

Writer: Hana Arikat & Ahmad Bayadreh

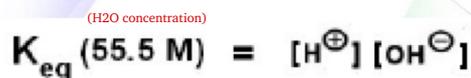
Science: Haitham Alsaifi

Grammar: Haitham Alsaifi

Doctor: Diala Abu Hassan

pH and Buffers

K_w



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

- K_w is called the ion product for water.

By calculating this constant we were able to calculate [H⁺] and [OH⁻]

In any solution.

- In aqueous solutions, [OH⁻] = [H⁺] = 10⁻⁷ M

TABLE 2.3 Relation of [H[⊕]] and [OH[⊖]] to pH

pH	[H [⊕]] (M)	[OH [⊖]] (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

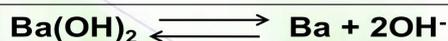
Examples

Find the K_a of a 0.04 M weak acid HA whose [H⁺] is 1 x 10⁻⁴?



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

What is the [H⁺] of a 0.05 M Ba(OH)₂?

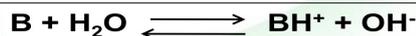


$$[OH^-] = 2 \times 0.05 = 0.10 \text{ M} = 1 \times 10^{-1}$$

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



The [H⁺] of a 0.03 M weak base solution is 1 x 10⁻¹⁰ M. Calculate pK_b?



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

$$K_b = (10^{-4} \times 10^{-4}) / 0.03 = 3.33 \times 10^{-7} \text{ M}$$

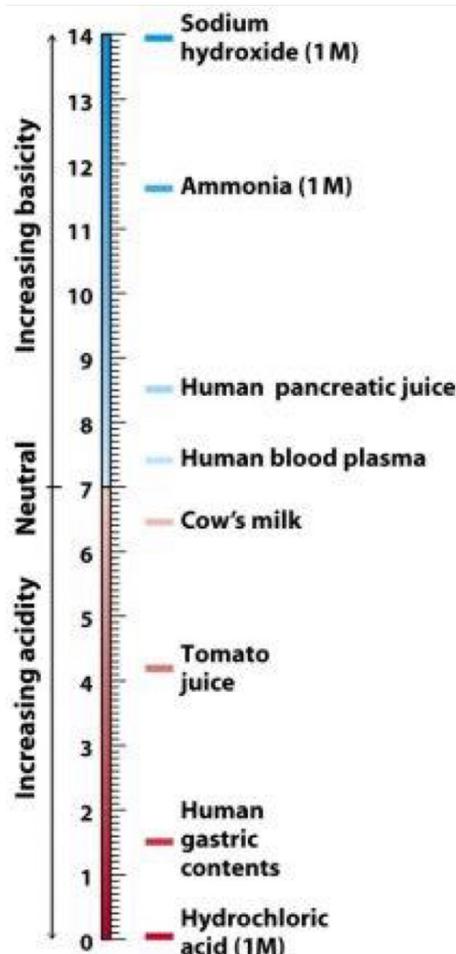
$$pK_b = -\log K_b = 6.48$$

What is pH ?

- A quantitative measure of the acidity or basicity of the solution.
- In terms of scale it ranges from 0 to 14.

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

- High concentration of H^+ means low concentration of OH^- and low pH.
- In acidic solutions like gastric acid $[\text{H}^+] > [\text{OH}^-]$
Whereas in basic solutions like ammonia $[\text{H}^+] < [\text{OH}^-]$.



*Notes on the table:

1) pH of female urine is more acidic (more towards 5) than male urine (which is more towards 8).

2) relating to the pH of saliva we have slight differences between individuals because of cleaning habits or different types of diets .

*The normal pH of saliva is 6.6 but if we have an individual that doesn't take care of his teeth for example, the pH will be less than 6.6 and will have higher probability to develop dental cavities.

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

*Only the highlighted ones are required.

•The pH scale is a logarithmic scale. One pH unit difference implies a 10-fold difference in $[H^+]$.

•The pH of the lemon juice for example is 2 units less than the orange juice (100 times).

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

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

Determination of pH

1) Acid-base indicators:

A) Litmus paper. (least accurate)

Once you add a base to the red one it becomes blue and once you add an acid to the blue one it becomes red.

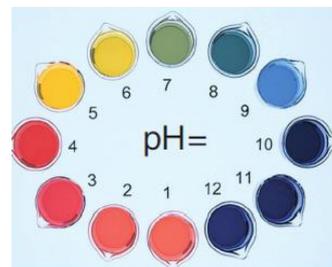
B) Universal indicator.

*Acid-base indicators give us an idea whether we have acid or base but they don't determine the exact value of pH.

Red litmus paper with a drop of base here

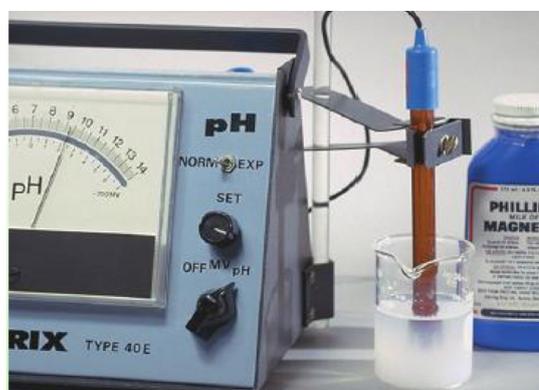


Blue litmus paper with a drop of acid here



2) Electronic pH meter (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.



Exercises

- What is the pH of
 - 0.01 M HCl? **pH=2**
 - 0.01 N H₂SO₄? **pH=2**
 - 0.01 N NaOH? **pH=12**
 - 1 x 10⁻¹¹ HCl? (this is a tricky one) **pH=7**
 - 0.1 M of acetic acid (CH₃COOH)? Remember **K_a = 1.8 x 10⁻⁵**
pH=2.87

Henderson-Hasselbalch Equation

Let's do some connection between [H⁺] and K_a value of a solution and how would these affect the distribution of different types of molecules in a solution.

- The dissociation of a weak acid is as follows:



- The acid dissociation constant is as follows:

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

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

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

- 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

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

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

Regarding to the equation above:

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

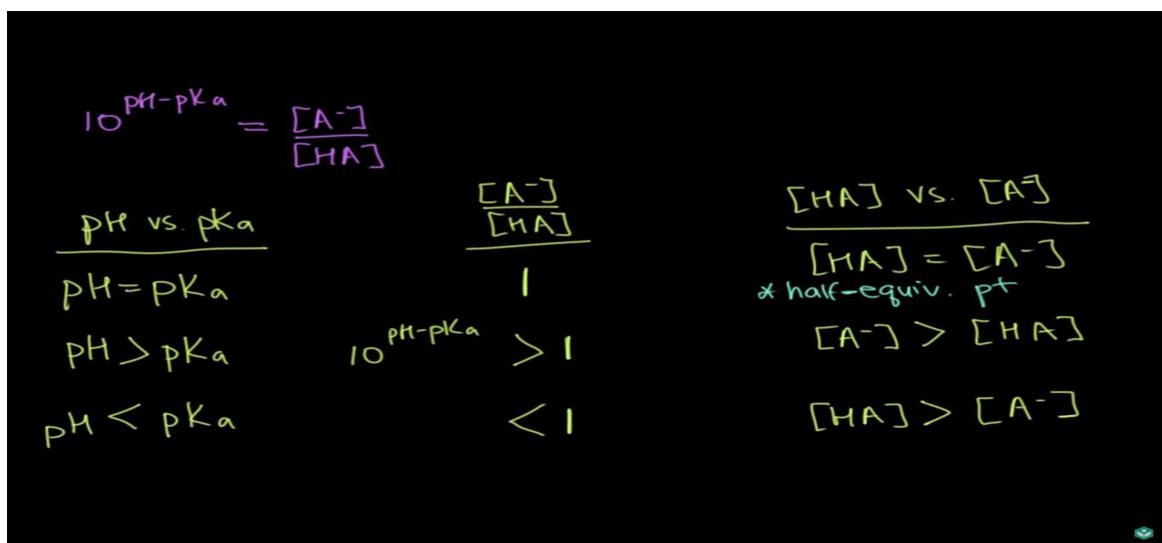
*get rid of log

$$10^{pH - pK_a} = \frac{[A^-]}{[HA]}$$

Notes:

- pK_a is a constant value for each acid.
- pH is a characteristic of a solution.

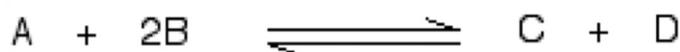
For example, if $pH=7$ and $pK_a=5$ then $10^2 = 100$ this means that $[A^-]$ is 100 times more than $[HA]$



Maintenance of equilibrium

Le Châtelier's principle

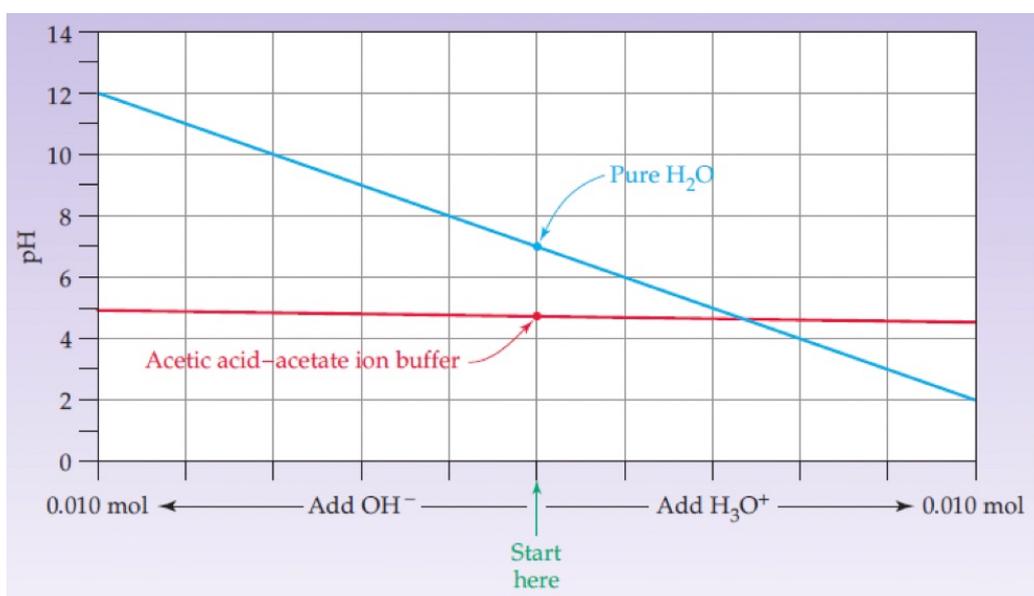
when more reactants, A and/or B is added, the equilibrium shifts to reduce A and B by producing more C and D



when more products, C and/or D is added, the equilibrium shifts to reduce C and D by producing more A and B

A comparison of the change in pH

(water vs. acetic acid)



- In the chart above we notice that pure H₂O can't do a role to protect the pH of the solution from decreasing/ increasing. But, in the solution of Acetic acid-acetate ion pH value stays nearly the same because it's a buffer solution.

*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.

So, what is a buffer?

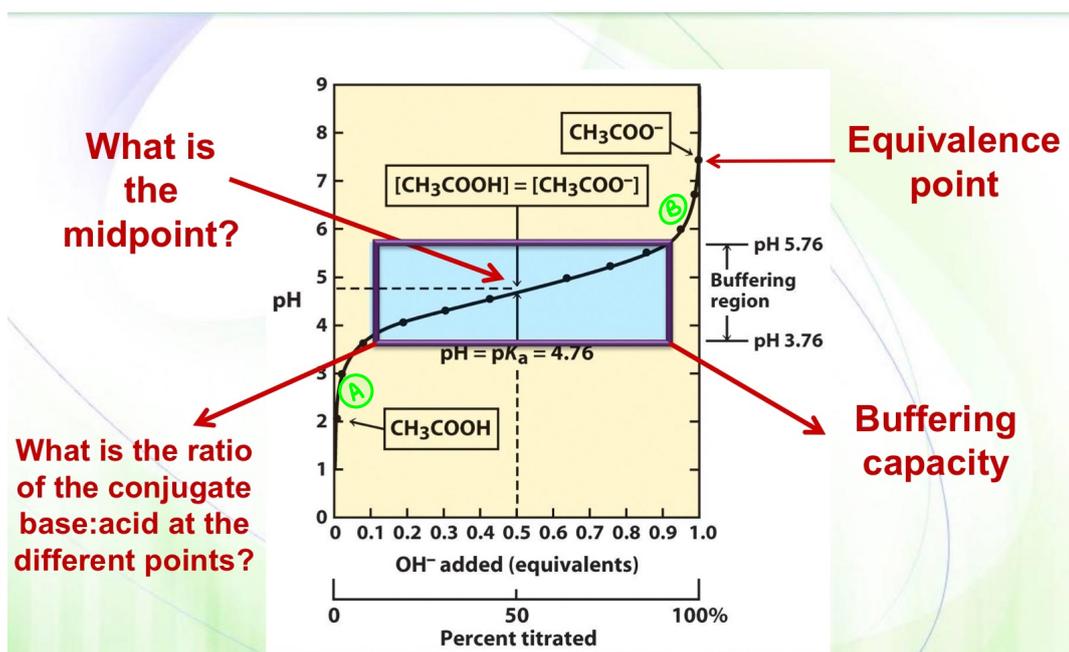
- Buffers are solutions that resist changes in pH by changing reaction equilibrium. They are composed of mixtures of a weak acid and a roughly equal concentration of its conjugate base.
- When H^+ is added to a buffer, the weak acid's conjugate base will accept a proton (H^+), thereby “absorbing” the H^+ before the pH of the solution lowers significantly. Similarly, when OH^- is added, the weak acid will donate a proton (H^+) to its conjugate base, thereby resisting any increase in pH before shifting to a new equilibrium point.

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: if you add an acid even if it's strong to a buffer solution there will be a very minor change in pH.

* Titration curve of buffer *

How to get a buffer solution from a weak acid or base and their salts:



1) We start with a 100% just weak acid (CH_3COOH) and we measure the pH and it's around 2.

2) We start adding a base (OH^-) to it to titrate or neutralize it.

*We use a strong base to guarantee a high concentration of OH^- .

3) OH^- is added gradually drop by drop, since the acid is monoprotic we would expect that if we had 1 eq of the acid we would need the same number of equivalents so we add 1 eq of OH^- .

- At the beginning (A) , there would be a sudden increase in the pH and then the pH value starts to increase slowly until it reaches a certain point (B) where it would go fast again.

- At point (B) we would have finished the process of neutralization (we finished all the molecules of CH_3COOH).

- When 50% of titration is done, 50% of OH^- was added at this point. The direction of the curve changes (inflection point) $\text{pH}=\text{pKa}$

- The end of titration is the equivalence point. At this point, pH doesn't have to be 7 it can be more or less depending on the pH that we started with in the first phase. **It's a matter of finishing the acid rather than having equal amounts of H^+ and OH^- .**

***What determines how fast pH is changing?**

At the beginning (A), there was a high concentration of the acid because nothing was titrated yet and a very small concentration of OH^- . So, there is a plenty of molecules of the acid to react that's why the reaction goes fast.

At the mid region (highlight in blue) the amounts of the acid and its conjugate base are very close to each other. The change in pH is going to be much slower.

At the end (B), almost all the acid reacted and a very small amount remained while we have a large amount of the base. So, there are many molecules of the base to react with. That's why the reaction goes fast.

- The buffering region is around the reflection point (1 unit above and 1 unit below). Whenever I'm in the buffering region, the buffer can act. But, when I'm in the edges the buffer will fail to act.

How do we make/choose a buffer?

- A buffer is made by combining weak acid/base and its salt.

- The ability of a buffer to function depends on:

1) Buffer concentration:
high buffer concentration means high number of molecules, more resistance to changes and more buffering capacity.

2) Buffering capacity

3) pKa of the buffer :

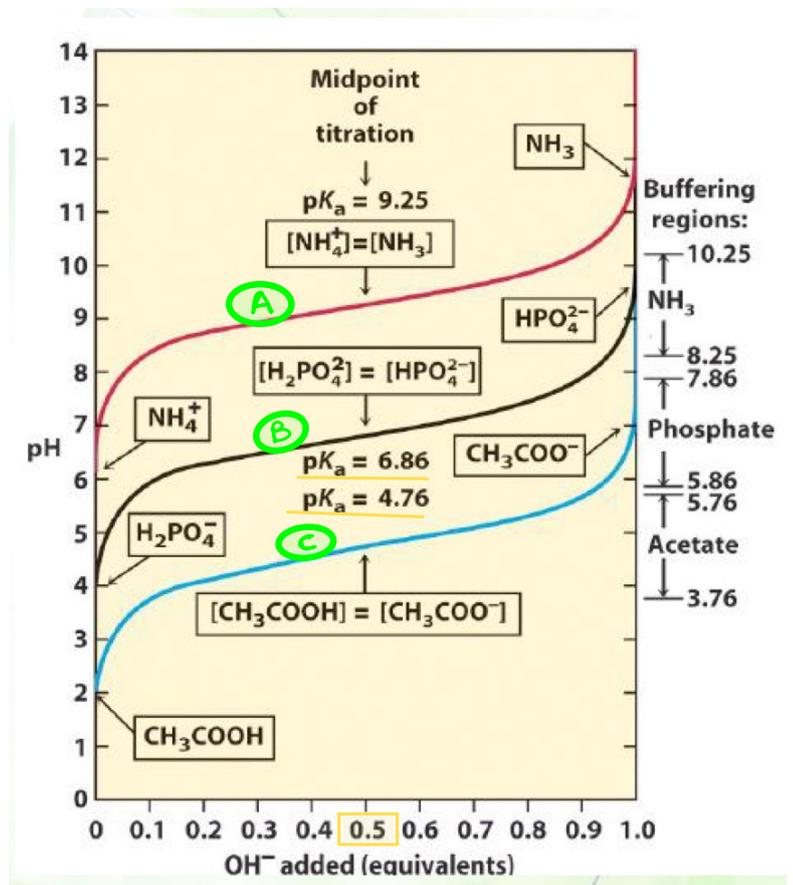
We can tell which acid is the strongest using pKa values.

4) The desired of pH

For example, a reaction is going to be carried and this reaction needs to be kept around 6.5-7 . Which solution would I choose (A,B or C)?

The answer is B.

- If we're talking about bases, it will be the same curve but in opposite direction.



Exercises

- 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

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

- Similarly, the pKa of an acid can be calculated

- Predict then calculate the pH of a buffer containing
 - 0.1M HF and 0.12M NaF? ($K_a = 3.5 \times 10^{-4}$) **pH= 3.5**
 - 0.1M HF and 0.1M NaF, when 0.02M HCl is added to the solution? **pH= 3.29**

- What is the pH of a lactate buffer that contain 75% lactic acid and 25% lactate? ($\text{p}K_a = 3.86$) **pH= 3.38**

- 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. **M= 0.89**
N= 0.89

Extra practice questions

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 $[CH_3COO^-]/[CH_3COOH]$ ratio in an acetate buffer at pH 5.00 ?

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

4. A buffer is made by adding 0.2 M $HC_2H_3O_2$ and 0.15 M $NaC_2H_3O_2$. If 0.005 mol of NaOH is added to 125ml of this buffer, what is the pH ?
 $K_a = 1.8 \times 10^{-5}$

5. The K_b for ammonia (NH_3) is 1.8×10^{-5} . What is its K_a value?

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: 1.8

Q3: 2.3

Q4: 4.8

Q5: 5.5×10^{-10}