ELECTROCHEMISTRY
3: CELL POTENTIALS AND EMF

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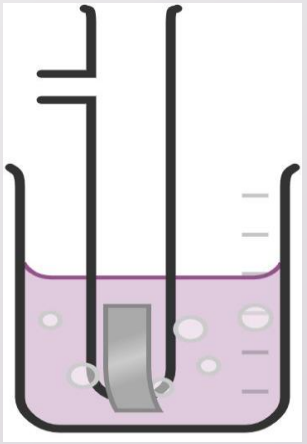
STANDARD ELECTRODE POTENTIAL

Standard electrode potential is calculated under standard conditions for hydrogen, H_2, 1atm and for concentration of HCl at 1 M. Standard electrode potential is written with the degree symbol on E^o.

- Standard **reduction** potential is measured relative to the standard hydrogen electrode (SHE).
  - Standard conditions (1 atm, 1 M HCl)
  - Hydrogen is assigned a value of 0 V
  - Reaction

    $2H^+ (1M) + 2e^- \longrightarrow H_2 (1atm) \qquad E^o = 0\ V$
  - A sample of the setup is shown on the right.

H_2 at 1 atm
With Pt electrode



1M HCl

STANDARD REDUCTION POTENTIAL

The standard hydrogen electrode (SHE) setup is used for measuring the electrode potential of all other elements against hydrogen. The voltage measured during the experiment indicates whether the hydrogen is getting reduced or oxidized depending on the other electrode element.

For example: zinc prefers to lose electrons to H^+ while copper prefers to gain electrons from H_2.

The equation used to calculate the cell potential or electromotive force (**EMF**) is:

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$

In case of SHE, hydrogen is always zero.

Next few slides show the electrode potential determination using SHE. SHE is always kept on the left, so the equation above can also be written as:

$$E^{o}_{cell} = E^{o}_{right} - E^{o}_{left}$$

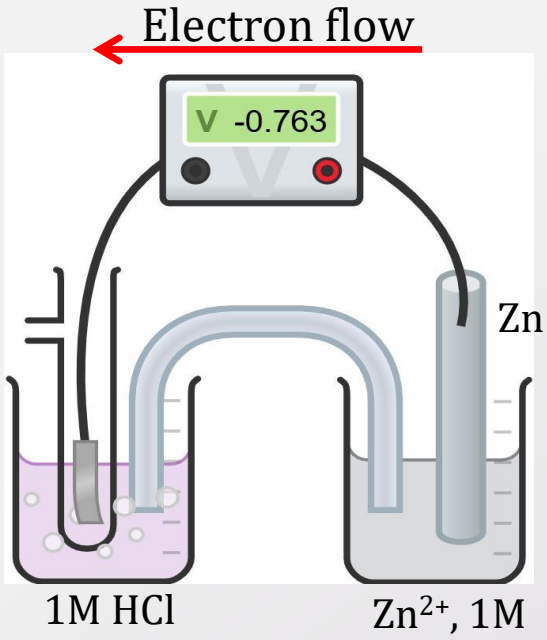
ELECTRODE POTENTIAL FOR H_2|Zn CELL

In a Zn and H_2 cell, the voltmeter reads -0.763 V. This means zinc is getting oxidized, giving electrons to hydrogen.

Anode (oxidation): $Zn_{(g)} \longrightarrow Zn^{2+}{}_{(aq)}(1\ M) + 2e^-$

Cathode (reduction): $2H^+{}_{(aq)}(1\ M) + 2e^- \longrightarrow H_{2\,(g)}(1\ atm)$

Overall: $Zn_{(s)} + 2H^+{}_{(aq)}(1\ M) \longrightarrow Zn^{2+}{}_{(aq)}(1\ M) + H_{2\,(g)}(1\ atm)$



$$E^o_{cell} = E^o_{right} - E^o_{left}$$

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

$$-0.760V = E^o_{Zn^{2+}/Zn} - 0\ V$$

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

*Note: *Zn should technically be the anode as it is giving electrons and should the left electrode in the electrochemical cell. Electron flow is always left to right in galvanic cells.*

Cell notation: $Zn_{(s)}|\ Zn^{2+}(1\ M)\ ||\ H^+\ (1\ M)\ |\ H_2\ (1\ atm)\ |\ Pt_{(s)}$

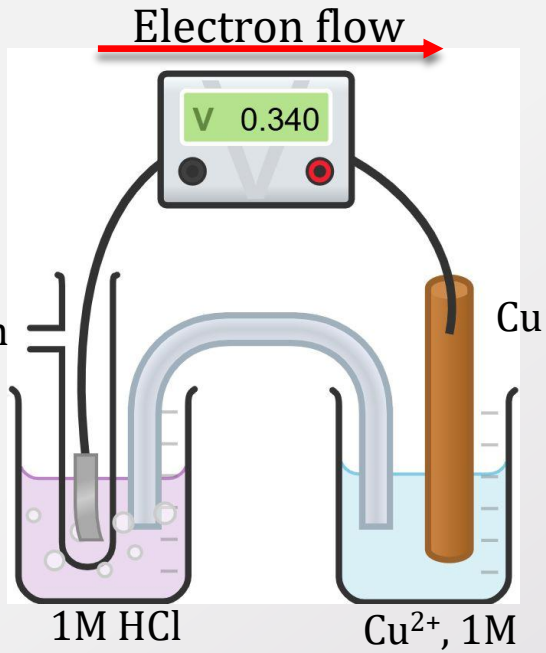
ELECTRODE POTENTIAL FOR H_2|Cu CELL

In a Cu and H_2 cell, the voltmeter reads +0.340 V. This means copper is getting reduced, taking electrons from hydrogen.

Anode (oxidation): $H_{2\,(g)}\,(1\text{ atm}) \longrightarrow 2H^+_{(aq)}\,(1\text{ M}) + 2e^-$

Cathode (reduction): $Cu^{2+}_{(aq)}\,(1\text{ M}) + 2e^- \longrightarrow Cu_{(s)}$

Overall: $H_{2\,(g)}(1\text{ atm}) + Zn^{2+}_{(aq)}\,(1\text{ M}) \longrightarrow 2H^+_{(aq)}\,(1\text{ M})\,Cu_{(s)}$



$$E^o_{cell} = E^o_{right} - E^o_{left}$$

$$E^o_{cell} = E^o_{Cu^{2+}/Cu} - E^o_{H^+/H_2}$$

$$0.34\text{ V} = E^o_{Cu^{2+}/Cu} - 0\text{ V}$$

$$E^o_{Cu^{2+}/Cu} = 0.34\text{ V}$$

Cell notation: $Pt(s) \mid H_2\,(1\text{ atm}) \mid H^+\,(1\text{ M}) \mid\mid Cu^{2+}(1\text{ M}) \mid Cu(s)$

WHAT DOES THIS REDUCTION POTENTIAL MEAN?

In these experiments we are measuring "reduction" potential which means how easily is something reduced (accepts electrons).

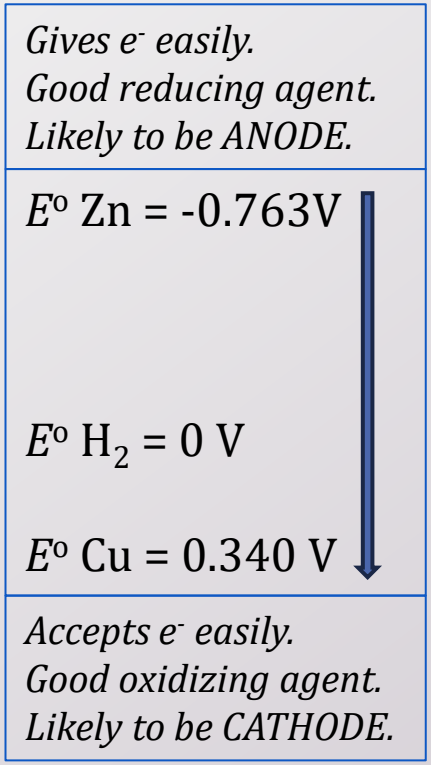
In a Zn and H_2 cell, the voltmeter reads -0.763 V. This means zinc is getting oxidized, giving electrons to hydrogen.

Hydrogen is getting reduced in presence of zinc.

In a Cu and H_2 cell, the voltmeter reads +0.340 V. This means copper is getting reduced, taking electrons from hydrogen.

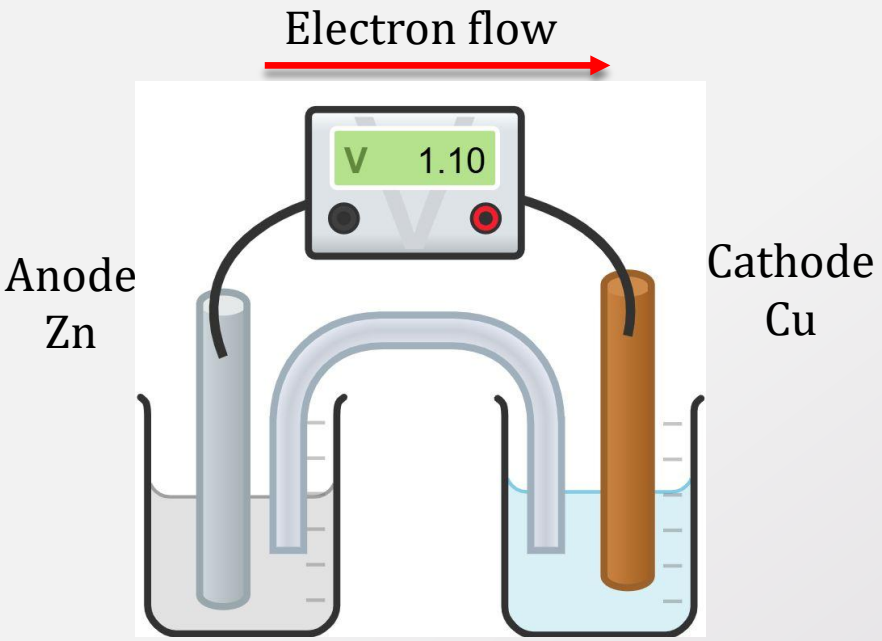
Copper is getting reduced in presence of hydrogen.

From these experiments we develop the "**activity series**" which tells us which elements are more readily reduced than others. This can eventually help us build galvanic cells (spontaneous reaction).



EMF OR CELL POTENTIAL FOR Zn|Cu CELL

In a Zn/Cu cell, the reduction potential for Zn is -0.76 V while Cu is +0.34 V. Zn is more negative thus is more likely to reduce Cu, therefor Zn is the anode and Cu is cathode. Their cell voltage (EMF) can be calculated as the below.



$$E^{o}_{cell} = E^{o}_{right} - E^{o}_{left}$$

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$

$$E^{o}_{cell} = E^{o}_{Cu^{2+}/Cu} - E^{o}_{Zn^{2+}/Zn}$$
$$= 0.34V - (-0.76V)$$
$$= 1.10\ V$$

STANDARD REDUCTION POTENTIALS

Likely to be anode as they prefer to lose e⁻

	Standard Potential E° (V)
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.38
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.68
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	0.83
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	-0.74
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.41
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	-0.40
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	-0.28
$V^{3+}(aq) + 2e^- \rightleftharpoons V^{2+}(aq)$	-0.26
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13
$Fe^{3+}(aq) + 3e^- \rightleftharpoons Fe(s)$	-0.04
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00

Likely to be cathode as they prefer to gain e⁻

Cathode (Reduction) Half reaction	Standard Potential E° (V)
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu^+(aq)$	0.16
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	0.34
$IO_3^-(aq) + H_2O + 2e^- \rightleftharpoons I^-(aq) + 2OH^-(aq)$	0.49
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	0.52
$I_2(g) + 2e^- \rightleftharpoons 2I^-(aq)$	0.54
$MnO_4^-(aq) + 4H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$	0.59
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	0.77
$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	0.80
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	0.80
$Hg^{2+}(aq) + e^- \rightleftharpoons Hg(l)$	0.85
$ClO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons Cl^-(aq) + 2OH^-(aq)$	0.90
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	0.90
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	0.96
$Br_2(g) + 2e^- \rightleftharpoons 2Br^-(aq)$	1.07
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{2+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	1.49
$Pb^{4+}(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq)$	1.69
$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O(l)$	1.70
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	1.78
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	2.01
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	2.87

APPLICATIONS OF REDUCTION POTENTIALS

Knowing the reduction potentials help us to determine the following:

1) Predicting oxidation and reduction of elements with respect to each other.
   a) The higher the standard potential value (more positive), the more likely it is to oxidize another (cause another to lose electrons).
   b) The more negative the standard potential value the more likely it is to lose electrons and reduce another element. (Usually metals.)
2) Construction of galvanic cells. Galvanic cells are spontaneous in nature. Electrons should transfer automatically without providing external energy.
   a) A galvanic cell where anode has a smaller standard potential than the cathode is spontaneous.
   b) The E_{cell} or EMF value from $E^{o}_{cathode} - E^{o}_{anode}$ equation should be <u>positive</u> for a cell to be spontaneous. If it is negative, then cell is nonspontaneous.

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 ($\mathbf{F_2}$ + 2 e^- -> $2F^-$).
- Found generally on the right side of the periodic table (e.g., nonmetals - 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. (Zn^{2+} + $2e^-$ -> **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+})?

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

- The standard (reduction) potentials are

  Sn^{2+} to Sn^{4+} $\quad E^o = 0.15$ V

  Fe to Fe^{2+} $\quad E^o = -0.41$ V

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

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

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

- The standard (reduction) potentials are

  Cl_2 to Cl^- $\quad E^o = 1.36$ V

  MnO_4^- to Mn^{2+} $\quad E^o = 1.49$ V

  The stronger oxidizing agent is MnO_4^- as it is more positive.

EXAMPLE: WILL REACTION OCCUR?

Will dichromate ion ($Cr_2O_7^{2-}$) oxidize manganese(II) ion (Mn^{2+}) to permanganate ion (MnO_4^-) in an acid solution under standard conditions?

Answer:

The question really is if dichromate will 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:

  $Cr_2O_7^{2-}$ to Cr^{3+} $\quad E° = 1.33$ V (*Cr is going from +6 to +3*)

  MnO_4^- to Mn^{2+} $\quad E° = 1.49$ V (*Mn is going from +7 to +2*)

- MnO_4^- has a larger reduction potential; i.e., Mn prefers to gain electrons when compared to Cr.
- $Cr_2O_7^{2-}$ will not oxidize Mn^{2+} to MnO_4^-.

EXAMPLE: CALCULATING CELL POTENTIALS - 1

Determine the a) $E°_{cell}$ and b) overall cell reaction, at 25 °C, of a galvanic cell made of an Al electrode in a 1.0 *M* $Al(NO_3)_3$ solution and a Cu electrode in a 1.0 *M* $Cu(NO_3)_2$ solution.

Answer:

a) Anode: $Al^{3+} + 3e^- \longrightarrow Al \quad E^o = -1.66\ V$

Cathode: $Cu^{2+} + 2e^- \longrightarrow Cu \quad E^o = +0.34V$

Cu is cathode because of higher EP

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$E^o_{cell} = E^o_{Cu^{2+}/Cu} - E^o_{Al^{3+}/Al}$$

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

b) Cell Reaction

$$3Cu^{2+} + \cancel{6e^-} \longrightarrow 3Cu$$

$$2\ Al \longrightarrow 2Al^{3+} + \cancel{6e^-}$$

$$3Cu^{2+} + 2Al \longrightarrow 2Al^{3+} + 3Cu$$

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

$$2H_{2(g)} + O_{2\,(g)} \longrightarrow 2H_2O_{\,(g)}$$

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

$$2H_2O_{(l)} + 2e^- \rightleftharpoons H_2(g) + 2OH^-_{\,(aq)} \qquad E° = -0.83\ V$$

$$O_{2\,(g)} + 2H_2O_{\,(l)} + 4e^- \rightleftharpoons 4OH^-_{\,(aq)} \qquad E° = 0.40\ V$$

Answer:

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

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

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

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

EXAMPLE: DETERMINING SPONTANEITY - 1

Can the following reactions occur spontaneously?

$$Cu^{2+}_{(aq)} + 2\ Fe^{2+}_{(aq)} \longrightarrow 2\ Fe^{3+}_{(aq)} + Cu_{(s)}$$

Answer

$$Cu^{2+}_{(aq)} + 2\ Fe^{2+}_{(aq)} \longrightarrow 2\ Fe^{3+}_{(aq)} + Cu_{(s)}$$

Copper is getting reduced -> cathode; Fe^{2+} is getting oxidized -> anode

$E^{o}_{Cu^{2+}/Cu}$ = +0.34 V (cathode) ; $E^{o}_{Fe^{3+}/Fe^{2+}}$ = +0.77 V (anode)

$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$

0.34 – (+0.77) = - 0.43 V **NONSPONTANEOUS**

EXAMPLE: DETERMINING SPONTANEITY - 2

Can the following reaction occur as written, or does it need to be reversed for spontaneous reaction?

$$2\ Mn^{2+}_{(aq)} + 2\ IO_3^-{}_{(aq)} + 2\ H_2O_{(l)} \longrightarrow 2MnO_4^-{}_{(aq)} + I_{2\,(s)} + 4H^+_{(aq)}$$

Answer

$$2\ Mn^{2+}_{(aq)} + 2\ IO_3^-{}_{(aq)} + 2\ H_2O_{(l)} \longrightarrow 2MnO_4^-{}_{(aq)} + I_{2\,(s)} + 4H^+_{(aq)}$$

Mn^{2+} is getting oxidized to MnO_4^- (anode), IO_3^- is getting reduced to I_2 (cathode).

$E^o_{MnO_4^-/Mn^{2+}}$ = 1.51V (anode); $E^o_{IO_3^-/I_2}$ = 1.20 V (cathode)

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

1.20 – (+1.51) = - 0.31 V **NONSPONTANEOUS**

The reaction will have to be reversed to be spontaneous.

KEY CONCEPTS

- Understand standard electrode potential and activity series.
- Predict oxidation and reduction.
- Predict what will be oxidizing and what will be reducing agent in a reaction.
- Calculating cell potential/EMF.
- Predicting reaction spontaneity using reduction potentials.