Chapter 2
“Polar Covalent Bonds; Acids and Bases”

Ionic bonding between different elements and covalent bonding between atoms of the same element can be thought of as limits of electron distribution in compounds, either uniformly shared or completely transferred.

But most covalent bonds occur between different elements, and in these bonds, electron distribution is not necessarily uniform. That is they do not share the electron pair equally.

\[
\begin{align*}
\text{Na}^+ & : \text{Cl}^- \\
\end{align*}
\]

Consider molecular hydrogen (H\textsubscript{2}) and hydrogen fluoride (HF). Both of these are molecular compounds which can be represented by the molecular models shown above.

For molecular hydrogen, the electrostatic potential map is uniform, showing equal distribution of electron density around both hydrogen atoms.

For hydrogen fluoride, however, the electrostatic potential map shows a significant polarization of the electron density, with the greatest charge associated with the fluorine atom.

The blue color is associated with positive charge.

For hydrogen fluoride, however, the electrostatic potential map shows a significant polarization of the electron density, with the greatest charge associated with the fluorine atom.

The red color is associated with a negative charge.

Molecular compounds in which electron distribution is unsymmetrical are called polar compounds and the direction of the polarization is often shown using an arrow with a positive charge on one end.

This unsymmetrical charge distribution is also called a dipole moment.
The formation of dipole moments in molecules is a result of differences in electronegativity between the elements in a covalent bond. These elements have the highest electronegativities.

In the Lewis structure for water, there is a single bond to each hydrogen and there are two unshared pairs of electrons on the oxygen. Because there are four “things” surrounding the oxygen, the molecular geometry of water is bent.

For the O–H bonds in water, the electronegativity of oxygen is 3.5 and the electronegativity of hydrogen is 2.1. The prediction is that the O–H bond in water should therefore be polar.

Because the molecular geometry of water is bent, the combination of the two local dipoles will generate a molecular dipole with enhanced negative charge towards the oxygen and enhanced positive charge towards the hydrogen.

The predicted molecular dipole of water is confirmed by the electrostatic potential map, which shows the oxygen being electron-rich and the hydrogens being electron-poor.

Alcohols, such as methanol (CH₃OH), are also polar compounds and we will see that many of the reactions of alcohols are a simple result of this polarity.

The concept of a formal charge in a molecular compound can be rationalized as follows:

One of these bonding electrons came from carbon, but now it’s gone! That means carbon must now have a positive charge!

Likewise, oxygen now has one extra electron. That means carbon must now have a negative charge!
In a molecular compound, each atom can be assigned a **formal charge** that can be calculated as follows:

First, take the Group number for the atom in the periodic table. Subtract 1/2 of the number of bonding electrons. Then, subtract the number of non-bonding (lone pair) valence electrons.

\[
\text{Formal Charge (FC)} = \text{Group} - \left(\frac{1}{2} \times \text{number of bonding electrons}\right) - \text{number of non-bonding electrons}
\]

**Group 4** - \(\left(\frac{1}{2} \times 6\right) - 0 = +1\)

\[
\text{Group 1} - \left(\frac{1}{2} \times 2\right) - 0 = 0
\]

**Calculate the formal charges of the nitrogen and oxygen atoms in trimethylamine-N-oxide.**

\[
\text{H}_3\text{C} - \text{N} - \text{O} \quad \text{H}_3\text{C}
\]

**In-Class Problem**

**Calculate the formal charges of each of the atoms in the azide anion (N}_3\)\.

\[
\cdot\text{N}=\text{N}=\text{N}:
\]

**In-Class Problem**

Azide anion can also be drawn in the Lewis structure shown below. Determine the formal charges on each atom.

\[
\cdot\text{N}=\text{N}=\text{N}:
\]

**In-Class Problem**

Draw the Lewis structure for nitrate anion (NO}_3\)\.

\[
\text{O} = \text{N} - \text{O} - \text{O}
\]

**In-Class Problem**

Draw the atoms and their associated electrons.
These structures are called resonance forms and because they differ only in the arbitrary placement of electrons, they are all equivalent.

The hybrid looks something like this.

In the hybrid, each oxygen is linked by “1/3 bonds” and each oxygen has ⅓ negative charge.

Benzene is an organic molecule with the molecular formula C₆H₆. The structure of benzene is best described as a ring of carbons, each with one hydrogen, linked by alternating double and single bonds.

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The electron and charge distribution in the hybrid is actually best described as a “cloud”, with the entire group having one net negative charge.

These rules apply for drawing resonance forms:

- Move only electrons, not atoms.
- All resonance structures must be legal Lewis structures.
- Electrons can move only between adjacent sp and sp² centers, and between heteroatoms attached to these centers.
- Always remember that resonance forms are electronic limits; just like a mathematical limit, you never get there! The actual molecule is the hybrid, it never looks like any of the limits, but is always something in between.
The resonance in benzene can be described as a cloud formed from the overlap of the adjacent electron orbitals. This electron-rich region is referred to as a π-cloud.

Another simple example of a resonance-stabilized system is the carboxylate anion.

In the tropylium cation, the positive charge is evenly distributed over all seven ring carbons...

Acetone (2-propanone) and 2,4-pentanedione undergo ionization to give the anions shown below. Draw resonance structures for these anions.
**Dipoles in Chemical Compounds**

In the Lewis structure for water, there is a single bond to each hydrogen and there are two unshared pairs of electrons on the oxygen. Because there are four “things” surrounding the oxygen, the molecular geometry of water is bent.

Valence shell electron pair repulsion theory predicts that the molecular geometry of water will be bent.

**Dipoles in Chemical Compounds**

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**Dipoles in Chemical Compounds**

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**Dipoles in Chemical Compounds**

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**Hydrogen Bonding**

Space-filling models showing extended hydrogen-bonded complexes in liquid water are shown below.

**Hydrogen Bonding in Nucleic Acids**

Hydrogen-bonding is a very important force in aqueous solution and hydrogen bonds such as these are well known to stabilize biological molecules such as proteins and nucleic acids. Base-pairing in DNA is shown in the model given below.
As described previously, liquid water consists of a dynamic complex of hydrogen-bonded water molecules. If this polar attraction is sufficiently strong, a water molecule can transfer a proton along a hydrogen bond to an adjacent water molecule, forming a pair of ions. The hydronium and hydroxide ions, $\text{H}_3\text{O}^+$ and $\text{HO}^-$, are very polar molecules with a high concentration of positive charge associated with the hydrogens of $\text{H}_3\text{O}^+$ and a negative charge associated with the oxygen of $\text{HO}^-$, as shown in the electrostatic potential maps shown here.
The hydronium ion, $\text{H}_3\text{O}^+$, itself is a very polar molecule with a high concentration of positive charge associated with the hydrogens and a negative charge associated with the oxygen, as shown in the electrostatic potential map given below.

The stabilizing effect of this hydrogen bonding is clearly shown by the electrostatic potential map for this complex, which is given below.

This type of stabilization can extend over many layers of adjacent water molecules, although a fairly stable structure is actually formed which involves hydrogen-bonding interactions between the hydronium ion and eight adjacent water molecules.

Just like water can promote the dissociation of the $\text{O}–\text{H}$ bond in water, polar molecular compounds can also undergo ionization in the presence of a polar solvent. Consider hydrogen fluoride: this highly polar molecule readily ionizes in water to form hydronium ion and fluoride anion.

$$\text{H–F} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{F}^-$$

Reactions which proceed in both directions are termed equilibria and are written using a double arrow.

$$\text{H–F} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$$

Compounds which ionize in the presence of water to form equilibrium concentrations of hydronium ion are termed acids. The distinction between strong and weak acids is simply in the relative amounts of hydronium ion which are present in the equilibrium mixture.

In Brønsted acid-base theory, a Brønsted acid is a proton donor and a Brønsted base is a proton acceptor. The products of the ionization of HF are hydronium ion and fluoride anion. As we have seen, it is also reasonable to suggest that hydronium ion can associate with the fluoride anion and donate the proton back, to reform molecular HF.

The reaction shown below described as an equilibrium dissociation of HF to form hydronium ion and fluoride anion.

$$\text{H–F} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$$

Compounds which ionize in the presence of water to form equilibrium concentrations of hydronium ion are termed acids. The distinction between strong and weak acids is simply in the relative amounts of hydronium ion which are present in the equilibrium mixture.
I. COMMON STRONG ACIDS:

- Hydrochloric acid
  \[ \text{H-Cl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^- \]
- Nitric acid
  \[ \text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_3^- \]
- perchloric acid
  \[ \text{HClO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}_4^- \]
- Sulfuric acid
  \[ \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^- \]
  \[ \text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-} \]

II. LAW OF MASS ACTION

The law of mass action can be summarized as:

- Equilibrium expressions may contain gasses as partial pressures, or solutes, expressed in molar concentrations.
- Solids and liquids do not appear in equilibrium expressions.
- The equilibrium constant, \( K \), is given by the ratio of the product of the pressures (or concentrations) of the products of a reaction, divided by the product of the pressures (or concentrations) of the reactants, each raised to the powers of their stoichiometric exponents.

\[ K = \frac{P_{\text{products}}}{P_{\text{reactants}}} \]

III. THE EQUILIBRIUM CONSTANT, \( K_a \)

Given the fact that, in pure water at 25°C, the concentration of \( \text{H}_2\text{O}^+ \) and \( \text{OH}^- \) are both \( 1.0 \times 10^{-7} \) M, write the equilibrium constant for the autoionization of water:

\[ 2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \]

\[ K_w = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \]

and, at 25°C, \( K_w = 1.0 \times 10^{-14} \)

Liquid water does not appear in the equilibrium expression.

IV. IONIZATION OF MOLECULAR COMPOUNDS:

Weak acids, such as HF and acetic acid (the acidic component of vinegar) dissociate into ions to a very small extent.

- HF:
  \[ \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \]
  \[ K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5} \]
  \[ -\log(1.8 \times 10^{-5}) = 4.74 = \text{p}K_a \]

Strong acids, such as HCl, HNO₃, and H₂SO₄, dissociate completely (or nearly so) into ions.

- HCl:
  \[ \text{H-Cl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^- \]
  \[ K_a = \frac{[\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{HCl}]} = 1 \text{, and } K_a \gg 1 \]

For strong acids, such as HCl, HNO₃, and H₂SO₄, the acid dissociation constant, \( K_a \), is large.

Weak acids, such as HF and acetic acid (the acidic component of vinegar) dissociate into ions to a very small extent. The smaller the value of \( K_a \), the stronger the acid.

- HF:
  \[ \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \]
  \[ K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5} \]
  \[ -\log(1.8 \times 10^{-5}) = 4.74 = \text{p}K_a \]
### PK Values for Some Common Acids

<table>
<thead>
<tr>
<th>Acid</th>
<th>Name</th>
<th>$pK_a$</th>
<th>Conjugate base</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>Water</td>
<td>15.74</td>
<td>$H^+$</td>
</tr>
<tr>
<td>$NH_4^+$</td>
<td>Hydrogen carbonate</td>
<td>9.31</td>
<td>$OH^-$</td>
</tr>
<tr>
<td>H$_3$PO$_4^-$</td>
<td>Phosphoric acid</td>
<td>7.21</td>
<td>$HPO_4^{2-}$</td>
</tr>
<tr>
<td>CH$_3$CO$_2$H</td>
<td>Acetic acid</td>
<td>4.76</td>
<td>$CH_3CO_2^-$</td>
</tr>
<tr>
<td>H$_3$PO$_4$</td>
<td>Phosphoric acid</td>
<td>2.16</td>
<td>$HPO_4^{2-}$</td>
</tr>
<tr>
<td>HNO$_2$</td>
<td>Nitric acid</td>
<td>-1.3</td>
<td>$NO_2^-$</td>
</tr>
<tr>
<td>HO$_2^-$</td>
<td>Hydroxyl acid</td>
<td>-7.1</td>
<td>$O^-$</td>
</tr>
</tbody>
</table>

### Lewis Acids and Bases

Lewis acids are electron pair acceptors; Lewis bases are electron pair donors.

- **Lewis base**
- **Lewis acid**

### Hydrogen Bonding

Of all of the intermolecular forces we will encounter in Organic Chemistry, hydrogen bonding is the **strongest** force. When the hydrogen is attached to nitrogen, oxygen or fluorine, hydrogen bonding will be the most important.

### Hydrogen Bonding in Polar Liquids

Hydrogen bonding readily occurs between water and polar solutes such as alcohols and ammonia, and indeed, hydrogen bonding is important in the structure and properties of other polar liquids.
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Hydrogen bonding and boiling point

The more polar and the more efficient the hydrogen-bonding in a molecule the higher the boiling point will be.

Other Types of Intermolecular Interactions

Induced dipole attractions. Polar molecules and ions can induce a re-distribution of the electron cloud surrounding a non-polar molecule, resulting in a net (weak) attraction.

Induced Dipoles

Although simple gasses such as oxygen and nitrogen are very non-polar, they readily dissolve in water. This is a result of the ability of water to induce a dipole in the non-polar molecules by deforming the electron cloud surrounding the molecule.

Induced Dipoles

Consider the high molecular weight, non-polar molecule I₂ dissolving in the polar solvent ethanol (CH₃CH₂OH). As the I₂ interacts with the ethanol, a dipole is induced, increasing the solubility.

Dispersion Forces

Dispersion forces. In non-polar molecules such as iodine, a temporary fluctuation of the electron distribution in one atom can induce a transient dipole in a neighboring molecule, resulting in a net (very weak) attraction.

Intermolecular forces arising between non-polar molecules are generally referred to as van der Waals forces.
In non-polar hydrocarbons, the boiling points increase regularly with increasing molar mass due to increased intermolecular forces.

**Molecular Shape and Boiling Point**

*n*-Pentane and neopentane (2,2-dimethylpropane) are two isomers of the hydrocarbon, C\(_5\)H\(_{12}\). The boiling points the two are 36.1 °C, and 9.5 °C, respectively. This difference can be attributed to the enhanced surface in *n*-pentane allowing more van der Waals interactions.

**In-Class Problem**

Any species that can accept electrons.
A bond between two atoms differing in electronegativity by 0.5 - 2.
A term used to describe a “water loving” species.
A compound that can donate a proton.
The ability of an atom to attract the shared electrons in a covalent bond.
A term used to describe a “water fearing” species.
Any species that can donate electrons.
A compound that can accept a proton.

**In-Class Problem**

Assign any formal charges to atoms in the representation of phenylalanine...

The oxygen atom labeled A. has _____ non-bonding electrons.
The oxygen atom labeled B. has _____ bonding electrons.

Use the δ⁺ - δ⁻ convention and the crossed arrow to show the direction of the expected polarity of the C–F and C–O bonds in the following compounds.

The C-Si bond in tetramethylsilane
**IN-CLASS PROBLEM**

Refer to the following...

\[
\text{A} \cdot \text{B} \quad \text{C} \quad \text{D}
\]

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

\[pK_a = 18 \quad pK_a = 15.7\]

The strongest Brønsted-Lowry acid in the equation is _______.

The strongest Brønsted-Lowry base in the equation is _______.

**IN-CLASS PROBLEM**

Identify the acids and bases in the compounds shown below:

\[
\text{CH}_3\text{OH} \quad \text{HCl} \quad \text{Br}_2 \quad \text{N} \quad \text{FeBr}_3
\]

**IN-CLASS PROBLEM**

Draw two resonance forms of the ion shown below:

\[
\text{O} \quad \text{CH}_3^-
\]

**IN-CLASS PROBLEM**

Draw two resonance forms of the ion shown below:

\[
\text{O} \quad \text{CH}_3^-
\]