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Chemistry
Teach Yourself Series
Topic 4: Redox

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Redox reactions

What are they?

As it appears in Unit 2

There are several categories of chemical reactions i.e.
hydrochloric acid reacts vigorously with sodium hydroxide.

$$HCl(aq) \quad + \quad NaOH(aq) \rightarrow NaCl(aq) \quad + \quad H_2O(l)$$

H^+

This is referred to as an **ACID-BASE** reaction. Characteristic – **proton** (H^+) is transferred.

Precipitation reaction – characteristic; a **precipitate** forms when two soluble ionic solutions are mixed.

Redox reactions are another category of reaction. Characteristic – **electrons transferred** from one reactant to another.

Example 1

$$Mg(s) \quad + \quad S(s) \quad \rightarrow \quad MgS(s)$$

$2e^-$ $\quad$ Mg^{2+} $\quad$ S^{2-}

During this reaction, each magnesium atom donates 2 electrons to each sulfur atom.

Redox: Involves electron transfer.
One substance must donate electrons and one substance must accept electrons
One substance **donates electrons**; this is defined as **oxidation**
One substance **gains electrons**; this is defined as **reduction**.

Oxidation

- loss of electrons (electrons on right hand side of half equation)
- increase in oxidation number
- gain of oxygen
- loss of hydrogen

Reduction

- gain of electrons (electrons on left hand side of half equation)
- decrease in oxidation number
- loss of oxygen
- gain of hydrogen

Example 2

$$Na(s) \quad + \quad AgCl(aq) \quad \rightarrow \quad NaCl(aq) \quad + \quad Ag(s)$$

e^- $\qquad$ Na^+ $\quad$ Cl^-

Sodium atoms are oxidized.
Silver ions are reduced.
Chloride ions are spectator ions.

Oxidant/Reductant

In the example above, sodium is oxidized, releasing electrons. These electrons allow a reduction reaction to occur.

The chemical oxidized is the reductant.

Na is oxidized, therefore it is the reductant.

The chemical reduced is the oxidant.

Ag^+ is reduced, therefore it is the oxidant.

Half equations

The reaction above is easier to outline if half equations are used.
One half equation shows oxidation, the other reduction.

$Na(s) \rightarrow Na^{+}(aq) + e$ (increase in oxidation number or electrons being donated = oxidation)

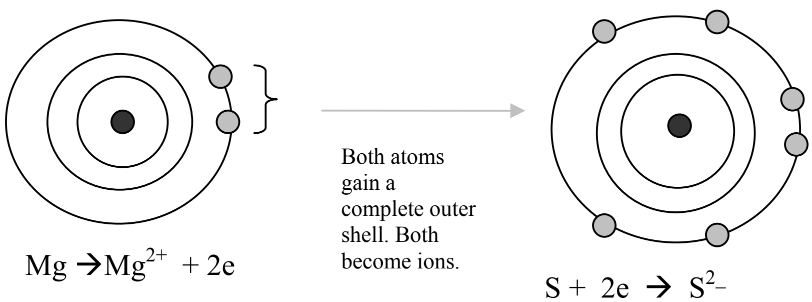
$Ag^{+}(aq) + e \rightarrow Ag(s)$ (decrease in oxidation number or electrons being accepted = reduction)

Why do redox reactions occur?

Many atoms are more stable if they have a complete outer shell.
Metals try and lose electrons to achieve this.
Non metals try and gain electrons to achieve this.
When substances are mixed, redox reactions occur if electrons are transferred from one reactant to another.

In example 1 above, the magnesium wants to lose electrons while sulfur wants to gain them. A reaction is no surprise.

$$Mg(s) + S(s) \rightarrow MgS(s)$$



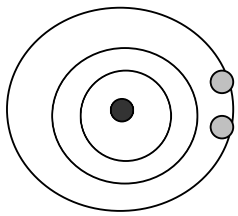
In example 2, both sodium and silver want to lose outer shell electrons but sodium can do this more readily so a reaction occurs.

$$Na(s) + AgCl(aq) \rightarrow NaCl(aq) + Ag(s)$$

No reaction will occur if silver is added to sodium chloride. Different substances have differing abilities to lose or gain electrons. As they have different nuclei and different electron structures this is no surprise.

Oxidation number

To determine if a redox reaction has occurred, it is important to be able to determine the oxidation number of a particular element.
The oxidation number reflects the electron structure.



The magnesium atom has a 2,8,2 electron configuration
It will lose two electrons in a redox reaction.
Therefore its oxidation number will be +2.

All elements in Group 2 will have the same oxidation number of +2.

Some of the elements have an oxidation number that is easily predicted from the Periodic Table.

Group 1 elements will have an oxidation number of +1.
Group 17 elements will have an oxidation number of -1.

Li
Na
K
Rb

If the oxidation number is not obvious, try the following;

- Hydrogen has an oxidation number of +1.
- Oxygen has an oxidation number of -2
- All substances present as elements have an oxidation state of 0.

Examples

1. Find the oxidation number of the element in bold print in each of the following

SO_3

each O atom is -2 => 3x-2 =- 6
S atom must be +6 to balance the O atoms

NH_3

each H atom is +1 => 3x1 =+3
N atom must be -3 to balance the H atoms

SO_4^{2-}

$(SO_4) = -2$
$(S + 4\text{x}-2) = -2$
$(S - 8) = -2$
$S = -2 + 8 = +6$

$Cr_2O_7^{2-}$

$(Cr_2O_7^{2-}) = -2$
$(2Cr + 7\text{x}-2) = -2$
$(2Cr - 14) = -2$
$2Cr = -2 + 14 = +12$
$Cr = +6$

2. Find the oxidation number of the element in bold print in each of the following equations to determine if oxidation or reduction has occurred

a. **Fe**$Cl_2(aq)$ + $Cl_2(g)$ → **Fe**$Cl_3(aq)$

Fe$Cl_2(aq)$ + $Cl_2(g)$ → **Fe**$Cl_3(aq)$
+2 +3

Cl^- has a charge of -1, therefore Fe changes from +2 to +3, therefore oxidation.

b. $2SO_2(g)$ + $O_2(g)$ → $2SO_3(g)$

$2SO_2(g)$ + $O_2(g)$ → $2SO_3(g)$

S changes from +4 to +6, therefore oxidation.

3. Is the reaction below a redox reaction?

$2CO(g)$ + $O_2(g)$ → $2CO_2(g)$

Oxygen changes from an element to a compound, therefore there is definitely an oxidation state change, therefore it is redox.
Carbon goes from +2 to +4 so it has been oxidised, while the oxygen goes from 0 to -2. This is reduction.

Review Questions

1. Determine the oxidation number of the element in bold print in each of the following

N$_2O_4$	**Fe**Cl_3
V$_2O_5$	**C**O_2
CO_3^{2-}	**P**O_4^{3-}

2. Find the oxidation number of the metals in each reaction below to identify the oxidant and the reductant.

Notes:

1. It is often easiest to start with the metal atoms as their oxidation numbers are easy.
2. Any element has an oxidation number of zero.
3. If you identify one of the oxidant or reductant, the other is usually obvious.)

a. $2Li(s)$ + $MgCl_2(aq)$ → $2LiCl(aq)$ + $Mg(s)$ _______________

b. $Ca(s)$ + $CuSO_4(aq)$ → $CaSO_4(aq)$ + $Cu(s)$ _______________

c. $4FeO(aq)$ + $O_2(g)$ → $2Fe_2O_3(s)$ _______________

d. Write half equations for the reactions above.

____

____

____

3.

a. Complete and balance the following half equations

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

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

$2Br^{-}(aq) \rightarrow Br(l)$

b. Label each of the half equations above as oxidation or reduction

4. Categorise the reactions below as acid/base, precipitation or redox.
Justify your answer.
(look for a transfer of a hydrogen or a precipitate or a change of oxidation state)

a. $HCO_3^{-}(aq) + H_2O(l) \rightarrow H_2CO_3(aq) + OH^{-}(aq)$

____

b. $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(aq)$

____

c. $LiCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + LiNO_3(aq)$

____

Writing more complex half equations

As it appears in Unit 4

1. Balance the oxygen atoms in the half equations, using water.
2. Balance the hydrogen atoms using hydrogen ions or water
3. Balance charges using electrons

Examples

Complete and balance the following half equations

1. $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$

Step 1. Balance oxygen atoms.
$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ (4 oxgyen requires 4 lots of H_2O)
Step 2. Balance hydrogen atoms
$MnO_4^-(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ (4 lots of water requires 8 H^+)
Step 3. Balance charges
$MnO_4^-(aq) + 8H^+(aq) + 5e \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ (-1 + 8+ -5 = +2)

2. $CH_3CH_2OH(aq) \rightarrow CH_3COOH(aq)$

Step 1. Balance oxygen atoms.
$CH_3CH_2OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq)$ (H_2O required to add extra O required)
Step 2. Balance hydrogen atoms
$CH_3CH_2OH(aq) + H_2O(l) \rightarrow CH_3COOH + 4H^+(aq)$ ($4H^+$ spare on right side)
Step 3. Balance charges
$CH_3CH_2OH(aq) + H_2O(l) \rightarrow CH_3COOH + 4H^+(aq) + 4e$ (4e added to balance)

Review Question

5. Complete and balance the following half equations

a. $Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$

____

____

b. $SO_2(g) \rightarrow SO_4^{2-}(aq)$

____

____

Will a reaction occur?

If the following reactants are mixed,

1. $Ni(s) \ + \ CaSO_4(aq) \rightarrow$

2. $Ca(s) \ + \ NiSO_4(aq) \rightarrow$

there will be a reaction in one beaker but not the other.
Note the reactions are the reverse of each other. One reaction is exothermic, hence the reverse (or other reaction) must be endothermic. The exothermic reaction will proceed; in this case reaction 2.
This can be predicted because calcium is more reactive than nickel, so it can pass its electrons to the nickel. If the reactivities of the elements are not known, the electrochemical series is used.

1. $Ni(s) \ + \ CaSO_4(aq) \rightarrow$ no reaction

2. $Ca(s) \ + \ NiSO_4(aq) \rightarrow CaSO_4(aq) \ + \ Ni(s)$

For a reaction to occur, the oxidant must be higher up the table than the reductant. Notice, the $\mathbf{Ni^{2+}}(aq)$ and the $\mathbf{Ca}(s)$ are shown in bold print. They are suitable to react.
$Ni(s)$ and $Ca^{2+}(aq)$ however, will not react as the reductant is above the oxidant.

Electrochemical series snippet

oxidants

$Cl_2(g) + 2e \Leftrightarrow 2Cl^-(aq)$

$Fe^{3+}(aq) + e \Leftrightarrow Fe^{2+}(aq)$

$\mathbf{Ni^{2+}}(aq) + 2e \Leftrightarrow Ni(s)$

$Ca^{2+}(aq) + 2e \Leftrightarrow \mathbf{Ca}(s)$

reductants

Ni^{2+} above Ca

Arbitrary choice to list all half equations as reduction reactions.
Arbitrary choice to make hydrogen the standard with a value of 00.00 V
All half equations shown as reversible, as the direction depends upon what other half cell is attached.

Will react		
$Cl_2(g)$	and	$Fe^{2+}(aq)$
$Fe^{3+}(aq)$	and	$Ni(s)$
$Cl_2(g)$	and	$Ca(s)$

Will not react		
$Ca^{2+}(aq)$	and	$Fe^{2+}(aq)$
$Ni(s)$	and	$\mathbf{Ca}(s)$
$Fe^{3+}(aq)$	and	$Cl^-(aq)$

The bigger the difference in voltage between the reactants, the greater the voltage produced. Chlorine with calcium will give the biggest voltage from those listed above.

Review Question

6. For each combination listed,
- will a reaction occur?
- write a balanced equation if it does.

a. $Cl_2(g)$ and $Ni(s)$

____

b. $Ni^{2+}(aq)$ and $Fe^{2+}(aq)$

____

c. $Ni^{2+}(aq)$ and $Ca(s)$

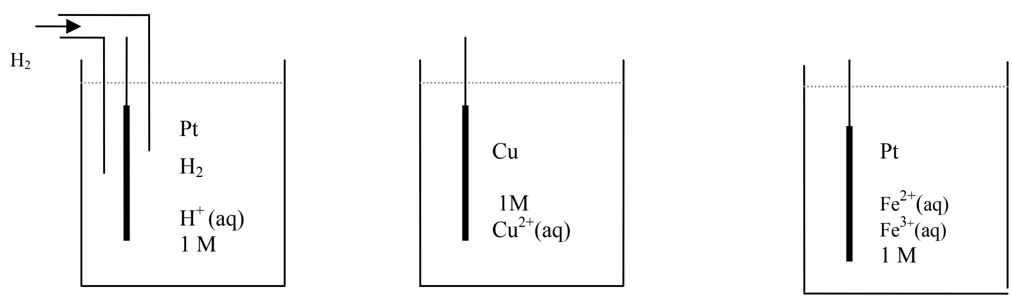
____

Half cells

It is easier to analyse redox reactions if the two half equations are conducted in separate half cells.

$$Fe^{3+}(aq) + e \Leftrightarrow Fe^{2+}(aq)$$
$$Cu^{2+}(aq) + 2e \Leftrightarrow Cu(s)$$
$$2H^{2+}(aq) + 2e \Leftrightarrow H_2(g)$$

The half cells for each half equation shown above would look like this.



Notes: $Fe^{3+}(aq) + e \Leftrightarrow Fe^{2+}(aq)$ does not list Fe(s) as an electrode, so platinum or graphite should be used.
Standard conditions requires 1.0 M solutions, 25 ^{0}C and a pressure of 1 atm if gases are involved.

Review Question

7. Draw the half cell for the following half equations
a. $Cl_2(g) + 2e \Leftrightarrow 2Cl^-(aq)$
b. $Ni^{2+}(aq) + 2e \Leftrightarrow Ni(s)$

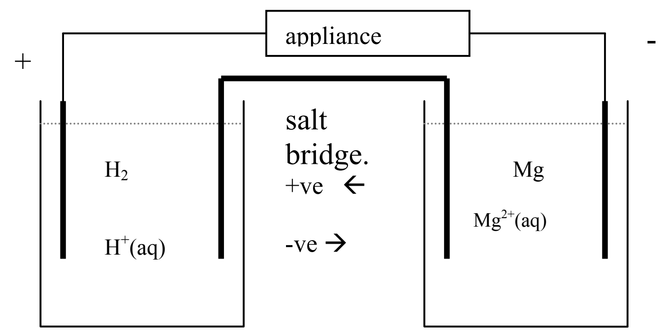
Galvanic cells

Galvanic cell – two half cells connected with leads and with salt bridge.
The whole point of a galvanic cell is that the flow of electrons is an electric current. This electric current is put to use as a portable power supply. A good galvanic cell needs to be safe, cheap and it needs to produce a reasonable voltage.

For a galvanic cell- **Oxidation** is always at the **anode** and the anode is **negative**.
Reduction is always at the **cathode** and the cathode is **positive.**

Example: $\mathbf{2H^+(aq)\ ,\ H_2(g)\ ||\ Mg^{2+}(aq),Mg(s)}$

H^+ is a stronger oxidant, so H^+ will react with Mg(s)



$2H^+(aq) + 2e \rightarrow H_2(g)$ $Mg(s) \rightarrow Mg^{2+}(aq) + 2e$

reduction at cathode, cathode positive
hydrogen gas evolved

oxidation at anode, anode negative
magnesium electrode will be corroded away

Salt bridge: Positive ions will move into the left beaker to replace H^+ ions.
Negative ions will move into the right beaker to match the Mg^{2+} ions.

Review Questions

8. Draw the galvanic cell that could be set up from the half cells

$Cl_2(g),Cl^-(aq)\ ||\ Zn^{2+}(aq),Zn(s)$

Label the anode and cathode and show the direction of electron flow.

9. Draw the galvanic cell required to generate an electric current from

$$Mg(s) + 2AgNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + 2Ag(s)$$

Write in the correct half equations and label the anode and cathode for the cell.

Putting it all together

A silver-zinc button cell has an overall equation

$$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow 2Ag(s) + Zn(OH)_2(s)$$

The whole point of this topic is to be able to analyse the processes occurring in a cell like this one. Therefore

- half equations are $Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e$ oxidation, anode, -ve
  $Ag_2O(s) + H_2O(l) + 2e \rightarrow 2Ag(s) + 2OH^-(aq)$ reduction, cathode, +ve
  (Zinc atoms are oxidized and silver ions are reduced)

Solutions to questions

1. N_2O_4 $2x = 8 \Rightarrow N = +4$ **Fe**Cl_3 $x = +3$

V$_2O_5$ $2x = -10 \Rightarrow V = +5$ **C**O_2 $x = +4$

CO_3^{2-} $(x + 3x - 2) = -2 \Rightarrow C = -2 + 6 = +4$
PO_4^{3-} $(x + 4x - 2) = -3 \Rightarrow P = -3 + 8 = +5$

2.
a. $2Li(s) + MgCl_2(aq) \rightarrow 2LiCl(aq) + Mg(s)$
$Li \rightarrow Li^+$ = oxidation = reductant => Mg = oxidant

b. $Ca(s) + CuSO_4(aq) \rightarrow CaSO_4(aq) + Cu(s)$
$Ca \rightarrow Ca^{2+}$ = oxidation = reductant => Cu = oxidant

c. $4FeO(aq) + O_2(g) \rightarrow 2Fe_2O_3(s)$
$Fe^{2+} \rightarrow Fe^{3+}$ = oxidation = reductant => O_2 = oxidant

3.

a. $Al^{3+}(aq) + 3e \rightarrow Al(s)$ reduction

$Ni(s) \rightarrow Ni^{2+}(aq) + 2e$ oxidation

$2Br^-(aq) \rightarrow Br_2(l) + 2e$ oxidation

4.
a. $HCO_3^-(aq) + H_2O(l) \rightarrow H_2CO_3(aq) + OH^-(aq)$ acid/base as H^+ transfer

b. $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(aq)$ redox, $Al \rightarrow Al^{3+}$

c. $LiCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + LiNO_3(aq)$ precipitation

5.
a. $Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

b. $SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq)$
$SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e$

6.

a. $Cl_2(g)$ and $Ni(s)$ Reaction - yes

$Cl_2(g) + Ni(s) \Leftrightarrow 2Cl^-(aq) + Ni^{2+}(aq)$

b. $Ni^{2+}(aq)$ and $Fe^{2+}(aq)$ No reaction

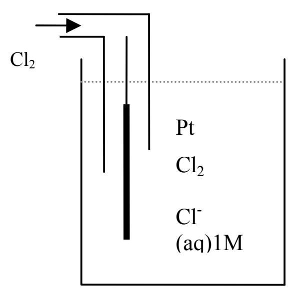
c. $Ni^{2+}(aq)$ and $Ca(s)$ Reaction - yes

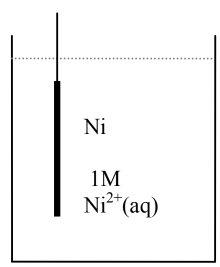
$Ni^{2+}(aq) + Ca(s) \rightarrow Ni(s) + Ca^{2+}(aq)$

7. Draw the half cell for the following half equations

a. $Cl_2(g) + 2e \Leftrightarrow 2Cl^-(aq)$

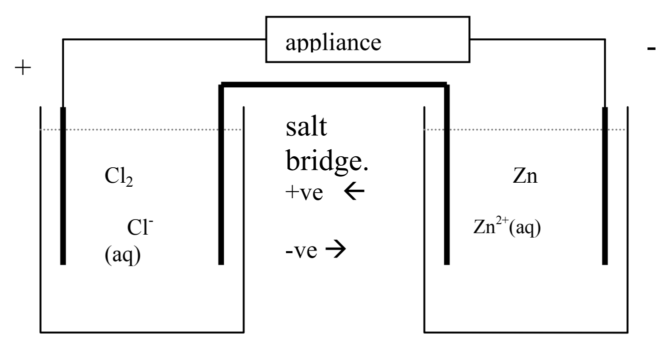
b. $Ni^{2+}(aq) + 2e \Leftrightarrow Ni(s)$





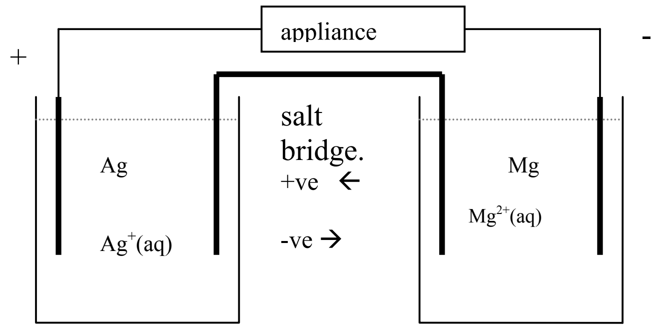
8. Draw the galvanic cell set up from the half cells

$Cl_2(g),Cl^-(aq) \,||\, Zn^{2+}(aq),Zn(s)$



$Cl_2(g) + 2e \rightarrow 2Cl^-(aq)$ $Zn(s) \rightarrow Zn^{2+}(aq) + 2e$

9. $Mg(s) + 2AgNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + 2Ag(s)$



$2Ag^+(aq) + 2e \rightarrow 2Ag(s)$ $Mg(s) \rightarrow Mg^{2+}(aq) + 2e$