Potentiometric Electrodes: Glass pH Electrode

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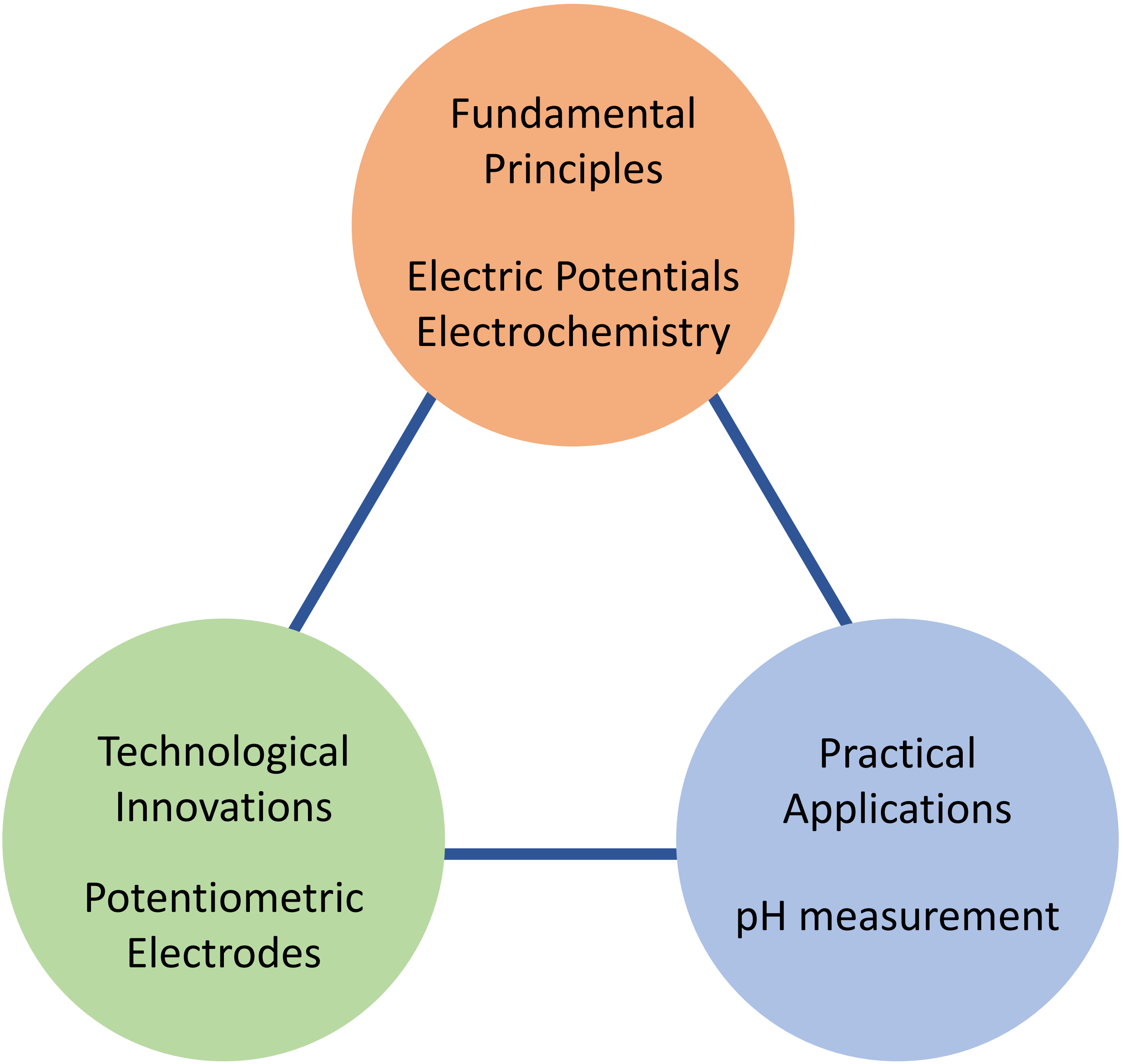
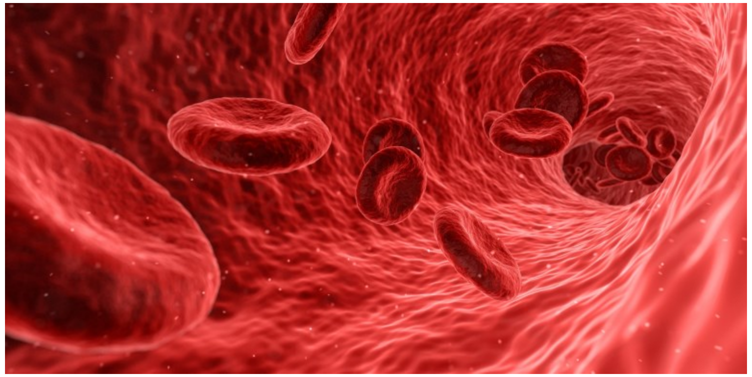

Fundamental Principles
Electric Potentials
Electrochemistry
Technological Innovations
Potentiometric Electrodes
Practical Applications
pH measurement

Why is pH important?

Biology



Blood: pH ~ 7.35 – 7.45
Tumor environment: pH < 7
Gastric acids: pH ~ 2

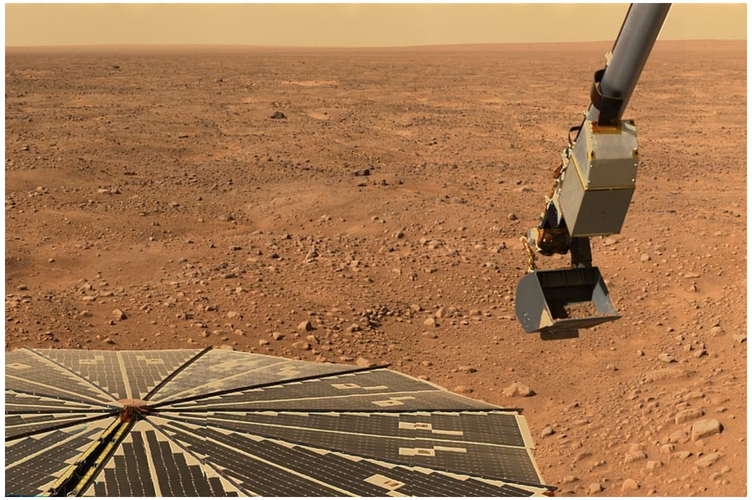
Ecology

Ocean acidification
Coral bleaching
Acid rain

Industry

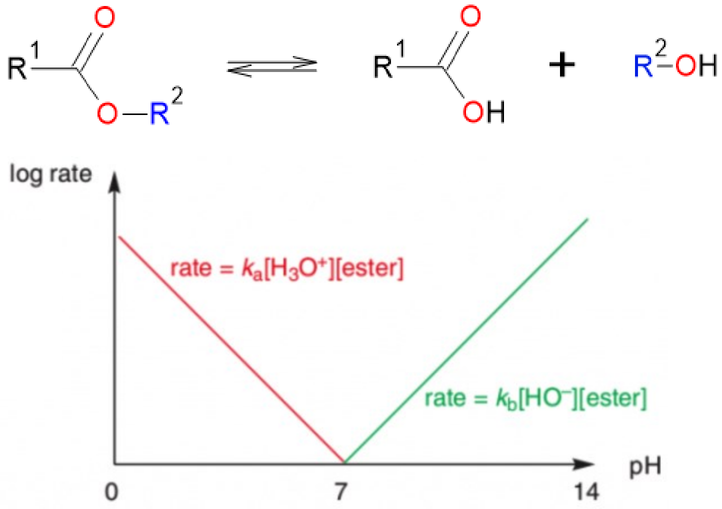
Food industry
Fermentation
Dyes

Geology



Soil analysis, planetary exploration

Synthesis



Catalysis and control of reactions

$$pH = -\log [H^+]$$

How can we measure pH?

How can we measure the ion concentrations?

Chemical Potential

rate of change in **energy** of the system with respect to the change in the concentration of species in a chemical reaction

$$chemical\ potential = \frac{potential\ energy}{number\ of\ molecules}$$

(at constant T, P, N, partial molar Gibbs free energy, $\bar{G}$, in J/mol)

If molecules are charged $\longrightarrow$ Electric Potential

$$electric\ potential = \frac{electrostatic\ potential\ energy}{charge}$$

E (J/C = V)

$$G = G^0 - RT \ln \frac{a_{products}}{a_{reactants}}$$

$\updownarrow$ E = G / n$\boxed{F}$

Nernst Equation

Driving force bringing the reaction to equilibrium

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{products}}{a_{reactants}}$$

Reaction product similar to an equilibrium constant… for a system that is NOT at equilibrium!

At equilibrium, potential is…

ZERO

E^0 = standard reduction potential (when a_i = 1)

R = gas constant, 8.314 J K^{-1} mol^{-1}

T = temperature, 298K

n = moles of electrons exchanged

F = Faraday constant, F = q_{e-} N_A = 96485.33 C mol^{-1}

a_i = activities (≈ concentrations, M)

How do we measure E?

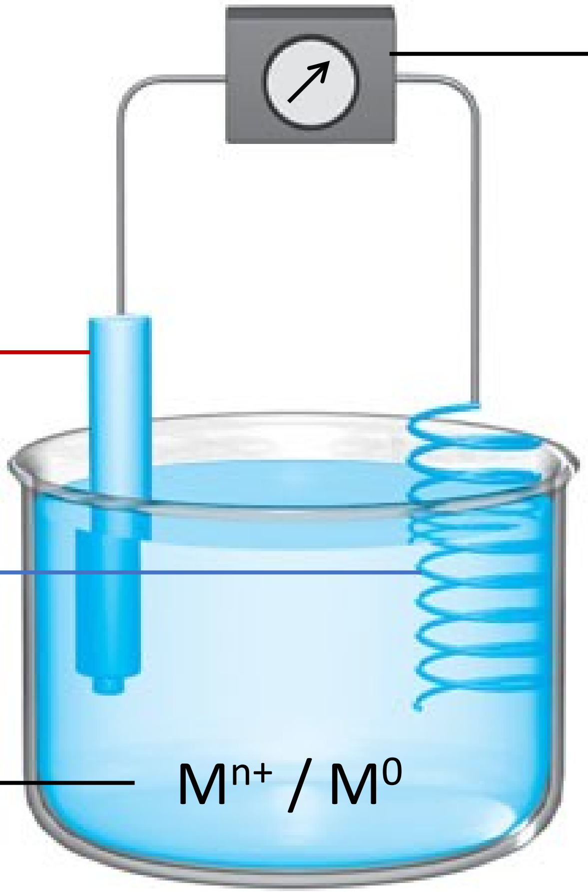
Potentiometry

Measurement of a difference in electric potential (a voltage) to obtain chemical information (concentration of charged species)

Measuring potential differences

Potential-measuring device

Voltmeter



Reference Electrode, E_{ref}

Indicator Electrode, E_{ind}

Test solution

$\Delta E = E_{ind} - E_{ref}$

Constant, known

Function of analyte concentration

Nernst Equation

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{products}}{a_{reactants}}$$

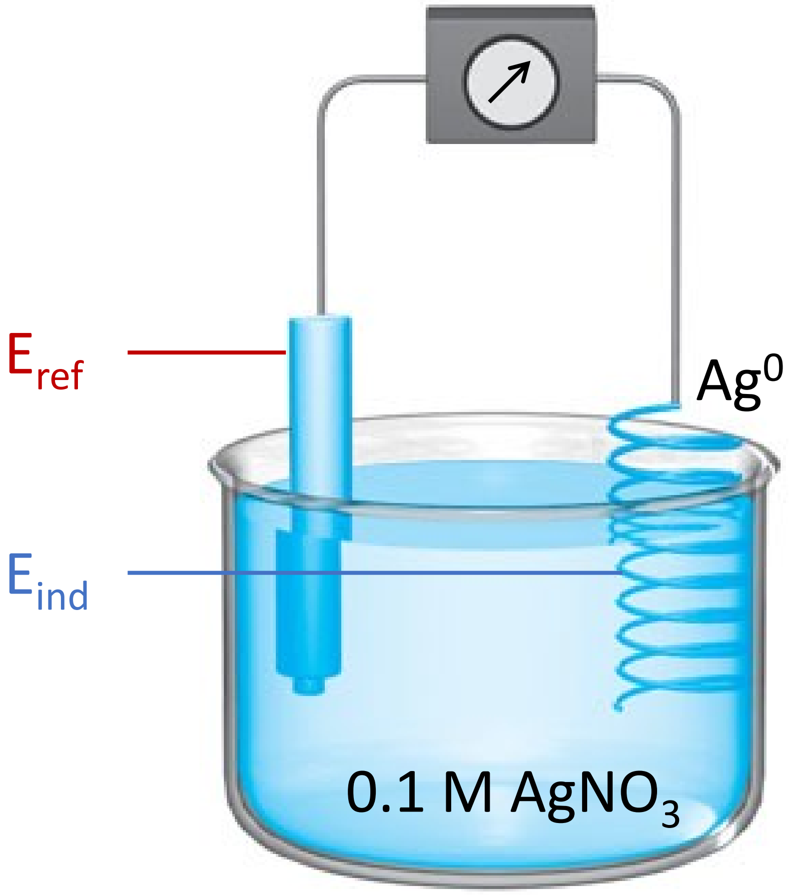
$M^+ + ne^- \rightarrow M^0$

$$\Delta E = E_{ind} - E_{ref}$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{products}}{a_{reactants}}$$

Ag|AgCl (sat. KCl): E_{ref} = + 0.197 V

E^0 (Ag^+|Ag^0) = + 0.799 V



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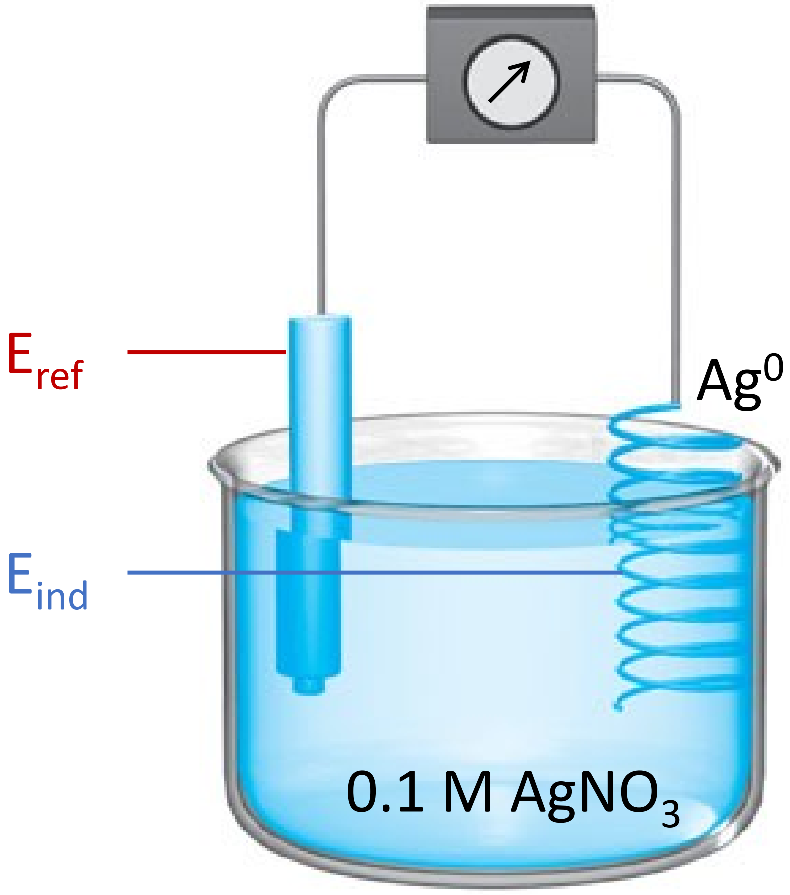


not generalizable to all metals, unspecific

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{products}}{a_{reactants}}$$

Ag^+ + e- → Ag^0 (s)

$$E = E^0 - \boxed{\frac{8.314 \cdot 298}{n \cdot 96485.33} 2.303} \log \frac{a_{products}}{a_{reactants}}$$

$$E = E^0 - \frac{0.0592}{n} \log \frac{a_{products}}{a_{reactants}}$$

$$E = 0.799 - \frac{0.0592}{1} \log \frac{1}{[Ag^+]}$$

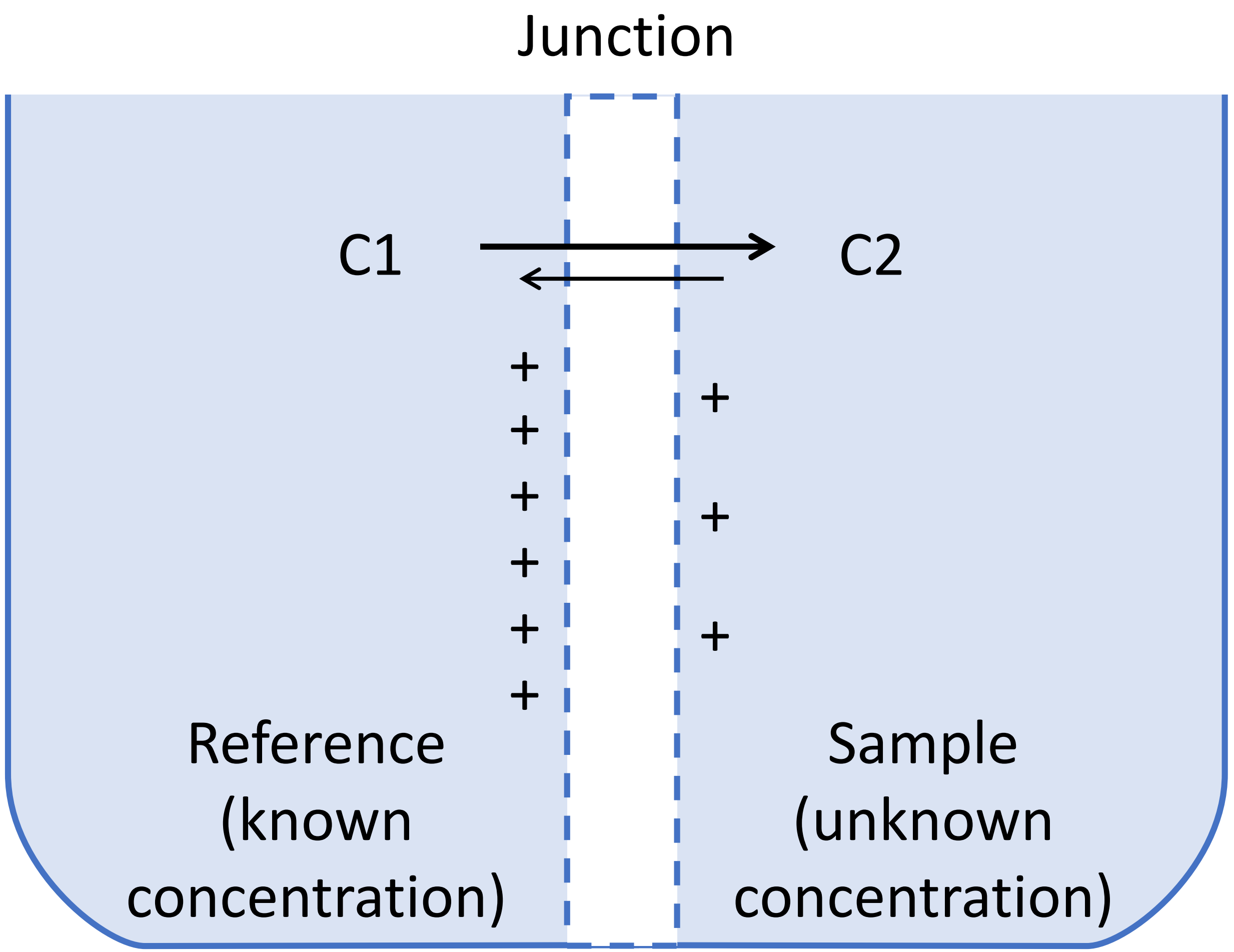
$$E = 0.799 - \frac{0.0592}{1} \log \frac{1}{0.1}$$

E_{ind} = 0.799 – 0.059 · 1 = 0.740 V

ΔE = 0.740 – 0.197 = **0.543 V**

How Else Can We Generate Potentials?

Junction Potentials



$\Delta C \longrightarrow$ chemical potential

If molecules are charged:

$\Delta C \longrightarrow$ electric potential, ΔE (V)

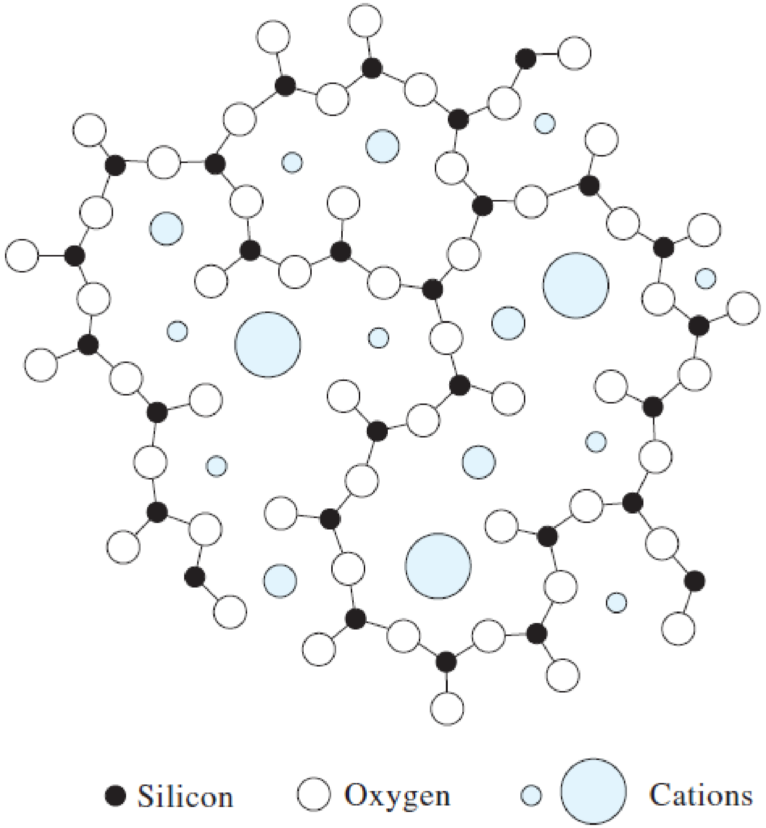
(as opposed to, e.g., fuel cells and batteries, this potential does not involve a redox process, but ***mass transport*** *of charged molecules)*

If the junction is selectively permeable to only one ion $\longrightarrow$ Ion-Selective Electrode!

Which Type of Membrane Is Selective for H^+?

Glass!!

Glass pH Electrode



Reference solution

Analyte solution

Known pH

Unknown pH

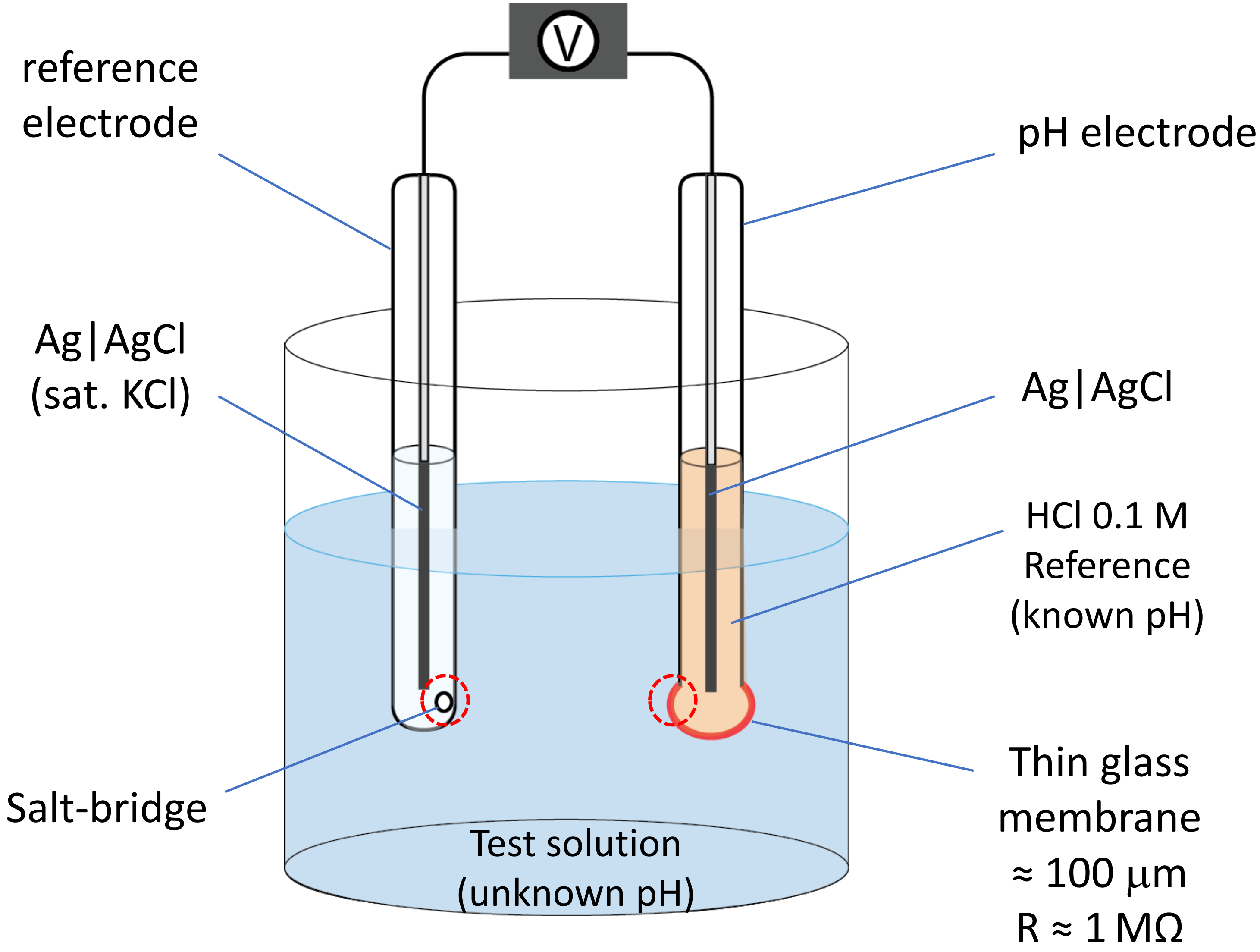
Potential at the membrane

$$E = E^0 - \frac{RT}{nF}\ 2.3\ \log\frac{a_{H^+,\ sol}}{a_{H^+,\ ref}}$$

$$E = E^0 - \ 0.0592\ \Delta pH$$

How can we measure this potential?

Glass pH Electrode



$$\Delta E = E_{ind} - E_{ref}$$

$$\Delta E = E_{ref}^{ind} + E_{membrane} - E_{ref}$$

$$E_{membrane} = 0.0592\,(pH_{sol} - pH_{ref})$$

$$E = constant + 0.0592 \cdot pH_{sol}$$

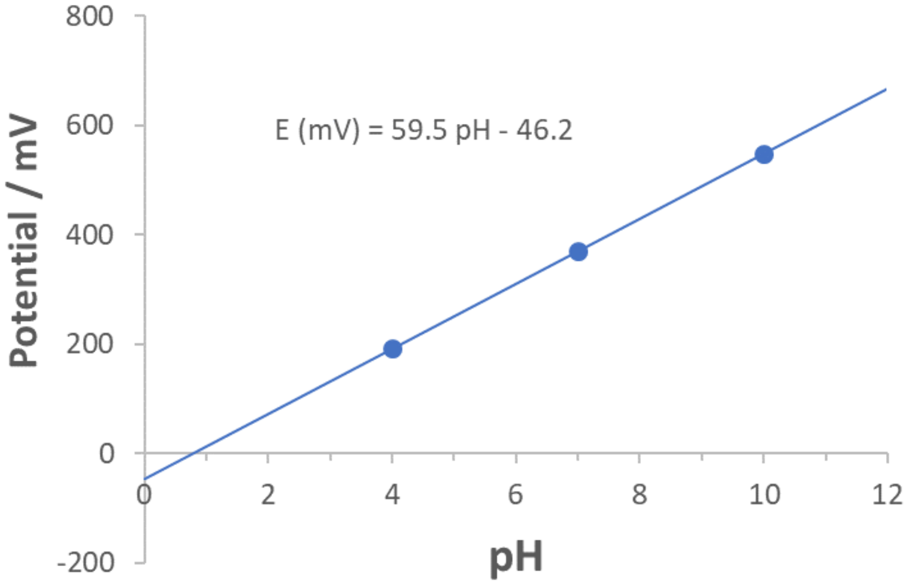
Beware of junction potentials!

$$E = constant + 0.0592 \cdot pH_{sol} + E_{juntion}$$

Unknown, not constant

6 mV ≈ 0.1 pH units

Glass pH Electrode



2-3 point calibration in the range of pH of your sample

$$E = E_{ref}^{ind} + E_{membrane} - E_{ref}^{ref}$$

$$E_{membrane} = 0.0592\,(pH_{sol} - pH_{ref})$$

$$E = constant + 0.0592 \cdot pH_{sol}$$

Beware of junction potentials!

$$E = constant + 0.0592 \cdot pH_{sol} + E_{juntion}$$

Unknown, not constant

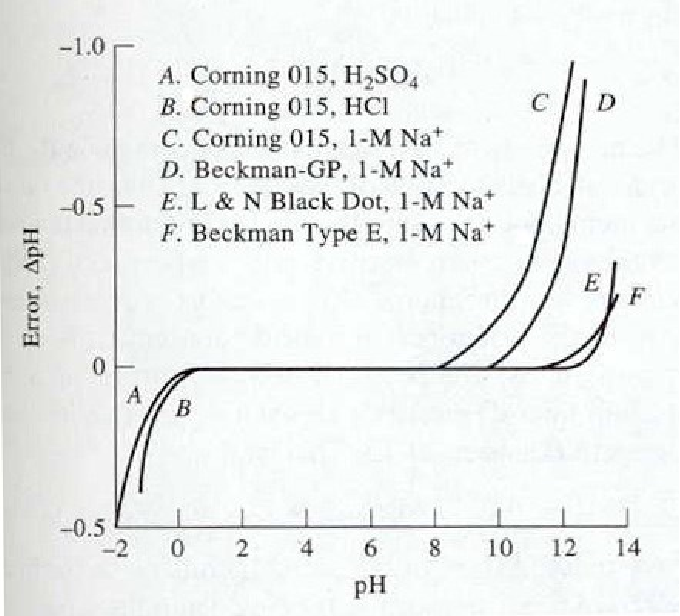
6 mV ≈ 0.1 pH units

Sources of Error

Calibration solution should be comparable to your sample
(pH, T, ionic strength)

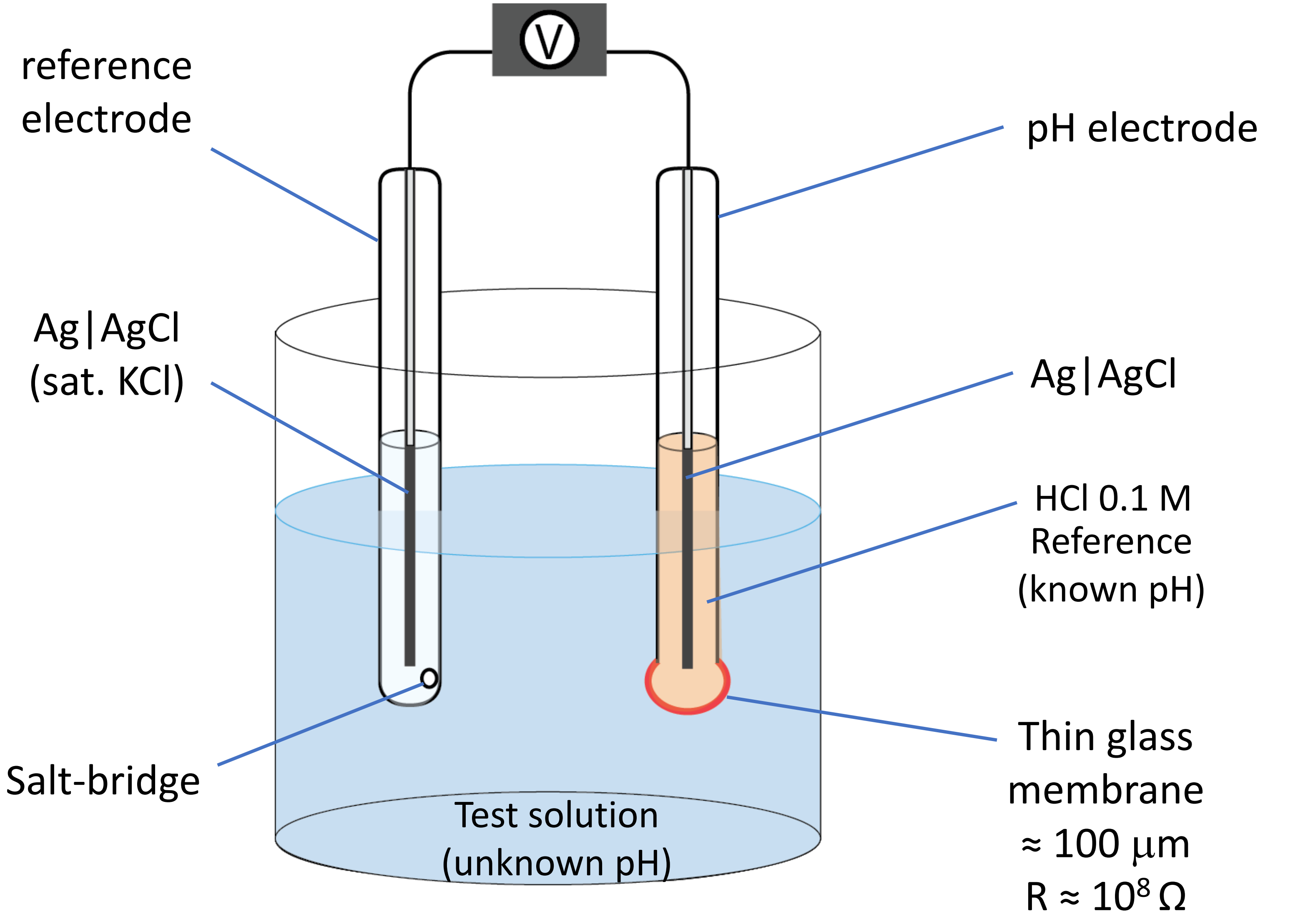
Selectivity: Na^+

Acidic error:
Saturation of glass membrane



Basic error
$[H^+]$ too low
$[Na^+]$ too high

Glass pH Electrode



Glass pH Electrode

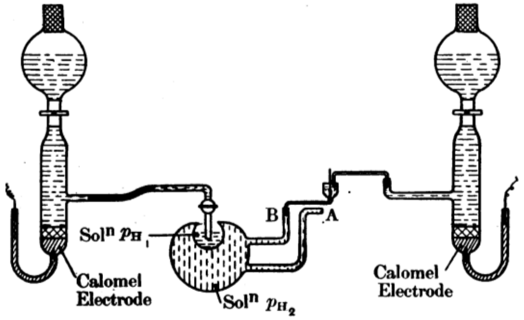
Phyllis Margaret Tookey Kerridge (1901-1940)

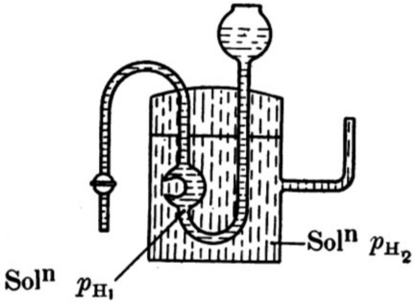
XCI. THE USE OF THE GLASS ELECTRODE IN BIOCHEMISTRY.

BY PHYLLIS TOOKEY KERRIDGE.

From the Institute of Physiology, University College, London.

(*Received June 18th, 1925.*)



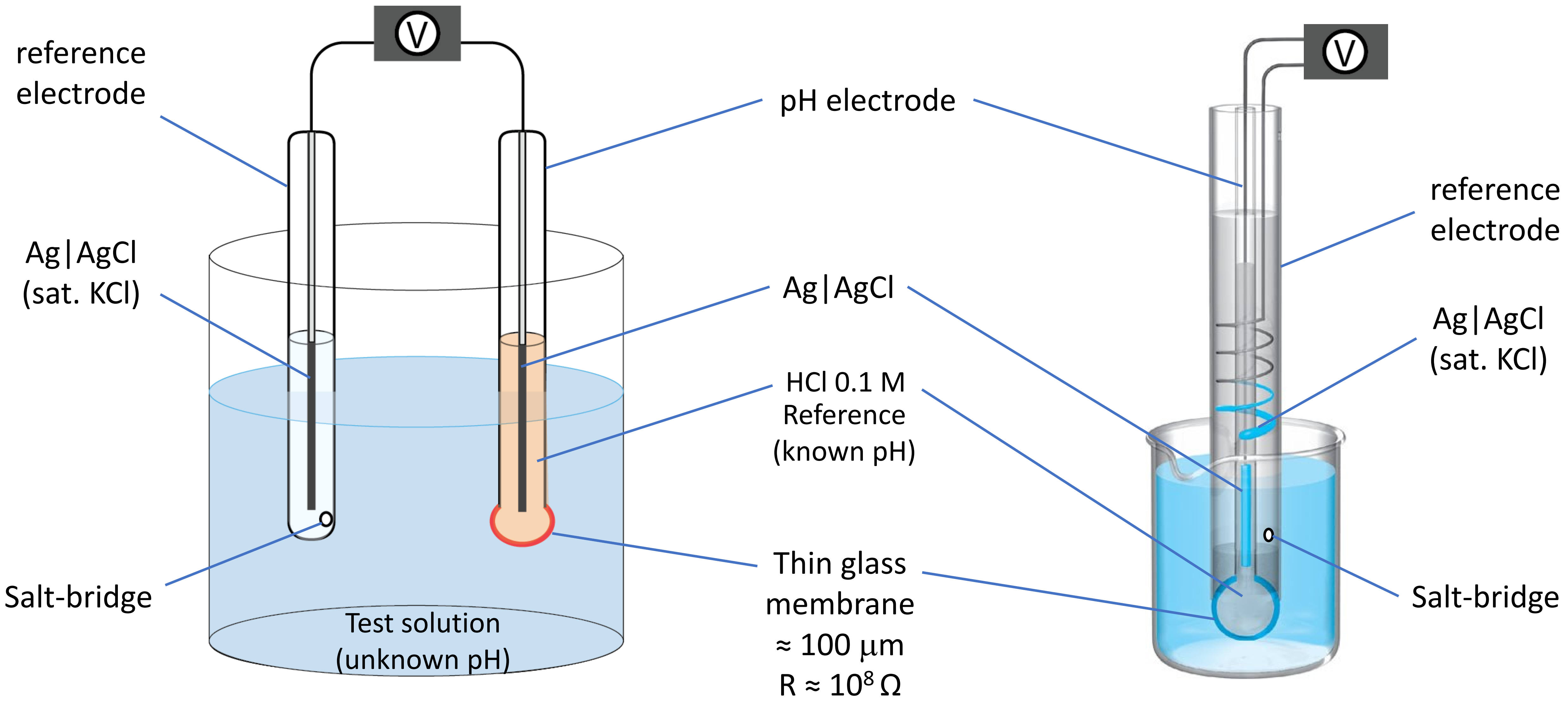


Arnold Beckman (1900-2004)

First “portable” pH meter, 1934

Beckman Model G pH Meter

Glass pH Electrode



Practical Considerations

Calibration!

Never let dry

To rinse it, gently pat the surface with a wipe.
Rubbing it will cause static electricity build-up.

The tip is extremely fragile (100 μm thick glass!)

Know when to you need a pH meter:

References & Links

Quantitative Chemical Analysis, 8th Ed. Daniel C. Harris

Chapters 13, 14

Fundamentals of Analytical Chemistry, 9th Ed. Skoog, West, Holler & Crouch

Chapter 21

Electrochemical Methods: Fundamentals & Applications, 2nd Ed. Bard & Faulkner

Chapter 2 (more advanced, rigorous treatment of electrostatic potentials and junctions)

***Bonus Track: Online Tutorial for DIY pH Electrode

https://www.instructables.com/cheap-DIY-electronic-pH-meter/