates an ***H⁺ ion***.

- An acid must contain H in its formula.

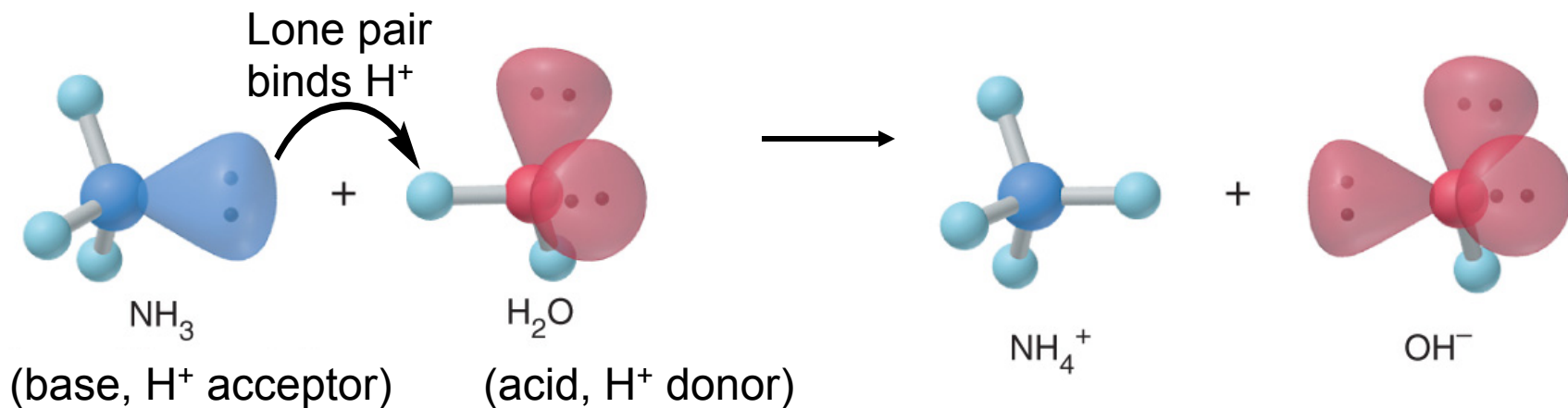
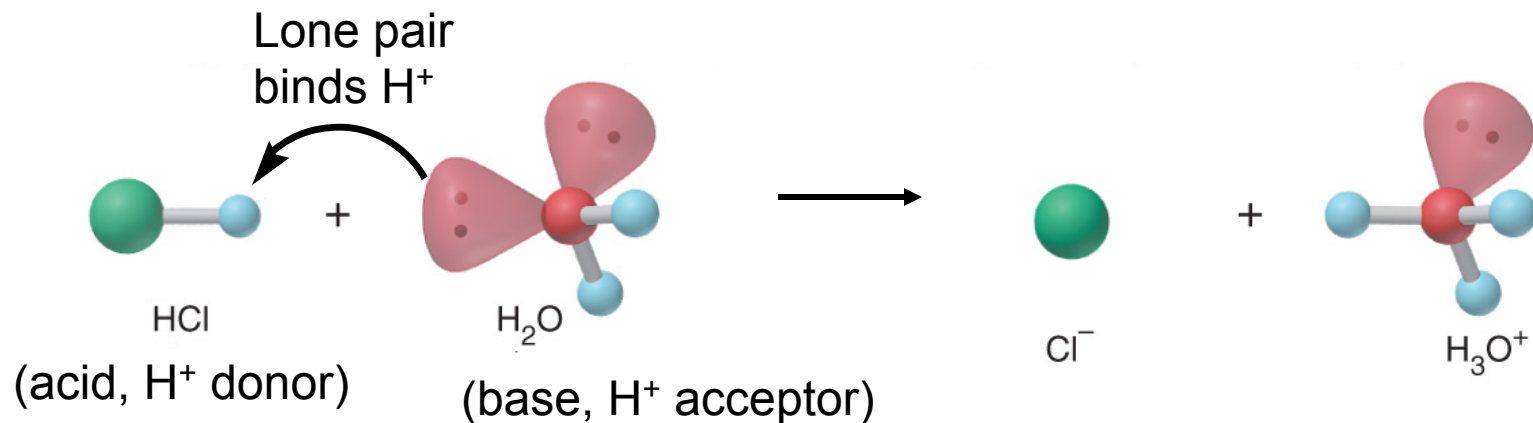
A base is a ***proton acceptor***, any species that accepts an ***H⁺ ion***.

- A base must contain a ***lone pair of electrons*** to bond to H⁺.

An acid-base reaction is a ***proton-transfer process***.

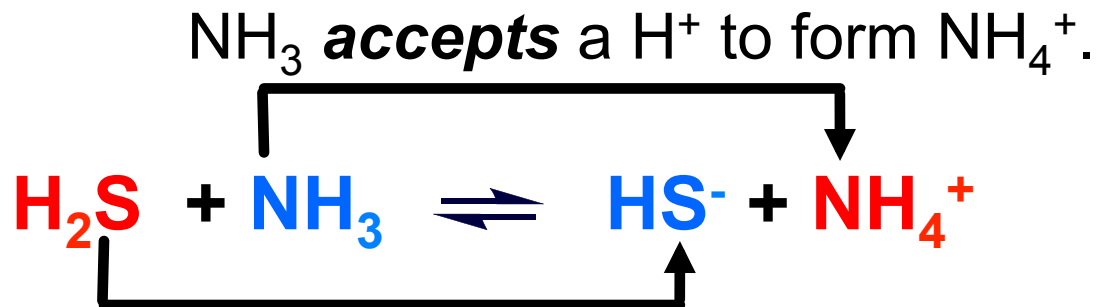


Figure 16.2 Dissolving of an acid or base in water as a Brønsted-Lowry acid-base reaction.



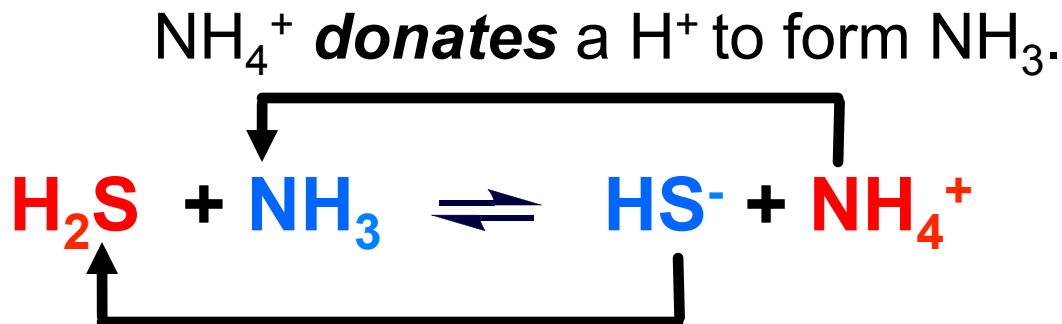
Conjugate Acid-Base Pairs

In the *forward* reaction:



H_2S *donates* a H^+ to form HS^- .

In the *reverse* reaction:



HS^- *accepts* a H^+ to form H_2S .



Conjugate Acid-Base Pairs



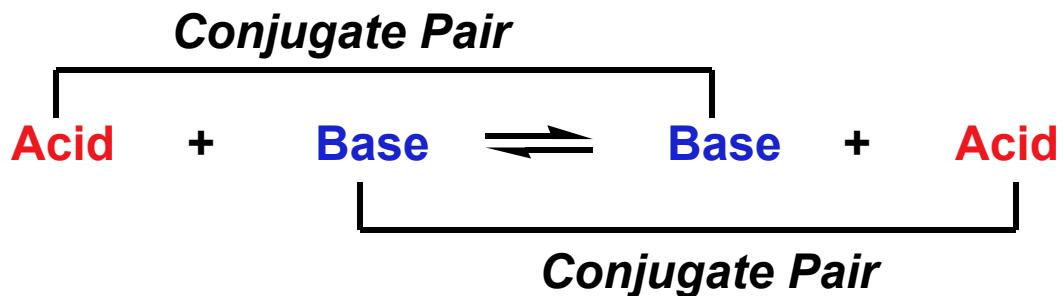
H₂S and HS⁻ are a **conjugate acid-base pair**.
HS⁻ is the **conjugate base** of the acid H₂S.

NH₃ and NH₄⁺ are a conjugate acid-base pair:
NH₄⁺ is the **conjugate acid** of the base NH₃.

A Brønsted-Lowry acid-base reaction occurs when an acid and a base react to form their **conjugate base** and **conjugate acid**, respectively.



Table 16.2 The Conjugate Pairs in some Acid-Base Reactions



Reaction 1	HF	+	H ₂ O	⇌	F ⁻	+	H ₃ O ⁺
Reaction 2	HCOOH	+	CN ⁻	⇌	HCOO ⁻	+	HCN
Reaction 3	NH ₄ ⁺	+	CO ₃ ²⁻	⇌	NH ₃	+	HCO ₃ ⁻
Reaction 4	H ₂ PO ₄ ⁻	+	OH ⁻	⇌	HPO ₄ ²⁻	+	H ₂ O
Reaction 5	H ₂ SO ₄	+	N ₂ H ₅ ⁺	⇌	HSO ₄ ⁻	+	N ₂ H ₆ ²⁺
Reaction 6	HPO ₄ ²⁻	+	SO ₃ ²⁻	⇌	PO ₄ ³⁻	+	HSO ₃ ⁻



Sample Problem 16.1

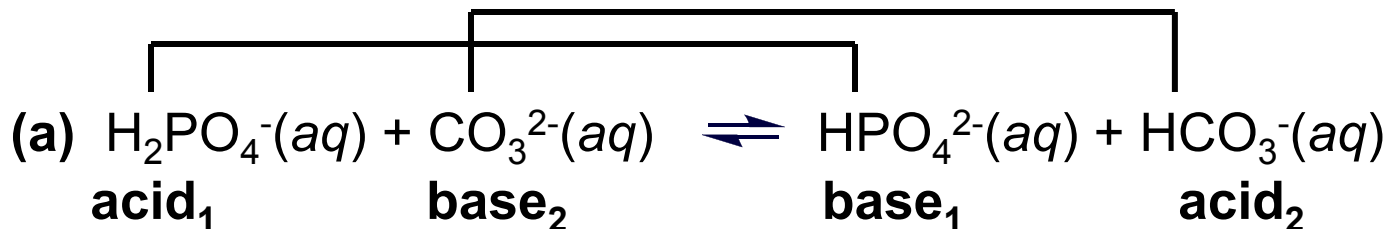
Identifying Conjugate Acid-Base Pairs

PROBLEM: The following reactions are important environmental processes. Identify the conjugate acid-base pairs.



PLAN: To find the conjugate pairs, we find the species that donated an H^+ (acid) and the species that accepted it (base). The acid donates an H^+ to become its conjugate base, and the base accepts an H^+ to become its conjugate acid.

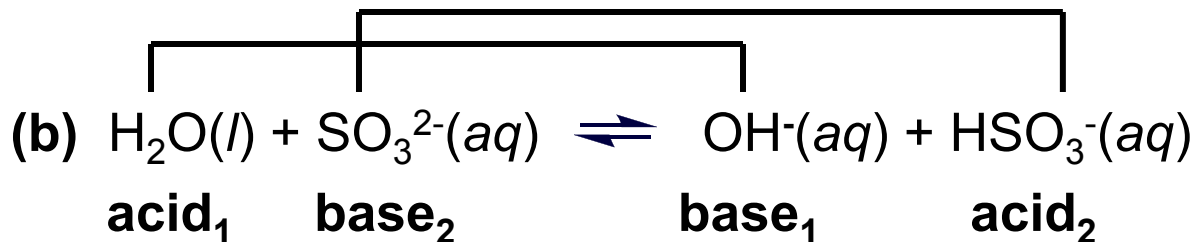
SOLUTION:



The conjugate acid-base pairs are $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and $\text{CO}_3^{2-}/\text{HCO}_3^-$.



Sample Problem 16.1



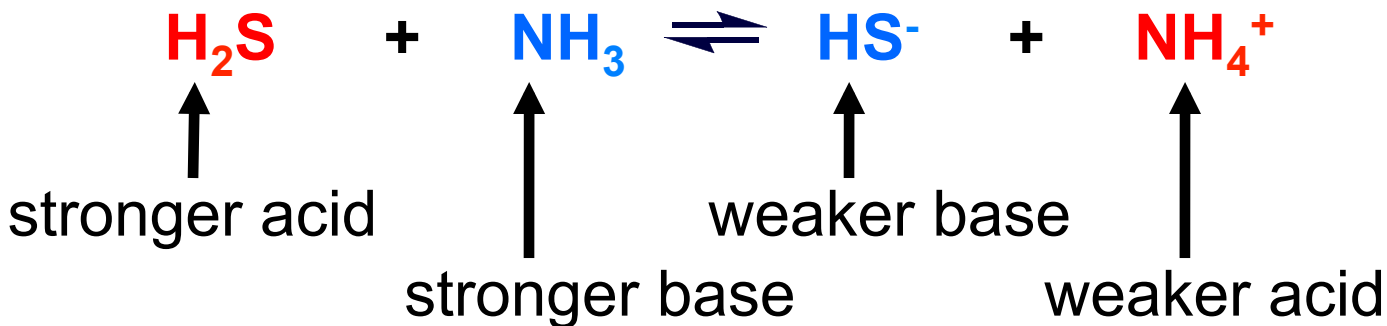
The conjugate acid-base pairs are H₂O/OH⁻ and SO₃²⁻/HSO₃⁻.



Net Direction of Reaction

The **net** direction of an acid-base reaction depends on the **relative** strength of the acids and bases involved.

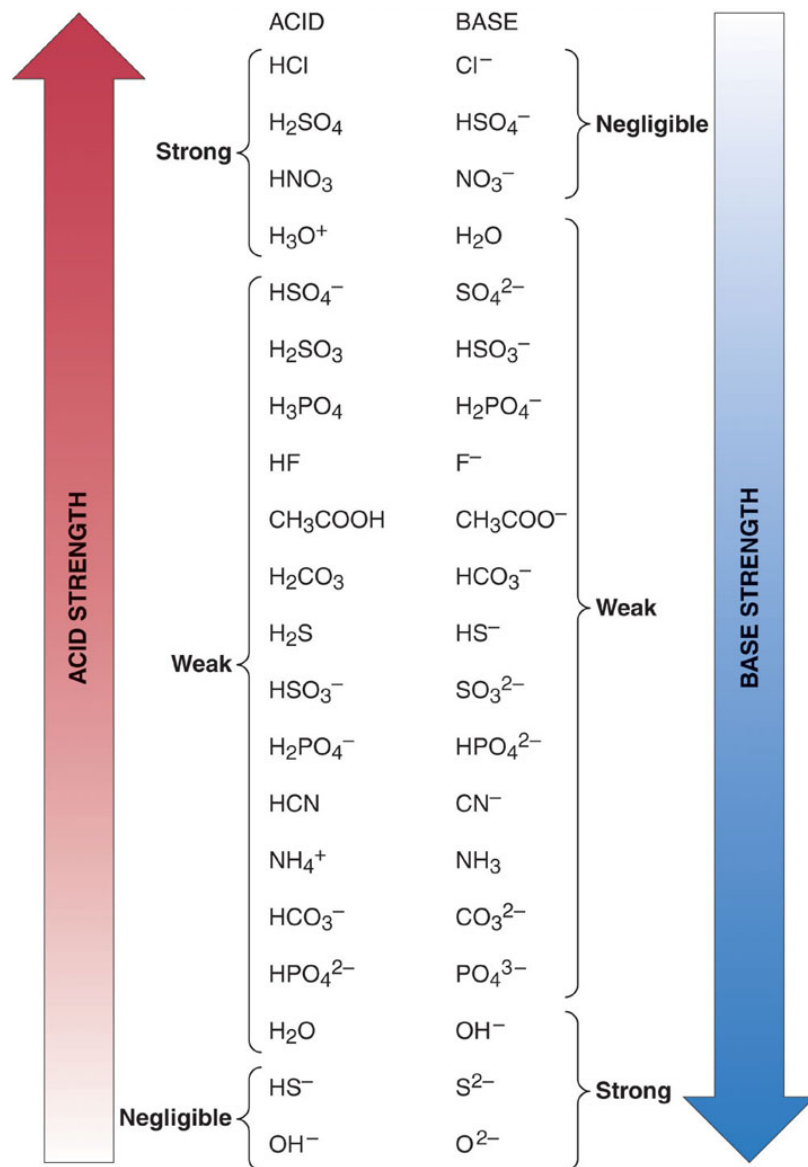
A reaction will favor the formation of the **weaker** acid and base.



This reaction favors the formation of the **products**.



Figure 16.3 Strengths of conjugate acid-base pairs.



The stronger the acid is, the weaker its conjugate base. When an acid reacts with a base that is farther down the list, the reaction proceeds to the **right** ($K_c > 1$).



Sample Problem 16.2

Predicting the Net Direction of an Acid-Base Reaction

PROBLEM: Predict the net direction and whether K is greater or less than 1 for each of the following reactions (assume equal initial concentrations of all species):



PLAN: We identify the conjugate acid-base pairs and consult figure 18.8 to see which acid and base are stronger. The reaction favors the formation of the weaker acid and base.

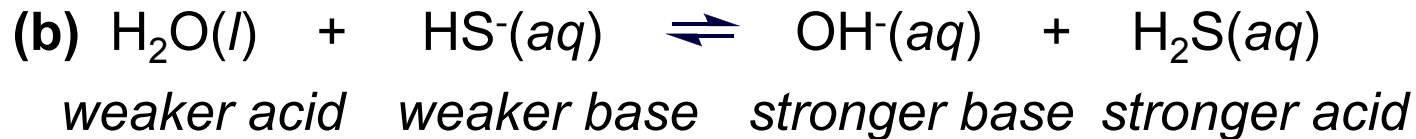
SOLUTION:



The net direction for this reaction is to the right, so $K > 1$.



Sample Problem 16.2



The net direction for this reaction is to the left, so $K < 1$.

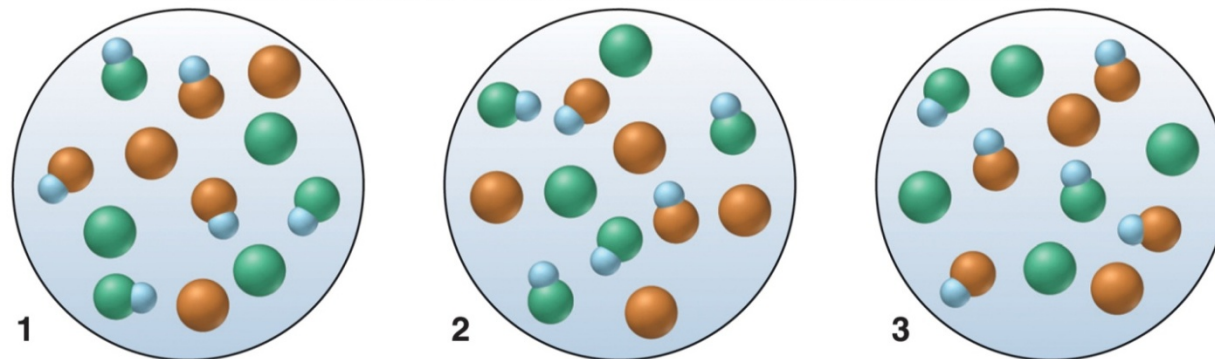


Sample Problem 16.3

Using Molecular Scenes to Predict the Net Direction of an Acid-Base Reaction

PROBLEM: Given that 0.10 M of HX (*blue and green*) has a pH of 2.88, and 0.10 M HY (*blue and orange*) has a pH 3.52, which scene best represents the final mixture after equimolar solutions of HX and Y^- are mixed?

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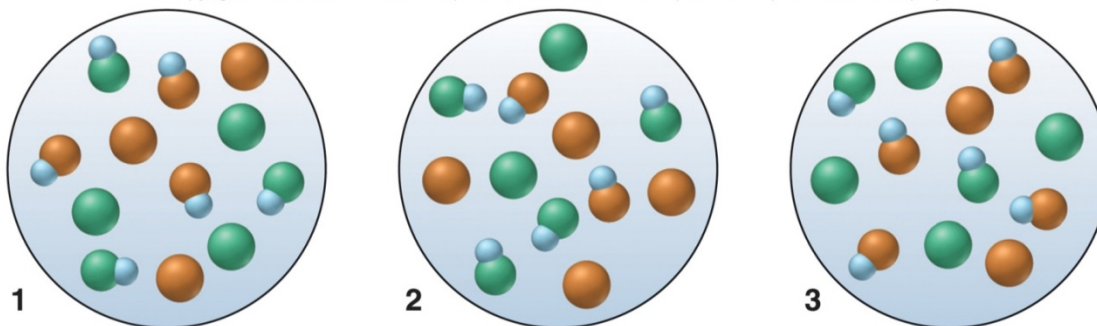
PLAN: A stronger acid and base yield a weaker acid and base, so we have to determine the relative acid strengths of HX and HY to choose the correct molecular scene. The concentrations of the acid solutions are equal, so we can recognize the stronger acid by comparing the pH values of the two solutions.



Sample Problem 16.3

SOLUTION:

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The HX solution has a lower pH than the HY solution, so HX is the stronger acid and Y^- is the stronger base. The reaction of HX and Y^- has a $K_c > 1$, which means the equilibrium mixture will contain more HY than HX.

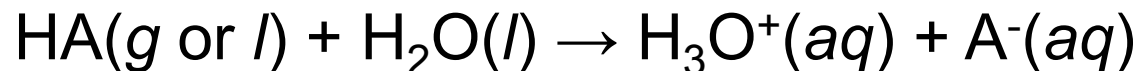
Scene 1 has equal numbers of HX and HY, which could occur if the acids were of equal strength. Scene 2 shows fewer HY than HX, which would occur if HY were the stronger acid.

Scene 3 is consistent with the relative acid strengths, because it contains more HY than HX.



Strong and Weak Acids

A **strong** acid dissociates **completely** into ions in water:



A dilute solution of a **strong** acid contains **no HA molecules**.

A **weak** acid dissociates **slightly** to form ions in water:



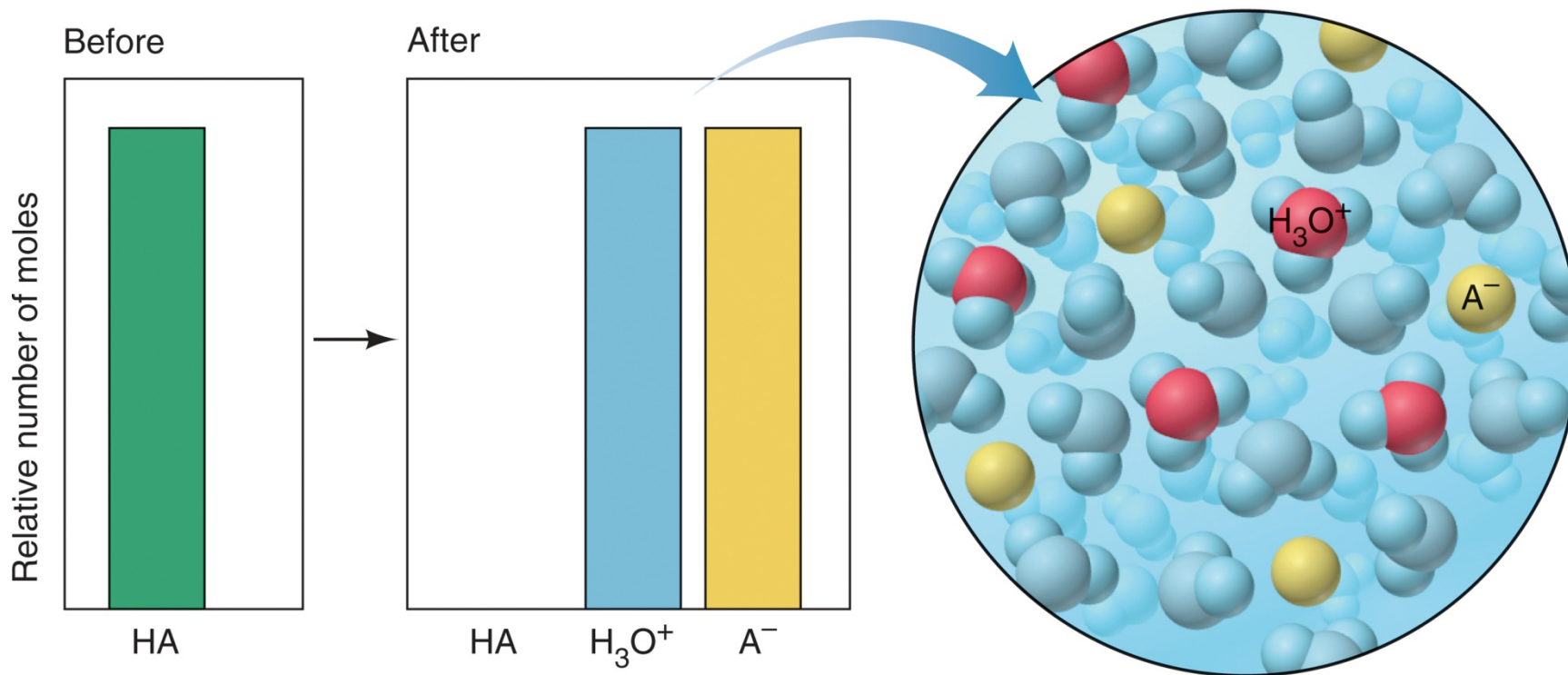
In a dilute solution of a **weak** acid, **most HA molecules are undissociated**.

$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \text{ has a very } \mathbf{small} \text{ value.}$$



Figure 16.4A The extent of dissociation for strong acids.

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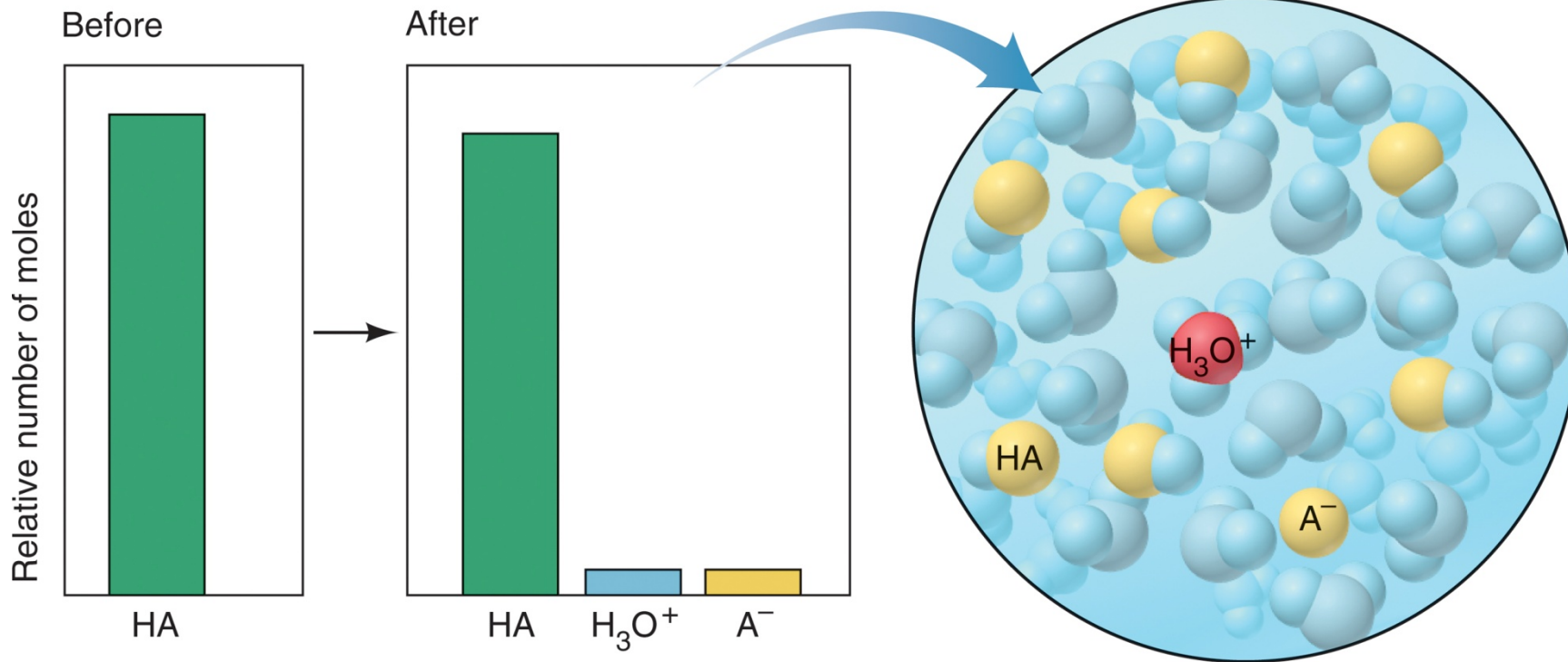


There are no HA molecules in solution.



Figure 16.4B The extent of dissociation for weak acids.

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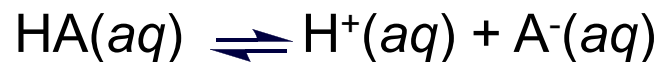
Most HA molecules are undissociated.



The Acid Dissociation Constant, K_a



OR



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

The value of K_a is an indication of acid strength.

Stronger acid \longrightarrow **higher $[\text{H}_3\text{O}^+]$** \longrightarrow **larger K_a**

Weaker acid \longrightarrow **lower % dissociation of HA** \longrightarrow **smaller K_a**



Table 16.4 K_a Values for some Monoprotic Acids at 25°C

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Name (Formula)	Lewis Structure*	K_a	pK_a
Chlorous acid (HClO ₂)	$\text{H}-\ddot{\text{O}}-\ddot{\text{Cl}}=\ddot{\text{O}}$	1.1×10^{-2}	1.96
Nitrous acid (HNO ₂)	$\text{H}-\ddot{\text{O}}-\ddot{\text{N}}=\ddot{\text{O}}$	7.1×10^{-4}	3.15
Hydrofluoric acid (HF)	$\text{H}-\ddot{\text{F}}:$	6.8×10^{-4}	3.17
Formic acid (HCOOH)	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{H}-\text{C}-\ddot{\text{O}}-\text{H} \end{array}$	1.8×10^{-4}	3.74
Acetic acid (CH ₃ COOH)	$\begin{array}{c} \text{H} \quad \text{:O:} \\ \quad \parallel \\ \text{H}-\text{C}-\text{C}-\ddot{\text{O}}-\text{H} \\ \\ \text{H} \end{array}$	1.8×10^{-5}	4.74
Propanoic acid (CH ₃ CH ₂ COOH)	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{:O:} \\ \quad \quad \parallel \\ \text{H}-\text{C}-\text{C}-\text{C}-\ddot{\text{O}}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	1.3×10^{-5}	4.89
Hypochlorous acid (HClO)	$\text{H}-\ddot{\text{O}}-\ddot{\text{Cl}}:$	2.9×10^{-8}	7.54
Hydrocyanic acid (HCN)	$\text{H}-\text{C}\equiv\text{N}:$	6.2×10^{-10}	9.21



*Red type indicates the ionizable proton; all atoms have zero formal charge.



Classifying the Relative Strengths of Acids

- **Strong acids** include
 - the hydrohalic acids (HCl, HBr, and HI) and
 - oxoacids in which the number of O atoms exceeds the number of ionizable protons by two or more (eg., HNO₃, H₂SO₄, HClO₄.)
- **Weak acids** include
 - the hydrohalic acid HF,
 - acids in which H is not bonded to O or to a halogen (eg., HCN),
 - oxoacids in which the number of O atoms equals or exceeds the number of ionizable protons by one (eg., HClO, HNO₂), and
 - carboxylic acids, which have the general formula RCOOH (eg., CH₃COOH and C₆H₅COOH.)



Classifying the Relative Strengths of Bases

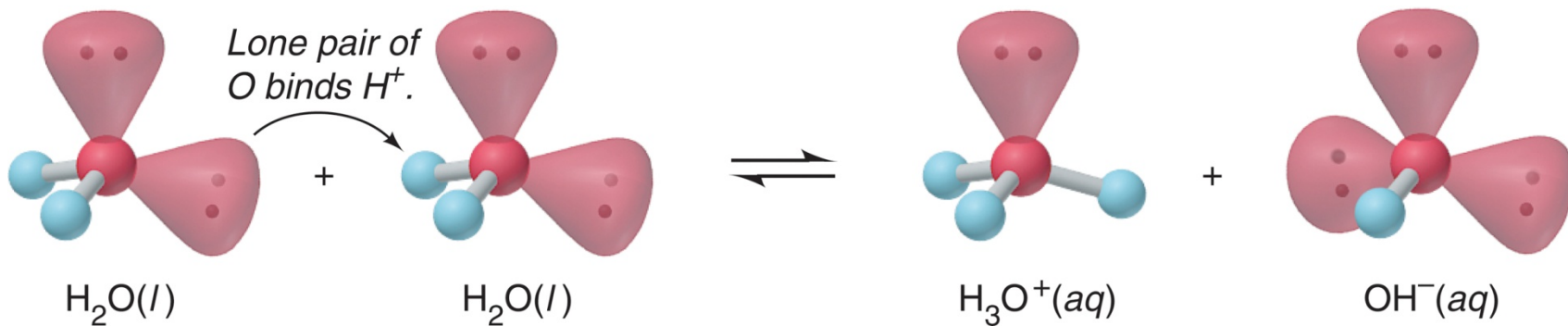
- **Strong bases** include
 - water-soluble compounds containing O^{2-} or OH^- ions.
 - The cations are usually those of the most active metals:
 - M_2O or MOH , where M = Group 1 metal (Li, Na, K, Rb, Cs)
 - MO or $M(OH)_2$ where M = group 2 metal (Ca, Sr, Ba).
- **Weak bases** include
 - ammonia (NH_3),
 - amines, which have the general formula $R\ddot{N}H_2$, $R_2\ddot{N}H$, or $R_3\ddot{N}$
 - The common structural feature is an N atom with a lone electron pair.



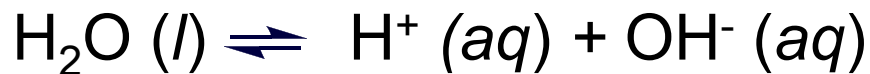
16.2

Autoionization of Water

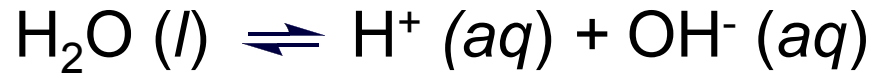
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Water dissociates very slightly into ions in an equilibrium process known as **autoionization** or **self-ionization**.



The Ion-Product Constant for Water (K_w)



$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

In pure water,
 $[\text{H}^+] = [\text{OH}^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ (at } 25^\circ\text{C)}$

Both ions are present in all aqueous systems.



A change in $[\text{H}_3\text{O}^+]$ causes an inverse change in $[\text{OH}^-]$, and vice versa.

Higher $[\text{H}^+]$ \longrightarrow lower $[\text{OH}^-]$

Higher $[\text{OH}^-]$ \longrightarrow lower $[\text{H}^+]$

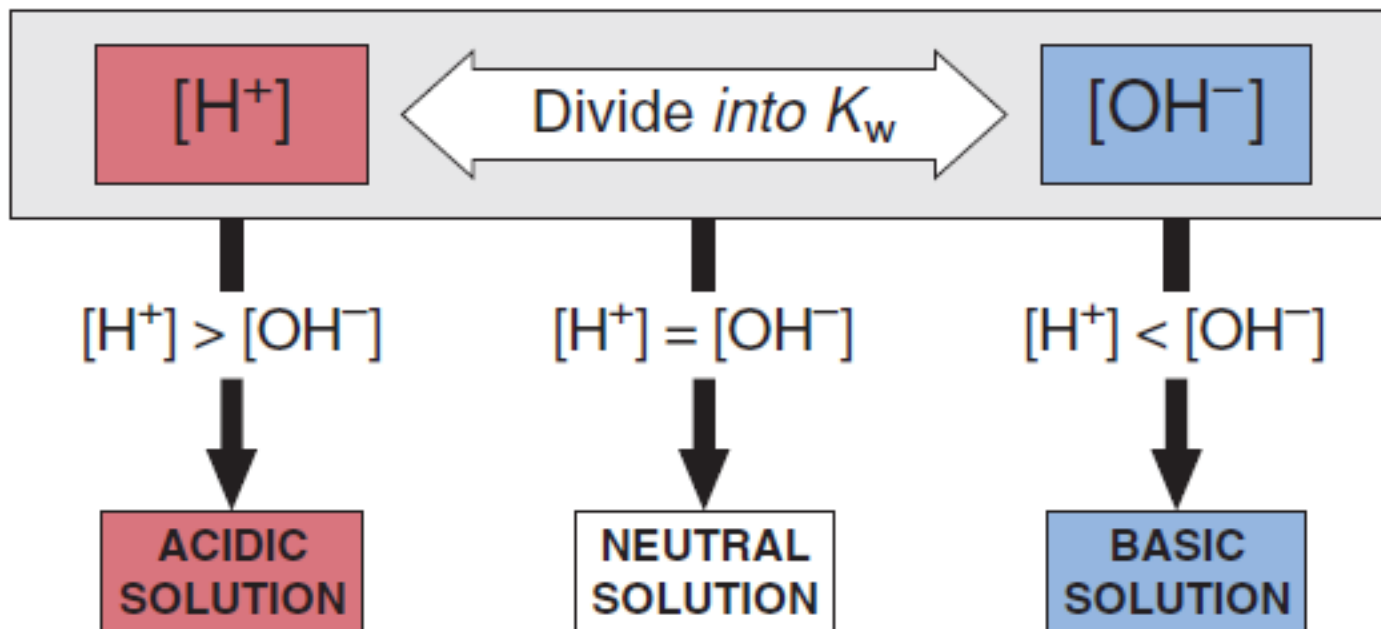
We can define the terms “acidic” and “basic” in terms of the relative concentrations of H_3O^+ and OH^- ions:

In an acidic solution,	$[\text{H}^+] > [\text{OH}^-]$
In a neutral solution,	$[\text{H}^+] = [\text{OH}^-]$
In basic solution,	$[\text{H}^+] < [\text{OH}^-]$



Figure 16.6 The relationship between $[H_3O^+]$ and $[OH^-]$ and the relative acidity of solutions.

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Sample Problem 16.5

Calculating $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ in an Aqueous Solution

PROBLEM: A research chemist adds a measured amount of HCl gas to pure water at 25°C and obtains a solution with $[\text{H}_3\text{O}^+] = 3.0 \times 10^{-4} \text{ M}$. Calculate $[\text{OH}^-]$. Is the solution neutral, acidic, or basic?

PLAN: We use the known value of K_w at 25°C (1.0×10^{-14}) and the given $[\text{H}^+]$ to solve for $[\text{OH}^-]$. We can then compare $[\text{H}_3\text{O}^+]$ with $[\text{OH}^-]$ to determine whether the solution is acidic, basic, or neutral.

SOLUTION:

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

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-4}} = \boxed{3.3 \times 10^{-11} \text{ M}}$$

$[\text{H}^+]$ is $>$ $[\text{OH}^-]$ and the solution is acidic.



The pH Scale

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

The pH of a solution indicates its relative acidity:

In an acidic solution,	pH < 7.00
In a neutral solution,	pH = 7.00
In basic solution,	pH > 7.00

The **higher** the pH, the **lower** the $[\text{H}^+]$ and the **less acidic** the solution.



pH, pOH, and pK_w

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

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

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

$$\text{p}K_w = \text{pH} + \text{pOH} = 14.00 \text{ at } 25^\circ\text{C}$$

$\text{pH} + \text{pOH} = \text{p}K_w$ for any aqueous solution at any temperature.

Since K_w is a constant, the values of pH, pOH, $[H^+]$, and $[OH^-]$ are interrelated:

- If $[H^+]$ increases, $[OH^-]$ decreases (and vice versa).
- If pH increases, pOH decreases (and vice versa).



Figure 16.8 The relations among $[H_3O^+]$, pH, $[OH^-]$, and pOH.

	$[H_3O^+]$	pH	$[OH^-]$	pOH
↑ MORE BASIC	1.0×10^{-15}	15.00	1.0×10^1	-1.00
	1.0×10^{-14}	14.00	1.0×10^0	0.00
	1.0×10^{-13}	13.00	1.0×10^{-1}	1.00
	BASIC 1.0×10^{-12}	12.00	1.0×10^{-2}	2.00
	1.0×10^{-11}	11.00	1.0×10^{-3}	3.00
	1.0×10^{-10}	10.00	1.0×10^{-4}	4.00
	1.0×10^{-9}	9.00	1.0×10^{-5}	5.00
	1.0×10^{-8}	8.00	1.0×10^{-6}	6.00
NEUTRAL	1.0×10^{-7}	7.00	1.0×10^{-7}	7.00
↓ MORE ACIDIC	1.0×10^{-6}	6.00	1.0×10^{-8}	8.00
	1.0×10^{-5}	5.00	1.0×10^{-9}	9.00
	1.0×10^{-4}	4.00	1.0×10^{-10}	10.00
	ACIDIC 1.0×10^{-3}	3.00	1.0×10^{-11}	11.00
	1.0×10^{-2}	2.00	1.0×10^{-12}	12.00
	1.0×10^{-1}	1.00	1.0×10^{-13}	13.00
	1.0×10^0	0.00	1.0×10^{-14}	14.00
	1.0×10^1	-1.00	1.0×10^{-15}	15.00



Sample Problem 16.6

Calculating $[H^+]$, pH, $[OH^-]$, and pOH

PROBLEM: In an art restoration project, a conservator prepares copper-plate etching solutions by diluting concentrated HNO_3 to 2.0 mol/L, 0.30 mol/L, and 0.0063 mol/L HNO_3 . Calculate $[H^+]$, pH, $[OH^-]$, and pOH of the three solutions at 25°C.

PLAN: HNO_3 is a strong acid so it dissociates completely, and $[H^+] = [HNO_3]_{init}$. We use the given concentrations and the value of K_w at 25°C to find $[H^+]$ and $[OH^-]$. We can then calculate pH and pOH.

SOLUTION:

Calculating the values for 2.0 mol/L HNO_3 :

$$[H^+] = 2.0 \text{ M} \quad \text{pH} = -\log[H_3O^+] = -\log(2.0) = \mathbf{-0.30}$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{2.0} = \mathbf{5.0 \times 10^{-15} \text{ mol/L}}$$

$$\text{pOH} = -\log[OH^-] = -\log(5.0 \times 10^{-15}) = \mathbf{14.30}$$



Sample Problem 16.6

Calculating the values for 0.30 mol/L HNO₃:

$$[\text{H}^+] = 0.30 \text{ M} \quad \text{pH} = -\log[\text{H}^+] = -\log(0.30) = \mathbf{0.52}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{0.30} = \mathbf{3.3 \times 10^{-14} \text{ mol/L}}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(3.3 \times 10^{-14}) = \mathbf{13.48}$$

Calculating the values for 0.0063 mol/L HNO₃:

$$[\text{H}_3\text{O}^+] = 0.0063 \text{ mol/L} \quad \text{pH} = -\log[\text{H}^+] = -\log(0.0063) = \mathbf{2.20}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{0.0063} = \mathbf{1.6 \times 10^{-12} \text{ mol/L}}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.6 \times 10^{-12}) = \mathbf{11.80}$$

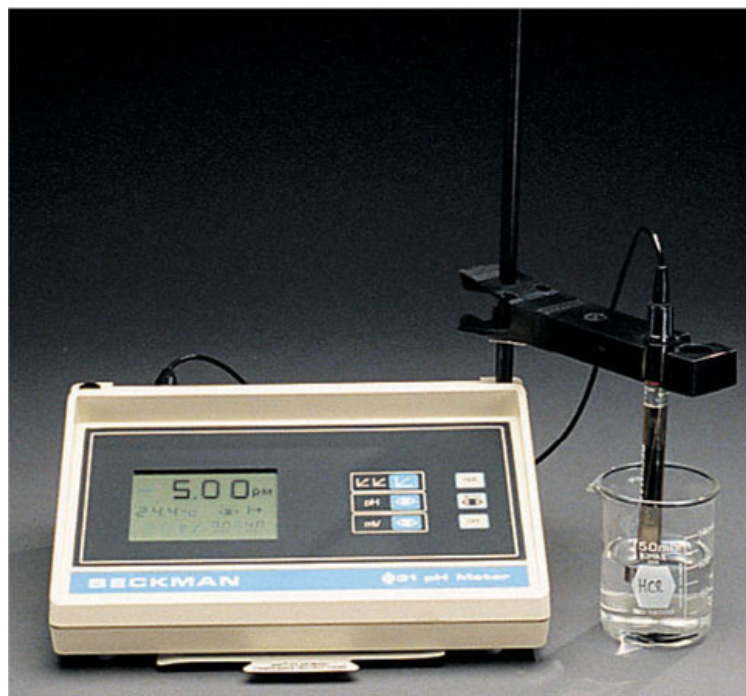


Figure 16.9 Methods for measuring the pH of an aqueous solution.

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pH paper



pH meter



16.3

Weak Bases

A Brønsted-Lowry base is a species that accepts an H^+ . For a weak base that dissolves in water:



The ***base-dissociation*** or ***base-ionization constant*** is given by:

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

Note that ***no base actually dissociates*** in solution, but ***ions*** are produced when the base reacts with H_2O .



Figure 16.10 Abstraction of a proton from water by the base methylamine.

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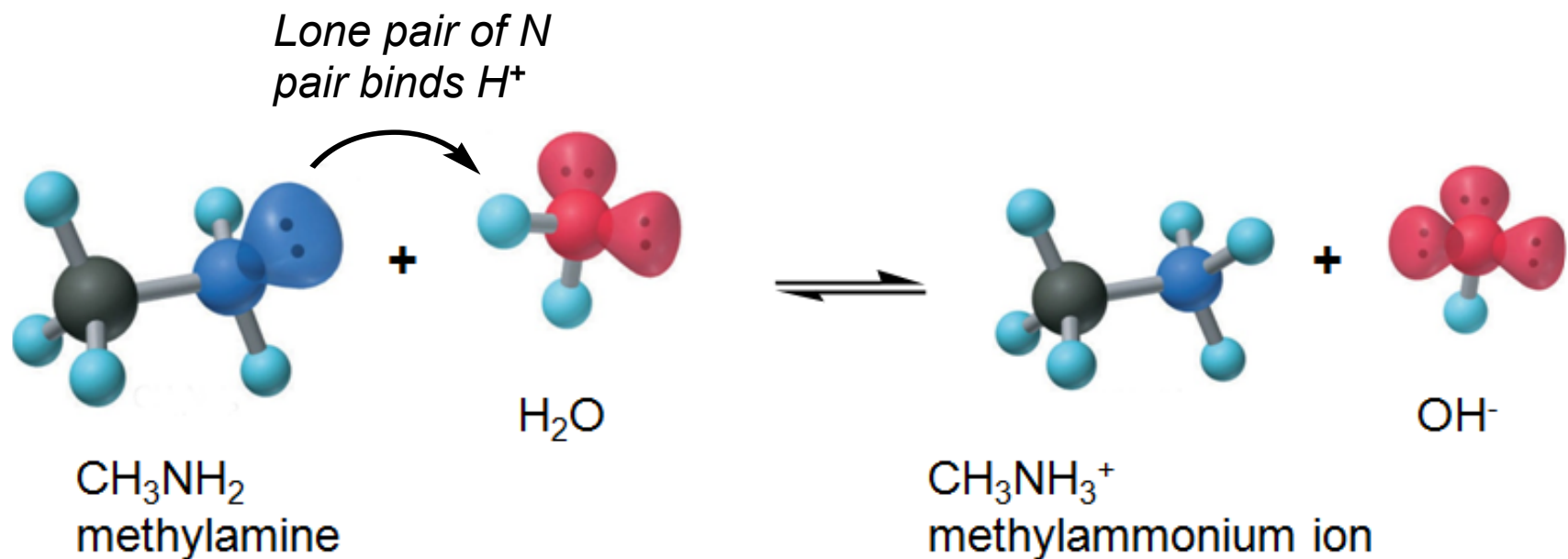


Table 16.6 K_b Values for Some Molecular (Amine) Bases at 25°C

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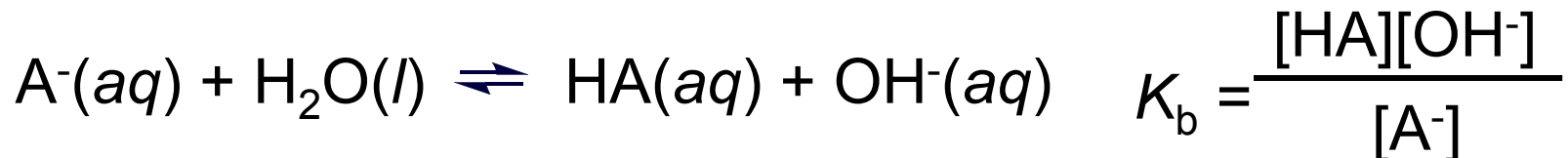
Name (Formula)	Lewis Structure*	K_b
Diethylamine [(CH ₃ CH ₂) ₂ NH]		8.6×10^{-4}
Dimethylamine [(CH ₃) ₂ NH]		5.9×10^{-4}
Methylamine (CH ₃ NH ₂)		4.4×10^{-4}
Ammonia (NH ₃)		1.76×10^{-5}
Pyridine (C ₅ H ₅ N)		1.7×10^{-9}
Aniline (C ₆ H ₅ NH ₂)		4.0×10^{-10}

BASE STRENGTH

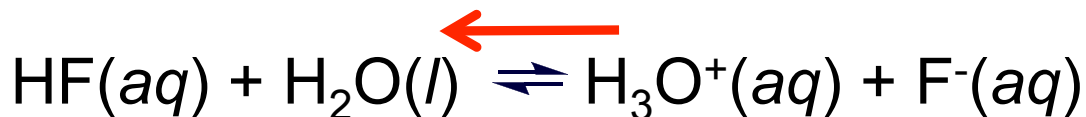
*Blue type indicates the basic nitrogen and its lone pair.

Anions of Weak Acids as Weak Bases

The *anions* of weak acids often function as *weak bases*.



A solution of HA is *acidic*, while a solution of A⁻ is *basic*.

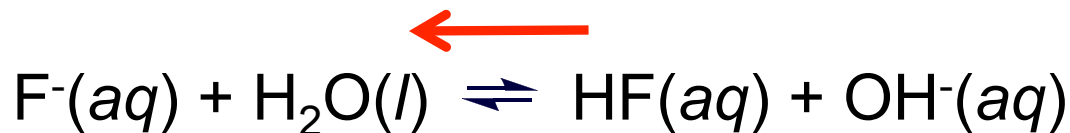


HF is a weak acid, so this equilibrium lies to the left.

$[HF] \gg [F^{-}]$, and $[H_3O^{+}]_{\text{from HF}} \gg [OH^{-}]_{\text{from H}_2\text{O}}$;
the solution is therefore *acidic*.



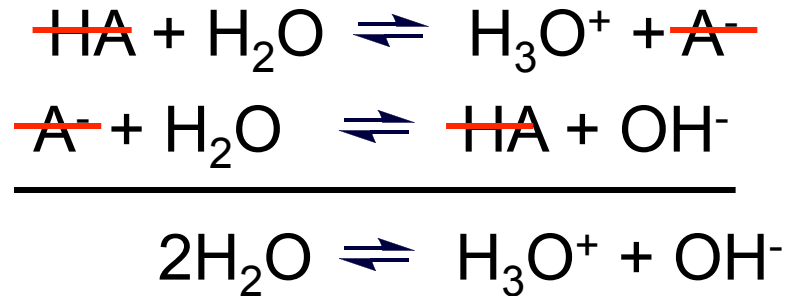
If NaF is dissolved in H₂O, it dissolves completely, and F⁻ can act as a weak base:



HF is a weak acid, so this equilibrium also lies to the left. [F⁻] >> [HF], and [OH⁻]_{from F⁻} >> [H₃O⁺]_{from H₂O} ; the solution is therefore **basic**.



K_a and K_b for a Conjugate Acid-Base Pair



K_c for the overall equation = $K_1 \times K_2$, so

$$\frac{[\text{H}_3\text{O}^+]\cancel{[\text{A}^-}]}{\cancel{[\text{HA}]}} \times \frac{\cancel{[\text{HA}]}\text{[OH}^-]}{\cancel{[\text{A}^-]}} = [\text{H}_3\text{O}^+][\text{OH}^-]$$
$$K_a \quad \times \quad K_b \quad = \quad K_w$$

This relationship is true for any ***conjugate acid-base pair***.



Solving Problems Involving Weak-Acid/Base Equilibria

The notation system

- Molar concentrations are indicated by [].
- A bracketed formula with ***no subscript*** indicates an ***equilibrium concentration***.

The assumptions

- $[\text{H}_3\text{O}^+]$ from the autoionization of H_2O is negligible.
- A weak acid has a small K_a and its dissociation is negligible. $[\text{HA}] \approx [\text{HA}]_{\text{init}}$.
OR for weak bases, $[\text{B}] \approx [\text{B}]_{\text{init}}$.



Sample Problem 16.7

Finding K_a of a Weak Acid from the Solution pH

PROBLEM: A substance called 2-phenylacetic acid ($C_6H_5CH_2COOH$, simplified here as HPAC) builds up in the blood of persons with phenylketonuria, an inherited disorder that, if untreated, causes mental retardation and death. A study of the acid shows that the pH of 0.12 mol/L HPAC is 2.62. What is the K_a of phenylacetic acid?

PLAN: We start with the balanced dissociation equation and write the expression for K_a . We assume that $[H_3O^+]$ from H_2O is negligible and use the given pH to find $[H_3O^+]$, which equals $[PAC^-]$ and $[HPAC]_{dissoc}$. We assume that $[HPAC] \approx [HPAC]_{init}$ because HPAC is a weak acid.



$$K_a = \frac{[H_3O^+][PAC^-]}{[HPAC]}$$



Sample Problem 16.7



Initial	0.12	-	0	0
Change	- x	-	+ x	+ x
Equilibrium	$0.12 - x$	-	x	x

$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 2.4 \times 10^{-3} \text{ mol/L}$ which is $\gg 10^{-7}$ (the $[\text{H}_3\text{O}^+]$ from water)

$$x \approx 2.4 \times 10^{-3} \text{ M} \approx [\text{H}_3\text{O}^+] \approx [\text{PAc}^-] \quad [\text{HPAc}] = 0.12 - x \approx 0.12 \text{ mol/L}$$

$$\text{So } K_a = \frac{(2.4 \times 10^{-3})(2.4 \times 10^{-3})}{0.12} = \boxed{4.8 \times 10^{-5}}$$

Checking the assumptions by finding the percent error in concentration:

$$[\text{H}_3\text{O}^+]_{\text{from H}_2\text{O}} = \frac{1 \times 10^{-7} \text{ mol/L}}{2.4 \times 10^{-3} \text{ mol/L}} \times 100 = 4 \times 10^{-3} \% (< 5\%; \text{ assumption is justified}).$$

$$[\text{HPAc}]_{\text{dissoc}} = \frac{2.4 \times 10^{-3} \text{ mol/L}}{0.12 \text{ mol/L}} \times 100 = 2.0 \% (< 5\%; \text{ assumption is justified}).$$



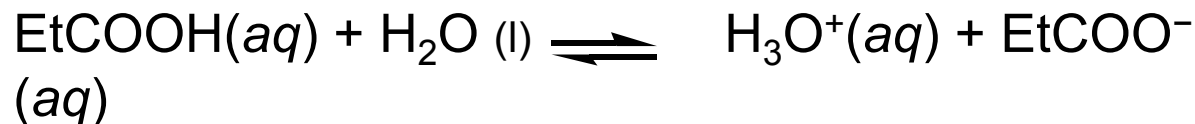
Sample Problem 16.8

Determining Concentration from K_a and Initial [HA]

PROBLEM: Propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$, which we simplify as EtCOOH) is a carboxylic acid whose salts are used to retard mold growth in foods. What is the $[\text{H}_3\text{O}^+]$ of 0.10 mol/L EtCOOH ($K_a = 1.3 \times 10^{-5}$)?

PLAN: We write a balanced equation and the expression for K_a . We know $[\text{EtCOOH}]_{\text{init}}$ but not $[\text{EtCOOH}]$ (i.e., the concentration at equilibrium). We define x as $[\text{EtCOOH}]_{\text{dissoc}}$ and set up a reaction table. We assume that, since EtCOOH has a small K_a value, it dissociates very little and therefore $[\text{EtCOOH}] \approx [\text{EtCOOH}]_{\text{init}}$.

SOLUTION:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{EtCOO}^-]}{[\text{EtCOOH}]}$$



Sample Problem 16.8

Concentration (M)	$\text{EtCOOH}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	EtCOO^-
Initial	0.10		-	(aq)	0		0
Change	$-x$		-		$+x$		$+x$
Equilibrium	$0.10 - x$		-		x		x

Since K_a is small, we will assume that $x \ll 0.10$ and $[\text{EtCOOH}] \approx 0.10 \text{ mol/L}$.

$$K_a = 1.3 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{EtCOO}^-]}{[\text{EtCOOH}]} = \frac{x^2}{0.10}$$

$$x = \sqrt{(0.10)(1.3 \times 10^{-5})} = 1.1 \times 10^{-3} \text{ mol/L} = [\text{H}_3\text{O}^+]$$

Check: $[\text{EtCOOH}]_{\text{diss}} = \frac{1.1 \times 10^{-3} \text{ mol/L}}{0.10 \text{ mol/L}} \times 100 = 1.1\% (< 5\%; \text{assumption is justified.})$



Sample Problem 16.9

Determining pH from K_b and Initial [B]

PROBLEM: Dimethylamine, $(\text{CH}_3)_2\text{NH}$, a key intermediate in detergent manufacture, has a K_b of 5.9×10^{-4} . What is the pH of 1.5 mol/L $(\text{CH}_3)_2\text{NH}$?

PLAN: We start with the balanced equation for the reaction of the amine with H_2O , remembering that it is a weak base. We then write the expression for K_b , set up a reaction table and solve for $[\text{OH}^-]$. From $[\text{OH}^-]$ we can calculate $[\text{H}_3\text{O}^+]$ and pH. We make similar assumptions to those made for weak acids. Since $K_b \gg K_w$, the $[\text{OH}^-]$ from H_2O is negligible. Since K_b is small, we can assume that the amount of amine reacting is also small, so $[(\text{CH}_3)_2\text{NH}] \approx [(\text{CH}_3)_2\text{NH}]_{\text{init}}$.

SOLUTION: $(\text{CH}_3)_2\text{NH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]}$$



Sample Problem 16.9



Initial	1.50	-	0	0
Change	-x	-	+x	+x
Equilibrium	$1.50 - x$	-	x	x

Since K_b is small, $x \ll 1.50$ and $1.50 - x \approx 1.50$

$$K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]} = 5.9 \times 10^{-4} \approx \frac{x^2}{1.5}$$

$$x = [\text{OH}^-] = 3.0 \times 10^{-2} \text{ mol/L}$$

Check assumption:

$$\frac{3.0 \times 10^{-2} \text{ mol/L}}{1.5 \text{ mol/L}} \times 100 = 2.0\% (< 5\%; \text{ assumption is justified}).$$



Sample Problem 16.9

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-2}} = 3.3 \times 10^{-13} \text{ mol/L}$$

$$\text{pH} = -\log (3.3 \times 10^{-13}) = \mathbf{12.48}$$



Sample Problem 16.11

Determining the pH of a Solution of A⁻

PROBLEM: Sodium acetate (CH₃COONa, or NaOAc for this problem) has applications in photographic development and textile dyeing. What is the pH of 0.25 mol/L NaOAc? K_a of acetic acid (HAc) is 1.8×10^{-5} .

PLAN: Sodium salts are soluble in water and acetate is the anion of HAc so it acts as a weak base. We write the base dissociation equation and the expression for K_b , and solve for [OH⁻]. We recall that any soluble ionic salt dissociates completely in solution, so [OAc⁻]_{init} = 0.25 mol/L.



$$K_b = \frac{[\text{HAc}][\text{OH}^-]}{[\text{OAc}^-]}$$



Sample Problem 16.11

Concentration (mol/L)	$\text{OAc}^-(aq)$	+ $\text{H}_2\text{O}(l) \rightleftharpoons$	$\text{HOAc}(aq)$	+ $\text{OH}^-(aq)$
Initial	0.25	-	0	0
Change	- x	-	+ x	+ x
Equilibrium	$0.25 - x$	-	x	x

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

$$K_b = 5.6 \times 10^{-10} = \frac{[\text{HOAc}][\text{OH}^-]}{[\text{OAc}^-]} \approx \frac{x^2}{0.25} \quad \text{so } x = [\text{OH}^-] = \mathbf{1.2 \times 10^{-5} \text{ mol/L}}$$

Checking the assumption:

OK!



Sample Problem 16.11

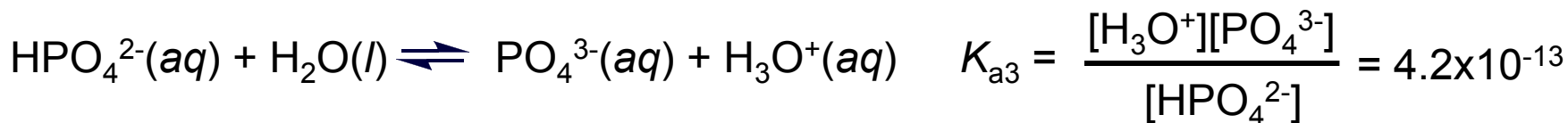
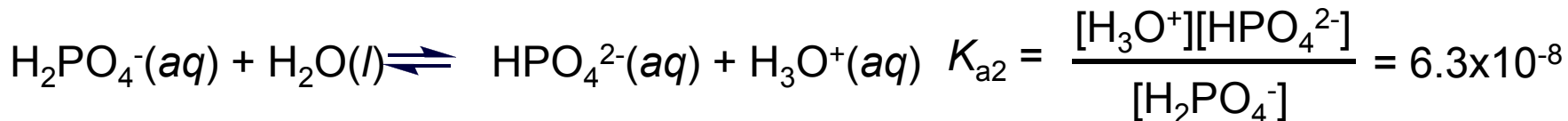
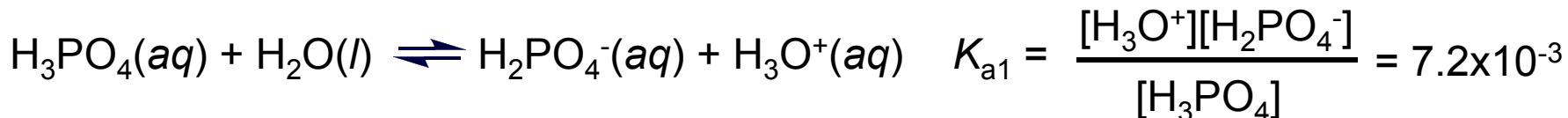
$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-5}} = 8.3 \times 10^{-10} \text{ mol/L}$$

$$\text{pH} = -\log (8.3 \times 10^{-10}) = \mathbf{9.08}$$



Polyprotic Acids

A **polyprotic acid** is an acid with more than one ionizable proton. In solution, each dissociation step has a different value for K_a :



$$K_{a1} > K_{a2} > K_{a3}$$

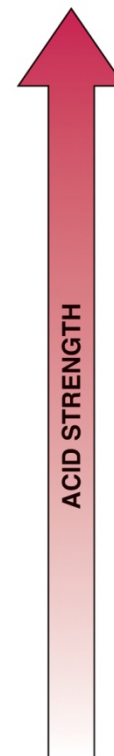
We usually neglect $[\text{H}_3\text{O}^+]$ produced after the first dissociation.



Table 16.7 Successive K_a values for Some Polyprotic Acids at 25°C

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Name (Formula)	Lewis Structure*	K_{a1}	K_{a2}	K_{a3}
Oxalic acid ($H_2C_2O_4$)	$ \begin{array}{c} \text{:O:} \quad \text{:O:} \\ \parallel \quad \parallel \\ \text{H}-\ddot{\text{O}}-\text{C}-\text{C}-\ddot{\text{O}}-\text{H} \end{array} $	5.6×10^{-2}	5.4×10^{-5}	
Sulfurous acid (H_2SO_3)	$ \begin{array}{c} \text{:O:} \\ \parallel \\ \text{H}-\ddot{\text{O}}-\ddot{\text{S}}-\ddot{\text{O}}-\text{H} \end{array} $	1.4×10^{-2}	6.5×10^{-8}	
Phosphoric acid (H_3PO_4)	$ \begin{array}{c} \text{:O:} \\ \parallel \\ \text{H}-\ddot{\text{O}}-\text{P}-\ddot{\text{O}}-\text{H} \\ \\ \text{:O}-\text{H} \end{array} $	7.2×10^{-3}	6.3×10^{-8}	4.2×10^{-13}
Arsenic acid (H_3AsO_4)	$ \begin{array}{c} \text{:O:} \\ \parallel \\ \text{H}-\ddot{\text{O}}-\text{As}-\ddot{\text{O}}-\text{H} \\ \\ \text{:O}-\text{H} \end{array} $	6×10^{-3}	1.1×10^{-7}	3×10^{-12}
Carbonic acid (H_2CO_3)	$ \begin{array}{c} \text{:O:} \\ \parallel \\ \text{H}-\ddot{\text{O}}-\text{C}-\ddot{\text{O}}-\text{H} \end{array} $	4.5×10^{-7}	4.7×10^{-11}	
Hydrosulfuric acid (H_2S)	$ \text{H}-\ddot{\text{S}}-\text{H} $	9×10^{-8}	1×10^{-17}	



*Red type indicates the ionizable protons.



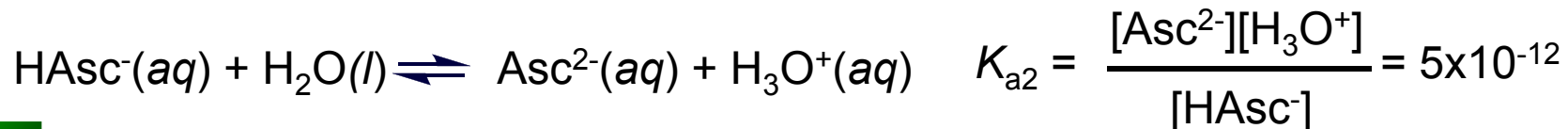
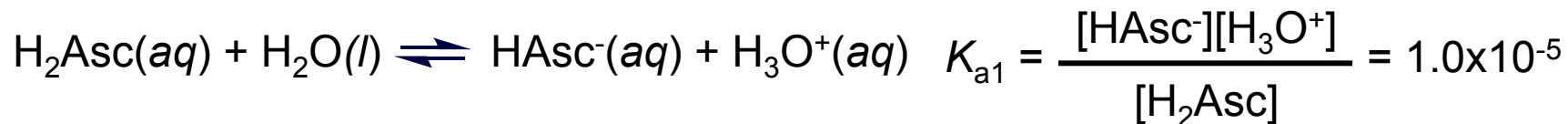
Sample Problem 16.12

Calculating Equilibrium Concentrations for a Polyprotic Acid

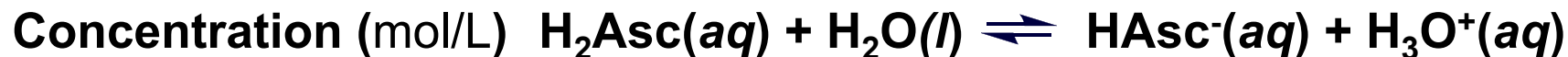
PROBLEM: Ascorbic acid ($\text{H}_2\text{C}_6\text{H}_6\text{O}_6$; H_2Asc for this problem), known as vitamin C, is a diprotic acid ($K_{a1} = 1.0 \times 10^{-5}$ and $K_{a2} = 5 \times 10^{-12}$) found in citrus fruit. Calculate $[\text{H}_2\text{Asc}]$, $[\text{HAsc}^-]$, $[\text{Asc}^{2-}]$, and the pH of $0.050 \text{ mol/L H}_2\text{Asc}$.

PLAN: We first write the dissociation equations and the associated K_a expressions. Since $K_{a1} \gg K_{a2}$, we can assume that the first dissociation produces almost all the H_3O^+ . Also, since K_{a1} is small, the amount of H_2Asc that dissociates can be neglected. We set up a reaction table for the first dissociation, with x equal to $[\text{H}_2\text{Asc}]_{\text{dissoc}}$, and solve for $[\text{H}_3\text{O}^+]$ and $[\text{HAsc}^-]$.

SOLUTION:



Sample Problem 16.12



Initial	0.050	-	0	0
Change	-x	-	+x	+x
Equilibrium	$0.050 - x$	-	x	x

$$K_{a1} = \frac{[\text{HAsc}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{Asc}]} = 1.0 \times 10^{-5} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

$$x = [\text{H}_3\text{O}^+] = [\text{HAsc}^-] = \sqrt{(0.050)(1.0 \times 10^{-5})} = 7.1 \times 10^{-4} \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(7.1 \times 10^{-4}) = 3.15$$



Sample Problem 16.12

Checking assumptions:

1. $[\text{H}_3\text{O}^+]_{\text{from HAsc}^-} \ll [\text{H}_3\text{O}^+]_{\text{from H}_2\text{Asc}}$: For any second dissociation,

$$[\text{H}_3\text{O}^+]_{\text{from HAsc}^-} \approx \frac{[\text{HAsc}^-](K_{a2})}{[\text{HAsc}^-] + K_{a2}} = \frac{(7.1 \times 10^{-4})(5 \times 10^{-12})}{7.1 \times 10^{-4} + 5 \times 10^{-12}} = 6 \times 10^{-8} \text{ mol/L}$$

This is even less than $[\text{H}_3\text{O}^+]_{\text{from H}_2\text{O}}$, so the assumption is justified.

2. $[\text{H}_2\text{Asc}]_{\text{dissoc}} \ll [\text{H}_2\text{Asc}]_{\text{init}}$:

$$\frac{7.1 \times 10^{-4} \text{ M}}{0.050 \text{ M}} \times 100 = 1.4\% (< 5\%; \text{ assumption is justified}).$$



16.5 Acid Strength of Nonmetal Hydrides

For nonmetal hydrides (E-H), acid strength depends on:

- the electronegativity of the central nonmetal (E), and
- the strength of the E-H bond.

Across a period, acid strength ***increases***.

Electronegativity increases across a period, so the acidity of E-H increases.

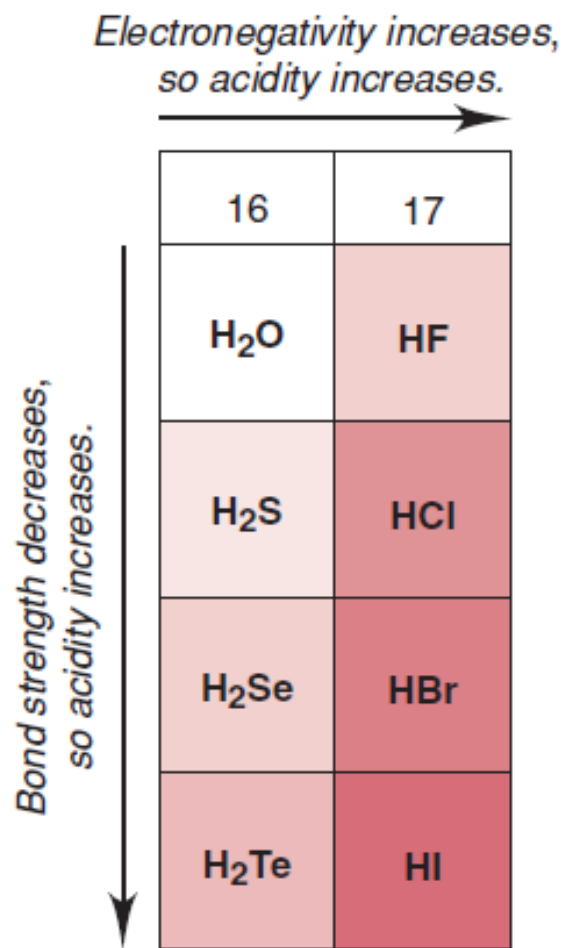
Down a group, acid strength ***increases***.

The length of the E-H bond increases down a group and its bond strength therefore decreases.



Figure 16.11 The effect of atomic and molecular properties on nonmetal hydride acidity.

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Acid Strength of Oxoacids

All oxoacids have the acidic H bonded to an **O atom**.

Acid strength of oxoacids depends on:

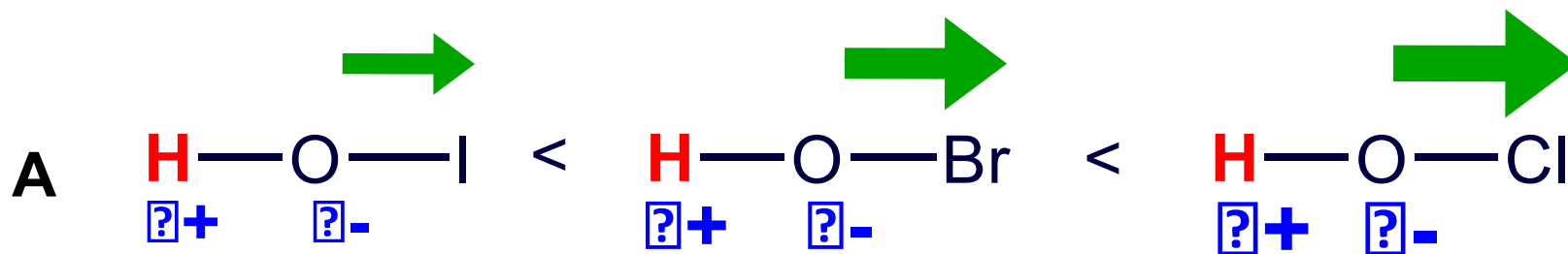
- the electronegativity of the central nonmetal (E), and
- the number of O atoms around E.

For oxoacids with the **same** number of O atoms, acid strength increases as the electronegativity of E increases.

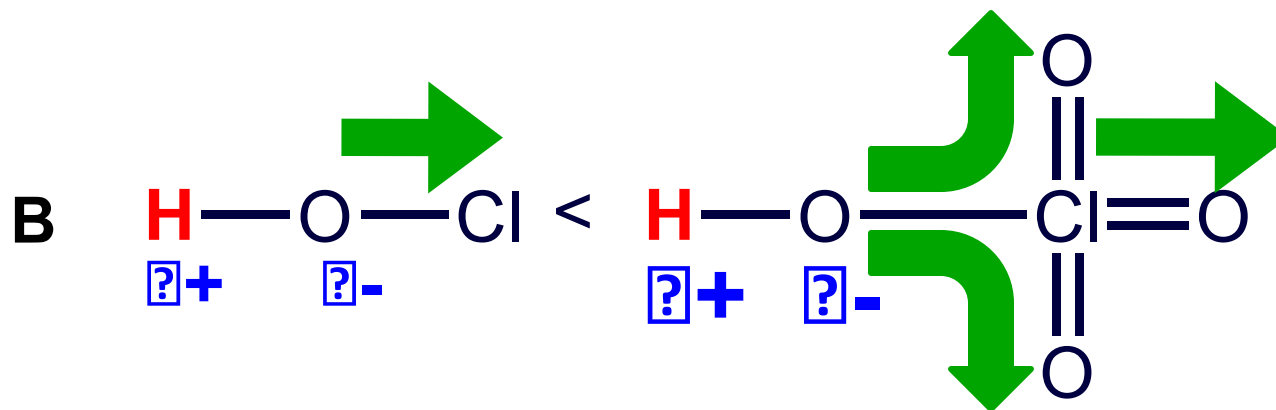
For oxoacids with **different** numbers of O atoms, acid strength increases with the number of O atoms.



Figure 16.12 The relative strengths of oxoacids.



Electronegativity increases, so acidity increases.



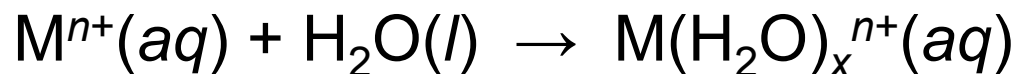
Number of O atoms increases, so acidity increases.



Hydrated Metal Ions

Some **hydrated** metal ions are able to transfer an H^+ to H_2O . These metal ions will form **acidic** solutions.

Consider a metal ion in solution, M^{n+} :

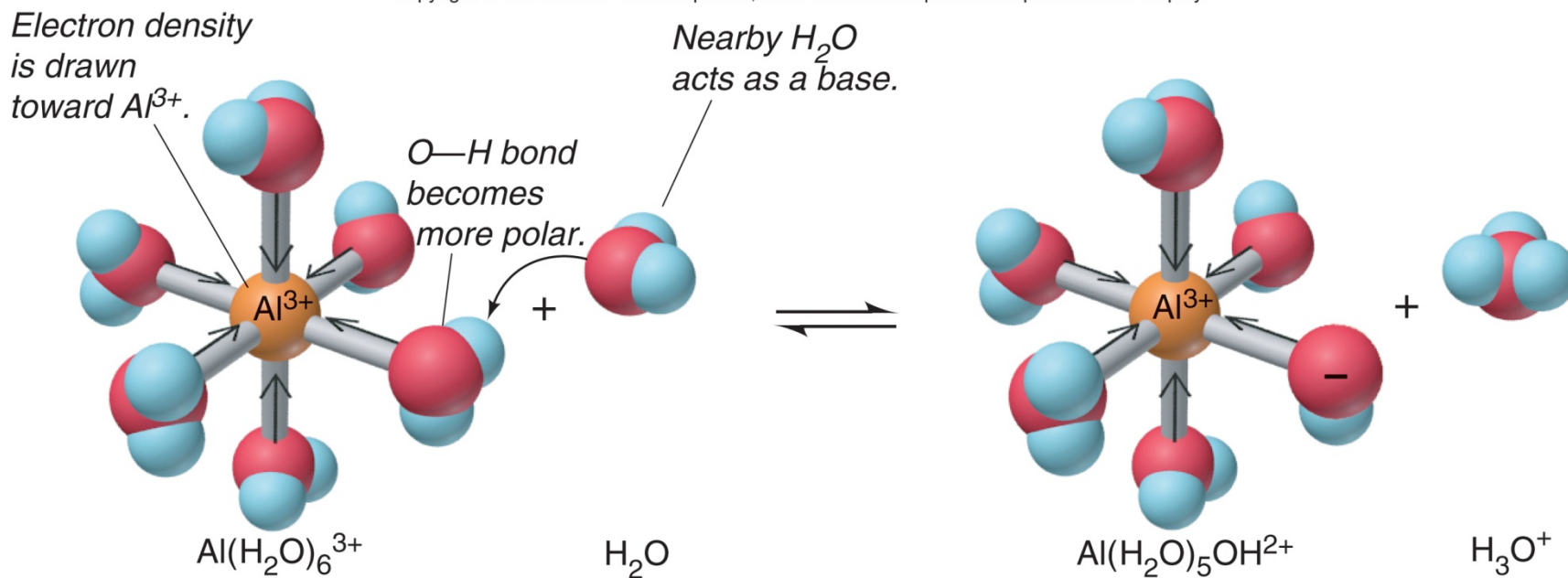


If M^{n+} is **small** and **highly charged**, it will withdraw enough e^- density from the O-H bonds of the bound H_2O molecules to release H^+ :



Figure 16.13 The acidic behavior of the hydrated Al^{3+} ion.

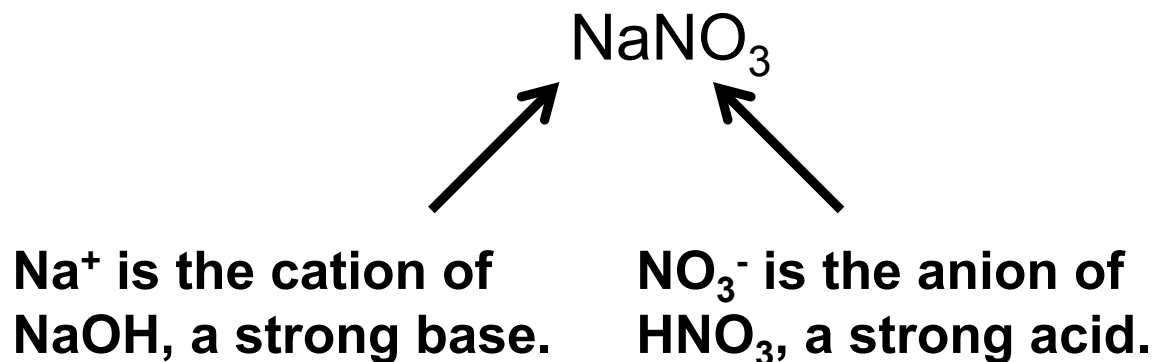
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16.6

Salts that Yield Neutral Solutions

A salt that consists of the ***anion*** of a ***strong acid*** and the ***cation*** of a ***strong base*** yields a ***neutral*** solution.

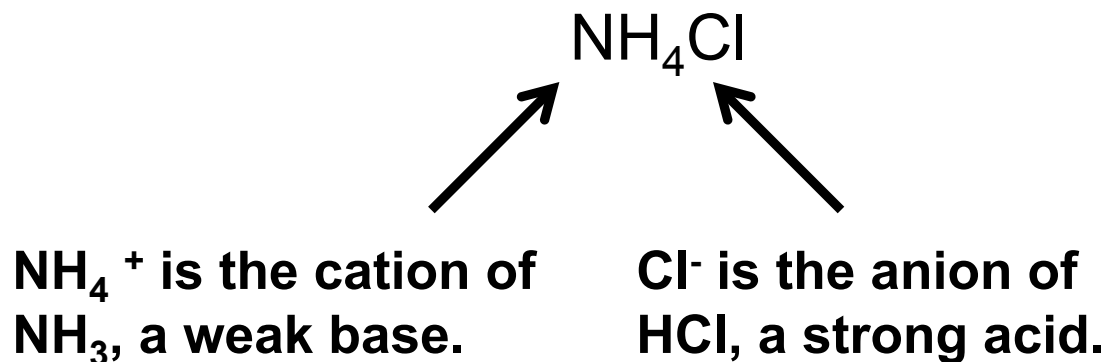


This solution will be neutral, because neither Na^+ nor NO_3^- will react with H_2O to any great extent.



Salts that Yield Acidic Solutions

A salt that consists of the **anion** of a **strong acid** and the **cation** of a **weak base** yields an **acidic** solution.

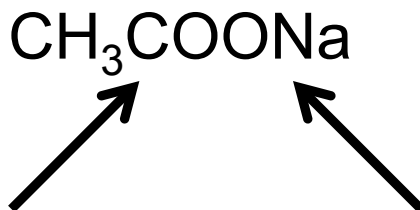


This solution will be **acidic**, because NH_4^+ will react with H_2O to produce H_3O^+ :



Salts that Yield Basic Solutions

A salt that consists of the ***anion*** of a ***weak acid*** and the ***cation*** of a ***strong base*** yields a ***basic*** solution.



CH_3COO^- is the anion of
 CH_3COOH , a weak acid.

Na^+ is the cation of
 NaOH , a strong base.

This solution will be ***basic***, because CH_3COO^- will react with H_2O to produce OH^- :



Sample Problem 16.13

Predicting Relative Acidity of Salt Solutions from Reactions of the Ions with Water

PROBLEM: Predict whether aqueous solutions of the following are acidic, basic, or neutral, and write an equation for the reaction of any ion with water:

- (a) Potassium perchlorate, KClO_4 (b) Sodium benzoate, $\text{C}_6\text{H}_5\text{COONa}$
(c) Chromium(III) nitrate, $\text{Cr}(\text{NO}_3)_3$

PLAN: We identify the cation and anion from the formula for each salt. Depending on an ion's ability to react with water, the solution will be neutral (strong-acid anion with strong-base cation), acidic (weak-base cation with strong-acid anion), or basic (weak-acid anion and strong-base cation).

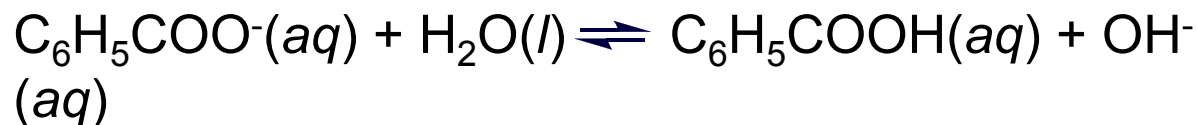
SOLUTION:

- (a) K^+ is the cation of a strong base (KOH) while ClO_4^- is the anion of a strong acid (HClO_4). **This solution will be neutral.**



Sample Problem 16.13

(b) Na^+ is the cation of a strong base (NaOH) while the benzoate anion ($\text{C}_6\text{H}_5\text{COO}^-$) is the anion of a weak acid (benzoic acid). The benzoate ion will react with H_2O to produce OH^- ions:



This solution will be basic.

(c) NO_3^- is the anion of a strong acid (HNO_3) and will not react with H_2O to any great extent. Cr^{3+} is a small metal cation with a fairly high charge density. It will become hydrated and the hydrated ion will react with H_2O to form H_3O^+ ions:

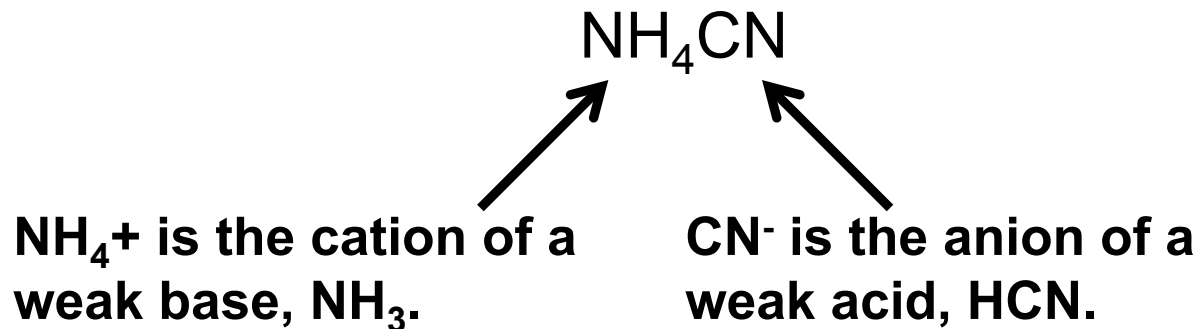


This solution will be acidic.



Salts of Weak Conjugate Acids and Weak Conjugate Bases

If a salt that consists of the **anion** of a **weak acid** and the **cation** of a **weak base**, the pH of the solution will depend on the relative acid strength or base strength of the ions.



The reaction that proceeds farther to the right determines the pH of the solution, so we need to compare the K_a of NH_4^+ with the K_b of CN^- .

$$K_a \text{ of } \text{NH}_4^+ = \frac{K_w}{K_b \text{ of } \text{NH}_3} = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.7 \times 10^{-10}$$

$$K_b \text{ of } \text{CN}^- = \frac{K_w}{K_a \text{ of } \text{HCN}} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$

Since K_b of $\text{CN}^- > K_a$ of NH_4^+ , CN^- is a stronger base than NH_4^+ is an acid. A solution of NH_4CN will be basic.



16.7

The Levelling Effect

All strong acids and bases are ***equally strong*** in water.

All strong acids dissociate completely to form H_3O^+ , while all strong bases dissociate completely to form OH^- .

In water, the strongest acid possible is H_3O^+ and the strongest base possible is OH^- .

H_2O exerts a ***leveling effect*** on any strong acid or base.

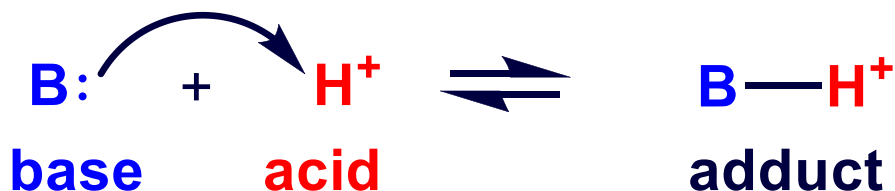


16.8

The Lewis Acid-Base Definition

A **Lewis base** is any species that **donates** an **electron pair** to form a bond.

A **Lewis acid** is any species that **accepts** an **electron pair** to form a bond.



The Lewis definition views an acid-base reaction as the **donation and acceptance of an electron pair** to form a **covalent bond**.

