UNIT B

ELECTROCHEMISTRY

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Background Material:
What is a Net Ionic Equation?
A net ionic equation represents the active species in a chemical reaction while omitting the inactive species. It is a brief but accurate description of the chemical change.

Steps involved when writing a net ionic equation

1. Write the chemical equation (**non-ionic equation**)

$$Pb(NO_3)_2(aq) + 2\,KI(aq) \rightarrow 2\,KNO_3(aq) + PbI_2(s)$$

2. Rewrite the equation dissociating all electrolytes into their component ions. (total **ionic equation**)

$$Pb^{2+}(aq) + 2\,NO_3^-(aq) + 2\,K^+(aq) + 2\,I^-(aq) \rightarrow 2\,K^+(aq) + 2\,NO_3^-(aq) + PbI_2(s)$$

3. Cancel all species that do not change. (these species are not really part of the chemical change) What remains is the **net ionic equation**.

$$Pb^{2+}(aq) + 2\,I^-(aq) \rightarrow PbI_2(s)$$

Write a net ionic equation for the following

A copper strip is placed in a solution of silver nitrate

Theoritical Definition

- explained using a 1/2 reactions

1/2 reaction - an equation that we write to show what a particular species does as it reacts
- is a balanced chemical equation that represents either a gain or loss of electrons in a substance

Reduction - a reaction whereby a species gains e^-

Oxidation - a reaction whereby a species loses an e^-

Oxidation and reduction reactions occur simultaneously within the overall reaction. Each reaction causes the other reaction to occur.

agent - chemical species that causes another species to do something

oxidizing agent

- causes oxidation by removing (gaining) electrons in a redox reaction and is itself reduced
- a strong oxidizing agent (OA) **forms a strong reduction 1/2 reaction**

reducing agent

- promotes reduction by donating (losing) electrons in a redox reaction and is itself oxidized
- a strong reducing agent (RA) **forms a strong oxidation 1/2 reaction**

The sum of the oxidation 1/2 reaction and reduction 1/2 reaction is called a **Redox reaction.**

For each of the following, write a redox reaction. Also determine OA, RA, RS, OS.

eg #1 $Al(s) + Cd(NO_3)_2(aq) \longrightarrow Al(NO_3)_3(aq) + Cd(s)$

eg. #2 $Au(s) + Br_2(l) \longrightarrow$

eg.#3 $Fe^{3+}(aq) + Cu(s) \longrightarrow Fe^{2+}(aq) + Cu^{2+}(aq)$

Recall **- charge or oxidation number ↑** **- oxidation – LEO**

- charge or oxidation number ↓ **- reduction - GER**

1. **State whether the following changes are oxidation or reduction**

a. Fe^{2+} → Fe^{3+} ____________________

b. $2\ O^{2-}$ → O_2 ____________________

c. $2\ N^{3-}$ → N_2 ____________________

d. X^{5-} → X^{7-} ____________________

e. Br_2 → $2\ Br^{-}$ ____________________

2. **State whether the following changes are oxidation or reduction and write the electrons in the equation.**

a. X_2 → $2X^{2-}$ ____________________

b. Mn^{4+} → Mn^{2+} ____________________

c. P_4 → $4P^{3-}$ ____________________

d. Z^{5-} → Z^{2-} ____________________

e. $6N^{3-}$ → $3\ N_2$ ____________________

f. J^{4+} → J^{2-} ____________________

3. Write the two half-reactions for each of the following net ionic equations. (label the two reactions)

a. $2\ Al(s) + 6\ H^{+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ H_2(g)$

b. $2\ Ba(s) + O_2(g) \rightarrow 2Ba^{2+}(aq) + 2\ O^{2-}(aq)$

c. $Cl_2(g) \quad + \quad 2\,Br^-(aq) \rightarrow 2\,Cl^-(aq) \quad + \quad Br_2(aq)$

d. $2\,Z^{4-}(aq) \quad + \quad 3\,Q^{2+}(aq) \rightarrow 2\,Z^{1-}(aq) \quad + \quad Q_3(aq)$

4. For each of the following reactions indicate:OS, RS, OA, RA.
   a. $Br_2(aq) \quad + \quad Sn^{2+}(aq) \rightarrow 2\,Br^-(aq) \quad + \quad Sn^{4+}(aq)$

   b. $Pb^{2+}(aq) \quad + \quad 2\,K(s) \rightarrow 2\,K^+(aq) \quad + \quad Pb(s)$

   c. $X^{2-}(aq) \quad + \quad J(s) \rightarrow X^{3+}(aq) \quad + \quad J^{4-}(aq)$

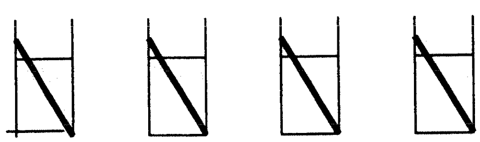
DEMONSTRATION – Introduction to Redox

Procedure:

1. Four sets of the following solutions are prepared
   $Cu(NO_3)_2(aq)$ $Zn(NO_3)_2(aq)$ $MgNO_3)_2(aq)$ $AgNO_3(aq)$

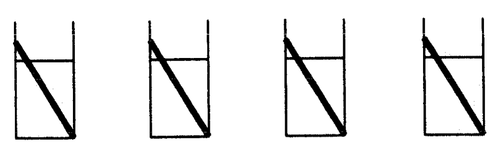
2.

Strips of **copper** are placed in the 1st set of solutions



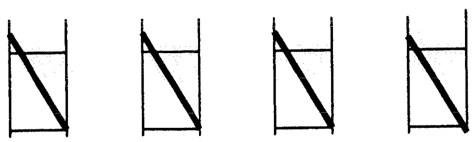
$Cu(NO_3)_2(aq)$ $Zn(NO_3)_2(aq)$ $Mg(NO_3)_2(aq)$ $AgNO_3(aq)$

Strips of **zinc** are placed in the 2nd set of solutions



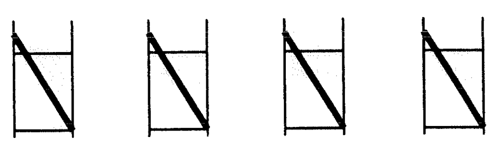
$Cu(NO_3)_2(aq)$ $Zn(NO_3)_2(aq)$ $Mg(NO_3)_2(aq)$ $AgNO_3(aq)$

Strips of **magnesium**are placed in the 3rd set of solutions



$Cu(NO_3)_2(aq)$ $Zn(NO_3)_2(aq)$ $Mg(NO_3)_2(aq)$ $AgNO_3(aq)$

Strips of **silver** are placed in the 4th set of solutions



$Cu(NO_3)_2(aq)$ $Zn(NO_3)_2(aq)$ $Mg(NO_3)_2(aq)$ $AgNO_3(aq)$

Observations:

	$Cu^{2+}(aq)$	$Zn^{2+}(aq)$	$Mg^{2+}(aq)$	$Ag^{+}(aq)$
Cu(s)	NR	NR	NR	R
Zn(s)	R	NR	NR	R
Mg(s)	R	R	NR	R
Ag(s)	NR	NR	NR	NR

NR – no reaction **R – spontaneous reaction**

1. If the forward reaction is spontaneous, will the reverse reaction also be spontaneous?

2. Does a metal react spontaneously with its own ion?

3. List the metallic ions in order of their tendency to form metals. Write ½ reactions for these ions. What type of ½ reactions are these?

4. List the metals in order of their tendency to form ions. Write ½ reactions for these metals. What type of ½ reactions are these?

5. How does the list for question 3 compare to the list for question 4?

Analysis: From the lab, we found that when listing the oxidizing agents in order of reactivity according to their half reactions, we got the following reduction half reaction table.

SOA

increasing strength of OA ↑	$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$	↓ increasing strength of RA
	$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$	
	$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$	
	$Mg^{2+}(aq) + 2e^{-} \rightarrow Mg(s)$	

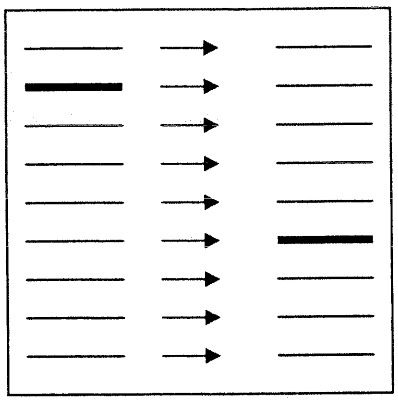
SRA

Spontaneity Rule

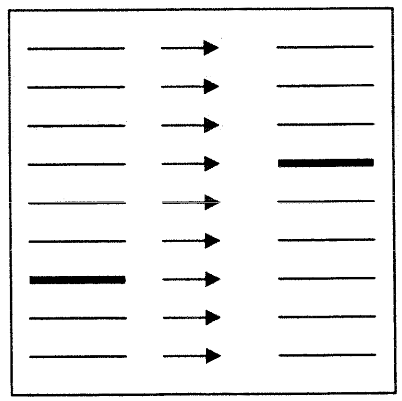
A spontaneous reaction only occurs if the OA is above the RA on the reduction half-reaction table

Spontaneous	Nonspontaneous
O.A.	R.A. (on the table)
is above the	is below the
R.A. (on the table)	O.A.

If the RA is above the OA on the reduction half-reaction table the reaction will not be spontaneous



SPONTANEOUS



NONSPONTANEOUS

Building Reduction ½ reaction tables.

eg.1 Metals K, L, M and N and their salts are selectively reacted and yield the following data:

$L^{2+}(aq) + 2\,K(s) \rightarrow L(s) + 2\,K^{+}(aq)$

$K(s) + N^{+}(aq) \rightarrow$ no change

$K^{+}(aq) + M(s) \rightarrow K(s) + M^{+}(aq)$

$N(s) + M^{+}(aq) \rightarrow N^{+}(aq) + M(s)$

Using the above data:

a. The strongest oxidizing agent is ________

b. The strongest reducing agent is ________

c. The substance most readily oxidized is ______

d. The weakest oxidizing agent is ______ eg.2 Metals M, N, O, and P and their salts are reacted and yield the following results:

$2\ M^+(aq) + N(s) \rightarrow N^{2+}(aq) + 2\ M(s)$

$O^{2+}(aq) + N(s) \rightarrow$ no reaction

$P^{3+}(aq) + 3\ M(s) \rightarrow P(s) + 3\ M^+(aq)$

a. The strongest reducing agent is _____
b. The strongest oxidizing agent is _____
c. The species that attracts electrons most readily is _____

eg.3 The following reactions were observed to occur:

$Y_2 + X^{2+} \rightarrow 2\ Y^- + X^{4+}$

$3\ Q^{2-} + 2\ P \rightarrow 3\ Q^{4-} + 2\ P^{3+}$

$2\ P^{3+} + 6\ Y^- \rightarrow 2\ P + 3\ Y_2$

$3\ X^{4+} + 3\ V^{2-} \rightarrow V_3 + 3\ X^{2+}$

From the above data, construct a mini-reduction ½ reaction table. Include electrons.

Previous Diploma Exam Questions:

1. As part of a laboratory procedure, a student recorded observations after placing strips of metal into aqueous solutions according to the following combinations.
N/C = no change and R = reaction.

	$Be^{2+}(aq)$	$Cd^{2+}(aq)$	$Ra^{2+}(aq)$	$V^{2+}(aq)$
Be(s)	N/C	R	N/C	R
Cd(s)	N/C	N/C	N/C	N/C
Ra(s)	R	R	N/C	R
V(s)	N/C	R	N/C	N/C

The grouping in which the oxidizing agents are arranged from weakest to strongest is

a) Cd(s), V(s), Be(s), Ra(s)
b) Ra(s), Be(s), V(s), Cd(s)
c) $Ra^{2+}(aq)$, $Be^{2+}(aq)$, $V^{2+}(aq)$, $Cd^{2+}(aq)$
d) $Cd^{2+}(aq)$, $V^{2+}(aq)$, $Be^{2+}(aq)$, $Ra^{2+}(aq)$

2. In the reaction
$2\ Ag^{1+}(aq) + Cu(s) \rightarrow 2\ Ag(s) + Cu^{2+}(aq)$,
the silver ion is

a) oxidized
b) the reducing agent
c) losing an electron
d) the oxidizing agent

3. In redox reactions,
a) oxidizing agents lose electrons and are oxidized
b) reducing agents lose electrons and are reduced
c) oxidizing agents gain electrons and are reduced
d) reducing agents gain electrons and are oxidized

4. Four elements Z, T, X, and R, form diatomic molecules and negative ions. The following observations are made:

$Z_2 + 2X^{1-}(aq) \rightarrow 2Z^{1-}(aq) + X_2$

$T_2 + 2R^{1-}(aq) \rightarrow$ no reaction

$X_2 + 2R^{1-}(aq) \rightarrow 2X^{1-}(aq) + R_2$

When the elements are arranged in order from

least reactive to most reactive, the list is

a) Z_2, X_2, R_2, T_2
b) T_2, R_2, X_2, Z_2
c) T_2, R_2, Z_2, X_2
d) T_2, X_2, R_2, Z_2

5. A student determined that the following combinations of unidentified metals and their aqueous ions would react spontaneously.

$A(s) + B^{2+}(aq) \rightarrow A^{2+}(aq) + B(s)$

$B(s) + C^{2+}(aq) \rightarrow B^{2+}(aq) + C(s)$

$C(s) + D^{2+}(aq) \rightarrow C^{2+}(aq) + D(s)$

$B(s) + E^{2+}(aq) \rightarrow B^{2+}(aq) + E(s)$

$D(s) + E^{2+}(aq) \rightarrow D^{2+}(aq) + E(s)$

The student should predict that the strongest reducing agent is

a) E(s)
b) A(s)
c) B(s)
d) C(s)

6. For the reaction
$Fe(s) + Sn^{4+}(aq) \rightarrow Sn^{2+}(aq) + Fe^{2+}(aq)$, a true statement is

a) $Sn^{4+}(aq)$ causes Fe(s) to be reduced
b) $Sn^{2+}(aq)$ is the oxidizing agent
c) Fe(s) causes $Sn^{4+}(aq)$ to be reduced
d) $Fe_{(s)}$ is the oxidizing agent

7. In the reaction
$X(s) + T^{3+}(aq) \rightarrow X^{1+}(aq) + T^{2+}(aq)$, the reducing agent is

a) X(s)
b) $X^{1+}(aq)$
c) $T^{3+}(aq)$
d) $T^{2+}(aq)$

<u>Answers</u>	
1. C	2. D
3. C	4. B
5. B	6. C
7. A	

Predicting Redox Reactions:

When several reducing agents and oxidizing agents are added together, a reaction will occur between the substance most readily oxidized and the substance most readily reduced. A reduction ½ reaction table must be used to determine the reacting species.

1. List all species mentioned

- **all soluble ionic compounds must be dissociated into their component ions**
- **strong acids dissociate into $H^+(aq)$ ions and their negative partner ions**
- **acidic solution , list $H^+(aq)$**
- **everything else must be left as is (weak acids, molecular compounds)**
- **From the reduction ½ reaction table determine if the substance is an OA or RA**

Note: $H_2O(l)$, $Fe^{2+}(aq)$, $Sn^{2+}(aq)$, and $Cr^{2+}(aq)$ may act as either OA or RA. Label both possibilities on your list.

2. **Look at the reduction ½ reaction table and determine the substance most readily reduced.(SOA) Write the reduction ½ reaction as it appears on the table.**
3. **Look again at the reduction ½ reaction table and determine the substance most readily oxidized. (SRA) Write the oxidation ½ reaction in reverse to what it appears on the table.**
4. **Multiply one or both the ½ reaction by a number so that the number of electrons gained will equal the number of electrons lost.**
5. **Add the two half-reactions together and determine if spontaneous or not.**

Questions

1. A copper strip is placed in a solution of lead (II) nitrate.

2. An aluminum wire is placed in a solution of nitric acid.

3. A potassium dichromate solution is titrated with an acidic tin (II) chloride solution.

4. Oxygen gas is bubbled through a solution of iron (II) nitrate.

5. A student uses hydrobromic acid to acidify a potassium dichromate solution for later use as an oxidizing solution.

6. A laboratory technician stores an aqueous solution of iron (III) chloride in a nickel plated container.

7. An iron bolt is exposed to air and water (a reaction which causes many millions of dollars damage each year on Earth).

8. Oxygen gas is bubbled over a silver mesh immersed in a solution of potassium iodide

Old Related Diploma Questions

1. The substance that does NOT act as both an oxidizing and a reducing agent is

a) $Fe^{2+}(aq)$
b) $Sn^{2+}(aq)$
c) $H_2O(l)$
d) $Cd^{2+}(aq)$

2. The balanced net ionic (redox) equation for the reaction between Pb(s) and $Ag^{1+}(aq)$ is

a) $Pb(s) + 2\,Ag^{1+}(aq) + 2\,e^{1-} \rightarrow 2\,PbAg(s)$
b) $Pb(s) + Ag^{1+}(aq) \rightarrow Pb^{2+}(aq) + Ag(s)$
c) $Pb(s) + 2\,Ag^{1+}(aq) \rightarrow Pb^{2+}(aq) + 2\,Ag(s)$
d) $Pb(s) + Ag^{1+}(aq) + 2e^{1-} \rightarrow Pb^{2+}(aq) + 2\,Ag(s) + 2\,e^{1-}$

3. Which of the following reactions would occur spontaneously?

   a) $Fe(s) + 2 Cl^{1-}(aq) \rightarrow Fe^{2+}(aq) + Cl_2(g)$
   b) $2 Ag(s) + Cu^{2+}(aq) \rightarrow 2 Ag^{1+}(aq) + Cu(s)$
   c) $Cu^{2+}(aq) + Sn^{2+}(aq) \rightarrow Cu(s) + Sn^{4+}(aq)$
   d) $MnO_4^{1-}(aq) + 8 H^{1+}(aq) + Pb^{2+}(aq) \rightarrow Pb(s) + Mn^{2+}(aq) + 4 H_2O(l)$

4. The species that will oxidize $Pb(s)$ to $Pb^{2+}(aq)$ but will not oxidize $I^{1-}(aq)$ to $I_2(s)$ are

   a) $F_2(g)$ and $Fe^{3+}(aq)$
   b) $Cu^{2+}(aq)$ and $Br_2(l)$
   c) $Cd^{2+}(aq)$ and $Ag^{1+}(aq)$
   d) $Cu^{2+}(aq)$ and $Sn^{4+}(aq)$

5. Predict which metal could be used to construct a storage container for an $AgNO_3(aq)$ solution.

   a) tin
   b) iron
   c) gold
   d) copper
   e)

6. All redox reactions must involve a transfer of

   a) protons
   b) electrons
   c) neutrons
   d) heat

7. $Sn^{2+}(aq)$ ions are more readily reduced than

   a) $Zn^{2+}(aq)$
   b) $Pb^{2+}(aq)$
   c) $Cu^{2+}(aq)$
   d) $Hg^{2+}(aq)$

8. Laboratory wastes must be carefully collected and stored for proper disposal. Which of the following materials would be suitable as a container in which to store an aqueous solution of nickel(II) nitrate?

   a) aluminum
   b) chromium
   c) tin
   d) zinc

9. In which change, are electrons gained?

   a) $Ca^{2+}(aq)$ to $Ca(s)$
   b) $2 Cl^{1-}(aq)$ to $Cl_2(g)$
   c) $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$
   d) $NaCl(s)$ to $Na^{1+}(aq)$ and $Cl^{1-}(aq)$

Answers

1. D	2. C
3. C	4. D
5. C	6. B
7. A	8. C
9. A	

Writing Complex Half-Reaction Equations For redox Reactions

Many metals and non-metals commonly have simple half-reaction equations, however polyatomic ions and molecular compounds have more complicated half-reactions that are generally done in an acidic or basic solution. In these half-reactions, $H_2O(l)$, $OH^-(aq)$, and $H^+(aq)$ play an important role, therefore a new method must be used to write these half-reactions

THE HALF-REACTION METHOD:

This method involves working out the half reaction step by step and then adding them together:

For acidic solutions:

Example: Balance the following equation by the half-reaction method:

$$HClO_2 + I^- \rightarrow Cl_2 + HIO \quad \text{(acidic solution)}$$

Step 1: Break the unbalanced equation into 2 skeleton half-reactions

$$HClO_2 \rightarrow Cl_2$$

$$I^- \rightarrow HIO$$

Step 2: Balance the main actor first! (everything but hydrogen and oxygen)

$$2\ HClO_2 \rightarrow Cl_2$$

$$I^- \rightarrow HIO$$

Step 3: Balance the **oxygen atoms** in each half-reaction by adding **H_2O** to the side **low** in oxygen:

$$2\ HClO_2 \rightarrow Cl_2 + 4H_2O$$

$$I^- + H_2O \rightarrow HIO$$

Step 4: Balance the **hydrogen atoms** by adding **H^+** to the side **low** in hydrogen:

$$2\ HClO_2 + 6\ H^+ \rightarrow Cl_2 + 4H_2O$$

$$I^- + H_2O \rightarrow HIO + H^+$$

Step 5: Balance the **charge** by adding **electons** to the side **high in positive** charge

$$2\ HClO_2 + 6\ H^+ + 6e^- \rightarrow Cl_2 + 4H_2O$$

$$I^- + H_2O \rightarrow HIO + H^+ + 2\ e^-$$

Step 6: Add the two half-reactions together to cancel out the electrons

$$2\ HClO_2 + 6\ H^+ + 6e^- \rightarrow Cl_2 + 4H_2O$$

$$\underline{I^- + H_2O \rightarrow HIO + H^+ + 2\ e^-\ (x3)}$$

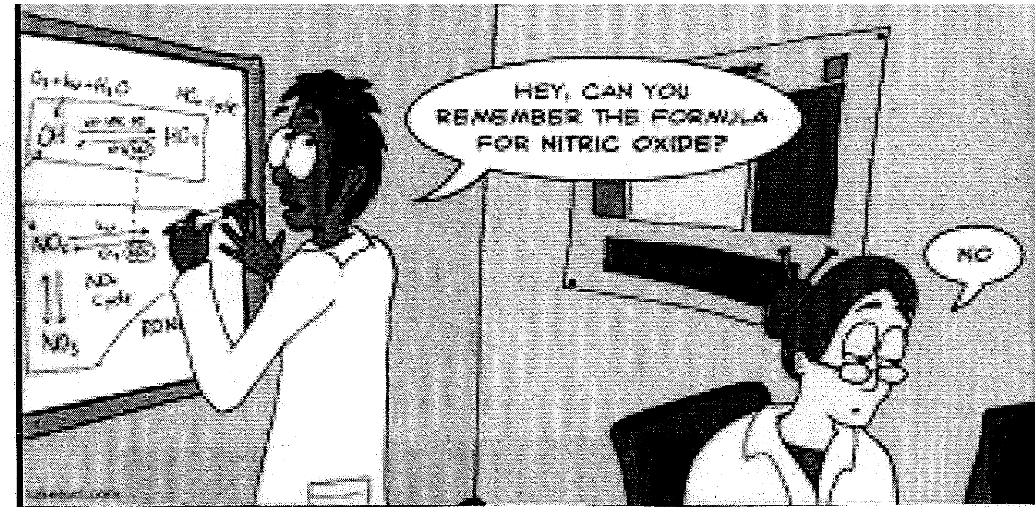
$$2\ HClO_2 + 6\ H^+ + 3\ I^- + 3\ H_2O \rightarrow Cl_2 + 3\ HIO + 4\ H_2O + 3\ H^+$$

Reduced to: $2\ HClO_2 + 3\ H^+ + 3\ I^- \rightarrow Cl_2 + H_2O + 3\ HIO$

Exercise: Balance the following Equations

1. $Zn + NO_3^- \rightarrow Zn^{2+} + N_2O$ (acidic solution)

2. $AsO_3^{3-} + BrO_3^- \rightarrow AsO_4^{3-} + Br^-$ (acidic solution)



Balance the following half-reactions:

4. P_4 → $H_2PO_4^-$ (acidic solution)

5. NO → N_2O (basic solution) – omit

6. IO_3^- → I^- (acidic solution)

Disproportionation (Auto-oxidation) Reactions

A disproportionation reaction is a reaction in which some atoms in a single element in a reactant are oxidized and others are reduced. For such a reactant behavior to be possible, the reactant must contain an element that is capable of having at least 3 oxidation numbers – its original number plus one higher and one lower oxidation number. Note that any given atom is not both oxidized and reduced. Some are oxidized and other atoms of the same element are reduced.

Example: **3 Br₂ + 3 H₂O → HBrO₃ + 5 HBr**

$$3\,\underline{Br}_2\;(0) + 3\,H_2O \rightarrow H\underline{Br}O_3\;(+5) + 5\,H\underline{Br}\;(-1)$$

Some bromine atoms have been oxidized and some have been reduced.
When balancing these equations, we simply write the formula for the substance undergoing disproportionation twice. (We pretend it is two different substances and proceed as before)

Questions: Balance the following disproportionation equations

1. $NO_2 \rightarrow NO_3^- + NO$ (acidic solution)

2. $S \rightarrow S^{2-} + SO_3^{2-}$ (basic solution)

3. $H_5IO_6^- + I^- \rightarrow I_2$ (acidic solution)

<u>Answers:</u>

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1. $4\,Zn + 10\,H^+ + 2\,NO_3^- \rightarrow 4\,Zn^{2+} + N_2O + 5\,H_2O$
2. $3\,AsO_3^{3-} + BrO_3^- \rightarrow 3\,AsO_4^{3-} + Br^-$
3. $2\,MnO_4^- + 6\,H^+ + 5\,SO_3^{2-} \rightarrow 2\,Mn^{2+} + 3\,H_2O + 5\,SO_4^{2-}$

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1. $2\,CrO_4^{2-} + 3\,SO_3^{2-} + H_2O \rightarrow 2\,CrO_2^- + 3\,SO_4^{2-} + 2\,OH^-$
2. $SeO_3^{2-} + Cl_2 + 2\,OH^- \rightarrow SeO_4^{2-} + 2\,Cl^- + H_2O$
3. $3\,CuO + 2\,NH_3 \rightarrow 3\,Cu + 3\,H_2O + N_2$
4. $16\,H_2O + P_4 \rightarrow 4\,H_2PO_4^- + 24\,H^+ + 20\,e^-$
5. $2\,NO + H_2O + 2\,e^- \rightarrow N_2O + 2\,OH^-$
6. $6\,H^+ + IO_3^- + 6\,e^- \rightarrow I^- + 3\,H_2O$

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1. $3\,NO_2 + H_2O \rightarrow 2\,NO_3^- + NO + 2H^+$
2. $3\,S + 6\,OH^- \rightarrow 3\,H_2O + 2\,S^{2-} + SO_3^{2-}$
3. $14\,H^+ + 2\,H_5IO_6^- + 12\,I^- \rightarrow 7\,I_2 + 12\,H_2O$

Oxidation States

An oxidation number is the real or apparent charge an atom or ion has when all bonds are assumed to be ionic. In this system, the ***oxidation state*** of an atom in an entity defined as the apparent net electrical charge that an atom would have if electron pairs in covalent bonds belonged entirely to the more electronegative atom. The false assumption is made that all bonds are ionic. An oxidation state is a useful idea for keeping track of electrons, but does not represent the actual charge of an atom; oxidation states are arbitrary charges that should not be confused with actual electric charges. The purpose of this assumption is to be able to determine if oxidation or reduction has taken place in situations where it is not obvious.

RULES FOR DETERMINING OXIDATION NUMBERS:

1. All **pure elements** have an oxidation number of zero.

$Mg(s)$ = 0	$Ca(s)$ = 0	$S_8(s)$ = 0
$P_4(s)$ = 0	$He(g)$ = 0	$Cl_2(g)$ = 0
$Hg(l)$ = 0	$Br_2(l)$ = 0	$Ba(s)$ = 0

2. All **simple ions** have an oxidation number of the charge of the ion.

$Mg^{2+}(aq)$ = +2	$O^{2-}(aq)$ = -2	$Al^{3+}(aq)$ = +3
$Br^{-}(aq)$ = -1	$P^{3-}(aq)$ = -3	$S^{2-}(aq)$ = -2
$N^{3-}(aq)$ = -3	$Ca^{2+}(aq)$ = +2	$F^{-}(aq)$ = -1

3. The oxidation number of all the **alkali metals** in any compound is **1+**, as in K^+, Li^+, and Na^+.

4. The oxidation number of the **alkaline earth metals** in compounds is **2+**. as in Ca^{2+}, Mg^{2+}, and Ba^{2+}.

5. The oxidation number for **oxygen in compounds** is almost always **2-**. However in **peroxides** oxygen is **1-** as in H_2O_2.

6. In molecular compounds that do **not contain hydrogen or oxygen**, the more electronegative element is assigned an oxidation number equal to the negative charge it is usually has when it is in ionic compounds. e.g. The oxidation number in PCl_3 is -1 and in CS_2 , the sulfur is -2.

7. The oxidation number for **hydrogen in compounds** is almost always **1+**. However in **metallic hydrides** like NaH, CaH_2, or BaH_2, hydrogen is **1-**.

8. All other oxidation numbers are assigned so that the sum of the oxidation numbers equals the net charge on the molecule or polyatomic ion.

EXAMPLE: Provide the oxidation number of each of the underlined species

$H_2\underline{S}O_4$	$\underline{N}O_3^-$	$\underline{P}_2O_5$	$Ca\underline{I}_2$	$\underline{P}O_4^{3-}$	$\underline{C}O_3^{2-}$
$\underline{6+}$	$\underline{5+}$	$\underline{5+}$	$\underline{1-}$	$\underline{5+}$	$\underline{4+}$

Exercise

1. Give the oxidation number of the following underlined species:

a. $H_3\underline{B}O_3$ $\underline{C}H_4$ $O\underline{Br}_3^+$ $\underline{S}O_3^{2-}$ $H\underline{C}O_3^{1-}$ $\underline{Mn}O$ $\underline{H}_2O_2$

_____ _____ _____ _____ _____ _____ _____

b. $\underline{V}O_2^+$ $\underline{C}_2H_5OH$ $H\underline{N}O_2$ $\underline{Cr}_2O_7^{2-}$ $\underline{Xe}O_4^{6-}$ $\underline{S}_2O_6^{2-}$ $H\underline{Xe}O$

_____ _____ _____ _____ _____ _____ _____

2. State whether the following changes involve oxidation or reduction:

a. $AsO_3^- \rightarrow AsO_2$ __________

b. $MnO_4^- \rightarrow MnO_2$ __________

c. $H_2O_2 \rightarrow O_2$ __________

d. $C_2H_5OH \rightarrow CO_2$ __________

e. $C_2O_4^{2-} \rightarrow CH_4$ __________

f. $Na_2HPO_4 \rightarrow P_2O_5$ __________

3. For each of the following reactions, identify the **oxidizing agent** and **reducing agent:**

a. $Sn + NO_3^- \rightarrow SnO_2 + NO$

b. $PbCl_4 + O^{2-} \rightarrow PbCl_2 + O_2$

c. $H_3PO_2 + Cr_2O_7^{2-} \rightarrow H_3PO_4 + Cr^{3+}$

d. $CrO_2^- + S_2O_8 \rightarrow CrO_4^{2-} + SO_4^{2-}$

Recall from the beginning of this Unit

- If the oxidation number increases: Oxidation is the taking place
  The reactant species is the RA
- If the oxidation number is decreasing :Reduction is taking place
  The reactant species is the OA

Photosynthesis is a redox reaction that occurs in plants

solar energy + $6\ CO_2(g)$ + $6\ H_2O(l)$ → $C_6H_{12}O_6(s)$ + $6\ O_2(g)$

$C_6H_{12}O_6(s)$ (glucose) is manufactured and stored.

1. Show that the above reaction is a redox reaction by assigning oxidation numbers to all species.

2. Show the half reactions for the above reaction: (assume acidic)

3. In animals the reverse of the above reaction occurs, what is it called?

4. One redox reaction important to many people is the combustion of natural gas ($CH_4(g)$)
   a. Write the equation for the combustion of methane

   b. Justify that the methane reaction is a redox reaction by assigning oxidation numbers to all species.

BALANCING REDOX REACTION USING OXIDATION NUMBERS

Rules:
1. Assign oxidation numbers to all species
2. Determine the number of e- transferred per atom or ion
3. Determine the number of e- transferred per OA&RA
4. Balance the number of e- using appropriate coeffients for the OA & RA in the equation.
5. Balance the remaining species by inspection and by charge if necessary.

e.g.

__ $Cr_2O_7^{2-}(aq)$ + __ $H^+(aq)$ + __ $C_2H_5OH(aq)$ → __ $Cr^{3+}(aq)$ + __ $H_2O(l)$ + __ $CH_3COOH(aq)$

Balance the following redox reactions using oxidation numbers

1. __ $CuO(s)$ + __ $NH_3(g)$ → __ $N_2(g)$ + __ $H_2O(l)$ + __ $Cu(s)$

2. __ $MnO_4^-(aq)$ + __ $H_2Se(g)$ + __ $H^+(aq)$ → __ $Se(s)$ + __ $Mn^{2+}(aq)$ + __ $H_2O(l)$

3. __ $PbO_2(s)$ + __ $Pb(s)$ + __ $H_2SO_4(aq)$ → __ $PbSO_4(s)$ + __ $H_2O(l)$

Sometimes all the reactants and products are not known. Only the main reactants and products are given along with the type of reaction (acidic or basic). After the initial reactants and products are balanced using oxidation numbers, $H_2O(l)$, $H^+(aq)$, $OH^-(aq)$ are added to balance the remainder of the reaction.

e.g.

1. Balance the following chemical equations for reactions in an **acidic solution:**

   a. __ $Cr_2O_7^{2-}(aq)$ + __ $Cl^-(aq)$ → __ $Cr^{3+}(aq)$ + __ $Cl_2(aq)$

   b. __ $IO_3^-(aq)$ + __ $HSO_3^-(aq)$ → __ $SO_4^{2-}(aq)$ + __ $I_2(s)$

2. Balance the following chemical equations for reactions in a **basic solution:**

a. __ $MnO_4^-(aq)$ + __ $SO_3^{2-}(aq)$ → __ $SO_4^{2-}(aq)$ + __ $MnO_2(s)$

b. __ $ClO_3^-(aq)$ + __ $N_2H_4(aq)$ → __ $NO(g)$ + __ $Cl^-(aq)$

3. __ $CH_3OH(aq)$ + __ $MnO_4^-(aq)$ → __ $Mn^{2+}(aq)$ + __ $CH_2O(aq)$ (acidic solution)

CHEMISTRY 30 - Stoichiometry Review

Step 1	**Equation Step**	**Step 3**	**Ratio Step**
Step 2	**Mole Step**	**Step 4**	**Answer step**

Solve the following stoichiometry problems. Show ALL work and steps.

1. When gasoline burns in an automobile engine water vapour is produced. What mass of water would be produced from the complete combustion of 15.0g of $C_8H_{18}(l)$ (one of the components of gasoline)? (ans: 21.3g)

2. In the laboratory preparation of oxygen, potassium chlorate is heated. The products are potassium chloride and oxygen. What mass of potassium chlorate must be decomposed to produce 6.40g of oxygen gas? (ans: 16.3g)

3. An excess of barium chloride solution was added to 400mL of silver nitrate solution and 5.10g of precipitate was formed. What was the concentration of the silver nitrate solution? (ans: 0.0890mol/L)

4. If 25.0mL of a sulfuric acid solution reacts completely with 15.0mL of a 0.200mol/L solution of sodium hydroxide, what is the concentration of the sulfuric acid solution? (ans: 0.0600mol/L)

Redox Stoichiometry

- The stoichiometric method is used to predict and analyze the quantity of substance involved in a chemical reaction.
- The most common method used is titration.
- In redox reactions, one reagent (the titrant) which is usually a strong reducing agent or strong oxidizing agent is slowly added to another (sample) until an abrupt change in a property (endpoint) occurs.
- Two very common oxidizing agents that are used are acidic solution of permanganate of dichromate ions. Both undergo a colour change as they react with a reducing agent as shown below.

$MnO_4^-(aq)$ + $H^+(aq)$ 5 e- → $Mn^{2+}(aq)$ + 4 $H_2O(l)$

Purple-pink **colourless**

$Cr_2O_7^{2-}(aq)$ + 14 $H^+(aq)$ + 6 e- → 2 $Cr^{3+}(aq)$ + 7 $H_2O(l)$

Orange **green**

Step 1 - Equation Step (Redox Reaction)
From the given information, make a chemistry 30 redox reaction

a. List all the chemical species as they would actually appear in solution.
b. Find the SOA and write its reduction ½ reaction using the data book
c. Find the SRA and write its oxidation ½ reaction using the data book
d. Write a redox reaction by adding up the two ½ reactions ($\#e^-_{lost} = \#e^-_{gained}$)

At this point, determine what substance has sufficient information to find the number of moles(called the **Given** substance). Also determine what substance you require more information on (called the **Required** substance).

Step 2 - Mole Step

a. If the numbers in the question are already in moles – do nothing and proceed to step 3
b. If the numbers in the question are in units other than moles, then those numbers must be changed into mole units.

Check: How is my information expressed

In grams or kg	In mol/L and Litres	In kPa, litre and °C
Use n = m/MM (from chem 20)	Use n = Cv (from chem 20)	n = PV/RT (from chem 20)

* Note: All expressed answers are to expressed as

<u>**Number**</u> <u>**unit**</u> **of** <u>**what**</u> eg. 2.34 g of NaCl
(by chemical formula)

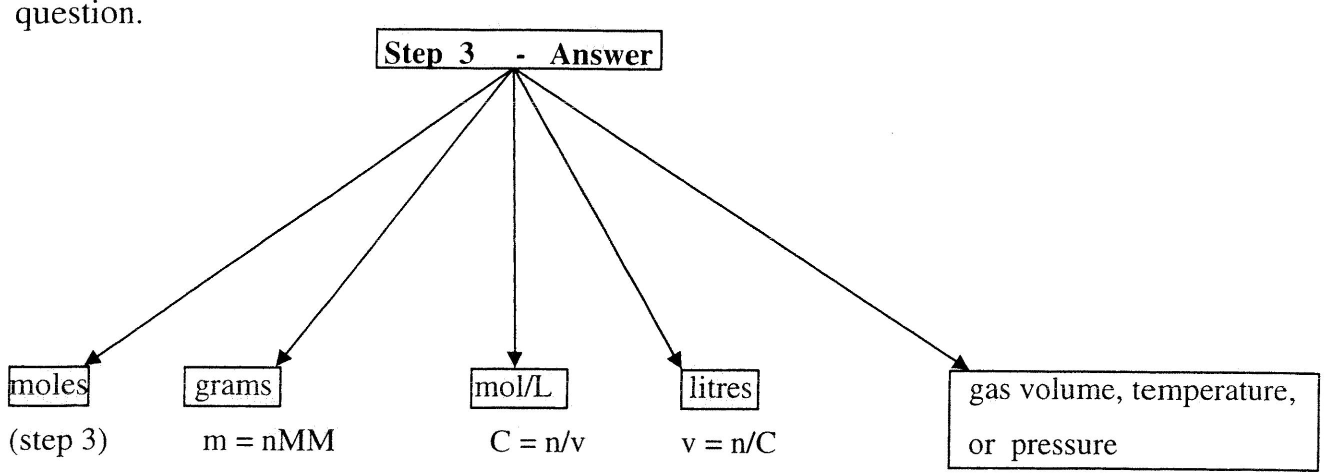
<u>Step 3 - Mole Ratio Step</u>
Set up a mole ratio using the coefficients in your balanced chemical equation of your required to your given substance.

$$\text{Moles of required} = \text{Moles of given (from step 2)} \times \frac{\text{coefficient of Required substance}}{\text{coefficient of given substance}}$$

* Note: Again calculated answers are to be expressed as
<u>**Number**</u> <u>**unit**</u> **of** <u>**what**</u>
(by chemical formula)

Step 4 - Answer Step

Take your calculated answer in moles from step 3 and express in the units desired in the question.



Express your final answer in Number unit of what
(by chemical formula)

V = nRT/P
P = nRT/V
T = PV/nR

CHEMISTRY 30 - Redox Stoichiometry

Solve the following problems. Show complete steps as taken in class.

1. 31.0 grams of chromium metal is used in a reaction with tin(IV)nitrate solution. Determine the volume of 0.200 mol/L tin(IV)nitrate solution used for this reaction. (ans: 2.98 L)

2. What volume of 0.845 mol/L acidic potassium permanganate solution is needed to completely react with 20.9 grams of iron? (ans: 177 mL)

3. A 0.120 mol/L acidified tin(II)chloride solution reacts with 200 mL of a 0.335 mol/L potassium dichromate solution. What volume of tin(II)chloride solution is required? (ans: 1.68 L)

4 In an experiment aqueous 0.0525 mol/L potassium dichromate was used in an acidic solution to oxidize Fe^{2+}(aq) ions to Fe^{3+}(aq) ions. The following data was obtained:

volume of Fe^{2+}(aq) solution	25.0 mL
final buret reading($K_2Cr_2O_7$(aq))	48.7 mL
initial buret reading	3.7 mL

What was the concentration of the Fe^{2+}(aq) ions in the solution? (ans: 0.567 mol/L)

5 25.0 grams of nickel metal is placed in a beaker containing 0.15 mol/L iron(III)chloride solution and allowed to react. What volume of iron(III) chloride solution should be used.(ans: 5.7 L)

6. 0.245 mol/L silver chloride solution is mixed with 50.0 mL of 0.200 mol/L zinc iodide solution. What volume of silver chloride solution is needed for a complete reaction?
(ans: 81.6 mL)

7 In an experiment, a solution of 2.40 mol/L barium hydroxide was used to reduce a solution containing $Au^{3+}(aq)$ ions

Trial	1	2	3	4
volume of $Au^{3+}(aq)$ solution used	20.0 mL	20.0 mL	20.0 mL	20.0 mL
initial buret reading ($Ba(OH)_2$)	1.9 mL	18.8 mL	1.8 mL	18.1 mL
final buret reading ($Ba(OH)_2$)	18.8 mL	35.0 mL	18.1 mL	34.5 mL

Use the above data to determine the concentration of $Au^{3+}(aq)$ ions in the solution.
(ans: 1.30 mol/L)

Electrochemical Cells

An **electrochemical cell** is a cell that either converts chemical energy to electrical energy (electric or voltaic cell) or electrical energy into chemical energy (electrolytic cell)

- **Voltaic Cells**
  - An arrangement of two half cells, separated by a porous boundary, that spontaneously produces electricity.
  - e.g. A battery

- **Electrolytic Cell**
  - a cell in which a non-spontaneous reaction is force to occur; a combination of two electrodes, an electrolyte, and an external power source.
  - e.g. electroplating, electrolysis

Consumer, Commercial, and Industrial Cells

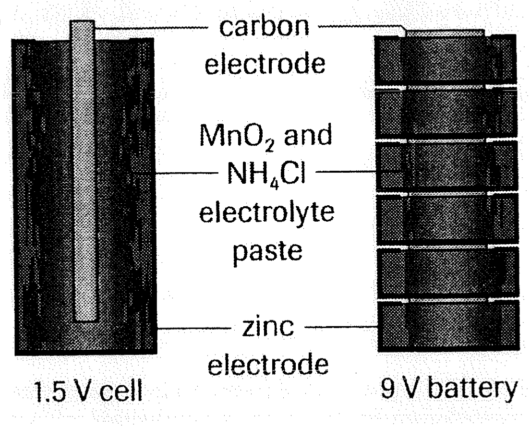


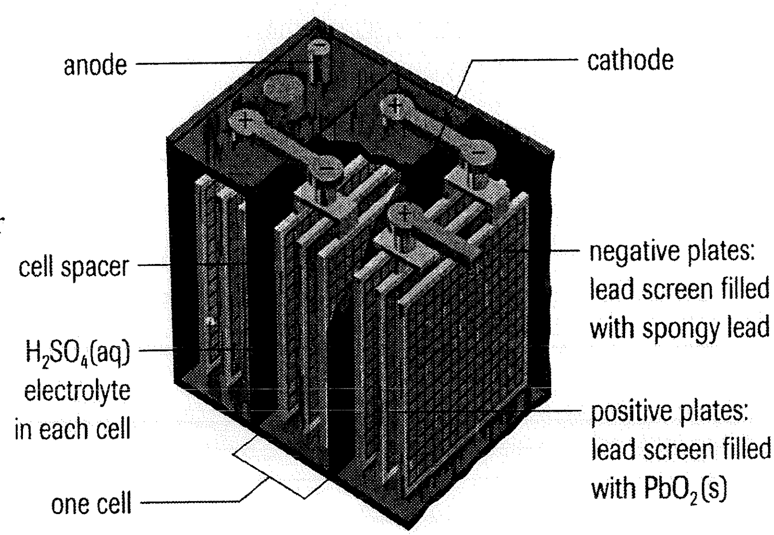
Figure 6
Like a flashlight D cell, the zinc chloride dry cell on the left has a voltage of 1.5 V. The 9 V battery on the right is made up of six 1.5 V dry cells in series.

- In these cells, the chemical eventually become depleted
- Irreversible reaction prevent them from being recharge.
- Called ***primary cells***

alkaline dry cell (1.5 V)	$2\,MnO_2(s) + H_2O(l) + 2\,e^- \rightarrow Mn_2O_3(s) + 2\,OH^-(aq)$ $Zn(s) + 2\,OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2\,e^-$	• longer shelf life; higher currents for longer periods compared with dry cell • same uses as dry cell

Figure 7
The anodes of a lead–acid car battery are composed of spongy lead and the cathodes are composed of lead(IV) oxide on a metal screen. The large electrode surface area is designed to deliver sufficient current to start a car engine.

- Reactions are reversible
- Recharged by reversing the reaction by using electricity
- Called secondary cell



lead-acid cell (2.0 V)	$PbO_2(s) + 4\,H^+(aq) + SO_4^{2-}(aq) + 2\,e^- \rightarrow PbSO_4(s) + 2\,H_2O(l)$ $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2\,e^-$	• very large currents; reliable for many recharges • all vehicles

Fuel Cells

- Produce electricity by having the fuel that is reacting continuously being supplied to the cell
- Increases the life of the battery since the cell should be able to operate as long as fuel is supplied.
- Fuel is directly converted to electricity unlike the conventional method of power plants where it is first burned to thermal energy and then to electricity (30-40% efficiency).

- As a result the fuel cell is much more efficient (70% efficiency) and does not produce harmful greenhouse emissions.

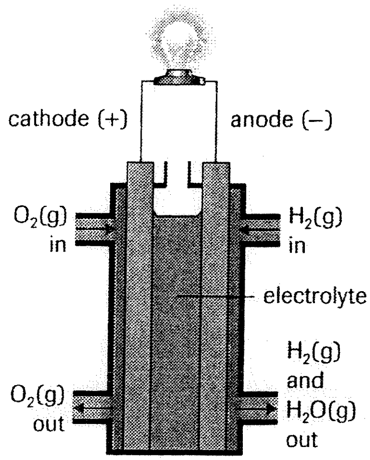


Figure 8
A hydrogen–oxygen fuel cell. Hydrogen and oxygen gases are continuously pumped into the cell, and each reacts at a different electrode. Unused gases are removed, filtered, and then recycled.

hydrogen-oxygen cell (1.2 V)	$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$	• lightweight; high efficiency; can be adapted to use hydrogen-rich fuels • vehicles and space shuttle

Voltaic cell

- chemical energy to electrical energy
- measured in volts
- voltage is called reduction potential difference or ΔE°_{cell} value
- $\Delta E^\circ_{cell} = E^\circ_{r(cathode)} - E^\circ_{r(anode)}$ (potential difference)

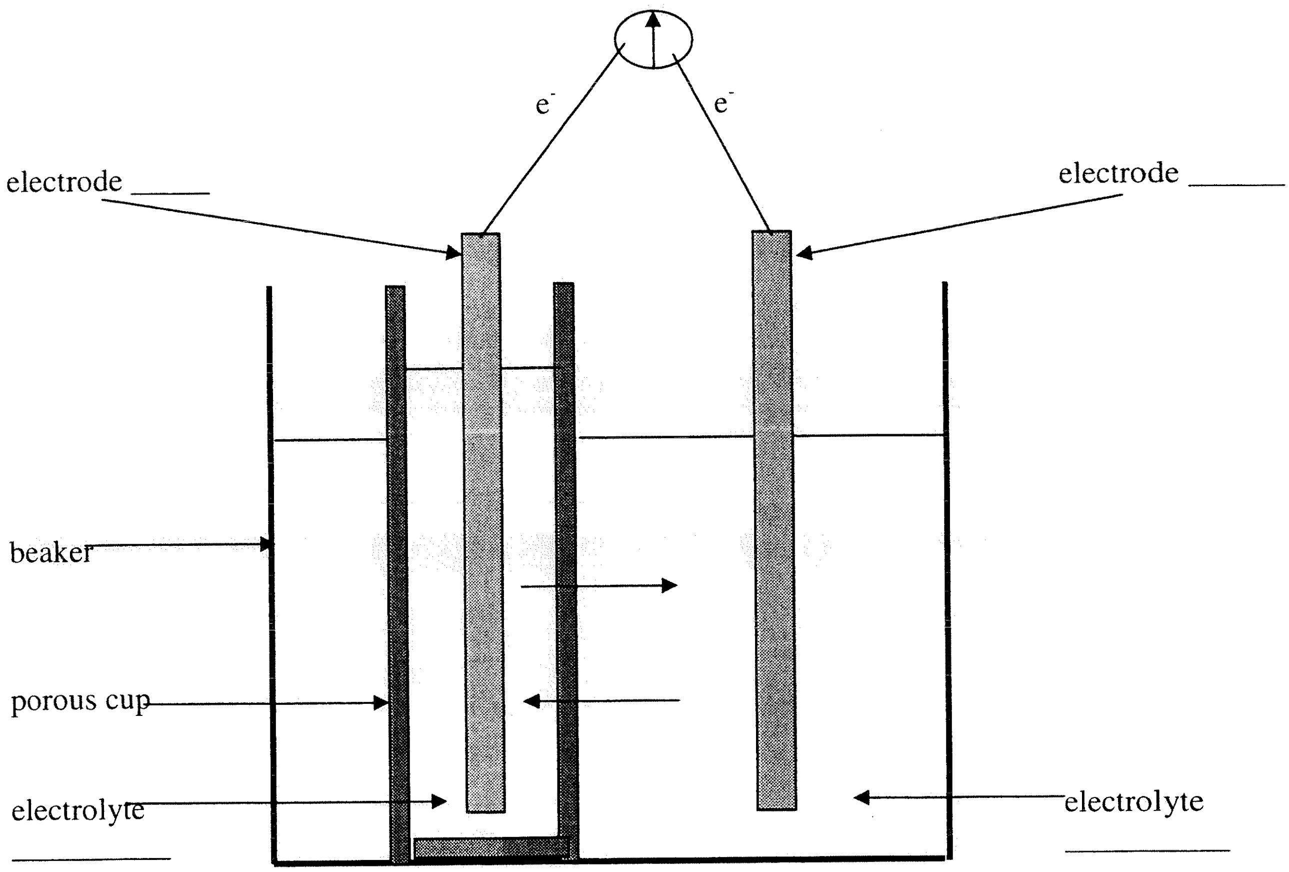
If the reacting species is

- **a metal,** - **electrode used is made up of that metal**
  - electrolyte has the same metal ion.
  - ie. Fe(s) electrode- will use $Fe(NO_3)_2(aq)$ electrolyte.

- **gas, liquid or solution**- use an inert electrode of C(s) or Pt(s)
  - use solution made of that electrolyte
  - eg. sol'n / electrolyte, $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{2+}(aq) + 7H_2O(l)$
  - will use an inert electrode since there is no solid metal in the equation.

CHEMISTRY 30 – Voltaic Cell

eg. $Zn(s) / Zn^{2+}(aq), NO_3^-(aq) // Cu^{2+}(aq), NO_3^-(aq) / Cu(s)$

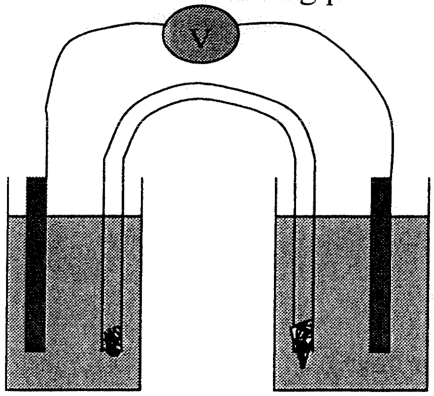


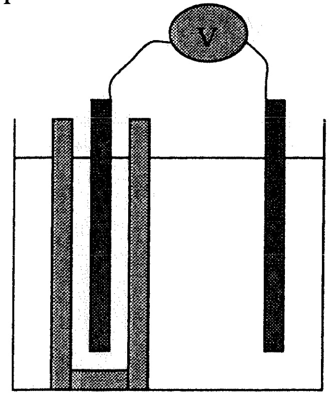
Complete

1. label electrodes and electrolytes
2. SOA & ½ reaction
3. SRA & ½ reaction
4. net redox reaction & $E°_{cell}$
5. spon / nonspon
6. direction of electron flow
7. pos / neg electrode
8. label cathode & anode
9. direction of electron flow

COMPONENTS OF A VOLTAIC CELL

Define and label the following parts as they apply to the types of voltaic cells





Cell Notation: Cu(s) / $CuSO_4$(aq) // $ZnSO_4$(aq) / Zn(s)

electrode

electrolyte

represents the porous boundary

represents interface between electrode and electrolytes

Anode reaction:

Cathode reaction

Half –cell - an electrode/electrolyte combination forming one half of a complete cell

Electrodes - a solid conductor generally a metal (or a $C_{(s)}$ or $Pt_{(s)}$ rod) which are also the site of oxidation & reduction rxns.

Anode - negative electrode where oxidation occurs (LEOA)

Cathode - positive elctrode wher reduction occurs (GERC)

Electrolytes - solute that dissociate in solution, able to carry an electrical current.
- chosen such that it will not react with its electrode.

Cations - positively charged ion

Anions - negatively charged ion

Voltage - name that rpresents the potential difference in volts between the anode and cathode ½ -reactions

Voltaic Cells – Chemical energy → Electrical Energy

Anions are all negatively charged ions in both half cells.

Cations are all positively charged ions in both half cells.

Ions can move only through the solutions (they can pass through the porous cup or the salt bridge)

Electrons can move only through the electrodes and wire (They move from the anode to cathode)

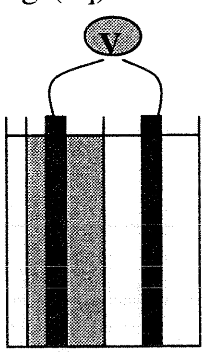
eg. In the following cell $Cu(s) / Cu^{2+}(aq) // Zn^{2+}(aq) / Zn(s)$

SOA SRA

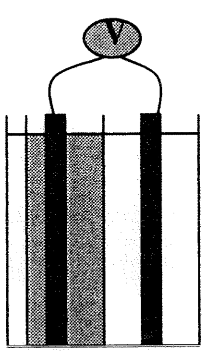
Cathode reaction:	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$E^\circ_r = 0.34\ V$
Anode reaction:	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	$E^\circ_r = -0.76\ V$
Net Reaction:	$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$	$\Delta E_{cell} = 1.10\ V$

Label the parts for the following cells. Write out the cathode,anode, and net reactions. Determine the potential difference of each cell.

1. $Ag(s) / Ag^+(aq) // Cd^{2+}(aq) / Cd(s)$



2. $C(s) / K^+(aq), Cr_2O_7^{2-}(aq), H^+(aq) // Fe^{2+}(aq), SO_4^{2-}(aq) / Fe(s)$



3. What is a salt bridge?

4. Anodes often ___________________ in size.

5. Complete the prediction section of the following investigation report.
Problem: What is the complete cell description (half-reactions, net reactions, cell potential, electrodes, electrolytes, cathodes and anodes with polarities, and the electron ion flow) of the maximum voltage cell from the materials available?

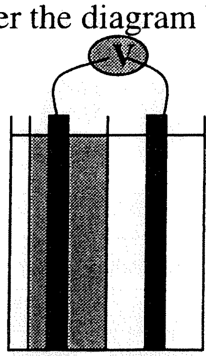
Materials: metal strips of iron, copper, lead and tin. Beakers, 1.0 mol.L solutions of the metal ion nitrates, connecting wires, porous cup, and voltmeter.

6. A half cell consisting of a palladium rod dipping into a 1.00 mol/L solution of $Pd(NO_3)_{2(aq)}$ solution is connected with a copper/copper(II)nitrate half cell. The cell voltage is 0.65 V and the copper electrode is the anode. Determine the E° for $Pd_{(s)}$.

$$\mathbf{Pd^{2+}(aq) \quad + \quad 2\,e^- \rightarrow Pd(s)}$$

7. Consider the diagram below and answer the following questions:

Ag(s)



Mg(s)

$AgNO_3(aq)$

$Mg(NO_3)_2(aq)$

a. When the cell is operating the anode will be _______________

b. As the cell operates the ______________(composition) electrode will gain mass.

c. The $\Delta E°_{cell}$ for this cell is _________________ .

8. **Calculate the $\Delta E°_{cell}$ values for the following Electrochemical Cells.**

1. $Fe(s) / Fe^{2+}(aq) // Cu^{2+}(aq) / Cu(s)$ $\Delta E°_{cell}$ = ____________________

2. $Pb(s) / Pb^{2+}(aq) // Ag^{+}(aq) / Ag(s)$ $\Delta E°_{cell}$ = ____________________

3. $Ni(s) / Ni^{2+}(aq) // Cr_2O_7^{2-}(aq), H^{+}(aq), Cr^{3+}(aq) / C(s)$ $\Delta E°_{cell}$ = ____________________

4. $Al(s) / Al^{3+}(aq) // Sn^{2+}(aq) / Sn(s)$ $\Delta E°_{cell}$ = ____________________

Notes

Find the reduction potential of the unknown substance

e.g.#1 $Cr(s) \mid Cr^{2+}(aq) \parallel X^{2+}(aq) \mid X(s)$ $E°_{cell} = +0.63$ V

Anode

What is a possible identity of substance X(s)

e.g.#2 $3Fe^{3+}(aq) + Y(s) \rightarrow 3Fe^{2+}(aq) + Y^{3+}(aq)$ $E°_{cell} = +2.43$ V

e.g. #3 Write the standard cell notation for a gold-tin(IV) cell

e.g. #4 If the reference half cell was change to a standard silver – silver ion half cell. What would the reduction potential be for the:

a. standard chlorine ½ cell

b. standard cobalt ½ cell

Corrosion of Iron

Rxn of iron with oxygen and water

e.g.	red	$O_2(g) + 2\,H_2O(l) + 4e^- \rightarrow 4\,OH^-(aq)$	$E^o_r = +0.40$ V
	oxid	$[Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^-]\times 2$	$E^o_r = -0.45$ V
	redox	$O_2(g) + 2\,H_2O(l) + 2\,Fe(s) \rightarrow 2Fe^{2+}(aq) + 4\,OH^-(aq)$	$E^o_{cell} = +0.85$ V
		$\rightarrow 2\,Fe(OH)_2(s)$	

Note:

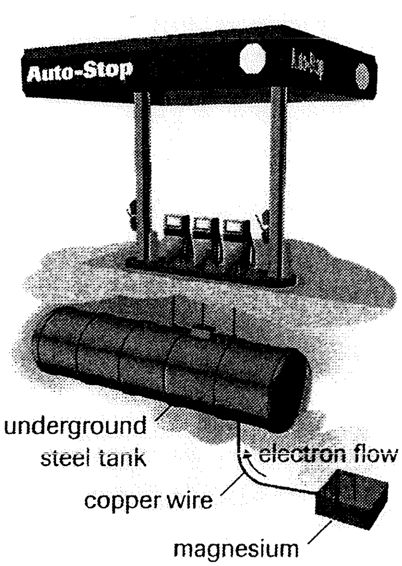
- If water or oxygen in the water is removed from the environment, this will make the corrosion reaction impossible.
- If oxidizing agents other than water such as $H^+(aq)$ (an acidic environment) is available, corrosion can still take place.
- If electrolytes such as salt are present, they can accelerate corrosion since speed up charge transfer

How Can Corrosion Be Prevented?

- The easiest method to prevent corrosion is to coat the metal with paint, plastic etc. to prevent it from being exposed to the environment. However any damage to the coating will allow corrosion to proceed.

- Metals such as tin (cans) or zinc (galvanizing) are used to coat metal like iron..
  - If the tin is damaged the exposed iron would react before the tin and become the anode and corrosion will proceed
  - However if the zinc coating is damaged, the zinc will react before the iron since it is a SRA. As a result the iron will continue to be protected even if the Zn coating is damaged.

- Another method to protect iron from corrosion is called **cathodic protection.**



  - In this situation the iron is forced to become a cathode by supplying the iron with an impressed current (hooked up to a weak power source that forces electrons on to the iron) or by a **sacrificial anode.**
  - A metal is attached to the iron directly or by a wire that is a SRA than the iron. The SRA will corrode away first before the iron (ie. Is sacrificed) to prevent the corrosion of the protected metal. The iron will be protected as long as sacrificial metal is available.
  - As the sacrificial metal is oxidized, it is producing electrons which pass directly to the iron forcing the iron to act as a cathode. (Cathodic protection)

This method is used to protect underground tanks, pipeline, ship hulls and hot water tanks.

Rxn of magnesium with oxygen and water

e.g. red $O_2(g) + 2\,H_2O(l) + 4e^- \rightarrow 4\,OH^-(aq)$ $E^o_r = +0.40$ V

oxid $[Mg(s) \rightarrow Mg^{2+}(aq) + 2\,e^-]\times 2$ $E^o_r = -2.37$ V

redox $O_2(g) + 2\,H_2O(l) + 2\,Fe(s) \rightarrow 2Fe^{2+}(aq) + 4\,OH^-(aq)$ $E^o_{cell} = +2.77$ V

$\rightarrow 2\,Mg(OH)_2(s)$

Notice that the E^o_{cell} is higher for magnesium than for iron (page 34) meaning that it is more spontaneous and will take place before the iron.

Electrolysis and Electrolytic Cells

Electrolysis is the reverse of a voltaic cell

- electrical energy is used to force a nonspontaneous reaction to occur
- electrical energy is supplied using an external power source(ie. Battery)
- endothermic reaction
- ΔE^o_{cell} is negative
- Electrolytes – may be one or more ionic solutions mixed together
- One container

$$\text{Reactants} \underset{\text{electrolytic}}{\overset{\text{voltaic}}{\rightleftarrows}} \text{products} + \text{electrical energy}$$

- Method is used commercially to force chemical changes with electricity
  a. electroplating metals ie. Chrome bumpers, gold plated jewellery, tin cans etc
  b. electrolysis of water into $H_{2(g)}$ and $O_{2(g)}$
  c. breakdown of compounds (metal ores) into pure metals

  Bauxite ($Al_2O_3(s)$) to pure aluminum

  ie $Al_2O_3(s)$ + electrical energy $\rightarrow Al(s) + O_2(g)$

eg Electrolysis of cadmium nitrate using inert electrodes

$C(s)$ / $Cd(NO_3)_2(aq)$ / $C(s)$ **(cell notation for electrolytic cells)**

Using the five step method determine the minimum voltage

Give evidence of reaction at the anode

Give evidence of reaction at the cathode

Electrolysis

Write cathode, anode and net reaction and determine the minimum voltage for the following reactions.

1. Electrolysis of aqueous aluminum bromide (ans: 1.90 V)

2. Electrolysis of potassium sulfate (ans: 2.06 V)

3. An aqueous solution of nickel II chloride is electrolyzed (ans 1.62 V)

The Chloride Anomaly

- Like regular reactions, some redox ½ reactions require a certain activation energy to get them started, there fore the actual voltage and the reported voltage are quite different. This is called half-cell overvoltage.

- This overvoltage is quite high for the reaction of water to $O_2(g)$ while the reaction of chlorine has a lower overvoltage precedes the reaction with water.
- In other words, the reaction of water is very slow; therefore the reaction of chlorine takes place instead.

As a general rule, during electrolysis if a choice for reducing agent must be made between $H_2O(l)$ and $Cl^-(aq)$, the choice of reducing agent should be $Cl^-(aq)$.

ELECTROLYSIS OF MOLTEN IONIC COMPOUNDS

Solid Ionic compounds **cannot conduct** electricity

When an **ionic** compound is **melted**, the ions are free to move around, and therefore ionic compounds **are conductors** of electricity.
In a molten ionic compound, there are only two species, the positive ion and the negative partner ion.

Example
Write the cathode, anode, and net reactions for the electrolysis of molten **aluminum oxide**:

Min Voltage cannot be calculated for molten cells. Data book values are for aqueous cells only.

Species: $Al^{3+}(l)$, $O^{2-}(l)$

Cathode reaction: $Al^{3+}(l) + 3e^- \rightarrow Al(s)$

Anode reaction: $2O^{2-}(l) \rightarrow O_2(g) + 4e^-$

Net Reaction: $4Al^{3+}(l) + 6O^{2-}(l) \rightarrow 4Al(s) + 3O_2(g)$

Exercise

1. Write equations for:
   a. Electrolysis of molten sodium iodide

   b. Electrolysis of molten calcium phosphide

c. Electrolysis of molten aluminum iodide

2. Describe briefly how you would electroplate a teaspoon with silver.

3. Impure copper is purified in an electrolytic cell. Design an electrolytic cell that would allow you to carry out this process.

	Electrolytic Cell	**Voltaic cell**
Reaction at the Cathode		
Reaction at the Anode		
Anion Movement		
Cation Movement		
Electron Movement		
Use of Salt Bridge/ porous cup		
Use of Power Source		

Voltage		
Position of Reducing Agent		
Position of Oxidizing Agent		
Spontaneous or Nonspontaneous		
Anode Appearance		
Cathode Appearance		

QUANTITATIVE ASPECTS OF ELECTROLYSIS

Electrolytic Stoichiometry

1. An appropriate half reaction of substance reacted
2. Calculation of moles of given species
3. Ratio step to find moles required
4. Answer step

Formulas:

$$n_{e^-} = \frac{IT}{F}$$

where $F = 9.65 \times 10^4 \frac{C}{mol}$

Solve the following problems. Show all work and steps.

1. Determine the number of moles of electrons supplied by a dry cell supplying a current of 0.100 A for 50.0 min to an Ipod. (ans: 3.11×10^{-3} mol)

2. If 20.0 A of current flows through an electrolytic cell containing molten aluminum oxide for 1.00 h, what mass of aluminum will be deposited at the cathode (ans: 6.71 g)

3. An electroplating firm wishes to plate 10.0 g of copper onto a pair of baby shoes from a $Cu(NO_3)_2$ solution. If a 2.00 A current is used, calculate the time required. At which electrode would the shoes be attached? (ans: 4.22 h)

4. If 80.0 g of fluorine gas are required, what current would have to flow for 10.0 hours to produce the fluorine from molten NaF? At which electrode would this reaction occur? (ans: 11.3A)

5. A $Pt_{(s)}$ / $Cl_2(aq)$, $Cl^-(aq)$ // $Cd^{2+}(aq)$ / Cd(s) voltaic cell delivers 1.93 A for 2.00 hours. During this time the greatest mass change would occur where? (ans: anode 8.09 g compared to 5.10 g)

6. In the electrolysis of molten aluminum chloride, if 20.0 grams of chlorine are collected at the anode, what mass of aluminum is produced at the cathode? (ans: 5.07 g)

Old Diploma Written Response Questions

1. An astute chemistry student pointed out to the teacher that problems could develop in the biology salt-water aquarium. The student indicated that the air pump which was made of iron, could corrode in the presence of oxygen and water in the aquarium.

   a. The student suggested that the attachment of a small piece of zinc metal to the pump would prevent the corrosion of iron. Would this suggestion solve the problem? Support your answer by utilizing any:
      - relevant chemical equations,
      - calculations and
      - accepted theories,

      relating to this unit which would explain the use of zinc as an advantage or disadvantage.

   b. How much zinc would be used after 1 year (assuming 365 days) if an electron flow of 0.58 mA is produced? (ans: 6.2 g)

2. You are given the following metals and solutions of their ions;

$Cu(s)$ and $CuSO_4(aq)$
$Ni(s)$ and $Ni(NO_3)_2(aq)$
$Fe(s)$ and $Fe(NO_3)_2(aq)$

a. Draw a diagram of an working electrochemical cell that would produce a voltage of 0.19V. Label the cathode and anode. Name and label the metals and solutions used. Use labeled arrows to show the direction of flow of electrons, cations and anions. Be neat and complete.

b. Calculate the change of mass at the cathode, if the anode undergoes a mass change of 3.14 g. Include all steps (ans: 3.30 g)

In the table below, the time in hours that each of three cells would operate for particular devices is given. The cost of each cell is also given.

	Type of D Cell		
	Leclanché	**Zinc Chloride**	**Alkaline**
Motor Toy	1.0 h	3.0 h	11.0 h
Cassette Tape Player	1.0 h	2.5 h	5.7 h
Flashlight	1.0 h	2.0 h	4.6 h
Pocket Radio	1.0 h	1.8 h	4.1 h
Cost of Cell	$0.75	$0.95	$2.25

Leclanché Cell ($Zn(s)/MnO_2(s)$)

Overall Reaction

$2\ MnO_2(s) + 2\ NH_4Cl(aq) + Zn(s) \rightarrow ZnCl_2 \cdot 2NH_3(s) + Mn_2O_3 \cdot 5H_2O(s)$

Operating Temperature Range -5°C to 55°C

Voltage 1.5 V

Zinc Chloride Cell ($Zn(s)/MnO_2(s)$)

Overall Reaction

$8\ MnO_2(s) + 4\ Zn(s) + ZnCl_2(s) + 9\ H_2O(l) \rightarrow 8\ MnOOH(s) + ZnCl_2 \cdot 4ZnO \cdot 5H_2O(l)$

Operating Temperature Range -20°C to 55°C

Voltage 1.5 V

Alkaline/Manganese Dioxide Cell ($Zn(s)/MnO_2(s)$)

Overall Reaction

$2\ Zn(s) + 3\ MnO_2(s) \rightarrow 2\ ZnO(s) + Mn_3O_4(s)$

Operating Temperature Range -30°C to 55°C

Voltage 1.5 V

3 a. Identify the anode common to all of the D cells. Indicate the change in oxidation number for the anode.

b. For how many hours could a Leclanché Cell at 0.300 A if the limiting reagent was a 10.0 g anode?

c. Which type of D cell battery would you use to operate a portable cassette player outside on a mild day when the temperature was -12°C? Justify your choice from two different perspectives.