Republic of Iraq
Ministry of Higher Education & Scientific research
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Analytical Chemistry

For

First Year Student

Lecture 4

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Acid-Base Equilibria

Acid-base theories:-

1) Arrhenius Theory (H^+ and OH^-):-

Acid:-any substance that ionizes (partially or completely) in water to give hydrogen ion (which associate with the solvent to give hydronium ion H_3O^+):

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

Base:-any substance that ionizes in water to give hydroxyl ions. Weak (partially ionized) to generally ionize as follows:-

$$B + H_2O \leftrightarrow BH^+ + OH^-$$

While strong bases such as metal hydroxides (e.g. NaOH) dissociate as

$$M(OH)n \leftrightarrow M^{n+} + nOH^-$$

This theory is obviously restricted to water as the solvent.

2) Bronsted-Lowry Theory (taking and giving protons, H^+):-

Acid:-any substance that can donate a proton.

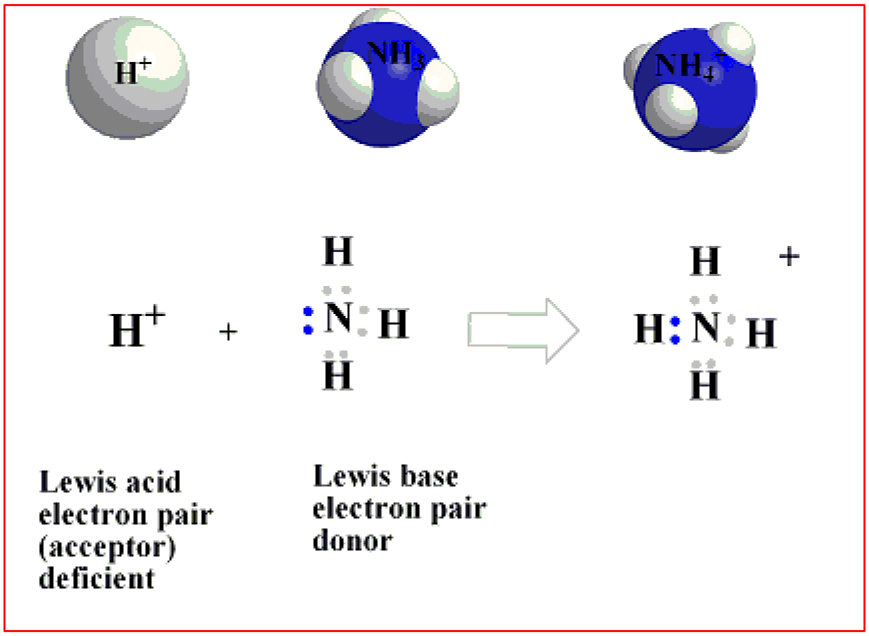
Base:-any substance that can accept a proton. Thus, we can write a half reaction:

$$\mathbf{Acid = H^+ + Base}$$

3) Lewis Theory (taking and giving electrons):-

Acid:-a substance that can accept an electron pair.

Base:-a substance that can donate an electron pair.



Strong acids: - H_2SO_4, $HClO_4$, HNO_3, HI and HCl .

Strong bases: - LiOH, KOH, NaOH and $Ca(OH)_2$.

Acid-Base Equilibria in water

when an acid or base is dissolved in water, it will dissociate, or ionize, the amount of ionization being dependent on the strength of the acid or base. A strong electrolyte is completely dissociated, while a weak electrolyte is partially dissociated.

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$ (strong acid, completely ionized)

$HOAC + H_2O \longrightarrow H_3O^+ + OAC^-$ (weak acid, partially ionized)

$$Ka = \frac{[H3O+][OAC-]}{[HOAC]}$$

$$2\ H_2O \rightleftharpoons H_3O^+ + OH- \quad \text{or}$$

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

Some of H_2O molecule gives H^+ to other H_2O molecule to produce H_3O^+ ions and OH^- ions.

$$Ka=[H_3O^+][OH-]/[H_2O]^2$$

$$K\ [\ H_2O\ ]^2 = [\ H3O^+\ ]\ [\ OH^-\ ] = Kw$$

$$Kw = [\ H_3O^+]\ [\ OH-\ ] = 1\ x10^{-14}\ mol^2\ /\ L^2 \text{ at } 25^Oc$$

Kw is **temperature dependant** it increases with temperature rise , and decreases with its decrease. **Kw** is used only for water.

Temperature ºC	kw
0.0	1.14×10^{-15}
25	1.01×10^{-14}
40	2.92×10^{-14}
50	5.47×10^{-14}
70	2.30×10^{-13}
10	4.90×10^{-13}

Example :

Calculate the hydronium [H_3O^+] and hydroxide ion [OH^-] concentrations of pure water at 25ₒC and 100ₒC ($Kw = 4.9 \times 10^{-13}$) ?

solution:

Because OH^- and H_3O^+ are formed from the dissociation of water only, then their concentrations are equal,

$$2\ H_2O \rightleftharpoons H_3O^+ + OH$$

then

$$: [H_3O^+] = [OH^-]$$

$$Kw = [\ H_3O^+]\ [\ OH^-\ ]$$

Subsititution in the above equation gives :

$$Kw = [\ H_3O^+\ ]^2 \text{ also } Kw = [\ OH^-\ ]^2$$

$$[\ H_3O^+\ ] = \sqrt{Kw} \text{ and } [\ OH-\ ] = \sqrt{Kw}$$

$$\text{At } 25\ ^oC\ [\ H_3O^+\ ]= \sqrt{Kw} = \sqrt{1.01\ x\ 10^{-14}} = 1.01 \text{ x } 10^{-7}$$

$$pH= -\log\ (1.01x10^{-7}\ ) = 7.00$$

$$[\ OH-\ ] =\sqrt{Kw} = \sqrt{1.01\ x\ 10^{-14}} = 1.01 \text{ x } 10^{-7}$$

At 100o C

$$[\ H3O+\ ] = \sqrt{Kw} = \sqrt{49\ x10^{-14}} = 7.0 \text{ x } 10^{-7}$$

$$pH = -\log\ (7 \text{ x } 10^{-7}) = 6.15$$

$$[\ OH-\ ] = \sqrt{Kw} = \sqrt{49\ x10^{-14}} = 7.0 \text{ x } 10^{-7}$$

Exercise:

Calculate the change in pH of pure water on heating from 25ºC to 50ºC(Kw = $5.47x10^{-14}$) .

Buffer solution

is a solution that resist any change in pH(maintain pH approximately constant) when added amount of an acid or base.

Types of Buffer Solution

The two primary types into which buffer solutions are broadly classified into are acidic and alkaline buffers.

Acidic Buffers

are made from a weak acid and its salts.

Example:

CH_3COOH – CH_3COONa

• CH_3COOH (weak acid)

Basic Buffers

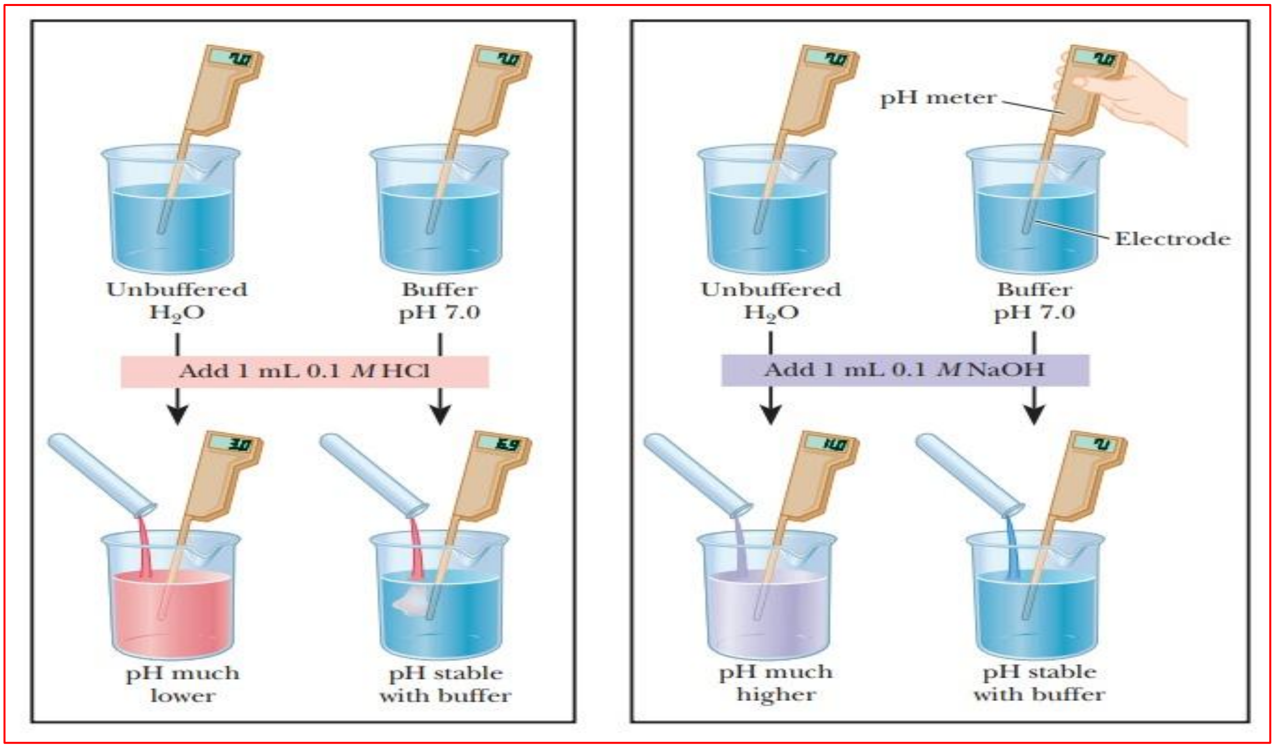
are made from a weak base and its salts.

Example:

NH_3 – NH_4Cl

• NH3 (weak base)

• NH4Cl (salt)



The Henderson-Hasselbalch equation is an equation that is often used to perform the calculations required in preparation of buffers for use in the laboratory.

Buffer solution that formed of weak acid and its salt:

$$CH_3COOH + H_2O \rightleftarrows CH_3\,COO^- + H_3O^+$$

$$HA \rightleftarrows H_+ + A_-$$

$$Ka= [H^+][A^-]/[HA] \text{ Or } [H+]=ka\times[HA^+]acid/[A^-]salt$$

$$Log\,[H^+]=log\,Ka + Log[acid]/[salt]$$

Multiply by −1

$$-Log\,[H^+]=-log\,Ka + Log[salt]/[acid]$$

$$pH= pKa+ Log[salt]/[acid]$$

Buffer solution formed of weak base and its salt:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \longrightarrow NH_4 + Cl^-$$

$$Kb=[NH^+{}_4][OH^-]/[NH_3] \text{ or } [OH^-]= Kb \times[NH_3]/[NH_4^+]$$

$$\text{Log } [OH^-]= \text{Log } Kb+ \text{Log } [base]/[salt]$$

Multiply by −1

$$-\text{Log } [OH^+]=-\log Kb + \text{Log}[salt]/[base]$$

$$pOH= pKb+ \text{Log}[salt]/[base]$$

Problem 1/ Calculate the pH of buffer of 0.3M CH_3COONa in 0.09M CH_3COOH? $Ka = 1.8\times10^{-5}$

Solution:

$$pH= pKa+ \text{Log}[salt]/[acid]$$

$$pH = -\log 1.8\times10^{-5} + \log (0.3 / 0.09)$$

$$pH = 4.74 + 0.522$$

$$pH = 5.262$$

Problem 2/ Calculate the pH of buffer of 0.28M NH_4Cl in0.07M NH_3? $Kb = 1.76\times10^{-5}$

Solution:

$$pOH= pKb+ \text{Log}[salt]/[base]$$

$$pOH = -\log 1.76\times10^{-5} + \log (0.28 / 0.07)$$

$$pOH = 4.75 + 0.602$$

$$pOH = 5.352$$

$$pH = 14 - 5.352$$

$$pH = 8.648$$