Doctor 022

Biochemistry

Sheet no. 3

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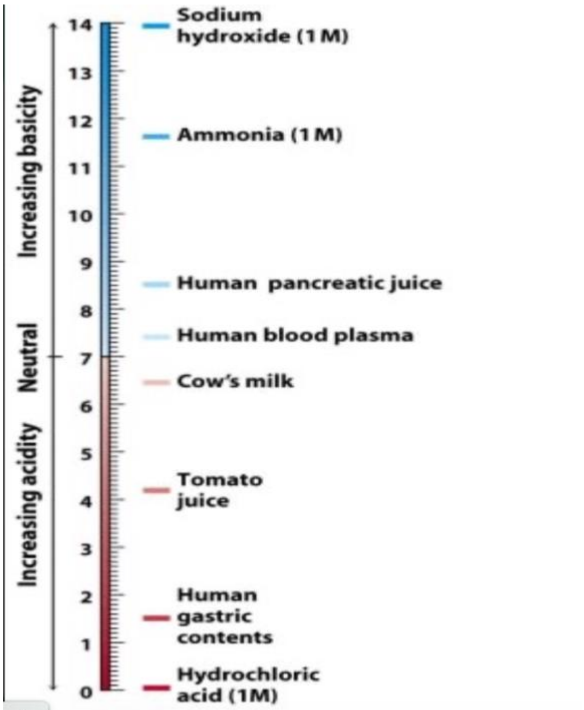
pH and buffers

-K_w is called the "ion product constant for water" and has the value of 10^{-14} M^2:

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

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

The ion product constant of water applies for all solutions, but the concentration of $[H^+]$ and $[OH^-]$ ions is only equal in pure H2O solutions. This means that K_w maintains the constant value of 10^{-14} in all aqueous solutions, but the individual concentration of each of water's ions ($[H^+]$ and $[OH^-]$) may differ in different solutions.
IF one increases, the other decreases and vice versa; to maintain the constant value of 10^{-14} for K_w.



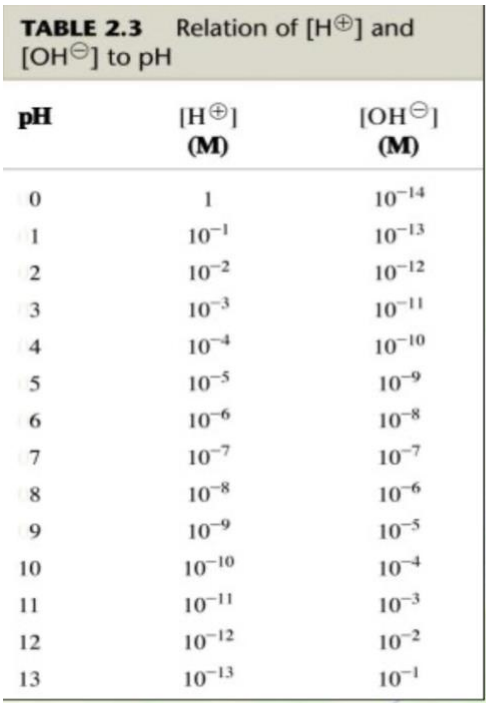


TABLE 2.3 Relation of $[H^{\oplus}]$ and $[OH^{\ominus}]$ to pH

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}

PH + POH = 14
POH = -log[OH-]
IF PH = 3, the POH= 11

Can the PH be less than zero?
Theoretically, yes, for example, if there was 10 M of HCl the pH = -1

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

The value of $[H^+]$ can range from 10^{-14} to 1 (10^0), covering a wide range of values. Similar to when calculating the value of pK_a from the value of K_a, instead of using the exact concentration of H^+ ions, we use a logarithmic formula to represent this concentration in a simpler way. The result of the logarithmic formula is known as the pH of the solution, where the greater the value of $[H^+]$ in the solution, the lower its pH becomes. The logarithmic scale of pH allows us to represent this range of concentrations using positive numbers and integers, making calculations and comparisons easier.

Similar to K_a and pK_a, pH= -log $[H^+]$ and if pH increases H^+ decreases and vice versa.

Let's take some examples of solutions and their pH (pH values mentioned are approximate ranges or typical values for the given solutions, as pH can vary depending on specific conditions.)

The pH of blood plasma is around 7.4, which is a little basic near to neutral.

The pH of saliva differs from person to person (depending on condition of the environment maintained in their mouths) but it is normally around 6.1, which is a little acidic, although it might be a bit more acidic for people that neglect basic oral hygiene.

The pH of urine has a range (not a specific number) from 5.8 to 8 where females usually have more acidic urine readings (closer to 5.8).

Some examples of acidic liquids are vinegar, lemon juice (pH=2), orange juice (pH=4), and milk (pH= 6)

Although pK_a is indeed a property of an acid and remains constant for a given acid regardless of the solution's dilution (concentration), there isn't a constant pH value for each acid. pH is solely a property given to describe a solution; it represents the hydrogen ion concentration and can vary with changes in the concentration of the acid or base present in it.
For example, we can make two solutions of HCl one with pH =1 and the other with pH =2 just by changing the concentration of HCl in each solution (0.1 M and 0.01 M respectively) but we can't change Ka or PKa

-Example 1:

Find the K_a of a 0.04M weak acid HA whose $[H^+]$ Is $1x10^{-4}$?

$HA \rightarrow H^+ + A^-$ Note: [H+]=[A-]

$K_a = [A^-][H^+]/[HA] = [H^+]^2 /[HA] = 10^{-4}x10^{-4}/0.04 = 2.5x10^{-7}$

Note: [HA] after dissociation = [HA] -X ; X: is a small negligible amount of acid that had been dissociated, so because it is negligible, the [HA] is considered not effected

-Example 2:

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

$Ba(OH)_2 \rightarrow Ba + 2OH^- \rightarrow [OH^-] = 2x\ 0.05 = 0.10\ M = 1\ x\ 10^{-1} \rightarrow [H^+] = 1x\ 10^{-13}$

-Example 3: (

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

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

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

$K_b = (10^{-4}x10^{-4})/0.03 = 3.33x10^{-7}M \rightarrow pK_b = -\log K_b = 6.48$

What is the pH of:

0.01 M HCl? 2

0.01 N H_2SO_4? 2

0.01 N NaOH? 12

$1\ x\ 10^{-11}$ M HCl? (this is a tricky one) 6.999

When strong acids have low concentrations in aqueous solutions, their effect becomes very negligible because the concentration of H^+ ions resulting from dissociating water molecules (10^{-7} M) is greater than the amount resulting from the dissociation of the acid (in this case 10^{-11} M). (2 sources of protons)

It is calculated as: $-\log(10^{-7}+10^{-11})$.

0.1 M of acetic acid (CH_3COOH)? (We can't solve it without knowing K_a)

N = normality =M * n
n: number of protons
In polyprotic acids N=[H^+] if its acid and N=[OH^-] in bases

Determination of pH

• Acid-base indicators: Acid-base indicators give us an idea if we have an acid or a base but they do not determine the exact value of pH.

1- Litmus paper (least accurate): It has an acidic/basic compound in its self, it either accepts or donates protons. If we use red litmus on an acid it remains red but we can't distinguish between two acids by this way
*** Base (Red to Blue)**
*** Acid (Blue to Red)**
2- Universal indicator.

• An electronic pH meter (most accurate): Is a device that has an electrode that is dipped in the solution with an unknown pH to give 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.

Henderson-Hasselbalch equation:

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

pH = acidity of a buffer solution
pKa = negative logarithm of Ka
Ka = acid disassociation constant
[HA] = concentration of an acid
[A-] = concentration of conjugate base

The dissociation of a weak acid is as follows:
$HA \Longleftrightarrow H^+ + A^-$
The acid dissociation constant is as follows:
$K_a = [H^+]*[A^-]/[HA]$
Rearranging this expression in terms of the parameter of interest [H+] gives the following:
$[H^+] = K_a[HA]/ [A^-]$
Take the log of both sides:
$\log[H^+] = \log(K_a[HA]/ [A^-])$

Change the signs, remember $pK_a = -\log K_a$:
$-\log[H^+] = -\log(K_a[HA]/ [A^-])$
$pH= pK_a + \log([A^-]/[HA])$

Henderson-Hasselbalch Equation Links the changes in pH of a solution with the changes of the ionization status of the molecules (and not with pK_a since it is constant).

-The value of pK_a becomes the value of pH when 50% of acid is dissociated into its conjugate base ([acid]=[conjugate base])

-pH affects the amount of ionization only and not the strength of dissociation (pK_a).

Examples: find the unknown ratios

1) **Preparing a solution with pH =5, pKa= 5**

5 = 5+ log [A-]/[HA]
Log[A-]/[HA] =0
***log (1) =0 [A-]/[HA] =1**
The ratio of [Conjugated base] to the [acid] is 1:1 which means that 50% of acid is ionized while 50% remains protonated.

2) Preparing another solution of the same acid (same pK_a) with pH =3

3 = 5+ log [A-]/[HA]
log [A-]/[HA] = -2
[A-]/[HA] = 0.01
One molecule gets ionized while 100 remain protonated

3) Preparing another solution of the same acid (same pK_a) with pH = 7

7 = 5+ log [A-]/[HA]
log [A-]/[HA] = 2
[A-]/[HA] = 100
100 molecules get ionized and turns to conjugated base while 1 remains protonated.

If the pH is greater than pK_a the more the acid is ionized and vice versa.

To explain this, analyze this example imagine you have a playground with two friends, خالد and ابراهيم, playing on a swing set. خالد represents the acid, and ابراهيم represents the conjugate base. Imagine that خالد starts swinging higher than ابراهيم. This represents a situation where the pH is more than the pK_a. As خالد swings higher, he gains more energy and momentum, making it easier for him to jump off the swing (ionize) and become a conjugate base. On the other hand, ابراهيم finds it harder to gain momentum and swing higher, so he remains as the conjugate base.

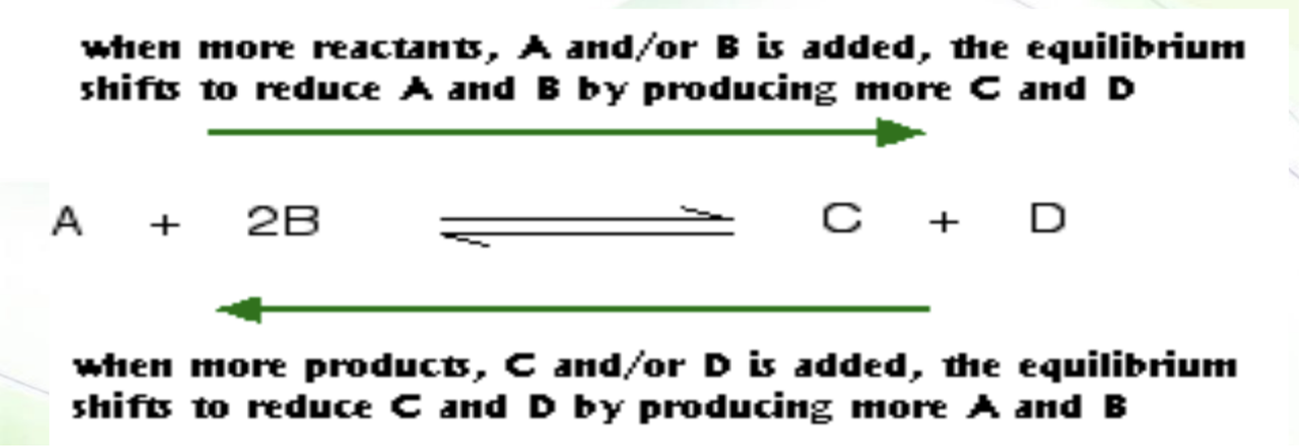
In this analogy, it means that when the pH is more than the pK_a, the acid has an increased tendency to ionize and donate a proton, while the conjugate base has a decreased tendency to accept a proton.

Another example

الدكتورة شبهت الموضوع بشخصين، واحد منهم لديه عضلات كبيرة (حمض قوي) والآخر لديه عضلات قليلة (حمض ضعيف). إذا قورن الشخص الذي يمتلك عضلات أقل بأشخاص يمتلكون عضلات أكبر منه، فلن يتفاخر بعضلاته (أي أن التأين ضعيف). أما الشخص الآخر، فإذا قورن بأشخاص يمتلكون عضلات أقل منه، فسيتفاخر بعضلاته (أي أن التأين كبير)".

Maintenance of equilibrium:

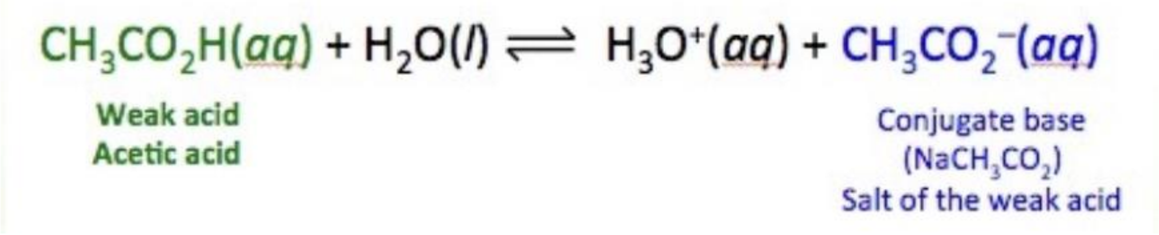
Le Châtelier's principle



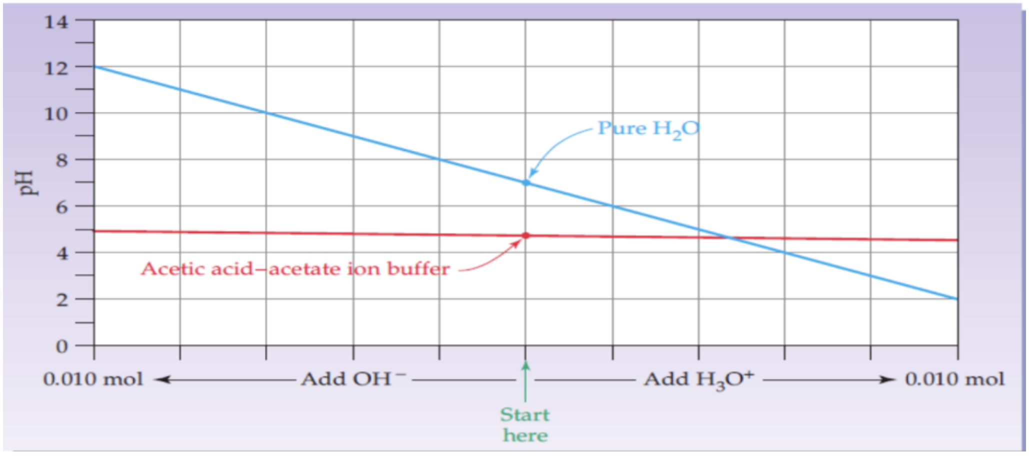
A comparison of the change in pH:

Water vs. Acetic acid (a weak acid)

0.010 mol of a base are added to 1.0 L of pure water and to 1.0 L of an acetate buffer composed of 0.10 M acetic acid and 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.



$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$



Addition of a small amount of acid to pure water results in reducing pH value significantly, you can observe this when squeezing some lemon in a cup of water, the taste becomes sour, as a result, water is not a true buffer because it doesn't resist changes in pH, but it can contribute in the function of the buffer.

In contrast, if we add 0.5 mol of NaOH to one mole of acetic acid CH3COOH (weak acid), they will react with each other and produce salt (the conjugate base of acetic acid) and water.
HC2H3O2 + NaOH ----> NaC2H3O2 (salt) + H2O
0.5 mol of NaOH reacts with 0.5 mol of acetic acid , 0.5 mol of acetic acid remains unreacted. The final solution is composed of 0.5 mol of acid, 0.5 mol of salt, and 0.5 mol of water and we call it a BUFFER.
The buffer could be acidic (pH<7) or basic (pH>7).

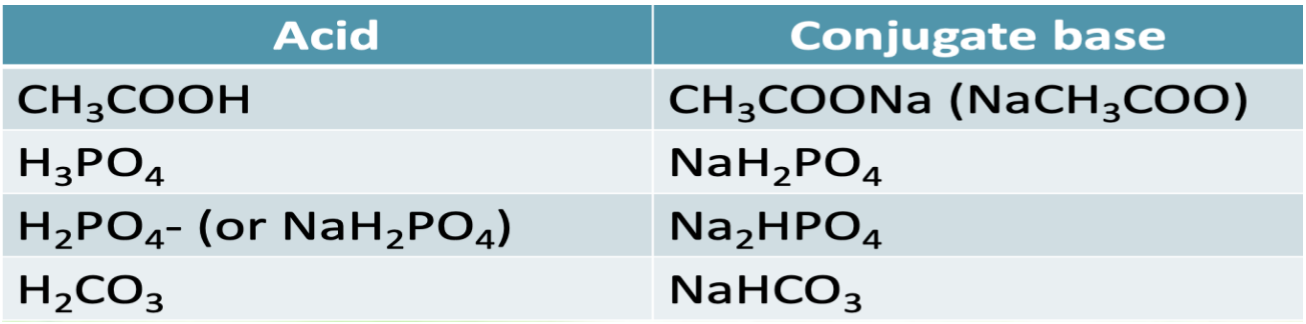
What is a buffer?

Buffers are solutions that resist changes in pH by changing reaction equilibrium.How is that? By the dissociation of the acid to protons and conjugate base or by the association of the conjugate base with the protons

Acidic buffers: starting with weak acid adding to it a strong base in smaller amount (weak acid and its conjugate base).

Basic buffers: starting with weak base adding to it a strong acid in smaller amount (weak base and its conjugate acid).

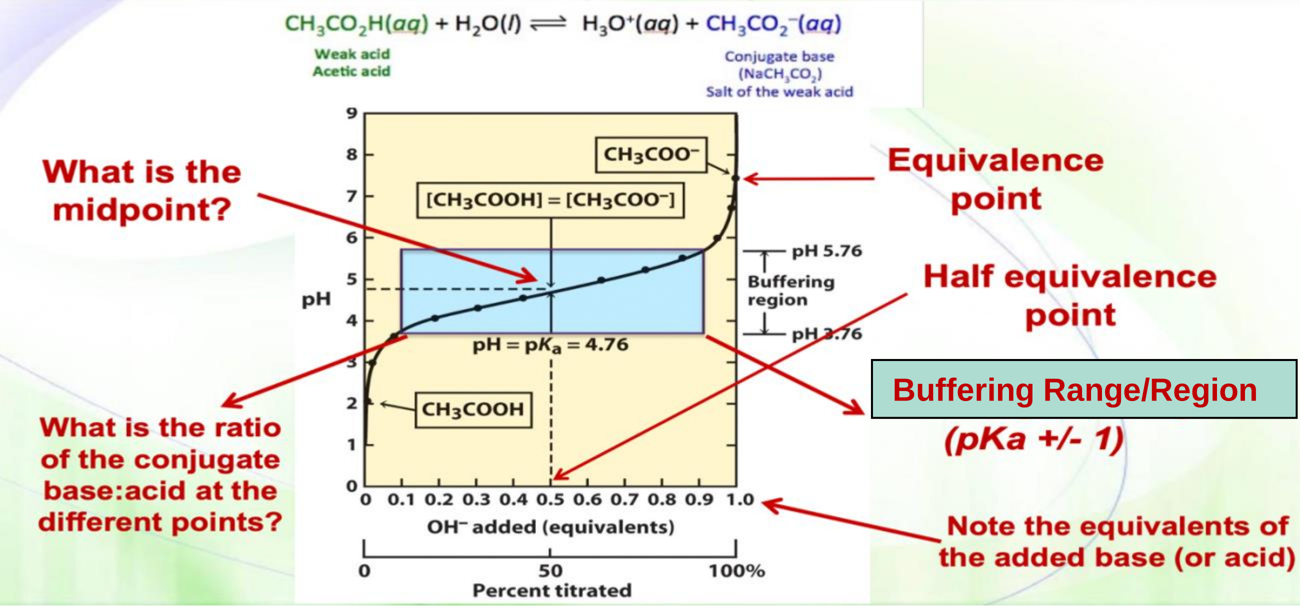
They are usually composed of mixtures of a weak acid and an equal concentration of its conjugate base (*salt*). **This means that the pH of these buffers would be equal to their pK_a values, remember Henderson-Hasselbalch's Equation!**



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	$NaHCO_3$

Note that the strong acids and bases cannot work as buffer because it is unidirectional (not reversible), which means that they dissociate completely.

Titration curve of buffers:

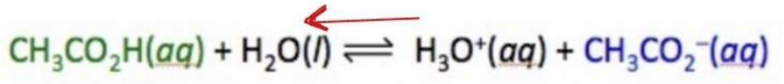


-The curve starts at low pH (acidic) and ends at a higher one (more basic), because we are titrating an acid. In this curve, we are titrating acetic acid which is weak.

 # We can titrate strong or weak acids/bases.

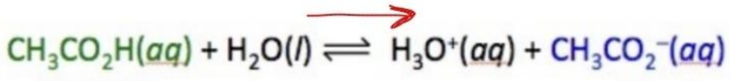
 # The added acid or base must be strong (in order to react completely with the buffer acid or base)

When adding strong acid HCL,the conjugate base will absorb the extra protons [H+]increases→ [CH3CO2-] decreases→ [CH3CO2H]increases.



$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

When adding strong base, OH- will grab the protons so the acetic acid will dissociate to recoup يعوض the lost protons, till all the acid is dissociated [H+]decreases→[CH3CO2H]decreases → [CH3CO2-] increases,



$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

-In the *middle*, the values were almost *equal*, that's why the reaction was slow, and the curve was almost flat. This phenomenon occurs because the concentration of the acid and its conjugate base (or base and its conjugate acid) are roughly equal, resulting in a slower change in pH as more titrant is added).

In the midpoint the curve shifted from concave downward to upward, this point is called the inflection point.

-Using Henderson-Hasselbalch equation:

pH = pKa + log[A-]/[HA]
*** [A-]/[HA] = 1**
Log (1) = 0

--> pH = pK_a in the inflection point.

-Buffering range/region is constant for the same buffer ($pK_a \pm 1$).
-Buffering capacity on the other hand, increases when the concentration is increased.

-The Equivalence point: where the amount of conjugate base (salt) is equal to the amount acid in the beginning of reaction, and it's not necessarily equal to 7 or around this value, it depends on the value of pK_a of the acid which represents the strength of the acid, and the values will be around the pK_a (greater or less than it).

Question from past papers

Question: If we have two solutions, the first with a pH of 7 and the second with a pH of 6.5, what is the difference between them?

A) The first solution has a $[H^+]$ concentration that is 10 times lower than the second solution.

B) The first solution has a $[H^+]$ concentration that is 10 times higher than the second solution.

C) The first solution has a $[H^+]$ concentration that is 3.16 times lower than the second solution.

D) The first solution has a $[H^+]$ concentration that is 3.16 times higher than the second solution.

The answer is: C

{فَقُلْتُ اسْتَغْفِرُوا رَبَّكُمْ إِنَّهُ كَانَ غَفَّارًا}

اي من تُريدون الجزاء جنان
صلوا على من بالرشاد أتانَ
صلوا عليه وأكثروا من ذكره
بل ذكّروا الأحباب والاخوانَ

V2

Page1 .

PH + POH = 14

POH = -log[OH-]

IF PH = 3, the POH= 11

Can the PH be less than zero?

Theoretically, yes, for example, if there was 10 M of HCl the pH = -1

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Note: [H+]=[A-]

Note: [HA] after dissociation = [HA] -X ; X: is a small negligible amount of acid that had been dissociated, so because it is negligible, the [HA] is considered not effected

Page 9

How is that? By the dissociation of the acid to protons and conjugate base or by the association of the conjugate base with the protons

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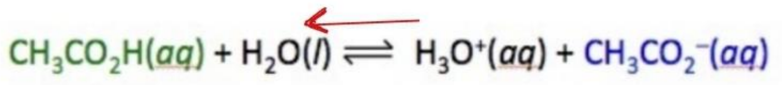
When adding strong acid HCL,the conjugate base will “absorb” the extra protons [H+]increases→ [CH3CO2-] decreases→ [CH3CO2H]increases.



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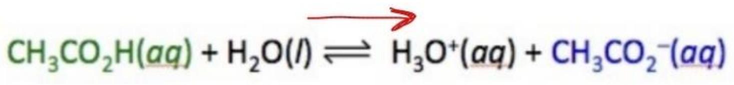

$$CH_3CO_2H(aq) + H_2O(l) \overset{\longrightarrow}{\rightleftharpoons} H_3O^+(aq) + CH_3CO_2^-(aq)$$