

## 8.2: Buffered Solutions

When it comes to buffer solution one of the most common equation is the [Henderson-Hasselbalch approximation](#). An important point that must be made about this equation is it's useful only if stoichiometric or initial concentration can be substituted into the equation for equilibrium concentrations.

### Origin of the Henderson-Hasselbalch Equation

Where the Henderson-Hasselbalch approximation comes from



where,

- $A^-$  is the conjugate base
- $HA$  is the weak acid

We know that  $K_a$  is equal to the products over the reactants and, by definition,  $H_2O$  is essentially a pure liquid that we consider to be equal to one.

$$K_a = [H_3O^+][A^-] \quad (8.2.2)$$

Take the  $-\log$  of both sides:

$$-\log K_a = -\log([H_3O^+][A^-]) \quad (8.2.3)$$

$$-\log K_a = -\log[H_3O^+] - \log[A^-] \quad (8.2.4)$$

Using the following two relationships:

$$-\log[K_a] = pK_a \quad (8.2.5)$$

$$-\log[H_3O^+] = pH \quad (8.2.6)$$

We can simplify the above equation:

$$pK_a = pH - \log[A^-] \quad (8.2.7)$$

If we add  $\log[A^-]$  to both sides, we get the **Henderson-Hasselbalch approximation**:

$$pH = pK_a + \log[A^-] \quad (8.2.8)$$

This approximation is only **valid** when:

1. The conjugate base / acid falls between the values of 0.1 and 10
2. The molarity of the buffers exceeds the value of the  $K_a$  by a factor of at least 100

#### ✓ Example 8.2.1

Suppose we needed to make a buffer solution with a pH of 2.11. In the first case, we would try and find a weak acid with a  $pK_a$  value of 2.11. However, at the same time the molarities of the acid and the its salt must be equal to one another. This will cause the two molarities to cancel; leaving the  $\log[A^-]$  equal to  $\log(1)$  which is zero.

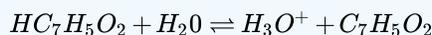
$$pH = pK_a + \log[A^-] = 2.11 + \log(1) = 2.11$$

This is a very unlikely scenario, however, and you won't often find yourself with Case #1

#### ✓ Example 8.2.2

What mass of  $NaC_7H_5O_2$  must be dissolved in 0.200 L of 0.30 M  $HC_7H_5O_2$  to produce a solution with pH = 4.78? (Assume solution volume is constant at 0.200L)

**Solution**



$$K_a = 6.3 \times 10^{-5}$$

$$K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} = 6.3 \times 10^{-5}$$

$$[H_3O^+] = 10^{-pH} = 10^{-4.78} = 16.6 \times 10^{-6} \text{ M} \quad [HC_7H_5O_2] = 0.30 \text{ M} \quad [C_7H_5O_2^-] =$$

$$[C_7H_5O_2^-] = K_a \times \frac{[HC_7H_5O_2]}{[H_3O^+]}$$

$$1.14 \text{ M} = 6.3 \times 10^{-5} \times \frac{0.30}{16.6 \times 10^{-6}}$$

Mass = 0.200 L x 1.14 mol C<sub>7</sub>H<sub>5</sub>O<sub>2</sub><sup>-</sup> / 1L x 1mol NaC<sub>7</sub>H<sub>5</sub>O<sub>2</sub> / 1 mol C<sub>7</sub>H<sub>5</sub>O<sub>2</sub><sup>-</sup> x 144 g NaC<sub>7</sub>H<sub>5</sub>O<sub>2</sub> / 1 mol NaC<sub>7</sub>H<sub>5</sub>O<sub>2</sub> = 32.832 g NaC<sub>7</sub>H<sub>5</sub>O<sub>2</sub>

## References

1. Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey 2007.

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