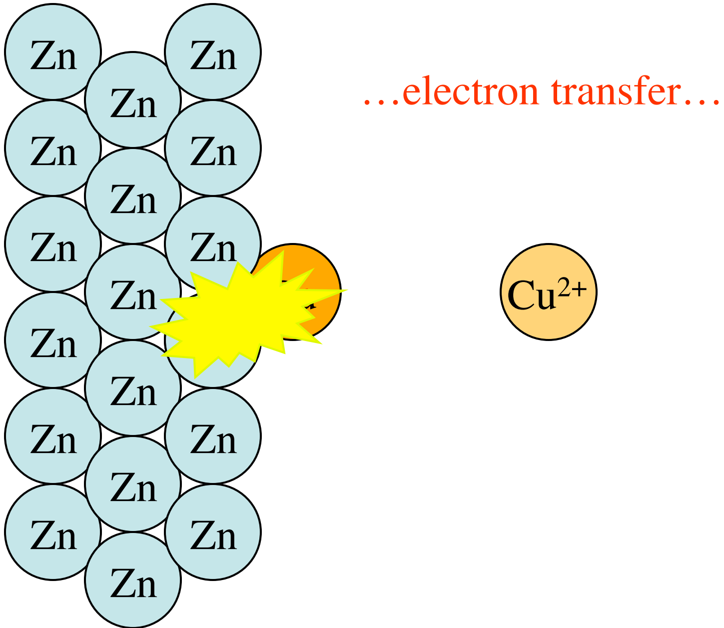
Consider the reaction between Zn and Cu^{2+}

$$Zn + Cu^{2+} \leftrightarrows Zn^{2+} + Cu$$

This will take place spontaneously in solution (i.e., $\Delta G^o < 0$, $K_{eq} > 1$)



Oxidation-reduction reactions

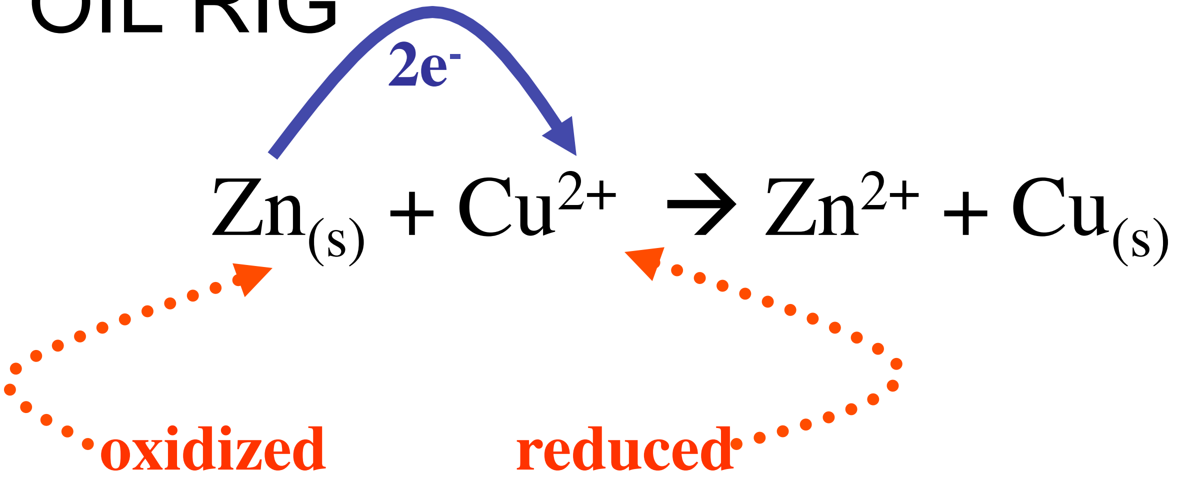
- Oxidation: Loss of electrons

  (consider <u>oxidation</u> of Fe to Fe^{3+} as in Fe_2O_3, rust)

- Reduction: Gain of electrons

  (<u>Reduction</u> of formal charge)

OIL RIG



$$Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+} + Cu_{(s)}$$

Electrochemical Terms

Redox Rxn: Reactions that involve the transfer of electrons from one species to another.

In an electrochemical reaction, both an oxidation and a reduction must occur.

Oxidation: A species loses electrons

Species that *are oxidized* are known as *reducing agents*

$$Al \rightarrow Al^{3+} + 3e^-$$

$$Zn \rightarrow Zn^{2+} + 2e^-$$

Reduction: A species gains electrons

Species that *are reduced* are known as *oxidizing agents*

$$Fe^{3+} + 1e^- \rightarrow Fe^{2+}$$

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Overall Rxn—Both oxidation and reduction must occur…

$2e^-$ net transferred

$$2\ Fe^{3+} + Zn \rightarrow 2\ Fe^{2+} + Zn^{2+}$$

Zn is reducing agent
Fe is oxidizing agent

Electric Potential (E) – work is needed to move electrons in a wire or to move ions through solution to an electrode. With electricity we need work to move charge from a region of high electrical potential (high electrical pressure) to a region at another potential (lower electrical pressure). The work needed to move an electric charge through a conductor (e.g. wire) depends on total charge moved and potential difference.

Work (Joules) = E (volts) x Q (coulombs)   units: V=J/C

E_p= (E)(e)

E_p*: electrostatic potential energy in J*;
e: charge of an e in C;
E: *potential in V*

The potential energy (E_p) of an electron (1.6×10^{-19} C) in a 1 V field is 1.6×10^{-19} J = 1 eV

Electrochemical Terms

Electric Charge (C) – magnitude of charge on one mole of electrons is known as the Faraday constant, F.

$Q = n\ F$ $\quad F = 96500\ \text{C/mol e}^-$ $\quad 1.6\text{x}10^{-19}\ \text{C per e}^-$

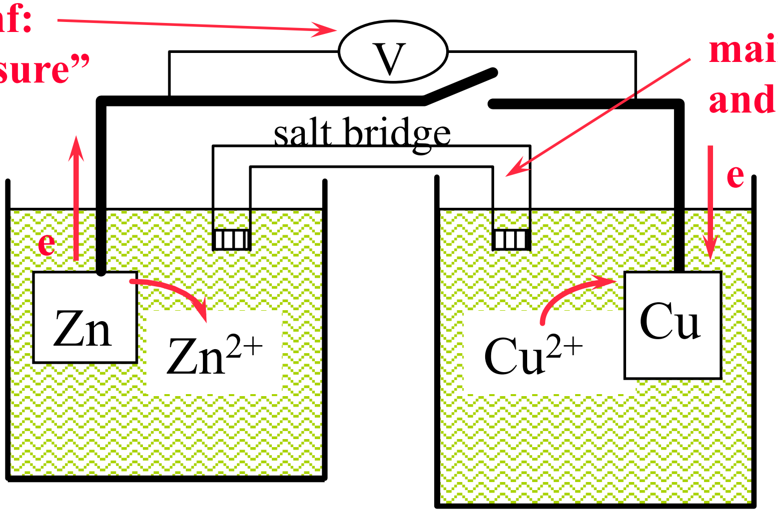
Current (A) – quantity of charge that flows per second.

$$i = \frac{\partial q}{\partial t} = C\frac{\partial E}{\partial t}A$$

Ampere (A) A=C/s

Faraday's Law: mole of substance reacting = it/nF

The electrochemical cell



Measure of emf:
“electron pressure”

maintains electrical neutrality
and “electrical connection

oxidation
ANODE

reduction
CATHODE

Implied reaction:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

(Note: Reax may not proceed as written when switch is closed in circuit!)

Half cell reactions:

$$Zn \longrightarrow Zn^{2+} + 2e^{-}$$
$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

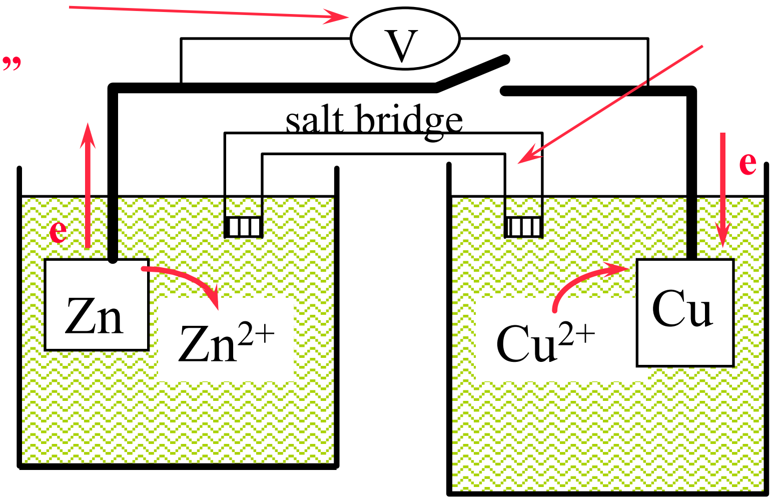
Electrochemical Cell

An **electrochemical cell** is a system consisting of two half cell reactions connected in such a way that chemical reactions either uses or generates an electric current

A **voltaic cell** or **galvanic cell** is an electrochemical cell in which a ***spontaneous reaction*** generates an electric current.

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Measure of emf:
"electron pressure"

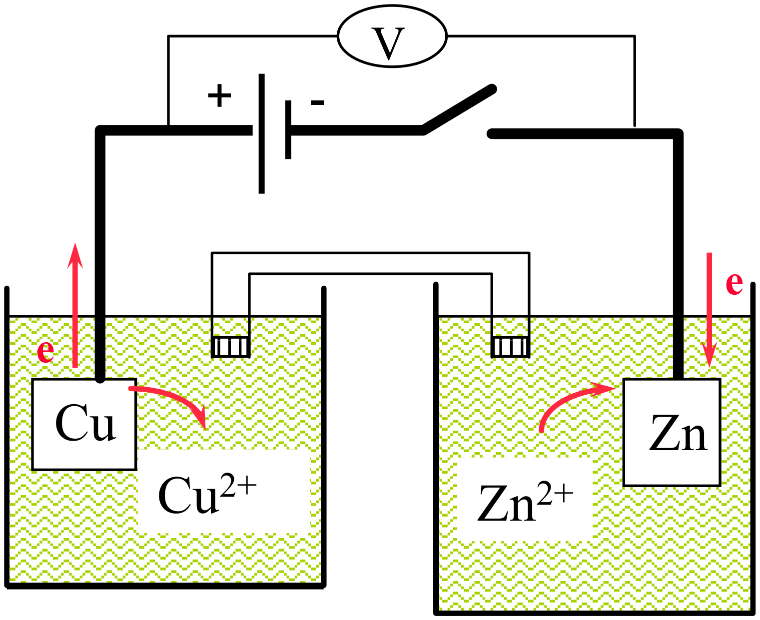


oxidation
ANODE

reduction
CATHODE

Electrochemical Cell

An **electrolytic cell** is an electrochemical cell in which an *electric current drives* an otherwise ***nonspontaneous reaction***.



Oxidation
STILL takes
place at
anode!

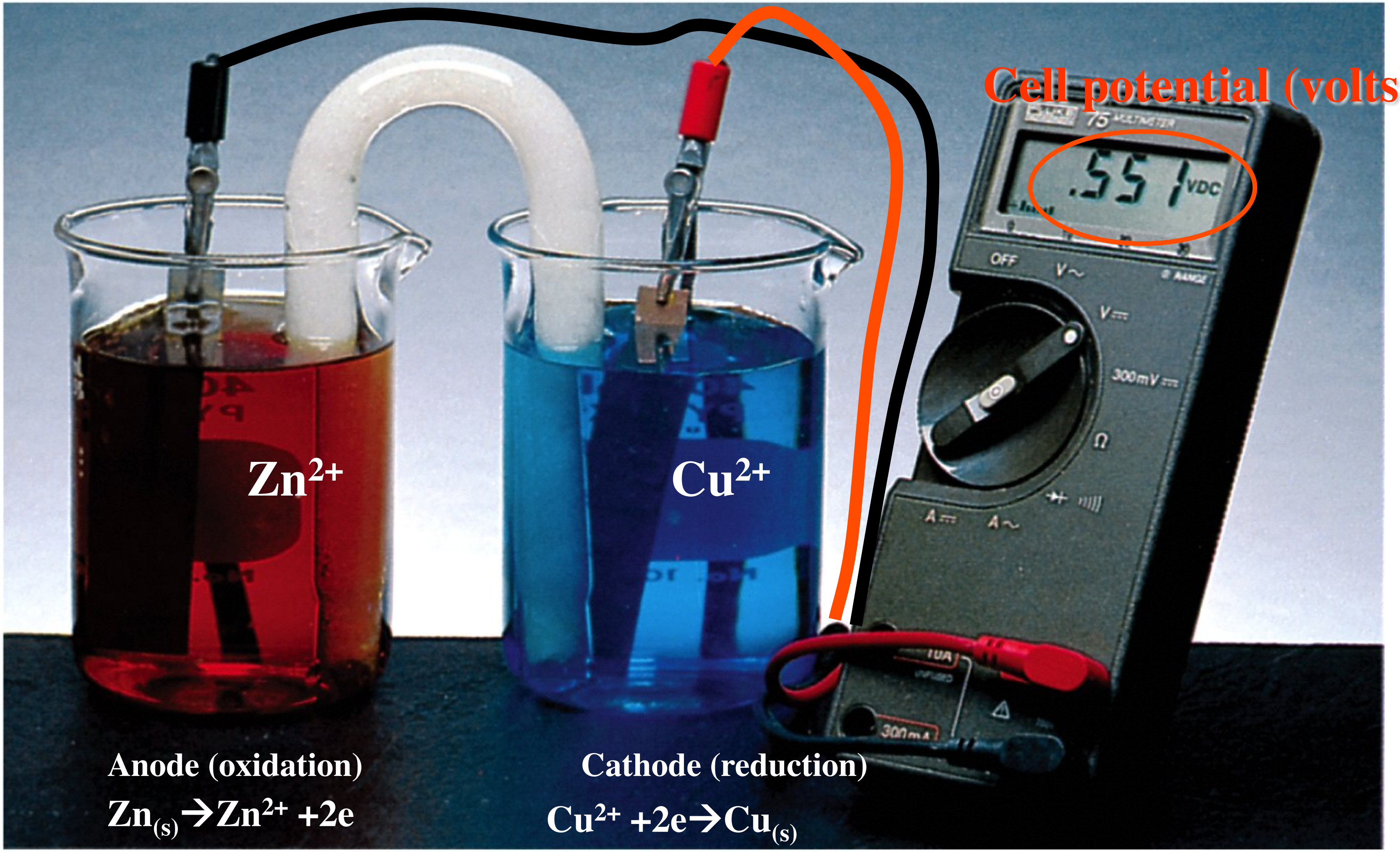
oxidation
ANODE

Reduction
STILL takes
place at
cathode!

reduction
CATHODE

$Zn^{2+} + Cu \rightarrow Zn + Cu^{2+}$

Note that the reaction is reversed from previous slide, i.e., Cu is oxidized.



Cell potential (volts)

Zn^{2+}

Cu^{2+}

Anode (oxidation)

$Zn_{(s)} \rightarrow Zn^{2+} + 2e$

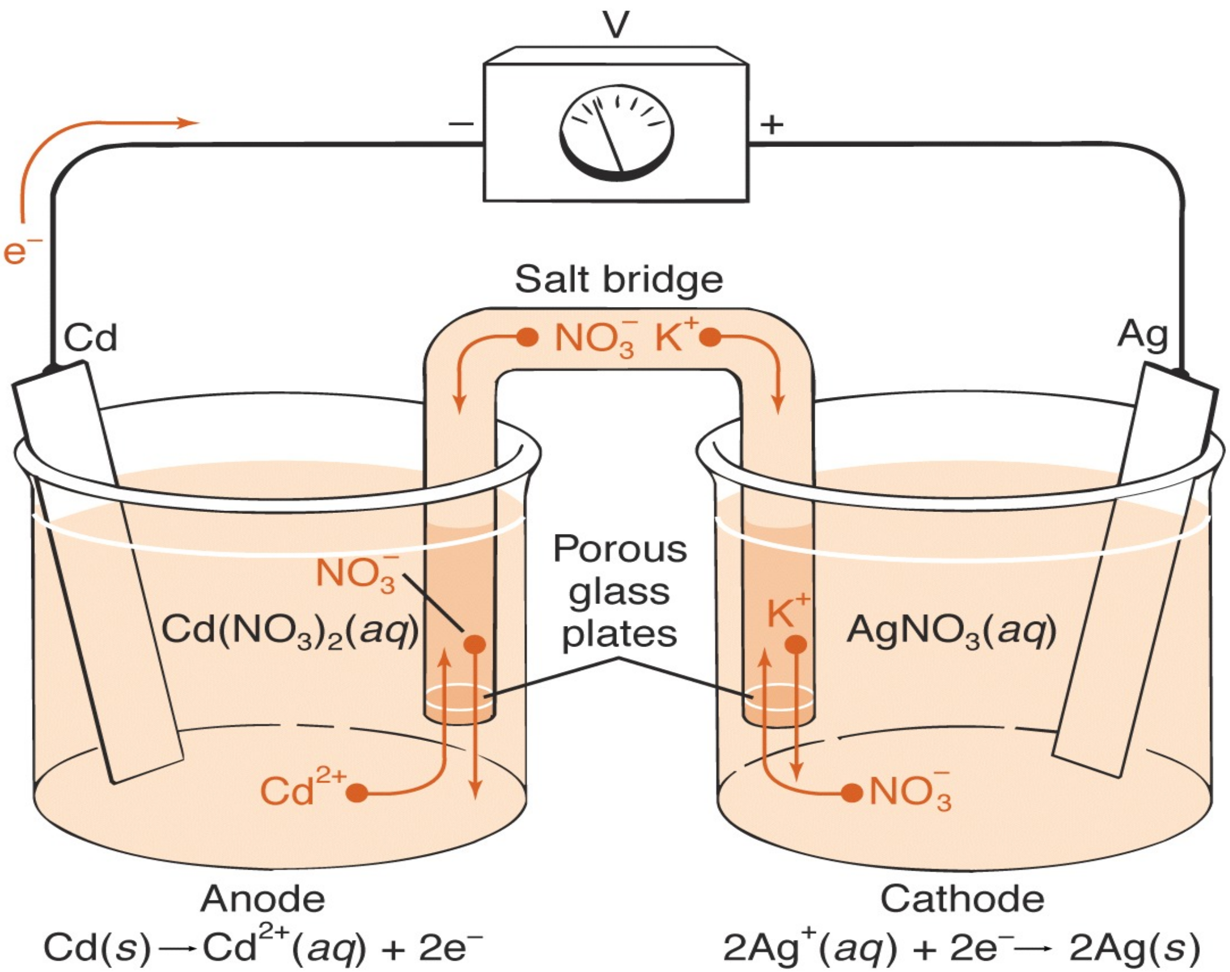
Cathode (reduction)

$Cu^{2+} + 2e \rightarrow Cu_{(s)}$

$$Zn_{(s)+} Cu^{2+} + \cancel{2e} \rightarrow Zn^{2+} Cu_{(s)} + \cancel{2e}$$

$$Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+} Cu_{(s)}$$

Cell layout



Anode
$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$

Cathode
$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

Shorthand notation

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}$$

anode

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+}\ (\underline{\quad\quad}\mathrm{M}) \parallel \mathrm{Cu}^{2+}(\underline{\quad\quad}\mathrm{M}) \mid \mathrm{Cu}$$

cathode

Phase boundary with junction potential

NO liquid junction potential (e.g., salt bridge

Other examples:

$$\mathrm{Pt} \mid \mathrm{H}_{2(g)}\ (a=1) \mid \mathrm{H}^{+}\ (a=1) \parallel \mathrm{Cu}^{2+}(0.01\mathrm{M}) \mid \mathrm{Cu}$$

$$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2} \mid \mathrm{KCl\ (sat'd)} \parallel \mathrm{Fe}^{2+}(0.001\mathrm{M}) \mid \mathrm{Pt}$$

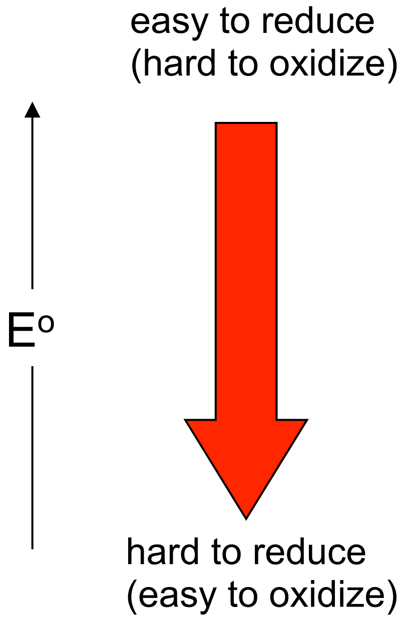
Standard Potentials, E°

ALWAYS written as reduction reactions

$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad E^o = -0.762\ V$$

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad E^o = +0.339\ V$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad E^o = +0.771\ V$$



E° assumes unit activity for all species!

Potentials are relative to <u>Standard hydrogen electrode</u> (SHE)

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^o = 0.000\ V$$

E° value is indication of driving force for reduction

E° is a constant!

Formal Potentials, E°'

Potentials for unique conditions (all species NOT at unit activity)

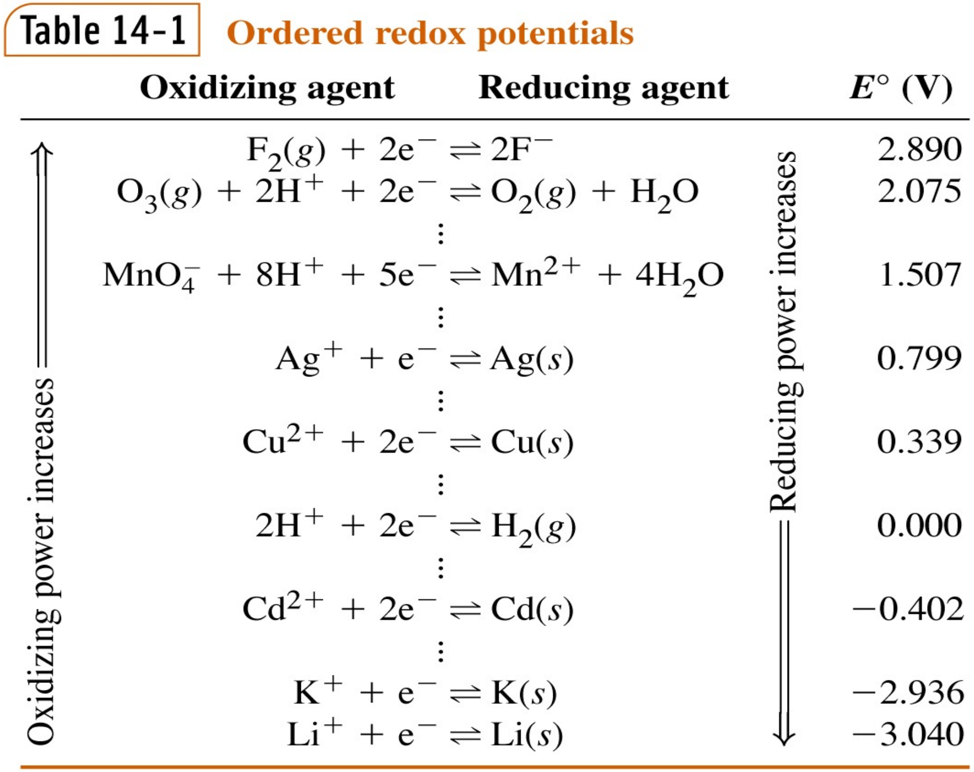


Table 14-1 Ordered redox potentials

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

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Zn is reducing agent

Cu^{2+} is oxidizing agent

E_{cell} calculation

$$E^o_{cell} = E^o_{cat} - E^o_{an}$$

$Zn \mid Zn^{2+}$ (0.2 M) $\parallel Cu^{2+}$(0.3M) $\mid Cu$

$Zn^{2+} + 2e^- \longrightarrow Zn$ E^o= -0.762 V

$Cu^{2+} + 2e^- \longrightarrow Cu$ E^o= +0.339 V

$$E^o_{cell} = E^o_{cat} - E^o_{an}$$

= 0.339-(-0.762)=+1.101 V

Electrochemical potentials and thermodynamics

$$\boxed{\Delta G^o = -nFE^o} \; where F = 96{,}500 coul / eq;$$

$$n = \text{number of e}^- \text{transferred}$$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{nFE^o}{RT}$$

$$\boxed{E^o = \frac{RT}{nF}\ln K = \frac{0.059}{n}\log K}$$

Nernst equation:

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

or

$$\boxed{E = E^o - \frac{0.059}{n}\log Q} \; (T = 298K)$$

at equilibrium: Q=K, E=0

E has units of volts (J/coul)

Determining E_{cell}

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

or

$$E = E^o - \frac{0.059}{n} \log Q \quad (T = 298K)$$

If E is for whole cell, then Q looks like “K” for the complete balanced reaction and E^o is E^o_{cell}

$$E_{cell} = E^o_{cell} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}$$

This can also be for half cells ! In this case, “Q” is the expression in the E^o (reduction) equation, i.e., “reduced over oxidized”. For example:

$$E_{Cu} = E^o_{Cu} - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]}$$

$$E_{Zn} = E^o_{Zn} - \frac{0.059}{2} \log \frac{1}{[Zn^{2+}]}$$

$$E_{cell} = E^o_{Cu} - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]} - \left\{ E^o_{Zn} - \frac{0.059}{2} \log \frac{1}{[Zn^{2+}]} \right\}$$

$$E_{cell} = (E^o_{Cu} - E^o_{Zn}) - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Table 14-2 Reduction potentials of biological interest

Reaction	$E°$ (V)	$E°'$ (V)
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229	+0.816
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771	+0.771
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.535	+0.535
Cytochrome *a* (Fe^{3+}) + e^- $\rightleftharpoons$ cytochrome *a* (Fe^{2+})	+0.290	+0.290
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.695	+0.281
Cytochrome *c* (Fe^{3+}) + e^- $\rightleftharpoons$ cytochrome *c* (Fe^{2+})	—	+0.254
2,6-Dichlorophenolindophenol + $2H^+ + 2e^-$ $\rightleftharpoons$ reduced 2,6-dichlorophenolindophenol	—	+0.22
Dehydroascorbate + $2H^+ + 2e^-$ $\rightleftharpoons$ ascorbate + H_2O	+0.390	+0.058
Fumarate + $2H^+ + 2e^-$ $\rightleftharpoons$ succinate	+0.433	+0.031
Methylene blue + $2H^+ + 2e^-$ $\rightleftharpoons$ reduced product	+0.532	+0.011
Glyoxylate + $2H^+ + 2e^-$ $\rightleftharpoons$ glycolate	—	−0.090
Oxaloacetate + $2H^+ + 2e^-$ $\rightleftharpoons$ malate	+0.330	−0.102
Pyruvate + $2H^+ + 2e^-$ $\rightleftharpoons$ lactate	+0.224	−0.190
Riboflavin + $2H^+ + 2e^-$ $\rightleftharpoons$ reduced riboflavin	—	−0.208
FAD + $2H^+ + 2e^-$ $\rightleftharpoons$ $FADH_2$	—	−0.219
(Glutathione-S)$_2$ + $2H^+ + 2e^-$ $\rightleftharpoons$ 2 glutathione-SH	—	−0.23
Safranine T + $2e^-$ $\rightleftharpoons$ leucosafranine T	−0.235	−0.289
$(C_6H_5S)_2 + 2H^+ + 2e^- \rightleftharpoons 2C_6H_5SH$	—	−0.30
$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH$	−0.105	−0.320
$NADP^+ + H^+ + 2e^- \rightleftharpoons NADPH$	—	−0.324
Cystine + $2H^+ + 2e^-$ $\rightleftharpoons$ 2 cysteine	—	−0.340
Acetoacetate + $2H^+ + 2e^-$ $\rightleftharpoons$ L-β-hydroxybutyrate	—	−0.346
Xanthine + $2H^+ + 2e^-$ $\rightleftharpoons$ hypoxanthine + H_2O	—	−0.371
$2H^+ + 2e^- \rightleftharpoons H_2$	0.000	−0.414
Gluconate + $2H^+ + 2e^-$ $\rightleftharpoons$ glucose + H_2O	—	−0.44
$SO_4^{2-} + 2e^- + 2H^+ \rightleftharpoons SO_3^{2-} + H_2O$	—	−0.454
$2SO_3^{2-} + 2e^- + 4H^+ \rightleftharpoons S_2O_4^{2-} + 2H_2O$	—	−0.527

$$\boxed{\Delta G = -nFE}$$

Free Energy and Potential – the maximum work obtainable from a balanced electrochemical rxn can be related to molar amounts of reactants. The sign and magnitude of the potential can be used to determine spontaneity of rxn and to measure total energy produced

$\Delta G > 0$ or $E < 0$ then reaction is nonspontaneous

$\Delta G < 0$ or $E > 0$ then reaction is spontaneous

Electrochemical Terms

Electric Charge (C) – magnitude of charge on one mole of electrons is known as the Faraday constant, F.

$Q = n\ F$ $F = 96500$ C/mol e^- $1.6\text{x}10^{-19}$ C per e^-

Current (A) – quantity of charge that flows per second.

$$i = \frac{\partial q}{\partial t} = C\frac{\partial E}{\partial t}\ A$$

Ampere (A) A=C/s

Faraday's Law: mole of substance reacting = it/nF

Ohm's Law – current flowing through circuit is directly proportional to potential

$$E = IR$$

Power – is the work done per unit time

$P=IE$ or $P=I^2R$ P=watt (VC/s or J/s)