Buffer action challenge question

CH102 General Chemistry, Spring 2009

http://quantum.bu.edu/notes/GeneralChemistry/BufferActionChallenge.pdf
Last updated Monday, April 6, 2009 16:20:46-05:00

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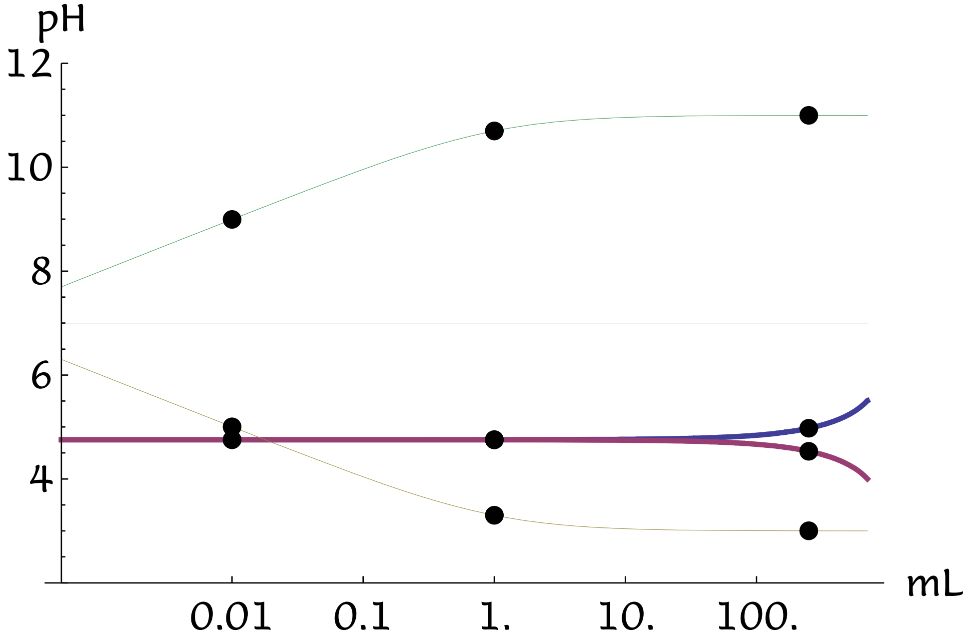

The figure compares the effect on pH of adding 0.001 M strong acid (downward changing curves) and 0.001 M strong base (upward changing curves) to 1 mL = 0.001 L of water (thin lines) and to 1000 mL = 1 L of a buffer (thick lines) consisting of 0.001 M acetic acid $\left(K_a = 1.76 \times 10^{-5}\right)$ and 0.001 M sodium acetate. The horizontal line marks pH = 7 of pure water. Note that the volume is on a logarithmic scale, and extends to 500 mL of added acid or base. The figure illustrates how the buffer is able to resist significant change in pH over a wide range of added acid or base.

The challenge is to calculate the twelve pH values corresponding to three dots on each curve, namely for volumes of added acid and base equal to 0.01, 1, and 250 mL.

■ Answer

In the numerical examples below, each quantity is treated as having three significant figures, but trailing zeros are not shown.

Adding strong acid to a buffer

When strong acid is added to a buffer solution, the added acid reacts the buffer conjugate base, A^-, to form additional buffer undissociated acid, HA. This changes the composition of the buffer to

$$c_a \to \frac{\text{moles of buffer HA} + \text{moles of added acid}}{\text{total volume}} = \frac{c_a\,V_\text{buffer} + c_{a,\text{added}}\,V_{a,\text{added}}}{V_\text{buffer} + V_{a,\text{added}}},$$

$$c_b \to \frac{\text{moles of buffer A}^- - \text{mol es of added acid}}{\text{total volume}} = \frac{c_b\,V_\text{buffer} - c_{a,\text{added}}\,V_{a,\text{added}}}{V_\text{buffer} + V_{a,\text{added}}},$$

and so the concentration ratio becomes

$$\frac{c_a}{c_b} \to \frac{c_a\,V_\text{buffer} + c_{a,\text{added}}\,V_{a,\text{added}}}{c_b\,V_\text{buffer} - c_{a,\text{added}}\,V_{a,\text{added}}}.$$

For the example of 250 mL of 0.001 M HCl added to 1 L of a 0.001 M acetic acid equimolar buffer, the hydronium concentration is

$$\begin{aligned}\left[H_3O^+\right] &= K_a\,\frac{c_a}{c_b} \to 1.76\times10^{-5}\,\frac{c_a\,V_\text{buffer} + c_{a,\text{added}}\,V_{a,\text{added}}}{c_b\,V_\text{buffer} - c_{a,\text{added}}\,V_{a,\text{added}}}\\ &= 1.76\times10^{-5}\,\frac{0.001\times1 + 0.001\times0.25}{0.001\times1 - 0.001\times0.25} = 2.93\times10^{-5}\end{aligned}$$

and so the pH is $-\log\left(2.93\times10^{-5}\right) = 4.533$.

Adding strong base to a buffer

When strong base is added to a buffer solution, the added base reacts the buffer acid, HA, to form additional buffer conjugate base, A^-. This changes the composition of the buffer to

$$c_a \to \frac{\text{moles of buffer HA} - \text{moles of added base}}{\text{total volume}} = \frac{c_a\,V_\text{buffer} - c_{b,\text{added}}\,V_{b,\text{added}}}{V_\text{buffer} + V_{b,\text{added}}},$$

$$c_b \to \frac{\text{moles of buffer A}^- + \text{moles of added base}}{\text{total volume}} = \frac{c_b\,V_\text{buffer} + c_{b,\text{added}}\,V_{b,\text{added}}}{V_\text{buffer} + V_{b,\text{added}}},$$

and so the concentration ratio becomes

$$\frac{c_a}{c_b} \to \frac{c_a\,V_\text{buffer} - c_{b,\text{added}}\,V_{b,\text{added}}}{c_b\,V_\text{buffer} + c_{b,\text{added}}\,V_{b,\text{added}}}.$$

For the example of 1 mL of 0.001 M NaOH added to 1 L of a 0.001 M acetic acid equimolar buffer, the hydronium concentration is

$$\left[H_3O^+\right] = K_a \frac{c_a}{c_b} \to 1.76\times10^{-5}\,\frac{c_a\,V_{\text{buffer}} - c_{b,\text{added}}\,V_{b,\text{added}}}{c_b\,V_{\text{buffer}} + c_{b,\text{added}}\,V_{b,\text{added}}}$$

$$= 1.76\times10^{-5}\,\frac{0.001\times1 - 0.001\times0.001}{0.001\times1 + 0.001\times0.001} = 1.756\times10^{-5}$$

and so the pH is $-\log\left(1.756\times10^{-5}\right) = 4.755$.

Adding to strong acid to pure water

When strong acid is added to water, reaction with water is effectively 100 %, and so the hydronium ion concentration is the moles of acid added divided by the total volume,

$$\left[H_3O^+\right] = \frac{\text{mol acid}}{\text{total volume}} = \frac{c_a\,V_a}{V_a + V_w}$$

where c_a and V_a are the concentration and volume of the added acid and V_w is the volume of the water. For the example of 250. mL of 0.001 M HCl added to 1.00 L of water,

$$\left[H_3O^+\right] = \frac{0.00100\ \text{mol}/\text{L}\times0.25\ \text{L}}{0.25\ \text{L} + 0.001\ \text{L}} = \frac{2.5\times10^{-4}\ \text{mol}}{0.251\ \text{L}} = 9.96\times10^{-4}\ \text{mol}/L.$$

and so the pH is $-\log\left(9.96\times10^{-4}\right) = 3.002$.

Adding to strong base to pure water

When strong base is added to water, reaction with water is effectively 100%, and so the hydroxide ion concentration is the moles of base added divided by the total volume,

$$[OH^-] = \frac{\text{mol base}}{\text{total volume}} = \frac{c_b\,V_b}{V_b + V_w}$$

where c_b and V_b are the concentration and volume of the added base and V_w is the volume of the water. For the example of 0.0100 mL of 0.00100 M NaOH added to 1.00 mL of water,

$$[OH^-] = \frac{0.001\ \text{mol}/\text{L}\times1\times10^{-5}\ \text{L}}{1\times10^{-5}\ \text{L} + 1\times10^{-3}\ \text{L}} = \frac{1\times10^{-8}\ \text{mol}}{1.01\times10^{-3}\ \text{L}} = 9.90\times10^{-6}\ \text{mol}/\text{L}$$

and so the pH is $14 + \log\left(9.90\times10^{-6}\right) = 8.996$.