Biochemists Use $E^0'$

Perhaps the most important redox reaction in living organisms are involved in respiration, in which molecules of food are oxidized by $O_2$ to yield energy or metabolic intermediates. The standard reduction potentials that we have been using so far apply to systems in which all activities of reactants and products are unity. If $H^+$ is involved in the reaction, $E^0'$ applies when $pH=0$. Whenever $H^+$ appears in a redox reaction, or whenever reactants or products are acids or bases, reduction potentials are pH dependent.

Because the pH inside a plant or animal cell is in the neighborhood of 7, reduction potentials that apply at pH 0 are not particularly appropriate. For example, at pH 0, ascorbic acid (vitamin C) is a more powerful reducing agent than succinic acid (琥珀酸，丁二酸) is. However, at pH 7, this order is reversed. It is the reducing strength at pH 7, not at pH 0, that is relevant to a living cell.

The standard potential for a redox reaction is defined for a galvanic cell (原电池) in which all activities are unity. The formal potential is the reduction potential that applies under a specified set of conditions (including pH, ionic strength, and concentration of complexing agents). Biochemists call the formal potential at pH 7 $E^0'$ (read “E zero prime”).

Example Finding the Formal Potential

Find $E^0'$ for the reaction

\[
\begin{align*}
&\text{Dehydroascorbic acid (oxidized)} \\
&D + 2H^+ + 2e^- \leftrightarrow H_2A + H_2O \\
&\text{Ascorbic acid (Vitamin C) (reduced)} \\
&W_pK_1=4.10 \quad W_pK_2=11.79
\end{align*}
\]

**SOLUTION** Abbreviating dehydroascorbic acid as D, and ascorbic acid as $H_2A$, we rewrite the reduction as

\[
D + 2H^+ + 2e^- \leftrightarrow H_2A + H_2O
\]

for which the Nernst equation is

\[
E = E^0 - \frac{0.05916}{2} \log \frac{[H_2A]}{[D][H^+]^2}
\]  

(14-33)

D is not an acid or a base, so its formal concentration equals its molar concentration: $F_D = [D]$.
the diprotic acid $H_2A$, we use Equation
\begin{equation}
[H_2A] = \alpha_{H_2A} F = \frac{[H^+]^2 F}{[H^+]^2 + [H^+]K_1 + K_1K_2}
\end{equation}

to express $[H_2A]$ in terms of $F_{H_2A}$:

\[ [H_2A] = \frac{[H^+]^2 F_{H_2A}}{[H^+]^2 + [H^+]K_1 + K_1K_2} \]

Putting these values into Equation 14-33 gives

\begin{equation}
E = E^0 - \frac{0.05916}{2} \log \left( \frac{[H^+]^2 F_{H_2A}}{[H^+]^2 + [H^+]K_1 + K_1K_2} \right) \frac{1}{F_D [H^+]^2}
\end{equation}

Which can be rearranged to the form

\begin{equation}
E = E^0 - \frac{0.05916}{2} \log \left( \frac{1}{[H^+]^2 + [H^+]K_1 + K_1K_2} \right) - \frac{0.05916}{2} \log \frac{F_{H_2A}}{F_D} \tag{14-34}
\end{equation}

Putting the values of $E^0$, $K_1$, and $K_2$ into Equation 14-34 and setting $[H^+] = 10^{-7.00}$, we find $E^0 = +0.062 \text{v}$. 

\[ \text{Formal potential } (= E^0 \text{ if pH=7}) \]

\[ \Rightarrow +0.062 \text{v} \]