

Applying Henderson-Hasselbalch Equation in pH Determination of Buffer (Acetic acid-Sodium Acetate) Solution at Temperature, 298K

ABSTRACT

In article, we have reported the applying of Henderson-Hasselbalch equation in determination of pH of acetic acid and sodium acetate buffer solutions at about 298 Kelvin as room temperature. In preparation of these buffer solutions, we have taken 1.5 ml of glacial acetic acid into 100 ml of standard flask for making up 0.2M of acetic acid solution, and 0.64 gm of sodium acetate were dissolved into 100 ml distilled water. Now, we taken 36.2 ml prepared solution of sodium acetate into 100 ml of standard flask and added 14.8 ml of prepared acetic acid to make its volume 100 ml by using of distilled water, it is a buffer. In measuring of pH of prepared buffer solutions, we have been using a calibrated digital pen pH meter for accurate and quick reading. In observation, the pH of buffer solutions a quite fluctuation was appeared. But, it has gradually raised by adding small amount of basic 5N NaOH solution into buffer sample, and, an adjusted pH was being to 4.7 as well.

Keywords: Henderson-Hasselbalch equation, acetic acid, sodium acetate, pH, buffer solution.

GRAPHICAL ABSTRACT



[1]- INTRODUCTION:

Indeed, the solubility of an ionic compounds in buffer solutions is decreased by the presence a common ions and it obey the Le Chatelier's principle¹. These principle states that, if a dynamic equilibrium is disturbed by the changing the conditions, the equilibrium position is shifts to

counteract the change to reestablish an equilibrium. The dissociation of any substances like as solute into solvents²⁻⁶, was earlier proved by Nernst in 1891 with given partition law, $K = C_A/C_B$ ⁷. A literature survey have reported about the determination of pH of buffer solutions with bellow described relationships as well⁸⁻¹⁵. A buffer solution contains either a weak acid and its salt with a strong base, or a weak base and its salt with strong acid. The buffer solution is a solution that can resist pH change by addition of an acidic or basic substances. Because of common ion effect in acetic acid-sodium acetate buffer solution which is the suppression of the degree of dissociation of a weak electrolyte by the addition of a strong electrolyte having an ion common with that of the weak electrolyte¹⁶. The general pH relation which was given by Peter Sorensen (1909) is,

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

Where, the log is the base -10 logarithm, and, the $[\text{H}^+]$ is stands for the concentration of H^+ ions in solution, as given in mole per litre. The pH or concentration of H^+ ions in solution is a measure of the acidity or basicity of solution. From equation (1), the pH is a negative logarithm of hydrogen (H^+) ions concentration. In our present article, we have reported the Henderson equation, which latter on modified by Hasselbalch for determination of potential of hydrogen (pH) of the acetic acid-sodium acetate buffer solutions at room temperature (298 Kelvin) by using of digital pH meter. According to the mass law, the ionization reaction of pure solution for a weak acid is as $\text{HA} = \text{H}^+ + \text{A}^-$, the equilibrium condition are defined by the equation of the concentration law, $K (\text{HA}) = (\text{H}^+)(\text{A}^-)$. Where, the enclosed quantities is stand for concentrations of the respective substances and K is the ionization constant of the acid. This relation may be written as in more convenient form is, $(\text{H}^+) = K (\text{HA}) / (\text{A}^-)$ ¹⁷. For buffer solutions the described Henderson equation is modified as follows,

$$\text{pH} = \text{pKa} + \log [\text{salt/acid}] \dots\dots\dots (2)$$

This above equation (2) is known as Henderson-Hasselbalch equation and it applicable for all buffer solutions. Here, the [salt] and [acid] is the concentration of the salt and acid in buffer, respectively. And, the pKa is the value of pK of acid and, when the concentration of acid and the salt is equal then pH of buffer solution is equal to the pKa, (pH = pka). By applying equation (2) we can calculated the pH value of a given buffer solutions¹⁸. For example, the buffer of acetic acid and sodium acetate is an acidic buffer with pH 5.36 and, the pKa of acetic acid is given as 4.76. Hence, from equation (2) we get,

By substituting of given values,

$$4.76 = 4.76 + \log [\text{salt/acid}]$$

$$\text{Or, } 4.76 - 4.76 = \log [\text{salt/acid}] = 0$$

Thus, $[\text{salt}] = [\text{acid}]$ as $\log 1 = 0$. For buffer solutions, the above equation (2) can be written as,

$$\text{pH} = \text{pK}_a + \log_{10} \left(\frac{[\text{A}^-]}{[\text{HA}]} \right) \dots\dots\dots(3)$$

Where, $[\text{A}^-]$ and $[\text{HA}]$ is as concentration of weak acid with its salt or, conjugated acid-base pair in buffer solutions.

[2]- EXPERIMENTAL:

In experimental, the all required materials, chemicals and reagents are being an analytical graded and laboratory based standard which have been used further as without purification for study. Here, the glacial acetic acid (CH_3COOH ; 99-100%) is of Merck Specialities Private Limited and the sodium acetate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) crystal pure of E. Merck (India) Pvt. Ltd., Worli, Mumbai-400018, India. Typically, the carbonate free a basic NaOH solution of 5N is prepared well by adopting of Vogel procedure¹⁹. Here, firstly, we have prepared a 0.2M of acetic acid by taken 1.5 ml of glacial acetic acid into distilled water and make the total volume upto 100 ml. After then, for preparation of solution of sodium acetate we take a 0.64 gm of sodium acetate was dissolved into 100 ml distilled water. Now, we pipette out about 36.2 ml of prepared sodium acetate solution and poured it into a 100 ml of standard flask and added 14.8 ml of acetic acid, and by using distilled water make it volume 100 ml, respectively. These mixed both solutions are as buffer solution. Now, we measured the pH of this prepared buffer solution with using Wellon's digital pen pH meter for accurate and quick resolution of reading. Notably, before measuring of pH, the pH meter is standardized or calibrated first with its electrode tip and junction submerged in buffer and wash the electrode with distilled water and then introduced into prepared 0.2M acetic acid-sodium acetate buffer solutions.

[3]- RESULTS AND DISCUSSION:

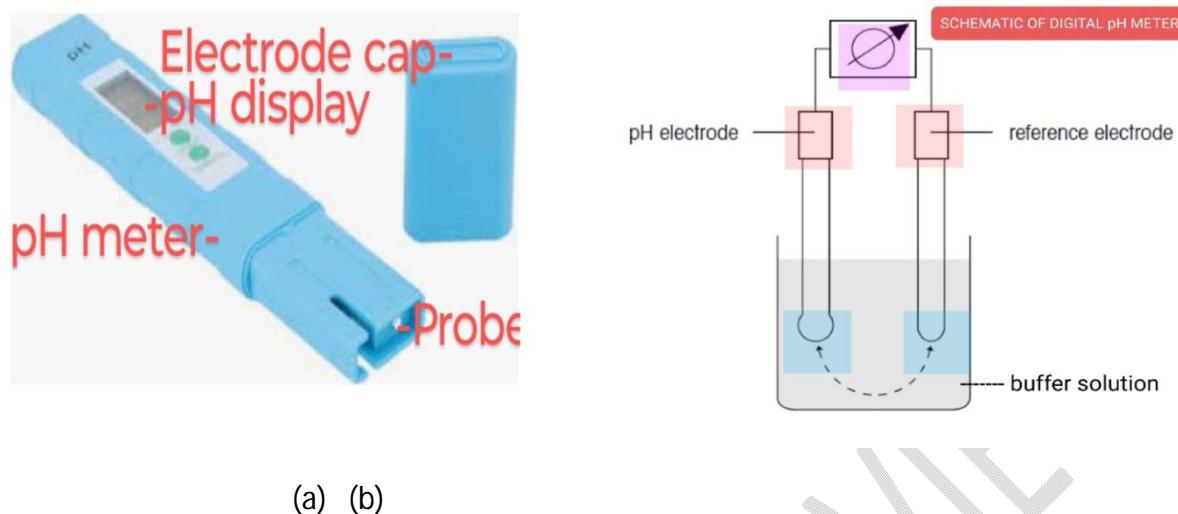


Figure 1. (a)-A digital pen pH meter and,(b)- pH electrodes working representation scheme.

In pH measurement, we applied Wellon's digital pen type pH meter or tester, in these an electrical potential is developed by electrode pair pins when it dip into a buffer solutions (figure 1, (a)). A digital pH meter has a pH probe to conduct the electrical signals to pH meter that voltage count or display in the range of pH value for buffer solution²⁰. These pH probe contain two electrodes naming as internal or sensor pH electrode and a reference electrode, as in figure 1, (b). Although, the electrode system of pH meter is sensitive to change in concentration of H^+ ion for taken solutions²¹. The potential of electrode is raise with pH value in respect of the concentration of H^+ of the solution. Hence, a slight variation is show in pH range which provides a significant changing in the quality of using solution. In preparation of 0.2M acetic acid-sodium acetate buffer solution we have taken about 36.2 ml of prepared sodium acetate and 14.8 ml of glacial acetic acid which were mixed well and buffer was prepared. Here, in measuring of pH value of buffer solution the electronic digital pen pH meter was used. In using pH meter, the pH value is measured an initial reading was observed 4.0, which raised upto 3.1 to 4.7 with 5N NaOH²². Initially, the pH is due to pure CH_3COOH (acetic acid) and as NaOH (sodium hydroxide) is added with CH_3COOH forming its conjugate base, the CH_3COONa salt. In other words, the buffer of acetic acid-sodium acetate ($CH_3COOH-CH_3COONa$) is composed of an equilibrium of weak acid (CH_3COOH) and its conjugate base (acetate ion from sodium acetate). When if adding an acid to buffer, the acetate ions neutralized the extra H^+ ion to reform an acid and thus it preventing a decrease in pH²³.

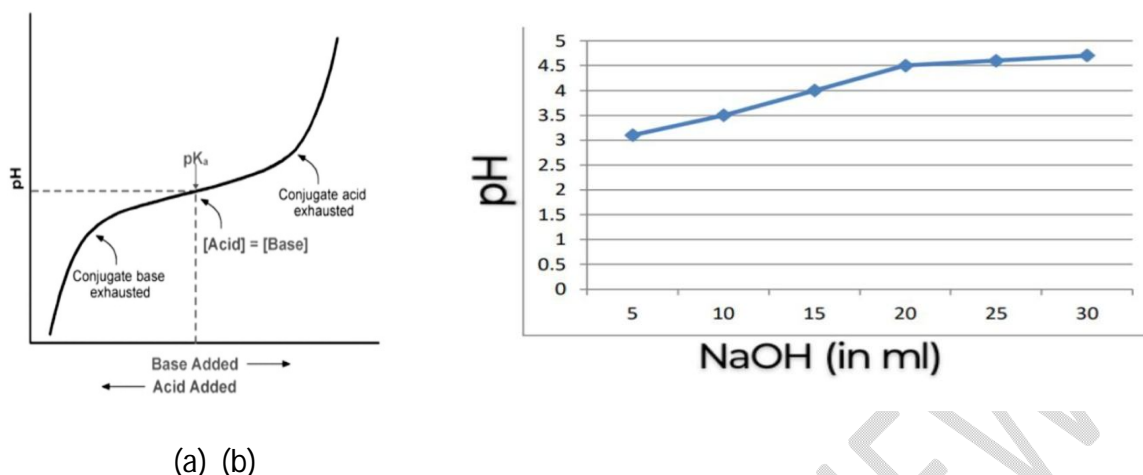
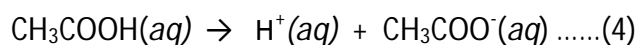


Figure 2. (a)- A schematic graph of buffer solutions and, (b)- pH of buffer (acetic acid-acetate) solution against basic 5N NaOH, at 298 K.

Although, there are various factors which influence the pH of a buffer solution like as the temperature, ionic strength, activity of H^+ ions, dilution of buffer and addition of electrolyte salt etc. A buffer can prevent a sudden drop or increase in the pH of a solution after the addition of a strong base or acid up to its buffering capacity²⁴. On dipping a pH meter into a buffer solution of acetic acid-sodium acetate, the pH value of the sample solution suddenly decreases before in fast and then gradually increases. But, when we pour the drop by drop solution of 5N NaOH, then the range of pH is raised from below 3.1 to 4.0 and up to 4.7. Graphically, Figure 2 (a) shows the schematic diagram of acid-base solutions in which the plot is raised in forward for pK_a value, and, (b) a pH of buffer (acetic acid-acetate) with 5N basic NaOH solution, at room temperature (298 K). Here, in our present observation, a quite fluctuation was appeared. This fluctuation may occur when so much acid or base are added to the buffer solution they become the excess reactants. If a preparing buffer having more acid than base, more H^+ ions are likely to be present and then pH falls, and, if a buffer has more base than acid, more OH^- ions are present thus pH rises. The acetic acid-sodium acetate buffer is a buffer and has the ability to resist in changing of pH at a certain pH range. When we added a small volume (5.0 to 30 ml) of 5N NaOH solution, then it effectively provided the OH^- ions and increased the pH of the buffer solution. Thus, by addition of salts of the conjugate acid-base pair to a solution increases the pH range due to the common ion effect²⁵. This observation has been reported for CH_3COONa (sodium acetate) which acts as a base and by adding base to a solution of weak acid (CH_3COOH) may increase the pH^{26,27}.

The acetic acid (CH_3COOH) is a weak acid and undergoes ionization in small extent to give the common acetate (CH_3COO^-) ion with H^+ ion as shown in the following reaction^{28,29}.



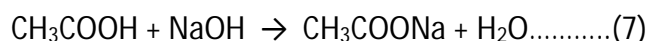
Where, the equilibrium or dissociation constant of acetic acid (CH_3COOH) is as -

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \dots\dots\dots(5)$$

When, a strong electrolyte such as sodium acetate (CH_3COONa) is added to that acetate ion, then CH_3COONa get ionizes as-



And,



By that ionization process, the concentration of CH_3COO^- ions is increases and equilibrium (equation 4) shifted in backward direction. Hence, the degree of dissociation of CH_3COOH is suppressed. Resulting, the concentration of H^+ ions is decreases and thus concentration of OH^- ions increases^{30,31}. And, therefore, the pH of buffer solution is increases. In buffer, the sodium hydroxide (NaOH) is reacts with acetic acid, a sodium acetate and water (H_2O) as product (a typical neutralization reaction). Notably, in $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$ (acetic acid-sodium acetate) buffer solution the role of sodium (Na^+) ions are as a spectator ion and it has no effect on position of equilibrium, so can be ignored^{32,33}.

[4]- CONCLUSIONS:

In conclusions, we have reported the applying of Henderson-Hasselbalch equation for determination of pH of acetic acid and sodium acetate buffer solutions at 298 Kelvin as room temperature. In the preparation of buffer solutions, firstly, we have taken 1.5 ml of glacial acetic acid into 100 ml of standard flask for making up 0.2M of acetic acid solution, and 0.64 gm of sodium acetate were dissolved into 100 ml distilled water. After then, a prepared 36.2 ml of sodium acetate solution into 100 ml of standard flask and added 14.8 ml of prepared acetic acid to make its volume 100 ml by using distilled water, it is a buffer. In measuring the pH of this prepared buffer solutions, we have been using a calibrated digital pen pH meter for accurate and quick resolution reading. In observation, a quite fluctuation was appeared. But, by adding basic 5N NaOH solution in acetic acid-acetate buffer solutions the pH of buffer sample have adjusted to shown about 4.7.

REFERENCES:

1. J. Arthur Campbell, Le Chatelier's principle, temperature effects, and entropy, *J. Chem. Educ.*, 1985;62(3):231-232.
2. I. L. Finar, *Organic Chemistry*, Vol-1, 6th Edition, Dorling Kindersley (India) Pvt. Ltd., (2007).
3. F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, 6th Edition, John Welly and Sons, Inc., (1999).
4. S. P. Mishra, Introducing of thermodynamic Van't Hoff equation in aqueous solubility and dissociation process of benzoic acid at ordinary temperature range, *Chem.Sci. Int. J.*, 2022;31(1):8-14. S. P. Mishra and R. P. Singh, Gibbs free energy change in aqueous dissociation of benzoic acid at temperature 'K' : A thermodynamic study, *Chem. Sci. Int. J.* 2022;31(2):44-52.
5. S. P. Mishra, Titrimetric study of solubility of solute benzoic acid and their partition in water and benzene solvents, *Chemical Sci. Int. J.*, 2021;30(3):40-45. S. P. Mishra, Concentration effect of sodium chloride salt on benzoic acid solubility and dissociation into water at 298K temperature, *Int. Res. J. Pure & Appl. Chem.*, 2021;22(6):47-52.
6. S. P. Mishra, Phenolphthalein indicator in titrimetric estimation of benzoic acid solubility and distribution in water and benzene-buffer solutions, *Asian J. of Chemical Sciences*, 2022;11(4):1-7.
7. W. Nernst, *Z. Phys. Chem.*, 1891;8:110-139.
8. Henry N, Po and N. M. Senozan, The Henderson-Hasselbalch equation: Its history and limitations, *J. Chem. Educ.*, 2001;78(11):1499.
9. R. Q. Blackwell, Verification of the Henderson-Hasselbalch equation, *J. Chem. Educ.*, 1954;31(3):138.
10. M. Hayert, J.-M. P.-Cornet, and P. Gervais, A simple method for measuring the pH of acid solutions under high pressure, *J. Phys. Chem. A*, 1999;103(12):1785-1789.
11. S. E. Kulevich, R. S. Herrick, and K. V. Mills, A discovery Chemistry experiment on buffers, *J. Chem. Educ.*, 2014;91(8):1207-1211.
12. K. R. Harris, The determination of pH of standard buffer solutions: a laboratory experiment, *J. Chem. Educ.*, 1985;62(4):350.
13. Adon A. Gordus, Chemical equilibrium: VI. Buffer solutions, *J. Chem. Educ.*, 1991;68(8):656.
14. J. H. Jordon, H. S. Ashbaugh, J. T. Mague and B. C. Gibb, Buffer and salt effects in aqueous host-guest system: screening, competitive binding, or both ?, *J. Am. Chem. Soc.*, 2021;143(44):18605-18616.

15. Bruce M. Thompson and Michael A. Kessick, On the preparation of buffer solutions, *J. Chem. Educ.*, 1981;58(9):743.
16. J. I. Partanen and A. K. Covington, Determination of stoichiometric dissociation constants of acetic acid in aqueous solutions containing acetic acid, sodium acetate and sodium chloride at (0 to 60) °C, *J. Chem. & Engineering Data*, 2003;48(4):797-807.
17. Lawrence J. Henderson, Concerning the relationship between the strength of acids and their capacity to preserve neutrality, *Am. J. Physiol.*, 1908;21(2):173-179.
18. Charles A. Lucy, Is your Henderson-Hasselbalch calculation of buffer pH correct ?, *J. Chem. Educ.*, 2023;100(6):2418-2422.
19. Vogel A. Text book of Quantitative Chemical Analysis, 5th Edition, Longman, Harlow, London,(1989).
20. Guy Schmitz, pH of sodium acetate solutions, *J. Chem. Educ.*, 2002;79(1):29.
21. M. Paabo, R. A. Robinson, and R. G. Bates, Reference buffer solutions for pH measurements in 50% methanol. Dissociation constant of acetic acid and dihydrogen phosphate ion from 10 to 40°, *J. Am. Chem. Soc.*, 1965;87(3):415-418.
22. H. S. Harned and R. W. Ehlers, The dissociation constant of acetic acid from 0 to 35°C, *J. Am. Chem. Soc.*, 1932;54(4):1350-1357.
23. Z. Luz and S. Meiboom, Kinetics of proton exchange in aqueous solutions of acetate buffer, *J. Am. Chem. Soc.*, 1963;85(24):3923-3925.
24. C. J. Donahue and M. G. Panek, Buffer capacity of various acetic acid-sodium acetate systems: A lecture experiment, *J. Chem. Educ.*, 1985;62(4):337.
25. Elwyn. F. Chase, A study of acetic acid –acetate buffers in KCl and NaCl solutions using the quinhydrone electrode, *J. Am. Chem. Soc.*, 1933;55(8):3072-3075.
26. Arthur W. Davidson, An introduction to the chemistry of acetic acid solutions, *Chem. Rev.*, 1931;8(2):175-190.
27. A. Pergantis, L. Saridakis, A. Lyratzakis, L. Mavroudakis, and T. Montagnon, Buffer squares: A graphical approach for the determination of buffer pH using logarithmic concentration diagrams, *J. Chem. Educ.*, 2019;96(5):936-943.
28. D. A. MacInnes and T. Shedlovsky, The determination of the ionization constant of acetic acid at 25°, from conductance measurements, *J. Am. Chem. Soc.*, 1932; 54(4):1429-1438.

29. N. F. Hall and F. Meyer, The acidity scale in glacial acetic acid. II. Buffer solutions- $1.6 < H_0 < 3.8$, *J. Am. Chem. Soc.*, 1940;62(9):2493-2500.

30. H. S. Harned and F. C. Hickey, The ionization of acetic acid in aqueous sodium chloride solutions from 0 to 40°, *J. Am. Chem. Soc.*, 1937;59(7):1284-1288.

31. E. T. Urbansky, B. T. Cooper, and D. W. Margerum, Disproportionation kinetics of hypiodous acid as catalyzed and suppressed by acetic acid-acetate buffer, *Inorg. Chem.*, 1997;36(7):1338-1344.

32. A. A. Green, The preparation of acetate and phosphate buffer solutions of known pH and ionic strength, *J. Am. Chem. Soc.*, 1933;55(6):2331-2336.

33. R.E. Mesmer, C. S. Patterson, R. H. Busey, and H. F. Holmes, The ionization of acetic acid in aqueous sodium chloride media: a potentiometric study to 573K and 130 bar, *J. Phys. Chem.*, 1989;93(21):7483-7490.

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