

Potentiometric titrations using the pH meter and determination of pI

**Materials
required**

Sodium hydroxide solution (0.1 M and 0.25 N)
Phosphoric acid (0.1 N)
Dilute hydrochloric acid (0.1 N)
KCl solution (1M) (for preparing ref electrode)
Glycine

**Equipment
and special
glassware**

pH meter
100 ml beaker
Burette
Tissue paper

**Time
required**

3 hours

**Key
references**

1. Harris, D. C., *Quantitative Chemical Analysis*, 6th ed
W. H. Freeman, 2003.
2. Clark Westcott C., *pH Measurements*, Academic Press, 1978.

PRINCIPLES

Analytical methods that are based on electrode potential measurements are termed potentiometric methods. Potentiometry deals with the measurement of potential difference between two electrodes which are combined to form an electrochemical cell. EMF is the potential difference of the electrochemical cell when no current is flowing through the circuit. In this experiment the pH meter, which is a direct reading potentiometer will be utilized to measure potentials and pH as well as carry out potentiometric titrations.

pH and its measurement

The pH of a substance is a measure of its acidity just as a degree is a measure of temperature. The term pH, introduced by Danish chemist S. P. L. Sørensen in 1909, means hydrogen ion exponent and is defined in terms of hydrogen ion activity, "a". The name, pH, may have come from a variety of sources including: *pondus hydrogenii* (Latin), *potentiel hydrogène* (French), and *potential of hydrogen* (English). When we measure pH with a pH meter, we are actually measuring the negative logarithm of the hydrogen ion activity, not its concentration.

$$\text{pH} = -\log_{10} a_{\text{H}}^+ \quad \text{or} \quad 10^{-\text{pH}} = a_{\text{H}}^+$$

The activity is the effective concentration of the hydrogen ions in that solution. It is to be noted that for every decade change in activity, the pH changes by one unit.

Note: Chemists use the term *activity* to describe quantitatively the effective concentration of participants in an equilibrium at any given ionic strength. Substituting activity in place of concentration in an equilibrium-constant expression frees the numerical value of the constant from dependence on ionic strength. Activity is almost the same as concentration in very dilute solutions.

pH values of common substances	
Substance	pH
Hydrochloric acid, 10M	-1.0
Car battery acid	0.5
Gastric acid	1.5-2.0
Lemonade	2.3
Vinegar	2.9
Orange juice	3.5
Beer	4.5
Coffee	5.0
Tea	5.5
Milk	6.5
Pure water	7.0
Blood	7.34-7.45
Seawater	7.7-8.3
Hand soap	9.0-10.0
Ammonia	11.5
Bleach	12.5
Caustic soda	13.9

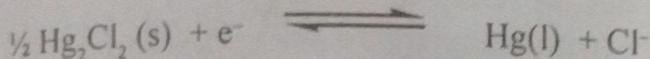
Electrodes

To measure potential, one requires electrodes. The electrode potential of a single electrode can be determined only with respect to a standard reference electrode. The electrode, which responds to the species being analyzed, is normally called the indicator electrode. The reference electrode has a fixed composition and a constant potential. There are two main types of standard reference electrodes.

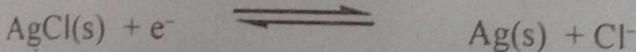
Primary reference electrode The standard hydrogen electrode is the primary reference electrode and its potential is taken as 0 volts. It consists of a 1 M solution of HCl with a

platinum wire having a platinized foil immersed in it. Pure and dry H_2 is passed at 1 atm through the solution. However, this electrode is inconvenient to prepare and handle under normal conditions, so secondary reference electrodes are often used in its place.

Secondary reference electrodes There are many secondary electrodes such as the calomel electrode ($Hg/Hg_2Cl_2/KCl$) and the silver-silver chloride electrode. The calomel electrode is based on the reaction:



The standard potential of this reaction is +0.268 V. However, if the cell is saturated with KCl at 25°C, the potential lowers to +0.241 V (This is because the activity of Cl^- is not unity in a saturated solution of KCl. The solution is saturated not only with KCl but also with Hg_2Cl_2 and the saturation concentration of highly soluble KCl is well above 1.0 M and hence the potential is only 0.241 V). A calomel electrode saturated with KCl is called a saturated calomel electrode (SCE). The advantage of using saturated KCl is that the concentration of Cl^- does not change if some liquid evaporates. Although calomel reference electrodes were popular, these days due to mercury toxicity, they have been replaced by safer electrodes such as the silver-silver chloride electrode. The silver-silver chloride electrode is based on the reaction.



The standard reduction potential for the $AgCl | Ag$ couple is +0.222 V at 25°C. But as it is kept in a saturated KCl solution, due to the reasons mentioned above, the potential of the electrode is reduced to +0.197 V with respect to the standard hydrogen electrode.

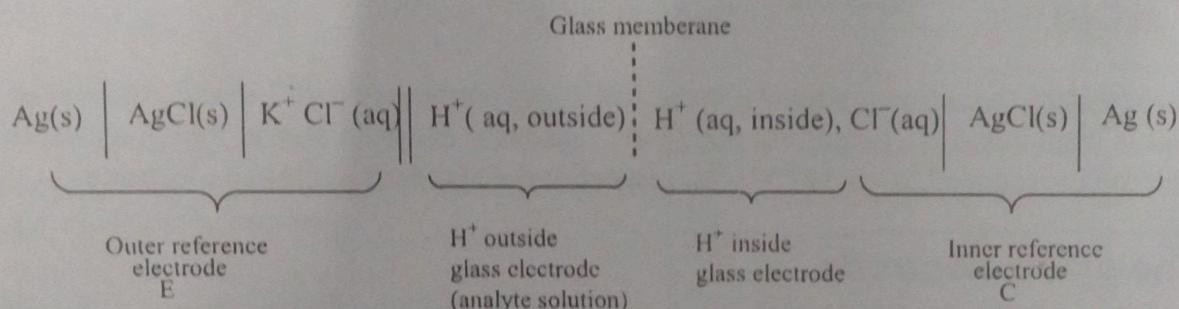
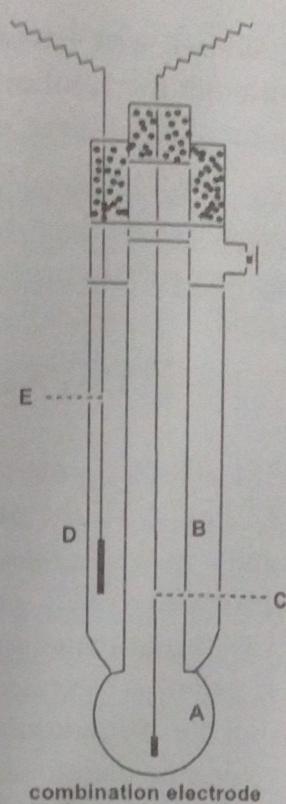
The glass electrode

To determine the pH value or hydrogen ion concentration for a solution, we shall need an electrode reversible to H^+ ions. In pH meters, glass electrode is employed as an indicator electrode for this purpose. A glass electrode has an electrode membrane made of special glass that responds to pH. The property one seeks for this glass material is that it must generate a potential that accurately corresponds to the pH of the solution and even though it must be very sensitive to acidity and alkalinity, it must not be damaged by them. The glass membrane is normally made of a special glass with an approximate composition of 72 % SiO_2 , 22 % Na_2O and 6 % CaO . This type of glass has the desirable properties of low melting point, relatively high electrical conductivity and a hygroscopic nature. The material is good for the pH range 1–9. However in solutions of high alkalinity, this electrode gets subjected to an 'alkaline error'. Nowadays, lithium-based glasses are exclusively used for hydrogen response glass electrodes when dealing with high pH values.

Glass electrodes may also be used in solutions containing oxidizing or reducing substances, colloids or biological fluids. The determination of hydrogen ion concentration depends upon the fact that when a thin glass membrane is in contact with solutions having different hydrogen ion concentration on its two sides, a difference of potential is

developed across the membrane. The magnitude of the potential difference depends on the difference in concentrations of the hydrogen ions in the two solutions.

Glass electrodes are now available as *combination electrodes* which contain the indicator electrode (a thin glass bulb) and a reference electrode (silver–silver chloride) combined in a single unit as shown in the figure. This produces a simple, compact unit for immersing in the test solution and has the added advantage that the two cells are in close proximity (with the reference cell normally completely surrounding the sensor element), thus minimizing the effect of any stray electrostatic fields or any inhomogeneity in the test solution. The thin glass bulb A and the narrow tube B to which it is attached are filled with hydrochloric acid (normally 0.1M) and carry a silver–silver chloride electrode C. The wide tube D is fused to the lower end of tube B and contains saturated KCl solution which is also saturated with silver chloride. It carries a silver–silver chloride electrode E. The assembly is sealed with an insulation cap through which the two leads from the electrodes are taken. The line diagram of this cell can be written as follows:

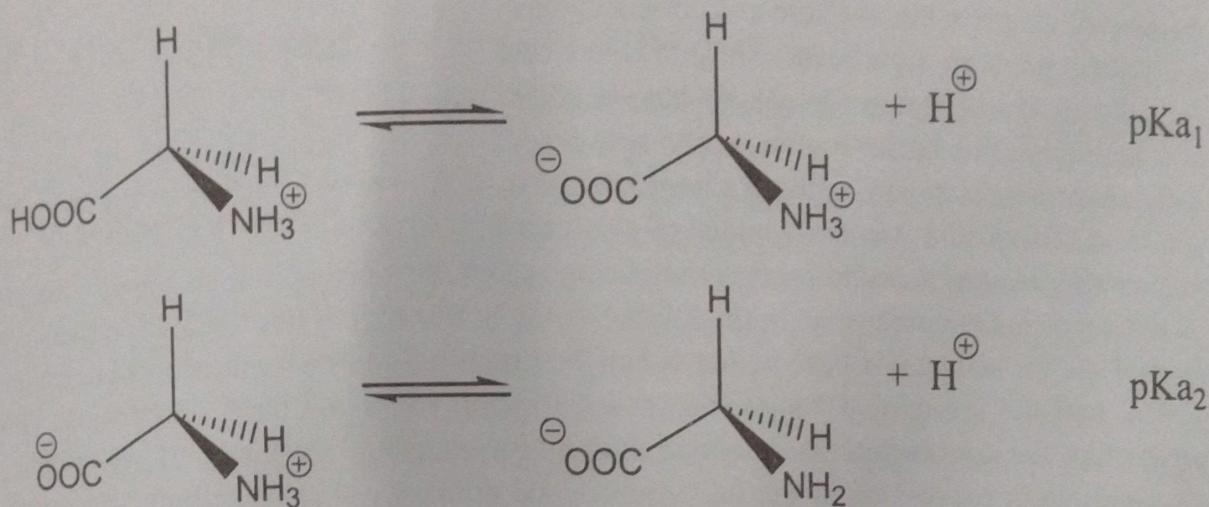


Provided that the internal hydrochloric acid solution is maintained at constant concentration, the potential of the silver–silver chloride electrode inserted into it will be constant and so too will the potential between the hydrochloric acid solution and the inner surface of the glass bulb. Hence the only potential which can vary is that existing between the outer surface of the glass bulb and the test solution in which it is immersed. Therefore the overall potential of the electrode will be decided by the hydrogen ion concentration of the test solution.

Isoelectric Point

The *isoelectric point* (commonly denoted as pI) is the pH at which a molecule or surface carries no net electrical charge. It is at this pH that the molecule will not show any motion in an electric field. In order to have a sharp isoelectric point, a molecule (or surface) must be amphoteric, meaning it must have both acidic and basic functional groups. Proteins and amino acids are common molecules that meet this requirement.

For an amino acid with only one amine and one carboxyl group, the pI can be calculated from the pKa values of this molecule. Glycine, the simplest amino acid, for example can exist in three possible ionic forms $\text{H}_3\text{N}^+ - \text{CH}_2 - \text{COOH}$ (pH 1), $\text{H}_3\text{N}^+ - \text{CH}_2 - \text{COO}^-$ (pH 6) and $\text{H}_2\text{N} - \text{CH}_2 - \text{COO}^-$ (pH 11). The two pKa values for glycine arise from the following equilibria.



$$\text{pI} = \frac{\text{pK}_{\text{a}1} + \text{pK}_{\text{a}2}}{2}$$

For amino acids with more than two ionizable groups, such as lysine for example, the same formula is used, but this time the two pKas used are those of the two groups that lose and gain a charge from the neutral form of the amino acid. Proteins can be separated according to their isoelectric point in a process known as isoelectric focusing. At a pH below the pI, proteins carry a net positive charge. Above the pI, they carry a net negative charge. This has implications for running gel electrophoresis which is a method used in biochemistry and molecular biology to separate DNA, RNA, or protein molecules by size.

Potentiometric titrations

The determination of the equivalence point of titrations based on potential measurements is called potentiometric titrations. The electrode potential of an electrode depends upon the concentration of its ions in the solution. Hence, the potential of an indicator electrode goes on changing with respect to a standard reference electrode by the change of the concentration of the ions during titration. In other words, finding the difference in potential of the indicator electrode can be used as an indicator in volumetric titration. The equivalence point is indicated by a fairly large change in potential. A good potentiometric titration requires a suitably selected indicator electrode and a standard reference electrode. This is where the pH meter can be used.

To understand the type of information one can gather from a potentiometric titration, let us consider as an example, the titration of acetic acid versus sodium hydroxide.

The equivalence point, when enough base is added to react with all the acid present, exhibits a sharp increase in pH. This happens when the moles of the base added equals the moles of the acid in the sample. The flat portion of the titration curve before the equivalence point is called the buffer region. In this part of the pH scale, the acid and conjugate base are both present in significant concentrations and the solution resists changes in pH. As base is added to a solution in this buffer region, acetic acid reacts with it to form acetate ion, without a large change in pH. If additional acid was to be added to a solution in the buffer region, it would react with the conjugate base, acetate ion, and, again, the pH would not change appreciably. In the middle of the buffer region lies the half-equivalence point. Here the volume of base added is half that required to reach the equivalence point – also half the acetic acid has been converted to the conjugate base, acetate ion. This means that the concentrations of acetic acid and acetate ion are equal. If we examine the equilibrium expression at the half-equivalence point, we find something interesting:

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

At the half-equivalence point, $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$, so

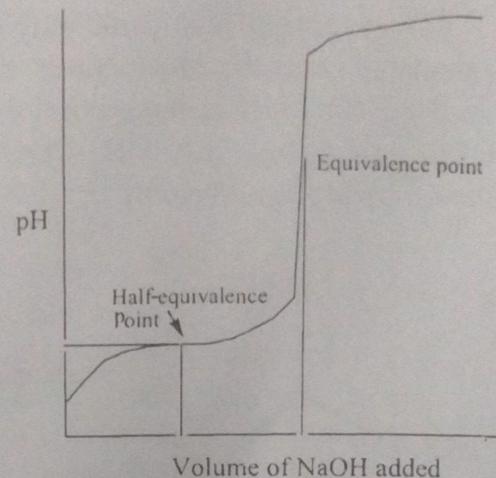
$$K_a = [\text{H}_3\text{O}^+]$$

And taking the log and multiplying both sides by -1 yields

$$\text{p}K_a = \text{pH}$$

So at the half-equivalence point, half the acetic acid has been converted to the conjugate base, acetate ion, and the pH will be equal to the $\text{p}K_a$ of the acid. This gives us an experimental way to determine the $\text{p}K_a$ of a weak acid.

The advantages of potentiometric titrations over conventional methods are that these titrations are applicable even to colored and turbid solutions; they are rapid and can be carried out in micro-scale; the results are highly accurate; and one can also use the method for weak acid-weak base titrations.



PROCEDURE

A Determination of hydrogen ion concentration and pH of a given solution

1. Switch on the pH meter and allow the instrument to warm up for 10 minutes.
2. Set the temperature control to room temperature.
3. Insert the electrode assembly into the buffer solution.

4. Set the selector switch of the instrument to read pH.
5. Remove the electrode assembly, rinse in distilled water and place it back into the beaker containing distilled water.
6. Measure the pH of different solutions given to you and determine their hydrogen ion concentration.

B Potentiometric titration of an acid versus base

1. Take 25 ml of the given acid in a beaker and measure its pH as described above. Also measure its potential.
2. Add known volumes of NaOH (0.25 N) from a burette to the acid in the beaker. Shake the mixture and measure its pH as well as potential.
3. Initially, add 0.5 ml of the base after each reading till 5 ml of the base has been added. After which, add 0.2 ml and measure the pH (and potential) a little over the end point (indicated by sharp change in pH and potential).
4. Plot pH (y-axis) versus volume of the base added (x-axis) and obtain the end point from the graph. Also plot voltage (mV) versus volume and obtain the end point from the graph.

C To titrate a polybasic acid (H_3PO_4) against a base

1. Take 25 ml of the given phosphoric acid in a beaker and measure pH as given in part (A). Also measure its potential.
2. Add known volumes of NaOH (0.25 N) from a burette to it. Shake the mixture and measure its pH as well as potential.
3. Continue the addition and measurement of pH (and potential) a little over the end point.
4. Plot pH (y-axis) versus volume of NaOH added (x-axis) and obtain the end point from the graph. Also plot voltage (mV) versus volume and obtain the end point from the graph.
5. Obtain the dissociation constants from the titration plot. (HINT: Use the Henderson-Hasselbach equation, $pH = pK_a - \log [acid]/[base]$).

D Determination of pI of glycine

1. Take 25 ml of the given glycine in a beaker and dilute with 25 ml of distilled water.
2. Add 0.3 ml of NaOH solution (from a burette; NaOH of approximate strength 0.1 M).
3. Measure the pH and continue to add 0.3 ml of NaOH and measure the pH till the NaOH volume reaches around 65 ml.
4. Plot a graph with volume of NaOH on the x-axis and pH on the y-axis.
5. The two almost horizontal parts of the graph gives the values of pK_{a_1} and pK_{a_2} for glycine. Use mid-points of these regions to get the values.
6. The average of these values (pK_{a_1} and pK_{a_2}) gives the pI of glycine.