CHEM 1120- 20.2.1

[SPELL CARD]

Electrochemical processes are oxidation-reduction reactions in which:

- The energy released by a spontaneous reaction is converted to electricity or
- Electrical energy is used to cause a nonspontaneous reaction to occur

$$\overset{0}{2Mg}\,(s) + \overset{0}{O_2}\,(g) \longrightarrow \overset{2+\,2-}{2MgO}\,(s)$$

$2Mg \longrightarrow 2Mg^{2+} + 4e^-$ ***Oxidation*** half-reaction (lose e^-)

$O_2 + 4e^- \longrightarrow 2O^{2-}$ ***Reduction*** half-reaction (gain e^-)

"REDOX" reactions

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CHEM 1120- 20.2.2

[SPELL CARD]

Half-Reaction Method of Balancing Redox Equations

- Separate an oxidation–reduction equation into two half-equations, one for oxidation and one for reduction
- $Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^-$ oxidation
- $2\,Ag^+(aq) + 2\,e^- \longrightarrow 2\,Ag(s)$ reduction
- Remember with all chemical equations, one must have ***mass* AND *charge*** balance

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CHEM 1120- 20.2.3

[SPELL CARD]

Half-Reaction Method of Balancing Redox Equations

- $Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^-$ oxidation
- $2\,Ag^+(aq) + 2\,e^- \longrightarrow 2\,Ag(s)$ reduction

$Cu(s) + \mathbf{2}\,Ag^+(aq) + \cancel{2e^-} \longrightarrow Cu^{2+}(aq) + \cancel{2e^-} + \mathbf{2}\,Ag(s)$

- Net chemical equation:

$Cu(s) + \mathbf{2}\,Ag^+(aq) \longrightarrow Cu^{2+}(aq) + \mathbf{2}\,Ag(s)$

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[SPELL CARD]

$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$

$Zn \longrightarrow Zn^{2+} + 2e^-$ Zn is oxidized

Zn is the ***reducing agent***

$Cu^{2+} + 2e^- \longrightarrow Cu$ Cu^{2+} is reduced

Cu^{2+} is the ***oxidizing agent***

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CHEM 1120- 20.2.5

[SPELL CARD]

Oxidation number

$\boxed{\text{The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.}}$

1. Free elements (uncombined state) have an oxidation number of zero.

   $Na, Be, K, Pb, H_2, O_2, P_4 = 0$

2. In monatomic ions, the oxidation number is equal to the charge on the ion.

   $Li^+, Li = +1$; $Fe^{3+}, Fe = +3$; $O^{2-}, O = -2$

3. The oxidation number of oxygen is **usually** -2. In H_2O_2 and O_2^{2-} it is -1.

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CHEM 1120- 20.2.6

[SPELL CARD]

4. The oxidation number of hydrogen is $+1$ *except* when it is bonded to metals in binary compounds. In these cases, its oxidation number is -1.
5. In molecules, Group IA metals are $+1$, IIA metals are $+2$
6. Halogens are always -1, except in homodiatomic form where they are 0. (ex. I_2, Cl_2, Br_2, and F_2)
7. The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion.
8. Oxidation numbers do not have to be integers. The oxidation number of oxygen in the superoxide ion, O_2^-, is $-\frac{1}{2}$.

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[SPELL CARD]

Redox reactions in acid solutions

- In these reactions, it will be necessary to **add molecules of water and protons (H^+)** to achieve a balanced equation

Redox reactions in basic solutions

- In these reactions, it will be necessary to solve as if it was in acid solution, but at the end add **one OH^- on each side for each H^+ present**, then balance by combining the side with both H^+ and OH^- to form molecules of water

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CHEM 1120- 20.3.1

[SPELL CARD]

Voltaic (or Galvanic) Cells

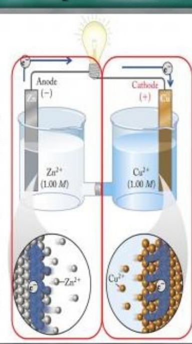
A **half-cell** consists of an electrode immersed in a solution of ions

Anodic half cell:

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

Cathodic half cell:

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



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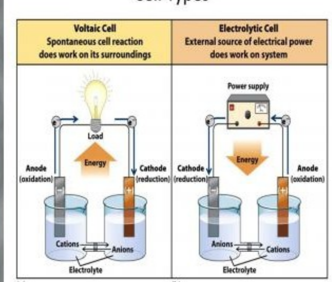
[SPELL CARD]

Cell Types



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[SPELL CARD]

Conventions of galvanic cells

- The anode is on the *left* side
- The cathode is on the *right* side
- Use a single vertical line (|) to represent the **boundary between different phases**, such as between an electrode and a solution
- Use a double vertical line (||) to represent a **salt bridge or porous barrier** separating two half-cells

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[SPELL CARD]

An Example Cell Diagram

Anode | Salt bridge | Cathode

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

Half-cell (oxidation) | Half-cell (reduction)

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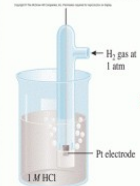
[SPELL CARD]

Standard Reduction Potentials

Standard reduction potential **(E^0)** is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 *M* and all gases are at 1 atm.



Reduction Reaction

$2e^- + 2H^+ (1\ M) \longrightarrow H_2 (1\ atm)$

$E^0 = 0$ V

Standard hydrogen electrode (SHE)

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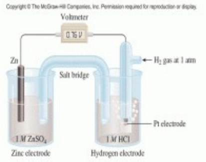
CHEM 1120- 20.4.2

[SPELL CARD]

Standard Reduction Potentials



$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ H^+\ (1\ M)\ |\ H_2\ (1\ atm)\ |\ Pt\ (s)$

Anode (oxidation): $Zn\ (s) \longrightarrow Zn^{2+}\ (1\ M) + 2e^-$

Cathode (reduction): $2e^- + 2H^+\ (1\ M) \longrightarrow H_2\ (1\ atm)$

$Zn\ (s) + 2H^+\ (1\ M) \longrightarrow Zn^{2+}\ (1\ M) + H_2\ (1\ atm)$

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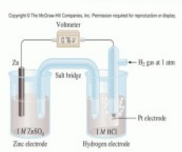
[SPELL CARD]

Standard Reduction Potentials



Standard emf **(*E^0_{cell}*)**

$$\boxed{E^0_{cell} = E^0_{cathode} - E^0_{anode}}$$

$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ H^+\ (1\ M)\ |\ H_2\ (1\ atm)\ |\ Pt\ (s)$

$E^0_{cell} = E^0_{H^+/H_2} - E^0_{Zn^{2+}/Zn}$

$0.76\ V = 0 - E^0_{Zn^{2+}/Zn}$

$E^0_{Zn^{2+}/Zn} = -0.76$ V

$Zn^{2+}\ (1\ M) + 2e^- \longrightarrow Zn \quad E^0 = -0.76$ V

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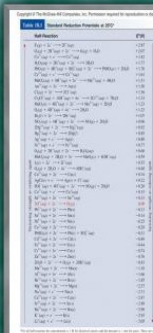
[SPELL CARD]



- Changing the stoichiometric coefficients of a half-cell reaction ***does not*** change the value of E^0
- $E^0_{cell} > 0$ for spontaneous rxns
- Always use **reduction** potential to solve $E^0 = E_{cathode} - E_{anode}$

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CHEM 1120- 20.4.5

[SPELL CARD]

We see that Br_2 will oxidize I^- but will not oxidize Cl^-. Therefore, the only redox reaction that will occur appreciably under standard-state conditions is

Oxidation: $2I^-(1\ M) \longrightarrow I_2(s) + 2e^-$

Reduction: $Br_2(l) + 2e^- \longrightarrow 2Br^-(1\ M)$

Overall: $2I^-(1\ M) + Br_2(l) \longrightarrow I_2(s) + 2Br^-(1\ M)$

Cell diagram:

$I^-\ (1\ M)\ |\ I_2\ (s)\ ||\ Br_2\ (l)\ |\ Br^-\ (1\ M)$

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CHEM 1120- 20.5.1

[SPELL CARD]

Voltage and Free Energy

- $\Delta G_{cell} = w_{elec}$
- $w_{elec} = -nFE_{cell}$
  - w_{elec} is the work done on a circuit
- $\Delta G = -n\ F\ E_{cell}$
  - Cell Potential (E_{cell}) or Electromotive Force is the voltage between the electrodes of a voltaic cell
  - V = J/C; C - coulomb
  - Faraday constant (F) is 9.65 x 10^4 C/(mol e^-)
  - n - number of moles of electrons transferred

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CHEM 1120- 20.5.2

[SPELL CARD]

Spontaneity of Redox Reactions

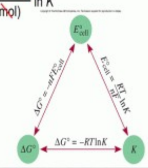
$\Delta G^0 = -nFE^0_{cell} \qquad F = 96{,}500 \frac{J}{V \cdot mol} = 96{,}500$ C/mol

$\Delta G^0 = -RT \ln K = -nFE^0_{cell}$

$E^0_{cell} = \frac{RT}{nF} \ln K = \frac{(8.314\ \cancel{J}/(\cancel{K} \cdot \cancel{mol}))(298\ \cancel{K})}{n\ (96{,}500\ \cancel{J}/(V \cdot \cancel{mol}))} \ln K$

$E^0_{cell} = \frac{0.0257\ V}{n} \ln K$

$E^0_{cell} = \frac{0.0592\ V}{n} \log K$



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CHEM 1120- 20.5.3

[SPELL CARD]

Spontaneity of Redox Reactions

Table 18.2 Relationships Among $\Delta G°$, K, and $E°_{cell}$

$\Delta G°$	K	$E°_{cell}$	Reaction Under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	=1	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

$$\Delta G^0 = -RT \ln K = -nFE^0_{cell}$$

CHEM 1120- 20.5.4

[SPELL CARD]

Calculate the equilibrium constant for the following reaction at 25°C:

$$Sn(s) + 2Cu^{2+}(aq) \rightleftharpoons Sn^{2+}(aq) + 2Cu^{+}(aq)$$

$$E^0_{cell} = \frac{0.0257\ V}{n} \ln K$$

CHEM 1120- 20.5.5

[SPELL CARD]

Solution

The half-cell reactions are

Anode (oxidation): $Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$

Cathode (reduction): $2Cu^{2+}(aq) + 2e^- \longrightarrow 2Cu^{+}(aq)$

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$E^0_{cell} = \frac{0.0257\ V}{n} \ln K$$

CHEM 1120- 20.5.6

[SPELL CARD]

Calculate the standard free-energy change for the following reaction at 25°C:

$$2Au(s) + 3Ca^{2+}(1.0\ M) \longrightarrow 2Au^{3+}(1.0\ M) + 3Ca(s)$$

$$\Delta G° = -nFE°_{cell}$$

CHEM 1120- 20.5.7

[SPELL CARD]

Solution

The half-cell reactions are

Anode (oxidation): $2Au(s) \longrightarrow 2Au^{3+}(1.0\ M) + 6e^-$

Cathode (reduction): $3Ca^{2+}(1.0\ M) + 6e^- \longrightarrow 3Ca(s)$

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$\Delta G° = -nFE°_{cell}$$

CHEM 1120- 20.6.1

[SPELL CARD]

The Effect of Concentration on Cell Emf

$$\Delta G = \Delta G^0 + RT \ln Q \qquad \Delta G = -nFE \qquad \Delta G^0 = -nFE^0$$

$$-nFE = -nFE^0 + RT \ln Q$$

Nernst equation

$$E = E^0 - \frac{RT}{nF} \ln Q$$

At 298 K

$$E = E^0 - \frac{0.0257\ V}{n} \ln Q \qquad E = E^0 - \frac{0.0592\ V}{n} \log Q$$

CHEM 1120- 20.6.2

[SPELL CARD]

Predict whether the following reaction would proceed spontaneously as written at 298 K:

$$Co(s) + Fe^{2+}(aq) \longrightarrow Co^{2+}(aq) + Fe(s)$$

given that $[Co^{2+}] = 0.15\ M$ and $[Fe^{2+}] = 0.68\ M$.

CHEM 1120- 20.6.3

[SPELL CARD]

Solution

The half-cell reactions are

Anode (oxidation): $Co(s) \longrightarrow Co^{2+}(aq) + 2e^-$

Cathode (reduction): $Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$

$$\begin{aligned} E°_{cell} &= E°_{cathode} - E°_{anode} \\ &= E°_{Fe^{2+}/Fe} - E°_{Co^{2+}/Co} \\ &= -0.44\ V - (-0.28\ V) \\ &= -0.16\ V \end{aligned}$$

CHEM 1120- 20.6.4

[SPELL CARD]

From Equation (18.8) we write

$$\begin{aligned} E &= E° - \frac{0.0257\ V}{n} \ln Q \\ &= E° - \frac{0.0257\ V}{n} \ln \frac{[Co^{2+}]}{[Fe^{2+}]} \\ &= -0.16\ V - \frac{0.0257\ V}{2} \ln \frac{0.15}{0.68} \\ &= -0.16\ V + 0.019\ V \\ &= -0.14\ V \end{aligned}$$

Because E is negative, the reaction is not spontaneous in the direction written.

CHEM 1120- 21

[SPELL CARD]

Review

Atomic number (Z) = number of protons in nucleus

Mass number (A) = number of protons + number of neutrons

= atomic number (Z) + number of neutrons

Mass Number $\longrightarrow$ A; Atomic Number $\longrightarrow$ Z; $^{A}_{Z}X \longleftarrow$ Element Symbol

	proton	neutron	electron	positron	α particle
	$^{1}_{1}p$ or $^{1}_{1}H$	$^{1}_{0}n$	$^{0}_{-1}e$ or $^{0}_{-1}\beta$	$^{0}_{+1}e$ or $^{0}_{+1}\beta$	$^{4}_{2}He$ or $^{4}_{2}\alpha$
A	1	1	0	0	4
Z	1	0	-1	+1	2