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UNIT I
ELECTROCHEMISTRY

I. OXIDATION NUMBER AND REDOX REACTIONS

A. Oxidation Number:

Oxidation number is the charge which an atom ***appears*** to have when:

a) electrons shared between two unlike atoms are counted with the more electronegative atom.

b) electrons shared between like atoms are divided equally between the sharing atoms.

The oxidation number is an ***arbitrary*** number based on a set of rules. it should not be confused with the real charge on an atom or a group of atoms.

The oxidation number is ***assigned*** according to the following set of rules:

1) The oxidation number of **oxygen** in almost all compounds is (-2) .

Examples: Na_2O H_2O CO_2

Exception: peroxides as : Na_2O_2, H_2O_2, and K_2O_2. Oxygen here is (-1) .

2) The oxidation number of **hydrogen** in a compound is (+1) .
Examples; HCl, H_2O
Exceptions: Metal hydrides as: NaH, and CaH_2. " H" here is (-1).
What is the oxidation number of H in NH_3 ? Answer: __________

3) Any free or **uncombined element** has an oxidation number of zero.
Examples: Ag, Au, N_2 , F_2, and P_4 .

4) The oxidation number of an **ion** is numerically equal to the charge on that ion.
Examples: Na^+ Cl^-

5) The **sum** of oxidation numbers of all elements in a **compound** is zero.
Examples: HNO_3

6) The sum of the oxidation numbers of the elements in a polyatomic ion is equal to the net charge on the ion.
Example: PO_4^{3-}

Exercise I:

Assign an oxidation state for each element in the following :

a) $K_2Cr_2O_7$ b) $Ca(ClO_2)_2$ c) Fe_2O_3 d) H_3AsO_4 e) $S_2O_3^{2-}$ f) $C_{12}H_{22}O_{11}$

g) $Cr_2(CO_3)_3$

Exercise II:

What is the oxidation state of "C" in each of the following:

a) CH_4 b) CH_3OH c) HCHO d) CO_2

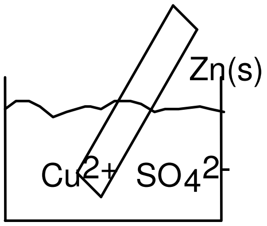
Writing **molecular** formula instead of the **structural** formula will result in an average oxidation state.

Example: NH_4NO_3	$N_2H_4O_3$
structural formula	molecular formula

It is possible to obtain **fractional** oxidation state due to writing molecular formula instead of structural formula.

Examples: Fe_3O_4 $Na_2S_4O_6$

B) Redox Reactions (Oxidation - Reduction Reactions)



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

$$Zn(s) \longrightarrow Zn^{2+}\,(aq) + 2\,e^{-} \quad \text{oxidation}$$

$$Zn(s) + Cu^{2+} \longrightarrow Cu\,(s) + Zn^{2+}$$

The total increase in oxidation number is equal to the total decrease in oxidation number. The number of electrons lost is equal to the number of electrons gained.

Cu^{2+} is reduced by Zn(s). Zn (s) is the reducing agent.

Zn(s) is oxidized by Cu^{2+}. Cu^{2+} is the oxidizing agent.

Summary:

Oxidation state. It is the charge an atom would appear to have if both electrons in the bond were assigned to the more electronegative element.
Oxidation: It is the process of **losing** electrons. There is an **increase** in the oxidation number.
Reduction: It is the process of **gaining** electrons. There is a **decrease** in the oxidation number.
Oxidizing agent: It is the material being reduced. (i.e. causing oxidation).
Reducing agent: It is the material being oxidized. (i.e. causing reduction).

C) Balancing Redox Equations:

Ion-electron Method (Half-reaction method):

Balancing Redox Equations for Reactions Taking place in <u>Acidic Media</u>

Example: MnO_4^- (aq) + $C_2O_4^{2-}$ (aq) ——> Mn^{2+} (aq) + CO_2 (g) (Acidic medium)

i) Write two half reactions , one involving oxidation and the other involving reduction. Half reactions are balanced separately.

MnO_4 aq) → Mn^{2+} (aq) $C_2O_4^{2-}$ (aq) → CO_2 (g)

ii) Atoms undergoing oxidation or reduction are balanced first.

MnO_4 aq) → Mn^{2+} (aq) $C_2O_4^{2-}$ (aq) → CO_2 (g)

iii) H_2O can be added to reactants or products to balance "O".

MnO_4 aq) → Mn^{2+} (aq) $C_2O_4^{2-}$ (aq) → CO_2 (g)

iv) If the reaction occurs in **acidic** solution, H^+ ions can be added to either reactants or products to balance "H"

MnO_4 aq) → Mn^{2+} (aq) $C_2O_4^{2-}$ (aq) → CO_2 (g)

v) Last, the charges are balanced by adding electrons.

MnO_4^- (aq) → Mn^{2+} (aq) $C_2O_4^{2-}$ (aq) → CO_2 (g)

Answer:

16 H^+ (aq)+ 2 MnO_4^- (aq) + 5 $C_2O_4^-$ (aq) → 2 Mn^{2+}(aq) + 8 H_2O (l) +10 CO_2 (g)

Example: Balance the following redox equation using the ion-electron method.
$FeSO_4$ (aq)+ $KMnO_4$(aq)+ H_2SO_4(aq) $\rightarrow$ $Fe_2(SO_4)_3$ + $MnSO_4$(aq) +K_2SO_4 (aq) + H_2O(l)
(Acidic solution)

Write the net- ionic equation for the above reaction. All strong acids, strong bases (soluble metal hydroxides), and soluble salts are ionizable.

i) Total-ionic equation:

Fe^{2+}(aq) + SO_4^{2-}(aq)+ K^+ (aq) + MnO_4^-(aq) $\rightarrow$ Fe^{3+}(aq)+SO_4^{2-}(aq)+Mn^{2+}(aq) + K^+ (aq)

ii) Net-ionic Equation is: Fe^{2+} (aq) + MnO_4^- (aq) $\rightarrow$ Fe^{3+} + Mn^{2+} (aq)

iii) Write two half reactions:

Fe^{2+} (aq) $\rightarrow$ Fe^{3+} (aq) MnO_4^- (aq) $\rightarrow$ Mn^{2+} (aq)

Answer:5 Fe^{2+} (aq) + 8 H^+ (aq) + MnO_4^- $\rightarrow$ (aq) 5 Fe^{3+} + Mn^{2+} (aq) + 4 H_2O (l)

Example: Balance the following equation by using the ion-electron method

NO_2^- (aq) + $Cr_2O_7^{2-}$ (aq) $\rightarrow$ Cr^{3+} (aq) + NO_3^- (aq)   (Acidic solution)

Answer:

Example: Balance the following equation by using the ion-electron method.

$SO_3{}^{2-}$ (aq) + $IO_3{}^{-}$ (aq) $\longrightarrow$ $SO_4{}^{2-}$ (aq) + I_2 (s) (Acidic medium)

Answer:

Balancing Redox Equations for Reactions Taking place in <u>Alkaline (Basic)</u> Media.

The two half reactions are balanced , as if they took place in acid solution, by the addition of appropriate H_2O and H^+. Since H^+ ions cannot exist in basic solutions, they are removed by adding OH^- to the **two** sides of the equation.

Example: Balance the following equation by using the ion-electron method.

$CrO_2{}^{-}$ (aq) + ClO^- (aq) $\longrightarrow$ $CrO_4{}^{2-}$ (aq) + Cl^- (aq) (Alkaline solution)

$CrO_2{}^{-}$ (aq $\longrightarrow$ $CrO_4{}^{2-}$ (aq) ClO^- (aq) $\longrightarrow$ Cl^- (aq)

Answer:

Example: Use the ion-electron method to balance the following equation.

PbO_2 (s) + Cl^- (aq) → ClO^- (aq) + $Pb(OH)_3^-$ (aq) (Basic solution)

Answer:

Example: Use the ion-electron method to balance the following equation:

CN^- (aq) + MnO_4^- (aq) → CNO^- (aq) + MnO_2 (s) (Basic medium)

Answer:

Example: Balance the following equation using the ion-electron method.

$$Mn(OH)_2\ (s) + O_2\ (g) \longrightarrow Mn(OH)_3\ (s)$$

$Mn(OH)_2\ (s) \longrightarrow Mn(OH)_3\ (s)$ $O_2\ (g) \longrightarrow$?

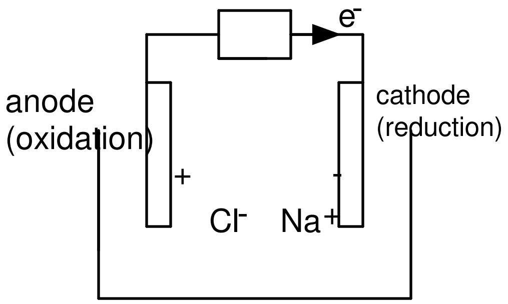
Answer:

D) ELECTROCHEMISTRY

Electrochemistry is the study of the relationship between electrical energy and chemical energy. **Electrochemical cells** are systems that incorporate redox reactions to utilize electrical energy. Electrochemical cells that utilize electrical energy to cause a nonspontaneous redox reaction to occur are called **Electrolytic cells.** Electrochemical cells that utilize a spontaneous redox reaction to provide electrical energy are called **Voltaic cells (or Galvanic cells).**

1) Electrolytic Cell: Electrical energy → chemical energy

a) Electrolysis of Molten Salt:



Anode:(positive electrode)

$2Cl^- \rightarrow Cl_2 + 2e^-$

Cathode :(negative electrode)

$Na^+ + e^- \rightarrow Na$

The overall cell reaction: $2\,Cl^- + 2\,Na^+ \rightarrow Cl_2\,(g) + 2\,Na\,(l)$

Electrolytic conduction: It is the movement of ionic charges through the liquid, due to the application of electricity.

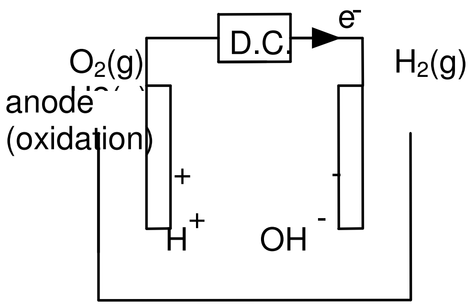
Electrolysis: It is the chemical reaction that occurs at the electrodes during electrolytic conduction.

The cathode is a sink for the electrons.

Electrical Neutrality: Even in the most minute part of the liquid, whenever a negative ion moves away, a positive ion must also leave or another negative ion must immediately take place. Every portion of the liquid is electrically neutral at all times.

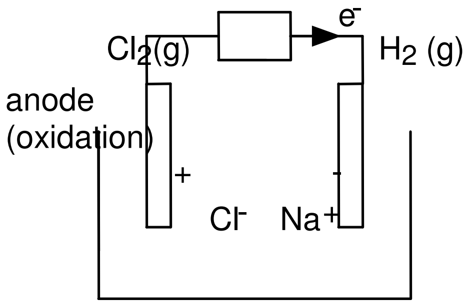
Assignment of cathode and anode for both, the Electrolytic cell and the Voltaic cell:
Cathode is the electrode where reduction takes place.
Anode is the electrode where oxidation takes place.

b) The Electrolysis of Water:



<u>Anode</u>(positive electrode)	<u>Cathode</u>:(negative electrode)
$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$	$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$

c) Electrolysis of Aqueous NaCl:



<u>Anode:</u>(positive electrode)	<u>Cathode</u>:(negative electrode)
$2Cl^- \rightarrow Cl_2 + 2e^-$	$Na^+ + e^- \rightarrow Na$
$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Conclusion: 1) It is easier to oxidize Cl^- to $Cl_2(g)$ than to oxidize H_2O to $O_2(g)$.

2) It is easier to reduce H_2O (l) to $H_2(g)$ than to reduce Na^+ to Na(l).

QUANTITATIVE ASPECTS OF ELECTROLYSIS

Michael Faraday determined experimentally that the amount of substance produced at each electrode is directly proportional to the amount of electric charge flowing through the cell.
We cannot measure charge, but we can measure current (that is , we can measure the charge flowing per unit time. The SI unit for current is Ampere (A), which is defined as the coulomb(which is the unit for charge) flowing through a conductor in one second.

Ampere = Coulomb/sec

That is, **1 coulomb= 1 Ampere x 1 sec**

The amount of electricity that must be supplied to a cell in order to deliver 1 mole of electrons is called a **Faraday**.

1 F = 96500 coulomb

$$\begin{array}{ccccc} Ag^{+}\ (aq) & + & 1\ e^{-} & \longrightarrow & Ag\ (s) \\ 1\,mole = 107.87\ g & & 1\ mole & & 1\ F \end{array}$$

To apply Faraday's law, we balance the half-reaction to find the number of moles of electrons needed per mole of product.
The following are examples to demonstrate the relationship among **current**, **time**, and the **amount of substance:**

Example:

In an electrolytic cell, how many grams of Cu will be deposited from the solution of $CuSO_4$ by a current of 1.5 A flowing for 2.0 hrs?

Example:

How long would it take to produce 25.0 g of Cr (s) from a solution of $CrCl_3$ by a current of 2.75 A ?

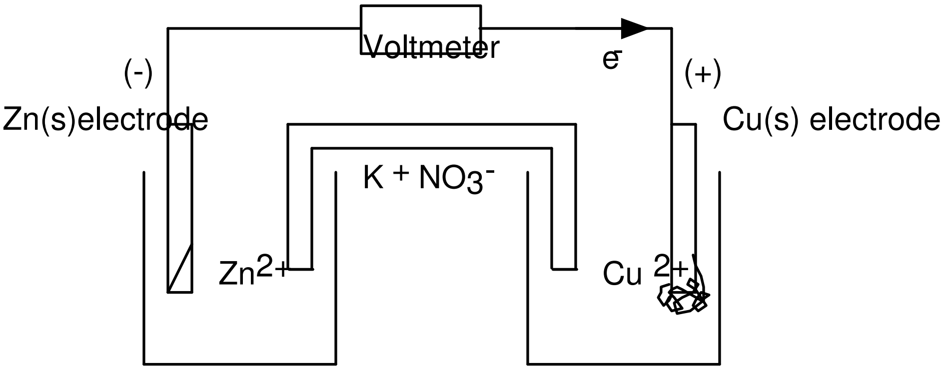
Answer: 14.0 hours

2) VOLTAIC CELL

In the previously mentioned Electrolytic cell, we made a nonspontaneous chemical reaction to take place by placing an electric current. In a Voltaic cell (Galvanic cell), an electron flow is produced as a result of spontaneous redox reaction. Recall,

$Cu^{2+} + 2e^- \rightarrow Cu(s)$ E° red = + 0.34 V

$Zn(s) \rightarrow Zn^{2+} + 2e^-$ E° red = - 0.76 V



Oxidation: (at anode)

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

-

Reduction (at cathode)

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

Overall cell reaction: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

In electrochemistry, in general, whether we are considering an Electrolytic cell or a Voltaic cell:

a) The **anode** is the electrode where **oxidation** takes place.

b) The **cathode** is the electrode where **reduction** takes place.

The signs of the electrodes in a Voltaic cell:

a) The **anode** is **negative**.

b) The **cathode** is **positive**.

Note: The above terminology is opposite of what we found previously in the Electrolytic cell.

The cathode is a sink for the electrons.

Shorthand notation for describing the components of a Voltaic cell:

Zn (s) I Zn^{2+} (aq) II Cu^{2+} (aq) I Cu (s)

Graphite I I^- (aq) I I_2 (s) II H^+ (aq), MnO_4^- (aq), Mn^{2+} (aq) I graphite

The anode compartment is written on the left. The vertical line represents a phase boundary, and the double vertical line represents the wire and salt bridge. A comma is used to separate the half-cell components in the same phase. The electrodes are written on the extreme left and right of the notation.

E) Cell Potential:

The force by which the electrons are pulled in the wire **(emf, electromotive force)** depends on the reduction potential of each electrode , that is, the tendency for the ion in each half cell to undergo reduction. The emf is measured in units of Volts.

The cell potential, E_{cell}, produced by a Voltaic cell depends on:

a) The type of electrode and type of ions in solution.
b) The concentration of the ions in the solution and the partial pressures of any gases that might be involved in the cell reaction.
c) The temperature.

Standard electrode potential, $E°_{cell}$: It is the emf when all ion concentrations are 1 M, all partial pressures of gases are 1 atm and the temperature of the cell is 25 °C. It is designated by **$E°_{cell}$**.

The Cell Potential

Each of Zn^{2+} and Cu^{2+} ions has a certain tendency to acquire electrons from its electrode and become reduced !

$$Cu^{2+} + 2e^- \longrightarrow Cu(s) \qquad E°red = +0.34\ V$$

$$Zn(s) \longrightarrow Zn^{2+} + 2e^- \qquad E°red = -0.76\ V$$

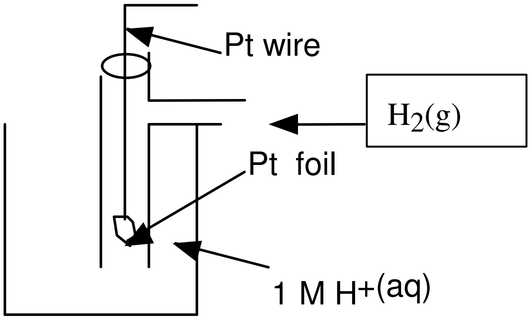
The larger the reduction potential, the greater the tendency for the reduction reaction to take place. When the cell reaction takes place, each of the species attempts to pull electrons.

The **potential that is measured** for the cell corresponds to the difference in the tendencies of the two ions to be reduced:

$E°$cell = $E°$red (substance that actually undergoes reduction) **-** **$E°$red** (substance that is forced to undergo oxidation)

= **$E°$red** **(cathode)** (right half -cell) **-** **$E°$red** (anode) (left half -cell)

How can we obtain the reduction potential for any specific half-cell ?
It is only possible to measure the overall cell potential. That is, we are only able to measure the differences between red, potential for any two substances.

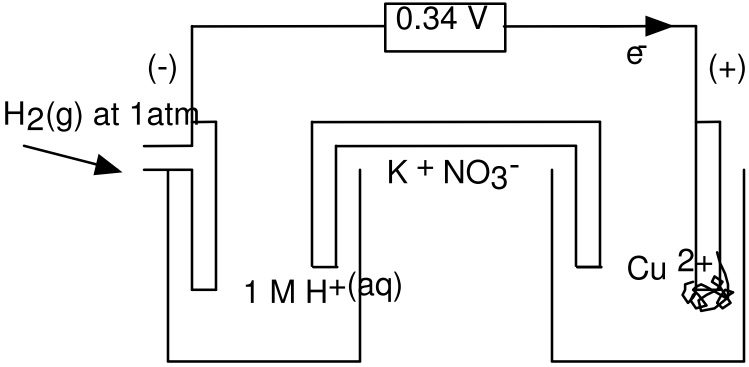


The Hydrogen electrode is chosen to be the **standard reference electrode.** Arbitrarily, a zero standard electrode potential, E°_{red} =0.00 V, is assigned for the Hydrogen electrode. All other half reactions are compared to this standard and a set of **relative values** of E°_{red} are obtained.

How is the standard hydrogen electrode used ?
When we connect a Voltmeter to a cell made of Cu half-cell and hydrogen standard electrode, "PROPER" reading of the voltmeter is possible only when the hydrogen electrode is attached to the **negative** terminal of the Voltmeter. Recall, that the negative electrode is the **anode** where **oxidation** takes place!

$H_2(g) \rightarrow 2H^+(aq) + 2e^-$ oxidation (anode)

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



Oxidation: <u>(at anode)</u>
$H_2(g) \rightarrow 2H^+ + 2e^-$

Reduction <u>(at cathode)</u>
$Cu^{2+} + 2e^- \rightarrow Cu(s)$

Now we will calculate the standard reduction potential for Cu^{2+} half cell, E°_{red}, from the **experimentally** measured cell potential.

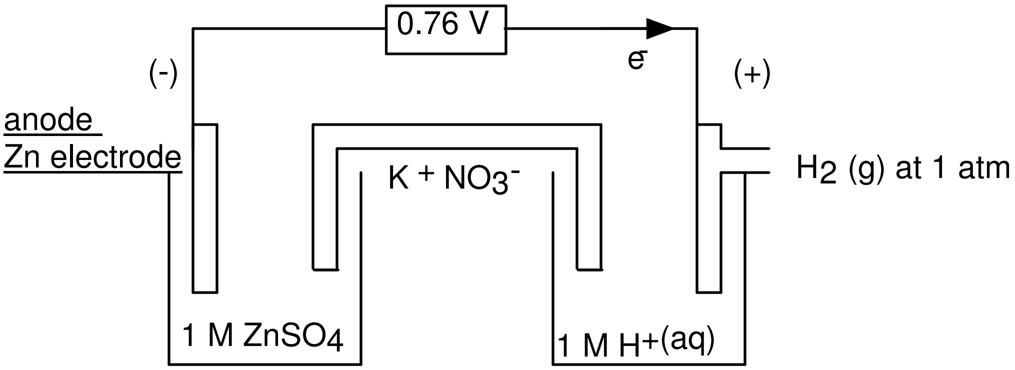
$E^\circ_{cell} = E^\circ_{red\,(Cu^{2+})} - E^\circ_{red\,(H^+)}$, $0.34\ V = E^\circ_{red\,(Cu^{2+})} - 0.00\ V$

$E^\circ_{red} = +0.34\ V$

Similarly, if we connect a voltmeter to a cell made of Zn half-cell and Hydrogen electrode, “PROPER” reading of the voltmeter is possible only when the hydrogen electrode is attached to the **positive** terminal of the voltmeter. Recall, that the **positive electrode** is the **cathode** where **reduction** takes place.

$Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2\,e^-$ oxidation (anode)

$2\,H^+\,(aq) + 2\,e^- \longrightarrow H_2\,(g)$ reduction (cathode)



Oxidation: (at anode)

$Zn(s) \longrightarrow Zn^{2+} + 2\,e^-$

Reduction (at cathode)

$2H^+ + 2e^- \longrightarrow H_2(g)$

The overall cell reaction is : $Zn\,(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)$

Now we will calculate the standard reduction potential for Zn^{2+} half-cell, $E^\circ_{red\,(Zn2+)}$, from the **experimentally** measured cell potential.

$$E^\circ_{cell} = E^\circ_{red\,(H^+)} - E^\circ_{red\,(Zn^{2+})}$$

$$0.76V = 0.00\,V - E^\circ_{red\,(Zn^{2+})}$$

$$E^\circ_{red\,(Zn^{2+})} = -0.76\,V$$

Note: The negative sign for E°_{red} reflects that it is easier to reduce H^+ than to reduce Zn^{2+}.

What is the use of knowing the reduction potentials of half-reactions?

We can predict:

a) the cell potential for any two half cells.

b) the spontaneous cell reaction.

The Reduction Potential Table

The table lists the standard reduction potential of a number of electrodes.

Strength ↑	Ag^{+} (aq, 1M) + 2 e^{-} $\rightleftharpoons$ Ag (s)	E° $_{red}$ = + 0.80 V	↓ **Strength**
increases as as	Cu^{2+} (aq,1M) + 2 e^{-} $\rightleftharpoons$ Cu (s)	E° $_{red}$ = + 0.34 V	**increases**
an oxidizing	Zn^{2+} (aq,1M) + 2 e^{-} $\rightleftharpoons$ Zn (s)	E° $_{red}$ = - 0.76V	**as a reducing**
agent.	Mg^{2+} (aq, 1M)+ 2 e^{-} $\rightleftharpoons$ Mg (s)	E° $_{red}$ = - 2.37 V	**agent.**

1) a) The more positive E° $_{red}$, the greater the tendency for the substance to be reduced.
b) The substance is considered to be a strong oxidizing agent as the value of E° $_{red}$ becomes more positive.
c) The more negative E° $_{red}$, the weaker the tendency for the substance to be reduced. Actually, the greater the tendency of the substance to be oxidized and it is considered to be a strong reducing agent.

2) The half reactions are reversible. Depending on the conditions, a given electrode can act as an anode or as a cathode.

3) Under standard conditions, any species on the left of a given half-cell reaction will react spontaneously with a substance on the right of any half-cell reaction having lower reduction potential. Therefore, Zn (s) will reduce Cu^{2+} (aq,1 M) spontaneously.
Cu^{2+} (aq,1 M) + Zn (s) $\rightleftharpoons$ Cu (s) + Zn^{2+} (aq, 1 M)

4) Changing the stoichiometric coefficients of a half-cell reaction does not effect the value of E° $_{red}$ because the electrode potential is an intensive property.

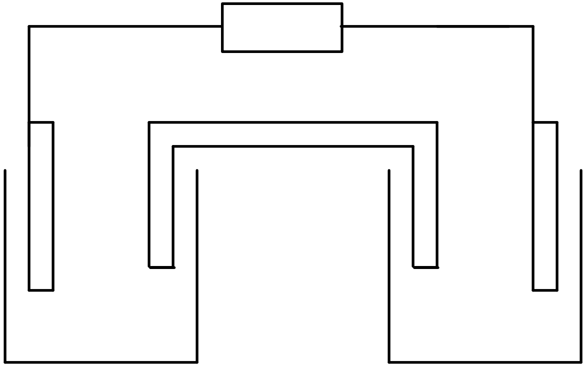
Example:

A Voltaic cell consists of a Mg electrode in a 1.0 M $Mg(NO_3)_2$ and a Ag electrode in a 1.0 M $AgNO_3$.

a) Calculate the **standard** emf of this electrochemical cell at 25° C.
b) Sketch the Galvanic cell for the spontaneous reaction .

Ag^{+} (aq, 1M) + 2 e^{-} $\rightleftharpoons$ Ag (s) E° $_{red}$ = + 0.80 V
Mg^{2+} (aq, 1M) + 2 e^{-} $\rightleftharpoons$ Mg (s) E° $_{red}$ = - 2.37 V

Apply the “diagonal “ rule:



Example:

Consider the reduction potential table to compute $E°_{cell}$ and use it to determine whether the following reactions will occur spontaneously.

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O(l)$ $E°_{red} = +1.49$ V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$ $E°_{red} = +1.36$V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O(l)$ $E°_{red} = +1.33$ V
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O(l)$ $E°_{red} = +1.23$ V
$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$ $E°_{red} = -0.13$ V

a) $Pb^{2+} + 2Cl^- \rightleftharpoons Pb(s) + Cl_2(g)$

a) Ans: ______

b) $6Mn^{2+} + 5Cr_2O_7^{2-} + 22H^+ \rightleftharpoons 6MnO_4^- + 10Cr^{3+} + 11H_2O(l)$

b) Ans:_____

c) $O_2(g) + 4Cl^- + 4H^+ \rightleftharpoons 2H_2O(l) + 2Cl_2(g)$

c) Ans: _______

Example:

Given the following sets of half-reactions, write the net reaction and calculate $E°_{cell}$ for the spontaneous changes that will occur.

a) $Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$ $E° = +0.27$ V
$PbSO_4(s) + 2e \rightleftharpoons Pb(s) + SO_4^{2-}$ $E° = -0.36$ V

b) $Al^{3+} + 3e^- \rightleftharpoons Al(s)$ $E° = -1.67$ V
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$ $E° = +1.09$ V

F) Concentration Effect on Cell Potential (Nernst Equation)

Thus far we have limited ourselves to those cells where the reactants are at unit concentration. However, in the lab, we do not usually restrict ourselves to only this one set of condition.

It is found that the **cell emf** and the **direction of the cell reaction**, can be controlled by the concentration of the species taking part in the reaction.

$$E_{cell} = E°_{cell} - \frac{RT}{nF} \ln Q$$

$$E_{cell} = E°_{cell} - \frac{0.0592}{n} \log Q \qquad \text{Nernst equation}$$

Example:

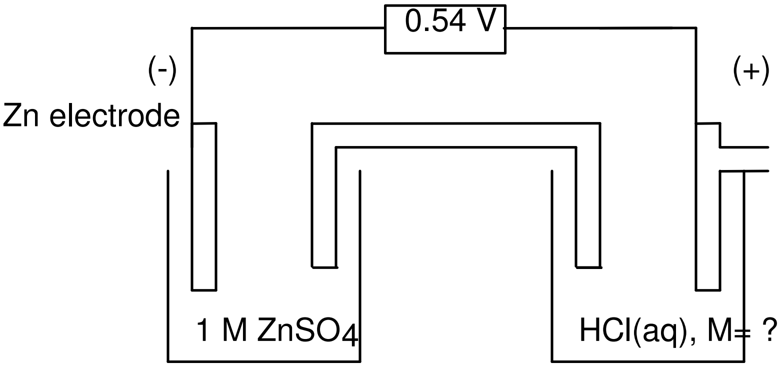
Calculate the emf of the Zn/Cu cell under the following conditions:

$$Zn\,(s) + Cu^{2+}\,(0.020M) \rightleftharpoons Cu\,(s) + Zn^{2+}\,(0.40\,M)$$

Given: $Cu^{2+} + 2\,e^- \rightleftharpoons Cu\,(s) \qquad E°_{red} = +0.34\,V$

$Zn^{2+} + 2\,e^- \rightleftharpoons Zn\,(s) \qquad E°_{red} = -0.76\,V$

Example:
Consider the Galvanic cell shown in the figure below



In a certain experiment, the emf of the cell is found to be 0.54 V at 25 °C. Suppose that $[Zn^{2+}]$ = 1.00 M and P_{H_2} = 1.0 atm. Calculate the concentration of the $[H^+]$.

Given: $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ $E°_{red} = -0.76V$

Example:
What is the potential of the cell represented by the following:

$$5\ Fe^{2+} + MnO_4^- + 8\ H^+ \rightleftharpoons 5\ Fe^{3+} + Mn^{2+}\ \ 4\ H_2O$$

when the concentration of **each** of the solute species is 0.010 M at 25° C?

Given: $Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$ $E°_{red} = -0.76V$

$MnO_4^- + 8\ H^+ + 5\ e^- \rightleftharpoons Mn^{2+} + 4\ H_2O$ $E°_{red} = +1.50\ V$

Answer=0.54 V

Example:
Calculate the cell potential.

a) $PbO_2\,(s) + SO_4^{\,2-}(0.010\ M) + 4H^+\ (0.10\ M) + Cu(s) \rightleftharpoons PbSO_4(s) + 2H_2O(l) + Cu^{2+}(0.0010M)$

Given: $PbO_2\,(s) + SO_4^{\,2-} + 4\,H^+ + 2\,e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$ $E°_{red} = +\ 1.69\ V$

$Cu^{2+} + 2\,e^- \rightleftharpoons Cu\ (s)$ $E°_{red} = +\ 0.34\ V$

Answer: 1.26 V

b) $3\,Zn\,(s) + 2\,Cr^{3+}\ (0.010\ M) \rightleftharpoons 3\ Zn^{2+}\ (0.020\ M) + 2\ Cr\,(s)$

Given: $Cr^{3+} + 3\,e^- \rightleftharpoons Cr\ (s)$ $E°_{red} = -\,0.74\ V$

$Zn^{2+} + 2\,e^- \rightleftharpoons Zn\ (s)$ $E°_{red} = -\,0.76\ V$

Answer: 0.03 V

Determining the pH of a solution by measuring the E_{cell}:

Here we will calculate the concentration of a single ionic species from the experimentally measured potential of a carefully designed cell.

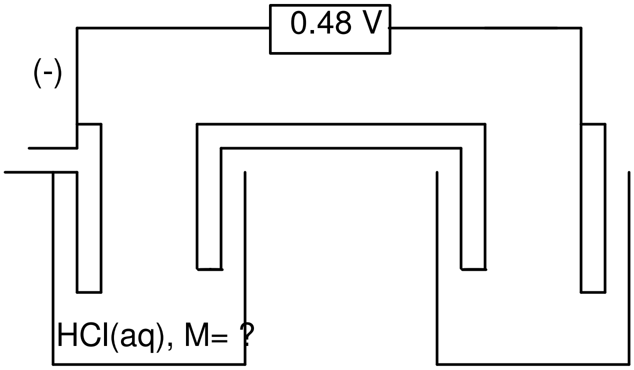
A Cu/H_2 cell is used to measure the [H^+] concentration. Voltage can be measured when the Cu electrode is connected to the **positive** terminal .Is the Cu electrode acting as a cathode or an anode?

Answer: ______

Is it an oxidation or a reduction reaction that is taking place in the Cu half-cell? **Answer** _____

The unknown was placed in the Hydrogen electrode compartment and the pressure of the hydrogen gas was controlled at 1 atm. The concentration of Cu^{2+} was adjusted to 1 M and the emf of the cell at 25 °C was determined to be 0.48 V. Calculate the pH of the unknown solution.

Given: $Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$ $E^\circ_{red} = +\ 0.34$ V



Reaction at the anode:

Reaction at the cathode:

The overall cell reaction is:

Setup:

Answer: pH= 2.40

By measuring E_{cell}, we can calculate the concentration of a specific ion in the solution. Hence, we can determine the solubility product constant, K_{sp}, of an insoluble salt of that specified ion.

Example:

A Galvanic cell is prepared and was consisted of Pb/Pb^{2+} and Sn/Sn^{2+}. Sn^{2+} concentration was held constant at 1.00 M. SO_4^{2-} is added to precipitate $PbSO_4$ (s). The SO_4^{2-} concentration in the lead compartment is then adjusted until it is 1.00 M. The emf of the cell is measured as 0.22 V. It is also observed that the Pb electrode is **negative** with respect to Sn.

$Pb(s) \rightleftharpoons Pb^{2+} + 2e^-$ $E^\circ_{red} = -0.13$ V

$Sn^{2+} + 2e^- \rightleftharpoons Sn(s)$ $E^\circ_{red} = -0.14$ V

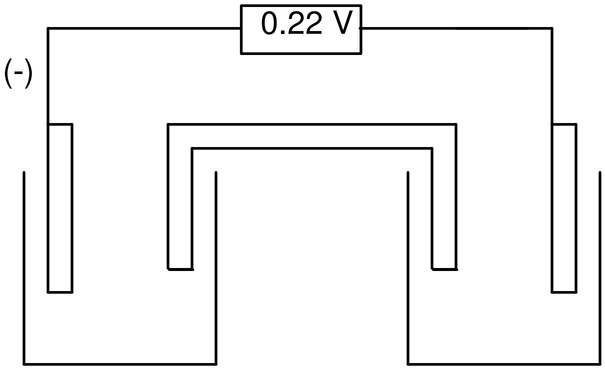
a) Choose the correct answer: The above information indicates that Pb is undergoing **(oxidation, reduction)**,at the **(anode, cathode)**, while Sn^{2+} is **(reduced, oxidized)**.

b) Write the reaction taking place at the **anode** .

c) Write the reaction taking place at the **cathode** .

d) Write the cell reaction .

e) Sketch the cell:



f) Calculate the concentration of Pb^{2+} .
Setup:

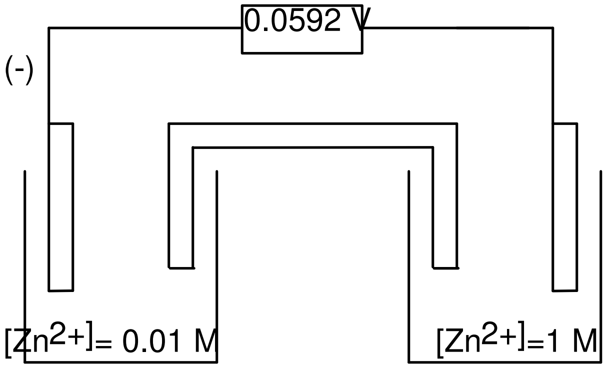
Answer: $[Pb^{2+}]$= __________M

g) Calculate the solubility product constant, K_{sp}, for $PbSO_4$ (s).
Setup:

Answer: K_{sp} = ___________

G) Concentration Cell

Because the reduction potential of an electrode depends on the concentration of the ions in solution, it is possible to construct a cell in which the cathode and anode compartments contain the **same electrode materials** but **different concentration of the ions**



Dilute: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

Concentrated: $Zn^{2+} + 2e^- \longrightarrow Zn(s)$

When the circuit is completed a spontaneous reaction takes place in a direction that tends to make the two $[Zn^{2+}]$ concentrations become equal. In the **more concentrated** side, $[Zn^{2+}]$ ions disappear forming Zn(s) in order to decrease $[Zn^{2+}]$ concentration. In the **more dilute** side, more Zn^{2+} will be produced.

At the **more dilute** compartment: $Zn(s) \longrightarrow Zn^{2+}_{dil}\ (0.010M) + 2e^-$

At the **more concentrated** compartment: $Zn^{2+}_{conc}(1.0M) + 2e^- \longrightarrow Zn(s)$

Cell reaction: $\underset{(conc)}{Zn(s) + Zn^{2+}(1.0\ M)} \longrightarrow \underset{(dil)}{Zn^{2+}(0.010\ M)} + Zn(s)$

The **reduction potential** of the individual half-reactions:

$$E_{red\ (conc)} = E°_{red\ (Zn)} - \frac{0.0592}{2} \log \frac{1}{[Zn^{2+}]_{conc}}$$

$$E_{red\ (dil)} = E°_{red\ (Zn)} - \frac{0.0592}{2} \log \frac{1}{[Zn^{2+}]_{dil}}$$

$$E_{cell} = E_{red\ (conc)} - E_{red\ (dil)}$$

$$= E°_{red\ (Zn)} - \frac{0.0592}{2} \log \frac{1}{[Zn^{2+}]_{conc}} - I\ E°_{red\ (Zn)} - \frac{0.0592}{2} \log \frac{1}{[Zn^{2+}]_{dil}}$$

$$\boxed{E_{cell} = 0.0 - \frac{0.0592}{2} \log \frac{[Zn^{2+}]_{dil}}{[Zn^{2+}]_{conc}}}$$

The **short notation** or the above cell reaction is: $Zn(s)\ |\ Zn^{2+}_{(dil)}\ ||\ Zn^{2+}_{(conc)}\ |\ Zn(s)$

Summary:
In general, for any concentration cell:

a) The voltage obtained from this type of cell is usually **small** and will continually decrease as the concentration in the two compartments approach each other.

b) The voltage becomes zero when the concentrations are the **same** in the two compartments.

The potential of the cell described in the previous page would be calculated as:

$$E_{cell} = 0.0 - \frac{0.0592}{2} \log \frac{0.010}{1.0}$$
$$= +\ 0.0592\ \text{V}$$

Example:
A concentration cell containing Cu(s) electrodes in two compartments. The concentration of Cu^{2+} of one solution is 0.500 M Cu^{2+} and the other solution is 1.25 M Cu^{2+}.

$$Cu^{2+}\ (aq, 1\ M) + 2\ e^- \rightleftharpoons Cu\ (s) \qquad E^\circ red = +0.34$$

a) Write the reaction taking place at the **negative** electrode.

b) Write the reaction taking place at the **positive** electrode.

c) Give the equation for the overall reaction.

d) Determine the potential of the above cell.
Setup:

Answer: + 0.0118 V

H. Calculation of the Equilibrium Constant, K, from the Standard Cell Potential., E°$_{cell}$.

Example:

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

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

Given: $Sn^{2+} (aq) + 2e^{-} \rightleftharpoons Sn (s)$ $E°_{red} = -0.14$ V

$2Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu^{+} (aq)$ $E°_{red} = +0.15$ V

Setup:

Answer: 6.0×10^{9}

Is the above reaction **spontaneous** at standard condition?Answer: _________

b) $2 Fe^{3+} (aq) + 2 I^{-} (aq) \rightleftharpoons I_2 (s) + 2 Fe^{2+} (aq)$

Given : $Fe^{3+} (aq) + e^{-} \rightleftharpoons Fe^{2+} (aq)$ $E°_{red} = +0.77$ V

$I_2 (s) + 2 e^{-} \rightleftharpoons 2 I^{-} (aq)$ $E°_{red} = +0.53$ V

Setup:

Answer: $K = 1.3 \times 10^{8}$

Is the above reaction **spontaneous** at standard condition? Answer: _______

Example:

Consider the reaction: $Pb^{2+} (0.50M) + Zn (s) \rightleftharpoons Pb (s) + Zn^{2+} (0.25 M)$

$Pb^{2+} (aq) + 2 e^{-} \rightleftharpoons Pb (s)$ $E°_{red} = -0.126V$

$Zn^{2+} (aq) + 2 e^{-} \rightleftharpoons Zn (s)$ $E°_{red} = -0.763$ V

a) Caculate E°$_{cell}$.

b) Caculate E$_{cell}$.

Setup:

c) Is the cell reaction spontaneous? You must justify your answer.

d) Identify the anode and cathode reaction.

Anode reaction:

Cathode reaction:

e) Calculate the equilibrium constant, K.

Setup: