

ELECTROCHEMISTRY – 2

GALVANIC CELLS AND CELL POTENTIAL - EMF

Dr. Sapna Gupta

ELECTROCHEMICAL CELLS

An **electrochemical cell** is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current.

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

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

GALVANIC CELLS

- **Galvanic cell** - the experimental apparatus for generating electricity through the use of a spontaneous reaction
- **Electrodes**
 - Anode (oxidation)
 - Cathode (reduction)
- **Half-cell** - combination of container, electrode and solution
- **Salt bridge** - conducting medium through which the cations and anions can move from one half-cell to the other.
- **Ion migration**
 - Cations – migrate toward the cathode
 - Anions – migrate toward the anode
- **Cell potential (E_{cell})** – difference in electrical potential between the anode and cathode
 - Concentration dependent
 - Temperature dependent
 - Determined by nature of reactants

GALVANIC CELLS CONSTRUCTION

Zn-Cu cell



Zn loses two electrons
forming Zn^{2+} ions.

oxidation/loss of e

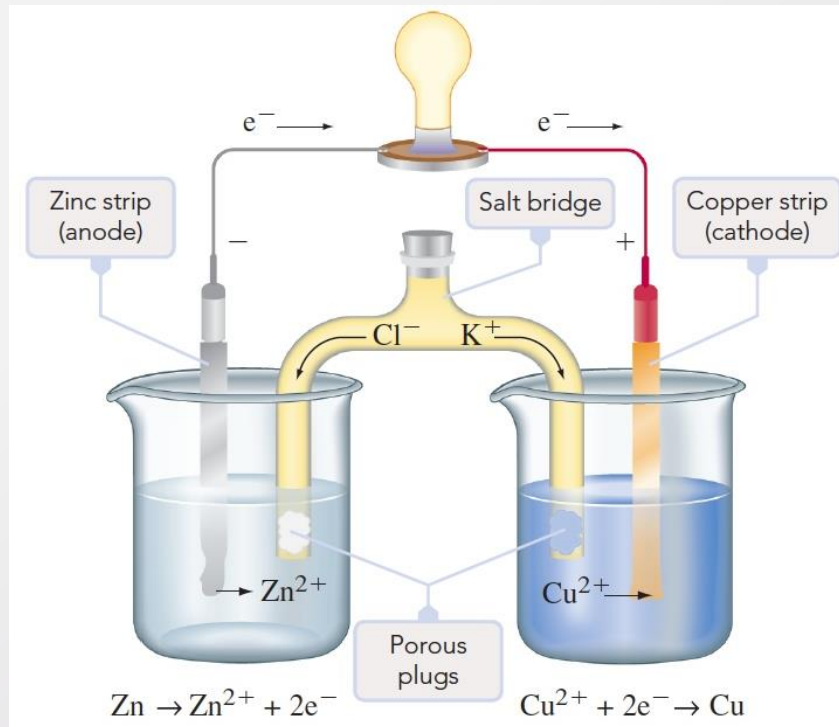
Cu^{2+} ions gain two electrons,
forming solid copper

reduction/gain of e

Electrons flow from anode to cathode

ANODE

CATHODE

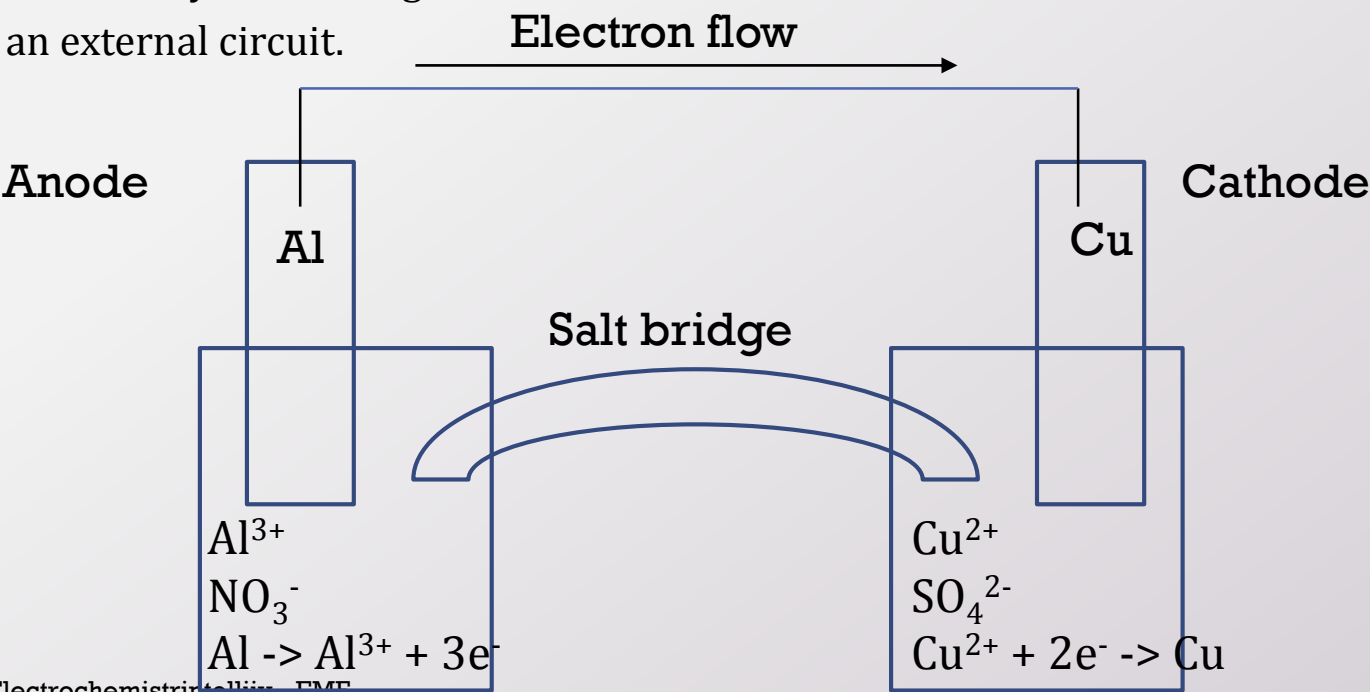


EXAMPLE: CONSTRUCTING AN Al/Cu GALVANIC CELL

Sketch the voltaic cell and label the anode and the cathode, showing the corresponding half-reactions. Indicate the direction of electron flow in the external circuit. Hint: The aluminum is oxidized.

Solution:

- 1) Construct a half-cell by inserting an aluminum metal strip in a solution of aluminum nitrate and write the equation. (Anode)
- 2) Construct the other half-cell of a voltaic cell by inserting a copper metal strip into a solution of copper(II) sulfate and write the equation. (Cathode)
- 3) Connect the half-cells by a salt bridge.
- 4) Connected to an external circuit.



VOLTAIC CELL NOTATION

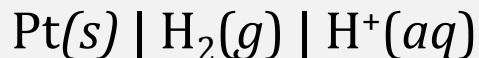


- This is a shorthand way of writing a cell instead of drawing the cell.
- The oxidation half-cell, the anode, is written on the left.
- The reduction half-cell, the cathode, is written on the right.
- The cell terminal is written on the outside: left for the anode and right for the cathode.
- Phase boundaries are shown with a single vertical bar, |.
- Between the anode and cathode the salt bridge is represented by two vertical bars, ||.
- Left: Anode, the oxidation of Zn(s) to $\text{Zn}^{2+}(\text{aq})$ is shown as $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq})$.
- Right: Cathode, the reduction of $\text{Cu}^{2+}(\text{aq})$ to Cu(s) is shown as $\text{Cu}^{2+}(\text{aq}) | \text{Cu(s)}$.
- The complete notation for the reaction is

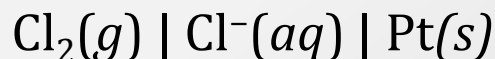


VOLTAIC CELL NOTATION WITH GASES

- When the half-reaction involves a gas, the electrode is an inert material such as platinum, Pt. It is included as a third substance in the half-cell.
 - For the oxidation of $\text{H}_2(g)$ to $\text{H}^+(aq)$, the notation is



- In this case, the electrode appears on the far left.
- In half-reaction of Cl_2 being reduced to Cl^- is written as follows:



- Because this is a reduction, the electrode appears on the far right.



With Concentrations:

- To completely specify a voltaic cell, concentrations of the solutions have to be written out too.
- For example, the oxidation of $\text{Cu}(s)$ to $\text{Cu}^{2+}(aq)$ at the anode and the reduction of $\text{F}_2(g)$ to $\text{F}^-(aq)$ at the cathode is written as follows:



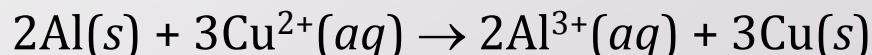
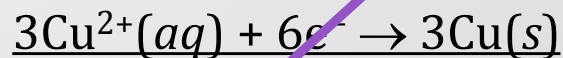
EXAMPLE: VOLTAIC CELL TO EQUATION

Write the cell reaction for the following cell notation for a voltaic cell.



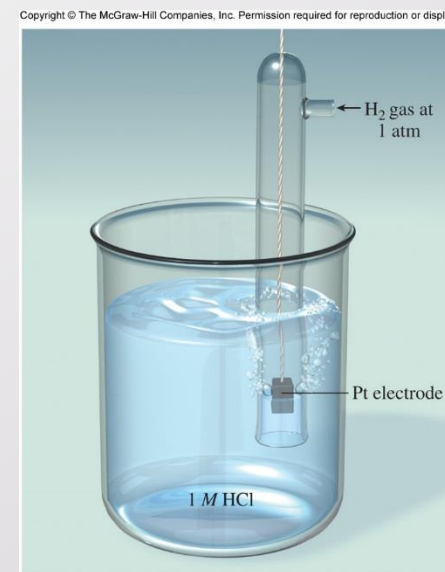
Solution:

- Write and balance each half-reaction, and then to combine the half-reactions to give the overall cell reaction.
- The skeleton oxidation reaction is $\text{Al}(s) \rightarrow \text{Al}^{3+}(aq)$.
 - Balanced eq.: $\text{Al}(s) \rightarrow \text{Al}^{3+}(aq) + 3e^{-}$
- The skeleton reduction reaction is $\text{Cu}^{2+}(aq) \rightarrow \text{Cu}(s)$.
 - Balanced eq.: $\text{Cu}^{2+}(aq) + 2e^{-} \rightarrow \text{Cu}(s)$
- Balance the electrons in the equations by multiplying by 2 and 3 respectively.
- Add the two equations by cancelling the electrons.

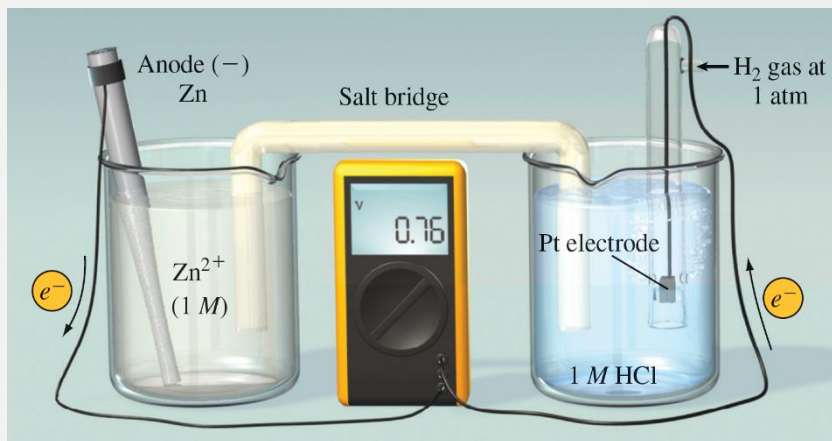
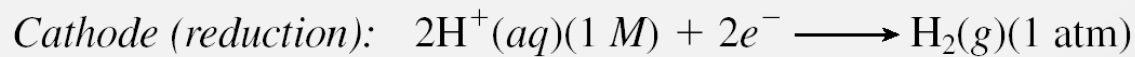
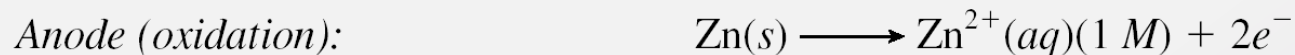
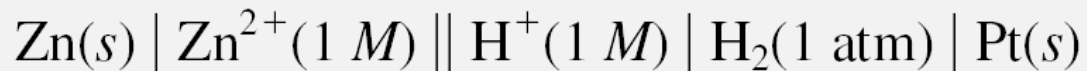


STANDARD ELECTRODE POTENTIAL

- Designated E°
- Measured relative to the standard hydrogen electrode (SHE)
 - Standard conditions
 - Assigned a value of 0 V
 - Reaction



ELECTRODE POTENTIAL FOR ZINC/H₂ CELL



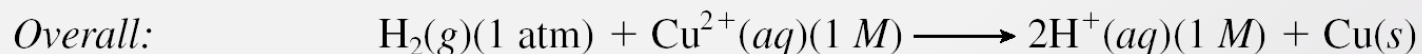
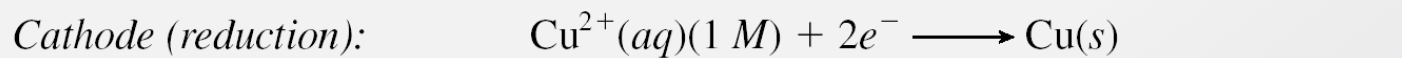
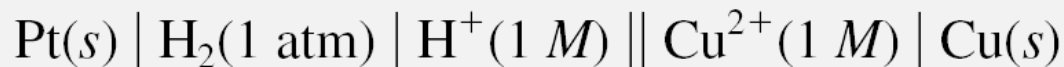
$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = E_{\text{H}^{+}/\text{H}_2}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

$$0.76\text{ V} = 0\text{ V} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76\text{ V}$$

ELECTRODE POTENTIAL FOR H₂|Cu CELL



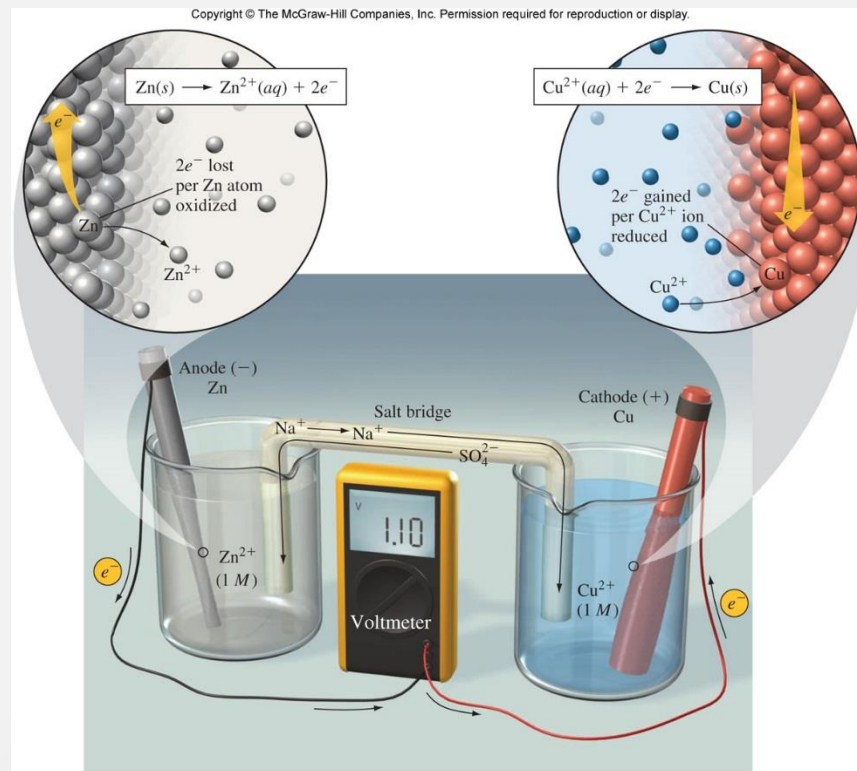
$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{H}^+/\text{H}_2}^{\circ}$$

$$0.34 \text{ V} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - 0 \text{ V}$$

$$E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.34 \text{ V}$$

ELECTRODE POTENTIAL FOR Zn|Cu CELL



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

$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = 0.34\text{V} - (-0.76\text{V})$$

$$E_{\text{cell}}^{\circ} = 1.10\text{V}$$

CELL POTENTIALS

Likely to be anode as they prefer to lose e^-

Cathode (Reduction) Half-Reaction	Standard Potential, $E^\circ(\text{V})$
$\text{Li}^+(\text{aq}) + e^- \rightleftharpoons \text{Li}(\text{s})$	-3.04
$\text{Na}^+(\text{aq}) + e^- \rightleftharpoons \text{Na}(\text{s})$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mg}(\text{s})$	-2.38
$\text{Al}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Al}(\text{s})$	-1.66
$2\text{H}_2\text{O}(\text{l}) + 2e^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Zn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$\text{Cr}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Cr}(\text{s})$	-0.74
$\text{Fe}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Fe}(\text{s})$	-0.41
$\text{Cd}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Cd}(\text{s})$	-0.40
$\text{Ni}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Ni}(\text{s})$	-0.23
$\text{Sn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Sn}(\text{s})$	-0.14
$\text{Pb}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Pb}(\text{s})$	-0.13
$\text{Fe}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Fe}(\text{s})$	-0.04
$2\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{Sn}^{4+}(\text{aq}) + 2e^- \rightleftharpoons \text{Sn}^{2+}(\text{aq})$	0.15
$\text{Cu}^{2+}(\text{aq}) + e^- \rightleftharpoons \text{Cu}^+(\text{aq})$	0.16
$\text{Cu}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Cu}(\text{s})$	0.34

Cathode (Reduction) Half-Reaction	Standard Potential, $E^\circ(\text{V})$
$\text{IO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2e^- \rightleftharpoons \text{I}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.49
$\text{Cu}^+(\text{aq}) + e^- \rightleftharpoons \text{Cu}(\text{s})$	0.52
$\text{I}_2(\text{s}) + 2e^- \rightleftharpoons 2\text{I}^-(\text{aq})$	0.54
$\text{Fe}^{3+}(\text{aq}) + e^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	0.77
$\text{Hg}_2^{2+}(\text{aq}) + 2e^- \rightleftharpoons 2\text{Hg}(\text{l})$	0.80
$\text{Ag}^+(\text{aq}) + e^- \rightleftharpoons \text{Ag}(\text{s})$	0.80
$\text{Hg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Hg}(\text{l})$	0.85
$\text{ClO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2e^- \rightleftharpoons \text{Cl}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.90
$2\text{Hg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Hg}_2^{2+}(\text{aq})$	0.90
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3e^- \rightleftharpoons \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	0.96
$\text{Br}_2(\text{l}) + 2e^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	1.07
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6e^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	1.33
$\text{Cl}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	1.36
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5e^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	1.49
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	1.78
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2e^- \rightleftharpoons 2\text{SO}_4^{2-}(\text{aq})$	2.01
$\text{F}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{F}^-(\text{aq})$	2.87

Likely to be cathode as they prefer to gain e^-

COMPARING OXIDIZING/REDUCING STRENGTH

The **oxidizing agent**:

- Causes another substance to get oxidized (lose electrons)
- Itself gets reduced (gains electrons)
- Is the species on the left of the reduction half-reaction ($\text{F}_2 + 2 \text{e}^- \rightarrow 2\text{F}^-$)
- Found generally on the right side of the periodic table (e.g. non metals - groups V to VII)

Consequently, the strongest oxidizing agent is the product of the half-reaction with the **largest (most positive) E° value**.

The **reducing agent**:

- Causes another substance to get reduced (gain electrons)
- Itself gets oxidized (loses electrons)
- Is the species on the right of the reduction half-reaction. ($\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$)
- Found on the left side of periodic table (all metals!)

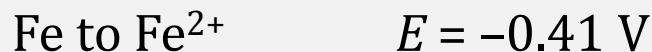
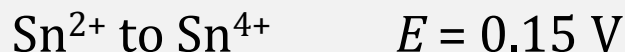
Consequently, the strongest reducing agent is the reactant in the half-reaction with the **smallest (most negative) E° value**.

EXAMPLE: COMPARE REDOX STRENGTH

Question: Which is the stronger reducing agent under standard conditions: Sn^{2+} (to Sn^{4+}) or Fe (to Fe^{2+})?

Solution: (*stronger reducing agent will be oxidized; loses electrons readily*)

- The standard (reduction) potentials are

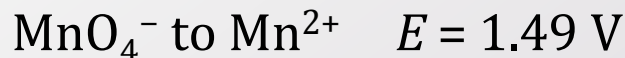
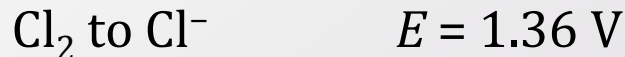


The stronger reducing agent is Fe (to Fe^{2+}).

Question Which is the stronger oxidizing agent under standard conditions: Cl_2 or MnO_4^- ?

Solution: (*The stronger oxidizing agent will be reduced – gains electrons*)

- The standard (reduction) potentials are



The stronger oxidizing agent is MnO_4^- .

EXAMPLE: WILL REACTION OCCUR?

Will dichromate ion oxidize manganese(II) ion to permanganate ion in an acid solution under standard conditions?

Solution:

- Will dichromate accept electrons from Mn^{2+} ion (causing Mn^{2+} to oxidize to Mn^{7+})?
- For dichromate to accept electrons it must have higher E value than Mn^{2+}
- Standard reduction potentials

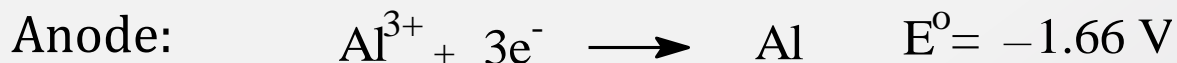


- MnO_4^- has a larger reduction potential; it will oxidize Cr^{3+} to $\text{Cr}_2\text{O}_7^{2-}$. (i.e. Mn prefers to gain electrons when compared to Cr)
- $\text{Cr}_2\text{O}_7^{2-}$ will not oxidize Mn^{2+} to MnO_4^- .

EXAMPLE: CALCULATING CELL POTENTIALS - 1

Determine the overall cell reaction and E°_{cell} (at 25°C) of a galvanic cell made of an Al electrode in a 1.0 M $\text{Al}(\text{NO}_3)_3$ solution and a Cu electrode in a 1.0 M $\text{Cu}(\text{NO}_3)_2$ solution.

Solution:

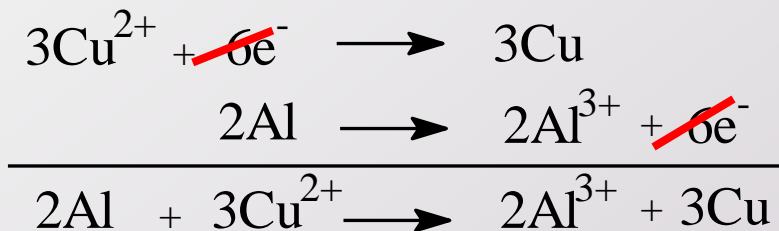


$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Al}^{3+}/\text{Al}}$$

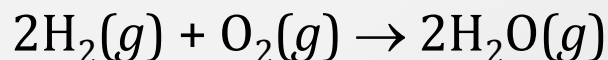
$$E^\circ_{\text{cell}} = +0.34 \text{ V} - (-1.66 \text{ V}) = 2.00 \text{ V}$$

Cell Reaction



EXAMPLE: CALCULATING CELL POTENTIAL - 2

A fuel cell is simply a voltaic cell that uses a continuous supply of electrode materials to provide a continuous supply of electrical energy. A fuel cell employed by NASA on spacecraft uses hydrogen and oxygen under basic conditions to produce electricity. The water produced in this way can be used for drinking. The net reaction is



Calculate the standard EMF of the oxygen–hydrogen fuel cell.

- $2\text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq) \quad E^\circ = -0.83 \text{ V}$
- $\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightleftharpoons 4\text{OH}^-(aq) \quad E^\circ = 0.40 \text{ V}$

Solution:

Anode (loss of electrons) reaction is the first one, since water gaining electrons is lower in voltage (prefers to lose electrons).

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

$$E_{\text{cell}} = 0.40 \text{ V} - (-0.83 \text{ V})$$

$$E_{\text{cell}} = 1.23 \text{ V}$$

KEY CONCEPTS

- Constructing a galvanic cell
- Calculating cell potential
- Predicting reactions