Chapter 4
Acids and Bases

William H. Brown • Beloit College

http://academic.cengage.com/chemistry/brown
In 1884, Svante Arrhenius proposed these definitions

- **acid**: A substance that produces $\text{H}_3\text{O}^+$ ions aqueous solution.
- **base**: A substance that produces $\text{OH}^-$ ions in aqueous solution.

- this definition of an acid is a slight modification of the original Arrhenius definition, which was that an acid is a substance that produces $\text{H}^+$ in aqueous solution.
- today we know that $\text{H}^+$ reacts immediately with a water molecule to give a **hydronium ion**.

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

Hydronium ion
Brønsted-Lowry Definitions

- **Acid:** A proton donor.
- **Base:** A proton acceptor.

![Diagram of Brønsted-Lowry acid-base reaction]

[Diagram showing the proton transfer from an acid to a base, with labeled proton donors and acceptors.]
**Conjugate Acids & Bases**

- **Conjugate base**: The species formed from an acid when it donates a proton to a base.
- **Conjugate acid**: The species formed from a base when it accepts a proton from an acid.
- **Acid-base reaction**: A proton-transfer reaction.
- **Conjugate acid-base pair**: Any pair of molecules or ions that can be interconverted by transfer of a proton.

\[
\begin{align*}
\text{HCl}(aq) & \quad + \quad \text{H}_2\text{O}(l) & \rightarrow & \quad \text{Cl}^- (aq) & \quad + \quad \text{H}_3\text{O}^+ (aq) \\
\text{Hydrogen chloride} & \quad \text{(acid)} & \quad \text{Water} & \quad \text{(base)} & \quad \text{Chloride ion} & \quad \text{(conjugate base of HCl)} & \quad \text{Hydronium ion} & \quad \text{(conjugate acid of H}_2\text{O)}
\end{align*}
\]
Conjugate Acids & Bases

• Brønsted-Lowry definitions do not require water as a reactant.
• Consider the following reaction between acetic acid and ammonia.

\[
\text{CH}_3\text{COOH} + \text{NH}_3 \quad \text{CH}_3\text{COO}^- + \text{NH}_4^+ \\
\text{(acid)} \quad \quad \text{Ammonia} \quad \quad \text{Acetate ion} \quad \quad \text{Ammonium ion} \\
\text{(base)} \quad \quad \text{(conjugate base}} \quad \quad \text{(conjugate acid}} \\
\text{acetic acid) \quad \quad \text{of ammonia)}
\]
Conjugate Acids & Bases

• We can use curved arrows to show the flow of electrons in an acid-base reaction.

\[
\text{CH}_3\text{-C}-\overset{\circ}{\text{O}}\overset{\circ}{\text{H}} + \overset{\circ}{\text{N}}\overset{\circ}{\text{H}} \rightleftharpoons \text{CH}_3\text{-C}-\overset{\circ}{\text{O}}\overset{\circ}{\text{H}}^- + \overset{\circ}{\text{H}}\overset{\circ}{\text{N}}\overset{\circ}{\text{H}}^+
\]

Acetic acid (proton donor) Ammonia (proton acceptor) Acetate ion Ammonium ion
Many organic molecules have two or more sites that can act as proton acceptors.

In this chapter, we limit our discussion to carboxylic acids, esters, and amides.

In these molecules, the favored site of protonation is the one in which the charge is more delocalized.

Question: Which oxygen of a carboxylic acid is protonated?

\[
\begin{align*}
\text{CH}_3\text{C}-\text{O}-\text{H} + \text{H}_2\text{SO}_4 & \rightleftharpoons \text{CH}_3\text{C}-\text{O}^+\text{H}^- & \\
\text{or CH}_3\text{C}-\text{O}-\text{H} + \text{HSO}_4^- & \\
\text{A} & \text{B} & \\
\text{(protonated on the carbonyl oxygen)} & \text{(protonated on the hydroxyl oxygen)}
\end{align*}
\]
For protonation on the carbonyl oxygen, we can write three contributing structures.

Two place the positive charge on oxygen, one places it on carbon.

- A-1 and A-3 make the greater contribution because all atoms have complete octets.
- The positive charge is delocalized over three atoms with the greater share on the two equivalent oxygens.
For protonation on the hydroxyl oxygen, we can write two contributing structures.

B-1 makes only a minor contribution because of charge separation and adjacent positive charges.

Therefore, we conclude that protonation of a carboxylic acid occurs preferentially on the carbonyl oxygen.
**Problem 4.3** Does proton transfer to an amide group occur preferentially on the amide oxygen or the amide nitrogen?

\[
\text{CH}_3\text{-C-} \quad \text{N-H} \quad + \quad \text{HCl} \quad \xrightarrow{\text{protonation}} \quad \text{CH}_3\text{-C-} \quad \text{N-H} \quad + \quad \text{Cl}^{-}
\]

A (protonation on the amide oxygen)

B (protonation on the amide nitrogen)

Acetamide (an amide)
Problem 4.3.

Proton transfer to carbonyl oxygen

Favored

\[
\begin{align*}
\text{CH}_3\text{C} & \equiv \text{N} \equiv \text{H} \\
\text{A1} & \quad \iff \quad \text{CH}_3\text{C} & \equiv \text{N} & \equiv \text{H} \\
\text{A2} & \quad \iff \quad \text{CH}_3\text{C} & \equiv \text{N}^+ & \equiv \text{H} \\
\text{A3}
\end{align*}
\]

Proton transfer to amide nitrogen

\[
\begin{align*}
\text{CH}_3\text{C} & \equiv \text{N}^+ \equiv \text{H} \\
\text{B1} & \quad \iff \quad \text{CH}_3\text{C} & \equiv \text{N}^+ & \equiv \text{H} \\
\text{B2}
\end{align*}
\]
Pi Electrons As Basic Sites

- Proton-transfer reactions occur with compounds having pi electrons, as for example the pi electrons of carbon-carbon double and triple bonds.
  - The pi electrons of 2-butene, for example, react with HBr by proton transfer to form a new C-H bond.

\[
\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 + \text{H-Br} \rightarrow \text{CH}_3-\text{C}\text{-}\text{C}-\text{CH}_3 + \text{Br}^-
\]

2-Butene

\[\text{sec-Butyl cation} \quad (\text{a } 2^\circ \text{ carbocation})\]

- The result is formation of a carbocation, a species in which one of its carbons has only six electrons in its valence shell and carries a charge of +1.
Problem 4.4 Draw Lewis structures for the two possible carbocations formed by proton transfer from HBr to 2-methyl-2-butene.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 - \text{C}=\text{CH}-\text{CH}_3 + \text{H}-\text{Br} \\
2\text{-Methyl-2-butene} & 
\end{align*}
\]
The strength of an acid is expressed by an equilibrium constant. The acid dissociation of acetic acid is given by the following equation.

\[
\text{CH}_3\text{COH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}^- + \text{H}_3\text{O}^+
\]

Acetic acid \hspace{1cm} Water \hspace{1cm} Acetate ion \hspace{1cm} Hydronium ion
Weak Acids and Bases

We can write an equilibrium expression for the dissociation of any uncharged acid, HA, as:

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

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

Water is a solvent and its concentration is a constant equal to approximately 55.5 mol/L.

We can combine these constants to give a new constant, \( K_a \), called an acid dissociation constant.

\[ K_a = K_{\text{eq}}[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \]
Chem Activity 8: Acid-Base Reactions

- Split quickly in groups of 4
- Red handout chapter 4 (Chem Activity 8)
- Work on the critical thinking questions (1-9)
- You have 20 min
- We will discuss the questions in 10 min
# $pK_a$ - Some Organic & Inorganic Acids

<table>
<thead>
<tr>
<th>Acid</th>
<th>Formula</th>
<th>$pK_a$</th>
<th>Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>$\text{CH}_3\text{CH}_3$</td>
<td>51</td>
<td>$\text{CH}_3\text{CH}_2^-$</td>
</tr>
<tr>
<td>Ethylene</td>
<td>$\text{CH}_2=\text{CH}_2$</td>
<td>44</td>
<td>$\text{CH}_2=\text{CH}^-$</td>
</tr>
<tr>
<td>Ammonia</td>
<td>$\text{NH}_3$</td>
<td>38</td>
<td>$\text{NH}_2^-$</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>$\text{H}_2$</td>
<td>35</td>
<td>$\text{H}^+$</td>
</tr>
<tr>
<td>Acetylene</td>
<td>$\text{HC}≡\text{CH}$</td>
<td>25</td>
<td>$\text{HC}≡\text{C}^-$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>$\text{CH}_3\text{CH}_2\text{OH}$</td>
<td>15.9</td>
<td>$\text{CH}_3\text{CH}_2\text{O}^-$</td>
</tr>
<tr>
<td>Water</td>
<td>$\text{H}_2\text{O}$</td>
<td>15.7</td>
<td>$\text{HO}^-$</td>
</tr>
<tr>
<td>Methylammonium ion</td>
<td>$\text{CH}_3\text{NH}_3^+$</td>
<td>10.64</td>
<td>$\text{CH}_3\text{NH}_2$</td>
</tr>
<tr>
<td>Bicarbonate ion</td>
<td>$\text{HCO}_3^-$</td>
<td>10.33</td>
<td>$\text{CO}_3^{2-}$</td>
</tr>
<tr>
<td>Phenol</td>
<td>$\text{C}_6\text{H}_5\text{OH}$</td>
<td>9.95</td>
<td>$\text{C}_6\text{H}_5\text{O}^-$</td>
</tr>
<tr>
<td>Ammonium ion</td>
<td>$\text{NH}_4^+$</td>
<td>9.24</td>
<td>$\text{NH}_3$</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>$\text{H}_2\text{S}$</td>
<td>7.04</td>
<td>$\text{HS}^-$</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>$\text{H}_2\text{CO}_3$</td>
<td>6.36</td>
<td>$\text{HCO}_3^-$</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>$\text{CH}_3\text{COOH}$</td>
<td>4.76</td>
<td>$\text{CH}_3\text{COO}^-$</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>$\text{C}_6\text{H}_5\text{COOH}$</td>
<td>4.19</td>
<td>$\text{C}_6\text{H}_5\text{COO}^-$</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>$\text{H}_3\text{PO}_4$</td>
<td>2.1</td>
<td>$\text{H}_2\text{PO}_4^-$</td>
</tr>
<tr>
<td>Hydronium ion</td>
<td>$\text{H}_3\text{O}^+$</td>
<td>-1.74</td>
<td>$\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>$\text{H}_2\text{SO}_4$</td>
<td>-5.2</td>
<td>$\text{HSO}_4^-$</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>$\text{HCl}$</td>
<td>-7</td>
<td>$\text{Cl}^-$</td>
</tr>
<tr>
<td>Hydrogen bromide</td>
<td>$\text{HBr}$</td>
<td>-8</td>
<td>$\text{Br}^-$</td>
</tr>
<tr>
<td>Hydrogen iodide</td>
<td>$\text{HI}$</td>
<td>-9</td>
<td>$\text{I}^-$</td>
</tr>
</tbody>
</table>

**Notes:**
- Weaker acid
- Stronger acid
- Conjugate base
- Weaker conjugate base
Acid-Base Equilibria

Equilibrium favors reaction of the stronger acid and stronger base to give the weaker acid and weaker base.

\[
\begin{align*}
\text{Acetic acid} \quad &\quad \text{Ammonia} \quad &\quad \text{Acetate ion} \quad &\quad \text{Ammonium ion} \\
pK_a \quad &\quad \text{(stronger base)} \quad &\quad \text{(weaker base)} \quad &\quad \text{(weaker acid)} \\
\text{p}K_a \quad &\quad 4.76 \quad &\quad \text{(stronger acid)} \quad &\quad 9.24
\end{align*}
\]

\[
pK_{eq} = 4.76 - 9.24 = -4.48
\]

\[
K_{eq} = 3.0 \times 10^4
\]
Consider the reaction between acetic acid and sodium bicarbonate.

- We can write the equilibrium as a net ionic equation.
- We omit Na\(^+\) because it does not undergo any chemical change in the reaction.

\[
\text{CH}_3\text{COH} + \text{HCO}_3^- \rightleftharpoons \text{CH}_3\text{CO}^- + \text{H}_2\text{CO}_3
\]

Acetic acid  Bicarbonate ion  Acetate ion  Carbonic acid

\(pK_a\) 4.76 (stronger acid)

\(pK_a\) 6.36 (weaker acid)

- Equilibrium lies to the right.
- Carbonic acid forms, which then decomposes to carbon dioxide and water.
Thermochemistry & Mechanisms

- **Reaction mechanism**: A step-by-step description of how a chemical reaction occurs.

- **Thermochemistry**: The study of the energy of an entire system at each and every instant of a reaction.

- **Reaction coordinate diagram**: A graph showing the energy changes that occur during a chemical reaction. Energy is plotted on the vertical axis and reaction progress is plotted along the horizontal axis.
Most chemical reactions occur via collisions.

- During collisions, the structure of a molecule contorts and flexes. Collisions of higher energy lead to larger distortions in structure.
- During collisions, the kinetic energy of the reactants is converted to potential energy, which is stored in the chemical structures in the form of structural strains.
- During a collision process that yields a reaction, a transition state is formed which possesses partially broken and partially formed bonds.
- Chemists use reaction coordinate diagrams to show the changes in energy for the molecules involved in a chemical reaction.
A reaction coordinate diagram for a one step reaction between H-A and B.
Thermochemistry & Mechanisms

- For reactions at constant pressure, the change in Gibbs free energy, \( \Delta G^\circ \), is used.
  - This kind of energy controls the rates and equilibrium of reactions.
  - The change in Gibbs free energy between reactants and products is related to the equilibrium constant through this equation:
    \[
    \Delta G^\circ = -RT \ln K_{eq}
    \]
    where \( R = 8.31 \text{J/K mol} \) and \( T \) is the temperature in kelvins.
  - Free energy of activation: The difference in energy between reactants and the transition state.
Molecular Structure and Acidity

◆ The overriding principle in determining the relative acidities of uncharged organic acids is the stability of the anion, $A^-$, resulting from the loss of a proton.
  ◆ the more stable the anion, the greater the acidity of HA

◆ Ways to stabilize anions include having the negative charge:
  ◆ on a more electronegative atom.
  ◆ on a larger atom.
  ◆ delocalized through resonance.
  ◆ delocalized by the inductive effect.
  ◆ in an orbital with more s character.
A. Electronegativity of the atom bearing the negative charge

- Within a period, the greater the electronegativity of the atom bearing the negative charge, the more strongly its electrons are held, the more stable the anion is, and the stronger the acid.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Conjugate base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>CH$_3$–O$^-$:– Methoxide ion</td>
</tr>
<tr>
<td>pK$_a$ 16</td>
<td></td>
</tr>
<tr>
<td>Methylamine</td>
<td>CH$_3$–N$^-$:– Methylamide ion</td>
</tr>
<tr>
<td>pK$_a$ 38</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>CH$_3$–C$^-$:– Ethyl anion</td>
</tr>
<tr>
<td>pK$_a$ 51</td>
<td></td>
</tr>
</tbody>
</table>
B. Size of the atom bearing the negative charge

- Within a column of the Periodic Table, acidity is related to the size of the atom bearing the negative charge.
- Atomic size increases from top to bottom of a column.
- The larger the atom bearing the charge, the greater its stability.

\[
\text{CH}_3\text{S}^- + \text{CH}_3\text{O}^- \rightleftharpoons \text{CH}_3\text{S}^\text{2-} + \text{CH}_3\text{O}^\text{2-}
\]

Methanethiol \( pK_a \) 7.0 (stronger acid)
Methoxide ion (stronger base)
Methanethiolate ion (weaker base)
Methanol \( pK_a \) 16 (weaker acid)
C. Resonance delocalization of charge in A⁻

- The more stable the anion, the farther the position of equilibrium is shifted to the right.
- Compare the acidity of alcohols and carboxylic acids.
- Ionization of the O-H bond of an alcohol gives an anion for which there is no resonance stabilization.

\[
\text{CH}_3\text{CH}_2\text{O}^-\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{O}^- + \text{H}_3\text{O}^+ \quad \text{pK}_a = 15.9
\]

An alcohol \hspace{1cm} An alkoxide ion
**Molecular Structure and Acidity**

- Ionization of a carboxylic acid gives a resonance-stabilized anion.
- The $pK_a$ of acetic acid is 4.76

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

---

*Equivalent contributing structures; the carboxylate anion is stabilized by delocalization of the negative charge.*

- Carboxylic acids are stronger acids than alcohols as a result of the resonance stabilization of the carboxylate anion.
D. Electron-withdrawing inductive effect

- The polarization of electron density of a covalent bond due to the electronegativity of an adjacent covalent bond.

\[
\begin{align*}
\text{Ethanol} & : F & \quad F\text{-C-CH}_2\text{-O-H} \\
pK_a & : 15.9 & \text{pK}_a & : 12.4
\end{align*}
\]

- Stabilization by the inductive effect falls off rapidly with increasing distance of the electronegative atom from the site of negative charge in the conjugate base.

\[
\begin{align*}
\text{CF}_3\text{-CH}_2\text{-OH} & \quad \text{CF}_3\text{-CH}_2\text{-CH}_2\text{-OH} & \quad \text{CF}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH} \\
2,2,2\text{-Trifluoroethanol} & : \text{pK}_a 12.4 & 3,3,3\text{-Trifluoro-1-propanol} & : \text{pK}_a 14.6 & 4,4,4\text{-Trifluoro-1-butanol} & : \text{pK}_a 15.4
\end{align*}
\]
Molecular Structure and Acidity

• We also see the operation of the inductive effect in the acidity of halogen substituted carboxylic acids.

\[
\begin{align*}
\text{Butanoic acid} & \quad pK_a 4.82 \\
\text{4-Chlorobutanoic acid} & \quad pK_a 4.52 \\
\text{3-Chlorobutanoic acid} & \quad pK_a 3.98 \\
\text{2-Chlorobutanoic acid} & \quad pK_a 2.83
\end{align*}
\]
E. Hybridization

- For anions differing only in the hybridization of the charged atom, the greater the percentage s character to the hybrid orbital of the charged atom, the more stable the anion.

- Consider the acidity of alkanes, alkenes, and alkynes (given for comparison are the acidities of water and ammonia).

<table>
<thead>
<tr>
<th>Weak Acid</th>
<th>Conjugate Base</th>
<th>( pK_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>HO(-)H</td>
<td>HO(^-)</td>
</tr>
<tr>
<td>Alkyne</td>
<td>HC(\equiv)C(-)H</td>
<td>HC(\equiv)C(^-)</td>
</tr>
<tr>
<td>Ammonia</td>
<td>H(_{2})N(-)H</td>
<td>H(_{2})N(^-)</td>
</tr>
<tr>
<td>Alkene</td>
<td>CH(_{2}) = CH(-)H</td>
<td>CH(_{2}) = CH(^-)</td>
</tr>
<tr>
<td>Alkane</td>
<td>CH(<em>{3})CH(</em>{2})(-)H</td>
<td>CH(<em>{3})CH(</em>{2})^-</td>
</tr>
</tbody>
</table>

Increasing acidity
Lewis Acids and Bases

- **Lewis acid**: Any molecule of ion that can form a new covalent bond by accepting a pair of electrons.

- **Lewis base**: Any molecule of ion that can form a new covalent bond by donating a pair of electrons.

![Diagram showing Lewis acid and base reacting to form a new covalent bond.](image-url)
Lewis Acids and Bases

- Examples

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3^+ + \text{Br}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]

sec-Butyl cation (a carbocation)  Bromide ion  2-Bromobutane

\[
\text{CH}_3\text{CH}_2\text{O}^- + \text{BF}_3 \rightarrow \text{CH}_3\text{CH}_2\text{O}^+\text{BF}_3^-
\]

Diethyl ether (a Lewis base)  Boron trifluoride (a Lewis acid)  A BF$_3$-ether complex
Acids and Bases

End Chapter 4