pH Measurement
General Chapters:<791> pH USP38

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Outline

- Introduction
- pH measurement system
- Instrument requirements
- Buffer solutions
- Calibration
- Operation
Introduction

pH (in an aqueous solution)

→ a measure of hydrogen and hydroxide ions

At 25°C, water contains

- $1 \times 10^{-7}$ mol/l of $H^+$ and
- $1 \times 10^{-7}$ mol/l of $OH^-$

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

$K_w$ is dissociation constant
pH is often expressed as

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

Example:

Hydrogen ion concentration = \(1 \times 10^{-3}\) mol/l, pH = 3.00

If add base, change the hydrogen ion concentration to \(1 \times 10^{-11}\) mol/l, pH = 11.0
The Nernst equation:

\[ E = E_0 + 2.3 \frac{RT}{nF} \log[a_{H^+}] \]

- \( E \) = measured potential
- \( E_0 \) = constant, standard potential
- \( R \) = gas constant
- \( T \) = temperature in Kelvin
- \( n \) = ionic charge
- \( F \) = Faraday constant
The Nernst equation:

\[ E = E_0 + 2.3 \frac{RT}{nF} \log[a_{H^+}] \]

\[ Y = a + bX \]

Slope is the Nernst factor at 25°C, slope = -59.16 mV/pH unit
Theoretically ideal

At 25°C, slope = -59.16 mV/pH and 0 mV at pH = 7 (offset or zero point)
Temperature influences

**Isothermal point of electrode**: intersection point of calibration lines plotted for different temperatures

**Ideal electrode**:  
Isothermal intersection point at zero point (0 mV at pH 7) for different temperature

**Real electrode**:  
Hardly ever coincides with the zero point of the electrode
Different between Real and theoretical isothermal intersection point

↓

Measurement error
pH meter has to be adjusted to compensate for any deviations due to non-ideal behaviour of the electrode from theoretical values by

“Calibration”

2 parameters: offset and slope
Offset adjustment of pH electrode

Slope adjustment of pH electrode

--- Ideal behavior

-------- Real behavior
Automatic temperature compensation (ATC)

automatic calculation of pH from the measured potential and temperature, using an adjusted slope to the measured temperature
It is recommended to do a calibration and sample measurement at the same temperature.

The most accurate pH value
pH measurement system

consists of

-measuring electrode

\((potential \ directly \ proportional \ to \ pH)\)

-reference electrode

\((potential \ independent \ of \ pH)\)

-voltage measurement system with temperature device
Instrument requirements

- capable of performing a 2-point pH calibration

- resolution of pH measurement system at least 0.01 pH

- capable of temperature compensation (convert mV to pH units at any temperature), either automatic temperature device or manual entry
- accuracy of temperature measurement system ±1°C

- resolution of temperature measurement System at least 0.1°C

- lab-based pH measurement performed at 25 ± 2°C
Buffer solutions

-prepared as directed in Table 2 by using purified water

or

-used commercial buffer solutions which is traceable to NIST or other national authorities, labeled with a pH value accurate to 0.02 pH unit
Table 2. pH Values of Buffer Solutions for Standardization

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Potassium Tetraoxalate, 0.05 m</th>
<th>Potassium Hydrogen Tartrate Saturated at 25°</th>
<th>Potassium Dihydrogen Citrate, 0.05 M</th>
<th>Potassium Biphthalate, 0.05 m</th>
<th>Equimolar Phosphate, 0.05 m</th>
<th>Potassium Dihydrogen Phosphate, 0.0087 M, and Disodium Hydrogen Phosphate, 0.0303 M</th>
<th>Sodium Tetraborate, 0.01 m</th>
<th>Sodium Carbonate, 0.025 M, and Sodium Bicarbonate, 0.025 M</th>
<th>Calcium Hydroxide, Saturated at 25°</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.67</td>
<td>--</td>
<td>4.00</td>
<td>6.92</td>
<td>--</td>
<td>9.33</td>
<td>--</td>
<td>13.00</td>
<td></td>
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<tr>
<td>15</td>
<td>1.67</td>
<td>--</td>
<td>3.80</td>
<td>4.00</td>
<td>6.90</td>
<td>7.45</td>
<td>9.28</td>
<td>10.12</td>
<td>12.81</td>
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<tr>
<td>20</td>
<td>1.68</td>
<td>--</td>
<td>3.79</td>
<td>4.00</td>
<td>6.88</td>
<td>7.43</td>
<td>9.23</td>
<td>10.06</td>
<td>12.63</td>
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<tr>
<td>25</td>
<td>1.68</td>
<td>3.56</td>
<td>3.78</td>
<td>4.01</td>
<td>6.86</td>
<td>7.41</td>
<td>9.18</td>
<td>10.01</td>
<td>12.45</td>
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<tr>
<td>35</td>
<td>1.69</td>
<td>3.55</td>
<td>3.76</td>
<td>4.02</td>
<td>6.84</td>
<td>7.39</td>
<td>9.10</td>
<td>9.93</td>
<td>12.13</td>
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<td>40</td>
<td>1.69</td>
<td>--</td>
<td>--</td>
<td>4.04</td>
<td>6.84</td>
<td>--</td>
<td>9.07</td>
<td>--</td>
<td>11.98</td>
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<tr>
<td>45</td>
<td>1.70</td>
<td>--</td>
<td>--</td>
<td>4.05</td>
<td>6.83</td>
<td>--</td>
<td>9.04</td>
<td>--</td>
<td>11.84</td>
</tr>
<tr>
<td>50</td>
<td>1.71</td>
<td>--</td>
<td>--</td>
<td>4.06</td>
<td>6.83</td>
<td>--</td>
<td>9.01</td>
<td>--</td>
<td>11.71</td>
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<tr>
<td>55</td>
<td>1.72</td>
<td>--</td>
<td>--</td>
<td>4.08</td>
<td>6.83</td>
<td>--</td>
<td>8.99</td>
<td>--</td>
<td>11.57</td>
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<td>60</td>
<td>1.72</td>
<td>--</td>
<td>--</td>
<td>4.09</td>
<td>6.84</td>
<td>--</td>
<td>8.96</td>
<td>--</td>
<td>11.45</td>
</tr>
<tr>
<td>ΔpH/Δ°C</td>
<td>0.0010</td>
<td>-0.0014</td>
<td>-0.0022</td>
<td>0.0018</td>
<td>-0.0016</td>
<td>-0.0028</td>
<td>-0.0074</td>
<td>-0.0096</td>
<td>-0.0310</td>
</tr>
</tbody>
</table>
Buffer solutions

Buffer solutions greater than 11,

- containers are resistant to or reduce CO$_2$ intrusion

- be prepared and used fresh

** CO$_2$ would lower the pH of buffer **
Buffer solutions

Buffer solutions *lower* than 11,

-be prepared at intervals not to exceed 3 months
Temperature coefficient
the change in pH of a solution with temperature (ΔpH/°C)

Ex. Buffer solution pH 8.00 (20°C)

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>ΔpH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>+0.015</td>
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<tr>
<td>5</td>
<td>+0.10</td>
</tr>
<tr>
<td>10</td>
<td>+0.07</td>
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<tr>
<td>15</td>
<td>+0.004</td>
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<td>20</td>
<td>±0</td>
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<tr>
<td>25</td>
<td>-0.04</td>
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<tr>
<td>30</td>
<td>-0.06</td>
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<tr>
<td>35</td>
<td>-0.08</td>
</tr>
<tr>
<td>40</td>
<td>-0.10</td>
</tr>
<tr>
<td>50</td>
<td>-0.15</td>
</tr>
</tbody>
</table>
Calibration

Standardization

Calibration process
1\textsuperscript{st} buffer \quad 2\textsuperscript{nd} buffer

Verification
3\textsuperscript{rd} buffer

cover the expected of pH of the sample

between calibration buffer
Calibration process

1. Rinse the electrode with water
2. Rinse the electrode with 1\textsuperscript{st} buffer
3. Immerse the electrode in 1\textsuperscript{st} buffer
4. 2-point calibrate according to instruction
remove the electrode

rinse the electrode with water

rinse the electrode with 2nd buffer

Immerse the electrode in 2nd buffer

2- point calibrate according to instruction
verify the slope and offset

*Slope from 90-105%  
Offset ±30 mV (0.5pH units at 25°C)*

If not in acceptance limit, cleaned, replenished, serviced or replaced the electrode.

repeat the 2-point calibration
Verification

1. Rinse the electrode with water

2. Rinse the electrode with 3rd buffer

3. Immerse the electrode in 3rd buffer

4. Read the pH according to instruction
verify the pH reading

pH reading within ±0.05 pH of the pH value at the buffer solution temperature
Operation

rinse the electrode with water

↓

rinse the electrode with sample

↓

Immerse the electrode in sample

↓

read the pH and temperature according to instruction
-prepare the sample by using purified water unless otherwise specified in the monograph

-allow sufficient time for stabilization of the temperature and pH measurement
Reference:

- USP 38

- A guide to pH Measurement - the Theory and Practice of pH Applications, Metter Toledo