ACID-BASE EQUILIBRIA

1. Arrhenius acids and bases (aqueous system)
   acid - is a substance which produces H^+ ions when placed in water
   base - is a substance which produces OH^- ions when placed in water

2. Lowry-Bronsted acids and bases
   acid - is a substance which is a proton donor
   base - is a substance which is a proton acceptor

3. Lewis acids and bases
   acid - is a substance which is an electron pair acceptor
   base - is a substance which is an electron pair donor

4. For acids, we define $K_a = [H_3O^+][A^-]/[HA]$
   If $K_a < 0.1$, it is called a weak acid.

5. For base, we define $K_b = [BH^+][OH^-]/[B]$
   If $K_b < 0.1$, it is called a weak base.

6. Self-ionization of water: $H_2O + H_2O \leftrightharpoons H_3O^+ + OH^-$
   $K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$ at 25°C

7. For pure water at 25°C, $[H_3O^+] = [OH^-] = [1 \times 10^{-14}]^{\frac{1}{2}} = 1 \times 10^{-7}\ M$

8. Definitions: $pH = -\log[H_3O^+]$ and $pOH = -\log[OH^-]$
   $pK_a = -\log K_a$ and $pK_b = -\log K_b$

9. All strong acid solutions result in 100% ionization (i.e. all acid becomes H_3O^+). e.g. 0.100 *M* HCl has $[H_3O^+] = 0.100\ M$.

10. In weak acid solutions, only a small amount of ionization occurs (i.e. only a small amount of H_3O^+ is formed. The equilibrium state is determined in point #11.

11. <u>Weak acid problem:</u> calculate the $[H_3O^+]$ and pH of a 0.100 *M* acetic acid solution.

	CH_3COOH	$\leftrightharpoons$	CH_3COO^-	+	H^+
initially	0.100		0		0
at equil.	0.100 - x		x		x

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x^2}{0.100 - x} \cong \frac{x^2}{0.100}$$

$[H_3O^+] = [H^+] = x = (K_a \times 0.100)^{\frac{1}{2}} = (1.8 \times 10^{-5} \times 0.100)^{\frac{1}{2}} = 1.34 \times 10^{-3}\ M$ and pH = 2.87

12. For weak bases the treatment is identical except for the fact that you use K_b for the dissociation constant of the weak base and you obtain the $[OH^-]$ instead of the $[H^+]$. The pH is obtained by making use of the fact that at 25°C $pK_{water} = pH + pOH = 14.0$

13. Buffer solutions:
-solution of a weak acid + salt of the weak acid **or** solution of a weak base + salt of the weak base.
-such a solution resists pH changes when small amounts of acid or base are added to it.

14. For weak acids the following equation can be obtained from the equilibrium expression for a weak acid along with the definitions of pH and pK_a:

$$pH = pK_a + \log \{[A^-]/[HA]\}$$

For weak bases a similar expression can be obtained:

$$pOH = pK_b + \log \{[BH^+]/[B]\}$$

15. Hydrolysis:
a. In a solution of a salt of a weak acid, the anion acts like a weak base,

$$CN^- + H_2O \leftrightharpoons HCN + OH^-$$

$$K_{hydrolysis} = K_w / K_a = \frac{[HCN][OH^-]}{[CN^-]}$$

b. In a solution of a salt of a weak base, the cation acts like a weak acid,

$$NH_4^+ + H_2O \leftrightharpoons NH_3 + H_3O^+$$

$$K_{hydrolysis} = K_w/K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

16. Indicators are weak organic acids or bases.
At this time we will assume it is a weak organic acid:

$$HInd + H_2O \leftrightharpoons H_3O^+ + Ind^-$$

The color of the HInd species is different than for the Ind^- species.

$$K_{indicator} = \frac{[H_3O^+][Ind^-]}{[HInd]}$$

$$\text{therefore} \quad \frac{[Ind^-]}{[HInd]} = \frac{K_{ind}}{[H_3O^+]}$$

a. If $[H_3O^+] > K_{ind}$ then $[HInd] > [Ind^-]$ and the solution will have the color of the HInd.
b. If $[H_3O^+] < K_{ind}$ then $[HInd] < [Ind^-]$ and the solution will have the color of the Ind^-.

17. Polyprotic acids (e.g. H_2CO_3, H_2S, H_2SO_3, H_3PO_4)

Example:

$$H_2CO_3 + H_2O \leftrightharpoons HCO_3^- + H_3O^+ \quad K_1 = 4.5 \times 10^{-7}$$

$$HCO_3^- + H_2O \leftrightharpoons CO_3^{2-} + H_3O^+ \quad K_2 = 5.6 \times 10^{-11}$$

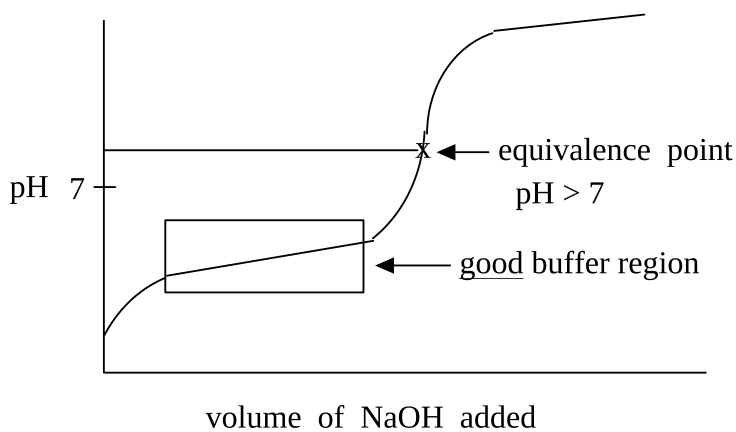
18. Titration
To an unknown amount of acid is added a solution of base of known concentration. The equivalence point is that point at which equal moles of H^+ and OH^- have reacted. The endpoint is that point at which the indicator used changes color to indicate the end of the titration has been reached. Therefore it is critical that the correct indicator be selected to indicate the correct endpoint of a titration.

19. Titration of a strong acid vs. strong base

Example: 0.10 *M* HCl vs. 0.10 *M* NaOH
At the endpoint we have a 0.05 *M* NaCl solution which neither the salt of a weak base nor a strong acid and therefore does not undergo hydrolysis. The pH at the equivalence point of such a titration at 25°C would then be 7.0 due to the self-ionization of water.

20. Titration of a weak acid vs. strong base

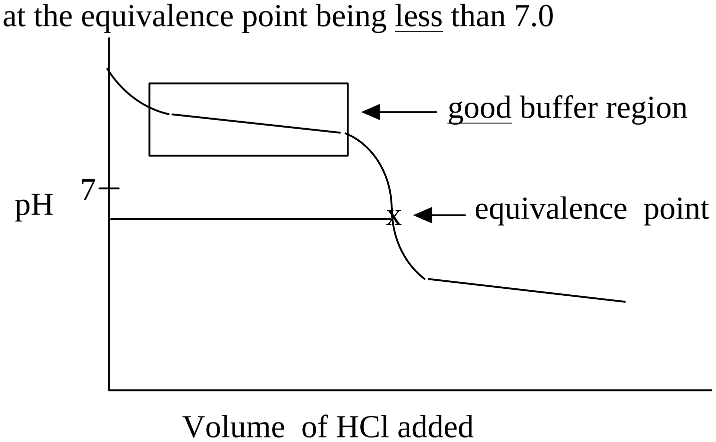
Example: 0.10 *M* CH_3COOH vs. 0.10 *M* NaOH
At the equivalence point we have a 0.05 *M* sodium acetate solution. Since the acetate ion is the salt of the weak acid, acetic acid, it will act as a weak base and undergo hydrolysis resulting in the pH at the equivalence point being greater than 7.0



(1) Determine the pH initially (before any base is added) as in the weak acid problem.
(2) Determine the pH as base is added as in buffer problem.
(3) Determine the pH at the equivalence point as in hydrolysis problem.
(4) Determine the pH after the equivalence point from the amount of excess strong base added.

21. Titration of a weak base vs. strong acid

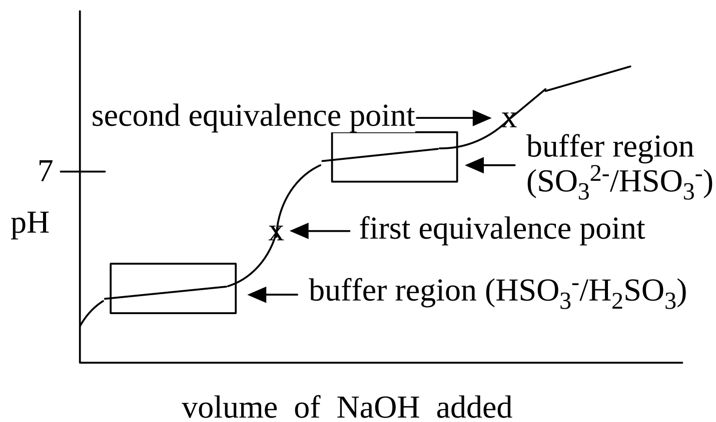
Example: 0.10 *M* NH_3 vs. 0.10 *M* HCl
At the equivalence point we have a 0.05 *M* ammonium chloride solution. Since the ammonium ion is the salt of the weak base, ammonia, it will act as a weak acid and undergo hydrolysis resulting in the pH at the equivalence point being less than 7.0



(1) Determine the pH initially (before any acid is added) as in the weak base problem.
(2) Determine the pH as acid is added as in buffer problem.
(3) Determine the pH at the equivalence point as in hydrolysis problem.
(4) Determine the pH after the equivalence point from the amount of excess strong acid added.

22. Titration of weak polyprotic acid vs. strong base

Example: 0.10 *M* H_2SO_3 vs 0.10 *M* NaOH
The first equivalence point occurs when pH = $\frac{1}{2}(pK_1 + pK_2)$. For H_2SO_3 pK_1 = 1.77 and pK_2 = 7.23 and therefore at the first equivalence point of this titration the pH = 4.50.
At the second equivalence point we have a 0.033 *M* sodium sufite solution. Since the sulfite ion is the salt of a weak acid, the bisulfite ion (HSO_3^-), it will act as a weak base and undergo hydrolysis resulting in the pH at the equivalence point being greater than 7.0



(1) Determine the pH initially (before any base is added) as in the weak polyprotic acid case.
(2) Determine the pH as base is added as in a buffer problem involving $[HSO_3^-]/[H_2SO_3]$.
(3) Determine the pH at the first equivalence point as mentioned above.
(4) Determine the pH as base is added as in a buffer problem involving $[SO_3^{2-}]/[HSO_3^-]$.
(5) Determine the pH at the second equivalence point as in a hydrolysis problem involving the SO_3^{2-} ion.
(6) Determine the pH after the second equivalence point from the amount of excess strong base added.