Bronsted-Lowry Acids

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

- **An acid is a substance that can donate a proton**
- **A base is a substance that can accept a proton**
- **In the above equation, HA is the acid and H_2O is the base**
- **A^- is the conjugate base of HA, and H_3O^+ is the conjugate acid of H_2O.**

$$\underset{\text{Acid}}{CH_3COOH} \rightleftharpoons H^+ + \underset{\text{Conjugate base}}{CH_3COO^-}$$

Proton Hydration

- **Protons do not exist free in solution.**
- **They are immediately hydrated to form hydronium ions (H_3O^+).**

$$K_{eq} = \frac{[H^+]\,[OH^-]}{[H_2O]}$$

- **A hydronium ion is a water molecule with a proton associated with one of the nonbonding electron pairs.**
- **Hydronium ions are solvated by nearby water molecules.**

What Is pH?

$$\mathbf{pH = -\log[H^+]}$$

$$K_w = [H^+][OH^-] = 1 \cdot 10^{-14} M^2$$

$$-\log[H^+] - \log[OH^-] = +14$$

$$pH + pOH = 14$$

- **pH is defined as the negative logarithm of the hydrogen ion concentration.**
- **Simplifies equations**
- **The pH and pOH must always add up to 14.**
- **In neutral solution, $[H^+]$ = $[OH^-]$ and the pH is 7.**

$[H^+]$ (M)	pH	$[OH^-]$ (M)	pOH[a]
10^0 (1)	0	10^{-14}	14
10^{-1}	1	10^{-13}	13
10^{-2}	2	10^{-12}	12
10^{-3}	3	10^{-11}	11
10^{-4}	4	10^{-10}	10
10^{-5}	5	10^{-9}	9
10^{-6}	6	10^{-8}	8
10^{-7}	7	10^{-7}	7
10^{-8}	8	10^{-6}	6
10^{-9}	9	10^{-5}	5
10^{-10}	10	10^{-4}	4
10^{-11}	11	10^{-3}	3
10^{-12}	12	10^{-2}	2
10^{-13}	13	10^{-1}	1
10^{-14}	14	10^0 (1)	0

Buffers

Buffer

- It is a chemical system that tends to resist large changes in pH upon the addition of small amounts of H^+ or OH^- ions.
- Common buffer mixtures contain two substances, a conjugate acid and a conjugate base.

- **Buffers are mixtures of weak acids and their conjugate base**
- **Each acid has a conjugate base**
- **For example B^- is the conjugate base of the acid HB**

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

$$HSO_4 + H_2O \longrightarrow H_3O^+ + SO_4^-$$

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$HBr + H_2O \longrightarrow H_3O^+ + Br^-$$

$$H_2O \quad + \quad H_2O \rightleftharpoons H_3O^+ \quad + \quad OH^-$$

- **Weak acids dissociate weakly because they have strong conjugate base that bind hydrogen.**
- **Strong acids ionize easily to give H^- because they have weak conjugate base**
- **Acids are proton donors**
- **Bases are proton acceptors**

- **At pH = pKa, there is a 50:50 mixture of acid and anion forms of the compound.**
- **Buffering capacity is lost when the pH differs from pKa by more than 1 pH unit.**
- **Buffering capacity of acid/anion system is greatest at pH = pKa.**

Types of buffer

Acidic buffer

contains a weak acid and a salt of the weak acid (conjugate base).

Basic buffer

contains a weak base and a salt of the weak base (conjugate acid).

- **Together the two species (conjugate acid plus conjugate base)**
- **Resist large changes in pH by partially absorbing additions of [H^+] or [OH^-] ions to the system.**

- **If H^+ ions are added to the buffered solution, they react partially with the conjugate base present to form the conjugate acid. ⇒ Thus some H^+ ions are taken out of circulation.**
- **If OH^- ions are added to the buffered solution, they react partially with the conjugate acid present to form water and the conjugate base. ⇒ Thus, some OH^- are taken out of circulation.**

Example of acidic buffer

- (CH_3COOH/CH_3COO^-)
- (H_2CO_3/ HCO_3^-)

Example

How can this acidic buffer **(H_2CO_3/ HCO_3^-)** resist change in pH.

- $$HCO_3^- \xrightarrow{H^+} H_2CO_3$$

- $$H_2CO_3 \xrightarrow{OH^-} HCO_3^-$$

- **The buffer working range is determined by the pKa of the conjugate acid.**

- **The best buffering region is one pH unit on either side of the pKa value**

$$pH = pKa \pm 1$$

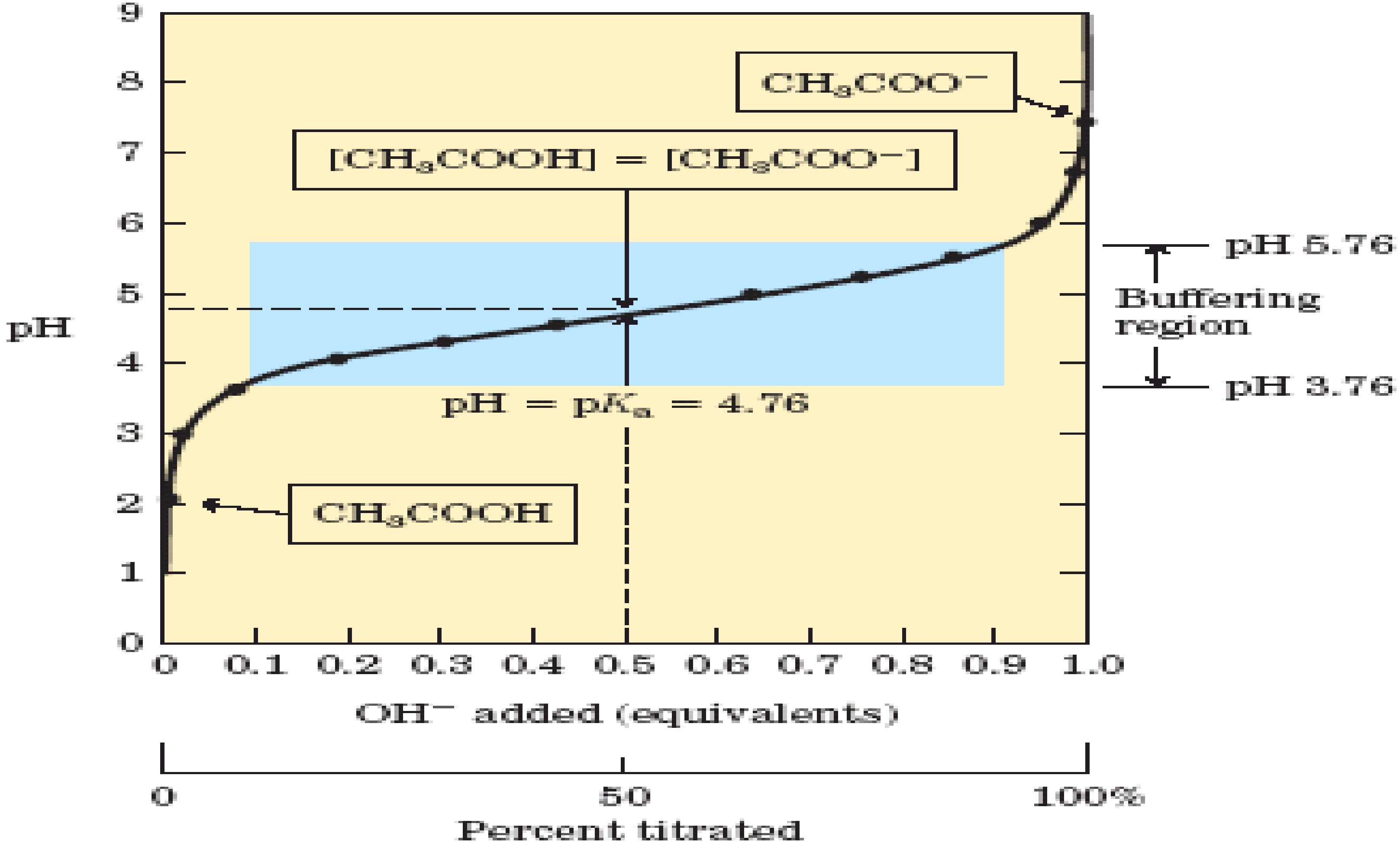
Titration curve

- **It is a plot of pH against the amount of NaOH added.**
- **A measured volume of the acid is titrated with a base solution, usually sodium hydroxide (NaOH) of known concentration.**
- **The NaOH is added in small increments until the acid is consumed (neutralized).**

Example:

Titration curve of acetic acid

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$



Henderson–Hasselbalch Equation

$HA \leftrightarrows H^+ + A^-$

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

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

$$\downarrow$$

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

$$\downarrow$$

$$\downarrow$$

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[A^-]}{[HA]}$$

Biological Buffer Systems

- **Maintenance of intracellular pH is vital to all cells.**
  - **Enzyme-catalyzed reactions have optimal pH.**
  - **Solubility of polar molecules depends on H-bond donors and acceptors.**
  - **Equilibrium between CO_2 gas and dissolved HCO_3^- depends on pH.**

- **Buffer systems *in vivo* are mainly based on:**
  - **phosphate, concentration in millimolar range**
  - **bicarbonate, important for blood plasma**
  - **histidine, efficient buffer at neutral pH**