Acid – Base Titration
part 1

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Acid base titration

Strong-, weak acid and base

Ka, Kb, Kw, PH, POH

Polyprotic acid

Buffer

Salts

Titration curves

indicators

Applications and calculations

Titration in non-aqueous media

Neutralization titration (Acid-Base titration)

The neutralization of an acid (or a base) by a base (or by an acid) results in salt and water.

Analyte - Titrant

Types of acid base titration:

1- strong acid - strong base titration

2- Strong base - strong acid titration

3- weak acid - strong base titration

4- weak base - strong acid titration

Neutralization titration (Acid-Base titration)

$$\text{Acid} + \text{Base} \longrightarrow \text{Salt} + H_2O$$

Define what is acid?? What is base??

Acid & Base

Arhenius theory

Bronsted lowery theory

Lewis acid base

Definitions

Arrhenius Theory

- *Acid: substance that produces H+ in aqueous solution*
- *Base: substance that produces OH- in aqueous solution*

Acid $HCl \xrightarrow{H2O} H^+(aq) + Cl^-(aq)$

Base $NaOH \xrightarrow{H2O} Na^+ (aq) + OH^-(aq)$

Definitions

Brönsted-Lowery theory

A Brönsted acid releases a proton, a proton donator.

A Brönsted base accepts a proton, a proton acceptor.

Lewis theory

Lewis acid: is an electron pair acceptor
Lewis base: is an electron pair donor
The reaction between lewis acid and base results in a formation of covalent or coordination bonds.

$SO_3 + H_2O \longrightarrow H_2SO_4$

$NH_3 + BF_3 \longrightarrow H_3NI \rightarrow BF_3$

$2\,CN^{-} + Ag^{+} \longrightarrow [Ag\,(CN)_2]^{-}$

Acid - Base titration

Bronsted lowery theory

Acid

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

$HNO_3 + H_2O \longrightarrow NO_3^- + H_3O^+$

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

$CH_3COOH + H_2O \longleftrightarrow CH_3COO^- + H_3O^+$

$HOCl + H_2O \longleftrightarrow OCl^- + H_3O^+$

$HNO_2 + H_2O \longleftrightarrow NO_2^- + H_3O^+$

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

$HCO_3^- + H_2O \longleftrightarrow CO_3^{-\,2} + H_3O^+$

Strong

Weak

Neutral compound

Cationic

Anionic

Acid - Base titration

Bronsted lowery theory

Base

Neutral compoud

Anionic

$NaOH + H_2O \longrightarrow Na^+ + OH^-$

$KOH + H_2O \longrightarrow Na^+ + OH^-$

$Ba(OH)_2 + H_2O \longrightarrow Ba^{+2} + 2\,OH^-$

Strong

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

$OCl^- + H_2O \longleftrightarrow HOCl + OH^-$

$HCO_3^- + H_2O \longleftrightarrow H_2CO_3 + OH^-$

$CH_3COO^- + H_2O \longleftrightarrow CH_3COOH + OH^-$

Weak

Conjugate acids and bases:

Conjugate bases are the species formed when an acid lose a proton

$$\text{Acid 1} \longrightarrow \text{Base 1 + Proton}$$

Conjugate acids are the species formed when a base accept a proton

$$\text{Base 2 + Proton} \longrightarrow \text{Acid 2}$$

$$\underset{\text{Base}}{NH_3} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{conjugate acid}}{NH_4^+} + \underset{\text{conjugate base}}{OH^-}$$

$$\underset{\text{acid}}{CH_3COOH} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{conjugate base}}{CH_3COO^-} + \underset{\text{conjugate acid}}{H_3O^+}$$

Amphoterism

A substance behaves as an acid and as a base is called *amphoteric* like Water, ethanol, methanol.

Water is amphoteric (see above example)

Methanol is amphoteric.

$$NH_3 + CH_3OH \rightleftharpoons NH_4^+ + CH_3O^-$$

$$CH_3OH + HNO_2 \rightleftharpoons CH_3OH_2^+ + NO_2^-$$

Base1	Acid2	conjugate acid 1	conjugate base 2

Amphoteric species: HCO_3^- , HPO_4^{-2}, HSO_4^-

Amphoterism

For Example: **: HCO_3^-**

$HCO_3^- + H_2O \longleftrightarrow H_2CO_3 + OH^-$ **Base**

$HCO_3^- + H_2O \longleftrightarrow CO_3^{-\,2} + H_3O^+$ **Acid**

Hydrogen Carbonate ion is a weak base, and Carbonic acid is conj. Acid

Hydrogen carbonate ion is a weak acid, and Carbonate is conj. Base

Carbonic acid is only a weak acid, Hydrogen carbonate is weak conj. base

Carbonate ion is only a weak base, Hydrogen carbonate is weak conj. acid

Autoprotolysis

Amphiprotic solvents behave self-ionization to form a pair of ionic species.

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

$$2\,CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^-$$

$$2\,NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

Autoprotolysis

The ion-product constant for water (K_w)

$$2\ H_2O \longleftrightarrow H_3O^+ \quad + \quad OH^-$$

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

$Kw : 1.011 \times 10^{-14}$ at 25 °C

$$\log K_w = -\log [H_3O^+] + -\log [OH^-]$$
$$pK_w = pH + pOH = 14$$

Strength of acids and bases (K_a & K_b)

Strong acids:
HCl,
$HClO_4$
HNO_3
H_2SO_4 (the first hydrogen),
HI
HBr
organic sulfonic acids (RSO_3H).

Conj. Bases:
Neglected
basicity

Strength of acids and bases (K_a & K_b)

Strength of an acid depends on the ability to donate a proton.

For a base it is the affinity to accept a proton.

Strong acids: dissociate ***completely*** in water to give H_3O^+ and a very weak conjugate base (neglected).

$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

1.2 M 1.2 M 1.2 M

Acid fully dissociates.

No equilibrium occurs between the acid and its ions.

Strength of acids and bases (K_a & K_b)

Weak acids:	**Conj. Bases:**
CH_3COOH	Weak bases
HNO_2	
H_2CO_3	
H_3BO_3	
HF	
NH_4+	
HCO_3^-	

Strength of acids and bases (K_a & K_b)

Weak acids:

- only dissociate partially in water.

- Their conjugate bases are weak bases

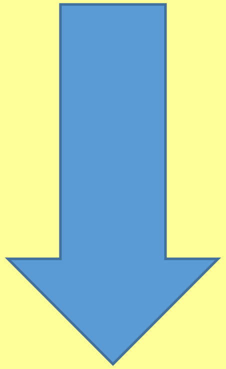
- There is an equilibrium constant

$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

- **The Ka is (1.8×10^{-5}).**
- **Some of the CH_3COOH remains undissociated**

Now we know Strong & weak

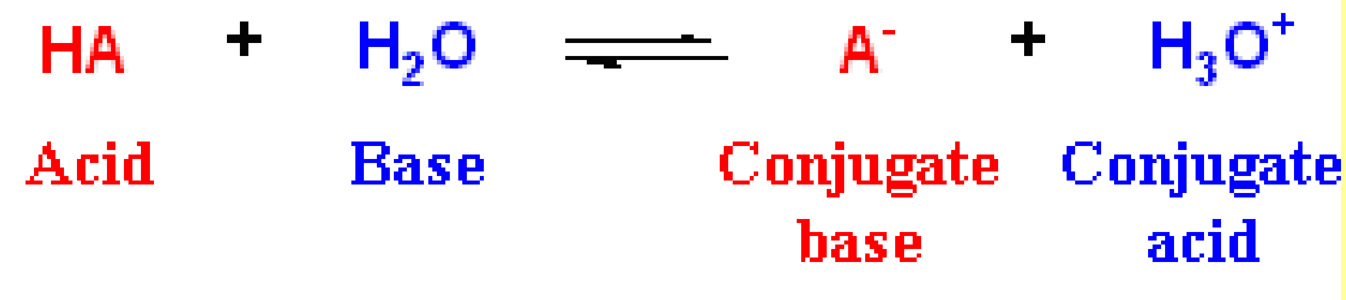
How to differentiate weak acids and weak bases among each other



K_a & K_b

Strength of acids and bases (K_a & K_b)

The ionization equation of a weak acid HA :



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

Acid, Base, Conjugate base, Conjugate acid

The equilibrium constant *K_a*, called **acidity constant** (Dissociation constant, or ionization constant)

$$Ka = \frac{[A-]\,[H3O+]}{[HA]}$$

After HA (acid) loses its proton it is converted into A- (base).
Therefore HA and A- are conjugate acid-base pairs.
Conjugate acid-base pairs differ by only one proton.

Strength of acids and bases ($K_{a\ \&}\ K_b$)

Strong bases are completely dissociated in water.

–They have a great attraction to protons.

–They have a pair of electrons to form a bond with the proton.

Strong bases are NaOH, KOH, $Ba(OH)_2$ and quaternary ammonium hydroxide R_4NOH where R is CH_3- or C_2H_5- group, O^{-2}, H^-.

Example:

$$\boxed{O^{2-}(aq) + H_2O(l) \rightarrow OH\text{-}(aq) + OH\text{-}(aq)}$$

Strength of acids and bases (K_{a} & K_{b})

Weak bases are molecules or ions that are partially ionized in water to give OH-

–They are poor proton acceptors

- Their conjugated acids are weak acids.

– examples: NH3, $CH_3CO_2^-$, OCl^-, NO_2^-, organic amines, alkaloids.

$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+ (aq)$

The equilibrium constant, Kb, is 1.8×10^{-5}.

Some NH_3 molecules remain undissociated.

Strength of acids and bases (K_{a} & K_{b})

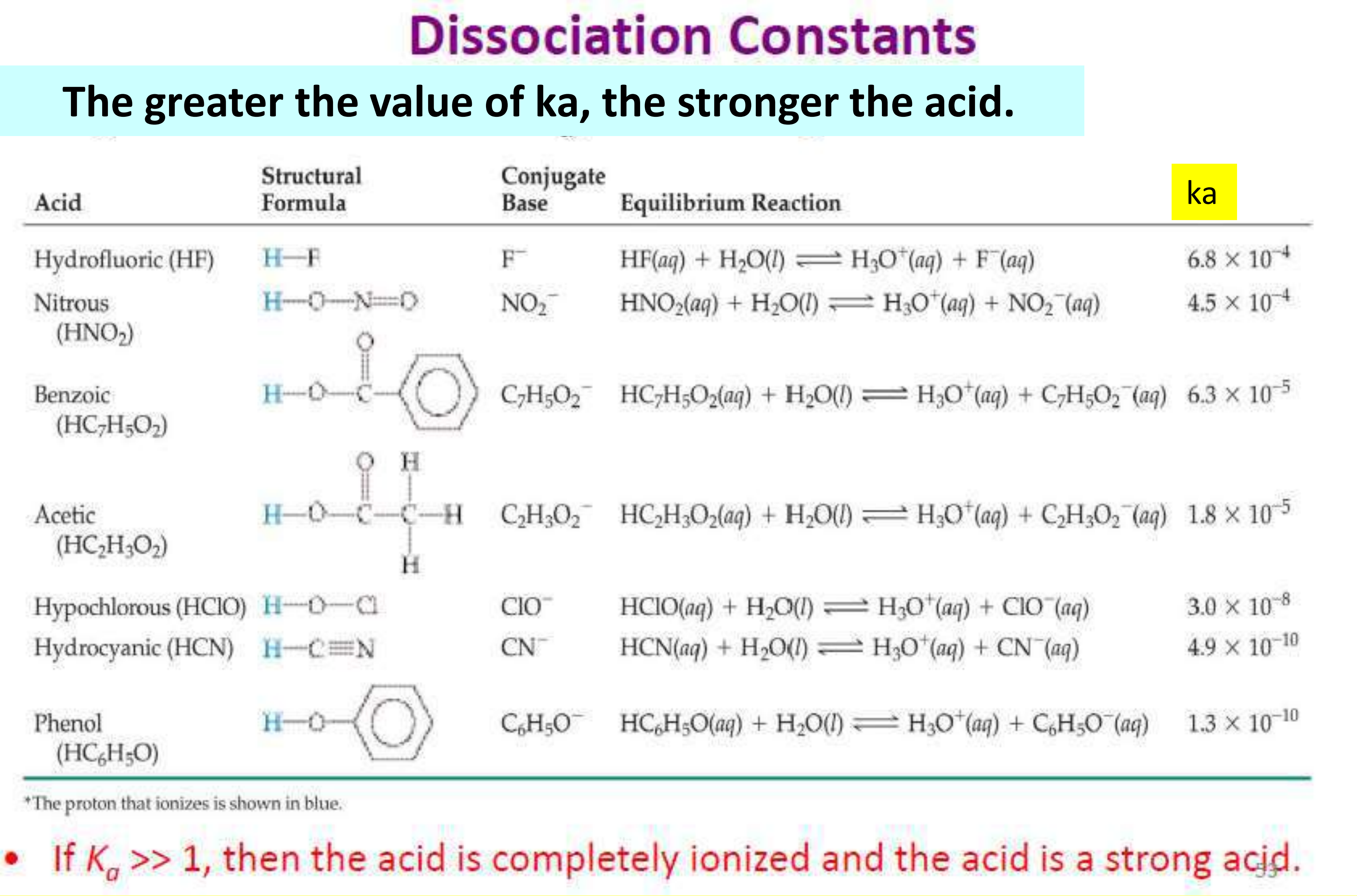
The ionization equation of a weak base B

$$\underset{\text{base}}{B} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{conjugate acid}}{HB^+} + \underset{\text{conjugate base}}{OH^-}$$

$$\mathbf{Kb} = \frac{[HB^+]\,[OH-]}{[B]}$$

The equilibrium constant K_b, called **bacisity constant** (or dissociation constant, or ionization constant)

Strength of acids and bases (K_{a} & K_{b})



Dissociation Constants

The greater the value of ka, the stronger the acid.

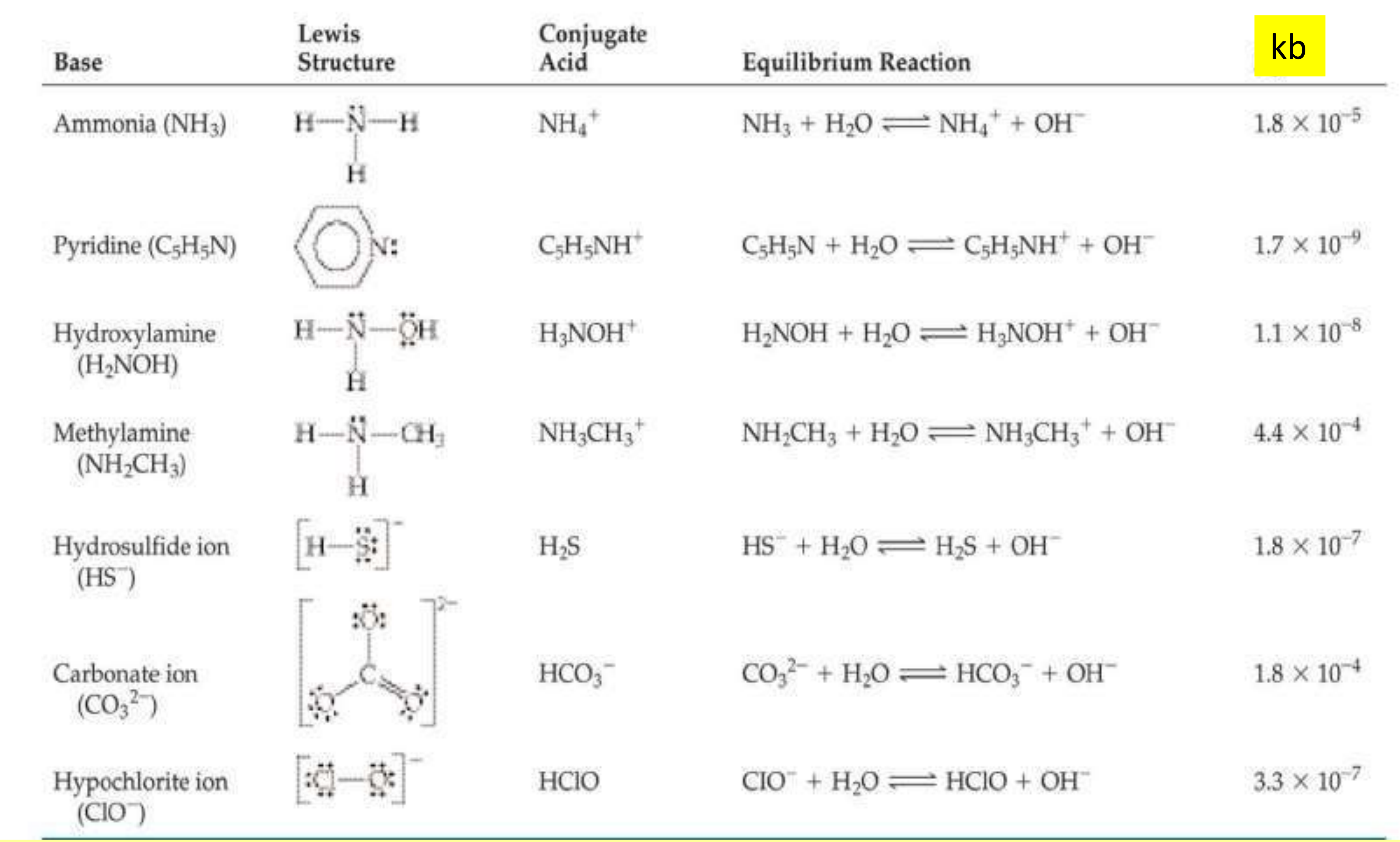
Acid	Structural Formula	Conjugate Base	Equilibrium Reaction	ka
Hydrofluoric (HF)	H—F	F^-	$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$	6.8×10^{-4}
Nitrous (HNO_2)	H—O—N=O	NO_2^-	$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$	4.5×10^{-4}
Benzoic ($HC_7H_5O_2$)		$C_7H_5O_2^-$	$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_7H_5O_2^-(aq)$	6.3×10^{-5}
Acetic ($HC_2H_3O_2$)		$C_2H_3O_2^-$	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$	1.8×10^{-5}
Hypochlorous (HClO)	H—O—Cl	ClO^-	$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$	3.0×10^{-8}
Hydrocyanic (HCN)	H—C≡N	CN^-	$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol (HC_6H_5O)		$C_6H_5O^-$	$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

*The proton that ionizes is shown in blue.

- If $K_a >> 1$, then the acid is completely ionized and the acid is a strong acid.

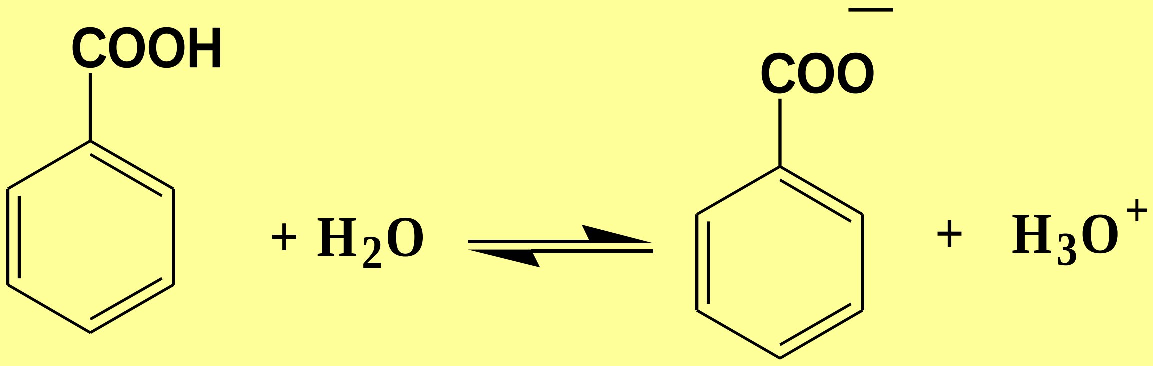
Strength of acids and bases ($K_{a\ \&}\ K_b$)

The greater the value of kb, the stronger the base.

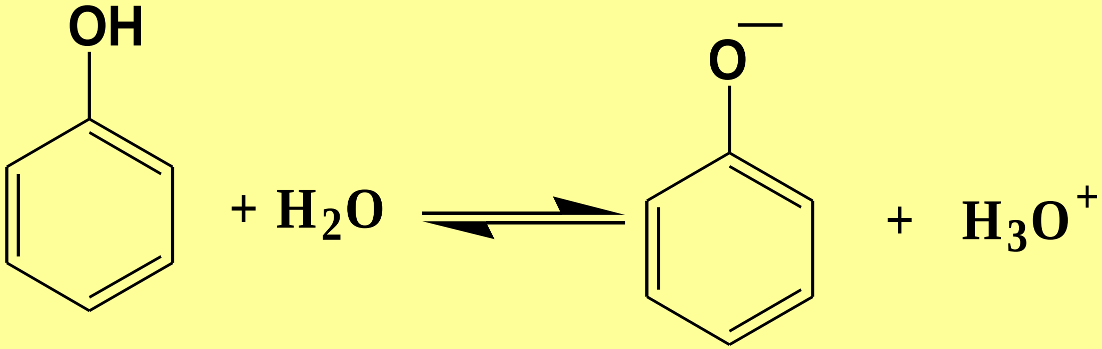


Base	Lewis Structure	Conjugate Acid	Equilibrium Reaction	kb
Ammonia (NH_3)	$\mathrm{H-\ddot{N}-H}$ H	NH_4^+	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine (C_5H_5N)		$C_5H_5NH^+$	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Hydroxylamine (H_2NOH)	$\mathrm{H-\ddot{N}-\ddot{\underset{\cdot\cdot}{O}}H}$ H	H_3NOH^+	$H_2NOH + H_2O \rightleftharpoons H_3NOH^+ + OH^-$	1.1×10^{-8}
Methylamine (NH_2CH_3)	$\mathrm{H-\ddot{N}-CH_3}$ H	$NH_3CH_3^+$	$NH_2CH_3 + H_2O \rightleftharpoons NH_3CH_3^+ + OH^-$	4.4×10^{-4}
Hydrosulfide ion (HS^-)	$\left[\mathrm{H-\ddot{\underset{\cdot\cdot}{S}}:}\right]^-$	H_2S	$HS^- + H_2O \rightleftharpoons H_2S + OH^-$	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	1.8×10^{-4}
Hypochlorite ion (ClO^-)	$\left[\mathrm{:\ddot{\underset{\cdot\cdot}{Cl}}-\ddot{\underset{\cdot\cdot}{O}}:}\right]^-$	$HClO$	$ClO^- + H_2O \rightleftharpoons HClO + OH^-$	3.3×10^{-7}

Acetic acid + H_2O ⟷ Acetate + H_3O^+

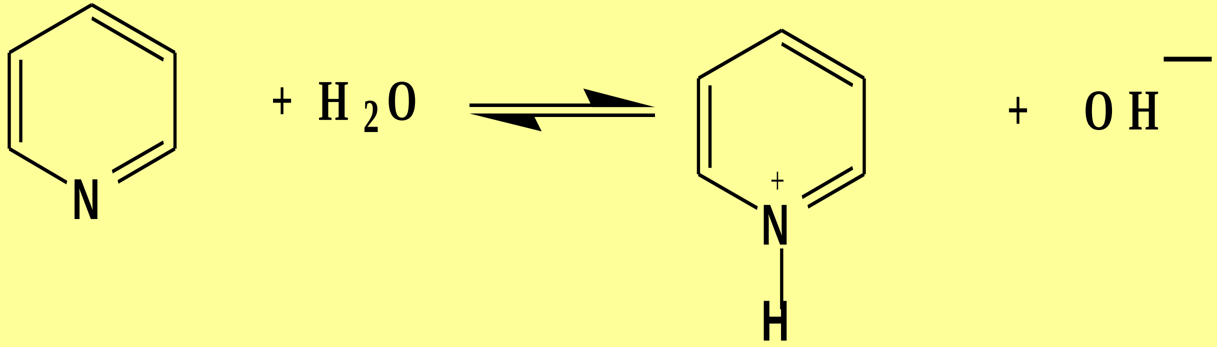


Benzoic acid **Benzoate**



Phenol **Phenolate**

Ammonia + H_2O $\longleftrightarrow$ Ammonium + OH^-



Pyridine

Pyridinium

$$H_3C{-}NH_2 + H_2O \rightleftharpoons H_3C{-}NH_3^+ + OH^-$$

Methylamine

Methylammonium

Question

Compare acidity strength between HCN and HF?

Ka of HCN = $4.9*10^{-10}$, HF = $6.8*10^{-4}$

Acidity HF > HCN Or HF is stronger as acid than HCN

Remember both of them
HCN and HF are weak acids

Remember HBr is a strong acid completely dissociate in water

Relation between K_a and K_b

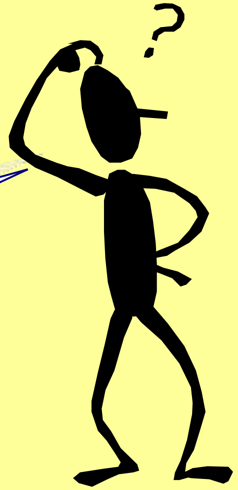
For a conjugate pair acetic acid/acetate

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_a = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$K_b = \frac{[OH^-]\,[CH_3COOH]}{[CH_3COO^-]}$$



$$K_a * K_b = K_w$$

Relation between K_a and K_b

For a conjugate pair ammonia/ammonium

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

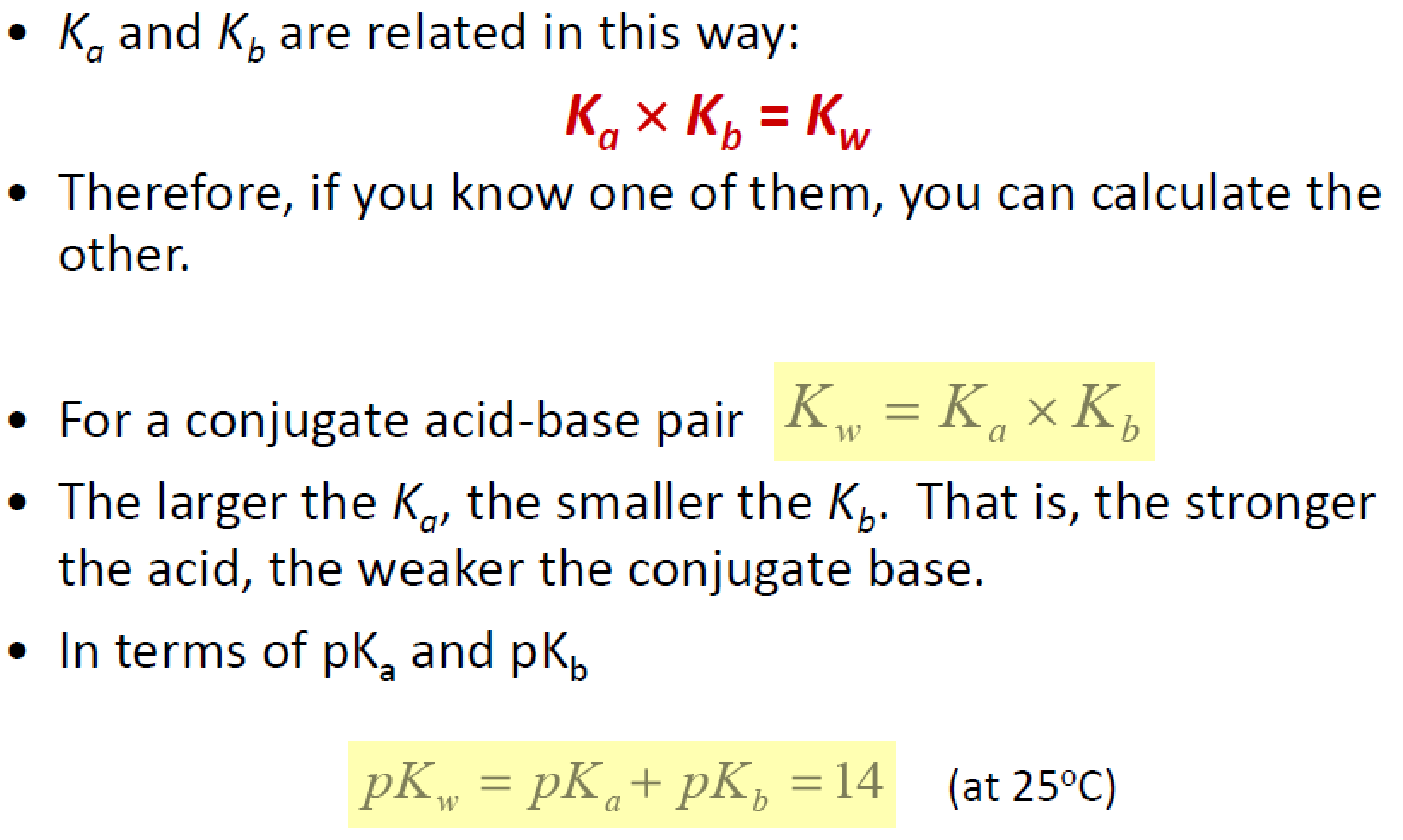
$$K_b = \frac{[OH^-]\,[NH_4^+]}{[NH_3]}$$

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

$$K_a = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]}$$

$$K_a * K_b = [OH^-]\,[H_3O^+] = K_w$$

Relation between K_a and K_b



- K_a and K_b are related in this way:

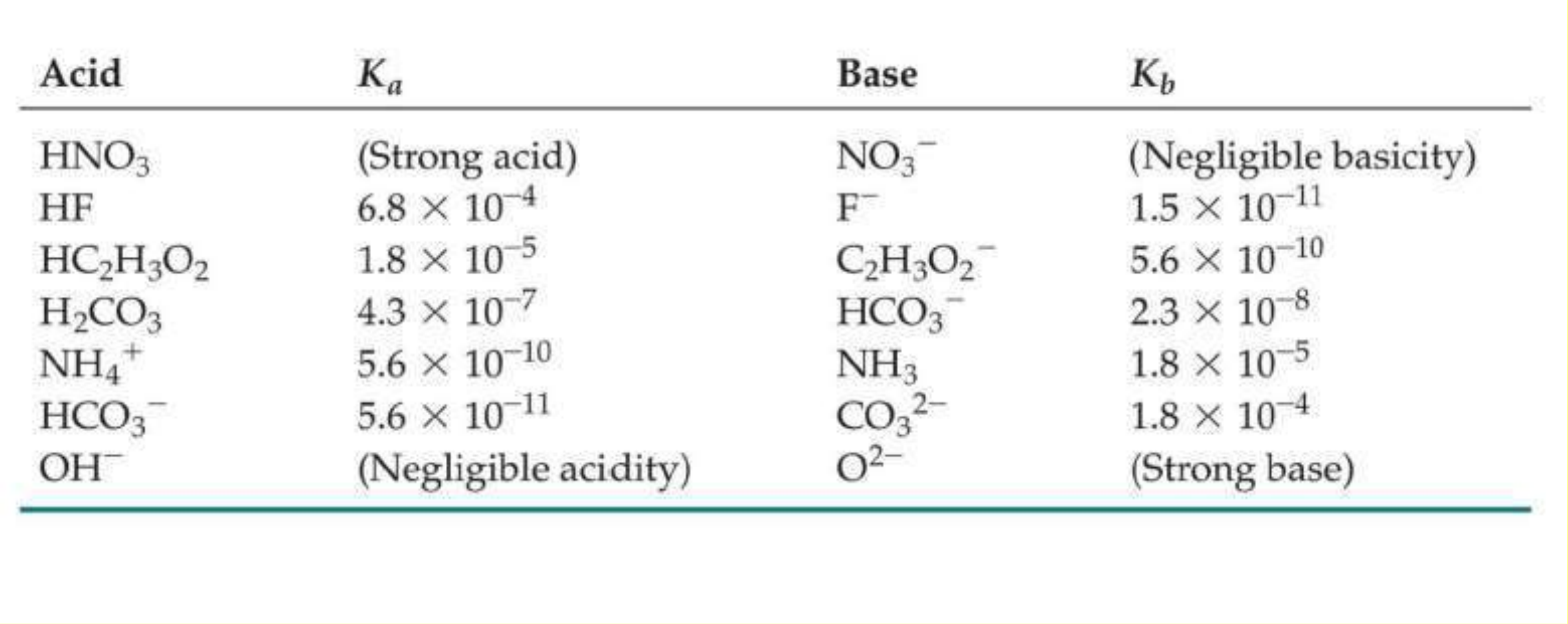
$$K_a \times K_b = K_w$$

- Therefore, if you know one of them, you can calculate the other.

- For a conjugate acid-base pair $K_w = K_a \times K_b$
- The larger the K_a, the smaller the K_b. That is, the stronger the acid, the weaker the conjugate base.
- In terms of pK_a and pK_b

$$pK_w = pK_a + pK_b = 14$$ (at 25°C)

Relation between K_a and K_b



Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

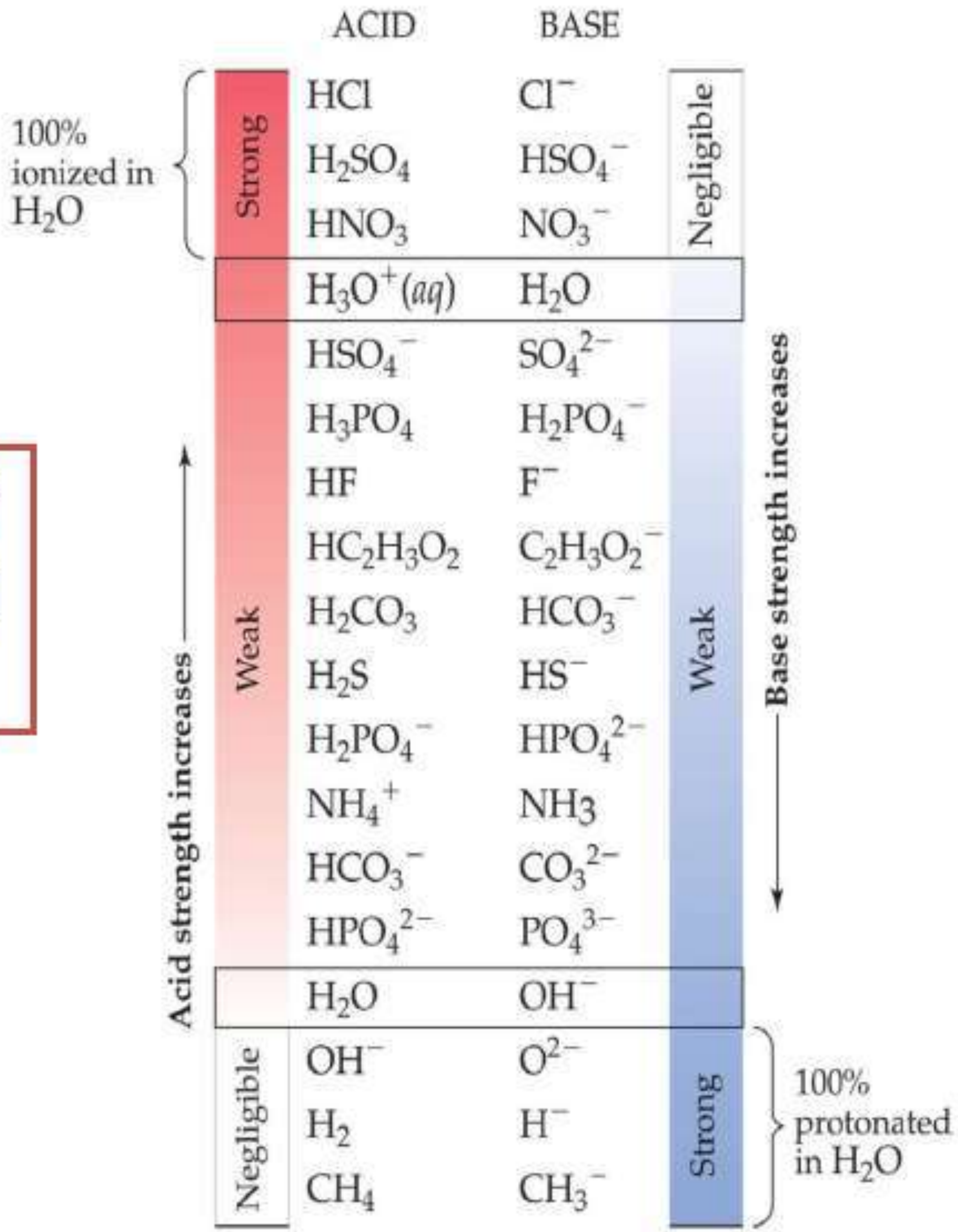
Relation between K_a and K_b

A base-acid couple (Conjugate)

$$K_a * K_b = K_w$$

$$pK_a + pK_b = 14$$

Relative strengths of some conjugate-acid base pairs.



	ACID	BASE	
Strong	HCl	Cl^-	Negligible
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$H_3O^+(aq)$	H_2O	
Weak	HSO_4^-	SO_4^{2-}	Weak
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	
Negligible	OH^-	O^{2-}	Strong
	H_2	H^-	
	CH_4	CH_3^-	

100% ionized in H_2O

Acid strength increases

Base strength increases

100% protonated in H_2O

P-Value

$pX = -\log [X] = \log [X]^{-1}$

$pH = -\log [H_3O^+]$

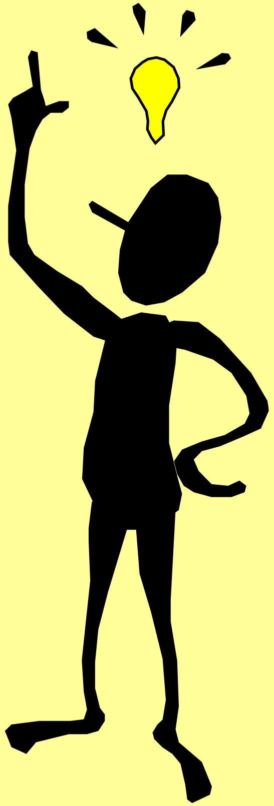
$pOH = -\log [OH^-]$

$pKa = -\log Ka$

$pKb = -\log Kb$

$pAg = -\log [Ag^+]$

$pCa = -\log [Ca^{+2}]$



P-Value

↑ Ka ↓ pka ↑ Acidity

↑ Kb ↓ pkb ↑ Basicity

Pka & pkb

pK_a	Acid	Base	pK_b
-1.32	HNO_3	NO_3^-	15.32
3.45	HF	F^-	10.55
4.75	CH_3COOH	CH_3COO^-	10.25
11.96	HS^-	S^{-2}	2.04

very strong acid (base) pK_a $(pK_b) \leq 0$

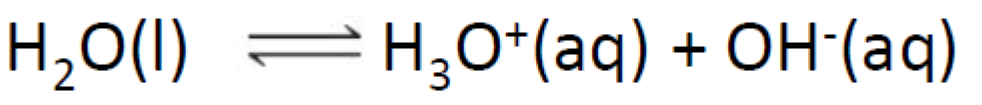
strong acid (base) pK_a $(pK_b) = 0$ to 4

weak acid (base) pK_a $(pK_b) = 4$ to 10

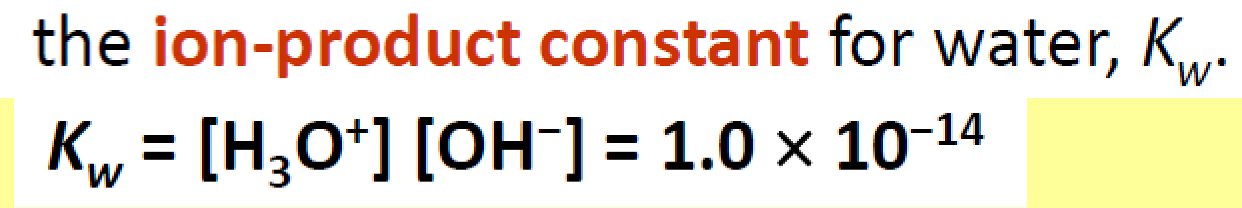
very weak acid (base) pK_a $(pK_b) = 10$ to 14

Extreme weak acid (base) pK_a $(pK_b) \geq 14$

PH Scale

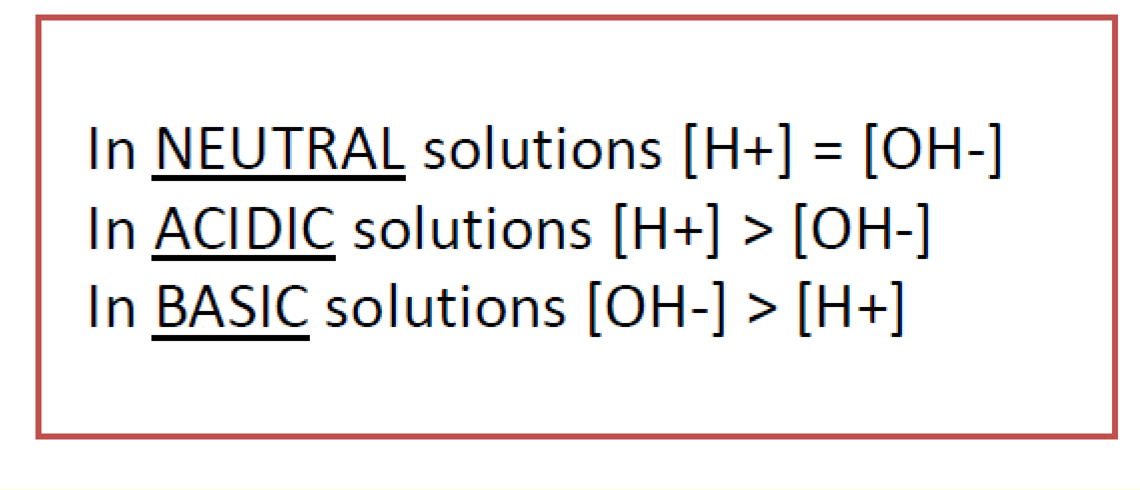


$$H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$



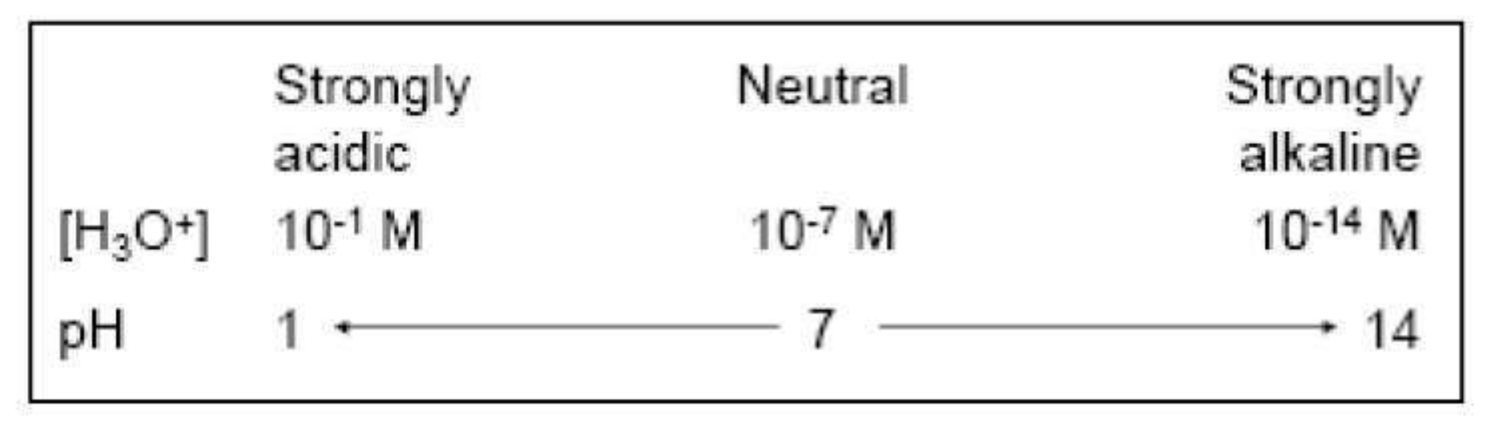
the **ion-product constant** for water, K_w.

$$K_w = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}$$

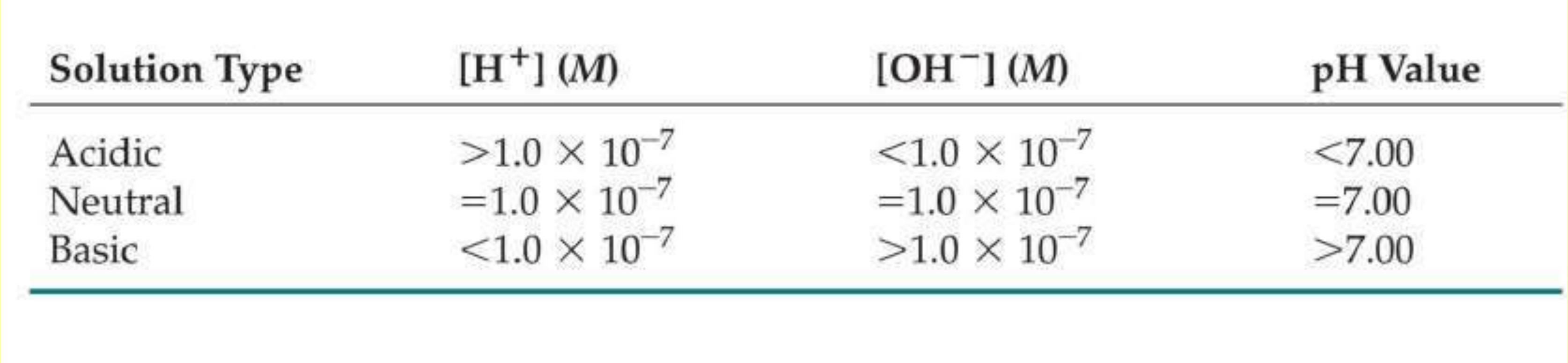


In NEUTRAL solutions [H+] = [OH-]
In ACIDIC solutions [H+] > [OH-]
In BASIC solutions [OH-] > [H+]

PH Scale

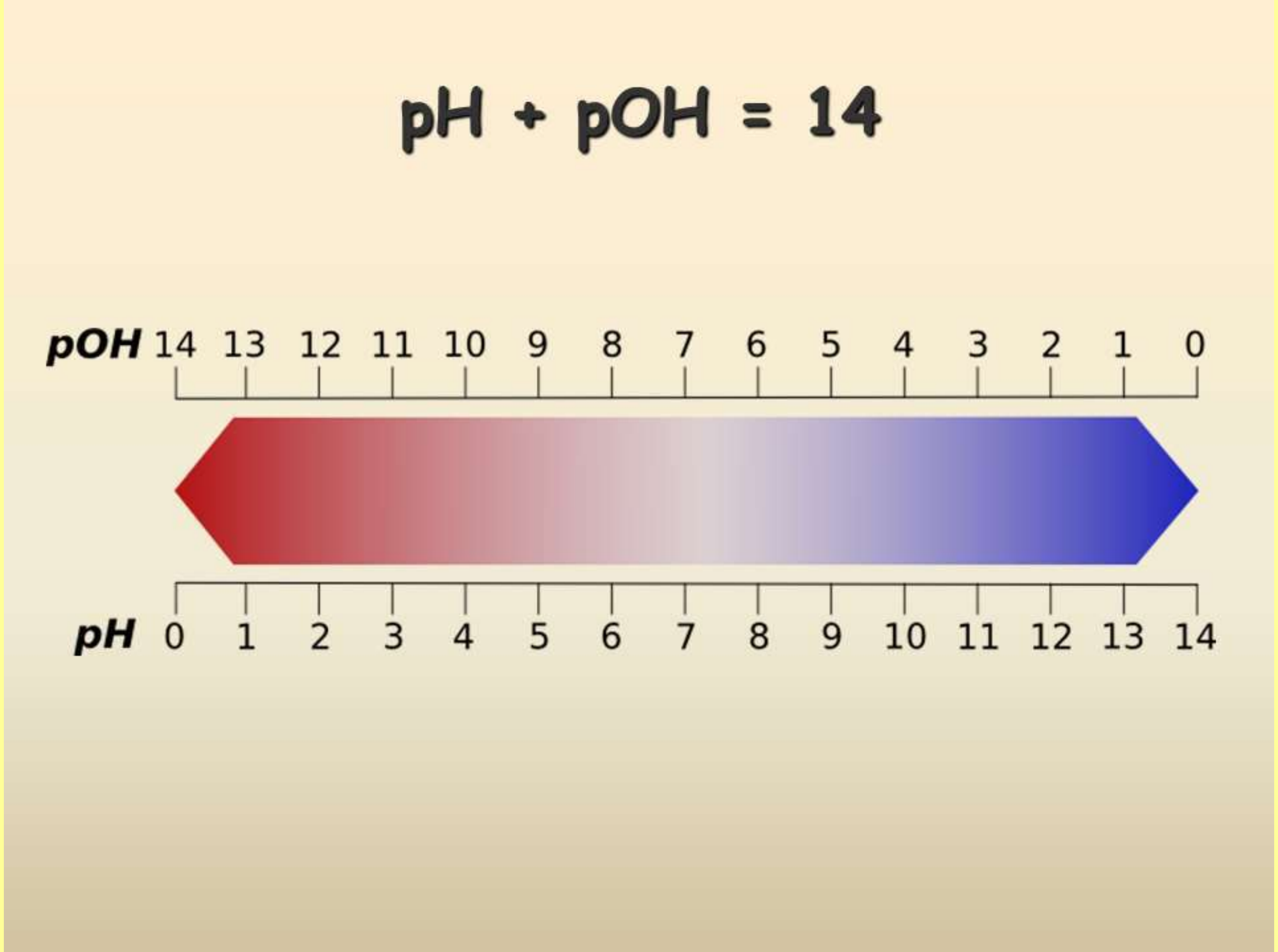


	Strongly acidic	Neutral	Strongly alkaline
$[H_3O^+]$	10^{-1} M	10^{-7} M	10^{-14} M
pH	1 ←	7	→ 14



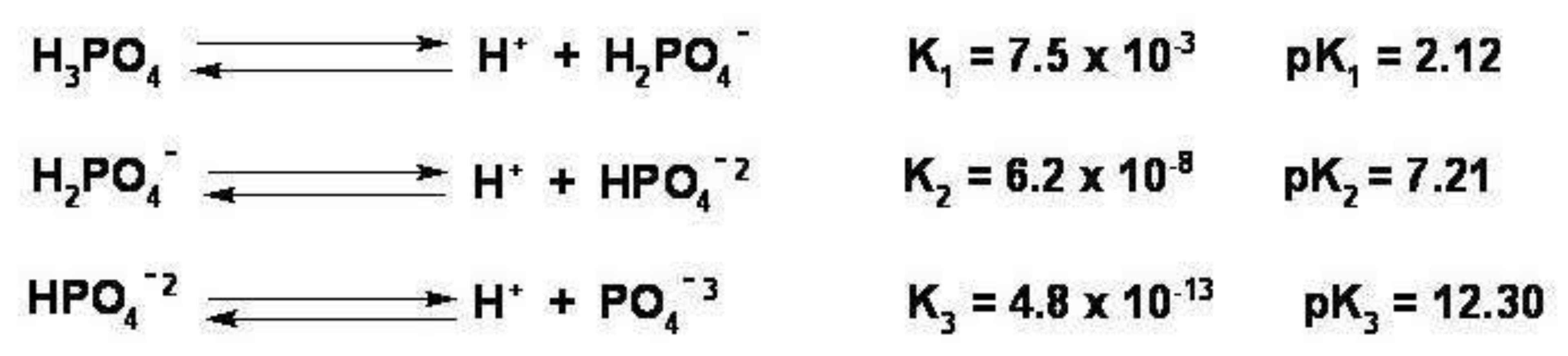
Solution Type	$[H^+]$ (*M*)	$[OH^-]$ (*M*)	pH Value
Acidic	$>1.0 \times 10^{-7}$	$<1.0 \times 10^{-7}$	<7.00
Neutral	$=1.0 \times 10^{-7}$	$=1.0 \times 10^{-7}$	$=7.00$
Basic	$<1.0 \times 10^{-7}$	$>1.0 \times 10^{-7}$	>7.00

PH Scale



pH + pOH = 14
pOH
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
pH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14

Polyprotic acid



$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $K_1 = 7.5 \times 10^{-3}$ $pK_1 = 2.12$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2}$ $K_2 = 6.2 \times 10^{-8}$ $pK_2 = 7.21$

$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3}$ $K_3 = 4.8 \times 10^{-13}$ $pK_3 = 12.30$

$$K1 = \frac{[H+]\,[H_2PO_4^-]}{[H_3PO_4]}$$

$$K2 = \frac{[H+]\,[HPO_4^{-2}]}{[H_2PO_4^-]}$$

$$K3 = \frac{[H+]\,[PO_4^{-3}]}{[HPO_4^{-2}]}$$

Polyprotic acid

For the sum reaction,

$H_3PO_4 \longleftrightarrow 3H^+ + PO_4^{-3}$

K1 > K2 >>> K3

$$K = \frac{[PO_4^{-3}]\,[H^+]^3}{[H_3PO_4]}$$

The equilibrium constant for the sum reaction K

K = K1 * K2 * K3

Polyprotic acid

$H_3PO_4 \longleftrightarrow 3H^+ + PO_4^{-3}$

Using K1, K2, K3 of $H_3PO_4$and calculate Kb for PO_4^{-3}, HPO_4^{-2}, $H_2PO_4^{-1}$

Remember

Acids – proton donors (cation, anion, neutral)

Bases – proton acceptors (anion, neutral)

Weak acids and weak bases – partly dissociate

Strong acids and strong bases – fully dissociate

Conjugate acid-base pair – one H+ difference

Ka is dissociation constant of weak acid

Kb is dissociation constant of weak base

Kw is ion product constant of water

A weak acid had weak conjugated base

A weak base had a weak conjugated acid

If ka acid 1 > ka acid 2 then kb conjugated base 1< kb conjugated base 2.

Acid – Base Titration
part 2

Dr. Mai Ramadan

PH Scale

$$H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

the **ion-product constant** for water, K_w.

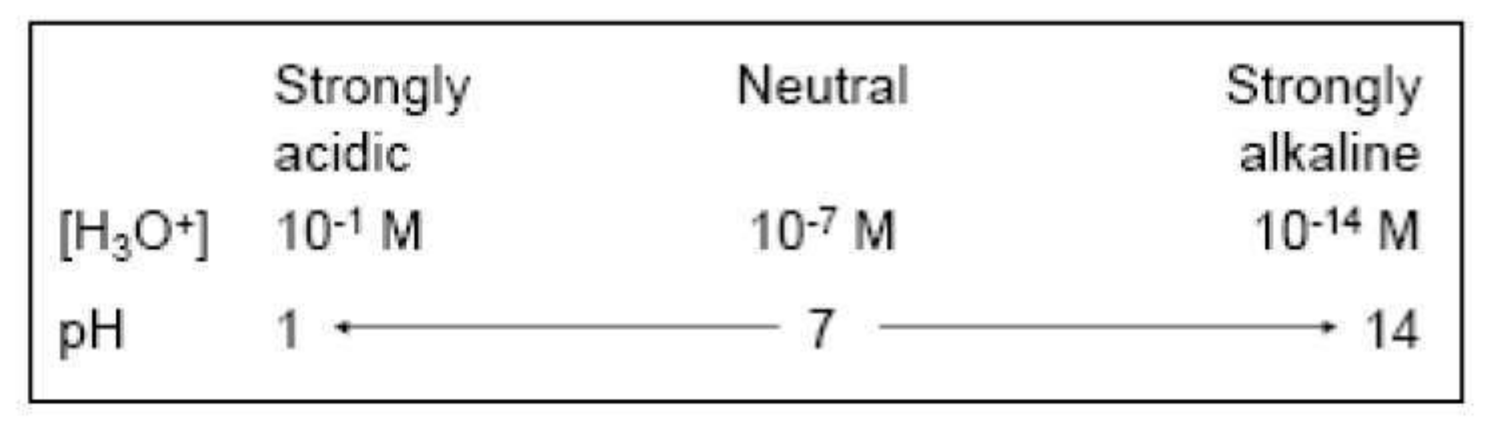
$$K_w = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}$$

In NEUTRAL solutions [H+] = [OH-]

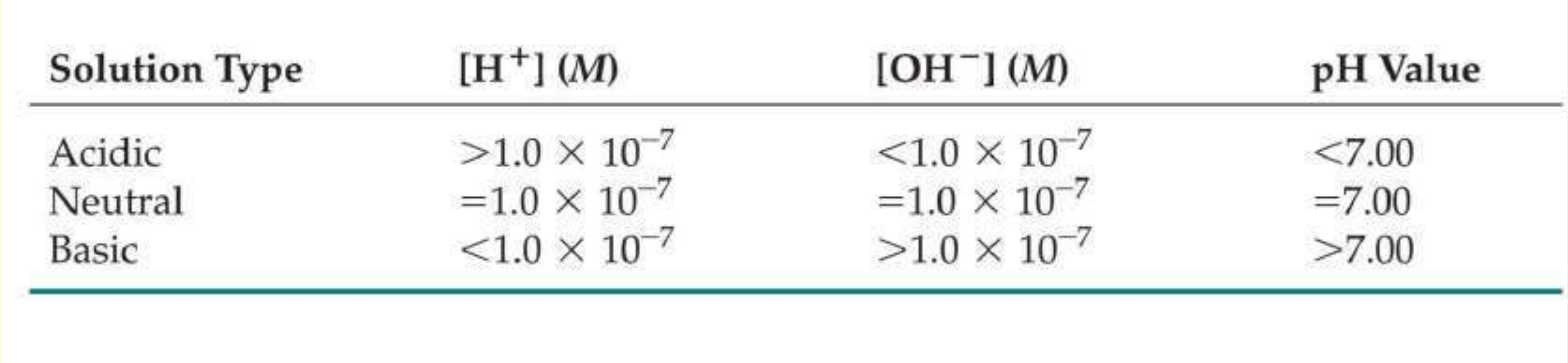
In ACIDIC solutions [H+] > [OH-]

In BASIC solutions [OH-] > [H+]

PH Scale

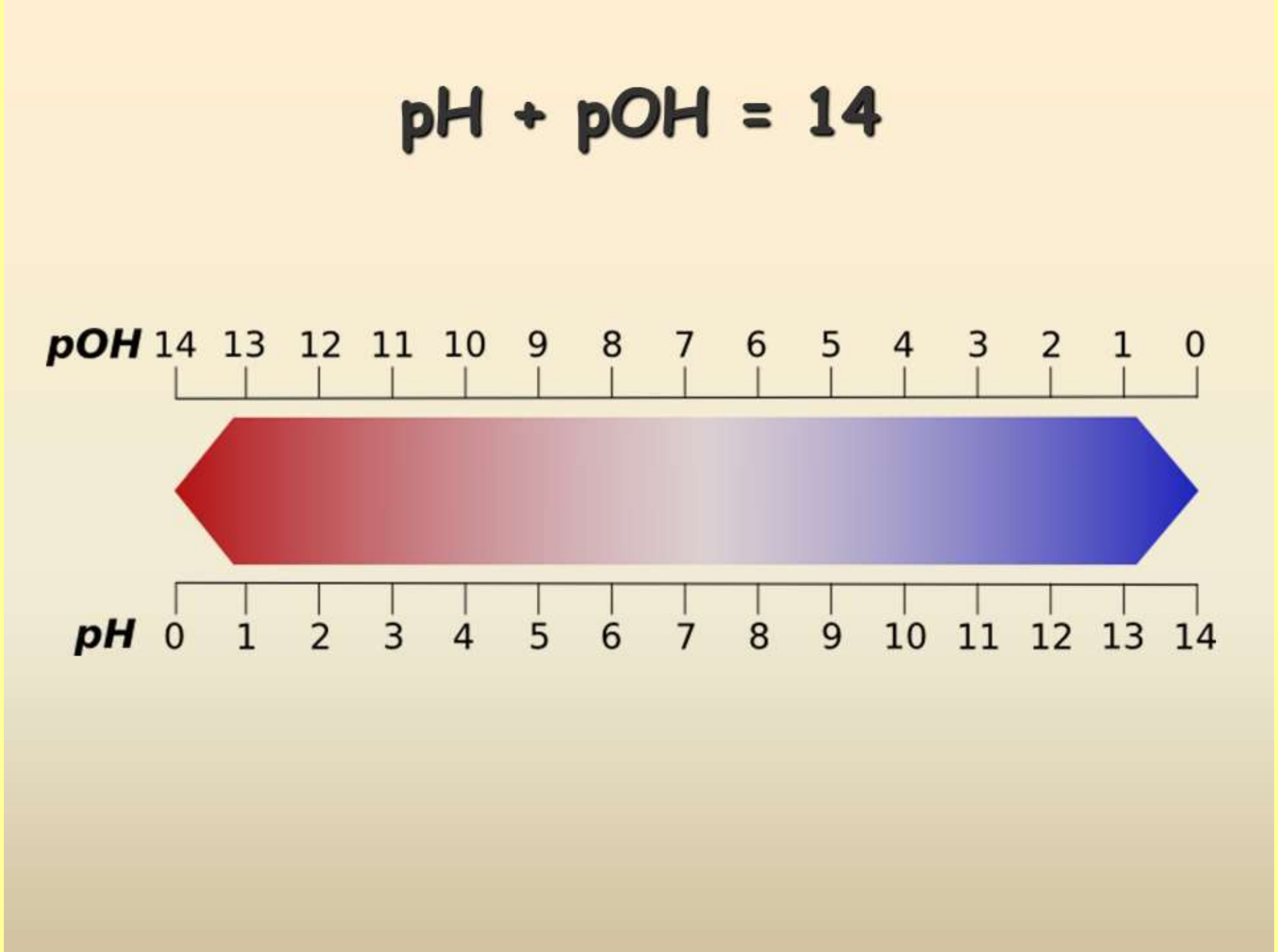


	Strongly acidic	Neutral	Strongly alkaline
$[H_3O^+]$	10^{-1} M	10^{-7} M	10^{-14} M
pH	1 ←	7	→ 14

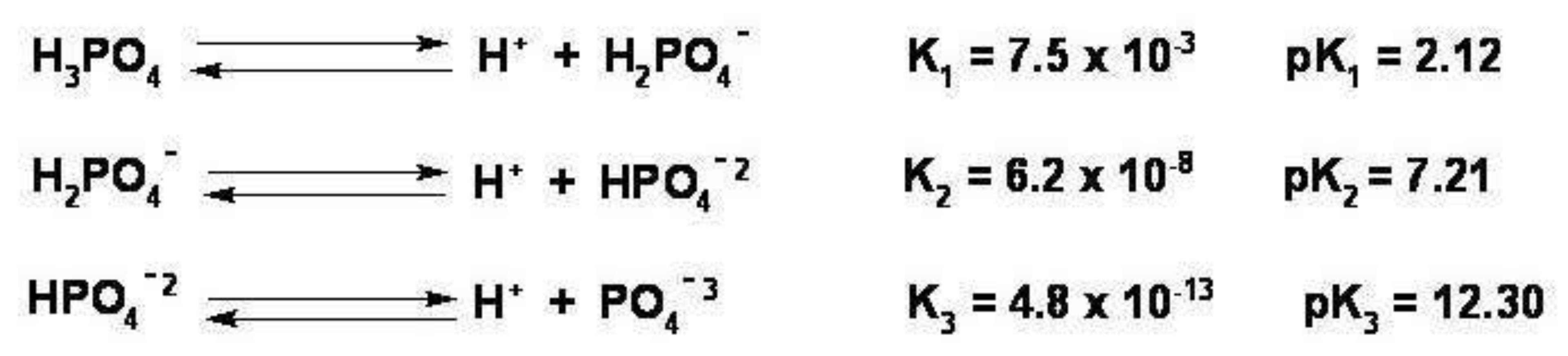


Solution Type	**$[H^+]$ (M)**	**$[OH^-]$ (M)**	**pH Value**
Acidic	$>1.0 \times 10^{-7}$	$<1.0 \times 10^{-7}$	<7.00
Neutral	$=1.0 \times 10^{-7}$	$=1.0 \times 10^{-7}$	$=7.00$
Basic	$<1.0 \times 10^{-7}$	$>1.0 \times 10^{-7}$	>7.00

PH Scale


pH + pOH = 14
pOH 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
pH 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

Polyprotic acid



$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	$K_1 = 7.5 \times 10^{-3}$	$pK_1 = 2.12$
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2}$	$K_2 = 6.2 \times 10^{-8}$	$pK_2 = 7.21$
$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3}$	$K_3 = 4.8 \times 10^{-13}$	$pK_3 = 12.30$

$$K1 = \frac{[H+]\,[H_2PO_4^-]}{[H_3PO_4]}$$

$$K2 = \frac{[H+]\,[HPO_4^{-2}]}{[H_2PO_4^-]}$$

$$K3 = \frac{[H+]\,[PO_4^{-3}]}{[HPO_4^{-2}]}$$

Polyprotic acid

For the sum reaction,

$$H_3PO_4 \longleftrightarrow 3H^+ + PO_4^{-3}$$

K1 > K2 >>> K3

$$\mathbf{K} = \frac{[PO_4^{-3}]\,[H^+]^3}{[H_3PO_4]}$$

The equilibrium constant for the sum reaction K

K = K1 * K2 * K3

Polyprotic acid

$$H_3PO_4 \longleftrightarrow 3H^+ + PO_4^{-3}$$

Using K1, K2, K3 of $H_3PO_4$and calculate Kb for PO_4^{-3}, HPO_4^{-2}, $H_2PO_4^{-1}$

To summarize the definition and Formula

Acids – proton donors (cation, anion, neutral)

Bases – proton acceptors (anion, neutral)

Weak acids and weak bases – partly dissociate

Strong acids and strong bases – fully dissociate

Conjugate acid-base pair – one H+ difference

Ka is dissociation constant of weak acid

Kb is dissociation constant of weak base

Kw is ion product constant of water

A weak acid had weak conjugated base

A weak base had a weak conjugated acid

If ka acid 1 > ka acid 2 then kb conjugated base 1< kb conjugated base 2.

For acid-base conjugate $Ka*Kb = Kw$

$pH + pOH = 14$

$pka + pkb = 14$

$pH = –log[H+]$

$pOH = -log\ [OH^-]$

$Pka = -\ log\ ka$

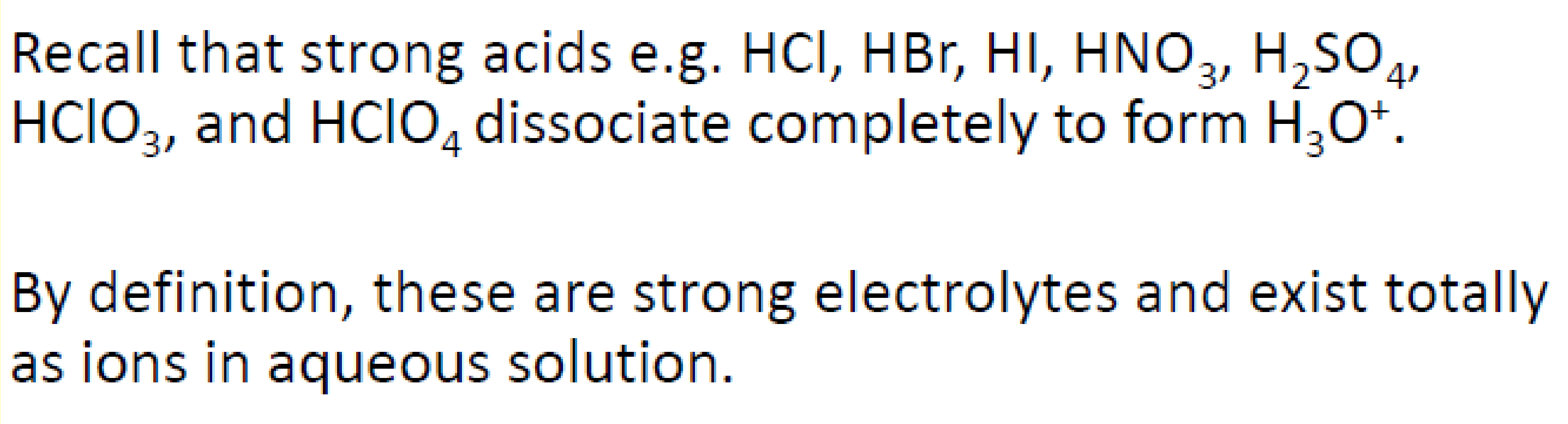
$Pkb = -\ log\ kb$

pH Calculations

Strong acid

pH Calculations

Strong acid



Recall that strong acids e.g. HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, and $HClO_4$ dissociate completely to form H_3O^+.

By definition, these are strong electrolytes and exist totally as ions in aqueous solution.

HA strong acid completely dissociated ($pK_a \leq 0$)

pH Calculations
Strong acid

For monoprotic acid

$$[H_3O^+] = [Acid]$$

$$pH + pOH = 14$$

$$pH = -\log [H_3O^+]$$

pH Calculations
Strong acid

$HA + H_2O \longrightarrow A^- + H_3O^+$ equilibrium 1

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

Note : the introduction of a strong acid HA into water drives equilibrium 2 towards the left !

If $[HA]_0$ is the total concentration of acid initially introduced into the aqueous solution.

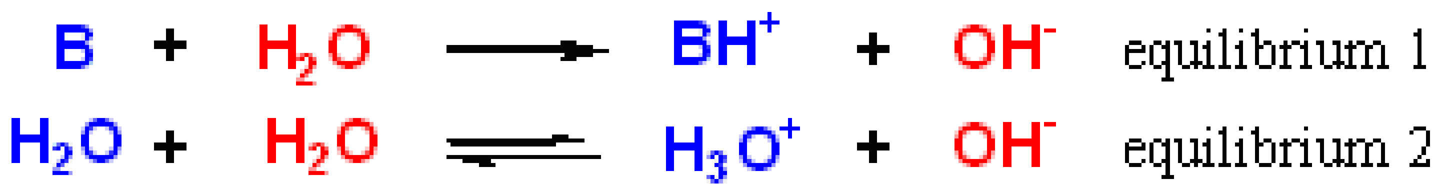
$[HA]_0 > 10^{-7}$ M : the H_3O^+ ions present in the solution come primarily from the dissociation of HA.

pH Calculations

Strong base

pH Calculations
Strong base

A strong base is completely dissociate in water.
The following two equations have to be taken into account :



$$B + H_2O \longrightarrow BH^+ + OH^- \quad \text{equilibrium 1}$$

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

Note : the introduction of the strong base B into water drives equilibrium 2 towards the left !

If $[B]_0$ is the total concentration of base initially introduced into the aqueous solution.

$[B]_0 > 10^{-7}$ M : one can assume that the OH- come exclusively from the dissociation of H2O protons under the action of B.

$[OH^-] = [Base]$

$pOH = -\log [B]$

pH Calculations
Strong base

$$[OH\ -] = [Base]$$

$$pOH = -\log [B]$$

pH Calculations

Strong Acids & Bases

Problems

pH Calculations

Calculate the pH of the following:

1. **Solution made of 0.723 g perchloric acid (FW = 100.46) in 500 mL of the solution?**

$$[HClO_4] = \frac{0.723\ (g) / 100.46\ (g/mol)}{0.5\ (L)} = 0.014\ M$$

pH= - log [HClO4] = 1.85

2. **0.1 M NaOH?**

$[OH^-]$ = [NaOH] = 0.1 M, pOH = 1, pH = 14 – pOH = 13

3. **0.005 M $Ba(OH)_2$?**

$$Ba(OH)_2 \longrightarrow Ba^{+2} + 2\ OH^-$$

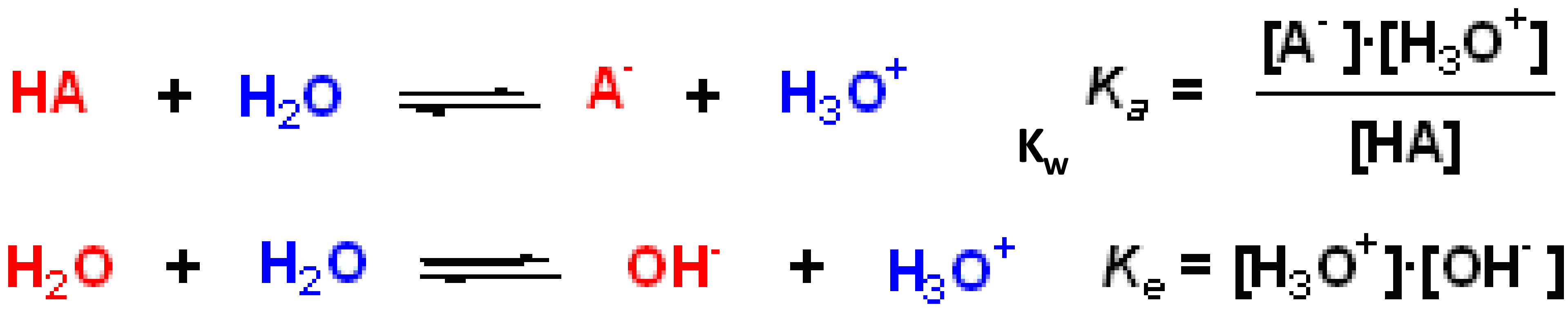
$[OH^-]$ = $2[Ba(OH)_2]$ = 0.01 M, pOH = 2, pH = 14 – pOH = 12

pH Calculations

Weak acid

pH Calculations
Weak acid

A weak acid HA is dissociated partially.



$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad K_a = \frac{[A^-]\cdot[H_3O^+]}{[HA]}$$

K_w

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+ \qquad K_e = [H_3O^+]\cdot[OH^-]$$

pH Calculations
Weak acid

$[H_3O^+] \simeq [A^-]$, $[H_3O^+] \lll [HA]$

$$[H_3O^+] = \sqrt{K_a \times C_{HA}}$$

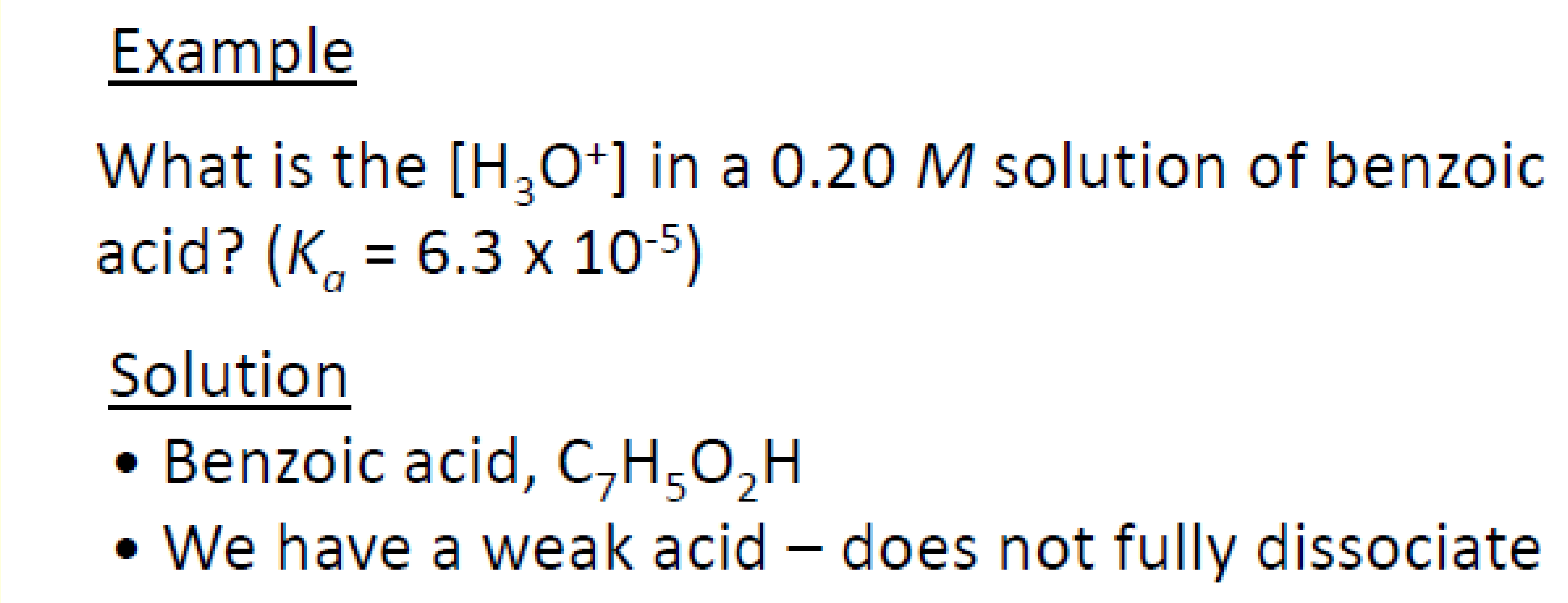
$$\text{Relative error} = \frac{[H_3O+] \; * \; 100\%}{[HA]} = \; > 5\%$$

pH Calculations
Weak acid

- ❑ Use quadratic equation if $[H_3O+]$ is out by more than 5% of the original acid concentration.
- ❑ The $[H_3O^+]$ should be calculated using the positive solution of quadratic equation.

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2}$$

pH Calculations
Weak acid



Example

What is the $[H_3O^+]$ in a 0.20 *M* solution of benzoic acid? (K_a = 6.3 x 10^{-5})

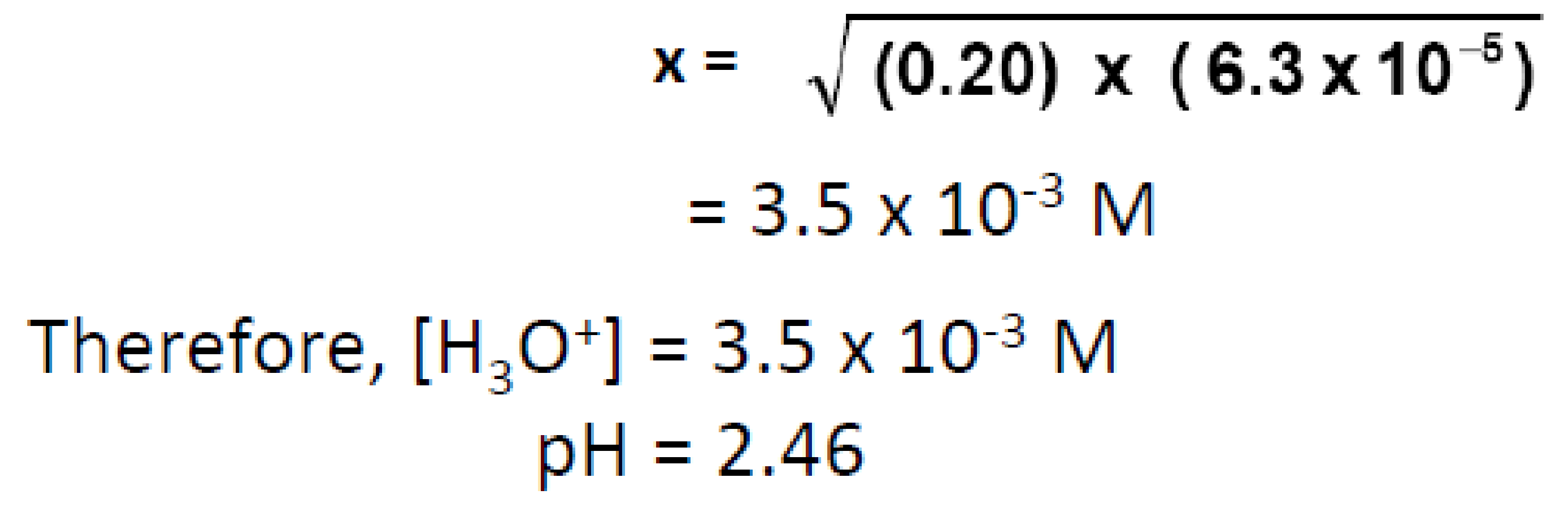
Solution

- Benzoic acid, $C_7H_5O_2H$
- We have a weak acid – does not fully dissociate

pH Calculations
Weak acid

Using assumption that :

$X = [H_3O^+] = [A^-]$, $[H_3O^+] <<< [HA]$



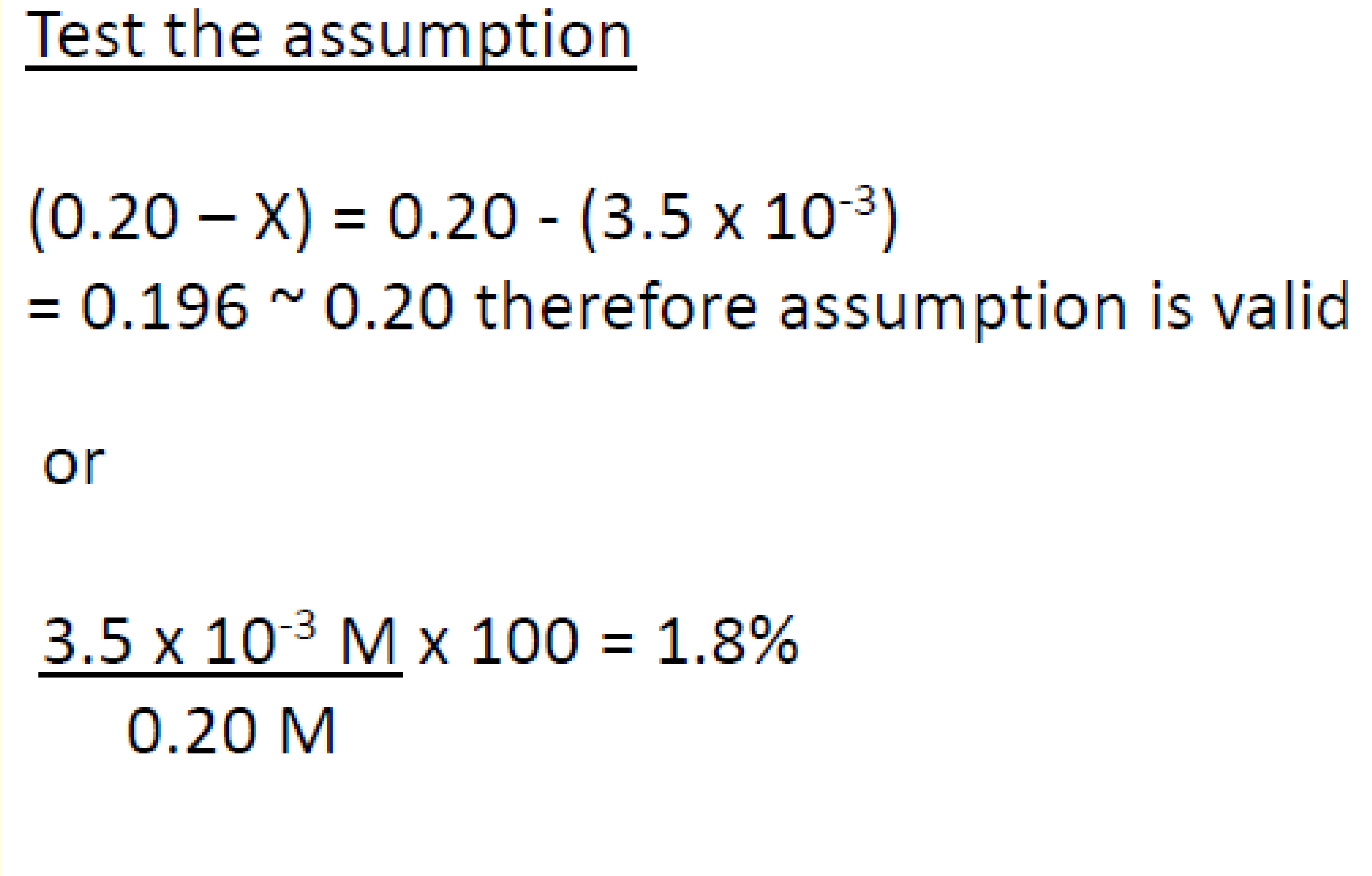
$$x = \sqrt{(0.20) \times (6.3 \times 10^{-5})}$$

$$= 3.5 \times 10^{-3}\ M$$

Therefore, $[H_3O^+] = 3.5 \times 10^{-3}\ M$

$pH = 2.46$

pH Calculations
Weak acid



Test the assumption

$(0.20 - X) = 0.20 - (3.5 \times 10^{-3})$

$= 0.196 \sim 0.20$ therefore assumption is valid

or

$$\frac{3.5 \times 10^{-3}\ \text{M}}{0.20\ \text{M}} \times 100 = 1.8\%$$

pH Calculations
Weak acid

Calculate the $[H_3O+]$ in 0.12 M nitrous acid (HNO_2) Ka = $5.1*10^{-4}$?

Assumption $[HNO_2]- [H_3O+] = [HNO_2]$

$[H_3O+] = 7.8*10^{-3}$ M **Relative error = 6.5%**

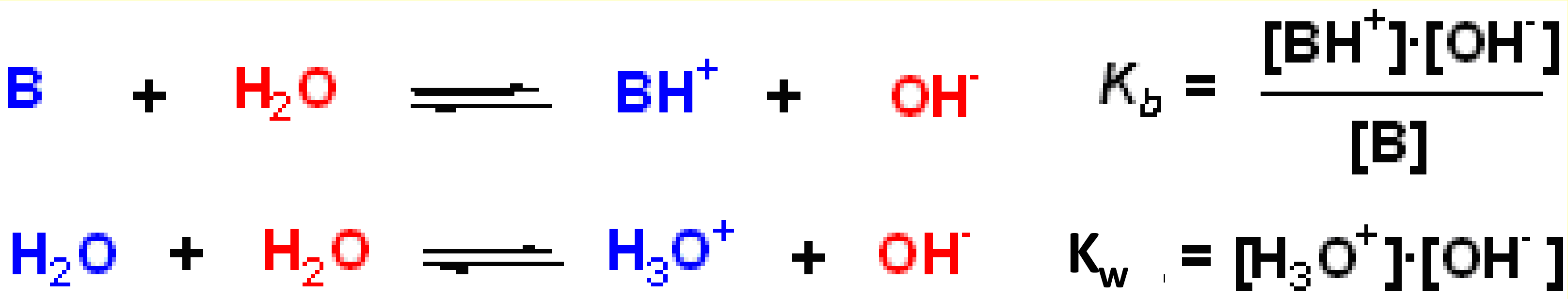
Using quadratic equation:

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2}$$

$[H_3O+] = 8.9*10^{-3}$ M

pH Calculations
Weak base

A weak base B is dissociated partially.



$$B + H_2O \rightleftharpoons BH^+ + OH^- \qquad K_b = \frac{[BH^+]\cdot[OH^-]}{[B]}$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad K_w = [H_3O^+]\cdot[OH^-]$$

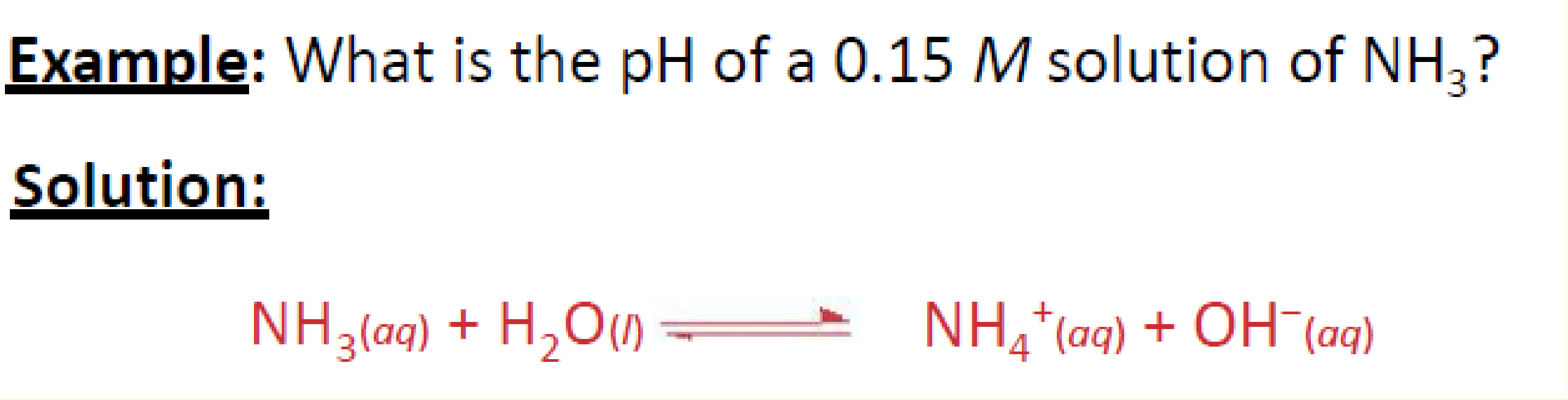
Assume that autoionization of water is very small and should be neglected.

$$[OH^-] \simeq [BH^+],$$

$$[OH^-] <<< [B] \longrightarrow [B] - [OH^-] = [B]$$

$$[OH^-] = \sqrt{K_b \times C_B}$$

pH Calculations
Weak base



Example: What is the pH of a 0.15 *M* solution of NH_3?

Solution:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

Using assumption $[OH^-] <<< [B]$

pH Calculations
Weak base

Using assumption:

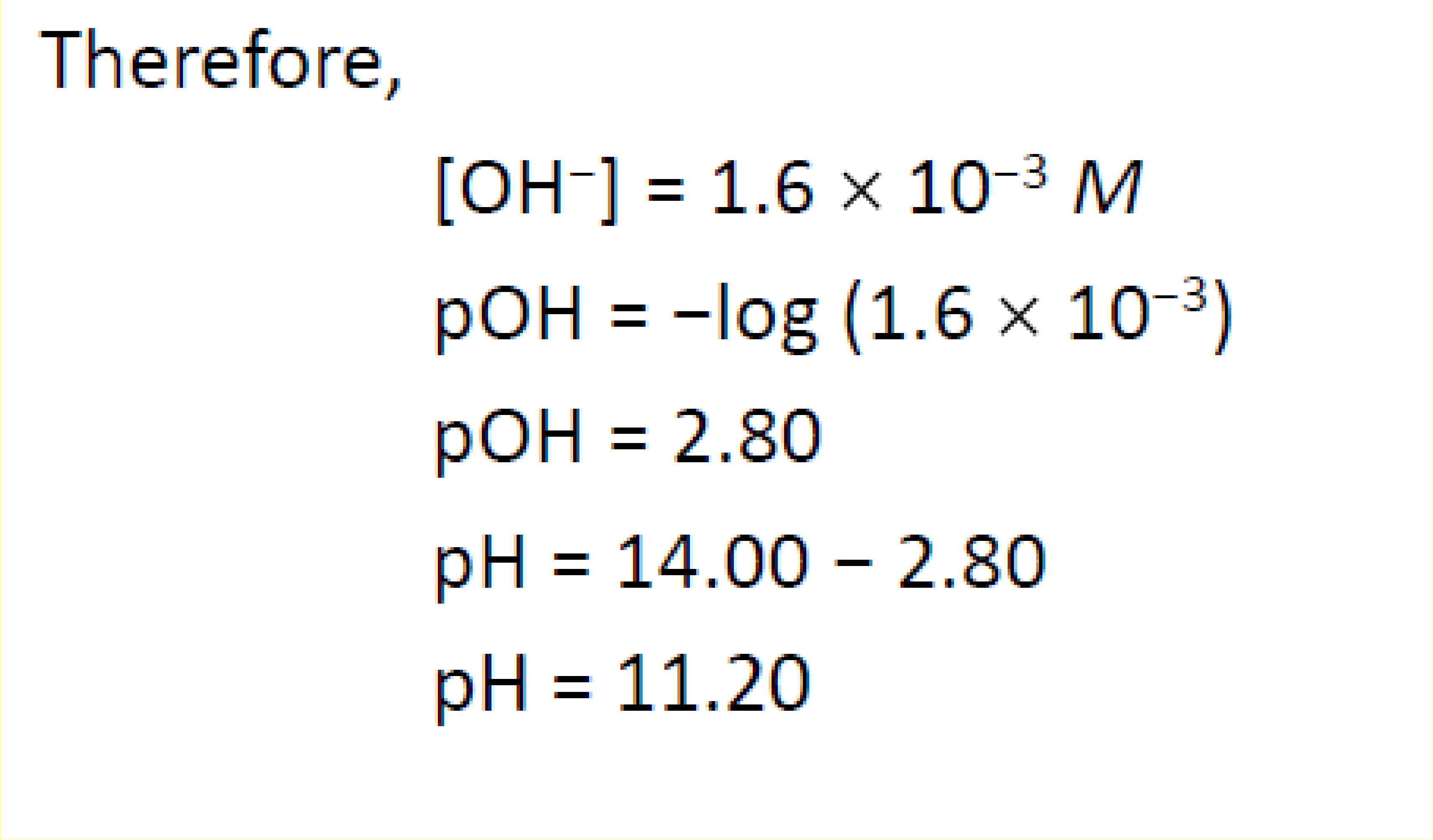
$$[OH^-] = \sqrt{K_b \times C_B}$$

$[OH^-] = 1.6 \times 10^{-3}$ M

Test the assumption

Relative error = 1.07%

pH Calculations
Weak base



Therefore,

$$[OH^-] = 1.6 \times 10^{-3}\ M$$

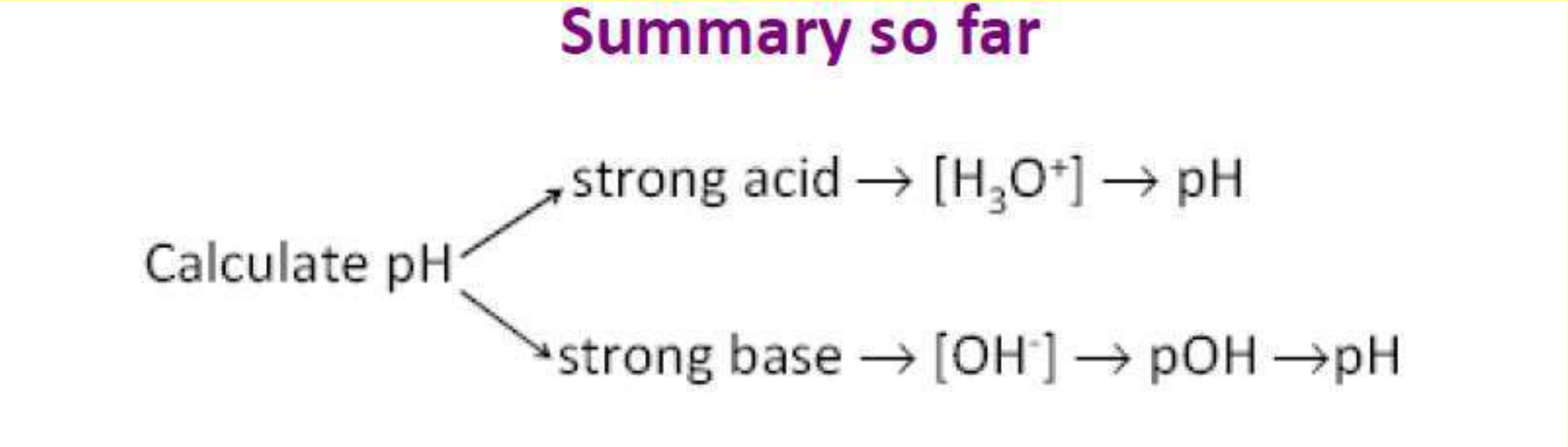
$$pOH = -\log(1.6 \times 10^{-3})$$

$$pOH = 2.80$$

$$pH = 14.00 - 2.80$$

$$pH = 11.20$$

pH Calculations



Summary so far

Calculate pH

strong acid → $[H_3O^+]$ → pH

strong base → $[OH^-]$ → pOH → pH

pH Calculations

Weak acid

Assume $X = [H_3O^+] = [A^-], [H_3O^+] <<< [HA]$

$$[H_3O^+] = \sqrt{K_a \times C_{HA}}$$

If the relative error = $[H_3O^+]/C_{HA} * 100 > 5\%$
then use quadratic equation

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2}$$

pH Calculations

Weak base

Assume $X = [OH^-] <<< [B], \quad [OH^-] = [BH^+]$

$$[OH^-] = \sqrt{K_b \times C_B}$$

If the relative error $= [OH^-]/C_B * 100 > 5\%$
then use quadratic equation

$$[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_bC_B}}{2}$$

Acid – Base Titration
part 3

Dr. Mai Ramadan

pH Calculations
Weak acid

$[H_3O^+] \simeq [A^-]$, $[H_3O^+] <<< [HA]$

$$[H_3O^+] = \sqrt{K_a \times C_{HA}}$$

$$\text{Relative error} = \frac{[H_3O^+]}{[HA]} * 100\% = > 5\%$$

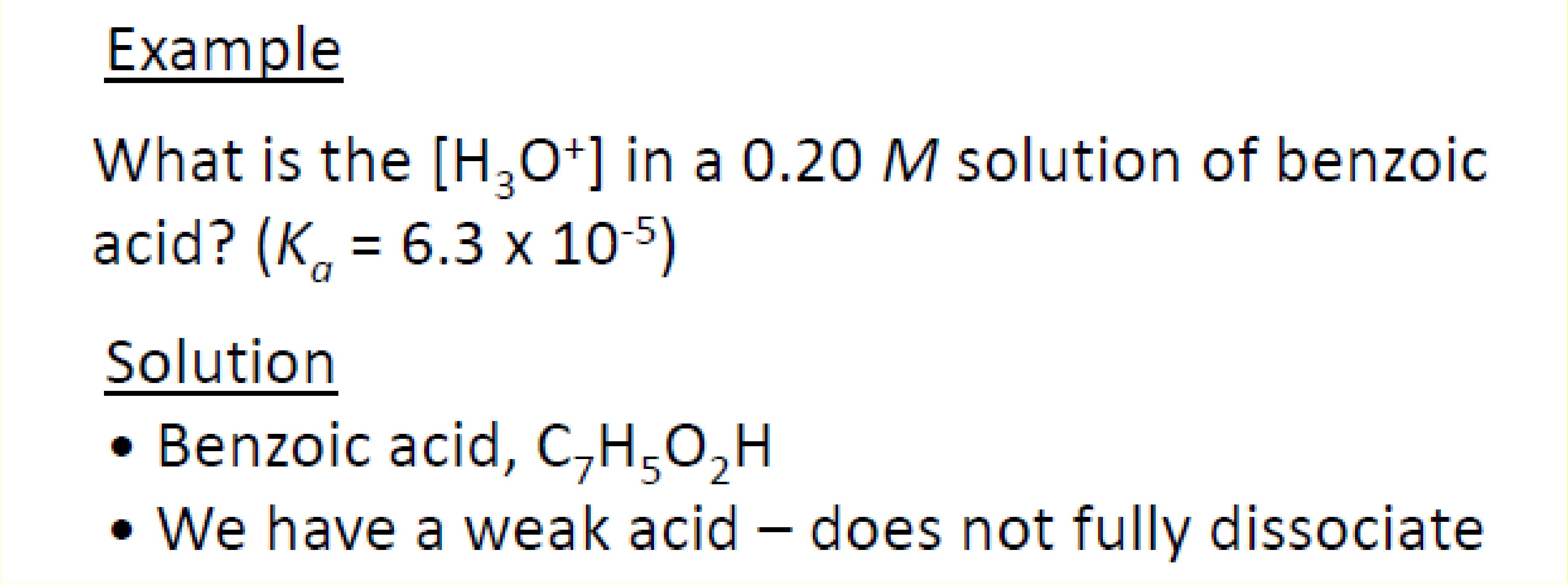
pH Calculations
Weak acid

- ❑ Use quadratic equation if $[H_3O+]$ is out by more than 5% of the original acid concentration.

- ❑ The $[H_3O^+]$ should be calculated using the positive solution of quadratic equation.

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2}$$

pH Calculations
Weak acid



Example

What is the $[H_3O^+]$ in a 0.20 *M* solution of benzoic acid? ($K_a = 6.3 \times 10^{-5}$)

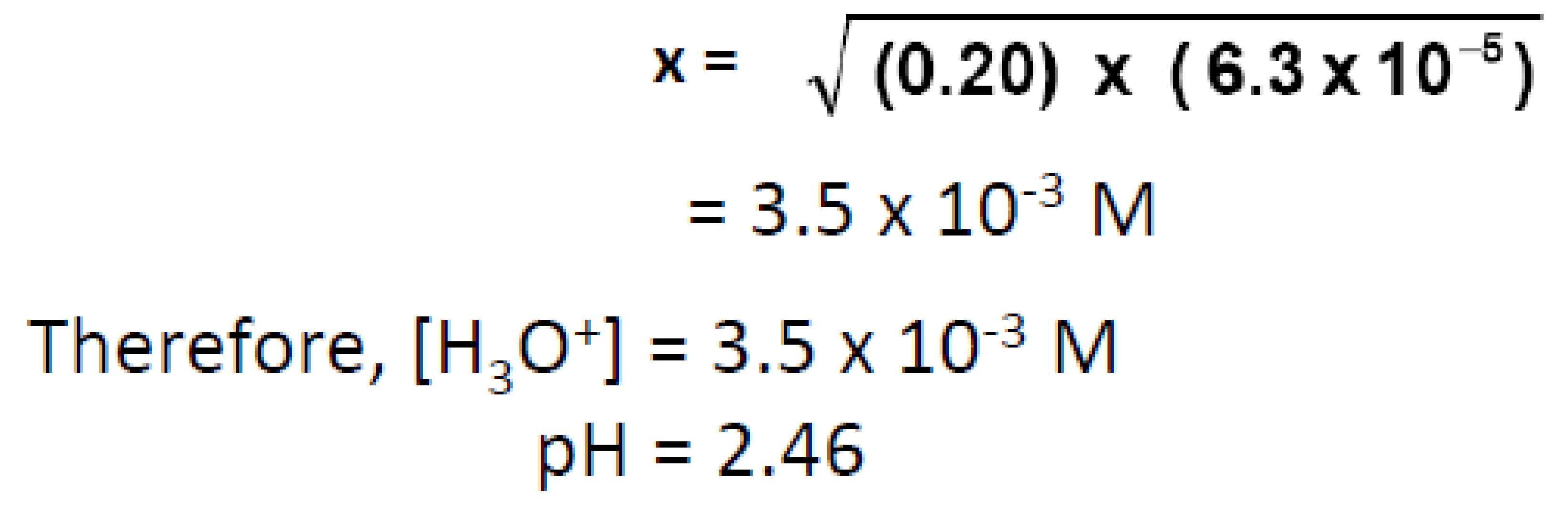
Solution

- Benzoic acid, $C_7H_5O_2H$
- We have a weak acid – does not fully dissociate

pH Calculations
Weak acid

Using assumption that :

$X = [H_3O^+] = [A^-]$, $[H_3O^+] <<< [HA]$



$$x = \sqrt{(0.20) \times (6.3 \times 10^{-5})}$$

$$= 3.5 \times 10^{-3}\ M$$

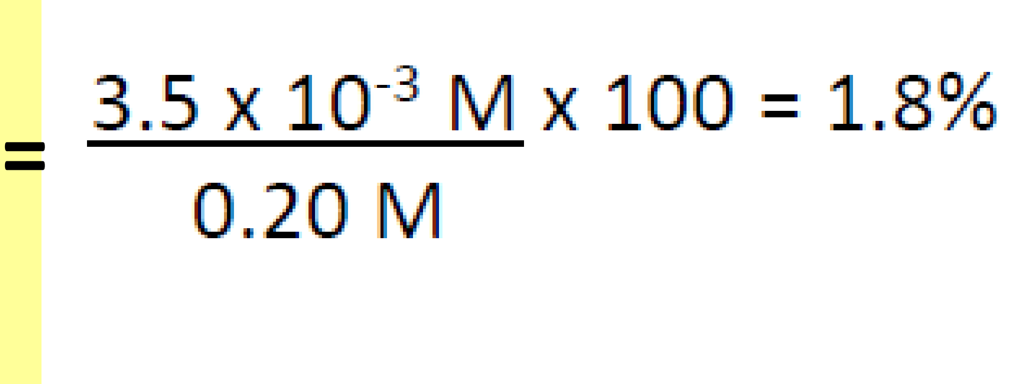
Therefore, $[H_3O^+] = 3.5 \times 10^{-3}$ M

pH = 2.46

pH Calculations
Weak acid

$$\text{Relative error} = \frac{[H_3O^+]}{[HA]} * 100\% =$$

Relative error =



$$\frac{3.5 \times 10^{-3}\ M}{0.20\ M} \times 100 = 1.8\%$$

$< 5\%$

The calculation is finished

pH Calculations
Weak acid

Calculate the $[H_3O+]$ in 0.12 M nitrous acid (HNO_2) Ka = $5.1*10^{-4}$?

Assumption $[H_3O+] <<< [HNO_2]$

$[H_3O+] = 7.8*10^{-3}$ M **Relative error = 6.5%**

Using quadratic equation:

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2}$$

$[H_3O+] = 8.9*10^{-3}$ M

pH Calculations
Weak base

A weak base B is dissociated partially.

$$B + H_2O \rightleftharpoons BH^+ + OH^- \qquad K_b = \frac{[BH^+]\cdot[OH^-]}{[B]}$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad K_w = [H_3O^+]\cdot[OH^-]$$

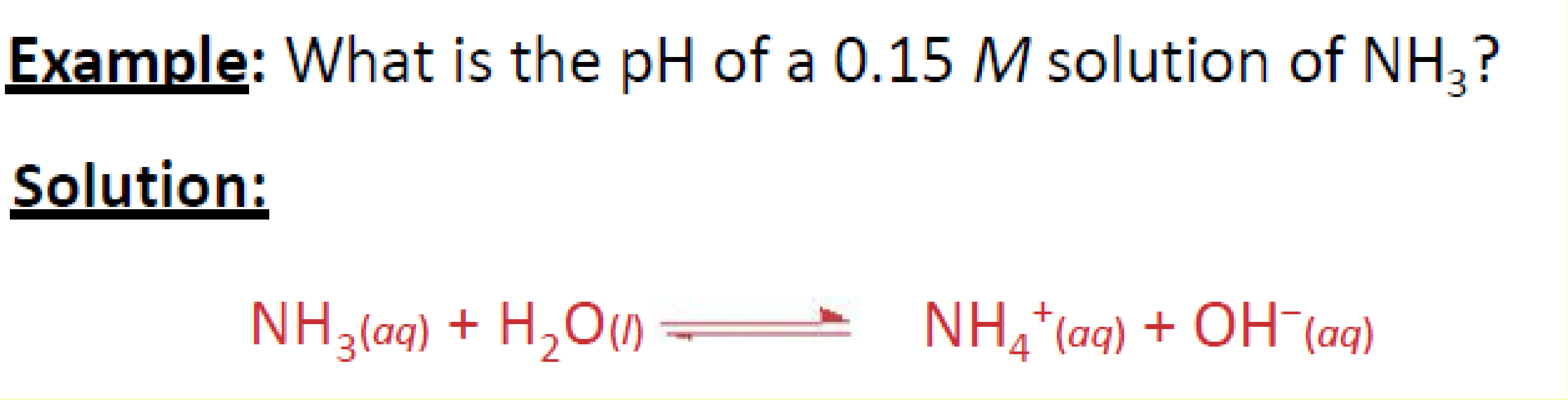
Assume that autoionization of water is very small and should be neglected.

$$[OH^-] \simeq [BH^+],$$

$$[OH^-] \lll [B] \longrightarrow [B] - [OH^-] = [B]$$

$$[OH^-] = \sqrt{K_b \times C_B}$$

pH Calculations
Weak base



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Using assumption [OH^-] <<<[B]

pH Calculations
Weak base

Using assumption:

$$[OH^-] = \sqrt{K_b \times C_B}$$

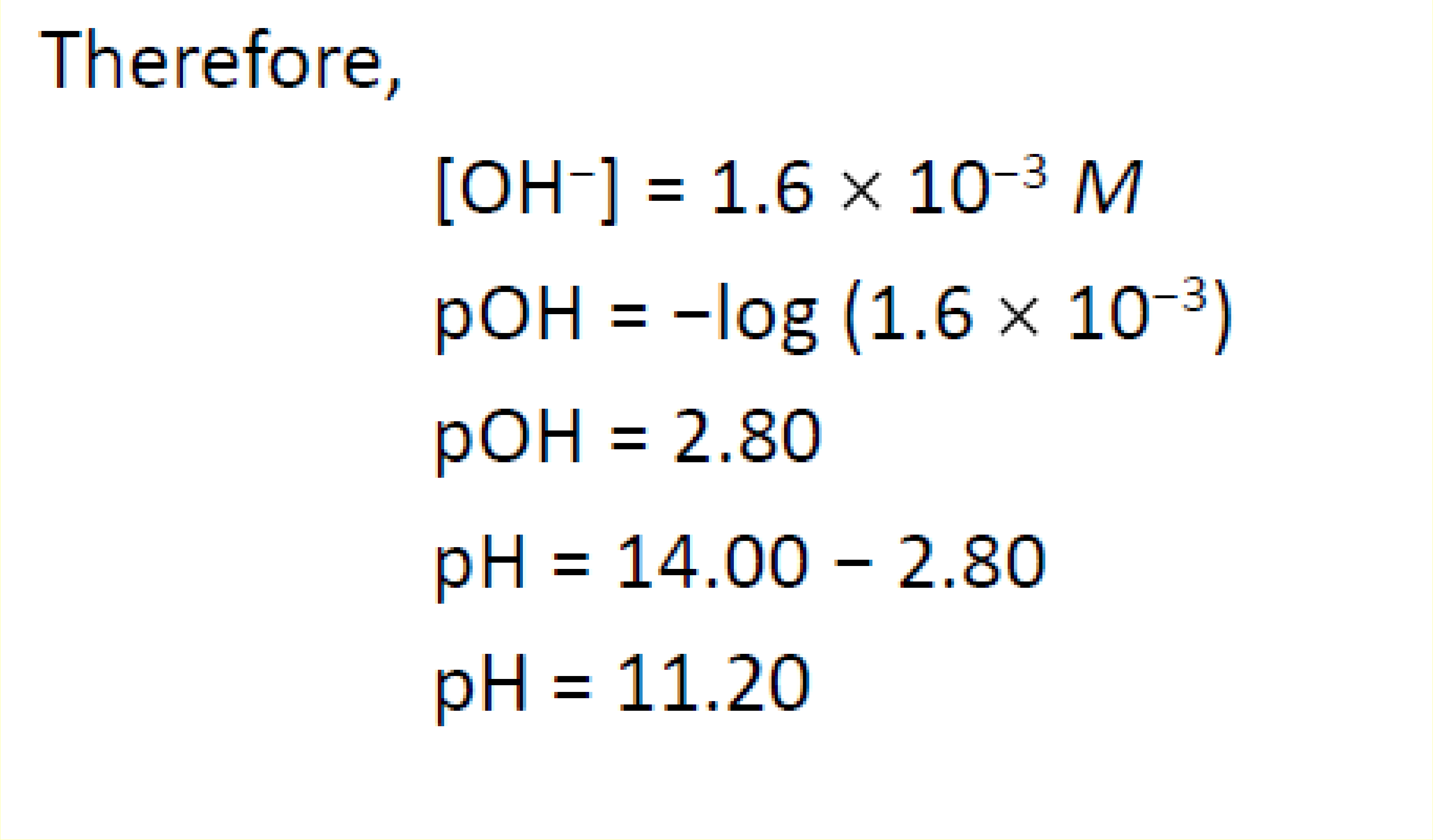
$$[OH^-] = 1.6 * 10^{-3}\ M$$

Test the assumption

Relative error = 1.07%

< 5%

pH Calculations
Weak base



Therefore,

$$[OH^-] = 1.6 \times 10^{-3}\ M$$

$$pOH = -\log(1.6 \times 10^{-3})$$

$$pOH = 2.80$$

$$pH = 14.00 - 2.80$$

$$pH = 11.20$$

pH Calculations
Weak base

If relative error is more than 5% of the original weak base concentration, Use the quadratic equation to calculate $[OH^-]$

$$\text{Relative error} = \frac{[OH^-] \; * \; 100\%}{[B]} = \; > 5\%$$

$$[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_bC_B}}{2}$$

To summarize formulae for pH calculation of weak acid & weak base again

pH Calculations

Weak acid

Assume $X = [H_3O^+] = [A^-]$, $[H_3O^+] <<< [HA]$

$$[H_3O^+] = \sqrt{K_a \times C_{HA}}$$

If the relative error = $[H_3O^+]/C_{HA}$ *100 = > 5% then use quadratic equation

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2}$$

pH Calculations

Weak base

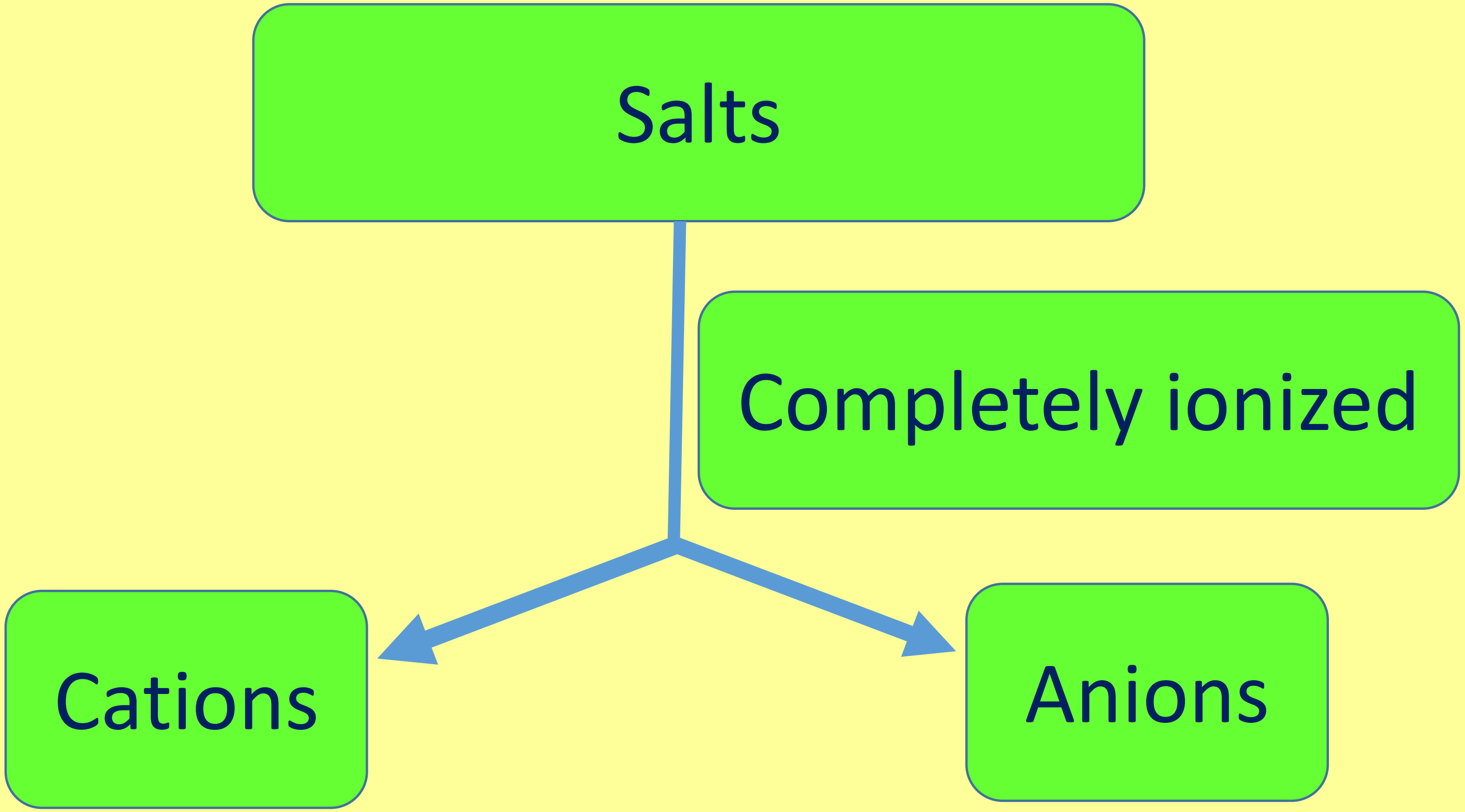
Assume **$X = [OH^-] <<< [B]$, $[OH^-] = [BH^+]$**

$$[OH^-] = \sqrt{K_b \times C_B}$$

If the relative error = $[OH^-]/C_B$ *100= > 5%
then use quadratic equation

$$[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_bC_B}}{2}$$

Acid base properties of solution



Salts

Completely ionized

Cations

Anions

What is pH of salts

Acid base properties of solution

Salts

pH = 7
neutral

pH > 7
basic

pH < 7
acidic

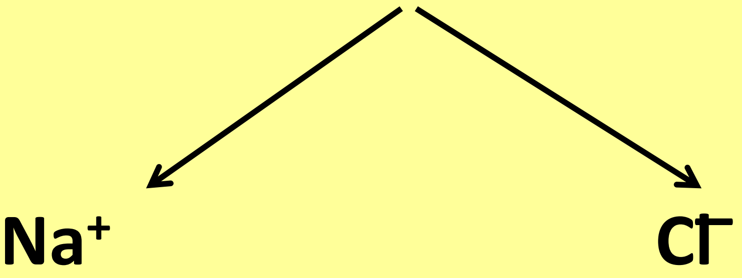
Cations and anions are weak acid and weak base

Amphoteric

Acid base properties of solution

Salts of strong acids and strong bases

NaCl solution is **neutral**



Na^+ Cl^-

The acidic and basic properties of cation and anion is neglected since they are conjugate of strong acid and strong base

Acid base properties of solution

Salts of weak acids and strong bases

$(CH_3COO)Na$ solution is basic

Na^+
Neutral

CH_3COO^-
weak base

$$CH_3COO^- + H_2O \xleftrightarrow{K_b} CH_3COOH + OH^-$$

Acid base properties of solution

Salts of weak acids and strong bases

NaOCl solution is basic

Na^+
Neutral

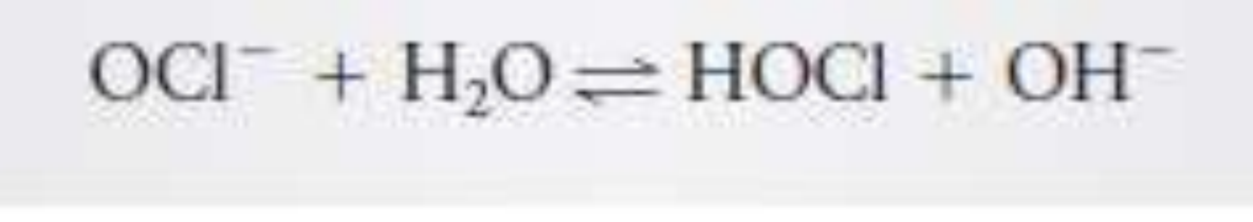
OCl^-
weak base

$$OCl^- + H_2O \overset{K_b}{\longleftrightarrow} HOCl + OH^-$$

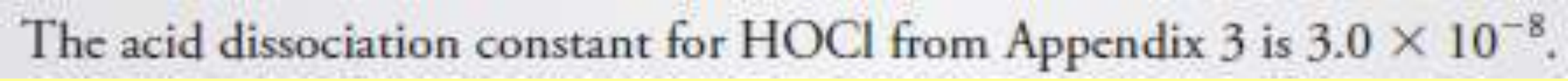
Acid base properties of solution

Calculate the hydroxide ion concentration in a 0.0100 M sodium hypochlorite solution.

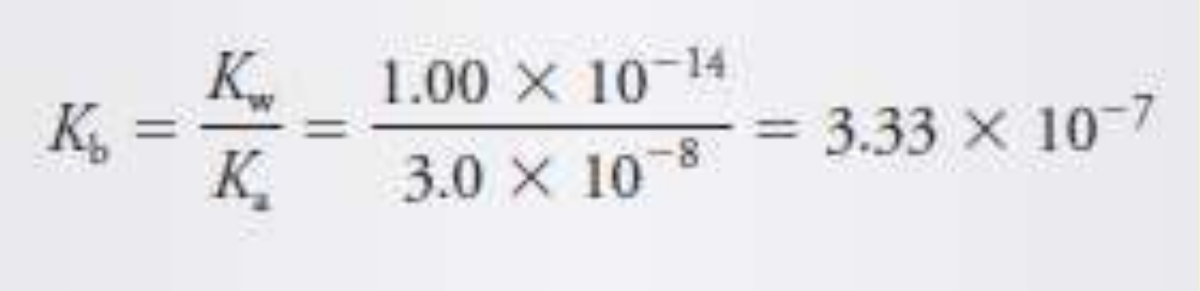
Na+ is neutral, OCl^- is a weak base had the following equilibrium



$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$$



The acid dissociation constant for HOCl from Appendix 3 is 3.0×10^{-8}.



$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{3.0 \times 10^{-8}} = 3.33 \times 10^{-7}$$

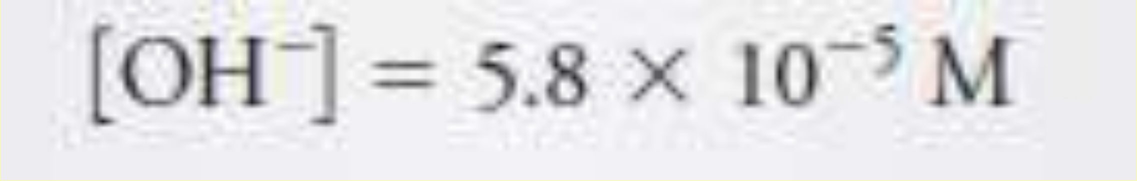
Acid base properties of solution

Calculate the hydroxide ion concentration in a 0.0100 M sodium hypochlorite solution.

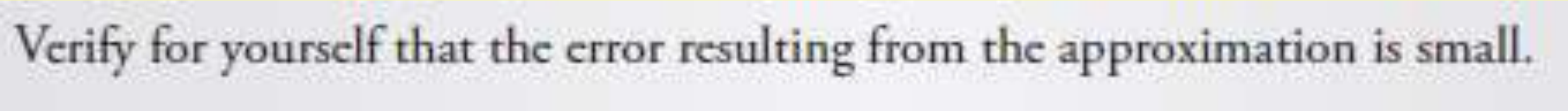
Assuming that

$[OH^-] \ll 0.0100.$

$$[OH^-] = \sqrt{k_b * C_B}$$



$$[OH^-] = 5.8 \times 10^{-5}\ M$$



Verify for yourself that the error resulting from the approximation is small.

Acid base properties of solution

Salts of strong acids and weak bases

NH_4Cl solution is **acidic**

NH_4^+
Weak acid

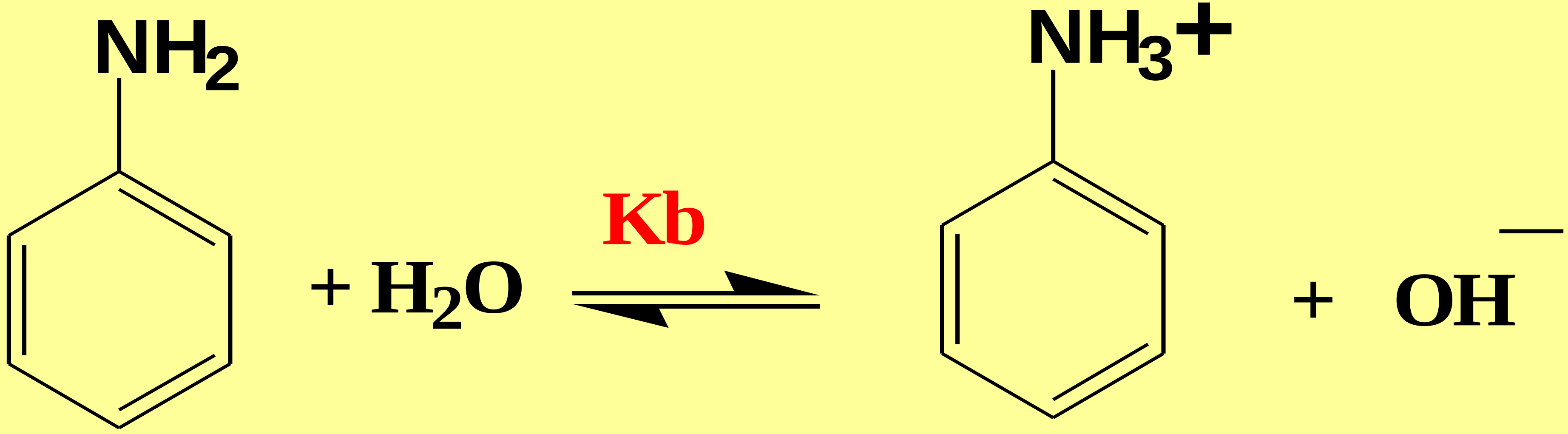
Cl^-
neutral

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

Acid base properties of solution

Calculate the hydronium ion concentration in a solution that is 2.0 * 10¯4 M in **aniline hydrochloride**, $C_6H_5NH_3Cl$ (Anilinium chloride).

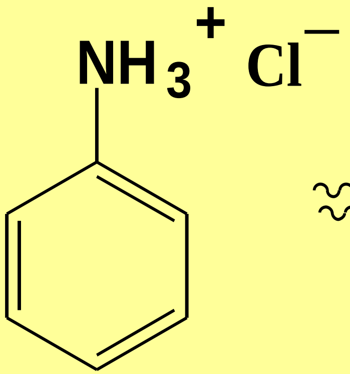
$$B + H_2O \xrightleftharpoons{Kb} BH^+ + OH^-$$



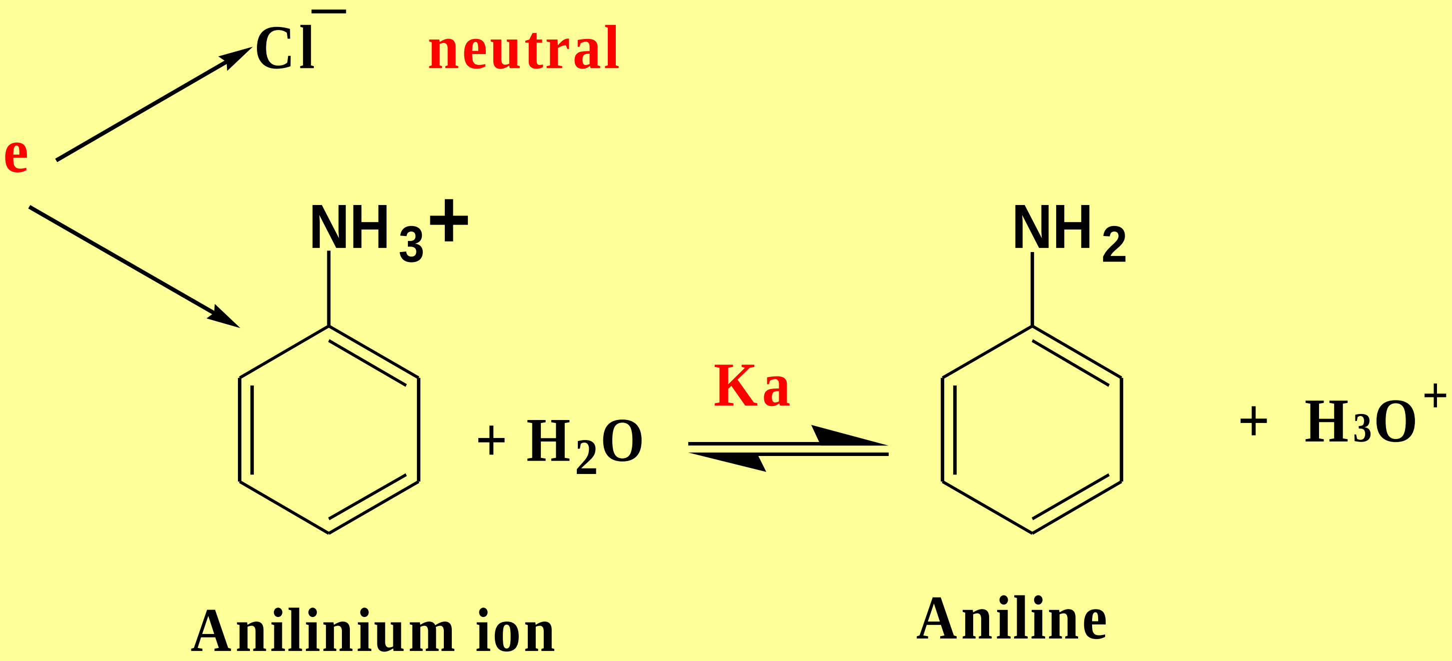
Aniline

Anilinium ion

Anilinium Chloride
is
a salt



≈ BH^+Cl^- ≈ $C_6H_5NH_3Cl$



Cl^- **neutral**

Anilinium Chloride

$$\text{Anilinium ion} + H_2O \overset{Ka}{\rightleftharpoons} \text{Aniline} + H_3O^+$$

$$BH^+ + H_2O \overset{Ka}{\rightleftharpoons} B + H_3O^+$$

Acid base properties of solution

In aqueous solution, dissociation of the salt to Cl^- and C6H5NH3$^+$ is complete. The weak acid $C_6H_5NH_3^+$ dissociates as follows:

$$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$$

Anilinium cation

Ka for Anilinium ion $= \dfrac{\mathbf{Kw}}{\mathbf{Kb\ (aniline)}} = 2.51*10^{-5}$

Kb of aniline: $3.94*10^{-10}$

Assume that

$$[H_3O^+] \ll 2.0 \times 10^{-4},$$

$$[H_3O+] = \sqrt{K_a * C_{HA}}$$

Acid base properties of solution

$$[H_3O^+] = \sqrt{5.02 \times 10^{-9}} = 7.09 \times 10^{-5}\ M$$

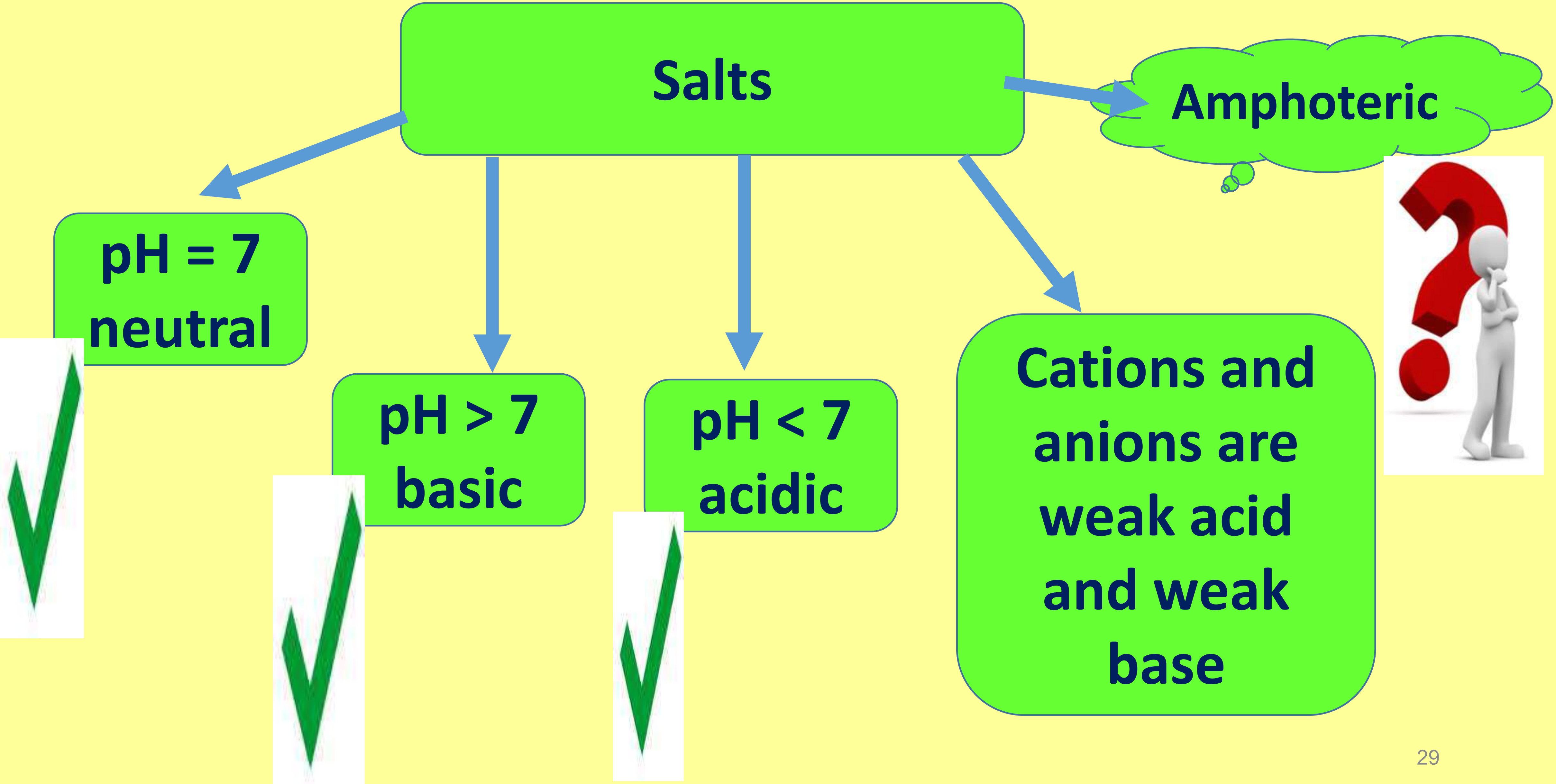
Verify your assumption relative error is 35%

Use quadratic equation then:

$$[H_3O^+] = \frac{-2.51 \times 10^{-5} + \sqrt{(2.54 \times 10^{-5})^2 + 4 \times 5.02 \times 10^{-9}}}{2}$$

$$= 5.94 \times 10^{-5}\ M$$

Acid base properties of solution



Salts

pH = 7
neutral
✓

pH > 7
basic
✓

pH < 7
acidic
✓

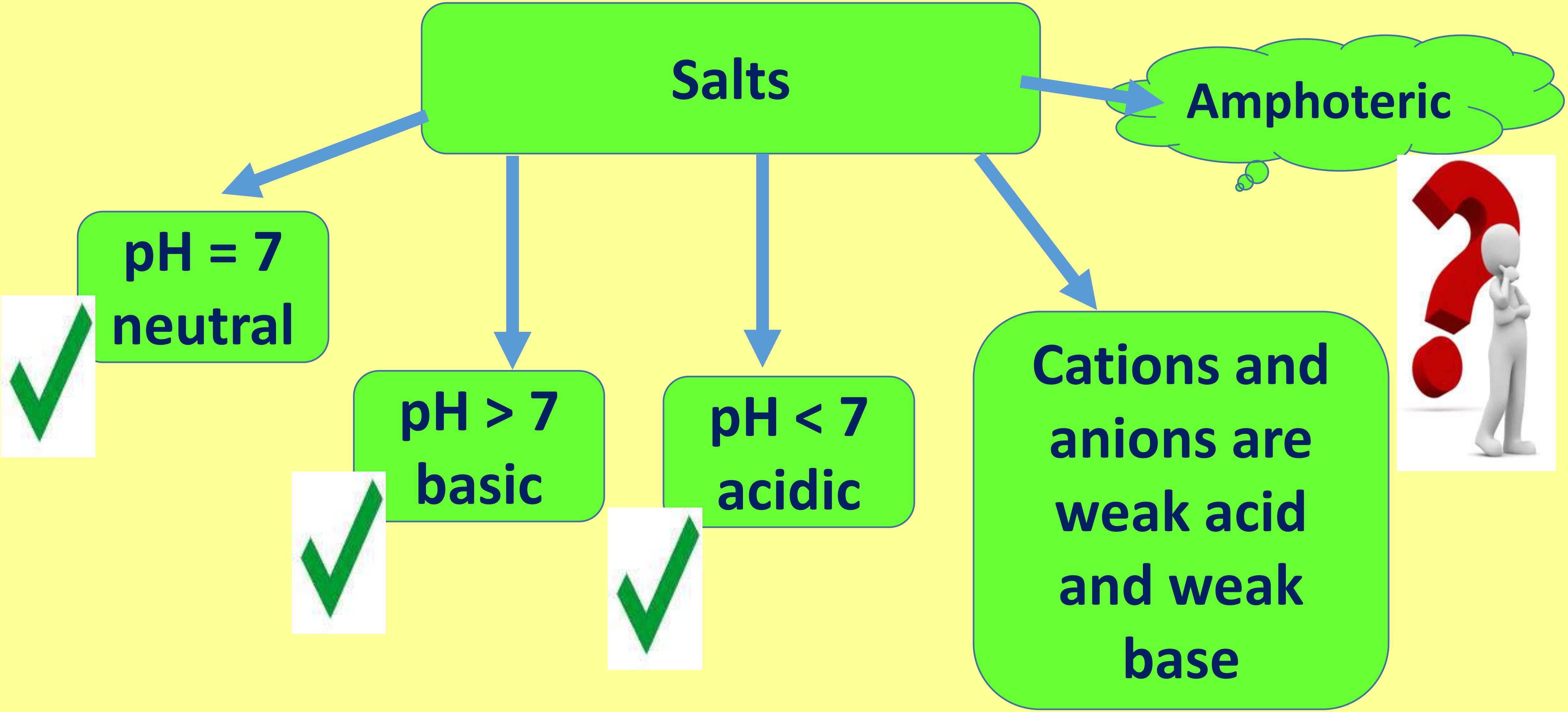
Cations and anions are weak acid and weak base

Amphoteric

Acid – Base Titration
part 4

Dr. Mai Ramadan

Acid base properties of solution



Salts

Amphoteric

pH = 7
neutral ✓

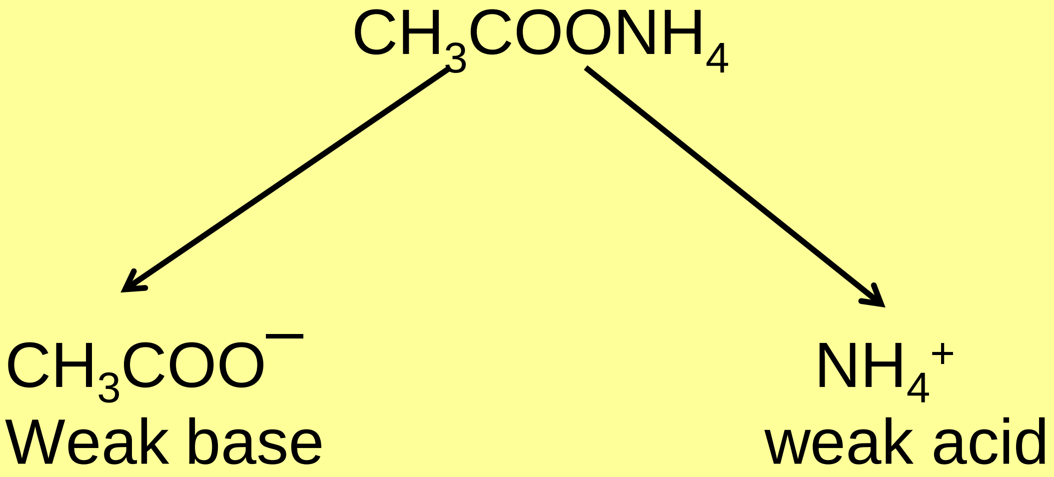
pH > 7
basic ✓

pH < 7
acidic ✓

Cations and anions are weak acid and weak base

Acid base properties of solution

Salts of weak bases and weak acids



CH_3COONH_4

CH_3COO^-
Weak base

NH_4^+
weak acid

$$CH_3COO^- + H_2O \longleftrightarrow CH_3COOH + OH^-$$

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

$$NH_4^+ + CH_3COO^- \longleftrightarrow CH_3COOH + NH_3$$

Acid base properties of solution

Salts of weak bases and weak acids

$$[H_3O^+] = \sqrt{\frac{K_w * K_a}{K_b}}$$

When a solution contain a conjugate of a weak acid and a conjugate of a weak base then the effect on pH depends on Ka and Kb

If $pK_a < pK_b$ the salt solution is acidic

If $pK_a > pK_b$ the salt solution is basic

Acid base properties of solution

Salts of weak bases and weak acids

$$[H_3O^+] = \sqrt{\frac{K_w * K_a}{K_b}}$$

Example:

What is the pH of 0.1 M **$HCOONH_4$** , ka (NH_4^+) = 5.7*10^{-10} , Ka (HCOOH) = 1.8*10^{-4}?

$$[H_3O^+] = \sqrt{\frac{K_w * K_{aNH4+} * k_{aHCOOH}}{K_w}}$$

$[H_3O^+]$ = 3.2*10^{-7} M , pH = 6.5

Acid base properties of solution

Salts of weak bases and weak acids

Example:

What is the pH of 0.1 M **NH_4CN**, ka (NH_4^+) = $5.7*10^{-10}$, Ka (HCN) = $6.2*10^{-10}$?

$$[H_3O^+] = \sqrt{\frac{K_w * K_{aNH4^+} * k_{aHCN}}{K_w}}$$

$[H_3O^+] = 5.9*10^{-10}$ M , pH = 9.2

How should you calculate pH of $NaHCO_3$

Na^+
neutral

HCO_3^-
Amphoteric

HCO_3^- : Amphoteric spieces

$HCO_3^- + H_2O \xleftrightarrow{Kb} H_2CO_3 + OH^-$ **Base** $K_b = \dfrac{K_w}{K_1}$

$HCO_3^- + H_2O \xleftrightarrow{Ka} CO_3^{-2} + H_3O^+$ **Acid** $K_a = K_2$

Calculation

For an amphiprotic salt $NaHCO_3$ what is the pH for 0.1 M solution of sodium hydrogencarbonate?

Dissociation constant of H_2CO_3 : $K_1 = 4.45*10^{-7}$, $K_2 = 4.7*10^{-11}$

See your book--------

$$[H_3O^+] = \sqrt{K_1 \times K_2}$$

pH Calculations

Calculate pH of the following: for ka values see appendix 3

0.1 M, 100 ml HCl mixed with 400 ml H_2O?

0.1 M, 100 ml HCl mixed with 0.05 M, 200 ml NaOH?

0.1 M , 100 ml HCl mixed with 0.1 M , 100 ml NH_3?

0.2 M, 50 ml NaOH mixed with 10 mmol HNO_3?

0.2 M , 50 ml NaOH mixed with 10 mmol HOCl?

pH Calculations

Calculate pH of the following: for ka values see appendix 3

0.1 M, 100 ml HCl mixed with 400 ml H_2O?

$$[HCl] = \frac{\text{no mmol HCl}}{\text{total volume}} = \frac{10\ (\text{mmol})}{(100 + 400)\ (\text{mL})} = 0.02\ \text{M}$$

$[H_3O^+] = [HCl] = 0.02$ M

pH = $-\log [H_3O^+] = 1.69$

pH Calculations

Calculate pH of the following: for ka values see appendix 3

0.1 M, 100 ml HCl mixed with 0.05 M, 200 ml NaOH?

$$\begin{array}{ccccc} \mathrm{HCl} & + & \mathrm{NaOH} & \longrightarrow & \mathrm{NaCl} + \mathrm{H_2O} \\ 10\ \mathrm{mmol} & & 10\ \mathrm{mmol} & & \text{———} \\ \text{———} & & \text{———} & & 10\ \mathrm{mmol} \end{array}$$

The mixture is a solution of salt $[\mathrm{NaCl}] = \dfrac{10\ \mathrm{mmol}}{300\ \mathrm{mL}} = 0.03\ \mathrm{M}$

$pH = 7$

The case is complete neutralization

pH Calculations

Calculate pH of the following: for ka values see appendix 3

0.1 M , 100 ml HCl mixed with 0.1 M , 100 ml NH_3?

NH_3	+	HCl	$\longrightarrow$	NH_4Cl	
10 mmol		10 mmol		______	
______		______		10 mmol	**complete neutralization**

$$[NH_4Cl] = \frac{10\ \text{mmol}}{200\ \text{mL}} = 0.05\ M$$

NH_4Cl is acidic salt ka $NH_4^+ = \frac{kw}{kb} = 5.7*10^{\mathbf{-10}}$

$[NH_4+] = [NH_4Cl] = 0.05\ M$

$$\mathbf{[H_3O^+] = \sqrt{K_a \times C_{HA}}}$$

Calculate pH of the following: for ka values see appendix 3

0.2 M , 50 ml NaOH mixed with 10 mmol HOCl?

NaOH	+	HOCl	$\longrightarrow$	NaOCl	+	H_2O
10 mmol		10 mmol		———		
———		———		10 mmol	**complete neutralization**	

$$[NaOCl] = \frac{10\ mmol}{50\ mL} = 0.2\ M$$

NaOCl is basic salt $kb\ OCl^{-} = \frac{kw}{ka_{\ HOCl}} = 3.33 * 10^{-7}$

$[OCl^{-}] = [Na\ OCl] = 0.2\ M$

$$\mathbf{[OH^{-}] = \sqrt{K_b \times C_B}}$$

Calculate the pH of the following

0.01 M HBr

0.03 M acetic acid

0.05 M anilinium bromide

0.02 M NaBr

0.05 M KNO_2

0.085 M pyridinium chloride

0.1 M sodium benzoate

0.3 M potassium butanoate

0.15 M ethylammonium chloride

Calculate the pH of the following

0.085 M pyridinium chloride

Pyridinium bromide

BH^+ (weak acid) Br^- (neutral)

$$BH^+ + H_2O \xrightleftharpoons{Ka} B + H_3O^+$$

Pyridinium pyridine

$$Ka = \frac{K_w}{K_{b\ \text{Pyridine}}}$$

$$[H_3O^+] = \sqrt{K_a \times C_{HA}}$$

Calculate the pH of the following

0.085 M pyridinium chloride

$$Ka = \frac{K_w}{K_{b\ \text{Pyridine}}} = 5.88*10^{-6}$$

$$[H_3O^+] = \sqrt{K_a \times C_{HA}} = 7*10^{-4}\ M$$

Relative error =0.83% , the approximation is accepted.

Calculate the pH of the following

0.1 M sodium benzoate

Sodium benzoate

Na^+ (neutral) A^- (weak base)

$$A^- + H_2O \xleftrightarrow{Kb} HA + OH^-$$

benzoate Benzoic acid

$$Kb = \frac{K_w}{K_{a\ \text{benzoic acid}}}$$

$$[OH^-] = \sqrt{K_b \times C_B}$$

Calculate the pH of the following

0.1 M sodium benzoate

$$Kb = \frac{K_w}{K_{a\ \text{benzoic acid}}} = 1.62*10^{-10}$$

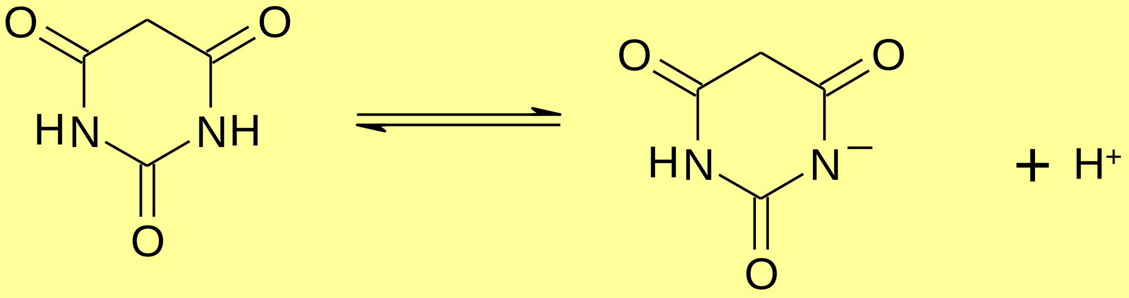
$$[OH^-] = \sqrt{K_b \times C_B} = 4*10^{-6}\ M$$

Relative error = 0.004%

pOH= 5.4   pH=8.6

Calculation

Barbituric acid dissociate as follows



Barbituric acid, HA

Barbiturate, A^-

K_a of the above reaction is $9.8 * 10^{-5}$. Calculate the pH of 0.01 M barbituric acid and of 0.01 M potassium barbiturate.

Calculation

$$[H_3O^+] = \sqrt{K_a \times C_{HA}}$$

Barbituric acid is a weak acid donates one proton Ka= $9.8 * 10^{-5}$

$[H_3O+] = 9.89*10^{-4}$ M

pH = 3

Calculation

Potassium barbiturate 0.01 M,
[barbiturate ion] = 0.01 M which is a weak base (conj. Base)

$$[OH^{-}] = \sqrt{K_{b\ barbiturate} \times C_{B\ barbiturate}}$$

$$[OH-] = \sqrt{\frac{K_w}{K_a} \; X \; C_b} = 1*10^{-6}\ M,$$

POH = 6 → PH = 14 – POH= 8

Calculation

Examples: 7-8 to 7-12

Problems: chapter 7 questions 2, 4,5,6,8, 20, 21, 22

The next subject is buffer and indicator

Acid – Base Titration
part 5

Dr. Mai Ramadan

Buffer

A *buffer solution* is a solution able to absorb a certain quantity of acid or base without undergoing a strong variation in pH.

A *buffer solution* is a solution that resists changes in pH within the buffer capacity.

A buffer solution is a mixture of a weak acid HA and its conjugate base A- or a mixture of a weak base B and of its conjugate acid BH+.

Buffer

Buffer capacity is the number of moles of strong acid or strong base that causes 1.00 L of the buffer to undergo a 1.00 unit change in pH

pH = pKa ± 1 (pH range of buffer ability)

Buffer

pH of buffer: (***Henderson-Hasselbalch-relationship***)

For a mixture of weak acid and its conjugate base HA/A^-

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

For a mixture of weak base and its conjugate acid B/HB^+

$$pOH = pK_b + \log \frac{[HB+]}{[B]}$$

$$\mathbf{0.1} \leq \frac{[A^-]}{[HA]} \leq \mathbf{10}$$

Buffer

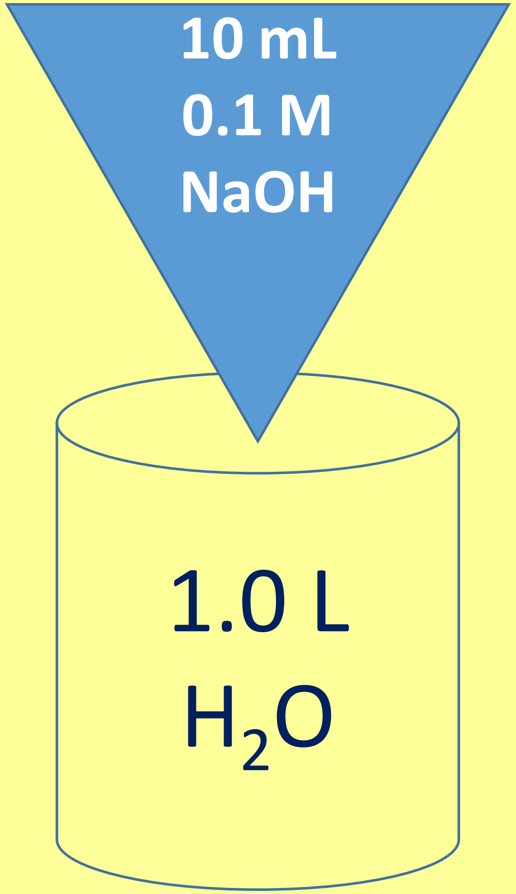
Maximum buffer capacity when pH = Pka

pOH =pKb

When $\frac{[A^-]}{[HA]} = 1 \longrightarrow [A^-] = [HA] \longrightarrow \quad \longrightarrow$ **pH = Pka**

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

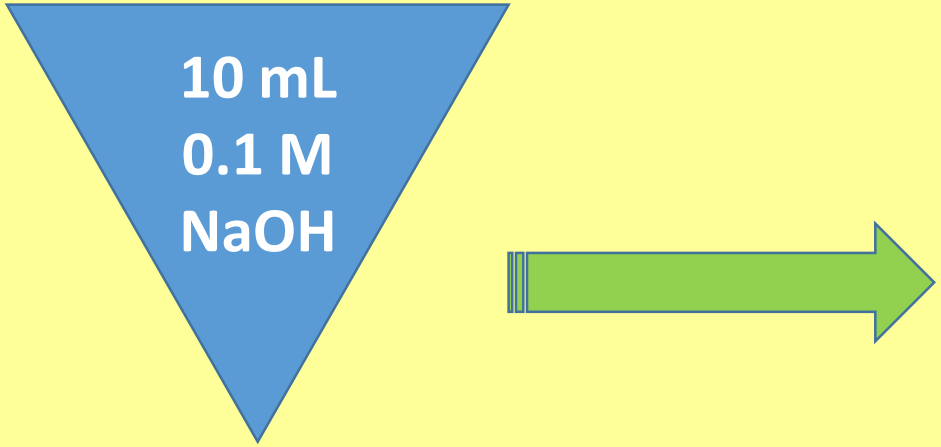
When $[BH+] = [B] \longrightarrow pOH = pK_b + \log \frac{[HB+]}{[B]} \longrightarrow \quad \longrightarrow$ **pOH =pKb**



10 mL
0.1 M
NaOH

1.0 L
H_2O

Initial pH of H_2O = 7



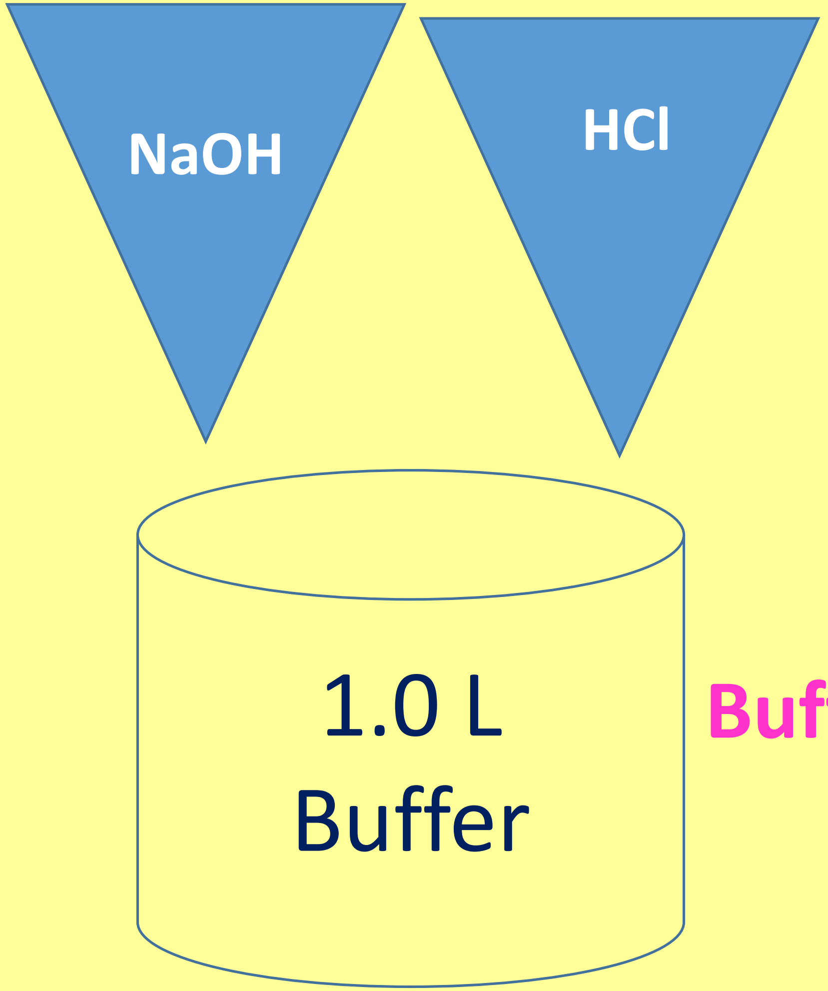
10 mL
0.1 M
NaOH

Δ pH= +4

pH of H_2O = 11

$[OH^-]$ = 1 mmol/1010 mL= $9.9*10^{-4}$

pOH= 3 pH= 11



A liter of water has pH of 7 when 10 ml, 0.1 M NaOH is Added then the pH of water is changed to 11.

When the same amount of NaOH is added to a liter buffer solution then pH changes is minimum (Δ pH < 1)

Buffer is a mixture of HA & A^- → **Δ pH < 1**

Buffer

Why does a buffer resist changes in pH?

It does because the strong acid or strong base is consumed by A- or HA, When HCl is added, A- is converted to HA. When NaOH is added then HA is converted to A-. As long as we do not use up HA and A- (by adding HCl and NaOH) the log term of the henderson-Hesslbalch equation does not change very much and pH remains constant.

The buffer has **a maximum capacity when** pH= pka

See the next example

Buffer

Calculate change in pH of a buffer solution that is 1 liter, 1.0 M CH_3COOH and 0.3 M $Na(CH_3COO)$

a. when a 100 ml 1.0 M HCl is added?

b. when 100 ml 1.0 M NaOH is added?

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

$CH_3COOH + HCl \xrightarrow{\quad\quad}$ *no reaction*

$CH_3COO^- + HCl \xrightarrow{\quad\quad} CH_3COOH + Cl^-$

pH original = *4.24*

After addition of 100 ml, 1.0 M HCl then

No mol CH3COOH = 1 mol (original) + 0.1 mol (formed)

No mol CH3COO$^-$ = 0.3 mol (orginal) – 0.1 mol (consumed)

$$pH = 4.76 + \log \frac{0.2\ mol/\cancel{Vol}}{1.1\ mol/\ \cancel{Vol}} = 4.02 \Longrightarrow \Delta pH = 0.22$$

Buffer

Calculate change in pH of a buffer solution that is 1 liter, 1.0 M CH_3COOH and 0.3 M $Na(CH_3COO)$

a. when a 100 ml 1.0 M HCl is added?

b. when 100 ml 1.0 M NaOH is added?

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

$$CH_3COOH + NaOH \longrightarrow CH_3COO^- + Na^+ + H_2O$$

$CH_3COO^- + NaOH \longrightarrow$ *no reaction*

pH original *= 4.24*

After addition of 100 ml, 1.0 M NaOH then

No mol CH3COOH = 1 mol (original) - 0.1 mol (consumed)

No mol $CH3COO^-$ = 0.3 mol (orginal) + 0.1 mol (formed)

$$pH = 4.76 + \log \frac{0.4\ mol/\cancel{Vol}}{0.9\ mol/\cancel{Vol}} = 4.41 \Longrightarrow \Delta pH = -0.17$$

How to prepare a buffer

Mixing

HA & A^- OR B & BH^+

$CH_3COOH + Na(CH_3COO)$

$HCOOH + K(HCOO)$

$NH_3 + NH_4Cl$

$$0.1 \le \frac{[A^-]}{[HA]} \le 10$$

Mixing

HA & strong base OR

B & strong acid

One condition

Partial neutralization

No. mol HA > no. mol strong base

No. mol B > no. mol strong acid

Preparation of buffer

What is the pH of 0.1 M NH_3 solution? ***How many milliliters*** *of 0.2 M HCl should be added to 250 ml ammonia solution to have pH 9?*

For a weak base $[OH^-] = \sqrt{K_b \times C_B}$

$[OH^-] = 1.3*10^{-3}$ M → pH = 11.12

	NH_3	+ HCl	$\longrightarrow$	$NH_4^+ + Cl^-$
Intial:	0.025 mol	X mol		--------
Change:	(0.025-X) mol	------		X mol

Through **partial neutralization** of a weak base a buffer is produced,

$$pOH = pK_b + \log \frac{[HB+]}{[B]}$$

Preparation of buffer

What is the pH of 0.1 M NH_3 solution? ***How many milliliters*** *of 0.2 M HCl should be added to 250 ml ammonia solution to have pH 9?*

$$pOH = pK_b + \log \frac{[HB+]}{[B]}$$

Since the ratio of concentration is the ratio of number of moles then

$$14 - 9 = 4.76 + \log \frac{X}{(0.025 - X)}$$

X = 0.0159 (mol)

Volume of HCl = $\frac{\text{no mol}}{\text{Conc. (M)}}$ = 0.079 L = **79 ml**

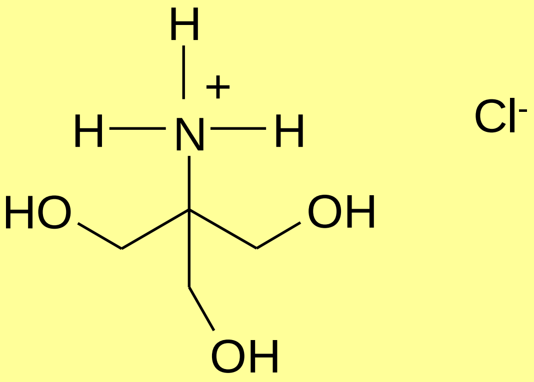
Acid – Base Titration
part 6

Dr. Mai Ramadan

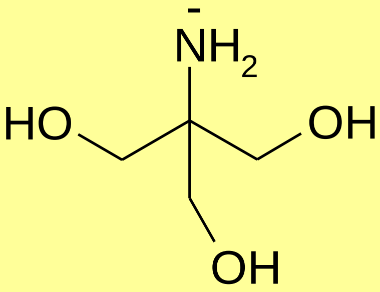
Continue with Buffer Problems

Preparation of buffer

Calculate how many milliliters of 0.05 M NaOH should be addede to 10.0 g of tris-hydrochloride (FW = 157.59, pKa 8.075) to give a pH of 7.6 in a final volume of 250 ml?



Trishydrochloride **($BH^+ Cl^-$)**



Tris **(B)**

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

Since the ratio of concentration is the ratio of number of moles then

Remember that

B.HCl $\cong$ BH^+Cl^- Acidic salt

Cation BH^+ Weak conjugated acid

Anion Cl^- No influence on pH

Preparation of buffer

$$\mathbf{BH^+Cl^- + NaOH \longrightarrow B + NaCl + H_2O}$$

	BH^+Cl^-	NaOH	B
Initial:	0.063 mol	X mol	----
Change:	(0.063-X)	--------	X

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

Since the ratio of concentration is the ratio of number of moles then

$$7.6 = 8.075 + \log \frac{X \text{ mol}}{(0.063 - X) \text{ mol}}$$

X = 0.0158 mol

No mol NaOH = 0.0158 (mol)   Vol of NaOH = 0.0316 L= 31.6 mL

Preparation of buffer

Preparation of buffer in real life:

Weigh out 10 g of tris hydrochloride and dissolve in a beaker containing about 150 ml of water

Place pH electrode in the solution and monitor pH

Add NaOH (0.05 M) until pH is exactly 7.6

Transfer the solution into a volumetric flask and wash the beaker a few times. Adding the washing to volumetric flask.

Dilute to 250 ml mark and mix.

To prepare a buffer of a desired pH

Choose a buffer whose pK_a is close to pH

Calculation

pK_b of nitrite ion NO_2^- is 10.85. Find the quotient $[HNO_2]/[NO_2^-]$ in a solution of sodium nitrite at pH 2 and at pH 10?

$$NO_2^- + H_2O \longleftrightarrow HNO_2 + OH^-$$

$$POH = PK_b + \log \frac{[HNO_2]}{[NO_2^-]}$$

At pH =2, pOH = 12 using the above equation

$$\frac{[HNO_2]}{[NO_2^-]} = 14$$

At pH =12, pOH = 2 using the above equation

$$\frac{[HNO_2]}{[NO_2^-]} = 1.4*10^{-9}$$

Calculation

In the above question it is clear that for a weak base B
In acidic media the main specie present is BH+ ionized form
In basic media the main specie present is B non ionized form

The importance in pharmacy that a drug is considered as a weak base B

↓

The non-ionized (lipophillic , ready to be absorbed) form concentration differs according to pH of media (biological pH differs along GI-tract)

Calculation

Calculate pH for the following mixture:

1- 100 ml, 0.1 M NH3 + 100 ml, 0.1 M HCl
(Complete neutralization)

2- 100 ml, 0.1 M HCOOH + 100 ml, 0.1 M NaOH
(Complete neutralization)

3- 100 ml, 0.1 M HCOOH + 50 ml, 0.1 M NaOH
(**Buffer, maximum buffer capacity pH= pka)**

4- 100 ml , 0.1 M HCOOH + 20 ml, 0.1 M NaOH
(Partial neutralization of weak acid, buffer)

5- 100 ml, 0.1 M HCl + 20 ml, 0.1 M NaOH
(Partial neutralization, <u>not a buffer</u>)

Calculation

Calculate pH for the following mixture:
1- 100 ml, 0.1 M NH3 + 100 ml, 0.1 M HCl **(Complete neutralization)**

NH_3	+	$HCl \longrightarrow$	NH_4Cl
10 mmol		10 mmol	______
______		______	10 mmol

$$[NH_4Cl] = \frac{10\ mmol}{200\ mL} = 0.05\ M$$

NH_4Cl is acidic salt ka $NH_4^+ = \frac{K_w}{K_{bNH3}} = 5.7*10^{\mathbf{-10}}$

$[NH_4+] = [NH_4Cl] = 0.05\ M$

$\mathbf{[H_3O^+] = \sqrt{K_a \times C_{HA}}}$ $= 5.3*10^{-6}$ M , relative error is very small, pH= 5.3

Calculation

Calculate pH for the following mixture:

3- 100 ml, 0.1 M HCOOH + 50 ml, 0.1 M NaOH

(**Buffer, maximum buffer capacity pH= pka)**

$HCOOH$	+	$NaOH$	$\longrightarrow$	$HCOONa$	+ $H2O$
10 mmol		5 mmol		______	
5 mmol		______		5 mmol	

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

$$pH = 3.75 + \log \frac{5\ \text{mmol}}{5\ \text{mmol}}$$ **= pKa = 3.75**

Calculation

Calculate pH for the following mixture:

4- 100 ml , 0.1 M HCOOH + 20 ml, 0.1 M NaOH

(Partial neutralization of weak acid, buffer)

HCOOH	+	NaOH	$\longrightarrow$	HCOONa	+ H_2O
10 mmol		2 mmol		———	
8 mmol		———		2 mmol	

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

$$pH = 3.75 + \log \frac{2\ \text{mmol}}{8\ \text{mmol}} = 3.15$$

pH Calculations

Calculate pH for the following mixture:

5- 100 ml, 0.1 M HCl + 20 ml, 0.1 M NaOH

(Partial neutralization, not a buffer)

$$\begin{array}{ccccccc} \text{HCl} & + & \text{NaOH} & \longrightarrow & \text{NaCl} & + & \text{H}_2\text{O} \\ 10\ \text{mmol} & & 2\ \text{mmol} & & \underline{\hspace{3em}} & & \\ 8\ \text{mmol} & & \underline{\hspace{3em}} & & 2\ \text{mmol} & & \end{array}$$

$$[\text{HCl}]_{\text{residual}} = \frac{\text{no mmol HCl unreacted}}{\text{total volume}} = \frac{8\ \text{mmol}}{120\ \text{mL}} = 0.067\ \text{M}$$

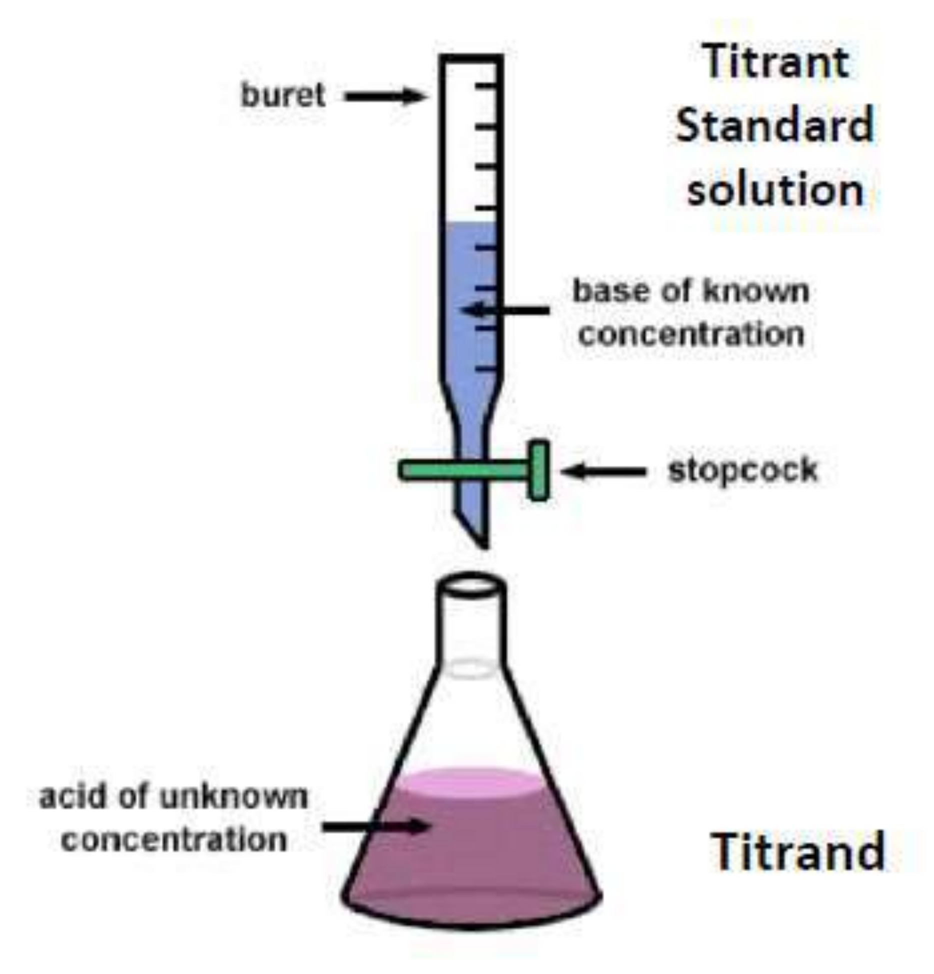
$$\text{pH} = -\log[\text{HCl}]_{\text{residual}} = 1.17$$

Note : the solution after mixing is a mixture of residual HCl and salt NaCl formed. pH depends only on HCl , NaCl has no effect.

Acid – Base Titration
part 6 continue

Dr. Mai Ramadan

Indicators



How to know that the reaction during titration is completed

How to **stop** the titration process

End point

Detection in lab

Indicators

☐ Different chemical compound

Instruments

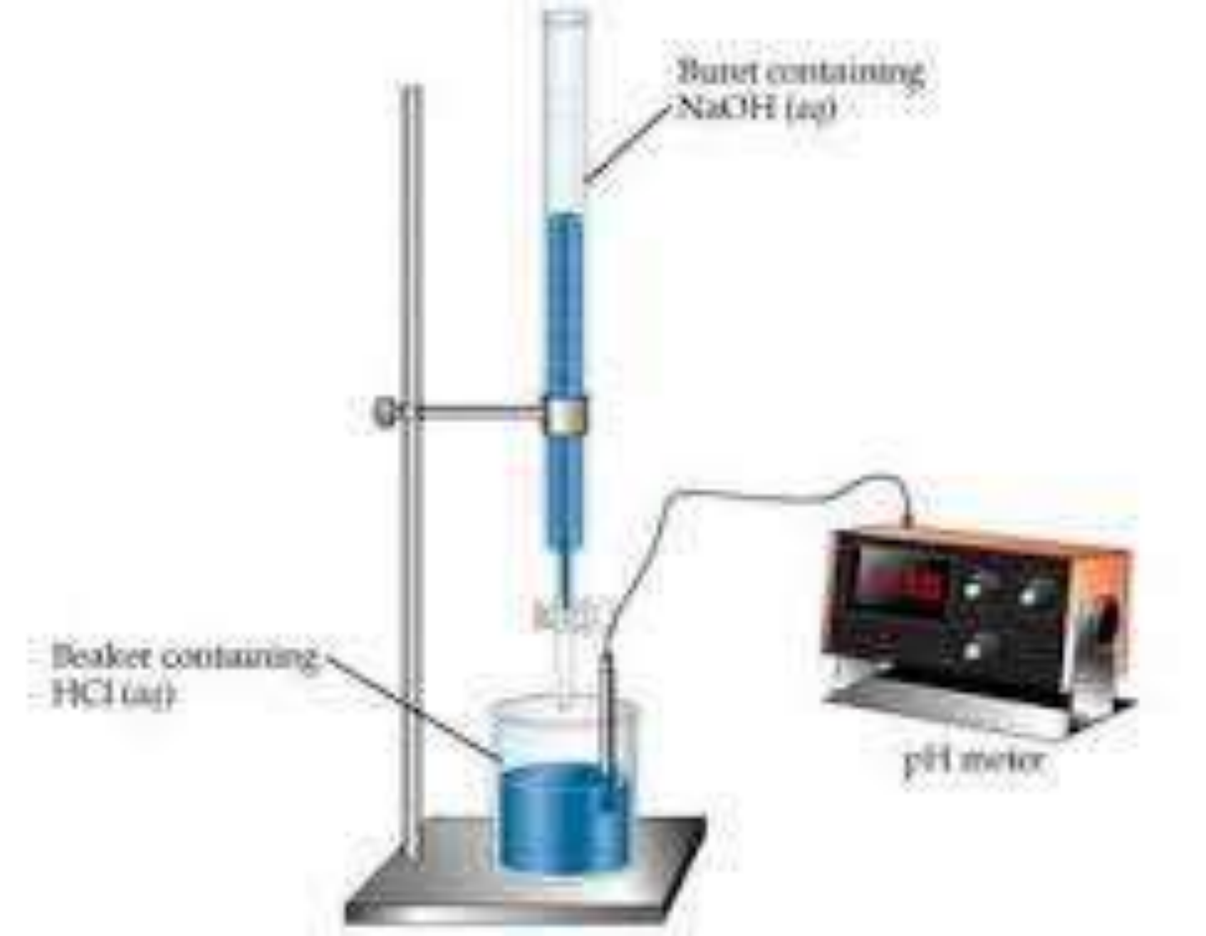
☐ Potentiometric end point detection

Indicators

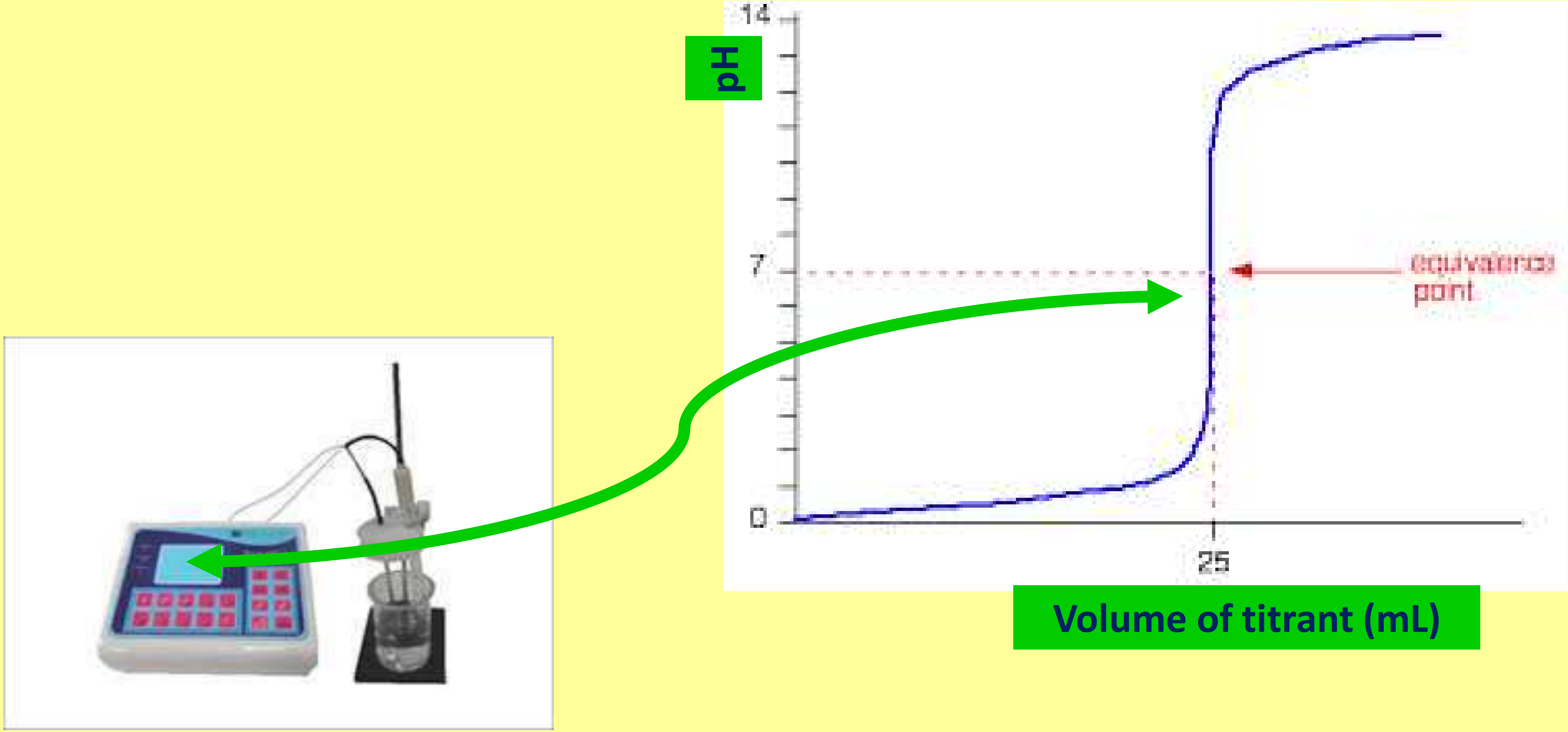
pH: 7

pH: 10

Phenolphthaleine


Buret containing NaOH (aq)
Beaker containing HCl (aq)
pH meter


140 ml
120
100
80
60
40


14
pH
7
0
equivalence point
25
Volume of titrant (mL)

Indicator

An acid/base indicator is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate base or its conjugate acid form

$\underset{\text{acid color}}{HIn} + H_2O \longleftrightarrow H_3O^+ + \underset{\text{base color}}{In^-}$ acid type Indicator

$\underset{\text{base color}}{In} + H_2O \longleftrightarrow \underset{\text{acid color}}{InH^+} + OH^-$ base type indicator

$$pH = pK_a + \log \frac{[In^-]}{[HIn]}$$

pH-rang of indicator: pKa ± 1

Indicator

The human eye is not very sensitive to color differences in a solution containing a mixture of HIn and In¯, particularly when the ratio [HIn]/[In¯] is greater than about 10 or smaller than about 0.1.

HIn, exhibits its pure acid color when

$$\frac{[\mathrm{HIn}]}{[\mathrm{In}^-]} \geq \frac{10}{1}$$

its base color when

$$\frac{[\mathrm{HIn}]}{[\mathrm{In}^-]} \leq \frac{1}{10}$$

Indicator

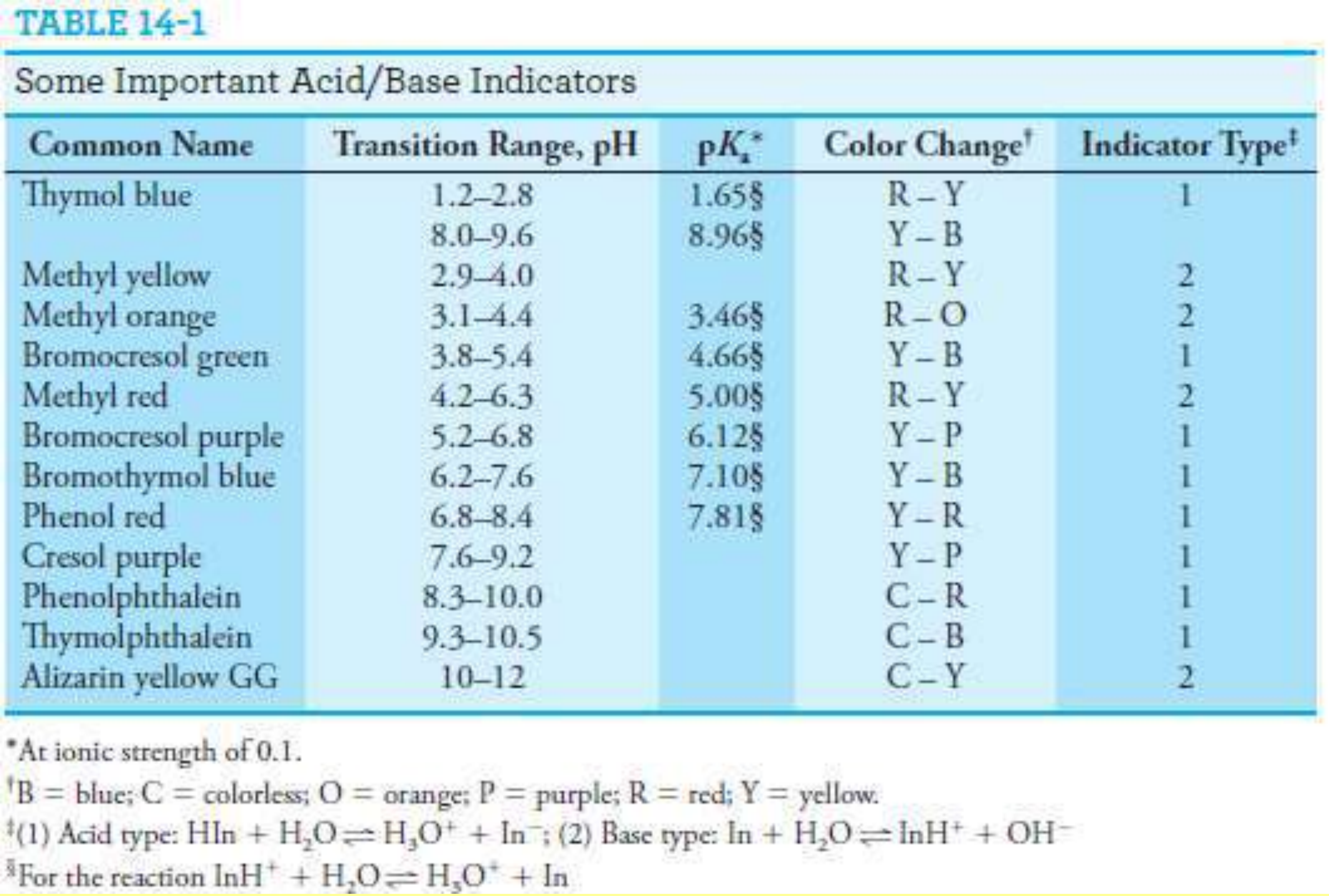


TABLE 14-1

Some Important Acid/Base Indicators

Common Name	Transition Range, pH	pK_a[*]	Color Change[†]	Indicator Type[‡]
Thymol blue	1.2–2.8	1.65[§]	R – Y	1
	8.0–9.6	8.96[§]	Y – B	
Methyl yellow	2.9–4.0		R – Y	2
Methyl orange	3.1–4.4	3.46[§]	R – O	2
Bromocresol green	3.8–5.4	4.66[§]	Y – B	1
Methyl red	4.2–6.3	5.00[§]	R – Y	2
Bromocresol purple	5.2–6.8	6.12[§]	Y – P	1
Bromothymol blue	6.2–7.6	7.10[§]	Y – B	1
Phenol red	6.8–8.4	7.81[§]	Y – R	1
Cresol purple	7.6–9.2		Y – P	1
Phenolphthalein	8.3–10.0		C – R	1
Thymolphthalein	9.3–10.5		C – B	1
Alizarin yellow GG	10–12		C – Y	2

[*] At ionic strength of 0.1.

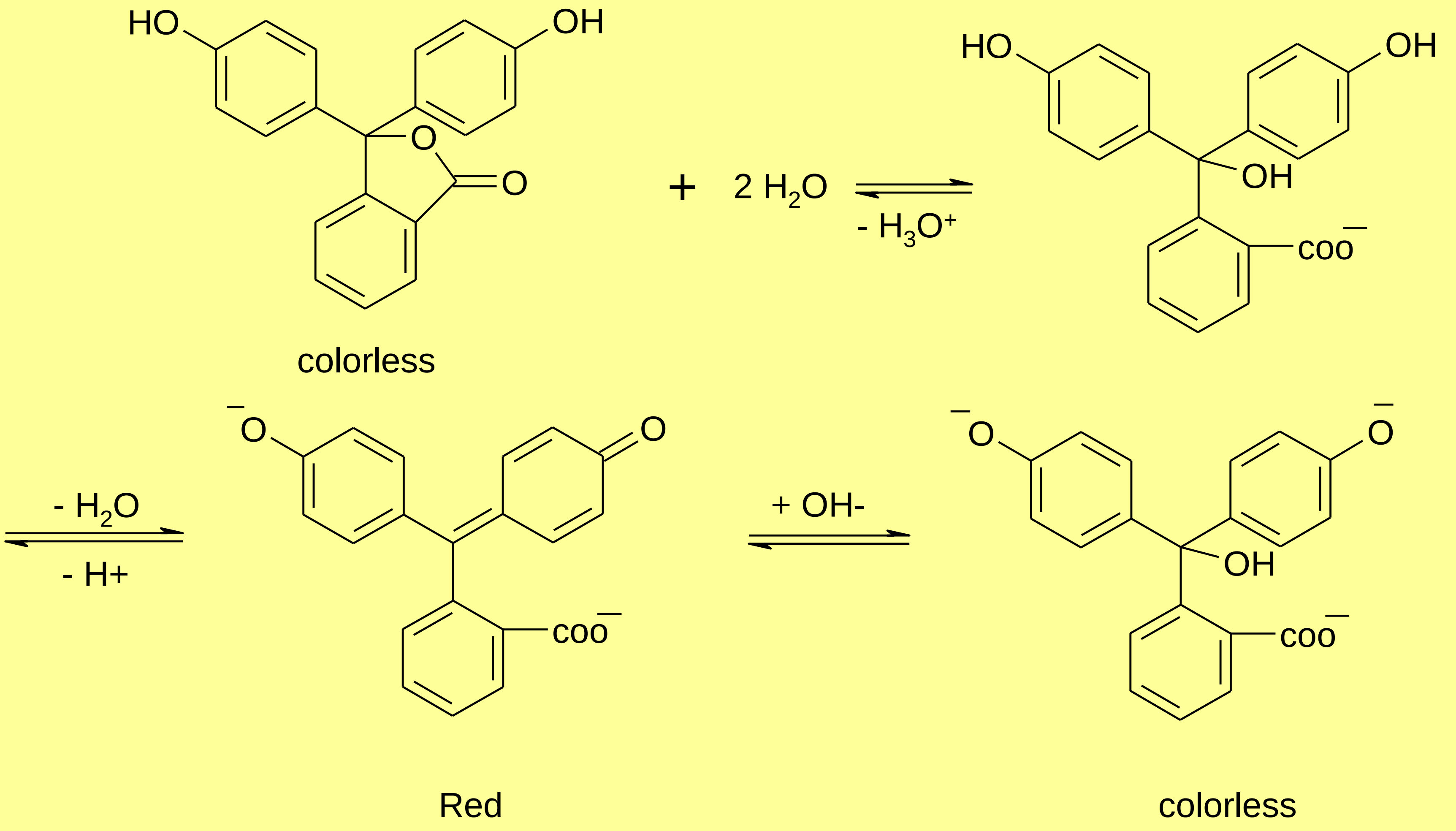
[†] B = blue; C = colorless; O = orange; P = purple; R = red; Y = yellow.

[‡] (1) Acid type: $HIn + H_2O \rightleftharpoons H_3O^+ + In^-$; (2) Base type: $In + H_2O \rightleftharpoons InH^+ + OH^-$

[§] For the reaction $InH^+ + H_2O \rightleftharpoons H_3O^+ + In$

Examples of indicators

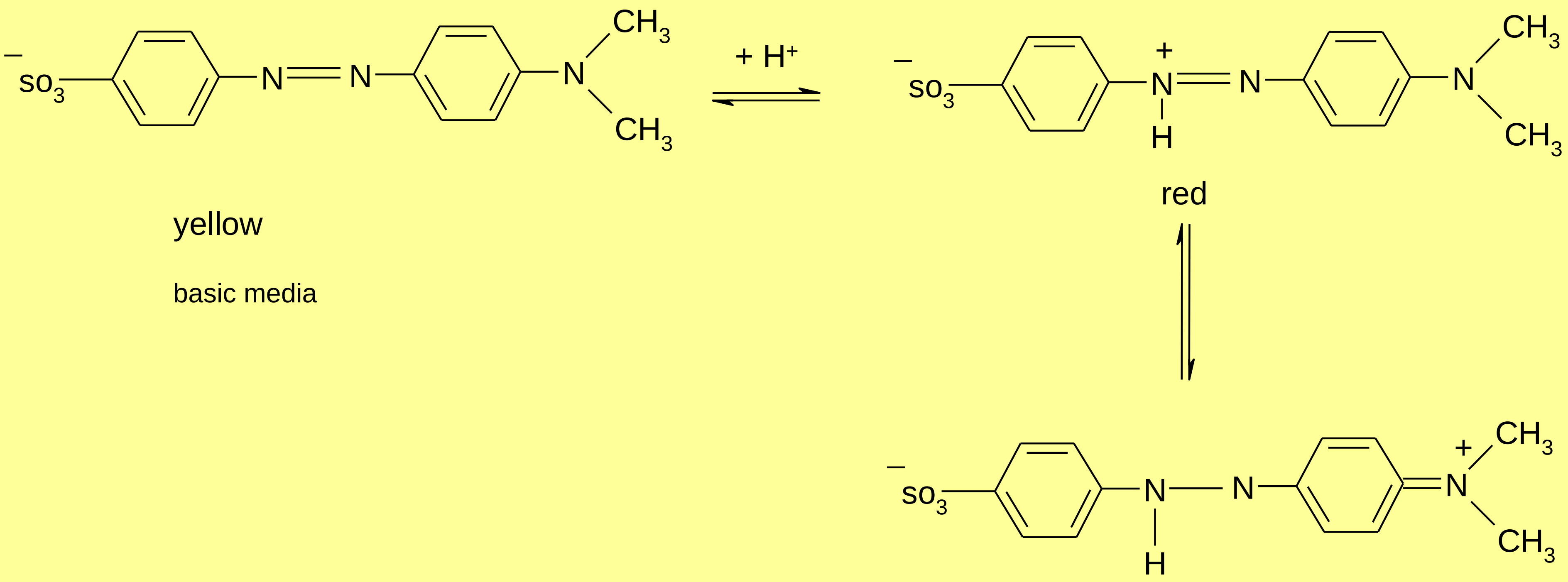
1- Phthalein indicator: Phenolphthalein



Examples of indicators

2- Sulphonphthalein indicator: Phenol red

3-Azo indicator: Methyl orange



Acid – Base Titration
part 7

Dr. Mai Ramadan

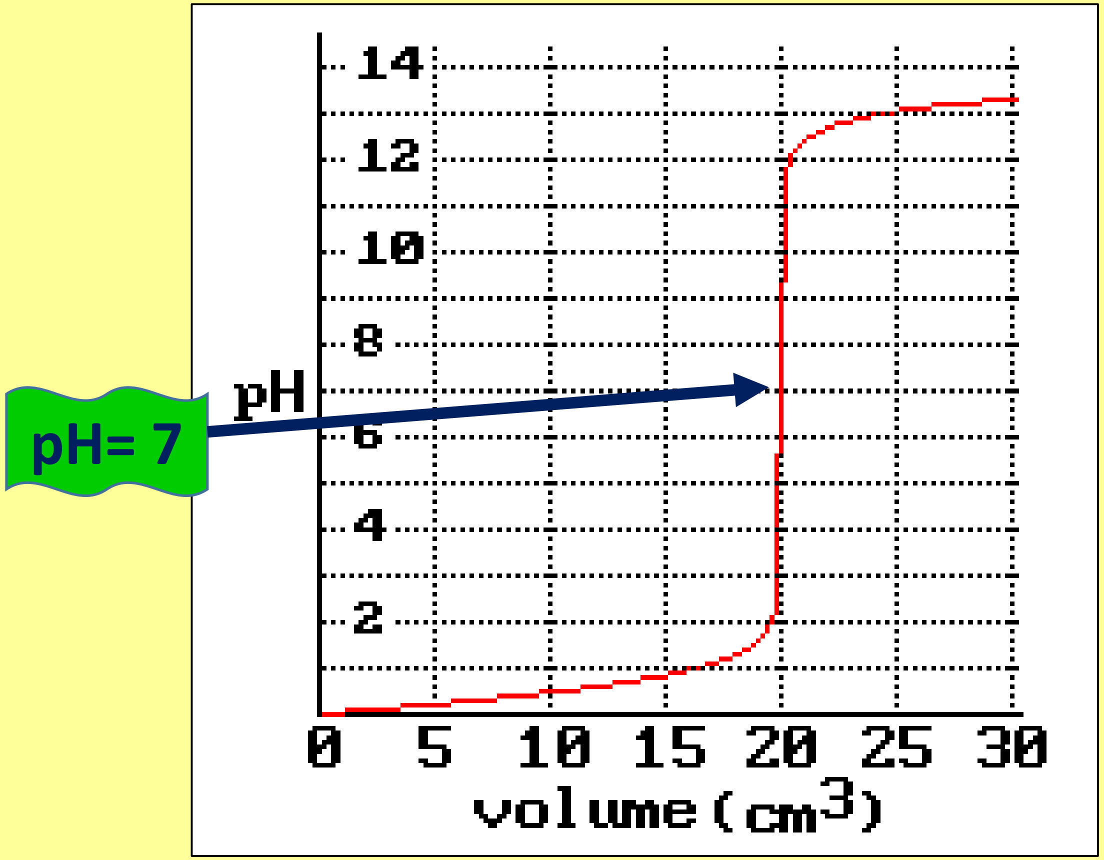
Titration curves

A **titration curve** is a graph of the pH as a function of the amount of titrant (acid or base) added.
The equivalence point for **a strong acid – strong base** has pH = 7

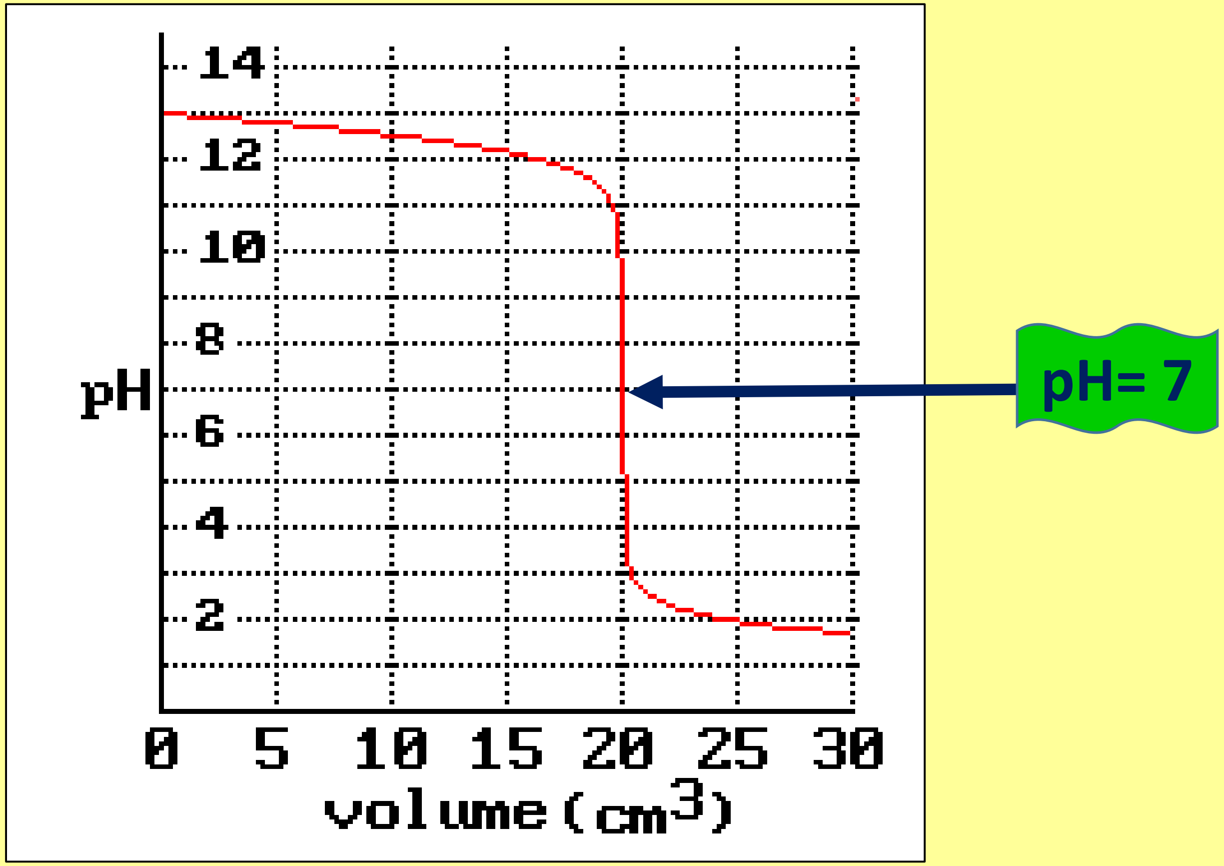
The equivalence point for a **weak acid-strong base** titration has a pH > 7.00.

The equivalence point for a **weak base-strong acid** titration has a pH < 7.00.

Titration curves

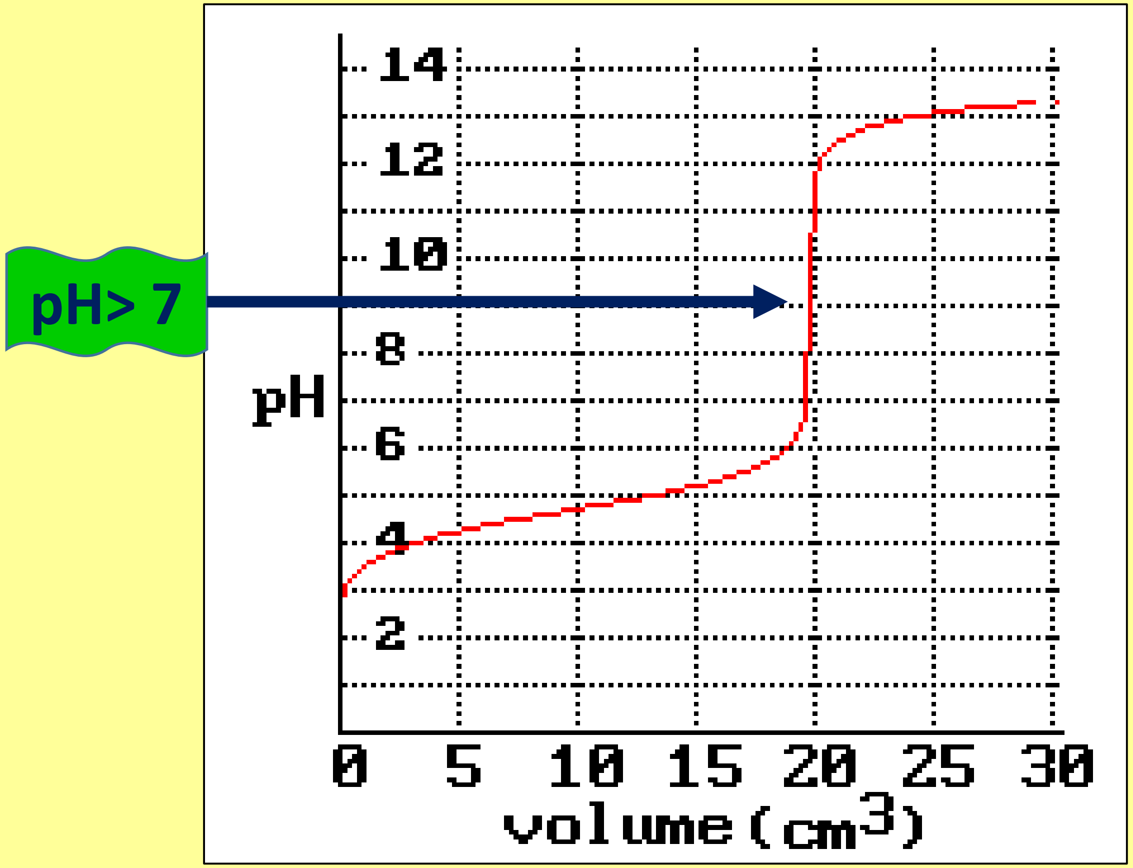


Strong acid –strong base

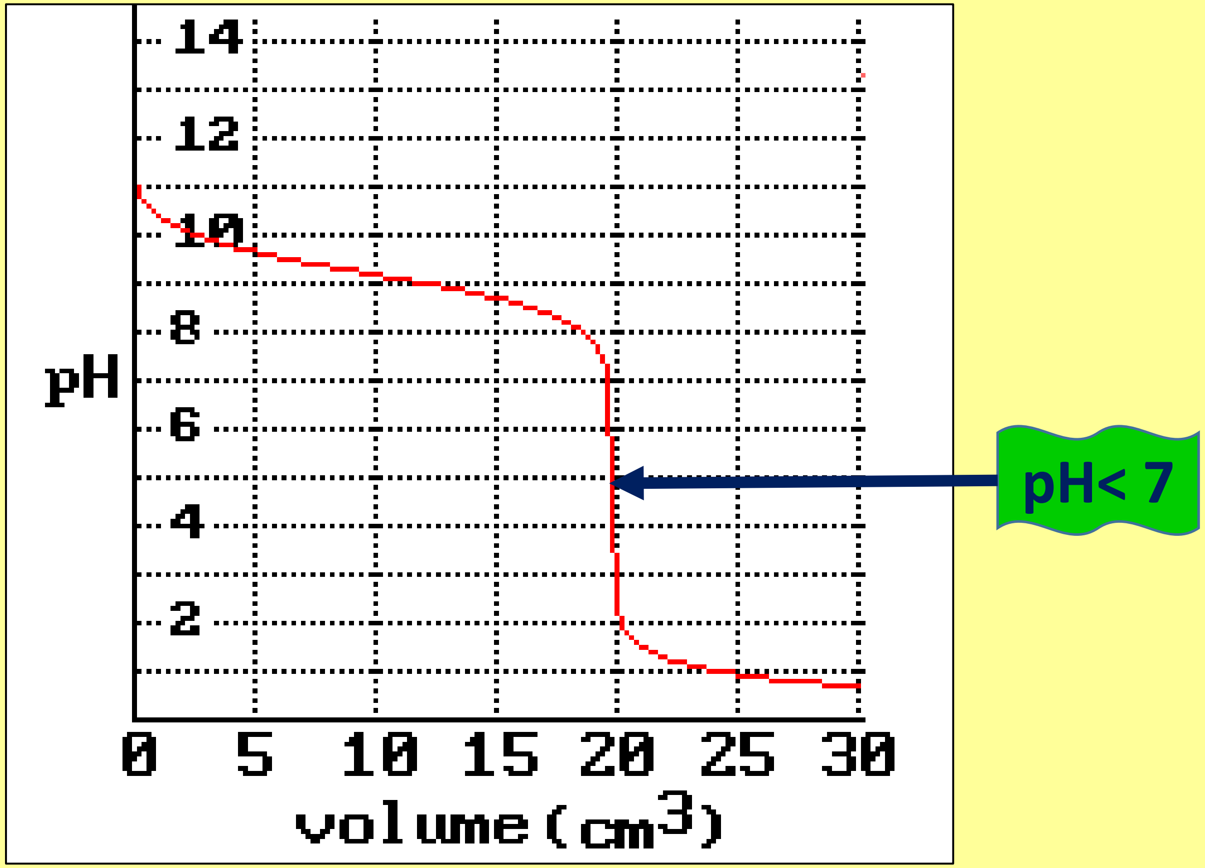


Strong base-strong acid

Titration curves



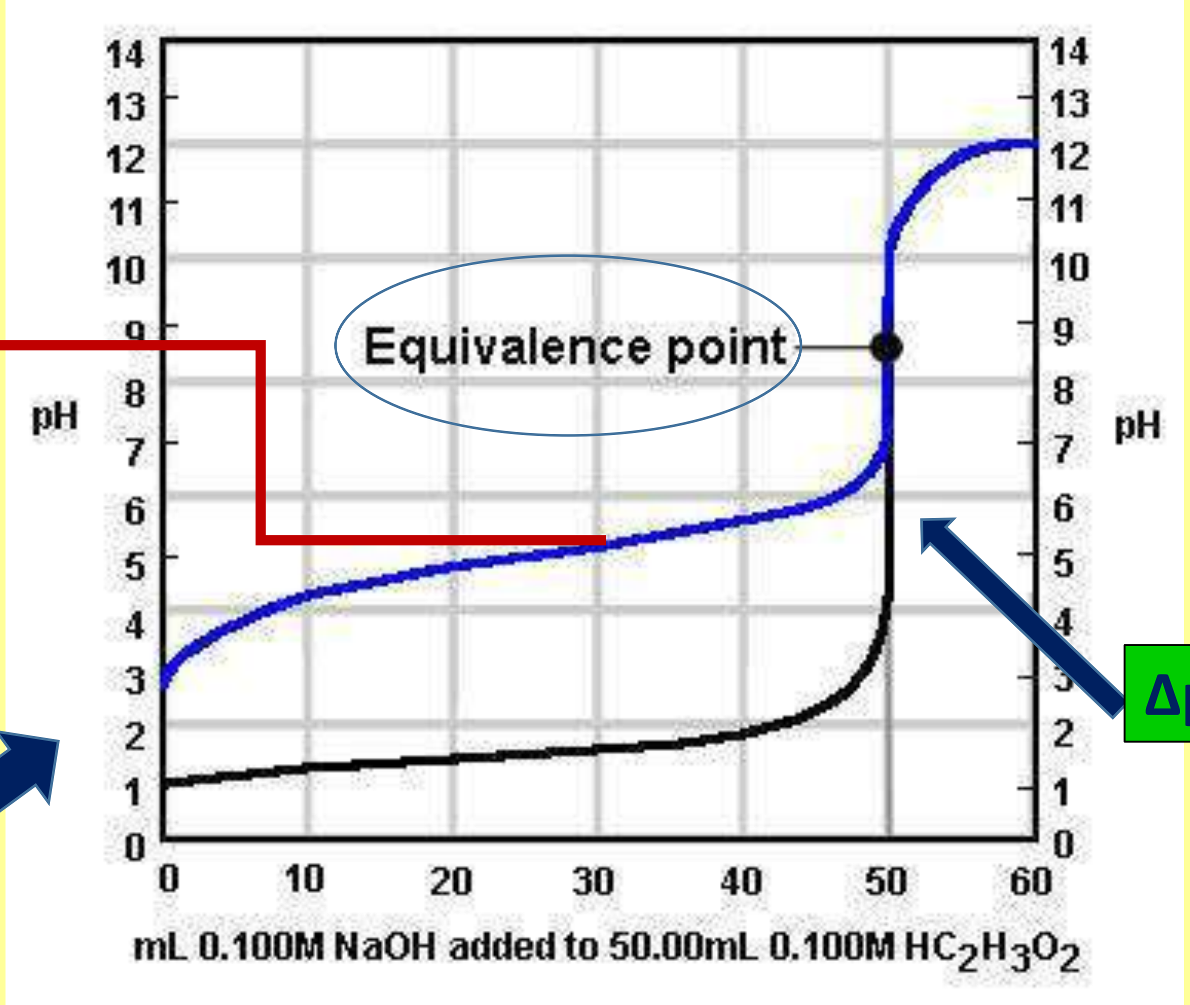
Weak acid –strong base



Weak base-strong acid

Titration curves

Titration Curves of strong acid-strong base in comparison with weak acid strong base



Buffer zone

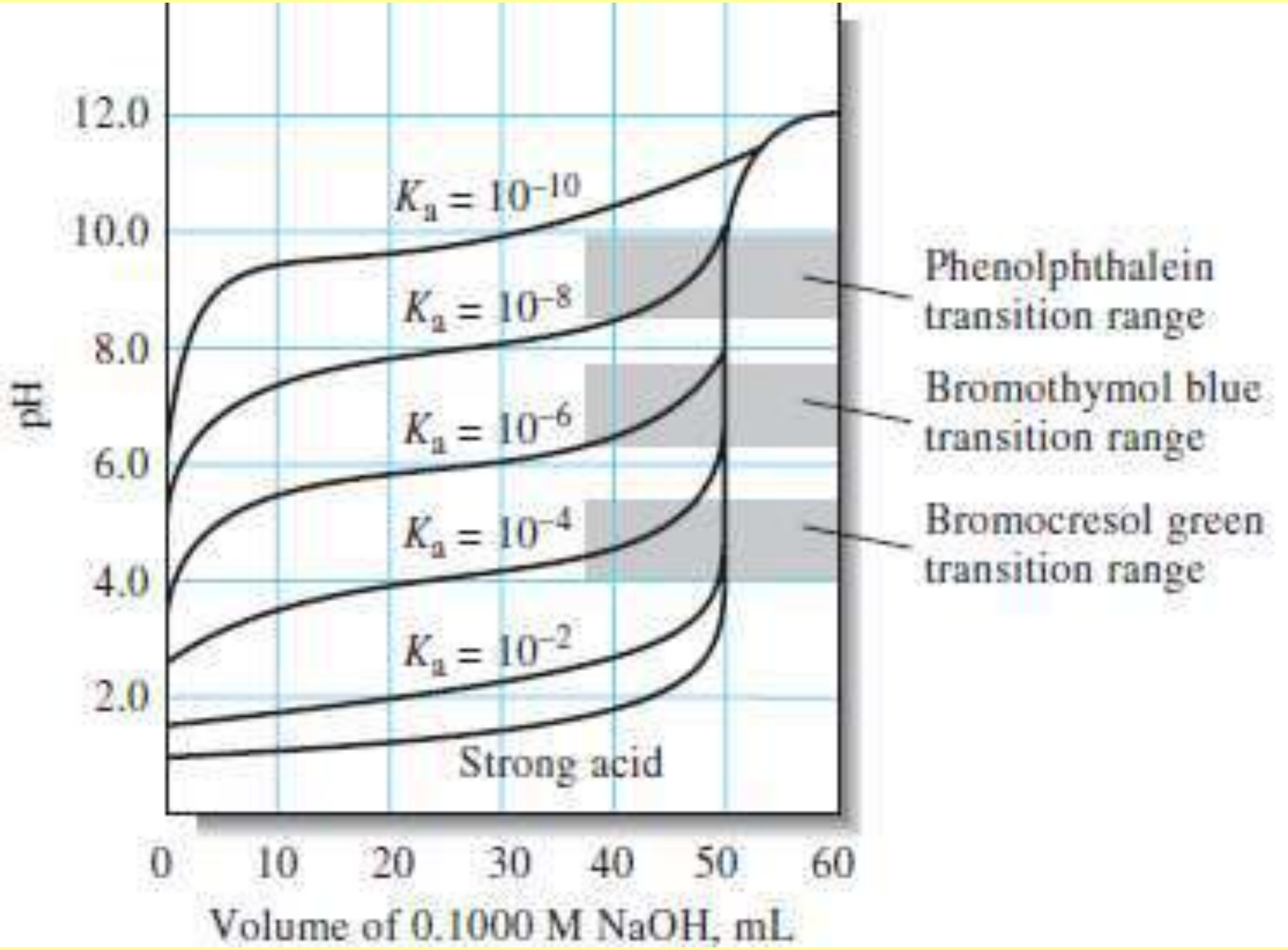
vol. Eq P/2 →

pH= Pka

Initial pH

ΔpH at Eq.P

Titration curves



The effect of acid strength (dissociation constant) on titration curves. Each curve represents the titration of 50.00 mL of 0.1M weak acid with 0.1 M strong base.

Strong acid-Strong base titration curve

Volume of titrant added to analyte	pH of analyte solution
Vol = 0.0 ml	
Vol < Eq. P	
Vol = Eq. P	
Vol > Eq. P	

Strong base

Strong acid

Titrating a Strong Acid with a Strong Base

Initial pH:

The solution is only a strong acid. pH = - log [acid]

Pre-equivalence point:

we calculate the pH from the molar concentration of unreacted acid.

At the equivalence point:

The solution is neutral, and pH = pOH. Both pH and pOH = 7.00, at 25°C.

Post equivalence point:

We first calculate pOH from the excess added strong base.

Remember that pH = 14 - pOH.

Titrating a Strong Acid with a Strong Base

Generate the hypothetical titration curve for the titration of 50.00 mL of 0.05 M HCl with 0.10 M NaOH at 25°C.

Initial Point: Vol = 0.0 mL

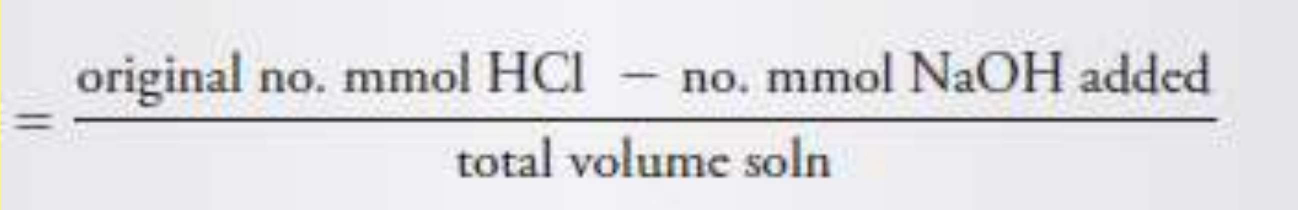
Before any base is added, the solution is 0.05 M in H_3O^+, and

pH = $-\log[H_3O^+] = 1.30$

Pre Equivalence point (Pre-Eq P): Vol= 10 mL

HCl	+	$NaOH$	$\longrightarrow$	$NaCl + H_2O$
2.5 mmol		1 mmol		-------
(2.5 – 1)mmol		----------		1 mmol

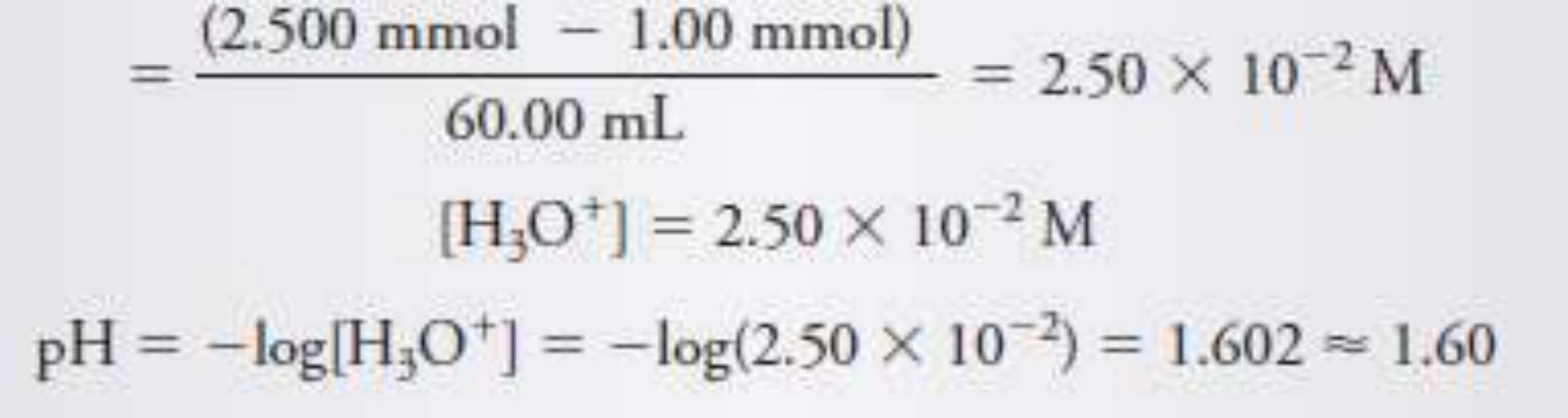
There is partial neutralization of strong acid, the unreactred acid determine pH



$$[HCl] = \frac{\text{original no. mmol HCl} - \text{no. mmol NaOH added}}{\text{total volume soln}}$$

Titrating a Strong Acid with a Strong Base

Pre Equivalence point (Pre-Eq P): Vol= 10.0 mL



$$= \frac{(2.500\text{ mmol} - 1.00\text{ mmol})}{60.00\text{ mL}} = 2.50 \times 10^{-2}\text{ M}$$

$$[H_3O^+] = 2.50 \times 10^{-2}\text{ M}$$

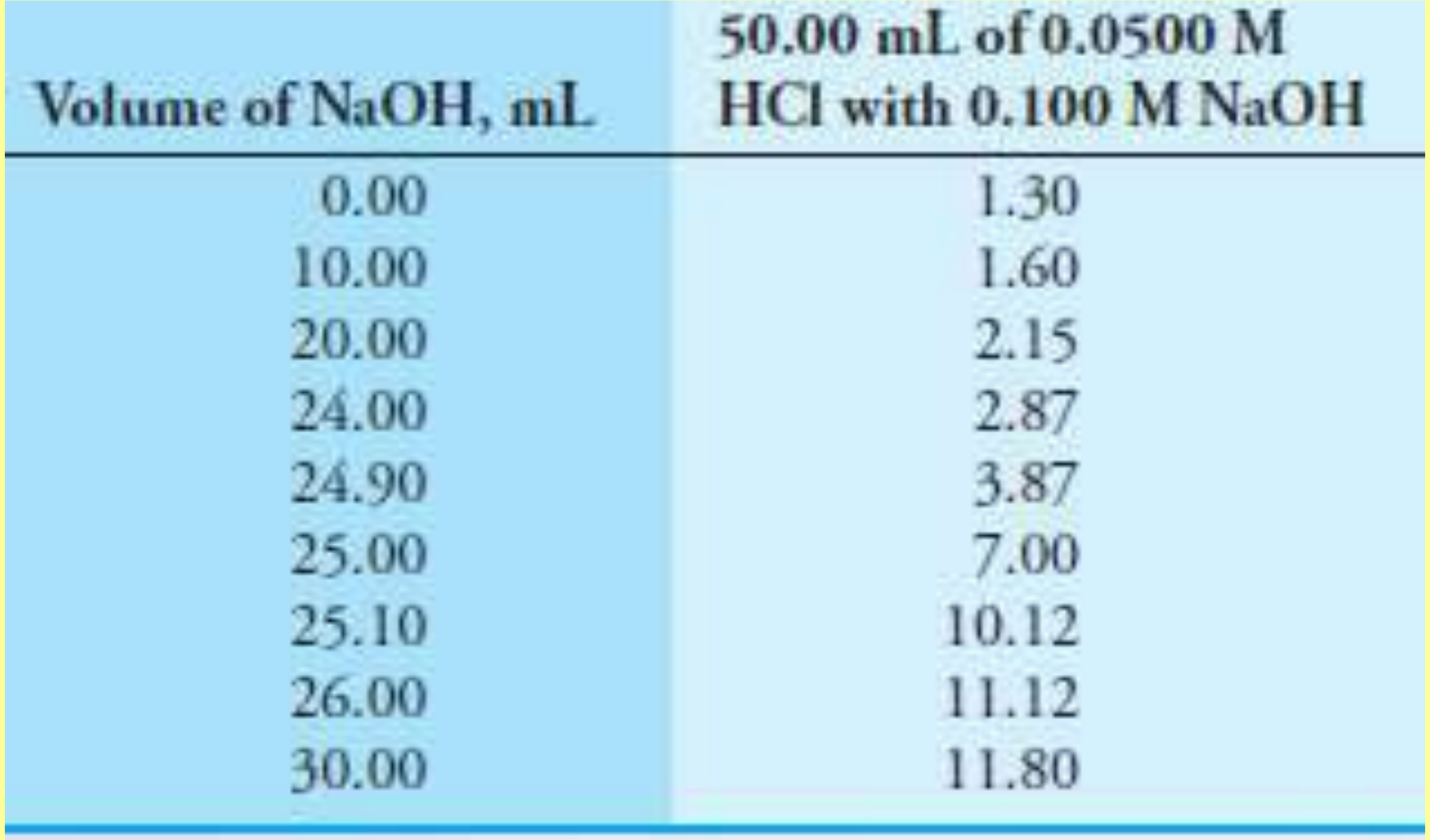
$$\text{pH} = -\log[H_3O^+] = -\log(2.50 \times 10^{-2}) = 1.602 \approx 1.60$$

Pre Equivalence point: Vol= 24.00 mL pH = 2.87
Pre Equivalence point: Vol= 24.90 mL pH = 3.87

Titrating a Strong Acid with a Strong Base

Changes in pH during titration of strong acid with strong base

pH



Volume of NaOH, mL	50.00 mL of 0.0500 M HCl with 0.100 M NaOH
0.00	1.30
10.00	1.60
20.00	2.15
24.00	2.87
24.90	3.87
25.00	7.00
25.10	10.12
26.00	11.12
30.00	11.80

Titrating a Strong Acid with a Strong Base

At Equivalence Point : Vol = 25.0 mL

The strong acid is completely neutralized. There is only salt

pH = 7

HCl	+	NaOH	→	NaCl + H2O
2.5 mmol		2.5 mmol		-------
------------		----------		2.5 mmol

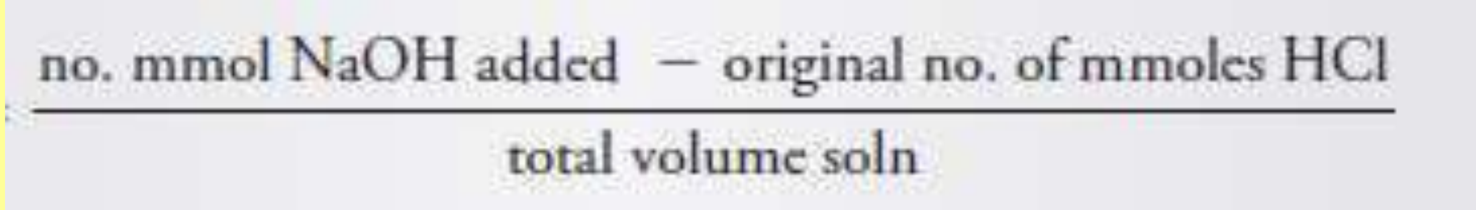
Titrating a Strong Acid with a Strong Base

Post Equivalence Point : Vol = 25.1 mL

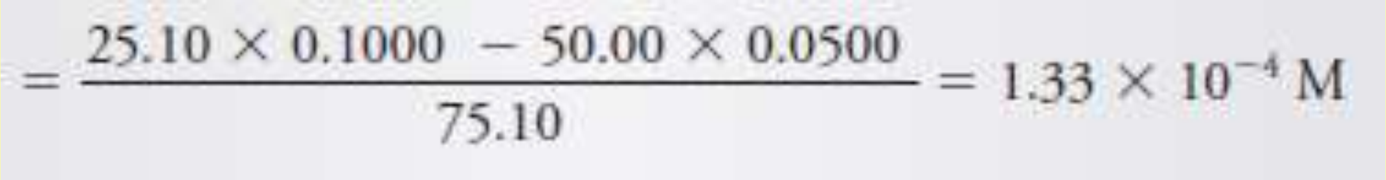
There is an excess of strong base added

HCl	+	NaOH	$\longrightarrow$	NaCl + H2O
2.5 mmol		2.51 mmol		-------
------------		0.01 mmol		2.5 mmol

[NaOH] =



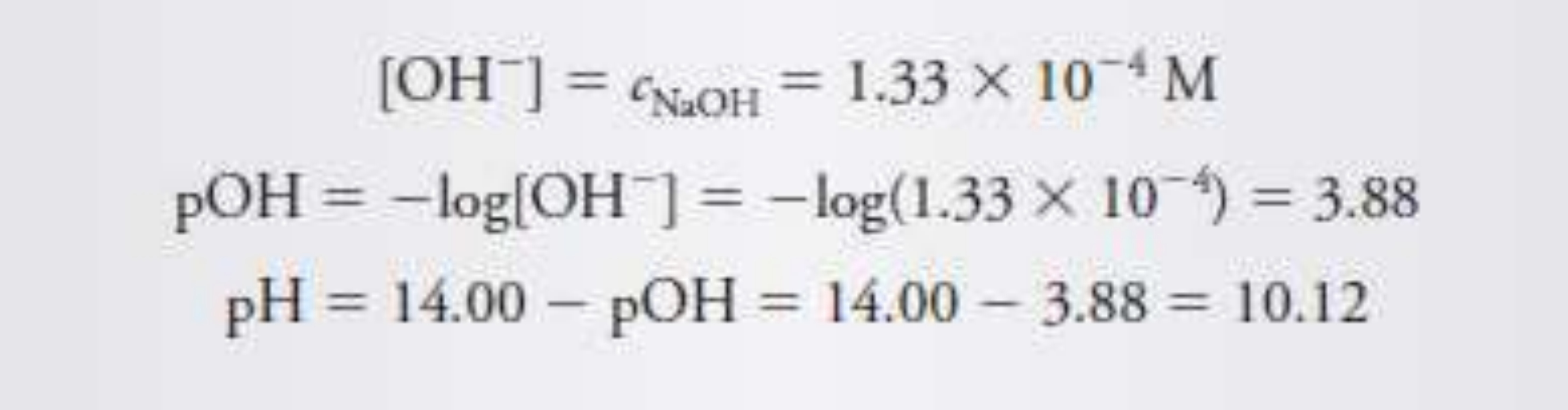
$$\frac{\text{no. mmol NaOH added} - \text{original no. of mmoles HCl}}{\text{total volume soln}}$$



$$= \frac{25.10 \times 0.1000 - 50.00 \times 0.0500}{75.10} = 1.33 \times 10^{-4}\ \mathrm{M}$$

Titrating a Strong Acid with a Strong Base

Post Equivalence Point : Vol = 25.1 mL



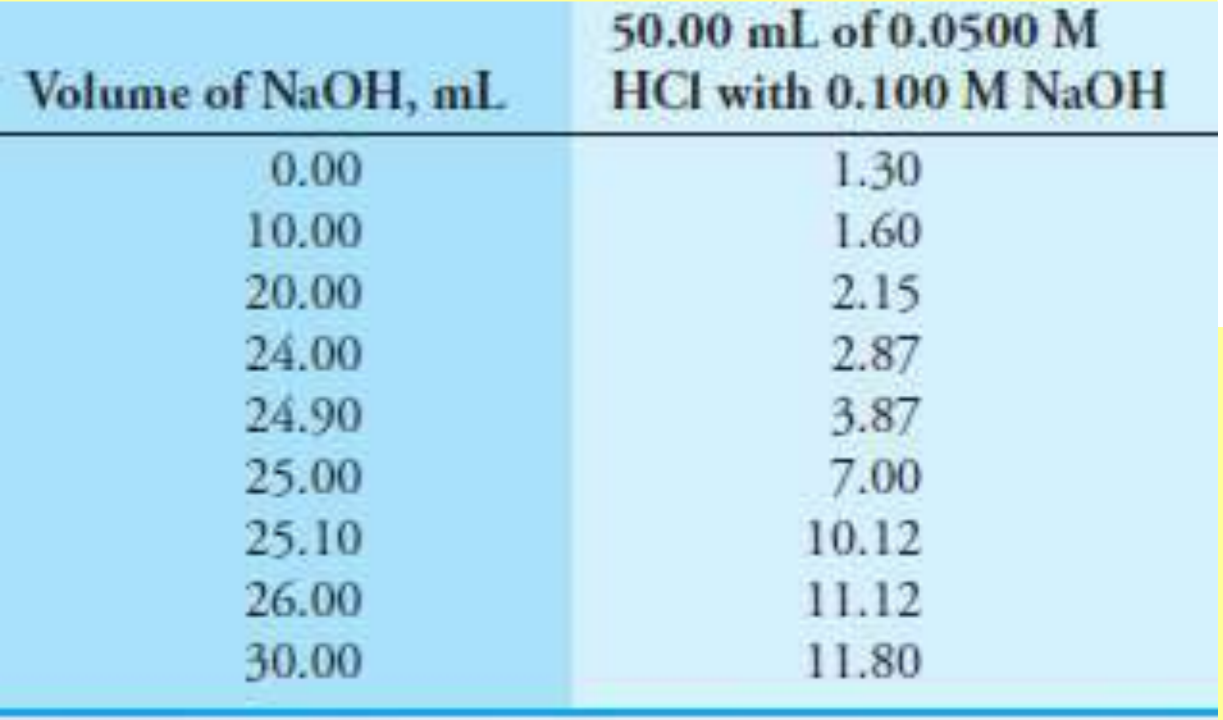
$$[\mathrm{OH^-}] = c_{\mathrm{NaOH}} = 1.33 \times 10^{-4}\ \mathrm{M}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.33 \times 10^{-4}) = 3.88$$

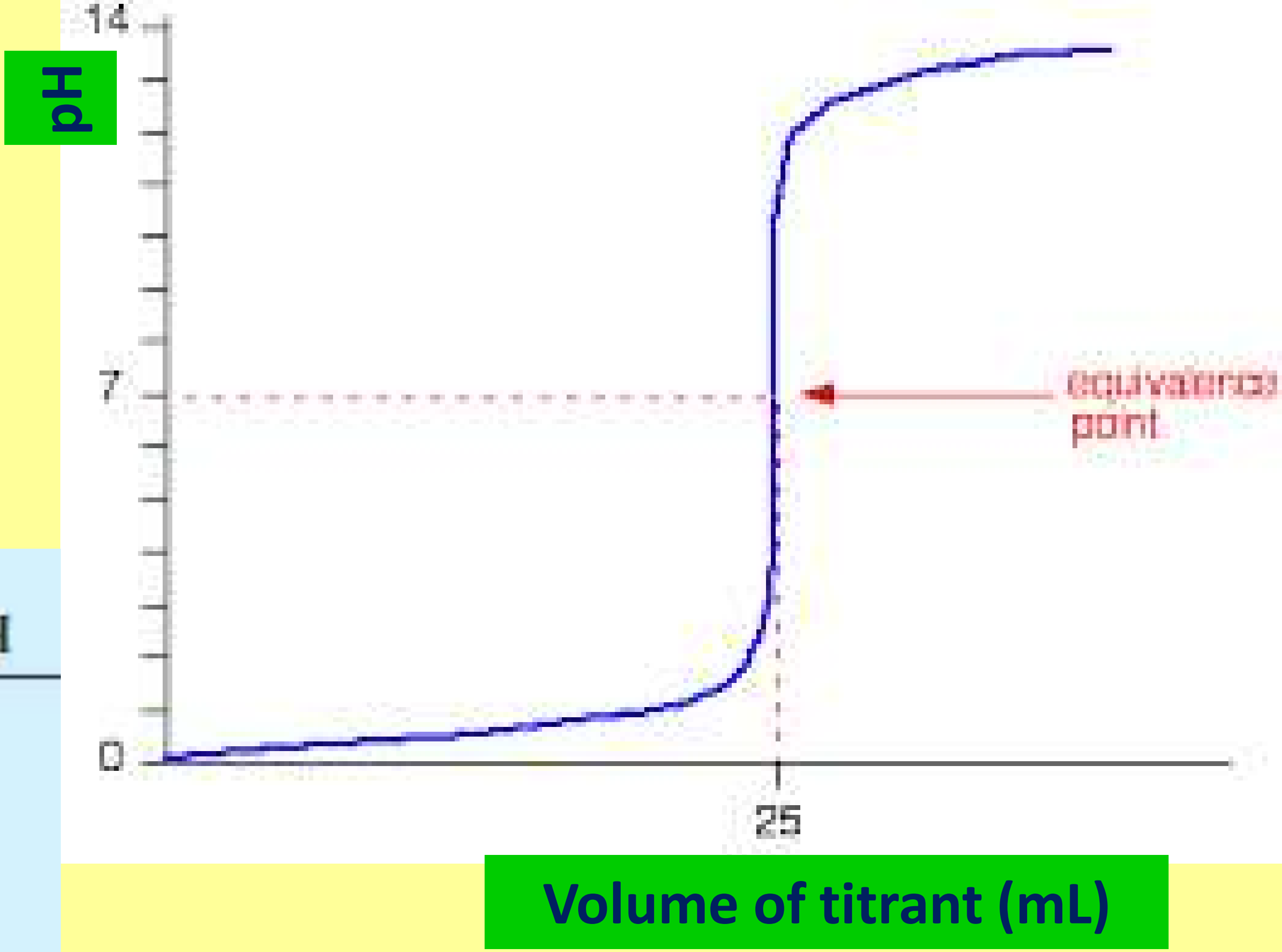
$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 3.88 = 10.12$$

Vol 26.0 mL pH = 11.12

Vol 30.0 mL pH= 11.80

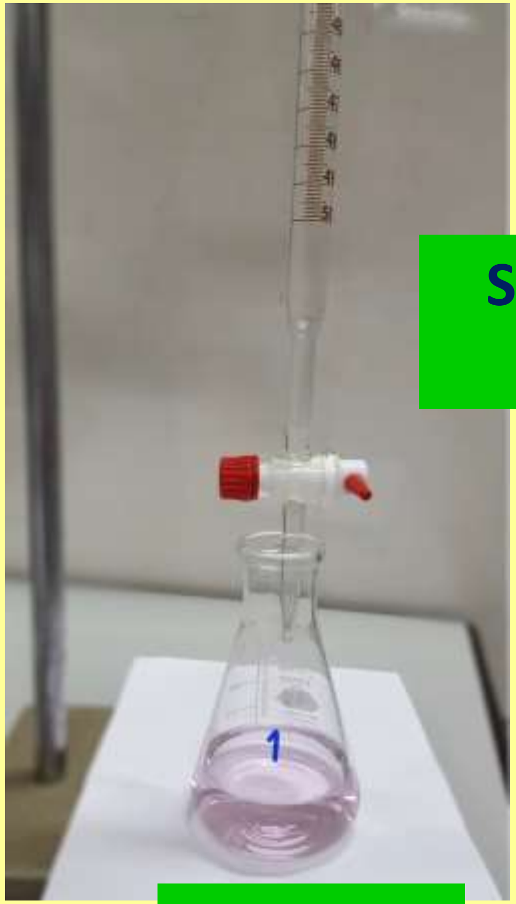


Volume of NaOH, mL	50.00 mL of 0.0500 M HCl with 0.100 M NaOH
0.00	1.30
10.00	1.60
20.00	2.15
24.00	2.87
24.90	3.87
25.00	7.00
25.10	10.12
26.00	11.12
30.00	11.80



Strong base-Strong acid titration curve

Volume of titrant added to analyte	pH of analyte solution
Vol = 0.0 ml	
Vol < Eq. P	
Vol = Eq. P	
Vol > Eq. P	

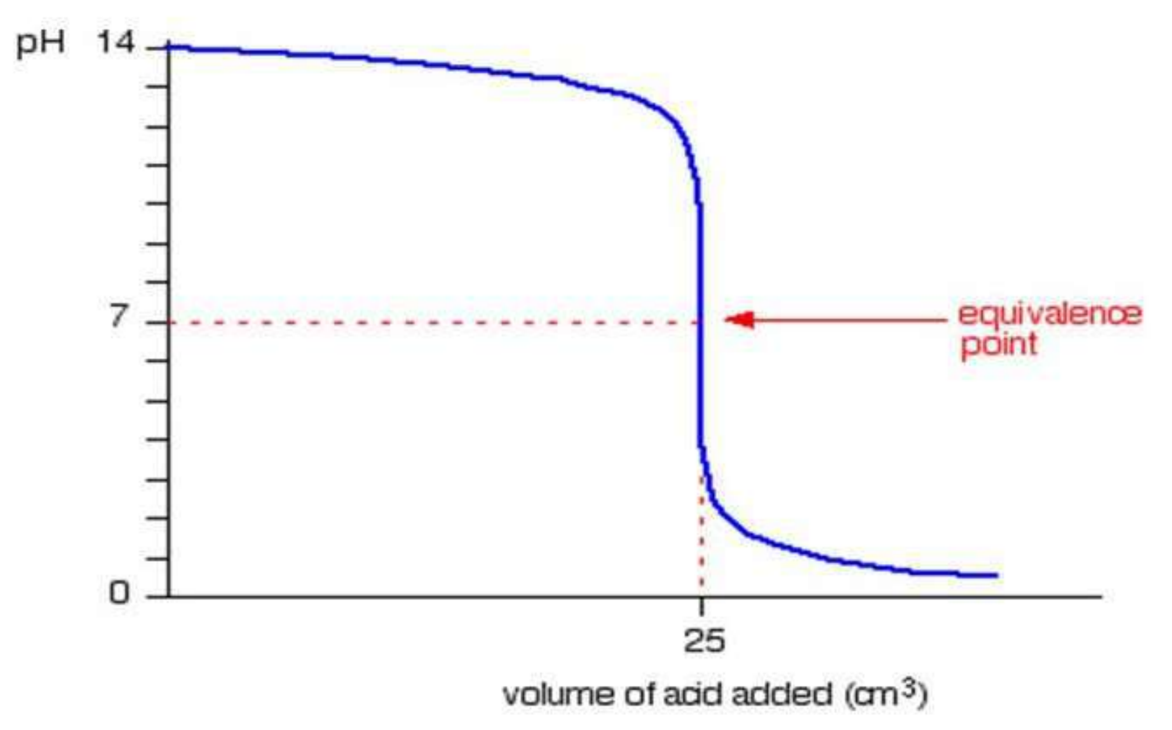


Strong acid

Strong base

Strong base-Strong Acid titration curve

Volume of titrant added to analyte	pH of analyte solution
Vol = 0.0 ml	
Vol < Eq. P	
Vol = Eq. P	
Vol > Eq. P	



Titrating a Strong Base with a Strong Acid

Calculate the pH during the titration of 50.00 mL of 0.05 M NaOH with 0.10 M HCl at 25°C after the addition of the following volumes of reagent: 0.00, 10.00, 24.50 , 25.00 mL, 25.50 mL??

Initial Point: Vol = 0.0 mL

Before any acid is added, the solution is 0.05 M $[OH^-]$

pH = 14 - pOH = 12.7

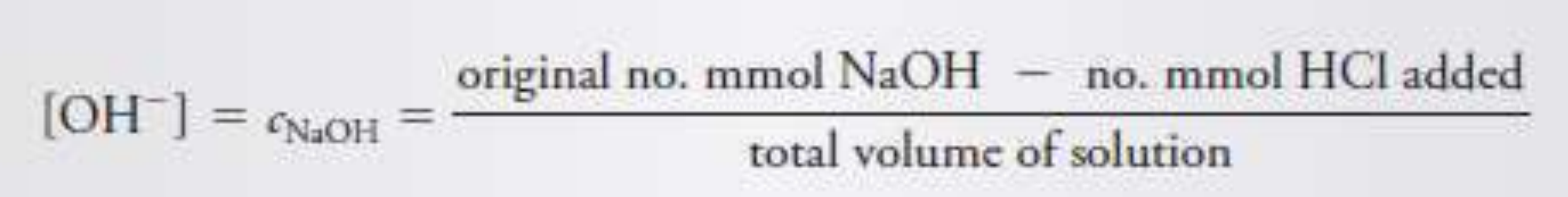
Pre Equivalence point (Pre-Eq P): Vol= 10 mL

HCl	+	NaOH	$\longrightarrow$	NaCl + H2O
1 mmol		2.5 mmol		-------
------		(2.5-1) mmol		1 mmol

There is partial neutralization of strong base, the unreactred base determine pH

Titrating a Strong Base with a Strong Acid

Pre Equivalence point (Pre-Eq P): Vol= 10 mL



$$[OH^-] = c_{NaOH} = \frac{\text{original no. mmol NaOH} - \text{no. mmol HCl added}}{\text{total volume of solution}}$$

$[NaOH] = 2.5 * 10^{-2}$ M

pH = 14 -1.6= 12.4

Pre Equivalence point (Pre-Eq P): Vol= 24.5 mL

$[NaOH] = 6.71*10^{-4}$ M

pH = 10.83

Titrating a Strong Base with a Strong Acid

At Equivalence point: Vol= 25 mL

The strong base is completely neutralized. There is only salt

pH = 7

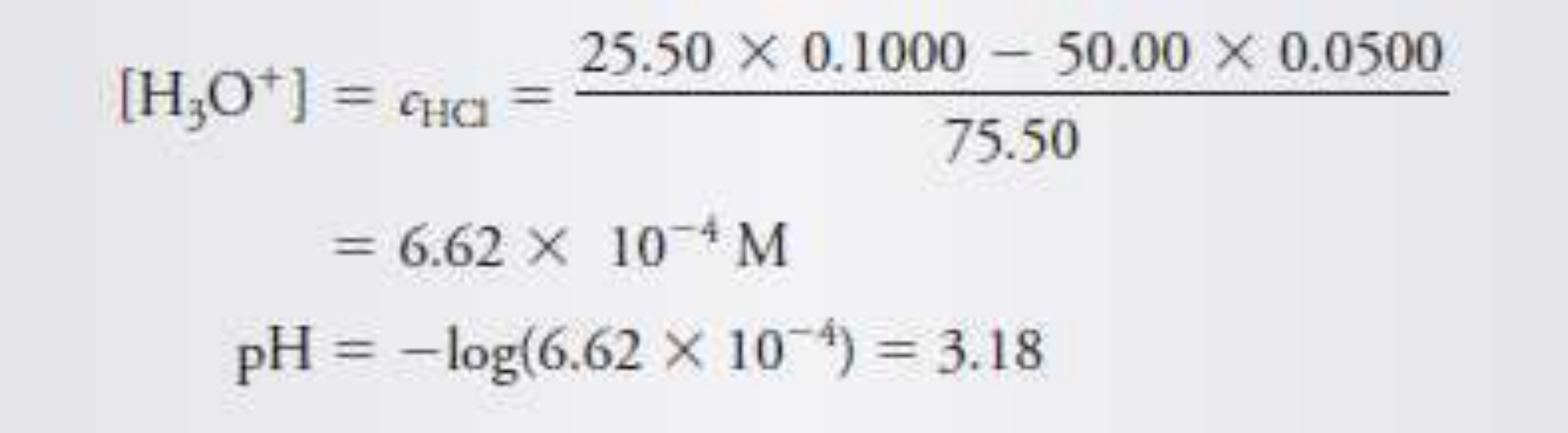
HCl	+	NaOH	$\longrightarrow$	NaCl + H2O
2.5 mmol		2.5 mmol		-------
------------		----------		2.5 mmol

Titrating a Strong Base with a Strong Acid

Post Equivalence point: Vol= 25.5 mL

There is an excess of strong acid added

HCl	+	NaOH	$\longrightarrow$	NaCl + H_2O
2.55 mmol		2.5 mmol		-------
0.05 mmol		--------- mmol		2.5 mmol



$$[H_3O^+] = c_{HCl} = \frac{25.50 \times 0.1000 - 50.00 \times 0.0500}{75.50}$$

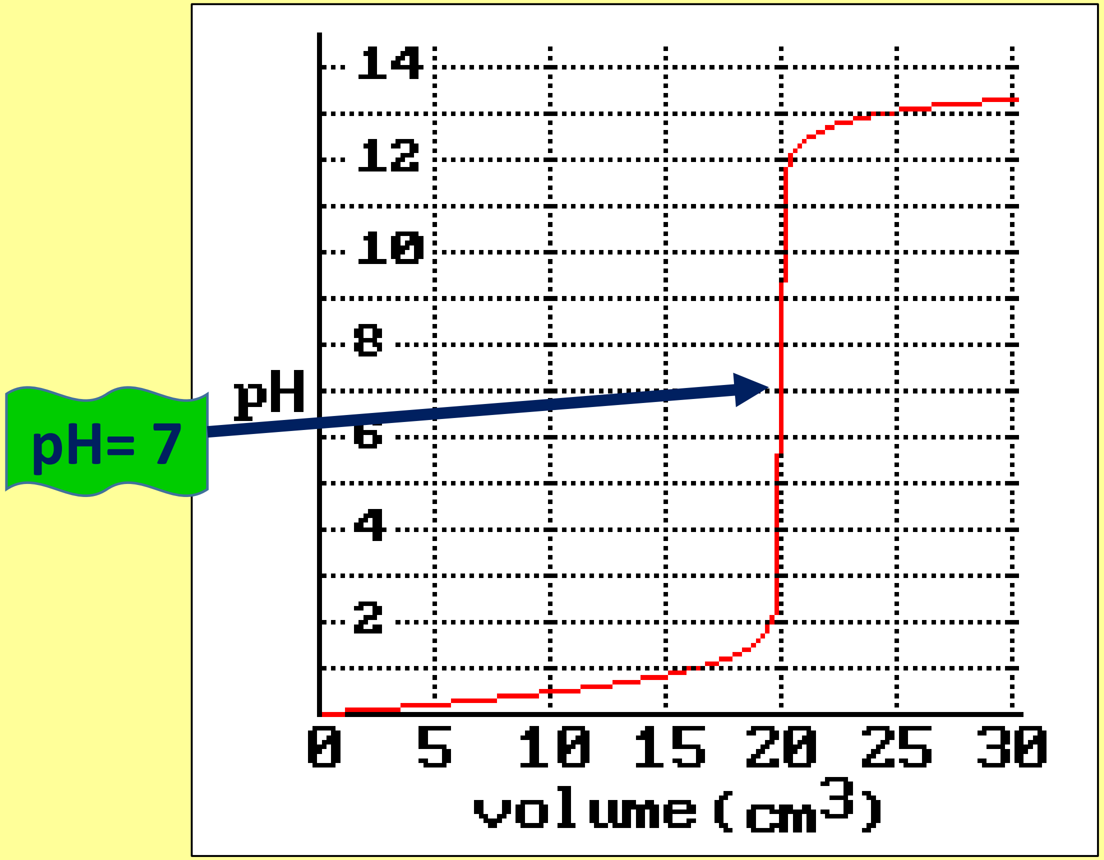
$$= 6.62 \times 10^{-4}\ M$$

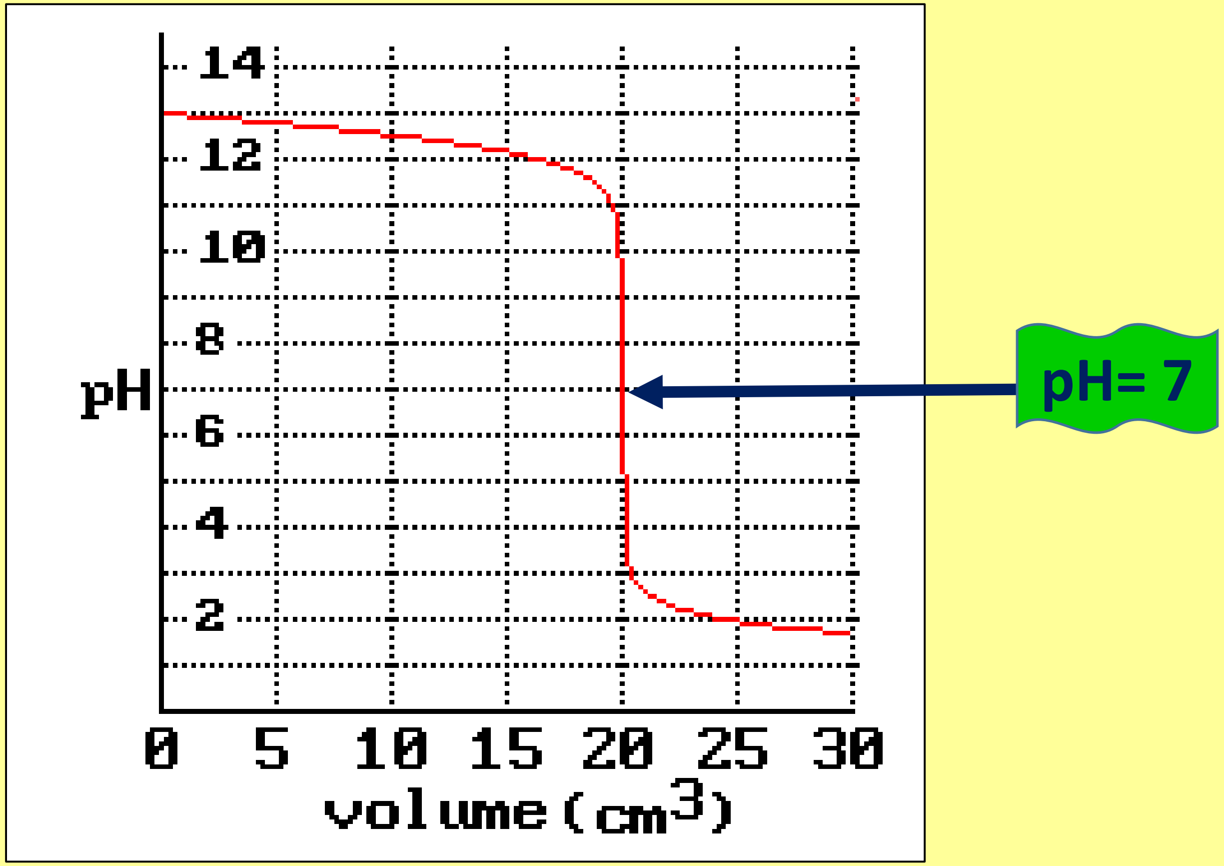
$$pH = -\log(6.62 \times 10^{-4}) = 3.18$$

Acid – Base Titration
part 8

Dr. Mai Ramadan

Titration curves

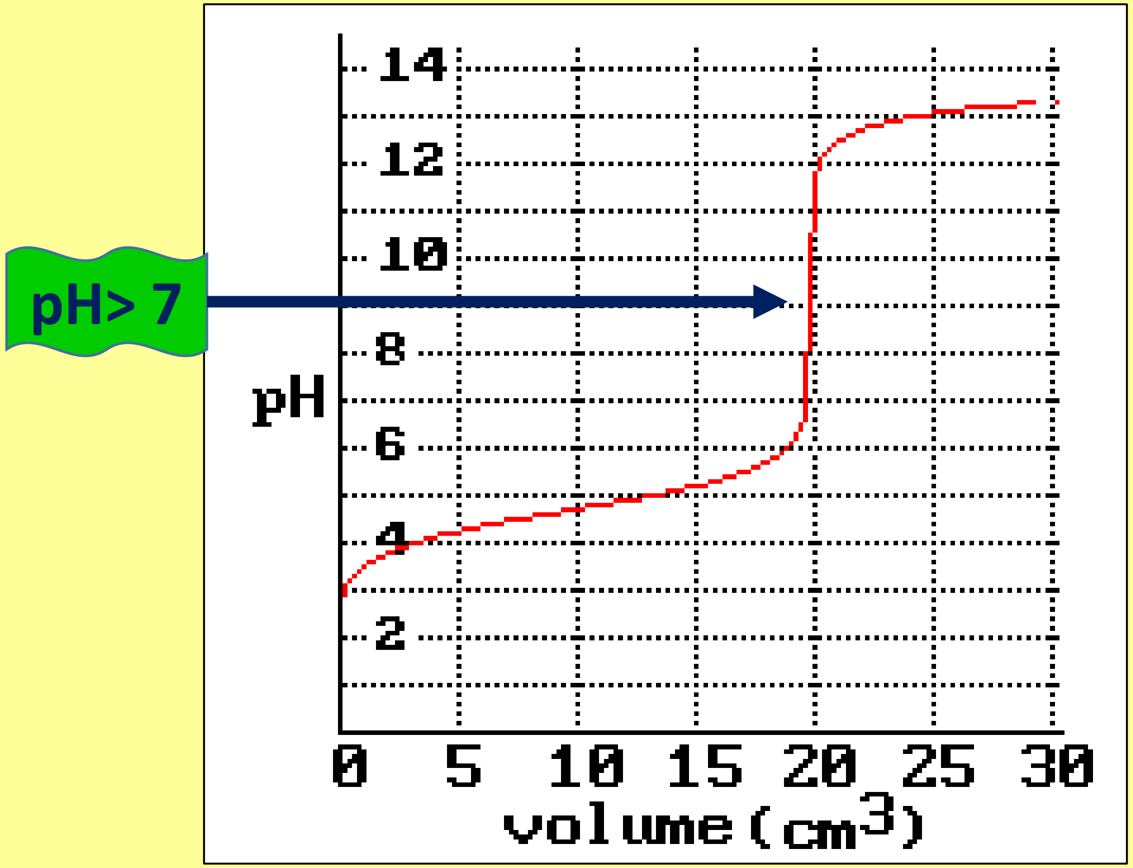




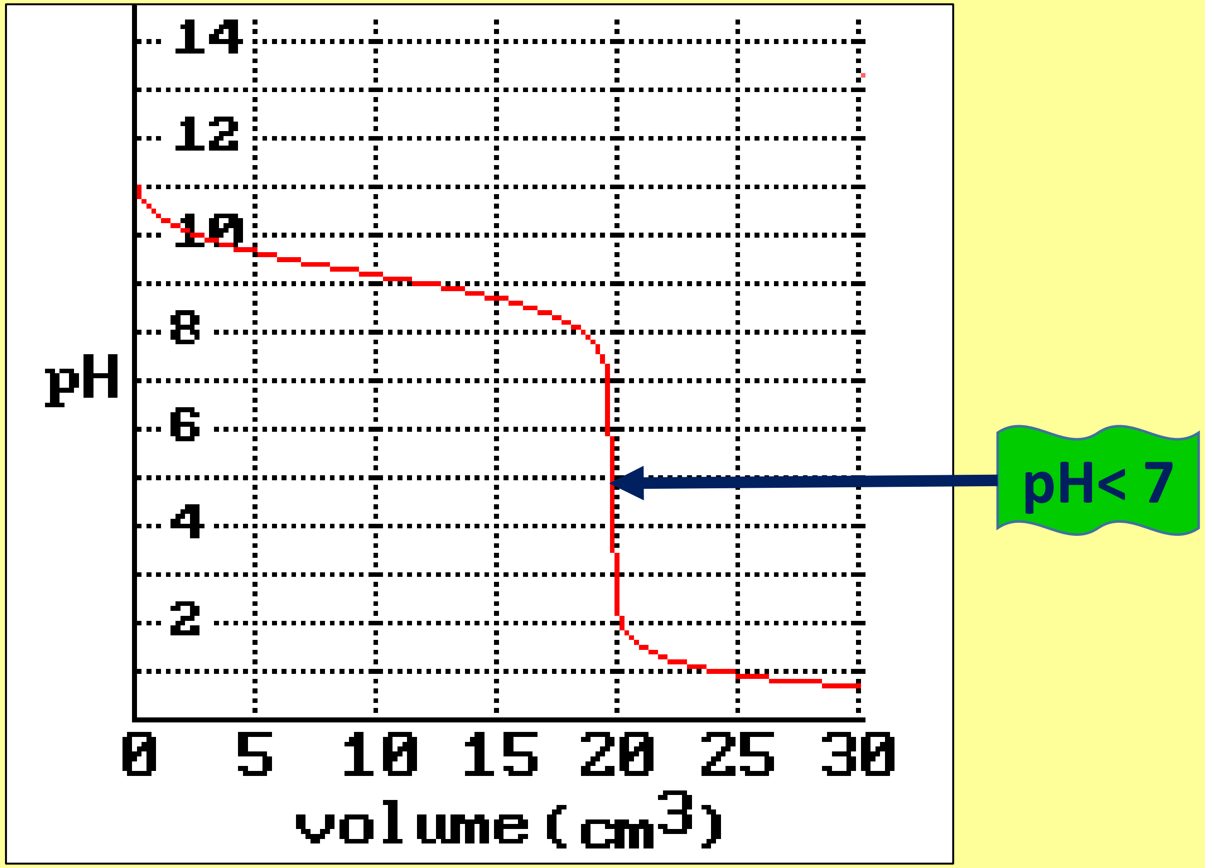
Strong acid –strong base

Strong base-strong acid

Titration curves


pH> 7

Weak acid –strong base


pH< 7

Weak base-strong acid

Weak acid-Strong base titration curve

Volume of titrant added to analyte	pH of analyte solution
Vol = 0.0 ml	
Vol < Eq. P	
Vol = Eq. P	
Vol > Eq. P	

Strong base

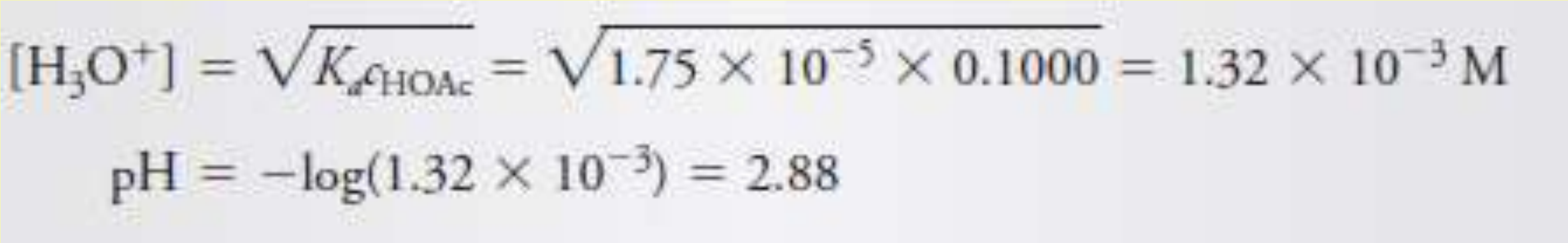
Weak acid

Titrating a Weak Acid with a Strong Base

Generate the hypothetical titration curve for the titration of 50.00 mL of 0.1 M CH_3COOH with 0.10 M NaOH at 25°C.

Initial Point: Vol = 0.0 mL

Before any base is added, the solution is 0.1 M of a weak acetic acid, Ka = $1.75*10^{-5}$



$$[H_3O^+] = \sqrt{K_a c_{HOAc}} = \sqrt{1.75 \times 10^{-5} \times 0.1000} = 1.32 \times 10^{-3}\ \text{M}$$

$$\text{pH} = -\log(1.32 \times 10^{-3}) = 2.88$$

Titrating a Weak Acid with a Strong Base

Pre Equivalence point (Pre-Eq P): Vol= 10.0 mL

CH3COOH	+	NaOH	⟶	Na(CH3COO) + H2O
5 mmol		1 mmol		-------
(5 – 1)mmol		----------		1 mmol

There is partial neutralization of weak acid, there is a buffer

$$\mathbf{pH = Pka + \log \frac{[A-]}{[HA]}}$$

$$\mathbf{pH = 4.76 + \log \frac{1}{4} = 4.15}$$

Titrating a Weak Acid with a Strong Base

Pre Equivalence point (Pre-Eq P): Vol= 25.0 mL

CH3COOH	+	NaOH	$\longrightarrow$	Na(CH3COO)	+ H2O
5 mmol		2.5 mmol		-------	
(5 – 2.5)mmol		----------		2.5 mmol	

At half titration point (Vol = Eq P/2)

$$\mathbf{pH = Pka + \log \frac{[A-]}{[HA]}}$$

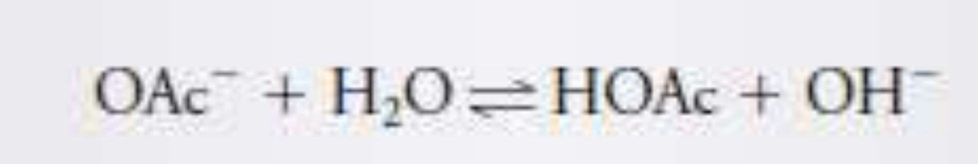
$$\mathbf{pH = Pka = 4.76}$$

Titrating a Weak Acid with a Strong Base

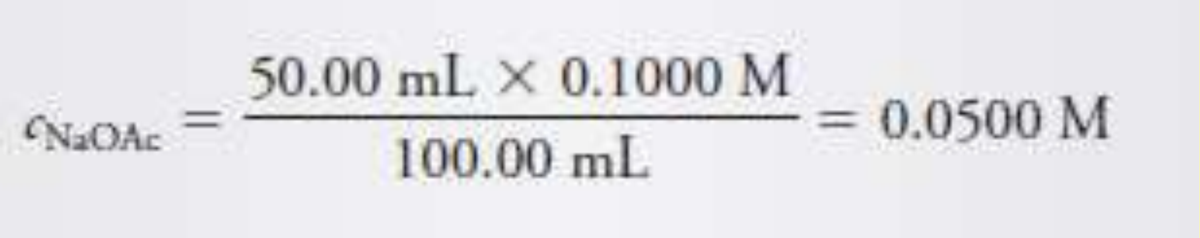
At Equivalence point (Eq P): Vol= 50.0 mL

CH3COOH	+	NaOH	$\longrightarrow$	Na(CH3COO)	+ H2O
5 mmol		5 mmol		-------	
------------		----------		5 mmol	

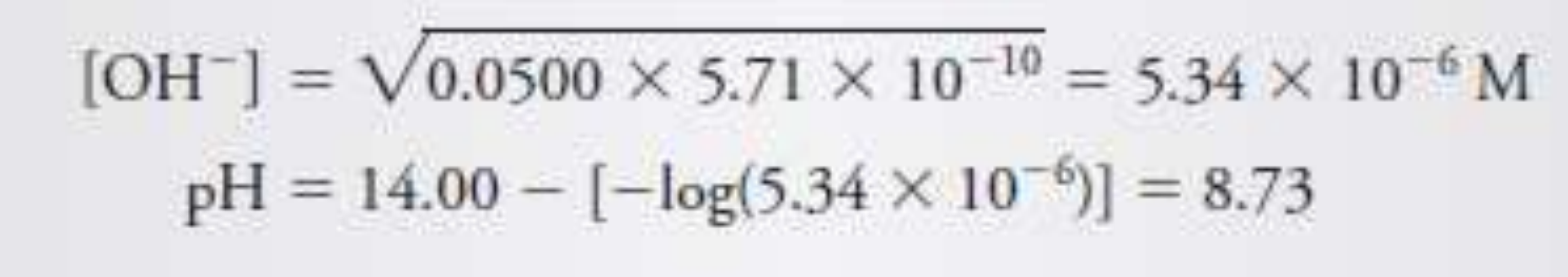
There is complete neutralization of weak acid, there is a basic salt



$$OAc^- + H_2O \rightleftharpoons HOAc + OH^-$$



$$c_{NaOAc} = \frac{50.00\ mL \times 0.1000\ M}{100.00\ mL} = 0.0500\ M$$



$$[OH^-] = \sqrt{0.0500 \times 5.71 \times 10^{-10}} = 5.34 \times 10^{-6}\ M$$

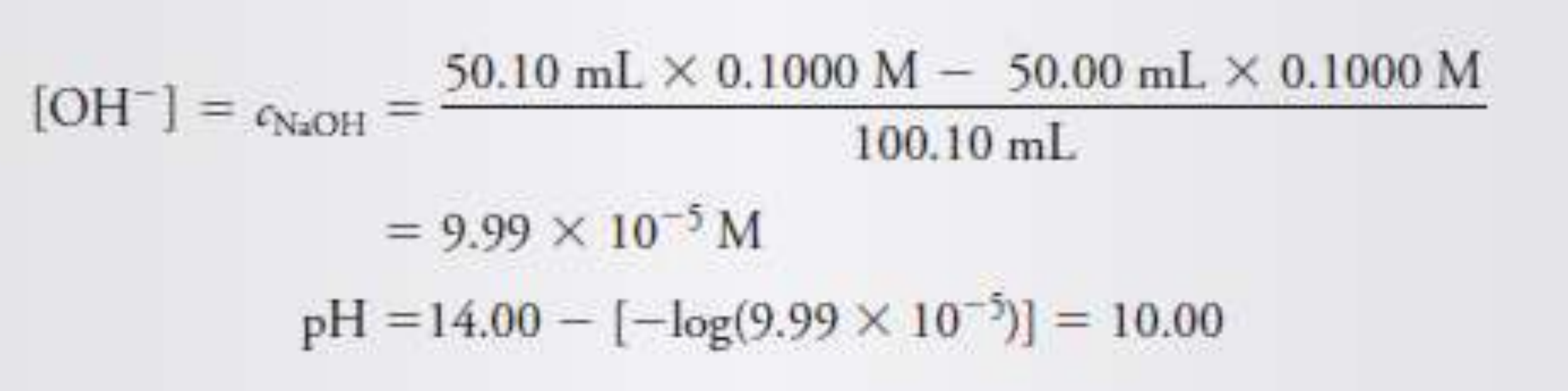
$$pH = 14.00 - [-\log(5.34 \times 10^{-6})] = 8.73$$

Titrating a Weak Acid with a Strong Base

Post Equivalence point (Post-Eq P): Vol= 50.1 mL

CH_3COOH	+	NaOH	$\longrightarrow$	$Na(CH_3COO)$	+ H2O
5 mmol		5.01 mmol		--------------	
-----------		0.01 mmol		5 mmol	

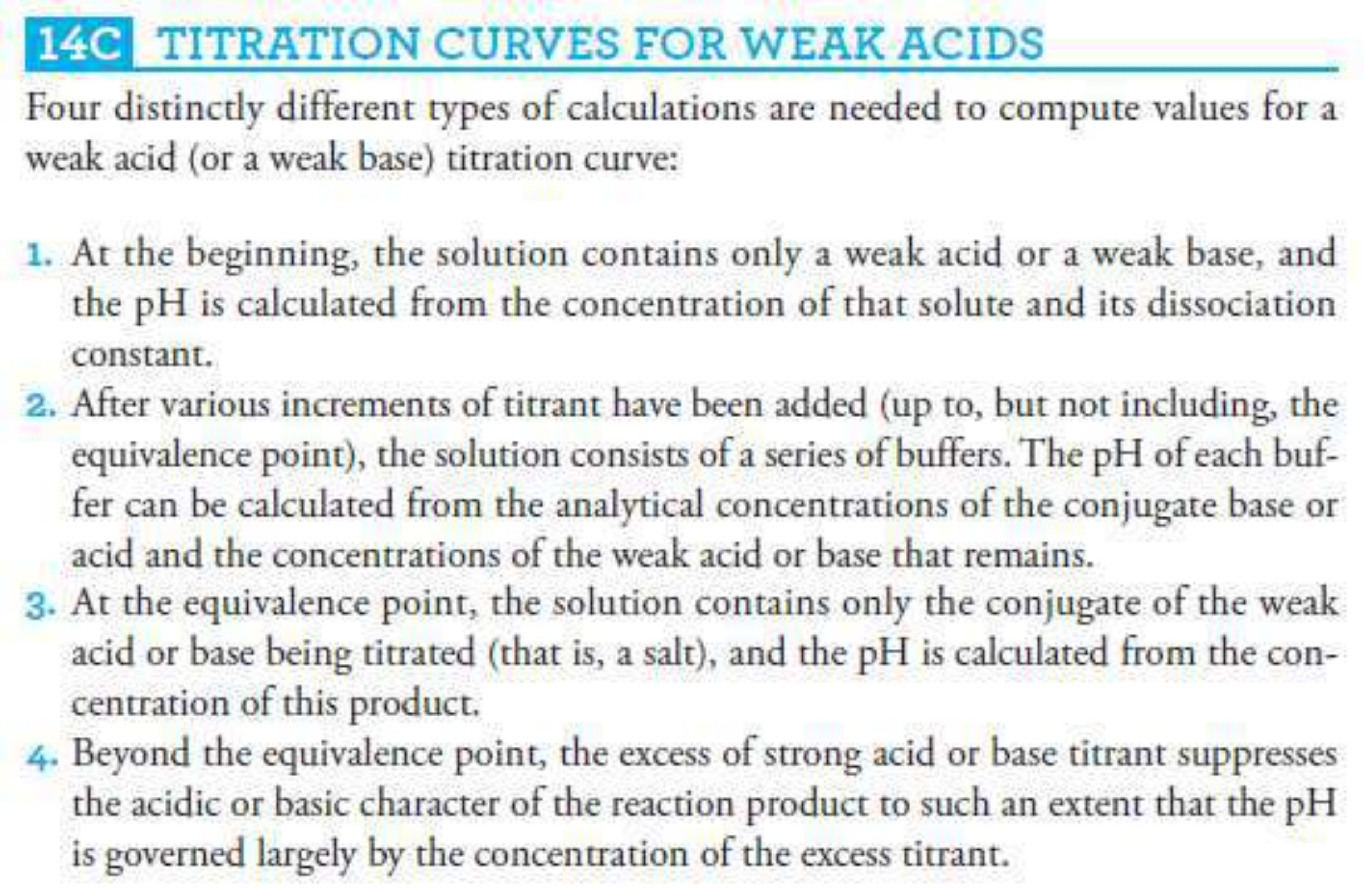
There is excess of added strong base and a weak basic salt, the pH depends only on strong base



$$[OH^-] = c_{NaOH} = \frac{50.10\text{ mL} \times 0.1000\text{ M} - 50.00\text{ mL} \times 0.1000\text{ M}}{100.10\text{ mL}}$$

$$= 9.99 \times 10^{-5}\text{ M}$$

$$pH = 14.00 - [-\log(9.99 \times 10^{-5})] = 10.00$$



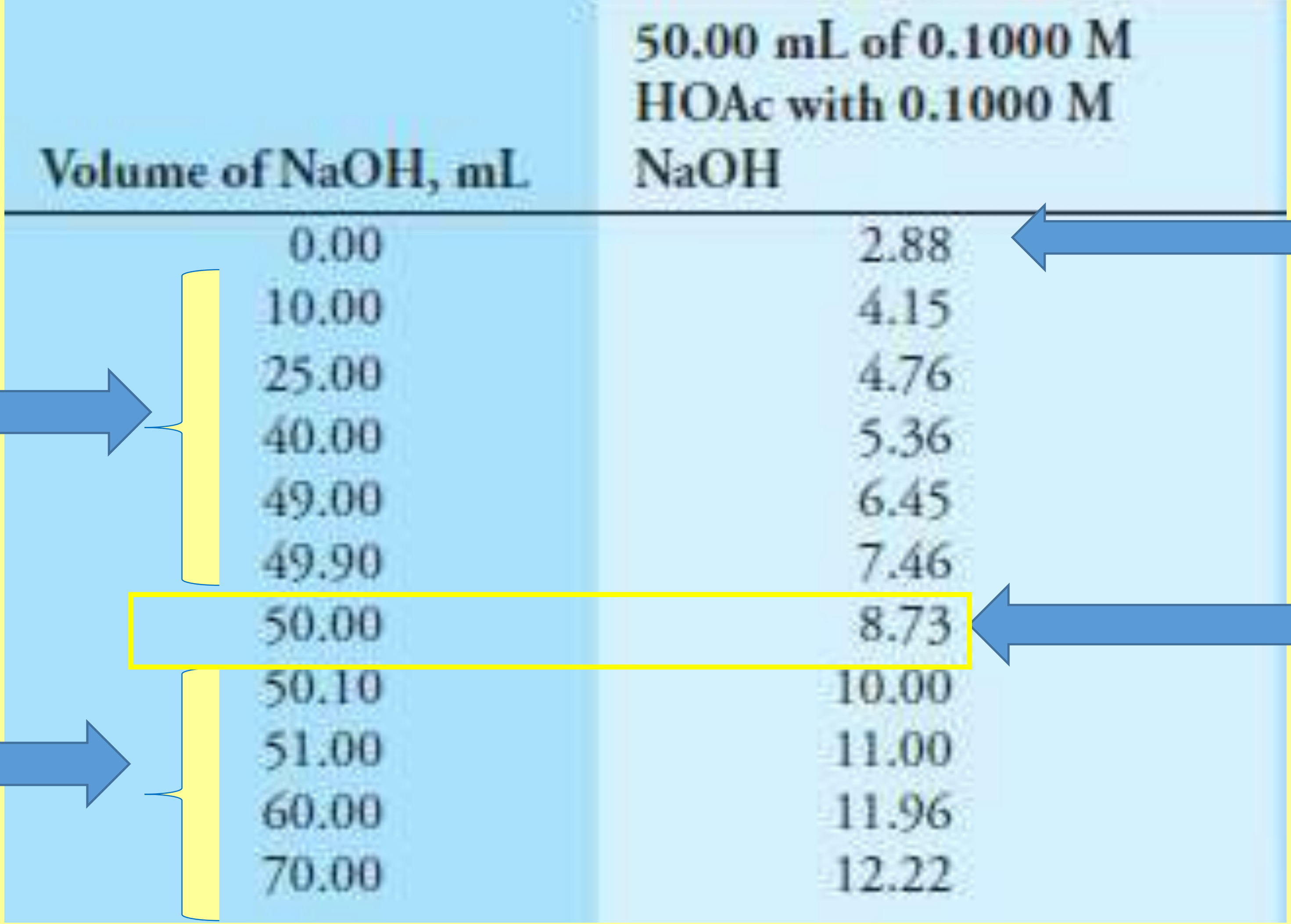
14C TITRATION CURVES FOR WEAK ACIDS

Four distinctly different types of calculations are needed to compute values for a weak acid (or a weak base) titration curve:

1. At the beginning, the solution contains only a weak acid or a weak base, and the pH is calculated from the concentration of that solute and its dissociation constant.
2. After various increments of titrant have been added (up to, but not including, the equivalence point), the solution consists of a series of buffers. The pH of each buffer can be calculated from the analytical concentrations of the conjugate base or acid and the concentrations of the weak acid or base that remains.
3. At the equivalence point, the solution contains only the conjugate of the weak acid or base being titrated (that is, a salt), and the pH is calculated from the concentration of this product.
4. Beyond the equivalence point, the excess of strong acid or base titrant suppresses the acidic or basic character of the reaction product to such an extent that the pH is governed largely by the concentration of the excess titrant.

Titrating a Weak Acid with a Strong Base

Changes in pH during titration of weak acid with strong base



	pH
Volume of NaOH, mL	50.00 mL of 0.1000 M HOAc with 0.1000 M NaOH
0.00	2.88
10.00	4.15
25.00	4.76
40.00	5.36
49.00	6.45
49.90	7.46
50.00	8.73
50.10	10.00
51.00	11.00
60.00	11.96
70.00	12.22

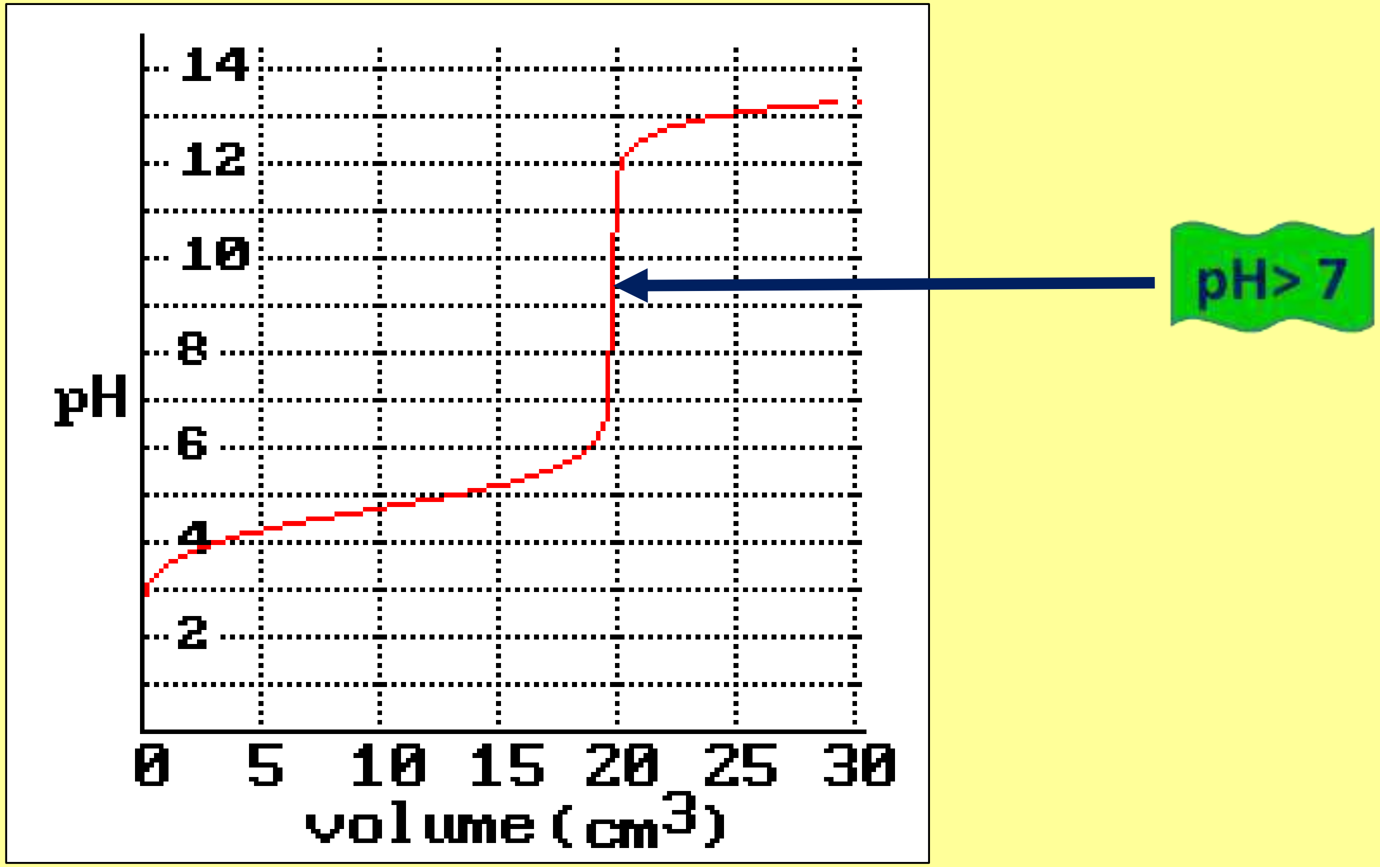
Initial point

Pre. Eq. P
Buffer

Eq. P
Complete neutralization

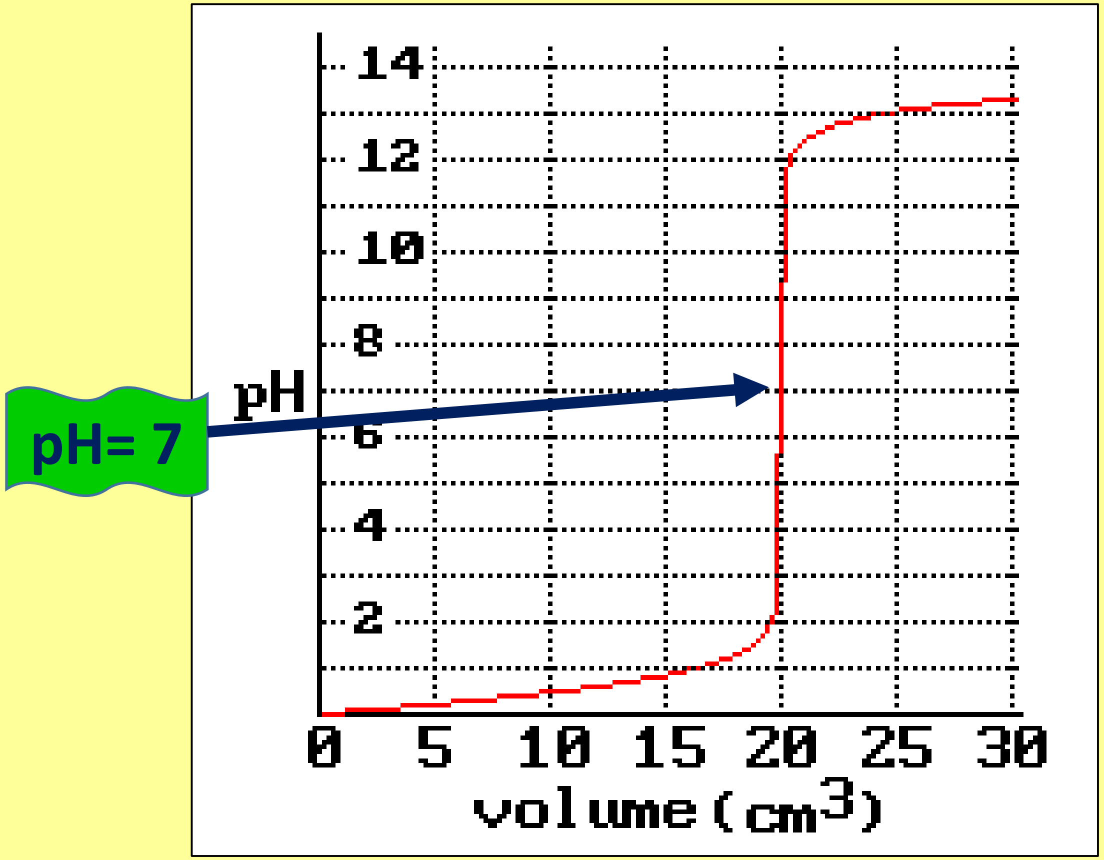
Post Eq. P

Titration curves



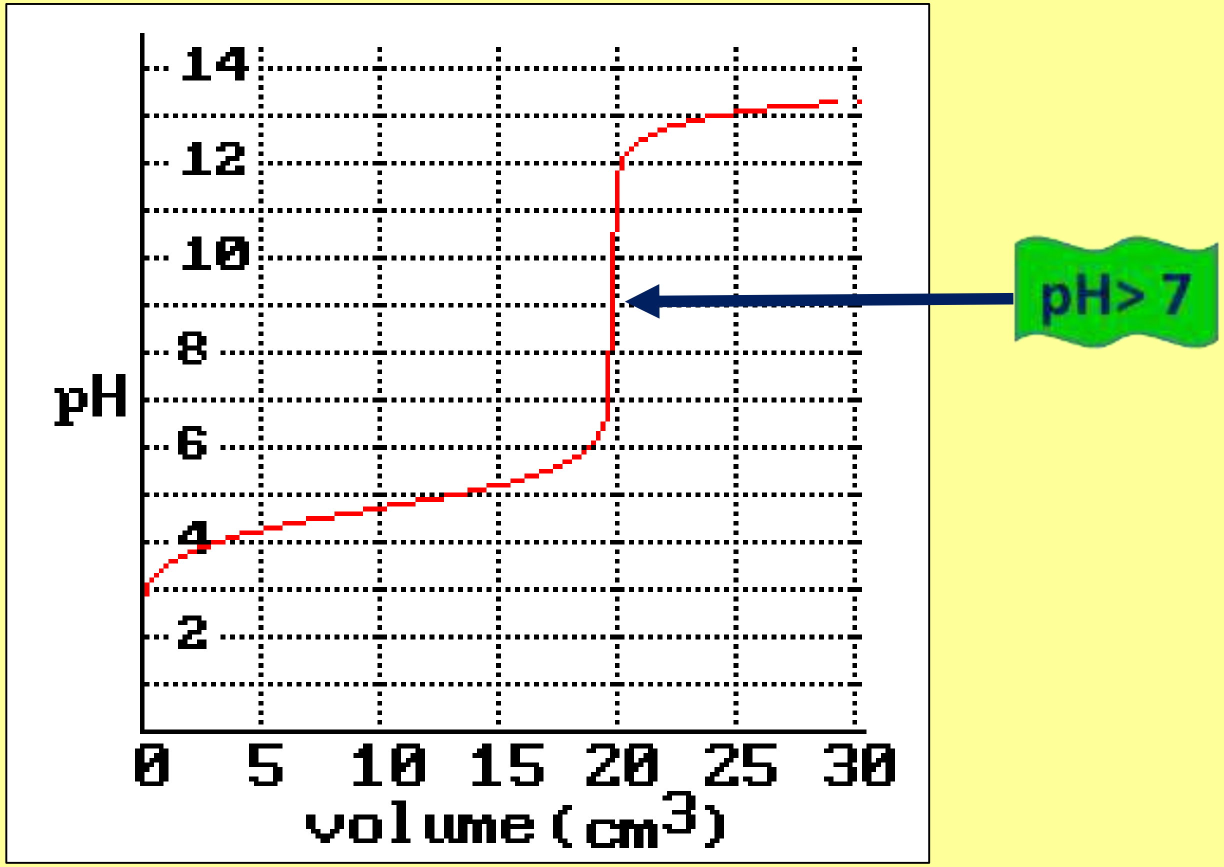
Weak acid-strong base

Titration curves



pH= 7

Strong acid –strong base



pH> 7

Weak acid-strong base

Acid – Base Titration
part 8 continue

Dr. Mai Ramadan

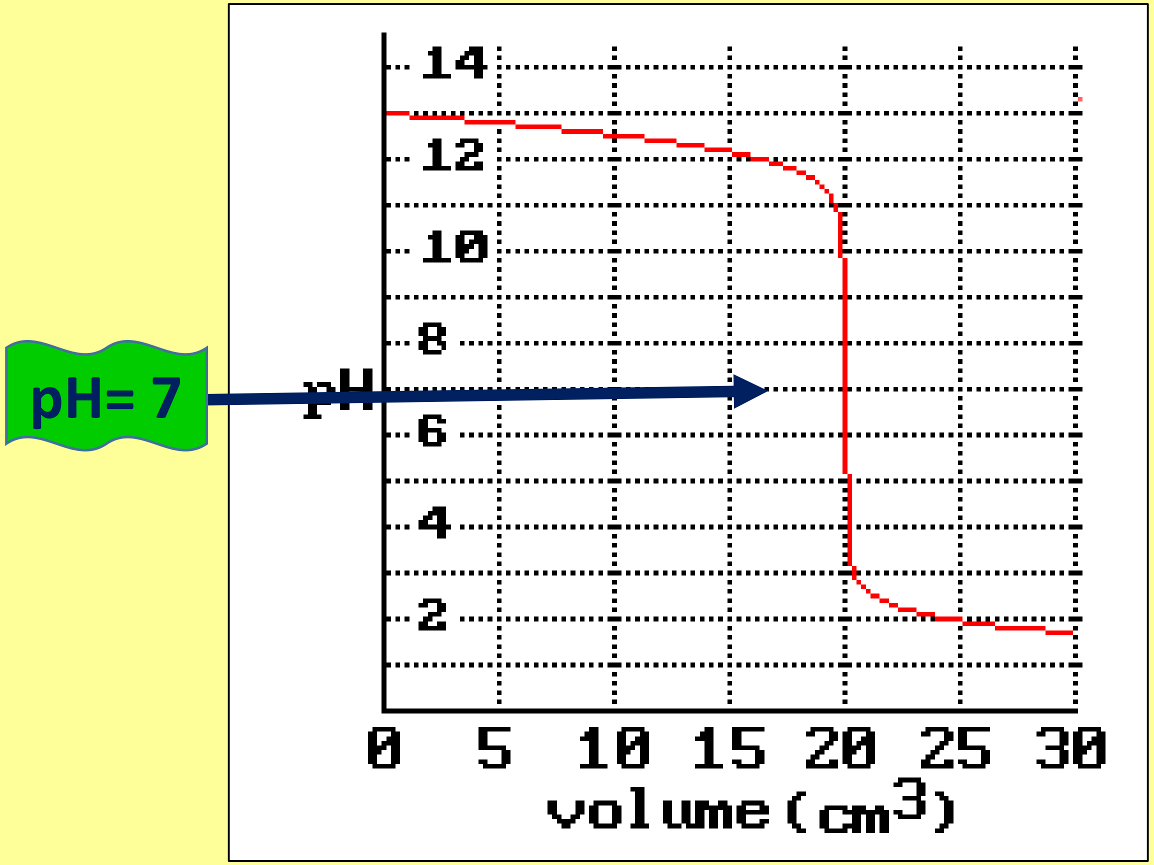
Weak base-Strong acid titration curve

Volume of titrant added to analyte	pH of analyte solution
Vol = 0.0 ml	
Vol < Eq. P	
Vol = Eq. P	
Vol > Eq. P	

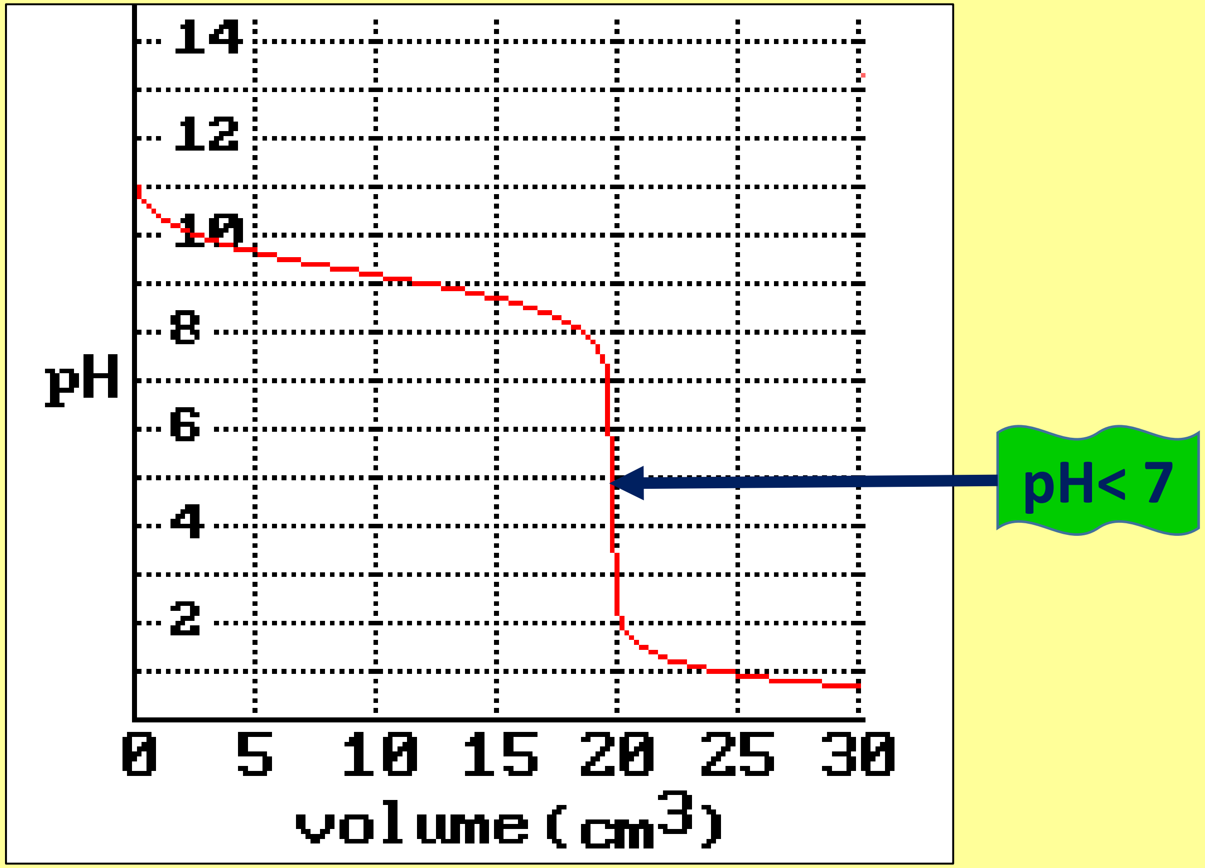
Strong acid

Weak base

Titration curves



Strong base-Strong acid



Weak base-Strong acid

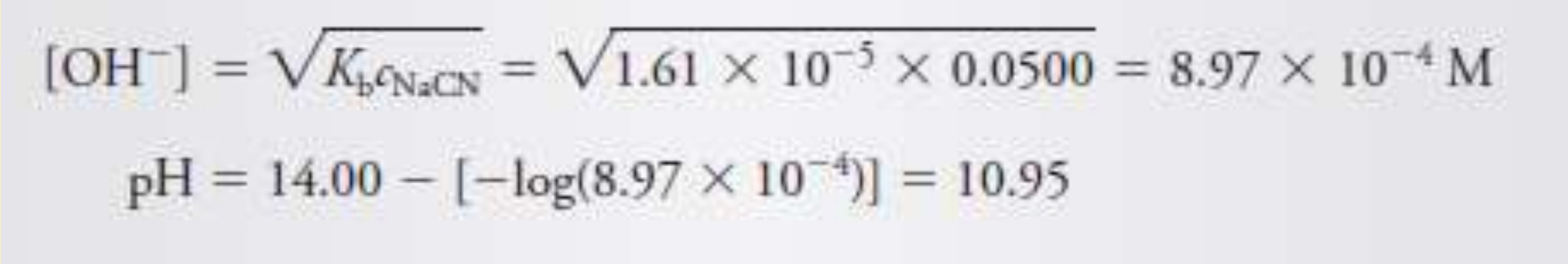
Titrating a Weak Base with a Strong Acid

A 50.00-mL aliquot of 0.05 M NaCN (*Ka for HCN = 6.2 * 10*$^{-10}$*) is titrated* with 0.1 M HCl.

Calculate the pH after the addition of: 0.00, 10.00, 25.00, and 26.00 mL of acid.

$$CN^{-} + HCl \longrightarrow HCN + Cl^{-}$$

At volume = 0.0 mL the solution is a weak base



$$[OH^{-}] = \sqrt{K_b c_{NaCN}} = \sqrt{1.61 \times 10^{-5} \times 0.0500} = 8.97 \times 10^{-4}\ M$$

$$pH = 14.00 - [-\log(8.97 \times 10^{-4})] = 10.95$$

Titrating a Weak base with a Strong acid

Pre Eq. P: At volume = 10.0 mL

CN^-	+	HCl	$\longrightarrow$	HCN	+	Cl^-
2.5 mmol		1 mmol		-----------		
(2.5-1) mmol		----------		1 mmol		

Partial neutralization of a weak base , buffer.

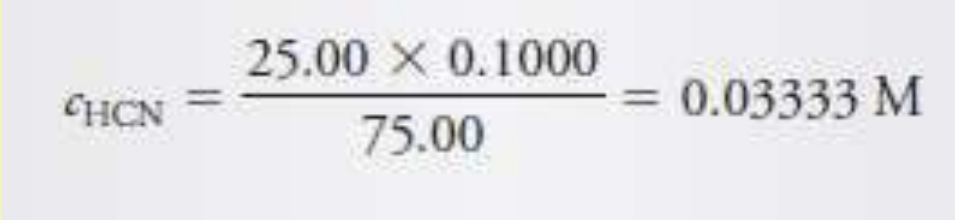
$$\mathbf{pOH = Pkb \quad + \log \frac{[BH+]}{[B]}}$$

pH = 9.38

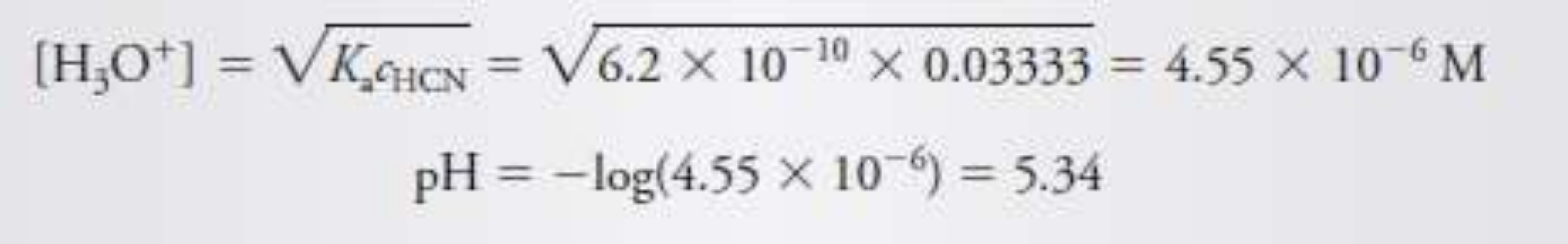
Titrating a Weak base with a Strong Acid

At Eq. P: At volume = 25.0 mL

CN^-	+	HCl	$\longrightarrow$	HCN	+	Cl^-
2.5 mmol		2.5 mmol		-----------		
-----------		----------		2.5 mmol		



$$c_{HCN} = \frac{25.00 \times 0.1000}{75.00} = 0.03333\ M$$



$$[H_3O^+] = \sqrt{K_a c_{HCN}} = \sqrt{6.2 \times 10^{-10} \times 0.03333} = 4.55 \times 10^{-6}\ M$$

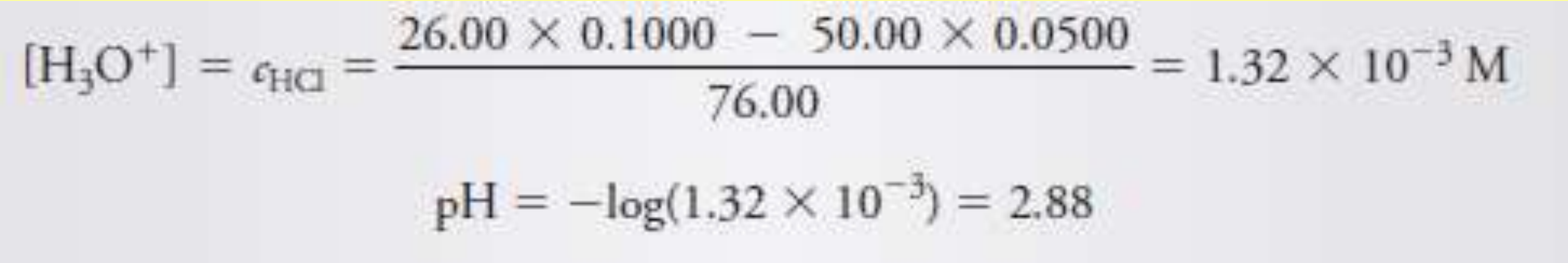
$$pH = -\log(4.55 \times 10^{-6}) = 5.34$$

Titrating a Weak Base with a Strong Acid

Post Eq. P: At volume = 26.0 mL

CN^-	+	HCl	→	HCN	+	Cl^-
2.5 mmol		2.6 mmol		-----------		
------------		0.1 mmol		2.5 mmol		

There is an excess of strong acid and a weak acid. The excess of strong acid should now suppresses the dissociation of HCN to the point that the contribution to pH is neglegted.



$$[H_3O^+] = c_{HCl} = \frac{26.00 \times 0.1000 - 50.00 \times 0.0500}{76.00} = 1.32 \times 10^{-3}\ M$$

$$pH = -\log(1.32 \times 10^{-3}) = 2.88$$

Acid – Base Titration
part 9

Dr. Mai Ramadan

Titration curve of polyprotic acid

Carbonic acid

$H_2CO_3 + H_2O \longleftrightarrow H_3O^+ + HCO_3^-$ $K_1 = 4.45 * 10^{-7}$

$HCO_3^- + H_2O \longleftrightarrow H_3O^+ + CO_3^{2-}$ $K_2 = 4.7 * 10^{-11}$

The titration curve had two equivalence point

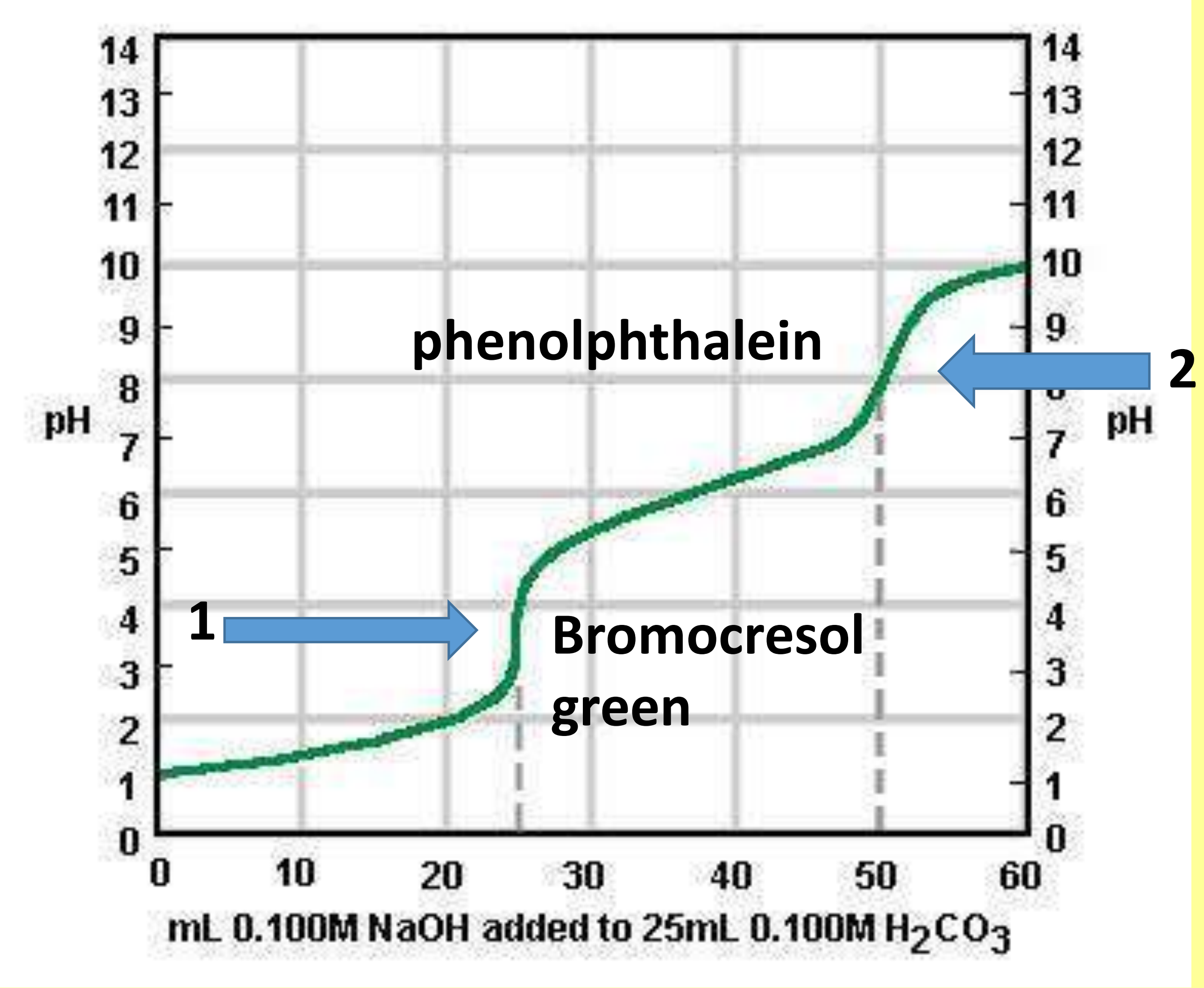
1- $H_2CO_3 + NaOH \longrightarrow HCO_3^- + Na^+ + H_2O$

2- $HCO_3^- + NaOH \longrightarrow CO3^{-2} + Na^+ + H_2O$

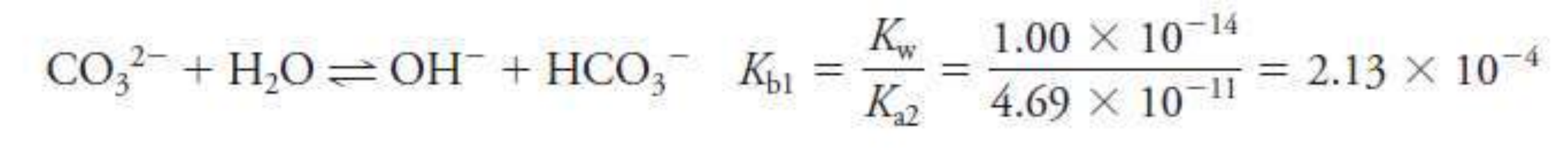
$H_2CO_3 + 2\,NaOH \longrightarrow CO3^{-2} + 2\,Na^+ + 2\,H_2O$

Titration curve of polyprotic acid

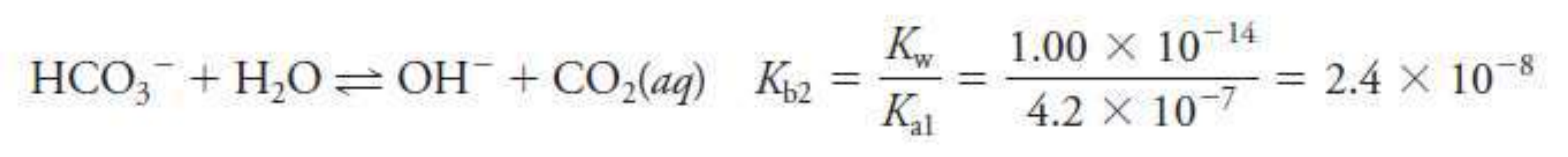
The titration curve of H_2CO_3 with NaOH using two indicators



Titration curve of poly functional bases



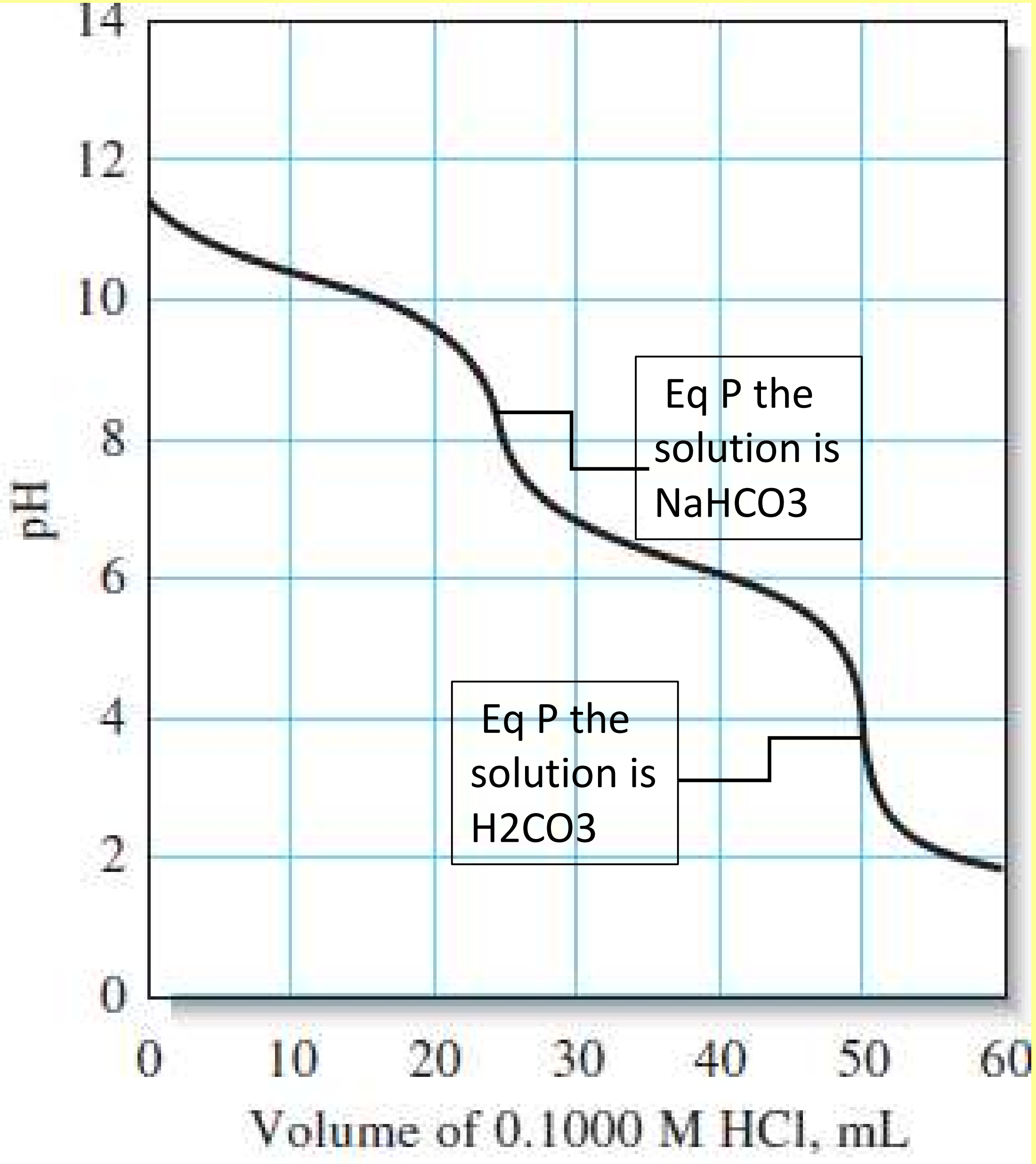
$$CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^- \quad K_{b1} = \frac{K_w}{K_{a2}} = \frac{1.00 \times 10^{-14}}{4.69 \times 10^{-11}} = 2.13 \times 10^{-4}$$



$$HCO_3^- + H_2O \rightleftharpoons OH^- + CO_2(aq) \quad K_{b2} = \frac{K_w}{K_{a1}} = \frac{1.00 \times 10^{-14}}{4.2 \times 10^{-7}} = 2.4 \times 10^{-8}$$

The titration curve of 25 mL of 0.1 M Na_2CO_3 with 0.1M HCl on the next slide

Titration curve of poly functional bases



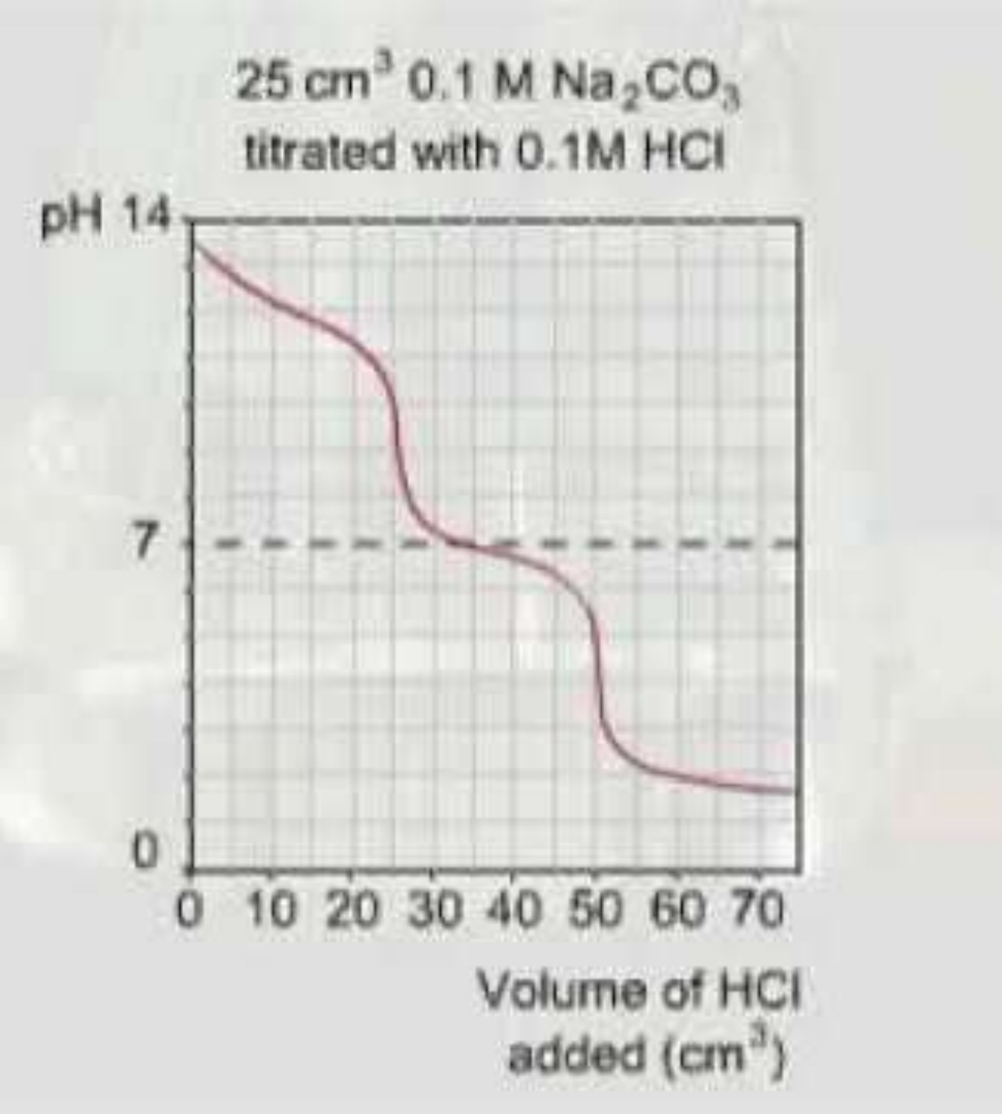
Eq P the solution is NaHCO3

Eq P the solution is H2CO3

Titration curve of polyprotic acid

See Video for the titration:

https://youtu.be/ZloiJuiEaI8



Calculation

For an amphiprotic salt $NaHCO_3$ what is the pH for 0.1 M solution of sodium hydrogencarbonate?

See in your book example **11-5**

Calculation

Examples: 6-11, 6-15, 10-1, 10-2, 10-3, 10-4, 10-5, 10-6, 10-7

Problems: 6-20, 6-22, 6-25
Chapter 10 : 1, 2, 3, 5, 6,7, 8, 9, 10, 11, 12,19, 26, 28, 27, 30, 32, 34, 35, 43, 47, 45, 50, 51.
Chapter 12: 8, 14, 15, 16 (a&c), 20,23, 26,34-39.

Acid – Base Titration
part 10

Dr. Mai Ramadan

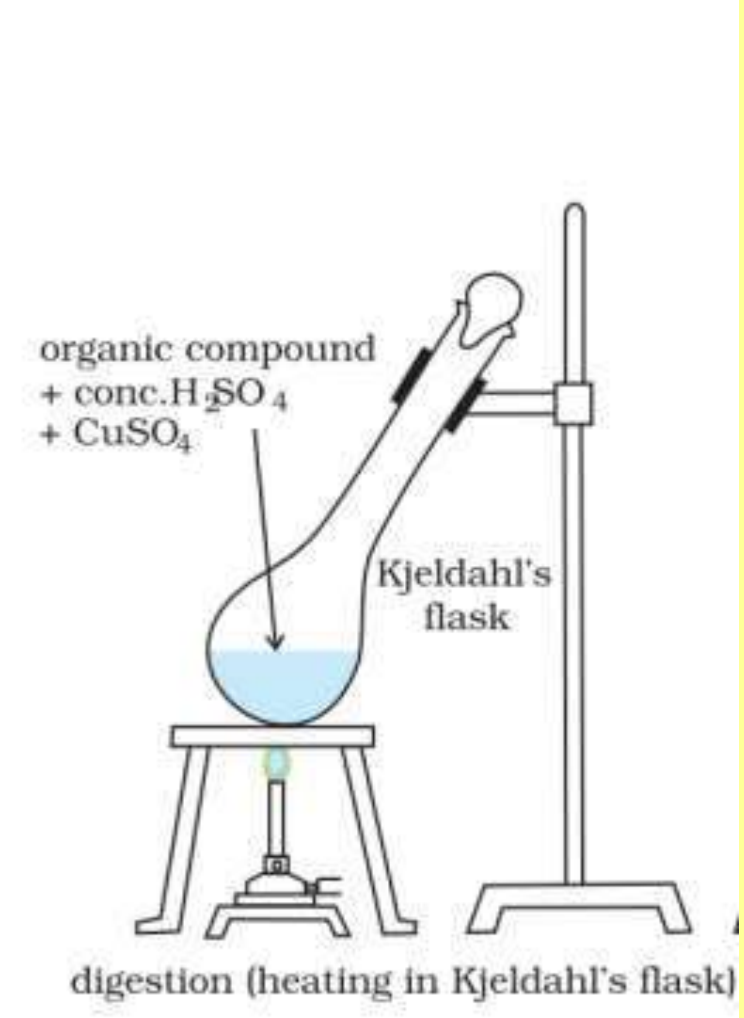
Application of acid base titration

The Kjeldahl method

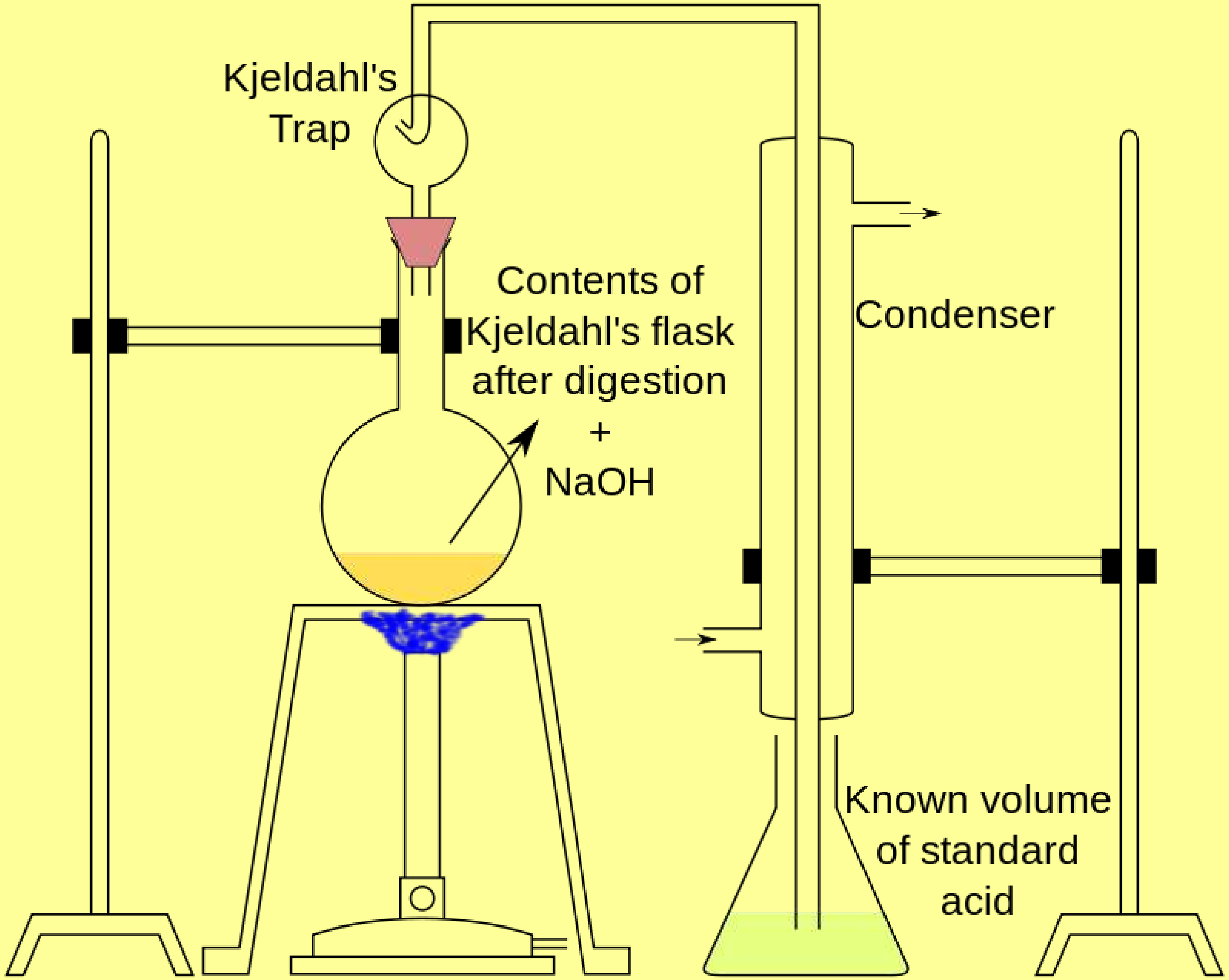
The most common method for determining organic nitrogen is the **Kjeldahl method, which is based on a neutralization titration**

The Kjeldahl method was developed by the Danish chemist Johan Kjeldahl, who first described it in 1883 (J. Kjeldahl, *Z. Anal. Chem.,**1883, 22, 366).*** ***Working*** at the Carlsberg Laboratory, Kjeldahl developed the method **to determine the protein content** of various grains to be used in brewing beer.

The Kjeldahl method



digestion (heating in Kjeldahl's flask)



1. Digestion

$$\text{Organic N} + H_2SO_4\ \text{(Conc.)} \xrightarrow{\triangle} NH_4^+ + SO_4^{-2}$$

2. Add base & Distillation

$$NH_4^+ \text{ (aq.)} + NaOH \text{ (Conc.)} \xrightarrow{\Delta} NH_3 \text{ (g)} + Na^+ + H_2O$$

3. Collection of NH_3

A

$$2\ NH_3\ (g) + H_2SO_4 \longrightarrow 2\ NH_4^{+}\ (aq.) + SO_4^{-2}$$

Volume and concentration are known before collection

4. Back titration of excess acid

$$H_2SO_{4\ (Excess)} + 2\ NaOH \longrightarrow 2\ Na^+\ (aq.) + SO_4^{-2} + 2\ H_2O$$

Titrant:
Volume is measured & concentration is known

Calculation

A

No moles H_2SO_4 (Total) = Conc. (M) * Vol. (L)

No moles H_2SO_4 (Excess) = $\frac{1}{2}$ * no. moles NaOH

No. moles H_2SO_4 (reacted) = Total – excess

No moles NH_3 (liberated) = $\frac{2}{1}$ * no moles H_2SO_4 (reacted)

No moles NH_3 (liberated) = No moles N = No moles N in organic material

3. Collection of NH_3

B

$$NH_3\,(g) + H_3BO_3 \longrightarrow NH_4^+\,(aq.) + H_2BO_3^-$$

Unknown amount of H_3BO_3

4. Titration

$$H_2BO_3^- + HCl \rightarrow H_3BO_3 + Cl^-$$

Titrant:
Volume is measured & concentration is known

Calculation

B

No moles $H_2BO_3^-$ = no moles HCl = Conc. (M) * Vol. (L)
No moles No. $H_2BO_3^-$ = no moles NH_3 (liberated)

No moles NH_3 (liberated) = No moles N = No moles N in organic material

The Kjeldahl method

Steps:
Digestion of organic sample with H2SO4 (conc): organic substance decomposes and nitrogen transformed to ammonium ion

Distillation: after cooling of digestive mixture base is added and liberated ammonia should be distilled.

Collection of ammonia in absorption media: distilled ammonia is collected through reacting with known amount of acid (Conc, Volume known) or unknown amount of boric acid. It transformed again to NH4+ ion soluble in solution.

Back-titration: titrate un-reacted acid of collection media with a strong base **(Acid base titration).**

The Kjeldahl method

Example:

A 0.5843-g sample of a plant food preparation was analyzed for its **N content by the Kjeldahl method**, the liberated NH3 being collected in 50.00 mL of 0.1062 N HCl. The excess acid required an 11.89 mL back-titration with 0.0925 N NaOH. Express the results of this analysisin terms of

(a) %N.

(b) %urea, H2NCONH2.

(c) %(NH4)2SO4.

(d) %(NH4)3PO4

The Kjeldahl method

$NH3 + HCl_{reacted} \longrightarrow NH_4^+ + Cl^-$

$HCl_{unreacted} + NaOH \longrightarrow NaCl + H_2O$

$\text{Conc (M)} = \dfrac{N}{a}$ a: no of protons given or gained

No mmol HCl (total) = Conc (M) * Vol (mL)

= 0.1062 (M) * 50 (ml) = 5.31 mmol

No mmol HCl (unreacted) = no mmol NaOH

= 0.0925 (M)* 11.89 (mL)= 1.0998 mmol

No mmol HCl (reacted) = Total – unreacted =4.2102 mmol

The Kjeldahl method

No mmol NH_3 = 4.2102 mmol

No mmol N = No. mmol NH3 = 4.2102 mmol

$$\% \text{ N} = \frac{4.2102 \text{ mmol} * 14 \text{ mg/mmol} * 10^{-3} \text{ g}}{0.5843\text{-g}} * 100 = 10.09\ \%$$

$$\text{No mmol } (NH_4)_2SO_4 = \frac{1}{2} \text{ no mmol N} = 2.1051 \text{ mmol}$$

$$\% \ (NH_4)_2SO_4 = \frac{2.1051 \text{ mmol} * 132.14 \text{ mg/ mmol} * 10^{-3} \text{ g}}{0.5843\text{-g}} * 100 = 47.61\%$$

% urea = 21.64%, % $(NH_4)_3PO_4$ = 35.81%

The Kjeldahl method

Neohetramine, $C_{16}H_{21}ON_4$ (285.37 g/mol), is a common antihistamine. A 0.1247-g sample containing this compound was analyzed by the Kjeldahl method. The ammonia produced was collected in H3BO3, the resulting H2BO3¯ was titrated with 26.13 mL of 0.01477 M HCl. Calculate the percentage of neohetramine in the sample.

$$NH_3 + H_3BO_3 \longrightarrow NH_4^+ + H_2BO_3^-$$

$$H_2BO_3^- + H_3O^+ \longrightarrow H_3BO_3 + H_2O$$

No mmol HCl = no mmol $H_2BO_3^-$ = no mmol NH_3 = 0.3859 mmol

No mmol neohetramine= $\frac{1}{4}$ mmol NH_3 = 0.0965 mmol

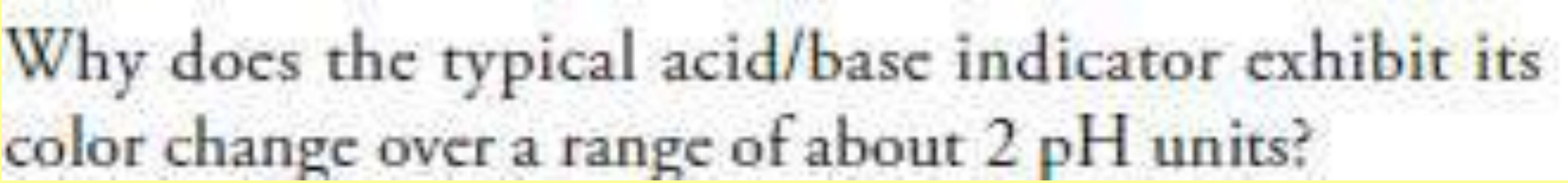
$$\%\ \text{neohetramine} = \frac{0.0965*10\text{-}3\ \text{mol} * 285.37\ \text{g/mol}}{0.1247\ \text{g}} * 100 = 22.08\%$$

Problems to test your self

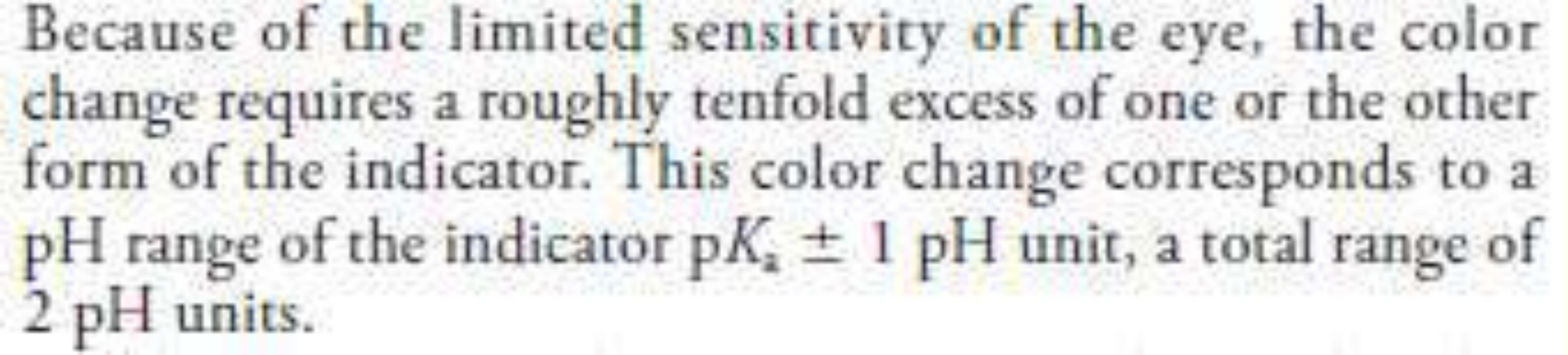
Acid-base titration

Indicator & titration curves

Problems

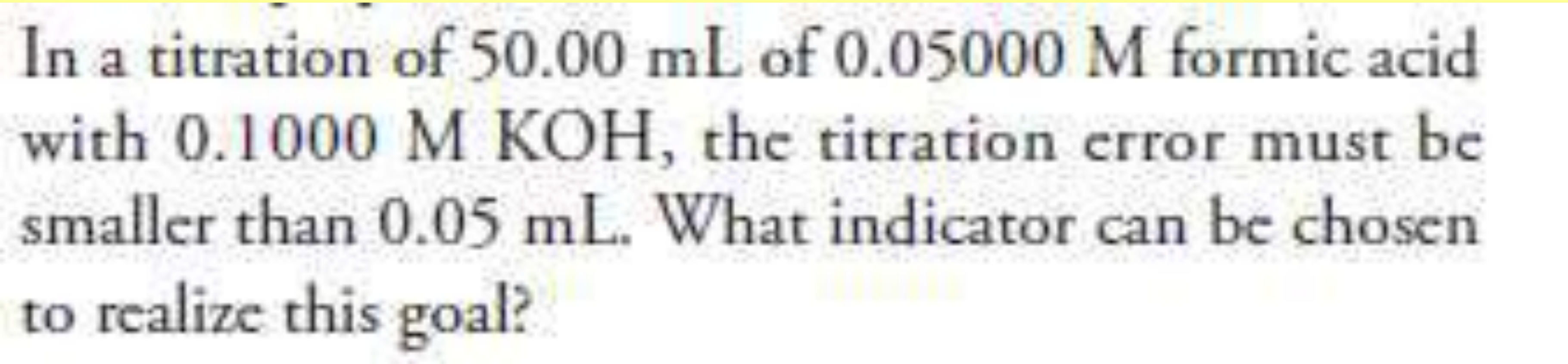


Why does the typical acid/base indicator exhibit its color change over a range of about 2 pH units?

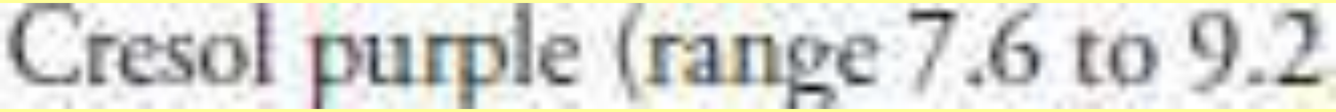


Because of the limited sensitivity of the eye, the color change requires a roughly tenfold excess of one or the other form of the indicator. This color change corresponds to a pH range of the indicator $pK_a \pm 1$ pH unit, a total range of 2 pH units.

Problems

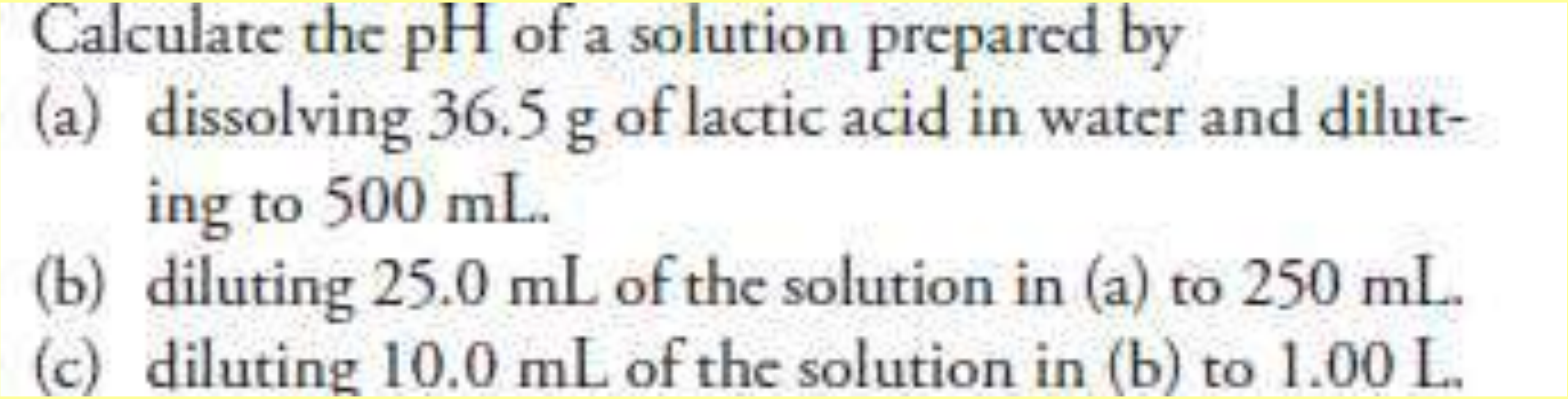


In a titration of 50.00 mL of 0.05000 M formic acid with 0.1000 M KOH, the titration error must be smaller than 0.05 mL. What indicator can be chosen to realize this goal?



Cresol purple (range 7.6 to 9.2

Problems

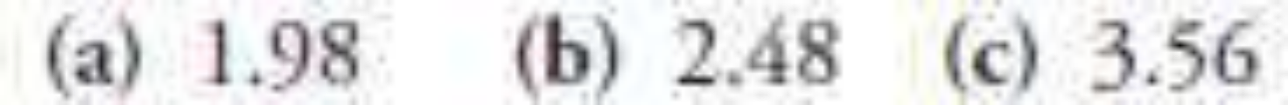


Calculate the pH of a solution prepared by

(a) dissolving 36.5 g of lactic acid in water and diluting to 500 mL.

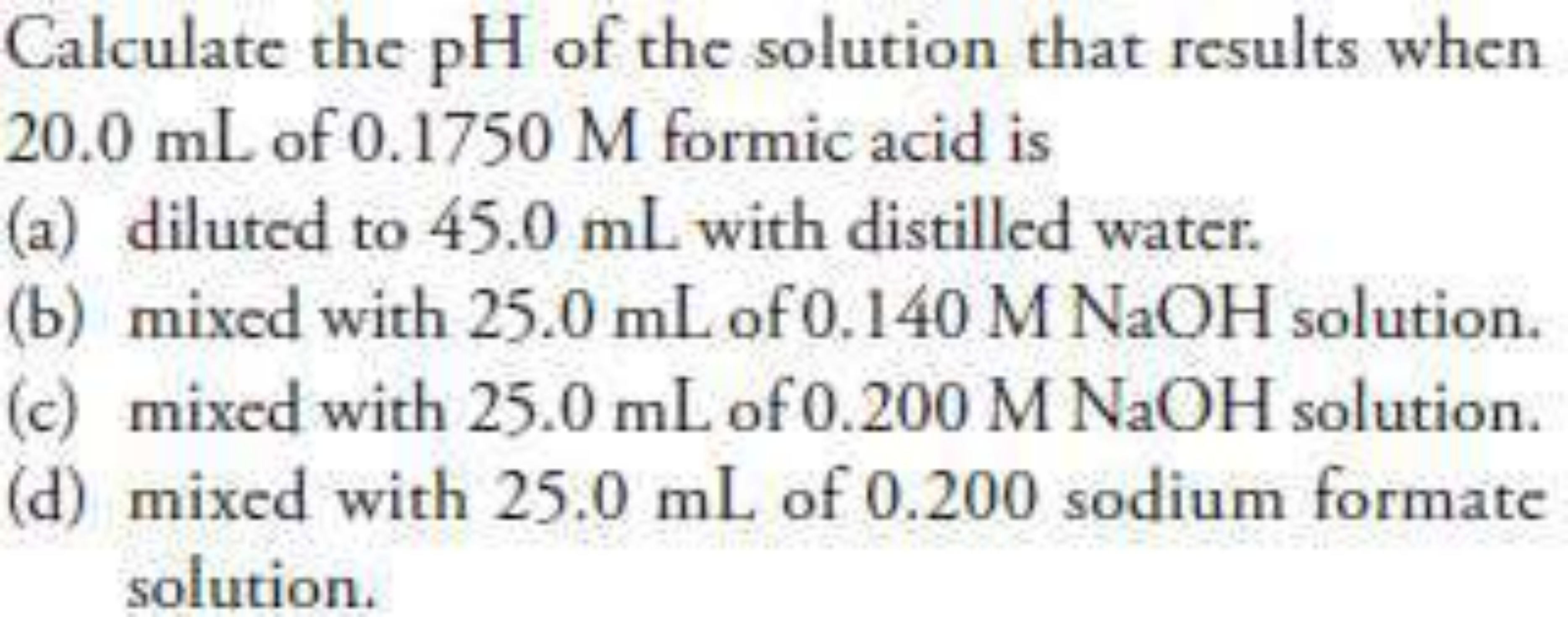
(b) diluting 25.0 mL of the solution in (a) to 250 mL.

(c) diluting 10.0 mL of the solution in (b) to 1.00 L.



(a) 1.98 (b) 2.48 (c) 3.56

Problems



Calculate the pH of the solution that results when 20.0 mL of 0.1750 M formic acid is

(a) diluted to 45.0 mL with distilled water.

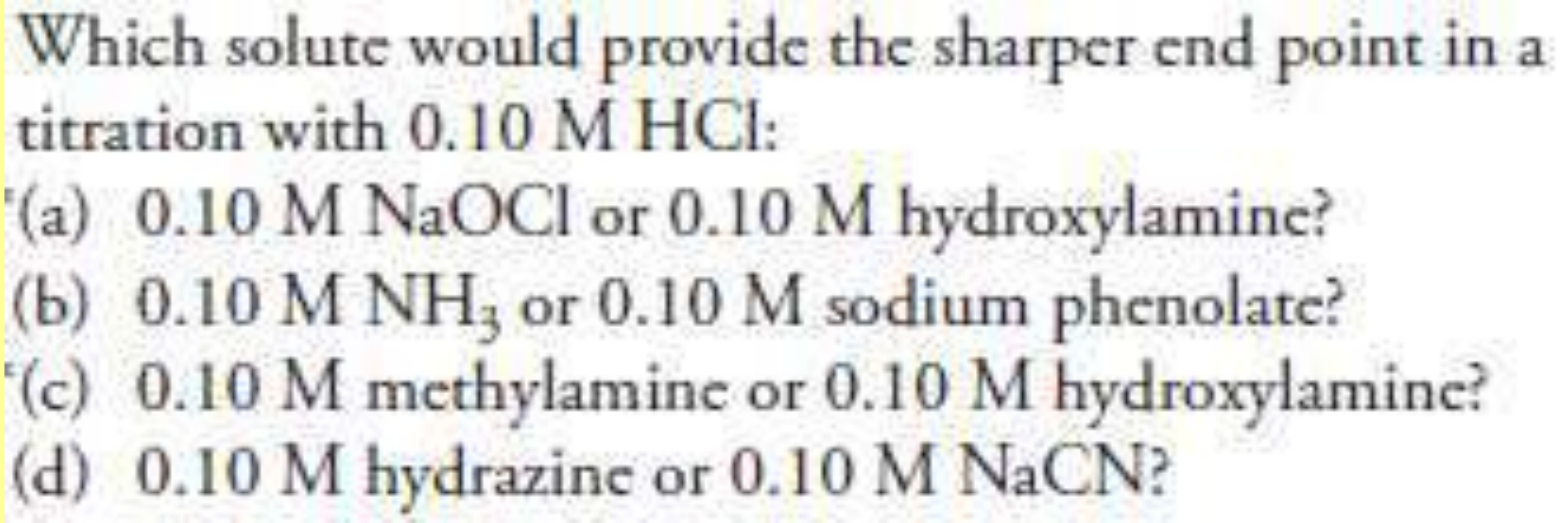
(b) mixed with 25.0 mL of 0.140 M NaOH solution.

(c) mixed with 25.0 mL of 0.200 M NaOH solution.

(d) mixed with 25.0 mL of 0.200 sodium formate solution.

(a) 2.44 (b) 8.32 (c) 12.52 (d) 3.90

Problems



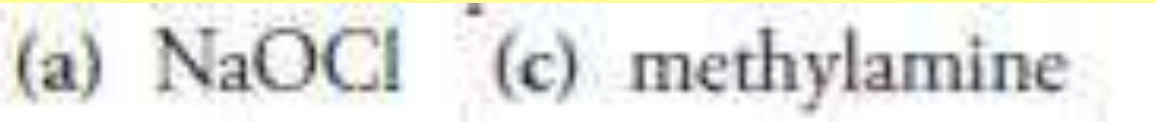
Which solute would provide the sharper end point in a titration with 0.10 M HCl:

(a) 0.10 M NaOCl or 0.10 M hydroxylamine?

(b) 0.10 M NH_3 or 0.10 M sodium phenolate?

(c) 0.10 M methylamine or 0.10 M hydroxylamine?

(d) 0.10 M hydrazine or 0.10 M NaCN?



(a) NaOCl (c) methylamine

Calculation

Examples: 6-11, 6-15, 10-1, 10-2, 10-3, 10-4, 10-5, 10-6, 10-7

Problems: 6-20, 6-22, 6-25
Chapter 10 : 1, 2, 3, 5, 6,7, 8, 9, 10, 11, 12,19, 26, 28, 27, 30, 32, 34, 35, 43, 47, 45, 50, 51.
Chapter 12: 8, 14, 15, 16 (a&c), 20,23, 26,34-39.

The next subject is kjeldhal method

Acid – Base Titration Problems continue

Dr. Mai Ramadan

Acid base titration problems

A 0.4723-g sample of **primary-standard-grade** Na_2CO_3 required 34.78 mL of an H_2SO_4 solution to reach the end point in the reaction

$$CO_3^{-2} + 2\,H^+ \longrightarrow H_2O + CO_2\,(g)$$

What is the molar concentration of the H_2SO_4?

$$\text{No mol } Na_2CO_3 = \frac{0.4723\text{ g}}{105.99\text{ g/mol}} = 4.46*10^{-3}\text{ mol}$$

$$\text{No mol } H_2SO_4 = \text{no mol } Na_2CO_3 = \text{Conc (M)} * \text{Vol (L)}$$

$$\text{Conc (M)} = \frac{4.46*10^{-3}\text{ mol}}{34.78*10^{-3}\text{ L}} = 0.1282\text{ (M)}$$

Acid base titration problems

A 25.0 mL aliquot of vinegar was diluted to 250 mL in a volumetric flask . Titration of 50 mL aliquot of the diluted solution required an average of 34.88 mLof 0.096 M NaOH. Express the acidity of vinegar in terms of the percentage w/v of acetic acid?

$CH_3COOH + NaOH \longrightarrow Na(CH_3COO) + H2O$

No mmol CH_3COOH (50 ml)= 34.88 (mL) * 0.096 (M)= 3.348 mmol

No mmol CH_3COOH (250 mL) = 16.74 mmol (no mmol acetric acid in 25 ml vinegar)

$$\% \text{ acetic acid} = \frac{16.74 * 10^{-3} \text{ mol} * 60.05 \text{ g/mol}}{25 \text{ ml}} * 100 = 4.02\%$$

Acid base titration problems

A diluted perchloric acid solution was standarized by dissolving 0.2445 g **primary sodium carbonate** in 50.00 ml of the acid, boiling to eliminate CO_2, and back-titration with 4.13 ml of diluted NaOH. In a separate titration 25.00 ml portion of the acid required 26.88 ml of the base. Calculate the molar concentration of the acid and the base.

$$2\ HClO_{4\ \text{reacted}} + Na_2CO_3 \longrightarrow 2\ NaClO_4 + CO_2 + H2O$$

$$HClO_{4\ \text{unreacted}} + NaOH \longrightarrow NaClO_4 + H2O$$

No mol $Na_2CO_3 = 2.31*10^{-3}$ mol

No mol $HClO_{4\ \text{reacted}} = 2 *$ no mol $Na_2CO_3 = 4.62*10^{-3}$ mol

A diluted perchloric acid solution was standarized by dissolving 0.2445 g **primary sodium carbonate** in 50.00 ml of the acid, boiling to eliminate CO_2, and back-titration with 4.13 ml of diluted NaOH. In a separate titration 25.00 ml portion of the acid required 26.88 ml of the base. Calculate the molar concentration of the acid and the base.

$$\text{Vol of } HClO_4 \text{ unreacted} = \frac{25 * 4.13}{26.88} = 3.84 \text{ mL}$$

Vol of $HClO_4$ reacted = 50- 3.84 = 46.16 mL

$$\text{Conc M of } HClO_4 = \frac{4.62*10^{-3} \text{ mol}}{46.16*10^{-3} \text{ L}} = 0.1 \text{ M}$$

$$\text{Conc M NaOH} = \frac{0.1 \text{ M} * 25 \text{ mL}}{26.88 \text{ mL}} = 0.093 \text{ M}$$

Calculation

Examples: Notes

Problems: Chapter 10

10-42, 10-39 (a,c,e,g), 10-48, 10-52 (a, c), 11-4, 12-19, 12-12 , 12-21, 12-24, 12-26.

To compare your answers with the ideal answers of the book

An Answers pdf file will be send to you per moodle