Homework #5 Solutions

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^{-3}F NaOCl solution and draw a titration curve for this solution indicating the pH at the beginning, middle and end of the titration.

Approach

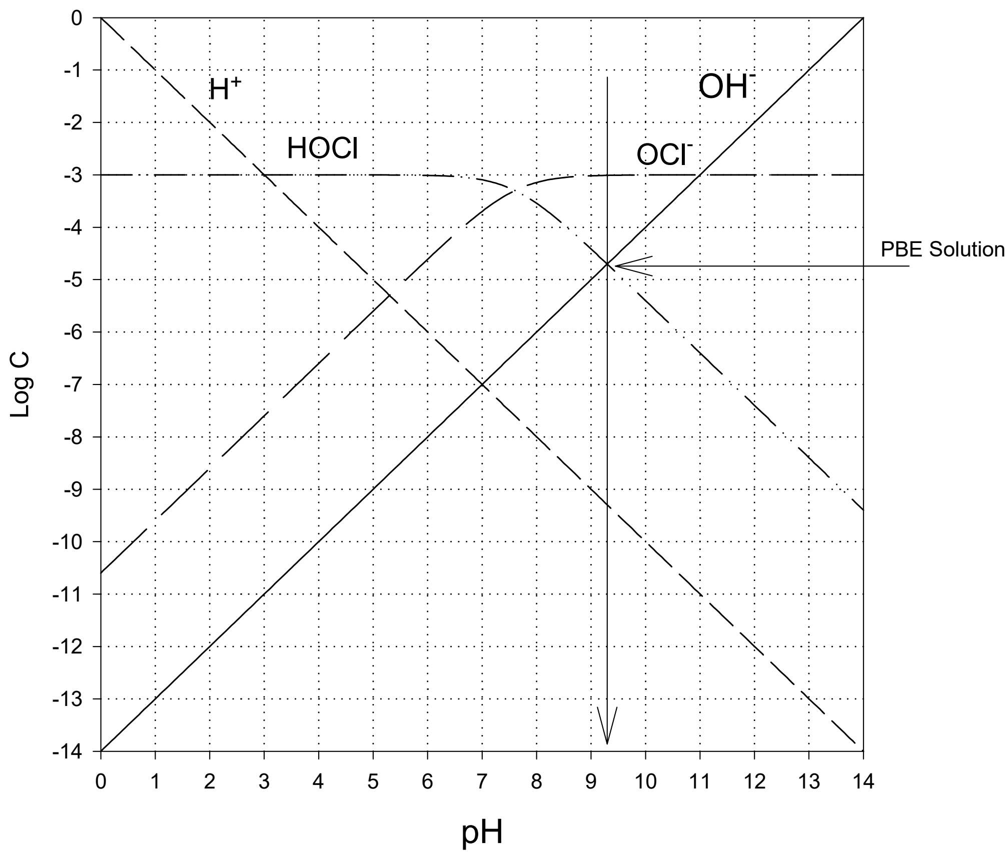
- addition of a simple monoprotic acid to water
- prepare Log C vs pH diagram and solve using the two possible PBEs

Starting pH, Use PBE for a pure OCl- solution

$$[H^+] + [HOCl] = [OH^-]$$

solution lies at intersection of HOCl and OH^- lines

Log C vs pH Diagram



Find major titration points

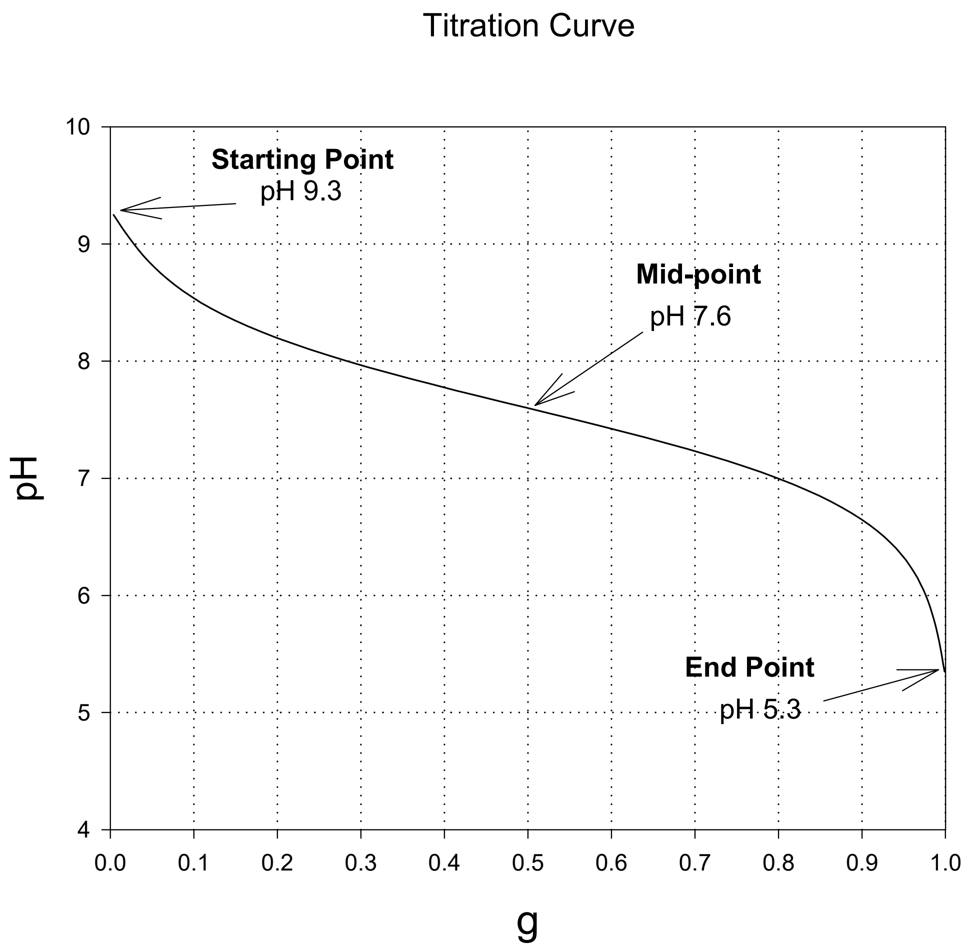
For titration curve, one needs the mid-point pH (pKa) and the endpoint pH. This comes from the other PBE (i.e., pure HOCl solution)

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

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.

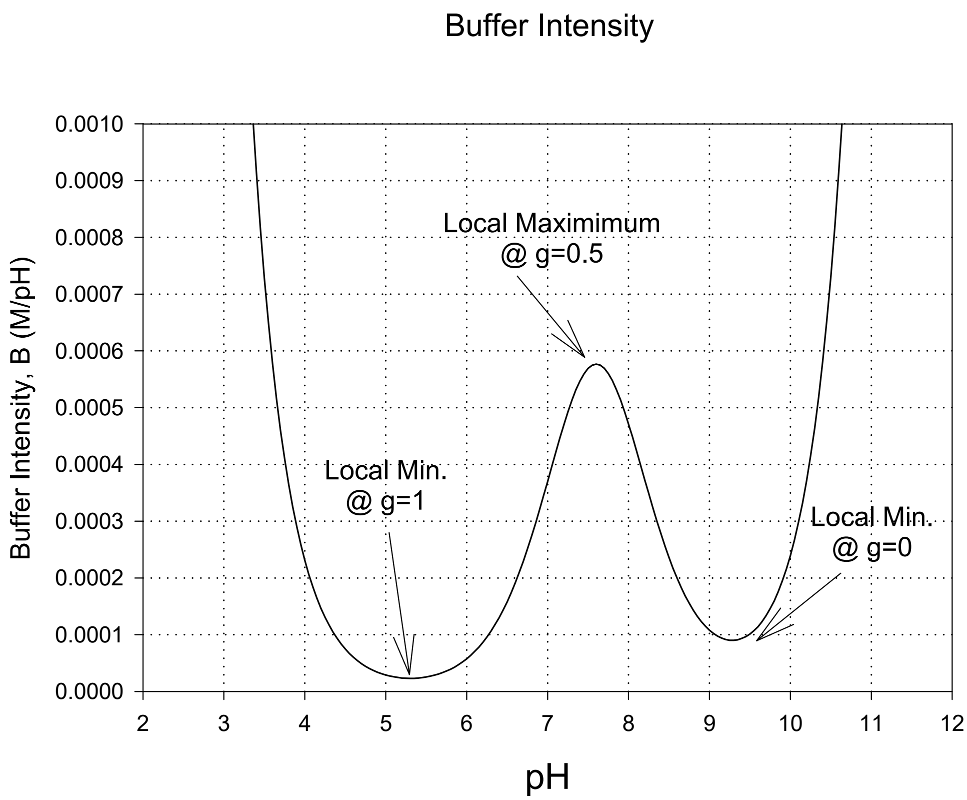
Calculate Local Minima & Maximum

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

- @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



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 NaH_2PO_4 to Na_2HPO_4 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

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

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:

$$\beta \approx 2.303\left(C_T\alpha_1\alpha_2 + C_T\alpha_2\alpha_3\right)$$

and substituting in for the alphas, we get:

$$\beta \approx 2.303\left(\begin{array}{l} C_T\left(\dfrac{1}{\dfrac{[H^+]}{K_1}+1+\dfrac{K_2}{[H^+]}+\dfrac{K_2K_3}{[H^+]^2}}\right)\left(\dfrac{1}{\dfrac{[H^+]^2}{K_1K_2}+\dfrac{[H^+]}{K_2}+1+\dfrac{K_3}{[H^+]}}\right) \\ +C_T\left(\dfrac{1}{\dfrac{[H^+]^2}{K_1K_2}+\dfrac{[H^+]}{K_2}+1+\dfrac{K_3}{[H^+]}}\right)\left(\dfrac{1}{\dfrac{[H^+]^3}{K_1K_2K_3}+\dfrac{[H^+]^2}{K_2K_3}+\dfrac{[H^+]}{K_3}}\right)\end{array}\right)$$

and since $K_2 >> [H^+] >> K_3$, then we can simplify:

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

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

$$\begin{aligned}\beta &\approx 2.303C_T(0.0826+0.000009)\\ &\approx 0.1904C_T\end{aligned}$$

and our buffering criteria are:

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

now solve for C_t in moles/L

$$\begin{aligned}0.005 &\approx 0.1904C_T\\ C_T &\approx 0.026\end{aligned}$$