1 Ionic Equilibria

1.1 Ionic Product of Water

$$H_2O \rightleftharpoons H^+ + OH^-$$

Definition 1.1: Ionic Product of Water K_w

The product of concentrations of H^+ and OH^- are always K_w=$1 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$ at 298 K.

As a result of this property of the equilibrium between disassociating H_2O, the concentration of one ion can be calculated once the concentration of the other is known.

1.2 pH and pOH

Equation 1.1: p Function

For some quantity X:

$$pX = \log_{10} X$$

Definition 1.2: pH

pH is a measure of the concentration of H^+ in a solution, calculated as:

$$pH = \log_{10} [H^+]$$

Definition 1.3: pOH

pH is a measure of the concentration of OH^- in a solution, calculated as:

$$pOH = \log_{10} [OH^-]$$

Note that at 298 K, $pH + pOH = pK_w = 14$.

1.3 Acid and Base Models

Ionic Equilibria typically use the Brønsted Acid and Base model, which involves the transfer of H^+.

Definition 1.4: Brønsted Acids and Bases

Brønsted-Lowry Acids are substances which donate protons while Brønsted-Lowry Bases receive protons.

Definition 1.5: Conjugate Acids and Bases

A Conjugate Acid or Base is the chemical substance obtained after a base recieves H^+ or a acid donates H^+ respectively.

1.4 Strength of Acids and Bases

$$HA \longrightarrow H^+ + A^-$$
$$BOH \longrightarrow B^+ + OH^-$$

Definition 1.6: Strong Acids and Bases

Strong Acids and Bases are substances which fully disassociate into H^+ and OH^- in aqueous solution.

$$HA \rightleftharpoons H^+ + A^-$$
$$BOH \rightleftharpoons B^+ + OH^-$$

Definition 1.7: Weak Acids and Bases

Weak Acids and Bases are substances which only partially disassociate into H^+ and OH^- in aqueous solution.

1.5 Weak Acids and Bases

Weak acids and bases disassociate according to a incomplete reaction and exist in equilibrium, hence acid and base disassociation reactions can be quantified through equilibrium constants as well.

$HA + H_2O \rightleftharpoons H_3O^+ + A^- \; K_C = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$

$BOH + H_2O \rightleftharpoons BH^+ + OH^- \; K_C = \frac{[BH^+][OH^-]}{[BOH][H_2O]}$

Notice that the non-simplified reactions of weak acid and weak base disassociation are psuedo-order with respect to H_2O because H_2O is present in large excess. As such, a simplified equilibrium constant for weak acid and weak base disassociation can be used instead.

Equation 1.2: Weak Acid Equilibrium Constant

For a weak acid which dissociates to equilibrium concentrations $[H^+]$, $[A^-]$ and $[HA]$,its equilibrium constant K_A is given by the equation

$$K_A = \frac{[H^+][A^-]}{[HA]}$$

Equation 1.3: Weak Base Equilibrium Constant

For a weak base which dissociates to equilibrium concentrations $[B^+]$, $[OH^-]$ and $[BOH]$,its equilibrium constant K_A is given by the equation

$$K_B = \frac{[B^+][OH^-]}{[HA]}$$

As with other equilibrium constants, the values of K_A and K_B are constant at any given temperature and do not vary with concentration.

Definition 1.8: Disassociation Constant

The disassociation constant α of a weak acid or base is the proportion of disassociated acid or base to original concentration of acid or base.

Equation 1.4: Disassociation Constant

$$\alpha = \frac{[A^-]_{\text{equilibrium}}}{[HA]_{\text{initial}}}$$

1.6 Salt Hydrolysis

Definition 1.9: Salt Hydrolysis

The disassociation of acids and bases will form H^+ or OH^- as well as a conjugate base A^- or acid B^+. If a solution contains these conjugate bases or acids, their reverse reaction of Salt Hydrolysis can occur.

$$A^- + H_2O \rightleftharpoons HA + OH^-$$
$$B^+ + H_2O \rightleftharpoons H^+ + BOH$$

As such, a 'fully reacted' weak acid or base solution still contains conjugate base or acids which will alter their pH.

Also notice that the product of the equilibrium constants of the initial disassociation reaction and the salt hydrolysis equation will be equal to that of K_w.

Equation 1.5: Relationship of K_A and K_B

$$K_A \times K_B = K_w$$

1.7 Buffer Solutions

Definition 1.10: Buffer Solution

A Buffer Solution is a solution which can resist change in its pH. Usually it contains a weak acid and its conjugate base in comparable proportions or a weak base and its conjugate acid in comparable proportions.

Equation 1.6: Henderson Hasselbach Equation

$$pH = pK_A + \lg \frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$pOH = pK_B + \lg \frac{[\mathrm{B^+}]}{[\mathrm{BOH}]}$$

Definition 1.11: Effective Buffer Region

The effective buffer region is the region of pH where a buffer solution is able to resist changes in pH, typically present within $pK_A \pm 1$ or $pK_B \pm 1$

Definition 1.12: Maximum Buffer Capacity

A Buffer solution is at maximum buffer capacity if it can resist the addition of acid and the addition of base equally well.

At maximum buffer capacity, the concentration of acid or base is equal to the concentration of conjugate salt. At this point in time, the lg term is numerically equal to zero, hence $pH = pK_a \text{or} pK_b$. As a result of this property, the point of maximum buffer capacity in a titration occurs at half of the volume of the equivalence point, where $pH = pK_A$.

1.8 Acid-Base Titration Curves

For a titration of weak acid against strong base:

Equation 1.7: Initial pH

Assuming $[\mathrm{HA}]_{\text{initial}} \approx [\mathrm{HA}]_{\text{equilibrium}}$

$$pH = -\lg \sqrt{K_A[\mathrm{HA}]}$$

Equation 1.8: pH in Buffer Region

When $|\lg \frac{[\mathrm{A^-}]}{[\mathrm{HA}]}| < 1$

$$pH = pK_A + \lg \frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

Equation 1.9: Equivalence Point pH

Assuming $[\mathrm{HA}]_{\text{initial}} \approx [\mathrm{A^-}]_{\text{endpoint}}$

$$pH = 14 - pOH = 14 + \lg \sqrt{\frac{K_w}{K_A}[\mathrm{HA}]}$$

1.9 Solubility Product

$$\mathrm{M_aX_b(s)} \rightleftharpoons \mathrm{aM^+(aq) + bX^-(aq)}\ K_C = \frac{[\mathrm{M^+}]^a[\mathrm{X^-}]^b}{[\mathrm{M_aX_b}]}$$

Since $[\mathrm{M_aX_b}]$ is approximately constant, the equilibrium constant of dissociation of a sparingly soluble salt can be presented as psuedo-order with respect to its solid salt.

Equation 1.10: Solubility Product K_sp

The Solubility Product K_{sp} of a sparingly soluble which disassociates to equilibrium concentrations $[\mathrm{M^+}]$ and $[\mathrm{A^-}]$ is given by the equation

$$K_{sp} = [\mathrm{M^+}]^a[\mathrm{X^-}]^b$$