Typically, the pH of solutions will change as temperature changes. The reasons why depend on the context, but even a simple solution of a weak acid (HA) will exhibit a (weak) temperature dependence.

**Basis of Dependence**

The pH is given by the [Henderson-Hasselbalch approximation](#):

\[
pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{1}\]

where \(K_a\) is the equilibrium constant for the acid dissociation reaction

\[
HA \rightleftharpoons H^+ + A^- \tag{2}\]

with

\[
K_a = \dfrac{[H^+][A^-]}{[HA]} \tag{3a}\]

and

\[
pK_a = -\log(K_a) \tag{3b}\]

As with all equilibrium constants, \(K_a\) is a function of temperature, since it is related to the Gibbs free energy of reaction \((\Delta G)\) by the equation:

\[
\Delta G = -RT \ln(K_a) = -2.303 RT \log(K_a) = 2.303 RT \; pK_a \tag{4}\]

Hence

\[
pK_a = \dfrac{\Delta G}{2.303 \; RT} \tag{5}\]

and \(\Delta G\) is itself given by (under constant pressure and temperature)

\[
\Delta G = \Delta H - T \Delta S \tag{6}\]

with

- \(\Delta H\) is the enthalpy of reaction and
- \(\Delta S\) is the entropy of reaction.

Combining these, we get

\[
pK_a = \dfrac{\Delta H}{2.303 \; RT} - \dfrac{\Delta S}{2.303 \; R} \tag{7}\]

Assuming that \(\Delta H\) and \(\Delta G\) are approximately independent of temperature \(T\) (which is not a bad approximation over a narrow temperature range), then the variation with temperature is determined exclusively by the sign of \(\Delta H\).
• **Endothermic dissociation**: If \(\Delta H > 0\), then \(pK_a\) gets smaller as the temperature gets larger; this results in an increase in \(K_a\), which means that the reaction favors dissociation more as temperature increases (in agreement with Le Châtelier's principle). This increases \([H^+]\) and decreases the pH.

• **Exothermic dissociation**: If \(\Delta H < 0\), then the opposite effect will be observed.

Either way, we expect the pH to depend on temperature (unless \(\Delta H = 0\)). These arguments can be extended to strong acids too. Things get complicated when there are multiple chemical reactions. Biological systems can use enzyme-catalyzed reactions to keep the pH constant even when T varies (within limits, of course).

### Weak Dependence

The general equation for the change of an equilibrium constant is:

\[
\frac{d}{dT} \ln(K_{eq}) = \frac{\Delta H}{RT^2} \tag{8}
\]

where

- the "d's" mean the change in the natural log of Keq,
- the temperature \(T\) in Kelvin,
- \(\Delta H\) is the heat of reaction (change of enthalpy),
- and \(R\) is the gas constant.

Since pH is already a "log" function of \(K_{eq}\) and the change in \(K_{eq}\) is again a "log" function of the heat of reaction, \(\Delta H\) the change in pH is not a very sensitive function of temperature. In addition, the heat of the ionization reaction \(\Delta H\) for weak acids (partially dissociated) like acetic acid, formic acid etc. is very small. To a reasonable approximation for such acids, \(\Delta H\) is less than 1-2 kcal per mol, which is very small. So pH does not change greatly with temperature. More details can be found in an article in the Journal of Chemical Education, Vol. 48, pg.338, 1971.

### Temperature Dependence of pH for Commonly Used Buffers

The apparent \(pK_a\), and therefore the pH, of any buffer are temperature dependent. Consequently, the pH of prepared concentrated buffer solutions will change with temperature.

<table>
<thead>
<tr>
<th>Buffer System</th>
<th>(pK_a)/20°C</th>
<th>(\Delta pK_a)/10°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MES</td>
<td>6.15</td>
<td>0.110</td>
</tr>
<tr>
<td>ADA</td>
<td>6.60</td>
<td>0.110</td>
</tr>
<tr>
<td>PIPES</td>
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<td>0.085</td>
</tr>
<tr>
<td>ACES</td>
<td>6.90</td>
<td>0.200</td>
</tr>
<tr>
<td>BES</td>
<td>7.15</td>
<td>0.160</td>
</tr>
<tr>
<td>Buffer</td>
<td>pH</td>
<td>ΔpH</td>
</tr>
<tr>
<td>----------</td>
<td>-------</td>
<td>-----</td>
</tr>
<tr>
<td>MOPS</td>
<td>7.20</td>
<td>−0.013</td>
</tr>
<tr>
<td>TES</td>
<td>7.50</td>
<td>−0.200</td>
</tr>
<tr>
<td>HEPES</td>
<td>7.55</td>
<td>−0.140</td>
</tr>
<tr>
<td>Tricine</td>
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<td>−0.210</td>
</tr>
<tr>
<td>Tris</td>
<td>8.30</td>
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<tr>
<td>Bicine</td>
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<td>−0.180</td>
</tr>
<tr>
<td>Glycylglycine</td>
<td>8.40</td>
<td>−0.280</td>
</tr>
</tbody>
</table>


References


Contributors

- [http://www.newton.dep.anl.gov/askasc.../chem00920.htm](http://www.newton.dep.anl.gov/askasc.../chem00920.htm)
- Vince Calder
- Prof. Topper