Practical pH Measurement and Theoretical Approach: Acid-Base System

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Abstract This study proposes a laboratory experiment for undergraduate students based on the comparison of Classical method (Acid-base titration) with Instrumental method (pH metric titration) and response of glass electrode towards dilute solution of acid/base. Current methodology inculcate the students better about the theoretical approach and practical outcomes of pH measurement for a dilute acid/base solution.

Keywords: classical method, acid-base titration, instrumental method, pH metric titration, glass electrode

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With the availability of inexpensive glass electrodes and pH meters, most of the laboratory experiments of undergraduate chemistry curriculum are based on pH determination as a tool for quantitative analytical measurements. Classical methods of analysis is one of the upper division under graduate lab courses which is designed to acquaint the students about non-instrumental methods, for quantitative determination. Usually instrumental methods are considered more reliable than classical methods but in some cases instrumental techniques also get fail. Previous reports are based on uses and construction of electrodes extensively [1,2,3,4] but don't emphasize on simple experiment by which a student can learn and understand better about these electrodes. A laboratory experiment is needed to be designed for students in this context to make them understand when they switch from classical method to instrumental one and to teach them better about the deviation of practical pH measurement from theoretical approach for a dilute acid/base system. This approach is considered in this paper.
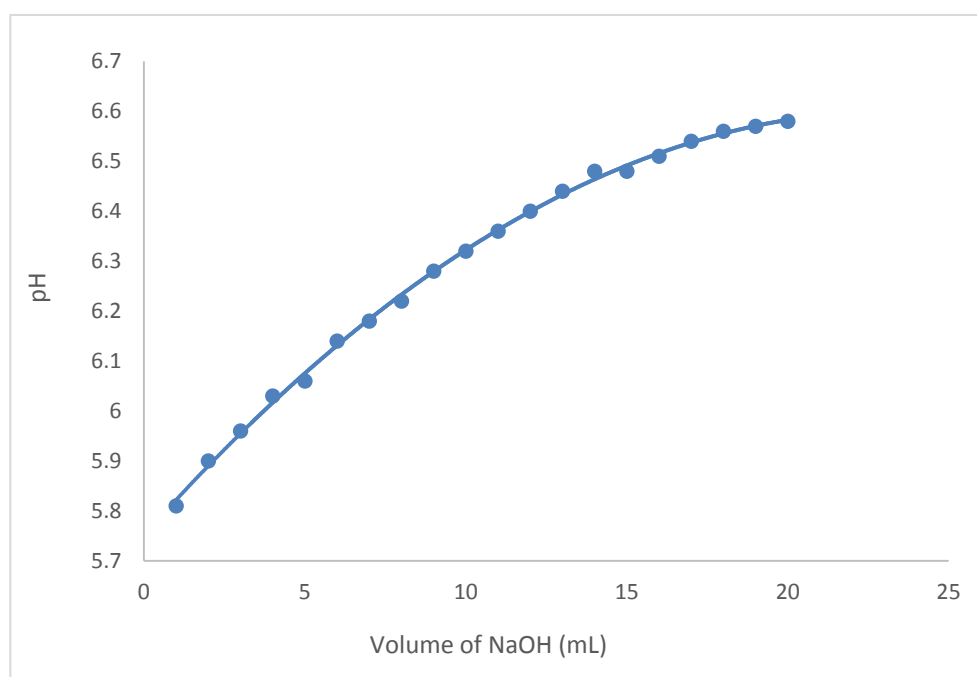

Figure 1. Change in pH of 10^{-4}M HCl by the addition of 10^{-4}M NaOH solution.
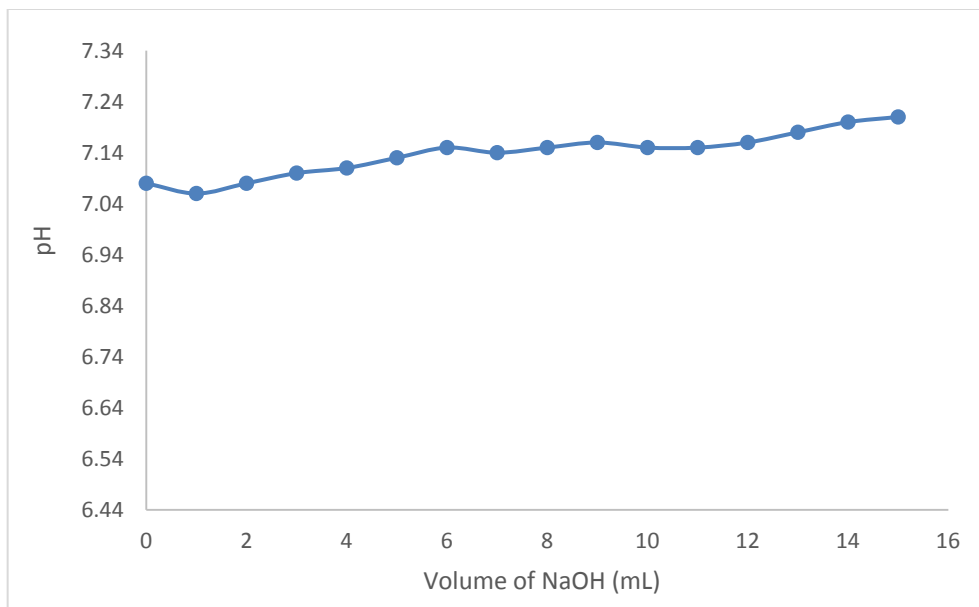
Figure 2. Change in pH of 10^{-5}M HCl by the addition of 10^{-5}M NaOH solution.
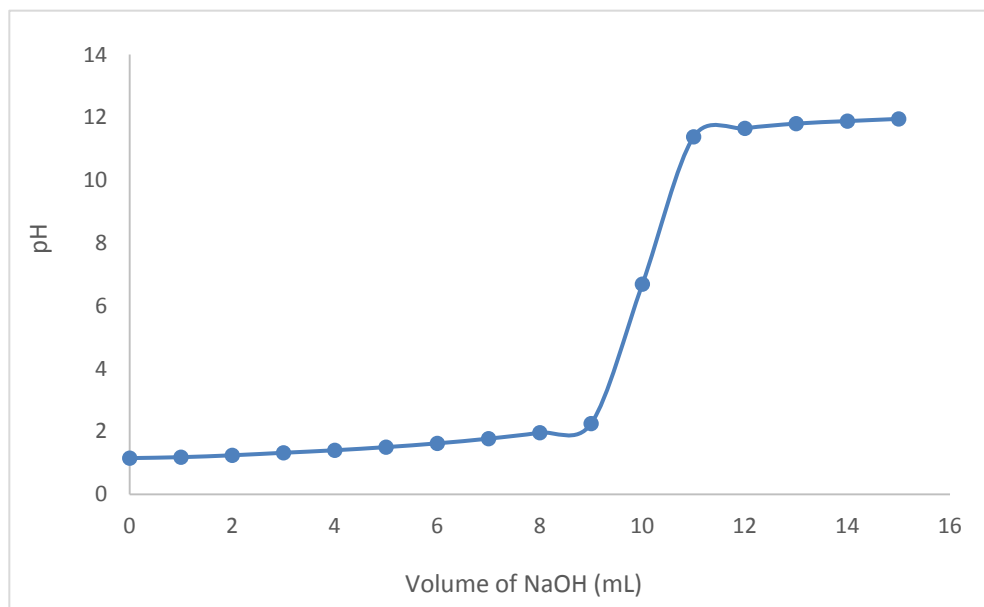

Figure 3. Change in pH of 0.1M HCl by the addition of 0.1M NaOH solution

The classical part of this experiment is the titration of strong acid (HCl) with strong base (NaOH) in the presence of phenolphthalein indicator. This titration is repeated after successive 10 times dilution of both acid and base solutions. It was observed that when 10 mL 0f 0.1, 0.01 and 0.001M HCl is titrated against standardized NaOH, the end point appeared around 10 mL of 0.1, 0.01 and 0.001 M NaOH respectively, whereas the titration of 10 mL of 0.0001 M HCl with 0.0001 M NaOH couldn't give the endpoint. This means phenolphthalein fails to perceive the end point at this dilution. Now common opinion is to switch from classical to instrumental method, but it may possible that the instrumental method may also not reliable at this dilution level. To check the instrumental response (pH electrode response) for this diluted (10^{-4}M) solution of acid, pH was noted with glass electrode. It was observed that for 10mL of 10^{-4}M HCl solution, pH was just changed from around pH 6 to 7 with the successive 1.00mL addition of 10^{-4}M NaOH, even, the addition upto 20 mL of

NaOH couldn't produce any sharp change in pH (Figure 1). In addition to that the pH of 10^{-5}M acid solution was recoded as 7.08 and it changed slightly up to 7.21 by the successive 1 mL addition of 10^{-5}M base with no detection of equivalence point (Figure 2). Consequently pH meter is also failed to show equivalence point. It means that classical and pH metric titration both aren't reliable at this concentration range i.e. 10^{-4} M of both acid and base.

In theoretical point of view, if the concentration of added OH$^-$ or H$^+$ is high i.e. $\geq 10^{-6}$M, the pH has the value we can calculate by just considering the concentration of added OH$^-$ or H$^+$. The contribution of water ions must be considered in the case when OH$^-$ or H$^+$ concentrations are in the intermediate range i.e. 10^{-6}-10^{-8}M and thus for pH calculation systematic treatment of equilibrium become necessary [5]. Practically this trend is not observed. The solution of diluted acid has the concentration 10^{-4}M so theoretical pH of the solution should be 4 and experimental pH must be around 4 in the absence of base

but experimentally this pH was not recorded. Ideal Nernst equation represents the relationship of potential and pH as, E = K – 2.303RT/F pH, where K contributes some factors like the potential of the reference electrode, the asymmetric potential of the glass membrane, any liquid junction potential and concentration of analyte in the internal solution of electrode [6]. Asymmetric potential is a nonzero potential which is observed when opposite sides of the membrane are in contact with identical solutions. This asymmetric potential is developed due to small imperfections in manufacturing of glass membrane and it can also be ascribed because over the electrode life time inner and outer gel layers experience very different environments. It should not be exceeded from ± 47 mV (± pH 0.8) at a pH value of 7. Since the potential of the reference electrode is remains constant, so deviation in the pH of diluted solution, is may be due to the change ascends in other contributing potentials. It can be checked and measured by the intercept of the curve (potential Vs pH curve), means that either the intercept of the curve increases or not for diluted solution. This discussion is incomplete without conferring the sensitivity of the glass electrode, that is, slope of the curve. Determination of slope of the curve is a well-known method to estimate the sensitivity of the glass electrode. In theory, the slope should be -59.16 mV/pH unit at 25°C.In practice, it is observed that a new and well hydrated pH electrode has slope which is 99.8% of the theoretical value. This slope is decreases with time. In order to optimize the electrode performance the calibration of electrode is advised. pH electrode output response follows Nernst equation as closely as possible. In order to check the pH electrode output response and to find the cause of deviation in the experimental pH of 10^{-4}M acid solution, a graph is plotted between potentials (mV) and pH of this solution with the addition of 10^{-4}M NaOH (Table 2, Figure 4). For comparison, a graph of potential Vs pH is also plotted for 0.1M acid solution with the addition of 0.1M NaOH (Figure 3 & Figure 5). If this deviation in pH is appeared due to the different response of the glass electrode, the slope and intercept of the curve obtained for 10^{-4} M solution must differ significantly from the slope and intercept of 0.1 M solution. Contrary to that for both of the solution, the values of slope and intercept obtained, aren't differ significantly and remained close to the theoretical values (Figure 6).

Table 1. pH and potentials of Acid (HCl) solutions

| S.No.	Vol. of NaOH (mL)	pH	Potential (mV)
$1x10^{-4}$ M Acid solution Vs $1x10^{-4}$ M Base			
1	0.0	6.34	37.0
2	1.0	6.60	26.1
3	2.0	6.71	13.0
4	3.0	6.87	9.3
5	4.0	6.93	3.1
6	5.0	6.95	3.2
7	6.0	6.98	0.9
8	7.0	7.06	-3.5
9	8.0	7.14	-9.0
10	9.0	7.23	-13.5
11	10.0	7.28	-17.3
12	11.0	7.37	-21.7
13	12.0	7.44	-26.3
14	13.0	7.52	-30.5
15	14.0	7.59	-35.5
16	15.0	7.67	-39.9
0.1M Acid solutionVs 0.1 M Base			
1	0.0	1.15	346.7
2	1.0	1.18	344.7
3	2.0	1.24	340.6
4	3.0	1.32	336.4
5	4.0	1.40	330.8
6	5.0	1.50	325.5
7	6.0	1.62	317.8
8	7.0	1.77	309.9
9	8.0	1.96	298.1
10	9.0	2.25	280.7
11	10.0	6.69	17.5
12	11.0	11.38	-258.9
13	12.0	11.65	-275.1
14	13.0	11.80	-283.7
15	14.0	11.88	-288.9
16	15.0	11.95	-292.9
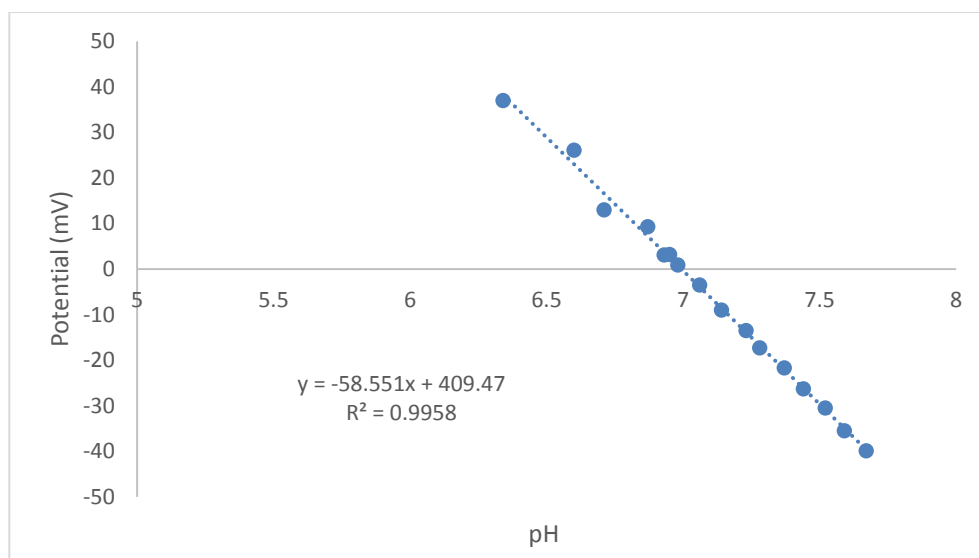
Figure 4. pH Vs potential curve for 0.0001M solution
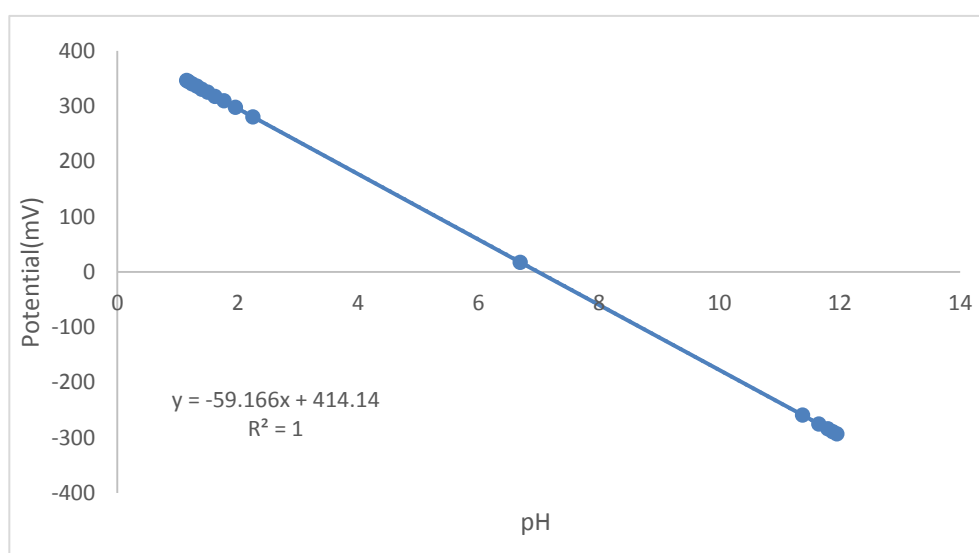

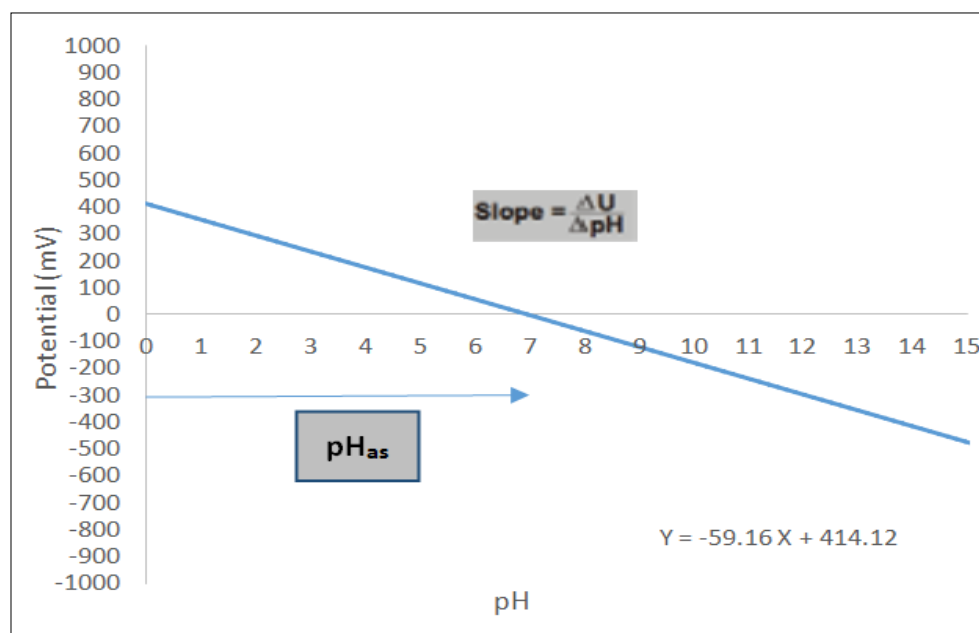**Figure 5.** pH Vs potential curve for 0.1M solution

Figure 6. Theoretical slope and asymmetry potential of a glass electrode assembly

This simple methodology describes that the deviation in experimental pH of diluted solution is not due to response of glass electrode. There is no uncertainty in the response of glass electrode so any deviation in pH is may be due to the reason that 0.0001M solution become extremely sensitive to traces of alkali from the glass of containing vessel and to ammonia from the air. Likewise a solution of sodium hydroxide (0.0001M), which should have a pH of 10, is sensitive to traces of carbon dioxide from the atmosphere.

In short there is a great need of implementation of such simple experiments in the curriculum of undergraduate students in order to inculcate them better about theoretical approach and practical outcomes of pH measurements.

References

[1] Goldcamp, M.J.; Conklin, A.; Nelson, K.; Marchetti,J.; Brashear, R.; Epure ,E. *J. Chem. Educ.* 2010, 87, 1262-1264.

[2] Graham, D. G.; Jaselskis, B.; Moore, C.E. *J. Chem. Educ.* 2013, 90, 345-351.

[3] Scholz, F.; Steinhardt, T.; Kahlert, H.; Porksen, J.R. *J. Chem. Educ.* 2005, 82, 782-786.

[4] Martin, C. R.; Freiser, H. *J. Chem. Educ.* 1980, 57, 512-514.

[5] Quantitative Chemical Analysis by Daniel C. Harris. Acid Base Equilibria, Ch: 10, Third Edition.

[6] Modern Analytical Chemistry by David Harvey. Electrochemical Methods of Analysis, Ch: 11.