Acid/Base Equilibria

CHEM 361A: Introduction to Physical Chemistry

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Lecture 13

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Learning Objective: Apply activity coefficients for ionic solutions to acid/base equilibria.

References:

- Atkins and de Paula Focus 5D - 5F
- Chang Chapter 11

Acid Equilibria

Consider the following reaction:

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

The equilibrium expression would be written as

$$K_a = \frac{a_{A^-}\ a_{H_3O^+}}{a_{HA}} = \frac{\gamma_\pm \frac{m_{A^-}}{m^\circ}\ \gamma_\pm \frac{m_{H_3O^+}}{m^\circ}}{\frac{m_{HA}}{m^\circ}}$$

The percent ionization is calculated by

$$\text{percent ionization} = \frac{m_{H_3O^+}}{m_{HA_0}} \times 100\%$$

The pH is calculated by

$$pH = -\log(a_{H_3O^+})$$

Acid Equilibrium Review

HA is an acid with $K_a = 1.0 \times 10^{-3}$. If 0.1 mol of HA is mixed into 1 kg of water, determine the equilibrium pH. Assume that $\gamma_{\pm} = 1$.

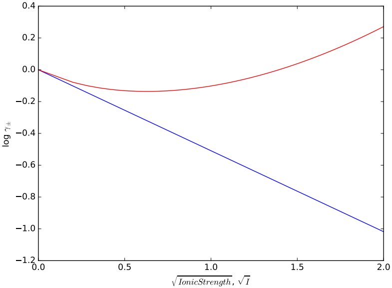
Debye-Hückel Law

Recall that we have a way to describe the average activity coefficient for ions in solution:

- The Debye-Hückel Limiting Law is only for dilute solutions (low I).

$$\log \gamma_\pm = -A \left|z_+ z_-\right| I^{\frac{1}{2}}$$

- The Davies Equation is an empirical correction to fit the data better at high I

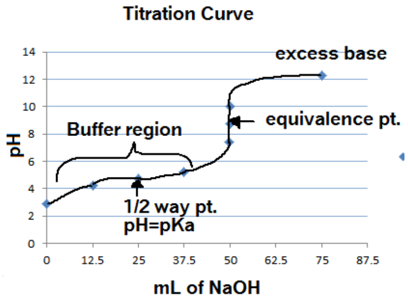


$$\log \gamma_\pm = -0.509|z_+ z_-| \left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.3I \right)$$

Acid Equilibrium with Debye-Hückel

1. HA is an acid with $K_a = 1.0 \times 10^{-3}$. If 0.1 mol of HA is mixed into 1 kg of water, determine the percent ionization and equilibrium pH.
2. Suppose you were to make the same solution with 0.18 M NaCl. Determine the percent ionization and pH.
3. Suppose you were to make the same solution with 10 M NaCl. Determine the percent ionization and pH.

Buffers



A buffer is when an equivalent amounts of weak acid exist with its conjugate base

- Resist changes to pH when small amounts of acid or base are added to the mixture
- When equal amounts of weak acid and conjugate base are in the system, the pH of the buffer is the acid's pKa

Henderson-Hasselbalch Equation

To calculate the expected pH of a buffer we will use the Henderson-Hasselbalch equation. It is derived from the standard equilibrium expression:

$$K_a = \frac{a_{A^-}\ \ a_{H_3O^+}}{a_{HA}} = \frac{\gamma_\pm \frac{m_{A^-}}{m^\ominus}\ \ a_{H_3O^+}}{\frac{m_{HA}}{m^\ominus}}$$

Taking the $-\log$ of both sides

$$-\log K_a = -\log\left[\frac{\gamma_\pm \frac{m_{A^-}}{m^\ominus}\ \ a_{H_3O^+}}{\frac{m_{HA}}{b^\ominus}}\right]$$

$$pKa = -\ log\gamma_\pm - \log\frac{m_{A^-}}{m_{HA}} - \log a_{H_3O^+}$$

$$\log\gamma_\pm + \log\frac{m_{A^-}}{m_{HA}} + pKa = pH$$

Henderson-Hasselbatch (cont.)

$$pH = pKa + \log \frac{m_{A^-}}{m_{HA}} + \log \gamma_{\pm}$$

This is the **modified Henderson-Hasselbatch equation**.

- The ideal equation is highlighed in blue
- Including the effect that there are ions in solution is included in the $\log \gamma_{\pm}$ term.
    - Can use either the Debye-Hückel Limiting Law, or the Davies Equation depending on the ionic strength

The Henderson-Hasselbalch equation is most effective when

- $$-1 < \log \frac{m_{A^-}}{m_{HA}} < 1$$
- The molarity of the buffer should be at least 100x higher than K_a

Henderson-Hasselbatch Example

A solution is prepared such that the final mixture is 0.1 molal CH_3COOH with 0.09 molal $NaCH_3COO$. Determine the pH of this buffer where the K_a for CH_3COOH is 1.76×10^{-5}.

Summary

- Acid/base equilibria include ions in solution which deviate properties of mixtures from ideal conditions
- The deviation is quantified in the average activity coefficient which can be calculated using
  - The Debye-Hückel Limiting Law (low ionic strength)

$$\log \gamma_\pm = -A\ |z_+ z_-|\ I^{\frac{1}{2}}$$

  - The Davies Equation (high ionic strength: $\sqrt{I} > 0.2$)

$$\log \gamma_\pm = -0.509|z_+ z_-| \left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.3I \right)$$

- The average activity coefficient can also be incorporated into the Henderson-Hasselbatch equation to give

$$pH = pKa + \log \frac{m_{A^-}}{m_{HA}} + \log \gamma_\pm$$