

Overview of acid-base calculations, CHI02 Spring 2017

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In lectures we will present a framework based on a weak acid solution to which may be added different amounts of a sodium hydroxide solution. Here is a brief overview of the kinds of calculations you will need to know,

The goal is to calculate the hydronium ion concentration for the following four circumstances: (1) the initial weak acid solution, (2) the solution resulting from adding some hydroxide ion, but not enough to react with all of the weak acid present, (3) the solution resulting from adding exactly as many moles of hydroxide ion as there were moles of weak acid originally present (the equivalence point), and (4) the solution resulting from adding more moles of hydroxide ion than there were moles of weak acid originally present.

When you are confronted with an acid-base problem, determine which of the four circumstances applies, and then carry out the corresponding calculations. In the example below, assume the temperature is 25 °C.

1. Pure weak acid

The hydronium ion concentration of a weak acid solution is given by

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

As we have seen in lectures, since $K_a \ll 1$ the equilibrium concentration of the unreacted acid, $[\text{HA}]_e$, is approximately that of the unreacted acid, c_a . Also, as we have seen, since $K_a \gg K_w$, the amount of acid that reacts with water, x , is much greater than the hydronium ion concentration initially present in pure water, and so $[\text{H}_3\text{O}^+] \approx [\text{A}^-]_e = x$. With these approximations, we can express the hydronium concentration as

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]_e}{[\text{A}^-]_e} \approx x \approx K_a \frac{c_a}{x}$$

and so

$$x \approx \sqrt{K_a c_a}$$

As example, the hydronium concentration of a 0.32 M solution of acid with $K_a = 1.6 \times 10^{-6}$ is 7.2×10^{-4} M.

2. Some weak acid and some of its conjugate base

If volume V_b of hydroxide ion solution of concentration c_b is added, $c_b V_b$ moles of hydroxide ion will react with that number of moles of acid to form conjugate base. If the moles of hydroxide ion added is not enough to react with all of the weak acid present, then the concentration of unreacted acid will be

$$[\text{HA}]_e \approx \frac{c_a V_a - c_b V_b}{V_a + V_b}$$

and the concentration of its conjugate base will be

$$[\text{A}^-]_e \approx \frac{c_b V_b}{V_a + V_b}$$

The reason these are each approximately equal to the equilibrium concentrations is again that $K_a \ll 1$. Therefore, we can express the hydronium concentration as

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]_e}{[\text{A}^-]_e} \approx x \approx K_a \frac{(c_a V_a - c_b V_b)/(V_a + V_b)}{c_b V_b/(V_a + V_b)}$$

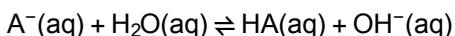
and so

$$x \approx K_a \frac{c_a V_a - c_b V_b}{c_b V_b}$$

As example, adding 240. mL of 0.32 M NaOH solution to 500. mL of a 0.32 M solution of acid with $K_a = 1.6 \times 10^{-6}$, the resulting hydronium concentration is 1.7×10^{-6} M.

3. Pure conjugate base (exact neutralization)

If the moles of hydroxide ion added equals the moles of acid initially present, then all of the acid will be converted to conjugate base. In this case (and in this case only), we need to use a different chemical equilibrium, namely the reaction of the conjugate base with water to reform the weak acid,



We will see in lecture that the equilibrium constant is $K_b = K_w/K_a$, and because $K_a \gg K_w$, K_b will be small compared to 1; that is, the conjugate base of a weak acid acts as a weak base. This means that at equilibrium, most of the conjugate base will remain unreacted,

$$[\text{A}^-]_e \approx \frac{c_b V_b}{V_a + V_b}$$

and the small amount, y , that does react gives the equilibrium concentrations of the reformed weak acid and of hydroxide ion,

$$y \approx [\text{HA}]_e = [\text{OH}^-]_e$$

Using the equilibrium constant for the reaction of the weak acid conjugate base with water, the hydroxide ion concentration is as

$$[\text{OH}^-] = K_b \frac{[\text{A}^-]_e}{[\text{HA}]_e} \approx y \approx K_b \frac{c_b V_b/(V_a + V_b)}{y}$$

and so

$$y \approx \sqrt{K_b \frac{c_b V_b}{V_a + V_b}}$$

Once the hydroxide ion concentration is calculated, the hydronium ion concentration can be calculated from $[\text{H}_3\text{O}^+] = K_w/[\text{OH}^-]_e = K_w/y$. As example, adding 500. mL of 0.32 M NaOH solution to 500. mL of a

0.32 M solution of acid with $K_a = 1.6 \times 10^{-6}$, the resulting hydroxide concentration is 3.2×10^{-5} M and the corresponding hydronium concentration is 3.2×10^{-10} M.

4. Excess strong base (past exact neutralization)

If the moles of hydroxide ion added exceeds the moles of acid initially present, then all of the acid will be converted to conjugate base and there will be $c_b V_b - c_a V_a$ moles of hydroxide ion left over. Again, the weak acid conjugate base will react with water to form additional hydroxide ions, but because the weak acid conjugate base is a weak base, this additional source of hydroxide ions will be negligible compared with the left over hydroxide ions, Therefore, in this case,

$$[\text{OH}^-]_e = \frac{c_b V_b - c_a V_a}{V_a + V_b}$$

and so

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]_e}$$

As example, adding 525. mL of 0.32 M NaOH solution to 500. mL of a 0.32 M solution of acid with $K_a = 1.6 \times 10^{-6}$, the resulting hydroxide concentration is 0.0078 M and the corresponding hydronium concentration is 1.3×10^{-12} M.