3.1 Bronsted-Lowry Acids and Bases

- **Brønsted-Lowry definition**
  - **Acids donate** a proton
  - **Bases accept** a proton

- Recall from General Chemistry this classic example

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

**Acid** (proton donor)  
**Base** (proton acceptor)  
**Conjugate base**  
**Conjugate acid**
3.1 Conjugate Acids and Bases

• Brønsted-Lowry definition
  – A **conjugate acid results** when a base accepts a proton
  – A **conjugate base results** when an acid gives up a proton

• Label the acid, base, and the conjugates in the reaction below
3.2 Curved Arrows in Reactions

- Consider a specific acid/base example

\[
\begin{align*}
\text{Base} & : \text{OH}^- + \\
\text{Acid} & : \text{H}^+ - \text{O} \rightarrow \\
\text{Conjugate acid} & : \text{H}_2\text{O} + \\
\text{Conjugate base} & : \text{O}^- - \text{O} \\
\end{align*}
\]

- The base “attacks” the acid, using a pair of electrons
- The acid cannot lose its proton without the base taking it. All acid/base reactions occur in one step
- The mechanism shows two arrows indicating that two pairs of electrons move simultaneously (one shows a bond breaking, the other shows the bond being made
A multistep reaction mechanism is shown below. Which steps below are proton transfers?

Before long, you will be drawing mechanisms like this one. For now, just worry about correctly using curved arrows to show acid-base reactions (i.e. proton transfers).

Practice with SkillBuilder 3.1
3.3 Quantifying Acidity

- Recall from General Chemistry, how do “strong” acids/bases differ from “weak” acids/bases?

- The strength of an acid or base is helpful to predict how reactions will progress
  
  - We will learn to do Quantitative strength analysis – using $pK_a$ values to compare the strengths of acids
  
  - We will learn to do Qualitative strength analysis – comparing the general stability of structures.
3.3 Quantifying Acidity

- Quantitative strength analysis – using numerical data to compare how strong acids are.

- $K_a$ is the acid dissociation constant of an acid *dissolved in water*. It is the measurement of an acid’s strength when water is the base.

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

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

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

- If the acid is strong, will $K_a$ be bigger than 1, or smaller than 1?
3.3 Quantifying Acidity

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

- \( K_a \) values range from \(10^{-50}\) to \(10^{10}\) and so the size of these numbers (very small or very big) are hard to work with.

- If you take the -log of the \( K_a \), that will focus you on the exponent of the \( K_a \) value, which ranges from -10 to 50.

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

\[
pK_a = -\log K_a
\]

- So, pKa values range from -10 to 50. **Lower pka = stronger acid**
3.3 Quantifying Acidity

- There are more acids and pK\textsubscript{a} values in Table 3.1 and the inside cover of your textbook

- Each pK\textsubscript{a} unit represents an order of magnitude or a power of 10.

- For example, H\textsubscript{2}SO\textsubscript{4} (pKa = -9) is 100 times stronger acid than HCl (pKa = -7)

- Practice with SkillBuilder 3.2
You can also use $pK_a$ values to compare the strengths of bases because...

... The stronger an acid the weaker its conjugate base.

• Practice with SkillBuilder 3.3
3.3 Using $pK_a$ values to predict equilibria

- With the relevant $pK_a$ values, you can predict which direction an acid/base equilibrium will favor. **Higher $pK_a$ = weaker acid**

- This reaction demonstrates what is ALWAYS true in an acid-base reaction: **equilibrium favors the weaker acid and weaker base!!**
3.3 Using pKₐs to analyze Equilibria

- Subtracting the pKₐ values, (50 - 15.7 ≈ 34) also tells you that there will be ≈ 10^{34} more products than reactants.

- It’s not really much of an equilibrium, and more like an irreversible reaction

- Practice with SkillBuilder 3.4 and checkpoint 3.12
3.4 Qualifying Acidity

- to determine the relative strength of two acids, without knowing their pKa values, we compare the stability of their conjugate bases

- The stronger the acid, the more stable it’s conjugate base!

- When an acid loses a proton, it forms the conjugate base, which has a lone pair of electrons that resulted from the lose of H+

- To determine the stability of a conjugate base, we are actually looking at the stability of the lone pair
3.4 Qualifying Acidity

• The more effectively a conjugate base can stabilize its negative charge (i.e. lone pair), the stronger the acid.

• Four main factors affect the stability of a negative charge:
  
  – The type of **atom** that carries the charge
  – **Resonance**
  – **Induction**
  – The type of **orbital** where the charge resides

• These factors can be remembered with the acronym, **ARIO**
3.4 Qualifying Acidity

- **ARIO** - The type of atom that carries the charge

In order to compare the acidity of the two compounds below

- **Butane**
- **Propanol**

We need to draw and then analyze the stability of the negative charge on the conjugate bases
3.4 Qualifying Acidity

- ARIO - The type of atom that carries the charge

Here, we can determine whether an oxygen or a carbon will better stabilize a negative charge

(1) The larger the atom, the more stable a negative charge will be (size is the most important factor)

(2) Since C and O are in the same period, they are similar sizes. In this case, the more electronegative atom will better stabilize the negative charge
3.4 Qualifying Acidity

- **ARIO** - The type of *atom* that carries the charge

The relative stability of the bases tells us the relative strength of the acids.

![Diagram showing comparisons of stability and acidity between Butane and Propanol](https://via.placeholder.com/150)

- **Less stable**
  - Butane
  - Propanol

- **More stable**
  - Propanol

- **Less acidic**
  - Butane
  - Propanol

- **MORE ACIDIC**
  - Propanol
3.4 Qualifying Acidity

- A hogy Resonance stabilizes a negative charge (i.e. lone pair) by spreading it out across multiple atoms.

- Compare the acidity of the two compounds below by comparing the stabilities of their conjugate bases.

![Ethanol](image1)

![Acetic acid](image2)
3.4 Qualifying Acidity

- **ARIO - Resonance**

  Compare the stability of these conjugate bases

  ![Charge localization diagrams](image)

  Charge is localized (less stable) versus Charge is delocalized (more stable)

  Now we know the relative stability of the acids (which can be confirmed by looking up their pKa values)

  Ethanol
  Less acidic

  Acetic acid
  MORE ACIDIC

  Practice with Skillbuilder 3.6
3.4 Qualifying Acidity

- ARIO - **Induction** can also stabilize a formal negative charge by spreading it out. How is induction different from resonance?

- Electron withdrawing atoms/groups inductively withdraw electron density from their surroundings, thus stabilizing a negative charge.

![Acetic acid](image1)  ![Trichloroacetic acid](image2)

**Less acidic**  **More acidic**
3.4 Qualifying Acidity

- More electron withdrawing groups = more stable conjugate base
- The closer the electron withdrawing groups to the negative charge = more stable the conjugate base

\[
\begin{align*}
\text{CH}_3\text{CO}_2\text{H} & \quad \text{p}K_a = 4.75 \\
\text{Cl}_2\text{CH}_2\text{CO}_2\text{H} & \quad \text{p}K_a = 2.87 \\
\text{Cl}_2\text{CH}_2\text{CO}_2\text{H} & \quad \text{p}K_a = 1.25 \\
\text{Cl}_2\text{CH}_2\text{CO}_2\text{H} & \quad \text{p}K_a = 0.70
\end{align*}
\]

- Practice with SkillBuilder 3.7
3.4 Qualifying Acidity

- ARIO - The type of orbital also can affect the stability of a formal negative charge.

- The closer electrons are held to the nucleus, the more stable they are.

- The shorter the atomic orbital, the closer to the nucleus.
3.4 Qualifying Acidity

- **ARIO** - The type of orbital also can affect the stability of a formal negative charge.
- Consider the relative stability of the H’s indicated below:

  ![Image showing two possible conjugate bases]

- To predict which H is more acidic, we first have to draw the two possible conjugate bases.

- Which carbanion is more stable?
3.4 Qualifying Acidity

• ARI O - The type of orbital also can affect the stability of a negative charge. The more s-character in the orbital, the more stable the negative charge.

Lone pair in a $sp^2$ orbital, not as close to the nucleus
LESS STABLE

Lone pair in a $sp$ orbital, closer to the nucleus
MORE STABLE

Less acidic

MORE ACIDIC
3.4 Qualifying Acidity

• Compare the acidity of the compounds below by comparing the stabilities of their conjugate bases.

- Ethane $pK_a = 50$
- Ethylene $pK_a = 44$
- Acetylene $pK_a = 25$

• Practice with SkillBuilder 3.8
3.4 Qualifying Acidity

• When assessing the acidity of protons, we generally use ARIO as the order of importance of these stabilizing effects.

  1. The type of atom that carries the charge
  2. Resonance
  3. Induction
  4. The type of orbital where the charge resides

• It is typically helpful to use this order of priority when comparing the stability of conjugate bases, but it isn’t 100% reliable: there are exceptions
3.4 Qualifying Acidity

- Ethanol is more acidic than propylene. Therefore, the conjugate base of ethanol must be more stable.

- The type of atom (O vs. C) is consistent with this fact.
- But, propylene’s conjugate base is resonance stabilized, which would suggest it is more stable.
- So, in this case, our order of priority (ARIO) is accurate.
3.4 Qualifying Acidity

- **ARIO** is only a guideline of priority... it sometimes fails
- In this example, we know **equilibrium lies to the right** because we know the pka values

\[
\text{H–C≡C–H} + \text{NH}_2^- \rightarrow \text{H–C≡C∶}^- + \text{NH}_3
\]

- If we had judged the conjugate base stability, we would’ve concluded that negative charge on N is more stable than C, and predicted equilibrium to lie to the left, and we would’ve been wrong

- **Conclusion:** for some acids, we simply need to know the pKa values because they are exceptions to the **ARIO** priority rule.
3.4 Qualifying Acidity

- **Practice the Skill 3.23** – Predict which proton (red vs. blue) is more acidic in each of these compounds.

(a) ![Structure](image1)

(b) ![Structure](image2)

(c) ![Structure](image3)

- Keep practicing with the other examples in Practice the Skill 3.23
3.5 Predicting Equilibrium Position

- Consider any acid base reaction:

\[
\text{H—A} + \text{B}^- \rightleftharpoons \text{A}^- + \text{H—B}
\]

- There are two distinct ways to predict which side is favored at equilibrium:
  1. the \( pK_a \) values of H-A and H-B (the higher \( pK_a \) will be favored)
  2. The relative stability of the bases, B⁻ and A⁻

See Skillbuilder 3.10
Another important skill is to be able to choose an appropriate solvent for a acid/base reaction.

The solvent should be able to surround the reactants and facilitate their collisions without itself reacting.

Because water can act as an acid or a base, it has a leveling effect on strong acids and bases.

- Acids stronger than H$_3$O$^+$ can not be used in water.

- Bases stronger than OH$^-$ can not be used in water. WHY? – see next few slides.
3.6 Leveling Effect

- Appropriate use for water as a solvent – when the base is not stronger than hydroxide:

\[
\begin{align*}
\text{\textit{CH}_3\text{CO}_2^-} & \quad \text{\textit{H}_2\text{O}} \\
pK_a &= 15.7 & & pK_a = 4.75
\end{align*}
\]

- With water as the solvent, the \textit{CH}_3\text{CO}_2^- will react with the water, but the equilibrium greatly favors the left side, so water is an appropriate solvent
3.6 Leveling Effect

- Because water can act as an acid or a base, it has a leveling effect on strong acids and bases

  - Acids stronger than $\text{H}_3\text{O}^+$ cannot be used in water. For example, water would react with sulfuric acid producing $\text{H}_3\text{O}^+$. Virtually no sulfuric acid will remain if we wanted it to be available to react with another reagent.

\[
\begin{align*}
\text{H}_2\text{SO}_4 + \text{H}_2\text{O} &\rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^- \\
\text{pK}_a &= -9 \\
\text{pK}_a &= -1.7
\end{align*}
\]
3.6 Leveling Effect

- Because water can act as an acid or a base, it has a leveling effect on strong acids and bases
  - Bases stronger than OH\(^-\) cannot be used in water. For example, we wouldn’t be able to perform the following acid-base reaction in water

\[
\begin{align*}
\text{H} & \quad + \quad \text{N}^- \\
\text{H} & \quad + \quad \text{H}^- \\
\text{N}^- & \quad + \quad \text{H}^-
\end{align*}
\]

- Which of the following solvents would be a better choice?
3.7 Solvating Effects

• Because they are so similar, ARIO cannot be used to explain the $pK_a$ difference comparing ethanol and tert-Butanol.

![Chemical structures of ethanol and tert-Butanol with $pK_a$ values]

$\text{tert-Butanol}$
$pK_a = 18$

$\text{Ethanol}$
$pK_a = 16$

• As with all acids, the difference in acidity is due to the relative stability of their conjugate bases.

• The ability of the solvent to stabilize conjugate bases comes into play for this example.
The solvent must form ion-dipole attractions to stabilize the formal negative charge.

If the tert-Butoxide is sterically hindered, it won’t be as well solvated as the ethoxide. That is why t-butanol is not as acidic as ethanol.
3.9 Lewis Acids and Bases

• Lewis acid/base definition
  – A **Lewis acid accepts** a pair of **electrons**
  – A **Lewis base donates** a pair of **electrons**

• Acids under the Brønsted-Lowry definition are also acids under the Lewis definition

• Bases under the Brønsted-Lowry definition are also bases under the Lewis definition

• this reaction fits both definitions

\[
\begin{align*}
\text{H}_2\text{O} & \quad + \quad \text{H}^-\text{Cl}^+ \\
\text{H}_2\text{O} & \quad + \quad \text{H}^+\text{Cl}^- \\
\end{align*}
\]
3.9 Lewis Acids and Bases

- Lewis acid/base definition
  - A Lewis acid accepts and shares a pair of electrons
  - A Lewis base donates and shares a pair of electrons
- Some Lewis acid/base reactions cannot be classified using the Brønsted-Lowry definition
- Explain how this reaction fits the Lewis definition but not the Brønsted-Lowry definition

![Chemical structure](image)

- Practice with SkillBuilder 3.12