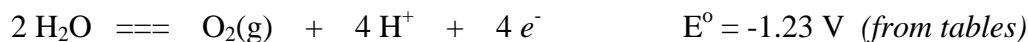
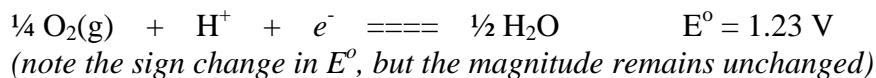


Oxidation/Reduction Limits for H₂O

Consider the **Oxidation** of H₂O to yield O₂(g), the half reaction can be written as;



Re-writing this as a reduction (by convention) and dividing by 4 (for convenience) yields;



Writing an equilibrium expression for the half reaction yields;

$$K_{\text{eq}} = \frac{1}{P_{\text{O}_2}^{1/4} \{\text{H}^+\} \{\text{e}^-\}} = P_{\text{O}_2}^{-1/4} \{\text{H}^+\}^{-1} \{\text{e}^-\}^{-1}$$

Isolating {e⁻}⁻¹ yields; {e⁻}⁻¹ = K_{eq} P_{O₂}^{1/4} {H⁺}

and taking log of both sides yields; log {e⁻}⁻¹ = log K_{eq} + log P_{O₂}^{1/4} + log {H⁺}

Defining pe = -log {e⁻} and pH = -log {H⁺} yields;

$$pe = \log K_{\text{eq}} + \log P_{\text{O}_2}^{-1/4} - \text{pH}$$

At the boundary of chemical oxidation of H₂O, the P_{O₂} = 1 atm and so;

$$pe = \log K_{\text{eq}} - \text{pH}$$

$$\text{Since, } K_{\text{eq}} = 10^{\frac{\Delta G^\circ}{2.3RT}}, \log K_{\text{eq}} = \frac{-\Delta G^\circ}{2.3RT} \text{ and } \Delta G^\circ = -nFE^\circ, \text{ then}$$

$$\log K_{\text{eq}} = \frac{nFE^\circ}{2.3RT} \text{ and}$$

$$pe = \frac{nFE^\circ}{2.3RT} - \text{pH}$$

In the present case, where n = 1 and E° = 1.23 V, the dependence of pe on pH is given by;

pe = 20.8 – pH for the boundary for the oxidation of H₂O to O₂
 where F = 96,485 C/mol, R = 8.314 J/mol K, T = 298 K and 1 CV = J/mol.

When H⁺ is at standard state (i.e., 1 M, pH = 0) at 25°C, then

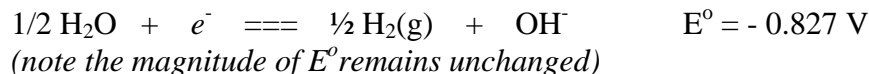
$$pe = pe^\circ = \frac{nFE^\circ}{2.3RT} = 20.8 \text{ (for the oxidation of H}_2\text{O to O}_2\text{)}$$

In general; $pe^\circ = \log K_{\text{eq}} = \frac{-\Delta G^\circ}{2.3RT} = \frac{E^\circ}{0.0591}$, **and** $pe = \frac{E}{0.0591}$ **for any one electron process at 25°C.**

Consider the **Reduction** of H₂O to yield H₂(g), the half reaction can be written as;



Re-writing this reduction dividing by 2 (for convenience) yields;



Writing an equilibrium expression for the half reaction yields;

$$K_{\text{eq}} = P_{\text{H}_2}^{1/2} \{ \text{OH}^- \} \{ e^- \}^{-1}$$

Isolating $\{ e^- \}^{-1}$ and taking log of both sides yields;

$$\log \{ e^- \}^{-1} = \log K_{\text{eq}} + \log P_{\text{H}_2}^{-1/2} + \log \{ \text{OH}^- \}^{-1}$$

Defining $pe = -\log \{ e^- \}$ and $p\text{OH} = -\log \{ \text{OH}^- \}$ yields;

$$pe = \log K_{\text{eq}} + \log P_{\text{O}_2}^{-1/2} + p\text{OH}$$

At the boundary of chemical reduction of H₂O, the $P_{\text{H}_2} = 1 \text{ atm}$ and so;

$$pe = \log K_{\text{eq}} + p\text{OH}$$

Since $pK_w = p\text{OH} + \text{pH}$, we can substitute $p\text{OH} = pK_w - \text{pH}$ thus;

$$pe = \log K_{\text{eq}} + pK_w - \text{pH}$$

As before,

$$\log K_{\text{eq}} = \frac{nFE^\circ}{2.3RT} \text{ and}$$

$$pe = \frac{nFE^\circ}{2.3RT} + pK_w - \text{pH}$$

In the present case, where $n = 1$, $E^\circ = -0.827 \text{ V}$ and $pK_w = 14$, the dependence of pe on pH is given by;

$$pe = \frac{(1)(96485)(-0.827)}{2.3(8.314)(298)} + 14 - \text{pH} = -\text{pH} \text{ (note that the units in } nFE^\circ/2.3RT \text{ cancel)}$$

When H^+ is at standard state (i.e., 1 M , $\text{pH} = 0$) at 25° , then $pe = pe^\circ = 0$ for the reduction of H₂O to H₂.

At other $\{ \text{H}^+ \}$, the boundary between H₂O and H₂ is given by; **$pe = -\text{pH}$**