16.7 The pH in Solutions of Strong Acids and Strong Bases

A strong monoprotic acids (E.g HCl, HNO_3 etc..) – 100% dissociated in aqueous solution

- Contains a single dissociable proton

$$HA_{(aq)} + H_2O_{(l)} \xrightarrow{100\%} H_3O^+_{(aq)} + A^-_{(aq)}$$

$[H_3O^+] = [A^-] = [HA]_{ini}$

Undissociated $HA]_{ini} = 0$

Strong Bases: Water-soluble ionic solids

- Alkali metal hydroxide, MOH

$$MOH_{(aq)} \xrightarrow{100\%} OH^-_{(aq)} + M^+_{(aq)}$$

$[MOH]_{ini} = [^-OH]$

- Exits in aqueous solution as alkali metal cations and hydroxide anions
- Alkaline earth metal hydroxide, $M(OH)_2$ where M= Mg, Ca, Sr, Ba

$$M(OH)_{2(aq)} \xrightarrow{100\%} 2OH^-_{(aq)} + M^{+2}_{(aq)}$$

$2 \times [M(OH)_2] = [-OH]$

- Less soluble than alkali hydroxide, therefore lower [-OH]

Example: Calculate the $[^-OH]$ and pH of 1.25×10^{-2} M $HClO_4$

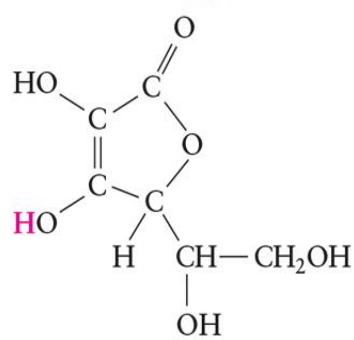
Example: Calculate the pH of a solution prepared by dissolving 0.25 g of CaO in enough water to make 1.50 L of solution.

Example: The pH of an unknown acid solution is 2.45. What is the initial concentration of this acid solution? Assume it fully dissociated.

16.8 Equilibria in Solutions of Weak Acids

It's important to realize that a weak acid is not the same thing as a dilute solution of a strong acid. Whereas a strong acid is 100% dissociated in aqueous solution, a weak acid is only partially dissociated. The equilibrium constant for the dissociation reaction, denoted is called the acid-dissociation constant, Ka.

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^- \qquad K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

	Acid	Molecular Formula	Structural Formula*	K_a	pK_a†
Stronger acid	Hydrochloric	HCl	H—Cl	2×10^{6}	−6.3
	Nitrous	HNO_2	H—O—N=O	4.5×10^{-4}	3.35
	Hydrofluoric	HF	H—F	3.5×10^{-4}	3.46
	Formic	HCO_2H	H—C(=O)—O—H	1.8×10^{-4}	3.74
	Ascorbic (vitamin C)	$C_6H_8O_6$		8.0×10^{-5}	4.10
	Acetic	CH_3CO_2H	CH_3—C(=O)—O—H	1.8×10^{-5}	4.74
	Hypochlorous	$HOCl$	H—O—Cl	3.5×10^{-8}	7.46
Weaker acid	Hydrocyanic	HCN	H—C≡N	4.9×10^{-10}	9.31
	Methanol	CH_3OH	CH_3—O—H	2.9×10^{-16}	15.54

* The proton that is transferred to water when the acid dissociates is shown in red.
† $pK_a = -\log K_a$.

Example: The pH of a 0.10 M solution of lactic acid ($HC_3H_5O_3$) is 2.42. Calculate the K_a and pK_a for lactic acid.

16.9 Calculating Equilibrium Concentrations in Solutions of Weak Acids

- **Step 1:** Write the balance equation for weak acid and water
- **Step 2:** Identify the principle reaction (the reaction that has larger K_a)
- **Step 3:** Generate an ICE table
- **Step 4:** Solve for x
- **Step 5:** Calculate pH and all other concentrations (HA, H_3O^+ and A^-)

Example: What is the pH of a 0.125 *M* HClO (hypochlorous acid) solution? $K_a = 3.5 \times 10^{-8}$

Example: Determine the concentration of all species present (H_3O^+, $CH_3CO_2^-$, CH_3CO_2H) and pH of a 0.150 M CH_3CO_2H $K_a = 1.8 \times 10^{-5}$

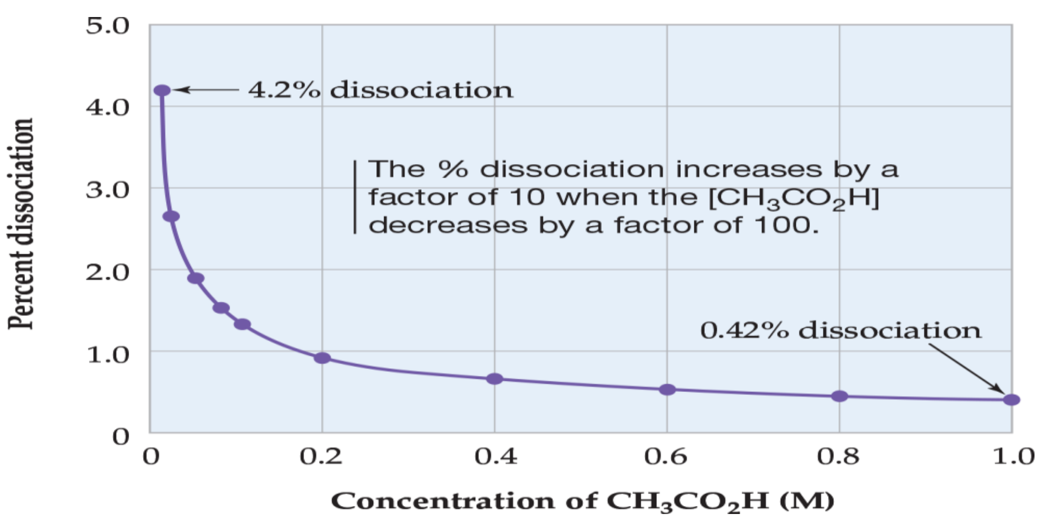
16.10 Percent Dissociation in Solutions of Weak Acids

Another measure of the strength of an acid is its percent ionization. The percent ionization of a weak acid is the ratio of its concentration of the ionized acid to the initial acid concentration, times 100:

$$\%\ \text{ionization} = \frac{[\text{HA}]_{\text{dissociated}}}{[\text{HA}]_{\text{ini}}} \times 100 \quad \text{OR} \quad = \frac{[H_3O^+]}{[\text{HA}]_{\text{ini}}} \times 100$$

The smaller the value of K_a, the smaller % ionization BUT do not confuse a weak acid with a diluted acid.

For a given weak acid, the percent dissociation increases with decreasing concentration, as shown in Figure 16.8



Why Doesn't the Increase in H_3O^+ Keep Up with the Increase in HA?

- The reaction for ionization of a weak acid is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons A^-_{(aq)} + H_3O^+_{(aq)}$$

- According to Le Châtelier's principle, if we reduce the concentrations of all the (*aq*) components, the equilibrium should shift to the right to increase the total number of dissolved particles.
  - We can reduce the (*aq*) concentrations by using a more dilute initial acid concentration.
- The result will be a larger $[H_3O^+]$ in the dilute solution compared to the initial acid concentration. This will result in a larger percent ionization

16.11 Polyprotic acids

Acids that contain more than one dissociable proton are called polyprotic acids. Polyprotic acids dissociate in a stepwise manner, and each dissociation step is characterized by its own acid-dissociation constant, K_{a1},K_{a2} and so forth,

$$H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO_3^-{}_{(aq)} \qquad K_{a1} = \frac{[H_3O^+]\,[HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}$$

$$HCO_3^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CO_3^{-2}{}_{(aq)} \qquad K_{a2} = \frac{[H_3O^+]\,[CO_3^{-2}]}{[HCO_3^-]} = 5.6 \times 10^{-11}$$

- Generally, the difference in K_a values is great enough so that the second ionization does not happen to a large enough extent to affect the pH.
  - $K_{a1} > K_{a2} > K_{a3}$
  - Because of electrostatic forces, it's more difficult to remove a positively charged proton from a negative ion, such as than from an uncharged molecule, such as H_2CO_3 so $K_{a1} > K_{a2}$.
  - Most pH problems just do first ionization.
  - Except $H_2SO_4 \Rightarrow$ uses $[H_2SO_4]$ as the $[H_3O^+]$ for the second ionization.
- $[A^{2-}] = K_{a2}$ as long as the second ionization is negligible.

Ionization in H_2SO_4

- The ionization constants for H_2SO_4 are as follows:

$$H_2SO_{4(aq)} + H_2O(l) \rightarrow HSO_4^-{}_{(aq)} + H_3O^+_{(aq)} \qquad K_{a1} = \text{strong}$$
$$HSO_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons SO_4^{2-}{}_{(aq)} + H_3O^+_{(aq)} \qquad K_{a2} = 1.2 \times 10^{-2}$$