2.4 Resonance

Two different ways to draw the acetate ion

- Double bond placement
  - Neither structure correct by itself
  - True structure is intermediate between the two
  - Two structures are known as resonance forms

Resonance forms
- Individual line-bond structures of a molecule or ion that differ only in the placement of \( \pi \) and nonbonding valence electrons
- Indicated by " \( \cdots \) "
- Resonance forms contribute to a single, unchanging structure that is the resonance hybrid of the individual forms and exhibits the characteristics of all contributors

Resonance
Benzene has two equivalent resonance forms
- The true structure of benzene is a hybrid of the two individual forms, and all six carbon-carbon bonds are equivalent
- Symmetrical distribution of electrons is evident in an electrostatic potential map of benzene
Rule 1 – Individual resonance forms are imaginary, not real
- Real structure is a composite

Rule 2 – Resonance forms differ only in the placement of their π or nonbonding electrons

The red curved arrow indicates that a lone pair of electrons moves from the top oxygen atom to become part of a C=O double bond.

Simultaneously, two electrons from the C=O double bond move onto the bottom oxygen atom to become a lone pair.

The new resonance form has a double bond here...

and has a lone pair of electrons here.

Rule 3 – Different resonance forms of a substrate do not have to be equivalent

This resonance form has the negative charge on carbon.

This resonance form has the negative charge on oxygen.

Acetyl CoA

Acetyl CoA anion (two resonance forms)
Rules for Resonance Forms

**Rule 4** – Resonance forms obey normal rules of valency (follow the octet rule)

![Resonance forms example](image)

**Rule 5** – The resonance hybrid is more stable than any individual resonance form
- Resonance leads to stability

---

2.6 Drawing Resonance Forms

In general any three-atom grouping with a $p$ orbital on each atom has two resonance forms:

![Resonance forms example](image)

- The atoms X, Y, and Z in the general structure might be C, N, O, P, or S
- The asterisk (*) on atom Z for the resonance form on the left might mean that the $p$ orbital is:
  - Vacant
  - Contains a single electron
  - Contains a lone pair of electrons

---

Drawing Resonance Forms

Reaction of pentane-2,4-dione with a base
- H⁺ is removed
- An anion is formed

![Resonance forms example](image)

Resonance of the anion product:
Worked Example 2.2

Drawing Resonance Forms of an Anion

Draw three resonance forms for the carbonate ion, CO$_3^{2-}$.

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\]

Carbonate ion

Worked Example 2.3

Drawing Resonance Forms for a Radical

Draw three resonance forms for the pentadienyl radical. A radical is a substance that contains a single, unpaired electron in one of its orbitals, denoted by a dot (•).

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H} \\
\text{C} \\
\text{C} \\
\text{H}
\end{array}
\]

Pentadienyl radical

2.7 Acids and Bases: The Brønsted-Lowry Definition

Two frequently used definitions of acidity

- The Brønsted-Lowry definition
- Lewis definition

**Brønsted-Lowry acid**

- A substance that donates a hydrogen ion (proton; H$^+$) to a base

**Brønsted-Lowry base**

- A substance that accepts a hydrogen ion (proton; H$^+$) from an acid
**Conjugate acid**
- The product that results from protonation of a Brønsted-Lowry base

**Conjugate base**
- The anion that results from deprotonation of a Brønsted-Lowry acid

In a general sense

\[
\begin{align*}
\text{Acid} & \quad + \quad \text{Base} & \quad \rightleftharpoons & \quad \text{Conjugate} & \quad \text{Conjugate} \\
& & & \text{base} & \quad \text{acid}
\end{align*}
\]

---

**2.8 Acid and Base Strength**

Acids differ in their ability to donate H⁺
- The exact strength of a given acid, HA, in water solution is described using the equilibrium constant \( K_{eq} \) for the acid-dissociation equilibrium

\[
\begin{align*}
\text{HA} + \text{H}_2\text{O} & \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+ \\
K_{eq} & = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} 
\end{align*}
\]
The concentration of water, \([H_2O]\), remains nearly constant at 55.5 M at 25 °C.

• Can rewrite equilibrium expression using new quantity called the acidity constant \(K_a\).

**Acidity constant \(K_a\):**

• A measure of acid strength in water.
• For any weak acid \(HA\), the acidity constant is given by the expression:

\[
K_a = K_{eq} \frac{[H_2O]}{[HA]}
\]

Equilibria for stronger acids favor the products (to the right) and thus have larger acidity constants.

Equilibria for weaker acids favor the reactants (to the left) and thus have smaller acidity constants.

Acid strengths are normally expressed using \(pK_a\) values.

\[
pK_a = -\log K_a
\]

• Stronger acids (larger \(K_a\)) have smaller \(pK_a\).
• Weaker acids (smaller \(K_a\)) have larger \(pK_a\).

**Table 2.3**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Name</th>
<th>(pK_a)</th>
<th>Conjugate base</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_2O)</td>
<td>Water</td>
<td>15.74</td>
<td></td>
<td>(H_2O^+)</td>
</tr>
<tr>
<td>(H_3N)</td>
<td>Hydrazine</td>
<td>9.33</td>
<td></td>
<td>(CN^-)</td>
</tr>
<tr>
<td>(H_2PO_4^-)</td>
<td>Dihydrogen phosphate ion</td>
<td>7.21</td>
<td></td>
<td>(HPO_4^{2-})</td>
</tr>
<tr>
<td>(HCO_2H)</td>
<td>Acetic acid</td>
<td>4.76</td>
<td></td>
<td>(CH_3COO^-)</td>
</tr>
<tr>
<td>(H_3PO_4)</td>
<td>Phosphoric acid</td>
<td>2.18</td>
<td></td>
<td>(H_2PO_4^-)</td>
</tr>
<tr>
<td>(HNO_2)</td>
<td>Nitrous acid</td>
<td>3.55</td>
<td></td>
<td>(NO_2^-)</td>
</tr>
<tr>
<td>(HCl)</td>
<td>Hydrochloric acid</td>
<td>7.04</td>
<td></td>
<td>(Cl^-)</td>
</tr>
</tbody>
</table>