The **Common-Ion Effect**

Le Chatelier's Principle for the equilibrium of an ionic solution: The shift in equilibrium caused by the addition of solute that is an ion initially present prior to the addition.

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

In which direction will the equilibrium above shift if HCl(aq) is added?

Since HCl is a strong acid, a dilute aqueous solution of it will contain only \(\text{H}_3\text{O}^+\) and \(\text{Cl}^-\). Addition of this solution to the equilibrium above will cause a shift to the left. Why?

In which direction will the equilibrium shift if NaSH(s) is added to the solution? Why?

In which direction will the equilibrium shift if NaOH(aq) is added to the solution? Why?

**Buffers**

A buffer is a solution that is capable of resisting changes in pH when limited amounts of acid or base are added to it.

Buffers are either solutions of a weak acid (HA) and the salt of its conjugate base (MA) or a weak base (B) and the salt of its conjugate acid (BHX).

(\(M^+=\) metal cation such as \(\text{Na}^+\), \(X^-\)= non-metal anion like \(\text{Cl}^-\), note \(M^+\) and \(X^-\) are spectator ions)

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

or

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

Buffer solutions are identified by their pH and buffer capacity, i.e. the amount of acid or base that the buffer can handle before showing a significant pH change. Typically the ratio of acid and conjugate base or the ratio of base and conjugate acid is close to 1 (between 0.1 and 10). This means that the buffer has a range of ±1 pH unit.

**Blood Buffer (only one component is shown)**

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

weak acid

conjugate base
Henderson-Hasselbalch Equation

Calculating the pH of a buffer solution:

When the buffer is made from HA and MA the equation is: \[ \text{pH} = \text{p}K_a + \log([A^-]/[HA]) \] where \( \text{p}K_a \) is the \( \text{p}K_a \) of HA.

When the buffer is made from B and BHX the equation \[ \text{pH} = \text{p}K_a + \log([B]/[BH^+]) \] where \( \text{p}K_a \) is the \( \text{p}K_a \) of BH^+.

Example: 0.108 moles of NaH_2PO_4 and 0.106 moles of Na_2HPO_4 are dissolved to make 1.00 liter of buffer solution. What is the pH of this buffer?

1) \( \text{p}K_a = -\log(K_a) \)

2) \( K_a = 6.2 \times 10^{-8} \) (this is given or looked up in a reference)

3) The acid is H_2PO_4^- and the base is HPO_4^{2-}

4) \( [A^-] = 0.106 \text{ moles}/1.00 \text{ liter} \) and \( [HA] = 0.108/1.00 \text{ L} \)

5) \[ \text{pH} = 7.21 + -0.00812 = 7.20 \] The buffer's pH is based on the \( \text{p}K_a \) of the acid. This is a general practice in making up buffers of a particular pH. If you want a buffer of a particular pH choose the weak acid whose \( \text{p}K_a = \text{pH} \). For an acidic buffer one looks up the \( \text{p}K_a \) of the weak acid (HA), for the base buffer one looks up the \( \text{p}K_a \) of the base’s conjugate acid (BH^+). In reality one doesn’t always find a perfect match of pH to \( \text{p}K_a \), but realize that the ratio of base to acid can tune the pH effectively.


A titration is a procedure in which increments of a known reagent solution-the titrant-are added to analyte until the reaction is complete, i.e. a stoichiometric amount of titrant has been added to completely react with the analyte.

An indicator is a compound with a physical property (usually color) that changes abruptly when a titration is complete. The change is caused by the disappearance of analyte or the appearance of excess titrant.

The equivalence point occurs when the quantity of titrant added is the exact amount necessary for stoichiometric reaction with analyte.

The equivalence point is the ideal result one seeks in a titration. What is usually measured is the endpoint which is marked by the sudden change in a physical property of the solution (indicator color change is one example).

\[
\begin{align*}
\text{NaOH (aq)} & \text{ + } \text{HCl (aq)} & \rightarrow & \text{H}_2\text{O(l)} & \text{ + } & \text{NaCl(aq)} \\
30 \text{ ml of 0.10M} & \text{ titrant} & \text{ + } & 15 \text{ ml of } ? \text{ M analyte} & & \\
\end{align*}
\]

What’s the concentration of HCl?
Phenolphthalein as Indicator

Phenolphthalein is a diprotic acid in its own right. If too much base is added one can fully deprotonate the indicator which absorbs light and appears dark pink. The endpoint of phenolphthalein is a very light pink. Why is this? What does this mean?