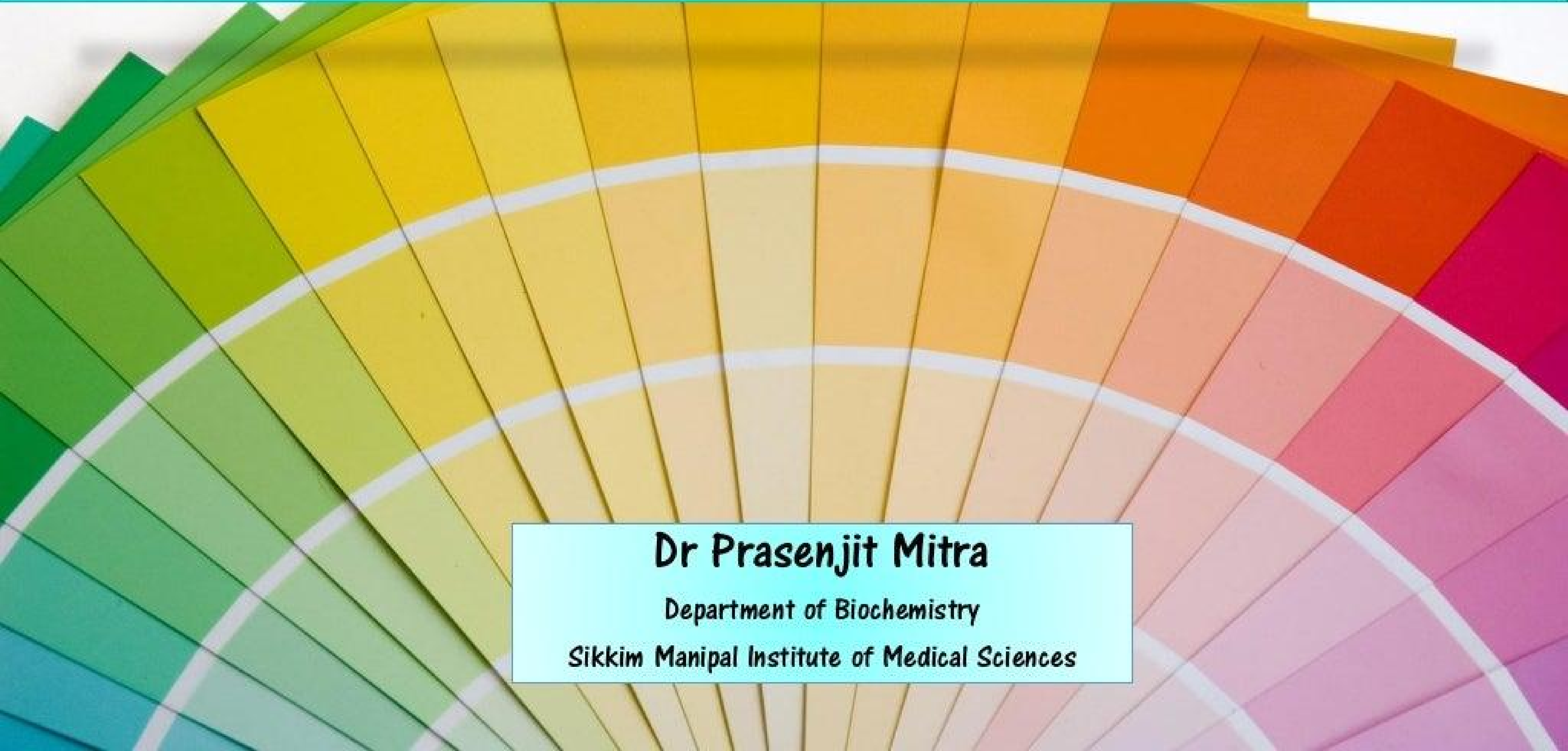
pH & its Measurement



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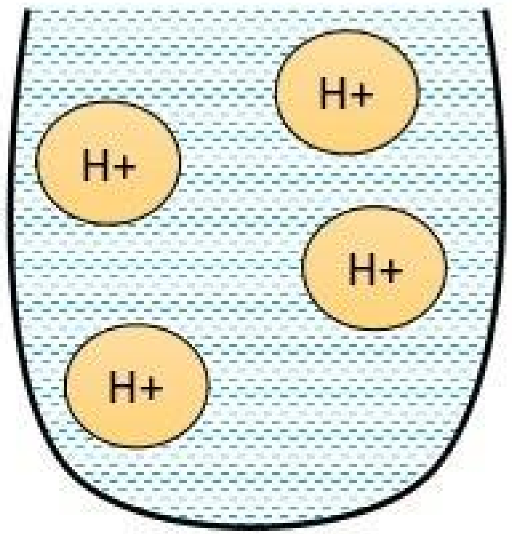
Origin of pH

Number of Hydrogen ions (H+) determine acidity or alkalinity



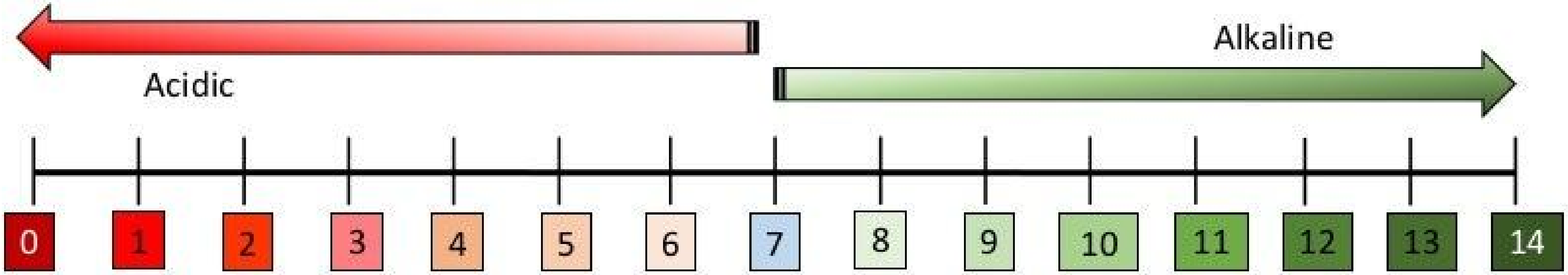
- Number of Hydrogen ions (H^+) in water = 0.0000001 mol/L

- Logarithm of H^+ Concentration
  - Log (0.0000001) = log (10^{-7}) = -7

- Negative Logarithm of H^+ Concentration
  - -[Log (0.0000001)] = -log (10-7) = -(-7) = 7

Søren P. L. Sörenson
(1868-1939)

power of Hydrogen



pH Scale

Determination of pH

Indicators

- Litmus paper
- pH paper

Colorimeter

pH meters

pH meters - History

Arnold Orville Beckman
(1900-2004)

pH meters - Types

- Handheld pH meter
- Bench top pH meter
- Continuous in line pH meter

pH meters – pH Electrode

- Glass electrode
- Reference electrode
- Combination electrode
- 3 in 1 electrode

pH meter -- Glass Electrode

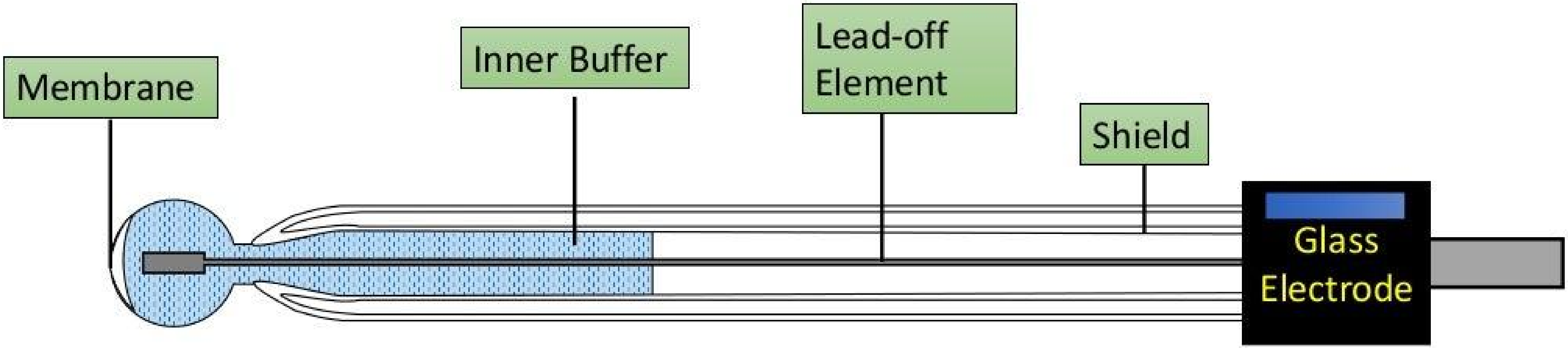


Fig Measuring (Glass) electrode

pH Reference Electrode

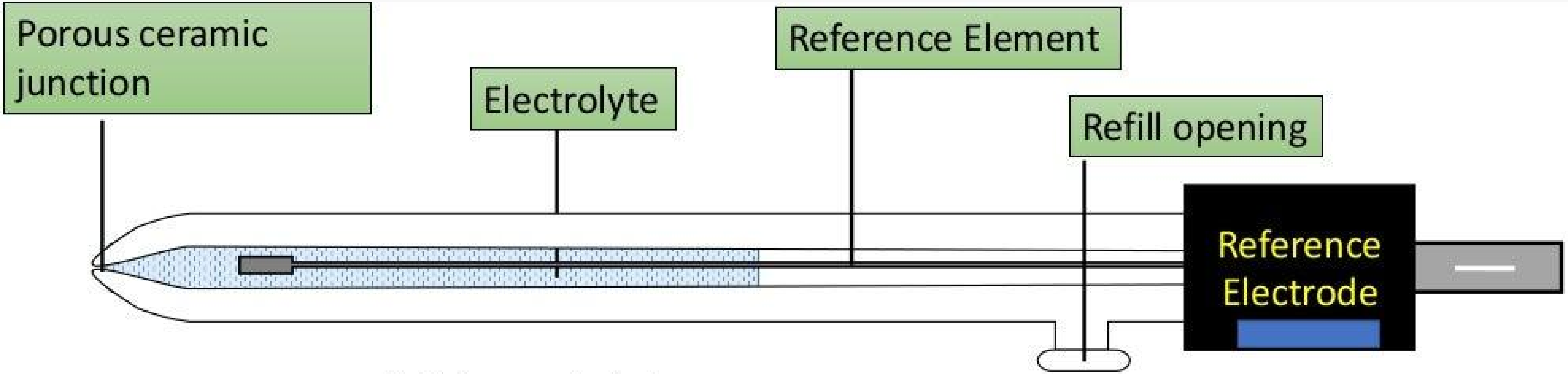


Fig Reference electrode

Reference electrolyte

- Inert
- High ion concentration → Low electrical resistance
- Contact with measuring solution

Popular Reference Systems

- Mercury/calomel
- Silver/Silver chloride

pH meter – Combination Electrode

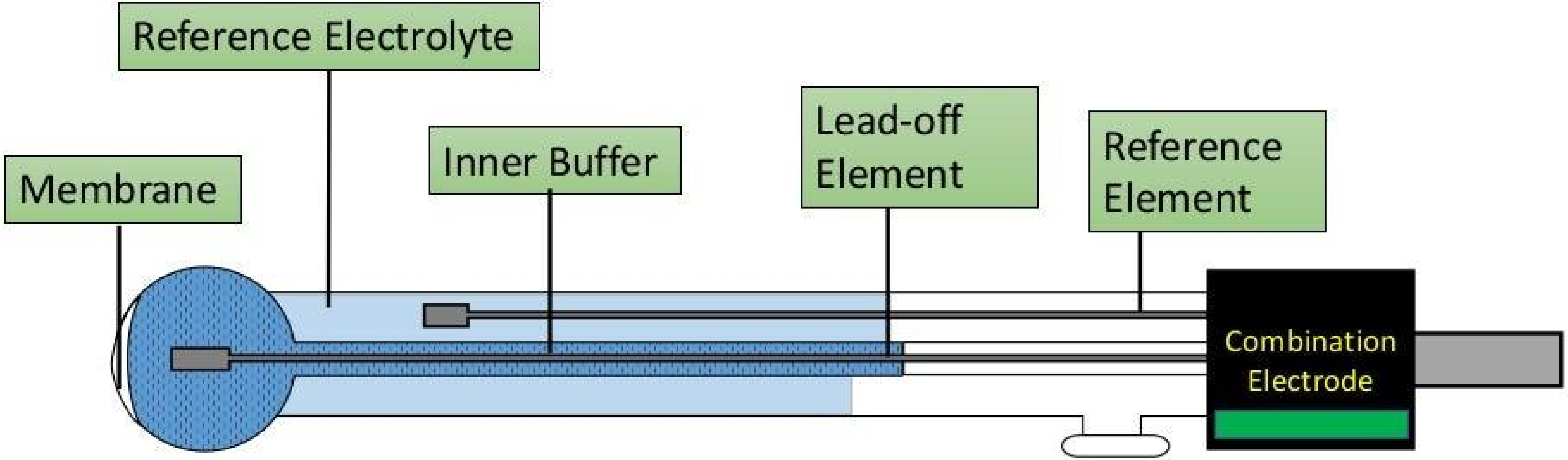


Fig Combination electrode

pH meter- Working principle

The potential of glass electrode is measured against that of reference electrode

$$E = E^0 + \boxed{\frac{2.303\, RT}{nF}} \log a_{H+}$$

Standard potential when a_{H+} = 1mol/L

Nernst potential (E_N)/Slope factor
Change in potential per pH unit.
Depends on absolute temperature

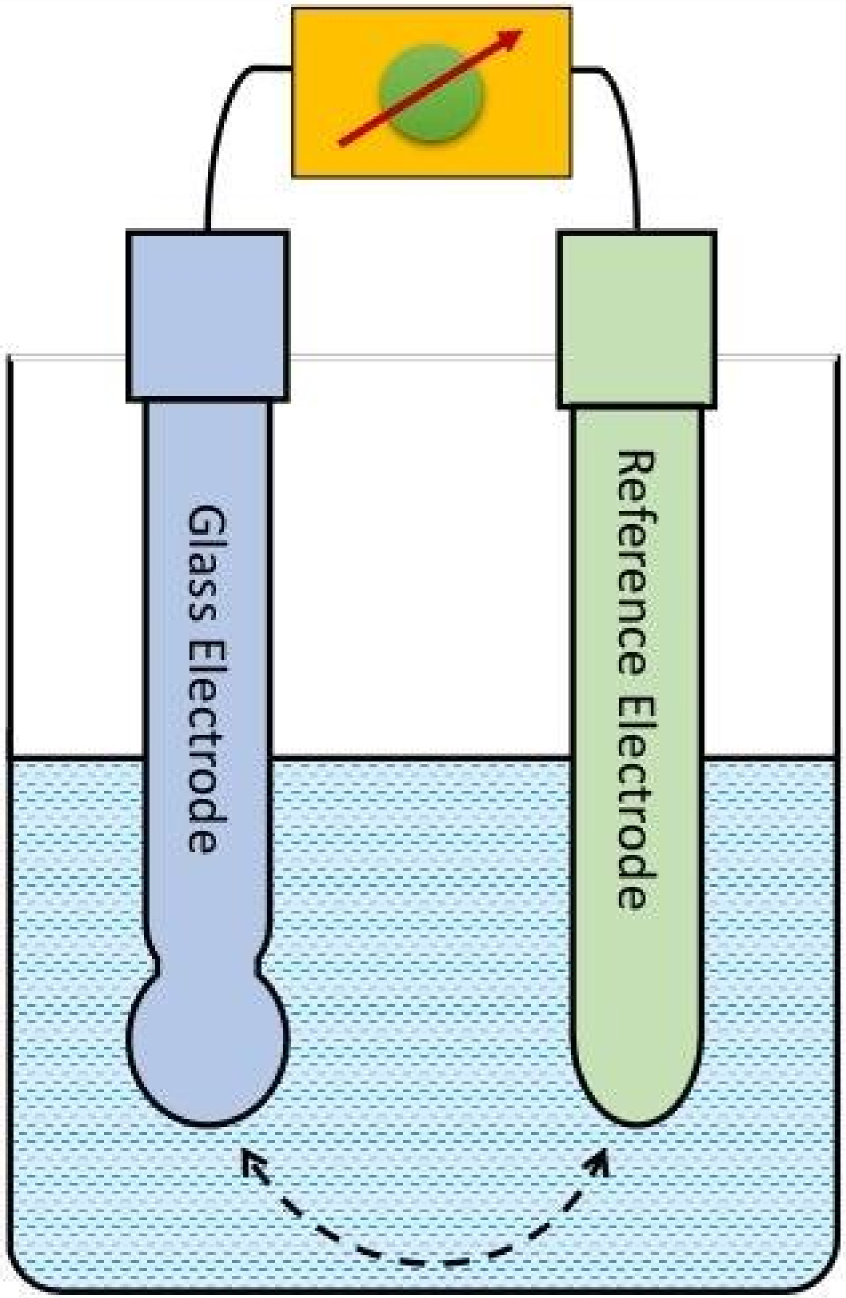


Fig Closed circuit of pH meter

pH Electrode – Working principle

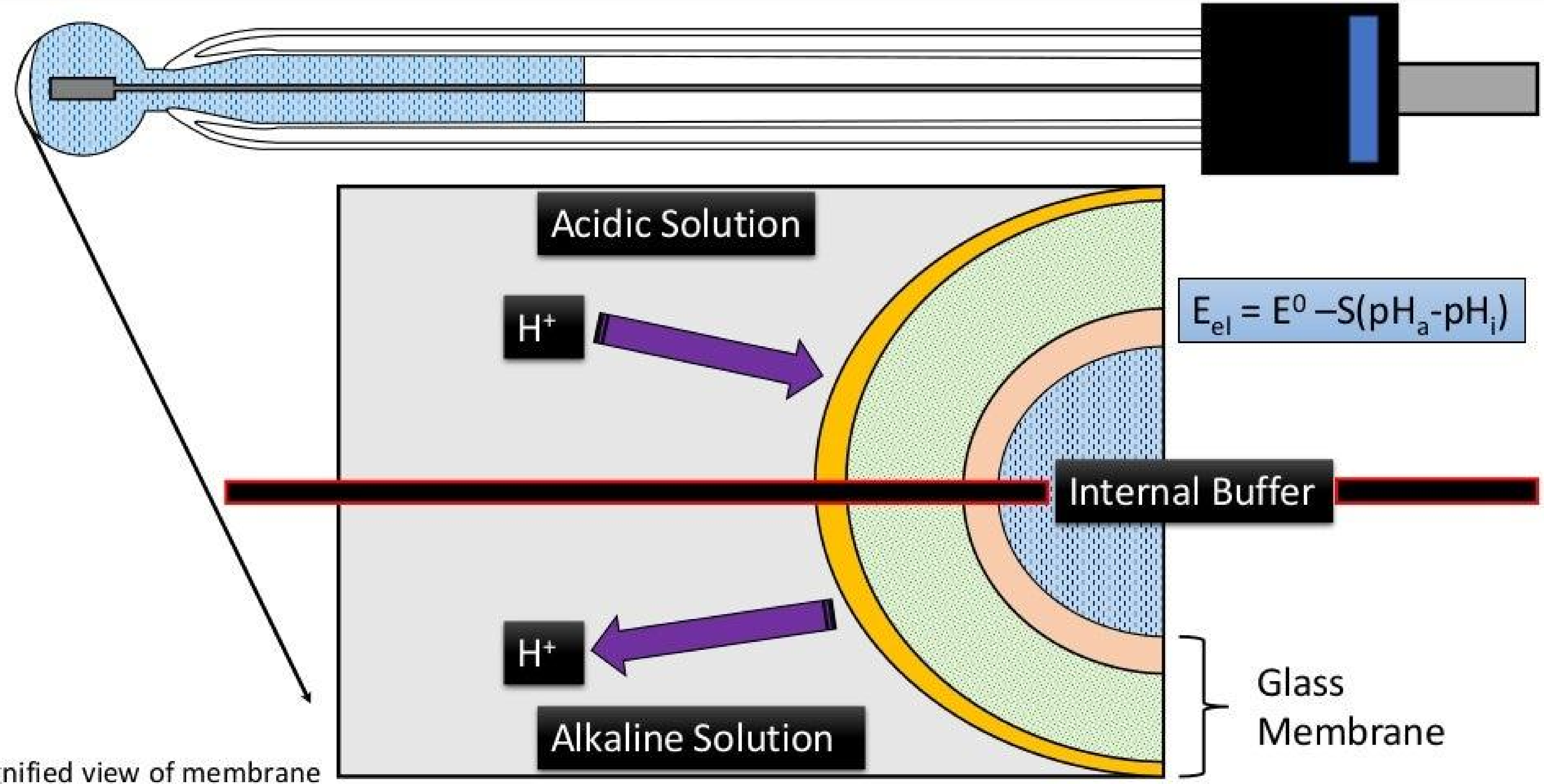


Fig Magnified view of membrane

pH meter – working principle

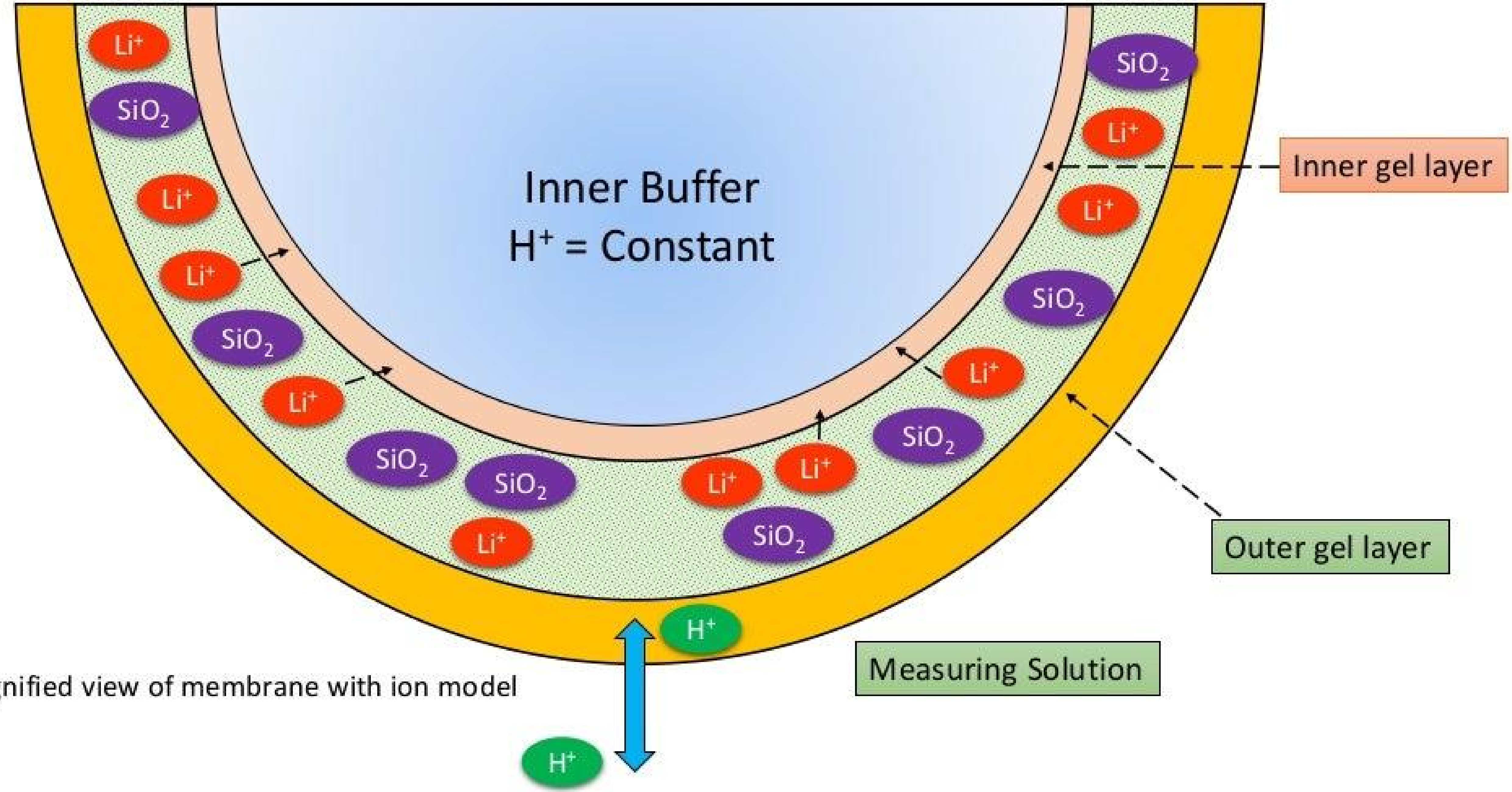


Fig Magnified view of membrane with ion model

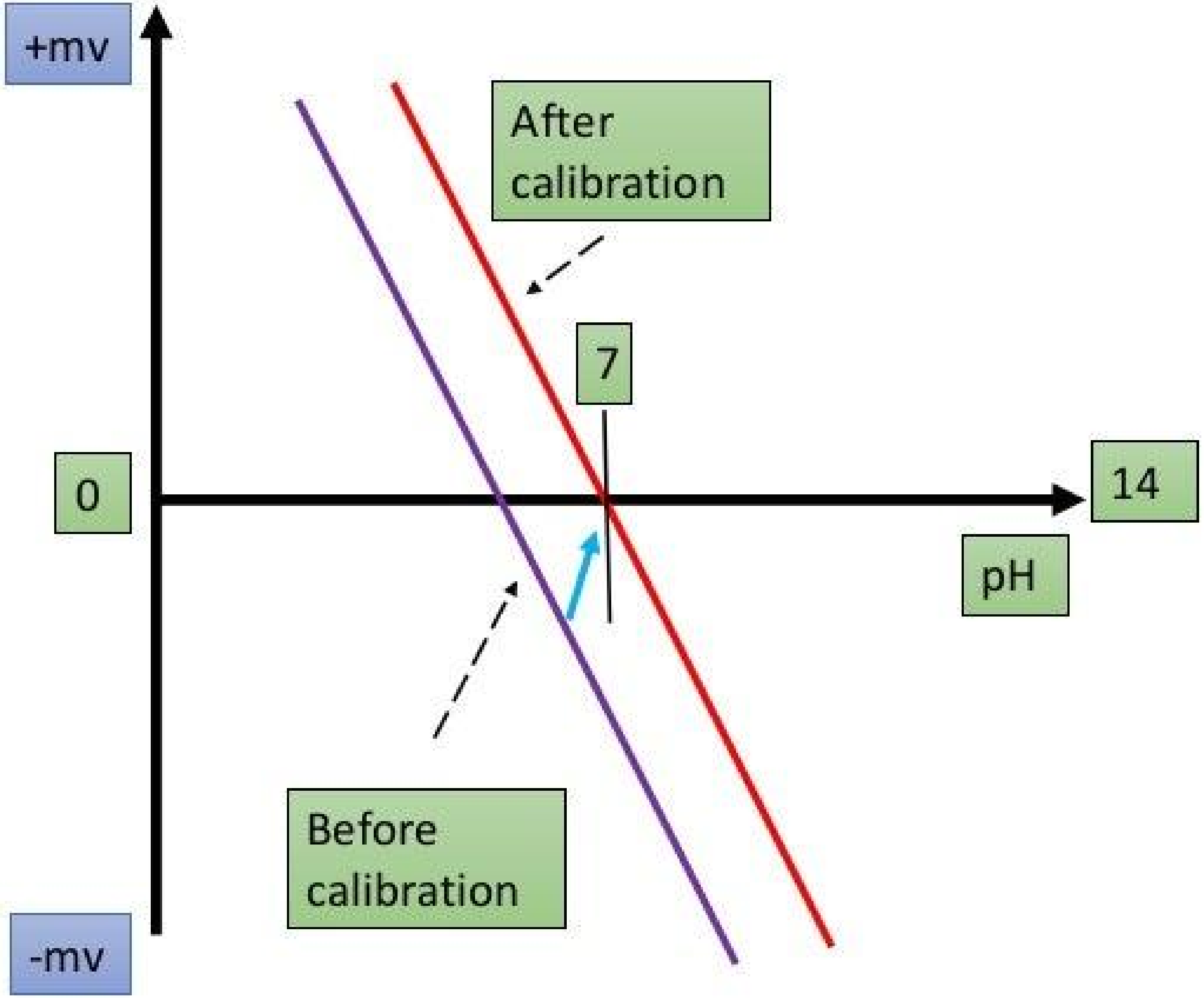
Calibration of pH meter

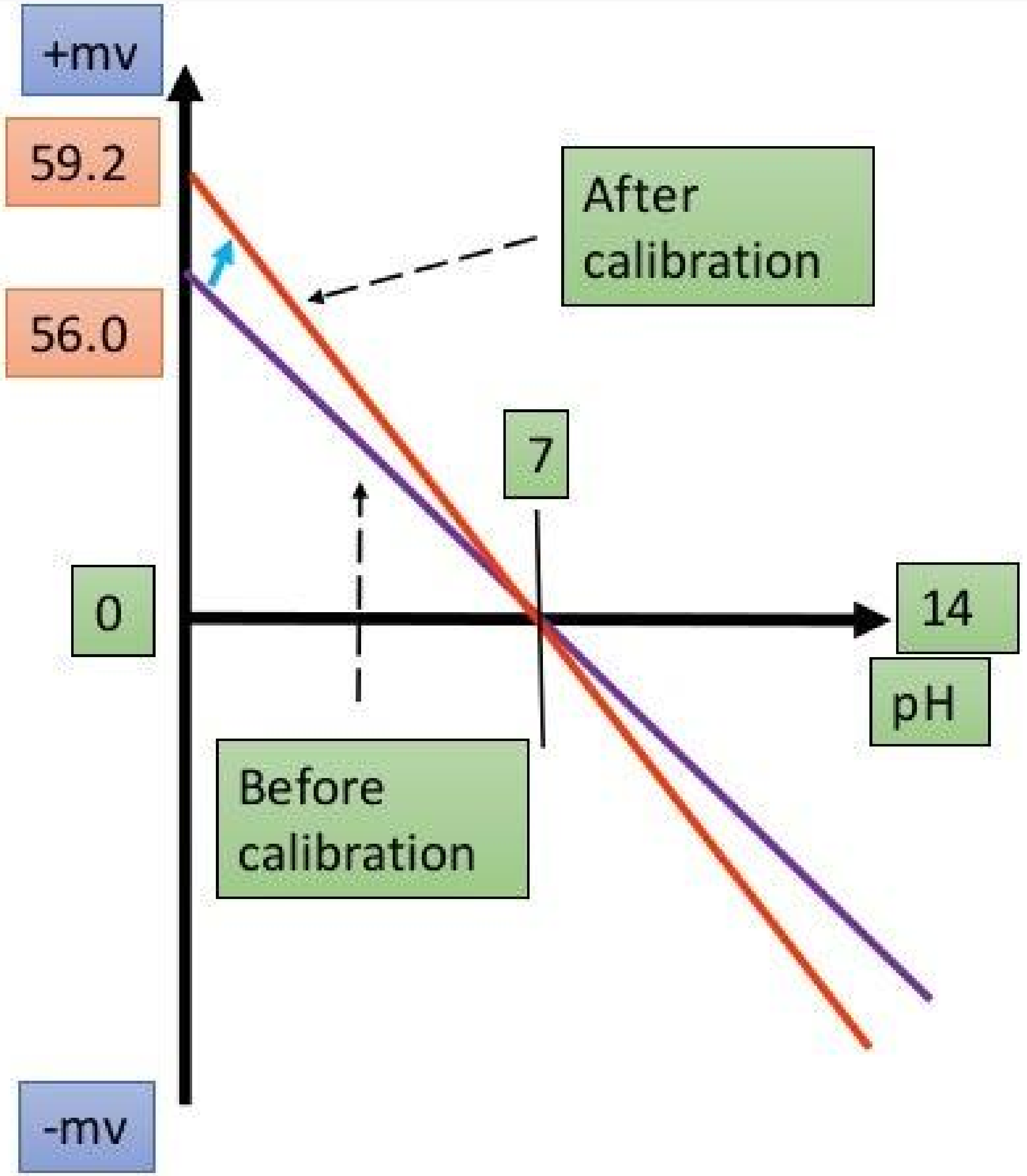
The measuring electrode and reference electrode, when put in a zero solution (7.0 pH buffer) provides a zero mV output.

Factors causing differences or changes in potential

- Contamination of the reference electrolyte solution.
- Electrolyte evaporation/depletion
- Chemical attack of the silver/silver chloride wire.
- Junction potential.
- Aging of the measuring electrode.

Calibration of pH meter





Calibration of pH meter

- 2 point calibration
- Multi point calibration

Fig pH meter with calibrators

Errors in determination of pH

- Alkaline error
- Acidic error
- Due to reactivity of reference electrolyte
- Error due to temperature variation

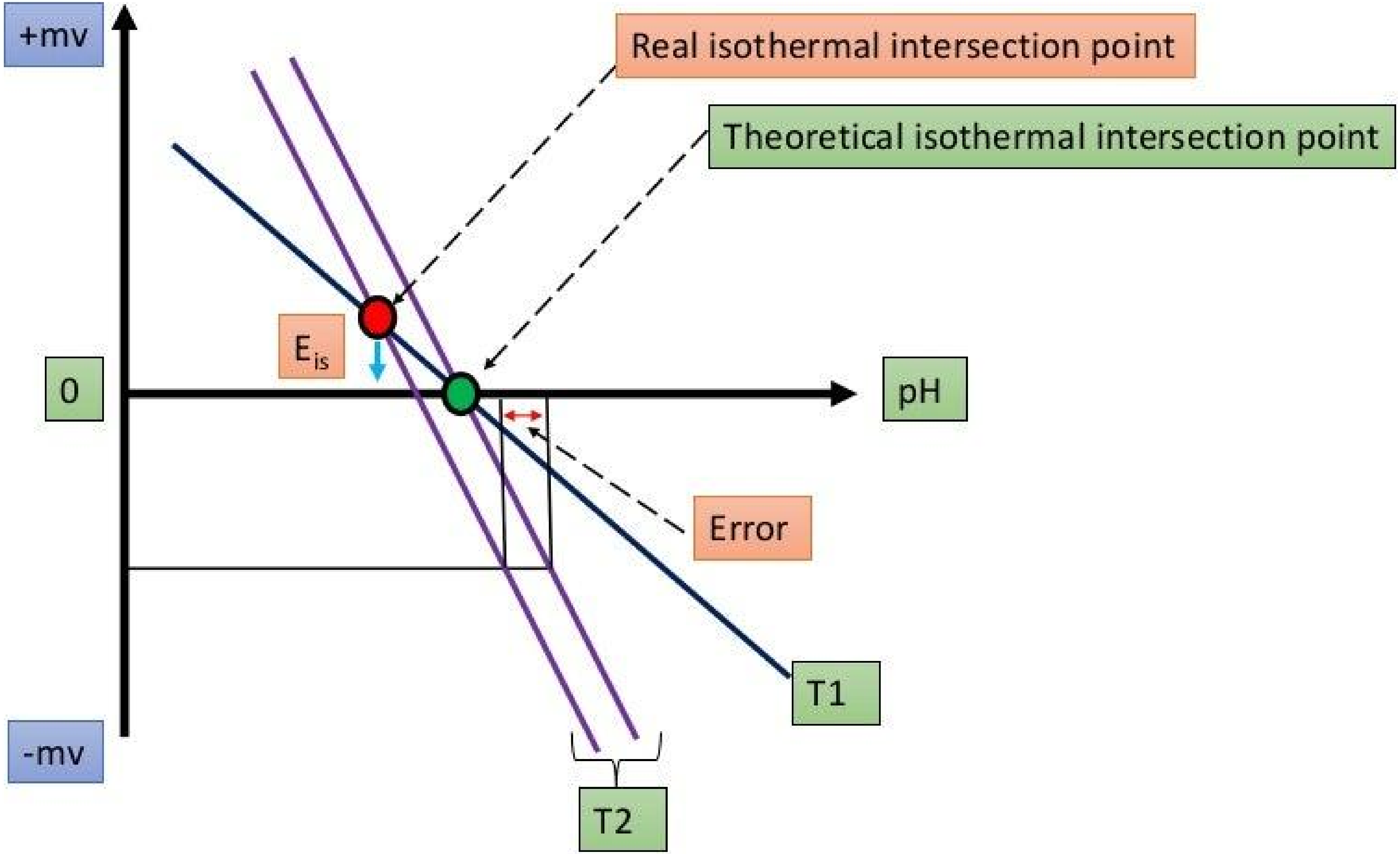
Temperature Compensation

Type of Solution	pH value at	
	20^0C	30^0C
0.001 Mol/L HCl	3.00	3.00
0.001 Mol/L NaOH	11.17	10.83
Phosphate Buffer	7.43	7.40
Tris Buffer	7.84	7.56

Table – Changes in pH with change in temperature

The linear function for temperature versus pH change → 0.003 pH error/pH unit/°C

Automated temperature compensation (ATC)



Maintenance & Storage of pH electrode

Dehydration

- Dehydration of glass electrode
- Dehydration of reference electrode

Factors detrimental to electrode life

- Chemical attack
- Stripping of gel layer

Transport

- Avoidance of freezing, extreme heat, mechanical shock and vibration

Storage

- At ambient temperatures (10-30 ^{0}C)
- Capped
- Ideal storage solution → 3 -3.5 M KCl solution

Definition of pH – a misnomer

- Concentration versus activity
- Activity depends on ionic strength of a solution
- $pH = -\{\log[H^+] \times [f]\}\ where\ f\ is\ activity\ co-efficient$
- Activity co-efficient depends on total molality of a solution

Molality	**0.001**	**0.005**	**0.01**	**0.05**	**0.1**
Activity co-efficient	0.964	0.935	0.915	0.857	0.829

pH of 0.01 M HCl
= -log (0.01 x 0.915)
=2.04

pH of 0.01 M HCl with 0.09 M KCl
= -log (0.01 x 0.829)
=2.08

pH is negative logarithm of hydrogen ion activity in a solution