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Do yourself a solid.
3.091: Introduction to Solid State Chemistry Maddie Sutula, Fall 2018 Recitation 23

## 1 Acids and bases

In lecture, we talked about Brønsted-Lowry acids and bases as well as Lewis acids and bases. The BrønstedLowry definition of acids and bases is more narrow: a Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor: to be clear here, the proton is a hydrogen ion, $\mathrm{H}^{+}$. More generally, a Lewis acid is an electron acceptor, while a Lewis base is an electron donor. Water is amphoteric: it can be either an acid or a base. Water serves as the solvent for many acid-base reactions. Consider adding a generic acid to water:

$$
H A(a q)+H_{2} O(l) \rightarrow H_{3} O^{+}(a q)+A^{-}(a q)
$$

Similarly, consider adding a generic base to water:

$$
B^{-}(a q)+H_{2} O(l) \rightarrow H B(a q)+O H^{-}(a q)
$$

These serve as prototypical acid-base reactions: we can identify conjugate acid-base pairs to relate species that lost/gained a proton (or electron) on either side of the reaction.

Example: Identify the conjugate acid-base pairs in the following reaction:

$$
\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}(\mathrm{aq})+\mathrm{NH}_{3}(\mathrm{aq}) \rightarrow \mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{NH}_{4}^{+}
$$



## 2 Dissociation

In the same way we wrote a general equilibrium constant, we can write an acid/base specific equivalent. The equilibrium constant for our acid dissociation reaction above would be

$$
K_{e q}=\frac{\left[H_{3} O^{+}\right]\left[A^{-}\right]}{\left[H_{2} O\right][H A]}
$$

However, since the water is acting as a solvent and is present in excess, it has a constant concentration: we therefore define the acid constant as

$$
K_{a}=K_{e q}\left[H_{2} O\right]=\frac{\left[H_{3} O^{+}\right]\left[A^{-}\right]}{[H A]}
$$

Similarly, the base dissocation constant is

$$
K_{b}=\frac{[H B]\left[O H^{-}\right]}{[B-]}
$$

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The product of the acid and base constants for a given dissociation is constant and called $K_{W}$, where W is for water. $K_{W}=10^{-14}$

The stronger the acid or base, the more readily it dissolves in solution, and the greater the magnitude of $K_{a}$ or $K_{b}$. There are only a few strong acids- acids that fully dissociate into their constituent ions. These include $\mathrm{HCl}, \mathrm{HBr}, \mathrm{HI}, \mathrm{HNO}_{3}, \mathrm{HClO}_{3}, \mathrm{HCLO}_{4}$, and $\mathrm{H}_{2} \mathrm{SO}_{4}$. The strong bases are mostly alkali salts, including $\mathrm{LiOH}, \mathrm{NaOH}, \mathrm{KOH}, \mathrm{RbOH}, \mathrm{CsOH}, \mathrm{Ca}(\mathrm{OH})_{2}, \mathrm{Sr}(\mathrm{OH})_{2}, \mathrm{Ba}(\mathrm{OH})_{2}$. Of course, the strength of an acid or base is related to its bond energy: polar acids with big differences in electronegativity have a low bond energy rapidly dissociate when placed in water, for example.

Example: Write an expression for the dissociation and for the acid or base dissociation constants for these acids ( $\left.\mathrm{HF}, \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right)$ and bases $\left(\mathrm{NH}_{3}, \mathrm{NaOH}\right)$.

Hydrofluoric acid, HF, is a strong acid. In water, the proton dissociates:

$$
H F(a q)+H_{2} O(l) \rightarrow H_{3} O^{+}(a q)+F^{-}(a q)
$$

Its acid dissociation constant is

$$
K_{a}=\frac{\left[H_{3} O^{+}\right]\left[F^{-}\right]}{[H F]}
$$

We can take a similar approach for acetic acid, a weak acid.

$$
\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(l) \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}(\mathrm{aq})
$$

The acid dissociation constant is

$$
K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right]}
$$

For ammonia, the base gains a proton when placed in water:

$$
\mathrm{NH}_{3}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightarrow \mathrm{NH}_{4}^{+}(a q)+\mathrm{OH}^{-}(a q)
$$

The base dissociation constant for ammonia is

$$
K_{b}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]}
$$

Finally, sodium hydroxide fully dissociates:

$$
\mathrm{NaOH}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightarrow \mathrm{Na}^{+}(a q)+\mathrm{OH}^{-}(a q)
$$

The base dissociation constant is

$$
K_{b}=\frac{[N a+]\left[O H^{-}\right]}{[N a O H]}
$$

Example: Which of these acids is the strongest? sulfurous acid $\left(\mathrm{H}_{2} \mathrm{SO}_{3} ; \mathrm{K}_{a}=1.54 \times 10^{-2}\right)$, phosphoric $\operatorname{acid}\left(\mathrm{H}_{2} \mathrm{PO}_{4}^{-} ; \mathrm{K}_{a}=6.23 \times 10^{-8}\right)$, citric acid $\left(\mathrm{H}_{3} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7} ; \mathrm{K}_{a}=8.4 \times 10^{-4}\right)$

Stronger acids have larger acid dissociation constants, so sulfurous acid is stronger than citric acid and phosphoric acid.

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