Essentials of pH Measurement

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Thermo Scientific Electrochemistry Products

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What is pH?

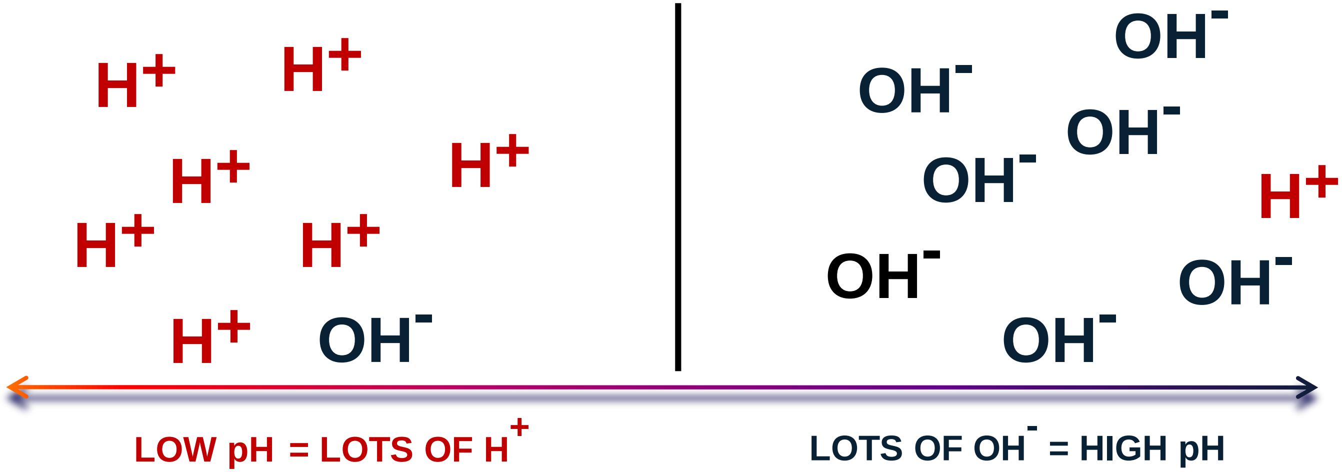
- **The Theoretical Definition**

$$\mathbf{pH = -\log a_H}$$

- a_H is the free hydrogen ion *activity* in a sample, not total ions.
- In solutions that contain other ions, activity and concentration are not the same. The activity is an *effective* concentration of hydrogen ions, rather than the true concentration; it accounts for the fact that other ions surrounding the hydrogen ions will shield them and affect their ability to participate in chemical reactions.
- These other ions effectively change the hydrogen ion concentration in any process that involves H^+. pH electrodes are an ISE for hydrogen.

What is pH?

- pH = “Potential Hydrogen” or Power of Hydrogen
- The pH of pure water around room temperature is about 7. This is considered "neutral" because the concentration of hydrogen ions (H^+) is exactly equal to the concentration of hydroxide (OH^-) ions produced by dissociation of the water.
- Increasing the concentration of H^+ in relation to OH^- produces a solution with a pH of less than 7, and the solution is considered "acidic".
- Decreasing the concentration H^+ in relation to OH^- produces a solution with a pH above 7, and the solution is considered "alkaline" or "basic".



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What is pH?

- The pH Scale

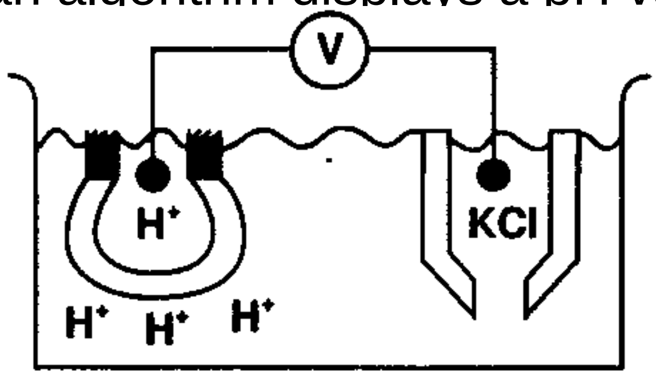
- Each pH unit is a factor 10 in $[H^+]$
  - pH of Cola is about 2.5. This is 10x more acidic than Orange Juice (pH of 3.5)
  - Cola is 100x more acidic than Beer! (pH of 4.5)

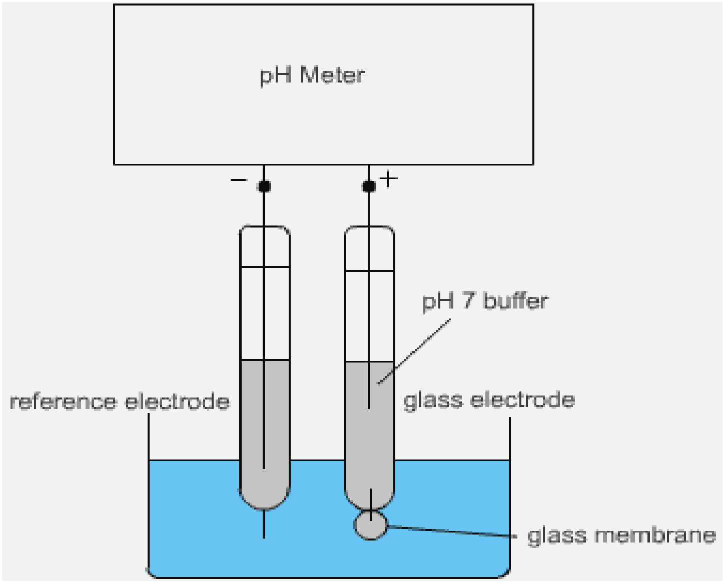
Representative pH values

Substance	pH
Hydrochloric Acid, 10M	-1.0
Lead-acid battery	0.5
Gastric acid	1.5 – 2.0
Lemon juice	2.4
Cola	2.5
Vinegar	2.9
Orange or apple juice	3.5
Beer	4.5
Acid Rain	<5.0
Coffee	5.0
Tea or healthy skin	5.5
Milk	6.5
Pure Water	7.0
Healthy human saliva	6.5 – 7.4
Blood	7.34 – 7.45
Seawater	7.7 – 8.3
Hand soap	9.0 – 10.0
Household ammonia	11.5
Bleach	12.5
Household lye	13.5

pH Measurement System

- When two solutions containing different concentrations of H^+ ions are separated by a glass membrane, a voltage potential is developed across the membrane. (Sensing electrode)
- A voltage potential is also generated from the reference electrode.
- The pH meter measures the voltage potential difference (mV) between the sensing electrode and the outside sample (reference electrode) and via an algorithm displays a pH value.





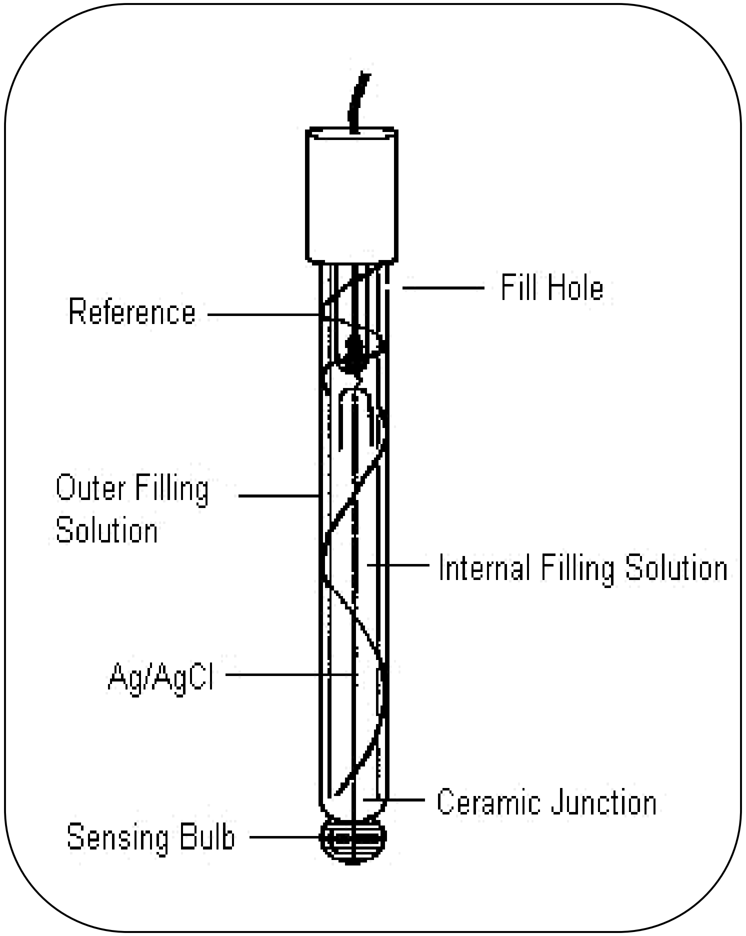
pH Measurement System

- The pH Meter
  - Acts as a volt meter
  - Translates electrode potential (mV) to pH scale
- Meter functions
  - Stores calibration curve
  - Adjusts for temperature changes
  - Adjusts electrode slope
  - Signals when reading is stable
- Features
  - mV and relative mV scales
  - Recognizes US Standard Buffers
  - Number of calibration points
  - Display information
  - RS232 or recorder outputs
  - Datalogging
  - GLP/GMP compliant

Measuring pH

- How do electrodes work?
  - If two solutions are separated by an ion-permeable membrane, they will equilibrate.
  - If the electrode membrane is permeable to ONLY one ion species, a charge will quickly develop that opposes further ion movement.
  - The charge that develops across the membrane is proportional to the difference in the ion concentration on the other side.

pH Measurement System



The pH Electrode

- Combination
- Sensing Half-Cell
- Reference Half-Cell

Internal filling solution (Sensing)

- Buffer solution

Outer Filling solution (Reference)

- Saturated AgCl, KCl

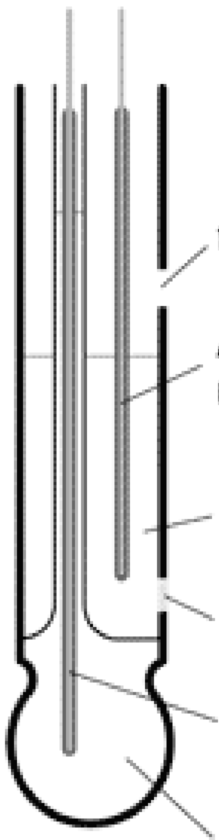
Common References

- Calomel (going, going…..)
- Ag/AgCl
- ROSS™

pH Measurement System – Reference Electrode

- In a two electrode system a reference electrode is needed to complete the "circuit".
  - Combination electrode has the reference built in.
- The reference wire or element is typically encased in Saturated AgCl or KCl
- The reference must have a "liquid" connection to the sample in order to generate a voltage potential.

Common Questions – Electrode Types



- What is a combination electrode?
  - A combination pH electrode is one that has a sensing half-cell and a reference half-cell built into one electrode body instead of existing as two separate electrodes. (Same size as a reference or sensing electrode.)
- What is a triode?
  - A triode is a combination electrode (sensing and reference together) plus an ATC (automatic temperature compensation thermistor) all built into one electrode body. (Same size as a reference, sensing or combination electrode.)

pH Measurement System – Reference Types

- **Calomel Reference (Hg/Hg_2Cl_2) (Going, going ……….)**
- Calomel electrodes is very stable and is ideally suited for use with TRIS buffers and sample solutions containing proteins and other biological media.
  - Also used where samples contain metal ions, sulfides, or other substances that will react with Ag or AgCl .
- Advantages
  - Low Cost, Good Precision (±0.02 pH)
- Disadvantages
  - Limited body styles, Temperature Hysteresis, Contains Mercury!

pH Measurement System – Reference Types

Single Junction Silver/Silver Chloride Reference (Ag/AgCl)	• Recommended for all applications **except** those involving TRIS buffer, proteins, metal ions, sulfides or other substances that will react with either Ag or AgCl.
Advantages	• Mid-range cost, Variety of body styles, Refillable or gel-filled, Good Precision (±0.02 pH)
Disadvantages	• Temperature Hysteresis, complexation in samples such as: TRIS, proteins, sulfides

pH Measurement System – Reference Types

Double Junction Silver/Silver Chloride Reference (Ag/AgCl)	• The double junction Ag/AgCl reference isolates the reference, making it ideally suited for all types of samples.
Advantages	• Mid-range cost, Variety of body styles, Refillable or gel-filled, Good Precision (±0.02 pH)
Disadvantages	• Temperature Hysteresis

Mercury Free alternative to the Calomel Reference

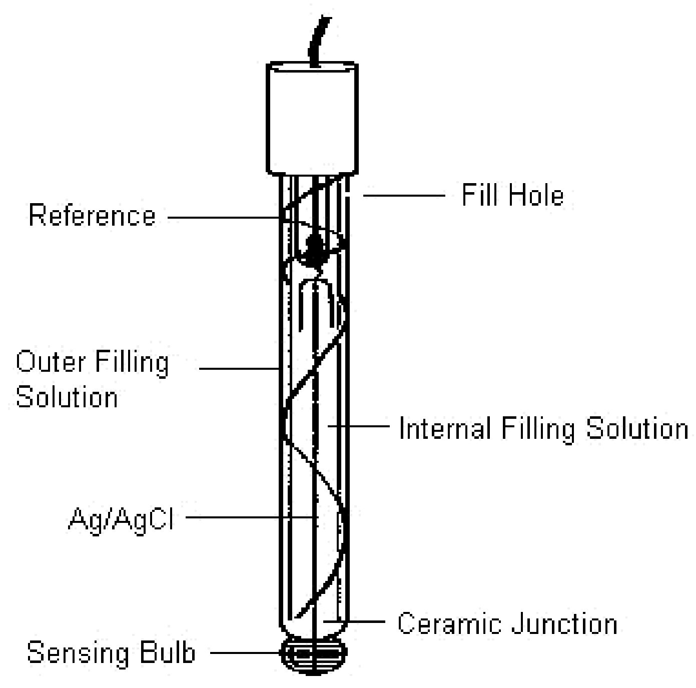
pH Measurement System – Reference Types

ROSS™ Reference	• Double Junction Iodine/Iodide redox couple • The ROSS™ reference is ideally suited for all sample types and all temperature ranges
Advantages	• Variety of body styles, Unmatched Precision (±0.01 pH), Fast response, Stable to 0.01 pH in 30 seconds over 50 ºC temperature change, Drift less than 0.002 pH units/day
Disadvantages	• Cost

Mercury Free alternative to the Calomel Reference

pH Measurement System - Junctions

- The electrode junction is where the Outer fill solution (reference) passes from inside the electrode body to the sample completing the “circuit”.
- The type of junction is a good indicator of how the electrode will perform in different samples.
- Three basic types of junctions
  - Wick
  - Ceramic
  - Open



pH Measurement System - Junctions

The Wick Junction

- Glass fiber, fiber optic bundles, Dacron, etc.

Advantages

- Used in rugged epoxy bodies
- Good for aqueous samples

Disadvantages

- Will clog if sample is “dirty” or viscous
- Not as “fast” as other junctions

pH Measurement System - Junctions

The Ceramic Junction	• Porous ceramics, wooden plugs, porous teflon, etc.
Advantages	• Good all-purpose junction • Ideally suited for most lab applications
Disadvantages	• Will clog if sample is “dirty” or viscous

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pH Measurement System - Junctions

The Open Junction

- Sure-Flow, Laser Drilled Hole, Ground Glass Sleeve, etc.

Advantages

- Junction will never clog
- Can be used in all sample types
- Ideal choice for “dirty” or viscous samples
- Can be used in non-aqueous samples

Disadvantages

- Sure-Flow Junction has a high flow rate of fill solution (2 ml/day)

Common Questions – Electrode Types

- Single Junction
  - There is one junction in the electrode body. This term applies to Ag/AgCl electrodes that have a silver reference wire and silver ions dispersed in the internal electrolyte fill solution.

- Double Junction
  - There are two junctions in the electrode body. This term applies to any electrode that is a ROSS or calomel electrode and to some Ag/AgCl electrodes.

pH Measurement System – Electrode Types

Refillable or Low Maintenance Gel?

Low Maintenance Gel Electrodes

- Easy to use
- Rugged epoxy body
- 0.05-0.1 pH precision
- Slower response rate
- 6 month average life
- Gel memory effects at junction

Refillable Electrodes

- Fill/drain electrode
- Wide applicability
- Glass or epoxy body
- 0.02 pH precision
- Faster response rate
- 1 year minimum life
- Replaceable fill solution

pH Measurement System – Electrode Types

Polymer or Low Maintenance Gel?

Low Maintenance Gel Electrodes

- Easy to use
- Rugged epoxy body
- 0.05-0.1 pH precision
- Slower response rate
- 6 month average life
- Gel memory effects at junction

Polymer Electrodes

- Low maintenance
- Easy to use
- Glass or epoxy body
- 0.02 pH precision
- Faster response rate
- 1 year minimum life
- Double junction design

pH Measurement System - Electrode Selection

- Select proper reference for application
  - ROSS™, Single or Double Junction Ag/AgCl
  - Remember that Calomel contains Mercury!
- Select proper junction for application
  - Wick, Ceramic, Open, Sure-Flow, etc.




- Select appropriate body style
  - Standard, semi-micro, micro, rugged bulb, spear tip, flat surface, NMR, 384
- Select appropriate body type
  - Glass body, epoxy body
- Other considerations
  - Refillable, Gel, or Polymer?
  - Built in Temperature Probe?

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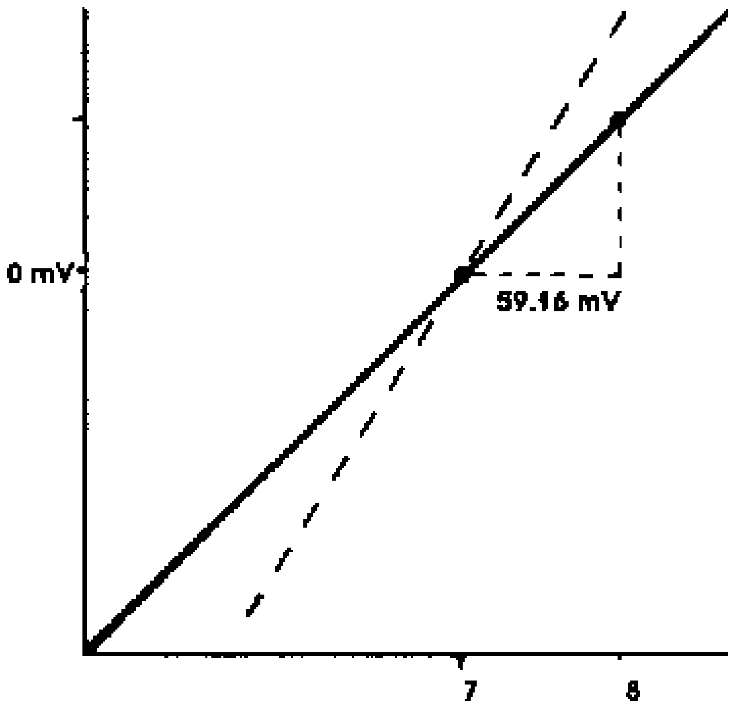
pH Calibration

- The Nernst Equation

$$\boldsymbol{E = E_0 - RT/nF \log a_H}$$

E = measured potential
E_0 = reference potential
R = Universal Gas Constant
T= Temperature (at 25 ^oC)
n = Number of electrons
F = Faraday Constant
a_H = Hydrogen Ion activity

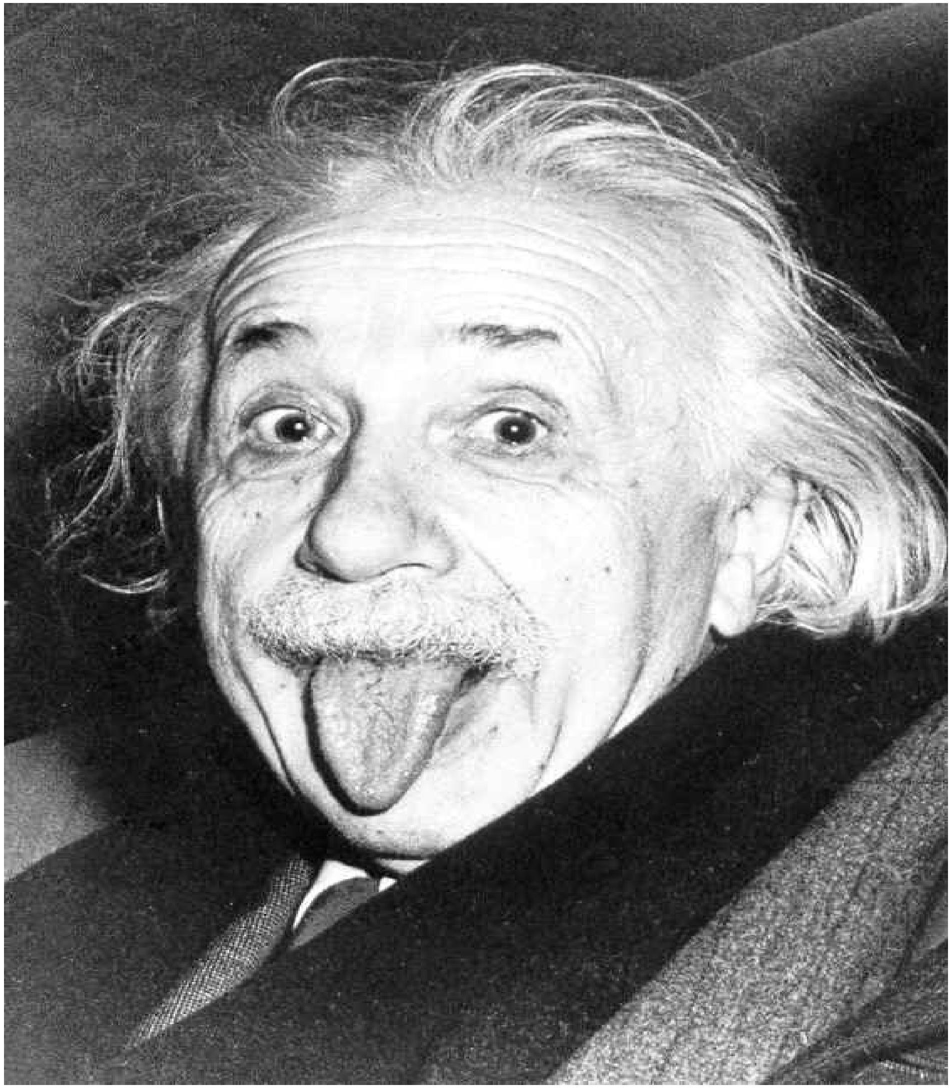
Slope = RT/nF = 59.16mv @ 25 ^oC



Walther Nernst

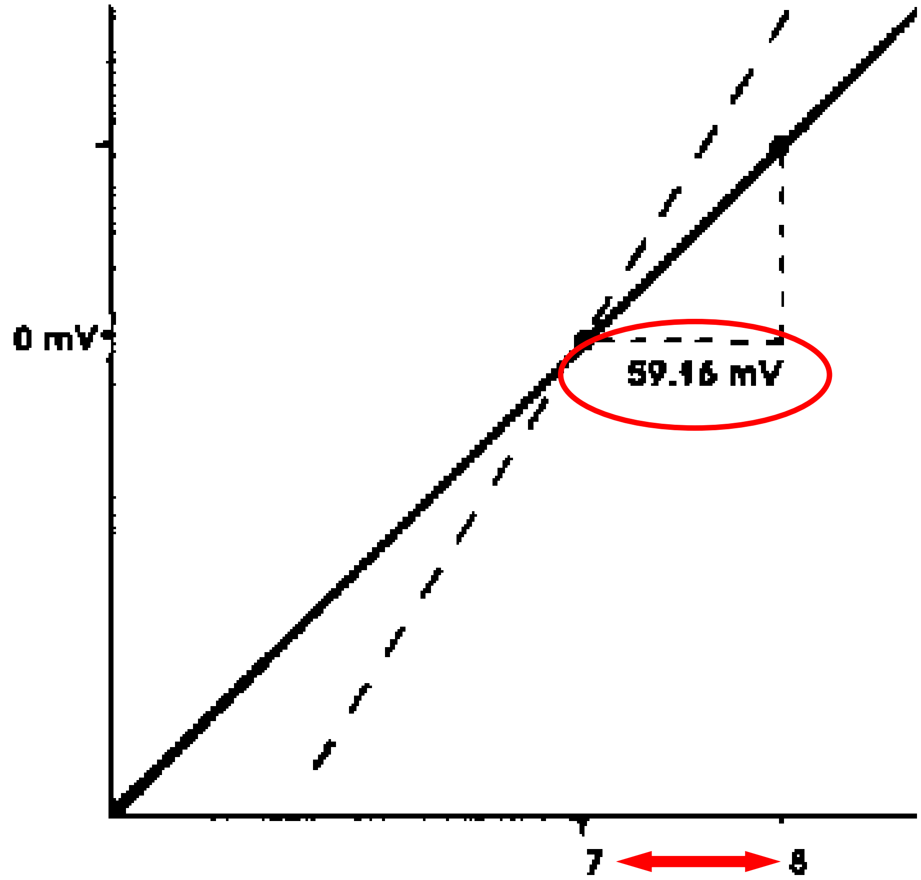
- Nobel Prize Winner in Chemistry in 1920
- Worked with other famous chemists, physicists and scientists.

Albert Einstein



pH Calibration

% slope is the change in mV value divided by the Nernstian theoretical value of 59.2 mV, the expected change in mV per pH unit at 25 ^{o}C



pH Calibration

- When you are calibrating, you are determining the electrodes slope as it relates to the theoretical slope defined by the Nernst Equation
- Newer meters automatically calculate slope
- Check slope manually by reading mV in buffers and comparing to Nernstian response (59.2 mV/pH unit)

- *Example:*
  - pH 7 = -10 mV
  - pH 4 = +150 mV
  - Slope = 160 mV/177.6 mV = **90.1%**
  - Where did this 177.6mV come from?
    - A change of 3 pH units (7-4)
    - 59.2 mV per pH unit x 3 equals 177.6 mV

Common Questions: *Calibration*

My samples range from pH 5 to 8. Can I use a 4 and 10 standard for my 2-point calibration?

- *The slope (or efficiency) of any electrode will not be consistent across a range of measurement.*
- *The greater the range between calibration points, the greater the measurement error.*
- *Calibration should include at least 2 buffers, but these buffers should be no more than 3 pH units apart from the next sequenced buffer.*
- *The 4-10 slope created across 6 decades of measurement will provide less accuracy than two point-to-point slopes using 4-7 (3 decades) and 7-10 (3 decades)*

Common Questions: *Calibration*

I have small containers on my bench that are labeled and filled with fresh buffer each week.
We re-use these buffers all week.
Will this practice affect my calibration?

Cal 1, using fresh 7 and 10 buffer:

- *slope between 7-10 = 96.7%*

Cal 2, using fresh 7 and old 10 buffer:*

- *slope between 7-10 = 93.4%*

** set on shelf uncovered for 8 hours*

ALWAYS use fresh buffer for each calibration.

Don’t re-use today’s buffer for tomorrow’s calibration!

pH Calibration - Guidelines

- Always calibrate with at least 2 buffers
- Check calibration drift with 1 buffer
- Always calibrate with buffers that bracket the expected measurement range
- Calibrate with buffers that are no more than 3 pH units apart
- Track calibration slope on a daily basis
- Calibration frequency
  - Electrode type
  - Sample type
  - Number of samples
- Electrode slope guidelines
  - Ideal range: 95% - 102%
  - Stable reading in 30 seconds

Effects of Temperature

Temperature can have a significant effect on pH measurements

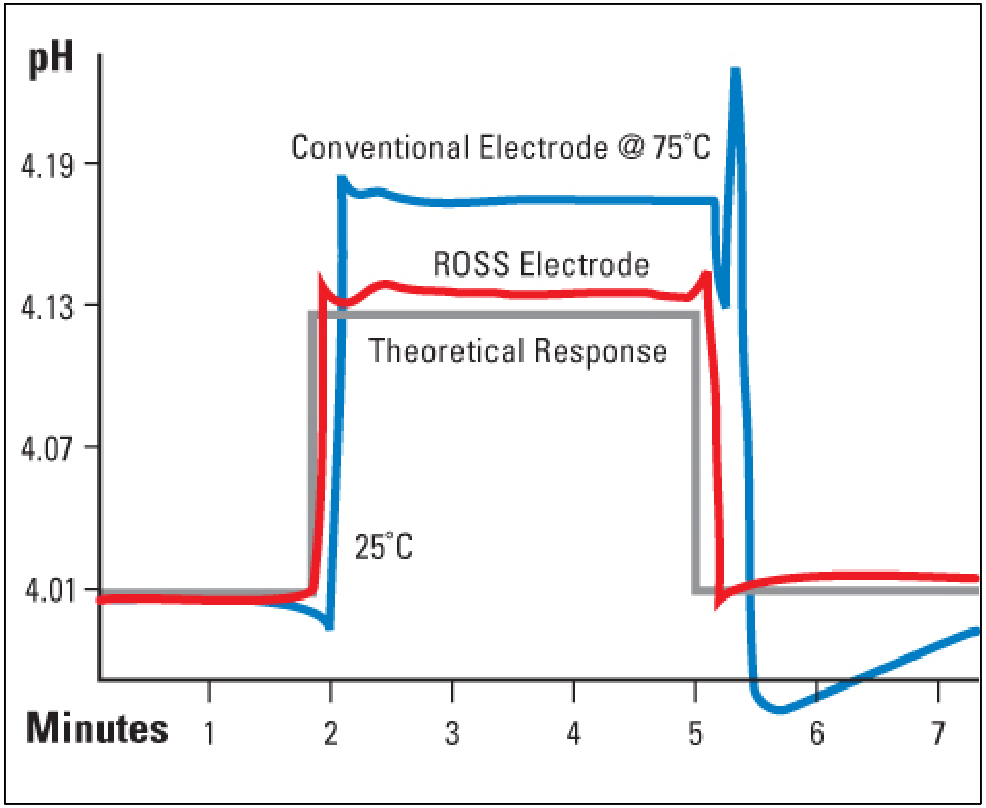
- Electrode
- Calibration
- Buffers
- Samples

Temperature Compensation Techniques

- Calibrate and measure at same temperature
- Manually temperature compensate using temperature control on meter
- Use automatic temperature compensator (ATC) or 3-in-1 Triode electrode
- Use LogR temperature compensation

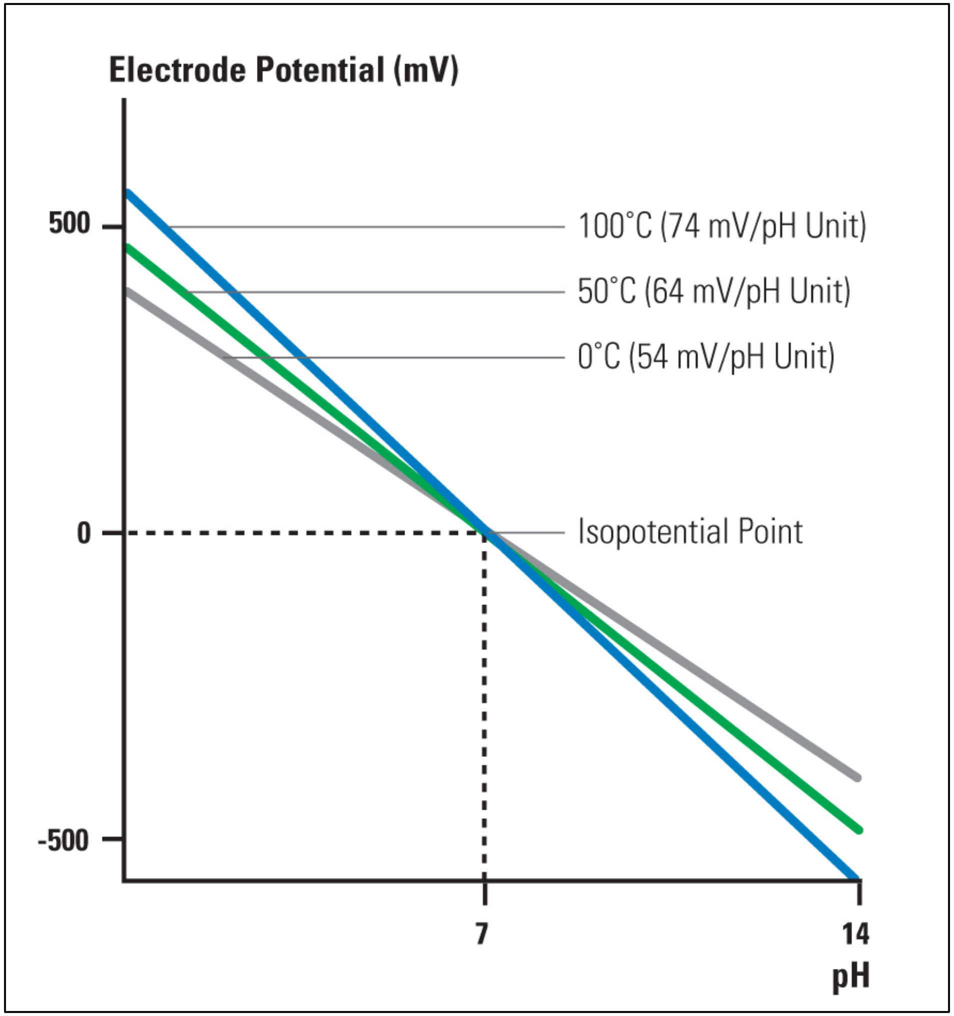
Effects of Temperature – Electrode Effects

- Temperature Hysteresis
  - AgCl or Hg_2Cl_2 references drift with temperature changes
  - 0.05 pH unit error with 4 °C difference
  - ROSS™ electrodes stabilize within seconds



Effects of Temperature – Calibration Effects

- Calibration Effects
  - Theoretical slope of electrode is 59.16mv at 25 ^{o}C
  - Temperature changes the calibration slope
  - Temperature compensation adjusts the calibration slope for temperature effects
  - The point at which temperature has no effect on mV is referred to as the isopotential point



Effects of Temperature – Buffer Effects

- Buffer Effects
  - Buffers have different pH values at different temperatures
  - Use the value of the buffer at the calibration temperature
  - New meters have NIST calibration tables pre-programmed
  - NIST Certified Values only at 25° C

25 C	0 C	5 C	10 C	20 C	30C	40 C	50 C	60 C	70 C	80 C	90 C
1.68	1.67	1.67	1.67	1.67	1.68	1.69	1.71	1.72	1.74	1.77	1.79
3.78	3.86	3.84	3.82	3.79	3.77	3.75	3.75				
4.01	4.00	4.00	4.00	4.00	4.02	4.03	4.06	4.08	4.13	4.16	4.21
6.86	6.98	6.95	6.92	6.87	6.85	6.84	6.83	6.84	6.85	6.86	6.88
7.00*	7.11	7.08	7.06	7.01	6.98	6.97	6.97				
7.41	7.53	7.50	7.47	7.43	7.40	7.38	7.37				
9.18	9.46	9.40	9.33	9.23	9.14	9.07	9.01	8.96	8.92	8.89	8.85
10.01	10.32	10.25	10.18	10.06	9.97	9.89	9.83				
12.46	13.42	13.21	13.01	12.64	12.30	11.99	11.71				

*Non-NIST Phosphate Buffer

Effects of Temperature – Sample Effects

- Sample effects
  - Temperature compensation corrects for changes in electrode slope not sample pH
  - It is not possible to normalize pH readings to a specific temperature
  - pH of samples will change with temperature changes
  - Record temperature with pH readings

Common Questions – Stable Readings

- Why does it take so long to get a stable reading?
  - Electrode performance and efficiency
  - Junction and bulb function (non-clogged and non-coated)
  - Electrode Type (gel effects, open junction, etc.)
  - Meter stabilization settings (if available)
  - Resolution settings (0.1 or 0.01 or 0.001)
  - Inner fill solution freshness
  - Low ionic strength samples
    - Use open junction electrode and stir samples when measuring
  - Air bubbles near junction

Electrode Care and Maintenance

- Electrode Storage
  - Short-term storage
    - Use appropriate electrode storage solution. (ROSS or Standard)
    - Alternatively, soak in 100 ml pH 7 buffer with 0.5 g KCl.
  - Long-term storage
    - Fill electrode, close fill hole, store with storage solution in protective cap
- Cleaning Solutions
  - Soak electrode in solvent that will remove deposits
    - Example: 0.1 M HCl for general cleaning
    - Example: 1% pepsin in HCl for proteins
    - Example: Bleach for disinfecting
    - Example: detergent for grease & oil

Electrode Care and Maintenance

- When do you need to clean your electrode?
  - Check slope range
    - Ideal range: 95% - 102%
    - Cleaning range: 92% - 95%
    - Replacement range: below 92%
  - Check response times in buffers
    - Electrode stability within 30 seconds
  - Check precision of electrode by reading buffers as samples
  - Check for any drift of electrode in pH buffer
    - Gel filled slower to respond can be seen as drift.
    - Size of sample.
    - Glass electrodes better than Epoxy to limit drift.
    - Static charge from stir bar or plastic container.
    - Verify your sample and electrode are at the same temperature.

Electrode Care and Maintenance

- General electrode bulb cleaning
  - Soak in Cleaning Solution for 30 minutes
  - Replace electrode fill solution
  - Soak in storage solution for at least 2 hours
- Electrode junction cleaning
  - Soak in 0.1M KCl for 15 minutes at 70 ^{o}C
  - Replace electrode fill solution
  - Soak in electrode storage solution for 2 hours
- Check junction by suspending in air for ten minutes
  - Observe KCl crystal formation

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Common Questions - Maintenance

- Is there a cleaning routine I can follow to keep my electrode working?
  - Refresh inner fill solution
  - Use recommended storage solution (premade or make your own)
    - ROSS vs. Standard
  - Close fill hole at end of the day
  - Use cleaning remedies and cleaning solutions if you suspect a coated bulb or coated junction is the cause of poor electrode slope.

Keys to Accuracy

- Always use fresh buffers
  - Check bottle expiration and date opened
    - pH 4 and pH 7 buffers expire within 12 months of being opened.
    - pH 10 buffer expires within 9 month of being opened.
  - Fresh buffer for each calibration
    - Calibrate only once in buffer… don’t re-use buffer
- Replace the fill solution in the electrode every week
  - Fill solution concentration is maintained
  - KCl crystallization is prevented
- Make sure to use the correct fill solution
  - Ross electrodes cannot use silver fill solutions

Keys to Accuracy

- Make sure level of fill solution is high
- Gently stir buffers and samples
- Shake any air bubbles out of the electrode
- Use insulation between stir plate and sample container to minimize heat transfer
- Blot electrodes between samples
- Uncover fill hole during measurement

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Troubleshooting pH Problems

- Common measurement problems
  - Readings not reproducible
  - Slow response
  - Noisy response
  - Drifty response
  - Inaccurate

- Troubleshooting Sequence
  - Meter
  - Buffers
  - Reference electrode
  - pH electrode
  - Sample
  - Technique

Troubleshooting pH Problems

- Troubleshooting pH Meters
  - Use meter shorting strap
  - Reading should be 0 mV +/- 0.2 mV
  - Use meter self-test procedure

- Troubleshooting Buffers
  - Use Fresh Buffers for calibration
  - Verify expiration date
    - 1 year after opening maximum
  - Stir buffers during calibration

Troubleshooting pH Problems

- Troubleshooting pH Electrodes
  - Clean bulb, junctions
  - Replace Fill solution
  - Uncover fill hole
  - Check for scratches on sensing bulb

- Troubleshooting Samples
  - Proper sample preparation
  - Stir samples

- Troubleshooting Technique
  - Treat samples and buffers the same
  - Clean and blot electrode between samples

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Electrode Check

- Check Slope Range (102% - 95%)
- Check response time in buffers (stable reading in 30 seconds)
- Verify mV readings are in the correct range for each buffer
  - pH 4.01 is +178 mV   +/- 30 mV
  - pH 7.00 is 0 mV   +/- 30 mV
  - pH 10.01 is -178 mV   +/- 30 mV

IF the Electrode Check FAILS:

- Check for air bubbles near bulb
- Verify correct filling solution is being used
- Check for salt crystal formation inside electrode
- Check junction is open by suspending in air for 10 minutes and KCl crystal formation should occur
- Use Junction cleaning procedures
- Re-check instruction manual for electrode conditioning procedures

Thermo Scientific – Technical Service

- **Contact us for any technical questions**
  - ***Technical Service: (800) 225-1480***
  - ***Web site: thermoscientific.com/water***
  - ***pH system check***

Thank You!

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