

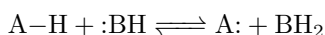
Topic IV

Hard-Soft Acid-Base and Donor-Acceptor Concepts of Transition Metals

IV.1 Module 24: Acid-Base Chemistry

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- Brønsted-Lowry Acid-Base Theory of Acids and Bases (1923).
 - Acid: Any chemical species (molecule or ion) that is able to lose, or “donate,” a hydrogen ion (proton).
 - Base: Any chemical species that is able to gain, or “accept”, a proton.
 - A base must have a pair of electrons available to share with the proton; this is usually present as an unshared pair, but sometimes is in a π orbital.
 - Acid-base reactions: The transfer of a proton from an acid to a base.



- Protons do not exist free in solution but must be attached to an electron pair.
 - Water is amphoteric.
- In the Brønsted-Lowry paradigm, we cannot separate the acids/bases from the solvent (no protons; only *solvated* protons). In a non-aqueous medium such as DMSO, however, we have much broader scope of acids and bases.
- **Carbon acid:** Any molecule containing a C–H bond can lose a proton forming the carbanion.
- Carborane ($\text{H}(\text{CHB}_{10}\text{Cl}_{11})$) is a superacid one million times stronger than sulfuric acid since its conjugate basis is incredibly stable (super easy to delocalize the charge).
- The base dissociation constant or K_b is a measure of basicity. $\text{p}K_b$ is the negative log of K_b and related to the $\text{p}K_a$ by the simple relationship $\text{p}K_a + \text{p}K_b = 14$. The larger the $\text{p}K_b$, the more basic the compound.
- **Superacid:** An acid with acidity greater than that of 100% pure sulfuric acid.
 - In water, the strongest acid you can have is H_3O^+ .
 - The strongest superacids are prepared by the combination of two components, a strong Lewis acid and a strong Brønsted-Lowry acid.
 - Fluoroantimonic acid HF-SbF_5 is 2×10^{19} stronger than 100% sulfuric acid.

- Olah's magic acid ($\text{FSO}_3\text{H}-\text{SbF}_5$) can dissolve paraffin (candle wax; extremely inert), converting methane into the t-butyl carbocation.

- **Hammett acidity function:** Can replace the pH in concentrated solutions. *Also known as H_0 .*

$$H_0 = \text{p}K_{\text{BH}^+} + \log \frac{[\text{B}]}{[\text{BH}^+]}$$

- Let BH^+ be the conjugate acid of a very weak base B, with a very negative $\text{p}K_{\text{BH}^+}$. In this way, it is rather as if the pH scale has been extended to very negative values.
- Hammett originally used a series of anilines with EWGs for the bases.

- **Superbase:** A compound that has a high affinity for protons.

- Again, these do not exist in water.
- Often destroyed by water, CO_2 , and O_2 .
- A superbase has been defined as an organic compound whose basicity is greater than that of proton sponge, which has conjugate $\text{p}K_{\text{a}}$ of 12.1.
- These are valuable in organic chemistry, which abounds in very weak acids.
- A common superbase is lithium diisopropylamide.