BioChem

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pH and buffers (part 1)

Kw (ion product of water) = 1.0 x 10^{-14} {constant}

Is the product of the concentrations of OH- and H+ ions in any solution.

However, in aqueous solutions there are equal concentrations of OH- and H+ ions, where each equals 1.0 x 10^{-7}.

The formula:- $$K_w = [H^{\oplus}][OH^{\ominus}] = 1.0 \times 10^{-14} M^2$$

The Kw constant can also be calculated using the formula shown below, where the equilibrium constant is multiplied by the concentration of water (55.5M).

$$K_{eq} (55.5 M) = [H^{\oplus}][OH^{\ominus}]$$

(RECAP)

From the last lecture it was said that if there is a high concentration of H+ in a solution then the concentration of OH- will be low (Vice-versa) in order to maintain the total number of ions in the solution as well as the Kw constant (1.0 x 10^{-14}).

Check this table which shows the changes in the concentrations of H+ and OH- respectively across different pH values.

TABLE 2.3 Relation of [H$^{\oplus}$] and [OH$^{\ominus}$] to pH

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

What is pH?

A figure (Quantitative measure) expressing the acidity or basicity of a solution, with values ranging from 0-14

It can be calculated using the following formula which is fairly similar to the way by which the pKa value is calculated from the Ka value of a solution

$$pH = \log_{10}(1/[H^+]) = -\log_{10}[H^+]$$

The pH is used to compare the acidity and basicity of different solutions through the pH scale which ranges from 0 to 14.

At a very low pH (almost 0) such as that of HCL (1M) the concentration of protons (H+) is extremely high!

Whereas the concentration of the protons produced by the dissociation of weaker acids when compared to HCL like (human gastric acid/ tomato, lemon and orange juices, etc..) is lower.

Once a pH of 7 (Middle point) is reached the concentrations of H+ and OH- are equal hence forming a neutral solution (Like water).

As the OH- concentration increases the pH value rises reaching 14 (wich means that the solution is very basic and the concentration of OH^- is higher when compared to the lower concentration of the H_3O^+).

Increasing basicity — Neutral — Increasing acidity

14 — Sodium hydroxide (1 M)
13
12 — Ammonia (1 M)
11
10
9
8 — Human pancreatic juice
7 — Human blood plasma
6 — Cow's milk
5
4 — Tomato juice
3
2 — Human gastric contents
1
0 — Hydrochloric acid (1M)

We've previously talked about acidic and basic solutions but how can we determine it? This can be achieved by the following techniques:

1)<mark>Acid-base indicator:</mark>

 A- Litmus paper(ورق عباد الشمس):- Which is the least accurate. We use it to determine if it's acidic or basic, but scientists have manufactured more accurate litmus paper, that can tell you what the PH almost exactly is. It gives you a scale with different colors. (It's quite accurate)

Note**The colors of a pH strip correspond to pH ranges, not to a specific pH. Consequently, when you use pH paper, you can't get an exact number. If you need a definite number for the work you're doing, pH paper won't be very helpful. You can estimate the pH, but you'll have a highly uncertain value; pH meters, by contrast, will give you a more exact figure.

Red litmus paper with a drop of base here

Blue litmus paper with a drop of acid here
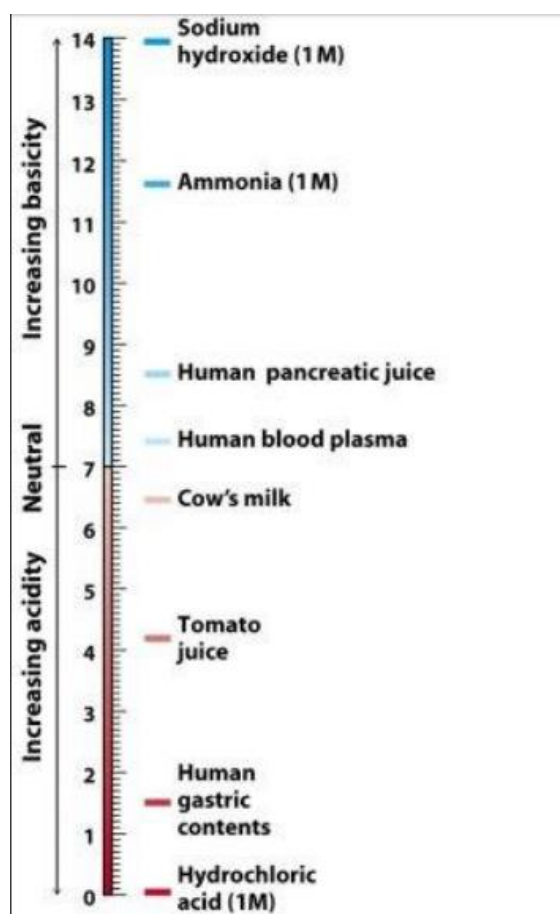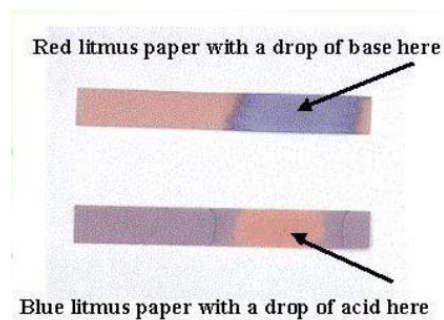
b- Universal indicator: - is a pH indicator made of a solution of several compounds that exhibits several smooth color changes over a wide range pH values to indicate the acidity or alkalinity of solutions, as shown below:

(a)   (b)
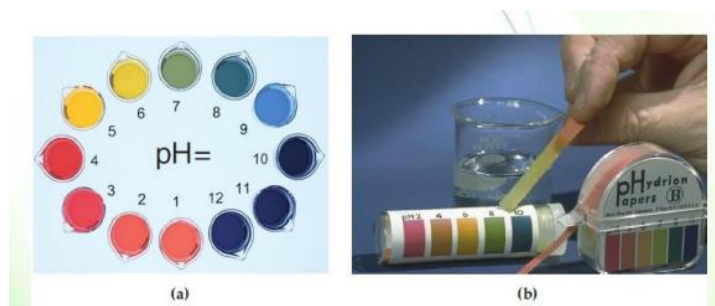
2) Electronic PH meter (which is the most accurate).

Is a device that has an electrode which is dipped in the solution with an unknown pH giving a numerical reading of the pH. However, before using it the electrode should be dipped in a standard solution with a known pH value, in order to ensure that the device is measuring the correct pH value.
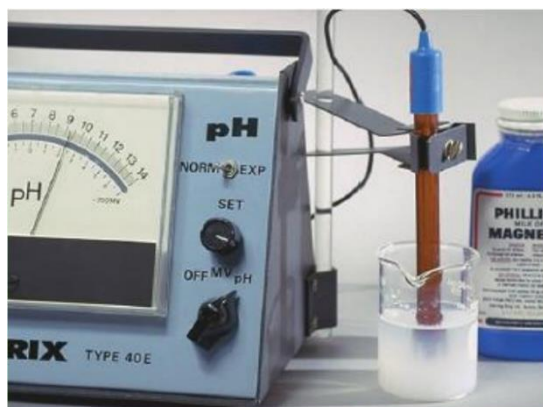
*Remember that pH is a logarithmic scale, in other words 1-unit difference between two pH values, which means that there is a 10-times difference in the concentration of protons among these pH values.

Example: -

As shown in the figure, the pH of the lemon juice (pH=2) is 2 units less than that of the Orange juice (pH=4), hence there is 100 times more (10^2) protons in the lemon juice than in the Orange juice.

Example 1 in the figure represents a usual calculation of pH by implying the formula:-
pH= -log[10^x]

(x= concentration of the solution in M)

Example: lemon juice at pH 2.0 contains more than 100 times as much H+ as orange juice at pH 4.0

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

$[H_3O^+] = 10^{-pH}$

Example 1: $[H_3O^+]$ in household bleach is 10^{-12} M

$pH = - \log [10^{-12}] = 12$

Example 2: Orange juice has a pH of 4

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

In addition, the proton concentration could be calculated from the pH value such as in example 2 of the figure.

Where **X=10^{-pH}**

Note* Not all the values present in the table are for memorization.

The list present on the side contains the pH values of many common fluids.

For example, the pH of Urine that ranges from 5 to 8, where the female urine is more acidic (more towards 5) than that of the male urine (more towards 8).

In addition, the blood plasma has a pH of 7.4, which will be discussed later on in more details.

The pancreatic fluid has a pH of almost 8 to allow the functioning of various pancreatic enzymes.

The pH of Various Common Fluids	
Fluid	**pH**
Household lye	13.6
Bleach	12.6
Household ammonia	11.4
Milk of magnesia	10.3
Baking soda	8.4
Seawater	8.0
Pancreatic fluid	7.8–8.0
Blood plasma	7.4
Intracellular fluids	
Liver	6.9
Muscle	6.1
Saliva	6.6
Urine	5–8
Boric acid	5.0
Beer	4.5
Orange juice	4.3
Grapefruit juice	3.2
Vinegar	2.9
Soft drinks	2.8
Lemon juice	2.3
Gastric juice	1.2–3.0
Battery acid	0.35

The saliva has a pH of 6.6 making it acidic. However, it varies from an individual to another based upon the differences in cleaning and eating habits (oral habits in general). For example, we expect that the pH of the saliva of an individual who doesn't take care of his teeth to be more acidic than normal (less than 6.6) thus increasing the probability of developing dental cavities.
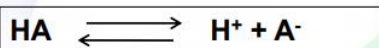
In the first example shown below, we should calculate the K_a of a weak acid having a concentration of 0.04M with [H+] of 1×10^{-4} M, we should assume that [H+]=[A-] since the weak acid dissociates into H+ and A- where both have the same ratio (1:1). After that substitute the values in the formula:

$$Ka=([H+]*[A-])/ [HA]$$

Example:

Find the K_a of a 0.04 M weak acid HA whose [H$^+$] is 1×10^{-4}?

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

$$K_a = [A^-] [H^+] / [HA] = [H^+]^2 / [HA] = 10^{-4} \times 10^{-4} / 0.04 = 2.5 \times 10^{-7}$$

In the second example shown below, we should calculate the concentration of protons [H+] in a **dibasic solution of Ba(OH)$_2$**, hence we should multiply the [OH-] by 2. Then since the product of [H+] and [OH-] is 1.0×10^{-14}.

Therefore, to find the [H+] the Kw constant (1.0×10^{-14}) should be divided by the [OH-]

Example:

What is the [H$^+$] of a 0.05 M Ba(OH)$_2$?

$$Ba(OH)_2 \rightleftharpoons Ba + 2OH^-$$

$$[OH^-] = 2 \times 0.05 = 0.10 \text{ M} = 1 \times 10^{-1}$$

$$[H^+] = 1 \times 10^{-13}$$

In the third example below, we should calculate the pKb of a weak base (0.03 M) given that the [H+] present in this basic solution (1.0×10^{-10}). First of all, the [OH-] should be calculated by dividing the Kw constant by the [H+]. Followed by the calculation of the K_b of the weak base by using the formula below **where [OH-]=[BH+]**
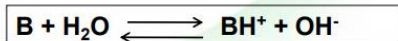
$$K_b=([OH-]*[BH+])/ [B]$$

Finally, the pK$_b$ is calculated by taking the negative logarithm of the K$_b$ value, as shown below: -

$$pK_b= -\log(K_b)$$

Example:

The [H$^+$] of a 0.03 M weak base solution is 1 x 10^{-10} M. Calculate pKb?

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

[OH$^-$] = 10^{-4}

K$_b$ = (10^{-4} x 10^{-4}) / 0.03 = 3.33 x 10^{-7} M

pK$_b$ = -log K$_b$ = 6.48

Henderson-Hasselbalch equation:

We use it when we want to know what is the relationship between the PH and the pKa.

 Remember that**, PH gives us an indication of how much protons are in a solution, and for that it gives us measurements. But pKa gives us the equilibrium of a weak acid (products/reactants), plus, showing us the strength of it → The lower the pKa, the stronger the acid is.

The images below show the derivative of the **Henderson-Hasselbalch equation:**

To begin with, for the dissociation of a weak acid, Ka value could be calculated by the formula:-   **Ka=([H+]*[A-])/ [HA].**

Followed by rearranging the formula and making [H+] the subject of the formula we get:

[H+]= (Ka*[HA])/[A-].

The dissociation of a weak acid is as follows:

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

The acid dissociation constant is as follows:

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

Rearranging this expression in terms of the parameter of interest [H+] gives the following:

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

After that we obtain the pH by taking the log of both sides, with some mathematical skills the final equation will be derived!

Bear in mind that pKa is Independent of the pH Since it is a constant! Hence a change in the pH of a solution is due to changes in the relative concentrations of the acid and its conjugate base

Take the log of both sides:

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

Change the signs, remember $pK_a = -\log K_a$:

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

or

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

What is the significance of **Henderson-Hasselbalch equation?**

➜ PH doesn't only depend on the concentration of the protons (as we took earlier), it also depends on the concentration of the conjugate base over the concentration of the acid. So, when I can say that PH of an acid equal to the pKa of it?

➜ When the acid is half dissociated, half of it is in the acidic form, and the other is in the conjugate base form. (½ over ½) gives us 1, and the log 1, equals to 0, therefore the PH value= pKa, as shown below:

pKa is the pH where 50% of acid is dissociated into conjugate base.

"However difficult life may seem, there is always something you can do and succeed at. It matters that you don't just give up." -Stephen Hawking.
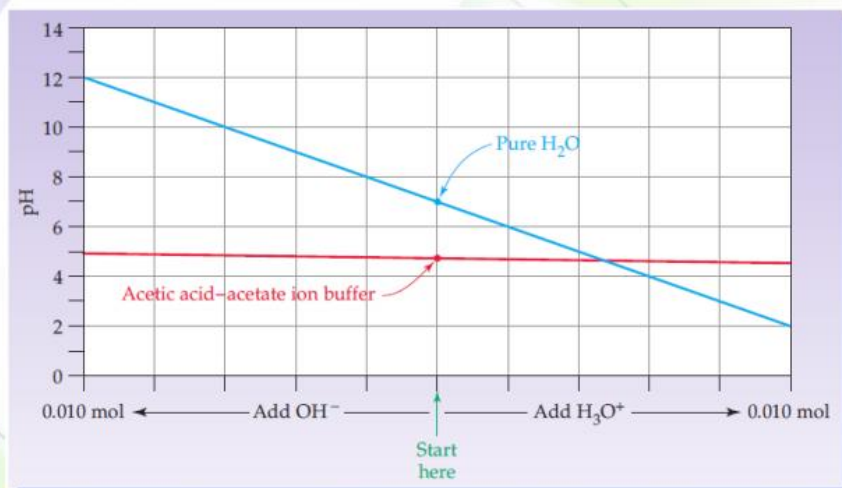
- 0.010 mol of base are added to 1.0 L of pure water and to 1.0 L of a 0.10 M acetic acid 0.10 M acetate ion buffer, the pH of the water varies between 12 and 2, while the pH of the buffer varies only between 4.85 and 4.68.

The figure above compares between the changes in pH of pure water (line in blue) and Acetic acid- acetate ion buffer system (line in red) as different concentrations of OH- and H+ (H3O+) were added.

To begin with as the [H+] increased (towards the right) there was a great drop in the pH of pure water. However, for the acetic acid- acetate ion buffer system there was a slight decline in pH (almost negligible).

On the other hand, as the [OH-] increased (towards the left) there was a upsurge in the pH (more basic). However, for the acetic acid-acetate ion buffer system there was a minimal increase in pH (almost negligible).

In conclusion, pure water cannot maintain the pH of a solution, while buffer systems such as the acetic acid- acetate ion system can almost maintain a constant pH when small concentrations of acid or base are added.

What is a pH buffer?

Buffer solution (محلول منظّم): - (basically weak acid or weak base and their conjugate acid/base) that resist changes in pH by changing reaction equilibrium. Contains at least two components (acidic form + conjugate base form, if we have more a greater amount of one of them, we will have less amount from the other).

What is a buffer?
- Buffers are solutions that resist changes in pH by changing reaction equilibrium.
- They are composed of mixtures of a weak acid and a roughly equal concentration of its conjugate base.

The figure below shows some examples of Acidic buffer systems, where the weak acid a long with its conjugate base resist changes in pH. Additionally, basic buffer systems works the same, as the weak base along with its conjugate acid resist changes in pH.

Acid	Conjugate base
CH_3COOH	CH_3COONa ($NaCH_3COO$)
H_3PO_4	NaH_2PO_4
H_2PO_4- (or NaH_2PO_4)	Na_2HPO_4
H_2CO_3	$NaHCO_3$

Titration curve of a buffer system

The figure shows the titration of acetic acid (pH=2) and its conjugate base (acetate ions) with OH- ions gradually (drop by drop).

This curve is divided into two parts the first half (concaved downwards) and the second half (concaved upwards). However, the focus here on the middle which represents the inflexion point in which the concavity of the curve changed, where the half-equivalence point is reached (mid-region of the buffer system where 50% of titration is over) .Bear in mind, that the pH=pKa at this point since the concentrations of acetic acid and acetate ions are equal.
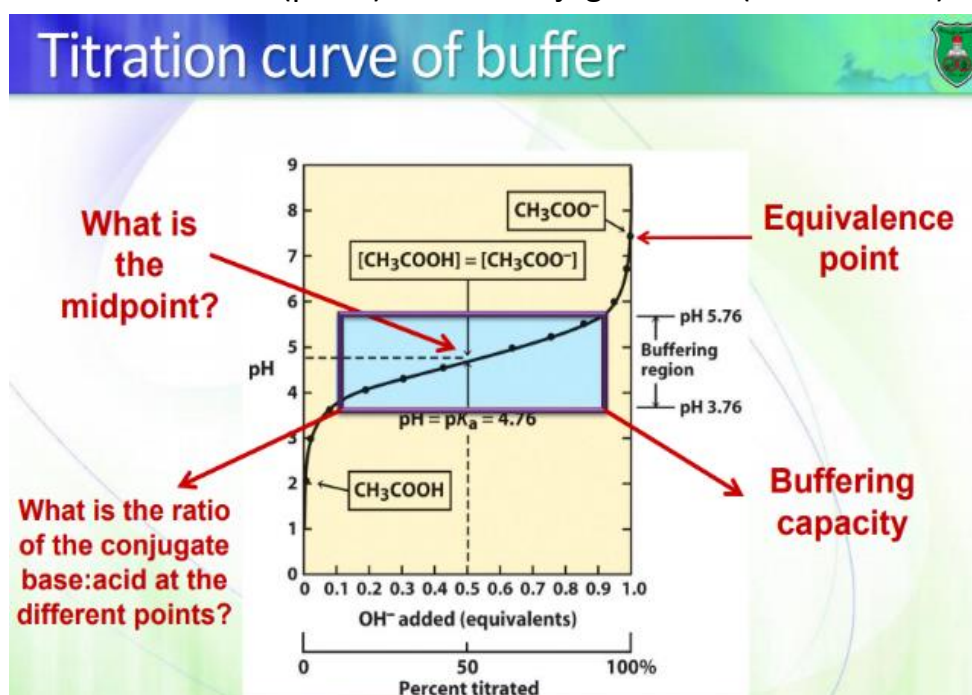
NOTE the equivalence point is not always equal to 7, it depends on the type of acid/base reacted.**

Right at the beginning of the titration there was a huge concentration of the acetic acid, hence increasing the rate of reaction causing a great change in pH. (before the buffer system gets into action).

Right at the end of the titration there was a huge concentration of the OH- ions and very little amount of acetic acid since it is almost got neutralised, hence there was a very large increase of pH (after the buffer system gets into action).

However, in the mid-region (blue rectangle) the concentrations of acetic acid and its conjugate base (acetate ions) were almost close to each other, hence this buffer system acted by decreasing the rate of change in pH of the reaction.

As you can notice below in the figure the range of the buffering region (buffering capacity) is +/-1 units above and below the half-equivalence point (5.76-3.76).

How to make and choose a buffer?

In order to choose the suitable buffer, we must ask ourselves, what is the PH value of the solution we want to maintain? If we want it to be 5, the best buffer to use is acetic acid/acetate buffer system. However, if we want it to be 9.25 the best buffer is the ammonia /ammonium ion buffer system.

Recap* The buffer is made by combining weak acid/base with its salt.

The ability of a buffer to function depends on two factors: -

1) Buffer concentration → it will not affect the buffering capacity, but it will affect the ability to resist the changing in the PH→ If you increase the concentration, the resistance will be increased because we have more base (or conjugate base) that will take or release protons, and the opposite is true).

 2) Buffering capacity. also known as buffering range, along which the buffering system can resist changes in pH.It highly depends on pKa of the buffer and the desired pH value
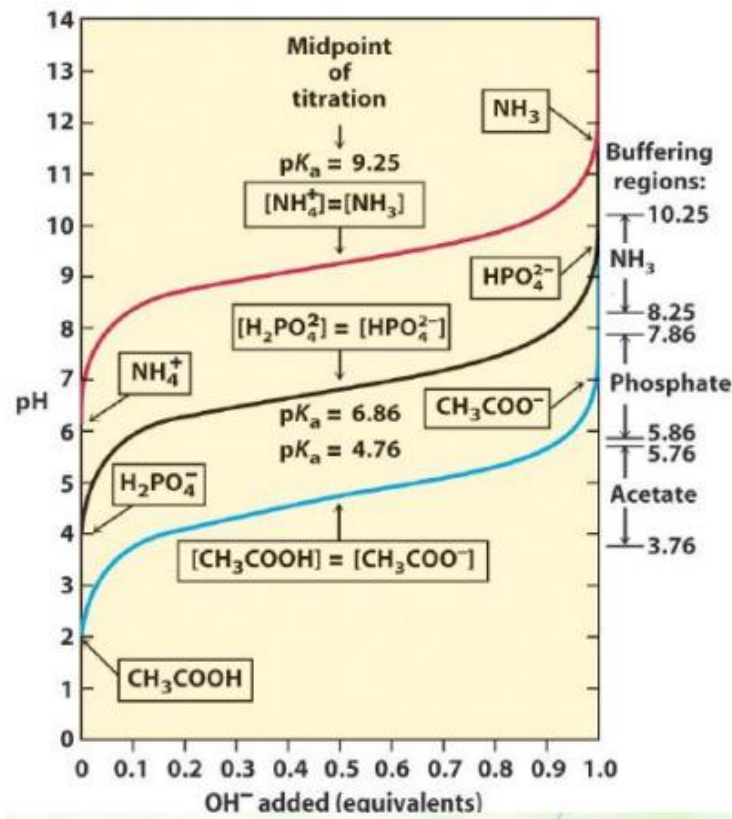
By applying **Henderson-Hasselbalch equation calculate the pH of the acetic acid/ acetate ion buffer system present in the below figure: -**

- A solution of 0.1 M acetic acid and 0.2 M acetate ion. The pKa of acetic acid is 4.8. Hence, the pH of the solution is given by

$$pH = 4.8 + \log(0.2/0.1) = 4.8 + \log 2.0 = 4.8 + 0.3 = 5.1$$

Similarly using the same equation the pKa could be also calculated.

في كلّ مرّة تظنّ بأنّك لن تجتاز ما تمرّ به الآن, تذكّر كلّ
الصّعاب السّابقة, وكيف أنّ يد الله مسحَت على قلبك,
وجعلَت من حاضرك الصعب ماضيًا كان مُرًّا, ومَرّ.

Below are a number of number of self-assessment questions, test yourself !

1) What is the pH of?

 a) 0.01 M HCl?

 b) 0.01 N H2 SO4?

 c) 0.01 N NaOH?

 d) 1 x 10-11 HCl? (this is a tricky one)

 e) 0.1 M of acetic acid (CH3COOH)? Remember Ka.

2) Predict then calculate the pH of a buffer containing :

 a) 0.1M HF and 0.12M NaF? (Ka = 3.5 x 10-4)

 b) 0.1M HF and 0.1M NaF, when 0.02M HCl is added to the solution?

3) What is the pH of a lactate buffer that contain 75% lactic acid and 25% lactate? (pKa = 3.86)

4) What is the concentration of 5 ml of acetic acid knowing that 44.5 ml of 0.1 N of NaOH are needed to reach the end of the titration of acetic acid? Also, calculate the normality of acetic acid.

Note for Q4**(The number of equivalents of OH- required for complete neutralization is equal to the number of equivalents of hydrogen ion present as H+ and HA)

** FOR MAIN IDEAS

** FOR EXPLAINATION

**FOR GENERAL INFO

تذكَّر دومًا: أنّ "لكلّ مجتهدٍ نصيب" وبما أنّ للعملةِ وجهان دائمًا, فهذا الوجه الأول، أما الآخر فهو التَّتمَّة. لكلّ مجتهدٍ نصيب، ولا مكانَ أو زمانَ أو هيئة لهذا النصيب. اليوم أو غدًا، في الدنيا أو الآخرة، هنا أو هناك، مع هذا أو ذاك, واجتهادُك ما كان أبدًا ليصيرَ هباءً منثورًا مع ربٍّ عادلٍ كريم, فنصيبُك سيصيبُك لا محالة. اطمئن!

1. Calculate the hydrogen ion concentration, [H+], for each of the following materials:

(a) Blood plasma, pH 7.4 (b) Orange juice, pH 3.5
(c) Human urine, pH 6.2
(d) Household ammonia, pH 11.5 (e) Gastric juice, pH 1.8

2. What is the [CH3COO–]/[CH3COOH] ratio in an acetate buffer at pH 5.00?

3. Calculate the pH of a buffer solution prepared by mixing 25 mL of 1.0 M lactic acid and 75 mL of 1.0 M sodium lactate

4. What is the ratio of concentrations of acetate ion and undissociated acetic acid in a solution that has a pH of 5.12? (pKa = 4.76)

5. What is the ratio of TRIS/TRIS-H1 in a TRIS buffer at pH 8.7? (pKa = 8.3)

ANSWERS

Q1)

Blood plasma, pH 7.4 $[H^+] = 4.0 \times 10^{-8}$ M
Orange juice, pH 3.5 $[H^+] = 3.2 \times 10^{-4}$ M
Human urine, pH 6.2 $[H^+] = 6.3 \times 10^{-7}$ M

Household ammonia, pH 11.5 $[H^+] = 3.2 \times 10^{-12}$ M
Gastric juice, pH 1.8 $[H^+] = 1.6 \times 10^{-2}$ M

Q2	Q3	Q4	Q5
1.7	4.34	2.3	2.5