Essentials of pH Measurement

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Thermo Scientific Electrochemistry Products
What is pH?

- The Theoretical Definition

\[ \text{pH} = - \log a_H \]

- \( a_H \) 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".

LOW pH = LOTS OF H$^+$

LOTS OF OH$^-$ = HIGH pH
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

<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>
</tr>
<tr>
<td>Lemon juice</td>
<td>2.4</td>
</tr>
<tr>
<td>Cola</td>
<td>2.5</td>
</tr>
<tr>
<td>Vinegar</td>
<td>2.9</td>
</tr>
<tr>
<td>Orange or apple juice</td>
<td>3.5</td>
</tr>
<tr>
<td>Beer</td>
<td>4.5</td>
</tr>
<tr>
<td>Acid Rain</td>
<td>&lt;5.0</td>
</tr>
<tr>
<td>Coffee</td>
<td>5.0</td>
</tr>
<tr>
<td>Tea or healthy skin</td>
<td>5.5</td>
</tr>
<tr>
<td>Milk</td>
<td>6.5</td>
</tr>
<tr>
<td>Pure Water</td>
<td>7.0</td>
</tr>
<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>
</tr>
<tr>
<td>Household ammonia</td>
<td>11.5</td>
</tr>
<tr>
<td>Bleach</td>
<td>12.5</td>
</tr>
<tr>
<td>Household lye</td>
<td>13.5</td>
</tr>
</tbody>
</table>
pH Measurement System

• When two solutions containing different concentrations of $\text{H}^+$ 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/Hg₂Cl₂) (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

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

![Image of pH electrode](image-url)
## pH Measurement System – Reference Types

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

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 °C 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
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?
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 = \( \frac{RT}{nF} = 59.16 \text{mv} @ 25 \, ^\circ\text{C} \)
Walther Nernst

• Nobel Prize Winner in Chemistry in 1920
• Worked with other famous chemists, physicists and scientists.
% slope is the change in mV value divided by the Nernstian theoretical value of $59.2 \text{ mV}$, the expected change in mV per pH unit at 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
- Slope = 160 mV/177.6 mV = 90.1%
- Where did this 177.6 mV come from?
  - A change of 3 pH units (7-4)
  - 59.2 mV per pH unit x 3 equals 177.6 mV
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!
PpH 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 Hg₂Cl₂ 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 °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

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>1.68</td>
<td>1.67</td>
<td>1.67</td>
<td>1.67</td>
<td>1.68</td>
<td>1.69</td>
<td>1.71</td>
<td>1.72</td>
<td>1.74</td>
<td>1.77</td>
<td>1.79</td>
</tr>
<tr>
<td>30°C</td>
<td>3.78</td>
<td>3.86</td>
<td>3.84</td>
<td>3.82</td>
<td>3.79</td>
<td>3.77</td>
<td>3.75</td>
<td>3.75</td>
<td>3.75</td>
<td>3.75</td>
<td>3.75</td>
</tr>
<tr>
<td>40°C</td>
<td>4.01</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.02</td>
<td>4.03</td>
<td>4.06</td>
<td>4.08</td>
<td>4.13</td>
<td>4.16</td>
<td>4.21</td>
</tr>
<tr>
<td>60°C</td>
<td>7.00*</td>
<td>7.11</td>
<td>7.08</td>
<td>7.06</td>
<td>7.01</td>
<td>6.98</td>
<td>6.97</td>
<td>6.97</td>
<td>6.97</td>
<td>6.97</td>
<td>6.97</td>
</tr>
<tr>
<td>70°C</td>
<td>7.41</td>
<td>7.53</td>
<td>7.50</td>
<td>7.47</td>
<td>7.43</td>
<td>7.40</td>
<td>7.38</td>
<td>7.37</td>
<td>7.37</td>
<td>7.37</td>
<td>7.37</td>
</tr>
<tr>
<td>100°C</td>
<td>12.46</td>
<td>13.42</td>
<td>13.21</td>
<td>13.01</td>
<td>12.64</td>
<td>12.30</td>
<td>11.99</td>
<td>11.71</td>
<td>11.71</td>
<td>11.71</td>
<td>11.71</td>
</tr>
</tbody>
</table>

*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 °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
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 months 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

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