Responses of Chemical Equilibria

Chapter 9 of Atkins: Section 9.5

The Response of Chemical Equilibria to Conditions

- Acid-base equilibria in water
- The pH of acids and bases
- Acid-base titrations
- The pH curve
- Buffers
- Indicators
The Response of Chemical Equilibria to pH

Proton transfer equilibria (acid and base reactions) are established on timescales as short as nanoseconds.

These types of reactions (characteristic of solutions of Brønsted acids and bases) are highly responsive to the activity of the hydronium ion, $H_3O^+$ (the best representation we have of the hydrogen ion species in solution).

Since the scale of $H_3O^+$ concentrations (activities) can range from $10^{-14}$ M and lower to $10$ M and beyond, we choose to use a convenient common logarithm scale.

$$pH = -\log a_{H_3O^+}$$
The pH Scale - Alkaline to Acidic

\[ pH = -\log a_{H_3O^+} \]
Acid-Base Equilibria

We measure pH using many sophisticated and non-sophisticated means. Early on we often make approximation that:

\[ a_{H_3O^+} = \left[ H_3O^+ \right] \]

Since many thermodynamic observables depend on pH itself (and not hydronium ion concentration specifically) there is often no need to make this approximation.

We need to consider three equilibrium constants to discuss the effect of pH on equilibria involving the transfer of protons between species.

\[ K_a, K_b, \text{ and } K_w \]
Equilibrium Constants

\[ \text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \]

\[ K_a = \frac{a_{\text{H}_3\text{O}^+} a_{\text{A}^-}}{a_{\text{HA}}} \]

\[ \text{B}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HB}^+(aq) + \text{OH}^-(aq) \]

\[ K_b = \frac{a_{\text{HB}^+} a_{\text{OH}^-}}{a_{\text{B}}} \]

\[ 2 \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \]

\[ K_w = a_{\text{H}_3\text{O}^+} a_{\text{OH}^-} \]
Equilibrium Constants

2 H₂O(l) ⇌ H₃O⁺(aq) + OH⁻(aq)  \[ K_w = a_{H_3O^+} a_{OH^-} \]

At 25°C, \( K_w = 1.008 \times 10^{-14} \)

\( pK_w = 14.00 \)

If we also use the notation:

\[ pOH = -\log a_{OH^-} \]

\[ pK_w = pH + pOH \]

Also, the equilibrium constant of the conjugate acid to B (the species HB⁺) is related to that of the base by:

\[ K_w = K_a K_b \]
Strong and Weak Acids and Bases

For a weak acid or base, the extent of the reaction is not very advanced. For a strong acid or base, the reaction heavily favors the products.

$$\text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$$
The pH of Acids and Bases

HA(aq) + H₂O(l) ⇌ H₃O⁺(aq) + A⁻(aq)

First, the approximation will be made that the activity of the species in solution are equivalent to the numerical values of concentration given in moles per liter (M).

For a weak acid, the extent of proton transfer is so small that it is usually assumed that the molar concentration of HA is unchanged from its nominal value. Also, the molar amounts of H₃O⁺ and A⁻ formed from the reaction are equal (we amount from the autoprotolysis of water is considered minimal), and we can find:

\[ K_a = \frac{[H_3O^+][A^-]}{[HA]} = \left(\frac{[H_3O^+]}{[HA]}\right)^2 \]

or

\[ [H_3O^+] = \sqrt{K_a[HA]} \]
The pH of Acids and Bases

HA(aq) + H₂O(l) ⇌ H₃O⁺(aq) + A⁻(aq)

\[ pH = \frac{1}{2} pK_a - \frac{1}{2} \log[HA] \]

Similarly for a weak base equilibrium:

B(aq) + H₂O(l) ⇌ HB⁺(aq) + OH⁻(aq)

\[ pH = pK_w - \frac{1}{2} pK_b + \frac{1}{2} \log[B] \]
Acid-Base Titrations

We can better understand the stages of chemical equilibrium in acid/base reactions by following the progress of a titration of a weak acid, HA, with a solution of a strong base, MOH.

Volume of acid = $V_A$
Molar concentration of acid is initially $A_0$

Molar concentration of base (titrant) is B.

Goal: calculate pH at any stage in the titration.

This can be done “exactly” - assuming that activities are given by concentrations - and approximately making certain assumptions.
Acid-Base Titrations

- \[ \text{pH} = \frac{1}{2} \text{p}K_a - \frac{1}{2} \log A_0 \]
- \[ \text{pH} = \frac{1}{2} \text{p}K_a + \frac{1}{2} \text{p}K_w + \frac{1}{2} \log S \]
- \[ \text{pH} = \text{p}K_w + \log B' \]
Acid-Base Titrations - Initial pH

Stoichiometric point (also called the equivalence point): enough titrant has been added for the amount of strong base it supplies to match the amount of weak acid in the analyte.

Upon the addition of $V_B$ of titrant, the total volume of the analyte solution is increased to $V = V_A + V_B$.

Assumptions:
- since HA is weak, amount of HA present is much greater than amount of A$^-$. 
- HA provides hydronium ions that far outnumber those arising from autoprotolysis of water.

At the starting point of the titration:

$$pH = \frac{1}{2} pK_a - \frac{1}{2} \log A_0$$
Acid-Base Titrations - Addition of Base

As some base is added (but well before stoichiometric point), the concentration of A- ions comes almost entirely from the following reaction (which formally is the formation of a salt, MA):

\[
HA(aq) + OH^-(aq) \rightarrow A^-(aq) + H_2O(l)
\]

Neglecting the small concentration of A- from the remaining weak acid, we can set \([A^-] = S\), where S is the salt concentration present after reaction of HA with the titrant.

At this point, \(n_{HA}\) remaining is \(A_0V_a\) minus the amount converted to salt, or:

\[
[HA] = A' = A_0V_a/V - S
\]

Then:

\[
K_a = \frac{a_{H_3O^+}a_{A^-}}{a_{HA}} = \frac{a_{H_3O^+}S}{A'}
\]

or:

\[
pH = pK_a - \log\frac{A'}{S}
\]
The Henderson-Hasselbelch Equation

\[ pH = pK_a - \log \frac{A'}{S} \]

\[ pH = pK_a - \log \frac{[\text{acid}]}{[\text{base}]} \]

When the molar concentration of acid and salt (acting as base) are equal:

\[ pH = pK_a \]

Hence the pKₐ of an acid can be measured directly from the pH of the mixture. Practically, this is accomplished by recording the pH during the titration and then examining the data for the pH halfway to the stoichiometric point.
Acid-Base Titrations

This buret contains the titrant.

This flask contains the solution to be titrated and the indicator.

\[ \text{pH} = \text{pK}_w + \log B' \]

\[ \text{pH} = \frac{1}{2} \text{pK}_a + \frac{1}{2} \text{pK}_w + \frac{1}{2} \log S \]

\[ \text{pH} = \text{pK}_a - \log(A'/S) \]

\[ \text{pH} = \frac{1}{2} \text{pK}_a - \frac{1}{2} \log A_0 \]

Volume of titrant

Half-way to the stoichiometric point

Stoichiometric point

Prof. Mueller

Chemistry 451 - Fall 2003

Lecture 22 - 15
Acid-Base Titrations - Stoichiometric Point

At the stoichiometric point, the hydronium ion concentration in the solution comes from the autoprotolysis of water, and the OH⁻ ions are produced by the reaction below:

\[ \text{A}^- (\text{aq}) + \text{H}_2\text{O (l)} \rightarrow \text{HA(aq)} + \text{OH}^- (\text{aq}) \]

Since only a small amount of HA is formed in this way, \([\text{A}^-] = S\), and \([\text{OH}^-] = [\text{HA}]\). Hence

\[ K_b = \frac{a_{HA}a_{OH^-}}{a_{A^-}} = \frac{[OH^-]^2}{S} \]

Using \(K_w = K_a K_b\), we can rearrange and substitute into the above equation and conclude that at the stoichiometric point:

\[ pH = \frac{1}{2} pK_a + \frac{1}{2} pK_w + \frac{1}{2} \log S \]
Acid-Base Titrations - “Exact” Solution

\[
\frac{V_B}{V_A} = \frac{K_a A_0 [H_3O^+]}{\left([H_3O^+] + K_a\right)^2 + B_0 [H_3O^+] - K_w}
\]

This equation is derived using

(a) Electrical neutrality
(b) Conservation of A- containing species
(c) Conservation of M⁺- containing species

and the definitions for \(K_a\) and \(K_w\).
Acid-Base Titrations - “Exact” Solution

\[
\frac{V_B}{V_A} = \frac{K_a A_0 [H_3O^+] + (K_w - [H_3O^+]^2)[H_3O^+] + K_a}{([H_3O^+] + K_a) ([H_3O^+]^2 + B_0 [H_3O^+] - K_w)}
\]
Buffer action takes advantage of the slow variation of the pH in the vicinity of $A' = S$ in the titration curve.

This gives the solution the ability to oppose changes in pH when small amounts of strong acids or bases are added.

Example: What is the pH of an aqueous buffer solution that contains 0.200 mol L$^{-1}$ KH$_2$PO$_4$ and 0.100 mol L$^{-1}$ K$_2$HPO$_4$?
Using Acid-Base Equilibria: Indicators

\[ \text{HIn(aq) + H}_2\text{O (l)} \rightleftharpoons \text{In}^- \text{(aq) + H}_3\text{O}^+(\text{aq}) \]

Normally, HIn is some large, water-soluble, weakly acidic organic molecule. Could be di-protic, such as phenolphthalein.

\[ \text{H}_2\text{In(aq) + 2H}_2\text{O} \rightleftharpoons \text{In}^2^- \text{(aq) + 2H}_3\text{O}^+ \]
Using Acid-Base Equilibria: Indicators

\[
\text{HIn}(aq) + \text{H}_2\text{O} \rightleftharpoons \text{In}^- (aq) + \text{H}_3\text{O}^+(aq)
\]

\[
K_{in} = \frac{a_{\text{H}_3\text{O}^+}a_{\text{In}^-}}{a_{\text{HIn}}}
\]

Then we can find the ratio of acid and base at a given pH:

\[
\log \left[ \frac{[\text{HIn}]}{[\text{In}^-]} \right] = pK_{in} - pH
\]

- pH < pK\text{in} \quad \text{indicator in acidic form}
- pH > pK\text{in} \quad \text{indicator in basic form}
- pH = pK\text{in} \quad \text{endpoint}

Choose an indicator so that the dramatic passing through the end-point coincides with the stoichiometric point of the titration.