All about pH!
Is it as simple as it seems?
The pH Workshop
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What is pH?

“Potential Hydrogen” or “Power of Hydrogen”

\textit{pH electrodes are a type of ion selective electrode (ISE) measuring free hydrogen ion activity}
Common Questions: *What is pH?*

**The Theoretical Definition:** \[ pH = - \log a_H \]

- \( a_H \) is the hydrogen ion *activity*.

- 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 \( H^+ \).
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".
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!

Representative pH values

<table>
<thead>
<tr>
<th>Substance</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric Acid, 10M</td>
<td>-1.0</td>
</tr>
<tr>
<td>Lead-acid battery</td>
<td>0.5</td>
</tr>
<tr>
<td>Gastric acid</td>
<td>1.5 – 2.0</td>
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<tr>
<td>Lemon juice</td>
<td>2.4</td>
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<tr>
<td>Cola</td>
<td>2.5</td>
</tr>
<tr>
<td>Vinegar</td>
<td>2.9</td>
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<tr>
<td>Orange or apple juice</td>
<td>3.5</td>
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<tr>
<td>Beer</td>
<td>4.5</td>
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<tr>
<td>Acid Rain</td>
<td>&lt;5.0</td>
</tr>
<tr>
<td>Coffee</td>
<td>5.0</td>
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<tr>
<td>Tea or healthy skin</td>
<td>5.5</td>
</tr>
<tr>
<td>Milk</td>
<td>6.5</td>
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<tr>
<td>Pure Water</td>
<td>7.0</td>
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<tr>
<td>Healthy human saliva</td>
<td>6.5 – 7.4</td>
</tr>
<tr>
<td>Blood</td>
<td>7.34 – 7.45</td>
</tr>
<tr>
<td>Seawater</td>
<td>7.7 – 8.3</td>
</tr>
<tr>
<td>Hand soap</td>
<td>9.0 – 10.0</td>
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<tr>
<td>Household ammonia</td>
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</tr>
<tr>
<td>Bleach</td>
<td>12.5</td>
</tr>
<tr>
<td>Household lye</td>
<td>13.5</td>
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</table>
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 measuring the outside sample and a stable reference electrode and translates this to the pH scale.
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
  - Autocalibration/autobuffer recognition
  - Number of calibration points
  - Display information
  - RS232 or recorder outputs
  - Datalogging
  - GLP/GMP compliant
Common Questions: *Electrode Composition*

**pH Electrode Composition**

- Sensing Bulb
- Reference
- Reference Solution
- Internal Fill Solution
- Junction

*This is a “combination pH electrode”*
Common Questions: Electrode Components

pH Electrode Reference Types

- Calomel reference
  - Fixed $\text{Hg}_2^{++}$ activity in contact with solid mercury
- Silver reference
  - Fixed Ag$^+$ activity in contact with silver wire
  - Single and double junction design
- ROSS reference
  - Redox couple (Iodide/Iodine)
  - Double junction design
Common Questions: *Electrode Components*

**pH Electrode Junction Types**

- **Wick junction**
  - *Glass fiber, fiber optical bundles, Dacron, etc.*
  - *Common in epoxy body electrodes*

- **Ceramic junction**
  - *Porous ceramic, wooden plug, porous Teflon, etc.*
  - *Common in glass body electrodes*
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
pH Measurement System - Junctions

- The Open Junction
  - Sure-Flow or Ground Glass Sleeve, Laser Drilled Hole, or Bundle of Capillary Tubes, etc.

- Advantages
  - Sure-Flow or Sleeve 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)
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
What is meant by a “single junction?”

• There is one junction in the electrode body.

This term applies to calomel electrodes or Ag/AgCl electrodes that have a silver reference wire and silver ions dispersed in the internal electrolyte fill solution.
What is meant by a “double junction?”

- There are two junctions in the electrode body.
  
  This term applies to any electrode that has a ROSS reference and also to some Ag/AgCl electrodes.
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
- Select appropriate body type
  - Glass body, epoxy body
- Other considerations
  - Refillable, Gel, or Polymer?
  - Built in Temperature Probe?
pH Calibration

- The Nernst Equation

\[ E = E_0 - \frac{RT}{nF} \log a_H \]

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

Slope = \( \frac{RT}{nF} \) = 59.16 mV @ 25 °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
    - $150 - (-10) = 160$ mV
    - 3 pH units $\times 59.2$ mV $= 177.6$ mV
    - Slope $= \frac{160 \text{ mV}}{177.6 \text{ mV}} \times 100 = 90.1\%$
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%
Common Questions: Temperature Compensation

Why is temperature compensation important when measuring pH?

• Samples / buffers have different pH values at different temperatures

• Temperature compensation will contribute to achieving accurate measurements
Common Questions: *Temperature Compensation*

- Temperature affects calibration slope because it affects the expected change in the mV value per pH unit.

- *Temperature compensation will adjust the calibration slope* across a wide temperature range.

- *It is not possible to normalize pH readings to a specific temperature*, but it is possible to get an accurate pH measurement for any sample temperature.
Common Questions: Temperature Compensation

Temperature Compensation Strategies

- Calibrate and measure at the same temperature
- Use automatic temperature compensator (ATC) or 3-in-1 Triode electrode
- Manually temperature compensate using temperature control on meter
- Use LogR temperature compensation
- Record temperature with pH readings
Effects of Temperature – Electrode Effects

- Temperature “Hysteresis”
  - AgCl or Hg₂Cl₂ references drift with temperature changes
  - 0.05 pH unit error with 4 °C difference
  - ROSS™ electrodes stabilize within seconds
  - With other Ion Selective Electrodes a 1 degree C temperature change creates up to a 2% error
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

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*Non-NIST Phosphate Buffer
Electrode Care and Maintenance

• Electrode Storage
  • Short-term storage
    • Use electrode storage solution
    • 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
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 °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
Keys to Accuracy

• Always use fresh buffers
  • Check bottle expiration and date opened
    • pH 4 and pH 7 buffers expire within 3 months of being opened
    • pH 10 buffer expires within 1 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
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
  - 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
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)
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!
Common Questions: Stable Readings

Why does it take so long to get a stable reading?

- electrode performance and efficiency
- inner fill-solution freshness
- electrode type (gel effects, open junction, etc.)
- junction and bulb function (non-clogged and non-coated)
- meter stabilization settings (if available)
- resolution settings
- low ionic strength samples
- air bubbles near bulb
- stirred or not?
What can be done to improve measurements made in low ionic strength samples?

- use an electrode with an open junction
- stir the samples during measurement
Common Questions: Maintenance

Is there a cleaning routine I can follow to keep my electrode working?

- refresh inner fill solution
- use recommended storage solution
- close fill hole at end of day
- use cleaning remedies if a coated bulb or a clogged junction is the suspected cause of a poor calibration slope
New Technologies

• LogR Temperature Compensation
  • Meter reads the resistance (R) from the bulb of any pH electrode
  • Resistance measurement is inverse to temperature: LogR = 1/T
  • Calibrate pH electrode for temperature
  • Direct temperature compensation without using ATC
New Technologies

• AquaPro Electrodes
  • Low maintenance sealed electrode
    • No fill solutions to worry about
  • Patented polymer reference gel
    • Performance and life equivalent to refillable electrodes
  • Double-junction design
    • Silver will not precipitate with sulfides, TRIS, or proteins
  • Laser-drilled open junction
    • Won’t clog in viscous samples
New Technologies

• **ROSS™ Ultra** Electrodes
  • Best of the Best!
    • *Superior Performance*
    • *Fast Response*
    • *Very Stable*
  • 2-Year Replacement Warranty
New Technologies

• ROSS™ Micro Electrode
  • Measure samples as small as 15µl in 384 well plates
  • Only needs to be immersed 4.5mm into the sample
  • PerpHect electrode, Ideal for LogR meters!

• Micro ATC probe
  • Stainless Steel
  • Measure samples as small as 10µl
  • Only needs to be immersed 3.0mm into the sample
Contact us for any technical questions concerning pH / Conductivity / ISE / Dissolved Oxygen / ORP / Turbidity / Colorimetry

- **Technical Support**: (800) 225-1480
- **Web site**: [www.thermoscientific.com/water](http://www.thermoscientific.com/water)
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Why We Analyze Water.....

WATER

The purity of brewing water is vital to the quality of GUINNESS.

Water used to brew GUINNESS is known for its purity. This is a soft water with a low mineral content. As it courses down the mountain side some calcium and magnesium sulphate are absorbed.
Thank you!

• Questions?