Calculating Species Concentrations
for
Pure Weak Acid or Pure Weak Base in Water

☞ A solution of pure weak acid or base in solution involves simultaneous equilibria, including the hydrolysis of the acid or base and water's autoprotolysis.

☞ We will consider the weak acid case first, analyzing the problem in some detail to see where we might be able to make certain routine simplifications.

✔ Once we have identified the conditions that warrant simplifying assumptions, we can subsequently invoke those simplifications directly whenever we are dealing with a solution that meets the appropriate criteria.

✔ When we consider the case of a pure weak base in water, we will be able to take an analogous approach and make the same kinds of simplifying assumptions.

Calculating All Species in a Solution
of
Pure Weak Acid in Water

☞ In an aqueous solution of any weak acid, HA, all concentrations in the K_a expression are the *total concentrations* of the species in solution.

 ✔ In the K_a expression, we need to assess the total concentrations of [HA], [H_3O^+], and [A^-] from all sources.

 ✔ Both K_a and K_w must be obeyed, and both related equilibria are potentially significant sources of [H_3O^+].

 ✔ From K_a we will be able to calculate [H_3O^+], [A^-], and [HA].

 ✔ Using the calculated value of [H_3O^+] we will be able to use K_w to calculate [OH^-].

Prototype Problem

Calculate the concentrations of all species in a 1.00×10^{-2} M solution of acetic acid, HOAc. What is the pH of the solution? $K_a = 1.76 \times 10^{-5}$

Simultaneous Equilibria
Pure Weak Acid in Water

$$HOAc \; + \; H_2O \; \rightleftharpoons \; H_3O^+ \; + \; OAc^-$$

$$2H_2O \; \rightleftharpoons \; H_3O^+ \; + \; OH^-$$
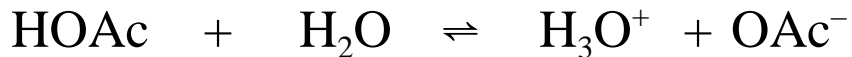
- Both K_a and K_w must be obeyed:

① $\quad K_a \; = \; \dfrac{[H_3O^+][OAc^-]}{[HOAc]} \; = \; 1.76 \times 10^{-5}$

② $\quad K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$

- Charge balance expression:

③ $\quad [H_3O^+] = [H_3O^+]_{acid} + [H_3O^+]_{water} = [OAc^-] + [OH^-]$

- Mass balance expression:

④ $\quad [HOAc] = C - [H_3O^+]_{acid} = C - [OAc^-]$

Or $\qquad C = [HOAc] + [OAc^-] = 1.00 \times 10^{-2} \; M$

Simplifications for Solutions
of Weak Acids at Moderate Concentration
Assumption I

③ $[H_3O^+] = [H_3O^+]_{acid} + [H_3O^+]_{water} = [OAc^-] + [OH^-]$

- Assumption I: This is an acidic solution at moderate concentration, so the concentration of hydroxide ion is so small as to be negligible in expression ③:

$$[H_3O^+]_{water} = [OH^-] \ll 10^{-7} \text{ M} \approx 0$$

Therefore, expression ③ simplifies to

$$[H_3O^+] \approx [OAc^-]$$

✓   This simplification means that we are assuming virtually all of the hydronium ion in the solution comes from the acid, and water's contribution is negligible.

Simplifications for Solutions
of Weak Acids at Moderate Concentration
Assumption II

④ $C = [\text{HOAc}] + [\text{OAc}^-] = 1.00 \times 10^{-2}$ M

- Assumption II: HOAc is a weak acid, so the equilibrium lies mainly to the left and

$$[\text{HOAc}] \gg [\text{OAc}^-]$$

Then, in expression ④, we ignore $[\text{OAc}^-]$ and write

$$[\text{HOAc}] \approx C = 1.00 \times 10^{-2} \text{ M}$$

✓   Making this assumption means that the amount of dissociation of HOAc is negligible and can be ignored.

Substituting the Simplified Expressions into K_a

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = 1.76 \times 10^{-5}$$

- Substituting $[H_3O^+] \approx [OAc^-]$ and $[HOAc] \approx C = 1.00 \times 10^{-2}$ M

$$K_a = 1.76 \times 10^{-5} = \frac{[H_3O^+]^2}{C} = \frac{[H_3O^+]^2}{1.00 \times 10^{-2}}$$

$[H_3O^+]^2 = 1.76 \times 10^{-7}$

$[H_3O^+] = 4.19_5 \times 10^{-4}$ M $= [OAc^-]$

pH = 3.38

- To find $[OH^-]$, substitute into K_w.

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{4.195 \times 10^{-4}} = 2.38 \times 10^{-11} \text{ M}$$

Checking the Assumptions

Assumption I:

- ✔ We assumed water's contribution to $[H_3O^+]$ is negligible.
- ✔ Water's contribution is $[H_3O^+]_{water} = [OH^-]$.
- ☺ For this solution, $[H_3O^+]_{water}$ is negligible:

$$[H_3O^+]_{water} = [OH^-] = 2.38 \times 10^{-11} \text{ M}$$
$$\ll [H_3O^+]_{acid} = 4.19_5 \times 10^{-4} \text{ M}$$

Assumption II:

- ✔ We ignored the dissociation of the acid.
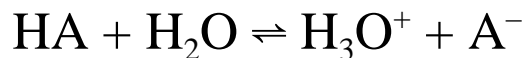- ✔ To check how good this assumption is, calculate **percent dissociation** of the acid.

$$\% \text{ dissociation} = \frac{[H_3O^+]}{C_{HA}} \times 100\%$$

$$\% \text{ dissociation} = \frac{4.19_5 \times 10^{-4}}{1.00 \times 10^{-2}} \times 100\% = 4.20\%$$

- ☺ This amount of dissociation represents a minor error in the exact mass balance expression:
  $C = [HOAc] + [OAc^-]$
  $= 1.00 \times 10^{-2} \text{ M} + 4.19_5 \times 10^{-4} \text{ M}$
  $= 1.04 \times 10^{-2} \text{ M}$

Weak Acid in Water Calculations

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

☞ Assumption I: If $C_{HA} >> 10^{-7}$ M, assume virtually all H_3O^+ comes from HA. Thus,

$$[H_3O^+] \approx [A^-]$$

☞ Assumption II: If $C_{HA} >> K_a$ (usually 2 powers of 10 or more), assume HA is negligibly dissociated. Thus,

$$[HA] \approx C_{HA}$$

☞ If both assumptions can be made

$$K_a \; = \; \frac{[H_3O^+][A^-]}{[HA]} \; = \; \frac{[H_3O^+]^2}{C_{HA}}$$
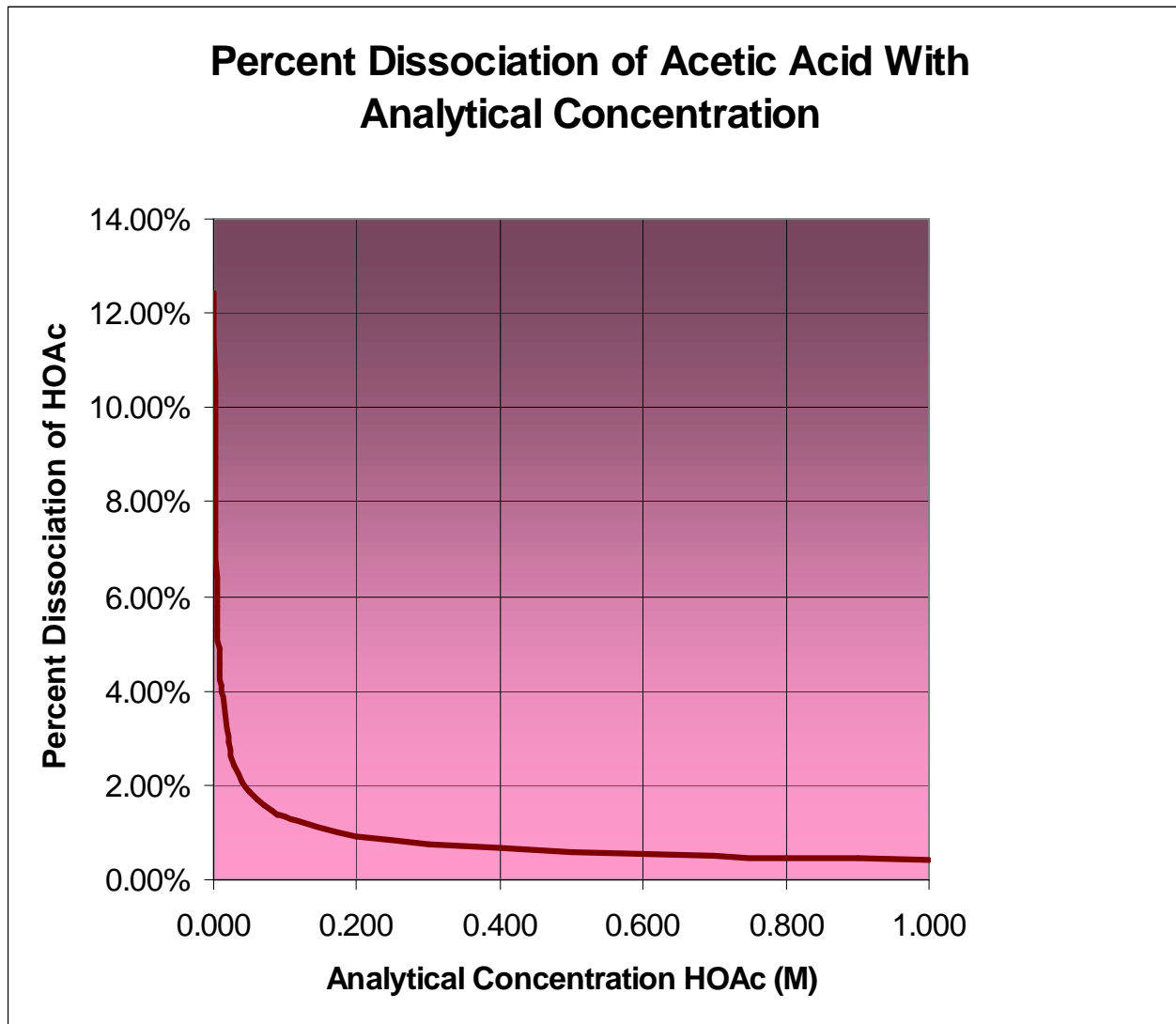
and

$$[H_3O^+] \; = \; \sqrt{C_{HA}K_a}$$

Percent Dissociation With Dilution

$$\% \text{ dissociation } = \frac{[A^-]}{C_{HA}} \times 100\%$$

☞ For a solution of a pure weak acid in water with any value of K_a, the percentage of the dissociation of the added acid increases with dilution.

Percent Dissociation of Acetic Acid With Analytical Concentration

Percent Dissociation Data for Acetic Acid

C_{HOAc}, M	$[H_3O^+]$	% Dissociation
1.00	4.19×10^{-3}	0.419%
0.100	1.32×10^{-3}	1.32%
0.0100	4.11×10^{-4}	4.11%
0.00100	1.24×10^{-4}	12.4%
0.000100	3.41×10^{-5}	34.1%

☞ In general, all acids are virtually completely dissociated at very high dilution, regardless of how small their K_a.

Breakdown of Assumption II

☞ Assumption II breaks down at appreciable percent dissociation.

☞ If $C_{HA} \approx K_a$ (within 2 powers of 10), dissociation of the acid cannot be ignored. Thus

$$[HA] = C_{HA} - [H_3O^+]$$

☞ Substituting this more exact expression into K_a with Assumption I gives

$$K_a = \frac{[H_3O^+]^2}{C_{HA} - [H_3O^+]}$$

$$[H_3O^+]^2 + K_a[H_3O^+] - K_a C_{HA} = 0$$

☞ Solve the quadratic equation for $[H_3O^+] = [A^-]$, ignoring the negative root.