Statistical Molecular Thermodynamics

Christopher J. Cramer

Video 13.3

Standard Potentials

Single Electrode Values of E°

For a given *full* electrochemical cell reaction:

$$\Delta_r G^\circ = \Delta_{oxid} G^\circ + \Delta_{red} G^\circ \Rightarrow -nFE^\circ$$

e.g., $Zn^{2+}(aq) + 2e^- \leftrightarrows Zn(s)$	$\Delta_{red} G^\circ = -2FE^\circ_{red}$	
$Cu(s) \leftrightarrows Cu^{2+}(aq) + 2e^-$	$\Delta_{ox} G^\circ = 2FE^\circ_{red}$	*sign change*
$Zn^{2+}(aq) + Cu(s) \leftrightarrows Cu^{2+}(aq) + Zn(s)$	$\Delta_r G^\circ = -2FE^\circ$	

But we can't measure the standard free energies of the half-cell reactions because electrons don't come in bottles for use as reagents! However, if by convention, we set any one half-cell potential, we can determine all of the others from summed full-cell potentials. So, by convention, we assign a relative E° value of 0.00 to the Standard Hydrogen Electrode (SHE).

$$E^\circ_{red}\left[H^+\left(aq.;\ a_\pm = 1\right) \middle| H_2\left(gas;\ 1\ bar\right)\right] = 0$$

concentration standard state (molar)

Standard Reduction Potentials

$$E^{o}_{red}\left[H^{+}\left(aq.;\ a_{\pm}=1\right)\middle|\ H_2\left(gas;\ 1\ bar\right)\right]=0$$

Then, if we have:

measured

$$AgCl_{(s)}+\frac{1}{2}H_{2(g)} \leftrightarrows H^{+}_{(aq)}+Cl^{-}_{(aq)}+Ag_{(s)} \qquad E^{o}=0.222\ V$$

$$AgCl_{(s)}+e^{-} \leftrightarrows Cl^{-}_{(aq)}+Ag_{(s)} \qquad E^{o}_{red}=0.222\ V$$

$$\frac{1}{2}H_{2(g)} \leftrightarrows H^{+}_{(aq)}+e^{-} \qquad -E^{o}_{red}=0.000\ V$$

by convention

With one electrode set, all other values can be determined. By convention, standard *reduction* potentials are tabulated, and these may be positive (favorable relative to oxidation of H_2) or negative (unfavorable relative to oxidation of H_2).

Self-assessment

The standard-state free energy required to "split" water into hydrogen (a very clean fuel, since burning it creates only water) and oxygen is indicated below

$$2H_2O_{(l)} \leftrightarrows 2H_{2(g)} + O_{2(g)} \qquad \Delta G_r^o = 474.3 \text{ kJ mol}^{-1}$$

What is the standard reduction potential for the below half-cell reaction?

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \leftrightarrows 2H_2O_{(l)}$$

Self-assessment Explained

Given $2H_2O_{(l)} \leftrightarrows 2H_{2(g)} + O_{2(g)} \qquad \Delta G_r^o = 474.3\ \text{kJ mol}^{-1}$

then $E^o = -\dfrac{\Delta G}{nF} = -\dfrac{1}{n}\dfrac{474.7\ \text{kJ mol}^{-1}}{96.485\ \text{kJ V}^{-1}\ \text{mol}^{-1}} = -\dfrac{4.92\ \text{V}}{n}$

sign change for reversed reaction

so using

$2H_{2(g)} + O_{2(g)} \leftrightarrows 2H_2O_{(l)} \qquad E^o = \dfrac{4.92}{n}\ \text{V}$

$2H_{2(g)} \leftrightarrows 4H^+_{(aq)} + 4e^- \qquad E^o = 0.00\ \text{V}$

$O_{2(g)} + 4H^+_{(aq)} + 4e^- \leftrightarrows 2H_2O_{(l)} \qquad E^o = x$

since $n = 4$ electrons, the standard reduction potential $x = 1.23\ \text{V}$

Tabulated Reduction Potentials

Half-Reaction	$\mathscr{E}°$ (V)	Half-Reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3-} + e^- \rightarrow Co^{2-}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^- + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Next: Activities and Other Thermodynamic Properties