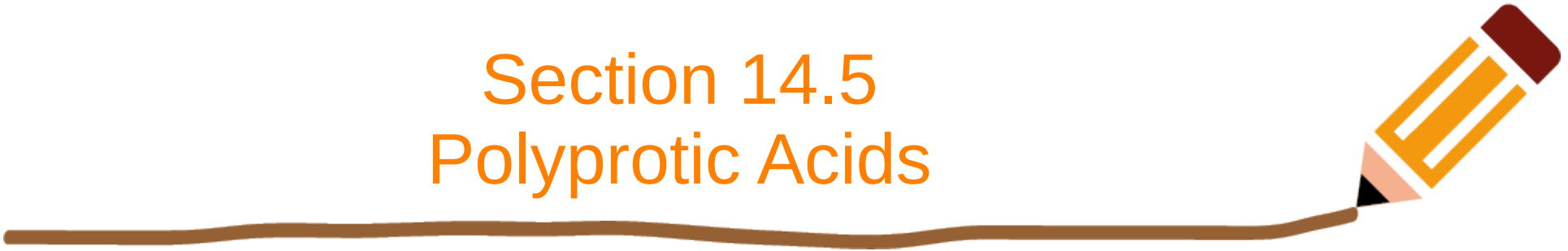
Section 14.5
Polyprotic Acids



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Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

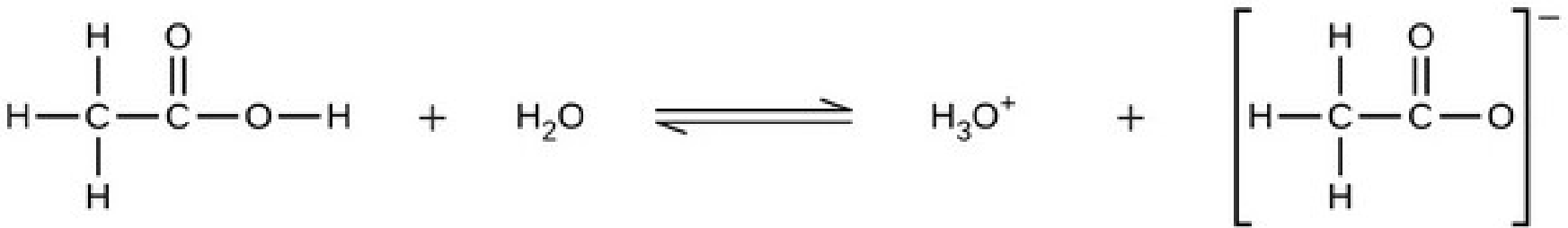
Monoprotic Acids

- Acids are classified by the number of protons per molecule that they can give up in a reaction.
- Acids that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids.**

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq)$$
$$\mathrm{HNO_3}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{NO_3^-}(aq)$$
$$\mathrm{HCN}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CN^-}(aq)$$

Multiple Hydrogens

- Not all of the hydrogens in an acid is acidic



Diprotic Acids

- **Diprotic acids** contain two ionizable hydrogen atoms per molecule
- Ionization of such acids occurs in two steps.
- The first ionization always takes place to a greater extent than the second ionization.

$$\text{First ionization: } \mathrm{H_2SO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HSO_4^-}(aq)$$

$$\text{Second ionization: } \mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq)$$

$$K_{a1} = \text{more than } 10^2$$

$$K_{a2} = 1.2 \times 10^{-2}$$

Stepwise Ionization

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

$$K_{H_2CO_3} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}$$

$$K_{HCO_3^-} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 4.7 \times 10^{-11}$$

- KH_2CO_3 is larger than $KHCO_3^-$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution.

Approximations

- If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization.

Triprotic Acid

- A **triprotic acid** is an acid that has three ionizable H atoms.
- Like diprotic acid, each successive ionization reaction is less extensive than the former
- This is reflected in decreasing values for the stepwise acid ionization constants.
  - This is a general characteristic of polyprotic acids
  - Successive ionization constants often differ by a factor of about 10^5 to 10^6.

Triprotic Acid Example

First ionization: $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$

Second ionization: $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$

Third ionization: $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$

$$K_{a1} = 7.5 \times 10^{-3}$$

$$K_{a2} = 6.2 \times 10^{-8}$$

$$K_{a3} = 4.2 \times 10^{-13}$$

Polyprotic Bases

- All of the concepts we've learned for polyprotic acids can be applied to bases.
- The carbonate ion is an example of a **diprotic base**, it can accept two protons.

$$\mathrm{H_2O}(l) + \mathrm{CO_3}^{2-}(aq) \rightleftharpoons \mathrm{HCO_3}^{-}(aq) + \mathrm{OH}^{-}(aq)$$

$$\mathrm{H_2O}(l) + \mathit{HCO_3}^{-}(aq) \rightleftharpoons \mathrm{H_2CO_3}(aq) + \mathrm{OH}^{-}(aq)$$

$$K_{\mathrm{b1}} = 2.1 \times 10^{-4}$$

$$K_{\mathrm{b2}} = 2.3 \times 10^{-8}$$