

Deep Dive: Bonus Buffer Problem

1. PROBLEM STATEMENT

We need to prepare an acetate buffer with pH = 6.420. On the shelf we have available a flask labeled **0.664 M Acetic Acid**

The flask contains 975 mL of solution.

- Find the pH of the contents of the flask.
- Create the buffer using two different methods:

Method A: By combining the entire contents of the flask with pure water.

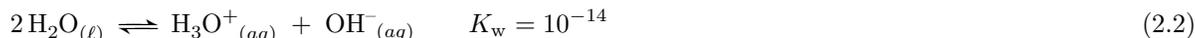
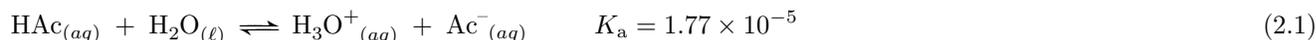
Method B: By combining the entire contents of the flask with 2.50 M KOH solution.

Find the volumes that would be needed for each method.

Data: For acetic acid is $K_a = 1.77 \times 10^{-5}$.

2. INITIAL FLASK

The flask contains 975 mL of 0.664 M acetic acid solution. Within that flask the following reactions have reached equilibrium (with their associated equilibrium constant)



What follows is a extremely detailed method of analyzing this problem. No matter how much of the HAc dissociates the following four things will be true.

- We will always have conservation of mass

$$\text{Conservation of Mass:} \quad [\text{HAc}] + [\text{Ac}^-] = 0.664 \text{ M} \quad (2.3)$$

- We will always have electroneutrality (conservation of charge)

$$\text{Conservation of Charge:} \quad [\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{Ac}^-] \quad (2.4)$$

- We will always have equilibrium expression for the dissociation of HAc

$$\text{Equilibrium WA:} \quad K_a = \frac{[\text{H}_3\text{O}^+] \cdot [\text{Ac}^-]}{[\text{HAc}]} \quad (2.5)$$

- We will always have equilibrium expression for the autoionization of water

$$\text{Equilibrium Water:} \quad K_w = [\text{H}_3\text{O}^+] \cdot [\text{OH}^-] \quad (2.6)$$

The equilibrium constants are known ($K_a = 1.77 \times 10^{-5}$ and $K_w = 10^{-14}$). Thus, the four equations eqs. (2.3) to (2.6) have these four unknowns

$$[\text{H}_3\text{O}^+] \quad \text{and} \quad [\text{OH}^-] \quad \text{and} \quad [\text{HAc}] \quad \text{and} \quad [\text{Ac}^-]$$

Solving numerically for the results we get (an unrealistic number of sig figs are shown and then rounded)

$$[\text{HAc}] = 0.66058060288 \quad \approx 0.661 \text{ M}$$

$$[\text{Ac}^-] = 3.41939711952 \times 10^{-3} \quad \approx 0.00342 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 3.41939712245 \times 10^{-3} \quad \approx 0.00342 \text{ M}$$

$$[\text{OH}^-] = 2.92449213762 \times 10^{-12} \quad \approx 2.92 \times 10^{-12} \text{ M}$$

Some observations:

- The flask initially contains the above (as well as water with $[\text{H}_2\text{O}] = 55.5 \text{ M}$). Apart from H_2O , the dominate species present in the flask initially is HAc. Its concentration is about 200 times larger than Ac^- and H_3O^+ and about 10^{11} times larger than OH^- .

- (ii) The concentration of the Ac^- and H_3O^+ are slightly different because of the autoionization of water. However, they match to eight sig figs which is way, way beyond anything experimental.
- (iii) The initial contents of the flask is quite acidic

$\text{pH} = 2.466$

3. QUICKER APPROXIMATION

Normally these type of weak acid problems are solved more simply. We first note that in this problem

$$K_a \gg K_w \quad \implies \quad K_w \approx 0$$

That is, K_a is so much larger than K_w that we could consider K_w to be essentially zero in this problem. In other words, reaction eq. (2.1) for HA dissociation dominates reaction eq. (2.2) for the dissociation of water.

We can use this observation to uncouple the four equations eqs. (2.3) to (2.6). Since K_w is so small we solve eq. (2.6) for the concentration of OH^- and then find

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} \approx 0$$

The concentration of the hydroxide ion is so small that the conservation of charge (eq. (2.4)) gives

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{Ac}^-] \quad \implies \quad [\text{H}_3\text{O}^+] \approx [\text{Ac}^-] \quad (\text{CENTRAL APPROXIMATION})$$

The concentration of mass (eq. (2.3)) becomes

$$[\text{HAc}] = 0.664 - [\text{Ac}^-] \quad \implies \quad [\text{HAc}] \approx 0.664 - [\text{H}_3\text{O}^+]$$

Using these in eq. (2.5) we get

$$K_a = \frac{[\text{H}_3\text{O}^+] \cdot [\text{Ac}^-]}{[\text{HAc}]} \quad \implies \quad K_a \approx \frac{[\text{H}_3\text{O}^+] \cdot [\text{H}_3\text{O}^+]}{0.664 - [\text{H}_3\text{O}^+]}$$

Plugging in for K_a and letting $x = [\text{H}_3\text{O}^+]$ we get

$$1.77 \times 10^{-5} = \frac{x \cdot x}{0.664 - x} \quad \implies \quad x = 3.4195 \times 10^{-3}$$

This numerical results here matches the previous ones to within several sig figs.

In fact, normally we even make a further approximation to simplify the quadratic equation

$$1.77 \times 10^{-5} = \frac{x \cdot x}{0.664 - x} \approx \frac{x \cdot x}{0.664} \quad \implies \quad x \approx \sqrt{0.664 \cdot 1.77 \times 10^{-5}} = 3.4282 \times 10^{-3}$$

This second approximation gives $[\text{H}_3\text{O}^+]$ that is only about 0.3% off from the exact result from the previous section.

The point here is not that the normal approximations save us time. That is obviously always true. The point is that we are making approximations not just in the mathematics but to the chemistry. We should be aware that these approximations may not always work.

If either K_a or the initial concentration of HAc were smaller in this problem, then the usual approximations would not work.

4. METHOD A: DILUTION USING PURE WATER

We need to dilute the solution in the flask. The initial concentration is 0.664 M with an initial volume of 0.975 L. We can use the dilute formula $M_1 \cdot V_1 = M_2 \cdot V_2$ to the initial HAc concentration

$$\underbrace{[\text{HAc}]_o \cdot V}_{\text{original}} = \underbrace{[\text{HAc}]_o \cdot V}_{\text{new}}$$

and get

$$(0.664 \text{ M}) \cdot (0.975 \text{ L}) = [\text{HAc}]_o \cdot V \quad \implies \quad [\text{HAc}]_o = \frac{0.664 \text{ M} \cdot 0.975 \text{ L}}{V} = \frac{0.6474}{V} \quad (4.1)$$

where V is the unknown final volume which is made up of the original 0.975 L and the unknown added water.

We know that the final pH must be 6.420. Therefore, the final equilibrium concentration of H_3O^+ will be

$$[\text{H}_3\text{O}^+] = 10^{-6.420} = 3.80 \times 10^{-7} \text{ M}$$

Using these changes, the four governing equations eqs. (2.3) to (2.6) would become

$$\begin{aligned}
 \text{Conservation of Mass:} & \quad [\text{HAc}] + [\text{Ac}^-] = \frac{0.6474}{V} \\
 \text{Conservation of Charge:} & \quad 3.80 \times 10^{-7} = [\text{OH}^-] + [\text{Ac}^-] \\
 \text{Equilibrium WA:} & \quad K_a = \frac{3.80 \times 10^{-7} \cdot [\text{Ac}^-]}{[\text{HAc}]} \\
 \text{Equilibrium Water:} & \quad K_w = 3.80 \times 10^{-7} \cdot [\text{OH}^-]
 \end{aligned}$$

where the unknowns are now

$$V \quad \text{and} \quad [\text{OH}^-] \quad \text{and} \quad [\text{HAc}] \quad \text{and} \quad [\text{Ac}^-]$$

Solving them we get

$$\begin{aligned}
 [\text{HAc}] &= 7.60135463698 \times 10^{-9} \approx 7.60 \times 10^{-9} \text{ M} \\
 [\text{Ac}^-] &= 3.53886716402 \times 10^{-7} \approx 3.54 \times 10^{-7} \text{ M} \\
 V &= 1.79093046733 \times 10^6 \approx 1.79 \times 10^6 \text{ L} \\
 [\text{OH}^-] &= 2.630267991 \times 10^{-8} \approx 2.63 \times 10^{-8} \text{ M}
 \end{aligned}$$

The final volume is insanely large

1.79 million Liters

This would fill more than two-thirds of an Olympic swimming pool.

In practice, to make the buffer just through dilution we would only a *tiny* sample from the original flask and then dilute that to achieve the desired pH. For example, we could pipette out one micro-liter (1.0×10^{-6} L) from the original flask and then enough water to that to make 1.84 L.

5. WHY DOES THE “DILUTION FORMULA” NOT WORK?

The so-called dilution formula is given in textbooks as

$$\boxed{M_1 \cdot V_1 = M_2 \cdot V_2} \tag{5.1}$$

One can apply this to the initial HAc charged into the flask. This is exactly what we did above in eq. (4.1). However, we would be using it only for the initial salt placed in the flask.

This formula can not be applied to the final equilibrium concentrations. That is, the original concentration of the hydronium ion is

$$\text{pH} = 2.466 \quad \implies \quad [\text{H}_3\text{O}^+]_{old} = 10^{-2.466}$$

and the desired concentration of the hydronium ion is

$$\text{pH} = 6.420 \quad \implies \quad [\text{H}_3\text{O}^+]_{new} = 10^{-6.420}$$

We can NOT use the dilution formula to write

$$10^{-2.466} \cdot (0.975 \text{ L}) = 10^{-6.420} \cdot V \quad \implies \quad V = 8770 \text{ L}$$

This volume is wrong. It is off by a factor of ~ 200 because we have ignored the equilibrium reaction eq. (2.1) for the weak acid HAc. The decrease in H_3O^+ concentration from dilute will cause more HAc to dissociate to produce more H_3O^+ but this requires more dilution.

The dilution formula eq. (5.1) really only works for initial amounts charged to flasks. It does work for equilibrium concentrations for salts and strong acids and bases because those completely dissociate. Those reactions are completely shifted to the right.

6. METHOD B: USING A STRONG BASE

Next, we need to add an unknown amount of the 2.50 M KOH to this flask so that the final pH = 6.420. Since KOH is a strong base its dissociation reaction is completely shifted to the right



Let V represent the final volume. This is made up of the original volume 0.975 L and the volume of the KOH added. The previous result eq. (4.1) can be used for the new initial HAc concentration

$$[\text{HAc}]_o = \frac{0.664 \text{ M} \cdot 0.975 \text{ L}}{V} = \frac{0.6474}{V}$$

The above will be used in the conservation of mass equation below. The final equilibrium concentration of H_3O^+ will be

$$[\text{H}_3\text{O}^+] = 10^{-6.420} = 3.80 \times 10^{-7} \text{ M}$$

This will be used in the conservation of charge equation below. Note also that K^+ is another positive ion in this problem and contributed to the conservation of charge. The final equilibrium concentration of the potassium ion is found using the dilution formula

$$\underbrace{[\text{K}^+] \cdot V}_{\text{added}} = \underbrace{[\text{K}^+] \cdot V}_{\text{at end}}$$

The added volume of the KOH is the final volume V minus the volume in the original flask 0.975 L

$$(2.50 \text{ M}) \cdot (V - 0.975 \text{ L}) = [\text{K}^+] \cdot V \quad \implies \quad [\text{K}^+] = 2.50 \text{ M} \cdot \frac{V - 0.975 \text{ L}}{V} = 2.50 - \frac{2.4375}{V}$$

The conservation of charge equation below includes this.

$$\text{Conservation of Mass:} \quad [\text{HAc}] + [\text{Ac}^-] = \frac{0.6474}{V} \quad (6.1)$$

$$\text{Conservation of Charge:} \quad 3.80 \times 10^{-7} + 2.50 - \frac{2.4375}{V} = [\text{OH}^-] + [\text{Ac}^-] \quad (6.2)$$

$$\text{Equilibrium WA:} \quad K_a = \frac{3.80 \times 10^{-7} \cdot [\text{Ac}^-]}{[\text{HAc}]} \quad (6.3)$$

$$\text{Equilibrium Water:} \quad K_w = 3.80 \times 10^{-7} \cdot [\text{OH}^-] \quad (6.4)$$

Solving numerically for the results we get (an unrealistic number of sig figs are shown and then rounded)

$$\begin{aligned} [\text{HAc}] &= 1.10812680035 \times 10^{-2} \approx 0.0111 \text{ M} \\ [\text{Ac}^-] &= 5.15896670345 \times 10^{-1} \approx 0.516 \text{ M} \\ V &= 1.22851442705 \approx 1.23 \text{ L} \\ [\text{OH}^-] &= 2.6302679919 \times 10^{-8} \approx 2.63 \times 10^{-8} \text{ M} \end{aligned}$$

The amount of KOH that needs to be added is

$$1.2285 \text{ L} - 0.975 \text{ L} = 0.253514427053 \text{ L} \quad \implies \quad \boxed{254 \text{ mL}} \quad (6.5)$$

7. QUICKER APPROXIMATION

There is a quicker way to solve this problem. First, substitute the HAc from the conservation of mass equation eq. (6.1) directly into the equilibrium expression for the weak acid eq. (6.3)

$$K_a = \frac{3.80 \times 10^{-7} \cdot [\text{Ac}^-]}{\frac{0.6474}{V} - [\text{Ac}^-]} \quad \text{or} \quad K_a = \frac{3.80 \times 10^{-7} \cdot V \cdot [\text{Ac}^-]}{0.6474 - V \cdot [\text{Ac}^-]}$$

Solve this for the product $V \cdot [\text{Ac}^-]$

$$V \cdot [\text{Ac}^-] = 0.6337865023888 \quad (7.1)$$

Note that the above is not an approximation. It represents the exact number of moles of Ac^- that remain at equilibrium.

Next, since K_w is small compared with K_a we can set $[\text{OH}^-] \approx 0$ in the conservation of charge equation

$$[\text{Ac}^-] \approx 3.80 \times 10^{-7} + 2.50 - \frac{2.4375}{V}$$

Multiply through by V and replace 2.4375 with $2.50 \cdot 0.975$ so we can factor out the 2.50

$$V \cdot [\text{Ac}^-] \approx 2.50 \cdot (V - 0.975) + V \cdot 3.80 \times 10^{-7}$$

The second term above is much smaller than the first term. We ignore it and get

$$V \cdot [\text{Ac}^-] \approx 2.50 \cdot (V - 0.975) \quad \implies \quad (V - 0.975) \approx \frac{V \cdot [\text{Ac}^-]}{2.50}$$

where $V - 0.975$ represents the volume of KOH solution added.

Using the previous exact result from eq. (7.1) on the right-hand side we get

$$(V - 0.975) \approx \frac{0.6337865023888}{2.50} = 0.253\,514\,600\,955\text{ L}$$

This matches the exact result from eq. (6.5) to six sig figs.