Chem 343

Summer 2002

Lecture 6

Topics

Recap on dipole moments, H-bonding, boiling points
van der Waals Forces
Introduction to Acids and Bases
Acid/Base Definitions
Strengths of Acids and Bases - $K_a$ & $pK_a$
Relationship between structure and Acidity
Trends & Relationships in Acid/Base Strengths
- The Inductive Effect
- The Resonance Effect

Props/Visuals/Demos

Announcements

Student hourly position
- synthesis & derivatiz. of peptides
  ~ 15 hrs/week
- course work in organic highly desirable.

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D. Van der Waals Forces (London forces)

What about the physical properties of non-polar organic compounds such as alkanes?

Why do alkanes have any tendency to condense into liquids or solids?

Answer: Van der Waals Forces

Van der Waals Forces - instantaneous dipole-induced-dipole forces.

\[
\begin{align*}
\text{CH}_3-\text{CH}_3 & \quad \text{b. p.} \quad -88^\circ \text{C} \\
\text{CH}_3-\text{CH}_2-\text{CH}_3 & \quad \text{b. p.} \quad -42^\circ \text{C} \\
\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3 & \quad \text{b. p.} \quad -0.5^\circ \text{C} \\
\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 & \quad \text{b. p.} \quad 38^\circ \text{C}
\end{align*}
\]
Chemistry 343 Lecture

Chapter 3 - Introduction to Organic Reactions: Acids and Bases

I. Introduction

Acid-base reactions are prevalent throughout all of chemistry, and organic chemistry is no exception - in fact, organic chemistry gives us a much broader perspective on acids and bases than the typical inorganic examples.

\[
\begin{align*}
\text{citric acid} & \quad \text{methylamine} \\
(\text{lemon juice}) & \quad (\text{fish})
\end{align*}
\]

In addition, to commonly considered acids like:

\[
\begin{align*}
\text{H}_2\text{SO}_4, & \quad \text{HCl}, \quad \text{HBr}, \quad \text{CH}_3\text{CO}_2\text{H}
\end{align*}
\]

we will consider acidity and acid/base reactions of organic compounds such as:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \quad \text{CH}_3\text{C} = \text{C} & \quad \text{CH}_3\text{C} = \text{C} - \text{H} \\
\text{ethanol} & \quad \text{acetylene} & \quad \text{acetylene}
\end{align*}
\]
In addition to considering common bases such as:

\[ \text{Na}^\circ \text{OH}^\circ, \quad \text{NH}_3, \quad \text{CH}_3-\text{CO}^\circ \text{Na}^\circ \]

we will consider bases such as:

\[ \text{CH}_3\text{CH}_2\text{O}^\circ \text{Na}^\circ \quad \text{Na}^\circ \text{NH}_2^\circ \quad \text{Li} \quad \text{N}[\text{CH}(_2\text{CH}_3)]_2 \]

sodium methoxide  sodium amide  lithium diisopropylamide

II. Acid Base Definitions
- good example of how a chemical theory can be systematically generalized.

A. Arrhenius Definition

**Acid** - substance which increases \( \text{H}_3\text{O}^\circ \) conc. when added to water.

**Base** - substance which increases \( \text{OH}^\circ \) concentration when added to water.

Examples:

\[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^\circ + \text{Cl}^\circ \]

\[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^\circ + \text{OH}^\circ \]
B. Brønsted-Lowry Definition

Acid - proton donor
Base - proton acceptor

Example:

\[ \text{HCl}(g) + \text{NH}_3(g) \rightarrow \text{NH}_4^+ \text{Cl}^- (s) \downarrow \]

* Note all Arrhenius Acids and Bases are Brønsted but not visa-versa.

C. Lewis Definition

Acid - e- pair acceptor
Base - e- pair donor

Example:

\[ \text{BF}_3 + \text{NH}_3 \rightarrow \text{H}_3\text{N} \rightarrow \text{BF}_3 \]
* Lewis Definition is the most general. All Brønsted Acids and Bases are Lewis but not vice-versa.

III. Strengths of Acids and Bases

A. Law of Mass Action -

- the rate of a single step chemical reaction is proportional to the product of the concentrations of reactants.

\[ A + B \rightarrow C + D \]

\[ \text{Rate}_f = k_f [A][B] \]

\[ \text{Rate}_r = k_r [C][D] \]

B. Equilibrium Constant

At equilibrium: \( \text{Rate}_f = \text{Rate}_r \)

\[ k_f [A][B] = k_r [C][D] \]

\[ K_{eq} = \frac{k_f}{k_r} = \frac{[C][D]}{[A][B]} \]
C. $K_a$ and $pK_a$

We still find it most useful to use $H_2O$ solvent and Arrhenius definition to quantify acid and base strengths.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

☆ Lower $pK_a$ is stronger acid.

D. Trends and Relationships in Acid/Base Strength.

1. Conjugate acid-base relationship

$$HA + B^- \rightleftharpoons HB + A^-$$

**Conjugate acid-base pair**

**Conjugate base/acid pair.**