Standard Reduction Potential

When the concentration of the Cu^{2+} and Zn^{2+} ions are both 1.0M,

We find the voltage or emf of the daniell cell is 1.10V at 25°c.

Notes

a) The measured emf of the cell can be treated as the sum of the electrical potential at the Zn and Cu electrodes.

b) Knowing one of these electrodes potential, we could obtained the other by subtraction from (1.10 V)

C) it's impossible to measure the potential of just single electrode, how can we do it?

By setting the potential value of a particular electrode at Zero such as "Hydrogen Electrode".

Hydrogen Electrode

Serves as a reference for measuring the potential of single electrode
The potential of hydrogen electrode is equal zero.

The composition of hydrogen cell

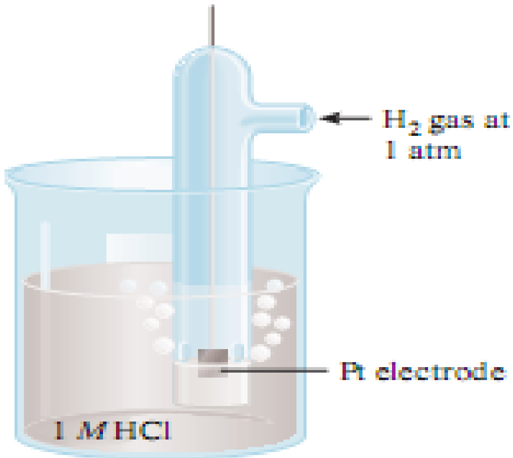
- Hydrogen gas
- 1M HCl solution
- Platinum electrode

Hydrogen gas is bubbled into a1M HCl at 25°c

Platinum electrode has two functions

*It provides a surface on which the dissociation of hydrogen molecules can take place.

*An electrical conductor to the external * circuit



$$H2 \rightarrow 2H^{+} + 2e$$

When P of H_2 =1atm concentration 1M

The potential for the reduction of H+ at 25°c is zero

$$H^{+}(1M) + 2e- \rightarrow H2\ (1atm) \qquad E° = 0V$$

E° the voltage associated with a reduction reaction at an electrode when all solutes are 1M and all gases are at 1 atm

Hydrogen electrode is called "Standard Hydrogen Electrode" (SHE)

Example

Calculate the potentials of

a) Cell containing Zn electrode

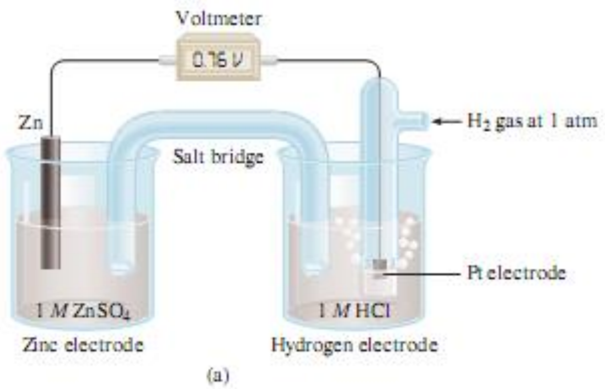
b) Cell containing Cu electrode

c) Danielle cell

By using (SHE) Solution

In 1st case

Zinc electrode is the anode and SHE is the cathode The oxidation reaction $Zn(s) \rightarrow Zn^{2+}{}_{(1M)} + 2e^-$



Zinc electrode is the anode and SHE is the cathode.

The oxidation reaction $Zn(s) \rightarrow Zn^{2+}{}_{(1M)} + 2e^-$

The cell diagram is

$Zn_{(s)} \mid Zn^{2+}{}_{(1M)} \parallel H^+{}_{(1M)} \mid H_{2\,(1atm)} \mid Pt_{(s)}$

The half-cell reaction is

Anode (oxidation) $Zn_{(s)} \rightarrow Zn^{2+}{}_{(1M)} + 2e^-$

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

Over all $Zn(s) + 2H^+{}_{(1M)} \rightarrow Zn^{2+}\ (1M) + H_{2\,(1atm)}$

The standard emf of the cell 0.76V

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

For the Zn –SHE cell, we write

$E°_{cell} = E°_{H+/H2} - E°_{Zn^{2+}/Zn}$

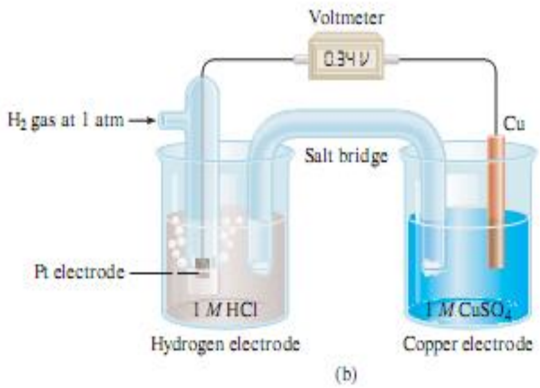
$0.76\ V = 0 - E°_{Zn2+/Zn}$

$E°_{Zn2+/Zn} = -0.76\ V$

In 2nd case

Copper electrode is the cathode ,Mentionwhy?

Because it's mass increases during the operation of the cell



The reduction reaction

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

$Pt_{(s)} | H_{2(1atm)} | H^+_{(1M)} || Cu^{2+}_{(1M)} | Cu_{(s)}$

The half cell reaction are :

Anode (oxidation) $H_{2(1atm)} \rightarrow 2H^+_{(1M)} + 2e^-$

Cathode (reduction) $Cu^{2+}_{(1M)} + 2e^- \rightarrow Cu_{(s)}$

Over all $H_{2(1atm)} + Cu^{2+}_{(1M)} \rightarrow 2H^+_{(1M)} + Cu_{(s)}$

The standard emf of the cell is 0.34 V

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

$E^o_{cell} = E^o_{Cu^{2+}/Cu} - E^o_{H+/H2}$

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

$E^oCu^{2+}/Cu = 0.34$ V

The 3rd case

For Danielle cell we can write

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

Cathode (reduction) Cu^{2+} (1M) +2e$^- \rightarrow Cu_{(s)}$

Over all $Zn_{(s)} + Cu^{2+}$ (1M) $\rightarrow Zn^{2+}$(1M) $+ Cu_{(s)}$

The emf for the cell

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

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

=0.34 v – (-0.67 V)

=1.10 V

We can use the sign of E^0 to predict the extent of redox reactions.

a)Positive E^0 :

means that the redox reaction

will favor the formation of products at equilibrium

b) Negative E^0 :

means that more reactant than product will be formed at equilibrium

Half-Reaction	$E°$(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

We note that

*SHE has an E° value of 0 V

-Below the SHE the negative standard reduction potentials increase.

-Above it, the positive standard reduction potentials increase.

- the more positive E° is the greater tendency for the substance to be reduced.

EX1 F_2 (1atm) +2e$^-$ → 2F$^-$(1M) E°=2.87 V

Has the highest positive E° value among all the half-cell reactions.

F_2 is the strongest oxidizing agent, rationalize??

Because it has the greatest tendency to be reduced.

EX2 Li^+ (1M) + e$^-$ → $Li_{(s)}$ E° = -3.05V

Has the most negative E° valve among all the half-cells reactions.

Li^+ is the weakest oxidizing agent, rationalize?

Because it's the most difficult species to reduce.

3) The oxidizing agent increase in the strength from bottom to top and the reducing agent increase in strength from the top to the bottom.

4) The half-cell reactions are reversible depending on the conditions; any electrode can act either as an anode or as a cathode.

Ex SHE is the cathode when coupled with Zn and becomes the anode when used in a cell with copper.

5) Diagonal rule

Any species on the left of a given half-cell reaction will react spontaneously with a species that appears on the right of any half-cell reaction.

In case of daniell cell

Cu^{2+} (1M) $+2e^- \rightarrow Cu_{(s)}$ $E^o=0.34V$

Zn^{2+} (1M) $+2e^- \rightarrow Zn_{(s)}$ $E^o = -0.76$ V

6) Changing the stoichiometric coefficients of a half-cell reaction doesn't affect the value of E^o, rationalize??

Because electrode potentials are intensive properties

What is the meaning of intensive property?

This means that the value of E^o is unaffected by the size of the electrodes or the amount of solutions present.

Ex $I_2(S) + 2e- \rightarrow 2I^-(1M)$ $E^o = 0.53$ V

$2I_2(S) + 4e- \rightarrow 4I^-(1M)$ $E^o = 0.53$ V

E^o doesn't change if we multiply the half _ reaction by 2

7) The sign of E^o changes but its magnitude remains the same when we reverse a reaction.

Example

Predict what will happen if molecular bromine (Br_2) is added to a solution containing NaCl and NaI at 25ºc assume all species are in their standard state.

Solution

We need to compare the standard reduction potentials of Cl_2, Br_2 and I_2 and apply the diagonal rule.

From table

Cl_2 (1atm) + $2e^- \rightarrow 2Cl^-$(1M)

$Br_{2\,(l)} + 2e^- \rightarrow 2Br^-$(1M)

$I_{2(S)} + 2e^- \rightarrow 2I^-$ (1M)

Br_2 will oxidize I^- but will not oxidize Cl^- the only redox reaction that will occur under standard state conditions is

Oxidation $2I^-(1M) \rightarrow I_{2(s)} + 2e^-$

Reduction $Br_{2\,(l)} + 2e^- \rightarrow 2Br^-$ (1M)

Over all $2I^-(1M) + Br_{2\,(l)} \rightarrow I_{2(s)} + 2Br^-(1M)$

Notes that

The Na^+ ions are inert and doesn't enter into the redox reactions

Ex2

A galvanic cell consists of a Mg electrode in a1.0M Mg $(No_3)2$ solutions and a Ag electrode in a1.0 M Ag No3 solution, calculate the standard emf of this cell at 25ºc.

Solution

Write the standard reduction potential of Ag and Mg and apply the diagonal rule to determine which the anode is and which the cathode is

The standard reduction potential

$Ag^+ (1.0M) + e^- \rightarrow Ag_{(s)}$

$Mg^{2+} (1.0M) + 2e^- \rightarrow Mg_{(s)}$

Apply the diagonal rule; we see that Ag^+ will oxidize Mg

Anode (oxidation) $Mg_{(s)} \rightarrow Mg^{2+} (1.0) + 2e^-$

Cathode (reduction) $2Ag^+ (1.0M) + 2e^- \rightarrow 2Ag_{(s)}$

Over all $Mg_{(s)} + 2Ag^+ (1.0M) \rightarrow Mg^{2+} (1.0M) + 2Ag_{(s)}$

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

$= E^o_{Ag^+/Ag} - E^o_{Mg2+/Mg}$

$= 0.80V - (-2.37\ V)$

$= 3.17\ V$

Examples

1) In Danielle cell when the concentrations of Cu^{2+} and Zn^{2+} ions are both (1M) at 25ºc, then emf is ……………

A) 1V
B) **1.10 V**
C) 0.1V
D) 2 V

2) The measured emf of the cell can be treated as…………..

A) The product of electrical potential of Zn and Cu electrode
B) The subtraction of electrical potential of Zn and Cu electrode
C) **The sum of electrical potential of Zn and Cu electrode**
D) None of the above

3) We can measure the potential value of a single electrode by using ………………

A) **H_2 electrode**
B) O_2 electrode
C) N_2 electrode
D) Cl_2 electrode

4) The standard potential of H_2 electrode is equal ………..

A) 0.5
B) 1
C) 2
D) **zero**

5) We use H2 electrode to measure the potential of a ………..

A) **Single electrode**
B) Double electrode
C) Triple electrode
D) All of the above

6) Hydrogen gas in H2 cell is bubbled in 1M of …………

A) H_2SO4
B) **Hcl**
C) Na Cl
D) NaOH

7) In hydrogen cell we use …….. To provide a surface on which the dissociation of hydrogen molecules can take place.

A) Zinc
B) Copper
C) Gold
D) **Platinum**

8) Is the voltage associated with a reduction reaction at an electrode when all solutes are (1M) and all gases are at (1atm)………..

A) Standard oxidation potential
B) **Standard reduction potential**
C) Potential difference
D) None of them

9) SHE refers to ……………………..

A) **Standard hydrogen electrode**
B) Standard helium electrode
C) Standard hydrogen emission
D) None of them

10) The standard emf of any cell is equal to ………………

A) E^o cathode +E^o anode
B) E^o anode -E^o cathode
C) E^o cathode/E^o anode
D) **E^o cathode - E^o anode**

11) When the redox reaction will favor the formation of reactant at equilibrium, then the value of E° is ……………..

A) **Positive value**
B) Negative value
C) zero
D) infinity

12) When the redox reaction will favor the formation of reactant at equilibrium, then the value of E° is ……………..

A) Positive value
B) **Negative value**
C) zero
D) infinity

13) Below the SHE the negative standard reduction potential ……………

A) **increase**
B) decrease
C) Remain constant
D) None of all

14) The more positive E°is , the greater tendency for the substance to be ……………….

.

A) increase
B) decrease
C) **reduced**
D) oxidized

15) The strongest oxidizing agent is ……….. While the weakest oxidizing agent is…………..

A) Li,F2
B) F2,H2
C) H2,Li
D) **F2,Li**

16) The weakest reducing agent is …………. While the strongest reducing agent is……………..

A) **F2,Li**
B) F2,H2
C) H2,Li
D) Li,F2

17) The oxidizing agent increases in strength from ……….to ………

A)	**Bottom -Top**	C)	Left-Right
B)	Top- Bottom	D)	Right -Left

18) The reducing agent increases in strength from ………….to ………….

A)	Bottom -Top	C)	Left-Right
B)	**Top- Bottom**	D)	Right -Left

19) Any electrode can act as ……………..

A)	anode	C)	**Cathode or anode**
B)	cathode	D)	None of them

20) SHE when coupled with Zn it acts as……………while when coupled with Cu it acts as …………..

A)	Anode - anode	C)	**Cathode- anode**
B)	Cathode - cathode	D)	Anode - cathode

21) Changing the stoichiometric coefficient of a half-cell reactions…….the value of E°

A	**Doesn't affect**	C)	decrease
B)	increase	D)	affect

22) The value of E° is …………by increasing the size of E°.

A)	affect	C)	decrease
B)	increase	D)	**Un affected**

23) The value of E° is …………… by increasing the amount of solutions present.

A)	**Un affected**	C)	decrease
B)	increase	D)	None of them

24) Calculated the value of E° cell for the following reaction.

$2Au_{(s)} + 3Ca^{2+}(aq) \rightarrow 2Au^{3+}{}_{(aq)} + 3Ca_{(s)}$.

A)	**-4.37 V**	C)	-11.6 V
B)	-1.37 V	D)	1.37 V

Solution

Anode (oxidation) $2Au_{(s)} \rightarrow 2Au^{3+} + 6e^-$ E° =1.5 V

Cathode (reduction) $3Ca^{2+} + 6e^- \rightarrow 3Ca_{(S)}$ E° = -2.87 V

Over all $2Au_{(s)} + 3Ca^{2+} \rightarrow 2Au^{3+} + 3Ca_{(s)}$

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

$= -2.87 - 1.5 = -4.37\ V$

25) Calculate $E°_{cell}$ for a silver-aluminum cell in which the cell reaction is $Al(s) + 3Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3Ag(s)$

A. -2.46 V
B. 0.86 V
C. -0.86 V
D. 2.46 V
E. none of these

Solution

Anode (oxidation) $Al(s) \rightarrow Al^{3+}_{(aq)} + 3e^-$ $E° = -1.66$ V
Cathode (reduction) $3Ag^{+}_{(aq)} + 3e^- \rightarrow 3Ag_{(s)}$ $E° = +0.8$ V
$E°_{cell} = E°_{cathode} - E°_{anode}$
$= 0.8 - (-1.66)$
$= 0.8 + 1.66$
$= 2.46$ V

26) Calculate $E°_{cell}$ for the following reaction:

$$2Fe^{2+}_{(aq)} + Cd^{2+}_{(aq)} \rightarrow 2Fe^{3+}_{(aq)} + Cd_{(s)}$$

A. -0.37 V
B. 0.37 V
C. -1.17 V
D. 1.17 V
E. none of these

Solution

Anode (oxidation) $2Fe^{2+} \rightarrow 2e^- + 2Fe^{3+}$ $E° = .77$ V
Cathode (reduction) $Cd^{2+} + 2e^- \rightarrow Cd_{(s)}$ $E° = -0.40$ V

Over all $2Fe^{2+} + Cd^{2+} \rightarrow 2Fe^{3+} + Cd_{(s)}$
$E°_{cell} = -0.40 - 0.77$
$= -1.17$ V

27) For the reaction $Ni^{2+}_{(aq)} + 2Fe^{2+}_{(aq)} \rightarrow Ni_{(s)} + 2Fe^{3+}_{(aq)}$, the standard cell potential $E°_{cell}$ is

A) +2.81 V.
B) +1.02 V.
C) +0.52 V.
D) -1.02 V.
E) -2.81 V.

Solution

Anode (oxidation) $2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$ $E° = 0.77$ V
Cathode (reduction) $Ni^{2+} + 2e^- \rightarrow Ni_{(s)}$ $E° = -0.25$ V

$E°_{cell} = E°_{cathode} - E°_{anode}$
$= -0.25 - 0.77$
$= -1.02$ V

24. Calculate the standard cell emf for the following cell:
$Mg\,|Mg^{2+}\,||\,NO_3^-$ (acid son)$|\,NO_{(g)}\,|\,Pt$

A. 3.33 V
B. 1.41 V
C. -1.41 V
D. 8.46 V
E. -8.46 V

Solution

Anode (oxidation) $3Mg \rightarrow 3Mg^{2+} + 6e^-$ $E° = -2.37$ V
Cathode (reduction) $2No^{3-} + 6e^- \rightarrow 2No$ $E° = 0.96$ V

$E°_{cell} = E°_{cathode} - E°_{anode}$
$= 0.96 + 2.37$
$= 3.33$ V.