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 Brønsted-Lowry 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, 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:

$$HA(aq) + H_2O(l) \to H_3O^+(aq) + A^-(aq)$$

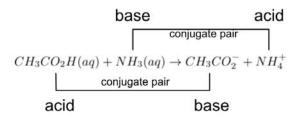
Similarly, consider adding a generic base to water:

$$B^-(aq) + H_2O(l) \rightarrow HB(aq) + OH^-(aq)$$

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:

$$CH_3CO_2H(aq) + NH_3(aq) \to CH_3CO_2^- + NH_4^+$$



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

$$K_{eq} = \frac{[H_3 O^+][A^-]}{[H_2 O][HA]}$$

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

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

Similarly, the base dissocation constant is

$$K_b = \frac{[HB][OH^-]}{[B-]}$$



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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 HCl, HBr, HI, HNO₃, HClO₃, HCLO₄, and H₂SO₄. The strong bases are mostly alkali salts, including LiOH, NaOH, KOH, RbOH, CsOH, Ca(OH)₂, Sr(OH)₂, Ba(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 (HF, CH₃CO₂H) and bases (NH₃, NaOH).

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

$$HF(aq) + H_2O(l) \to H_3O^+(aq) + F^-(aq)$$

Its acid dissociation constant is

$$K_a = \frac{[H_3 O^+][F^-]}{[HF]}$$

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

$$CH_3CO_2H(aq) + H_2O(l) \rightarrow H_3O^+(aq) + CH_3CO_2^-(aq)$$

The acid dissociation constant is

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$

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

$$NH_3(aq) + H_2O(l) \to NH_4^+(aq) + OH^-(aq)$$

The base dissociation constant for ammonia is

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Finally, sodium hydroxide fully dissociates:

$$NaOH(aq) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq)$$

The base dissociation constant is

$$K_b = \frac{[Na+][OH^-]}{[NaOH]}$$

Example: Which of these acids is the strongest? sulfurous acid (H_2SO_3 ; $K_a = 1.54 \times 10^{-2}$), phosphoric acid ($H_2PO_4^-$; $K_a=6.23 \times 10^{-8}$), citric acid ($H_3C_6H_5O_7$; $K_a=8.4 \times 10^{-4}$)

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

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