Buffers

Buffered Solutions.

- A buffered solution is one that resists a change in its pH when either hydroxide ions or protons (H_3O^+) are added.
- Very little change in pH is witnessed even when a strong acid or base is added.
- The components of a buffer are a conjugate acid-base pair.

Buffer Calculations

- Assume that the reaction goes to completion, and carry out the *stoichiometric* calculations (based on MOLES).
- Carry out the equilibrium calculations.

Problems

- Calculate the pH of a buffer of 0.50 M HF and 0.45 M F^- **(a)** before and **(b)** after the addition of 0.40 g NaOH to 1.0 L of the buffer.
- K_a of HF = 7.2×10^{-4}.

Answer part (a)

- HF ⇌ H^+ + F^-
- I .50M .45 M
- C -x +x +x
- E .50-x x .45+x
- $K_a = 7.2\times10^{-4} = x(x+.45)/(.5-x)$
- $x = [H^+] = 8.0\times10^{-4}$ M
- pH = 3.10

Answer part (b)

- The sodium hydroxide will react with the HF
- .40 g NaOH x 1 mol/39.988 g =.010003 mol
- It is 1 L so it is easy to convert to moles
- Assume this reaction goes to completion
- HF + OH^- → H_2O + F^-
- .50 mol .45 mol
- .01mol
- .49 mol .46 mol
- Now plug these values back into the equilibrium

Answer part (b) Cont

- HF ⇌ H^+ + F^-
- I .49M .46 M
- C -x +x +x
- E .49-x x .46+x
- $K_a = 7.2\times10^{-4} = x(x+.46)/(.49-x)$
- $x = [H^+] = 7.6\times10^{-4}$ M
- pH = 3.12

Buffers

- Buffered solutions are solutions of weak acids or bases containing a **common ion**.
- The pH calculations on buffered solutions are the same as last chapter.
- When a strong acid or base is added to a buffered solution, do the stoichiometric calculation first.
- Then do the equilibrium calculation.

How Buffers Work

- The equilibrium concentration of H_3O^+, and thus the pH, is determined by the ratio of *[HA]/[A⁻]*.
- HA + H_2O ⇌ A^- + H_3O^+
- $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$ so,
- $\mathbf{[H_3O^+] = K_a \dfrac{[HA]}{[A^-]}}$

Cont.

- If OH- is added to the system, HA is converted to A^-, and the ratio of *[HA]/[A⁻]* decreases.
- However, *if the amounts of HA and A- originally present are very large* compared with the amount of OH^- added, the change in the [HA]/[A^-] ratio will be very small.
- The reverse is true for adding H_3O^+ to a system

The Henderson-Hasselbach Equation.

- $[H_3O^+] = K_a \frac{[HA]}{[A^-]}$
- $-\log[H_3O^+] = -\log K_a - \log([HA]/[A^-])$
- $pH = pK_a - \log([HA]/[A^-])$
- $\mathbf{pH = pK_a + \log([A^-]/[HA])}$
- $\mathbf{= pK_a + \log([C.\ BASE]/[ACID])}$
- For a particular buffering system (conjugate base-acid pair), all solutions that have the same ratio [A^-]/[HA] will have the same pH.

The pH of a Buffered Solution I

- Calculate the pH of a solution containing 0.75 M lactic acid (K_a =1.4x 10^{-4}) and 0.25 M sodium lactate. Lactic acid ($HC_3H_5O_3$) is a common constituent of biological systems. For example, found in milk and is present in human muscle tissue during exertion.

The pH of a Buffered Solution II.

- A buffered solution contains 0.25 M NH_3 (K_b = 1.8 x 10^{-5}) and 0.40 M NH_4Cl. Calculate the pH of this solution.

Adding Strong Acid to a Buffered Solution I.

- Calculate the pH of the solution that results when 0.10 mol gaseous HCl is added to 1.0-L of the buffered solution in the previous example. *assume the volume does not change

Buffer Capacity.

- Buffer capacity represent the amount of protons or hydroxide ions the buffer can absorb without significantly changing the pH.
- The *pH* of a buffered solution is determined by the *ratio* of [A^-]/[HA]. The *capacity* of a buffered solution is determined by the *magnitudes* of [HA] and [A^-].

Adding Strong Acid to a Buffered Solution II.

- Calculate the change in pH that occurs when 0.0100 mol gaseous HCl is added to 1.0-L of each of the following substances:
- Solution A: 5.00 M HCH_3COO and 5.00 M $NaCH_3COO$
- Solution B: 0.050 M HCH_3COO and 0.050 M $NaCH_3COO$
- Solution C: 0.020 M HCH_3COO and 0.020 M $NaCH_3COO$
- For acetic acid, K_a = 1.8 x 10^{-5}

Preparing Buffers

- The most effective buffers have equal concentrations or weak acid to conjugate base or [A^-]/[HA] = 1
- $pH = pK_a + \log([A^-]/[HA])$
- Log(1) = 0
- The pK_a of the weak acid used should be as close as possible to the desired pH of the buffered solution.

Preparing a Buffer

- A chemist needs a solution buffered at pH 4.30 and can choose from the following acids and their salts:
- chloroacetic acid (K_a = 1.35 x 10^{-3})
- propanoic acid (K_a = 1.3 x 10^{-5})
- benzoic acid (K_a = 6.4 x 10^{-5})
- hypochlorous acid (K_a = 3.5 x 10^{-8})
- Calculate the ratio [A^-]/[HA] required to yield the pH 4.30.
- Which system works best?

Preparing a Buffer II

- How would you prepare a benzoic acid/benzoate buffer with pH 4.25, starting with 5.0-L of 0.050 M sodium benzoate (NaC_6H_5COO) solution and adding the acidic component?
- $K_a = 6.3 \times 10^{-5}$ of benzoic acid (C_6H_5COOH).