Chapter 20: Electrochemistry II



Chem 102 Jussi Eloranta



Spontaneous electrochemical reactions



This reaction occurs spontaneously at room temperature:

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

<u>Half reactions:</u> $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$





Galvanic Cells (Voltaic Cells)

- Can we make use of those electrons as they are transferred? (electrical work)
- We could separate the two metals and connect them with a wire. Electrons would travel through the wire to make the reaction occur (metals conduct electricity).
- This type of arrangement is called a Galvanic or Voltaic cell





Alessandro Volta

















- Electrodes: Solid metal (or graphite) surfaces placed in the solutions.
- The cell on the left will not produce current (or voltage) because the Ag⁺ can react directly with the Cd(s) electrode.
- <u>Must separate</u> the two half-cells to force the current through the wire (salt bridge).



FIGURE 13-5 A cell that will not work. The solution contains Cd(NO₃)₂ and AgNO₃. Harris, *Quantitative Chemical Analysis*, 8e © 2011 W. H. Freeman



FIGURE 13-6 A cell that works-thanks to the salt bridge!

Harris, Quantitative Chemical Analysis, 8e © 2011 W. H. Freeman



<u>Salt bridge</u>: Porous gel that allows counter ions to flow from one solution to another (but not the other ions):

Counter ions are not involved in the redox reactions, but without them, charge would build up on each electrode, stopping the reaction.





Anode: The electrode, at which oxidation occurs:

- "ox-an" you lose your electrons
- Can think of it as having a negative charge (-)
- Electrons flow <u>away</u> from the anode (it has a higher potential)





<u>Cathode</u>: The electrode, at which reduction occurs:

- Can think of it as having a positive charge (+)
- Electrons flow <u>toward</u> the cathode (it has a lower potential)



Anatomy of a voltaic cell – salt bridge



Without the salt bridge:

- Anode solution would become more and more positively charged as reaction proceeds (Zn is being converted to Zn²⁺ in the example below)
- Cathode would become more and more negatively charged as reaction proceeds (Cu²⁺ is being converted to Cu in the example below)
- Salt bridge: Counter anions flow from salt bridge into anode solution

Salt bridge: Counter cations flow from salt bridge into cathode solution



It is annoying to draw the diagrams, so we use a notation instead:

Zn(s) | Zn²⁺(aq) || Cu²⁺(aq) | Cu(s) phase change phase change electrodes are written on the outsides

Inert electrodes



inert

Sometimes the electrode is not reacting, it is just a way for electrons to be transferred into the solution:

 $Fe(s) | Fe^{2+}(aq) || MnO_4(aq), H^+(aq), Mn^{2+}(aq) |$ Pt(s)





Standard electrode potentials

- Think of each half-cell as having its own potential (relative quantity)
- The standard potential of the cell, E_{cell^o} is the resulting potential from combining the potentials of each half-cell

Higher the cell voltage, higher potential energy for electrons

• "Standard" means under standard conditions (1 M, 1 atm, 298 K)





Standard hydrogen electrode (SHE)

- Because the half-cell potential is *relative*, we need a common scale to compare the electrodes
- Use SHE as the standard and define its potential to be zero at standard conditions:

$$2 H^{+}(aq) + 2 e^{-} \rightarrow H_{2}(g) \qquad E^{\circ} = 0.00 V$$

• Compare everything to the SHE potential (reference point) so that everything is on the same scale.



Standard Hydrogen Electrode (SHE)



Standard cell potential

Measuring Half-Cell Potential with the SHE

Consider this cell:

- Cathode is SHE so its standard potential is 0 V
- Anode is a Zn(s) electrode with a solution of Zn²⁺(aq)
- The anode potential is -0.76 V (higher than the SHE potential)
- Reaction would be spontaneous and 2e⁻ would be transferred
- We could make such a measurement for any electrode (relat. to SHE)



Standard cell potential



- The overall cell potential can the be calculated from how much higher the anode potential is vs. the cathode potential
- We can get the overall cell potential from:

$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ}$$
 "right - left"

• In the case of $Zn(s) | Zn^{2+}(aq) || H^{+}(aq) | H_{2}(g) | Pt(s) cell$

$$E_{cell}^{\circ} = 0.00 \ V - (-0.76 \ V) = 0.76 \ V$$

Cell notation: Oxidation on the left and reduction on the right!

Standard electrode potentials:

- Always written as reductions: Standard reduction potentials
- Substances at the top tend to undergo reduction; they are good oxidizing agents
- Substances at the bottom tend to undergo oxidation; they are good reducing agents
- Any reduction listed is spontaneous when paired with the reverse of any reaction listed below it
- Do <u>not</u> multiply *E*_{cell}^o by any factors when, e.g., balancing equations!

duction Half-Rea	iction		E°(V)	
<u>.</u>	$F_{2}(g) + 2 e^{-1}$	> 2 F ⁻ (aq)	2.87	147. J.
stronger tidizing agent	$H_2O_2(aq) + 2 H^+(aq) + 2 e^-$	$\rightarrow 2 H_2O(l)$	1.78	 Weaker reducing agent
	$PbO_{2}(s) + 4 H^{+}(aq) + SO_{4}^{2-}(aq) + 2 e^{-}$	\longrightarrow PbSO ₄ (s) + 2 H ₂ O(<i>l</i>)	1.69	
	MnO ₄ ^{-(aq)} + 4 H ⁺ (aq) + 3 e ⁻	\longrightarrow MnO ₂ (s) + 2 H ₂ O(<i>l</i>)	1.68	
	MnO ₄ ^{-(aq)} + 8 H ⁺ (aq) + 5 e ⁻	\longrightarrow Mn ²⁺ (aq) + 4 H ₂ O(l)	1.51	
	Au ³⁺ (ag) + 3 e ⁻	\longrightarrow Au(s)	1.50	
	PbO ₂ (s) + 4 H ⁺ (aq) + 2 e ⁻	$\longrightarrow Pb^{2+}(aq) + 2 H_2O(l)$	1.46	
	$Cl_2(g) + 2 e^-$	\rightarrow 2 Cl ⁻ (aq)	1.36	
	Cr ₂ O ₇ ²⁻ (aq) + 14 H ⁺ (aq) + 6 e ⁻	$\longrightarrow 2 \operatorname{Cr}^{3+}(aq) + 7 \operatorname{H}_2O(l)$	1.33	-
	$O_2(g) + 4 H^+(aq) + 4 e^-$	$\longrightarrow 2 H_2O(I)$	1.23	
	$MnO_2(s) + 4 H^+(aq) + 2 e^-$	\longrightarrow Mn ²⁺ (aq) + 2 H ₂ O(l)	1.21	
	IO ₃ ^{-(aq)} + 6 H ⁺ (aq) + 5 e ⁻	$\longrightarrow \frac{1}{2}I_2(aq) + 3 H_2O(l)$	1.20	-
	$Br_2(l) + 2 e^-$	$\rightarrow 2 \text{ Br}^-(aq)$	1.09	
	V0 ₂ ⁺ (aq) + 2 H ⁺ (aq) + e ⁻	$\longrightarrow VO^{2+}(aq) + H_2O(l)$	1.00	-
	NO3 ⁻ (aq) + 4 H ⁺ (aq) + 3 e ⁻	\longrightarrow NO(g) + 2 H ₂ O(l)	0.96	
	$ClO_2(g) + e^-$	$\longrightarrow ClO_2^{-}(aq)$	0.95	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^{-}$	\longrightarrow Fe ²⁺ (aq)	0.77	
	$O_2(g) + 2 H^+(aq) + 2 e^-$	\longrightarrow H ₂ O ₂ (aq)	0.70	
	$MnO_{4}^{-}(aq) + e^{-}$	\longrightarrow MnO ₄ ²⁻ (aq)	0.56	
	l ₂ (s) + 2 e ⁻	> 2 I⁻(aq)	0.54	
	$Cu^+(aq) + e^-$	\longrightarrow Cu(s)	0.52	
	$O_2(g) + 2 H_2O(l) + 4 e^-$	\longrightarrow 4 OH ⁻ (aq)	0.40	
	Cu ²⁺ (aq) + 2 e ⁻	\longrightarrow Cu(s)	0.34	_
	SO ₄ ²⁻ (aq) + 4 H ⁺ (aq) + 2 e ⁻	\longrightarrow H ₂ SO ₃ (aq) + H ₂ O(<i>I</i>)	0.20	
	$Cu^{2+}(aq) + e^{-}$	\longrightarrow Cu ⁺ (aq)	0.16	_
	Sn ⁴⁺ (aq) + 2 e ⁻	\longrightarrow Sn ²⁺ (aq)	0.15	_
	2 H ⁺ (aq) + 2 e ⁻	$\longrightarrow H_2(g)$	0	
	Fe ³⁺ (aq) + 3 e ⁻	\longrightarrow Fe(s)	-0.036	
	Pb ²⁺ (aq) + 2 e ⁻	$\longrightarrow Pb(s)$	-0.13	
	Sn ²⁺ (aq) + 2 e ⁻	\longrightarrow Sn(s)	-0.14	
	Ni ²⁺ (aq) + 2 e ⁻	→ Ni(s)	-0.23	
	Cd ²⁺ (aq) + 2 e ⁻	\longrightarrow Cd(s)	-0.40	
	Fe ²⁺ (aq) + 2 e ⁻	\longrightarrow Fe(s)	-0.45	
	$Cr^{3+}(aq) + e^{-}$	$\longrightarrow Cr^{2+}(aq)$	-0.50	
	Cr ³⁺ (aq) + 3 e ⁻	\longrightarrow Cr(s)	-0.73	-
	Zn ²⁺ (aq) + 2 e ⁻	\longrightarrow Zn(s)	-0.76	
	2 H ₂ 0(<i>l</i>) + 2 e ⁻	\longrightarrow H ₂ (g) + 2 OH ⁻ (aq)	-0.83	
	$Mn^{2+}(aq) + 2 e^{-}$	→ Mn(s)	-1.18	
	Al ³⁺ (aq) + 3 e ⁻	\longrightarrow Al(s)	-1.66	
	Mg ²⁺ (aq) + 2 e ⁻	\longrightarrow Mg(s)	-2.37	
	$Na^+(aq) + e^-$	→ Na(s)	-2.71	
	Ca ²⁺ (aq) + 2 e ⁻	\longrightarrow Ca(s)	-2.76	
	Ba ²⁺ (aq) + 2 e ⁻	→ Ba(s)	-2.90	
117-1	K ⁺ (aq) + e ⁻	\longrightarrow K(s)	-2.92	
weaker kidizing agent	Li+(aq) + e ⁻	\longrightarrow Li(s)	-3.04	reducing agent
0 0				0 0

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SHE as the higher potential



Now imagine you had a half-cell that had a positive standard potential relative to the SHE.

Example: $Cu(s) | Cu^{2+}(aq) || H^{+}(aq) | H_{2}(g) | Pt(s)$

The way this cell is written, would be non-spontaneous (negative cell potential; -0.34 V).



Two-electrode cell



Example: $Cu(s) | Cu^{2+}(aq)$ and $Zn(s) | Zn^{2+}(aq)$

Which electrode would be the anode and which the cathode?

According to the redox table:

Cathode: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $E^{\circ} = +0.34 \text{ V}$ Anode: $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$ $E^{\circ} = -0.76 \text{ V}$

The more positive standard potential will gain electrons (as written). Reduction (right) at cathode.

The more negative standard potential will lose electrons (reverse written reaction). Oxidation (left) at anode.

$$E_{cell}^{\circ} = 0.34 \ V - (-0.76 \ V) = 1.10 \ V$$
 Positive!

"cathode - anode"

Summary of Standard Electrode Potentials

- The standard electrode potential (SHE) is (arbitrarily) defined to be 0 V (reference point).
- The electrode with greater *E*^o (i.e., more positive value) will undergo reduction (cathode; polarity +) and the other electrode will undergo oxidation (anode; polarity -).
- Redox table written as reductions (reverse for oxidation).
- Calculate the standard cell potential using:

$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ}$$

- *E*_{cell}^o is positive for spontaneous reactions and negative for non-spontaneous reactions as written.
- Do <u>not</u> multiply *E*_{cell}^o by any factors when balancing chemical equations (stoichiometric coefficients).

Example



Given the following two half-cell reactions, what reaction will occur at the anode, and what at the cathode? What is the E_{cell}^{0} and the overall reaction? What is the cell notation?

 $Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$ $E^{\circ} = -0.23 V$

 $Mn^{2+}(aq) + 2e^{-} \rightarrow Mn(s) E^{\circ} = -1.18 V$

1. Based on the E^o values, determine reduction (cathode; larger E^o) vs. oxidation (anode; smaller E^o) at the electrodes.

2. Calculate E_{cell}^{0} by subtracting the E^{0} values ("cathode – anode"). Positive value for spontaneous process.

3. Balance the number of electrons transferred, reverse the halfreaction that corresponds to oxidation, and add the two halfreactions to get the overall reaction.

4. Write the cell notation (oxidation on left; reduction on right)

Example





$Mn(s) | Mn^{2+}(aq) || Ni^{2+}(aq) | Ni(s)$



Cell potential, Free energy, and K

- Positive *E*_{cell}°
- •Negative ΔG°
- •K > 1 (Q = 1 at standard conditions)

- •Negative *E*_{cell}°
- Positive ΔG°
- •K < 1 (Q = 1 at standard conditions)

There must be some relationship between cell potential, free energy, and equilibrium constant!



$$\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + RTlnQ$$

At equilibrium, Q = K and $\Delta G_{rxn} = 0$ (not spontaneous in either direction)

 $0 = \Delta G_{rxn}^{\circ} + RTlnK$ (use K_{ρ} for gases, and K_{ρ} for solutions)

$$\Delta G^{\circ}_{rxn} = -RTlnK$$

- If K < 1, ΔG_{rxn}° is positive because ln(K) is negative
 Under standard conditions (Q = 1), Q > K, spontaneous in reverse direction
- If K > 1, ΔG_{rxn}^o is negative because In(K) is positive
 Under standard conditions (Q = 1), Q < K, spontaneous in forward direction
- If K = 1, ΔG_{rxn}° is zero, at equilibrium under standard conditions



Relationship between ΔG° and E_{cell}°

Electrical energy can be used to perform work:

$$w = -qE_{cell}^{o}$$
 (1 V = 1 J/C)

So, the maximum free energy available to do work:

$$\Delta G^{\circ} = -nFE_{cell}^{\circ}$$

F = Faraday's constant = 96,485 C/mol e⁻
(total charge on 1 mole of electrons).
n = number of moles of electrons transferred.



Relationship between *E*_{*cell*}^o **and** *K*

 $\begin{array}{ll} \displaystyle \underline{Recall:} & \Delta G_{rxn}^{\circ} = -RTlnK \\ \displaystyle -nFE_{cell}^{\circ} = -RTlnK \\ \displaystyle E_{cell}^{\circ} = \frac{RT}{nF}lnK \end{array}$

<u>At room temperature</u> and converting natural log (ln) to ten base logarithm (log):

$$E_{cell}^{\circ} = \frac{0.0592 \ V}{n} log K$$

"the pyramid" $\Delta \boldsymbol{G}^{\circ}$ $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$ $\Delta G^{\circ} = -RT \ln K$ $\boldsymbol{E}^{\circ}_{\text{cell}}$ K $E_{\rm cell}^{\circ} = \frac{0.0592 \,\,{\rm V}}{n} \,\log K$

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Use tabulated electrode potentials to calculate ΔG° and *K* for the reaction (temperature 298 K):

$2 \operatorname{Na}(s) + 2 \operatorname{H}_2 O(\ell) \longrightarrow \operatorname{H}_2(g) + 2 \operatorname{OH}^-(aq) + 2 \operatorname{Na}^+(aq)$

Na is oxidized and H_2O is reduced (2 el. transfer)

[Exercise]

 $(E_{cell}^{0} = 1.88 \text{ V} \text{ and use the equations on the previous slide})$

Calculation of *E*_{cell} under non-standard conditions

We know that under standard conditions:

 $\operatorname{Zn}(s) + \operatorname{Cu}^{2+}(\operatorname{aq}, 1 \operatorname{M}) \longrightarrow \operatorname{Zn}^{2+}(\operatorname{aq}, 1 \operatorname{M}) + \operatorname{Cu}(s) \quad E_{cell}^{\circ} = 1.10 V$

What if the concentrations were different? How would we calculate E_{cell} ?

For example, with $[Cu^{2+}] = 1.5$ M and $[Zn^{2+}] = 0.5$ M, the cell will be even more likely to go forward (Le Chatelier's principle), which means that E_{cell} should be > 1.10 V.

The Nernst Equation



$$\begin{split} \Delta G &= \Delta G^{\circ} + RT lnQ \\ -nFE_{cell} &= -nFE_{cell}^{\circ} + RT lnQ \\ E_{cell} &= E_{cell}^{\circ} - \frac{RT}{nF} lnQ \end{split}$$

At room temp and converting natural log to log:

$$E_{cell} = E_{cell}^{\circ} - rac{0.0592}{n} logQ$$

Calculation of Q for redox reactions

For an overall reaction

$$aA(s) + bB(aq) \longrightarrow cC(aq) + dD(s)$$

$$Q = \frac{[C]^c}{[B]^b}$$

Remember: Pure solids do not affect **Q**!





Calculate the cell potential of a voltaic cell based on the following reaction (temperature 298 K):

$$2 \ \mathrm{Fe}^{3+}(\mathrm{aq}) + 3 \,\mathrm{Mg}(\mathrm{s}) \longrightarrow 2 \,\mathrm{Fe}(\mathrm{s}) + 3 \,\mathrm{Mg}^{2+}(\mathrm{aq})$$

at a) standard condition

b)
$$[Fe^{3+}] = 1.0 \times 10^{-3} M$$
, $[Mg^{2+}] = 2.50 M$
(non-standard condition)

(Hint: use the Nernst equation in part b)

Equilibrium and the Nernst Equation



$$E_{cell} = E_{cell}^{\circ} - \frac{0.0592}{n} logQ$$

- Q = 1 (standard condition), $E_{cell} = E_{cell}^{\circ}$
- Q < 1, greater concentration of reactants vs. products: $E_{cell} > E_{cell}^o$
- Q > 1, greater concentration of products vs. reactants: $E_{cell} < E_{cell}^o$

Equilibrium and the Nernst Equation



$$E_{cell} = E_{cell}^{\circ} - \frac{0.0592}{n} logQ$$



If the cell reaches equilibrium, the potential will be 0 V:

- No electrochemical reaction will occur
- The cell is "dead"



This property of cells to change potential based on concentration of the reactants is useful because you can create a cell with one reactant/product.

Different concentrations for each half-cell

$$Cu(s) + Cu2+(aq, 2.0 M) \longrightarrow Cu2+(aq, 0.010 M) + Cu(s)$$

$$E^{\circ}_{cell} = 0 \vee \qquad E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} logQ$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} logQ = 0 - \frac{0.0592}{2} log\left(\frac{0.010 M}{2.0 M}\right) = 0.068 V$$





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