Chapter 17: Acids and Bases

Bronsted-Lowry Definition: An Acid is a proton (H⁺; H₃O⁺) donor
A Base is a proton (H⁺; H₃O⁺) acceptor.

Acids and Bases are discriminated by their “strength”.

17.1 Formulae, Names & Structures of Strong Acids

Binary Acids

HCl
HBr
HI

Oxy-Acids

HNO₃
HClO₄
H₂SO₄

Formulae, Names & Structures of Weak Acids

Oxy-Acids

HNO₂
HClO₃
HClO₂
HClO
H₂SO₃

H₃PO₄

Carboxylic Acids

HCO₂H

HC₂H₃O₂
CH₃CO₂H

HC₃H₅O₂
CH₃CH₂CO₂H

C₆H₅CO₂H
Acids dissolve in aqueous solution by forming conjugate acid/conjugate base ions.

Stabilization of aqueous Hydronium Ion by extensive hydrogen-bonding with water molecules.

Another Definition: Lewis Acids and Lewis Bases (sec. 18.1 p880)
Nitric Acid dissolving in water:
Strong Acid

Acetic Acid dissolving in water:
Weak Acid

Concentration Equilibrium Constant for acids: $K_a$ & $[H^+]$

$pK_a = -\log[K_a]$  
$pH = -\log[H^+]$
Relative Strengths of Acids and Bases in aqueous solutions depend on their extent of ionization. Defined by $K_a$ and/or %-ionization.
### Relative Strengths of Acids and their Conjugate Bases (anions)

#### Ionization Constants for Some Acids and Their Conjugate Bases at 25 °C

<table>
<thead>
<tr>
<th>Acid Name</th>
<th>Acid</th>
<th>$K_a$</th>
<th>Base</th>
<th>$K_b$</th>
<th>Base Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perchloric acid</td>
<td>HClO₄</td>
<td>large</td>
<td>ClO₄⁻</td>
<td>very small</td>
<td>perchlorate ion</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄</td>
<td>large</td>
<td>HSO₄⁻</td>
<td>very small</td>
<td>hydrogen sulfate ion</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>large</td>
<td>Cl⁻</td>
<td>very small</td>
<td>chloride ion</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>large</td>
<td>NO₃⁻</td>
<td>very small</td>
<td>nitrate ion</td>
</tr>
<tr>
<td>Hydronium ion</td>
<td>H₃O⁺</td>
<td>1.0</td>
<td>H₂O</td>
<td>$1.0 \times 10^{-14}$</td>
<td>water</td>
</tr>
<tr>
<td>Sulfurous acid</td>
<td>H₂SO₃</td>
<td>$1.2 \times 10^{-2}$</td>
<td>HSO₃⁻</td>
<td>$8.3 \times 10^{-13}$</td>
<td>hydrogen sulfite ion</td>
</tr>
<tr>
<td>Hydrogen sulfate ion</td>
<td>HSO₄⁻</td>
<td>$1.2 \times 10^{-2}$</td>
<td>SO₄²⁻</td>
<td>$8.3 \times 10^{-13}$</td>
<td>sulfate ion</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H₃PO₄</td>
<td>$7.5 \times 10^{-3}$</td>
<td>H₂PO₄⁻</td>
<td>$1.3 \times 10^{-12}$</td>
<td>dihydrogen phosphate ion</td>
</tr>
<tr>
<td>Hexaaquiron(III) ion</td>
<td>[Fe(H₂O)₆]³⁺</td>
<td>$6.3 \times 10^{-3}$</td>
<td>[Fe(H₂O)₅OH]²⁺</td>
<td>$1.6 \times 10^{-12}$</td>
<td>pentaaquahydroxiron(III) ion</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>HF</td>
<td>7.2</td>
<td>F⁻</td>
<td>$1.4 \times 10^{-11}$</td>
<td>fluoride ion</td>
</tr>
<tr>
<td>Nitrous acid</td>
<td>HNO₂</td>
<td>4.5</td>
<td>NO₂⁻</td>
<td>$2.2 \times 10^{-11}$</td>
<td>nitrite ion</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCO₂H</td>
<td>1.8</td>
<td>HCO₂⁻</td>
<td>$5.6 \times 10^{-11}$</td>
<td>formate ion</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>C₆H₅CO₂H</td>
<td>6.5</td>
<td>C₆H₅CO₂⁻</td>
<td>$1.6 \times 10^{-10}$</td>
<td>benzoate ion</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃CO₂H</td>
<td>1.8</td>
<td>CH₃CO₂⁻</td>
<td>$5.6 \times 10^{-10}$</td>
<td>acetate ion</td>
</tr>
<tr>
<td>Propanoic acid</td>
<td>CH₃CH₂CO₂H</td>
<td>1.3</td>
<td>CH₃CH₂CO₂⁻</td>
<td>$7.7 \times 10^{-10}$</td>
<td>propanoate ion</td>
</tr>
<tr>
<td>Hexaaquaaluminum ion</td>
<td>[Al(H₂O)₆]³⁺</td>
<td>$7.9 \times 10^{-6}$</td>
<td>[Al(H₂O)₅OH]²⁺</td>
<td>$1.3 \times 10^{-9}$</td>
<td>pentaaquahydroxaluminum ion</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>H₂CO₃</td>
<td>4.2</td>
<td>HCO₃⁻</td>
<td>$2.4 \times 10^{-8}$</td>
<td>hydrogen carbonate ion</td>
</tr>
<tr>
<td>Hexaaquacopper(II) ion</td>
<td>[Cu(H₂O)₆]²⁺</td>
<td>$1.6 \times 10^{-7}$</td>
<td>[Cu(H₂O)₅OH]⁺</td>
<td>$6.3 \times 10^{-8}$</td>
<td>pentaaquahydroxocopper(II) ion</td>
</tr>
<tr>
<td>Hydrogen sulfide ion</td>
<td>H₂S</td>
<td>9.5</td>
<td>HS⁻</td>
<td>$1 \times 10^{-7}$</td>
<td>hydrogen sulfide ion</td>
</tr>
<tr>
<td>Dihydrogen phosphate ion</td>
<td>H₂PO₄⁻</td>
<td>6.2</td>
<td>HPO₄²⁻</td>
<td>$1.6 \times 10^{-7}$</td>
<td>hydrogen phosphate ion</td>
</tr>
<tr>
<td>Hydrogen sulfate ion</td>
<td>HSO₄⁻</td>
<td>6.5</td>
<td>SO₄²⁻</td>
<td>$1.6 \times 10^{-7}$</td>
<td>sulfite ion</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>HClO</td>
<td>3.5</td>
<td>ClO⁻</td>
<td>$2.9 \times 10^{-7}$</td>
<td>hypochlorite ion</td>
</tr>
<tr>
<td>Hexaaqualeted(II) ion</td>
<td>[Pb(H₂O)₆]²⁺</td>
<td>$1.5 \times 10^{-8}$</td>
<td>[Pb(H₂O)₅OH]⁺</td>
<td>$6.7 \times 10^{-7}$</td>
<td>pentaaquahydroxolead(II) ion</td>
</tr>
<tr>
<td>Hexaaquacobalt(II) ion</td>
<td>[Co(H₂O)₆]³⁺</td>
<td>$1.3 \times 10^{-9}$</td>
<td>[Co(H₂O)₅OH]⁺</td>
<td>$7.7 \times 10^{-6}$</td>
<td>pentaaquahydroxocobalt(II) ion</td>
</tr>
<tr>
<td>Boric acid</td>
<td>B(OH)₃(H₂O)</td>
<td>$7.3 \times 10^{-10}$</td>
<td>B(OH)₄⁻</td>
<td>$1.4 \times 10^{-5}$</td>
<td>tetrahydroborate ion</td>
</tr>
<tr>
<td>Ammonium ion</td>
<td>NH₄⁺</td>
<td>5.6</td>
<td>NH₃</td>
<td>$1.8 \times 10^{-5}$</td>
<td>ammonia</td>
</tr>
<tr>
<td>Hydrocyanic acid</td>
<td>HCN</td>
<td>4.0</td>
<td>CN⁻</td>
<td>$2.5 \times 10^{-5}$</td>
<td>cyanide ion</td>
</tr>
<tr>
<td>Hexaaquiron(II) ion</td>
<td>[Fe(H₂O)₆]²⁺</td>
<td>$3.2 \times 10^{-10}$</td>
<td>[Fe(H₂O)₅OH]⁺</td>
<td>$3.1 \times 10^{-5}$</td>
<td>pentaaquahydroxiron(II) ion</td>
</tr>
<tr>
<td>Hydrogen carbonate ion</td>
<td>HCO₃⁻</td>
<td>4.8</td>
<td>CO₃²⁻</td>
<td>$2.1 \times 10^{-4}$</td>
<td>carbonate ion</td>
</tr>
<tr>
<td>Hexaaquanickel(II) ion</td>
<td>[Ni(H₂O)₆]²⁺</td>
<td>$2.5 \times 10^{-11}$</td>
<td>[Ni(H₂O)₅OH]⁺</td>
<td>$4.0 \times 10^{-4}$</td>
<td>pentaaquahydroxanickel(II) ion</td>
</tr>
<tr>
<td>Hydrogen phosphate ion</td>
<td>HPO₄²⁻</td>
<td>$3.6 \times 10^{-13}$</td>
<td>PO₄³⁻</td>
<td>$2.8 \times 10^{-2}$</td>
<td>phosphate ion</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>$1.0 \times 10^{-14}$</td>
<td>OH⁻</td>
<td>1.0</td>
<td>hydroxide ion</td>
</tr>
<tr>
<td>Hydrogen sulfide ion</td>
<td>HS⁻</td>
<td>$1 \times 10^{-19}$</td>
<td>S²⁻</td>
<td>$1 \times 10^{5}$</td>
<td>sulfide ion</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>very small</td>
<td>C₂H₅O⁻</td>
<td>large</td>
<td>ethoxide ion</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>very small</td>
<td>NH₂⁻</td>
<td>large</td>
<td>amide ion</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H₂</td>
<td>very small</td>
<td>H⁻</td>
<td>large</td>
<td>hydride ion</td>
</tr>
</tbody>
</table>
Concentration Equilibrium Constant for bases: $K_b$

Strong Bases

Strong Bases dissolving in water directly produce $\text{OH}^-$. 

Weak Bases
Weak Bases dissolving in water react with H₂O to form OH⁻.

Ammonia, NH₃, dissolving in water.

Equilibrium Constant for bases: 

\[ pK_b = -\log[K_b] \quad \text{and} \quad pOH = -\log[OH^-] \]
17.2  Kw & Autoionization of water.
\[ \text{pH} = -\log[H^+] \]

**pH scale**

More basic (higher pH)

14  
1 M NaOH (14.0)

13  
Drain cleaner (13.0)

12  
Household ammonia (11.7)

11  
Milk of magnesia (10.5)

10  
9  
8  
Baking soda (8.3)  
Seawater (8.2)  
Human blood (7.4)

7 Neutral

6  
Milk (6.5)

5  
Natural rainwater (5.6)

4  
Tomatoes (4.5)

3  
Oranges (3.5)  
Vinegar (2–3)  
Lemons (2.3)

2  
Stomach acid (1.5–2.0)

1  
0  
1 M HCl (0.0)

More acidic (lower pH)
Relationships between: pH, pOH, pKw, Kw, [H\(^+\)], [OH\(^-\)] Ka, Kb, pKa, pKb

17.3 Using these relationships in calculations

**Example Problems**

**What is the pH of a 1.80 \times 10^{-3} M solution of HNO_3?**

**What is the pH of a 4.27 \times 10^{-6} M solution of KOH?**
WHAT IS THE PH OF A SOLUTION OF 7.81 \times 10^{-7} \text{ M } \text{Ca(OH)}_2?

CALCULATE THE $[\text{H}_3\text{O}^+]$ AND pH OF AN 0.15 M SOLN OF ACETIC ACID: $\text{CH}_3\text{CO}_2\text{H}$

$K_a = 1.80 \times 10^{-5}$

$[\text{CH}_3\text{CO}_2\text{H}] = [\text{H}_3\text{O}^+] = [\text{CH}_3\text{CO}_2^-]$
Example: What are $[\text{OH}^-]$, $[\text{H}_3\text{O}^+]$ and pH of a 0.20 M solution of sodium hydrogen carbonate (sodium bicarbonate; baking soda)

$$\text{NaHCO}_3(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Na}^+ + \text{H}_2\text{CO}_3(aq) + \text{OH}^-$$

$$\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^- \quad \text{(all)}$$

H |  |  |  |  |
---|---|---|---|---|
C |  |  |  |  |
E |  |  |  |  |
Hypochlorous acid: HClO
An 0.010 M solution has a pH of 4.8; calculate $K_a$

$$[HClO] = [H_3O^+] + [ClO^-]$$

ICE

A 0.100 M ammonia solution has a pH = 11.124. Calculate $K_b$ for ammonia.
PH OF VERY DILUTE SOLUTIONS

WHEN $K_w$ IS IMPORTANT.

WHAT IS THE PH OF A SOLUTION THAT IS $4.00 \times 10^{-9}$ M IN HCOO$_2$?

17.4

DI PROTIC ACIDS > POLYPROTIC ACIDS

TRI PROTIC ACIDS

$$\text{H}_2\text{SO}_4_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons 2\text{H}_3\text{O}^+_{(aq)} + \text{SO}_4^{2-}_{(aq)}$$

OVERALL COMPLETE IONIZATION

Polyprotic Acids

$$\text{H}_2\text{SO}_4_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{SO}_4^{2-}_{(aq)}$$

$$\text{H}_2\text{SO}_4_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{SO}_4^{2-}_{(aq)}$$

$K_{a1} =$

$K_{a2} =$
17.5 Acid strength and molecular structure.
### ELECTRONEGATIVITY

**INDUCTIVE EFFECT**

O...H BOND POLARIZATION

<table>
<thead>
<tr>
<th>Acid</th>
<th>Structure</th>
<th>Cl oxidation number</th>
<th>Ka</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malonic Acid</td>
<td><img src="image1" alt="Structure" /></td>
<td>+1</td>
<td>2.8 x 10^-8</td>
</tr>
<tr>
<td>Chlorous Acid</td>
<td><img src="image2" alt="Structure" /></td>
<td>+3</td>
<td>1.1 x 10^-2</td>
</tr>
<tr>
<td>Chloric Acid</td>
<td><img src="image3" alt="Structure" /></td>
<td>+5</td>
<td>~1</td>
</tr>
<tr>
<td>Per-Chloric Acid</td>
<td><img src="image4" alt="Structure" /></td>
<td>+7</td>
<td>strong acid</td>
</tr>
</tbody>
</table>
17.6 pH of salt solutions

<table>
<thead>
<tr>
<th>Acid</th>
<th>Structure</th>
<th>EN of Halogen</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hypochlorous</td>
<td><img src="image1" alt="Hypochlorous Acid structure" /></td>
<td>3.0</td>
<td>2.9 x 10^{-8}</td>
</tr>
<tr>
<td>Hypobromous</td>
<td><img src="image2" alt="Hypobromous Acid structure" /></td>
<td>2.8</td>
<td>2.3 x 10^{-9}</td>
</tr>
<tr>
<td>Hypoiodous</td>
<td><img src="image3" alt="Hypoiodous Acid structure" /></td>
<td>2.5</td>
<td>2.3 x 10^{-11}</td>
</tr>
</tbody>
</table>
Distinguishing Acidic, Basic and Neutral Salts

Pg 840: Is an aqueous solution of NaClO (sodium hypochlorite) acidic, basic or neutral?

<table>
<thead>
<tr>
<th>Anion Is Derived from a</th>
<th>Cation Is Derived from a</th>
<th>pH of Aqueous Solutions</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong acid</td>
<td>Strong base</td>
<td>7</td>
<td>NaCl</td>
</tr>
<tr>
<td>Strong acid</td>
<td>Weak base</td>
<td>&lt;7</td>
<td>NH₄Cl</td>
</tr>
<tr>
<td>Weak acid</td>
<td>Strong base</td>
<td>&gt;7</td>
<td>NaF</td>
</tr>
<tr>
<td>Weak acid</td>
<td>Weak base</td>
<td>Depends on relative values of pKₐ and pK₆</td>
<td>pK₆ &lt; pKₐ, acidic; NH₄F pK₆ &gt; pKₐ, basic; NH₄HCO₃ pK₆ = pKₐ, neutral; CH₃COONH₄</td>
</tr>
</tbody>
</table>

Calculate the pH of an 0.040 M solution of sodium hypochlorite.
Is an aqueous solution of ammonium chloride acidic, basic or neutral?

Calculate the pH of 0.100 M NH₄Cl solution?

Aqueous Chemical Reactions of CO₂(g)—A world-altering environmental pollutant.
17.7 Review the Common Ion Effect. The Henderson-Hasselbalch Equation and Prelude to Buffers.

Common Ion Effect

17.8 Buffers

Buffers

Solutions that resist pH change

A buffer consists of a weak acid and its conjugate base

Henderson-Hasselbalch Eqn

\[ pH = pK_a + \log \frac{[\text{conj. base}]}{[\text{conj. acid}]} \]
### Buffer Systems That Are Useful at Various pH Values

<table>
<thead>
<tr>
<th>Desired pH</th>
<th>Weak Conjugate Acid</th>
<th>Weak Conjugate Base</th>
<th>Ka of weak conjugate acid</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Lactic acid (CH₃CHOHOOCOH)</td>
<td>Lactate ion (CH₃CHOHOOCO²⁻)</td>
<td>1.4 × 10⁻⁴</td>
<td>3.85</td>
</tr>
<tr>
<td>5</td>
<td>Acetic acid (CH₃COOH)</td>
<td>Acetate ion (CH₃COO⁻)</td>
<td>1.8 × 10⁻⁵</td>
<td>4.74</td>
</tr>
<tr>
<td>6</td>
<td>Carbonic acid (H₂CO₃)</td>
<td>Hydrogen carbonate ion (HCO₃⁻)</td>
<td>4.2 × 10⁻⁷</td>
<td>6.38</td>
</tr>
<tr>
<td>7</td>
<td>Dihydrogen phosphate ion (H₂PO₄⁻)</td>
<td>Monohydrogen phosphate ion (HPO₄²⁻)</td>
<td>6.2 × 10⁻⁸</td>
<td>7.21</td>
</tr>
<tr>
<td>8</td>
<td>Hypochlorous acid (HClO)</td>
<td>Hypochlorite ion (ClO⁻)</td>
<td>3.5 × 10⁻⁸</td>
<td>7.46</td>
</tr>
<tr>
<td>9</td>
<td>Ammonium ion (NH₄⁺)</td>
<td>Ammonia (NH₃)</td>
<td>5.6 × 10⁻¹⁰</td>
<td>9.25</td>
</tr>
<tr>
<td>10</td>
<td>Hydrogen carbonate ion (HCO₃⁻)</td>
<td>Carbonate ion (CO₃²⁻)</td>
<td>4.8 × 10⁻¹¹</td>
<td>10.32</td>
</tr>
</tbody>
</table>


### Buffer Calculations:

**pH of a Buffer Solution**

**Buffer: 1.00 L of Buffer Solution**

\[
\begin{align*}
[H_2CO_3]_{initial} & = 2.50 \times 10^{-3} \text{ M} \\
[NaHCO_3]_{initial} & = 2.60 \times 10^{-3} \text{ M}
\end{align*}
\]

\[
K_a (H_2CO_3) = 4.2 \times 10^{-7}
\]

**Buffer Equilibrium: H_2CO_3 + H_2O \rightleftharpoons H_2O^+ + HCO_3^- + Na^+**

\[
K_a \frac{[H_2CO_3]}{[HCO_3^-]}
\]

I C E

---

22
Add KOH to this buffer and calculate the new pH.

Illustrating that Acid/Base Reactions are most easily organized on the basis of moles of acid reacting with moles of base. (Instead of using molarity.)

Problem. To the preceding carbonic acid/Bicarbonate buffer $2.000 \times 10^{-4}$ moles of solid KOH are added. What is the resulting pH of the solution?

Problem. What would be the resulting pH if $1.000 \times 10^{-3}$ moles of solid KOH were added to the original buffer?
17.10 Indicators and Acid-Base Titrations.

As you know from CH. 4, real titrations involve a solution of titrant added to a solution of analyte. In an acid/base titration the pH of the analyte solution changes.

In the picture of the titration-setup at right the analyte solution contains an INDICATOR, that changes color near the end-point of the titration.

For acid-base reactions, the titration endpoint is the EQUVALENCE POINT.

At the EQUVALENCE POINT the Number of moles of acid = Number of moles of Base.

**WHAT IS AN INDICATOR?**

AN ACID-BASE INDICATOR:

1) IS TYPICALLY A COLORED WEAK ORGANIC (e. CARBOXYLIC) ACIDS

2) THEIR COLOR CHANGES UPON LOSS OF A PROTON TO FORM THE CONJUGATE BASE.

\[ \text{HIN}_\text{(aq)} + \text{H}_2\text{O}_\text{(aq)} \rightarrow \text{H}_3\text{O}_\text{(aq)} + \text{IN}_\text{(aq)} \]

ACID FORM

\[ \text{IN}_\text{(aq)} \]

BASE FORM

PROTONATION STATE OF AN INDICATOR DEPENDS ON SOLUTION pH.

Crystal violet
Thymol blue
2,4-Dinitrophenol
Bromphenol blue
Methyl orange
Bromresol green
Methyl red
Bromthymol blue
Phenol red
Phenolphthalein
Alizarin yellow R

![pH Chart](chart.png)
A titration curve of HCl with NaOH showing the behavior of three indicators near the Equivalence Point. (pH=7.00)

Neutralization Titrations of Strong Acid/Strong Base you learned in CH. 4. Here we study titrations between Strong Acids and Weak Bases, or Weak Acids and Strong Bases. These are called “Alkalinity Titrations”.

Titration of NH₃ (weak base; analyte) by HCl (strong Acid; titrant).
Qualitative Description of the titration curves.
One use of Acid/Base titrations is to determine the concentration of the analyte.
Pg 862: 10.00 mL of a commercial vinegar solution was titrated with 0.1050 M NaOH solution (titrant) to determine the concentration of Acetic Acid (CH₃CO₂H; the analyte) in the vinegar. It took 16.24 mL of the titrant to reach the Equivalence Point. What is the acetic acid concentration?

Problem. Calculating the titration curve for a NaOH (strong base) titration of Acetic Acid (weak acid). Fig. 17.18
Titration curve for carbonic acid (weak acid; analyte) titrated with HCl (strong acid; titrant)
Sample Exercise 17.15; page 866.

End Ch. 17 Notes.