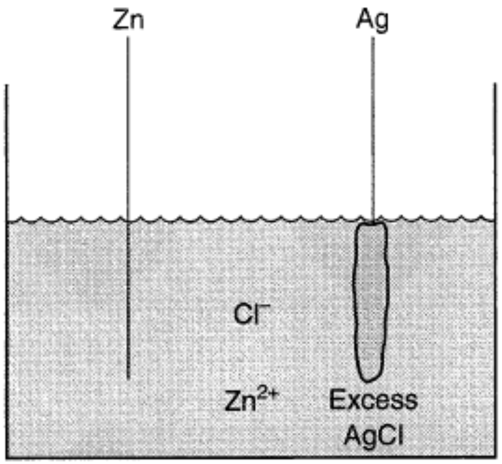
Working electrode

Working electrode

Most of the time, one is interested in only one of the two independent half-reactions

→ The electrode at which it occurs is called the working electrode.

→ The other electrode is called the counter electrode



Anode half-reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode half-reaction: $2AgCl(s) + 2e^- \longrightarrow 2Ag(s) + 2Cl^-(aq)$

Overall cell reaction: $Zn(s) + 2AgCl(s) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2Cl^-(aq)$

Reference electrode

Reference electrode

In order to easily compare with various electrochemical reactions at the working electrode,

→ one standardizes the other half of the cell (counter electrode) by using an electrode (called a reference electrode)

→ made up of phases having essentially constant composition.
(because composition affects a potential)

→ For more accurate measurement, counter and reference electrodes are experimentally separated (3-electrode cell)

The internationally accepted primary reference

→ the standard hydrogen electrode (SHE), or normal hydrogen electrode (NHE)

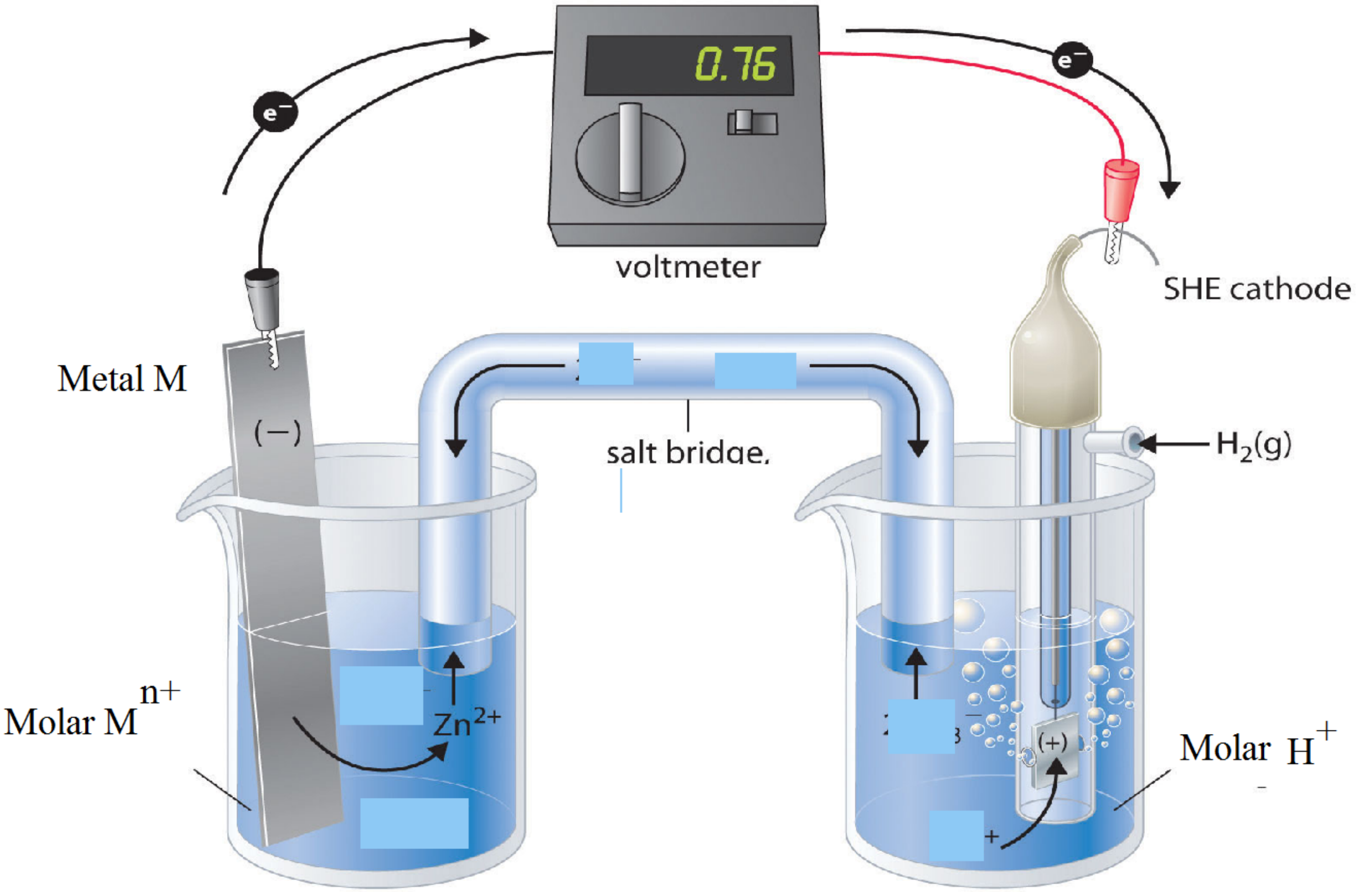
→ has all components at unit activity:

$$\mathrm{Pt/H_2}(a = 1)\mathrm{/H^+}(a = 1, \text{aqueous}) \qquad 2\ \mathrm{H^+(aq)} + 2\ e^- \leftrightarrow \mathrm{H_2(g)}$$

NHE: potential of a platinum electrode in 1 M acid solution (experimental)

SHE: potential of a platinum electrode in a theoretical ideal solution (the current **standard**)

Reference electrode



Reference electrode

Potentials are often measured with respect to reference electrodes other than the NHE

→ Because NHE is not very convenient from an experimental standpoint.

A common reference

→ the saturated calomel electrode (SCE), which is

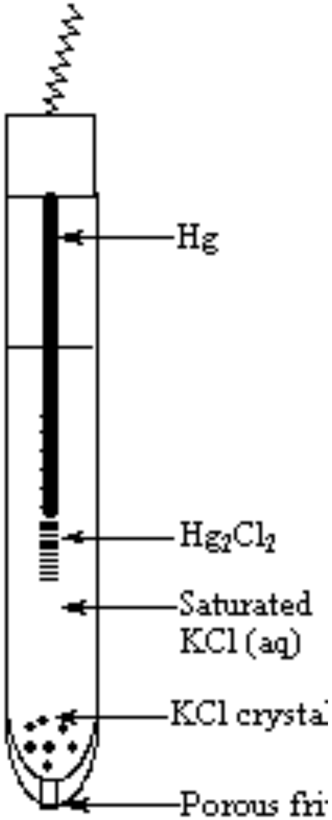
$$Hg/Hg_2Cl_2/KCl \text{ (saturated in water)}$$

→ the potential of SCE: 0.242 V vs. NHE.

$$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$$

$$Hg_2^{2+} + 2Cl^- \rightleftharpoons Hg_2Cl_2(s),$$

$$Hg_2Cl_2\,(s) + 2e^- \rightarrow 2\,Hg\,(s) + 2Cl^-\,(sat)$$



Reference electrode

Another is the silver-silver chloride electrode,

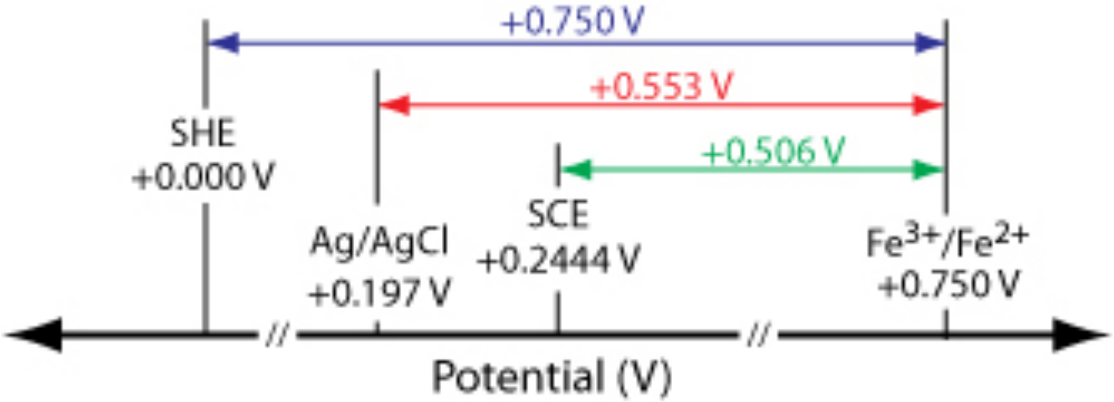
$$Ag^+ + e^- \rightleftharpoons Ag(s)$$

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$$

Ag/AgCl/KCl (saturated in water)

- → the potential of Ag/AgCl: 0.197 V vs. NHE.
- → Potentials identified in the literature as "vs. Ag/Ag$^+$" when this electrode is used.

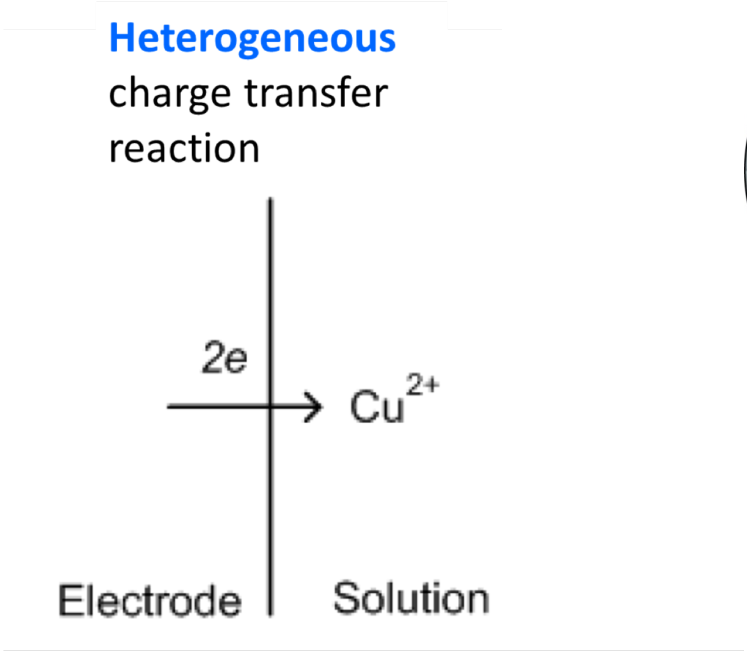


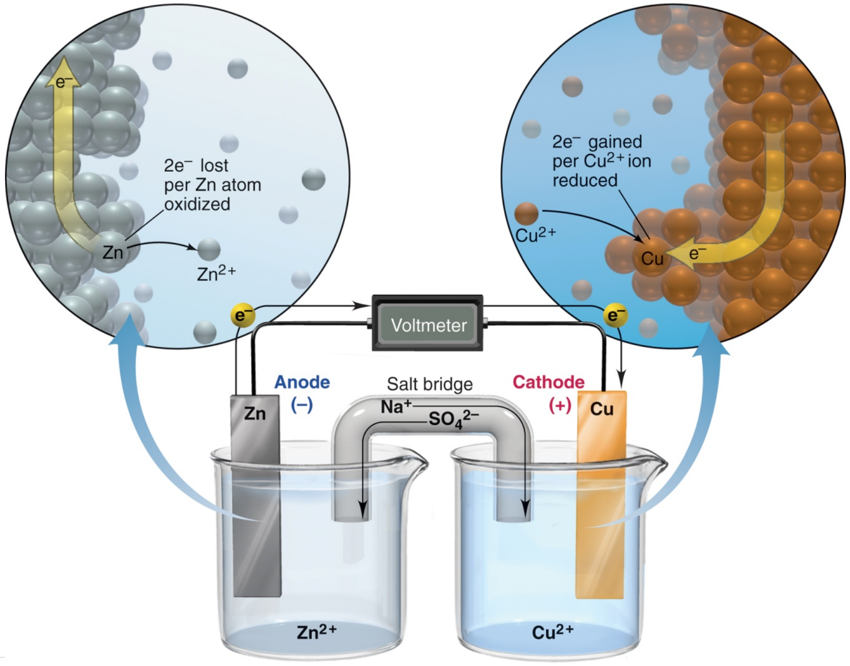
Electrochemical Cells and Reactions

An electrochemical reaction is often more complex than a chemical reaction occurring in solution or in the gas phase.

➔ The chemical reaction is called a homogeneous reaction, because it occurs everywhere within the medium at a uniform rate.

➔ In contrast, an electrode process is a heterogeneous reaction occurring only at the electrode-electrolyte interface.





Faradaic Processes

The current represents

→ the number of electrons reacting with Cd^{2+} per second,

→ or the number of coulombs of electric charge flowing per second

➔ the question "What is i?" is essentially the same as "What is the rate of the reaction, $Cd^{2+} + 2e \rightarrow Cd$?"

The following relations demonstrate the direct proportionality between faradaic current and electrolysis rate:

$$i \text{ (amperes)} = \frac{dQ}{dt} \text{ (coulombs/s)}$$

$$\frac{Q}{nF} \frac{\text{(coulombs)}}{\text{(coulombs/mol)}} = N \text{ (mol electrolyzed)}$$

➔ where n is the stoichiometric number of electrons consumed in the electrode reaction (e.g., 2 for reduction of Cd^{2+}).

$$\boxed{\text{Rate (mol/s)} = \frac{dN}{dt} = \frac{i}{nF}}$$

Heterogeneous reaction

Since electrode reactions are heterogeneous and occur at the electrode surface, their reaction rates are usually described in units of mol/s per unit area; that is,

$$\boxed{\text{Rate}\left(\text{mol s}^{-1}\text{ cm}^{-2}\right) = \frac{i}{nFA} = \frac{j}{nF}}$$

where j is the current density (A/cm^2).

POTENTIALS
AND THERMODYNAMICS
OF CELLS

Free Energy and Cell emf

- -ΔG: the maximum net work obtainable from the cell

$$\mathrm{Zn/Zn^{2+}}(a = 1),\ \mathrm{Cl^{-}}(a = 1)\mathrm{/AgCl/Ag}$$

$$|\Delta G| = \text{charge passed} \times \text{reversible potential difference}$$

$$|\Delta G| = nF|E|$$

- n: the number of electrons passed per atom of zinc reacted (or the number of moles of electrons per mole of Zn reacted)
- F: the charge on a mole of electrons, which is about 96,500 C.

Free Energy and Cell emf

$$|\Delta G| = \text{charge passed} \times \text{reversible potential difference}$$

$$|\Delta G| = nF|E|$$

The actual meaning of the signs - and +

➔ different for free energy and potential.

For free energy,

➔ - and + : energy lost or gained from the system

The free energy change has a sign associated with the direction of the net cell reaction.

➔ We can reverse the sign by reversing the direction.

Free Energy and Cell emf

$$|\Delta G| = \text{charge passed} \times \text{reversible potential difference}$$

$$|\Delta G| = nF|E|$$

For potential,

➔ - and + : the excess or deficiency of electronic charge

Only an infinitesimal change in the overall cell potential is required to reverse the direction of the reaction

➔ Hence E is essentially constant and independent of the direction of a (reversible) transformation.

We want to relate a direction-sensitive quantity (ΔG) to a direction-insensitive observable (E).

➔ This desire is the origin of almost all of the confusion that exists over electrochemical sign conventions.

Free Energy and Cell emf

We rationalize the relationship between free energy and potential

➔ by inventing a thermodynamic construct called the emf (electromotive force) of the cell reaction.

➔ emf has a directional aspect.

For the one in the following example,

$$\mathrm{Zn/Zn^{2+}}(a = 1),\ \mathrm{Cl^{-}}(a = 1)\mathrm{/AgCl/Ag}$$

➔ The reaction is

$$\mathrm{Zn} + 2\mathrm{AgCl} \rightarrow \mathrm{Zn^{2+}} + 2\mathrm{Ag} + 2\mathrm{Cl^{-}}$$

The right electrode corresponds to reduction in the implied cell reaction, and the left electrode is identified with oxidation.

Free Energy and Cell emf

$$\mathrm{Zn} + 2\mathrm{AgCl} \rightarrow \mathrm{Zn}^{2+} + 2\mathrm{Ag} + 2\mathrm{Cl}^-$$

Thus, the reverse of the above reaction would be associated with the opposite schematic:

$$\mathrm{Zn}^{2+} + 2\mathrm{Ag} + 2\mathrm{Cl}^- \rightarrow \mathrm{Zn} + 2\mathrm{AgCl}$$

$$\mathrm{Ag/AgCl/Cl}^-(a = 1), \mathrm{Zn}^{2+}(a = 1)/\mathrm{Zn}$$

(Sign convention) The cell reaction emf, E_{rxn},

→ is defined as the electrostatic potential of the electrode written on the right in the cell schematic with respect to that on the left.

$$\boxed{E_{\mathrm{rxn}} = E_{\mathrm{right}} - E_{\mathrm{left}}}$$

Free Energy and Cell emf

i) $\mathrm{Zn/Zn^{2+}}(a = 1), \mathrm{Cl^-}(a = 1)\mathrm{/AgCl/Ag}$

For example, in the above cell,

➔ thus the emf of the below reaction, the spontaneous direction, is +0.985 V.

$$\mathrm{Zn + 2AgCl \rightarrow Zn^{2+} + 2Ag + 2Cl^-}$$

ii) $\mathrm{Ag/AgCl/Cl^-}(a = 1), \mathrm{Zn^{2+}}(a = 1)\mathrm{/Zn}$

Likewise, the emf corresponding to the above cell is -0.985 V.

➔ The reaction is

$$\mathrm{Zn^{2+} + 2Ag + 2Cl^- \rightarrow Zn + 2AgCl}$$

Free Energy and Cell emf

i) $\mathrm{Zn + 2AgCl \rightarrow Zn^{2+} + 2Ag + 2Cl^{-}}$ +0.985 V.

ii) $\mathrm{Zn^{2+} + 2Ag + 2Cl^{-} \rightarrow Zn + 2AgCl}$ -0.985 V.

By adopting this convention,

→ we have managed to rationalize an electrostatic quantity (the cell potential difference),
which is not sensitive to the direction of the cell's operation,
with a thermodynamic quantity (the Gibbs free energy),
which is sensitive to that direction.

One can avoid completely the common confusion about sign conventions of cell potentials if one understands this formal relationship between electrostatic measurements and thermodynamic concepts.

Free Energy and Cell emf

Because our convention implies a positive emf when a reaction is spontaneous,

$$|\Delta G| = nF|E| \quad \Rightarrow \quad \boxed{\Delta G = -nFE_{\mathrm{rxn}}}$$

or as above, when all substances are at unit activity,

$$\boxed{\Delta G^0 = -nFE^0_{\mathrm{rxn}}}$$

: $E^0{}_{rxn}$ is called the standard emf of the cell reaction.

Practice

Determine. Cell rxns? Their emf? Spontaneous?

a) Ag/AgCl/K^+, Cl^-/Hg_2Cl_2/Hg

$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$	0.26816
$AgCl + e \rightleftarrows Ag + Cl^-$	0.2223

b) Pt/O_2 /Na^+, OH^- /H_2 /Pt

$O_2 + 2H_2O + 4e \rightleftarrows 4OH^-$	0.401
$2H_2O + 2e \rightleftarrows H_2 + 2OH^-$	−0.828

Half-Reactions and Reduction Potentials

TABLE C.1 Selected Standard Electrode Potentials in Aqueous Solutions at 25°C in V *vs.* NHE[a]

Reaction	Potential, V
$Ag^+ + e \rightleftarrows Ag$	0.7991
$AgBr + e \rightleftarrows Ag + Br^-$	0.0711
$AgCl + e \rightleftarrows Ag + Cl^-$	0.2223
$AgI + e \rightleftarrows Ag + I^-$	−0.1522
$Ag_2O + H_2O + 2e \rightleftarrows 2Ag + 2OH^-$	0.342
$Al^{3+} + 3e \rightleftarrows Al$	−1.676
$Au^+ + e \rightleftarrows Au$	1.83
$Au^{3+} + 2e \rightleftarrows Au^+$	1.36
p-benzoquinone $+ 2H^+ + 2e \rightleftarrows$ hydroquinone	0.6992
$Br_2(aq) + 2e \rightleftarrows 2Br^-$	1.0874
$Ca^{2+} + 2e \rightleftarrows Ca$	−2.84
$Cd^{2+} + 2e \rightleftarrows Cd$	−0.4025
$Cd^{2+} + 2e \rightleftarrows Cd(Hg)$	−0.3515
$Ce^{4+} + e \rightleftarrows Ce^{3+}$	1.72
$Cl_2(g) + 2e \rightleftarrows 2Cl^-$	1.3583
$HClO + H^+ + e \rightleftarrows \frac{1}{2}Cl_2 + H_2O$	1.630
$Co^{2+} + 2e \rightleftarrows Co$	−0.277
$Co^{3+} + e \rightleftarrows Co^{2+}$	1.92
$Cr^{2+} + 2e \rightleftarrows Cr$	−0.90
$Cr^{3+} + e \rightleftarrows Cr^{2+}$	−0.424
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftarrows 2Cr^{3+} + 7H_2O$	1.36
$Cu^+ + e \rightleftarrows Cu$	0.520
$Cu^{2+} + 2CN^- + e \rightleftarrows Cu(CN)_2^-$	1.12
$Cu^{2+} + e \rightleftarrows Cu^+$	0.159
$Cu^{2+} + 2e \rightleftarrows Cu$	0.340
$Cu^{2+} + 2e \rightleftarrows Cu(Hg)$	0.345
$Eu^{3+} + e \rightleftarrows Eu^{2+}$	−0.35
$1/2F_2 + H^+ + e \rightleftarrows HF$	3.053
$Fe^{2+} + 2e \rightleftarrows Fe$	−0.44
$Fe^{3+} + e \rightleftarrows Fe^{2+}$	0.771
$Fe(CN)_6^{3-} + e \rightleftarrows Fe(CN)_6^{4-}$	0.3610

(continued)

TABLE C.1 *(continued)*

Reaction	Potential, V
$2H^+ + 2e \rightleftarrows H_2$	0.0000
$2H_2O + 2e \rightleftarrows H_2 + 2OH^-$	−0.828
$H_2O_2 + 2H^+ + 2e \rightleftarrows 2H_2O$	1.763
$2Hg^{2+} + 2e \rightleftarrows Hg_2^{2+}$	0.9110
$Hg_2^{2+} + 2e \rightleftarrows 2Hg$	0.7960
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$	0.26816
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$ (sat'd. KCl)	0.2415
$HgO + H_2O + 2e \rightleftarrows Hg + 2OH^-$	0.0977
$Hg_2SO_4 + 2e \rightleftarrows 2Hg + SO_4^{2-}$	0.613
$I_2 + 2e \rightleftarrows 2I^-$	0.5355
$I_3^- + 2e \rightleftarrows 3I^-$	0.536
$K^+ + e \rightleftarrows K$	−2.925
$Li^+ + e \rightleftarrows Li$	−3.045
$Mg^{2+} + 2e \rightleftarrows Mg$	−2.356
$Mn^{2+} + 2e \rightleftarrows Mn$	−1.18
$Mn^{3+} + e \rightleftarrows Mn^{2+}$	1.5
$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{2+} + 2H_2O$	1.23
$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{2+} + 4H_2O$	1.51
$Na^+ + e \rightleftarrows Na$	−2.714
$Ni^{2+} + 2e \rightleftarrows Ni$	−0.257
$Ni(OH)_2 + 2e \rightleftarrows Ni + 2OH^-$	−0.72
$O_2 + 2H^+ + 2e \rightleftarrows H_2O_2$	0.695
$O_2 + 4H^+ + 4e \rightleftarrows 2H_2O$	1.229
$O_2 + 2H_2O + 4e \rightleftarrows 4OH^-$	0.401
$O_3 + 2H^+ + 2e \rightleftarrows O_2 + H_2O$	2.075
$Pb^{2+} + 2e \rightleftarrows Pb$	−0.1251
$Pb^{2+} + 2e \rightleftarrows Pb(Hg)$	−0.1205
$PbO_2 + 4H^+ + 2e \rightleftarrows Pb^{2+} + 2H_2O$	1.468
$PbO_2 + SO_4^{2-} + 4H^+ + 2e \rightleftarrows PbSO_4 + 2H_2O$	1.698
$PbSO_4 + 2e \rightleftarrows Pb + SO_4^{2-}$	−0.3505
$Pd^{2+} + 2e \rightleftarrows Pd$	0.915
$Pt^{2+} + 2e \rightleftarrows Pt$	1.188
$PtCl_4^{2-} + 2e \rightleftarrows Pt + 4Cl^-$	0.758
$PtCl_6^{2-} + 2e \rightleftarrows PtCl_4^{2-} + 2Cl^-$	0.726
$Ru(NH_3)_6^{3+} + e \rightleftarrows Ru(NH_3)_6^{2+}$	0.10
$S + 2e \rightleftarrows S^{2-}$	−0.447
$Sn^{2+} + 2e \rightleftarrows Sn$	−0.1375
$Sn^{4+} + 2e \rightleftarrows Sn^{2+}$	0.15
$Tl^+ + e \rightleftarrows Tl$	−0.3363
$Tl^+ + e \rightleftarrows Tl(Hg)$	−0.3338
$Tl^{3+} + 2e \rightleftarrows Tl^+$	1.25
$U^{3+} + 3e \rightleftarrows U$	−1.66
$U^{4+} + e \rightleftarrows U^{3+}$	−0.52
$UO_2^+ + 4H^+ + e \rightleftarrows U^{4+} + 2H_2O$	0.273
$UO_2^{2+} + e \rightleftarrows UO_2^+$	0.163

(continued)

TABLE C.1 *(continued)*

Reaction	Potential, V
$V^{2+} + 2e \rightleftarrows V$	−1.13
$V^{3+} + e \rightleftarrows V^{2+}$	−0.255
$VO^{2+} + 2H^+ + e \rightleftarrows V^{3+} + H_2O$	0.337
$VO_2^+ + 2H^+ + e \rightleftarrows VO^{2+} + H_2O$	1.00
$Zn^{2+} + 2e \rightleftarrows Zn$	−0.7626
$ZnO_2^{2-} + 2H_2O + 2e \rightleftarrows Zn + 4OH^-$	−1.285

Free Energy and Cell emf

Other thermodynamic quantities can be derived from electrochemical measurements

For example, the entropy change in the cell reaction is given by the temperature dependence of ΔG:

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_{\mathrm{P}}$$

hence

$$\Delta S = nF\left(\frac{\partial E_{\mathrm{rxn}}}{\partial T}\right)_{\mathrm{P}}$$

and

$$\boxed{\Delta H = \Delta G + T\Delta S = nF\left[T\left(\frac{\partial E_{\mathrm{rxn}}}{\partial T}\right)_{\mathrm{P}} - E_{\mathrm{rxn}}\right]}$$

Free Energy and Cell emf

The equilibrium constant of the reaction is given by

$$\Delta G = \Delta G^o + RT \ln Q$$

$$\boxed{RT \ln K_{\mathrm{rxn}} = -\Delta G^0 = nFE^0_{\mathrm{rxn}}}$$

Half-Reactions and Reduction Potentials

In the system

$$\mathrm{Pt/H_2}(a = 1)/\mathrm{H^+}(a = 1)//\mathrm{Ag^+}(a = 1)/\mathrm{Ag}$$

Thus, we say that the standard potential of the Ag^+/Ag couple is +0.799 V vs. NHE.

Another valid expression is that the standard electrode potential of Ag^+/Ag is +0.799 V vs. NHE.

$$\mathrm{Ag^+} + e \rightleftarrows \mathrm{Ag} \qquad E^0_{\mathrm{Ag^+/Ag}} = +0.799\ \mathrm{V}\ vs.\ \mathrm{NHE}$$

The standard emf of the Ag^+ reduction is also +0.799 V vs. NHE,

but that of the Ag oxidation is -0.799 V vs. NHE.

$$\boxed{E_{\mathrm{rxn}} = E_{\mathrm{right}} - E_{\mathrm{left}}}$$

emf and Concentration

Consider a general cell in which the half-reaction at the right-hand electrode is

$$\nu_O O + ne \rightleftarrows \nu_R R$$

where the v's are stoichiometric coefficients.

The cell reaction with NHE is then

$$\nu H_2 + \nu_O O \rightarrow \nu_R R + \nu H^+$$

and its free energy is given from basic thermodynamics by

$$\Delta G = \Delta G^o + RT \ln Q \qquad \Delta G = \Delta G^0 + RT \ln \frac{a_R^{\nu_R} a_H^{\nu_{H+}}}{a_O^{\nu_O} a_{H_2}^{\nu_{H_2}}}$$

where a_i is the activity of species i

emf and Concentration

Since $\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$,

$$\Delta G = \Delta G^0 + RT \ln \frac{a_{\mathrm{R}}^{\nu_{\mathrm{R}}} a_{\mathrm{H}^+}^{\nu_{\mathrm{H}^+}}}{a_{\mathrm{O}}^{\nu_{\mathrm{O}}} a_{\mathrm{H}_2}^{\nu_{\mathrm{H}_2}}} \quad \Rightarrow \quad E = E^0 - \frac{RT}{nF} \ln \frac{a_{\mathrm{R}}^{\nu_{\mathrm{R}}} a_{\mathrm{H}^+}^{\nu_{\mathrm{H}^+}}}{a_{\mathrm{O}}^{\nu_{\mathrm{O}}} a_{\mathrm{H}_2}^{\nu_{\mathrm{H}_2}}}$$

since $a_{\mathrm{H}^+} = a_{\mathrm{H}_2} = 1$,

$$\boxed{E = E^0 + \frac{RT}{nF} \ln \frac{a_{\mathrm{O}}^{\nu_{\mathrm{O}}}}{a_{\mathrm{R}}^{\nu_{\mathrm{R}}}}}$$

Nernst Equation

➔ provides the relationship between the potential of the O/R electrode vs. NHE and the activities of O and R.

emf and Concentration

$$E = E^0 - \frac{RT}{nF}\ln\frac{a_{\mathrm{R}}^{\nu_{\mathrm{R}}}}{a_{\mathrm{O}}^{\nu_{\mathrm{O}}}} \quad \text{or} \quad E^0 + \frac{RT}{nF}\ln\frac{a_{\mathrm{O}}^{\nu_{\mathrm{O}}}}{a_{\mathrm{R}}^{\nu_{\mathrm{R}}}}$$

$$\frac{RT}{nF} = \frac{8.3145J\cdot K^{-1}\cdot mol^{-1}\times 298K}{n\times 96487C\cdot mol^{-1}} = \frac{0.0257J\cdot C^{-1}}{n} = \frac{0.0257}{n}V$$

$$E = E^0 + \frac{0.0257}{n}\ln\frac{a_{\mathrm{O}}^{\nu_{\mathrm{O}}}}{a_{\mathrm{R}}^{\nu_{\mathrm{R}}}} = E^0 + \frac{0.0591}{n}\log\frac{a_{\mathrm{O}}^{\nu_{\mathrm{O}}}}{a_{\mathrm{R}}^{\nu_{\mathrm{R}}}} \qquad \text{[V]}$$

Formal Potentials

It is usually inconvenient to deal with activities in evaluations of half-cell potentials, because activity coefficients are almost always unknown.

➔ A device for avoiding them is the formal potential, $E^{0'}$.

For example,

$$\mathrm{Fe}^{3+} + e \rightleftarrows \mathrm{Fe}^{2+}$$

➔ Its Nernst relation is simply

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\mathrm{Fe}^{3+}}}{a_{\mathrm{Fe}^{2+}}} = E^0 + \frac{RT}{nF} \ln \frac{\gamma_{\mathrm{Fe}^{3+}} [\mathrm{Fe}^{3+}]}{\gamma_{\mathrm{Fe}^{2+}} [\mathrm{Fe}^{2+}]} \qquad a_i = \gamma_i (C_i/C^0)$$

where

C_i : the concentration of the solute

C^0 : the standard concentration (1 M)

Formal Potentials

$$E = E^0 + \frac{RT}{nF}\ln\frac{a_{\mathrm{Fe}^{3+}}}{a_{\mathrm{Fe}^{2+}}} = E^0 + \frac{RT}{nF}\ln\frac{\gamma_{\mathrm{Fe}^{3+}}\,[\mathrm{Fe}^{3+}]}{\gamma_{\mathrm{Fe}^{2+}}\,[\mathrm{Fe}^{2+}]}$$

$$E = \underbrace{E^0 + \frac{RT}{nF}\ln\frac{\gamma_{\mathrm{Fe}^{3+}}}{\gamma_{\mathrm{Fe}^{2+}}}} + \frac{RT}{nF}\ln\frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{2+}]}$$

$$E^{0'} = E^0 + \frac{RT}{nF}\ln\frac{\gamma_{\mathrm{Fe}^{3+}}}{\gamma_{\mathrm{Fe}^{2+}}} \quad \Rightarrow \quad E = \underline{E^{0'}} + \frac{RT}{nF}\ln\frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{2+}]}$$

formal potential, $E^{0'}$.

Formal Potentials

$E^{0'}$ will vary from medium to medium

→ because the ionic strength affects the activity coefficients

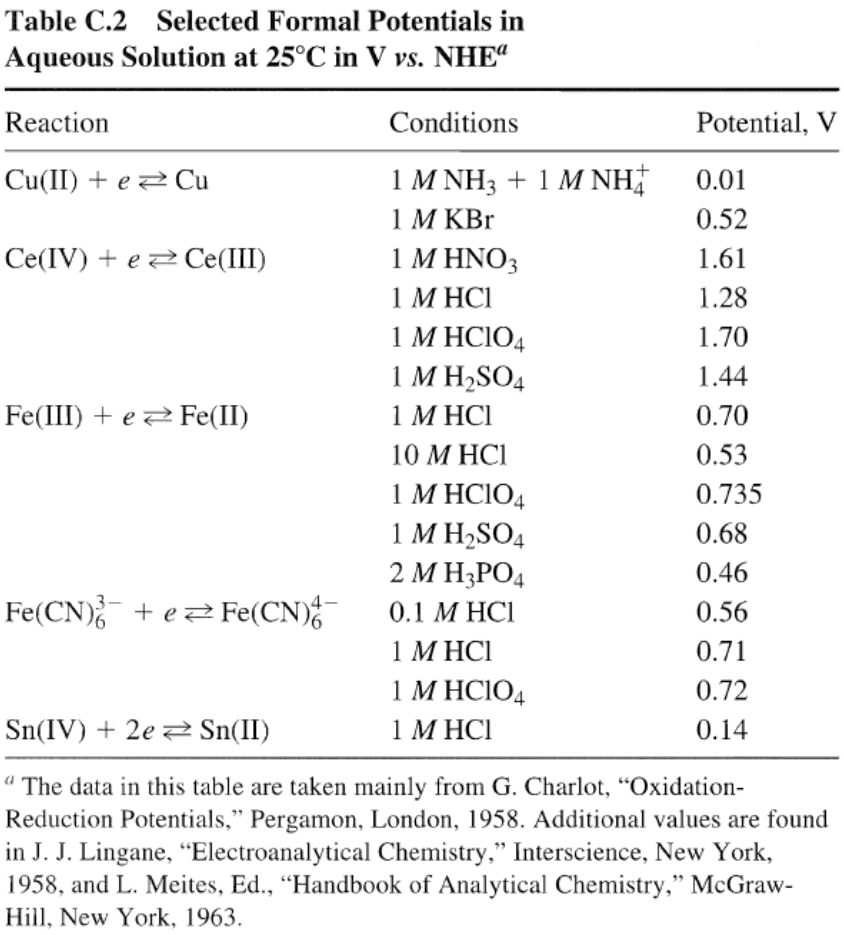


Table C.2 Selected Formal Potentials in Aqueous Solution at 25°C in V *vs.* NHE[a]

Reaction	Conditions	Potential, V
$Cu(II) + e \rightleftarrows Cu$	$1\,M\ NH_3 + 1\,M\ NH_4^+$	0.01
	$1\,M$ KBr	0.52
$Ce(IV) + e \rightleftarrows Ce(III)$	$1\,M\ HNO_3$	1.61
	$1\,M$ HCl	1.28
	$1\,M\ HClO_4$	1.70
	$1\,M\ H_2SO_4$	1.44
$Fe(III) + e \rightleftarrows Fe(II)$	$1\,M$ HCl	0.70
	$10\,M$ HCl	0.53
	$1\,M\ HClO_4$	0.735
	$1\,M\ H_2SO_4$	0.68
	$2\,M\ H_3PO_4$	0.46
$Fe(CN)_6^{3-} + e \rightleftarrows Fe(CN)_6^{4-}$	$0.1\,M$ HCl	0.56
	$1\,M$ HCl	0.71
	$1\,M\ HClO_4$	0.72
$Sn(IV) + 2e \rightleftarrows Sn(II)$	$1\,M$ HCl	0.14

[a] The data in this table are taken mainly from G. Charlot, "Oxidation-Reduction Potentials," Pergamon, London, 1958. Additional values are found in J. J. Lingane, "Electroanalytical Chemistry," Interscience, New York, 1958, and L. Meites, Ed., "Handbook of Analytical Chemistry," McGraw-Hill, New York, 1963.

Analytical Chemistry

Chapter 16. Redox Titrations

A redox titration

: based on an oxidation-reduction reaction between analyte and titrant.

This chapter introduces the theory of redox titrations

16.1 The shape of a redox titration curve

Consider the titration of iron(II) with standard cerium(IV), monitored potentiometrically with Pt and calomel electrodes as shown in Figure 16-1.

The titration reaction is

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$

Ce^{4+}	Fe^{2+}	Ce^{3+}	Fe^{3+}
Ceric titrant	Ferrous analyte	Cerous	Ferric

See Figure on P. 376

$$K \approx 10^{16} \text{ in } 1 \text{ M } HClO_4$$

Each mole of ceric ion oxidizes 1 mol of ferrous ion rapidly and quantitatively.

The titration reaction creates a mixture of Ce^{4+}, Ce^{3+}, Fe^{2+}, and Fe^{3+} in the beaker

16.1 The shape of a redox titration curve

At the Pt indicator electrode, two reactions come to equilibrium:

$$\text{Indicator half-reaction:} \quad Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^\circ = 0.767\ V$$

$$\text{Indicator half-reaction:} \quad Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^\circ = 1.70\ V$$

The Pt indicator electrode responds to
the relative concentrations (really, activities) of Ce^{4+} and Ce^{3+} or Fe^{3+} and Fe^{2+}.

We now set out to calculate how the cell voltage changes as Fe^{2+} is titrated with Ce^{4+}.

The titration curve has three regions.

16.1 The shape of a redox titration curve

Region 1: Before the Equivalence Point

$$\underset{\text{titrant}}{\underset{\text{Ceric}}{Ce^{4+}}} + \underset{\text{analyte}}{\underset{\text{Ferrous}}{Fe^{2+}}} \rightarrow \underset{\text{Cerous}}{Ce^{3+}} + \underset{\text{Ferric}}{Fe^{3+}}$$

As each aliquot of Ce^{4+} is added,

→ titration reaction consumes Ce^{4+}

→ and creates an equal number of moles of Ce^{3+} and Fe^{3+}.

Prior to the equivalence point, excess unreacted Fe^{2+} remains in solution.

Therefore, we can find the redox potential of Fe^{2+}/Fe^{3+}

$$E = E_+ - E_-$$

$$E = \left[\underset{\substack{\uparrow \\ \text{Formal potential for } Fe^{3+} \\ \text{reduction in} \\ 1\ M\ HClO_4}}{0.767} - 0.059\,16 \log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)\right] - \underset{\substack{\uparrow \\ \text{Potential of} \\ \text{saturated calomel} \\ \text{electrode}}}{0.241}$$

$$E = 0.526 - 0.059\,16 \log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)$$

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One special point is reached before the equivalence point.

When the volume of titrant is one-half of the amount required to reach the equivalence

point ($V = 1/2V_e$),

→ $[Fe^{3+}] = [Fe^{2+}]$.

→ In this case, the log term is 0

$$E = 0.526 - 0.059\,16 \log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)$$

The point at which $V = (1/2)V_e$ is analogous to the point at which pH = pKa when $V = (1/2)V_e$ in an acid-base titration.

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Region 2: At the Equivalence Point

Exactly enough Ce^{4+} has been added to react with all the Fe^{2+}.

Virtually all cerium is in the form Ce^{3+}, and virtually all iron is in the form Fe^{3+}.

Tiny amounts of Ce^{4+} and Fe^{2+} are present at equilibrium.

From the stoichiometry of Reaction 16-1, we can say that

$$[Ce^{3+}] = [Fe^{3+}] \qquad [Ce^{4+}] = [Fe^{2+}]$$

$$\underset{\substack{\text{Ceric}\\ \text{titrant}}}{Ce^{4+}} + \underset{\substack{\text{Ferrous}\\ \text{analyte}}}{Fe^{2+}} \rightarrow \underset{\text{Cerous}}{Ce^{3+}} + \underset{\text{Ferric}}{Fe^{3+}}$$