Introduction to Electrochemistry (Chapter 13)

Electrochemistry - study of the interchange of chemical energy and electrical energy based on processes that involve reduction and oxidation reactions

Electroanalytical chemistry - use of electrical measurements on a chemical system for analytical purposes:

Conductivity - bulk ionic concentrations

Amperometry - measure current resulting from a constant applied electrical potential

Coulometry - titration with electrons

Potentiometry - measure electrical potential when essentially no current flows

Voltammetry - measure current in response to a varied electrical potential.

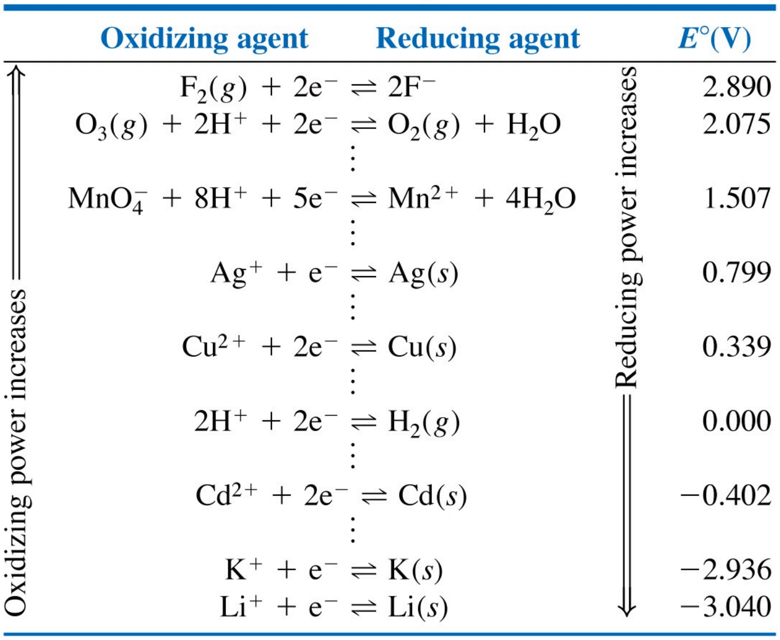
Redox reaction (titration) - transfer of electrons from one species to another

e.g., $2\ Fe^{3+} + Zn \rightleftharpoons 2\ Fe^{2+} + Zn^{2+}$

Oxidation: an increase in oxidation number; i.e., a process resulting from a loss of electrons.
Oxidizing agent or oxidant: substance causing the oxidation

Reduction: a decrease in oxidation number; i.e., a process resulting from a gain of electrons.
Reducing agent or reductant: substance causing the reduction

Table 13-1 Order standard reduction potential

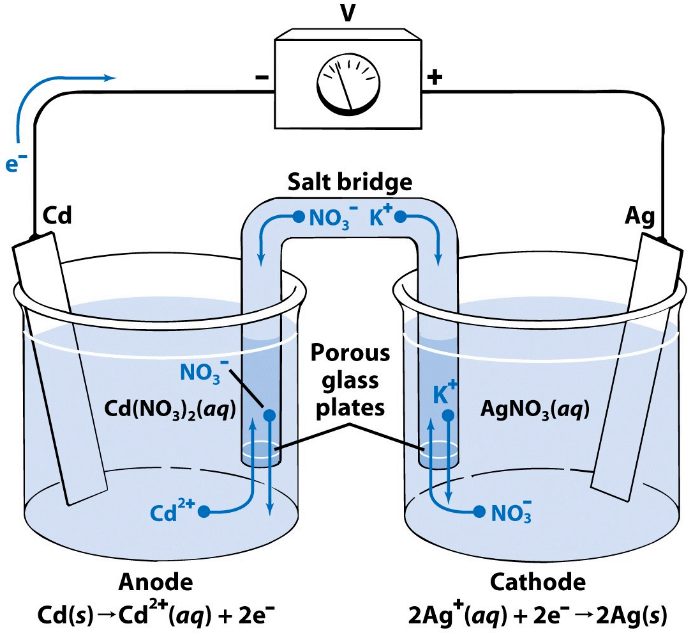


Oxidizing agent		Reducing agent	$E°$(V)
$F_2(g) + 2e^-$	$\rightleftharpoons$	$2F^-$	2.890
$O_3(g) + 2H^+ + 2e^-$	$\rightleftharpoons$	$O_2(g) + H_2O$	2.075
	⋮		
$MnO_4^- + 8H^+ + 5e^-$	$\rightleftharpoons$	$Mn^{2+} + 4H_2O$	1.507
	⋮		
$Ag^+ + e^-$	$\rightleftharpoons$	$Ag(s)$	0.799
	⋮		
$Cu^{2+} + 2e^-$	$\rightleftharpoons$	$Cu(s)$	0.339
	⋮		
$2H^+ + 2e^-$	$\rightleftharpoons$	$H_2(g)$	0.000
	⋮		
$Cd^{2+} + 2e^-$	$\rightleftharpoons$	$Cd(s)$	−0.402
	⋮		
$K^+ + e^-$	$\rightleftharpoons$	$K(s)$	−2.936
$Li^+ + e^-$	$\rightleftharpoons$	$Li(s)$	−3.040

Galvanic Cells (Sec 13-2)

Galvanic cell (voltaic cell) - generates a spontaneous voltage by a chemical redox reaction; e.g. battery

$$2\ Ag^+ + Cd \rightleftharpoons 2\ Ag(s) + Cd^{2+}$$



Cathode: electrode at which reduction occurs
Anode: electrode at which oxidation occurs

$Cd_{(s)}\ |\ Cd(NO_3)_{2(aq)}\ ||\ AgNO_{3(aq)}\ |\ Ag_{(s)}$

Line Notation (pg 286)
Anode on left
Cathode on right
"|" indicates phase boundary
"||" indicates salt bridge
Ignore spectator ions

If half-cell reaction has no solid species to serve as electrode, use an inert electrode such as Pt or graphite

Question: Write line notation for:
Anode: $Zn \rightarrow Zn^{2+} + 2e^-$
Cathode: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Standard Potentials (Sec 13-3)

Standard reduction potential (E°) is the electrode potential of a half-cell rxn (vs. SHE) when all reactants and products exist at unit activity (1 M conc or 1 atm).

(see table above)

Cell Potential

$E_{cell} = E_{cathode} - E_{anode}$
Calc the cell potential of Cd|Cd^{2+} (1 M) || Ag^{+} (1 M) | Ag

$E_{cell} = E_{cathode} - E_{anode}$

Nernst Equation (Sec 13-4)

$$E = E^\circ - \frac{RT}{nF}\ln Q$$

E^{o} = standard reduction potential (A=1)
R = gas constant = 8.314 J/(K·mol)
T = temperature (K)
n = number of electrons in half reaction
F= Faraday constant (96,490 C/mol)
Q = reaction quotient

At 25.00^{o}C, $E = E^\circ - \frac{0.05916\text{ V}}{n}\log Q$

Calc the cell potential of Cd|Cd^{2+} (1 M) || Ag^{+} (0.1 M) | Ag

$E_{cell} = E_{cathode} - E_{anode}$

Cathode half reaction: $Ag^{+} + 1e^{-} \rightarrow Ag(s)$

$$E_C = E_C^\circ - \frac{0.05916\text{ V}}{n}\log\frac{1}{[Ag^{+}]} = 0.799V - \frac{0.05916\text{ V}}{1}\log\frac{1}{0.1M} = 0.740\text{ V}$$

$E_{cell} = E_{cathode} - E_{anode} =$

Calc the cell potential of Cd|Cd^{2+} (0.1 M) || Ag^{+} (0.1 M) | Ag

Anode half reaction (as reduction): $Cd^{2+} + 2e^{-} \rightarrow Cd(s)$

$$E_A = E_A^\circ - \frac{0.05916\text{ V}}{2}\log\frac{1}{[Cd^{2+}]} = -0.402V - \frac{0.05916\text{ V}}{2}\log\frac{1}{0.1M}$$

$E_A = -0.432$ V

$E_{cell} = E_{cathode} - E_{anode} =$

Half-Reaction	**E^0 (V)**
$Li^+_{(aq)} + e^- \text{----->} Li_{(s)}$	-3.05
$K^+_{(aq)} + e^- \text{----->} K_{(s)}$	-2.93
$Ba^{2+}_{(aq)} + 2\ e^- \text{----->} Ba_{(s)}$	-2.90
$Sr^{2+}_{(aq)} + 2\ e^- \text{----->} Sr_{(s)}$	-2.89
$Ca^{2+}_{(aq)} + 2\ e^- \text{----->} Ca_{(s)}$	-2.87
$Na^+_{(aq)} + e^- \text{----->} Na_{(s)}$	-2.71
$Mg^{2+}_{(aq)} + 2\ e^- \text{----->} Mg_{(s)}$	-2.37
$Be^{2+}_{(aq)} + 2\ e^- \text{----->} Be_{(s)}$	-1.85
$Al^{3+}_{(aq)} + 3\ e^- \text{----->} Al_{(s)}$	-1.66
$Mn^{2+}_{(aq)} + 2\ e^- \text{----->} Mn_{(s)}$	-1.18
$2\ H_2O + 2\ e^- \text{----->} H_{2(g)} + 2\ OH^-_{(aq)}$	-0.83
$Zn^{2+}_{(aq)} + 2\ e^- \text{----->} Zn_{(s)}$	-0.76
$Cr^{3+}_{(aq)} + 3\ e^- \text{----->} Cr_{(s)}$	-0.74
$Fe^{2+}_{(aq)} + 2\ e^- \text{----->} Fe_{(s)}$	-0.44
$Cd^{2+}_{(aq)} + 2\ e^- \text{----->} Cd_{(s)}$	-0.40
$PbSO_{4(s)} + 2\ e^- \text{----->} Pb_{(s)} + SO_4^{2-}{}_{(aq)}$	-0.31
$Co^{2+}_{(aq)} + 2\ e^- \text{----->} Co_{(s)}$	-0.28
$Ni^{2+}_{(aq)} + 2\ e^- \text{----->} Ni_{(s)}$	-0.25
$Sn^{2+}_{(aq)} + 2\ e^- \text{----->} Sn_{(s)}$	-0.14
$Pb^{2+}_{(aq)} + 2\ e^- \text{----->} Pb_{(s)}$	-0.13
$2\ H^+_{(aq)} + 2\ e^- \text{----->} H_{2(g)}$	0.00
$Sn^{4+}_{(aq)} + 2\ e^- \text{----->} Sn^{2+}_{(aq)}$	+0.13
$Cu^{2+}_{(aq)} + e^- \text{----->} Cu^+_{(aq)}$	+0.13
$SO_4^{2-}{}_{(aq)} + 4\ H^+_{(aq)} + 2\ e^- \text{----->} SO_{2(g)} + 2\ H_2O$	+0.20
$AgCl_{(s)} + e^- \text{----->} Ag_{(s)} + Cl^-_{(aq)}$	+0.22
$Cu^{2+}_{(aq)} + 2\ e^- \text{----->} Cu_{(s)}$	+0.34
$O_{2(g)} + 2\ H_2 + 4\ e^- \text{----->} 4\ OH^-_{(aq)}$	+0.40
$I_{2(s)} + 2\ e^- \text{----->} 2\ I^-_{(aq)}$	+0.53
$MnO_4^-{}_{(aq)} + 2\ H_2O + 3\ e^- \text{----->} MnO_{2(s)} + 4\ OH^-_{(aq)}$	+0.59
$O_{2(g)} + 2\ H^+_{(aq)} + 2\ e^- \text{----->} H_2O_{2(aq)}$	+0.68
$Fe^{3+}_{(aq)} + e^- \text{----->} Fe^{2+}_{(aq)}$	+0.77
$Ag^+_{(aq)} + e^- \text{----->} Ag_{(s)}$	+0.80
$Hg_2^{2+}{}_{(aq)} + 2\ e^- \text{----->} 2\ Hg_{(l)}$	+0.85
$2\ Hg^{2+}_{(aq)} + 2\ e^- \text{----->} Hg_2^{2+}{}_{(aq)}$	+0.92
$NO_3^-{}_{(aq)} + 4\ H^+_{(aq)} + 3\ e^- \text{----->} NO_{(g)} + 2\ H_2O$	+0.96
$Br_{2(l)} + 2\ e^- \text{----->} 2\ Br^-_{(aq)}$	+1.07
$O_{2(g)} + 4\ H^+_{(aq)} + 4\ e^- \text{----->} 2\ H_2O$	+1.23
$MnO_{2(s)} + 4\ H^+_{(aq)} + 2\ e^- \text{----->} Mn^{2+}_{(aq)} + 2\ H_2O$	+1.23
$Cr_2O_7^{2-}{}_{(aq)} + 14\ H^+_{(aq)} + 6\ e^- \text{----->} 2\ Cr^{3+}_{(aq)} + 7\ H_2O$	+1.33
$Cl_{2(g)} + 2\ e^- \text{----->} 2\ Cl^-_{(aq)}$	+1.36
$Au^{3+}_{(aq)} + 3\ e^- \text{----->} Au_{(s)}$	+1.50
$MnO_4^-{}_{(aq)} + 8\ H^+_{(aq)} + 5\ e^- \text{----->} Mn^{2+}_{(aq)} + 4\ H_2O$	+1.51
$Ce^{4+}_{(aq)} + e^- \text{----->} Ce^{3+}_{(aq)}$	+1.61
$PbO_{2(s)} + 4\ H^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 2\ e^- \text{----->} PbSO_{4(s)} + 2\ H_2O$	+1.70
$H_2O_{2(aq)} + 2\ H^+_{(aq)} + 2\ e^- \text{----->} 2\ H_2O$	+1.77
$Co^{3+}_{(aq)} + e^- \text{----->} Co^{2+}_{(aq)}$	+1.82
$O_{3(g)} + 2\ H^+_{(aq)} + 2\ e^- \text{----->} O_{2(g)} + H_2O$	+2.07
$F_{2(g)} + 2\ e^- \text{----->} F^-_{(aq)}$	+2.87

Write the Nernst equation for the following reactions:

1) $Fe^{3+} + e \rightleftharpoons Fe^{2+}$

$$E = E^o - \frac{0.5916\ \text{V}}{1}\log\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

2) $Ni^{2+} + 2e \rightleftharpoons Ni\ (s)$

$$E = E^o - \frac{0.5916\ \text{V}}{2}\log\frac{1}{[\text{Ni}^{2+}]}$$

3) ¼ P_4 (s) + 3 H^+ + 3 e $\rightleftharpoons$ PH_3 (g)

$$E = E^o - \frac{0.5916\ \text{V}}{3}\log\frac{P_{\text{PH}_3}}{[\text{H}^+]^3}$$

3b) P_4 (s) + 12 H^+ + 12 e $\rightleftharpoons$ 4 PH_3 (g)

$$E = E^o - \frac{0.5916\ \text{V}}{12}\log\frac{P_{\text{PH}_3}{}^4}{[\text{H}^+]^{12}} = E^o - \frac{0.5916\ \text{V}}{12}4\log\frac{P_{\text{PH}_3}}{[\text{H}^+]^3}$$

$$E = E^o - \frac{0.5916\ \text{V}}{3}\log\frac{P_{\text{PH}_3}}{[\text{H}^+]^3}$$

If we multiply a half-cell rxn by any factor, the values of E° or E do not change.

A. Determination of cell potential (E)

4) Calculate the electrode potential of a half-cell containing 0.100 M $KMnO_4$ and 0.0500 M $MnCl_2$ in a pH 1.00 solution.

$MnO_4^- + 8\ H^+ + 5\ e \rightleftharpoons Mn^{2+} + 4\ H_2O$ $E^\circ_{MnO4-/Mn2+} = 1.51$ V

$$E = E^o - \frac{0.05916\ \text{V}}{5}\log\frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8}$$

$[H^+]$ = 0.10 M (pH = 1.00)

$$E = 1.51\ \text{V} - \frac{0.05916\ \text{V}}{5}\log\frac{0.0500}{0.100(0.100)^8} = 1.42\ \text{V}$$

5) What is the electrode potential of a half-cell consisting of a Pt electrode immersed in a 0.100 M HCl solution through which chlorine gas is being passed at a partial pressure of 1.15 atm?

Cl_2 (g) + 2 e $\rightleftharpoons$ 2 Cl^- $E^\circ_{Cl2/Cl-} = 1.36$ V

$$E = E^o - \frac{0.05916\ \text{V}}{2}\log\frac{[\text{Cl}^-]^2}{P_{\text{Cl}_2}} = 1.36\ \text{V} - \frac{0.05916\ \text{V}}{2}\log\frac{(0.100)^2}{1.15} = 1.42\ \text{V}$$

6) A beaker containing 50 mL of 0.15 M H_3AsO_3 and 0.061 M H_3AsO_4 in acidic solution has an electrode potential of 0.494 V. What is the pH?

$H_3AsO_4 + 2\,H^+ + 2\,e \rightleftharpoons H_3AsO_3 + H_2O \qquad E^{\circ} = 0.575\ V$

$$E = E^{o} - \frac{0.05916\ \mathrm{V}}{2}\log\frac{[\mathrm{H_3AsO_3}]}{[\mathrm{H_3AsO_4}][\mathrm{H^+}]^2}$$

$$0.494\ \mathrm{V} = 0.575\ \mathrm{V} - \frac{0.05916\ \mathrm{V}}{2}\log\frac{0.15}{0.061[\mathrm{H^+}]^2}$$

$[H^+]$ = 0.067 M or pH = -log0.067 = 1.17

7) Calculate the potential of the following cell:

Zn (s) | Zn^{2+} (0.120 M) || Cl^- (0.105 M) | Cl_2 (1.15 atm) | Pt

Cl_2 (g) + 2 e $\rightleftharpoons$ 2 Cl^- $\quad E^{\circ}_{Cl2/Cl-}$ =

$$E = E^{o} - \frac{0.05916\ \mathrm{V}}{2}\log\frac{[\mathrm{Cl^-}]^2}{P_{\mathrm{Cl_2}}} = 1.36\ \mathrm{V} - \frac{0.05916\ \mathrm{V}}{2}\log\frac{(0.105)^2}{1.15} = 1.42\ \mathrm{V}$$

Zn^{2+} + 2 e $\rightleftharpoons$ Zn $\quad E^{\circ}_{Zn2+/Zn}$ =

$$E = E^{o} - \frac{0.5916\ \mathrm{V}}{2}\log\frac{1}{[\mathrm{Zn^{2+}}]} = -0.762\ \mathrm{V} - \frac{0.5916\ \mathrm{V}}{2}\log\frac{1}{0.12} = -0.789\ \mathrm{V}$$

$E_{cell} = E_{cathode} - E_{anode}$ =

$E_{cell} > 0$, the overall cell rxn is spontaneous rxn, i.e., galvanic

8) A solution containing 0.0835 M Cr^{3+} and 0.119 M Cr^{2+} is mixed with another solution containing 0.0361 M V^{3+} and 0.0904 M V^{2+} to make a 25.0 mL final solution. Does a rxn occur and, if so, what reaction?

Cr^{3+} + e $\rightleftharpoons$ Cr^{2+} $\quad E^{\circ}_{Cr3+/Cr2+}$ =

$$E_{\mathrm{Cr}} = E^{o} - \frac{0.5916\ \mathrm{V}}{1}\log\frac{[\mathrm{Cr^{2+}}]}{[\mathrm{Cr^{3+}}]} = -0.407\ \mathrm{V} - \frac{0.5916\ \mathrm{V}}{1}\log\frac{0.119}{0.0835} = -0.416\ \mathrm{V}$$

V^{3+} + e $\rightleftharpoons$ V^{2+} $\quad E^{\circ}_{V3+/V2+}$ =

$$E_{\mathrm{V}} = E^{o} - \frac{0.5916\ \mathrm{V}}{1}\log\frac{[\mathrm{V^{2+}}]}{[\mathrm{V^{3+}}]} = -0.255\ \mathrm{V} - \frac{0.5916\ \mathrm{V}}{1}\log\frac{0.0904}{0.0361} = -0.279\ \mathrm{V}$$

For a spontaneous rxn to occur, $E_{cell} > 0$

So $E_{cell} = E_v - E_{cr}$ =

Cathode involves V^{3+}/V^{2+} and the anode involves Cr^{3+}/Cr^{2+} .

Cathode: reduction or $V^{3+} + e \rightarrow V^{2+}$

Anode: oxidation or $Cr^{2+} \rightarrow Cr^{3+} + e$

Overall rxn: $V^{3+} + Cr^{2+} \rightleftharpoons V^{2+} + Cr^{3+}$

B. Determining equilibrium constant

$$E^{o}_{cell} = \frac{RT}{nF}\ln K = \frac{0.05916V}{n}\log K$$

9) Calculate the equilibrium constant for the rxn,

$$2\,Fe^{3+} + H_3AsO_3 + H_2O \rightleftharpoons 2\,Fe^{2+} + H_3AsO_4 + 2\,H^{+}$$

$H_3AsO_4 + 2\,H^{+} + 2\,e \rightleftharpoons H_3AsO_3 + H_2O$ $E^{\circ}_{H3AsO4/H3AsO3}$=

and $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^{\circ}_{Fe3+/Fe2+} = 0.771$ V

n = 2: $\log K_{eq} = \frac{n\,(E_C - E_A)}{0.05916V} = \frac{2\times\ (0.771V - 0.575V)}{0.05916V} = 6.622$

$K_{eq} = 10^{6.622}$ =

10) What is the equilibrium constant for the following rxn?

$$Cu^{2+} + 2\,Ag \rightleftharpoons Cu + 2\,Ag^{+}$$

$Cu^{2+} + 2\,e \rightleftharpoons Cu$ $E^{\circ}_{Cu2+/Cu}$ =

and $Ag^{+} + e \rightleftharpoons Ag$ $E^{\circ}_{Ag+/Ag} = 0.800$ V

$E^{\circ}_{Ag+/Ag}$ =

n = 2: $\log K_{eq} = \frac{n\,(E_C - E_A)}{0.05916V} = \frac{2\times\ (0.337V - 0.800V)}{0.05916\ V} = -15.642$

$K_{eq} = 10^{-15.642}$ =

K_{eq} << 1 which means this rxn is not in favor to form the products, i.e., at the equilibrum $[Ag^{+}] << [Cu^{2+}]$.

C. Determination of concentration

Electrode of the first kind – develops a potential in response to a redox in which the electrode metal takes part.

11) What is the concentration of Ag^{+} within a solution when the potential of measured using a silver wire is 0.446V vs. SHE?

$$Ag^{+}_{(aq)} + e^{-} \rightleftharpoons Ag_{(s)} \qquad E^{o} = 0.80V$$

$$E = E^{o} - \frac{0.5916\ V}{1}\log\frac{1}{[Ag^{+}]}$$

$$0.446\text{ V} - 0.80\text{ V} = -\frac{0.05916\text{ V}}{1}\log\frac{1}{[\text{Ag}^{+}]}$$

log [Ag$^+$] = -5.98
[Ag$^+$] = 1.04 x 10^{-6} M

Electrode of the second kind – develops a potential in response to a species which is in equilibrium with the electrode metal redox

Ag$^+$(aq) + e- ⇌ Ag(s)   E^o = 0.80V

$$E = 0.80 - \frac{0.5916\text{ V}}{1}\log\frac{1}{[\text{Ag}^{+}]}$$

AgCl (s) ⇌ Ag$^+$(aq) + Cl$^-$ K_{sp}= 1.8x10^{-10}

$$[\text{Ag}^{+}] = \frac{K_{sp}}{[\text{Cl}^{-}]}$$

$$E = 0.80\text{ V} - \frac{0.05916\text{ V}}{1}\log\frac{[\text{Cl}^{+}]}{K_{sp}}$$

$$E = 0.80\text{ V} - \frac{0.05916\text{ V}}{1}\log\frac{1}{K_{sp}} - \frac{0.05916\text{ V}}{1}\log[\text{Cl}^{+}]$$

$$E = 0.223\text{ V} - 0.05916\text{ V}\log[\text{Cl}^{-}]$$

12) What is the concentration of Cl$^-$ when the potential measured using a Ag/AgCl electrode is 0.527V vs. SHE?

AgCl(s) + e- ⇌ Ag(s) + Cl$^-$ E^o = 0.223V

E= 0.223 V - 0.05916 V log [Cl$^-$]
0.527 V - 0.223 V = - 0.05916 V log [Cl$^-$]
-5.13$_9$ = log [Cl$^-$]
[Cl$^-$] = 7.3 x 10^{-6} M

Formal potential (E^{o}') (Sec 13-7)

• standard electrode potential (E°) is defined when [H$^+$] = 1 M and all other species concentrations = 1 M (or 1 atm for gas).

• **formal potential (E°')** is defined when **[H$^+$] = 10^{-7} M** or pH = 7 and all other species concentrations = 1 M (or 1 atm for gas)

H$^+$ participates in many biochemical redox reactions, and pH 7 is most common in life sciences. (see Harris for example)