Acids and Bases
and
Aqueous Equilibria

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Properties of Acids

1. Sour taste
   (examples: vinegar, citric acid, lemon juice)
2. Turns litmus from blue to red (also affects other indicators)
3. Reacts with metals to liberate H₂
4. Reacts with base losing its acid properties
5. Reacts with salts to give a new acid and a new salt
6. Conducts electricity (electrolyte)
Properties of Bases

1. Bitter taste (examples: baking soda, soap)
2. Turns litmus from red to blue (also affects other indicators – best known is phenolphthalein)
3. Soapy feel
4. Reacts with acid losing its basic properties
5. Conducts electricity (electrolyte)
A Review of Acid-Base Theories

1. The Arrhenius Theory
2. The Brønsted-Lowry Theory
3. The Lewis Theory
The Arrhenius Theory

- Svante August Arrhenius (1859 –1927)
  - Acid: Substance that produces hydrogen ions in water solution.
    \[ \text{HCl}_{(aq)} \rightarrow \text{H}^+_{(aq)} + \text{Cl}^-_{(aq)} \]
  - Base: Substance that produces hydroxide ions in water solution.
    \[ \text{NaOH}_{(aq)} \rightarrow \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)} \]
  - An acid neutralizes a base
    \[ \text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)} \]
The Arrhenius Theory

– Acid strength depends on the amount of hydrogen ions produced.
  Definition includes acids such as HCl, HBr, HI, HNO₃, H₂SO₄, HSO₄⁻, HC₄H₄O₂, etc.

– Base strength depends on amount of hydroxide ions produced.
  Definition includes bases such as NaOH, KOH, Ca(OH)₂, Mg(OH)₂, Al(OH)₃, etc.
The Arrhenius Theory

- Problems with the Arrhenius Theory
  - The solvent is limited to water, but water is not involved in the acid-base reaction
  - A solution of CO₂ in water is acidic, but H₂CO₃ exists at a concentration less than 1% of the CO₂
  - A solution of NH₃ in water is basic, but NH₄OH does not exist (Note: the formula NH₄OH was invented by Arrhenius to explain the basic nature of NH₃ solutions)
  - The reaction of HCl and NH₃ results in an acidic solution
A Generalized Arrhenius Theory

The solvent (water) can ionize to produce $\text{H}^+$ and $\text{OH}^-$ ions

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

**Acid:** Substance that increases the concentration of hydrogen ions in solution.

$$\text{HCl}_{(aq)} \rightarrow \text{H}^+_{(aq)} + \text{Cl}^-_{(aq)}$$

A strong acid is 100% dissociated
A weak acid is only slightly dissociated
A Generalized Arrhenius Theory

Base: Substance that increases the concentration of hydroxide ions in water solution.

\[ \text{NaOH}_{(aq)} \rightarrow \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)} \]

A strong base is 100% dissociated
A weak base is only slightly dissociated

Hydrolysis reactions can change H\(^+\) and OH\(^-\) concentration in water solution

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad \text{CO}_2 \text{ is an acid} \]
\[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \quad \text{NH}_3 \text{ is a base} \]
A Generalized Arrhenius Theory

If solvents other than water are used:
  The solvent can ionize to produce positive and negative ions
    Example: liquid ammonia, NH₃
      \[ 2 \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^- \]

Acid: Substance that increases the concentration of the positive ion in solution.
      \[ \text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Cl}^- \]

Base: Substance that increases the concentration of the negative ion in water solution.
      \[ \text{NaOH} + \text{NH}_3 \rightarrow \text{Na}^+ + \text{NH}_2^- + \text{H}_2\text{O}(l) \]
A Generalized Arrhenius Theory

Neutralization produces the solvent:

Example: In liquid ammonia, NH₃

\[ \text{NH}_4^+ + \text{NH}_2^- \rightarrow 2 \text{NH}_3 \]
The Brønsted–Lowry Theory

Johannes Nicolaus Brønsted (1879-1947) and Thomas Martin Lowry (1874-1936) independently proposed the proton definition of acids and bases in 1923.

Quoting Brønsted:

". . . acids and bases are substances that are capable of splitting off or taking up hydrogen ions, respectively."

or

An acid-base reaction consists of the transfer of a proton (or hydrogen ion) from an acid to a base.
The Brønsted–Lowry Theory

An acid is a proton donor

That is, an acid is a substance from which a proton (H\(^+\)) can be removed.

A Base is a proton acceptor

That is, a base is a substance that has a non-bonded electron pair that can bond with a proton from an acid.

No solvent is specified
The Brønsted–Lowry Theory

If a substance can either lose a proton or gain a proton, then it is **amphiprotic**

Some examples are

- $\text{HCO}_3^-$, $\text{HSO}_4^-$, and $\text{H}_2\text{O}$

Using $\text{HCO}_3^-$:

- as an acid: $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CO}_3^{2-}$
- as a base: $\text{HCO}_3^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{CO}_3 + \text{H}_2\text{O}$
The Brønsted–Lowry Theory

\[ \text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^- \]

Looking at the forward reaction:

HCl is an acid, because it has a proton available to be transferred.

H\(_2\)O is a base, since it bonds with the proton that the acid lost.

Looking at the reverse reaction:

H\(_3\)O\(^+\) is an acid, because it can give a proton to the Cl\(^-\)

Cl\(^-\) is a base, since it can bond with the proton from H\(_3\)O\(^+\)

Note that each pair HCl and Cl\(^-\), and, H\(_2\)O and H\(_3\)O\(^+\) differ by one proton. These pairs are called conjugate acid-base pairs.
The Brønsted–Lowry Theory

So, in the reaction:

\[ \text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^- \]

One acid-base conjugate pair is HCl and Cl\(^-\)

HCl is an acid, and Cl\(^-\) is the conjugate base of HCl

The second acid-base conjugate pair is H\(_2\)O and H\(_3\)O\(^-\)

H\(_2\)O is a base, and H\(_3\)O\(^+\) is the conjugate acid of H\(_2\)O
The Brønsted–Lowry Theory

When an Acid Dissolves in Water:

Water acts as a Brønsted–Lowry base and abstracts a proton (H\(^+\)) from the acid. As a result, the conjugate base of the acid and a hydronium ion are formed.
Conjugate Acids and Bases:

• “Conjugate” comes from the Latin word *conjugare*, meaning “to join together.”

• Reactions between acids and bases always yield their conjugate bases and acids.

\[
\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NO}_2^-(aq) + \text{H}_3\text{O}^+(aq)
\]

- Acid
- Base
- Conjugate base
- Conjugate acid

remove H\(^{+}\)

add H\(^{+}\)
The Lewis Theory

Gilbert Newton Lewis (1875-1946)

In a 1923 paper, Lewis wrote:

"We are so habituated to the use of water as a solvent, and our data are so frequently limited to those obtained in aqueous solutions, that we frequently define an acid or a base as a substance whose aqueous solution gives, respectively, a higher concentration of hydrogen ion or of hydroxide ion than that furnished by pure water. This is a very one sided definition..."
The Lewis Theory

Lewis wanted a general definition of an acid and a base:

"When we discuss aqueous solutions of substances which do not contain hydroxyl [ion], it is simplest to define a base as a substance which adds hydrogen ion. . . . Since hydrogen is a constituent of most of our electrolytic solvents, the definition of an acid or base as a substance which gives up or takes up hydrogen ion would be more general than the one we used before, but it would not be universal."

Lewis then gave his definition of an acid and a base:

"We are inclined to think of substances as possessing acid or basic properties, without having a particular solvent in mind. It seems to me that with complete generality we may say that a basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom, and that an acid is one which can employ a lone pair from another molecule in completing the stable group of one of its own atoms."
Lewis Acids

- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.
Lewis Bases

- Lewis bases are defined as electron-pair donors.
- Anything that could be a Brønsted–Lowry base is a Lewis base.
- Lewis bases can interact with things other than protons.
The Lewis Theory

The Lewis Theory can include many other reactions which can be classified as acid-base reactions:

In the reaction of Fe\(^{3+}\) with cyanide ions to form Fe(CN)\(_6\)\(^{3-}\):

\[
\text{Fe}^{3+} + 6 \text{[ :C≡N:]}^- \rightarrow [ \text{Fe(C≡N:)}_6 ]^{3-}
\]

The Fe\(^{3+}\) accepts an electron pair and acts as a Lewis acid and the :C≡N:⁻ has an available electron pair and acts as a Lewis base.
The Formation of Hydronium ion

Lewis Acid $\text{H}^+$ + Lewis Base $\text{H}_2\text{O}$ $\rightarrow$ Adduct $\text{H}_3\text{O}^+$
Formation of Ammonium ion

Lewis acid

$\text{H}^+$

$\text{NH}_3$

Adduct

$\text{NH}_4^+$
Hydrated ions can be viewed as Lewis acids and bases.
Complex ions can also be viewed as Lewis acids and bases.

\[
\text{Cu}^{2+}(\text{aq}) + 4\ \text{NH}_3(\text{aq}) \rightarrow [\text{Cu(NH}_3)_4]^{2+}(\text{aq})
\]

*Copper-ammonia coordinate covalent bond.*
The Lewis Acid-Base Chemistry of Nickel(II) Complex ions

End of Lewis acids and bases
## Acid and Base Strength

<table>
<thead>
<tr>
<th>Acid</th>
<th>Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Strong</strong></td>
<td><strong>Negligible</strong></td>
</tr>
<tr>
<td>HCl</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>HSO₄⁻</td>
</tr>
<tr>
<td>HNO₃</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>H₃O⁺(aq)</td>
<td>H₂O</td>
</tr>
<tr>
<td>HSO₄⁻</td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>H₂PO₄⁻</td>
</tr>
<tr>
<td>HF</td>
<td>F⁻</td>
</tr>
<tr>
<td>HC₂H₃O₂⁻</td>
<td>C₂H₃O₂⁻</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>HCO₃⁻</td>
</tr>
<tr>
<td>H₂S</td>
<td>HS⁻</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>HPO₄²⁻</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>NH₃</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>CO₃²⁻</td>
</tr>
<tr>
<td>HPO₄²⁻</td>
<td>PO₄³⁻</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Weak</strong></th>
<th><strong>Weak</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>OH⁻</td>
</tr>
<tr>
<td>OH⁻</td>
<td>O²⁻</td>
</tr>
<tr>
<td>H₂</td>
<td>H⁻</td>
</tr>
<tr>
<td>CH₄</td>
<td>CH₃⁻</td>
</tr>
</tbody>
</table>

### Strong Acids
- Strong acids are completely dissociated in water.
  - Their conjugate bases are quite weak.
- Weak acids only dissociate partially in water.
  - Their conjugate bases are weak bases.
Strong Acids

• The seven strong acids are HCl, HBr, HI, HNO$_3$, H$_2$SO$_4$, HClO$_3$, and HClO$_4$.

• These are, by definition, strong electrolytes and exist totally as ions in aqueous solution (i.e., they are 100% ionic in solution)

• For the monoprotic strong acids,

\[ [H_3O^+] = [\text{acid}] \]
Strong Acids

$\text{HNO}_3, \text{HCl, H}_2\text{SO}_4$ and $\text{HClO}_4$ are the most commonly used strong acids.

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

- hydrochloric acid
- strong electrolyte
- = 100% ionized
- water
- hydronium ion
- chloride ion
Acid and Base Strength

In any acid-base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base.

\[
\text{HCl}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)}
\]

H\(_2\)O is a much stronger base than Cl\(^-\), so the equilibrium lies so far to the right \(K\) is not measured \((K\gg 1)\).
Strong Acids - HCl

HCl completely ionizes in aqueous solution.

Note the hydrated ions in the solution.
Weak Acids

Acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, is a weak acid

$$\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$$

Acetate is a stronger base than $\text{H}_2\text{O}$, so the equilibrium favors the left side ($K<1$).

The equilibrium constant for a weak acid is denoted by the symbol $K_a$ (and for a weak base, it is $K_b$)

The equilibrium constants for weak acids and weak bases are tabulated as “aqueous equilibrium constants” or “ionization constants for weak acids and bases”
Weak Acids

Weak acids are much less than 100% ionized in water (usually 5% ionic or less)

One of the best known weak acids is acetic acid, \( \text{CH}_3\text{CO}_2\text{H} \)

\[
\text{H} : \text{O} : \quad \text{H} - \text{C} - \text{C} - \text{O} : \text{H(aq)} + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H} : \text{O} : \quad \text{H} - \text{C} - \text{C} - \text{O} : (\text{aq}) + \text{H}_3\text{O}^+(\text{aq})
\]

- acetic acid
- water
- acetate ion
- hydronium ion
Weak Acids – CH₃COOH

Acetic acid, CH₃CO₂H, ionizes only slightly in water.

Note the hydrated ions in the solution
Strong Bases

- Strong bases are the soluble hydroxides, which are the alkali metal and heavier alkaline earth metal hydroxides (Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$).

- Strong bases dissociate completely in aqueous solution (i.e., they are 100% ionic in solution).

- For a monohydroxy strong base

  \[[\text{OH}^-] = [\text{base}]\]
Strong Bases

A Strong Base is 100% dissociated in water.

$$\text{NaOH}_{(aq)} \rightarrow \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)}$$

Other common strong bases include KOH and Ca(OH)$_2$

$$\text{CaO \ (lime)} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \ (\text{slaked lime})$$
Weak Bases

A Weak base is less than 100% ionized in water

One of the best known weak bases is ammonia

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \]
Weak Bases

The weak base ammonia reacts to a small extent with water to give a weakly basic solution.

Note the hydrated ions in the solution.
Dissociation Constants

• For a generalized acid dissociation,

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

the equilibrium expression would be

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

• This equilibrium constant is called the acid-dissociation constant and is denoted by the symbol \( K_a \)
Dissociation Constant for Acetic Acid

Acetic acid is a weak acid

$$\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$$

The equilibrium expression for acetic acid is

$$K_a = \frac{[\text{H}_3\text{O}^+] [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$K_a^{\text{HC}_2\text{H}_3\text{O}_2} = 1.8 \times 10^{-5}$$
# Dissociation Constants

The greater the value of $K_a$, the stronger the acid.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Structural Formula</th>
<th>Conjugate Base</th>
<th>Equilibrium Reaction</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrofluoric (HF)</td>
<td>⚫(substrate)=F</td>
<td>F⁻</td>
<td>$\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$</td>
<td>$6.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Nitrous (HNO₂)</td>
<td>⚫(substrate)=O=N=O</td>
<td>NO₂⁻</td>
<td>$\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NO}_2^-(aq)$</td>
<td>$4.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Benzoic (HC₇H₅O₂)</td>
<td>⚫(substrate)=O-C-</td>
<td>C₇H₅O₂⁻</td>
<td>$\text{C}_7\text{H}_5\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_7\text{H}_5\text{O}_2^-(aq)$</td>
<td>$6.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Acetic (HC₂H₃O₂)</td>
<td>⚫(substrate)=O-C-C-H</td>
<td>C₂H₃O₂⁻</td>
<td>$\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$</td>
<td>$1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Hypochlorous (HClO)</td>
<td>⚫(substrate)=O-Cl</td>
<td>ClO⁻</td>
<td>$\text{HClO}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}^-(aq)$</td>
<td>$3.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>Hydrocyanic (HCN)</td>
<td>⚫(substrate)=C≡N</td>
<td>CN⁻</td>
<td>$\text{HCN}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq)$</td>
<td>$4.9 \times 10^{-10}$</td>
</tr>
<tr>
<td>Phenol (HC₆H₅O)</td>
<td>⚫(substrate)=O-C-C-C-</td>
<td>C₆H₅O⁻</td>
<td>$\text{HC}_6\text{H}_5\text{O}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_6\text{H}_5\text{O}^-(aq)$</td>
<td>$1.3 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

*The proton that ionizes is shown in blue.*
Polyprotic Acids

• Have more than one ionizable H

• A common polyprotic acid is sulfuric acid, H$_2$SO$_4$

• The dissociation of a polyprotic acid is written to take place in steps:

\[
\text{H}_2\text{SO}_4{}^{(aq)} + \text{H}_2\text{O}{}^{(l)} \rightleftharpoons \text{HSO}_4{}^{−(aq)} + \text{H}_3\text{O}{}^{+(aq)}
\]

\[
\text{HSO}_4{}^{−(aq)} + \text{H}_2\text{O}{}^{(l)} \rightleftharpoons \text{SO}_4{}^{2−(aq)} + \text{H}_3\text{O}{}^{+(aq)}
\]

• For a weak acid or weak base, each step has a separate dissociation constant.
Polyprotic Acids

\[ \text{H}_2\text{SO}_4(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HSO}_4^-(aq) + \text{H}_3\text{O}^+(aq) \]

\[ \text{HSO}_4^-(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{SO}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq) \]
Polyprotic Acids

- Have more than one acidic proton.
- If the difference between the $K_a$ for the first dissociation and subsequent $K_a$ values is $10^3$ or more, the pH generally depends only on the first dissociation.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>$K_{a1}$</th>
<th>$K_{a2}$</th>
<th>$K_{a3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic</td>
<td>H$_2$C$_6$H$_6$O$_6$</td>
<td>$8.0 \times 10^{-5}$</td>
<td>$1.6 \times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td>Carbonic</td>
<td>H$_2$CO$_3$</td>
<td>$4.3 \times 10^{-7}$</td>
<td>$5.6 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>Citric</td>
<td>H$_3$C$_6$H$_5$O$_7$</td>
<td>$7.4 \times 10^{-4}$</td>
<td>$1.7 \times 10^{-5}$</td>
<td>$4.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>Oxalic</td>
<td>H$_2$C$_2$O$_4$</td>
<td>$5.9 \times 10^{-2}$</td>
<td>$6.4 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>Phosphoric</td>
<td>H$_3$PO$_4$</td>
<td>$7.5 \times 10^{-3}$</td>
<td>$6.2 \times 10^{-8}$</td>
<td>$4.2 \times 10^{-13}$</td>
</tr>
<tr>
<td>Sulfurous</td>
<td>H$_2$SO$_3$</td>
<td>$1.7 \times 10^{-2}$</td>
<td>$6.4 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>Sulfuric</td>
<td>H$_2$SO$_4$</td>
<td>Large</td>
<td>$1.2 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>Tartaric</td>
<td>H$_2$C$_4$H$_4$O$_6$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$4.6 \times 10^{-5}$</td>
<td></td>
</tr>
</tbody>
</table>
Polyprotic Acids – $\text{H}_3\text{PO}_4$

\[\text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- \text{aq}) + \text{H}_3\text{O}^+(\text{aq})\]

\[K_{a1} = 7.5 \times 10^{-3}\]

\[\text{H}_2\text{PO}_4^- (\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} (\text{aq}) + \text{H}_3\text{O}^+(\text{aq})\]

\[K_{a2} = 6.2 \times 10^{-8}\]

\[\text{HPO}_4^{2-} (\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{PO}_4^{3-} (\text{aq}) + \text{H}_3\text{O}^+(\text{aq})\]

\[K_{a3} = 4.2 \times 10^{-13}\]
## Polyprotic Acids

<table>
<thead>
<tr>
<th>Acid Form</th>
<th>Amphiprotic Form</th>
<th>Base Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{S}$ (hydrosulfuric acid or hydrogen sulfide)</td>
<td>$\text{HS}^-$ (hydrogen sulfide ion)</td>
<td>$\text{S}^{2-}$ (sulfide ion)</td>
</tr>
</tbody>
</table>
| $\text{H}_3\text{PO}_4$ (phosphoric acid) | $\begin{cases} 
\text{H}_2\text{PO}_4^- \text{ (dihydrogen phosphate ion)} \\
\text{HPO}_4^{2-} \text{ (hydrogen phosphate ion)} 
\end{cases}$ | $\text{PO}_4^{3-}$ (phosphate ion) |
| $\text{H}_2\text{CO}_3$ (carbonic acid) | $\text{HCO}_3^-$ (hydrogen carbonate ion or bicarbonate ion) | $\text{CO}_3^{2-}$ (carbonate ion) |
| $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid) | $\text{HC}_2\text{O}_4^-$ (hydrogen oxalate ion) | $\text{C}_2\text{O}_4^{2-}$ (oxalate ion) |
Autoionization of Water

• Water is amphoteric.

• In pure water, a few molecules act as bases and a few act as acids.

\[
\text{H}_2\text{O}_{(l)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{OH}^-_{(aq)}
\]

• This process is referred to as autoionization.
Autoionization of Water

• The equilibrium expression for the autoionization of water is

\[ K_c = [H_3O^+] [OH^-] \]

• The equilibrium constant for water is denoted by the special symbol \( K_w \)

\[ K_w = [H_3O^+] [OH^-] = 1.00 \times 10^{-14} \text{ at } 25 \, ^\circ C \]

In a neutral solution \([H_3O^+] = [OH^-]\)

so \([H_3O^+] = [OH^-] = 1.00 \times 10^{-7} \text{ M}\)
A common way to express acidity and basicity is with pH.

pH is defined as the negative logarithm (to the base 10) of the hydrogen ion (hydronium) concentration:

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

In a neutral solution,

\[ [\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ at } 25^\circ\text{C} \]

\[ \text{pH} = - \log (1.00 \times 10^{-7}) \]
\[ = - (-7) = 7 \]
• Therefore, in pure water,
  \[ \text{pH} = \log (1.0 \times 10^{-7}) = 7.00 \]
• An acid has a higher \([H_3O^+]\) than pure water, so its pH is <7
• A base has a lower \([H_3O^+]\) than pure water, so its pH is >7.

<table>
<thead>
<tr>
<th>Solution Type</th>
<th>([H^+] , (M))</th>
<th>([OH^-] , (M))</th>
<th>pH Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic</td>
<td>&gt;1.0 \times 10^{-7}</td>
<td>&lt;1.0 \times 10^{-7}</td>
<td>&lt;7.00</td>
</tr>
<tr>
<td>Neutral</td>
<td>=1.0 \times 10^{-7}</td>
<td>=1.0 \times 10^{-7}</td>
<td>=7.00</td>
</tr>
<tr>
<td>Basic</td>
<td>&lt;1.0 \times 10^{-7}</td>
<td>&gt;1.0 \times 10^{-7}</td>
<td>&gt;7.00</td>
</tr>
</tbody>
</table>
pH

• The concept of pH was first introduced by Danish chemist Søren Peder Lauritz Sørensen (1868-1939), the head of the Carlsberg Laboratory’s Chemical Department, in 1909.

• Dr. Sørensen developed the pH scale during his pioneering research into proteins, amino acids and enzymes - the basis of today’s protein chemistry in a paper titled “Enzyme Studies II. The Measurement and Meaning of Hydrogen Ion Concentration in Enzymatic Processes”:

  The value of the hydrogen ion concentration will accordingly be expressed by the hydrogen ion based on the normality factor of the solution used, and this factor will have the form of a negative power of 10. Since in the following section I usually refer to this, I will explain here that I use the name "hydrogen ion exponent" and the designation $P_H$ for the numerical value of the exponents of this power.
pH

- Today, we refer to pH as meaning ‘the power of hydrogen’.
- The pH scale provides a simple and universal measurement of the amount of hydrogen ions in a solution, which affects its acidity and how it reacts chemically.
- Each value of pH means the $H^+$ concentration changes by a factor of 10
- As the $H^+$ concentration decreases, the $OH^-$ concentration increases

The pH scale according to the late Dr. Hubert Alyea, Princeton University
### pH values for some common substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>$[H^+] \ (M)$</th>
<th>pH</th>
<th>pOH</th>
<th>$[OH^-] \ (M)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gastric juice</td>
<td>$1 \times 10^{-0}$</td>
<td>0.0</td>
<td>14.0</td>
<td>$1 \times 10^{-14}$</td>
</tr>
<tr>
<td>Lemon juice</td>
<td>$1 \times 10^{-1}$</td>
<td>1.0</td>
<td>13.0</td>
<td>$1 \times 10^{-13}$</td>
</tr>
<tr>
<td>Cola, vinegar</td>
<td>$1 \times 10^{-2}$</td>
<td>2.0</td>
<td>12.0</td>
<td>$1 \times 10^{-12}$</td>
</tr>
<tr>
<td>Wine</td>
<td>$1 \times 10^{-3}$</td>
<td>3.0</td>
<td>11.0</td>
<td>$1 \times 10^{-11}$</td>
</tr>
<tr>
<td>Tomatoes</td>
<td>$1 \times 10^{-4}$</td>
<td>4.0</td>
<td>10.0</td>
<td>$1 \times 10^{-10}$</td>
</tr>
<tr>
<td>Banana</td>
<td>$1 \times 10^{-5}$</td>
<td>5.0</td>
<td>9.0</td>
<td>$1 \times 10^{-9}$</td>
</tr>
<tr>
<td>Black coffee</td>
<td>$1 \times 10^{-6}$</td>
<td>6.0</td>
<td>8.0</td>
<td>$1 \times 10^{-8}$</td>
</tr>
<tr>
<td>Rain</td>
<td>$1 \times 10^{-7}$</td>
<td>7.0</td>
<td>7.0</td>
<td>$1 \times 10^{-7}$</td>
</tr>
<tr>
<td>Saliva</td>
<td>$1 \times 10^{-8}$</td>
<td>8.0</td>
<td>6.0</td>
<td>$1 \times 10^{-6}$</td>
</tr>
<tr>
<td>Milk</td>
<td>$1 \times 10^{-9}$</td>
<td>9.0</td>
<td>5.0</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Human blood, tears</td>
<td>$1 \times 10^{-10}$</td>
<td>10.0</td>
<td>4.0</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Egg white, seawater</td>
<td>$1 \times 10^{-11}$</td>
<td>11.0</td>
<td>3.0</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>Baking soda</td>
<td>$1 \times 10^{-12}$</td>
<td>12.0</td>
<td>2.0</td>
<td>$1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Borax</td>
<td>$1 \times 10^{-13}$</td>
<td>13.0</td>
<td>1.0</td>
<td>$1 \times 10^{-1}$</td>
</tr>
<tr>
<td>Milk of magnesia</td>
<td>$1 \times 10^{-14}$</td>
<td>14.0</td>
<td>0.0</td>
<td>$1 \times 10^{-0}$</td>
</tr>
</tbody>
</table>
The Leveling Effect

• The pH scale ranges from 0 to 14
• Can an acid or base have a pH lower than 0 or higher than 14?
• When a strong acid, such as HCl, is dissolved in water, it reacts to form $\text{H}_3\text{O}^+$ in the following reaction:

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

• Any acid that is stronger than $\text{H}_3\text{O}^+$ reacts with $\text{H}_2\text{O}$ to form $\text{H}_3\text{O}^+$; therefore, no acid can be stronger than $\text{H}_3\text{O}^+$ in $\text{H}_2\text{O}$. 
The Leveling Effect

• In the same way, a base which is stronger than the conjugate base of water, such as sodium oxide, will react with water to give the weaker base which is the hydroxide ion, OH⁻:

\[ \text{Na}_2\text{O}_2(\text{s}) + \text{H}_2\text{O} \rightarrow 2\text{OH}^-_{\text{(aq)}} + 2\text{Na}^+_{\text{(aq)}} \]

Note: The actual base here is the oxide ion since the sodium ion is an extremely weak acid or base.

• All bases which are stronger than the hydroxide ion will react with water to produce hydroxide ion.

• Although oxide ion, amide ion, ethoxide ion, and methoxide ion are all stronger bases than hydroxide ion, their strength in aqueous solution is leveled to that of hydroxide ion.

• Any base that is stronger than OH⁻ reacts with H₂O to form OH⁻; therefore, no base can be stronger than OH⁻ in H₂O.
The Leveling Effect

• Can the strengths of strong acids or bases can be differentiated?

• The leveling effect operates in any protonic solvent. If a solvent other than water is used, differences between strengths of strong acids or bases can be measured.

• In liquid ammonia, for example, all acids are levelled to the strength of the ammonium ion, \( \text{NH}_4^+ \), and all bases are leveled to the strength of the amide ion, \( \text{NH}_2^- \).

\[
2 \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-
\]

• Many of the acids which are weak in water act as strong acids in liquid ammonia because they are stronger than ammonium ion.

• Not all of the bases which are strong in water are also strong in liquid ammonia.
The Leveling Effect

- Glacial acetic acid is another protonic solvent in which the leveling effect takes place.
  \[ \text{HC}_2\text{H}_3\text{O}_2 \quad \Leftrightarrow \quad \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^- \]
- Glacial acetic acid can be used to show that hydrogen chloride is a weaker acid than perchloric acid, since hydrogen chloride behaves as a weak acid in glacial acetic acid.
- Methanol is also a protonic solvent in which some of the acids which are strong (completely dissociated) in water are found partially in molecular form.
Uses of a pH-type Scale

In addition to pH, we can apply this method to:

\[
p\text{OH} = -\log [\text{OH}^-] \\
pK_w = -\log K_w \\
pK_a = -\log K_a \text{ (the equilibrium constant for a weak acid)} \\
pK_b = -\log K_b \text{ (the equilibrium constant for a weak base)}
\]
pH and pOH

Previous we saw:

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

If we take the negative log of \([H_3O^+]\) and \([OH^-]\)

\[\log [H_3O^+] + \log [OH^-] = \log K_w = 14.00\]

or, in other words,

\[\text{pH} + \text{pOH} = \text{p}K_w = 14.00\]
Measuring pH

• For a simple acid or base determination we use an indicator known as Litmus paper
  – Litmus is a water soluble mixture of different dyes extracted from lichens, especially *Roccella tinctoria*.
  – The name litmus comes from Middle English litemose (of Scandinavian origin; akin to Old Norse *litmosi*, dyer's herbs: litr, color, dye + mosi, bog, moss) and Middle English lykemose (from Middle Dutch lijkmoes, variant of lēcmoes: lēken, to drip + moes, moss).

“Red” litmus paper turns blue above ~pH = 8

“Blue” litmus paper turns red below ~pH = 5
Measuring pH

• pH test papers are made using a mixture of dyes to indicate pH values over a wide range or, for more accurate measurements, there are short range papers.
**Measuring pH**

Indicators are dyes or mixtures of dyes that can be added to solutions of acids or bases to determine pH.

Some common indicators and their color changes are shown in the chart below:

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH range for color change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl violet</td>
<td>Yellow → Violet</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>Red → Yellow → Blue</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>Red → Yellow</td>
</tr>
<tr>
<td>Methyl red</td>
<td>Red → Yellow</td>
</tr>
<tr>
<td>Bromthymol blue</td>
<td>Yellow → Blue</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>Colorless → Pink</td>
</tr>
<tr>
<td>Alizarin yellow R</td>
<td>Yellow → Red</td>
</tr>
</tbody>
</table>
Measuring pH

For more accurate measurements, a pH meter is used.

Using special glass electrodes, the meter measures the voltage of the solution as a function of the activity of the hydrogen ions near the tip of the electrode.
The pH Meter

• First pH meter was constructed in 1934 by Arnold Beckman (1900-2004).

• A glass pH electrode that had a potential dependent on activity of H⁺ ions had been constructed in 1906 by Fritz Haber and Zygmunt Klemensiewicz, but there were technical difficulties due to a large internal resistance of glass electrodes. To obtain reliable results one was forced to use very sensitive galvanoscope - expensive and difficult to maintain.

• To overcome the problem Arnold Beckman proposed to use simple high-gain amplifier made using two vacuum tubes. Amplified current was much easier to measure with cheap milliamperometers.

Beckman’s first pH meter, 1934 (middle photo)

The Model G pH meter, the first successful marketed pH meter, 1936 (bottom photo)
Calculating $K_a$ from the pH

• The pH of a $0.10 \, M$ solution of formic acid, $\text{HCOOH}$, at $25^\circ \text{C}$ is 2.38. Calculate $K_a$ for formic acid at this temperature.

• Solution:

The equation for the ionization of formic acid is

$$\text{HCOOH}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{HCOO}^-_{(aq)}$$

The $K_a$ expression is

$$K_a = \frac{[\text{H}_3\text{O}^+] \cdot [\text{HCOO}^-]}{[\text{HCOOH}]}$$
Calculating $K_a$ from the pH

Using the pH of 2.38, calculate the $[H_3O^+]$ concentration

\[ \text{pH} = -\log [H_3O^+] \]

Substitute the pH value

\[ 2.38 = -\log [H_3O^+] \]

Multiply both sides by -1

\[ -2.38 = \log [H_3O^+] \]

Take the antilog of both sides

\[ 10^{-2.38} = 10^{\log [H_3O^+]} = [H_3O^+] \]

\[ 4.2 \times 10^{-3} \text{ M} = [H_3O^+] \]
Calculating $K_a$ from pH

Using the initial concentration of HCOOH and the equilibrium concentration of $H_3O^+$, set up a concentration table:

<table>
<thead>
<tr>
<th></th>
<th>[HCOOH], M</th>
<th>[H$_3$O$^+$], M</th>
<th>[HCOO$^-$], M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change in concentration</td>
<td>$-4.2 \times 10^{-3}$</td>
<td>$+4.2 \times 10^{-3}$</td>
<td>$+4.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>Equilibrium concentration</td>
<td>$0.10 - 4.2 \times 10^{-3}$</td>
<td>$4.2 \times 10^{-3}$</td>
<td>$4.2 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$\approx 0.0958$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: For a weak acid, $K_a$ is usually small, so the equilibrium concentration of HA is essentially equal to the initial concentration of HA.
Calculating $K_a$ from the pH

The $K_a$ expression is:

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

Substitute the concentration values from the ICE table:

$$K_a = \frac{[4.2 \times 10^{-3}][4.2 \times 10^{-3}]}{[0.10]}$$

$$K_a = 1.8 \times 10^{-4}$$
Calculating Percent Ionization

• We can also calculate the percent ionization of a weak acid:

\[
\text{Percent Ionization} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_{\text{initial}}} \times 100
\]

In this example

\[
[\text{H}_3\text{O}^+]_{\text{eq}} = 4.2 \times 10^{-3} \text{ M}
\]

\[
[\text{HCOOH}]_{\text{initial}} = 0.10 \text{ M}
\]
Calculating Percent Ionization

Percent Ionization = \( \frac{4.2 \times 10^{-3}}{0.10} \times 100 \)

Percent Ionization = 4.2%
Calculating pH from $K_a$

Calculate the pH of a 0.30 $M$ solution of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, at 25°C.

**Solution:**

\[
\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})
\]

$K_a$ for acetic acid at 25°C is $1.8 \times 10^{-5}$. 
Calculating pH from $K_a$

The equilibrium constant expression is

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$
Calculating pH from $K_a$

Set up a table of concentrations:

<table>
<thead>
<tr>
<th></th>
<th>[HC₂H₃O₂], $M$</th>
<th>[H₃O⁺], $M$</th>
<th>[C₂H₃O₂⁻], $M$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial concentration</strong></td>
<td>0.30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Change in concentration</strong></td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td><strong>Equilibrium concentration</strong></td>
<td>$0.30 - x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
<tr>
<td></td>
<td>$\approx 0.30$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Since $K_a$ is small for acetic acid, we assume that $x$ will be very small compared to 0.30 and can be ignored.
Calculating pH from $K_a$

$$K_a = \frac{[H_3O^+] [C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Substitute the concentrations from the ICE table:

$$1.8 \times 10^{-5} = \frac{(x)^2}{(0.30)}$$

Solve for x:

$$(1.8 \times 10^{-5}) (0.30) = x^2$$

$$5.4 \times 10^{-6} = x^2$$

$$2.3 \times 10^{-3} \text{ M} = x$$
Calculating pH from $K_a$

Solve for pH:

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

\[ \text{pH} = -\log (2.3 \times 10^{-3}) \]

\[ \text{pH} = 2.64 \]
Weak Bases

Bases react with water to produce hydroxide ion.

\[ \text{Base} + \text{Acid} \rightarrow \text{Conjugate acid} \]

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \]

add $\text{H}^+$

remove $\text{H}^+$

Conjugate base
Weak Bases

The equilibrium constant expression for this reaction is

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

where $K_b$ is the base-dissociation constant.
Weak Bases

$K_b$ can be used to find $[\text{OH}^-]$ and, in the same method used for a weak acid, the pOH and the pH

<table>
<thead>
<tr>
<th>Base</th>
<th>Lewis Structure</th>
<th>Conjugate Acid</th>
<th>Equilibrium Reaction</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia (NH$_3$)</td>
<td><img src="image" alt="Lewis structure" /></td>
<td>NH$_4^+$</td>
<td>NH$_3$ + H$_2$O $\rightleftharpoons$ NH$_4^+$ + OH$^-$</td>
<td>$1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Pyridine (C$_5$H$_5$N)</td>
<td><img src="image" alt="Lewis structure" /></td>
<td>C$_5$H$_5$NH$_4^+$</td>
<td>C$_5$H$_5$N + H$_2$O $\rightleftharpoons$ C$_5$H$_5$NH$_4^+$ + OH$^-$</td>
<td>$1.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>Hydroxylamine (H$_2$NOH)</td>
<td><img src="image" alt="Lewis structure" /></td>
<td>H$_3$NOH$_4^+$</td>
<td>H$_2$NOH + H$_2$O $\rightleftharpoons$ H$_3$NOH$_4^+$ + OH$^-$</td>
<td>$1.1 \times 10^{-8}$</td>
</tr>
<tr>
<td>Methylamine (NH$_2$CH$_3$)</td>
<td><img src="image" alt="Lewis structure" /></td>
<td>NH$_3$CH$_3^+$</td>
<td>NH$_2$CH$_3$ + H$_2$O $\rightleftharpoons$ NH$_3$CH$_3^+$ + OH$^-$</td>
<td>$4.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydrosulfide ion (HS$^-$)</td>
<td><img src="image" alt="Lewis structure" /></td>
<td>H$_2$S</td>
<td>HS$^-$ + H$_2$O $\rightleftharpoons$ H$_2$S + OH$^-$</td>
<td>$1.8 \times 10^{-7}$</td>
</tr>
<tr>
<td>Carbonate ion (CO$_3^{2-}$)</td>
<td><img src="image" alt="Lewis structure" /></td>
<td>HCO$_3^-$</td>
<td>CO$_3^{2-}$ + H$_2$O $\rightleftharpoons$ HCO$_3^-$ + OH$^-$</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hypochlorite ion (ClO$^-$)</td>
<td><img src="image" alt="Lewis structure" /></td>
<td>HClO</td>
<td>ClO$^-$ + H$_2$O $\rightleftharpoons$ HClO + OH$^-$</td>
<td>$3.3 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
pH of Basic Solutions

What is the pH of a 0.15 M solution of NH₃?

\[ K_b_{NH_3} = 1.8 \times 10^{-5} \]

Solution:

NH₃ is a weak base. The equation for the dissociation of NH₃ is

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \]

The \( K_b \) expression is

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} \]
pH of Basic Solutions

Tabulate the data.

<table>
<thead>
<tr>
<th></th>
<th>[NH₃], M</th>
<th>[NH₄⁺], M</th>
<th>[OH⁻], M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration</td>
<td>0.15</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change in concentration</td>
<td>-x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Equilibrium concentration</td>
<td>0.15 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
**pH of Basic Solutions**

\[ 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3]} \]

Substitute values from the ICE table:

\[ 1.8 \times 10^{-5} = \frac{(x)^2}{(0.15)} \]

Solve for \(x\):

\[ (1.8 \times 10^{-5}) (0.15) = x^2 \]

\[ 2.7 \times 10^{-6} = x^2 \]

\[ 1.6 \times 10^{-3} = x = [\text{OH}^-] \]

Concentration is expressed as Molarity
pH of Basic Solutions

Since the calculation gave the [OH\(^-\)] concentration, solve for pOH:

\[
[\text{OH}^-] = 1.6 \times 10^{-3} \text{ M}
\]

and

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

\[
\text{pOH} = -\log (1.6 \times 10^{-3})
\]

\[
\text{pOH} = 2.80
\]

We know:

\[
\text{pH} + \text{pOH} = 14
\]

Solve for pH:

\[
\text{pH} = 14.00 - 2.80
\]

\[
\text{pH} = 11.20
\]
Relationship of $K_a$ and $K_b$

$K_a$ and $K_b$ are related:

$$K_a \times K_b = K_w = 1.0 \times 10^{-14}$$

Therefore, if you know one of them, you can calculate the other.
Acid-Base Properties of Salts

• Salts contain cations and anions which are conjugate acids or bases

• These ions can react with water in a hydrolysis reaction to form $\text{H}^+$ or $\text{OH}^-$ and the conjugate acid or base. For example, an anion can react with water

$$X^-_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{HX}_{(aq)} + \text{OH}^-_{(aq)}$$

A hydrolysis reaction is one where an anion or cation reacts with water and splits the water molecule.
Acid-Base Properties of Salts

Is a solution of \( MX + H_2O \) acidic or basic?

Consider \( \text{NH}_4\text{Cl} \):

\[
\text{NH}_4\text{Cl}_{(aq)} \rightleftharpoons \text{NH}_4^+_{(aq)} + \text{Cl}^-_{(aq)}
\]

First, consider the reaction of \( \text{Cl}^- \) with \( H_2O \):

\[
\text{Cl}^- + H_2O \rightleftharpoons H\text{Cl} + \text{OH}^- \\
\text{base} \quad \text{acid} \quad \text{acid} \quad \text{base}
\]

\( \text{Cl}^- \) ion is a \text{VERY} weak base because its conjugate acid is strong, so this equilibrium is shifted to the left.

Therefore, \( \text{Cl}^- \) forms a neutral solution
Acid-Base Properties of Salts

We are still considering a solution of NH$_4$Cl (from the previous slide)

\[ \text{NH}_4\text{Cl}_{(aq)} \rightleftharpoons \text{NH}_4^+_{(aq)} + \text{Cl}^-_{(aq)} \]

Second, consider the reaction of NH$_4^+$ with H$_2$O

\[ \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \]

acid base base acid

NH$_4^+$ ion is a moderate acid because its conjugate base is weak, so the equilibrium is shifted to the right.

Therefore, NH$_4^+$ forms an acidic solution

The salt, NH$_4$Cl, will form an acidic solution in water.
# Acid-Base Properties of Salts

## Acid and Base Properties of Some Ions in Aqueous Solution

<table>
<thead>
<tr>
<th>Neutral</th>
<th>Basic</th>
<th>Acidic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;COO&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>Br&lt;sup&gt;-&lt;/sup&gt;</td>
<td>HCO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>CN&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>I&lt;sup&gt;-&lt;/sup&gt;</td>
<td>CO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>PO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;3-&lt;/sup&gt;</td>
</tr>
<tr>
<td>S&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>S&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>HCO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>F&lt;sup&gt;-&lt;/sup&gt;</td>
<td>HS&lt;sup&gt;-&lt;/sup&gt;</td>
<td>NO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cations</th>
<th>[Al(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;5&lt;/sub&gt;(OH)]&lt;sup&gt;2+&lt;/sup&gt; (for example)</th>
<th>[Al(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;6&lt;/sub&gt;]&lt;sup&gt;3+&lt;/sup&gt; and hydrated transition metal cations (such as [Fe(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;6&lt;/sub&gt;]&lt;sup&gt;3+&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li&lt;sup&gt;+&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>NH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>K&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Ba&lt;sup&gt;2+&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>
Acid-Base Properties of Salts

As a general rule:

If the salt is formed from a strong acid and a strong base, the solution of the salt in water is neutral.

If the salt is formed from a strong acid and a weak base, the solution of the salt in water is acidic.

If the salt is formed from a weak acid and a strong base, the solution of the salt in water is basic.
Acid-Base Properties of Salts

A solution of NaCl is neutral (pH = 7)
This is a salt of a strong base and a strong acid.

A solution of NH₄Cl is acidic (pH = 3.5)
This is the salt of a weak base and a strong acid.

A solution of NaClO is basic (pH = 9.5)
This is the salt of a strong base and a weak acid.
Acid-Base Properties of Salts

Solutions of salts with indicators

<table>
<thead>
<tr>
<th>Salt</th>
<th>Indicator</th>
<th>Estimated pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO₃</td>
<td>Bromthymol blue</td>
<td>7.0</td>
</tr>
<tr>
<td>Ca(NO₃)₂</td>
<td>Bromthymol blue</td>
<td>6.9</td>
</tr>
<tr>
<td>Zn(NO₃)₂</td>
<td>Methyl red</td>
<td>5.5</td>
</tr>
<tr>
<td>Al(NO₃)₃</td>
<td>Methyl orange</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Hydrolysis: The Acid-Base Properties of Salt Solutions

Calculate the pH of a 0.10 M solution of NH₄Cl.

\[ K_{b \text{ NH}_3} = 1.8 \times 10^{-5} \]

Solution:

NH₄Cl is 100% ionic:

\[ \text{NH}_4\text{Cl}_{(aq)} \rightarrow \text{NH}_4^{+}_{(aq)} + \text{Cl}^{-}_{(aq)} \]

NH₄⁺ reacts with H₂O:

\[ \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \]

The reaction of NH₄⁺ with water is a hydrolysis reaction

(Note: Cl⁻ does not hydrolyze)
Hydrolysis: The Acid-Base Properties of Salt Solutions

Set up a concentration table:

<table>
<thead>
<tr>
<th></th>
<th>$[\text{NH}_4^+]$</th>
<th>$[\text{NH}_3]$</th>
<th>$[\text{H}_3\text{O}^+]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial conc</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.1</td>
<td>X</td>
<td>x</td>
</tr>
<tr>
<td>concentration</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Hydrolysis: The Acid-Base Properties of Salt Solutions

The equilibrium expression is:

\[ \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \]

\[ K_h = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \]

Where \( K_h \) is known as the hydrolysis constant and is defined as

\[ K_h = \frac{K_w}{K_b} \]

Note: Your textbook refers to \( K_h \) as a \( K_a \) for the ammonium ion.
Hydrolysis: The Acid-Base Properties of Salt Solutions

\[ K_h = \frac{K_w}{K_b} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \]

\[ K_h = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{[x][x]}{[0.1]} \]

\[ 5.56 \times 10^{-10} = \frac{[x]^2}{[0.1]} \]

\[ 5.56 \times 10^{-11} = [x]^2 \]

\[ 7.46 \times 10^{-6} \text{ M} = [x] = [\text{NH}_3] = [\text{H}_3\text{O}^+] \]
Hydrolysis: The Acid-Base Properties of Salt Solutions

\[ 7.46 \times 10^{-6} \text{ M} = [x] = [\text{NH}_3] = [\text{H}_3\text{O}^+] \]

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

\[ = - \log [7.46 \times 10^{-6}] \]

\[ \text{pH} = 5.13 \]
Hydrolysis: The Acid-Base Properties of Salt Solutions

Calculate the pH of a 0.10 M solution of Na₂CO₃.

\[ K_{a1} \text{H}_2\text{CO}_3 = 4.7 \times 10^{-7} \quad K_{a2} \text{H}_2\text{CO}_3 = 5.6 \times 10^{-11} \]

Solution:

Na₂CO₃ is 100% ionic:

\[ \text{Na}_2\text{CO}_3 (aq) \rightarrow 2 \text{Na}^+ (aq) + \text{CO}_3^{2-} (aq) \]

The hydrolysis equation is:

\[ \text{CO}_3^{2-} + \text{H}_2\text{O} \quad \Leftrightarrow \quad \text{HCO}_3^- + \text{OH}^- \]

Note: The reaction of HCO₃⁻ with H₂O is small and can be ignored.
Hydrolysis: The Acid-Base Properties of Salt Solutions

Set up a concentration table:

<table>
<thead>
<tr>
<th></th>
<th>$\text{CO}_3^{2-}$</th>
<th>$\text{HCO}_3^-$</th>
<th>$\text{OH}^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial conc</strong></td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td><strong>Equilibrium concentration</strong></td>
<td>0.1</td>
<td>$X$</td>
<td>$x$</td>
</tr>
</tbody>
</table>
Hydrolysis: The Acid-Base Properties of Salt Solutions

The hydrolysis equation is:

$$K_h = \frac{K_w}{K_a} = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]}$$

Substitute values from the ICE table:

$$K_h = \frac{1 \times 10^{-14}}{5.6 \times 10^{-11}} = \frac{[x][x]}{[0.1]}$$

Solve for $x$:

$$1.79 \times 10^{-4} = \frac{[x]^2}{[0.1]}$$

$$1.79 \times 10^{-5} = [x]^2$$

$$4.23 \times 10^{-3} \text{ M} = [x] = [\text{HCO}_3^-] = [\text{OH}^-]$$
Hydrolysis: The Acid-Base Properties of Salt Solutions

\[ 4.23 \times 10^{-3} \text{ M} = [x] = [\text{HCO}^-] = [\text{OH}^-] \]

Since the calculation resulted in the \([\text{OH}^-]\), solve for pOH:

\[
p\text{OH} = - \log [\text{OH}^-]
\]

\[
= - \log [4.23 \times 10^{-3}]
\]

\[
= 2.37
\]

Calculate the pH:

\[
pH = 14 - p\text{OH}
\]

\[
= 14 - 2.37
\]

\[
pH = 11.6
\]
Properties of Hydrated Cations with Water

- A cation such as NH$_4^+$ can donate a proton to a water molecule and lower the pH of a solution (i.e., more acidic).
- Most metal cations that are hydrated in solution also lower the pH of the solution:
  \[
  \text{Fe(H}_2\text{O)}_6^{3+} \rightleftharpoons \text{Fe(H}_2\text{O)}_5(\text{OH})^{2+} + \text{H}^+
  \]
- Attraction between nonbonding electrons on oxygen and the metal cation causes a shift of the electron density in the water molecule.
Properties of Hydrated Cations with Water

- The shift of the electron density in the water molecule toward the cation weakens the polar O-H bond and allows a proton to transfer to a nearby water molecule forming an $\text{H}_3\text{O}^+$ ion.
- The hydrated cation will form a hydrated $\text{M(H}_2\text{O)}_n\text{(OH)}^+$ ion and the acidity of the solution increases.
- The greater the charge and smaller the size of a cation, the stronger the acidity of the solution.
## Factors Affecting Acid Strength

In binary acids, the more polar the H-X bond and/or the weaker the H-X bond, the more acidic the compound.

Acidity increases from left to right across a row and from top to bottom down a group.
Factors Affecting Acid Strength

In oxyacids, in which an OH is bonded to another atom, Y, the more electronegative Y is, the more acidic the acid.
Factors Affecting Acid Strength

For a series of oxyacids, acidity increases with the number of oxygen atoms.
Factors Affecting Acid Strength

Resonance in the conjugate bases of carboxylic acids stabilizes the base and makes the conjugate acid more acidic.