

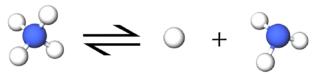
11.13: Conjugate Acid-Base Pairs

Through examples found in the sections on acids and bases proton-transfer processes are broken into two hypothetical steps: (1) donation of a proton by an acid, and (2) acceptance of a proton by a base. (Water served as the base in the acid example and as the acid in the base example [amphiprotic]). The hypothetical steps are useful because they make it easy to see what species is left after an acid donated a proton and what species is formed when a base accepted a proton. We shall use hypothetical steps or **half-equations** in this section, but you should bear in mind that free protons never actually exist in aqueous solution.

Suppose we first consider a weak acid, the ammonium ion. When it donates a proton to any other species, we can write the half-equation:

$$\mathrm{NH_4^+} \rightarrow \mathrm{H^+} + \mathrm{NH_3}$$

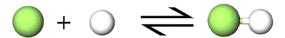
The submicroscopic representations below show the donation of the proton of ammonium. The removal of this proton results in NH₃, which is easily seen at the submicroscopic level.



But NH_3 is one of the compounds we know as a weak base. In other words, when it donates a proton, the weak acid NH_4^+ is transformed into a weak base NH_3 . Another example, this time starting with a weak base, is provided by fluoride ion:

$$F^- + H^+ \rightarrow HF$$

The submicroscopic representation above shows how the addition of a proton to fluoride converts a weak base (F- in green) into a weak acid (HF).



The situation just described for NH_4^+ and NH_3 or for F^- and HF applies to *all* acids and bases. Whenever an acid donates a proton, the acid changes into a base, and whenever a base accepts a proton, an acid is formed. An acid and a base which differ only by the presence or absence of a proton are called a **conjugate acid-base pair**. Thus NH_3 is called the conjugate base of NH_4^+ , and NH_4^+ is the conjugate acid of F^- , and F^- the conjugate base of HF.

Example 11.13.1 : Conjugate Pairs

What is the conjugate acid or the conjugate base of (a) HCl; (b) CH₃NH₂; (c) OH⁻; (d) HCO₃⁻.

Solution:

- a. HCl is a strong acid. When it donates a proton, a Cl⁻ ion is produced, and so Cl⁻ is the conjugate base.
- b. CH₃NH₂ is an amine and therefore a weak base. Adding a proton gives CH₃NH₃⁺, its conjugate acid.
- c. Adding a proton to the strong base OH⁻ gives H₂O its conjugate acid.
- d. Hydrogen carbonate ion, HCO_3^- , is derived from a diprotic acid and is amphiprotic. Its conjugate acid is H_2CO_3 , and its conjugate base is CO_3^{2-} .

The use of conjugate acid-base pairs allows us to make a very simple statement about relative strengths of acids and bases. *The stronger an acid, the weaker its conjugate base,* and, conversely, *the stronger a base, the weaker its conjugate acid.*



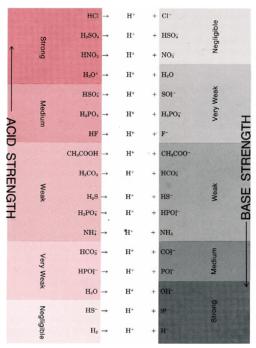


TABLE 11.13.1: Important Conjugate Acid-Base Pairs.

Table 11.13.1 gives a list of some of the more important conjugate acid-base pairs in order of increasing strength of the base. This table enables us to see how readily a given acid will react with a given base. The reactions with most tendency to occur are between the strong acids in the top left-hand comer of the table and the strong bases in the bottom right-hand comer.

If a line is drawn from acid to base for such a reaction, it will have a *downhill* slope. By contrast, reactions with little or no tendency to occur (between the weak acids at the bottom left and the weak bases at the top right) correspond to a line from acid to base with an *uphill* slope. When the slope of the line is not far from horizontal, the conjugate pairs are not very different in strength, and the reaction goes only part way to completion. Thus, for example, if the acid HF is compared with the base CH_3COO^- , we expect the reaction to go part way to completion since the line is barely downhill.

A strong acid like HCl donates its proton so readily that there is essentially no tendency for the conjugate base Cl^- to reaccept a proton. Consequently, Cl^- is a very weak base. A strong base like the H^- ion accepts a proton and holds it so firmly that there is no tendency for the conjugate acid H_2 to donate a proton. Hence, H_2 is a very weak acid.

Example 11.13.2 : Balanced Equation

Write a balanced equation to describe the reaction which occurs when a solution of potassium hydrogen sulfate, KHSO₄, is mixed with a solution of sodium bicarbonate, NaHCO₃.

Solution

The Na^+ ions and K^+ ions have no acid-base properties and function purely as spectator ions. Therefore any reaction which occurs must be between the hydrogen sulfate ion, HSO_4^- and the hydrogen carbonate ion, HCO_3^- . Both HSO_4^- and HCO_3^- are amphiprotic, and either could act as an acid or as a base. The reaction between them is thus either

$$\mathrm{HCO_3^-} + \mathrm{HSO_4^-} \rightarrow \mathrm{CO_3^{2-}} + \mathrm{H_2SO_4}$$

or

$$\mathrm{HSO_4^-} + \mathrm{HCO_3^-} \rightarrow \mathrm{SO_4^{2-}} + \mathrm{H_2CO_3}$$

Table 11.13.1tells us immediately that the second reaction is the correct one. A line drawn from HSO_4^- as an acid to HCO_3^- as a base is downhill. The first reaction cannot possibly occur to any extent since HCO_3^- is a very weak acid and HSO_4^- is a base whose strength is negligible



Example 11.13.3 : Reaction Prediction

What reactions will occur when an excess of acetic acid is added to a solution of potassium phosphate, K₃PO₄?

Solution

The line joining $\mathrm{CH_3COOH}$ to $\mathrm{PO_4^{3-}}$ in Table 11.13.1is downhill, and so the reaction

$$\mathrm{CH_{3}COOH} + \mathrm{PO_{4}^{3-}} \rightarrow \mathrm{CH_{3}COO^{-}HPO_{4}^{2-}}$$

should occur. There is a further possibility because HPO_4^{2-} is itself a base and might accept a second proton. The line from CH_3COOH to HPO_4^{2-} is also downhill, but just barely, and so the reaction

$$\mathrm{CH_{3}COOH} + \mathrm{HPO}_{4}^{2-} \rightarrow \mathrm{CH_{3}COO^{-}} + \mathrm{H_{2}PO}_{4}^{-}$$

can occur, but it does not go to completion. Hence double arrows are used. Although $H_2PO_4^-$ is a base and might be protonated to yield phosphoric acid, H_3PO_4 , a line drawn from CH_3COOH to $H_2PO_4^-$ is *uphill*, and so this does not happen.

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