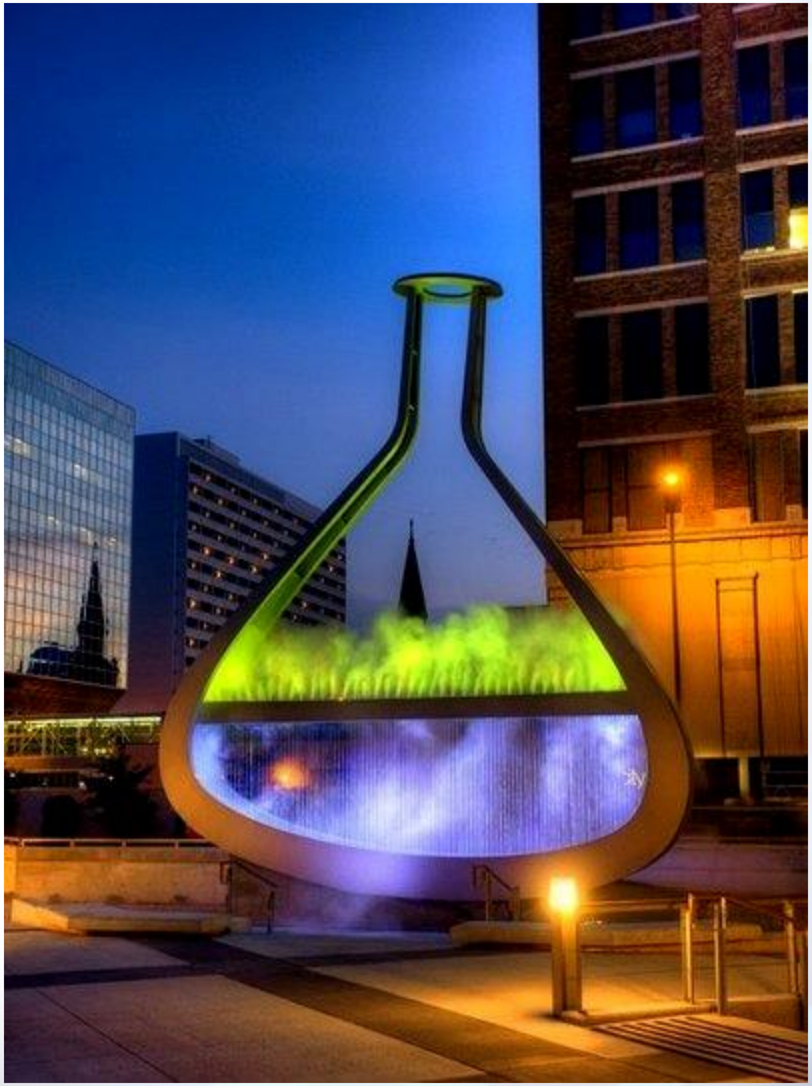
Analytical chemistry

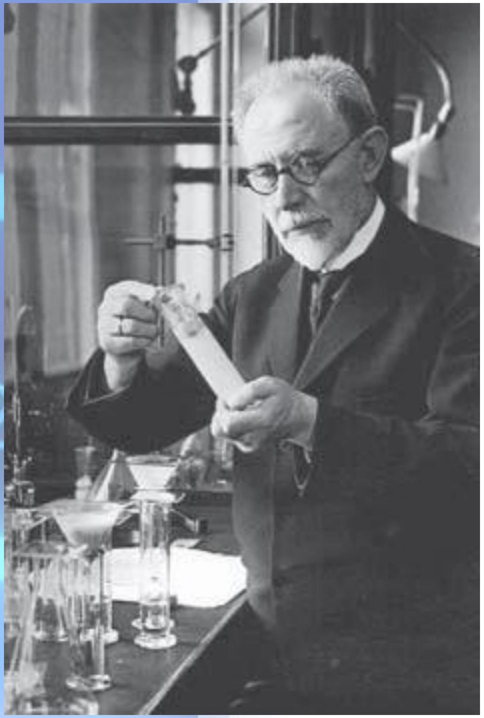
Lecture № 4

Acid - Base equilibria Part II



Acid-base equlibria in water

1816 year



Sören Sörenson

The pH scale

Sören Sörenson, head of the chemistry department at Carlsberg Laboratory (Carlsberg Brewery) invented the term *pH to describe this* effect and defined it as $-\log[H^+]$. The term *pH refers simply to "the* power of hydrogen." In 1924, he realized that the pH of a solution is a function of the "activit" of the H^+ ion, and published a second paper on the subject, defining it as $pH = -\log a_{H+}$.

$$pH = -\lg a_{H_3O^+} \qquad pH = -\lg[H_3O^+]$$

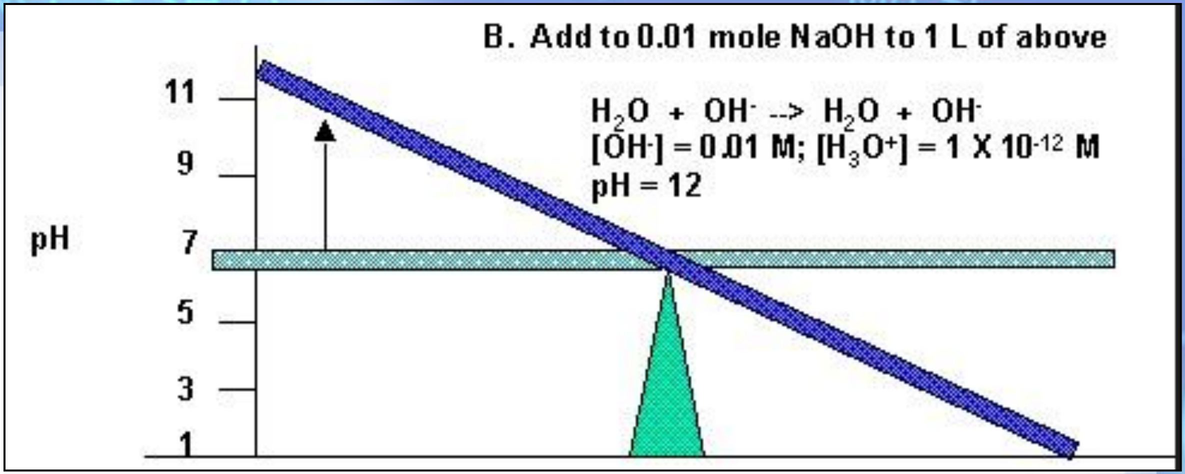
$$pOH = -\log[OH^-]$$

$$pK_w = pH + pOH$$

$$14.00 = pH + pOH$$

pAnything = −log Anything

0.01 M NaOH

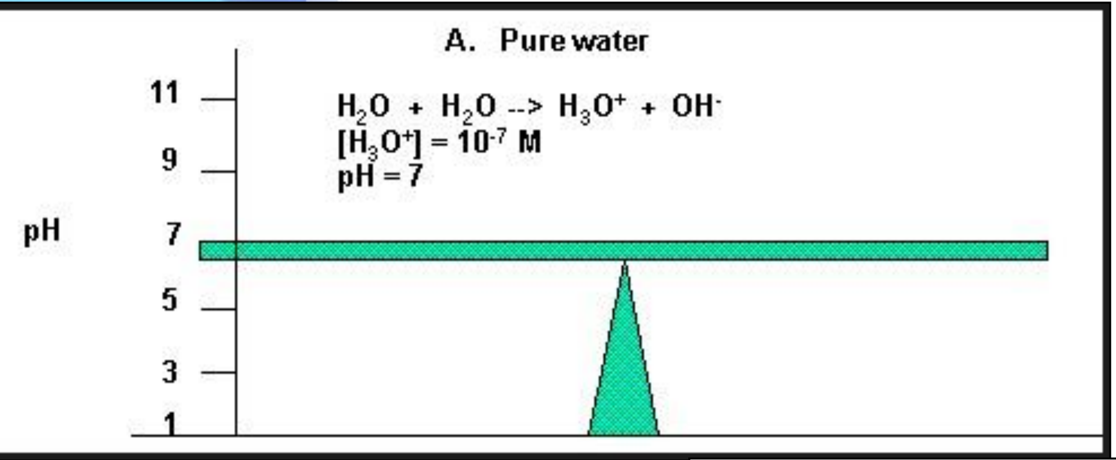


B. Add to 0.01 mole NaOH to 1 L of above

$H_2O + OH^- \text{-->} H_2O + OH^-$

$[OH^-] = 0.01$ M; $[H_3O^+] = 1 \times 10^{-12}$ M

pH = 12



A. Pure water

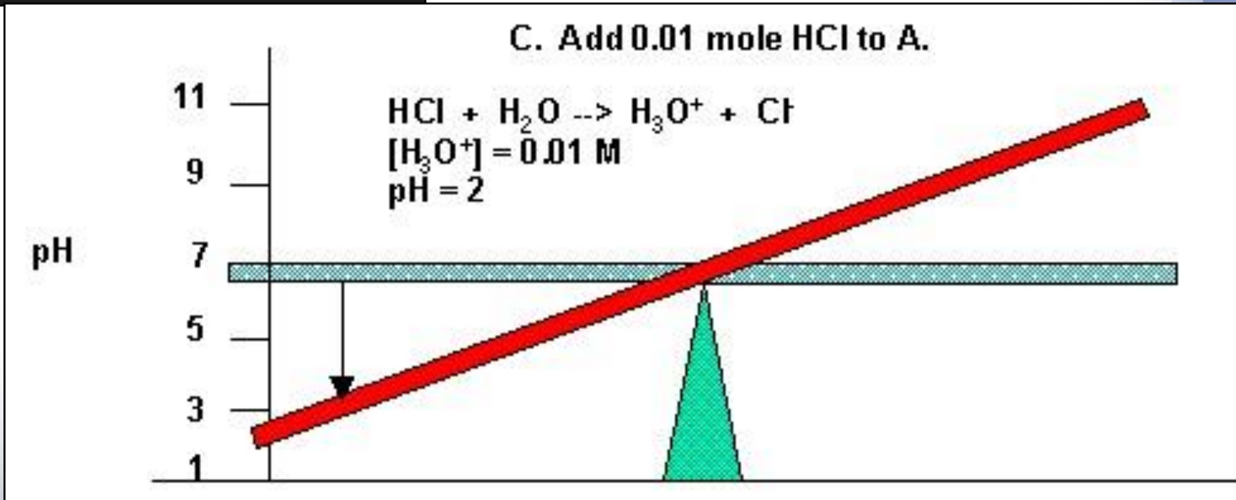
$H_2O + H_2O \text{-->} H_3O^+ + OH^-$

$[H_3O^+] = 10^{-7}$ M

pH = 7

Pure water

0.01 M HCl



C. Add 0.01 mole HCl to A.

$HCl + H_2O \text{-->} H_3O^+ + Cl^-$

$[H_3O^+] = 0.01$ M

pH = 2

ЗНАЧЕНИЯ pH- НЕКОТОРЫХ РАСТВОРОВ

0	🟥	Промышл. HCl (37 %)	-1,1
1	🟥	HCl (1:10)	0,0
2	🟥	Лимон	2,1
3	🟧	Яблочный сок, столовый уксус	2,3-2,5
4	🟥	Томатный сок	4,1
5	🟧	Черный кофе	5,0
6	🟨	Молоко	6,4-6,8
7	🟩	Вода	7,0
8	🟩	Слезы, кровь	7,0-7,4
9	🟫	Раствор пищевой соды 1% ($NaHCO_3$)	8,5
10	🟦		
11	🟦	Нашатырный спирт NH_4OH ; C = 0,1 моль/л	11,3
12	🟦	Раствор соды Na_2CO_3 ; C = 0,1 моль/л	11,5
13	⬛		
14	⬛	Раствор гидроксида натрия ; C = 0,1 моль/л	12,9

Calculations of pH Values in Aqueous Solutions

Strong acids

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

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

If $C_{HA} > 10^{-6}$ M, than we needn't to consider the H_3O^+ from autoprotolysis of water

$$\boxed{pH = -\lg C(HA)}$$

Strong acids

If the concentration of an acid is much less than 10^{-6} *M*, *then its contribution to the acidity will be negligible compared with the contribution* from water. Hence the sum of the two contributions must be taken.

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

$$[H_3O^+]'' = [OH^-]$$

$$[OH^-] = K_W/[H_3O^+]$$

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

$$[H_3O^+]' = C_{HA}$$

$$[H_3O^+] = [H_3O^+]' + [H_3O^+]''$$

$$[H_3O^+] = C_{HA} + \frac{K_W}{[H_3O^+]}$$

$$[H_3O^+]^2 - C_{HA}[H_3O^+] - K_W = 0$$

The pH of 10^{-9} *M HCl* *is not 9!*

Strong acids

Using the quadratic equation to solve

$$[H_3O^+] = \frac{C_{HA} + \sqrt{C_{HA}^2 + 4K_W}}{2}$$

$$pH = -\lg\left(\frac{C(HA) + \sqrt{C^2(HA) + 4Kw}}{2}\right)$$

Strong bases

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

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

If $C_B > 10^{-6}$ M, than we needn't to consider the H_3O^+ from autoprotolysis of water

$$C_B = [OH^-]$$

$$[OH^-] = K_W / [H_3O^+] = C_B$$

$$[H_3O^+] = K_W / C_B$$

$$\boxed{pH = pKw + \lg C(B)}$$

Strong bases

If the concentration of an base is much less than 10^{-6} *M, then its contribution to the acidity will be negligible compared with the contribution* from water. Hence the sum of the two contributions must be taken.

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

$$C_B = [OH^-]^{/}$$

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

$$[OH^-]^{//} = [H_3O^+]$$

$$[OH^-] = [OH^-]^{/} + [OH^-]^{//}$$

$$K_W = [H_3O^+][OH^-] = [H_3O^+](C_B + [H_3O^+])$$

$$[H_3O^+]^2 + [H_3O^+]C_B - K_W = 0$$

Using the quadratic equation to solve

Strong bases

$$[H_3O^+] = \frac{-C_B + \sqrt{C_B^2 + 4K_W}}{2}$$

$$pH = -\lg\left(\frac{-C(B) + \sqrt{C^2(B) + 4Kw}}{2}\right)$$

The contribution from the autoionization of water can be considered negligible if the concentration of protons or hydroxyl ions from an acid or base is 10^{-6} *M or greater.*

Weak acids

weak acids (or bases) are only partially ionized

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$

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

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

The ionization constant , the acidity constant

$$\alpha = \sqrt{\frac{K_a}{C_{HA}}}$$

Weak acids

For weak acids with α ≤ 5 % we neglect the contribution of hydrogen ions from the ionization of water and can to assume that $[HA] \approx C_{HA}$

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

$$[H_3O^+] = [A^-]$$

$$K_a = \frac{[H_3O^+]^2}{C_{HA}}$$

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

pH = 1/2 (pKa - lg C(HA)

Weak acids

For weak acids with $\alpha > 5\ \%$ we neglect the contribution of hydrogen ions from the ionization of water and can't to assume that $[HA] \neq C_{HA}$

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

$$[H_3O^+] = [A^-]$$

$$[HA] = C(HA) - [H_3O^+]$$

$$K_a = \frac{[H_3O^+]^2}{C_{HA} - [H_3O^+]}$$

$$[H_3O^+]^2 + K_a[H_3O^+] - K_a C_{HA} = 0$$

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

$$pH = -\lg\left(\frac{-Ka + \sqrt{Ka^2 + 4Ka \cdot C(HA)}}{2}\right)$$

Weak acids

If we have very weak acid with very small concentration ($C_{HA}K_a < 10^{-12}$ or $pK_a – lgC_{HA} < 12$) It's necessary to consider contribution of hydrogen ions from the ionization of water

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

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$

$$[H_3O^+] = [H_3O^+]' + [H_3O^+]''$$

$$[H_3O^+] = \frac{K_a C_{HA}}{[H_3O^+]} + \frac{K_W}{[H_3O^+]}$$

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

pH = - 1/2 lg (Ka•C(HA) + Kw)

Weak bases

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

$$BH^+ + H_2O \rightleftarrows B + H_3O^+$$

$$K_{BH^+} = \frac{[B][H_3O^+]}{[BH^+]}$$

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

$$K_H = K_b = \frac{[HOAc][OH^-]}{[OAc^-]}$$

K_H is called the hydrolysis constant of the salt and is the same as the basicity constant.

$$K_b = \frac{[HOAc][OH^-]}{[OAc^-]} \cdot \frac{[H^+]}{[H^+]}$$

$$K_a K_b = K_w$$

The product of K_a of any weak acid and K_b of its conjugate base is always equal to K_w

Weak bases

If α ≤ 5 %

$$pH = 1/2(pKw + pK_{BH+} + \lg C(B))$$

If α > 5 %

$$pH = -\lg\left(\frac{K_W + \sqrt{K_W^2 + 4Kw \cdot K_{BH+} \cdot C(B)}}{2C(B)}\right)$$

pH of a Monosalt of a Diacid Solution—pH of an Ampholyte Solution

Ampholyte

$$HA^{-} + H_2O \rightleftarrows H_3O^{+} + A^{2-}$$

$$HA^{-} + H_3O^{+} \rightleftarrows H_2A + H_2O$$

we neglect the contribution of hydrogen ions from the ionization of water; **HA^{-} - weak acid and weak base**

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

Mixture of 2 weak acids

For mixture of 2 weak acids HA_1 и HA_2 with Ka_1 и Ka_2.

$$[H_3O^+] = [A_1^-] + [A_2^-] + [OH^-]$$

$$[H_3O^+] = \frac{K_{a1}[HA_1]}{[H_3O^+]} + \frac{K_{a2}[HA_2]}{[H_3O^+]} + \frac{K_W}{[H_3O^+]}$$

$$[H_3O^+] = \sqrt{K_{a1}[HA_1] + K_{a2}[HA_2] + K_W}$$

Mixture of 2 weak acids

If $\alpha \leq 5\%$ **$[HA] \approx C_{HA}$**

if $K_a[HA] >> K_W$

$$[H_3O^+] = \sqrt{K_{a1}C_{HA_1} + K_{a2}C_{HA_2}}$$

For n weak acids:

$$[H_3O^+] = \sqrt{K_{a1}C_{HA_1} + \ldots + K_{a_n}C_{HA_n}}$$

Mixture of 2 weak acids

If HA_1 – strong, but a HA_2 – weak acid:

$$[H_3O^+] = [A_1^-] + [A_2^-] = C_{HA_1} + \frac{K_a[HA_2]}{[H_3O^+]}$$

$$[H_3O^+]^2 - C_{HA_1}[H_3O^+] - K_a[HA_2] = 0$$

$$[HA_2] \approx C_{HA_2}$$

$$\boxed{[H_3O^+] = \frac{C_{HA_1} + \sqrt{C_{HA_1}^2 + 4K_aC_{HA_2}}}{2}}$$

For 2 weak bases B_1 and B_2 with K_{BH^+1} и K_{BH^+2} .

Mixture of 2 weak bases

$$[OH^-] = [BH_1^+] + [BH_2^+]$$

$$\frac{K_W}{[H_3O^+]} = \frac{C_{B_1}[H_3O^+]}{K_{BH_1^+}} + \frac{C_{B_2}[H_3O^+]}{K_{BH_2^+}}$$

$$K_W = [H_3O^+]^2\left(\frac{C_{B_1}}{K_{BH_1^+}} + \frac{C_{B_2}}{K_{BH_2^+}}\right)$$

$$[H_3O^+] = \sqrt{\frac{K_W}{\frac{C_{B_1}}{K_{BH_1^+}} + \frac{C_{B_2}}{K_{BH_2^+}}}}$$

Mixture of a Strong and a Weak Acid

The addition of the strong acid induces the protonation of the conjugate base of the weak acid. The weak acid is less ionized when the strong acid is present than when it is alone at the same concentration. This phenomenon is called ***ionization repression*** ***(of the weak acid). The weak acid dissociation is repressed.***

Mixture of a Strong and a Weak Base

There is also an ionization repression of the weak base.

Solvents in Analytical Chemistry

Solvents are conveniently divided into those which promote the ionization of a solute (*ionizing solvents) and those which do not (non-ionizing solvents).* Some ionizing solvents are of major importance in analytical chemistry whilst others are of peripheral interest. A useful subdivision is into *protonic solvents such as water and the common acids, or nonprotonic solvents* which do not have protons available. Typical of the latter subgroup would be sulphur dioxide and bromine trifluoride. Non-protonic ionizing solvents have little application in chemical analysis. Ionizing solvents have one property in common, *self-ionization, which reflects their ability to produce ionization of a solute.* A final subdivision of ionizing protonic solvents can be made in terms of the behaviour of the solvent towards available protons from a solute. A basic or *protophilic solvent such as ammonia or an amine* will coordinate protons strongly, and in so doing accentuate the acidic properties of the acid.

$$\mathrm{RNH_2 + RCOOH = RNH_3^+ + RCOO^-}$$

On the other hand an acid or *protogenic solvent will be a poor proton acceptor, accentuating basic* properties. This effect is exemplified by the solution of nitric acid in anhydrous hydrofluoric acid, which shows how nitric acid (normally regarded as a strong acid) can behave as a Lowry–Brønsted base. Water and other hydroxylic solvents both donate and accept protons with reasonable facility and are termed *amphiprotic.*

FRACTIONS OF DISSOCIATING SPECIES AT A GIVEN pH: *α VALUES*

For acid H_2A

$$K_{a_1} = \frac{[HA^-][H_3O^+]}{[H_2A]} \qquad K_{a_2} = \frac{[A^{2-}][H_3O^+]}{[HA^-]}$$

$$C_{H_2A} = [H_2A] + [HA^-] + [A^{2-}]$$

$$C_{H_2A} = [A^{2-}]\frac{[H_3O^+]^2}{K_{a_1}K_{a_2}} + [A^{2-}]\frac{[H_3O^+]}{K_{a_2}} + [A^{2-}] =$$

$$[A^{2-}]\left(\frac{[H_3O^+]^2}{K_{a_1}K_{a_2}} + \frac{[H_3O^+]}{K_{a_2}} + 1\right) =$$

$$= [A^{2-}]\left(\frac{[H_3O^+]^2 + K_{a_1}[H_3O^+] + K_{a_1}K_{a_2}}{K_{a_1}K_{a_2}}\right)$$

$$\alpha(A^{2-}) = \frac{[A^{2-}]}{C_{H_2A}} = \frac{K_{a_1}K_{a_2}}{[H_3O^+]^2 + K_{a_1}[H_3O^+] + K_{a_1}K_{a_2}}$$

For acid H_2A

$$\alpha(HA^-) = \frac{[HA^-]}{C_{H_2A}} = \frac{[H_3O^+][A^{2-}]}{K_{a_2}C} = $$

$$= \frac{K_{a_1}[H_3O^+]}{[H_3O^+]^2 + K_{a_1}[H_3O^+] + K_{a_1}K_{a_2}}$$

$$\alpha(H_2A) = \frac{[H_2A]}{C_{H_2A}} = \frac{[H_3O^+]^2[A^{2-}]}{K_{a_1}K_{a_2}C} = $$

$$= \frac{[H_3O^+]^2}{[H_3O^+]^2 + K_{a_1}[H_3O^+] + K_{a_1}K_{a_2}}$$

For acid HA

$$\alpha(HA) = \frac{[H_3O^+]}{[H_3O^+] + K_a}$$

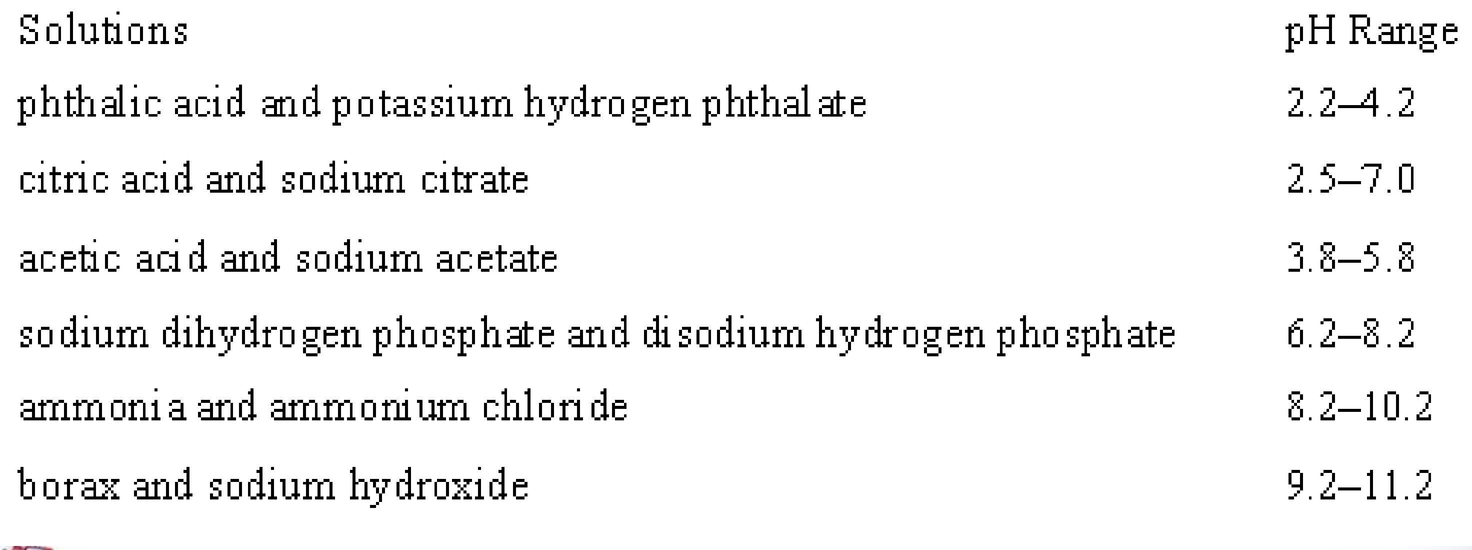
$$\alpha(HA) = \frac{1}{1 + 10^{pH - pK_a}}$$

$$\alpha(A^-) = \frac{K_a}{[H_3O^+] + K_a}$$

$$\alpha(A^-) = \frac{1}{1 + 10^{pK_a - pH}}$$

Buffer Solutions

A **buffer** is defined as a solution that **resists change in pH** when a small amount of an acid or base is added or when the solution is diluted. While carrying out a reaction, this is very useful for maintaining the pH within an optimum range. A buffer solution consists of a mixture of a weak acid and its conjugate base, or a weak base, and its conjugate acid at predetermined concentrations or ratios.



Solutions	pH Range
phthalic acid and potassium hydrogen phthalate	2.2–4.2
citric acid and sodium citrate	2.5–7.0
acetic acid and sodium acetate	3.8–5.8
sodium dihydrogen phosphate and disodium hydrogen phosphate	6.2–8.2
ammonia and ammonium chloride	8.2–10.2
borax and sodium hydroxide	9.2–11.2

Henderson–Hasselbach equation

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

$$pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$pH = pK_a + \log\frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

The buffer intensity is maximum *when the ratio is unity, when the pH = pKa.*

$$pH = pK_a \pm 1$$

The amount of acid or base that can be added without causing a large change in pH is governed by the *buffering capacity* of the solution.

$$\beta = dC_b/dpH,$$

$$\beta = -dC_a/dpH,$$

Buffer capacity – the amount of acid or base the buffer can react with before giving a significant pH change.

$$\beta = 2{,}3\frac{C_{HA}C_{A^-}}{C_{HA}+C_{A^-}}$$

$$\beta = 2{,}3[H_3O^+]\frac{K_a(C_{HA}+C_{A^-})}{(K_a+[H_3O^+])^2}$$

Mechanism of the Buffer Effect

$$[A^-] = C_A - C,$$

$$[HA] = C_{HA} + C.$$

$$\boxed{H_3O^+} + A^- \rightleftarrows \boxed{HA} + H_2O$$

$$\boxed{OH^-} + HA \rightleftarrows \boxed{A^-} + H_2O$$

The *C moles of hydroxonium ions added have been completely* transformed into *C moles of the weak acid HA. Briefly, due to the buffer effect, the* addition of *C mol/L of the strongest acid that can exist in water (H_3O^+) has been* commuted to the addition of *C mol/L of a weak acid that is very poorly dissociated.*

If the solution is diluted, the pH of the solution does not change.

Mechanism of the Buffer Effect

$$\boxed{H_3O^+} + A^- \rightleftarrows \boxed{HA} + H_2O$$

$$\boxed{OH^-} + HA \rightleftarrows \boxed{A^-} + H_2O$$

If a small amount of a strong acid is added, it will combine with an equal amount of the A^- to convert it to HA. That is, in the equilibrium HA $\rightleftharpoons$ H^+ + A^-, Le Chˆatelier’s principle dictates added H^+ will combine with A^- to form HA, with the equilibrium lying far to the left if there is an excess of A^-*. The change in the ratio* $[A^-]$*/[HA] is small and hence the change in pH is small. If the acid had been added* to an unbuffered solution (e.g., a solution of NaCl), the pH would have decreased markedly. If a small amount of a strong base is added, it will combine with part of the HA to form an equivalent amount of A^-*. Again, the change in the ratio is small.*