

Chapter 6 : Acids and Bases

Chapter 7 – Acids and Bases

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Chapter 8- Applications of Aqueous Equilibria

- 8.1 *Solutions of Acids and Bases containing a Common Ion*

The Nature of Acids and Bases

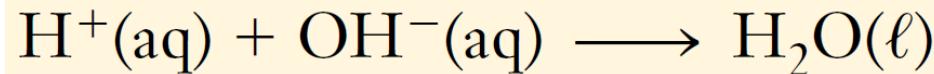
- **THE ARRHENIUS THEORY**

In the Arrhenius acid-base definition, acids and bases are classified in terms of their formulas and their behaviour in water:

- **An acid** is a substance that has H in its formula and dissociates in water to yield H_3O^+ .
- A base is a substance that has OH in its formula and dissociates in water to yield OH^- .

Some typical Arrhenius acids are HCl, HNO_3 , and HCN, and some typical bases are NaOH, KOH, and $\text{Ba}(\text{OH})_2$

Neutralization is defined as the combination of H^+ ions with OH^- ions to form H_2O molecules.



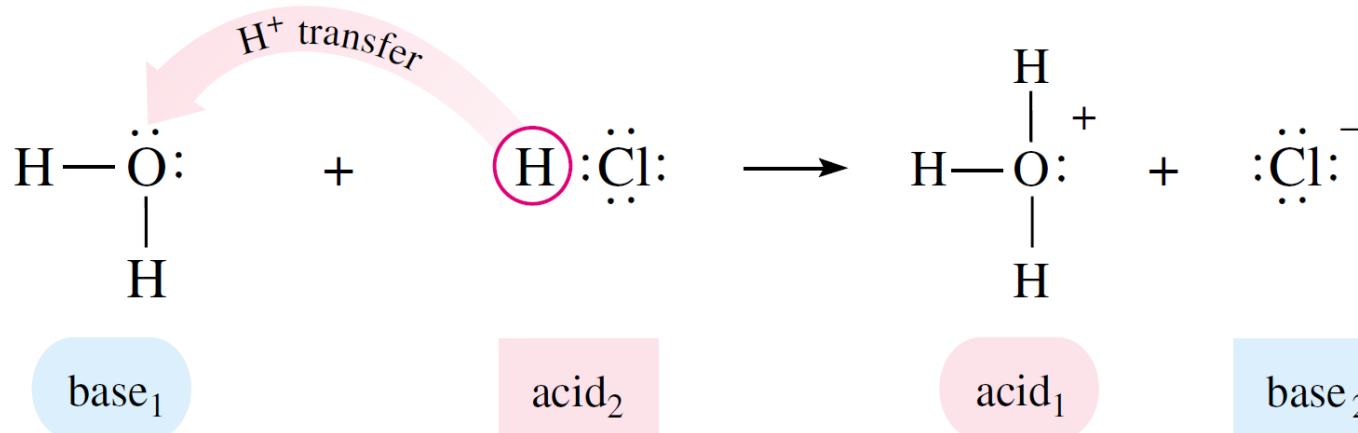
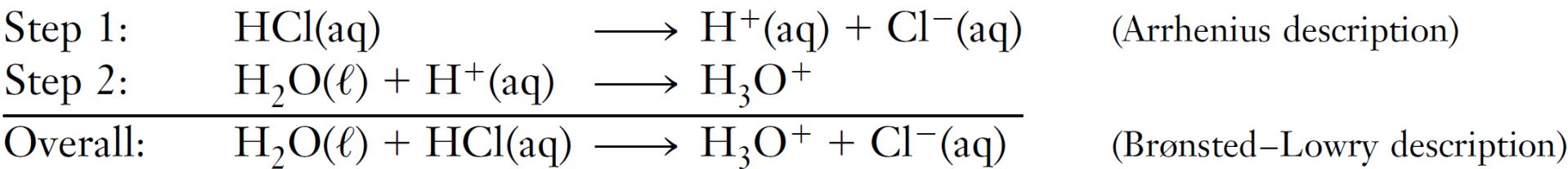
The Nature of Acids and Bases

• THE BRØNSTED–LOWRY THEORY

An **acid** is defined as a *proton donor* (H^+) and a **base** is defined as a *proton acceptor*.

An acid–base reaction is the transfer of a proton from an acid to a base.

Thus, the complete ionization of hydrogen chloride, HCl, a *strong acid, in water is an acid–base reaction in which water acts as a base or proton acceptor*

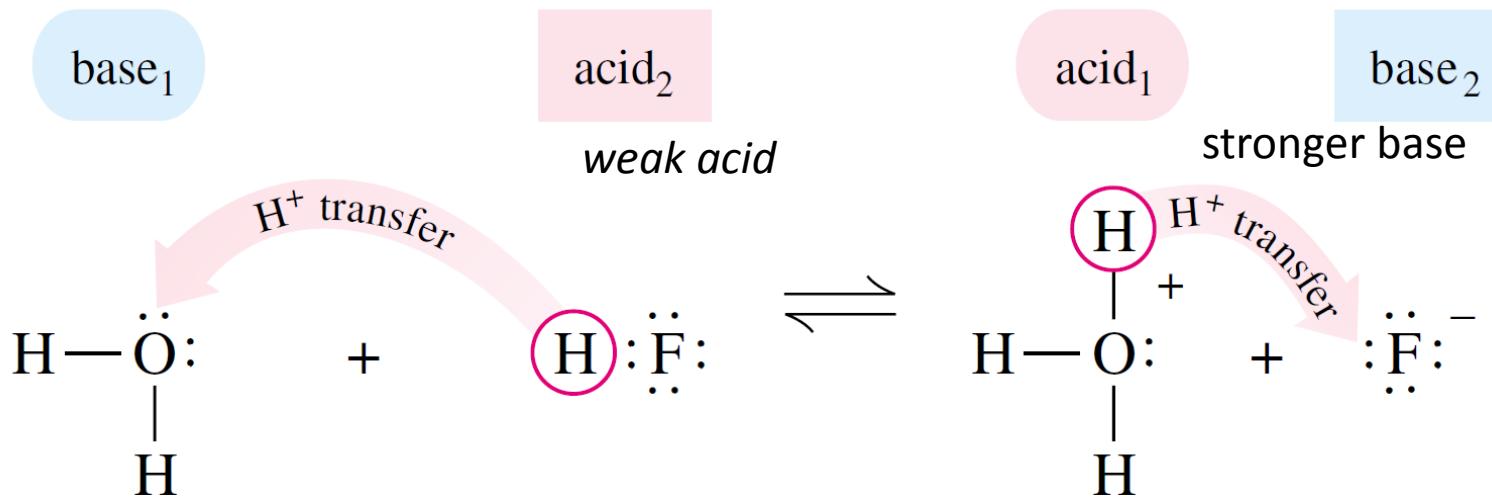


The Nature of Acids and Bases

- We can describe Brønsted–Lowry acid–base reactions in terms of **conjugate acid–base pairs**. $\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$

Acid	Base	Conjugate acid	Conjugate base
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- These are two species that differ by a proton.

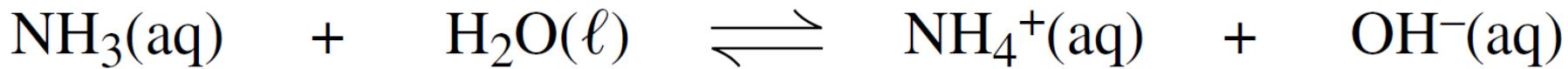


- In the equation, **HF (acid₂) and F[−](base₂) are one conjugate acid–base pair**, and **H₂O (base1) and H₃O⁺ (acid1) are the other pair**.

The stronger the acid, the weaker is its conjugate base; the weaker the acid, the stronger is its conjugate base.

The Nature of Acids and Bases

- Water acts as an acid (H^+ donor) in its reaction with NH_3 , whereas it acts as a base (H^+ acceptor) in its reactions with HCl and with HF

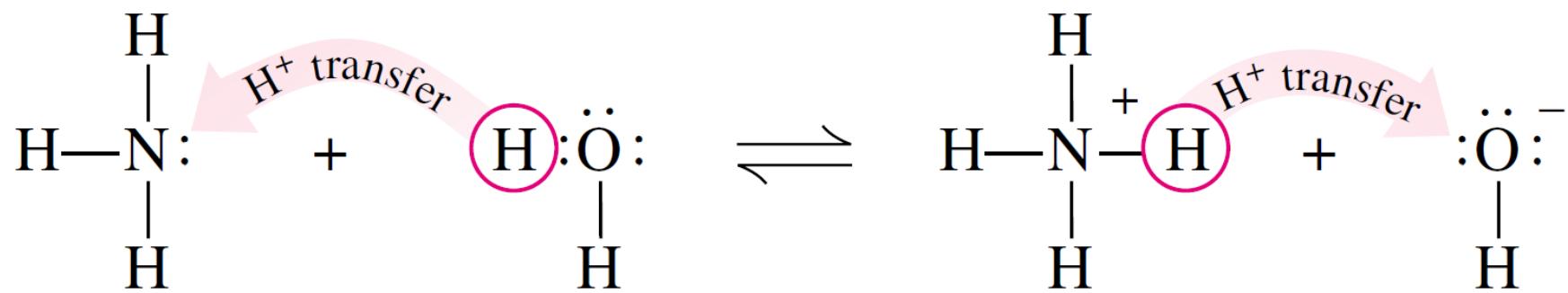


base 1

acid₂

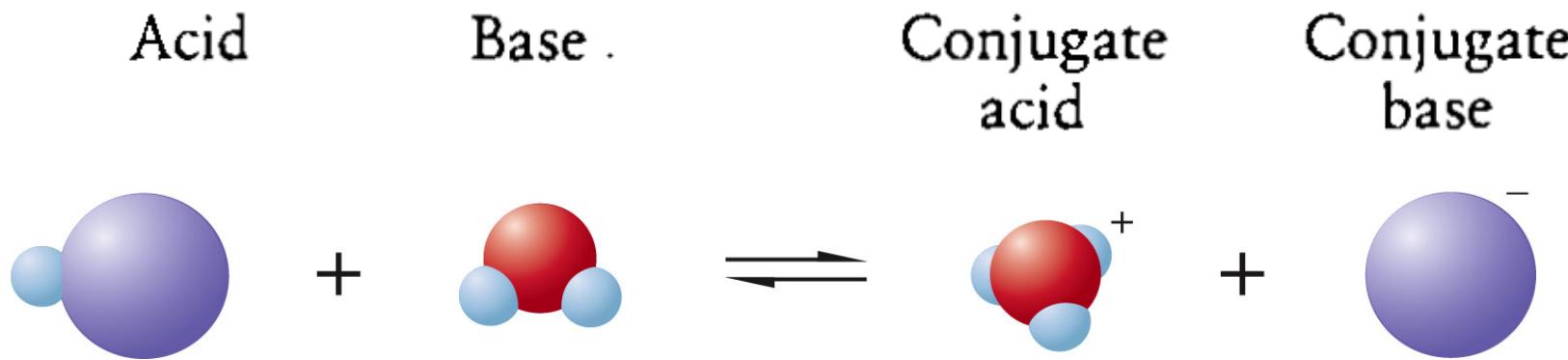
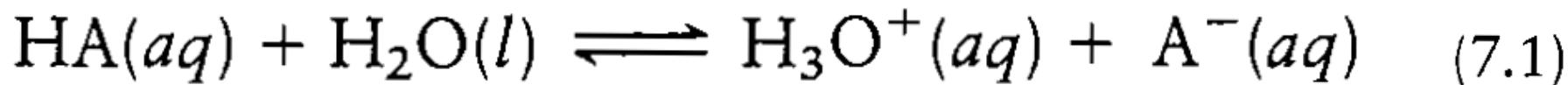
acid₁

base₂

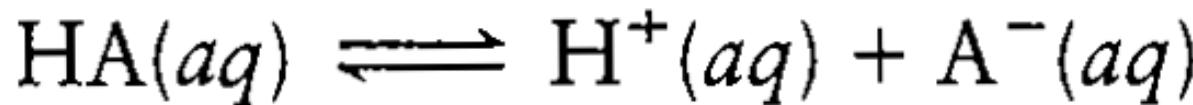


Whether water acts as an acid or as a base depends on the other species present.

The Nature of Acids and Bases



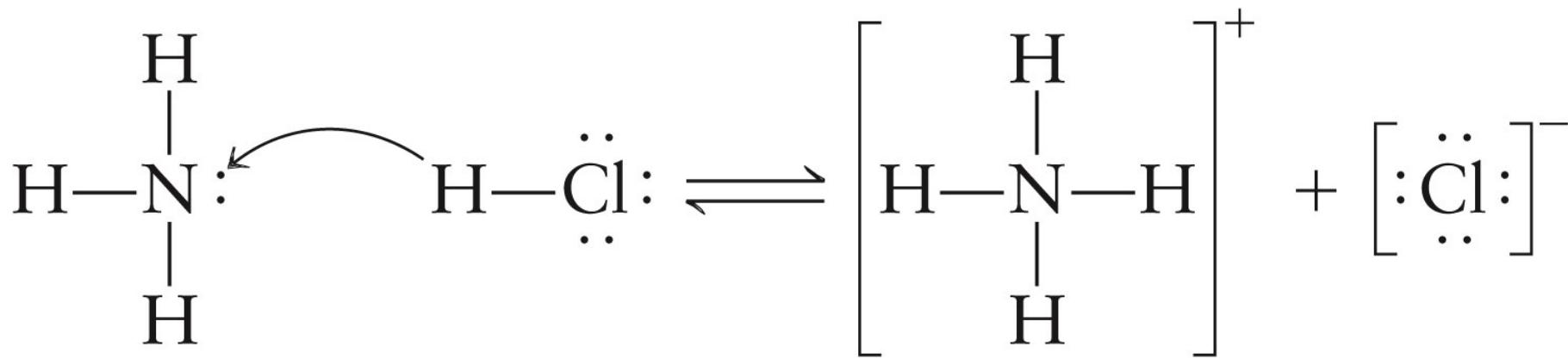
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (7.2)$$



The bigger the K_a , the stronger the acid

The Nature of Acids and Bases

- The Brønsted–Lowry definition is not limited to aqueous solutions; it can be extended to reactions in the gas phase
- Consider the reaction between $\text{HCl}_{(\text{g})}$ and ammonia (NH_3)



- Note that the reaction is not considered as acid-base reaction according to the Arrhenius concept.

Acid strength

- **Strong acids dissociate completely into ions in water, we can say that equilibrium lies far to the right**



virtually no HA molecules are present

$[\text{H}_3\text{O}^+] \approx [\text{HA}]_{\text{init}}$. In other words, $[\text{HA}]_{\text{eq}} \approx 0$

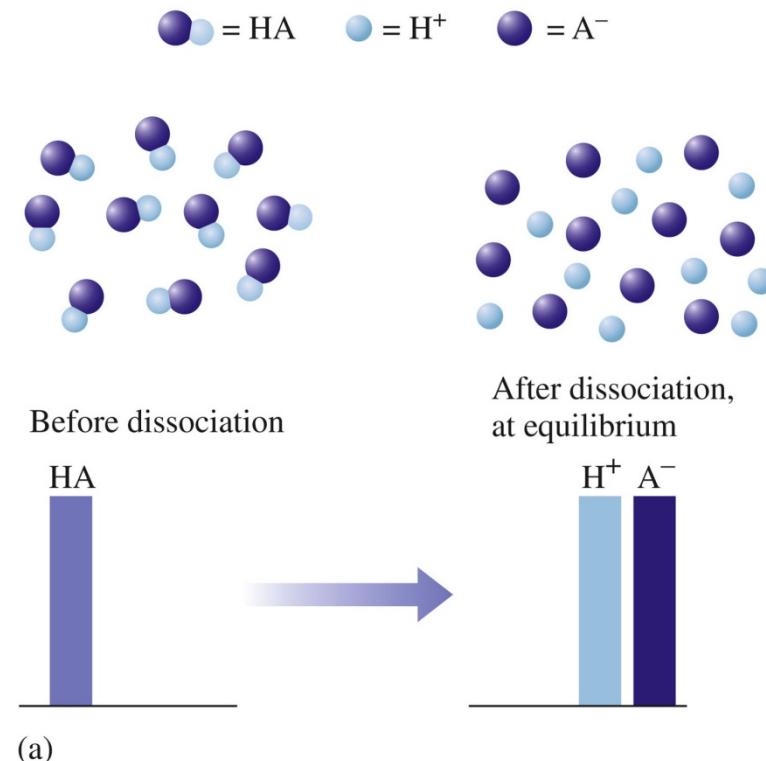


Figure 7.1 (a) - Graphical representation of the behavior of strong acid in aqueous solution.

Acid strength

- **Weak acids** dissociate very slightly into ions in water
- Equilibrium lies so far to the left



- In a dilute solution of a weak acid, the great majority of HA molecules are undissociated.

Thus, $[\text{H}_3\text{O}^+] \ll [\text{HA}]_{\text{init}}$. In other words, $[\text{HA}]_{\text{eq}} \approx [\text{HA}]_{\text{init}}$

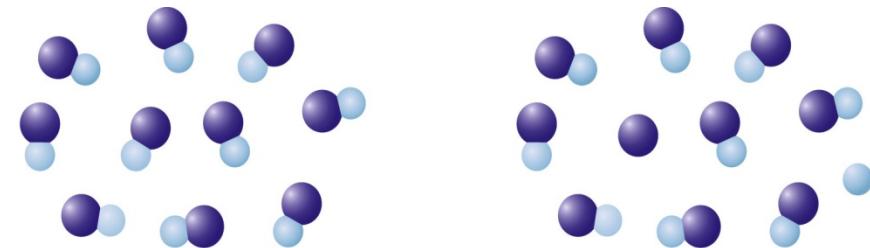
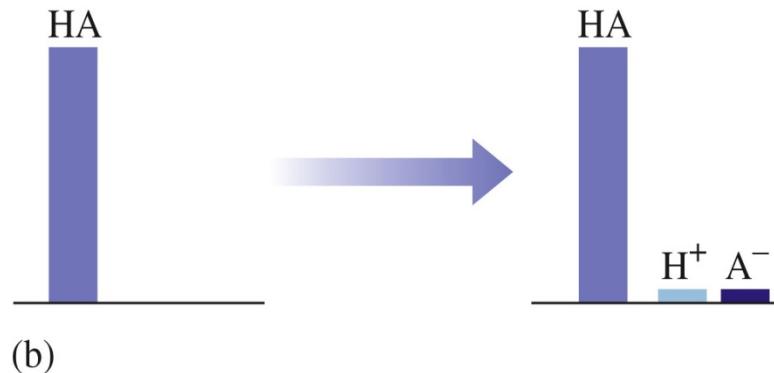


Figure 7.1 (b) Graphical representation of the behavior of weak acid in aqueous solution.



Acid strength

Specific equilibrium constant for acid dissociation K_a

- We simplify the equilibrium expression by multiplying $[H_2O]$ by K_c to define a new equilibrium constant, **the acid-dissociation constant (or acid-ionization constant), K_a**

$$K_c[H_2O] = K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Stronger acid \Rightarrow higher $[H_3O^+]$ \Rightarrow larger K_a

Thus, for solutions of the same initial HA concentration, the smaller the K_a , the lower the percent dissociation of HA

Smaller K_a \Rightarrow lower % dissociation of HA \Rightarrow weaker acid

$$K_a \leq 10^{-3}$$

Acid strength

Classifying the Relative Strengths of Acids and Bases

- **Strong acids:** 2 types of strong acids

1 . The **hydrohalic acids** HCl, HBr, and HI

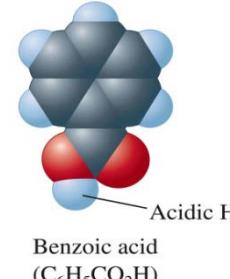
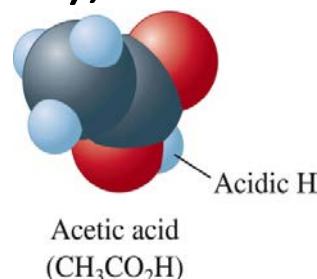
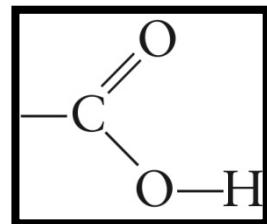
2. **Oxyacids** in which the number of O atoms exceeds the number of ionizable protons by two or more, such as HNO_3 , H_2SO_4 , and HClO_4 ;

in H_2SO_4 , 4 O's - 2 H's = 2

Acid strength

Weak acids. many more weak acids than strong ones. **Four types,**

1. The hydrohalic acid HF
2. Acids in which H is not bonded to O or to a halogen, (HCN and H_2S)
3. Oxyacids in which the number of O atoms equals or exceeds by one the number of ionizable protons, such as HClO , HNO_2 , and H_3PO_4
4. Carboxylic acids (general formula RCOOH , with the ionizable proton shown in red), such as CH_3COOH and $\text{C}_6\text{H}_5\text{COOH}$



Six Strong Acids, K_a too large

to measure accurately

Hydrogen Halides

HCl

HBr

HI

Oxyacids

H_2SO_4

HNO_3

$HClO_4$

Hydrochloric Acid

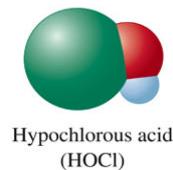
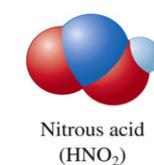
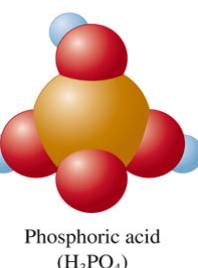
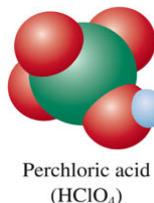
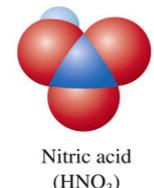
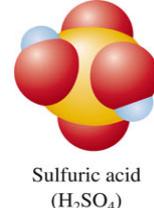
Hydrobromic Acid

Hydroiodic Acid

Sulfuric Acid

Nitric Acid

Perchloric Acid



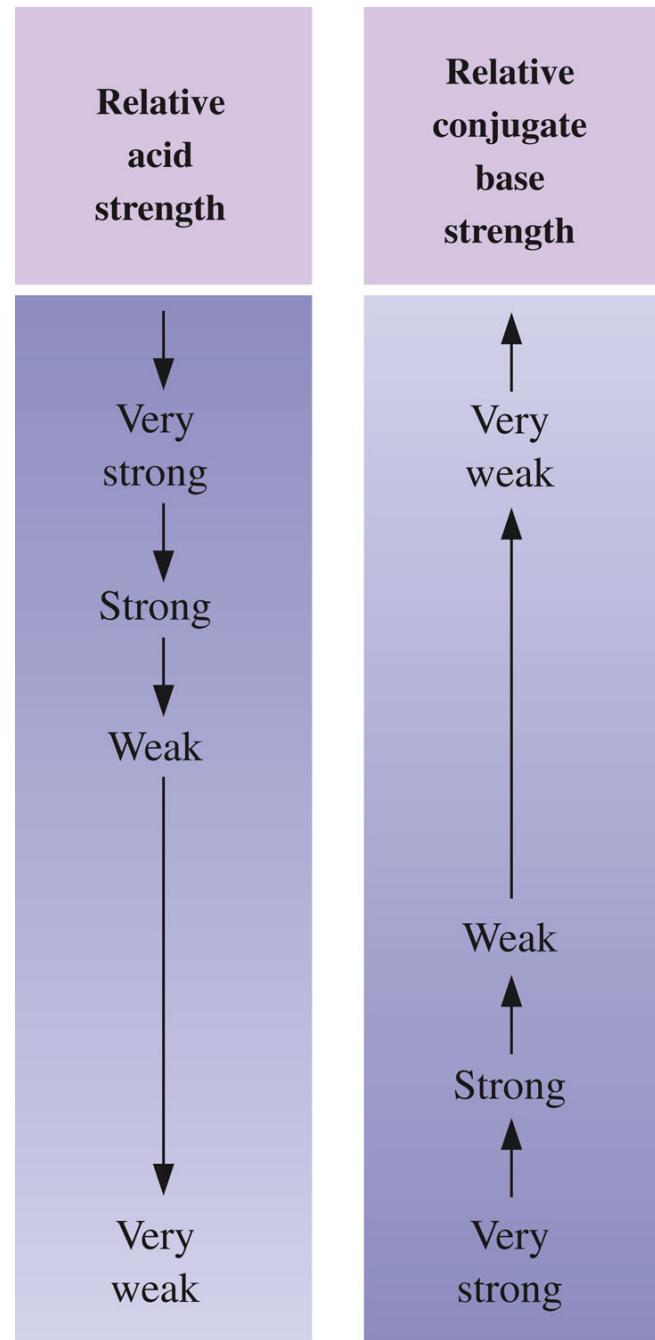
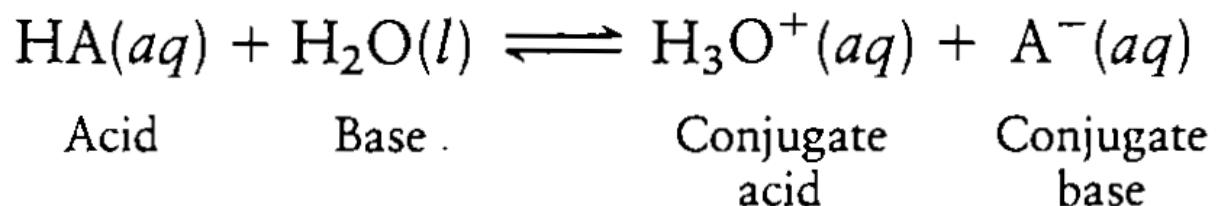


Figure 7.2 The relationship of acid strength and conjugate base strength

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

TABLE 7.2Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
HClO_2	Chlorous acid	1.2×10^{-2}
$\text{HC}_2\text{H}_2\text{ClO}_2$	Monochloracetic 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}

Increasing acid strength 

Example 7.1

Using Table 7.2, arrange the following species according to their strength as bases: H_2O , F^- , Cl^- , NO_2^- , and CN^- .

Solution

Remember that water is a stronger base than the conjugate base of a strong acid, but a weaker base than the conjugate base of a weak acid. This rule leads to the following order:

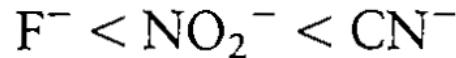


Weakest bases \longrightarrow Strongest bases

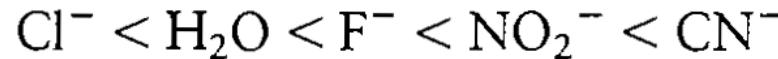
We can order the remaining conjugate bases by recognizing that the strength of an acid is *inversely related* to the strength of its conjugate base. From Table 7.2 we have



Thus the base strengths increase as follows:

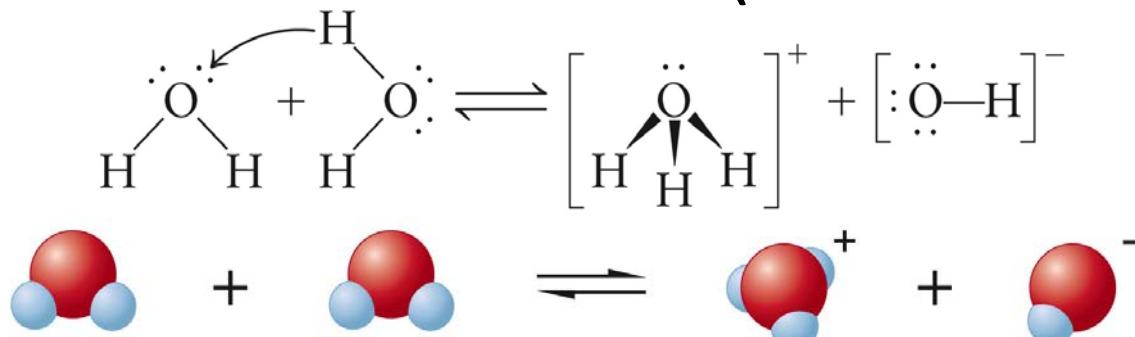


The combined order of increasing base strength is

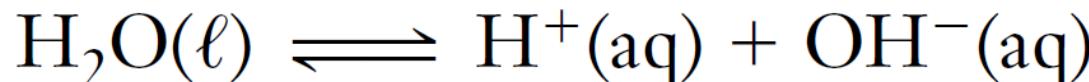


Acid strength

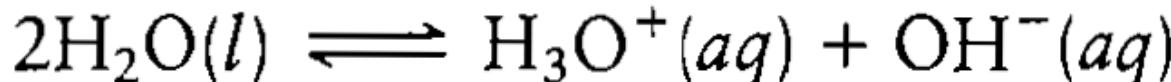
Water as an Acid and a Base (autoionization of water)



In simplified notation, we represent this reaction as



H_2O is amphoteric, can act as an acid and as a base



leads to the equilibrium expression

(known as ion product constant K_w)

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

Experiment shows that at 25°C $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$

$$\begin{aligned} K_w &= [\text{H}^+][\text{OH}^-] = (1.0 \times 10^{-7} \text{ mol/L})(1.0 \times 10^{-7} \text{ mol/L}) \\ &= 1.0 \times 10^{-14} \text{ mol}^2/\text{L}^2 \end{aligned}$$

Acid strength

Conversion between H⁺ AND OH⁻

- **The ion-product constant for water**

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

1. A change in [H₃O⁺] causes an inverse change in [OH⁻], and vice versa:

Higher [H₃O⁺] \Rightarrow lower [OH⁻] and Higher [OH⁻] \Rightarrow lower [H₃O⁺]

2. Both ions are present in all aqueous systems. Thus, all acidic solutions contain a low concentration of OH⁻ ions, and all basic solutions contain a low concentration of H₃O⁺ ions. The equilibrium nature of autoionization allows us to define “acidic” and “basic” solutions in terms of relative magnitudes of [H₃O⁺] and [OH⁻]:

In an *acidic* solution,

$$[\text{H}_3\text{O}^+] > [\text{OH}^-]$$

In a *neutral* solution,

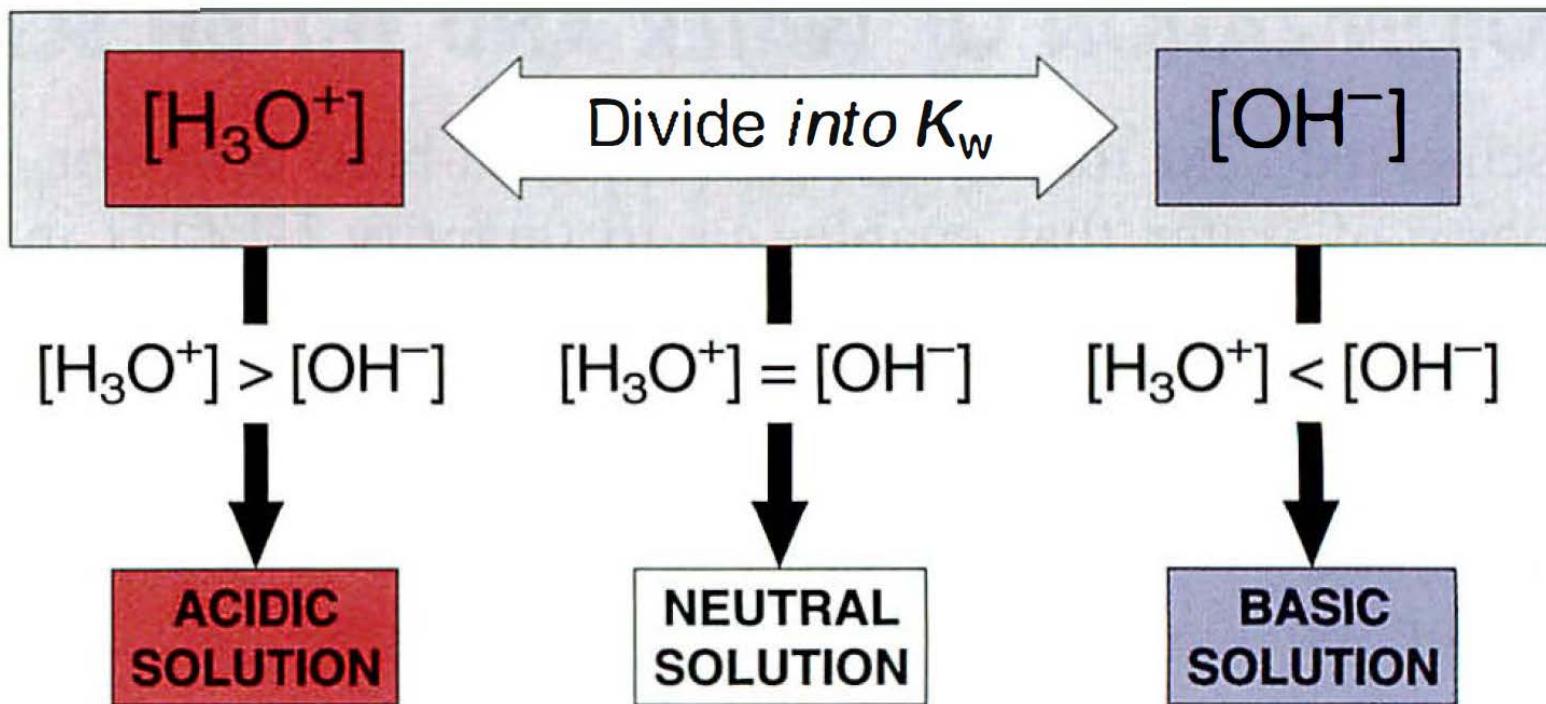
$$[\text{H}_3\text{O}^+] = [\text{OH}^-]$$

In a *basic* solution.

$$[\text{H}_3\text{O}^+] < [\text{OH}^-]$$

Acid strength

The relationship between $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ and the relative acidity of solutions

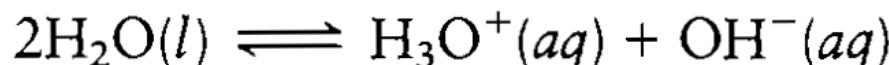


$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} \quad \text{or} \quad [\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]}$$

Example 7.2

At 60°C the value of K_w is 1×10^{-13} .

- a. Using Le Châtelier's principle, predict whether the reaction



is exothermic (releases energy) or endothermic (absorbs energy).

- b. Calculate $[\text{H}^+]$ and $[\text{OH}^-]$ in a neutral solution at 60°C.

Solution

- a. K_w increases from 1×10^{-14} at 25°C to 1×10^{-13} at 60°C. Le Châtelier's principle states that if a system at equilibrium is heated, it will adjust to consume energy. Since the value of K_w increases with temperature, we think of energy as a reactant, and so the process must be endothermic.

b. At 60°C $[\text{H}^+][\text{OH}^-] = 1 \times 10^{-13}$

For a neutral solution

$$[\text{H}^+] = [\text{OH}^-] = \sqrt{1 \times 10^{-13}} = 3 \times 10^{-7} \text{ M}$$

The pH scale



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

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

What is the pH of $10^{-12} M$ H_3O^+ solution?

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

Similarly, a $10^{-3} M$ H_3O^+ solution has a pH of 3, and a $5.4 \times 10^{-4} M$ H_3O^+ solution has a pH of 3.27: 

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = (-1)(\log 5.4 + \log 10^{-4}) = 3.27$$



The pH scale

pH of a neutral solution = 7.00

pH of an acidic solution < 7.00

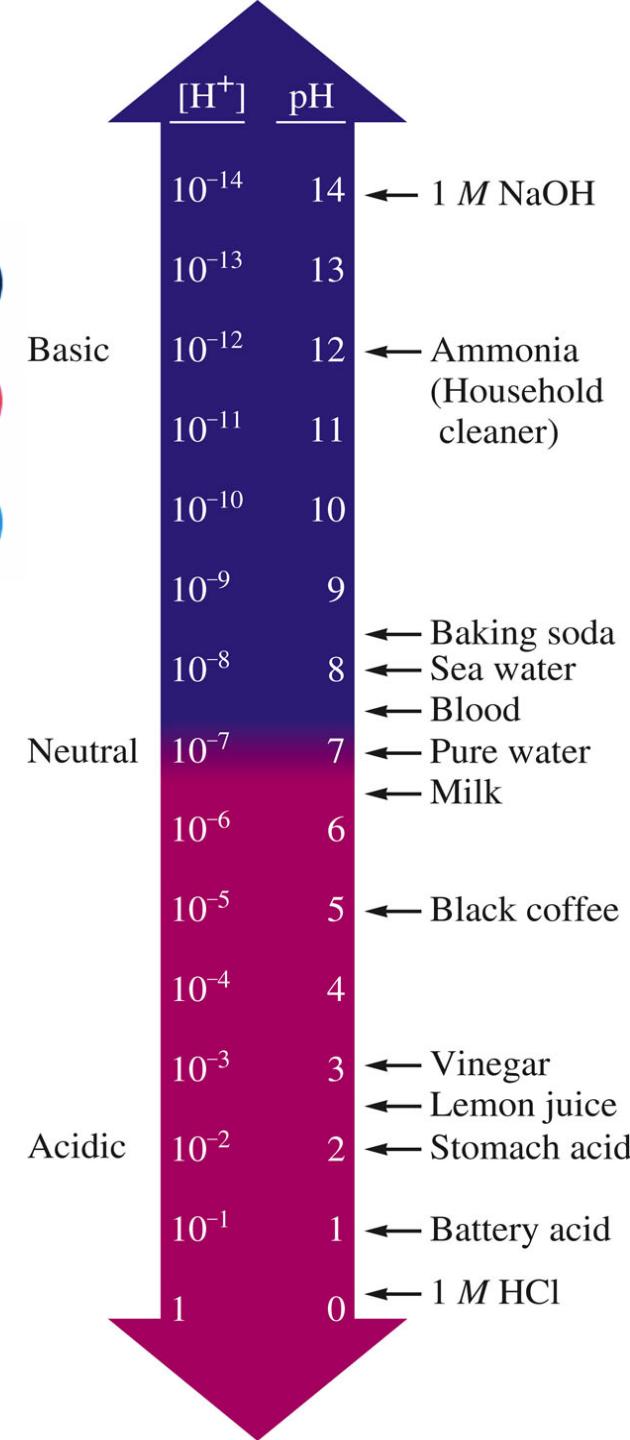
pH of a basic solution > 7.00

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

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

$$\text{p}K = -\log K$$

A low $\text{p}K$ corresponds to a high K .

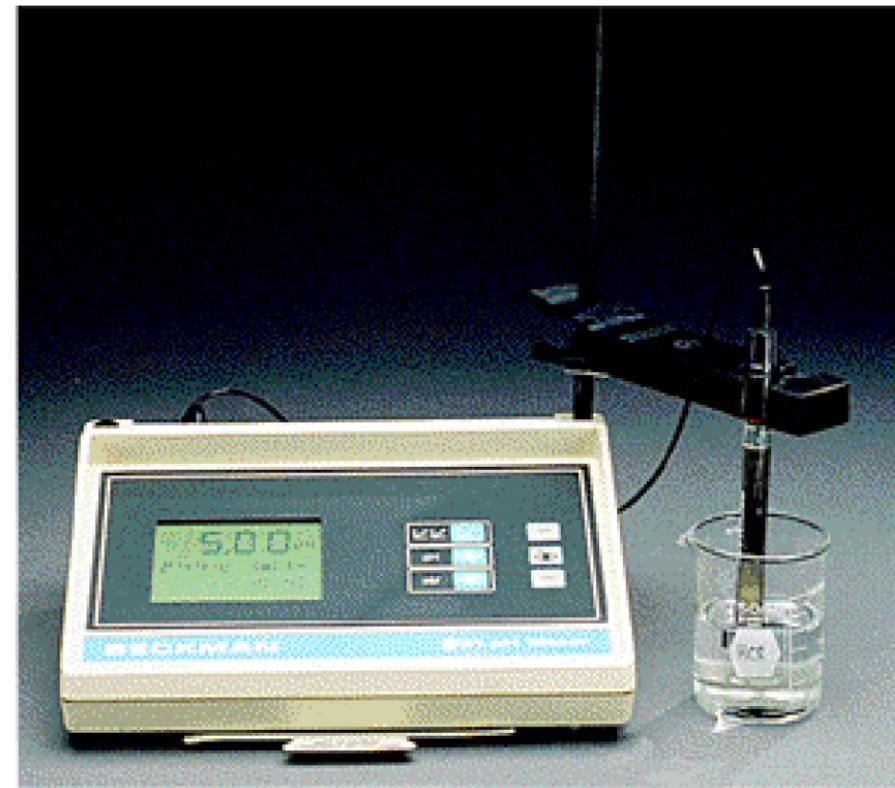


The pH scale

Methods for Measuring the pH of an Aqueous Solution



(a) pH paper



(b) Electrodes of a pH meter

The pH scale

The Relations Among pH, pOH, and pK_w

- Taking the negative log of both sides of the K_w expression gives a very useful relationship among pK_w , pH, and pOH

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

$$-\log K_w = (-\log [H_3O^+]) + (-\log [OH^-]) = -\log (1.0 \times 10^{-14})$$

$$pK_w = pH + pOH = 14.00 \quad (\text{at } 25^\circ\text{C})$$

With pH, pOH, $[H_3O^+]$, and $[OH^-]$ interrelated through K_w , knowing any one of the values allows us to determine the others.

Summary

General Strategies for Solving Acid-Base Problems

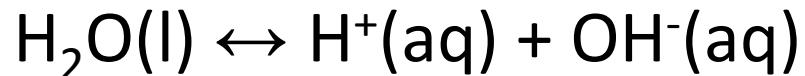
- *Think chemistry.* Focus on the solution components and their reactions. It will almost always be possible to choose one reaction that is the most important.
- *Be systematic.* Acid-base problems require a step-by-step approach.
- *Be flexible.* Although all acid-base problems are similar in many ways, 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 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 the pH of strong acid solutions

What are the major species in the solution?

What is the pH of a solution of 1.00 M HCl?

Major species: H^+ , Cl^- , and H_2O



But is autoionization an important source of H^+ ? **No** since $[\text{H}^+]$ in pure water is 10^{-7} M, and in 1 M HCl water will produce even less than 10^{-7} M H^+

$$\text{pH} = -\log [\text{H}^+] = -\log(1.0) = 0.00$$

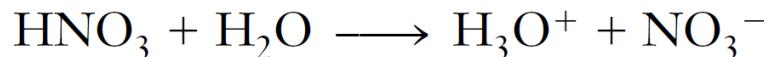
Calculating the pH of strong acid solutions

Calculate $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH for a 0.015 M HNO_3 solution.

Plan

We write the equation for the ionization of the strong acid HNO_3 , which gives us $[\text{H}_3\text{O}^+]$. Then we calculate pH. We use the relationships $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ and $\text{pH} + \text{pOH} = 14.00$ to find pOH and $[\text{OH}^-]$. At $25\text{ }^\circ\text{C}$

Solution



Because nitric acid is a strong acid (it ionizes completely), we know that

$$[\text{H}_3\text{O}^+] = 0.015\text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.015) = -(-1.82) = 1.82$$

We also know that $\text{pH} + \text{pOH} = 14.00$. Therefore,

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 1.82 = 12.18$$

Because $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$, $[\text{OH}^-]$ is easily calculated.

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{0.015} = 6.7 \times 10^{-13}\text{ M}$$

Calculating the pH of strong acid solutions

Calculate the pH of a solution in which the H_3O^+ concentration is 0.050 mol/L.

Plan

We are given the value for $[\text{H}_3\text{O}^+]$; so we take the negative logarithm of this value.

Solution

$$[\text{H}_3\text{O}^+] = 0.050 \text{ M} = 5.0 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [5.0 \times 10^{-2}] = 1.30$$

This answer contains only *two* significant figures. The “1” in 1.30 is *not* a significant figure; it comes from the power of ten.

Calculating the pH of strong acid solutions

The pH of a solution is 3.301. What is the concentration of H_3O^+ in this solution?

Plan

By definition, $\text{pH} = -\log [\text{H}_3\text{O}^+]$. We are given the pH, so we solve for $[\text{H}_3\text{O}^+]$.

Solution

From the definition of pH, we write

$$-\log [\text{H}_3\text{O}^+] = 3.301$$

Multiplying through by -1 gives

$$\log [\text{H}_3\text{O}^+] = -3.301$$

Taking the inverse logarithm (antilog) of both sides of the equation gives

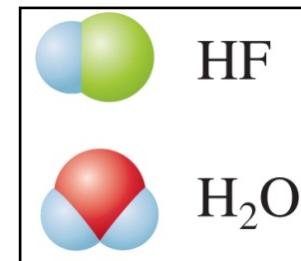
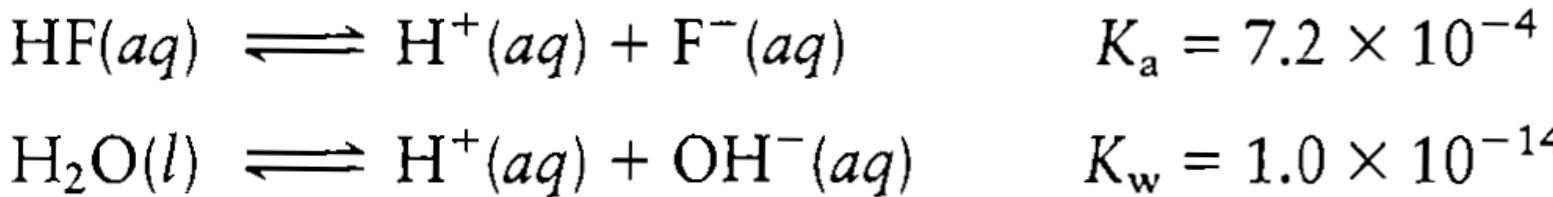
$$[\text{H}_3\text{O}^+] = 10^{-3.301} \quad \text{so} \quad [\text{H}_3\text{O}^+] = 5.00 \times 10^{-4} M$$

Calculating the pH of weak acid solutions

What is the pH of a solution of 1.00 M HF, $K_a = 7.2 \times 10^{-4}$?

Since HF is a weak acid, it will be dissociated only to a slight extent. It will be represented in its dominant form, as HF.

(1) Identify major species in solution: HF, and H_2O



(3) Is there a dominant species for H^+ (aq) production?

Because $K_a \gg K_w$, we can ignore contribution of H^+ from water.

Calculating the pH of weak acid solutions



The equilibrium expression is

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

The initial concentrations are:

$$[\text{HF}]_0 = 1.00 \text{ M}, \quad [\text{F}^-]_0 = 0, \quad [\text{H}^+]_0 = 10^{-7} \text{ M} \approx 0$$

The equilibrium concentrations can be defined in terms of x:

$$[\text{HF}] = [\text{HF}]_0 - x = 1.00 - x$$

$$[\text{F}^-] = [\text{F}^-]_0 + x = 0 + x = x$$

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

Substituting these equilibrium concentrations into the equilibrium expression gives

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

Calculating the pH of weak acid solutions

compared with 1.00, the term in the denominator can be approximated as follows:

$$1.00 - x \approx 1.00$$

The equilibrium expression then becomes

$$7.2 \times 10^{-4} = \frac{(x)(x)}{1.00 - x} \approx \frac{(x)(x)}{1.00}$$

which yields

$$x^2 \approx (7.2 \times 10^{-4})(1.00) = 7.2 \times 10^{-4}$$

$$x \approx \sqrt{7.2 \times 10^{-4}} = 2.7 \times 10^{-2}$$

How valid is the approximation that $[HF] = 1.00\text{ M}$? Because this question will arise often in connection with acid–base equilibrium calculations, we will consider it carefully. *The validity of the approximation depends on how much accuracy we demand for the calculated value of $[H^+]$.* Typically, the K_a values for acids are known to an accuracy of only about $\pm 5\%$. Therefore, it is reasonable to apply this figure when determining the validity of the approximation

$$[\text{HA}]_0 - x \approx [\text{HA}]_0$$

We will use the following test.

First calculate the value of x by making the approximation

$$K_a = \frac{x^2}{[\text{HA}]_0 - x} \approx \frac{x^2}{[\text{HA}]_0}$$

where

$$x^2 \approx K_a[\text{HA}]_0 \quad \text{and} \quad x \approx \sqrt{K_a[\text{HA}]_0}$$

Then compare the sizes of x and $[\text{HA}]_0$. If the expression

$$\frac{x}{[\text{HA}]_0} \times 100\%$$

is less than or equal to 5%, the value of x is small enough for the approximation

$$[\text{HA}]_0 - x \approx [\text{HA}]_0$$

to be considered valid.

In our example

$$x = 2.7 \times 10^{-2} \text{ mol/L}$$

$$[\text{HA}]_0 = [\text{HF}]_0 = 1.00 \text{ mol/L}$$

and

$$\frac{x}{[\text{HA}]_0} \times 100\% = \frac{2.7 \times 10^{-2}}{1.00} \times 100\% = 2.7\%$$

The approximation we made is considered valid, so the value of x calculated by using that approximation is acceptable. Thus

$$x = [\text{H}^+] = 2.7 \times 10^{-2} \text{ M} \quad \text{and} \quad \text{pH} = -\log(2.7 \times 10^{-2}) = 1.57$$

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 $[\text{HA}]_0 - x \approx [\text{HA}]_0$.
- Verify whether the approximation is valid (the 5% rule is the test in this case).
- Calculate $[\text{H}^+]$ and pH.

Calculating the pH of weak acid solutions

Percent Dissociation

What % of the acid is dissociated?

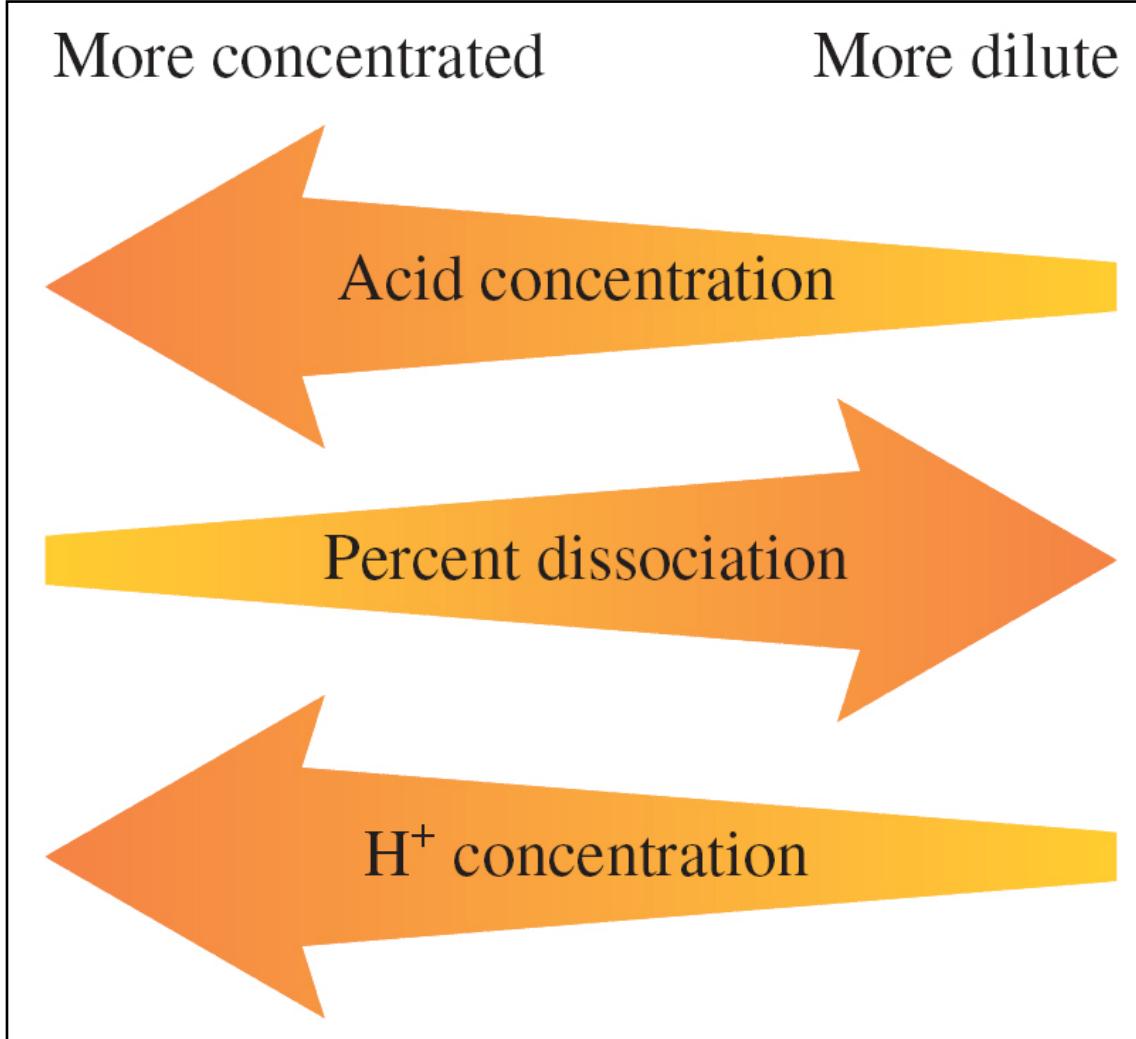
$$\text{Percent dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100\%$$

$$\text{Percent dissociation} = \frac{2.7 \times 10^{-2} \text{ mol/L}}{1.00 \text{ mol/L}} \times 100\% = 2.7\%$$

For a given weak acid, the percent dissociation increases as the acid becomes more dilute. For example, the percent dissociation of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$, $K_a = 1.8 \times 10^{-5}$) is significantly greater in a 0.10 M solution than in a 1.0 M solution.

Calculating the pH of weak acid solutions

Percent Dissociation



Percent dissociation

This phenomenon can be explained in the following way. Consider the weak acid HA with the initial concentration $[HA]_0$. At equilibrium

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

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

Thus

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

Now suppose enough water is added to dilute the solution by a factor of 10. The new concentrations before any adjustment occurs are

$$[A^-]_{\text{new}} = [H^+]_{\text{new}} = \frac{x}{10}$$

$$[HA]_{\text{new}} = \frac{[HA]_0}{10}$$

and Q , the reaction quotient, is

$$Q = \frac{(x/10)(x/10)}{[HA]_0/10} = \frac{1(x)(x)}{10[HA]_0} = \frac{1}{10} K_a$$

Since Q is less than K_a , the system must adjust to the right to reach the new equilibrium position. Thus the percent dissociation increases as the acid becomes more dilute.

Example 7.4

Lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) is a waste product that accumulates in muscle tissue during exertion, leading to pain and a feeling of fatigue. In a 0.100 M aqueous solution, lactic acid is 3.7% dissociated. Calculate the value of K_a for this acid.

Solution

The small value for the percent dissociation clearly indicates that $\text{HC}_3\text{H}_5\text{O}_3$ is a weak acid. Thus the major species in the solution are the undissociated acid and water:



Although $\text{HC}_3\text{H}_5\text{O}_3$ is a weak acid, it is much stronger than water and thus will be the dominant source of H^+ in the solution. The dissociation reaction is



and the equilibrium expression is

$$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]}$$

The initial and equilibrium concentrations are as follows:

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{HC}_3\text{H}_5\text{O}_3]_0 = 0.10$	$\xrightarrow{x \text{ mol/L}}$	$[\text{HC}_3\text{H}_5\text{O}_3] = 0.10 - x$
$[\text{C}_3\text{H}_5\text{O}_3^-]_0 = 0$	$\xrightarrow{\text{HC}_3\text{H}_5\text{O}_3 \text{ dissociates}}$	$[\text{C}_3\text{H}_5\text{O}_3^-] = x$
$[\text{H}^+]_0 \approx 0$		$[\text{H}^+] = x$

The change needed to reach equilibrium can be obtained from the percent dissociation and Equation (7.3). For this acid

$$\text{Percent dissociation} = 3.7\% = \frac{x}{[\text{HC}_3\text{H}_5\text{O}_3]_0} \times 100\% = \frac{x}{0.10} \times 100\%$$

and

$$x = \frac{3.7}{100}(0.10) = 3.7 \times 10^{-3} \text{ mol/L}$$

Now we can calculate the equilibrium concentrations:

$$[\text{HC}_3\text{H}_5\text{O}_3] = 0.10 - x = 0.10 \text{ M} \quad (\text{to the correct number of significant figures})$$

$$[\text{C}_3\text{H}_5\text{O}_3^-] = [\text{H}^+] = x = 3.7 \times 10^{-3} \text{ M}$$

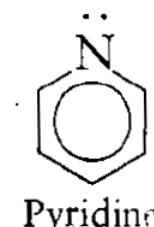
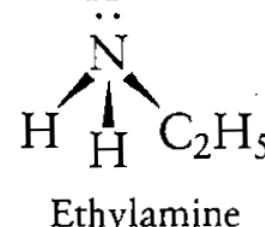
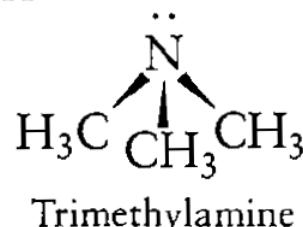
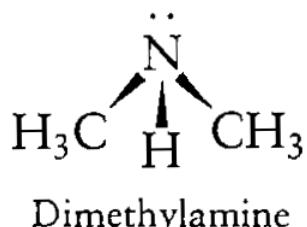
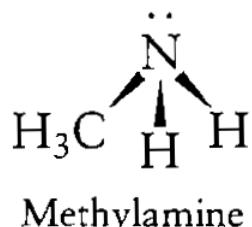
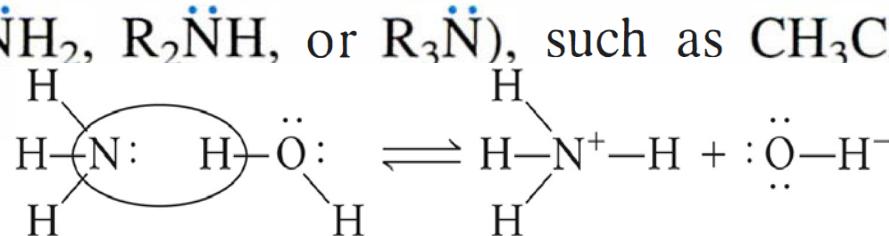
These concentrations can now be used to calculate the value of K_a for lactic acid:

$$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{(3.7 \times 10^{-3})(3.7 \times 10^{-3})}{0.10} = 1.4 \times 10^{-4}$$

Bases

Classifying the Relative Strengths of Acids and Bases

- *Strong bases.* Water-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) metal (Li, Na, K, Rb, Cs)
 2. MO or $\text{M}(\text{OH})_2$, where M = Group 2A(2) metal (Ca, Sr, Ba)
[MgO and $\text{Mg}(\text{OH})_2$ are only slightly soluble in water, but the soluble portion dissociates completely.]
- *Weak bases.* Many compounds with an electron-rich nitrogen atom are weak bases (none are Arrhenius bases). The common structural feature is an N atom with a lone electron pair (shown here in blue):
 1. Ammonia (NH_3)
 2. Amines (general formula $\text{R}\ddot{\text{N}}\text{H}_2$, $\text{R}_2\ddot{\text{N}}\text{H}$, or $\text{R}_3\ddot{\text{N}}$), such as $\text{CH}_3\text{CH}_2\ddot{\text{N}}\text{H}_2$, $(\text{CH}_3)_2\ddot{\text{N}}\text{H}$, and $(\text{C}_3\text{H}_7)_3\ddot{\text{N}}$



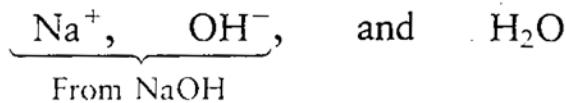
Strong Bases

Example 7.5

Calculate the pH of a $5.0 \times 10^{-2} M$ NaOH solution.

Solution

The major species in this solution are



Although the autoionization of water also produces OH^- ions, the pH will be determined by the OH^- ions from the dissolved NaOH. Thus in the solution

$$[\text{OH}^-] = 5.0 \times 10^{-2} M$$

The concentration of H^+ can be calculated from K_w :

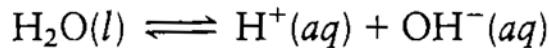
$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2.0 \times 10^{-13} M$$

$$\text{pH} = 12.70$$

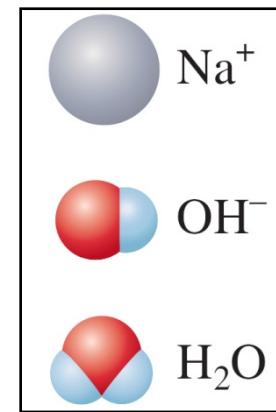
Note that this solution is basic:

$$[\text{OH}^-] > [\text{H}^+] \quad \text{and} \quad \text{pH} > 7$$

The added OH^- from the salt has shifted the water autoionization equilibrium



to the left, significantly lowering the $[\text{H}^+]$ compared with that in pure water.



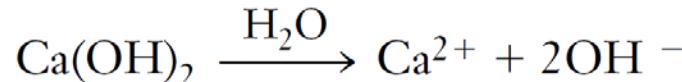
Strong Bases

Calculate $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH for a 0.015 M $\text{Ca}(\text{OH})_2$ solution.

Plan How to calculate the pH of strong base

We write the equation for the ionization of the strong base $\text{Ca}(\text{OH})_2$, which gives us $[\text{OH}^-]$. Then we calculate pOH. We use the relationships $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ and $\text{pH} + \text{pOH} = 14.00$ to find pH and $[\text{H}_3\text{O}^+]$.

Solution



Because calcium hydroxide is a strong base (it dissociates completely), we know that

$$[\text{OH}^-] = 2 \times 0.015\text{ M} = 0.030\text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (0.030) = -(-1.52) = 1.52$$

We also know that $\text{pH} + \text{pOH} = 14.00$. Therefore,

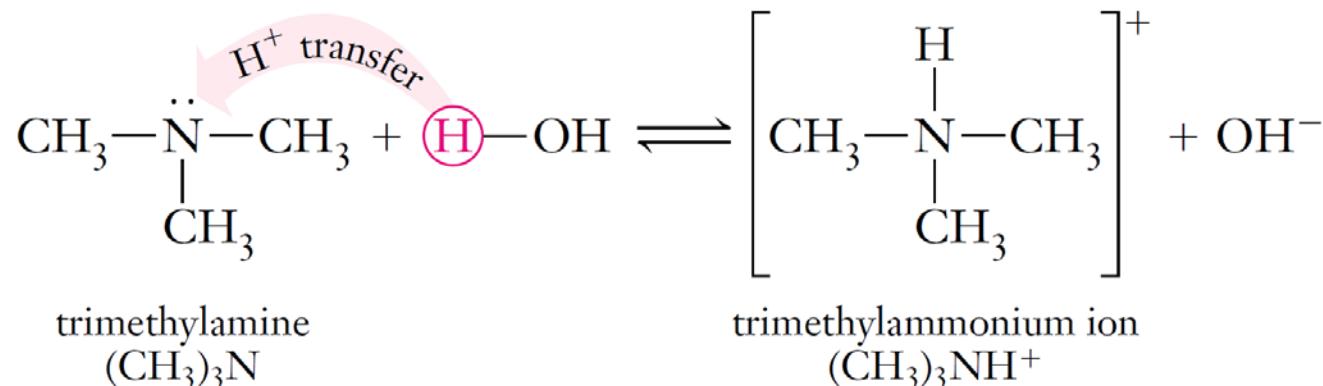
$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.52 = 12.48$$

Because $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$, $[\text{H}_3\text{O}^+]$ is easily calculated.

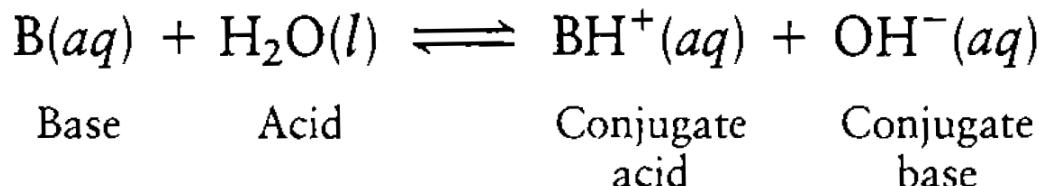
$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.030} = 3.3 \times 10^{-13}\text{ M}$$

Weak Bases

- A weak base does not have to contain the hydroxide ion to be base



The general reaction between a base (B) and water is given by



The equilibrium reaction for this general solution is

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

where K_b always refers to the reaction of a base with water to form the conjugate acid and the hydroxide ion.

Table 7.3Values 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}

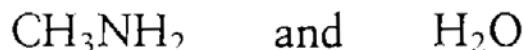
Weak Bases

Example 7.6

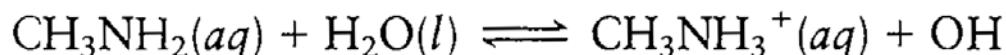
Calculate the pH of a 1.0 M solution of methylamine ($K_b = 4.38 \times 10^{-4}$).

Solution

Since methylamine (CH_3NH_2) is a weak base, the major species in solution are



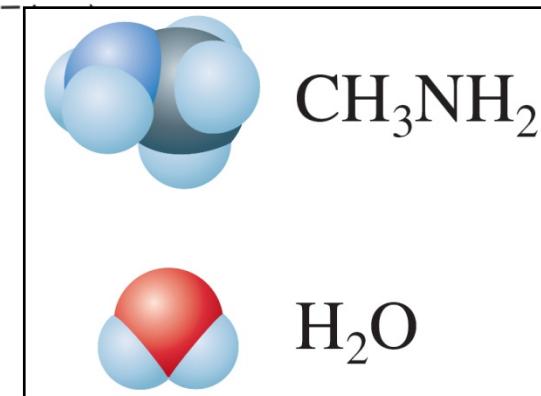
Both are bases; however, since water can be neglected as a source of OH^- , the dominant equilibrium is



and

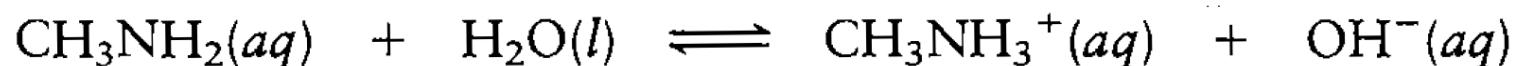
$$K_b = 4.38 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

The concentrations are as follows:



Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{CH}_3\text{NH}_2]_0 = 1.0$	x mol/L CH_3NH_2 reacts with H_2O to reach equilibrium	$[\text{CH}_3\text{NH}_2] = 1.0 - x$
$[\text{CH}_3\text{NH}_3^+]_0 = 0$		$[\text{CH}_3\text{NH}_3^+] = x$
$[\text{OH}^-]_0 \approx 0$		$[\text{OH}^-] = x$

Or, in shorthand form:



Initial:	1.0	—	0	0
Change:	$-x$	—	$+x$	$+x$
Equilibrium:	$1.0 - x$	—	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the usual approximation gives

$$K_b = 4.38 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(x)(x)}{1.0 - x} \approx \frac{x^2}{1.0}$$

$$x \approx 2.1 \times 10^{-2}$$

The approximation is valid by the 5% rule, so

$$[\text{OH}^-] = x = 2.1 \times 10^{-2} \text{ M and } \text{pOH} = 1.68$$

Note that since $[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$, $\text{pH} + \text{pOH} = 14$. Thus, $\text{pH} = 14.00 - 1.68 = 12.32$.

Weak Bases

Calculate the $[\text{OH}^-]$, pH, and percent ionization for a 0.20 M aqueous NH_3 solution.

Plan

Write the equation for the ionization of aqueous NH_3 and represent the equilibrium concentrations algebraically. Then, substitute into the K_b expression and solve for $[\text{OH}^-]$ and $[\text{NH}_3]_{\text{ionized}}$.

Solution

The equation for the ionization of aqueous ammonia and the algebraic representations of equilibrium concentrations follow. Let $x = [\text{NH}_3]_{\text{ionized}}$.

	NH_3	$+ \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$		
initial	0.20 M		0 M	$\approx 0\text{ M}$
change due to rxn	$-x\text{ M}$		$+x\text{ M}$	$+x\text{ M}$
at equil	$(0.20 - x)\text{ M}$		$x\text{ M}$	$x\text{ M}$

Weak Bases

Substitution into the ionization constant expression gives

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.20 - x)}$$

Again, we can simplify this equation. The small value of K_b tells us that the base is only slightly ionized, so we can assume that $x \ll 0.20$, or $(0.20 - x) \approx 0.20$, and we have

$$\frac{x^2}{0.20} = 1.8 \times 10^{-5} \quad x^2 = 3.6 \times 10^{-6} \quad x = 1.9 \times 10^{-3} \text{ M}$$

Then $[\text{OH}^-] = x = 1.9 \times 10^{-3} \text{ M}$, $\text{pOH} = 2.72$, and $\text{pH} = 11.28$.

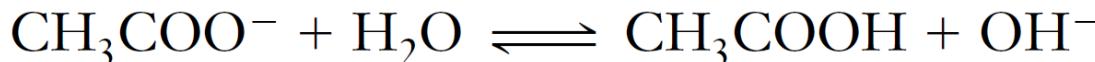
$[\text{NH}_3]_{\text{ionized}} = x$, so the percent ionization may be calculated.

$$\% \text{ ionization} = \frac{[\text{NH}_3]_{\text{ionized}}}{[\text{NH}_3]_{\text{initial}}} \times 100\% = \frac{1.9 \times 10^{-3}}{0.20} \times 100\% = 0.95\% \text{ ionized}$$

Relation between K_a and K_b

Calculating K_a and K_b

- The net result of the preceding equations can be written as a single equation. This equation describes the **hydrolysis of acetate ions**.



- The equilibrium constant for this reaction is called a (base) hydrolysis constant, or K_b for CH_3COO^- .

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

- We multiply the preceding expression by $[\text{H}_3\text{O}^+]/[\text{H}_3\text{O}^+]$ to give

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{[\text{CH}_3\text{COOH}]}{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]} \times \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{1}$$

- We recognize

$$K_b = \frac{1}{K_a(\text{CH}_3\text{COOH})} \times \frac{K_w}{1} = \frac{K_w}{K_a(\text{CH}_3\text{COOH})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

- which gives

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = 5.6 \times 10^{-10}$$

Relation between K_a and K_b

- We have calculated K_b , *the hydrolysis constant for the acetate ion, CH_3COO^-*
- We can do the same kind of calculations for the anion of any weak monoprotic acid and find that

$$K_b = K_w / K_a$$

— where K_a refers to the ionization constant for the weak monoprotic acid from which the anion is derived.

- This equation can be rearranged to

$$K_w = K_a K_b \quad (\text{valid for any conjugate acid-base pair in aqueous solution})$$

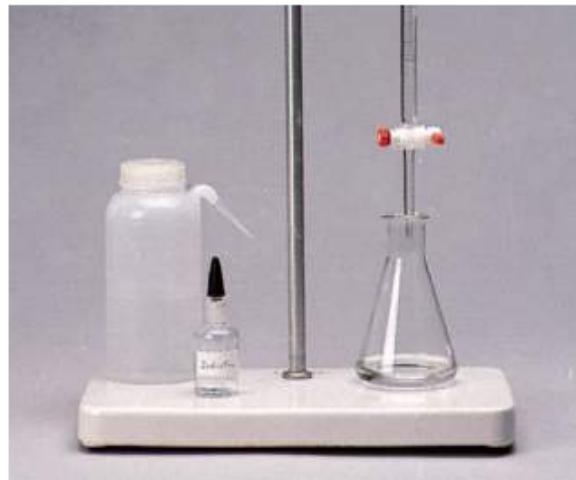
If either K_a or K_b is known, the other can be calculated.

Acid-Base Titration

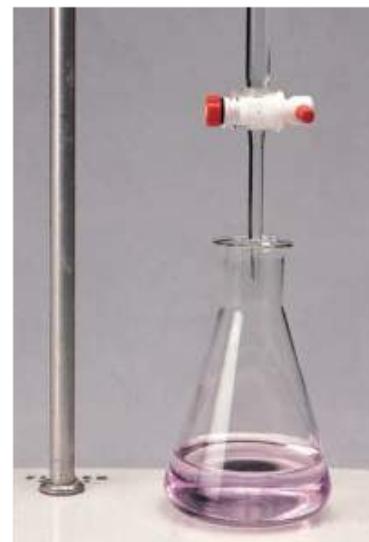
In a **titration** a solution of accurately **known** concentration is added gradually to another solution of **unknown** concentration until the chemical reaction between the two solutions is **complete**.

Equivalence point – the point at which the reaction is **complete**

Indicator – substance that changes color at (or near) the equivalence point



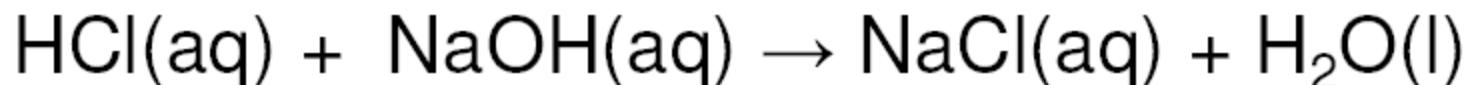
Slowly add base
to unknown acid
UNTIL
The indicator
changes color
(pink)



Acid- Base Titration

Acid- base titration involves the **complete** reaction between an acid and a base.

Neutralization reaction

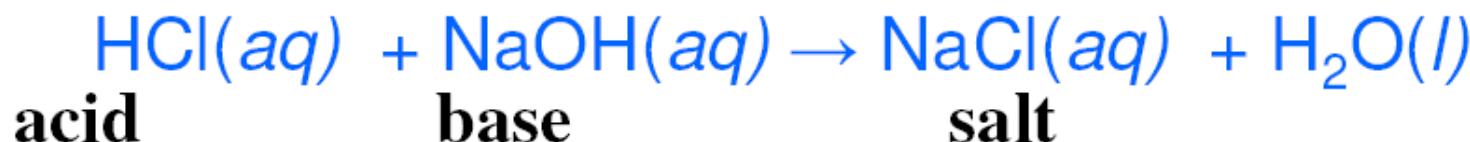


Net ionic equation of the reaction





42.00 mL of 0.150 M NaOH solution is required to neutralize 50.00 mL of hydrochloric acid solution. What is the molarity of the acid solution?



Complete neutralization:

$$\# \text{ of moles H}^+ = \# \text{ of moles OH}^-$$

Mole ratio of HCl:NaOH is **1:1**

$$\# \text{ of moles HCl} = \# \text{ of moles NaOH}$$

$$M_{\text{acid}} \times V_{\text{acid}} = M_{\text{base}} \times V_{\text{base}}$$

$$M_{\text{acid}} = \frac{0.150 \text{ M} \times 42.00 \text{ mL}}{50.00 \text{ mL}} = 0.126 \text{ M}$$



42.00 mL of 0.150 M NaOH solution is required to neutralize 50.00 mL of sulfuric acid solution. What is the molarity of the acid solution?



Complete neutralization:

$$\# \text{ of moles H}^+ = \# \text{ of moles OH}^-$$

Mole ratio of H_2SO_4 :NaOH is **1:2**

$$\# \text{ of moles H}_2\text{SO}_4 \times 2 = \# \text{ of moles NaOH}$$

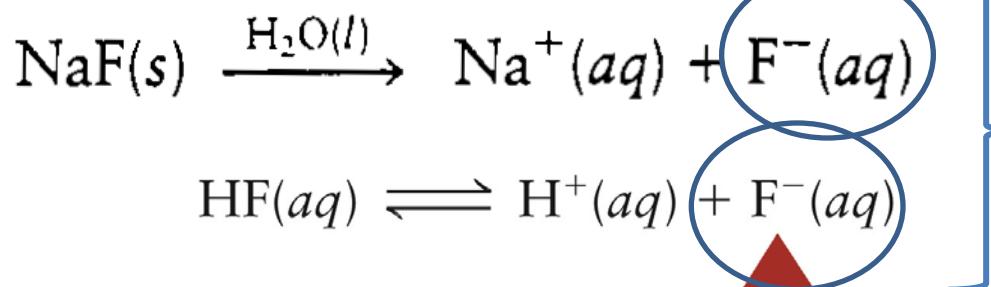
$$M_{\text{acid}} \times V_{\text{acid}} \times 2 = M_{\text{base}} \times V_{\text{base}}$$

$$M_{\text{acid}} = \frac{0.150 \text{ M} \times 42.00 \text{ mL}}{50.00 \text{ mL} \times 2} = 0.0630 \text{ M}$$

Solutions of Acids and Bases containing a Common Ion

- In this section we discuss solutions containing not only the weak acid HA but also its salt NaA
- The concept here is that the addition of a common ion can depress the dissociation of an acid. This is based on Le Chatelier's principle.
- Example : $\text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^- \quad \text{Ka}$
- Add CH_3COONa means adding CH_3COO^- which is a common ion. This imposes the stress on system. Shift to left. This will depress the amount of dissociation.

Suppose we have a solution containing the weak acid hydrofluoric acid (HF , $K_a = 7.2 \times 10^{-4}$) and its salt sodium fluoride (NaF). Recall that when a salt dissolves in water, it breaks up completely into its ions—it is a strong electrolyte:



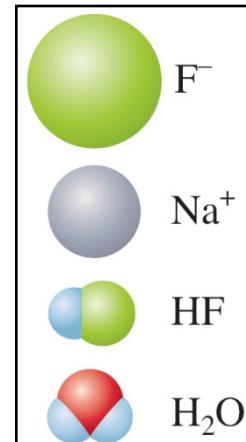
The common ion

So HF is
less acidic
in
presence
of NaF

Equilibrium shifts
away from added
component. Fewer
 H^+ ions present.

Added F^- ions
from NaF

According to Le
Chatelier's principle.

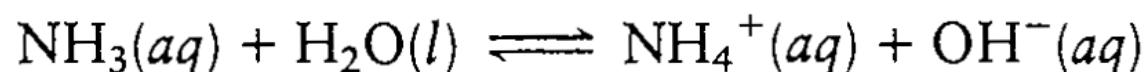


Since hydrofluoric acid is a weak acid and only slightly dissociated, the major species in the solution are HF , Na^+ , F^- , and H_2O .

The common ion effect is quite general. For example, when solid NH_4Cl is dissolved in a 1.0 M NH_3 solution



the added ammonium ions cause the position of the ammonia–water equilibrium



to shift to the left, reducing the concentration of OH^- ions.

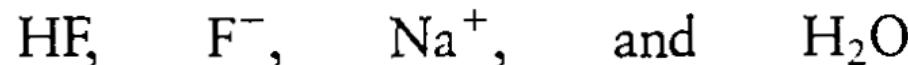
Example 8.1

In Section 7.5 we found that the equilibrium concentration of H^+ in a 1.0 M HF solution is 2.7×10^{-2} M and the percent dissociation of HF is 2.7%. Calculate $[\text{H}^+]$ and the percent dissociation of HF in a solution containing both 1.0 M HF ($K_a = 7.2 \times 10^{-4}$) and 1.0 M NaF.

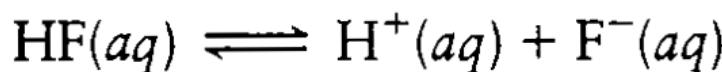
Solution

As the aqueous solutions we consider become more complex, it becomes increasingly important to be systematic and to *focus on the chemistry* occurring in the solution before thinking about mathematical procedures. *Always* write the major species first and consider the chemical properties of each component.

In a solution containing 1.0 M HF and 1.0 M NaF, the major species are



Since Na^+ ions have neither acidic nor basic properties, and since water is such a weak acid or base, the important species are HF and F^- ; they participate in the acid dissociation equilibrium that control $[\text{H}^+]$ in this solution. That is, the position of the equilibrium



will determine $[\text{H}^+]$ in the solution. The equilibrium expression is

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

The important concentrations are listed in the following table.

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{HF}]_0 = 1.0$ (from dissolved HF)		$[\text{HF}] = 1.0 - x$
$[\text{F}^-]_0 = 1.0$ (from dissolved NaF)	$\xrightarrow{x \text{ mol/L HF dissociates to reach equilibrium}}$	$[\text{F}^-] = 1.0 + x$
$[\text{H}^+]_0 = 0$ (neglect contribution from H_2O)		$[\text{H}^+] = x$

Note that $[\text{F}^-]_0 = 1.0 \text{ M}$ from the dissolved sodium fluoride and that the equilibrium $[\text{F}^-] > 1.0 \text{ M}$ because when the acid dissociates, it produces F^- as

well as H^+ . Then

$$K_a = 7.2 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(1.0 + x)}{1.0 - x} \approx \frac{(x)(1.0)}{1.0}$$

since x is expected to be small.

Solving for x gives

$$x = \frac{1.0}{1.0} (7.2 \times 10^{-4}) = 7.2 \times 10^{-4}$$

Noting that x is small compared with 1.0, we conclude that this result is acceptable. Thus

$$[\text{H}^+] = x = 7.2 \times 10^{-4} \text{ M} \quad (\text{The pH is 3.14.})$$

The percent dissociation of HF in this solution is

$$\frac{[\text{H}^+]}{[\text{HF}]_0} \times 100\% = \frac{7.2 \times 10^{-4} \text{ M}}{1.0 \text{ M}} \times 100\% = 0.072\%$$

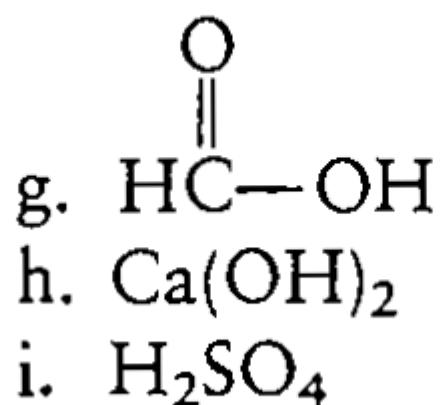
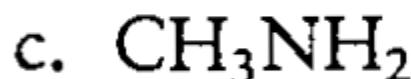
Compare these values for $[\text{H}^+]$ and percent dissociation of HF with those for a 1.0 M HF solution, where $[\text{H}^+] = 2.7 \times 10^{-2} \text{ M}$ and the percent dissociation is 2.7%. The large difference clearly shows that the presence of the F^- ions from the dissolved NaF greatly inhibits the dissociation of HF. The position of the acid dissociation equilibrium has been shifted to the left by the presence of F^- ions from NaF .

HOMEWORK

Chap.7: 27,32, 35, 53, 54, 62, 64, 96, 129

Chap. 8: 25

Classify each of the following as a strong acid, weak acid, strong base, or weak base in aqueous solution.



32

Calculate the $[\text{OH}^-]$ of each of the following solutions at 25°C. Identify each solution as neutral, acidic, or basic.

- a. $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$
- b. $[\text{H}^+] = 8.3 \times 10^{-16} \text{ M}$
- c. $[\text{H}^+] = 12 \text{ M}$
- d. $[\text{H}^+] = 5.4 \times 10^{-5} \text{ M}$

35

Calculate $[\text{H}^+]$ and $[\text{OH}^-]$ for each solution at 25°C. Identify each solution as neutral, acidic, or basic.

- a. $\text{pH} = 7.40$ (the normal pH of blood)
- b. $\text{pH} = 15.3$
- c. $\text{pH} = -1.0$
- d. $\text{pH} = 3.20$
- e. $\text{pOH} = 5.0$
- f. $\text{pOH} = 9.60$

53

A solution is prepared by dissolving 0.56 g of benzoic acid (C_6H_5COOH , $K_a=6.4 \cdot 10^{-5}$) in enough water to make 1 L of solution. Calculate $[C_6H_5COOH]$, $[C_6H_5COO^-]$, $[H^+]$, $[OH^-]$ and the pH of this solution.

54

Trichloroacetic acid (CCl_3CO_2H) is a corrosive acid that is used to precipitate proteins. The pH of a 0.050 M solution of trichloroacetic acid is the same as the pH of a 0.040 M $HClO_4$ solution. Calculate K_a for trichloroacetic acid.

62

A 0.15 M solution of a weak acid is 3% dissociated. Calculate K_a .

64

Use Table 7.3 to help answer the following questions.

- a. Which is the strongest acid, HClO_4 or $\text{C}_6\text{H}_5\text{NH}_3^+$?
- b. Which is the strongest acid, H_2O or $\text{C}_6\text{H}_5\text{NH}_3^+$?
- c. Which is the strongest acid, $\text{C}_6\text{H}_5\text{NH}_3^+$ or CH_3NH_3^+ ?

96

Consider a solution of an unknown salt having the general formula BHCl , where B is one of the weak bases in Table 7.3. A 0.10 M solution of the unknown salt has a pH of 5.82. What is the actual formula of the salt?

129

Calculate $[\text{OH}^-]$ in a solution obtained by adding 0.0100 mol of solid NaOH to 1.00 L of 15.0 M NH_3 .

25

Calculate the pH of a solution that is 0.60 M HF and 1.00 M KF.

TABLE 7.2Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
HClO_2	Chlorous acid	1.2×10^{-2}
$\text{HC}_2\text{H}_2\text{ClO}_2$	Monochloracetic 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}
HOCH_3	Phenol	1.6×10^{-10}

↑
Increasing acid strength

TABLE 7.3Values 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}

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	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	

*This is really $CO_2(aq)$.

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