

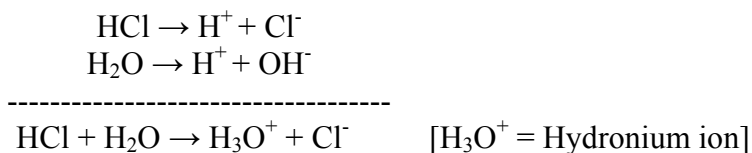
PAPER: MCBACOR03T (ACIDS, BASES, pH & BUFFER)

Dr. Sandip Bandopadhyay, WBES

Assistant Professor, Dept. of Microbiology

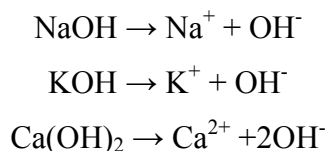
Bidhannagar College, Kolkata - 700064

Acids & Bases: a) According to the **Arrhenius concept**, acids are those molecules which in the aqueous solution produces H^+ ion. Eg: HCl (hydrochloric acid), H_2SO_4 , HNO_3 are acids in aqueous solution.



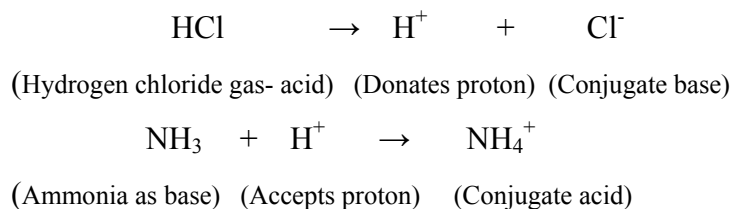
Similarly, in aqueous solution, $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$
 $HNO_3 \rightarrow H^+ + NO_3^-$

According to the **Arrhenius concept**, bases are those molecules which in the aqueous solution produces OH^- ion. Eg: NaOH, KOH, $Ca(OH)_2$ etc.



Drawbacks: Arrhenius concept relies only on aqueous solution, and therefore it fails to explain the acidity of Hydrogen chloride (HCl) gas as well as alkalinity of NH_3 gas. There are many acids and bases in the world which do not dissolve in aq. Solution and therefore they can not be designated as acid and bases respectively according to this concept.

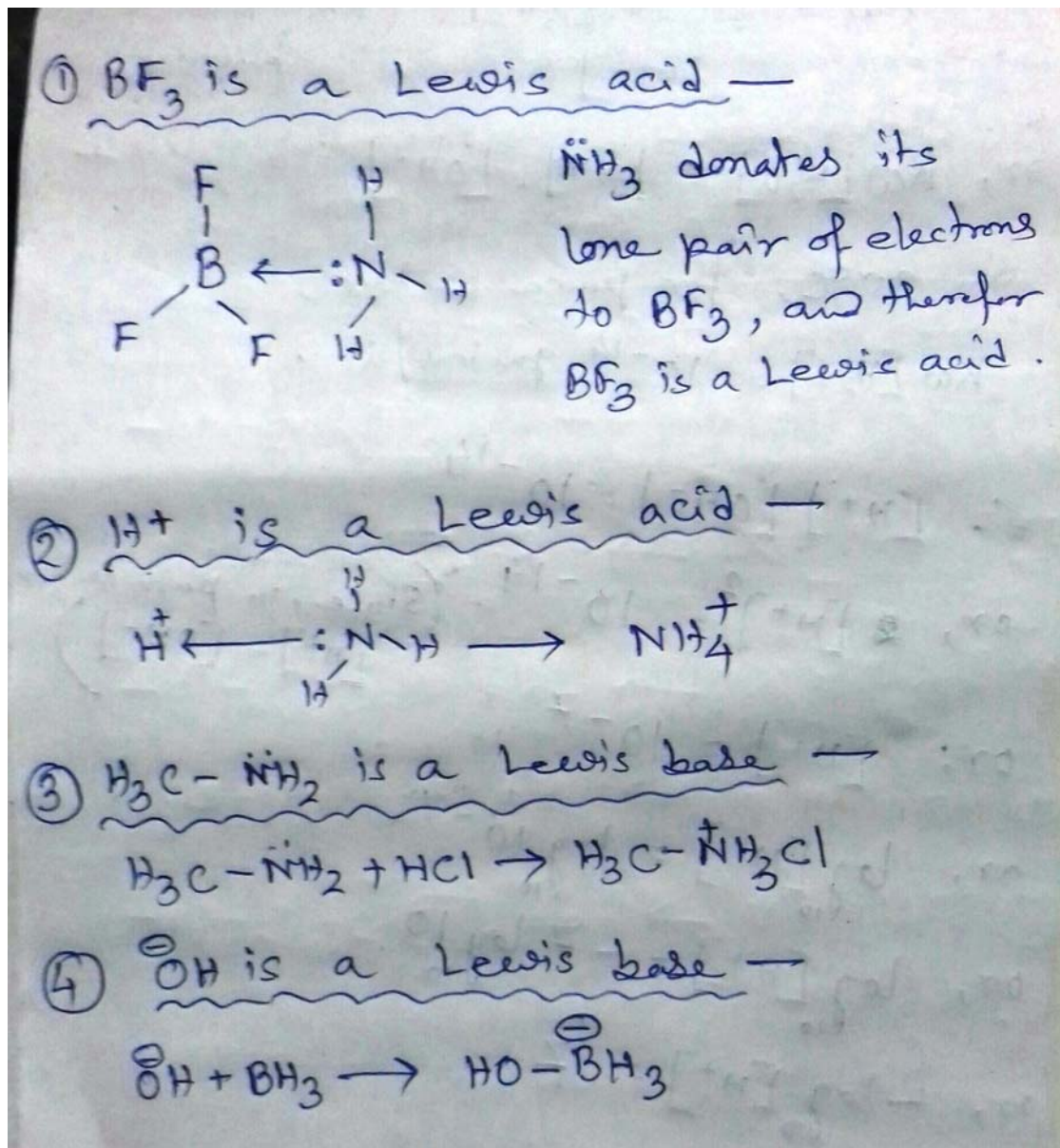
b) According to the **Bronsted-Lowry concept**, acids are simply proton (H^+) donor and bases are proton (H^+) accepter. It can explain the acidity of Hydrogen chloride (HCl) gas as well as alkalinity of NH_3 gas.



According to the **Bronsted-Lowry concept**, every acid (HCl) when donates proton it produces a conjugate base (Cl^-) and every base (NH_3) when receives proton it produces a conjugate acid (NH_4^+). Thus, upon dissociation, an acid or base produces a **conjugate acid-base pair**. For eg, HCl & Cl^- is a conjugate acid-base pair and NH_3 & NH_4^+ is also a conjugate acid-base pair. Similarly, H_2SO_4 is the acid and SO_4^{2-} is a conjugate base, and NaOH is a base and Na^+ is a conjugate acid.

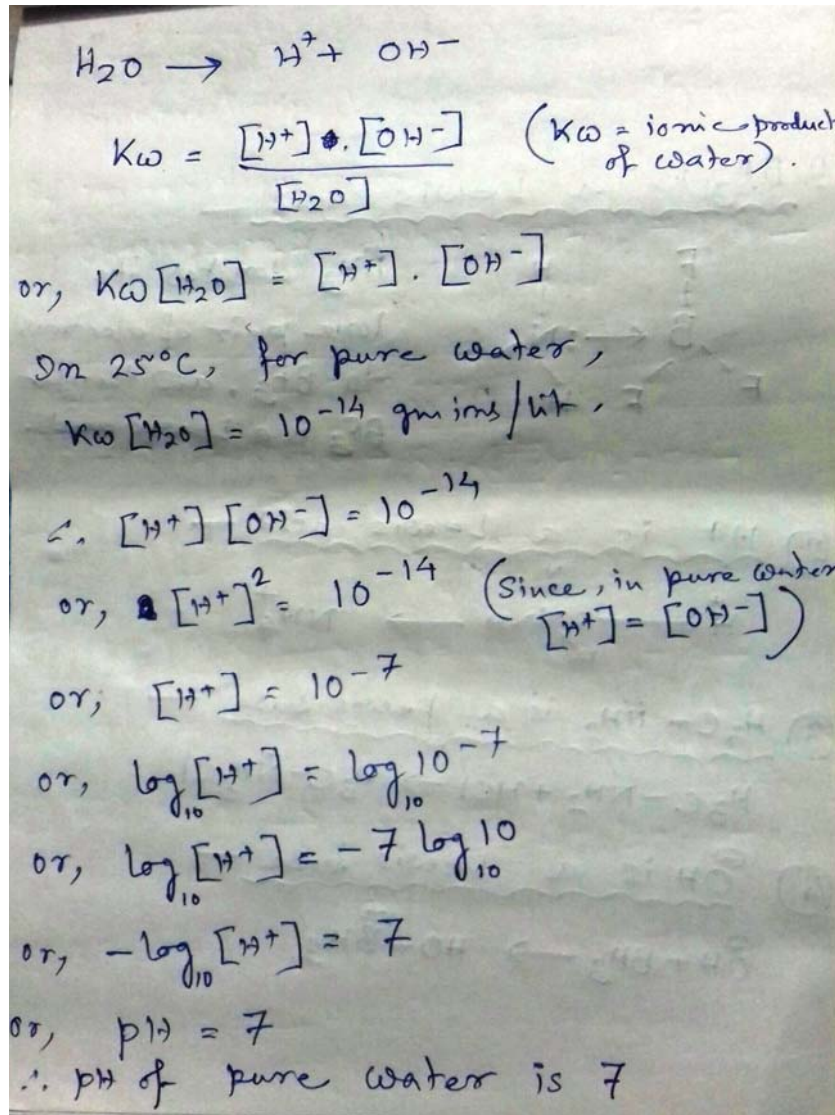
Drawbacks: There are some acids like BF_3 , which lacks any proton. Bronsted-Lowry concept fails to explain the acidity of that compound. Similarly, it fails to explain the basicity of $\text{NH}_2(\text{CH}_3)$.

c) According to the **Lewis concept**, Acids are the electron pair acceptor, where as, bases are electron pair donor. It can explain the acidity of BF_3 , and basicity of $\text{NH}_2(\text{CH}_3)$.

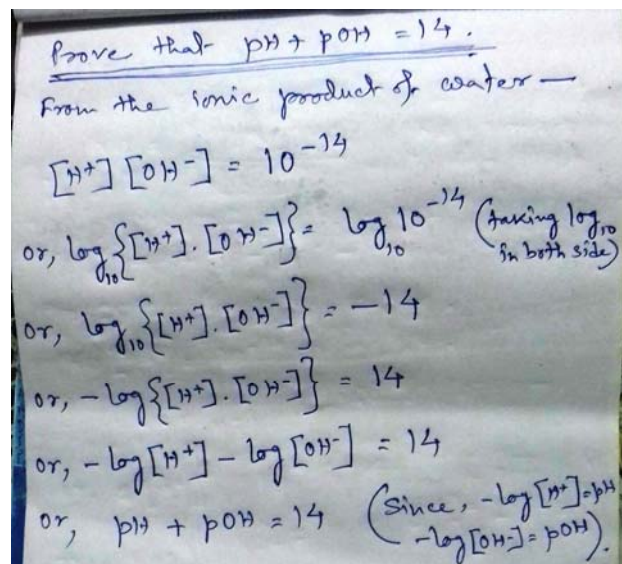


HSAB rule: Hard-Soft (Lewis) Acid-Base pair interaction is followed by HSAB rule. According to the HSAB rule, H^+ , Na^+ , K^+ , Zn^{2+} etc are hard acids, whereas, Ag^+ , Pt^{2+} , Ni^0 are soft acids. Ammonia, amines, COO^- , F^- , Cl^- are hard bases, where as CO , I^- etc are soft bases. Generally, **hard acids react with hard bases and soft acids react with soft bases**. The hard acid-hard base interaction is enthalpy favoured, whereas, soft acid-soft-base interaction is entropy favoured.

IONIC PRODUCT OF WATER



- **Definition of pH:** pH is the negative logarithm of hydrogen ion concentration of a solution. Eg: For pure water pH is 7.0.
- **Prove that $\text{pH} + \text{pOH} = 14$**



For pure water, we know, $\text{pH} = 7$, and $\text{pH} + \text{pOH} = 14$

Therefore, $\text{pH} + \text{pOH} = 14$

$$\text{Or, } 7 + \text{pOH} = 14$$

$$\text{Or, } \text{pOH} = 14 - 7$$

$$\text{Or, } \text{pOH} = 7 \text{ (Proved)}$$

• PROBLEMS

1. What is the pH of 10^{-1} N HCl?

A: $[\text{H}^+]$ of HCl = 10^{-1} N

Therefore, $[\text{H}^+] = 10^{-1}$

$$\text{Or, } \log [\text{H}^+] = \log 10^{-1} \quad (\text{Taking log in both side})$$

$$\text{or, } \log [\text{H}^+] = -1 \quad (\text{Since } \log 10 = 1)$$

$$\text{or, } \text{pH} = 1$$

2. What is the pH of 10^{-5} M H_2SO_4 ?

A: $[\text{H}^+]$ of $\text{H}_2\text{SO}_4 = 10^{-5}$ M

Therefore, $[\text{H}^+] = 10^{-5}$

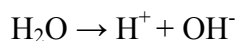
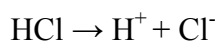
$$\text{Or, } \log [\text{H}^+] = \log 10^{-5} \quad (\text{Taking log in both side})$$

$$\text{or, } \log [\text{H}^+] = -5 \quad (\text{Since } \log 10 = 1)$$

$$\text{or, } \text{pH} = 5$$

3. What is the pH of 10^{-8} N HCl?

A: As the concentration of HCl is too low (10^{-8} N), therefore dissociation of water, i.e, aqueous solution should be considered.



Therefore, $[\text{H}^+] = [\text{H}^+]_{\text{H}_2\text{O}} + [\text{H}^+]_{\text{HCl}}$

$$\text{Or, } [\text{H}^+] = 10^{-7} + 10^{-8} \quad (\text{Since, } [\text{H}^+]_{\text{H}_2\text{O}} \text{ of pure water is } 10^{-7})$$

$$\text{Or, } \log [\text{H}^+] = \log \{10^{-7} + 10^{-8}\}$$

$$\text{Or, } \log [\text{H}^+] = \log \{10^{-7}(1+10^{-1})\}$$

$$\text{Or, } \log [\text{H}^+] = \log \{10^{-7} \times 1.1\}$$

$$\text{Or, } \log [\text{H}^+] = \log 10^{-7} + \log 1.1$$

$$\text{Or, } \log [\text{H}^+] = -7 + 0.04$$

$$\text{Or, } \log [\text{H}^+] = -6.96$$

$$\text{Or, } \text{pH} = 6.96$$

[Note: An acid solution, even in very dilute concentration pH remains below 7. Therefore, for the calculation of pH of a dilute acid, dissociation of water should be calculated]

4. What is the pH of 10^{-4} N NaOH?

A: $[\text{OH}^-] = 10^{-4}$ N

Therefore, $\log [\text{OH}^-] = \log 10^{-4}$ (taking log in both side)

Or, $\log [\text{OH}^-] = -4$

Or, $\text{pOH} = 4$

We know, $\text{pH} + \text{pOH} = 14$

Therefore, $\text{pH} = 14 - \text{pOH}$

Or, $\text{pH} = 14 - 4 = 10$

BUFFER SOLUTION

- **Definition:** buffer is an aqueous solution consisting of a mixture of a weak acid and its conjugate base, or vice versa. It resists the change of pH of the solution when a small amount of strong acid or base is added to it.

Eg: 1. **Acetate buffer** is the mixture of CH_3COOH (a weak acid) & its conjugate base CH_3COO^- .

2. **Phosphate buffer** is the mixture of NaH_2PO_4 , an acidic salt, with Na_2HPO_4 , a basic salt.

3. **Bicarbonate buffer** is the mixture of weak acid carbonic acid (H_2CO_3) and its conjugate base bicarbonate ion (HCO_3^-).

4. **Ammonium buffer** is the mixture of weak base NH_4OH and its conjugate acid NH_4^+

Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications. In nature, there are many systems that use buffering for pH regulation. For example, the **bicarbonate buffering system is used to regulate the pH of blood.**

- **Mechanism of Buffer action:**

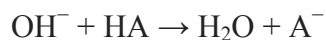
Buffer solutions achieve their resistance to pH change because of the presence of equilibrium between the weak acid HA and its conjugate base A^- :



When some **strong acid** is added to an equilibrium mixture of the weak acid and its conjugate base, [i.e., **hydrogen ions (H^+) are added**], the **equilibrium is shifted to the left, in accordance with Le Châtelier's principle**. Because of this, the hydrogen ion concentration increases by less than the acid added. The extra H^+ is taken up by the A^- ion present in the solution.



Similarly, if **strong alkali is added** to the mixture, the hydrogen ion concentration decreases by less than the amount expected for the quantity of alkali added. The hydrogen ion concentration decreases by less than the amount expected because most of the added hydroxide ion is consumed in the reaction -



Only a little is consumed in the neutralization reaction (which is the reaction that results in an increase in pH) $\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$

Once the acid is more than 95% **de-protonated**, the pH rises rapidly because most of the added alkali is consumed in the neutralization reaction.

- **Buffer capacity (β)**

Buffer capacity is a quantitative measure of the resistance to change of pH of a solution containing a buffering agent. It can be defined as follows:

$$\text{Buffer capacity } (\beta) = \frac{\text{Amount of acid/alkali added to the given solution}}{\text{Change of pH of the solution}}$$

- **Applications**

1. The pH of a solution containing a buffering agent can only vary within a narrow range, regardless of what else may be present in the solution. In biological systems this is an essential condition for **enzymes** to function correctly. For example, in **human blood** a mixture of **carbonic acid** (H_2CO_3) and **bicarbonate** (HCO_3^-) is present in the **plasma** fraction; this constitutes the major mechanism for maintaining the pH of blood between 7.35 and 7.45. Outside this narrow range (7.40 ± 0.05 pH unit), **acidosis** and **alkalosis** metabolic conditions rapidly develop, ultimately leading to death if the correct buffering capacity is not rapidly restored.

If the pH value of a solution rises or falls too much, the effectiveness of an enzyme decreases in a process, known as denaturation which is usually irreversible. The majority of biological samples that are used in research are kept in a buffer solution, often **phosphate buffered saline** (PBS) at pH 7.4.

2. In industry, buffering agents are used in **fermentation** processes and in setting the correct conditions for dyes used in colouring fabrics.

3. They are also used in chemical analysis and calibration of **pH meters**.

Preparation of Buffers: For buffers in acid regions (Like [Acetate buffer, pH range 3 – 5](#)), the pH may be adjusted to a desired value by adding a strong acid such as [hydrochloric acid](#) to the particular buffering agent. Acetate buffer can be made from a mixture of acetic acid and [sodium acetate](#).

For alkaline buffers (Like [Glycine-NaOH buffer, pH range 8 – 11](#)), a strong base such as [sodium hydroxide](#) may be added. Alternatively, a buffer mixture can be made from a mixture of an acid and its conjugate base. Similarly, an alkaline buffer can be made from a mixture of the base and its conjugate acid.

- **Universal buffer mixtures**

By combining substances with pK_a values differing by only two or less and adjusting the pH, a wide range of buffers can be obtained. [Citric acid](#) is a useful component of a buffer mixture because it has three pK_a values, separated by less than two. The buffer range can be extended by adding other buffering agents. The following mixtures ([McIlvaine's buffer solutions](#)) have a buffer range of pH 3 to 8.

A mixture containing [citric acid](#), [monopotassium phosphate](#), [boric acid](#), and [diethyl barbituric acid](#) can be made to cover the pH range 2.6 to 12.

Other universal buffers are the Carmody buffer and the [Britton–Robinson buffer](#), developed in 1931.

Calculating pH of the buffer

Buffer is the mixture of a weak acid (HA) and its conjugate base (A^-). Dissociation of acid in the buffer mixture can be designated as: $H^+ + A^- \rightleftharpoons HA$

Therefore, K_a , the dissociation constant of the acid is –

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

Or, $\log K_a = \log [H^+] + \log [A^-]/[HA]$ (taking log in both side)

Or, $-\log K_a = -\log [H^+] - \log [A^-]/[HA]$ (taking – sign in both side)

Or, $pK_a = pH - \log [A^-]/[HA]$

Or, **$pH = pK_a + \log [A^-]/[HA]$**

This equation is known as [Henderson-Hasselbalch equation](#).

- **Polyprotic acids**

Polyprotic acids are acids that can lose more than one proton. The constant for dissociation of the first proton may be denoted as K_{a1} , and the constants for dissociation

of successive protons as K_{a2} , K_{a3} etc. **Citric acid** and **Phosphoric acid** is an example of a polyprotic acid (H_3A), as it can lose three protons.

Dissociation of polyprotic acid:

Dissociation of Phosphoric Acid

$$H_3PO_4 \xrightleftharpoons{K_{a1}} H^+ + H_2PO_4^-$$

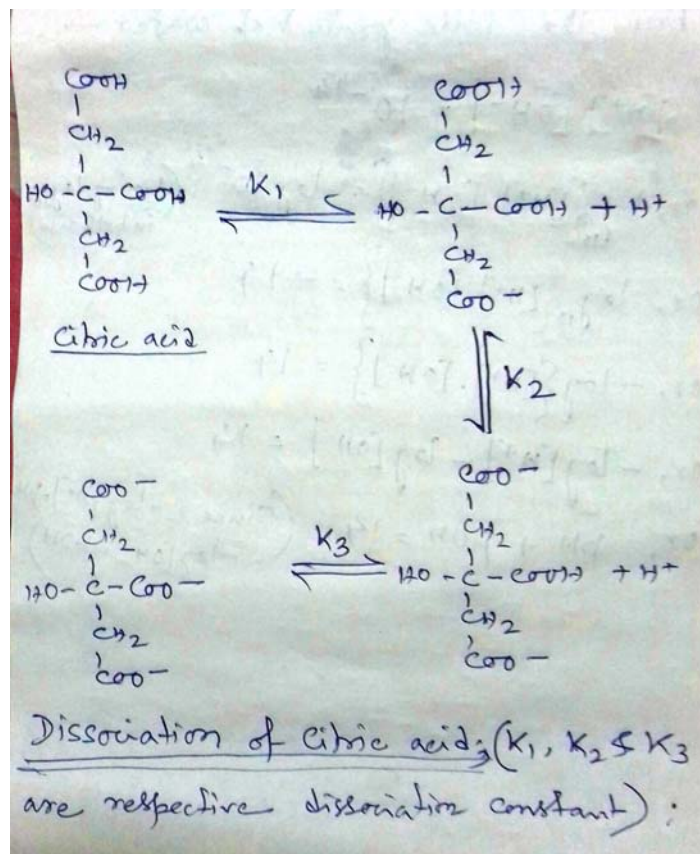
$$H_2PO_4^- \xrightleftharpoons{K_{a2}} H^+ + HPO_4^{2-}$$

$$HPO_4^{2-} \xrightleftharpoons{K_{a3}} H^+ + PO_4^{3-}$$

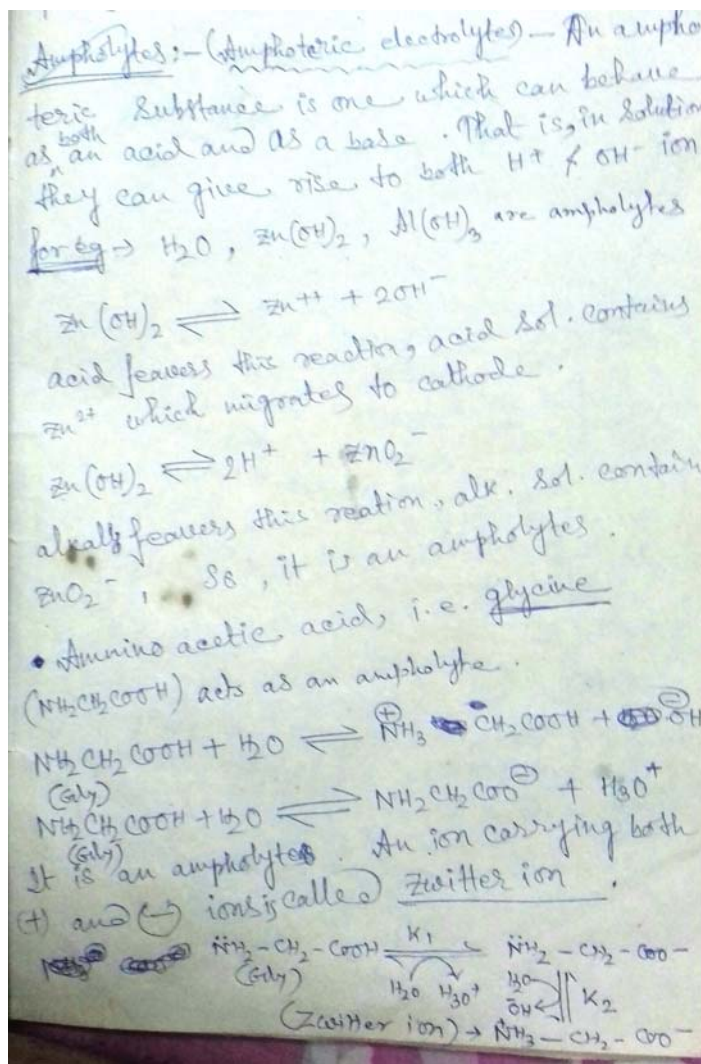
(K_{a1}, K_{a2}, K_{a3} are respective dissociation constant)

Titration curve of Polyprotic Acid

When polyprotic acid, like phosphoric acid is titrated with NaOH, the acid gradually loses its all protons by the alkali.



Ampholytes/Amphoteric Electrolyte



PROBLEMS ON BUFFER SOLUTION

1. Calculate the pH of a buffer solution made from 0.20 mol/L CH_3COOH and 0.50 mol/L CH_3COO^- . The acid dissociation constant of $HC_2H_3O_2$ is 1.8×10^{-5} .

Solution:

Plug the values into the Henderson-Hasselbalch equation for a weak acid and its conjugate base.



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

$$pH = -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.50 \text{ mol/L}}{0.20 \text{ mol/L}}\right)$$

$$pH = -\log(1.8 \times 10^{-5}) + \log(2.5)$$

$$pH = 4.74 + 0.40$$

$$pH = 5.14$$

2. How many moles of sodium acetate and acetic acid must you use to prepare 1.00 L of a 0.100 mol/L buffer with pH 5.00.

Solution

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$5.00 = 4.74 + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$\log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = 0.26$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{0.26} = 1.82$$

$$[\text{A}^-] = 1.82[\text{HA}]$$

$$\text{Also, } [\text{A}^-] + [\text{HA}] = 0.100 \text{ mol/L}$$

$$1.82[\text{HA}] + [\text{HA}] = 0.100 \text{ mol/L}$$

$$2.82[\text{HA}] = 0.100 \text{ mol/L}$$

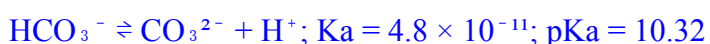
$$[\text{HA}] = \mathbf{0.0355 \text{ mol/L}}$$

$$[\text{A}^-] = (0.100 - 0.0355) \text{ mol/L} = \mathbf{0.0645 \text{ mol/L}}$$

Answer: You need 0.0355 mol of acetic acid and 0.0645 mol of sodium acetate to prepare 1 L of the buffer.

3. How you would make 100.0 ml of a 1.00 mol/L buffer solution with a pH of 10.80 to be made using only sodium carbonate, sodium hydrogen carbonate and water? How much sodium carbonate and sodium hydrogen carbonate would you use?

The chemical equation for the equilibrium is



Ans: The Henderson-Hasselbalch equation is

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$10.80 = 10.32 + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$\log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = 10.80 - 10.32 = 0.48$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = \text{Antilog of } 0.48 = 3.02$$

$$[\text{A}^-] = 3.02[\text{HA}]$$

$$\text{Also, } [\text{A}^-] + [\text{HA}] = 1.00 \text{ mol/L}$$

$$3.02[\text{HA}] + [\text{HA}] = 1.00 \text{ mol/L}$$

$$4.02[\text{HA}] = 1.00 \text{ mol/L}$$

$$[\text{HA}] = 1.00/4.02 = \mathbf{0.2488 \text{ mol/L}}$$

$$[\text{A}^-] = 3.02[\text{HA}] = 3.02 \times 0.2488 \text{ mol/L} = \mathbf{0.7512 \text{ mol/L}}$$

Calculate the masses of NaHCO_3 and of Na_2CO_3 in 100 ml, i.e., 0.1 L solution:

$$\text{Mass of NaHCO}_3 = 0.1 \text{ L} \times 0.2488 \text{ mol NaHCO}_3/\text{L} \times 84.01 \text{ g NaHCO}_3/\text{mol} = 2.09 \text{ g NaHCO}_3 \quad [\text{since MW of NaHCO}_3=84.01]$$

$$\text{Mass of Na}_2\text{CO}_3 = 0.1 \text{ L} \times 0.7512 \text{ mol Na}_2\text{CO}_3/\text{L} \times 106.0 \text{ g Na}_2\text{CO}_3/\text{mol} = 7.96 \text{ g Na}_2\text{CO}_3 \quad [\text{since MW of Na}_2\text{CO}_3=106.0]$$

You would transfer 2.09 g of NaHCO_3 and 7.96 g of Na_2CO_3 to a 100 mL volumetric flask and make up to the mark with distilled water.

Solve the problem:

4. What is the pH of a solution containing 0.02 M HA and 0.01 M A^- ? pK_a of HA = 5.0.
5. a) A solution was prepared by dissolving 0.02 moles of acetic acid (HOAc ; $\text{pK}_a = 4.8$) in water to give 1 liter of solution. What is the pH?
b) To this solution was then added 0.008 moles of concentrated sodium hydroxide (NaOH). What is the new pH? (In this problem, you may ignore changes in volume due to the addition of NaOH).
c) An additional 0.012 moles of NaOH is then added. What is the pH?