Problem # 1. Titration Curve (1 point)
Hypochlorous acid (HOCl) is used as a disinfectant in water and wastewater treatment. For purposes of disinfection HOCl is the preferred species in solution (HOCl can be as much as 100x as effective as OCl⁻ as a disinfectant). However, it is more convenient to add the chemical as NaOCl. Determine the pH of a 10⁻³F NaOCl solution and draw a titration curve for this solution indicating the pH at the beginning, middle and end of the titration.

Approach
- addition of a simple monoprotic acid to water
- prepare Log C vs pH diagram and solve using the two possible PBEs

Starting pH, Use PBE for a pure OCl⁻ solution
\[ [H^+] + [HOCl] = [OH^-] \]
solution lies at intersection of HOCl and OH⁻ lines
**Find major titration points**
For titration curve, one needs the mid-point pH (pKa) and the endpoint pH. This comes from the other PBE (i.e., pure HOCl solution)

\[ [H^+] = [OH^-] + [OCl^-] \]

solution lies at intersection of \(H^+\) and \(OCl^-\) lines

**Draw Smooth (alpha) curve through the points**
Note that minimum slope (maximum buffering) occurs at mid-point
Problem #2. (1 point)
Draw a figure showing buffer intensity vs pH for the above solution.

Calculate Local Minima & Maximum

\[ \beta = 2.303([H^+] + [OH^-]) + C_T \alpha_0 \alpha_1 \]

- @ pH where g=0 and g=1 (minima)
- @ pH where g=0.5 (maximum)
Draw Smooth Curve from these points

Or, if possible, use a computer to calculate additional points to plot

**Buffer Intensity**

![](image)

**Problem #3 Buffer Calculations (1 point)**

You wish to prepare a test solution that is buffered at pH 8.2. The reactor is to be operated at 25°C. After careful study you have chosen to use a phosphate buffer.

a. pH
What is the ratio of NaH₂PO₄ to Na₂HPO₄ that should be used?

b. Intensity
What is the minimum total phosphate concentration that must be used if the pH is not to deviate from 8.2 by more than 0.02 units, when 10⁻⁴ F strong acid or base is added?
**Approach**

- use buffer equation for part “a”
- use buffer intensity equation for part “b”

a.

\[ pH = pK_a + \log \frac{C_A}{C_{HA}} \]

\[ 8.2 = 7.2 + \log \frac{C_A}{C_{HA}} \]

\[ 1.0 = \log \frac{C_A}{C_{HA}} \]

\[ 10 = \frac{C_A}{C_{HA}} \]

\[ \frac{C_{HA}}{C_A} = \frac{C_{H_2PO_4}}{C_{HPO_4}} = 0.1 \]

b.

\[
\beta = \frac{dC_B}{dpH} = -\frac{dC_A}{dpH}
\]

refer to buffer example in class

\[
\beta \approx 2.303\left([OH^-] + [H^+] + C_1\alpha_0\alpha_1 + C_r\alpha_1\alpha_2 + C_r\alpha_2\alpha_3\right)
\]

and since the pH is near neutrality and it is between the second and third pK, we can drop the first phosphate-related term as well as the hydroxide and hydrogen ion terms:

\[
\beta \approx 2.303\left(C_r\alpha_1\alpha_2 + C_r\alpha_2\alpha_3\right)
\]

and substituting in for the alphas, we get:
and since $K_2 \gg [H^+] \gg K_3$, then we can simplify:

$$\beta \approx 2.303 \left( C_T \left( \frac{1}{[H^+] + 1 + \frac{K_2}{[H^+]} + \frac{K_2 K_3}{[H^+]}} \right) + C_T \left( \frac{1}{K_1 K_2} + 1 + \frac{K_3}{[H^+]} \right) \right)$$

and for the particular pH of 8.2, this reduces to:

$$\beta \approx 2.303 C_T \left( 0.0826 + 0.000009 \right)$$

$$\approx 0.1904 C_T$$

and our buffering criteria are:

$$\beta \equiv \frac{\partial C_B}{\partial pH} = \frac{10^{-4}}{0.02} = 0.005$$

now solve for $C_1$ in moles/L

$$0.005 \approx 0.1904 C_T$$

$$C_T \approx 0.026$$