# pH of a buffer solution

What is the pH of an $CH_3COOH/CH_3COONa$ buffer with $[CH_3COOH]$ = 0.700 M and $[CH_3COO^-]$ = 0.600 M?

| | $CH_3COOH$ | $+ H_2O$ | ⇔ | $CH_3COO^-$ | $+ H_3O^+$ |
|---|---|---|---|---|---|
| I | 0.700 M | | | 0.600 M | 0 |
| C | ~0 | | | ~0 | + x |
| E | 0.700 M | | | 0.600 M | x |

$$K_a = 1.8\times10^{-5} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{(0.600\ M)(x)}{(0.700\ M)} \rightarrow x = [H_3O^+] = \frac{[CH_3COOH](K_a)}{[CH_3COO^-]} = 2.1\times10^{-5} M$$

**pH** = –log(2.1 x $10^{-5}$ M) = **4.68**

# Henderson-Hasselbalch expression

Benzoic acid ($C_6H_5COOH$, 2.00 g) and sodium benzoate ($C_6H_5COONa$, 2.00 g) are dissolved in enough water to make 1.00 L of solution. Calculate the pH of the solution using the Henderson-Hasselbalch expression

$$2.00\ g\ C_6H_5COOH \times \frac{1\ mol}{122.12\ g} = 0.0164\ mol\ C_6H_5COOH$$

$$\frac{0.0164\ mol\ C_6H_5COOH}{1.00\ L} = 0.0164\ M\ C_6H_5COOH$$

$$2.00\ g\ C_6H_5COONa \times \frac{1\ mol}{144.11\ g} = 0.0139\ mol\ C_6H_5COONa$$

$$\frac{0.0139\ mol\ C_6H_5COONa}{1.00\ L} = 0.0139\ M\ C_6H_5COONa = 0.0139\ M\ C_6H_5COO^-$$

$$\boldsymbol{pH} = pK_a + log\frac{[\ C_6H_5COO^-]}{[\ C_6H_5COOH]} = -\log(6.3\times10^{-5}) + log\ \frac{0.0139\ M}{0.0164\ M} = \mathbf{4.13}$$

# Preparing a buffer solution

Describe how to prepare a buffer solution from $Na_2HPO_4$ and $NaH_2PO_4$ to have a pH of 7.5 ($pK_a$ of $H_2PO_4^-$ is 7.21)

$$pH = pK_a + log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \rightarrow 7.5 = 7.21 + log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \rightarrow \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 10^{7.5-7.21} = 2.0$$

Need 2.0 x moles of $Na_2HPO_4$ than moles of $NaH_2PO_4$.

For example, use 1.0 mol $Na_2HPO_4$ (140 g) and 0.5 mol $NaH_2PO_4$ (60. g); dissolve in appropriate volume of water.

# How does a buffer maintain constant pH?

What is the change in pH when 1.00 mL of 1.00 M HCl is added to (1) 1.000 L of pure water, and (2) 1.000 L of $CH_3COOH/CH_3COO^-$ buffer with $[CH_3COOH]$ = 0.700 M and $[CH_3COO^-]$=0.600 M?

$$0.00100\ L\ HCl \times \frac{1.00\ mol}{1\ L} = 1.00 \times 10^{-3} mol\ HCl = 1.00 \times 10^{-3}\ mol\ H_3O^+$$

$$\frac{1.00 \times 10^{-3}\ mol\ H_3O^+}{1.001\ L} = 9.99 \times 10^{-4}\ M H_3O^+$$

Pure water:

Initial pH = 7.00

Final pH = –log[9.99 x $10^{-4}$ M $H_3O^+$] = 3.000

# How does a buffer maintain constant pH?

What is the change in pH when 1.00 mL of 1.00 M HCl is added to (1) 1.000 L of pure water, and (2) 1.000 L of $CH_3COOH/CH_3COO^-$ buffer with $[CH_3COOH]$ = 0.700 M and $[CH_3COO^-]$=0.600 M?

$CH_3COOH/CH_3COO^-$ buffer: $CH_3COO^-$ can neutralize $H_3O^+$.

$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$ V = 1.001 L

| | $CH_3COO^-$ (aq) | + $H_3O^+$ (aq) | → | $CH_3COOH$ (aq) | + $H_2O$ (l) |
|---|---|---|---|---|---|
| Initial moles | 0.600 mol | $1.00 \times 10^{-3}$ mol | | 0.700 mol | |
| Change in moles | – $1.00 \times 10^{-3}$ mol | – $1.00 \times 10^{-3}$ mol | | + $1.00 \times 10^{-3}$ mol | |
| Final moles | 0.599 mol | 0 | | 0.701 mol | |

$$pH = pK_a + log\frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log\frac{0.599\ M}{0.701\ M} = 4.68$$

Initial pH was 4.68, so it didn't change.

# Calculating $K_{sp}$

- $CaF_2$, the main component of the mineral fluorite, dissolves to a slight extent in water. Calculate the $K_{sp}$ value for $CaF_2$ if $[Ca^{2+}]$ has been found to be $2.3 \times 10^{-4}$ M.
- $CaF_2\,(s) \Leftrightarrow Ca^{2+}\,(aq) + 2\,F^{-}\,(aq)$
- $[F^{-}] = 2[Ca^{2+}] = 4.6 \times 10^{-4}$ M
- $K_{sp} = [Ca^{2+}][F^{-}]^2 = (2.3 \times 10^{-4})(4.6 \times 10^{-4})^2 = \mathbf{4.9 \times 10^{-11}}$

# Solubility from $K_{sp}$

The $K_{sp}$ value for $MgF_2$ is $5.2 \times 10^{-11}$. Calculate the solubility of $MgF_2$ in (a) M, and (b) g/L

- $MgF_2\ (s) \Leftrightarrow Mg^{2+}\ (aq) + 2\ F^{-}\ (aq)$
- $K_{sp} = [Mg^{2+}][F^{-}]^2$
- $[F^{-}] = 2[Mg^{2+}]$
- $5.2 \times 10^{-11} = [Mg^{2+}](2[Mg^{2+}])^2$
- $5.2 \times 10^{-11} = 4[Mg^{2+}]^3$
- $[Mg^{2+}] = \sqrt[3]{\frac{5.2\times10^{-11}}{4}} = 2.4\times10^{-4}\ M$
- $2.4 \times 10^{-4}$ mol $MgF_2$ dissolves in 1 L of water
- $2.4\times10^{-4}\ mol\ MgF_2 \times \frac{62.3018\ g}{1\ mol\ MgF_2} = 0.015\ g\ MgF_2\ dissolves\ in\ 1\ L\ of\ water$

# Solubility and common ion effect

If AgCl (s) is placed in 1.00 L of 0.55 M NaCl, what mass of AgCl will dissolve?

| | AgCl (s) | ⇔ | $Ag^+$ (aq) | + $Cl^-$ (aq) |
|---|---|---|---|---|
| I | N/A | | 0 | 0.55 M |
| C | - x | | + x | + x |
| E | (N/A – x) | | x | ~0.55 |

$100K_{sp} < [A]_0$

- $K_{sp} = [Ag^+][Cl^-] \rightarrow 1.8\times10^{-10} = x(0.55) \rightarrow x = [Ag^+] = 3.3\times10^{-10}\ M$
- $3.3 \times 10^{-10}$ mol AgCl will dissolve in 1.00 L solution
- $3.3\times10^{-10}\ mol\ AgCl \times \frac{143.32\ g}{1\ mol} = \mathbf{4.7\times10^{-8}\ g\ AgCl\ will\ dissolve}$
- AgCl (s) is less soluble in solution containing one of its ions than in pure water

# Precipitation reactions

The concentration of $Ba^{2+}$ in a solution is 0.010 M. What concentration of $SO_4^{2-}$ is required to begin the precipitation of $BaSO_4$ (s)?

- Begin precipitation: $Q = K_{sp}$
- $BaSO_4$ (s) ⬄ $Ba^{2+}$ (aq) + $SO_4^{2-}$ (aq)
- $K_{sp} = [Ba^{2+}][SO_4^{2-}]$
- $1.1 \times 10^{-10} = [0.010\ M][SO_4^{2-}]$
- **$[SO_4^{2-}] = 1.1 \times 10^{-8}$ M**

# Precipitation reactions

The concentration of $Ba^{2+}$ in a solution is 0.010 M. When $[SO_4^{2-}]$ in the solution reaches 0.015 M, what $[Ba^{2+}]$ remains in the solution?

- $[SO_4^{2-}]$ at equilibrium = 0.015 M
- $BaSO_4\ (s) \Leftrightarrow Ba^{2+}\ (aq) + SO_4^{2-}\ (aq)$
- $K_{sp} = [Ba^{2+}][SO_4^{2-}]$
- $1.1 \times 10^{-10} = [Ba^{2+}][0.015\ M]$
- **$[Ba^{2+}] = 7.3 \times 10^{-9}$ M**

# Precipitation reactions

Suppose you mix 100.0 mL of 0.0200 M $BaCl_2$ (aq) with 50.0 mL of 0.0300 M $Na_2SO_4$ (aq). Will $BaSO_4$ precipitate?

- V = 150.0 mL     mol $Ba^{2+}$ = $2.00 \times 10^{-3}$ mol     mol $SO_4^{2-}$ = $1.50 \times 10^{-3}$ mol
- $K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$ M
- $[Ba^{2+}] = 0.013$ M     $[SO_4^{2-}] = 0.010$ M
- $Q = (0.013\text{ M})(0.010\text{ M}) = 1.3 \times 10^{-4} > K_{sp}$
- More ions in solution than equilibrium expression allows = **$BaSO_4$ (s) will precipitate**

# Complex ion equilibria

What is $[Cu^{2+}]$ in a solution prepared by adding 0.00100 mol of $Cu(NO_3)_2$ to 1.00 L of 1.50 M $NH_3$ (aq)?

- $Cu^{2+}$ (aq) + 4 $NH_3$ (aq) ⬄ $[Cu(NH_3)_4]^{2+}$ (aq) $K_f = 2.1 \times 10^{13}$
- **$K_f$ very large**; begin with the assumption that initially **all $Cu^{2+}$ (0.00100 M) is incorporated into the complex ion $[Cu(NH_3)_4]^{2+}$**
- $[Cu(NH_3)_4]^{2+}$ then **dissociates back** according to the equilibrium expression
  - $[Cu(NH_3)_4]^{2+}$ ⬄ $Cu^{2+}$ (aq) + 4 $NH_3$ (aq) **$K = K_f^{-1} = 4.8 \times 10^{-14}$**
- $100K < [A]_0$

| | $[Cu(NH_3)_4]^{2+}$ (aq) | ⬄ | $Cu^{2+}$ (aq) | + 4 $NH_3$ (aq) |
|---|---|---|---|---|
| I | 0.00100 M | | 0 | 1.50 M |
| C | - x | | + x | + 4x |
| E | ~0.00100 | | x | ~$(1.50)^4$ |

- $K = \frac{[Cu^{2+}][NH_3]^4}{[[Cu(NH_3)_4]^{2+}]} \rightarrow 4.8\times10^{-14} = \frac{x(1.50)^4}{(0.00100)} \rightarrow \boldsymbol{x = [Cu^{2+}] = 9.5\times10^{-18}\ M}$