9.9: Buffers

Buffer solutions, which are of enormous importance in controlling pH in various processes, can be understood in terms of acid/base equilibrium. A buffer is created in a solution which contains both a weak acid and its conjugate base. This creates to absorb excess H^+ or supply H^+ to replace what is lost due to neutralization. The calculation of the pH of a buffer is straightforward using an ICE table approach.

> **Example 9.9.1:**
>
> What is the pH of a solution that is 0.150 M in KF and 0.250 M in HF?
>
> **Solution**
>
> The reaction of interest is
>
> $$HF \rightleftharpoons H^+ + F^-$$
>
> Let's use an ICE table!
>
> | | HF | H^+ | F^- |
> |---|---|---|---|
> | **Initial** | 0.250 M | 0 | 0.150 M |
> | **Change** | -x | +x | +x |
> | **Equilibrium** | 0.250 M - x | x | 0.150 M + x |

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

$$10^{-3.17} M = \frac{x(0.150\,M + x)}{0.250\,M - x}$$

This expression results in a quadratic relationship, leading to two values of x that will make it true. Rejecting the negative root, the remaining root of the equation indicates

$$[H^+] = 0.00111\,M$$

So the pH is given by

$$pH = -log_{10}(0.00111) = 2.95$$

For buffers made from acids with sufficiently large values of pK_a the buffer problem can be simplified since the concentration of the acid and its conjugate base will be determined by their pre-equilibrium values. In these cases, the pH can be calculated using the Henderson-Hasselbalch approximation.

If one considers the expression for K_a

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

Taking the log of both sides and multiplying by -1 yields

$$pK_a = pH - \log_{10}\frac{[A^-]}{[HA]}$$

An rearrangement produces the form of the Henderson-Hasselbalch approxmimation.

$$pH = pK_a - \log_{10}\frac{[A^-]}{[HA]}$$

It should be noted that this approximation will fail if:

1. the pk_a is too small,
2. the concentrations $[A^-]$ is too small, or
3. $[HA]$ is too small,

since the equilibrium concentration will deviate wildly from the pre-equilibrium values under these conditions.
