

Acids and Bases

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Chapter 7 Acids and Bases

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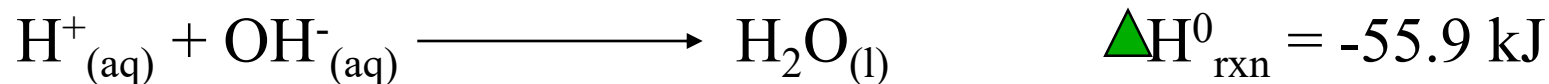
A circle of shiny pennies is created by the reaction between the citric acid of the lemon and the tarnish on the surface of the copper.



Arrhenius (or Classical) Acid-Base Definition

- An **acid** is a substance that contains hydrogen and dissociates in water to yield a hydronium ion : H_3O^+
- A **base** is a substance that contains the hydroxyl group and dissociates in water to yield : OH^-
- **Neutralization** is the reaction of an H^+ (H_3O^+) ion from the acid and the OH^- ion from the base to form water, H_2O .

The neutralization reaction is exothermic and releases approximately 56 kJ per mole of acid and base.



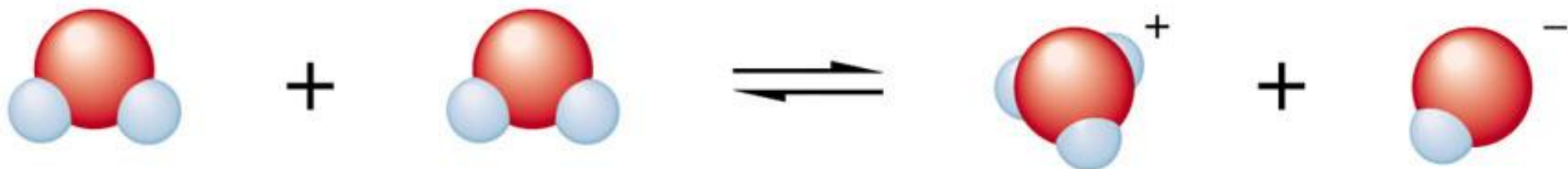
Brønsted-Lowry Acid-Base Definition

- An acid is a **proton donor**, any species that donates an H^+ ion.
An acid must contain H in its formula; HNO_3 and H_2PO_4^- are two examples, all Arrhenius acids are Brønsted-Lowry acids.
- A base is a **proton acceptor**, any species that accepts an H^+ ion.
A base must contain a lone pair of electrons to bind the H^+ ion; a few examples are NH_3 , CO_3^{2-} , F^- , as well as OH^- .
Brønsted-Lowry bases are not Arrhenius bases, but all Arrhenius bases contain the Brønsted-Lowry base OH^- .

Therefore in the Brønsted-Lowry perspective, *one species donates a proton and another species accepts it: an acid-base reaction is a proton transfer process.*

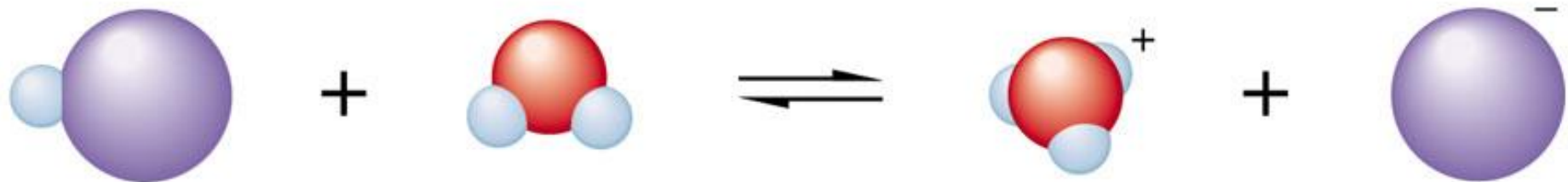
- Acids donate a proton to water
- Bases accept a proton from water

Molecular model: Two water molecules react to form H_3O^+ and OH^-



Brønsted-Lowry Acid-Base Reactions

Molecular model: The reaction of an acid HA with water to form H_3O^+ and a conjugate base.



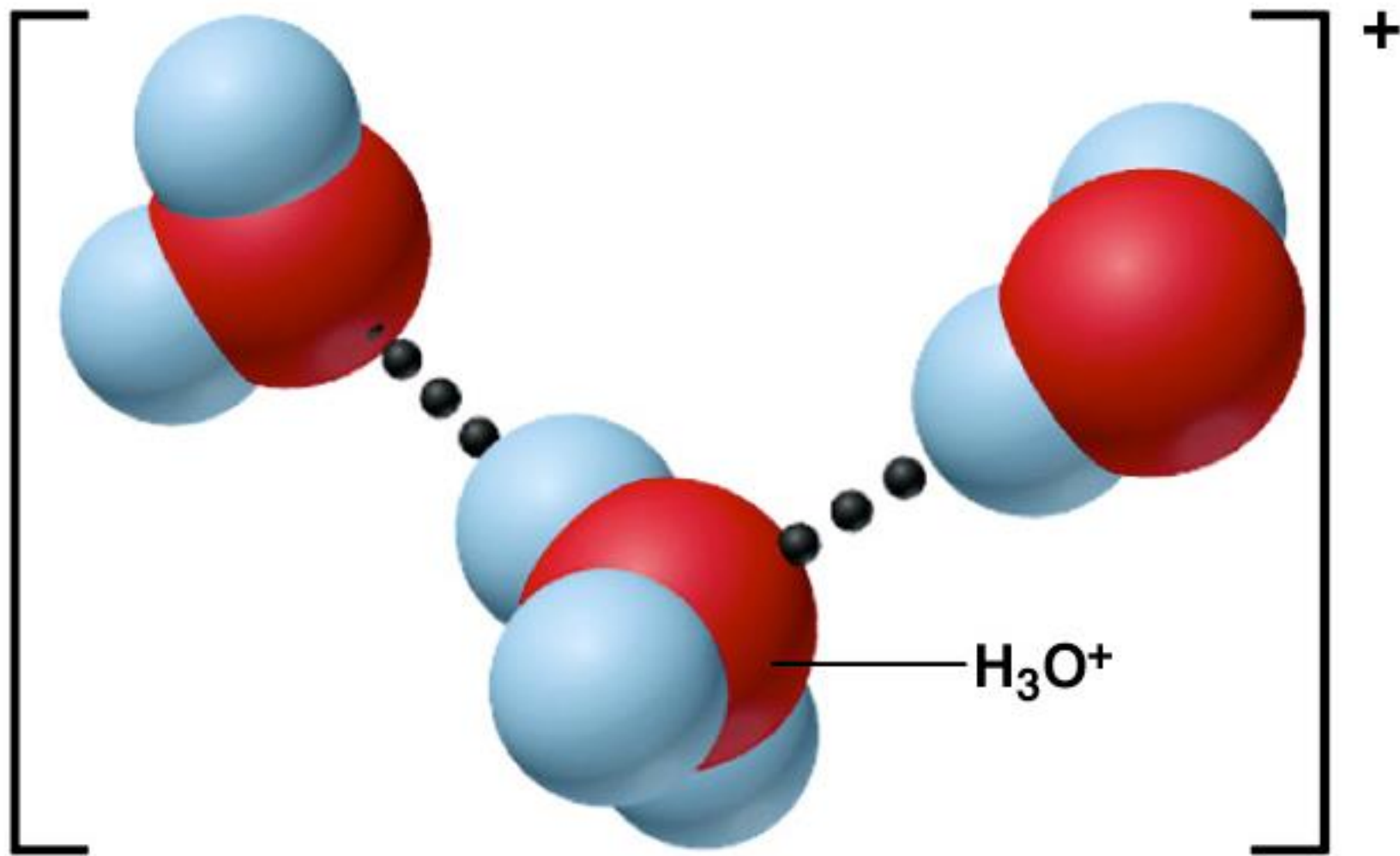
Acid

Base

**Conjugate
acid**

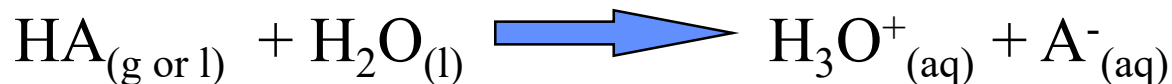
**Conjugate
base**

The Nature of the Hydrated Proton



The Acid-Dissociation Constant (K_a)

- Strong acids dissociate completely into ions in water:

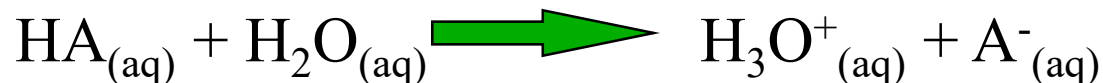


In a dilute solution of a strong acid, almost no HA molecules exist: $[\text{H}_3\text{O}^+] = [\text{HA}]_{\text{init}}$ or $[\text{HA}]_{\text{eq}} = 0$

$$Q_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \quad \text{at equilibrium, } Q_c = K_c \gg 1$$

Nitric acid is an example: $\text{HNO}_3_{(\text{l})} + \text{H}_2\text{O}_{(\text{l})} \longrightarrow \text{H}_3\text{O}^+_{(\text{aq})} + \text{NO}_3^-_{(\text{aq})}$

- Weak acids dissociate very slightly into ions in water:

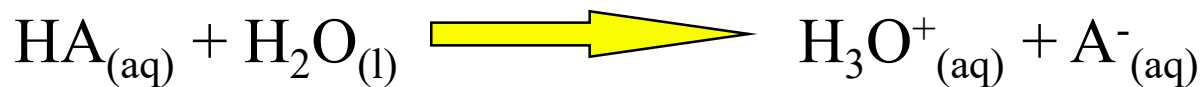


In a dilute solution of a weak acid, the great majority of HA molecules are undissociated: $[\text{H}_3\text{O}^+] \ll [\text{HA}]_{\text{init}}$ or $[\text{HA}]_{\text{eq}} = [\text{HA}]_{\text{init}}$

$$Q_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \quad \text{at equilibrium, } Q_c = K_c \ll 1$$

The Meaning of K_a , the Acid Dissociation Constant

For the ionization of an acid, HA:



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

Since the concentration of water is high, and does not change significantly during the reaction, its value is absorbed into the constant.

Therefore:

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

The stronger the acid, the higher the $[\text{H}_3\text{O}^+]$ at equilibrium, and the larger the K_a :

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

- For a weak acid with a relative high K_a ($\sim 10^{-2}$), a 1 M solution has $\sim 10\%$ of the HA molecules dissociated.
- For a weak acid with a moderate K_a ($\sim 10^{-5}$), a 1 M solution has $\sim 0.3\%$ of the HA molecules dissociated.
- For a weak acid with a relatively low K_a ($\sim 10^{-10}$), a 1 M solution has $\sim 0.001\%$ of the HA molecules dissociated.

Brønsted-Lowry Acid-Base Reaction

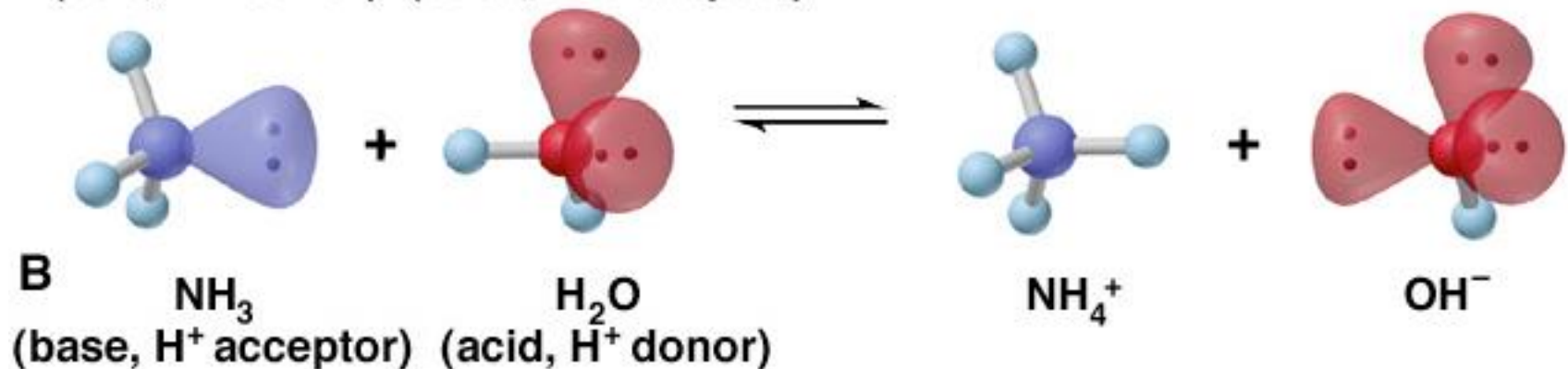
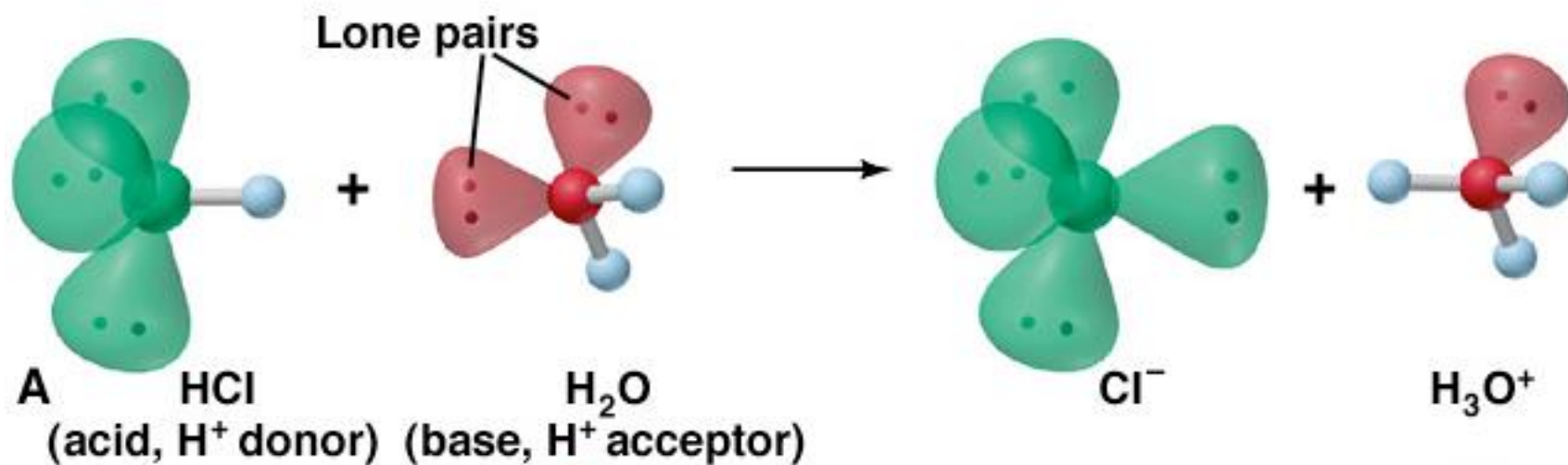
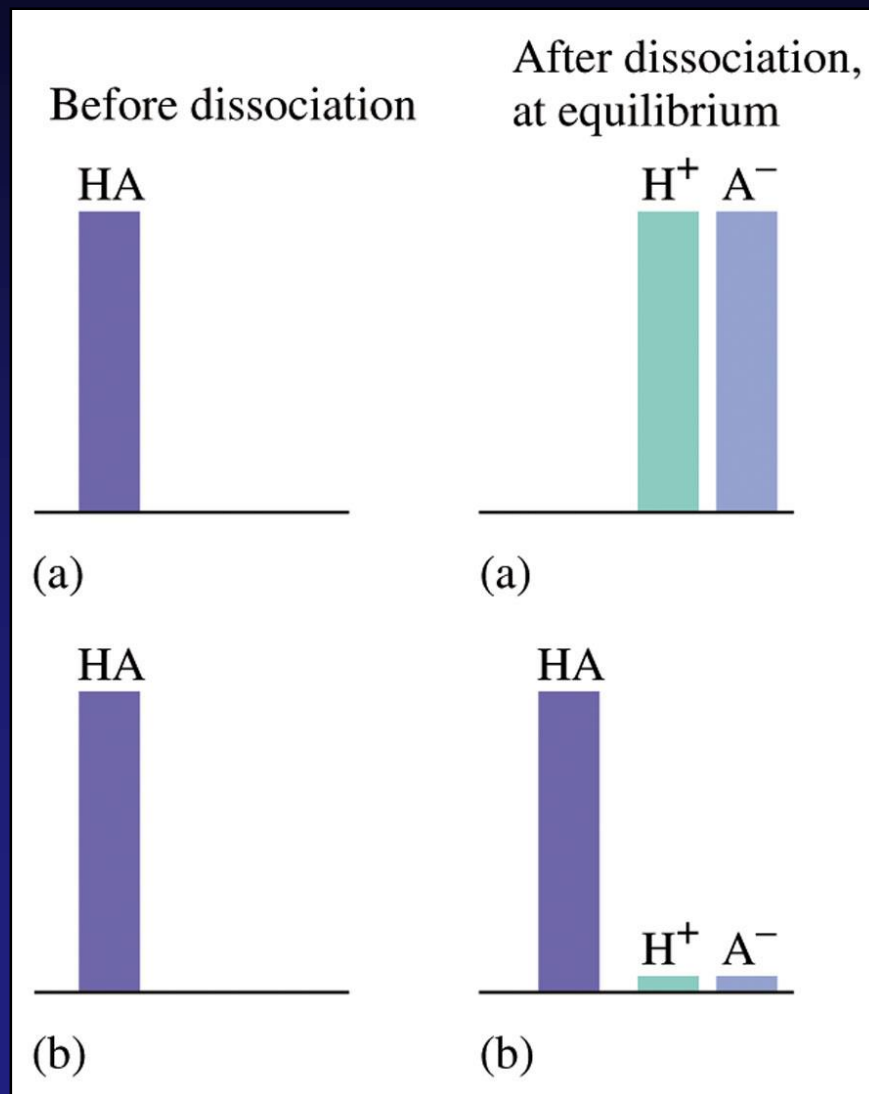


Figure 7.1: Graphical representation of the behavior of acids of different strengths in aqueous solution.



A Strong Acid

A Weak Acid

The Extent of Dissociation for Strong and Weak Acids

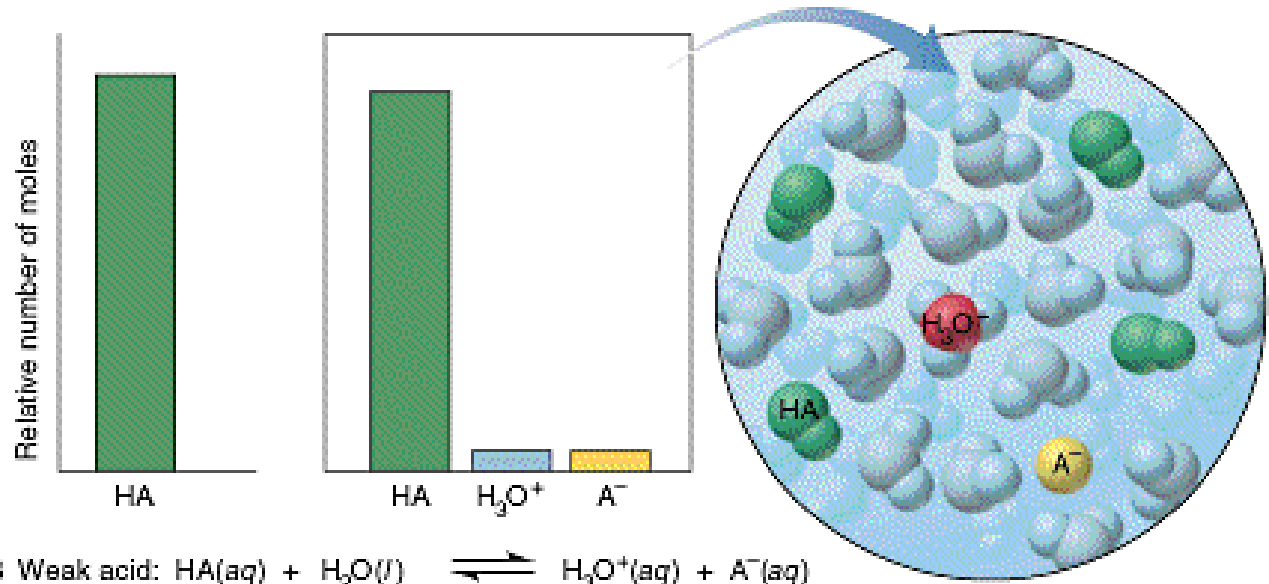
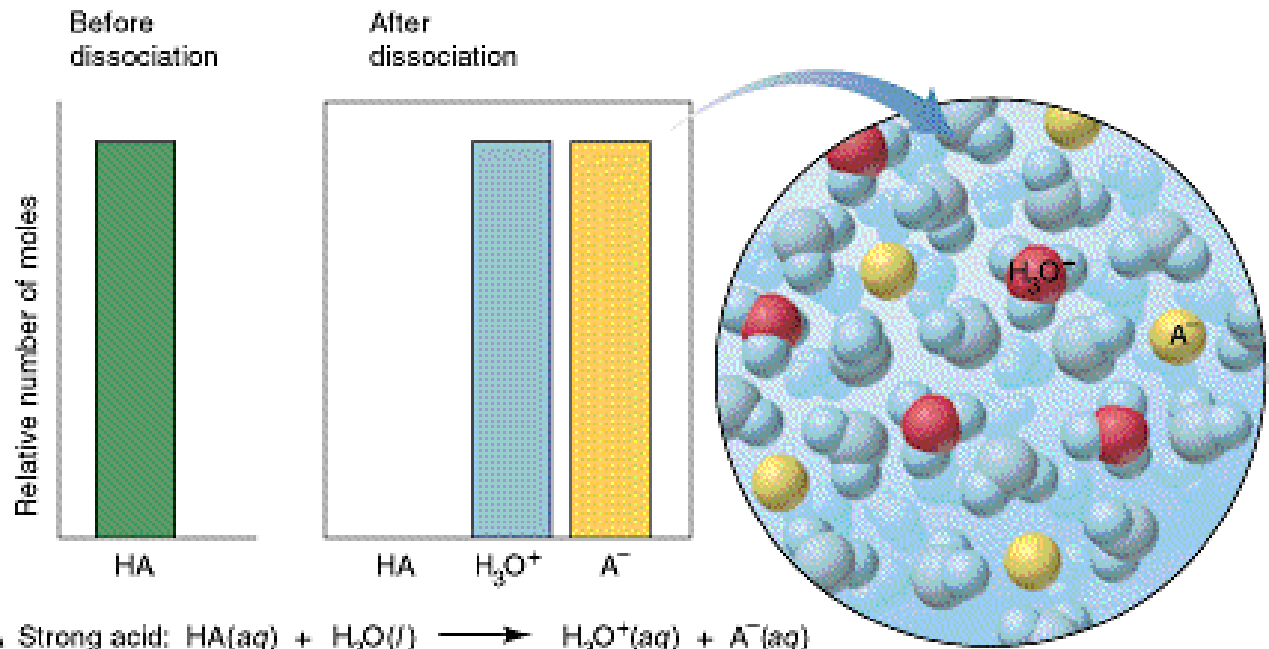
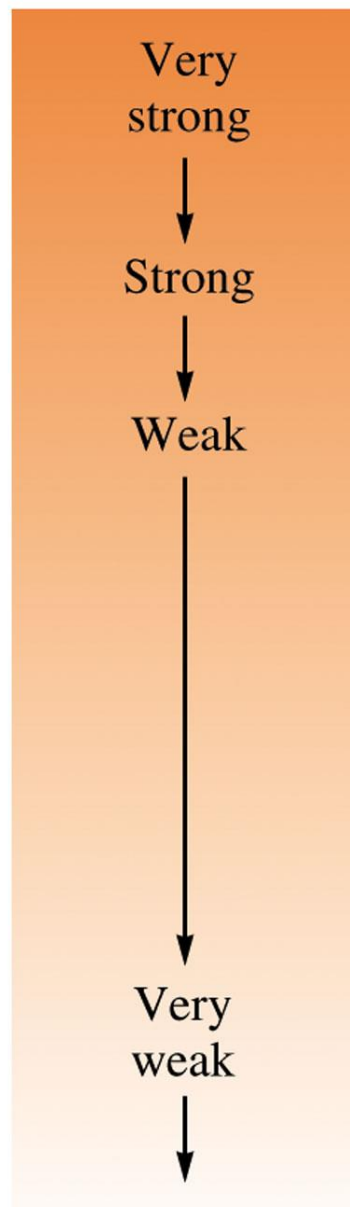


TABLE 7.1 Various Ways to Describe Acid Strength

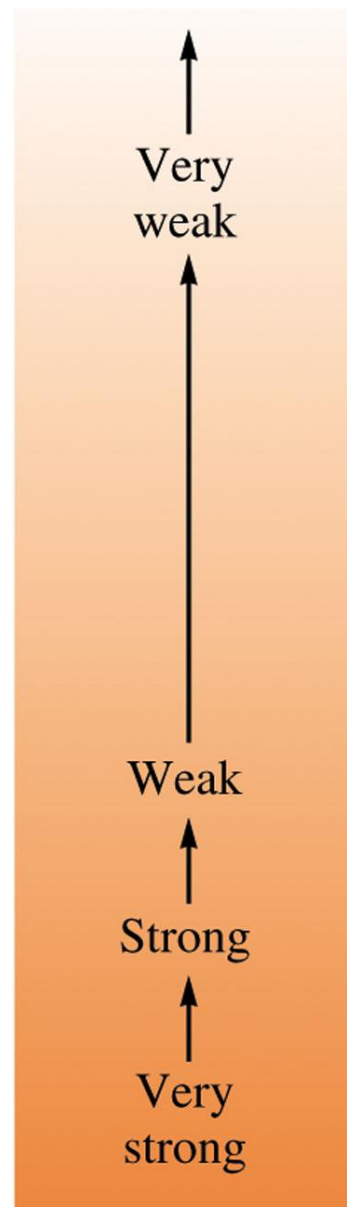
Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that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

Figure 7.2: Relationship of acid strength and conjugate base strength

Relative
acid strength



Relative
conjugate
base strength



The Six Strong Acids

Hydrogen Halides



Hydrochloric Acid



Hydrobromic Acid



Hydroiodic Acid

Oxyacids



Sulfuric Acid

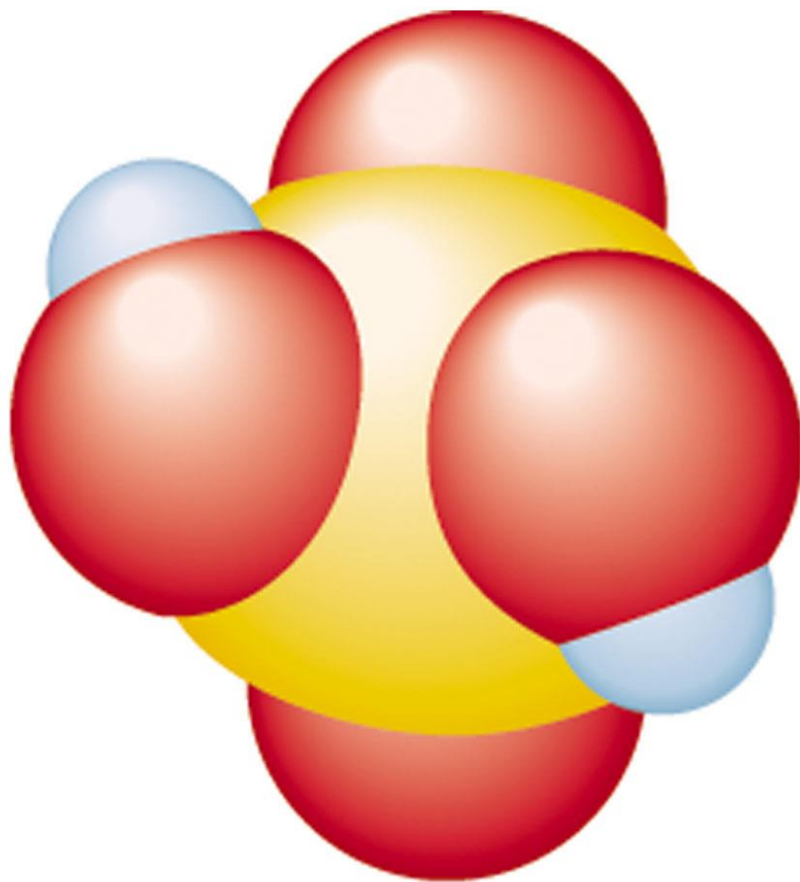


Nitric Acid



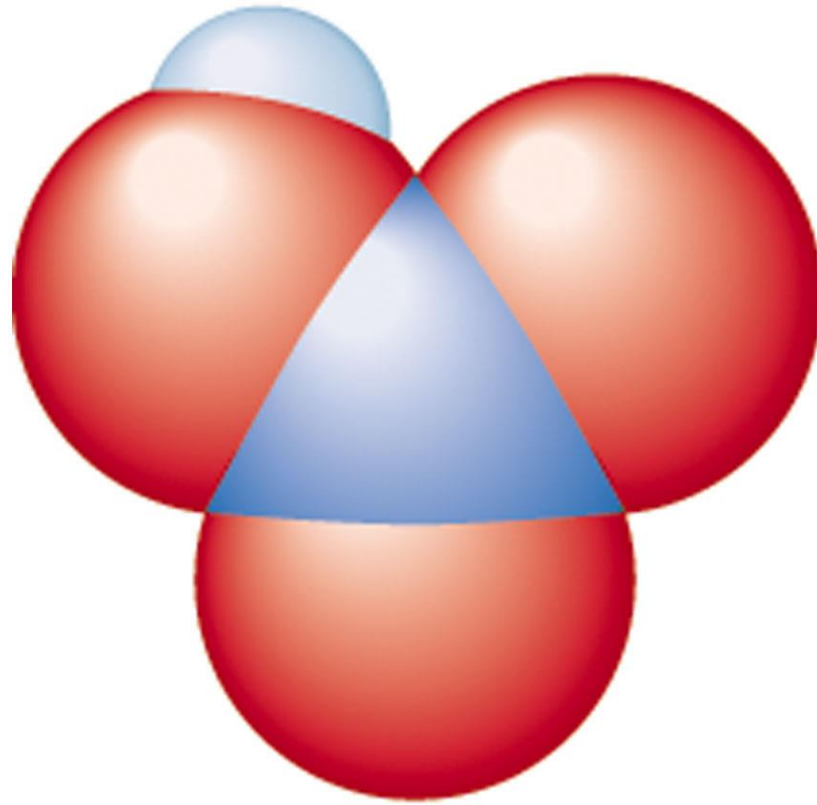
Perchloric Acid

Molecular model: Sulfuric acid



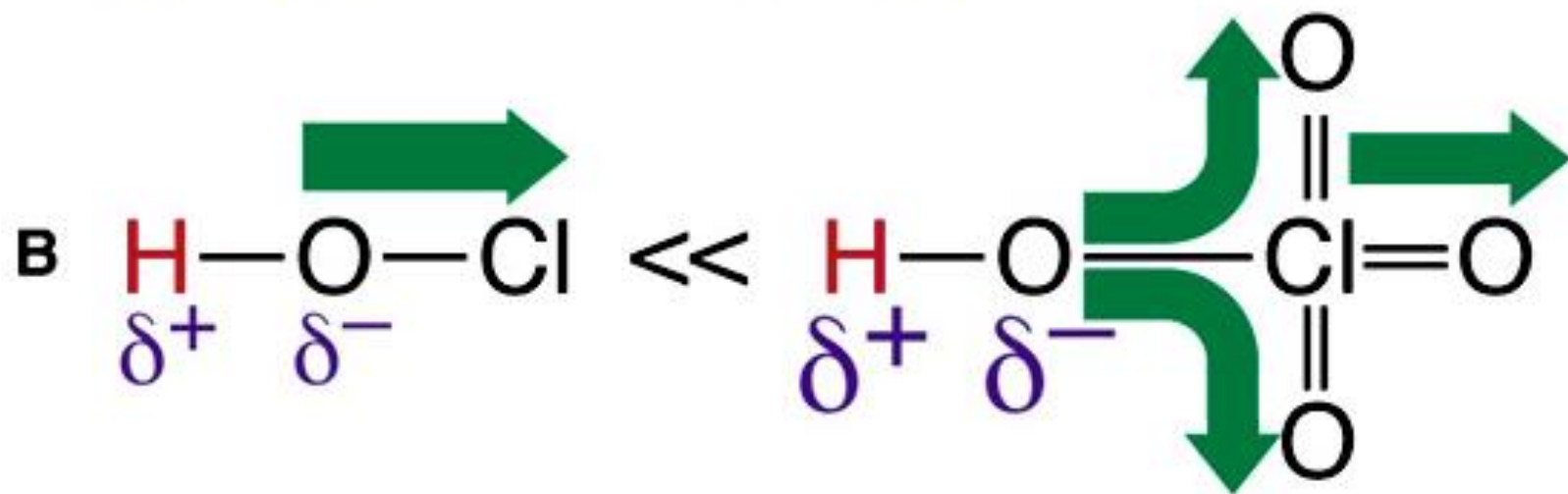
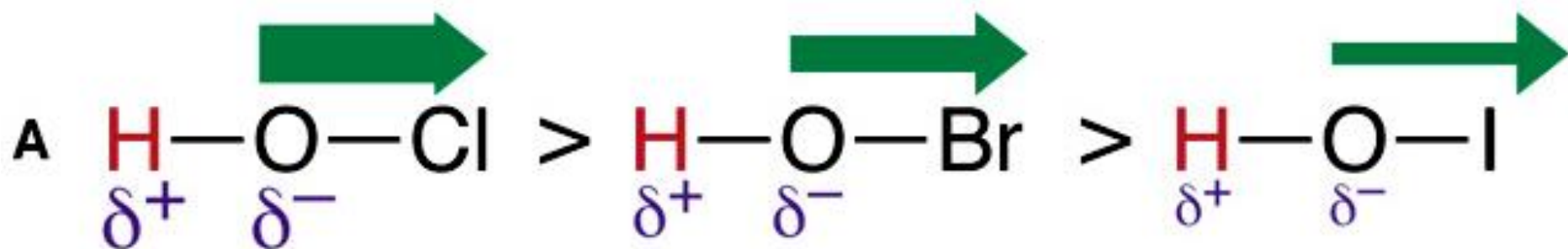
Sulfuric acid
(H_2SO_4)

Molecular model: Nitric acid

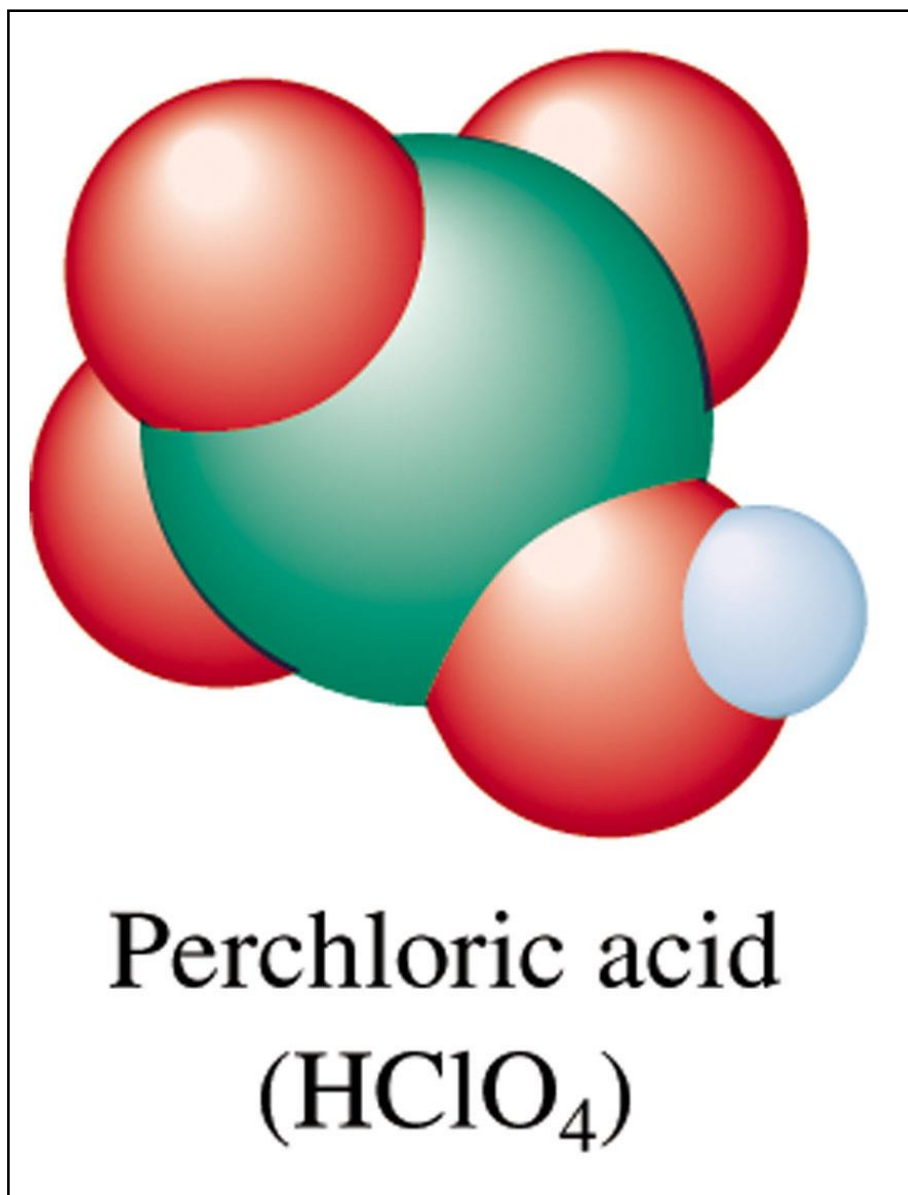


Nitric acid
(HNO_3)

The Relative Strengths of Oxoacids



Molecular model: Perchloric acid



The Stepwise Dissociation of Phosphoric Acid

Phosphoric acid is a weak acid, and normally only loses one proton in solution, but it will lose all three when reacted with a strong base with heat. The ionization constants are given for comparison.

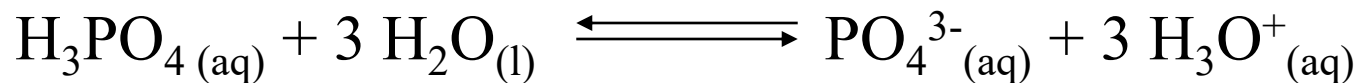
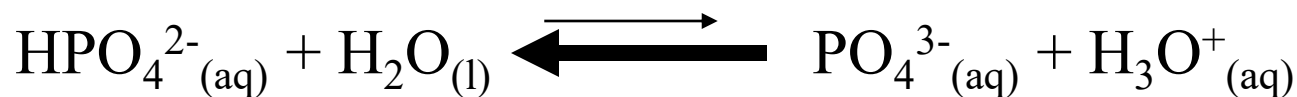
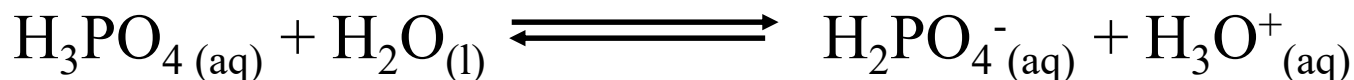


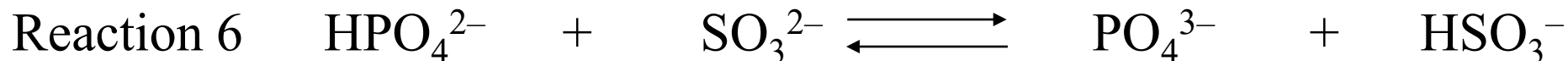
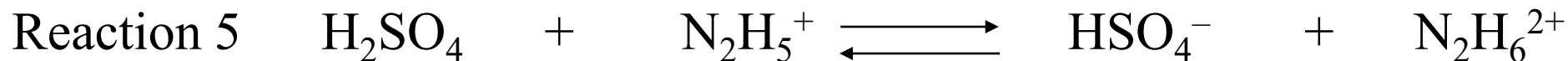
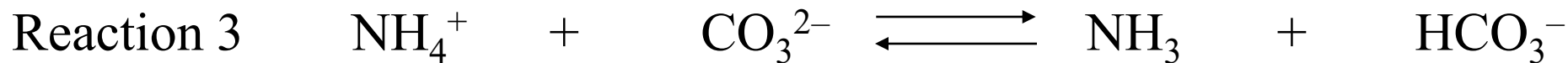
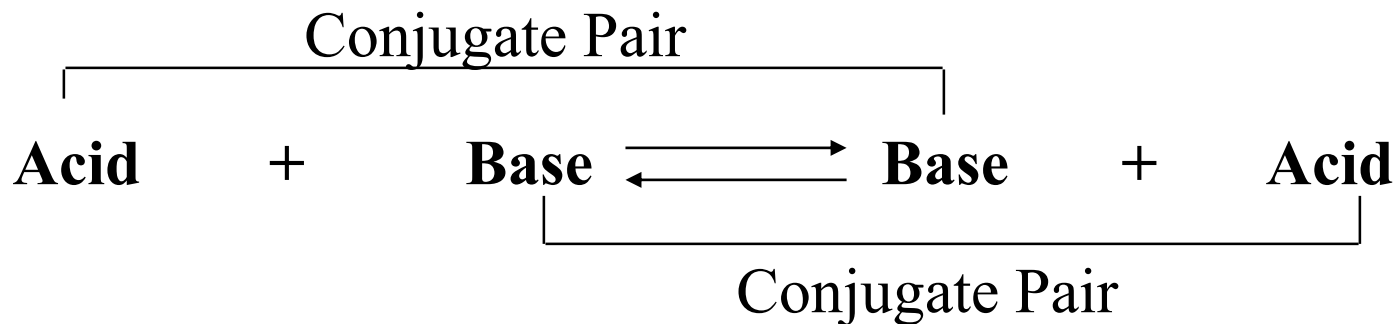
TABLE 7.2 Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a	
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}	↑ Increasing acid strength
HClO_2	Chlorous acid	1.2×10^{-2}	
$\text{HC}_2\text{H}_2\text{ClO}_2$	Monochloroacetic acid	1.35×10^{-3}	
HF	Hydrofluoric acid	7.2×10^{-4}	
HNO_2	Nitrous acid	4.0×10^{-4}	
$\text{HC}_2\text{H}_3\text{O}_2$	Acetic acid	1.8×10^{-5}	
$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}	
HOCl	Hypochlorous acid	3.5×10^{-8}	
HCN	Hydrocyanic acid	6.2×10^{-10}	
NH_4^+	Ammonium ion	5.6×10^{-10}	
HOC_6H_5	Phenol	1.6×10^{-10}	

Strengths of Conjugate Acid-Base Pairs

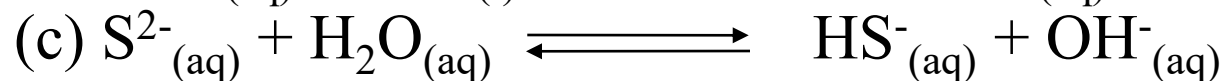
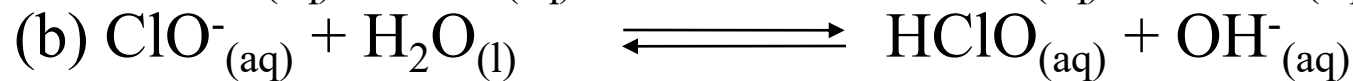
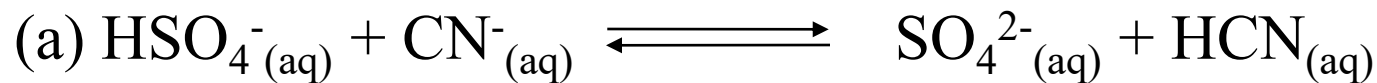
	ACID	BASE	
Strong	HCl	Cl ⁻	Negligible
	H ₂ SO ₄	HSO ₄ ⁻	
	HNO ₃	NO ₃ ⁻	
	H ₃ O ⁺	H ₂ O	
Weak	HSO ₄ ⁻	SO ₄ ²⁻	Weak
	H ₂ SO ₃	HSO ₃ ⁻	
	H ₃ PO ₄	H ₂ PO ₄ ⁻	
	HF	F ⁻	
	CH ₃ COOH	CH ₃ COO ⁻	
	H ₂ CO ₃	HCO ₃ ⁻	
	H ₂ S	HS ⁻	
	HSO ₃ ⁻	SO ₃ ²⁻	
	H ₂ PO ₄ ⁻	HPO ₄ ²⁻	
	NH ₄ ⁺	NH ₃	
Negligible	HCO ₃ ⁻	CO ₃ ²⁻	Strong
	HPO ₄ ²⁻	PO ₄ ³⁻	
	H ₂ O	OH ⁻	
	HS ⁻	S ²⁻	
	OH ⁻	O ²⁻	

The Conjugate Pairs in Some Acid-Base Reactions



Identifying Conjugate Acid-Base Pairs

Problem: The following chemical reactions are important for industrial processes. Identify the conjugate acid-base pairs.



Plan: To find the conjugate acid-base pairs, we find the species that donate H^+ and those that accept it. The acid (or base) on the left becomes its conjugate base (or acid) on the right.

Solution:

(a) The proton is transferred from the sulfate to the cyanide so:

$\text{HSO}_4^-_{(\text{aq})}/\text{SO}_4^{2-}_{(\text{aq})}$ and $\text{CN}^-_{(\text{aq})}/\text{HCN}_{(\text{aq})}$ are the two acid-base pairs.

(b) The water gives up one proton to the hypochlorite anion so:

$\text{ClO}^-_{(\text{aq})}/\text{HClO}_{(\text{aq})}$ and $\text{H}_2\text{O}_{(\text{l})}/\text{OH}^-_{(\text{aq})}$ are the two acid-base pairs.

(c) One of water's protons is transferred to the sulfide ion so:

$\text{S}^{2-}_{(\text{aq})}/\text{HS}^-_{(\text{aq})}$ and $\text{H}_2\text{O}_{(\text{l})}/\text{OH}^-_{(\text{aq})}$ are the two acid-base pairs.

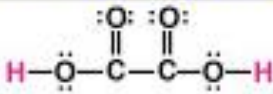
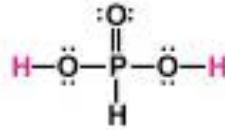
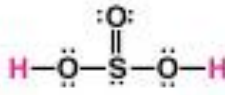
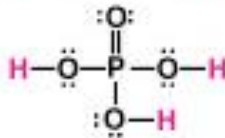
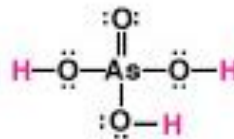
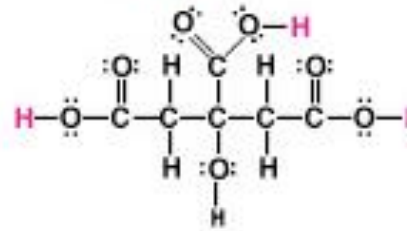
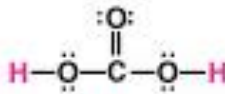
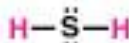
K_a Values for Some Monoprotic Acids

K_a Values for Some Monoprotic Acids at 25°C		
Name (Formula)	Lewis Structure*	K_a
Iodic acid (HIO_3)	$\text{H}-\ddot{\text{O}}-\overset{\text{O}}{\parallel}{\text{I}}-\ddot{\text{O}}$	1.6×10^{-1}
Chlorous acid (HClO_2)	$\text{H}-\ddot{\text{O}}-\overset{\text{O}}{\parallel}{\text{Cl}}-\ddot{\text{O}}$	1.12×10^{-2}
Nitrous acid (HNO_2)	$\text{H}-\ddot{\text{O}}-\overset{\text{O}}{\parallel}{\text{N}}-\ddot{\text{O}}$	7.1×10^{-4}
Hydrofluoric acid (HF)	$\text{H}-\ddot{\text{F}}$	6.8×10^{-4}
Formic acid (HCOOH)	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{H}-\text{C}-\ddot{\text{O}}-\text{H} \end{array}$	1.8×10^{-4}
Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$)	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{C}_6\text{H}_5-\text{C}-\ddot{\text{O}}-\text{H} \end{array}$	6.3×10^{-5}
Acetic acid (CH_3COOH)	$\begin{array}{c} \text{H} \text{ :O:} \\ \quad \parallel \\ \text{H}-\text{C}-\text{C}-\ddot{\text{O}}-\text{H} \\ \\ \text{H} \end{array}$	1.8×10^{-5}
Propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$)	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{:O:} \\ \quad \quad \parallel \\ \text{H}-\text{C}-\text{C}-\text{C}-\ddot{\text{O}}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	1.3×10^{-5}
Hypochlorous acid (HClO)	$\text{H}-\ddot{\text{O}}-\ddot{\text{Cl}}$	2.9×10^{-8}
Hypobromous acid (HBrO)	$\text{H}-\ddot{\text{O}}-\ddot{\text{Br}}$	2.3×10^{-9}
Hydrocyanic acid (HCN)	$\text{H}-\text{C} \equiv \text{N}$	6.2×10^{-10}
Phenol ($\text{C}_6\text{H}_5\text{OH}$)	$\text{C}_6\text{H}_5-\ddot{\text{O}}-\text{H}$	1.0×10^{-10}
Hypoiodous acid (HIO)	$\text{H}-\ddot{\text{O}}-\ddot{\text{I}}$	2.3×10^{-11}



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

Successive K_a Values for Some Polyprotic Acids at 25°C

Name (Formula)	Lewis Structure*	K_{a1}	K_{a2}	K_{a3}
Oxalic acid ($H_2C_2O_4$)		5.6×10^{-2}	5.4×10^{-5}	
Phosphorous acid (H_3PO_3)		3×10^{-2}	1.7×10^{-7}	
Sulfurous acid (H_2SO_3)		1.4×10^{-2}	6.5×10^{-8}	
Phosphoric acid (H_3PO_4)		7.2×10^{-3}	6.3×10^{-8}	4.2×10^{-13}
Arsenic acid (H_3AsO_4)		6×10^{-3}	1.1×10^{-7}	3×10^{-12}
Citric acid ($H_3C_6H_5O_7$)		7.5×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Carbonic acid (H_2CO_3)		4.5×10^{-7}	4.7×10^{-11}	
Hydrosulfuric acid (H_2S)		9×10^{-8}	1×10^{-17}	



*Red type indicates the ionizable protons.

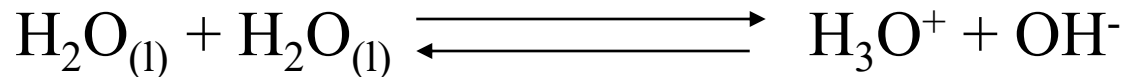
TABLE 7.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid*	H_2CO_3	4.3×10^{-7}	4.8×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid [†]	H_2S	1.0×10^{-7}	$\approx 10^{-19}$	
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	7.9×10^{-5}	1.6×10^{-12}	

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

[†]The K_{a_2} value for H_2S is quite uncertain. Its small size makes it very difficult to measure.

Autoionization of Water



$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

The ion-product for water, K_w :

$$K_c[\text{H}_2\text{O}]^2 = K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = \underline{1.0 \times 10^{-14}} \text{ (at } 25^\circ\text{C)}$$

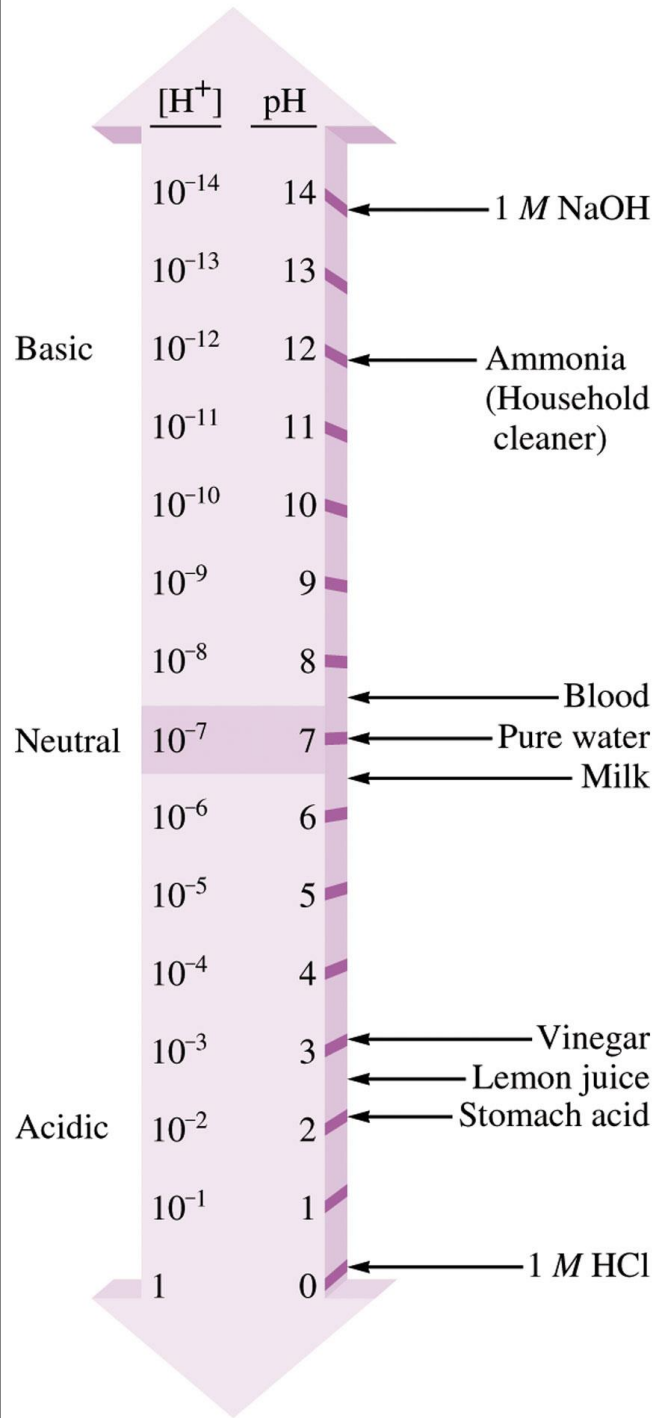
For pure water the concentration of hydroxyl and hydronium ions must be equal:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.0 \times 10^{-14}} = \underline{1.0 \times 10^{-7} \text{ M}} \text{ (at } 25^\circ\text{C)}$$

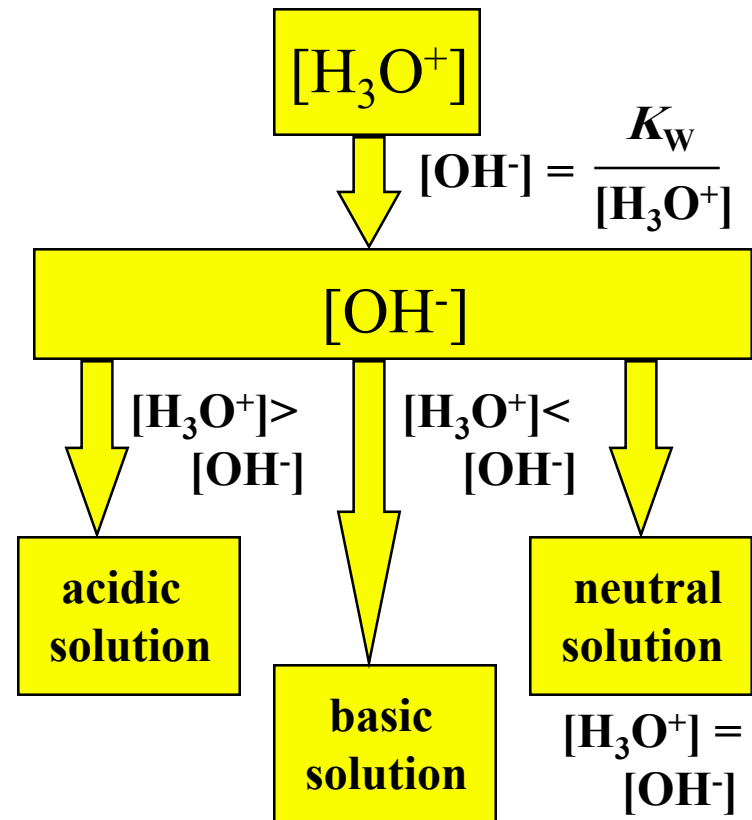
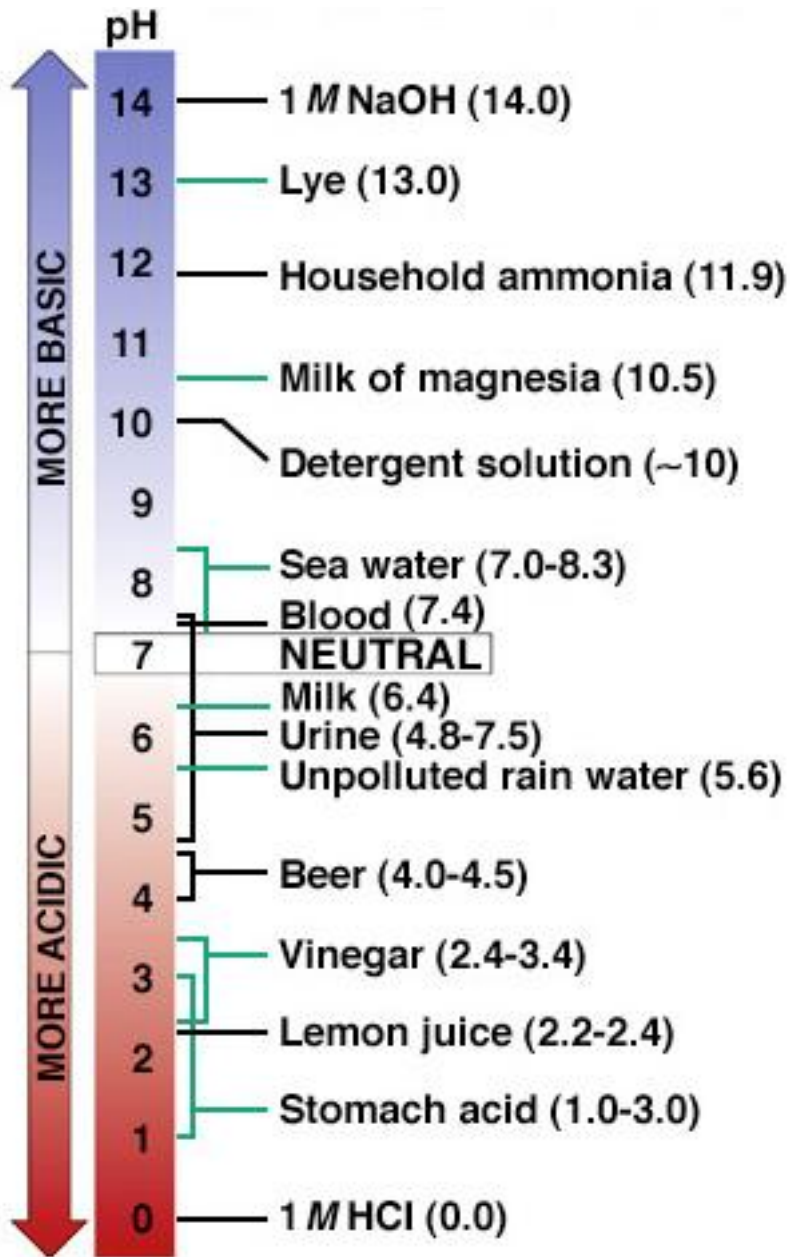
The molarity of pure water is: $\frac{1000\text{g/L}}{18.02 \text{ g/mol}} = \underline{\hspace{2cm}} \text{ M}$



Figure 7.3: The pH scale and pH values of some common substances



The pH Values of Some Familiar Aqueous Solutions



The Relationship Between K_a and pK_a

Acid Name (Formula)	K_a at 25°C	pK_a
Hydrogen sulfate ion (HSO_4^-)	1.02×10^{-2}	1.991
Nitrous acid (HNO_2)	7.1×10^{-4}	3.15
Acetic acid (CH_3COOH)	1.8×10^{-5}	4.74
Hypobromous acid (HBrO)	2.3×10^{-9}	8.64
Phenol ($\text{C}_6\text{H}_5\text{OH}$)	1.0×10^{-10}	10.00

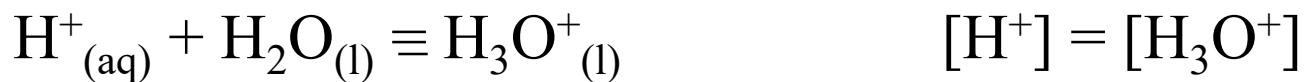
The Relations Among $[H_3O^+]$, pH, $[OH^-]$, and pOH



	$[H_3O^+]$	pH	$[OH^-]$	pOH
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
	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
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
	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

Acid and Base Character and the pH Scale

In acidic solutions, the protons that are released into solution will not remain alone due to their large positive charge density and small size. They are attracted to the negatively charged electrons on the oxygen atoms in water, and form hydronium ions.



To handle the very large variations in the concentrations of the hydrogen ion in aqueous solutions, a scale called the pH scale is used which is:

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

- What is the pH of a solution that is 10^{-12} M in hydronium ion ?

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = (-1)\log 10^{-12} = (-1)(-12) = 12$$

- What is the pH of a solution that is 7.3×10^{-9} M in H_3O^+ ?

$$\text{pH} = -\log(7.3 \times 10^{-9}) = -1(\log 7.3 + \log 10^{-9}) = -1[(0.863)+(-9)] = 8.14$$

pH of a neutral solution = 7.00

pH of an acidic solution < 7.00

pH of a basic solution > 7.00

Classifying the Relative Strengths of Acids and Bases–I

Strong acids. There are two types of strong acids:

1. The hydrohalic acids HCl, HBr, and HI
2. Oxoacids in which the number of O atoms exceeds the number of ionizable H atoms by two or more, such as HNO₃, H₂SO₄, HClO₄

Weak acids. There are many more weak acids than strong ones. Four types, with examples, are:

1. The hydrohalic acid HF
2. Those acids in which H is bounded to O or to halogen, such as HCN and H₂S
3. Oxoacids in which the number of O atoms equals or exceeds by one the number of ionizable H atoms, such as HClO, HNO₂, and H₃PO₄
4. Organic acids (general formula RCOOH), such as CH₃COOH and C₆H₅COOH

Classifying the Relative Strengths of Acids and Bases–II

Strong bases. Soluble compounds containing O^{2-} or OH^- ions are strong bases. The cations are usually those of the most active metals:

- 1) M_2O or MOH , where $M =$ Group 1A(1) metals (Li, Na, K, Rb, Cs)
- 2) MO or $M(OH)_2$, where $M =$ Group 2A(2) metals (Ca, Sr, Ba)
[MgO and $Mg(OH)_2$ are only slightly soluble, but the soluble portion dissociates completely.]

Weak bases. Many compounds with an electron-rich nitrogen are weak bases (none are Arrhenius bases). The common structural feature is an N atom that has a lone electron pair in its Lewis structure.

- 1) Ammonia ($:NH_3$)
- 2) Amines (general formula RNH_2 , R_2NH , R_3N), such as
 $CH_3CH_2NH_2$, $(CH_3)_2NH$, $(C_3H_7)_3N$, and C_5H_5N

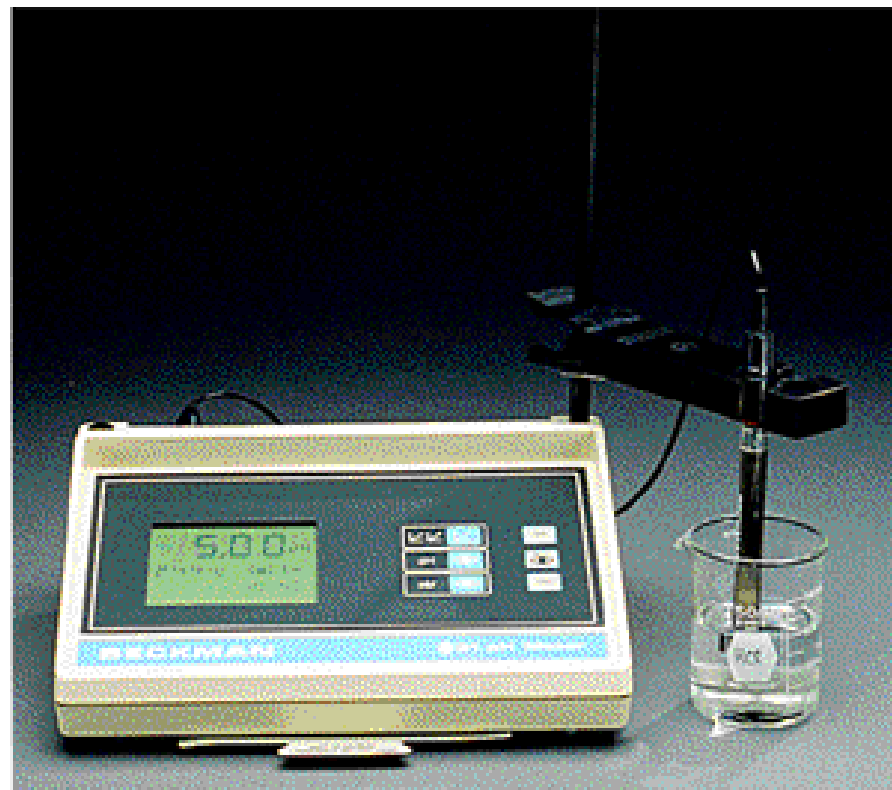
Figure 7.4: (a) Measuring the pH of vinegar. (b) Measuring the pH of aqueous ammonia.



Methods for Measuring the pH of an Aqueous Solution



(a) pH paper



(b) Electrodes of a pH meter

Summary: General Strategies for Solving Acid-Base Problems (P 233)

Think Chemistry, Focus on the solution components and their reactions. It will almost always be possible to choose one reaction that is the most important.

Be systematic, Acid-Base problems require a step-by-step approach.

Be flexible. Although all acid-base problems are similar in many ways, important differences do occur. Treat each problem as a separate entity. Do not try to force a given problem to match any you have solved before. Look for both the similarities and the differences.

Be patient. The complete solution to a complicated problem cannot be seen immediately in all its detail. Pick the problem apart into its workable steps.

Be confident. Look within the problem for the solution, and let the problem guide you. Assume that you can think it out. Do not rely on memorizing solutions to problems. In fact, memorizing solutions is usually detrimental, because you tend to try to force a new problem to be the same as one you have seen before. ***Understand and think; don't just memorize.***

Calculating $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH

Problem: A chemist dilutes concentrated hydrochloric acid to make two solutions: (a) 3.0 M and (b) 0.0024 M. Calculate the $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH of the two solutions at 25°C.

Plan: We know that hydrochloric acid is a strong acid, so it dissociates completely in water; therefore $[\text{H}_3\text{O}^+] = [\text{HCl}]_{\text{init.}}$. We use the $[\text{H}_3\text{O}^+]$ to calculate the $[\text{OH}^-]$ and pH as well as pOH.

Solution:

(a) $[\text{H}_3\text{O}^+] = 3.0 \text{ M}$ $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(3.0) = \underline{\hspace{2cm}}$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1 \times 10^{-14}}{3.0} = \underline{\hspace{2cm}} \text{ M}$$

$$\text{pOH} = -\log(3.333 \times 10^{-15}) = 15.000 - 0.477 = \underline{\hspace{2cm}}$$

(b) $[\text{H}_3\text{O}^+] = 0.0024 \text{ M}$ $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0024) = \underline{\hspace{2cm}}$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1 \times 10^{-14}}{0.0024} = \underline{\hspace{2cm}} \text{ M}$$

$$\text{pOH} = -\log(4.167 \times 10^{-12}) = 12.000 - 0.6198 = \underline{\hspace{2cm}}$$







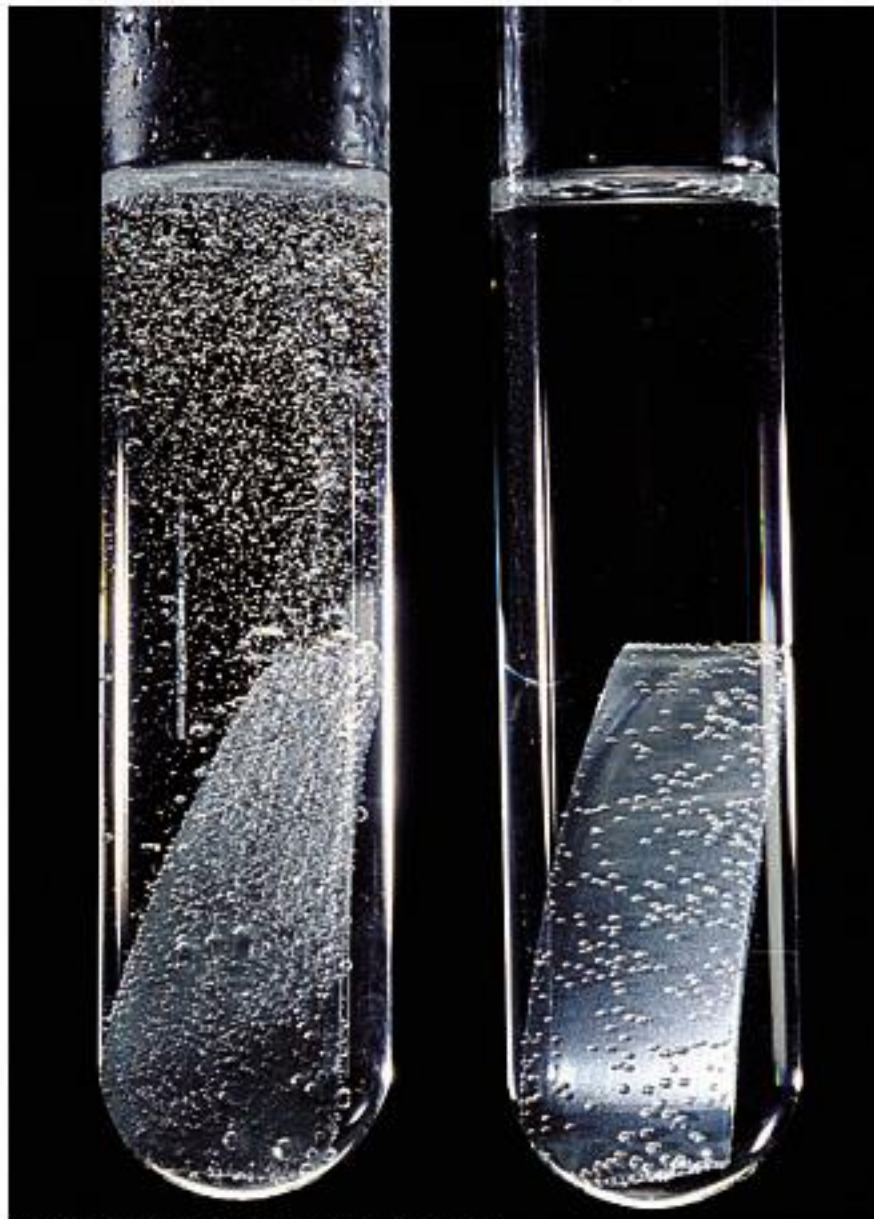
FABRIC
ACID DYE
11A

FABRIC ACID DYE
11B

FABRIC ACID DYE
11C



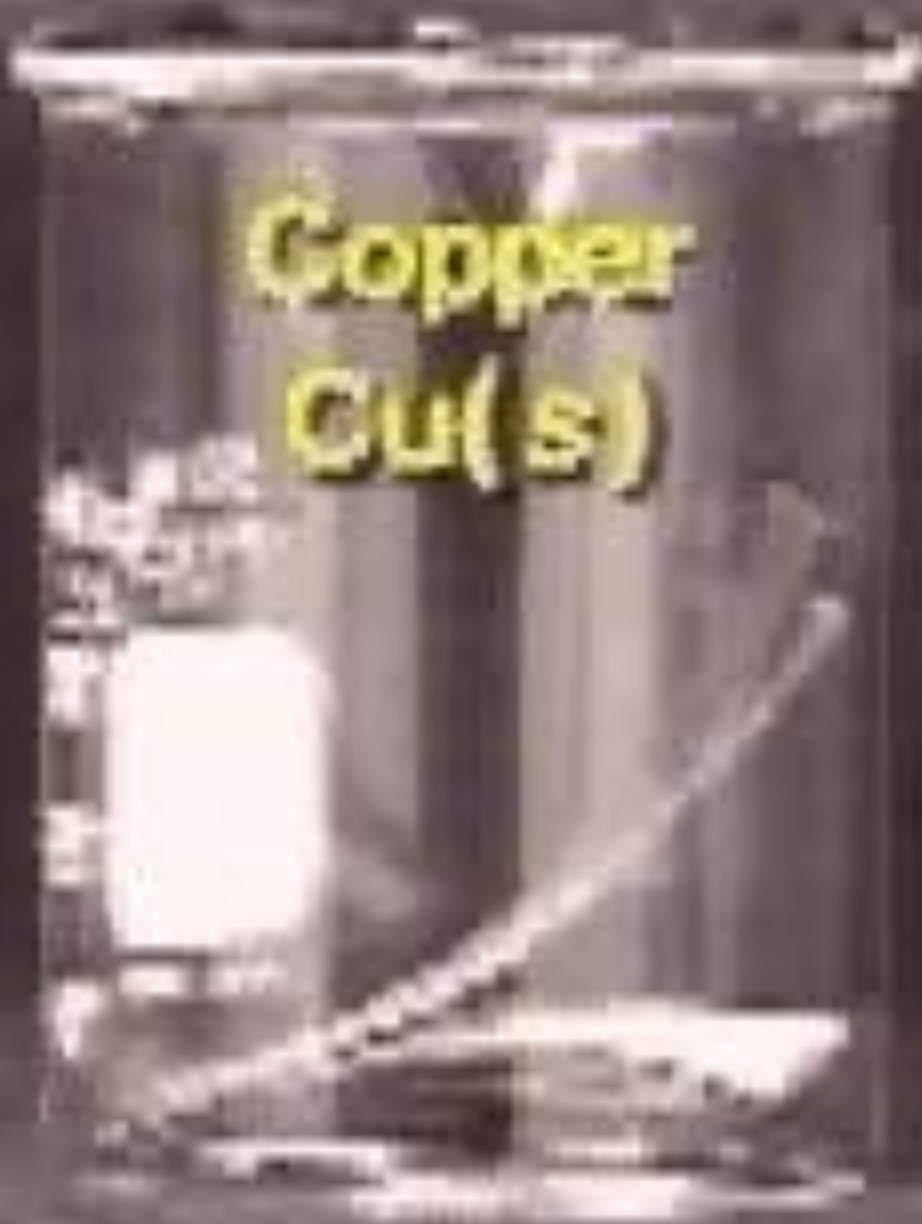
Reaction of Zinc with Strong vs. Weak Acid



© McGraw-Hill Higher Education/Stephen Frisch, photographer

Copper

$\text{Cu}(s)$



Cu

H_2SO_4 (aq)



Cu

HCl (aq)

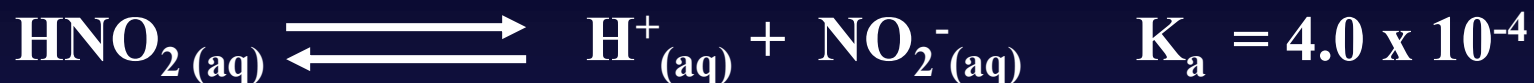




Calculate the pH of a 1.00 M HNO₂ Solution

Problem: Calculate the pH of a 1.00 M Solution of Nitrous acid HNO₂.

Solution:



Initial concentrations = $[\text{H}^+] = 0$, $[\text{NO}_2^-] = 0$, $[\text{HNO}_2] = 1.00 \text{ M}$

Final concentrations = $[\text{H}^+] = x$, $[\text{NO}_2^-] = x$, $[\text{HNO}_2] = 1.00 \text{ M} - x$

$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = 4.0 \times 10^{-4} = \frac{(x)(x)}{1.00 - x}$$

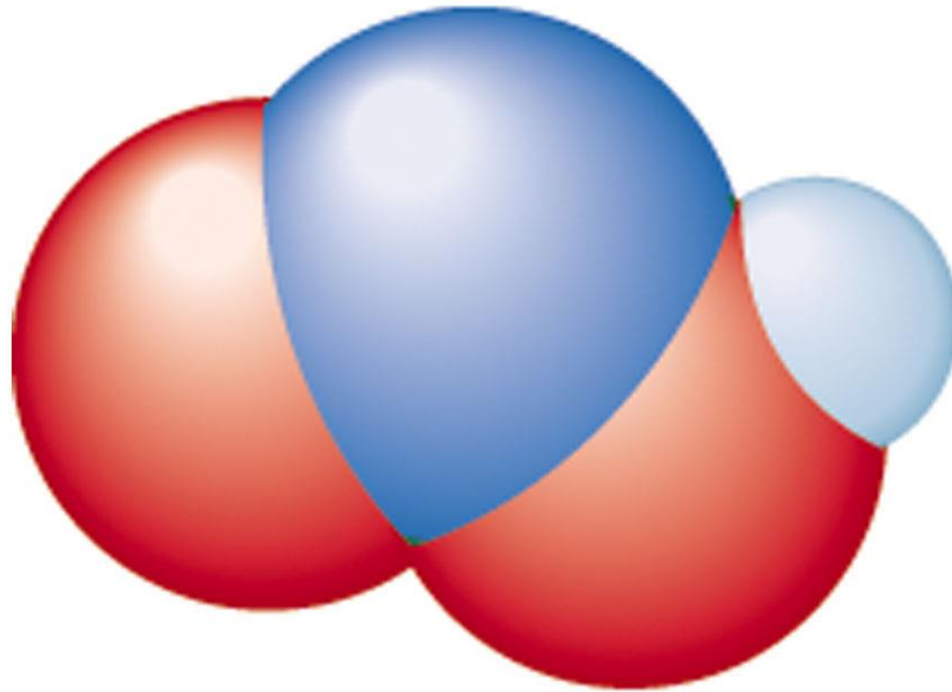
Assume $1.00 - x = 1.00$ to simplify the problem.

$$\frac{x^2}{1.00} = 4.0 \times 10^{-4} \quad \text{or} \quad x^2 = 4.0 \times 10^{-4}$$

$$x = 2.0 \times 10^{-2} = 0.02 \text{ M} = [\text{H}^+] = [\text{NO}_2^-]$$

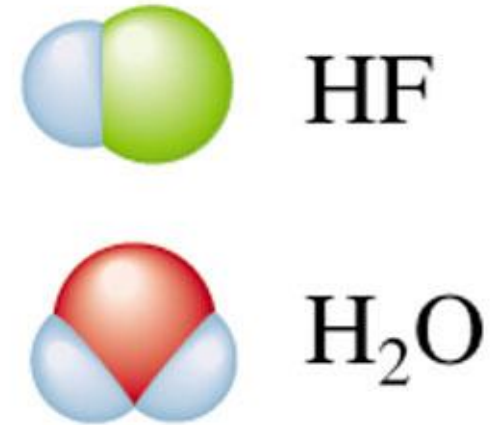
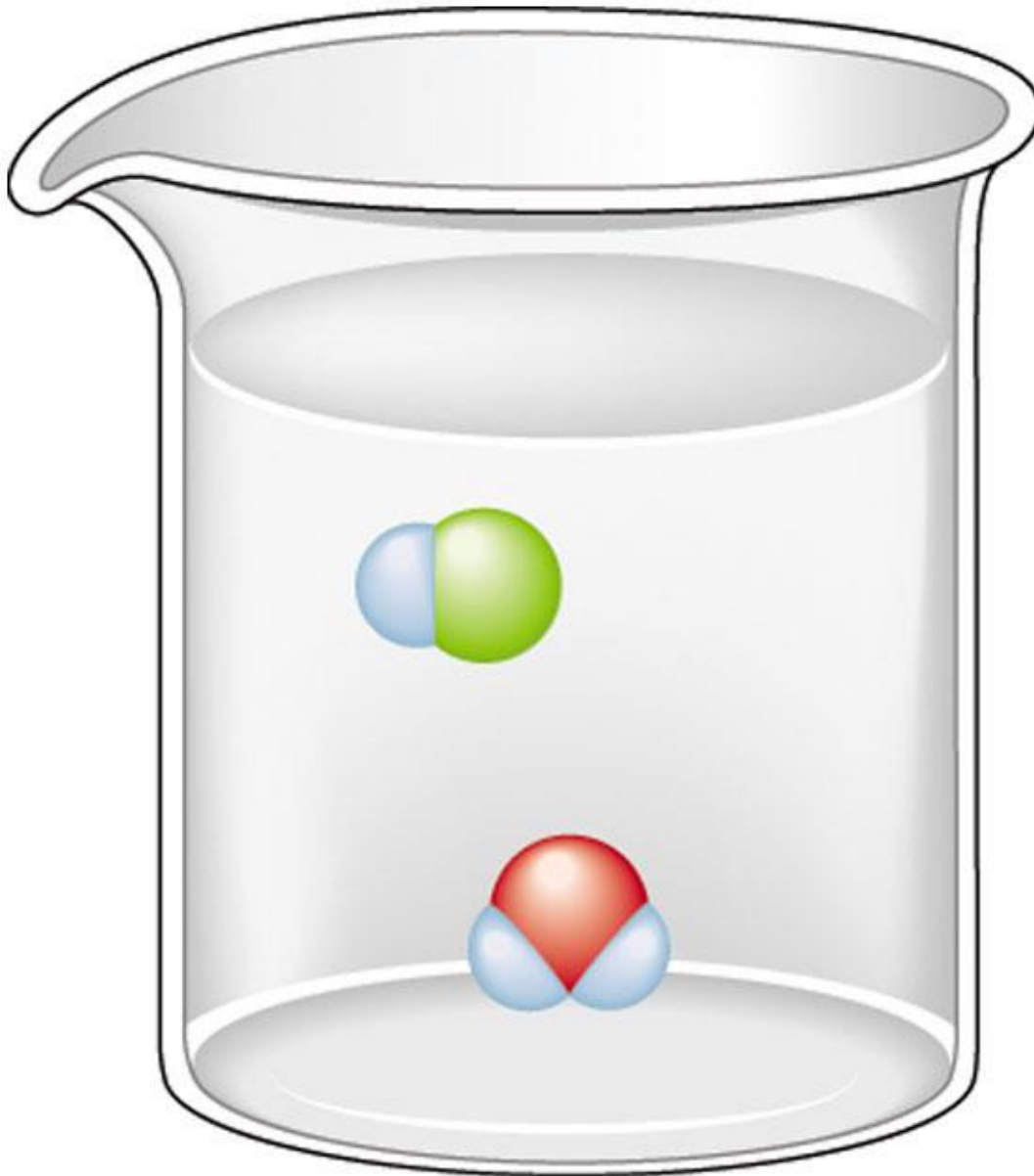
$$\text{pH} = -\log[\text{H}^+] = -\log(2.0 \times 10^{-2}) = 2.00 - 0.30 = \underline{\hspace{2cm}}$$

Molecular model: Nitrous acid



Nitrous acid
(HNO₂)

Molecular model: HF and H₂O



Summary:

(P 237)

Solving Weak Acid Equilibrium Problems

- List the major species in the solution.
- Choose the species that can produce H^+ , and write balanced equations for the reactions producing H^+ .
- Comparing the values of the equilibrium constants for the reactions you have written, decide which reaction will dominate in the production of H^+ .
- Write the equilibrium expression for the dominant reaction.
- List the initial concentrations of the species participating in the dominant reaction.
- Define the change needed to achieve equilibrium; that is, define x .
- Write the equilibrium concentrations in terms of x .
- Substitute the equilibrium concentrations into the equilibrium expression.
- Solve for x the “easy” way—that is, by assuming that $[\text{HA}]_0 - x = [\text{HA}]_0$
- Verify whether the approximation is valid (the 5% rule is the test in this case).
- Calculate $[\text{H}^+]$ and pH.

Like Example 7.3 (P 237)-I

Calculate the pH of a solution that contains 1.00 M HF ($K_a = 7.2 \times 10^{-4}$) and 5.00 M HOCl ($K_a = 3.5 \times 10^{-8}$). Also calculate the concentrations of the Fluoride and Hypochlorite ions at equilibrium.

Three components produce H^+ :



Even though HF is a weak acid, it has by far the greatest K_a , therefore it will be the dominate producer of H^+ .

$$K_a = \frac{[H^+][F^-]}{[HF]} = 7.2 \times 10^{-4}$$

Like Example 7.3 (P 236)-II

Initial Concentration
(mol/L)

Equilibrium Concentration
(mol/L)

$$\begin{aligned}[\text{HF}]_0 &= 1.00 \\ [\text{F}^-] &= 0 \\ [\text{H}^+] &\cong 0\end{aligned}$$

x mol HF
dissociates

$$\begin{aligned}[\text{HF}] &= 1.00 - x \\ [\text{F}^-] &= x \\ [\text{H}^+] &= x\end{aligned}$$

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 7.2 \times 10^{-4} = \frac{(x)(x)}{1.00-x} = \frac{x^2}{1.00} \quad x = 2.7 \times 10^{-2}$$

$x = 2.7 \times 10^{-2}$ using the 5% rule: $\frac{x}{[\text{HF}]_0} = \frac{2.7 \times 10^{-2}}{1.00} \times 100\% = 2.7\%$

Therefore,

$$[\text{F}^-] = [\text{H}^+] = x = 2.7 \times 10^{-2} \quad \text{and pH} = \underline{\hspace{2cm}}$$

Like Example 7.3 (P 236)-III

$$K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} = 3.5 \times 10^{-8}$$

The concentration of H^+ comes from the first part of this problem = $2.7 \times 10^{-2} \text{ M}$

$$[\text{HOCl}] = 5.00 \text{ M} ; [\text{OCl}^-] = x$$

$$3.5 \times 10^{-8} = \frac{(2.7 \times 10^{-2})[\text{OCl}^-]}{(5.00 - x)}$$

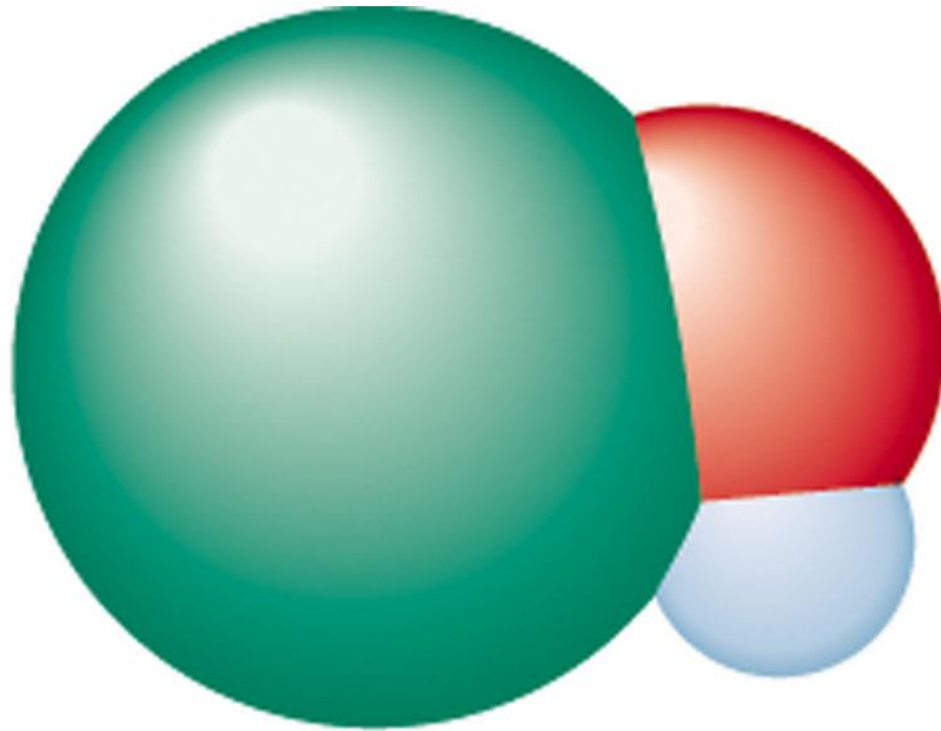
Assume: $5.00 - x = 5.00$

$$[\text{OCl}^-] = \frac{5.00 (3.5 \times 10^{-8})}{2.7 \times 10^{-2}} = 6.48 \times 10^{-6} \text{ M}$$

$$\text{pH} = 1.56$$

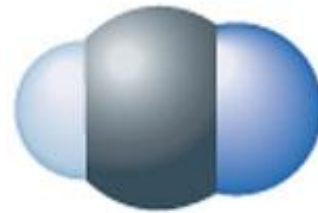
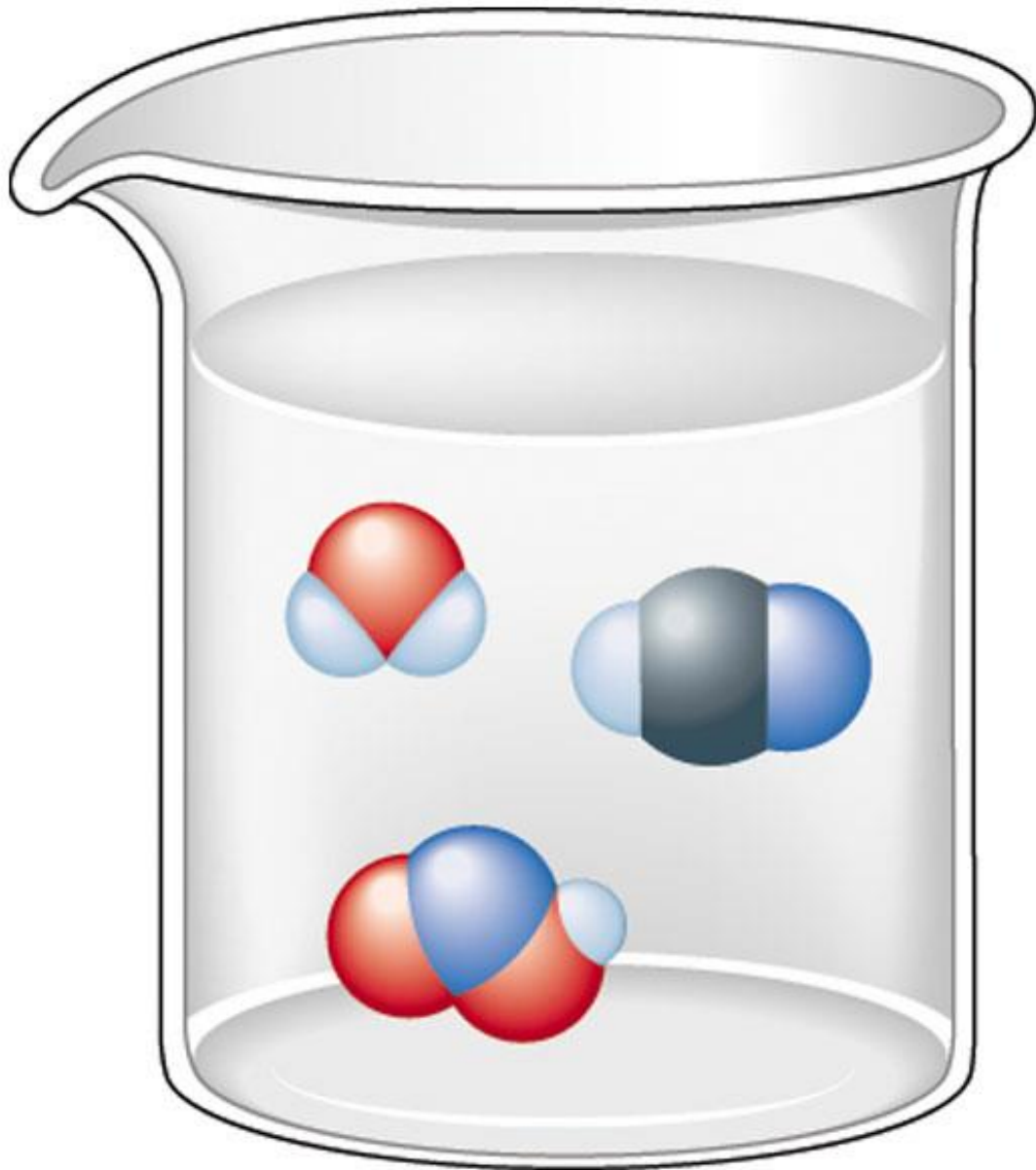
$$[\text{F}^-] = 2.7 \times 10^{-2} \text{ M} ; [\text{OCl}^-] = 6.48 \times 10^{-6} \text{ M}$$

Molecular model: Hypochlorous acid (HOCl)

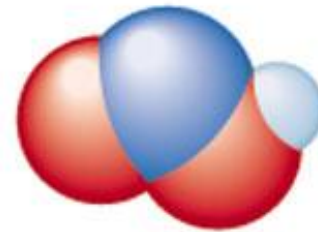


Hypochlorous acid
(HOCl)

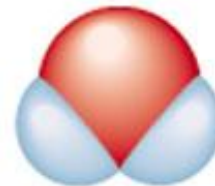
Molecular model: HCN, HNO₂, and H₂O



HCN

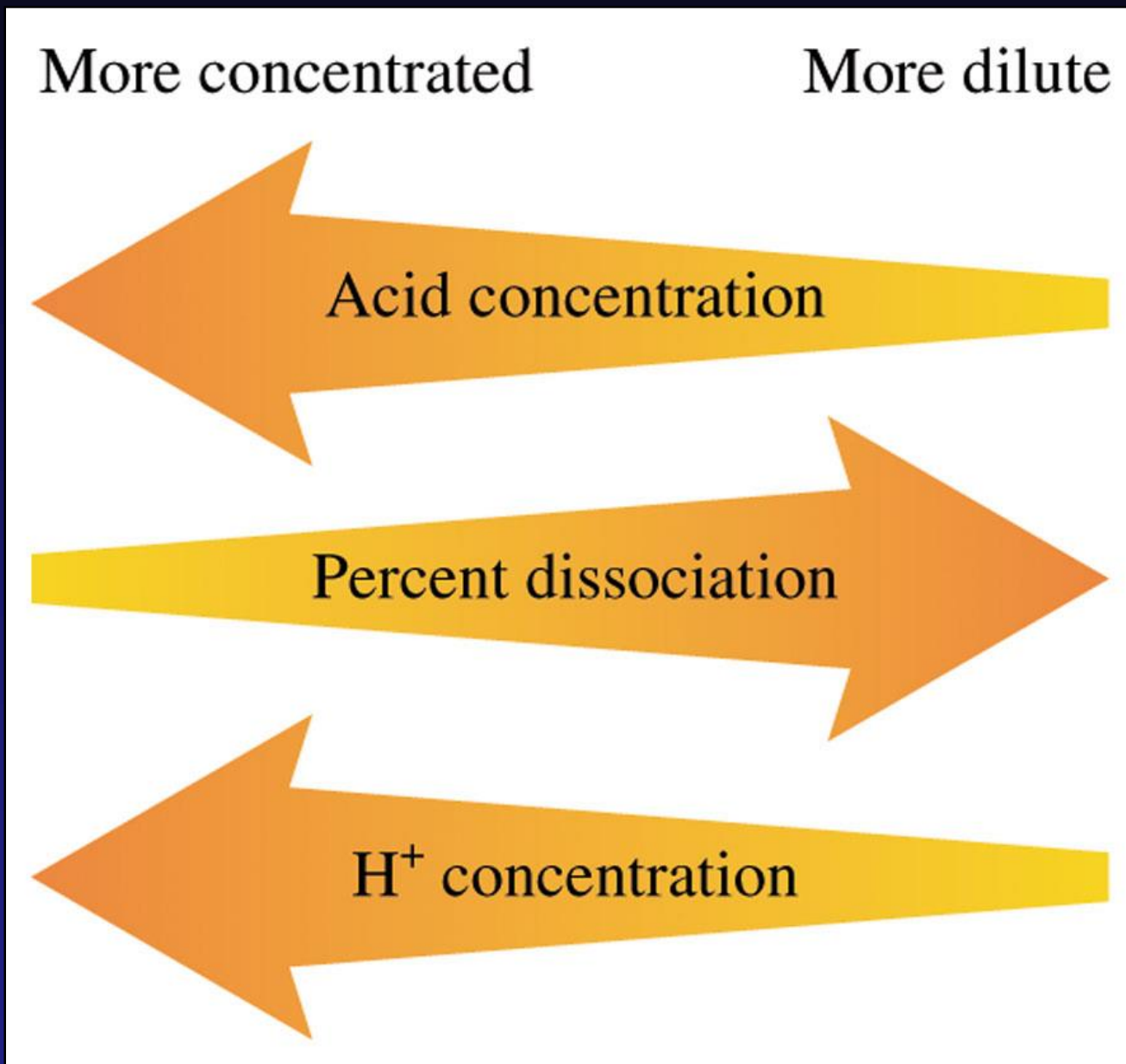


HNO₂



H₂O

Figure 7.5: Effect of dilution on the percent dissociation and $[H^+]$



Problem: Calculate the Percent dissociation of a 0.0100M Hydrocyanic acid solution, $K_a = 6.20 \times 10^{-10}$.



	HCN	H_3O^+	CN^-
Initial	0.0100M	0	0
Change	-x	+x	+x
Final	0.0100 - x	x	x

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

$$K_a = \frac{(x)(x)}{(0.0100-x)} = 6.20 \times 10^{-10}$$

Assume $0.0100-x = 0.0100$

$$K_a = \frac{x^2}{0.0100} = 6.2 \times 10^{-10}$$

$$x = 2.49 \times 10^{-6}$$

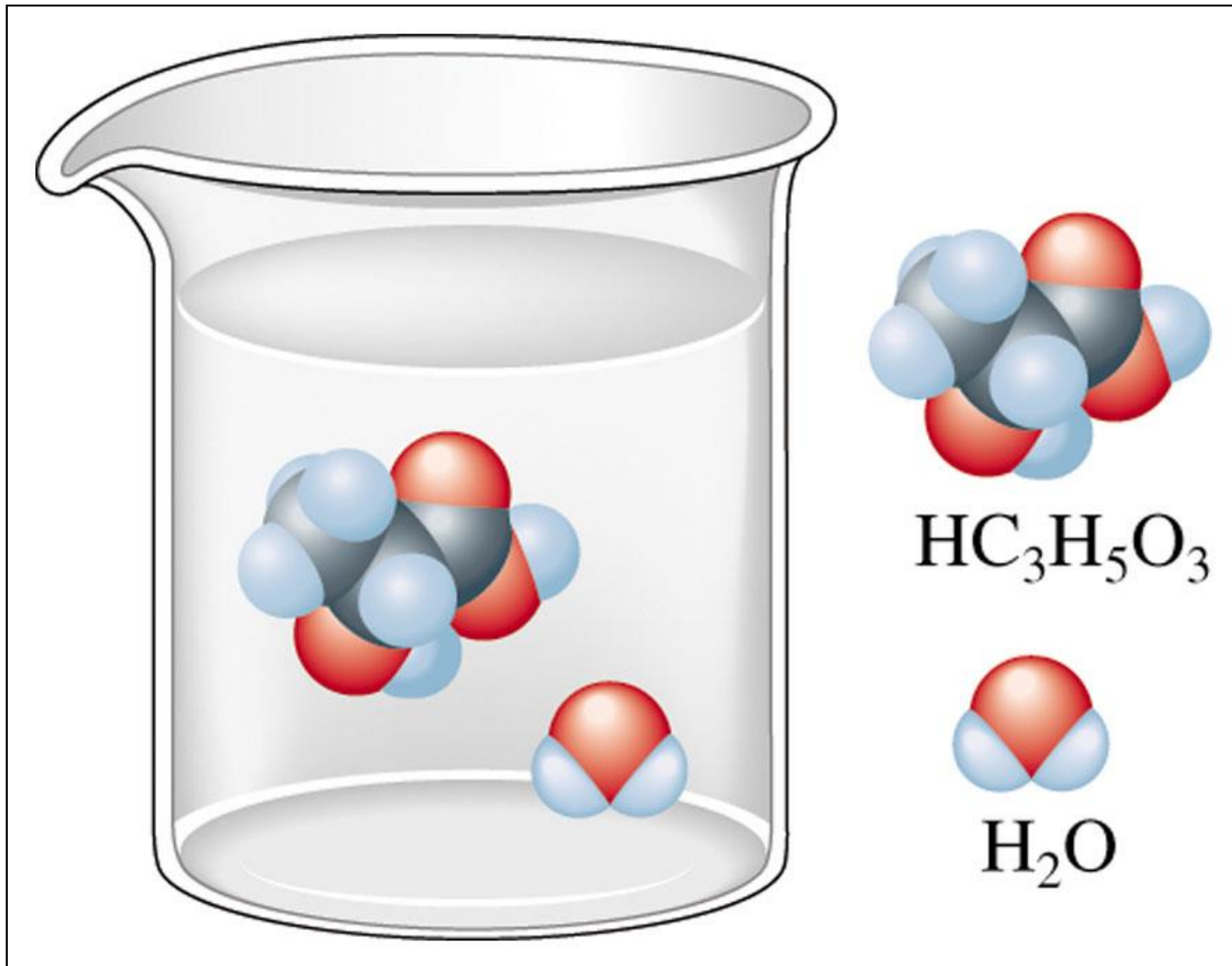
$$\% \text{ dissociation} = \frac{2.49 \times 10^{-6}}{0.0100} \times 100\% = \underline{\hspace{2cm}}$$

Runner struggles to top of a hill



Source: Corbis

Molecular model: $\text{HC}_3\text{H}_5\text{O}_3$ and H_2O



Finding the K_a of a Weak Acid from the pH of its Solution–I

Problem: The weak acid hypochlorous acid is formed in bleach solutions. If the pH of a 0.12 M solution of HClO is 4.19, what is the value of the K_a of this weak acid.

Plan: We are given $[\text{HClO}]_{\text{initial}}$ and the pH which will allow us to find $[\text{H}_3\text{O}^+]$ and, hence, the hypochlorite anion concentration, so we can write the reaction and expression for K_a and solve directly.

Solution:

Calculating $[\text{H}_3\text{O}^+]$: $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.19} = 6.46 \times 10^{-5} M$

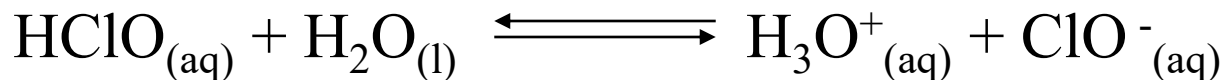


Initial	0.12		----		-----		-----
Change	-x		----		+x		+x
Equilibrium	0.12 -x		----		+x		+x

Assumptions: $[\text{H}_3\text{O}^+] = [\text{H}_3\text{O}^+]_{\text{HClO}}$

since HClO is a weak acid, we assume $0.12 M - x = 0.12 M$

Finding the K_a of a Weak Acid from the pH of its Solution–II



$$x = [\text{H}_3\text{O}^+] = [\text{ClO}^-] = 6.46 \times 10^{-5} \text{ M}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} = \frac{(6.46 \times 10^{-5} \text{ M})(6.46 \times 10^{-5} \text{ M})}{0.12 \text{ M}} = 348 \times 10^{-10}$$

$$K_a = 3.48 \times 10^{-8}$$

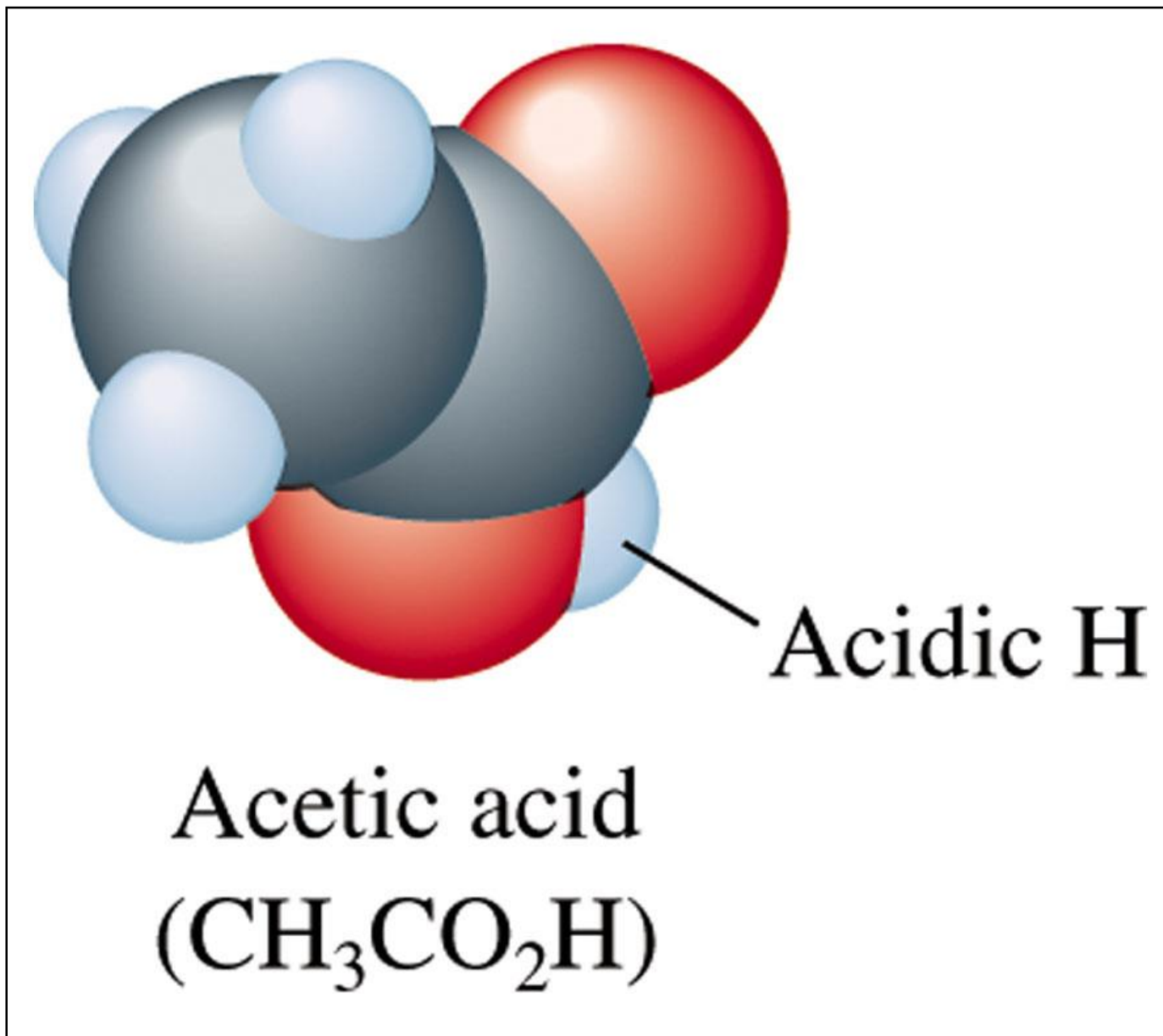
In text books it is found to be: 3.5×10^{-8}

Checking:

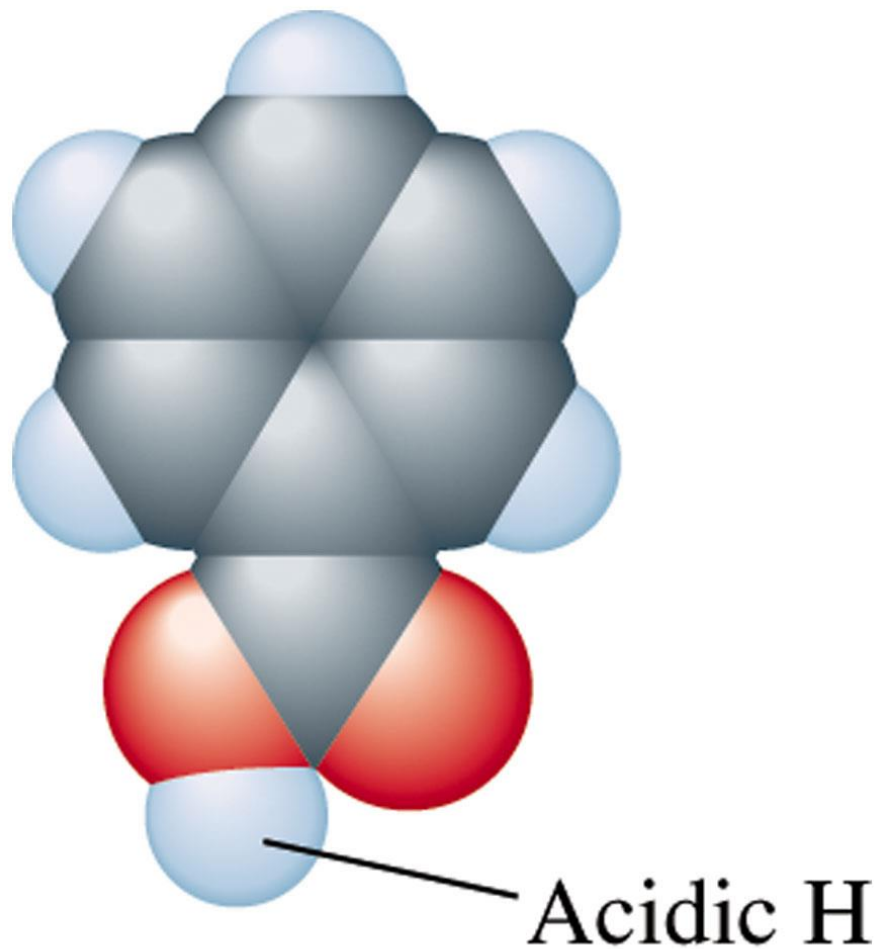
1. For $[\text{H}_3\text{O}^+]_{\text{from water}}$: $\frac{1 \times 10^{-7} \text{ M}}{6.46 \times 10^{-5} \text{ M}} \times 100 = 0.155\%$
assumption is OK

2. For $[\text{HClO}]_{\text{dissoc}}$: $\frac{6.46 \times 10^{-5} \text{ M}}{0.12 \text{ M}} \times 100 = 0.0538\%$

Molecular model: Acetic acid



Molecular model: Benzoic acid

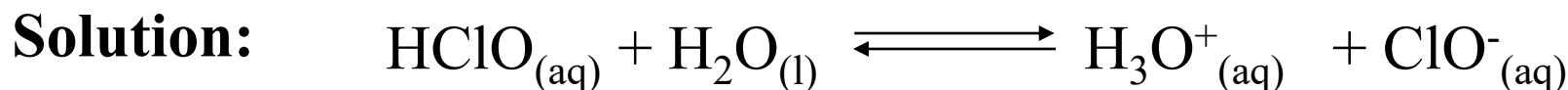


Benzoic acid
($\text{C}_6\text{H}_5\text{CO}_2\text{H}$)

Determining Concentrations from K_a and Initial [HA]

Problem: Hypochlorous acid is a weak acid formed in laundry bleach. What is the $[H_3O^+]$ of a 0.125 M HClO solution? $K_a = 3.5 \times 10^{-8}$

Plan: We need to find $[H_3O^+]$. First we write the balanced equation and the expression for K_a and solve for the hydronium ion concentration.



$$K_a = \frac{[H_3O^+][ClO^-]}{[HClO]} = 3.5 \times 10^{-8}$$

Concentration (M)	HClO	H ₂ O	H ₃ O ⁺	ClO ⁻
Initial	0.125	----	0	0
Change	-x	----	+x	+x
Equilibrium	0.125 - x	----	x	x

$$K_a = \frac{(x)(x)}{0.125-x} = 3.5 \times 10^{-8} \quad \text{assume } 0.125 - x = 0.125$$
$$x^2 = 0.4375 \times 10^{-8} \quad x = 0.661 \times 10^{-4}$$

Solving Problems Involving Weak-Acid Equilibria–I

There are two general types of equilibrium problems involving weak acids and their conjugate bases:

1. Given equilibrium concentrations, find K_a .
2. Given K_a and some concentration information, find the other equilibrium concentrations.

The problem-solving approach.

1. Write the balanced equation and K_a expression; these will tell you what to find.
2. Define x as the unknown concentration that changes during the reaction. Frequently, $x = [\text{HA}]_{\text{dissoc.}}$, the concentration of HA that dissociates which, through the use of certain assumptions, also equals $[\text{H}_3\text{O}^+]$ and $[\text{A}^-]$ at equilibrium.
3. Construct a reaction table that incorporates the unknown.
4. Make assumptions that simplify the calculation, usually that x is very small relative to the initial concentration.

Solving Problems Involving Weak-Acid Equilibria–II

5. Substitute the values into the K_a expression and solve for x .
6. Check that the assumptions are justified. We normally apply the 5% rule; if the value of x is greater than 5% of the value it is compared with, you must use the quadratic formula to find x .

The notation system. Molar concentrations of species are indicated by using square brackets around the species of interest. Brackets with no subscript refer to the molar concentration of the species at equilibrium.

The assumptions. The two key assumptions to simplify the arithmetic are:

1. The $[\text{H}_3\text{O}^+]$ from the autoionization of water is negligible. In fact, the presence of acid from whatever is put into solution will hinder the autoionization of water, and make it even less important.
2. A weak acid has a small K_a . Therefore, it dissociates to such a small extent that we can neglect the change in its concentration to find its equilibrium concentration.

Tanks in Miami, Florida



Source: Visuals Unlimited

Like Example 7.5 (P 243)

Calculate the pH of a 2.0×10^{-3} M solution of NaOH.

Since NaOH is a strong base, it will dissociate 100% in water.



Since $[\text{NaOH}] = 2.0 \times 10^{-3}$ M, $[\text{OH}^-] = 2.0 \times 10^{-3}$ M

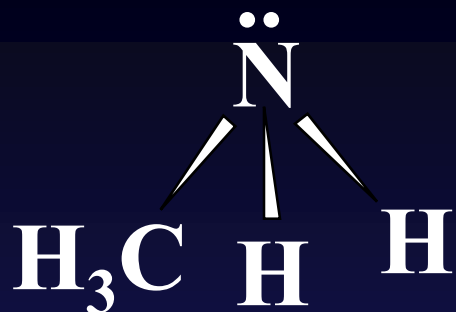
The concentration of $[\text{H}^+]$ can be calculated from K_w :

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12} \text{ M}$$

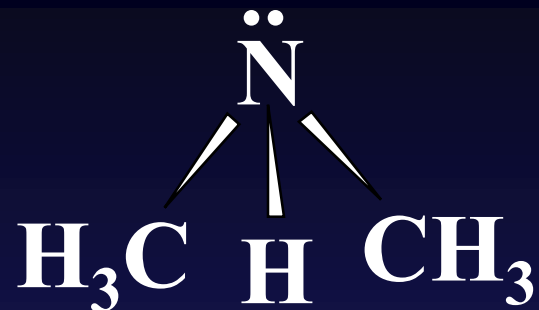
$$\text{pH} = -\log [\text{H}^+] = -\log(5.0 \times 10^{-12}) = 12.00 - 0.70 = \underline{\hspace{2cm}}$$



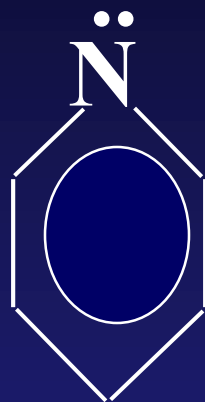
Amines: Bases with the Nitrogen Atom



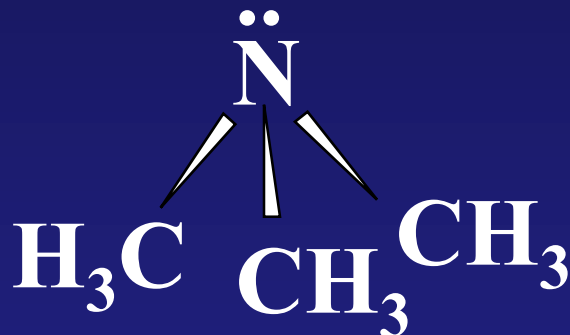
Methylamine



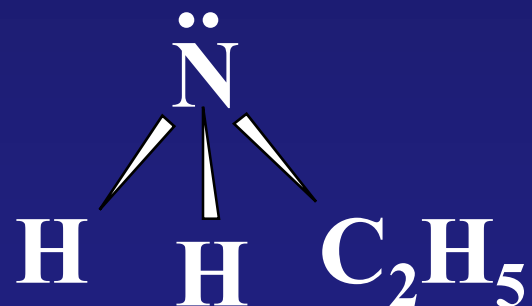
Dimethylamine



Pyridine



Trimethylamine



Ethylamine

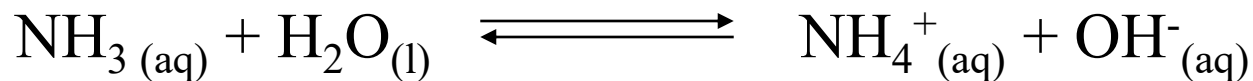
TABLE 7.3 Values of K_b for Some Common Weak Bases

Name	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	CH_3NH_3^+	4.38×10^{-4}
Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	$\text{C}_2\text{H}_5\text{NH}_3^+$	5.6×10^{-4}
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_5\text{NH}_3^+$	3.8×10^{-10}
Pyridine	$\text{C}_5\text{H}_5\text{N}$	$\text{C}_5\text{H}_5\text{NH}^+$	1.7×10^{-9}

Determining pH from K_b and Initial [B]–I

Problem: Ammonia is commonly used cleaning agent in households and is a weak base, with a K_b of 1.8×10^{-5} . What is the pH of a 1.5 M NH_3 solution?

Plan: Ammonia reacts with water to form $[\text{OH}^-]$ and then calculate $[\text{H}_3\text{O}^+]$ and the pH. The balanced equation and K_b expression are:



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

Concentration (M)	NH_3	H_2O	NH_4^+	OH^-
Initial	1.5	----	0	0
Change	-x	----	+x	+x
Equilibrium	$1.5 - x$	----	x	x

making the assumption: since K_b is small: $1.5 \text{ M} - x = 1.5 \text{ M}$

Determining pH from K_b and Initial [B]–II

Substituting into the K_b expression and solving for x:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(x)(x)}{1.5} = 1.8 \times 10^{-5}$$

$$x^2 = 2.7 \times 10^{-5} = 27 \times 10^{-6}$$

$$x = 5.20 \times 10^{-3} = [\text{OH}^-] = [\text{NH}_4^+]$$

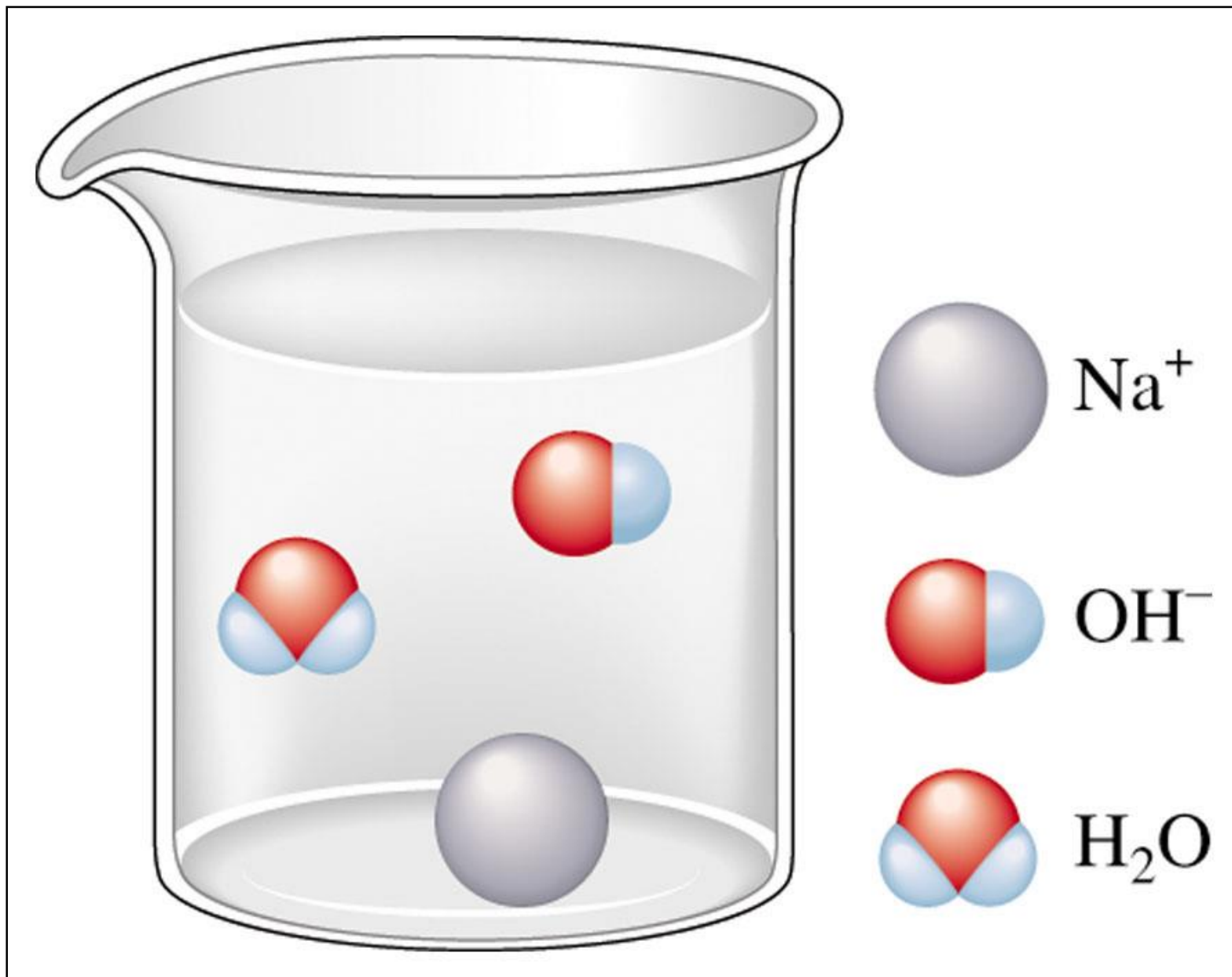
Calculating pH:

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.20 \times 10^{-3}} = 1.92 \times 10^{-12}$$

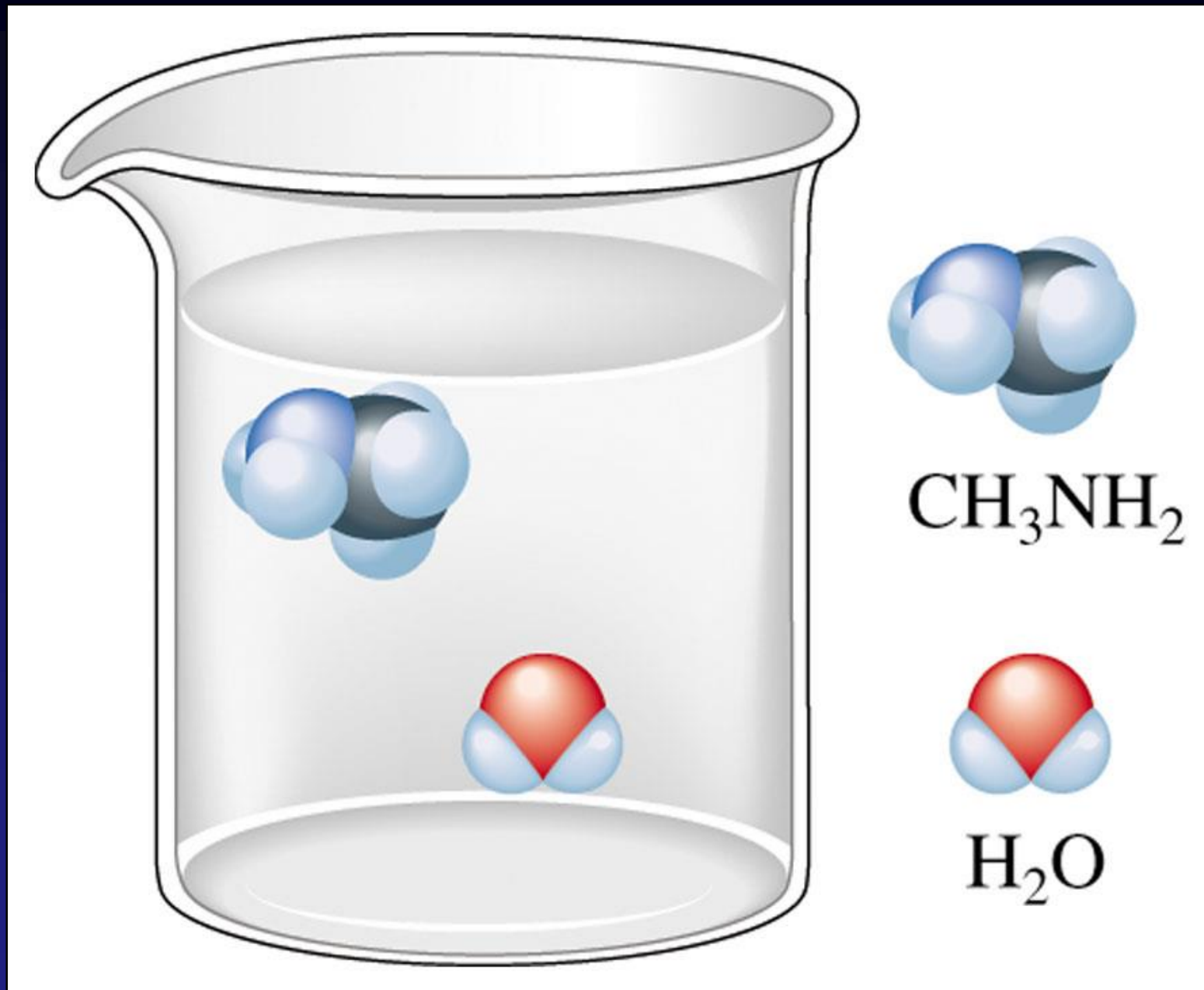
$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.92 \times 10^{-12}) = 12.000 - 0.283$$

pH = _____

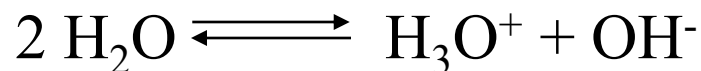
Molecular model: Na^+ and OH^- and H_2O



Molecular model: CH_3NH_2 and H_2O



The Relation Between K_a and K_b of a Conjugate Acid-Base Pair



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

$$K_w = K_a \times K_b$$

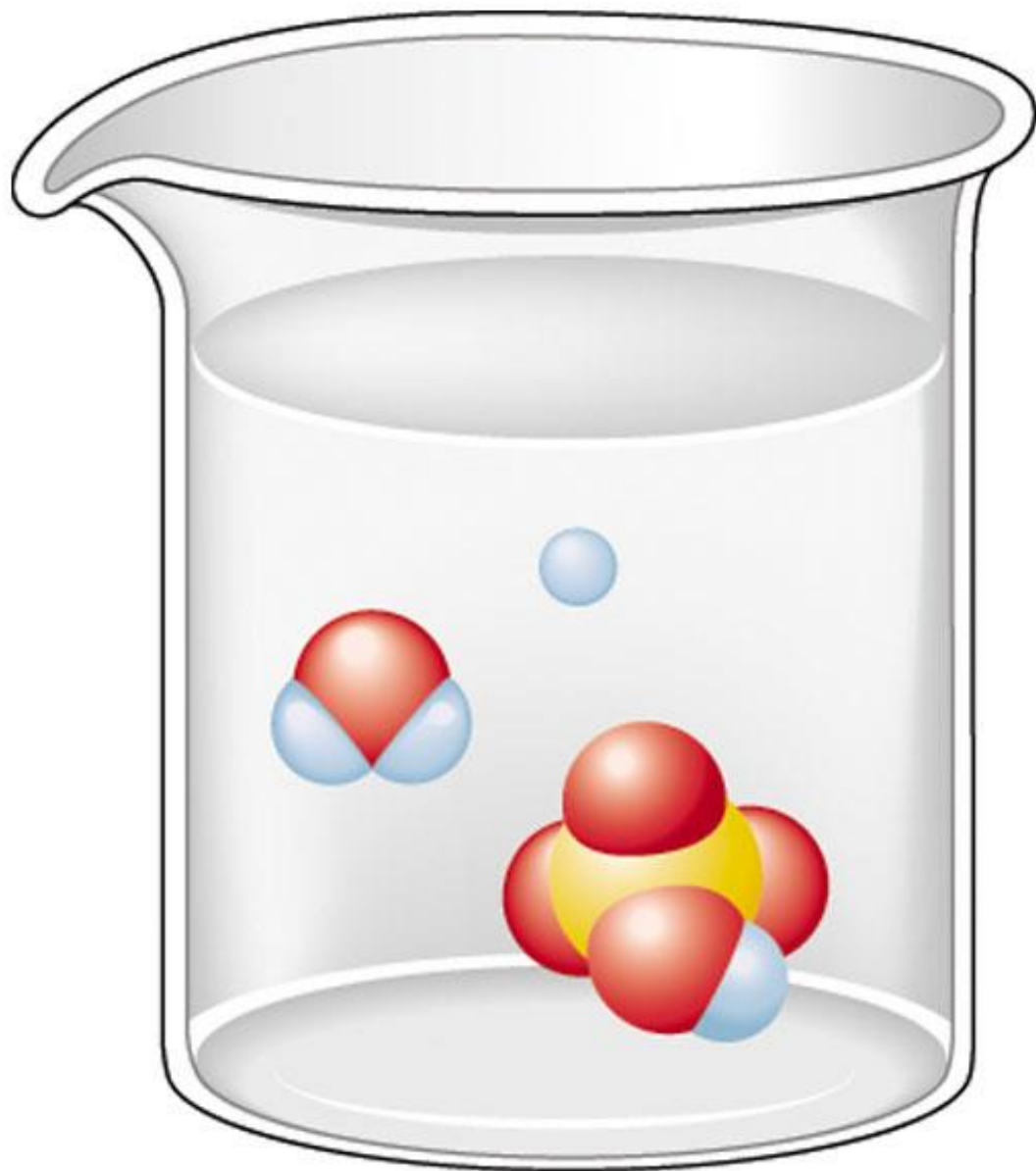
$$K_a = 4.5 \times 10^{-4}$$

For HNO_2 $\quad\quad\quad K_a \times K_b = (4.5 \times 10^{-4})(2.2 \times 10^{-11}) = 9.9 \times 10^{-15}$

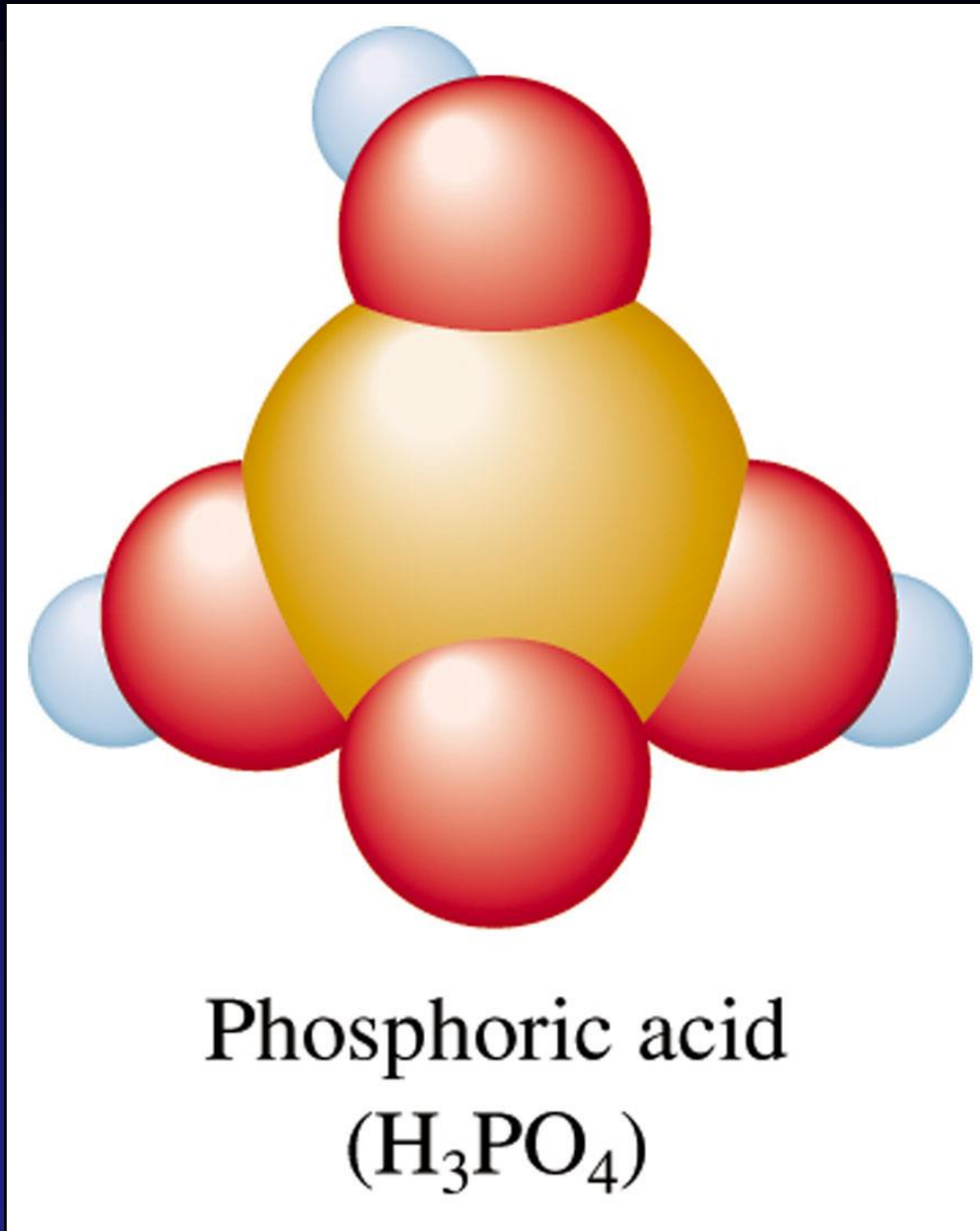
$$K_b = 2.2 \times 10^{-11}$$

$$\text{or } \sim 10 \times 10^{-15} = 1 \times 10^{-14} = K_w$$

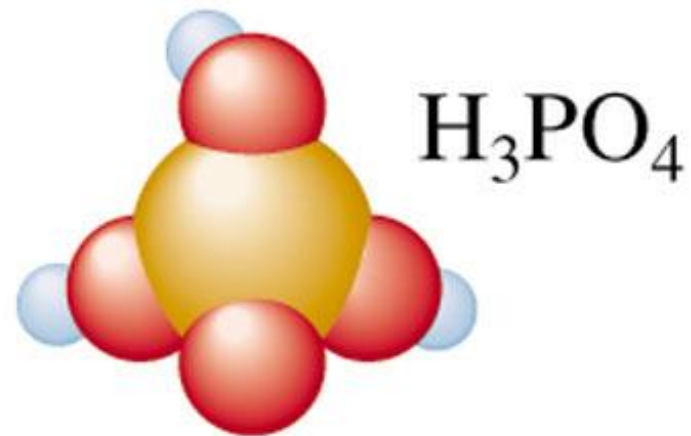
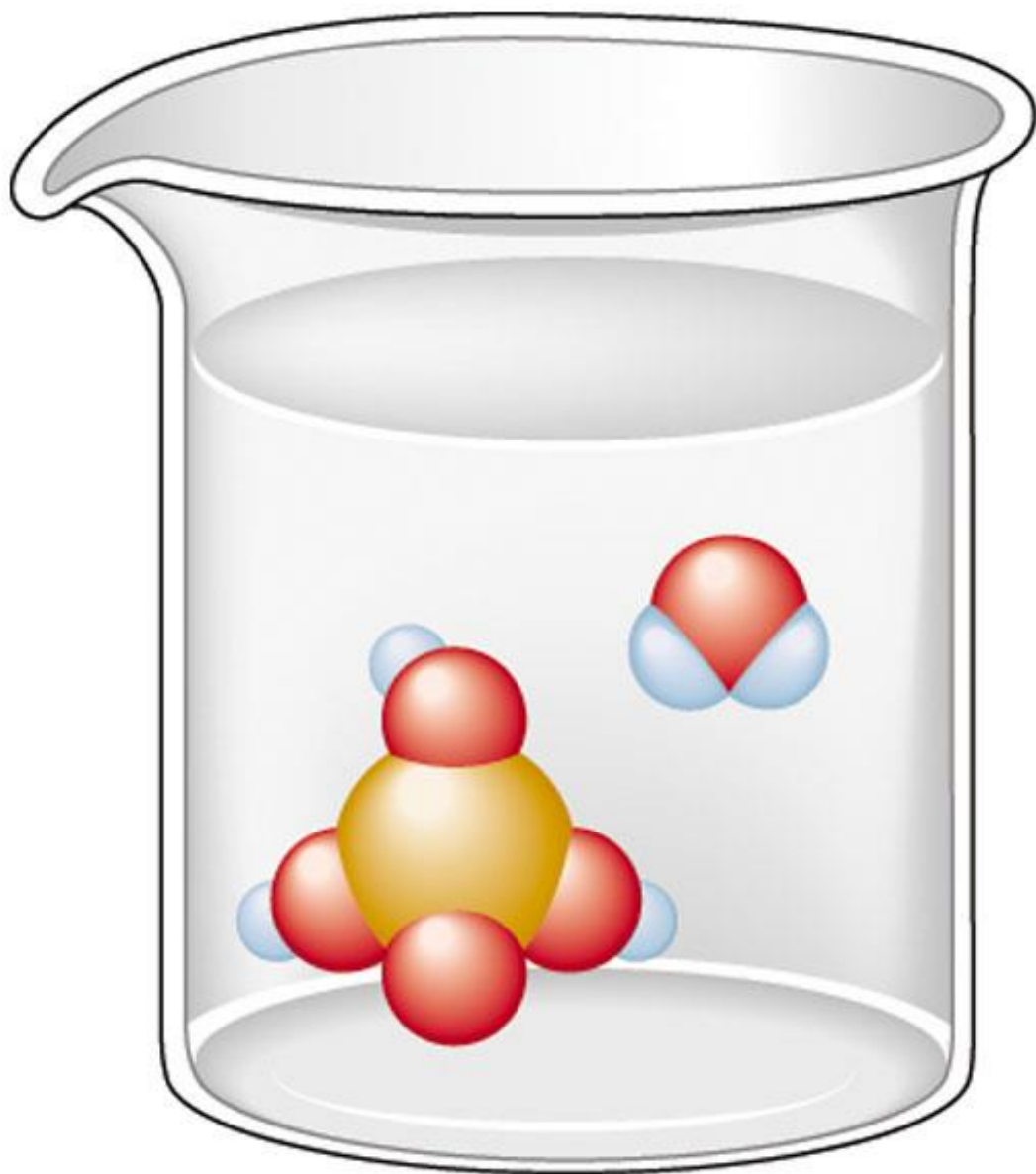
Molecular model: H^+ , HSO_4^- , and H_2O



Molecular model: Phosphoric acid



Molecular model: H_3PO_4 and H_2O



Like Example 7.7 (P247-8)-I

Calculate the pH of a 5.0 M H_3PO_4 solution and determine equilibrium concentrations of the species: H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} .

Solution:



$$K_a = 7.5 \times 10^{-3} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

Initial Concentration (mol/L)

$$[\text{H}_3\text{PO}_4]_0 = 5.0$$

$$[\text{H}_2\text{PO}_4^-]_0 = 0$$

$$[\text{H}^+]_0 = 0$$

Equilibrium Concentration (mol/L)

$$[\text{H}_3\text{PO}_4] = 5.0 - x$$

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

$$[\text{H}^+] = x$$

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

Like Example 7.7 (P247-8) - II

Solving for $x \cong 1.9 \times 10^{-1}$ Since 1.9×10^{-1} is less than 5% of 5.0, the approximation is acceptable and:

$$[\text{H}^+] = x = 0.19 \text{ M} = [\text{H}_2\text{PO}_4^-], \quad \text{pH} = 0.72 \quad [\text{H}_3\text{PO}_4] = 5.0 - x = 4.8 \text{ M}$$

The concentration of HPO_4^{2-} can be obtained from K_{a2} :

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

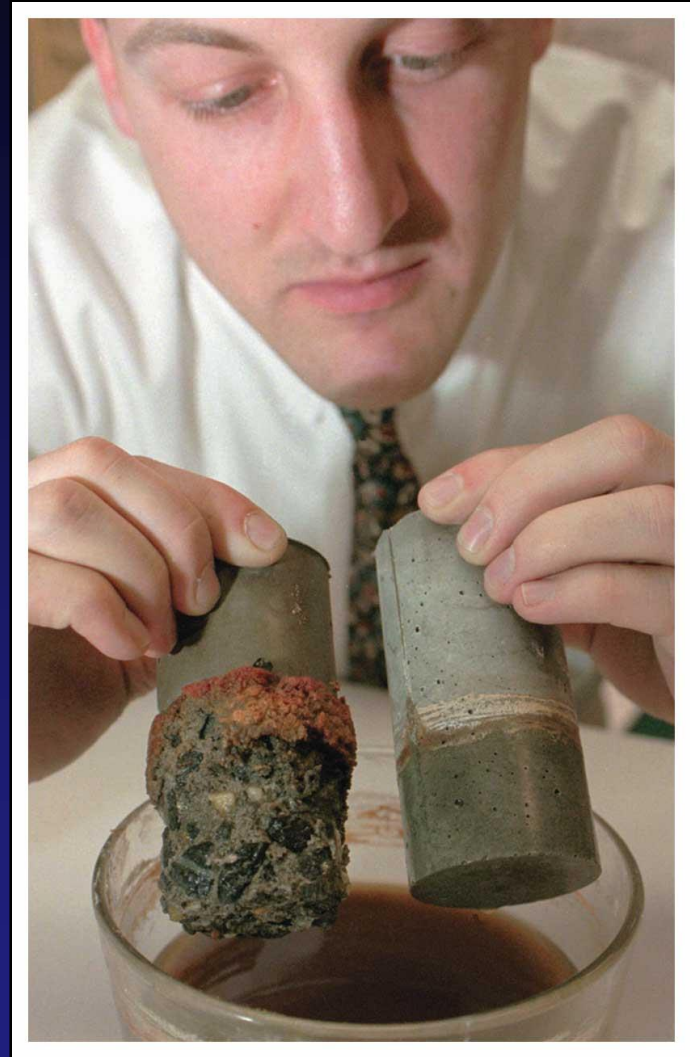
where: $[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.19 \text{ M}$; $[\text{HPO}_4^{2-}] = K_{a2} = 6.2 \times 10^{-8} \text{ M}$

To calculate $[\text{PO}_4^{3-}]$, we use the expression for K_{a3} , and the values obtained from the other calculations:

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

$$[\text{PO}_4^{3-}] = \frac{(4.8 \times 10^{-13})(6.2 \times 10^{-8})}{0.19} = \underline{\hspace{2cm}} \text{ M}$$

**A Drexel University
Chemist shows that
a new form of concrete
called ZeoTech
(on the right)
can withstand soaking
in sulfuric acid for 30
days**



Like Example 7.9 (P251-2)

Calculate the pH of a 3.00×10^{-3} M Sulfuric acid solution.

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
-------------------------------	--	-----------------------------------

$$[\text{HSO}_4^-]_0 = 0.00300$$

$$[\text{SO}_4^{2-}]_0 = 0$$

$$[\text{H}^+]_0 = 0.00300$$

From dissociation of H_2SO_4

x mol/L HSO_4^-

$\xrightarrow{\text{dissociates}}$
 to reach
 equilibrium

$$[\text{HSO}_4^-] = 0.00300 - x$$

$$[\text{SO}_4^{2-}] = x$$

$$[\text{H}^+] = 0.00300 + x$$

$$K_{a2} = 1.2 \times 10^{-2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(0.00300 + x)(x)}{(0.00300 - x)} \quad \begin{array}{l} \text{Assume} \\ x \ll 0.00300 \end{array}$$

When we solve for x we get $x = 1.2 \times 10^{-2}$, which is close to 0.00300 therefore the approximation is not valid, and we must solve with the quadratic formula. Multiplying the expression out we get:

$$0 = x^2 + 0.015x - 3.6 \times 10^{-5}$$

$$a = 1, b = 0.015$$

$$c = -3.6 \times 10^{-5}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = 2.10 \times 10^{-3}$$

$$[\text{H}^+] = 0.00300 + x = 0.00510$$

$$\text{pH} = 2.29$$

Figure 7.6: A plot of the fractions of H_2CO_3 , HCO_3^- and CO_3^{2-}

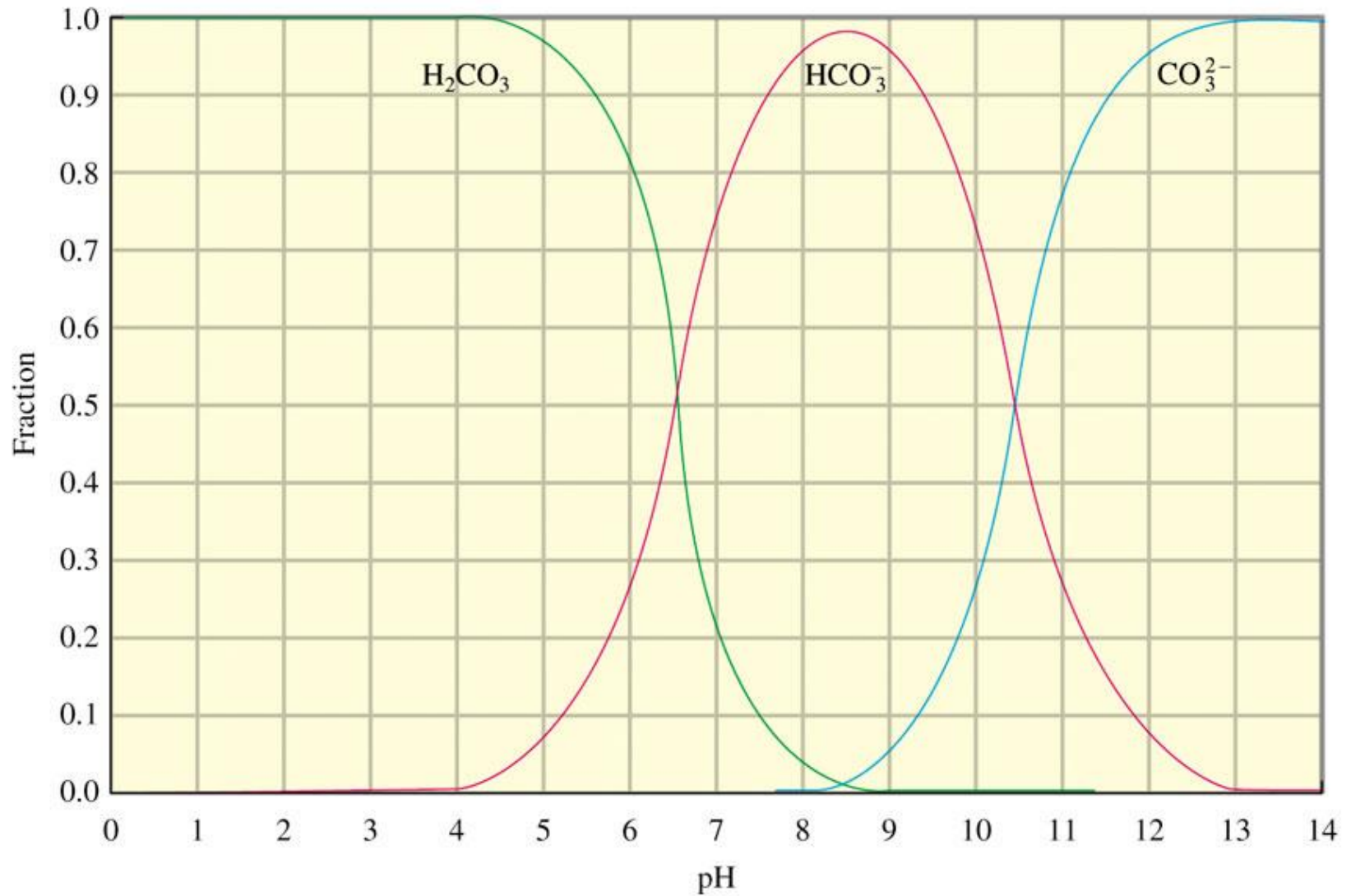


TABLE 7.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid*	H_2CO_3	4.3×10^{-7}	4.8×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid [†]	H_2S	1.0×10^{-7}	$\approx 10^{-19}$	
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	7.9×10^{-5}	1.6×10^{-12}	

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

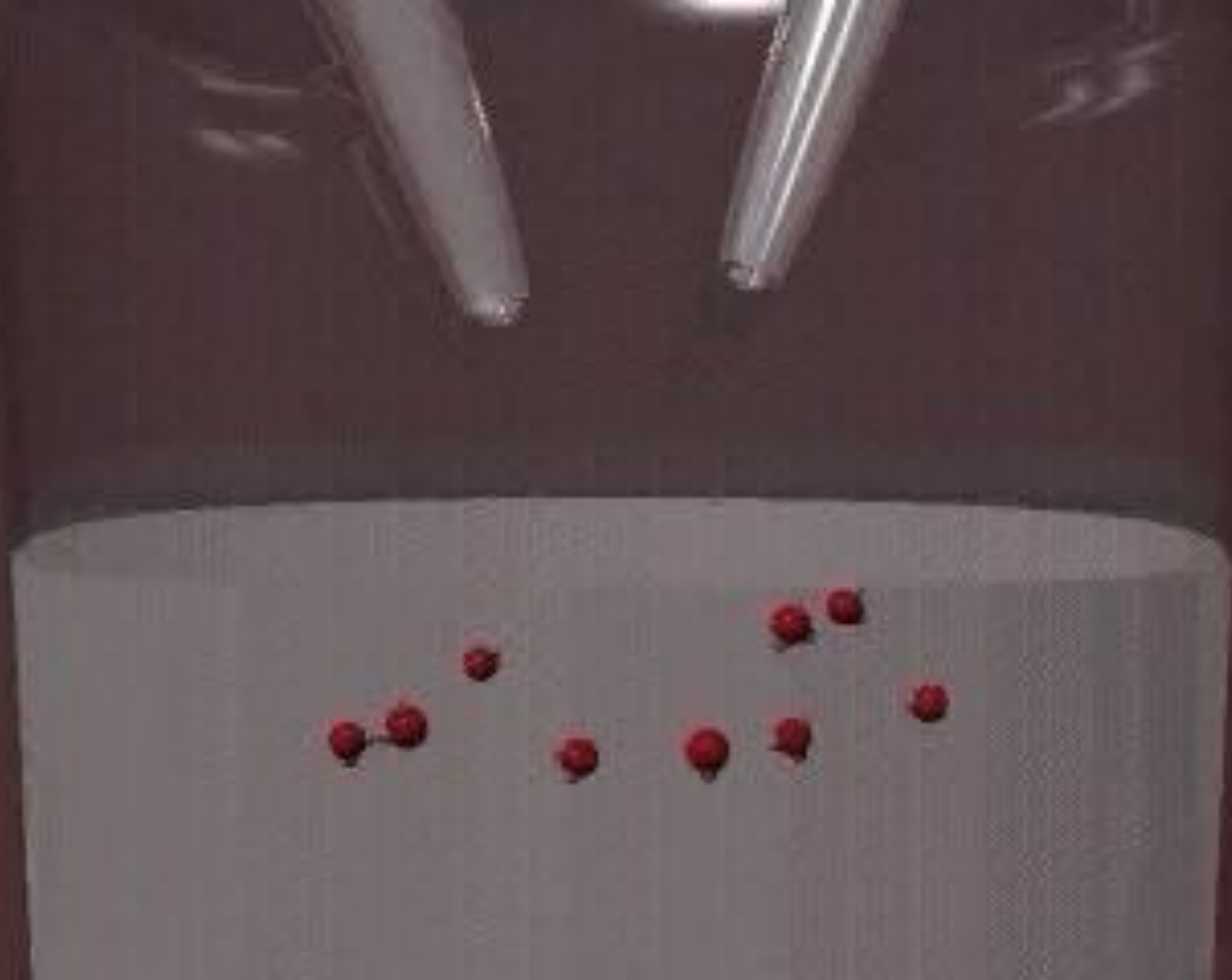
[†]The K_{a_2} value for H_2S is quite uncertain. Its small size makes it very difficult to measure.

The Effect of Atomic and Molecular Properties on Nonmetal Hydride Acidity

Electronegativity increases, acidity increases

Bond strength decreases, acidity increases

	6A(16)	7A(17)
	H ₂ O	HF
	H ₂ S	HCl
	H ₂ Se	HBr
	H ₂ Te	HI



Effects of Salts on pH and Acidity

Salts that consist of cations of strong bases and the anions of strong acids have no effect on the $[H^+]$ when dissolved in water.

Examples: $NaCl$, KNO_3 , Na_2SO_4 , $NaClO_4$, KBr , etc.

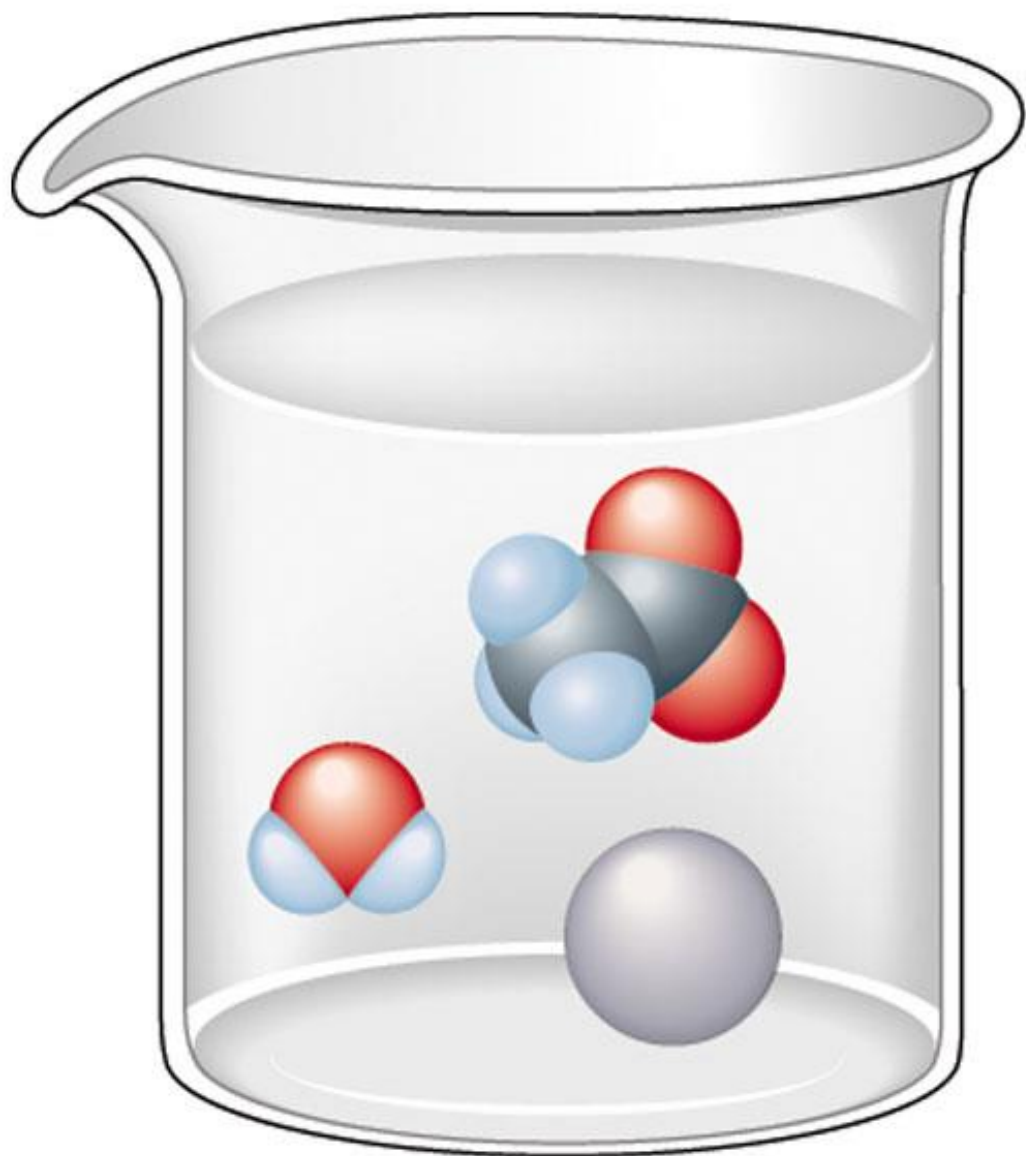
For any salt whose cation has neutral properties (such as Na^+ or K^+) and whose anion is the conjugate base of a weak acid, the aqueous solution will be basic.

Examples: NaF , KCN , $NaC_2H_3O_2$, Na_3PO_4 , Na_2CO_3 , K_2S ,
 $Na_2C_2O_4$, etc.

A salt whose cation is the conjugate acid of a weak base produces an acidic solution when dissolved in water.

Examples: NH_4Cl , $AlCl_3$, $Fe(NO_3)_3$, etc.

Molecular model: Na^+ , $\text{C}_2\text{H}_3\text{O}_2^-$, and H_2O



Na^+



$\text{C}_2\text{H}_3\text{O}_2^-$



H_2O

Like Example 7.11 (P255) - I

Calculate the pH of a 0.45M NaCN solution. The K_a value for HCN is 6.2×10^{-10} .

Solution: Since HCN is a weak acid, the Cyanide ion must have significant affinity for protons.



$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

The value of K_b can be calculated from K_w and the K_a value for HCN.

$$K_b = \frac{K_w}{K_a \text{ (for HCN)}} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.61 \times 10^{-5}$$

Initial Concentration (mol/L) Equilibrium Concentration (mol/L)

$$[\text{CN}^-]_0 = 0.45$$

$$[\text{HCN}]_0 = 0$$

$$[\text{OH}^-]_0 = 0$$

X mol/L CN^- reacts with


H₂O to reach equilibrium

$$[\text{CN}^-] = 0.45 - x$$

$$[\text{HCN}] = x$$

$$[\text{OH}^-] = x$$

Like Example 7.11 (P255) - II

Thus:

$$K_b = 1.61 \times 10^{-5} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{(x)(x)}{0.45 - x} \approx \frac{x^2}{0.45}$$

$$x \approx 2.69 \times 10^{-3}$$

Although this is not exactly valid by the 5% rule, it is only off by 1%, so we will use it for now!

$$x = [\text{OH}^-] = 2.69 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = 3 - 0.43 = 2.57$$

$$\text{pH} = 14.00 - 2.57 = \underline{\hspace{2cm}}$$

Behavior of Salts in Water

The Behavior of Salts in Water

Salt Solution (Examples)

pH

Nature of Ions

Ion That Reacts with Water

Neutral

7.0

Cation of
strong base
Anion of
strong acid

None

[NaCl, KBr,
Ba(NO₃)₂]



Acidic

<7.0

Cation of
weak base
Anion of
strong acid

Cation

[NH₄Cl, NH₄NO₃,
CH₃NH₃Br]



Acidic

<7.0

Small, highly
charged cation
Anion of
strong acid

Cation

[Al(NO₃)₃,
CrCl₃, FeBr₃]



Basic

>7.0

Cation of
strong base
Anion of
weak acid

Anion

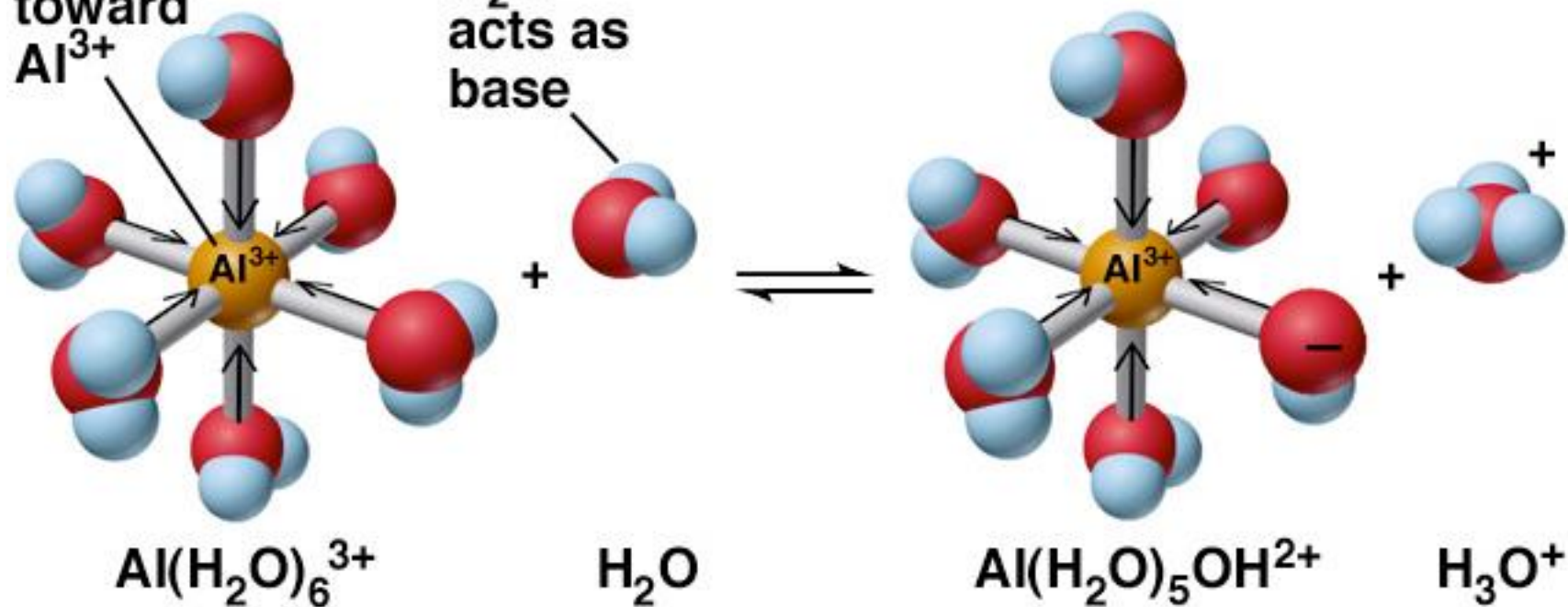
[CH₃COONa,
KF, Na₂CO₃]



Acidic Behavior of the Hydrated Al^{3+} Ion

Electron density drawn toward Al^{3+}

Nearby H_2O acts as base



Like Example 7.12 (P 255-6) - I

Calculate the pH of a 0.010 M AlCl_3 solution. The K_a value for the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion is 1.4×10^{-5} .

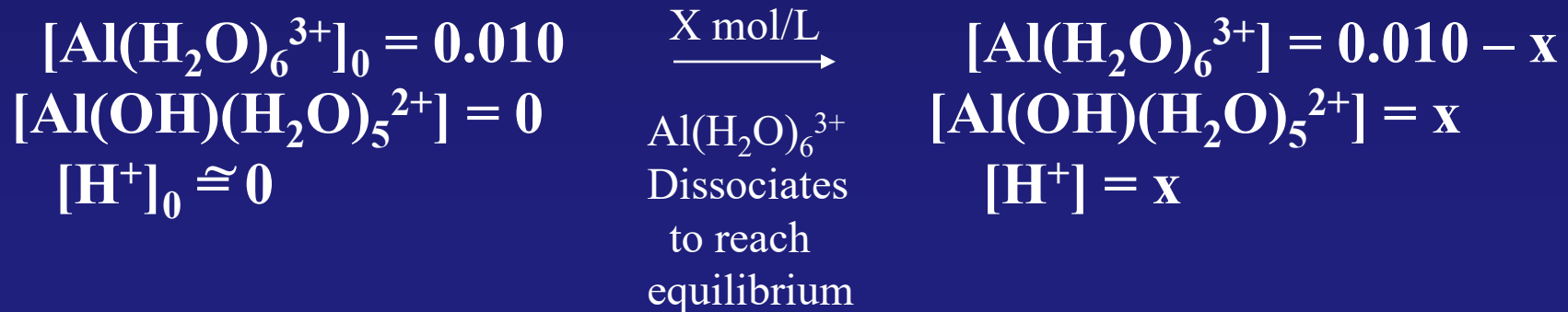
Solution:

Since the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion is a stronger acid than water, the dominant equilibrium will be:



$$1.4 \times 10^{-5} = K_a = \frac{[\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}][\text{H}^+]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]}$$

<u>Initial Concentration (mol/L)</u>		<u>Equilibrium Concentration (mol/L)</u>
--------------------------------------	--	--



Like Example 7.12 (P 255-6) - II

Thus:

$$1.4 \times 10^{-5} = K_a = \frac{[\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}][\text{H}^+]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]} =$$

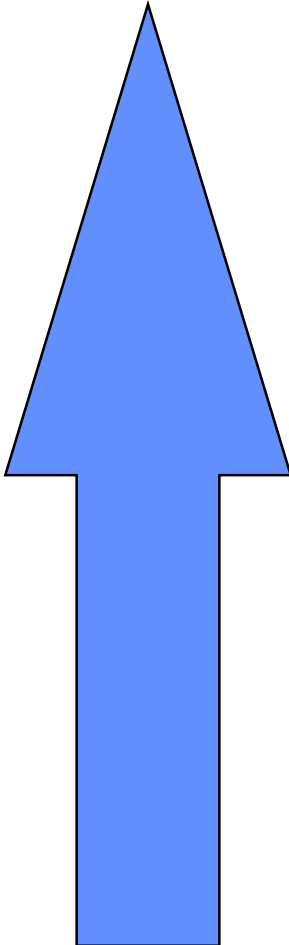
$$K_a = \frac{(x)(x)}{0.010 - x} = \frac{x^2}{0.010}$$

$$x = 3.7 \times 10^{-4}$$

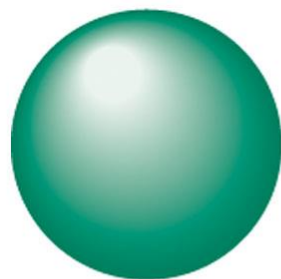
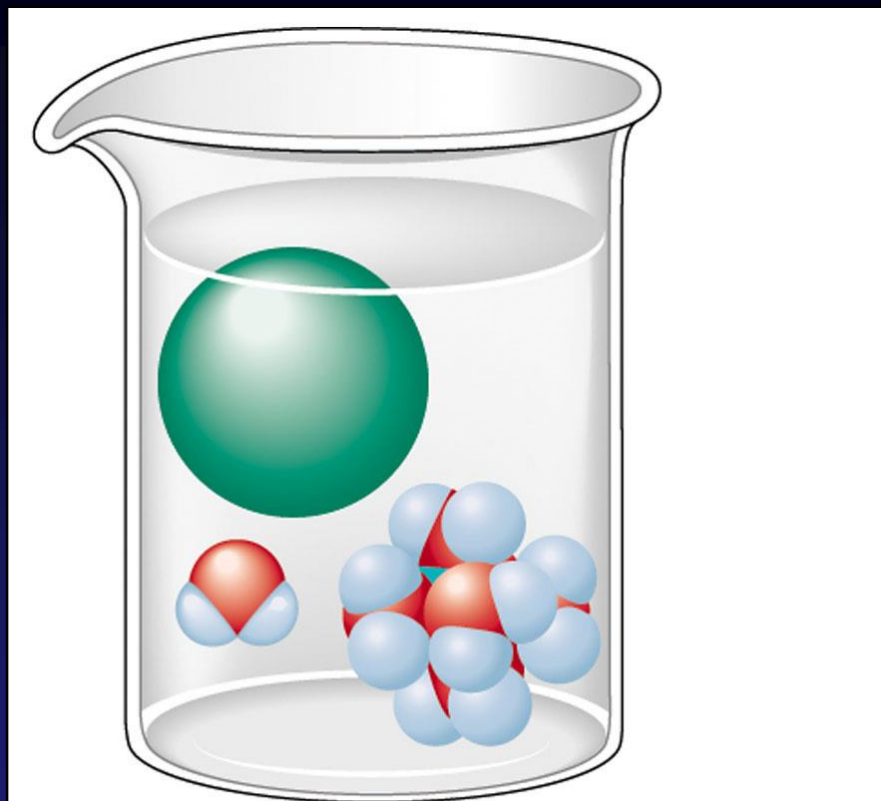
Since the approximation is valid by the 5% rule:

$$[\text{H}^+] = x = 3.7 \times 10^{-4} \text{ M} \quad \text{and} \quad \text{pH} = \underline{\hspace{2cm}}$$

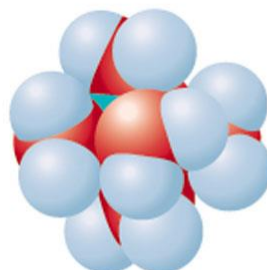
K_a Values of Some Hydrated Metal Ions at 25°C

Ion	K_a	Increasing acidity
$\text{Fe}^{3+} (\text{aq})$	6×10^{-3}	
$\text{Sn}^{2+} (\text{aq})$	4×10^{-4}	
$\text{Cr}^{3+} (\text{aq})$	1×10^{-4}	
$\text{Al}^{3+} (\text{aq})$	1×10^{-5}	
$\text{Be}^{2+} (\text{aq})$	4×10^{-6}	
$\text{Cu}^{2+} (\text{aq})$	3×10^{-8}	
$\text{Pb}^{2+} (\text{aq})$	3×10^{-8}	
$\text{Zn}^{2+} (\text{aq})$	1×10^{-9}	
$\text{Co}^{2+} (\text{aq})$	2×10^{-10}	
$\text{Ni}^{2+} (\text{aq})$	1×10^{-10}	

Molecular model: Cl^- , $\text{Al}(\text{H}_2\text{O})_6^{3+}$, H_2O



Cl^-



$\text{Al}(\text{H}_2\text{O})_6^{3+}$



H_2O

**A pH meter showing that the
pH of 0.1 M AlCl_3 is 2.93**

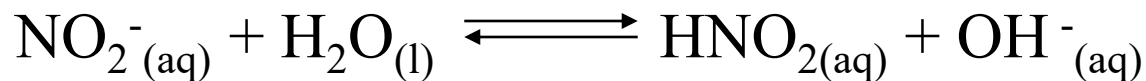
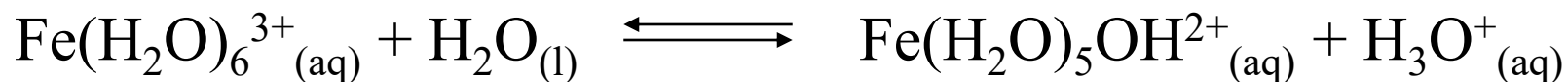


Predicting the Relative Acidity of Salt Solutions

Problem: Determine whether an aqueous solution of iron(III) nitrite, $\text{Fe}(\text{NO}_2)_3$, is acidic, basic, or neutral.

Plan: The formula consists of the small, highly charged, and therefore weakly acidic, Fe^{3+} cation and the weakly basic NO_2^- anion of the weak acid HNO_2 . To determine the relative acidity of the solution, we write equations that show the reactions of the ions with water, and then find K_a and K_b of the ions to see which ion reacts to form to a greater extent.

Solution: Writing the reactions with water:



Obtaining K_a and K_b of the ions: For $\text{Fe}^{3+}(\text{aq})$ $K_a = 6 \times 10^{-3}$.

For $\text{NO}_2^-(\text{aq})$, K_b must be determined:

$$K_b \text{ of } \text{NO}_2^- = \frac{K_w}{K_a \text{ of } \text{HNO}_2} = \frac{1.0 \times 10^{-14}}{7.1 \times 10^{-4}} = 1.4 \times 10^{-11}$$

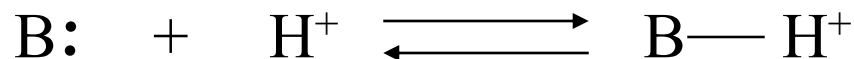
Since K_a of $\text{Fe}^{3+} > K_b$ of NO_2^- , the solution is **acidic**.

Electron-Pair Donation and the Lewis Acid-Base Definition

The Lewis acid-base definition :

- A **base** is any species that **donates** an electron pair.
- An **acid** is any species that **accepts** an electron pair.

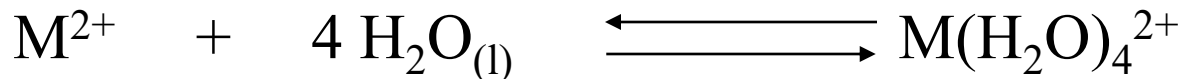
Protons act as Lewis acids in that they accept an electron pair in all reactions:



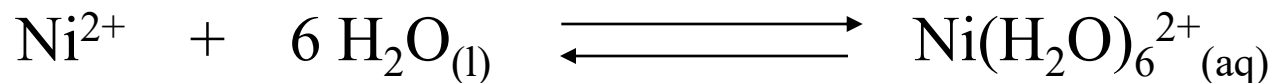
The product of any Lewis acid-base reaction is called an **adduct**, a single species that contains a new covalent bond:

- *A Lewis base is a lone pair of electrons to donate.*
- *A Lewis acid is a vacant orbital*

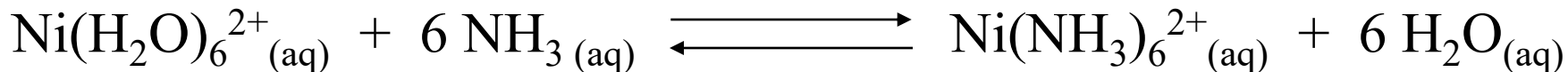
Metal Cations as Lewis Acids



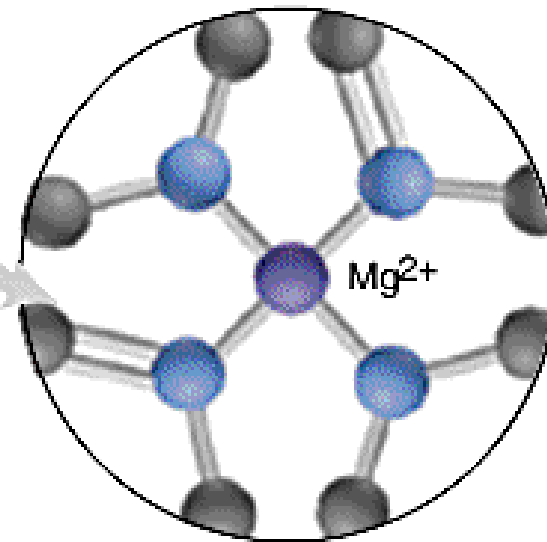
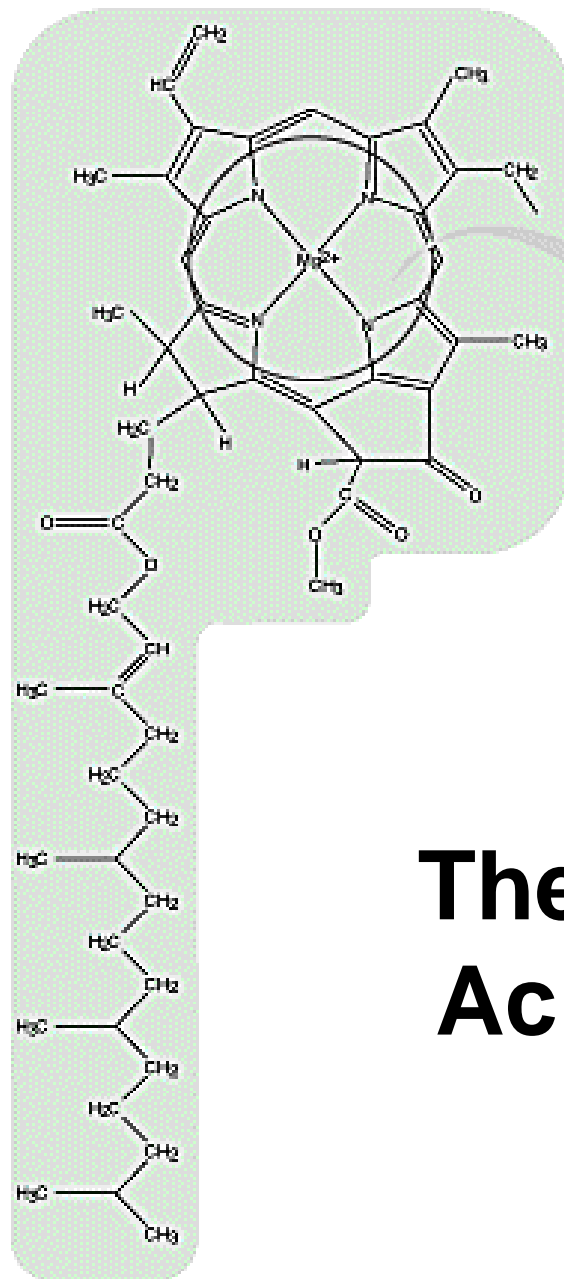
Metal ions can accept electron pairs from water molecules to form complexes. An example is nickel which forms an adduct with water to form the hexa aqua complex:



Ammonia is a stronger Lewis base than water because it displaces water from hydrated ions when aqueous ammonia is added.



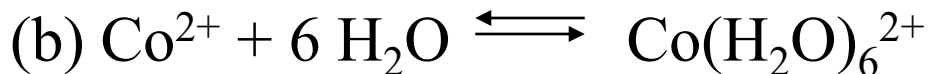
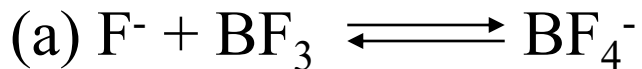
Many essential biomolecules are Lewis adducts with central metal ions. Chlorophyll is a Lewis adduct of a central Mg^{2+} ion. Vitamin B_{12} has a similar structure with a central Co^{3+} , as does heme with a central Fe^{2+} ion. Other metals such as Zn^{2+} , Mo^{2+} , and Cu^{2+} are bound to the active site in enzymes and participate in the catalytic action by virtue of their Lewis acidity.



The Mg^{2+} Ion as a Lewis Acid in the Chlorophyll Molecule

Identifying Lewis Acids and Bases

Problem: Identify the Lewis acids and bases in the following reactions:



Plan: We examine the species to see which species accepts the electron pair (Lewis acid) and which donates it (Lewis base) in the reactions.

Solution:

(a) The BF_3 accepted an electron pair from the fluoride ion.

BF_3 is the acid and F^- is the base.

(b) The Co^{2+} ion accepted the electron pairs from the water molecules.

Co^{2+} is the acid and H_2O is the base.

(c) The H^+ ion accepted the electron pair from the ammonia molecule.

H^+ is the acid and water is the base.

Example 7.14 (P259)

Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral.



Solution:

a) The ions are the ammonium and acetate ions, K_a for NH_4^+ is 5.6×10^{-10} , and K_b for $\text{C}_2\text{H}_3\text{O}_2^-$ is 5.6×10^{-10} . Since they are equal the solution will be neutral and the pH close to 7.

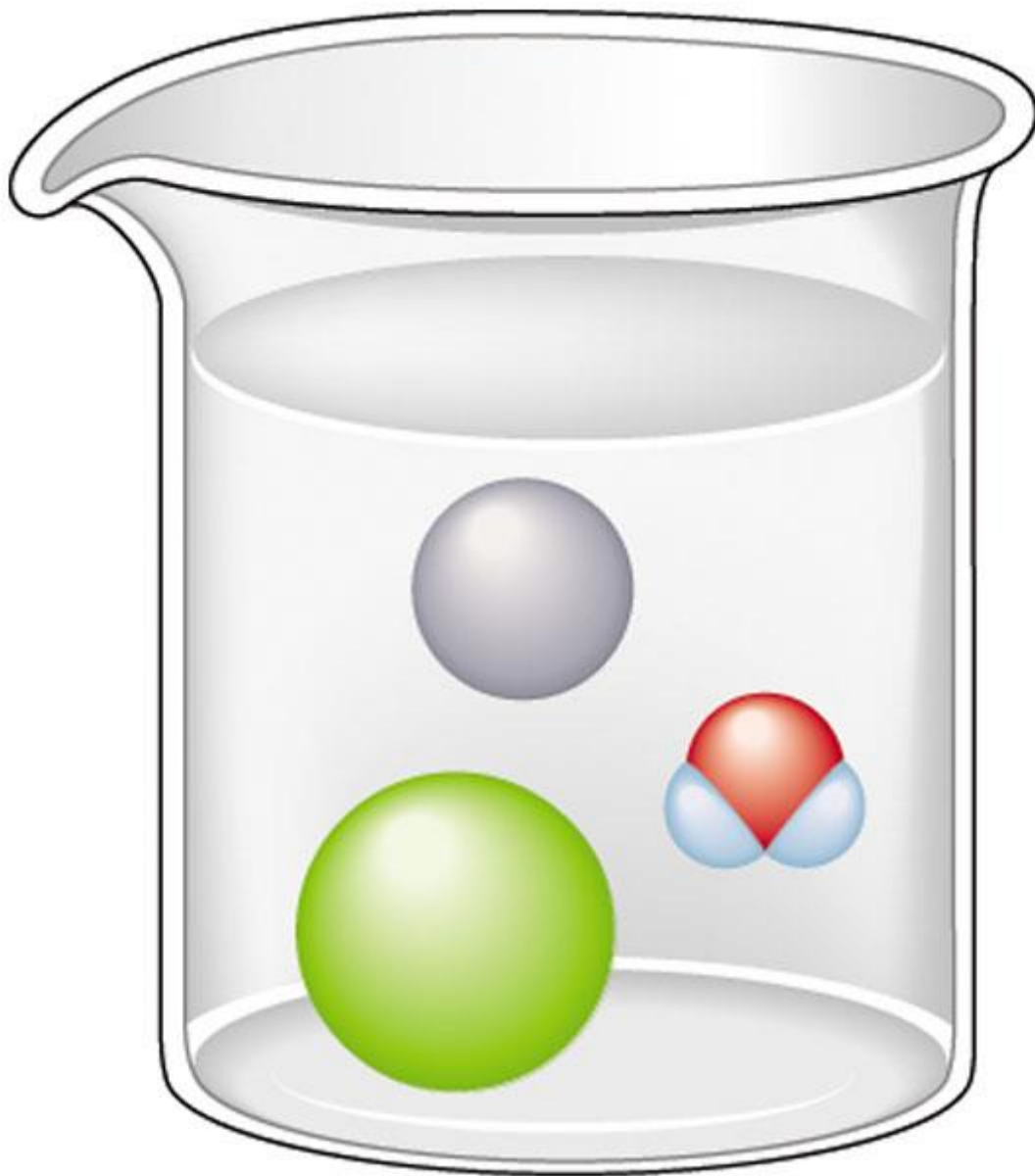
b) The solution will contain the ammonium and cyanide ions, the K_a value for NH_4^+ is 5.6×10^{-10} , and

$$K_b \text{ (for } \text{CN}^-) = \frac{K_w}{K_a \text{ (for HCN)}} = 1.6 \times 10^{-5}$$

Since K_b for CN^- is much larger than K_a for NH_4^+ , this solution will be basic.

c) This solution contains the hydrated Aluminum ion and the sulfate ion. K_a for $\text{Al}(\text{H}_2\text{O})_6^{3+} = 1.4 \times 10^{-5}$, for sulfate, $K_b = 8.3 \times 10^{-13}$; therefore this solution will be acidic.

Molecular model: Na^+ , F^- , H_2O



Na^+

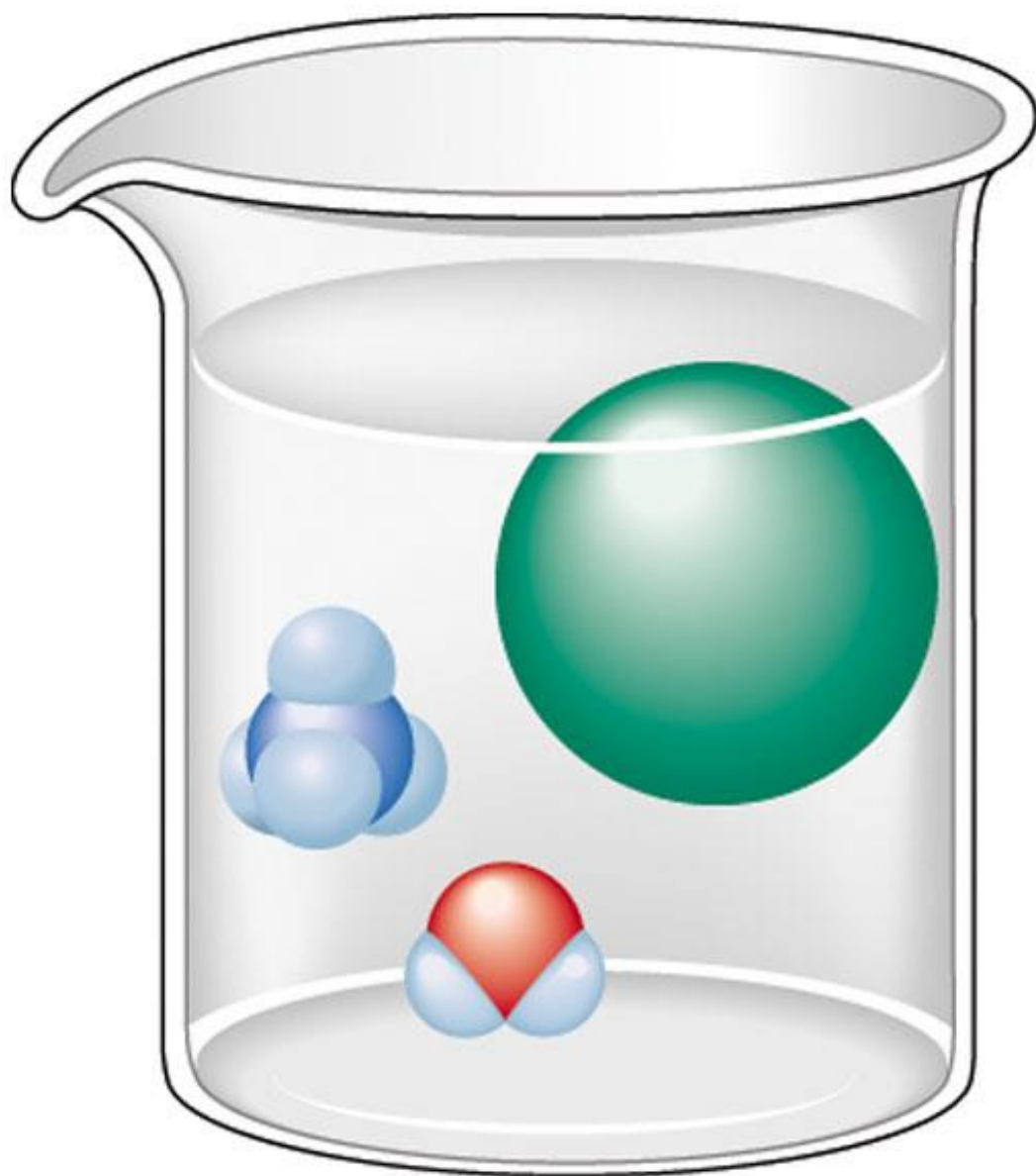


F^-



H_2O

Molecular model: Cl^- , NH_4^+ , and H_2O



Cl^-



NH_4^+



H_2O

**A pH meter showing that the
pH of 0.1 M HN_4Cl is 5.13**



TABLE 7.5 Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties

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

Table 7.6 (P 259) - I

Acid – Base Properties of Aqueous Solutions of Various Types of Salts

Type of Salt	Examples	Comment	pH of Solution
Cation is from strong base; anion is from strong acid	KCl, KNO ₃ NaCl, NaNO ₃	Neither acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	NaC ₂ H ₃ O ₂ KCN, NaF	Anion acts as a base; cation has no effect on pH	Basic
Cation is conjugate acid of weak base; anion is from strong acid	NH ₄ Cl, NH ₄ NO ₃	Cation acts as an acid; anion has no effect on pH	Acidic

Table 7.6 (P 259) - II

Acid – Base Properties of Aqueous Solutions of Various Types of Salts

Type of Salt	Examples	Comment	pH of Solution
Cation is conjugate acid of weak base anion is conjugate base of weak acid	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ NH_4CN	Cation acts as an acid; anion acts as a base	Acidic if : $K_a > K_b$ Basic if : $K_b > K_a$ Neutral if : $K_a = K_b$
Cation is highly charged metal ion; anion is from strong acid	$\text{Al}(\text{NO}_3)_3$, FeCl_3	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

Value of K_a - I

We start with the expression for the value of K_a , for the weak acid HA: From the conservation of charge equation:

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

$$[H^+] = [A^-] + [OH^-]$$

From the K_w expression for water:

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

The charge balance equation becomes:

$$[H^+] = [A^-] + \frac{K_w}{[H^+]} \quad \text{or:} \quad [A^-] = [H^+] - \frac{[K_w]}{[H^+]}$$

The material balance equation is:

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

Since:

$$[A^-] = [H^+] - \frac{K_w}{[H^+]}$$

We have:

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

Value of K_a - II

Now we substitute the expressions for $[A^-]$ and $[HA]$ into K_a :

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

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

Simplified, this equation becomes:

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

Like Example 7.16 (P264-5) -I

Calculate the $[H^+]$ in: a) 1.0 M HOCl and b) 1×10^{-4} M HOCl
for hypochlorous acid HOCl, $K_a = 3.5 \times 10^{-8}$

a) First do the weak acid problem in the normal way.

$$\frac{x^2}{1.0 - x} = 3.5 \times 10^{-8} \approx \frac{x^2}{1.0} \quad X = 1.87 \times 10^{-4} \text{ M} = [H^+]$$

b) First we do the weak acid problem in the normal way.

$$\frac{x^2}{1.0 \times 10^{-4} - x} = 3.5 \times 10^{-8} \approx \frac{x^2}{1.0 \times 10^{-4}} \quad X = 1.87 \times 10^{-6} \text{ M} = [H^+]$$

In this very dilute solution of HOCl we should use the full equation to obtain the correct H^+ concentration.

$$K_a = 3.5 \times 10^{-8} = \frac{[H^+]^2 - 10^{-14}}{1.0 \times 10^{-4} - \frac{[H^+]^2 - 10^{-14}}{[H^+]}}$$

Like Example 7.16 (P264-5) -II

To solve this we will use successive approximations, first substituting the value we obtained in the normal way: $1.87 \times 10^{-6} \text{ M}$ To do this we add in the correction for water ionization, $1.0 \times 10^{-7} \text{ M}$, giving as an approximation: $1.97 \times 10^{-6} \text{ M}$ for H^+ .

$$K_a = 3.5 \times 10^{-8} = \frac{[\text{H}^+]^2 - 10^{-14}}{1.0 \times 10^{-4} - \frac{([\text{H}^+]^2 - 10^{-14})}{1.97 \times 10^{-6}}}$$

$$3.5 \times 10^{-8} = \frac{[\text{H}^+]^2 - 10^{-14}}{1.0 \times 10^{-4} - 1.97 \times 10^{-6}} = \frac{[\text{H}^+]^2 - 10^{-14}}{9.8 \times 10^{-5}}$$

$$[\text{H}^+]^2 = 3.44 \times 10^{-12} \quad [\text{H}^+] = 1.85 \times 10^{-6}$$

Substituting 1.85×10^{-6} in to the equation in place of 1.97×10^{-6} yields $1.85 \times 10^{-6} \text{ M}$ so the approximation yields the same answer, so the final answer is $1.85 \times 10^{-6} \text{ M}$.

$$\text{pH} = -\log(1.85 \times 10^{-6}) = \underline{\hspace{2cm}}$$

Summary: The pH Calculations for an Aqueous Solution of a Weak Acid HA (major species HA and H₂O)

The full equation for this case is:

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

When the weak acid by itself produces $[H^+] \geq 10^{-6}$ M, the full equation becomes:

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

This corresponds to the typical weak acid case:

When:

$[HA]_0 \gg \frac{[H^+]^2 - K_w}{[H^+]}$ the full equation becomes:

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

Which gives:

$$[H^+] = \sqrt{K_a[HA]_0 + K_w}$$

Summary: Solving Acid-Base Equilibria Problems

- List the major species in solution.
- Look for reactions that can be assumed to go to completion, such as a strong acid dissociating or H^+ reacting with OH^- .
- For a reaction that can be assumed to go to completion:
 - a) Determine the concentrations of the products.
 - b) Write down the major species in solution after the reaction.
- Look at each major component of the solution and decide whether it is an acid or a base.
- Pick the equilibrium that will control the pH. Use known values of the dissociation constants for the various species to determine the dominant equilibrium.
 - a) Write the equation for the reaction and the equilibrium expression.
 - b) Compute the initial concentrations (assuming that the dominant equilibrium has not yet occurred—for example, there has been no acid dissociation).
 - c) Define x .
 - d) Compute the equilibrium concentrations in terms of x .
 - e) Substitute the concentrations into the equilibrium expression, and solve for x .
 - f) Check the validity of the approximation.
 - g) Calculate the pH and other concentrations as required.