Chapter 2 Acids and Bases

- A significant amount of chemistry can be described using different theories of acids and bases.
- We’ll consider three different acid-base theories (listed in order of increasing sophistication)
  1. Arrhenius theory
  2. Brønsted-Lowry theory
  3. Lewis theory

Arrhenius Acid and Base Theory

- In 1884, Svante Arrhenius proposed these definitions:
  - **Acid**: A substance that dissolves in water to produce hydronium ions (H$_3$O$^+$). H$^+$ + H$_2$O $\rightarrow$ H$_3$O$^+$
    - We’ll use hydronium ion interchangeably with hydrogen ion
  - **Base**: A substance that dissolves in water to produce hydroxide ions (OH$^-$).
    - In an Arrhenius acid – base reaction, hydrogen ion reacts with hydroxide ion to form water.

Brønsted-Lowry Acid and Base Theory

- Johannes Brønsted and Thomas Lowry proposed these definitions:
  - **Acid**: A substance that donates a hydrogen ion (proton donor).
  - **Base**: A substance that accepts a hydrogen ion (proton acceptor).
  - In a Brønsted-Lowry acid-base reaction, a hydrogen moves from acid to base. (proton transfer).
  - All Arrhenius acid-base reactions are Brønsted-Lowry acid-base reactions (not vice versa).

- When an acid donates a proton, the substance (missing a hydrogen ion) turns into a base.
- In the same way, when a base accepts a proton, the substance (with an extra hydrogen ion) turns into an acid.
- Pairs of substances that are different only by a hydrogen ion are called conjugate acid-base pairs.

• **Conjugate base**: The species formed from an acid when an acid donates a proton to a base.

  - Acid $\rightarrow$ Conjugate base
    - HCl $\rightarrow$ Cl$^-$
    - HC$_2$H$_2$O$_2$ $\rightarrow$ C$_2$H$_2$O$_2$$^-$
    - HCO$_3^-$ $\rightarrow$ CO$_3^{2-}$
    - NH$_4^+$ $\rightarrow$ NH$_3$
    - H$_2$O $\rightarrow$ OH$^-$

• **Conjugate acid**: The species formed from a base when a base accepts a proton from an acid.

  - Base $\rightarrow$ Conjugate acid
    - OH$^-$ $\rightarrow$ H$_2$O
    - C$_2$H$_2$O$_2$$^-$ $\rightarrow$ HC$_2$H$_2$O$_3$
    - HCO$_3^-$ $\rightarrow$ H$_2$CO$_3$
    - NH$_3$ $\rightarrow$ NH$_4^+$
    - NH$_2^-$ $\rightarrow$ NH$_3$
Brønsted-Lowry Acid-Base reaction

- An acid gives a hydrogen ion to the base.
- I.e., The reaction is a proton transfer reaction where the proton is transferred from the acid to the base.

Brønsted-Lowry Acid-Base reaction

- Conjugate acid-base pairs are connected via the proton transfer reaction.
- An acid turns into a base and a base turns into an acid.

Brønsted-Lowry definitions mean that an acid-base reaction does not need to involve water.

Acid and Base Strength

- Strong acids completely dissociate into hydrogen (hydronium) ion and conjugate base.

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

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

- Memorize list of strong acids
  - HCl, HBr, HI
  - HNO₃, H₂SO₄
  - HClO₃, HClO₄

Weak acids partially dissociate into hydronium ion and conjugate base.

\[
\text{HCH}_3\text{CO}_2 (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{CH}_3\text{CO}_2^- (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq})
\]

- In a weak acid, an equilibrium exists between the acid, the conjugate base and the hydronium ion.
- The degree of dissociation (the acid’s strength) is described using the acid-dissociation constant, \(K_a\).

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{HCH}_3\text{CO}_2]} = 1.8 \times 10^{-5}
\]

- The smaller an acid’s \(K_a\), the weaker the acid.
- Often we use an acid’s \(pK_a\) to describe its strength; thus, the larger the \(pK_a\), the weaker the acid. (This can be confusing!)

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

<table>
<thead>
<tr>
<th>Acid</th>
<th>(K_a)</th>
<th>(pK_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_3\text{PO}_4)</td>
<td>7.1 \times 10^{-3}</td>
<td>2.15</td>
</tr>
<tr>
<td>(\text{H}_2\text{C}_2\text{O}_3)</td>
<td>1.4 \times 10^{-4}</td>
<td>3.86</td>
</tr>
<tr>
<td>(\text{HCH}_3\text{CO}_2)</td>
<td>1.8 \times 10^{-5}</td>
<td>4.74</td>
</tr>
<tr>
<td>(\text{NH}_4^+)</td>
<td>5.5 \times 10^{-10}</td>
<td>9.26</td>
</tr>
</tbody>
</table>
• Commonly the strong bases are considered to be the soluble hydroxides; but, in organic chemistry, we’ll need to extend our definition as the conjugate bases of acids that are weaker than water.

- Strong bases completely dissociate into anion and cation.
  \[
  \text{NaOH (aq) } \rightarrow \text{Na}^+ (aq) + \text{OH}^- (aq)
  \]

- Weak bases partially react with water to form conjugate acid and hydroxide ion.
  \[
  \text{CH}_3\text{O}^- (aq) + \text{H}_2\text{O (l)} \rightarrow \text{CH}_3\text{OH (aq)} + \text{OH}^- (aq)
  \]

• The smaller a base’s \( K_b \), the weaker the base.
  Or the larger the \( pK_b \), the weaker the base.

\[
pK_b = -\log K_b = -\log (1.5 \times 10^{-11}) = 10.83
\]

<table>
<thead>
<tr>
<th>Base</th>
<th>( K_b )</th>
<th>( pK_b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_5\text{N}^- )</td>
<td>( 5.6 \times 10^{-6} )</td>
<td>4.25</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td>( 1.8 \times 10^{-5} )</td>
<td>4.74</td>
</tr>
<tr>
<td>( \text{F}^- )</td>
<td>( 1.5 \times 10^{-10} )</td>
<td>9.83</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{O}^- )</td>
<td>( 7.1 \times 10^{-11} )</td>
<td>10.14</td>
</tr>
</tbody>
</table>

• The strength of an acid and the strength of its conjugate base are deeply connected.

\[
pK_a \text{ (HF)} + pK_b \text{ (F}^-) = 14
\]
\[
3.17 + 10.83 = 14.00
\]
\[
pK_a \text{ (NH}_4^-) + pK_b \text{ (NH}_4) = 14
\]
\[
9.26 + 4.74 = 14.00
\]

• Understanding the strengths of acids (even extremely weak ones), aids in understanding of proton transfer reactions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Example</th>
<th>( pK_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkynes</td>
<td>( \text{CH}_2=\text{CH}_2 )</td>
<td>50</td>
</tr>
<tr>
<td>Alkynes</td>
<td>( \text{CH}_2=\text{CH}_2 )</td>
<td>45</td>
</tr>
<tr>
<td>Ammonia</td>
<td>( \text{NH}_3 )</td>
<td>37</td>
</tr>
<tr>
<td>Terminal Alkenes</td>
<td>( R=\text{CH}_2 )</td>
<td>25</td>
</tr>
<tr>
<td>Ketones</td>
<td>( \text{CH}_2(\text{CO})\text{CH}_3 )</td>
<td>20</td>
</tr>
<tr>
<td>Alcohols</td>
<td>( \text{CH}_3\text{CH}_2\text{OH} )</td>
<td>15 to 18</td>
</tr>
<tr>
<td>Water</td>
<td>( \text{H}_2\text{O} )</td>
<td>15.7</td>
</tr>
</tbody>
</table>

- Understanding that as an acid’s strength increases, the strength of its conjugate base decreases.

- The degree of reaction (base dissociation) is described using the base-dissociation constant, \( K_b \).

\[
K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = 1.5 \times 10^{-4}
\]

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pK_a \text{ (HF)} + pK_b \text{ (F}^-) = 14
\]
\[
3.17 + 10.83 = 14.00
\]
\[
pK_a \text{ (NH}_4^-) + pK_b \text{ (NH}_4) = 14
\]
\[
9.26 + 4.74 = 14.00
\]
Acid-Base Equilibria

• To determine the position of equilibrium in an acid-base reaction:
  • Identify the two acids in the equilibrium; one on the left and one on the right.
  • Use the information in a table of pKₐ's (Table 2.2) to determine which is the stronger acid and which is the weaker acid.
  • Remember that the stronger acid gives the weaker conjugate base, and the weaker acid gives the stronger conjugate base.
  • The stronger acid reacts with the stronger base to give the weaker acid and weaker base.
  • Equilibrium lies on the side of the weaker acid and the weaker base.

Structure and Acidity

• The most important factor in determining the relative acidity of an organic acid is the relative stability of the anion, A⁻, formed when the acid, HA, transfers a proton to another base.
• We consider these four factors:
  1. The electronegativity of the atom bonded to H in HA.
  2. Resonance stabilization of A⁻.
  3. The inductive effect.
  4. The size and delocalization of charge in 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 strongly electrons are held, the more stable the anion A⁻.
  • The more stable the anion A⁻, the greater the acidity of the acid HA.

Resonance delocalization of the charge on A⁻
• Compare the acidity of a carboxylic acid and an alcohol, both of which contain an –OH group.
• Carboxylic acids are weak acids. Values of pKₐ for most unsubstituted carboxylic acids fall within the range of 4 to 5.

CH₃COOH + H₂O ⇌ CH₃COO⁻ + H₃O⁺  pKₐ = 4.76
• Alcohols are very weak acids. Values of pKₐ for most alcohols fall within the range of 15 to 18.

CH₃CH₂OH + H₂O ⇌ CH₃CH₂O⁻ + H₃O⁺  pKₐ = 15.9

An alcohol      An alkoxide ion

The greater the resonance stabilization of the anion, the more acidic the compound.
• There is no resonance stabilization in an alkoxide anion.
• We can write two equivalent contributing structures for the carboxylate anion; the negative charge is spread evenly over the two oxygen atoms.
• When the carboxylate anion is near groups that have double bonds, resonance effects increase the acidity of the molecule.
• Resonance allows the “delocalization” of the negative charge which increases stability of the anion (and increases the acidity of the molecules).

• Inductive polarization of electron density transmitted through covalent bonds is caused by a nearby atom of higher electronegativity.
• The greater the inductive effect, the greater the acidity.

• The closer an electronegative atom is to the acidic hydrogen, the more acidic the molecule is.

• Groups that have electronegative atoms, no neighboring lone pairs of electrons, but has a carbon involved with multiple bonds.
• These groups are electron-withdrawing groups via induction and via resonance.

• Groups that are simply hydrocarbon branches (alkyl groups).
• These groups are electron-donating groups via induction.
• The more branching at the carbon, the more electron donating.

• A group of atoms that attracts electron density to itself is known as an electron-withdrawing group (EWG).
• A group of atoms that pushes electron density away from itself is known as an electron-donating group (EDG).
• Groups can be electron-withdrawing and electron-donating in two ways.
  • Inductive polarization (via electronegativity)
  • Resonance (via delocalization of charge)
• These groups can be divided into four classifications.

• Note that more electron-donating groups make the the O – H bond stronger; thus, making the molecule less acidic.
• Groups that have electronegative atoms but no neighboring lone pairs of electrons or multiple bonds.
  • These groups are **electron-withdrawing groups via induction only**.

![Trifluoromethyl and ammonium groups](image)

• Groups that have electronegative atoms and neighboring lone pairs of electrons.
  • These groups are **electron-withdrawing groups via induction and electron-donating via resonance**.

![Halogen, Alcohol, and Amino groups](image)

• Groups that have carbon – carbon double bonds.
  • These groups can be **electron-withdrawing or electron-donating groups via resonance**.
  • Whether these groups withdraw or donate electron density depends on the rest of the molecule.
  • These groups are excellent at distributing charge. (Molecules with these types of groups may have multiple resonance structures.)

![Vinyl and Phenyl groups](image)

• The larger the volume over which the charge on an anion (or cation) is delocalized, the greater the stability of the anion (or cation).
  • When considering the relative acidities of the hydrogen halides, (HI > HBr > HCl > HF), we need to consider the relative stabilities of the halide ions.
  • Recall from general chemistry that atomic size is a periodic property.
  • For main group elements, atomic radii increase going down a group and increase going across a period.

![Lewis Acid and Base Theory](image)

- For the halogens, iodine has the largest atomic radii, fluorine has the smallest (\(I > Br > Cl > F\)).
- Anions are always larger than the atoms from which they are derived. For anions, nuclear charge is unchanged but the added electron(s) introduce new repulsions and the electron clouds swell.
- Among the halide ions, \(I^-\) has the largest atomic radius, and \(F^-\) has the smallest atomic radius.
- Thus, HI is the strongest acid because the negative charge on iodide ion is delocalized over a larger volume than the negative charge on chloride, etc.
- A larger electron cloud has weaker bond overlap with hydrogen’s 1s orbital.

**Lewis Acid and Base Theory**

- Gilbert Lewis proposed these definitions:
  - **Acid**: A substance that accepts an electron pair (electrophile).
  - **Base**: A substance that donates an electron pair (nucleophile).
  - In a Lewis acid-base reaction, an base donates an electron pair to an acid to form a bond.
  - All Brønsted-Lowry acid-base reactions are Lewis acid-base reactions (not *vice versa*).
• Curved arrow notation
  • To show the flow of electrons in a Lewis acid-base reaction, we regularly use “curved arrows”.
  • The proper use of curved arrows allows us to see the bond breaking and bond making in a chemical reaction more easily.

![Lewis acid base reaction]

  • A “curved arrow” will always start at a source of electrons, a lone pair or a covalent bond.
  • A “curved arrow” will end on an atom (to show a lone pair or the formation of single bond) or between atoms (to show the formation of double or triple bond).

![An organic cation (a Lewis acid) + Bromide ion (a Lewis base) produces 2-Bromobutane]

• Lewis acid-base definitions mean that an acid-base reaction does not need to involve water (or hydrogen!).

![Bromine uses a lone pair of electrons to form a new bond to carbon]

• Note that in both examples, the first arrow illustrates the formation of a new bond.
  • The second arrow illustrates the electrons in a covalent bond moving to become a lone pair on chlorine atom. (These arrows are not drawn very well! They should better point to the chlorine atom.)

• Examples of stronger Lewis acids
  A. Neutral compounds containing group III elements: BF₃, BH₃, AlCl₃

  • Group III elements cannot have a filled octet without having a formal charge of –1. (Not likely for an electropositive element.)
  • Thus, neutral boron and aluminum compounds have an empty p-orbital that can accept a pair of electrons.

![Empty p-orbital]

  B. Carbocations: CH₃⁺, (CH₃)₃C⁺, etc.

  • Similar to the group III elements involved in three covalent bonds, carbocations also have an empty p-orbital.
  • Since they are in group IV, having just three bonds (and no lone pair electrons) results in a formal charge of +1 on the carbon (in addition to the empty orbital).
  • Thus, these are very strong electrophiles that often cannot be isolated, but instead are reactive intermediates.

![Empty p-orbital]
C. Sources of H⁺, i.e. strong acids: H₂SO₄, HCl, HBr, etc.

- A proton, H⁺, is a hydrogen atom with an empty 1s orbital and a formal positive charge. Therefore, it is a strong Lewis acid.
- In solution, an uncomplexed proton rarely exists. Instead, it is bound to some other element (often the solvent).
- Nonetheless, we can consider strong acids as sources of H⁺.

\[
\text{HO-S=O} \quad \text{H⁺}
\]

D. Electronegative atoms sharing electrons:

- O₂ (ozone);
- elemental forms of the halogens F₂, Cl₂, Br₂, I₂;
- compounds containing O=O single bonds, e.g., peroxides.

\[
\text{O-O} \quad \text{H-O-O-H}
\]

- Examples of weaker Lewis acids

A. Transition metal cations: Zn²⁺, Hg²⁺

- Since transition metals cations are larger than second row cations, their formal charge is spread over a larger area.
- These are often referred to as “soft” electrophiles or “soft” Lewis acids.
- “Hard” electrophiles have a positive charge concentrated in a small area, e.g. H⁺, CH₃CH₂⁺.
- Soft electrophiles will often complex to a lone pair of electrons located on a Lewis base.

B. Carbons bonded to electronegative atoms

- Examples include CH₃Br, H₂C=O
- A carbon bonded to an electronegative atom will have a δ (partial) positive charge.
- This carbon is referred to as an electrophilic carbon since it is electron deficient.
- Electrophilic carbons can react with nucleophiles (Lewis bases) in substitution or addition reactions.

B. Weaker Lewis Bases

- Compounds that contain π bonds can act as Lewis bases,
- Donation of a pair of π electrons results in the loss of an octet for one of the atoms involved in the double bond.
- Thus, the π-electrons are not donated as readily as lone pair electrons.
More examples of Lewis bases

<table>
<thead>
<tr>
<th>Halide ions</th>
<th>Water, alcohols, and ethers</th>
<th>Ammonia and Amines</th>
<th>Hydroxide and alkoxide ions</th>
<th>Amide ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl−</td>
<td>H2O− H</td>
<td>H− N− H</td>
<td>H2O−− H</td>
<td>H− N− H</td>
</tr>
<tr>
<td>Br−</td>
<td>CH32H− H</td>
<td>CH3N− H</td>
<td>CH3N−− H</td>
<td>CH3N− H</td>
</tr>
<tr>
<td>I−</td>
<td>CH32O− H</td>
<td>CH3N− H</td>
<td>CH3N−− H</td>
<td>CH3N− H</td>
</tr>
</tbody>
</table>

Very weak  Weak  Strong  Stronger  Very Strong