ACID-BASE REACTIONS/
THE PH CONCEPT.

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Lecture topics.

- 2 lectures dealing with some core chemistry:
  - acid/base reactions
  - the pH concept.
- We will study these concepts in more detail during the main lecture course later on.
- We will address the following questions/ideas:
  - What are acids and bases?
  - Can we provide a general definition of acid and base?
  - How can we quantify acidity and basicity?
  - Can we classify acid and base strength?
  - pH concept and pH scale.
  - Acid/base reactions: neutralization
  - How can we monitor an acid/base reaction in real time?
    - Acid/base titrations
Required Reading Material.

- **Silberberg, Chemistry, 4th edition.**
  - Chapter 18.
  - Chapter 19.
    - Ionic equilibria in aqueous systems. pp.814-862.

- **Kotz, Treichel and Weaver, 7th edition.**
  - Chapter 17&18, pp.760-859.

- **Burrows et al. Chemistry³ (OUP), 2009.Ch.6, pp.263-300.**

- Lecture notes available after course on School of Chemistry website located at:
Useful websites

- http://www.shodor.org/unchem/basic/ab/
- http://chemistry.about.com/od/acidsbases/
- http://www.chem.neu.edu/Courses/1221PAM/acidbase/index.htm
- http://dbhs.wvusd.k12.ca.us/webdocs/AcidBase/AcidBase.html
Acids

Have a sour taste. Vinegar owes its taste to acetic acid. Citrus fruits contain citric acid.

React with certain metals to produce hydrogen gas.

React with carbonates and bicarbonates to produce carbon dioxide gas

Bases

Have a bitter taste.

Feel slippery. Many soaps contain bases.
Acid and Bases

The tartness of lemons and oranges comes from the weak acid citric acid. The acid is found widely in nature and in many consumer products. (Charles D. Winters)

The sting of ants is due to the weak acid formic acid, HCO₂H. (Gallo Images/@ CORBIS)
Acid and Bases

Aspirin is a weak acid that has been used as an analgesic for over 100 years. (Charles D. Winters)

Glycine is representative of the amino acids that are the basis of proteins. The -CO₂H group is the acid portion of the molecule, and the -NH₂ group is the basic portion. (Charles D. Winters)
Acid and Bases

Caffeine is a well known stimulant and a weak base. (Charles D. Winters)

A sea slug excretes the strong acid sulfuric acid in self-defense. (Sharksong/M. Kazmers/Dembinski Photo Associates)
# Uses of Common Acids and Bases

## 18.1 Some Common Acids and Bases and Their Household Uses

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic acid (vinegar)</td>
<td>$\text{CH}_3\text{COOH}$ (or $\text{HC}_2\text{H}_3\text{O}_2$)</td>
<td>Flavoring, preservative</td>
</tr>
<tr>
<td>Citric acid</td>
<td>$\text{H}_3\text{C}_6\text{H}_6\text{O}_7$</td>
<td>Flavoring</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>$\text{H}_3\text{PO}_4$</td>
<td>Rust remover</td>
</tr>
<tr>
<td>Boric acid</td>
<td>$\text{B(OH)}_3$ (or $\text{H}_3\text{BO}_3$)</td>
<td>Mild antiseptic; insecticide</td>
</tr>
<tr>
<td>Aluminum salts</td>
<td>$\text{NaAl(SO}_4\text{)}_2\cdot12\text{H}_2\text{O}$</td>
<td>In baking powder, with sodium hydrogen carbonate</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>$\text{HCl}$</td>
<td>Brick and ceramic tile cleaner</td>
</tr>
<tr>
<td><strong>Bases</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium hydroxide (lye)</td>
<td>$\text{NaOH}$</td>
<td>Oven cleaner, unblocking plumbing</td>
</tr>
<tr>
<td>Ammonia</td>
<td>$\text{NH}_3$</td>
<td>Household cleaner</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>$\text{Na}_2\text{CO}_3$</td>
<td>Water softener, grease remover</td>
</tr>
<tr>
<td>Sodium hydrogen carbonate</td>
<td>$\text{NaHCO}_3$</td>
<td>Fire extinguisher, rising agent in cake mixes (baking soda), mild antacid</td>
</tr>
<tr>
<td>Trisodium phosphate</td>
<td>$\text{Na}_3\text{PO}_4$</td>
<td>Cleaner for surfaces before painting or wallpapering</td>
</tr>
</tbody>
</table>
Acid etching

The inside surfaces of these light bulbs are etched with HF.

Acids are used to wash away oxides of silicon and metals during the production of computer chips.
Arrhenius (or Classical) Acid-Base Definition

- An **acid** is a neutral substance that contains hydrogen and dissociates or ionizes in water to yield hydrated protons or hydronium ions $H_3O^+$.  

- A **base** is a neutral substance that contains the hydroxyl group and dissociates in water to yield hydrated hydroxide ions $OH^-$.  

- **Neutralization** is the reaction of an $H^+$ ($H_3O^+$) ion from the acid and the $OH^-$ ion from the base to form water, $H_2O$.  

- These definitions although correct are limited in that they are not very general and do not give a comprehensive idea of what acidity and basicity entails.

\[
\begin{align*}
HCl & \rightarrow H^+ (aq) + Cl^- (aq) \\
NaOH & \rightarrow Na^+ (aq) + OH^- (aq)  \\
HCl + NaOH & \rightarrow NaCl + H_2O
\end{align*}
\]
Arrhenius acid is a substance that produces $H^+ (H_3O^+)$ in water.

Arrhenius base is a substance that produces $OH^-$ in water.
Acids and bases: Bronsted/Lowry definition.

- **Bronsted/Lowry Acid (HA):**
  - An acid is a species which donates a proton.

- **Bronsted/Lowry Base (B):**
  - A base is a species which accepts a proton.

These definitions are quite general and refer to the reaction between an acid and a base.

- An acid must contain H in its formula; HNO₃ and H₂PO₄⁻ are two examples, all Arrhenius acids are Brønsted-Lowry acids.

- A base must contain a lone pair of electrons to bind the H⁺ ion; a few examples are NH₃, CO₃²⁻, F⁻, as well as OH⁻. Brønsted-Lowry bases are not Arrhenius bases, but all Arrhenius bases contain the Brønsted-Lowry base OH⁻.

• In the Brønsted-Lowry perspective: one species donates a proton and another species accepts it: an acid-base reaction is a proton transfer process.
Proton donation and acceptance are dynamic processes for all acids and bases. Hence a proton transfer equilibrium is rapidly established in solution.

The equilibrium reaction is described in terms of conjugate acid/base pairs.

The conjugate base (CB) of a BL acid is the base which forms when the acid has donated a proton.

The conjugate acid (CA) of a BL base is the acid which forms when the base has accepted a proton.

A conjugate acid has one more proton than the base has, and a conjugate base one less proton than the acid has.

If the acid of a conjugate acid/base pair is strong (good tendency to donate a proton) then the conjugate base will be weak (small tendency to accept a proton) and vice versa.
A Brønsted acid is a proton donor
A Brønsted base is a proton acceptor
### The Conjugate Pairs in Some Acid-Base Reactions

**Conjugate Pair**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Acid</th>
<th>Base</th>
<th>Conjugate Pair</th>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HF</td>
<td>H₂O</td>
<td>F⁻</td>
<td>H₃O⁺</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>HCOOH</td>
<td>CN⁻</td>
<td>HCOO⁻</td>
<td>HCN</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>NH₄⁺</td>
<td>CO₃²⁻</td>
<td>NH₃</td>
<td>HCO₃⁻</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>H₂PO₄⁻</td>
<td>OH⁻</td>
<td>HPO₄²⁻</td>
<td>H₂O</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>H₂SO₄</td>
<td>N₂H₅⁺</td>
<td>HSO₄⁻</td>
<td>N₂H₆²⁺</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>HPO₄²⁻</td>
<td>SO₃²⁻</td>
<td>PO₄³⁻</td>
<td>HSO₃⁻</td>
<td></td>
</tr>
</tbody>
</table>

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Quantifying acid/base strength.

- How can acid and base strength be quantified?
  - ‘Strong’ acids vs ‘weak’ acids
  - ‘Strong’ bases vs ‘weak’ bases
  - Key concept is extent or degree of ionization/dissociation.
  - Correlation exists between acid/base strength, degree of ionization in solution and extent to which solution exhibits ionic conductivity.
Strong and weak acids.

**Battery acid** \( H_2SO_4 \)

**Sulfuric acid**

**Vinegar** \( CH_3COOH \)

**Acetic acid**
The Extent of Dissociation for Strong and Weak Acids

Key concept:
Acid/base strength quantified in terms of extent or degree of dissociation.
An acid or base is classified as strong if it is fully ionized in solution (e.g. HCl, NaOH).
An acid or base is classified as weak if only a small fraction is ionized in solution (e.g. CH₃COOH, NH₃).
Strong Electrolyte - 100% dissociation

NaCl (s) $\xrightarrow{\text{H}_2\text{O}}$ Na$^+$ (aq) + Cl$^-$ (aq)

Weak Electrolyte - not completely dissociated

CH$_3$COOH $\rightleftharpoons$ CH$_3$COO$^-$ (aq) + H$^+$ (aq)

**Strong Acids** are strong electrolytes

HCl (aq) + H$_2$O (l) $\rightarrow$ H$_3$O$^+$ (aq) + Cl$^-$ (aq)

HNO$_3$ (aq) + H$_2$O (l) $\rightarrow$ H$_3$O$^+$ (aq) + NO$_3^-$ (aq)

HClO$_4$ (aq) + H$_2$O (l) $\rightarrow$ H$_3$O$^+$ (aq) + ClO$_4^-$ (aq)

H$_2$SO$_4$ (aq) + H$_2$O (l) $\rightarrow$ H$_3$O$^+$ (aq) + HSO$_4^-$ (aq)
Reactivity of strong and weak acids.

**1M HCl(aq)**
- Strong acid: Extensive $H_2$ evolution

**1M CH$_3$COOH(aq)**
- Weak acid: $H_2$ evolution
  - Not very extensive
Weak acids/bases.

- We can quantify the extent of dissociation of a weak acid or a weak base in aqueous solution by introducing:
  - the acid dissociation constant $K_a$
  - or
  - the base dissociation constant $K_b$.
- These are numbers which reflect acid or base strength and are computed by determining the equilibrium concentrations of all relevant species in the solution, and inputting this data into a theoretical expression for the relevant dissociation constant.
Weak acids.

$\text{CH}_3\text{CO}_2\text{H}$

Acetic acid

$\text{HCl}$ $\text{CH}_3\text{CO}_2\text{H}$
Weak Acids

\[ K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = 1.8 \times 10^{-5} \]

\[ pK_a = -\log(1.8 \times 10^{-5}) = 4.74 \]

lactic acid \( CH_3CH(OH)CO_2H \)

glycine \( H_2NCH_2CO_2H \)
**Weak Acids** are weak electrolytes

HF (aq) + H₂O (l) ⇌ H₃O⁺ (aq) + F⁻ (aq)

HNO₂ (aq) + H₂O (l) ⇌ H₃O⁺ (aq) + NO₂⁻ (aq)

HSO₄⁻ (aq) + H₂O (l) ⇌ H₃O⁺ (aq) + SO₄²⁻ (aq)

H₂O (l) + H₂O (l) ⇌ H₃O⁺ (aq) + OH⁻ (aq)

**Strong Bases** are strong electrolytes

NaOH (s) + H₂O ⇌ Na⁺ (aq) + OH⁻ (aq)

KOH (s) + H₂O ⇌ K⁺ (aq) + OH⁻ (aq)

Ba(OH)₂ (s) + H₂O ⇌ Ba²⁺ (aq) + 2OH⁻ (aq)
**Weak Bases** are weak electrolytes

\[
F^- (aq) + H_2O (l) \rightleftharpoons OH^- (aq) + HF (aq)
\]

\[
NO_2^- (aq) + H_2O (l) \rightleftharpoons OH^- (aq) + HNO_2 (aq)
\]

**Conjugate acid-base pairs:**

- The conjugate base of a strong acid has no measurable strength.
- \( H_3O^+ \) is the strongest acid that can exist in aqueous solution.
- The \( OH^- \) ion is the strongest base that can exist in aqueous solution.
Acid/base equilibria.

Weak acid solution at equilibrium

\[ \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \]

Weak base solution at equilibrium

\[ \text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^- \]
Mathematical interlude: the logarithm


The logarithm is the mathematical operation that is the inverse of exponentiation (raising a constant, the base, to a power). The logarithm of a number \( x \) in base \( b \) is the number \( n \) such that \( x = b^n \). It is usually written as \( \log_b(x) = n \).

If \( 10^x = y \) then \( \log_{10}y = x \), e.g. \( 10^2 = 10 \times 10 = 100 \), then \( \log_{10}(100) = 2 \).

The antilogarithm function is another name for the inverse of the logarithmic function. It is written \( \text{antilog}_b(n) \) and means the same as \( b^n \).

Logarithms can reduce multiplication operations to addition, division to subtraction, exponentiation to multiplication, and roots to division. Therefore, logarithms are useful for making lengthy numerical operations easier to perform.
Mathematical interlude: the logarithm

- The most widely used bases for logarithms are 10, the mathematical constant $e \approx 2.71828...$ and 2. When "log" is written without a base ($b$ missing from log $b$), the intent can usually be determined from context:
  - natural logarithm ($\log_e$) in mathematical analysis
  - common logarithm ($\log_{10}$) in engineering and when logarithm tables are used to simplify hand calculations
  - binary logarithm ($\log_2$) in information theory and musical intervals.

- The notation "ln($x$)" invariably means $\log_e(x)$, i.e., the natural logarithm of $x$, but the implied base for "log ($x$)" varies by discipline:
  - Mathematicians generally understand both "ln($x$)" and "log($x$)" to mean $\log_e(x)$ and write "$\log_{10}(x)$" when the base-10 logarithm of $x$ is intended.
  - Engineers, biologists, and some others write only "ln($x$)" or $\log_e(x)$" when they mean the natural logarithm of $x$, and take "log ($x$)" to mean $\log_{10}(x)$ or, sometimes in the context of computing, $\log_2(x)$.
  - On most calculators, the LOG button is $\log_{10}(x)$ and LN is $\log_e(x)$. 
http://mathworld.wolfram.com/Logarithm.html
## Operations with numbers

<table>
<thead>
<tr>
<th>Operation</th>
<th>Logarithmic identity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a \cdot b$</td>
<td>$\log(a \cdot b) = \log(a) + \log(b)$</td>
</tr>
<tr>
<td>$a/b$</td>
<td>$\log\left(\frac{a}{b}\right) = \log(a) - \log(b)$</td>
</tr>
<tr>
<td>$a^b$</td>
<td>$\log\left(a^b\right) = b \log(a)$</td>
</tr>
<tr>
<td>$\sqrt[b]{a}$</td>
<td>$\log\left(\sqrt[b]{a}\right) = \frac{\log(a)}{b}$</td>
</tr>
</tbody>
</table>
Acid strength: the acid dissociation constant $K_A$.

- It is easy to quantify the strength of strong acids since they fully dissociate to ions in solution.
- The situation with respect to weak acids is more complex since they only dissociate to a small degree in solution.
- The question is how small is small?
- We quantify the idea of incomplete dissociation of a weak acid HA by noting that the dissociation reaction is an equilibrium process and introducing the acid dissociation constant $K_A$.

$K_A$ values vary over a wide range so it is best to use a log scale.

$$pK_A = -\log_{10} K_A$$
The Relationship Between $K_a$ and $pK_a$

<table>
<thead>
<tr>
<th>Acid Name (Formula)</th>
<th>$K_a$ at 298 K</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulfate ion (HSO$_4^-$)</td>
<td>$1.02 \times 10^{-2}$</td>
<td>1.991</td>
</tr>
<tr>
<td>Nitrous acid (HNO$_2$)</td>
<td>$7.1 \times 10^{-4}$</td>
<td>3.15</td>
</tr>
<tr>
<td>Acetic acid (CH$_3$COOH)</td>
<td>$1.8 \times 10^{-5}$</td>
<td>4.74</td>
</tr>
<tr>
<td>Hypobromous acid (HBrO)</td>
<td>$2.3 \times 10^{-9}$</td>
<td>8.64</td>
</tr>
<tr>
<td>Phenol (C$_6$H$_5$OH)</td>
<td>$1.0 \times 10^{-10}$</td>
<td>10.00</td>
</tr>
</tbody>
</table>

When $K_a$ is small, $pK_a$ is large and the acid does not dissociate in solution to a large extent. A change in 1 $pK_a$ unit implies a 10 fold change in $K_a$ value and hence acid strength.
### Ionization Constants of Weak Acids and Bases

<table>
<thead>
<tr>
<th>Acid</th>
<th>Ionization Equilibrium</th>
<th>Ionization Constant $K_a$</th>
<th>p$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodic acid</td>
<td>$\text{HIO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{IO}_3^-$</td>
<td>$1.6 \times 10^{-1}$</td>
<td>0.80</td>
</tr>
<tr>
<td>Chlorous acid</td>
<td>$\text{HClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}_2^-$</td>
<td>$1.1 \times 10^{-2}$</td>
<td>1.96</td>
</tr>
<tr>
<td>Chloroacetic acid</td>
<td>$\text{HC}_2\text{H}_2\text{ClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_2\text{ClO}_2^-$</td>
<td>$1.4 \times 10^{-3}$</td>
<td>2.85</td>
</tr>
<tr>
<td>Nitrous acid</td>
<td>$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$</td>
<td>$7.2 \times 10^{-4}$</td>
<td>3.14</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$</td>
<td>$6.6 \times 10^{-4}$</td>
<td>3.18</td>
</tr>
<tr>
<td>Formic acid</td>
<td>$\text{HCHO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CHO}_2^-$</td>
<td>$1.8 \times 10^{-4}$</td>
<td>3.74</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>$\text{HC}_7\text{H}_5\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_7\text{H}_5\text{O}_2^-$</td>
<td>$6.3 \times 10^{-5}$</td>
<td>4.20</td>
</tr>
<tr>
<td>Hydrazoic acid</td>
<td>$\text{HN}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{N}_3^-$</td>
<td>$1.9 \times 10^{-5}$</td>
<td>4.72</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>$\text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_3\text{O}_2^-$</td>
<td>$1.8 \times 10^{-5}$</td>
<td>4.74</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>$\text{HOC}_1\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}^-$</td>
<td>$2.9 \times 10^{-8}$</td>
<td>7.54</td>
</tr>
<tr>
<td>Hydrocyanic acid</td>
<td>$\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-$</td>
<td>$6.2 \times 10^{-10}$</td>
<td>9.21</td>
</tr>
<tr>
<td>Phenol</td>
<td>$\text{HO}_2\text{C}_6\text{H}_5 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{O}^-$</td>
<td>$1.0 \times 10^{-10}$</td>
<td>10.00</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>$\text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HO}_2^-$</td>
<td>$1.8 \times 10^{-12}$</td>
<td>11.74</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Base</th>
<th>Ionization Equilibrium</th>
<th>Ionization Constant $K_b$</th>
<th>p$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylamine</td>
<td>$(\text{C}_2\text{H}_5)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{C}_2\text{H}_5)_2\text{NH}_2^+ + \text{OH}^-$</td>
<td>$6.9 \times 10^{-4}$</td>
<td>3.16</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>$\text{C}_2\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{NH}_3^+ + \text{OH}^-$</td>
<td>$4.3 \times 10^{-4}$</td>
<td>3.37</td>
</tr>
<tr>
<td>Ammonia</td>
<td>$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$</td>
<td>$1.8 \times 10^{-5}$</td>
<td>4.74</td>
</tr>
<tr>
<td>Hydroxylamine</td>
<td>$\text{HONH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HONH}_3^+ + \text{OH}^-$</td>
<td>$9.1 \times 10^{-9}$</td>
<td>8.04</td>
</tr>
<tr>
<td>Pyridine</td>
<td>$\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}_3^+ + \text{OH}^-$</td>
<td>$1.5 \times 10^{-9}$</td>
<td>8.82</td>
</tr>
<tr>
<td>Aniline</td>
<td>$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$</td>
<td>$7.4 \times 10^{-10}$</td>
<td>9.13</td>
</tr>
</tbody>
</table>
### Acid dissociation constants

#### Table 15.2: Acid-Dissociation Constants at 25°C

<table>
<thead>
<tr>
<th>Acid</th>
<th>Molecular Formula</th>
<th>Structural Formula*</th>
<th>$K_a$</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stronger acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrochloric</td>
<td>HCl</td>
<td>H—Cl</td>
<td>$2 \times 10^6$</td>
<td>-6.3</td>
</tr>
<tr>
<td>Nitrous</td>
<td>HNO$_2$</td>
<td>H—O—N=O</td>
<td>$4.5 \times 10^{-4}$</td>
<td>3.35</td>
</tr>
<tr>
<td>Hydrofluoric</td>
<td>HF</td>
<td>H—F</td>
<td>$3.5 \times 10^{-4}$</td>
<td>3.46</td>
</tr>
<tr>
<td>Acetylsalicylic (aspirin)</td>
<td>C$_7$H$_6$O$_4$</td>
<td></td>
<td>$3.0 \times 10^{-4}$</td>
<td>3.52</td>
</tr>
<tr>
<td>Formic</td>
<td>HCO$_2$H</td>
<td>H—C—O—H</td>
<td>$1.8 \times 10^{-4}$</td>
<td>3.74</td>
</tr>
<tr>
<td>Ascorbic (vitamin C)</td>
<td>C$_6$H$_8$O$_6$</td>
<td></td>
<td>$8.0 \times 10^{-3}$</td>
<td>4.10</td>
</tr>
<tr>
<td>Benzoic</td>
<td>C$_6$H$_5$CO$_2$H</td>
<td></td>
<td>$6.5 \times 10^{-5}$</td>
<td>4.19</td>
</tr>
<tr>
<td>Acetic</td>
<td>CH$_3$CO$_2$H</td>
<td>CH$_3$—C—O—H</td>
<td>$1.8 \times 10^{-3}$</td>
<td>4.74</td>
</tr>
<tr>
<td>Hypochlorous</td>
<td>HOCl</td>
<td>H—O—Cl</td>
<td>$3.5 \times 10^{-8}$</td>
<td>7.46</td>
</tr>
<tr>
<td>Hydrocyanic</td>
<td>HCN</td>
<td>H—C≡N</td>
<td>$4.9 \times 10^{-10}$</td>
<td>9.31</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH$_3$OH</td>
<td>CH$_3$—O—H</td>
<td>$2.9 \times 10^{-16}$</td>
<td>15.54</td>
</tr>
</tbody>
</table>

* The proton that is transferred to water when the acid dissociates is shown in color.

$^1pK_a = -\log K_a$
Acid-Base Properties of Water

\[ \text{H}_2\text{O} \rightarrow \text{H}^+ \text{(aq)} + \text{OH}^- \text{(aq)} \]

*autoionization* of water

\[ \text{H}^+ \text{(aq)} + \text{OH}^- \text{(aq)} \rightarrow \text{H}_2\text{O} \]

Acid

\[ \text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^- \]

Conjugate acid

Conjugate base

Base
The Ion Product of Water

\[ \text{H}_2\text{O} (l) \rightleftharpoons \text{H}^+ (aq) + \text{OH}^- (aq) \]

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

\[ [\text{H}_2\text{O}] = \text{constant} \]

\[ K_c[\text{H}_2\text{O}] = K_w = [\text{H}^+][\text{OH}^-] \]

The *ion-product constant* \( K_w \) is the product of the molar concentrations of \( \text{H}^+ \) and \( \text{OH}^- \) ions at a particular temperature.

At 25°C

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

**Solution Is**

- \( [\text{H}^+] = [\text{OH}^-] \) neutral
- \( [\text{H}^+] > [\text{OH}^-] \) acidic
- \( [\text{H}^+] < [\text{OH}^-] \) basic
Basicity Constant $K_b$.

- The proton accepting strength of a base is quantified in terms of the basicity constant $K_b$.
- The larger the value of $K_b$, the stronger the base.
- If $K_b$ is large then $pK_b$ will be small, and the stronger will be the base.
- Solve weak base problems like weak acids except solve for $[OH^-]$ instead of $[H^+]$.

$$B(aq) + H_2O \rightleftharpoons BH^+ (aq) + OH^- (aq)$$

$$K_c = \frac{[BH^+] [OH^-]}{[B][H_2O]}$$

$$K_b = K_c[H_2O] = \frac{[BH^+] [OH^-]}{[B]}$$

$$pK_b = -\log_{10} K_b$$

$$K_a K_b = K_w$$

$$pK_a + pK_b = pK_w$$
The pH concept.

- The best quantitative measure of acidity or alkalinity rests in the determination of the concentration of hydrated protons \([H_3O^+]\) present in a solution.
- The \([H_3O^+]\) varies in magnitude over quite a large range in aqueous solution, typically from 1 M to \(10^{-14}\) M.
- Hence to make the numbers meaningful \([H_3O^+]\) is expressed in terms of a logarithmic scale called the pH scale.
- The higher the \([H_3O^+]\), the more acidic the solution and the lower is the solution pH.

\[
pH = -\log_{10}[H_3O^+] = 10^{-pH}
\]
The pH Scale.

- pH is expressed on a numerical scale from 0 to 14.
- When \([H_3O^+] = 1.0 \text{ M (i.e. } 10^0\text{M})\), pH = 0.
- When \([H_3O^+] = 10^{-14} \text{ M}\), pH = 14.
- pH value < 7 implies an acidic solution.
- pH value > 7 implies an alkaline solution.
- pH value = 7 implies that the solution is neutral.
- The definition of pH involves logarithms.
- Hence a change in one pH unit represents a change in concentration of \(H_3O^+\) ions by a factor of 10.
**pH and pOH scales.**

<table>
<thead>
<tr>
<th>$[\text{H}_3\text{O}^+]$</th>
<th>pH</th>
<th>$[\text{OH}^-]$</th>
<th>pOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.00</td>
<td></td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>13.00</td>
<td></td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>12.00</td>
<td></td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>11.00</td>
<td></td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>10.50</td>
<td></td>
<td>3.50</td>
<td></td>
</tr>
<tr>
<td>10.00</td>
<td></td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td>9.00</td>
<td></td>
<td>5.00</td>
<td></td>
</tr>
<tr>
<td>8.00</td>
<td></td>
<td>6.00</td>
<td></td>
</tr>
<tr>
<td>7.00</td>
<td>7.00</td>
<td>7.00</td>
<td></td>
</tr>
<tr>
<td>6.00</td>
<td>8.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.00</td>
<td>9.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.50</td>
<td>9.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.00</td>
<td>10.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.00</td>
<td>11.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>12.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>13.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>14.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- $\text{pH} = - \log[\text{H}_3\text{O}^+]$
- $\text{pOH} = - \log[\text{OH}^-]$
Typical pH values.
Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 1997

Sites not pictured:
AK01  5.1
AK03  5.2

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu
pH Measurement.

- Approximate pH of a solution determined by use of acid/base indicators.
  - Indicators are substances (weak acids) which change colour over a specific pH range when they donate protons.
  - We add a few drops of indicator (which changes colour over the required pH range) to the test solution and record the colour change produced.
  - This procedure is utilized in acid/base titrations. Universal indicator (mixture of pH indicators) often used for making approximate pH measurements in range 3-10.
  - As solution pH increases, the indicator changes colour from red to orange to yellow to green to blue, and finally to purple.

- More accurate pH values determined using an electronic instrument called a pH meter.
  - The device (consisting of a probe electrode made of glass and associated electronics) measures the electrical potential generated across a glass membrane (which separates an internal solution of known \([H_3O^+]\) from the external test solution of unknown \([H_3O^+]\)) located at the electrode tip.
  - This membrane potential is proportional to the pH of the test solution.
  - A digital readout of solution pH is obtained.
  - The pH meter is essentially a voltmeter connected to a chemical sensor probe which is sensitive to the concentration of hydrated protons.
  - The pH meter is an example of a potentiometric chemical sensor system. In a potentiometric chemical sensor, the measured voltage is proportional to the logarithm of the analyte concentration.

\[ HIn(aq) + H_2O \rightarrow H_3O^+(aq) + In^- \]
Methods for Measuring the pH of an Aqueous Solution
Indicators: a visual estimation of pH.
Summary. pH - A Measure of Acidity

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

<table>
<thead>
<tr>
<th>Solution Is</th>
<th>At 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutral</td>
<td>([H^+] = [OH^-])</td>
</tr>
<tr>
<td>acidic</td>
<td>([H^+] &gt; [OH^-])</td>
</tr>
<tr>
<td>basic</td>
<td>([H^+] &lt; [OH^-])</td>
</tr>
</tbody>
</table>
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.

\[ \text{HA} + \text{MOH} \rightarrow \text{MA} + \text{H}_2\text{O} \]

**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)
**Strong Acid-Strong Base Titrations**

\[ \text{NaOH} \,(aq) + \text{HCl} \,(aq) \rightarrow \text{H}_2\text{O} \,(l) + \text{NaCl} \,(aq) \]

\[ \text{OH}^- \,(aq) + \text{H}^+ \,(aq) \rightarrow \text{H}_2\text{O} \,(l) \]

At equivalence point:

\[ n_A = n_B \]

\[ c_A V_A = c_B V_B \]

0.10 M NaOH added to 25 mL of 0.10 M HCl
HA + MOH → MA + H₂O
**Weak Acid-Strong Base Titrations**

\[
\text{CH}_3\text{COOH (aq)} + \text{NaOH (aq)} \rightarrow \text{CH}_3\text{COONa (aq)} + \text{H}_2\text{O (l)}
\]

\[
\text{CH}_3\text{COOH (aq)} + \text{OH}^- (aq) \rightarrow \text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O (l)}
\]

At equivalence point (pH > 7):

\[
\text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O (l)} \leftrightarrow \text{OH}^- (aq) + \text{CH}_3\text{COOH (aq)}
\]

<table>
<thead>
<tr>
<th>Volume NaOH added (mL)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.87</td>
</tr>
<tr>
<td>5.0</td>
<td>4.14</td>
</tr>
<tr>
<td>10.0</td>
<td>4.57</td>
</tr>
<tr>
<td>15.0</td>
<td>4.92</td>
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<tr>
<td>40.0</td>
<td>12.36</td>
</tr>
<tr>
<td>45.0</td>
<td>12.46</td>
</tr>
<tr>
<td>50.0</td>
<td>12.52</td>
</tr>
</tbody>
</table>
Weak Acid-Strong Base Titration Curve

Titration of 40.00 mL of 0.1000 M HPr with 0.1000 M NaOH

pKₐ of HPr = 4.89

[pH] = [Pr⁻]

Buffer region

pH = 8.80 at equivalence point

Methyl red

Strong acid-strong base curve

Volume of NaOH added (mL)

pH
Colors and Approximate pH Range of Some Common Acid-Base Indicators

Crystal violet
Thymol blue
2,4-Dinitrophenol
Bromphenol blue
Brom cresol green
Methyl red
Alizarin
Bromthymol blue
Phenol red
Phenolphthalein
Alizarin yellow R
Acid/base reactions represent an example of a fundamental class of chemical reactions. The process involves the transfer of a hydrated proton from a donor species (the acid) to an acceptor species (the base).

The degree of proton transfer can be quantified and enables a distinction between strong and weak acids/bases to be made.

The degree of acidity or alkalinity of a solution may be quantified in terms of the logarithmic pH scale. Acidic solutions have a low pH and basic solutions have a high pH.

The solution pH can be measured via use of indicators or via use of pH meter.

An acid/base reaction is termed a neutralization reaction and can be monitored by measuring the pH during the reaction.