DEEP DIVE: BUFFER PROBLEM WITH MOLES INSTEAD OF CONCENTRATIONS

(V 2.0, APRIL 27, 2021)

1. Purpose

This Deep Dive covers in detail **Problem #34** under the buffer problems. The problem is solved approximately and then an attempt is made to solve it exactly. It turns out that the problem can NOT be solved exactly.

2. Problem Statement

> You need to produce a buffer solution that has a pH of 5.270. You already have a solution that contains 10.0 mmol (millimoles) of acetic acid. How many millimoles of sodium acetate will you need to add to this solution? The pK_a of acetic acid is 4.752.

3. HH Quick Solution

Use the HH equation for a quick (but perhaps approximate) answer

$$pH = pK_a + \log_{10}\left\{\frac{[Ac^-]}{[HAc]}\right\}$$

The ratio of the concentrations equals the ratio of the moles

$$pH = pK_a + \log_{10}\left\{\frac{n(Ac^-)}{n(HAc)}\right\}$$

These are the *equilibrium* number of moles. **Assume** that these can be replaced by the *initial* number of moles

$$pH \approx pK_a + \log_{10}\left\{\frac{n_\circ(Ac^-)}{n_\circ(HAc)}\right\}$$

Note the "$\approx$" above. Plug in numbers

$$5.270 \approx 4.752 + \log_{10}\left\{\frac{n_\circ(Ac^-)}{10.0 \text{ mmol}}\right\}$$

Solve for the initial milli-moles of Ac^- and round to the appropriate place

$$n_\circ(Ac^-) = 32.\underline{9}6097 \qquad \longrightarrow \qquad \boxed{n_\circ(Ac^-) \approx 33.0 \text{ mmol}}$$

4. Attempting Exact Solution

In the above we assumed that the *equilibrium* amounts can be replaced by the *initial* amounts. This is the "usual" HH assumption. However, this approximation worsens as the amounts themselves get small. Here we are dealing with milli-moles so perhaps it is worth checking the above answer with the exact answer?

The detailed (exact) method of solving acid-base problems involves these four ideas.

4.1. Conservation of Mass (or moles as appropriate).

The acetate group CH_3COO or Ac is present initially in the acetic acid HA solution and present initially in the sodium acetate NaAc solution added. After equilibrium is reached, the Ac group will be present as acetic acid HAc and the acetate ion Ac^-. Thus we can write

$$n_\circ(HAc) + n_\circ(NaAc) = n(HAc) + n(Ac^-) \tag{4.1}$$

However, the initial moles of sodium acetate will equal the initial moles of sodium ion Na^+ and that is a spectator ion so its number of moles never change

$$n_\circ(NaAc) = n_\circ(Na^+) = n(Na^+)$$

The initial moles of HAc is given as 10.0 mmol = 0.0100 mol. We can use these to write eq. (4.1) as

$$\boxed{0.0100 + n(Na^+) = n(HAc) + n(Ac^-)}$$

4.2. **Conservation of Charge.** The total positive charge must equal the total negative charge at all times and in particular at equilibrium. The H^+ and Na^+ are the only positive ions while Ac^- and OH^- are the only negative ions

$$\boxed{n(H^+) + n(Na^+) = n(Ac^-) + n(OH^-)}$$

4.3. **Equilibrium of the Acid and Base.** Apply the Law of Mass Action to the weak acid HAc

$$K_a = \frac{[H^+] \cdot [Ac^-]}{[HAc]}$$

The ratio of two of the concentrations can be written as a ratio of moles

$$\boxed{K_a = [H^+] \cdot \frac{n(A^-)}{n(HA)}}$$

4.4. **Equilibrium of Water (Auto-Ionization).** Apply the Law of Mass Action to water H_2O

$$\boxed{K_w = [H^+] \cdot [OH^-]}$$

4.5. **Givens.** We are given the following values

$$K_a = 10^{-4.752} \qquad K_w = 10^{-14} \qquad [H^+] = 10^{-5.270}$$

4.6. **With Numbers.** If we plug these into the four boxed equations above we get

$$0.010 + n(Na^+) = n(HA) + n(A^-) \qquad \text{mole balance on species A}$$
$$n(H^+) + n(Na^+) = n(A^-) + n(OH^-) \qquad \text{charge balance}$$
$$10^{-4.752} = 10^{-5.270} \cdot \frac{n(A^-)}{n(HA)} \qquad \text{equilibrium for weak acid}$$
$$10^{-14} = 10^{-5.270} \cdot [OH^-] \qquad \text{equilibrium for water}$$

The last equation gives

$$[OH^-] = 10^{-8.730}$$

We could also write these two equations

$$[H^+] = 10^{-5.270} = \frac{n(H^+)}{V} \qquad \Longrightarrow \qquad n(H^+) = V \cdot 10^{-5.270}$$

$$\text{and} \qquad [OH^-] = 10^{-8.730} = \frac{n(OH^-)}{V} \qquad \Longrightarrow \qquad n(OH^-) = V \cdot 10^{-8.730}$$

We can use these to replace $n(H^+)$ and $n(OH^-)$ in the three remaining equations and get

$$0.010 + n(Na^+) = n(HA) + n(A^-)$$
$$V \cdot 10^{-5.170} + n(Na^+) = n(A^-) + V \cdot 10^{-8.730}$$
$$10^{-4.752} = 10^{-5.270} \cdot \frac{n(A^-)}{n(HA)}$$

We can do a lot of algebraic manipulation of the above but the fact remains that these three equations have these four unknowns

$$n(Na^+) \qquad n(HA) \qquad n(A^-) \qquad V$$

It is NOT possible to solve these and so it is NOT possible to solve this problem exactly.

5. Conclusion

The initial state gives 10.0 mmol of HA present instead of the concentration. The volume V does not cancel in the exact method so we need to know it. The problem statement is *extensive* (meaning the size of the system matters). If instead the initial <u>concentration</u> of HA had been given, then the problem would be *intensive* (meaning the size of the system does not matter). In that case, we could have solved the problem exactly.