

FIRST STAGE II

# Volumetric Analysis

The Second Lecture

## Lecture Objective

- Equilibrium Acid- base solution
- Neutralisation Reaction
- Ionic product constant of water
- Hydrogen- Ion Exponent (pH)
- Calculation of pH of acidic & basic solutions.
- Examples

## Second Lecture

### Equilibrium

### Neutralisation

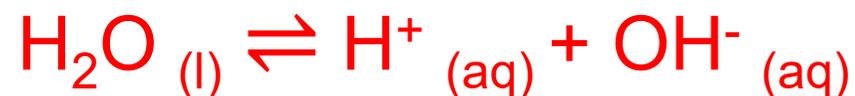
### $K_w$

### pH

### Calculation of pH

## Equilibrium

Water ( $\text{H}_2\text{O}$ ) – the most important molecule on earth. Even in pure water, there are small amounts of ions from the equilibrium below (“self-ionization of water” or “auto-ionization of water”).



More accurately:



$\text{H}_3\text{O}^+_{(aq)}$  = hydronium ion; often abbreviated as  $\text{H}^+_{(aq)}$

$\text{OH}^-_{(aq)}$  = hydroxide ion

$[\text{H}_3\text{O}^+] = [\text{OH}^-]$  in pure water

## Second Lecture

Equilibrium

Neutralisation

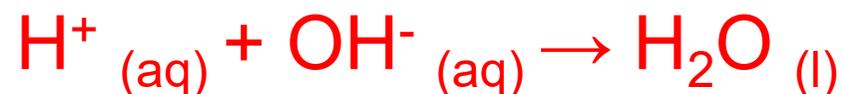
$K_w$

pH

Calculation of pH

## Neutralization

**Neutralization:** the reaction between an acid and a base called (neutralization reaction) and the water molecular is one of chief products



**Strengths** of Acids and Bases: (is depend to the amount of  $\text{H}^+$  or  $\text{OH}^-$  produced per mole of substance dissolved)

**Note:** Strong Acids And Bases Dissociate Completely (100%) In Water  
Most be know them

Stong Acids		Strong Bases	
Hydrobromic acid	HBr	Barium hydroxide	$\text{Ba}(\text{OH})_2$
Hydrochloric acid	HCl	Calsium hydroxide	$\text{Ca}(\text{OH})_2$
Hydroiodic acid	HI	Lithium hydroxide	LiOH
Nitric acid	$\text{HNO}_3$	Potassium hydroxide	KOH
Perchloric acid	$\text{HClO}_4$	Sodium hydroxide	NaOH
Sulfuric acid	$\text{H}_2\text{SO}_4$	Strontium hydroxide	$\text{Sr}(\text{OH})_2$

## Second Lecture

Equilibrium

Neutralisation

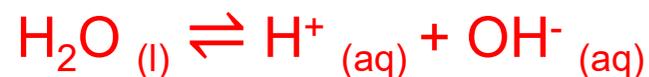
$K_w$

pH

Calculation of pH

## Ionic product constant of water $K_w$

Pure water is very slightly ionised and has little ability for electrical conductivity according to conductivity experiments done by **Kolrawsh** in 1894. Thus, water is slightly ionised into:



The equilibrium constant is  $K_{eq}$

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{\alpha_{H^+} \cdot \alpha_{OH^-}}{\alpha_{H_2O}} \dots\dots\dots(1)$$

$$\alpha_x = f_x \cdot [X] \dots\dots\dots(2) \text{ by Substitute in (1)}$$

$$K_{eq} = \frac{f_{H^+} \cdot [H^+] \times f_{OH^-} \cdot [OH^-]}{f_{H_2O} \cdot [H_2O]} \dots\dots\dots(3)$$

when the solution is very dilute  $f=1$

## Second Lecture

Equilibrium

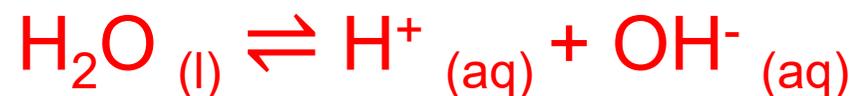
Neutralisation

**$K_w$**

pH

Calculation of pH

## Ionic product constant of water $K_w$



$$K_{\text{eq}} = \frac{[\text{H}^+] \times [\text{OH}^-]}{[\text{H}_2\text{O}]}$$
 .....(4) very small of water is ionised,  $\text{H}_2\text{O}$  is constant

After that the  $K_{\text{eq}}$  transform to  $K_w$

$$K_w = [\text{H}^+] \times [\text{OH}^-]$$
 .....(5)

Where  $K_w$  is ionic product constant of water which equals at 25 °C

$$10.01 \times 10^{-14}$$

**NOTE:** The  $K_w$  was increases with in increase the temperatures

## Second Lecture

Equilibrium

Neutralisation

$K_w$

pH

Calculation of pH

## Ionic product constant of water $K_w$

$$K_w = [H^+] \times [OH^-] \dots \dots (5)$$

$$10.01 \times 10^{-14} = [H^+] \times [OH^-]$$

At equilibrium of water ionization :  $[H^+] = [OH^-]$

$$[H^+] = [OH^-] = \sqrt{10.01 \times 10^{-14}} = 10^{-7}$$

When  $[H^+] > 10^{-7}$  the solution is acidic,

When  $[H^+] = 10^{-7}$  the solution is neutral,

When  $[H^+] < 10^{-7}$  the solution is basic.

**Also from eq (5)**

$$[H^+] = \frac{K_w}{[OH^-]} \quad \text{and} \quad [OH^-] = \frac{K_w}{[H^+]}$$

## Second Lecture

Equilibrium

Neutralisation

$K_w$

pH

Calculation of pH

## Hydrogen-Ion Exponent (pH):

It is preferred to express hydrogen ion concentration as ion exponent or *p-function* of hydrogen ion (pH), instead of using negative exponents:

$$\text{pH} = -\log[\text{H}^+] = \log \frac{1}{[\text{H}^+]} \text{ or } [\text{H}^+] = 10^{-\text{pH}}$$

$$\text{pOH} = -\log[\text{OH}^-] = \log \frac{1}{[\text{OH}^-]} \text{ or } [\text{OH}^-] = 10^{-\text{pOH}}$$

Therefore from equation (5):  $[\text{H}^+][\text{OH}^-] = K_w \times \log$

$$\bar{\mp} \log [\text{H}^+] \bar{\mp} \log [\text{OH}^-] = \bar{\mp} \log K_w$$

$$\text{pH} + \text{pOH} = \text{p}K_w = 14$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pOH} = 14 - \text{pH}$$

$$\text{pH} = \text{pOH} = 7$$

## Second Lecture

Equilibrium

Neutralisation

$K_w$

pH

Calculation of pH

## Hydrogen-Ion Exponent (pH):

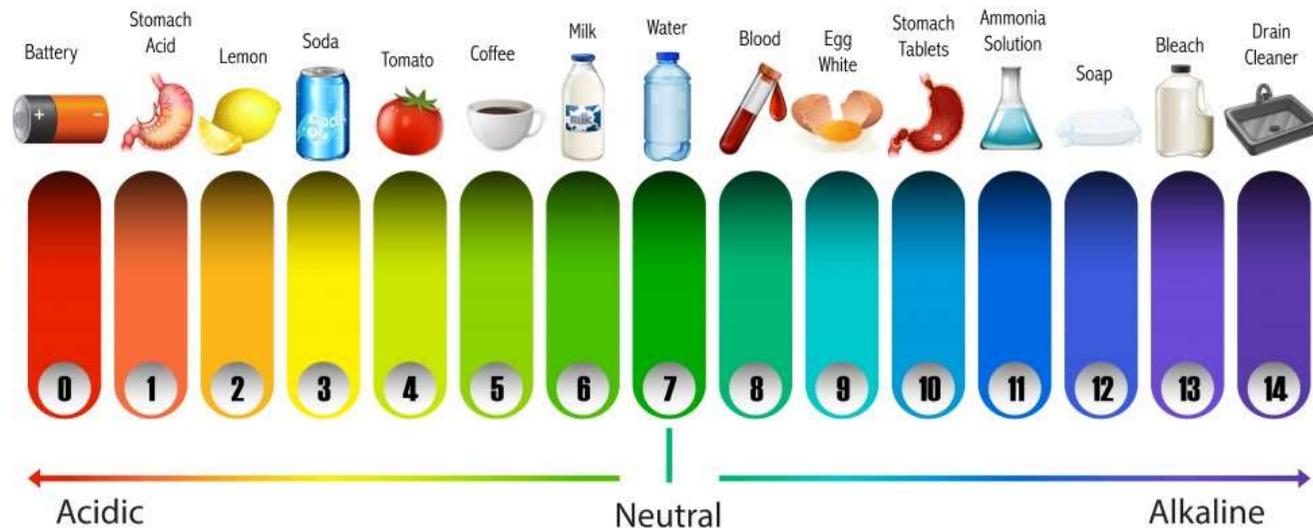
When **pH = 7**, the solution is neutral,

When **pH < 7**, the solution is acidic,

When **pH > 7**, the solution is basic.

Therefore, the pH range is from zero to 14

## The pH Scale



## Second Lecture

Equilibrium

Neutralisation

$K_w$

pH

Calculation of pH

## Calculation of pH

- Strong Acids

They are completely ionized such as HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>

**Ex.** Calculate the pH of 0.01 M of HCl and calculate its pOH ?

**Solution:**



$$[\text{H}^+] = 0.01\text{M} = 10^{-2}$$

$$\text{pH} = -\log[\text{H}^+] = -\log 10^{-2} = 2$$

$$\text{pH} = 2$$

$$\text{pOH} = 14 - \text{pH}$$

$$\text{pOH} = 14 - 2 = 12$$

$$\text{pOH} = 12$$

## Second Lecture

Equilibrium

Neutralisation

$K_w$

pH

Calculation of pH

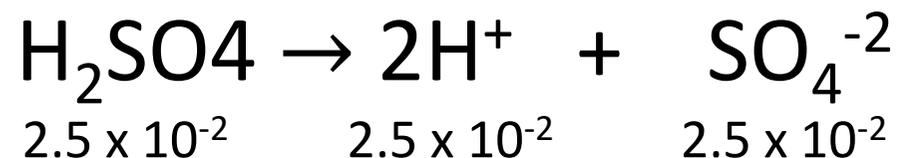
## Calculation of pH

- Strong Acids

They are completely ionized such as HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>

**Ex.** What is the pH and pOH of a  $2.5 \times 10^{-2}$  M solution of H<sub>2</sub>SO<sub>4</sub>

**Solution:**



$$[\text{H}^+] = 2 \times 2.5 \times 10^{-2}$$

$$\text{pH} = -\log[2 \times 2.5 \times 10^{-2}] = -\log 5.0 \times 10^{-2} = -0.7 + 2 = 1.3$$

**pH = 1.3**

$$\text{pOH} = 14 - \text{pH}$$

$$\text{pOH} = 14 - 1.3 = 12.7$$

**pOH = 12.7**

## Second Lecture

Equilibrium

Neutralisation

$K_w$

pH

Calculation of pH

## Calculation of pH

- Strong bases

They are completely ionized such as NaOH, KOH and Ba(OH)<sub>2</sub>.

**Ex.** Calculate the pOH of 0.01 M of NaOH and calculate its pH ?

**Solution:**



$$[\text{OH}^-] = 0.01\text{M} = 10^{-2}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log 10^{-2} = 2 \quad \text{pOH} = 2$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - 2 = 12 \quad \text{pH} = 12$$

## Second Lecture

Equilibrium

Neutralisation

$K_w$

pH

Calculation of pH

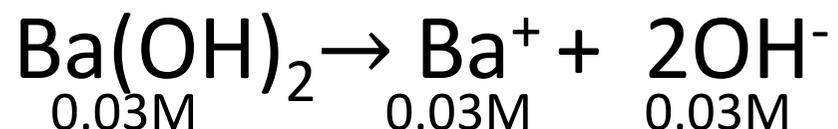
## Calculation of pH

- Strong bases

They are completely ionized such as NaOH, KOH and Ba(OH)<sub>2</sub>.

**Ex.** Calculate the pOH of 0.03 M of Ba(OH)<sub>2</sub> and calculate its pH ?

**Solution:**



$$[\text{OH}^-] = 2 \times 0.03M = 6 \times 10^{-2}$$

$$\text{pOH} = -\log[6 \times 10^{-2}] = -0.77 + 2 \quad \text{pOH} = 1.23$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - 1.23 = 12.77 \quad \text{pH} = 12.77$$

## Second Lecture

### REVIEW

- What's is the un equilibrium in chemistry ?
- Neutralization reaction
- The strength of an acid and a base in a solution depends on what ?
- Derive an equation of Ionic product constant of water  $K_w$
- Express of Hydrogen-Ion Exponent (pH)
- pH scale and know the difference between pH & pOH?
- Exercises for calculation the pH of strong acid & base

## Second Lecture

### Home Work

1. Calculate the pH and pOH of the following acidic solutions?
  - (a) 0.082 M  $\text{HNO}_3$
  - (b) 0.5 mL of 0.1M of HCl add to 50 ml water
2. Calculate the pH and pOH of the following basic solutions?
  - (a) 0.055 M KOH
  - (b) 0.8 mL of 0.2M of NaOH add to 50 ml water