

More Acid/Base Stuff – Polyprotic Systems & Buffers

Polyprotic Systems

Define –

polyprotic acids:

When a polyprotic acid dissociates, each proton dissociates _____, which means that each dissociation step has a different _____.

Write the equations and K_a expressions for the complete dissociation of phosphoric acid (H_3PO_4).

It is _____ for an H^+ ion to leave a singly charged anion than to leave a neutral molecule. Therefore, the K_a 's are ranked:

Examples:

6. Ascorbic acid ($H_2C_6H_6O_6$; H_2Asc), known as vitamin C, is a diprotic acid ($K_{a1}=1.0 \times 10^{-5}$ and $K_{a2} = 5 \times 10^{-12}$) found in citrus fruit. Calculate $[H_2Asc]$, $[HAsc^-]$, $[Asc^{2-}]$, and the pH of 0.050 M H_2Asc .

First, write the dissociation equations and K_a expressions:

Then, assume:

Now, solve:

7. Oxalic acid (HOOC-COOH , or $\text{H}_2\text{C}_2\text{O}_4$) is the simplest diprotic carboxylic acid. Its commercial uses include bleaching straw and leather and removing rust and ink stains. Calculate $[\text{H}_2\text{C}_2\text{O}_4]$, $[\text{HC}_2\text{O}_4^-]$, $[\text{C}_2\text{O}_4^{2-}]$, and the pH of a 0.150 M $\text{H}_2\text{C}_2\text{O}_4$ solution. ($K_{a1}=5.6 \times 10^{-2}$ and $K_{a2} = 5.4 \times 10^{-5}$).

Buffer Systems

Define –
acid-base buffer:

common-ion effect:

Henderson-Hasselbalch equation:

buffer capacity:

buffer range:

How does a buffer manage to resist pH changes upon addition of H_3O^+ or OH^- ?

Examples:

1. A student is told to prepare a buffer solution using acetic acid (CH_3COOH).

a. Write the acid dissociation equation for acetic acid.

b. What are the two main components (aside from H_2O) in this buffer?

c. Write the K_a expression for acetic acid.

d. Rearrange to solve for $[\text{H}_3\text{O}^+]$.

e. Since _____ is constant, $[\text{H}_3\text{O}^+]$ depends directly on the _____,
which is expressed as:

f. In generic terms, if the ratio _____ goes up, $[\text{H}_3\text{O}^+]$ goes _____.

Likewise, if the ratio _____ goes down, $[\text{H}_3\text{O}^+]$ goes _____.

2. Calculate the pH:

$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$, assume additions in b & c cause negligible volume change.

a. of a buffer solution consisting of 0.50 M CH_3COOH and 0.50 M CH_3COONa

b. after adding 0.020 mol of solid NaOH to 1.0 L of the buffer soln. in part (a)

c. after adding 0.020 mol of HCl to 1.0 L of the buffer soln in part (a)

3. Calculate the pH of a buffer consisting of 0.50 M HF and 0.45 M F⁻:

$$K_a(\text{HF}) = 6.8 \times 10^{-4}$$

a. before addition of 0.40 g NaOH to 1.0 L of the buffer soln.

b. after addition of 0.40 g NaOH to 1.0 L of the buffer soln.

Derivation of the H-H equation:

Buffers have greater buffer capacities when:

a.

b.

c.

Buffers have a usable range within _____ of the _____ of the acid component.

Four steps in preparing a buffer:

1.

2.

3.

4.

Examples:

4. An environmental chemist needs a carbonate buffer of pH 10.00 to study the effects of the acid rain on limestone-rich soils. How many grams of Na_2CO_3 must she add to 1.5 L of freshly prepared 0.20 M NaHCO_3 to make the buffer? $K_a(\text{HCO}_3^-) = 4.7 \times 10^{-11}$
(Note – you need the following molecular weights – Na = 22.99 g/mol, C = 12.01 g/mol, H = 1.008 g/mol, O = 16.00 g/mol)

5. How would you prepare a benzoic acid-benzoate buffer with $\text{pH}=4.25$, starting with 5.0 L of 0.050 M sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$) solution and adding the acidic component? $K_a(\text{C}_6\text{H}_5\text{COOH}) = 6.3 \times 10^{-5}$