SRM
INSTITUTE OF SCIENCE & TECHNOLOGY

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Virtual lab.

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Determination of strength of an acid using pH meter

Expt. No. : 7

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Experiment

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❑ **Aim :**

　　　　To find out the strength of given hydrochloric acid solution by titrating it against sodium hydroxide (0.05N) using pH meter

❑ **Materials required:**

　　　　pH meter, electrodes, beaker ,100mL standard flask, pipette, burette, funnel, glass rod

❑ **Chemicals required :**

　　　　Hydrochloric acid, NaOH solution, distilled water

pH of a solution

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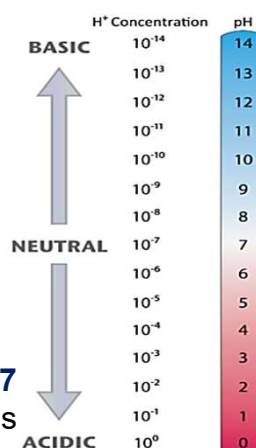
❑ The pH of a solution is the negative logarithm of the hydrogen ion concentration.

❑ pH may be represented mathematically as :

$$pH = - \log_{10} [H^+]$$

❑ If the $[H^+]$ concentration is greater than 1×10^{-7} M , pH is less than 7 and vice-versa.

❑ **pH < 7** indicate **acidic solution**, **pH > 7** indicate **basic solution** and **pH =7** means **neutral solution**.

H⁺ Concentration	pH
BASIC 10^{-14}	14
10^{-13}	13
10^{-12}	12
10^{-11}	11
10^{-10}	10
10^{-9}	9
10^{-8}	8
NEUTRAL 10^{-7}	7
10^{-6}	6
10^{-5}	5
10^{-4}	4
10^{-3}	3
10^{-2}	2
10^{-1}	1
ACIDIC 10^{0}	0

Potentiometric titration

❑ **Volumetric method** for the measurement of **changes in the e.m.f between two electrodes on the addition of titrant** of **known concentration to a solution of unknown concentration**.

❑ In this potentiometric titration setup an **indicator electrode (ISE electrode) and reference electrode (calomel) is coupled to form electrochemical cell.**

❑ The overall cell potential is calculated as :

$$E_{cell} = E_{ind} - E_{ref} + E_{sol}.$$

❑ E_{sol} is the **potential drop over the test solution** between the two electrodes which is recorded at intervals as the titrant is added.

Potentiometric titration

❑ We have seen that the potential of a metallic electrode arises from the tendency of an oxidation-reduction reaction to occur at an electrode surface (redox titration).

❑ In membrane electrodes, in contrast, the observed potential is a kind of junction potential that develops across a membrane that separates the analyte solution from a reference solution.

❑ **Requirements:** minimal solubility, need some electrical conductivity and selective reactivity with the analyte
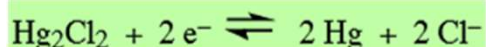
pH meter

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pH meter

❑A pH meter consists of two electrodes: **a glass electrode (ISE)**, which is sensitive to the concentration of hydrogen ions in solution, and **a calomel reference electrode**.

❑The reference electrode supplies a constant potential (**E° = +0.24 V** versus the SHE) as determined by the half-reaction :
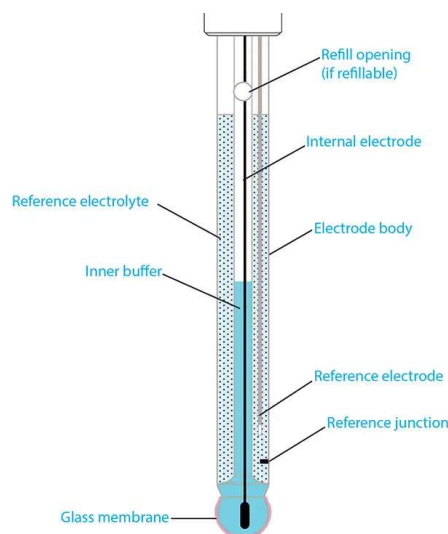
$$Hg_2Cl_2 + 2\,e^- \rightleftharpoons 2\,Hg + 2\,Cl^-$$

❑ The pH meter measures the total potential across the two electrodes and displays this measurement on a scale calibrated in pH units

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Principle

Refill opening (if refillable)

Internal electrode

Reference electrolyte

Electrode body

Inner buffer

Reference electrode

Reference junction

Glass membrane

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Principle

❑ In order to measure the voltage, two points with different electrical potential values are required.

❑ The reference electrode is designed to maintain a constant electrical potential that is independent of the sample composition and temperature.

❑ In contrast, the hydrogen ion selective electrode (ISE) with glass membrane provides an electrical potential that is dependent upon the activity of hydrogen (H^+) ions in the sample solution.

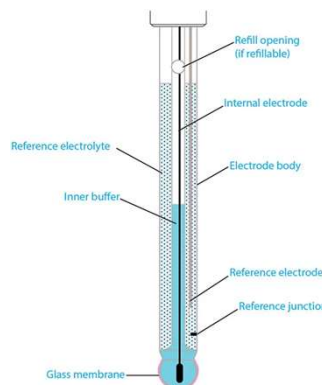❑ Therefore, both the reference electrode and the hydrogen ISE are needed when determining pH.
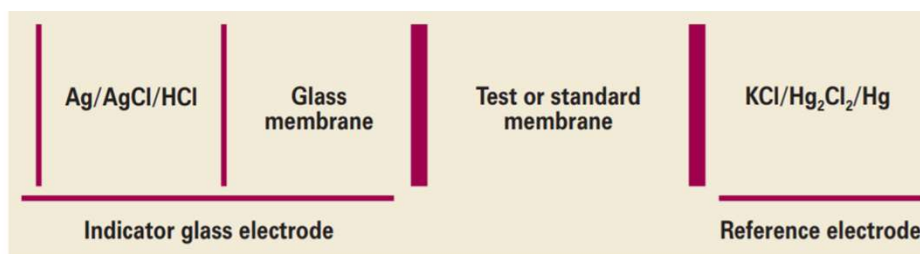
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Principle

- This membrane is filled with a buffer solution of known pH (typically pH = 7).

- This electrode design creates an environment with constant binding of H^+ ions on the inside of the glass membrane, while the outside of the glass membrane is exposed to the sample where a variable amount of H^+ ions exist.

- The difference in H^+ ions creates a potential that is read versus the stable potential of the reference electrode.

Refill opening (if refillable)
Internal electrode
Reference electrolyte
Electrode body
Inner buffer
Reference electrode
Reference junction
Glass membrane

Principle

Ag/AgCl/HCl | Glass membrane | Test or standard membrane | KCl/Hg$_2$Cl$_2$/Hg

Indicator glass electrode   Reference electrode

Principle

The ideal mixture was found to be 72% silicon dioxide, 6% calcium oxide and 22% disodium oxide.
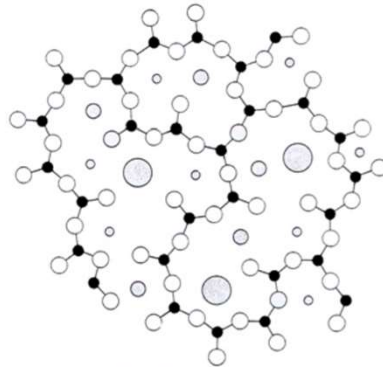
● Si   ○ Oxygen   ○ ◯ Cations

Structure of Silica pH Sensitive Glass

$$H^+ + -SiO^-Na^+ \rightleftharpoons -SiO^-H^+ + Na^+$$

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Principle

External solution ⟶   Hydrated gel ~10nm ⟷   Glass membrane 0.1mm ⟷   Hydrated gel ~10nm ⟷   ⟵ Internal solution

Unknown hydrogen activity: unknown pH of a test solution

Fixed hydrogen activity: known pH of a reference buffer solution (HCl)

Potential drop is established by partitioning of H+ and SiO-

Potential difference between the internal gel-solution interface and the external gel-solution interface: E_B, the boundary potential

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Principle

❑ The glass used in a pH electrode contains sodium (Na^+) ions.

❑ When placed in contact with a solution, a microscopically thin (10 nm thick) hydrated gel layer forms on the surface of the glass.

❑ Within this gel layer, hydrogen ions from the solution can migrate a very short distance into the glass and displace sodium ions.

❑ The number of H^+ ions that migrate into the gel layer depends directly on the concentration of H^+ in the solution.

Principle

❑ For the **internal solution, the concentration of H^+ is constant** so a fixed number of Na^+ ions are displaced from the gel layer by H^+ ions.

❑ For the **external solution, the number of H^+ ions changes with the pH** so the number of Na^+ ions displaced from the gel layer varies as a function of the pH.

❑ The ratio of **[H^+] to [Na^+] in the outside gel layer influences the magnitude of the membrane potential**.

❑ The reason the **membrane potential varies** with the ratio of the two ions is because the **smaller H+ ions have a higher mobility than the larger Na+ ions**.

Principle

- A voltmeter measures the voltage generated by the solution and displays it as a pH-measurement.

- An increase in voltage means more hydrogen ions and an increase in acidity, so the meter shows it as a decrease in pH; in the same way, a decrease in voltage means fewer hydrogen ions, more hydroxide ions, a decrease in acidity, an increase in alkalinity, and an increase in pH.

- ↑ voltage = more H+ /less OH - = ↑ acidity = ↓pH
- ↓ voltage = less H+ /more OH - = ↓ acidity = ↑pH

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Principle

- In order to measure pH, the cell is set up –

Ag| AgCl, 0.1.M HCl | glass | Unknown solution | sat.KCl| Hg2Cl2 | Hg

The glass electrode and calomel electrode are dipped in a solution of known pH.

$$E_{\text{cell}} = E_{\text{ref(int)}} - E_{\text{ref(samp)}} + E_{\text{mem}} + E_{\text{j}}$$

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Principle

$$E_{\text{mem}} = E_{\text{asym}} - \frac{RT}{zF} \ln \frac{(a_A)_{\text{int}}}{(a_A)_{\text{samp}}}$$

$$0.0592 \ \log \left[(\mathcal{A}_{\text{inner}}) / (\mathcal{A}_{\text{outer}}) \right]$$

(a_A)samp is the analyte's concentration in the sample, (a_A)int is the concentration of analyte in the ion-selective electrode's internal solution, and z is the analyte's charge. Ideally, E_{mem} is zero when (a_A)int = (a_A)samp. The term E_{asym}, which is an asymmetry potential, accounts for the fact that E_{mem} is usually not zero under these conditions.

Principle

❑The **pH values of the solution** at different stage of acid–base neutralization are determined and **plotted against the volume of alkali added.**

❑On **adding a base to an acid**, the **pH rises slowly** in the initial stages as the concentration of H^+ ion decreases gradually.

❑At the **equivalence point, it increases rapidly** as at the equivalent point H^+ ion concentration is very small and then it flattens out after the end point.

❑The end point of the titration can be detected where the pH value changes most rapidly.

Procedure

❑ Standardize the pH meter using different buffers of known pH, wash the electrode with distilled water.

❑ The given acid is diluted to 100 ml using distilled water. **10 ml** of this made up solution is pipetted out into a 250 mL clean beaker.

❑ 100 ml of distilled water is added to it, so that the electrode is completely dipped. Note the initial pH of the pure acid solution.

❑ Fill the burette with standard NaOH solution (**0.05 N**) and run down into the beaker in small increments (1 mL). Stir the solution well using glass rod.

Procedure contd..

❑ Note down the pH after every successive addition.

❑ Continue the titration till beyond the neutralization point as indicated by an abrupt change in pH. (at least 15-20 increments).

❑ Plot a pilot graph of volume of NaOH versus pH. The midpoint of the **'S' shaped curve** of the graph gives the equivalence point.

❑ In order to get an accurate end point, perform one more similar titration in a small volume range (3.0 mL on either side of the abrupt change in pH)
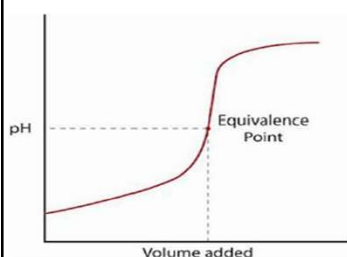
Procedure contd..
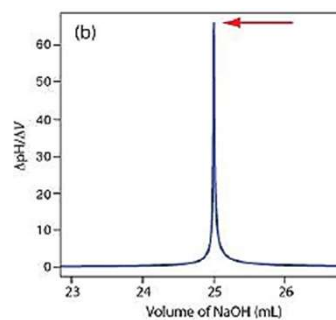
❑ Measure the pH after addition of every 0.2 mL of standard NaOH solution.

❑ Plot a fair graph of volume of NaOH versus Δ pH / ΔV.

❑ Find out the exact end point from the fair graph. The peak point of the curve from the fair graph gives the end point

Pilot Graph

Fair Graph

Tabular column

Table-1 : Pilot titration (HCl Vs NaOH)

S.No	Volume of NaOH (V) ml	pH
1.		
2.		
3.		
....		
16		

Tabular column

Table-2 : Fair titration (HCl Vs NaOH)

S.No.	Volume of NaOH (V) ml	pH	Δ pH	ΔV	Δ pH / ΔV
1.					
2.					
3.					
....					
20.					

Calculation

Volume of NaOH V_1 = ------------- ml [from FAIR graph]

Strength of NaOH N_1 = ------------ N

Volume of HCl V_2 = 10 ml

Strength of HCl N_2 =   N

Therefore strength of HCl (N_2) = $V_1 \times N_1 / V_2$

                                  = -----------N.

Result

☐ **The strength of the given HCl solution =   N**

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Table 1 Determination of the strength of an acid using pH meter

Sl.No.	Volume of NaOH (mL)	pH
1	0	2.84
2	1	2.86
3	2	2.90
4	3	2.94
5	4	3.00
6	5	3.07
7	6	3.15
8	7	3.26
9	8	3.40
10	9	3.61
11	10	4.13
12	11	7.11
13	12	9.85
14	13	10.41
15	14	10.67
16	15	10.84

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SI.No.	Volume of NaOH (mL)	pH	ΔpH	ΔV (mL)	ΔpH/ΔV
					SRM
1	9	3.69	------	-----	
2	9.2	3.73	0.04	0.2	0.2
3	9.4	3.83			
4	9.6	3.91			
5	9.8	4.07			
6	10	4.31			
7	10.2	4.86			
8	10.4	5.83			
9	10.6	6.29			
10	10.8	6.80			
11	11	7.20			
12	11.2	8.70			
13	11.4	9.26			
14	11.6	9.47			
15	11.8	9.72			
16	12	9.87			

Table 2 Determination of the strength of an acid using pH meter

17	12.2	10.05			
18	12.4	10.17			
19	12.6	10.25			
20	12.8	10.33			
21	13	10.42			
22	13.2	10.54			
23	13.4	10.72			