

Problem 5. (4 points)

Of the many acidic and basic compounds in seawater, the bicarbonate ion (HCO_3^-) and its conjugate base, carbonate ion (CO_3^{2-}), are present in the highest concentrations and establish the pH of seawater near 8. Given the dissociation constant for the bicarbonate ion $K_a = 4.68 \cdot 10^{-11} \text{ M}$, determine what fraction of the bicarbonate ion is present as a carbonate ion. Neglect the presence of all other buffers.

$$\text{pH} = 8 \Rightarrow [\text{H}^+] = 10^{-8} \text{ M}$$

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{K_a}{[\text{H}^+]} = 4.68 \cdot 10^{-3}$$

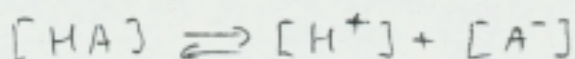
Total "carbonate" is $[\text{HCO}_3^-] + [\text{CO}_3^{2-}] = [\text{HCO}_3^-] \cdot (1 + 4.68 \cdot 10^{-3})$

The fraction present as carbonate ion is

$$\frac{[\text{CO}_3^{2-}]}{\text{tot. carbonate}} = \frac{4.68 \cdot 10^{-3}}{1 + 4.68 \cdot 10^{-3}} = 0.0047 \text{ or } 0.47\%$$

Problem 6. (total 24 points, 6 pts each) In this problem you must show your calculations and explain how you derived the results. Neglect changes in the total volume of your solution when an acid or base is added. Use the back of the page if you need more space.

(a) Cacodylic acid is a weak acid with $\text{p}K_a = 6.27$. You prepared 1L of 0.1M stock solution of this acid. Determine the pH of this solution.



If the amount of $[\text{HA}]$ that dissociated is x , then

$$[\text{A}^-] = x; [\text{HA}] = 0.1 \text{ M} - x; [\text{H}^+] = 10^{-7} \text{ M} + x.$$

$$K_a = \frac{(10^{-7} \text{ M} + x) \cdot x}{0.1 \text{ M} - x} \Rightarrow x^2 + x(10^{-7} \text{ M} + K_a) - K_a \cdot 0.1 \text{ M} = 0$$

$$x = \frac{-(10^{-7} \text{ M} + K_a) + \sqrt{(10^{-7} \text{ M} + K_a)^2 + 4 \cdot K_a \cdot 0.1 \text{ M}}}{2}$$

$$K_a = 10^{-6.27} \text{ M} = 5.37 \cdot 10^{-7} \text{ M}, \text{ hence } x = 2.31 \cdot 10^{-4} \text{ M}$$

$$[\text{H}^+] = 10^{-7} \text{ M} + x \approx x = 2.31 \cdot 10^{-4} \text{ M} \Rightarrow \text{pH} = 3.64$$

- (b) You added 1 mL 1M HCl to 200 mL of the stock solution that you prepared in problem (a). What is the pH of your solution?

The initial concentrations were (see previous problem)

$$[HA] = (0.1 - 2.31 \cdot 10^{-4}) M = 0.0998 M$$

$$[A^-] = 2.31 \cdot 10^{-4} M$$

The initial conc. of HCl (after 1:200 dilution) is $[HCl] = 5 \cdot 10^{-3} M$ which amounts to adding $5 \cdot 10^{-3} M H^+$.

Part of added H^+ will react with essentially all A^- .

$$\text{The conc. of the remaining } H^+ \text{ is } [H^+] = 5 \cdot 10^{-3} M - 2.31 \cdot 10^{-4} M = 4.77 \cdot 10^{-3} M$$

$$\text{Hence } pH = -\log [H^+] = \underline{2.32}$$

- (c) You added 1 mL 1M KOH to 200 mL of the stock solution that you prepared in problem (a). What is the pH of your solution?

The initial values of $[HA]$, $[H^+]$, $[A^-]$ are same as in (b).

We add $5 \cdot 10^{-3} M$ KOH, hence we make $5 \cdot 10^{-3} M OH^-$.

The OH^- will essentially completely neutralize H^+ ($2.31 \cdot 10^{-4} M$), and the amount of OH^- left ($5 \cdot 10^{-3} M - 2.31 \cdot 10^{-4} M = 4.77 \cdot 10^{-3} M$)

will react with HA to give A^- . The pH will then be

$$pH = pK_a + \log \frac{2.31 \cdot 10^{-4} M + 4.77 \cdot 10^{-3} M}{0.0998 M - 4.77 \cdot 10^{-3} M} = \underline{4.99}$$

- (d) What volume of 1M KOH you have to add to 200 mL of the original stock solution of the 0.1M cacodylic acid in order to bring its pH to the optimal buffering conditions?

Optimal buffering conditions: $pH = pK_a$, $\Rightarrow [HA] = [A^-]$

We have to add 0.05 M KOH: this will react with 0.05 M HA to give 0.05 M A^- . Final $[HA] = 0.05 M$.

If the required volume is x then the molar ^{KOH} amount we

$$\text{add is: } x \cdot 1 M = 200 \text{ mL} \cdot 0.05 M$$

$$\underline{x = 10 \text{ mL}}$$