

# Ionic Equilibria in Aqueous Systems

## 19.1 Acid-Base Buffers

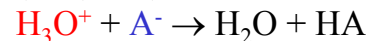
- Resist changes in  $pH$  upon addition of acids ( $H^+$ ) or bases ( $OH^-$ )

### The Buffer Action

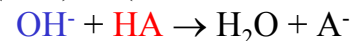
- Buffer solutions consist of two components
  - **Acid component** – reacts with added bases ( $OH^-$ )
  - **Base component** – reacts with added acids ( $H^+$ )
  - The two components must be a **conjugate acid-base pair**
  - The two components must be present in **high concentrations**

➤ **Weak acid buffer** – a solution of the weak acid, HA, and its conjugate base,  $A^-$  ( $HF/F^-$ , ...)

➤ Add  $H_3O^+$  (acid) → ( $A^-$  consumes the added  $H_3O^+$ )

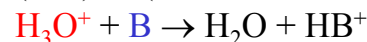


➤ Add  $OH^-$  (base) → (HA consumes the added  $OH^-$ )

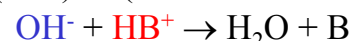


➤ **Weak base buffer** – a solution of the weak base, B, and its conjugate acid,  $HB^+$  ( $NH_4^+/NH_3$ , ...)

➤ Add  $H_3O^+$  (acid) → (B consumes the added  $H_3O^+$ )



➤ Add  $OH^-$  (base) → ( $HB^+$  consumes the added  $OH^-$ )



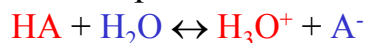
⇒ The addition of  $H_3O^+$  and  $OH^-$  changes the relative amounts of the buffer components ( $HA/A^-$  or  $HB^+/B$ )

### The $pH$ of a Buffer

- For a weak acid buffer ( $HA/A^-$ ),  $A^-$  can be supplied in solution by means of the salt, MA



- HA and  $A^-$  reach equilibrium

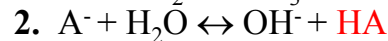
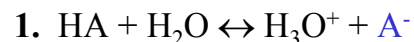


$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \Rightarrow [H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

⇒ The  $[H_3O^+]$  and  $pH$  depend on the ratio  $[HA]/[A^-]$

- If  $[HA]$  and  $[A^-]$  are relatively large, adding small amounts of  $H_3O^+$  or  $OH^-$  changes the ratio only slightly, so  $[H_3O^+] \approx \text{constant}$

- Both HA and  $A^-$  react with water



→ Both equilibria are shifted to the left, so the amounts of HA and  $A^-$  produced are often very small

compared to the total concentrations,  $C_{HA}$  and  $C_{A^-}$

⇒ Assume that  $[HA]_2$  and  $[A^-]_1 \ll C_{HA}$  and  $C_{A^-}$

$$[HA] = C_{HA} - [A^-]_1 + [HA]_2 \approx C_{HA} = C_a$$

$$[A^-] = C_{A^-} - [HA]_2 + [A^-]_1 \approx C_{A^-} = C_b$$

→  $C_a$  and  $C_b$  – total concentrations of the acid and base components of the buffer

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]} \Rightarrow [H_3O^+] = K_a \frac{C_a}{C_b}$$

→ Take a **-log()** of  $[H_3O^+] = K_a(C_a/C_b)$

$$-\log[H_3O^+] = -\log K_a - \log \frac{C_a}{C_b} = -\log K_a + \log \frac{C_b}{C_a}$$

$$\Rightarrow \mathbf{pH = pK_a + \log \frac{C_b}{C_a}} \quad \text{Henderson-Hasselbalch Equation}$$

→ The equation is valid only if  $C_a$  and  $C_b$  are large enough so that the assumptions  $[HA] \approx C_a$  and  $[A^-] \approx C_b$  are justified; If not,  $[HA]$  and  $[A^-]$  must be used

→ Works if  $C_a > 100 \times K_a$  and  $C_b > 100 \times K_b$

→ If  $C_a = C_b$ ,  $\log(C_a/C_b) = 0$  and  $\mathbf{pH = pK_a}$

⇒ If  $C_a$  and  $C_b$  are comparable, the **pH** of the buffer is close to the **pK<sub>a</sub>** of the acid component

**Example:** What is the **pH** of a buffer that is **0.50 M** in HF and **0.50 M** in KF? ( $K_a = 6.8 \times 10^{-4}$  for HF)

1. Use the *Hend.-Hass. Eq.* (HF – acid; F<sup>-</sup> – base)

$$C_a = 0.50 \quad C_b = 0.50$$

$$\mathbf{pH = pK_a + \log(0.50/0.50) = pK_a + \log(1) = pK_a + 0}$$

$$\mathbf{pH = pK_a = -\log(6.8 \times 10^{-4}) = 3.17}$$

2. Or use an *ice table*

|          |  |    |          |
|----------|--|----|----------|
| [ ]      | HF + H <sub>2</sub> O ↔ H <sub>3</sub> O <sup>+</sup> + F <sup>-</sup> |    |          |
| <i>i</i> | 0.50   | 0  | 0.50     |
| <i>c</i> | -x   | +x | +x       |
| <i>e</i> | 0.50 - x   | x  | 0.50 + x |

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} =$$

$$\frac{x(0.50 + x)}{(0.50 - x)} \approx \frac{x(0.50)}{(0.50)}$$

$$x = K_a = 6.8 \times 10^{-4} = [H_3O^+] \Rightarrow \mathbf{pH = -\log(6.8 \times 10^{-4}) = 3.17}$$

**Example:** For **1.0 L** of the same buffer, calculate the **pH** after the addition of **5.0 mL 2.0 M HCl**.

→ HCl is a strong acid and converts to H<sub>3</sub>O<sup>+</sup> which reacts with F<sup>-</sup> from the buffer

→ Calculate the starting moles of HF and F<sup>-</sup> in the buffer and the added moles of H<sub>3</sub>O<sup>+</sup> from HCl

$$\text{HF} \quad \rightarrow 1.0 \text{ L} \times 0.50 \text{ mol/L} = \mathbf{0.50 \text{ mol}}$$

$$\text{F}^- \quad \rightarrow 1.0 \text{ L} \times 0.50 \text{ mol/L} = \mathbf{0.50 \text{ mol}}$$

$$\text{H}_3\text{O}^+ \quad \rightarrow 0.0050 \text{ L} \times 2.0 \text{ mol/L} = \mathbf{0.010 \text{ mol}}$$

→ Use an “*srf*” table (*starting, reacted, final*) to calculate the final moles of HF and F<sup>-</sup>

|              |          |  |        |   |        |
|--------------|----------|--|--------|---|--------|
|              | [ ]      | F <sup>-</sup> + H <sub>3</sub> O <sup>+</sup> → H <sub>2</sub> O + HF |        |   |        |
| <b>moles</b> | <i>s</i> | 0.50   | 0.010  | – | 0.50   |
|              | <i>r</i> | -0.010   | -0.010 | – | +0.010 |
|              | <i>f</i> | 0.49   | 0.00   | – | 0.51   |

→ Use the *Hend.-Hass. Eq.* (HF – acid; F<sup>-</sup> – base)

→ Since the acid and base components of the buffer are in the same volume, the ratio of the concentrations is the same as the ratio of the moles →  $C_b/C_a = n_b/n_a$

$$\mathbf{pH = pK_a + \log \frac{n_b}{n_a} = -\log(6.8 \times 10^{-4}) + \log \frac{0.49}{0.51}}$$

$$= 3.17 + (-0.02) = \mathbf{3.15}$$

⇒ The **pH** is reduced by only **0.02 pH-units**

- The addition of strong acids or bases to unbuffered solutions has a much greater effect on  $pH$

**Example:** Calculate the  $pH$  after the addition of **5.0 mL 2.0 M HCl** to **1.0 L** of pure water .

→ The  $pH$  of pure water is **7.00**

→ After addition of the strong acid HCl:

$$[H_3O^+] = \frac{0.0050 \text{ L} \times \frac{2.0 \text{ mol}}{1 \text{ L}}}{(1.0 + 0.0050) \text{ L}} = 0.010 \text{ M}$$

$$pH = -\log(0.010) = \boxed{2.00}$$

⇒ The  $pH$  is reduced by **5.00 pH-units** (a much larger change compared to the buffered solution)

## Buffer Capacity and Buffer Range

- Buffer capacity (BC)** – a measure of the ability of the buffer to resist  $pH$  changes
  - $BC$  is higher for more concentrated buffers
    - ↑↑  $C_a$  and  $C_b \Rightarrow \uparrow\uparrow$  Buffer capacity
  - $BC$  is higher for buffers with similar component concentrations ( $BC$  is highest when  $C_a = C_b$ )
- Buffer range (BR)** – buffers act most efficiently when  $C_b/C_a$  is between **0.1** and **10**

$$pH = pK_a + \log(0.1) = pK_a - 1 \quad \Rightarrow \text{BR} = pK_a \pm 1$$

$$pH = pK_a + \log(10) = pK_a + 1$$

## Preparing Buffers

- **Choose the conjugate acid-base pair** (select a pair with an acid component having  $pK_a$  close to the desired buffer  $pH$ )
- **Calculate the ratio of  $C_b/C_a$**  needed to achieve the desired buffer  $pH$  (use the Hend.-Hass. Eq.)
- **Determine the buffer concentration** and the amounts of the two components to be mixed
- **Mix the components and adjust the pH** (final  $pH$  may be slightly off and can be adjusted by adding strong acid or base)
- Buffers can also be prepared by **partial neutralization** of weak acids (or bases) with strong bases (or acids) (Ex:  $HF + KOH \rightarrow KF + H_2O$ ; If only half of the HF is converted to KF → buffer)

**Example:** How many moles of  $NH_4Cl$  must be added to **1.0 L** of **0.20 M**  $NH_3$  solution to get a buffer with  $pH = 9.35$ ? ( $K_b = 1.8 \times 10^{-5}$  for  $NH_3$ )

→ Conjugate pair  $NH_4^+/NH_3$

$$\rightarrow K_a = K_w/K_b = 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$$

$$\rightarrow pK_a = -\log(5.6 \times 10^{-10}) = 9.25$$

$$\rightarrow n_b = 1.0 \text{ L} \times 0.20 \text{ mol/L} = 0.20 \text{ mol } NH_3 \quad n_a = ??$$

$$pH = pK_a + \log \frac{n_b}{n_a} \quad \rightarrow \quad 9.35 = 9.25 + \log \frac{0.20}{n_a}$$

$$\rightarrow 0.10 = \log(0.20/n_a) \quad \rightarrow \quad 10^{0.10} = 0.20/n_a$$

$$\rightarrow n_a = 0.20/10^{0.10} = 0.16 \text{ mol } NH_4^+ = 0.16 \text{ mol } NH_4Cl$$