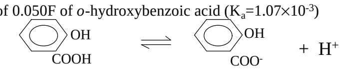
# Monoprotic acid-base equilibria (Ch 10)

- Weak acid equilibria
- Fraction of dissociation of a weak acid
- Weak base equilibria
- Fraction of association of a weak base
- When the dissociation of water cannot be neglected
- Buffer, Henderson-Hasselbalch equation and buffer capacity



## Weak acid equilibria

To calculate the pH of 0.050F of *o*-hydroxybenzoic acid ($K_a$=1.07×10$^{-3}$)



| | | | |
|---|---|---|---|
| Initial conc. (M) | 0.050 | 0 | 0 |
| Final conc. (M) | 0.050-x | x | x |

We assume that there is negligible contribution of $H^+$ from dissociation of water.

$$Since \quad K_a = \frac{[H^+][A^-]}{[HA]} \qquad 1.07\times10^{-3} = \frac{x^2}{0.050 - x}$$

$$x^2 + (1.07\times10^{-3})x - 5.35\times10^{-5} = 0$$

This is a quadratic equation: $ax^2+bx+c=0$

$$\therefore x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-1.07\times10^{-3} + \sqrt{(1.07\times10^{-3})^2 - 4(1)(-5.35\times10^{-5})}}{2(1)} = 6.80\times10^{-3}$$

The negative root is rejected.



## Weak acid equilibria

$$Since \quad [OH^-] = \frac{K_W}{[H^+]} = \frac{1.0\times10^{-14}}{6.80\times10^{-3}} = 1.4_7\times10^{-12} M$$

The amount of $H^+$, which is similar to $[OH^-]$, contributed from dissociation of water is very small and the above approximation is justified.

$$\therefore pH = -\log[H^+] = -\log x = 2.17$$

If the concentration of the acid is larger (e.g. 5.0F) and/or Ka is smaller, another approximation: 5.0-x ≈ 5.0 could also be made to avoid solving the quadratic equation.



## Fraction of dissociation of a weak acid

$$a = \frac{amount \ of \ dissociated \ conjugate \ base}{formal \ concentration \ of \ the \ acid}$$

$$= \frac{[A^-]}{[A^-]+[HA]} = \frac{x}{F}$$

$$a = \frac{6.80\times10^{-3} M}{0.0500 M} = 0.136$$

So 13.6% of the 0.050F acid has dissociated to give $H^+$ , leading to a rise in $[H^+]$, or a decrease in pH.



## Fraction of dissociation of a weak acid

Fig. 10-2: The fraction of dissociation of a weak electrolyte (e.g. a weak acid) increases as the concentration of the electrolyte decreases.

This does not mean [H+] increases (or pH decreases) as the conc. of the weak acid decreases.



## Weak base equilibria

To calculate the pH of 0.0372F of a weak base: cocaine ($K_b$=2.6×10$^{-6}$)

Similar to the weak acid calculation, note that x=$[OH^-]$, instead of $[H^+]$

$$Since \quad K_b = \frac{[OH^-][BH^+]}{[B]} \qquad 2.6\times10^{-6} = \frac{x^2}{0.0372 - x}$$

We assume that there is negligible contribution of $OH^-$ from dissociation of water.

We also make the approximation: 0.0372-x ≈ 0.0372

$$\therefore x = \sqrt{0.0372 \times 2.6\times10^{-6}} = 3.1\times10^{-4}$$

The negative root is rejected.

Note the above approximation is justified.

$$Since \quad [H^+] = \frac{K_W}{[OH^-]} = \frac{1.0\times10^{-14}}{3.1\times10^{-4}} = 3.2\times10^{-11} M$$

$$\therefore pH = -\log(3.2\times10^{-11}) = 10.49$$

# Fraction of association of a weak base

$$a = \frac{amount\ of\ dissociated\ conjugate\ acid}{formal\ concentration\ of\ the\ base}$$

$$= \frac{[BH^+]}{[BH^+]+[B]} = \frac{x}{F}$$

For 0.0372F cocaine,

$$a = \frac{3.1\times10^{-4}M}{0.0372M} = 0.0083$$

So only 0.83% of 0.0372F cocaine has associated with $H^+$, leading to a lowering in $[H^+]$, or rise in pH.



# When the dissociation of water cannot be neglected

What is the pH of $1.0\times10^{-8}$ M KOH?

If the dissociation of water is neglected,

$$\therefore\ pOH = -\log(1.0\times10^{-8}) = 8.00$$

$$pH = 14.00 - 8.00 = 6.00 < 7.00!!$$

When the dissociation of water must be considered,

$$H_2O \rightleftharpoons H^+ + OH^-$$

x    x + $1.0\times10^{-8}$

$$K_w = [H^+][OH^-]$$

$$1.0\times10^{-14} = x(x + 1.0\times10^{-8}) \qquad x^2 + (1.0\times10^{-8})x - 1.0\times10^{-14} = 0$$

$$x = \frac{-1.0\times10^{-8} + \sqrt{(1.0\times10^{-8})^2 - 4(1)(-1.0\times10^{-14})}}{2(1)} = 9.6\times10^{-8}$$

(The negative root is rejected)

$$\therefore\ pH = -\log(9.6\times10^{-8}) = 7.02$$



# Buffer

A buffer is a mixture of a conjugate weak acid and its conjugate base.

E.g. $CH_3CO_2H/CH_3CO_2Na$ and $NH_4Cl/NH_3$

A buffered solution resists changes in pH when acids or bases are added or when dilution occurs.

See Table 10-2 for other examples of buffers.



# Henderson-Hasselbalch equation

| | HA | $\rightleftharpoons$ | $H^+$ + | $A^-$ |
|---|---|---|---|---|
| Initial conc. (M) | $C_{HA}$ | | | $C_{A-}$ |
| Final conc. (M) | $C_{HA}$ - x | | x | $C_{A-}$ + x |

Approximation: $[HA] = C_{HA} - x \approx C_{HA}$ and $[A^-] = C_{A-} + x \approx C_{A-}$

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

$$-\log K_a = -\log[H^+] - \log\frac{[A^-]}{[HA]}$$

$$\therefore pH = pK_a + \log\frac{[A^-]}{[HA]} \approx pK_a + \log\frac{C_{A^-}}{C_{HA}}$$

Henderson-Hasselbalch equation

Similarly, for a conjugate pair of B and $BH^+$,

$$pOH = pK_b + \log\frac{[BH^+]}{[B]} \approx pK_b + \log\frac{C_{BH^+}}{C_B} \quad or \quad pH = pK_a + \log\frac{C_B}{C_{BH^+}}$$

$$K_a\ of\ BH^+ = \frac{K_W}{K_b\ of\ B}$$

treated as an acid: $BH^+$



# Buffer calculations

Example in Sec 10-5: Find the pH of a buffer prepared by dissolving 12.43g of tris (FW 121.136) plus 4.67g of tris hydrochloride (FW 157.597) in 1.00 L of water. (pKa=8.075)

tris: tris(hydroxymethyl)aminomethane   $(HOCH_2)_3C.NH_2$

$$C_B = \frac{12.43g/12.136g/mol}{1.0L} = 0.1026M$$

$$C_{BH^+} = \frac{4.67g/157.597g/mol}{1.0L} = 0.0296M$$

$$pH = pK_a + \log\frac{C_B}{C_{BH^+}} = 8.075 + \log\frac{0.1025}{0.0296} = 8.61$$

The same buffer can be prepared by adding sufficient HCl to tris or sufficient NaOH to tris hydrochloride.



# Buffer calculations

Example in Sec 10-5: Find the volume of 0.500M NaOH added to 10.0g of tris hydrochloride to give a pH of 7.60 in a final volume of 250mL.

Moles of tris hydrochloride initially present $= \dfrac{10g}{157.597g/mol} = 0.0635$

| | $BH^+$ + $OH^-$ | | → | B |
|---|---|---|---|---|
| Initial moles | 0.0635 | x | | |
| Final moles | 0.0635 - x | | | x |

$$pH = pK_a + \log\frac{C_B}{C_{BH^+}}$$

$$7.60 = 8.075 + \log\frac{x/0.250L}{(0.0635-x)/0.250L} \qquad x = 0.0159$$

$$\therefore\ volume\ of\ NaOH\ added = \frac{0.0159mol}{0.500mol/L} = 0.318L$$

# Buffer Capacity

Example in Sec 10-5: If we add 12.0mL of 1.00M HCl or NaOH to the first buffer with a final pH of 8.61, find the new pH.

Recall $C_B = 0.1026\,M$   Recall $C_{BH^+} = 0.0296\,M$

*moles of* $HCl$ (*or NaOH*) *added* $= 0.0120\,L \times 1.00\,mol/L = 0.0120$

| | $B$ + | $H^+$ → | $BH^+$ | $BH^+$ + | $OH^-$ → | $B$ |
|---|---|---|---|---|---|---|
| Initial moles | 0.1026 | 0.0120 | 0.0296 | 0.0296 | 0.0120 | 0.1026 |
| Final moles | 0.1026-0.0120 =0.0906 | | 0.0296+0.0120 =0.0416 | 0.0296-0.0120 =0.0176 | | 0.1026+0.0120 =0.1146 |

$$pH = pK_a + \log\frac{C_B}{C_{BH^+}} = 8.075 + \log\frac{0.0906}{0.0416} = 8.41$$

$$= 8.075 + \log\frac{0.1146}{0.0176} = 8.89$$

What will the new pH be if more than 0.1026 mol of acid is added?

What will the new pH be if more than 0.0296 mol of base is added?



# Buffer Capacity

Therefore, there must be comparable amounts of the conjugate acid and base (say, within a factor of 10) to have sufficient buffer capacity against fluctuations of acid and base content in the solution.

$$\log\frac{C_B}{C_{BH^+}} \quad or \quad \log\frac{C_{A^-}}{C_{HA}} = \log\frac{10}{1} = 1 \quad or \quad = \log\frac{1}{10} = -1$$

$$\therefore pH = pK_a \pm 1$$

Hence, based on the pH to be buffered, we prepare a buffer consisting the conjugate acid and base with a pKa close to the pH.



# Summary: Monoprotic acid-base equilibria

- To perform pH calculations on weak acid equilibria (Do Ex. 10-11)
- To determine the fraction of dissociation of a weak acid (Do Ex. 10-13)
- To perform pH calculations on weak base equilibria (Do Ex. 10-18)
- To determine the fraction of association of a weak base (Do Ex.10-22)
- To perform pH calculations when the dissociation of water cannot be neglected (Do Exercise 10-3)
- To derive Henderson-Hasselbalch equation and perform pH calculations for buffers. (Do Ex. 10-37 and 10-38)