OXIDATION REDUCTION REACTIONS

Objectives

At the end of this unit , the student is expected to be able to :

1- Understand the concepts of oxidation and reduction .

2- Distinguish between oxidizing and reducing agents in a redox reaction .

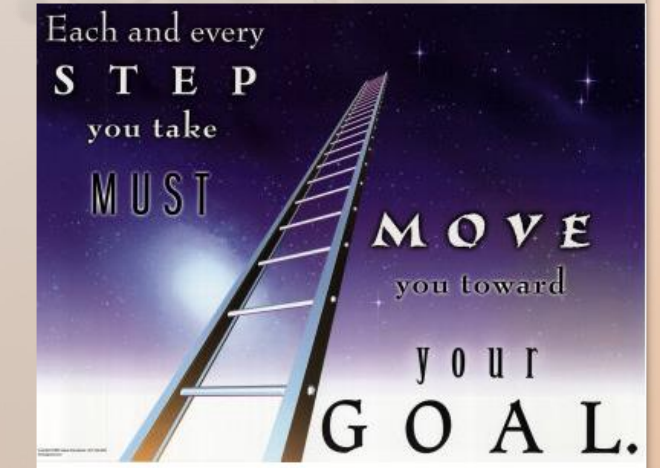
2- Write and Balance redox reaction equations .

3- Realize the role of standard potential in expecting the completeness and the direction of a redox reaction .

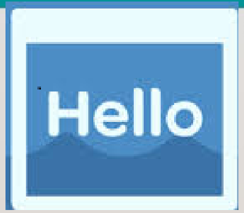
4- Understand and write the symbol for a galvanic cell reaction .

5- Calculate the electrode potential .

6- Calculate equilibrium constant K_{eq} for a redox reaction .

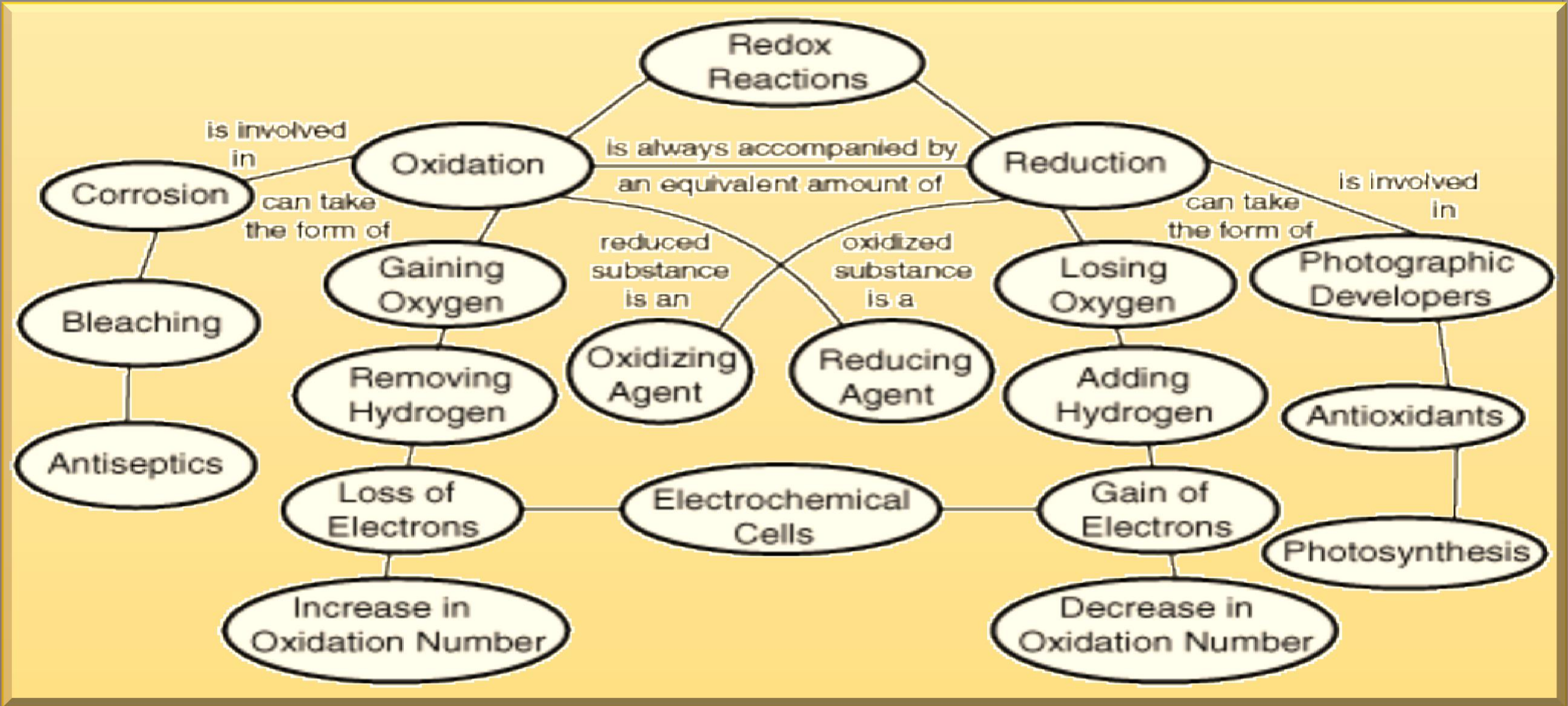


Introduction



Redox reactions are among the most common and most important chemical reactions in everyday life . **Combustion** is an example of a redox reaction that occurs so rapidly that noticeable heat and light are produced . **Corrosion** where most metals react with O_2 and might corrode so quickly that they became useless . Where plants and animals die, the organic compounds of which it are composed begin to react with O_2 , this process is called **decay** . Many of the changes that take place within living organisms (**biological processes**) are also redox reactions such as food digestion (metabolism) . Electricity, acid rain, paper making, photography, underwater welding and many more processes are redox reactions . There are numerous applications of redox reactions in analytical chemistry such as titrations of substances (see unit 11) , voltammetry , potentiometry and many more .

Introduction



Definitions

Redox reactions, or oxidation - reduction reactions , are a family of reactions that are concerned with the transfer of electrons between species. There is no oxidation reaction without a reduction reaction happening at the same time. Oxidation refers to the loss of electrons, while reduction refers to the gain of electrons. Each reaction by itself is called a "half-reaction", simply because we need two (2) half-reactions to form a whole redox reaction. In notating redox reactions, chemists typically write out the electrons explicitly:

$$\underset{(\text{Red})}{Zn^0(s)} \rightarrow \underset{(\text{Ox})}{Zn^{2+}(aq)} + 2e \qquad E^0 = -0.76\ V$$

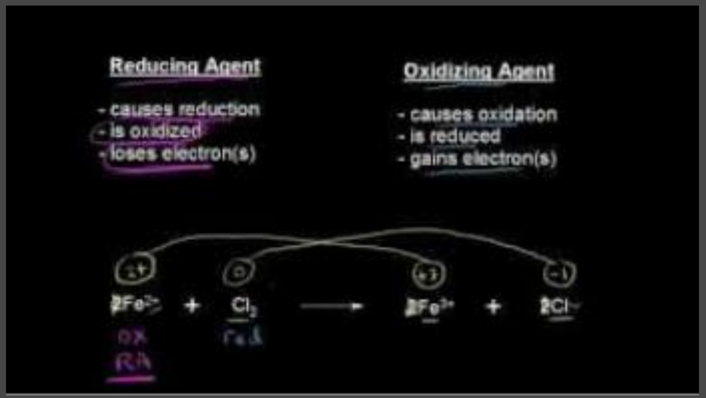
This half-reaction (electrode reaction in the galvanic cell) says that we have solid zinc (with no charge) being oxidized (losing two electrons) to form a zinc ion with a plus 2 charge. Notice that, like the stoichiometry notation, we have a "balance" between both sides of the reaction.

Definitions

We have one (1) zinc atom on both sides, and the charges balance as well. The symbol "e$^-$" represents a free electron with a negative charge that can now go out and reduce some other species, such as in the half-reaction:

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

(Ox) (Red)



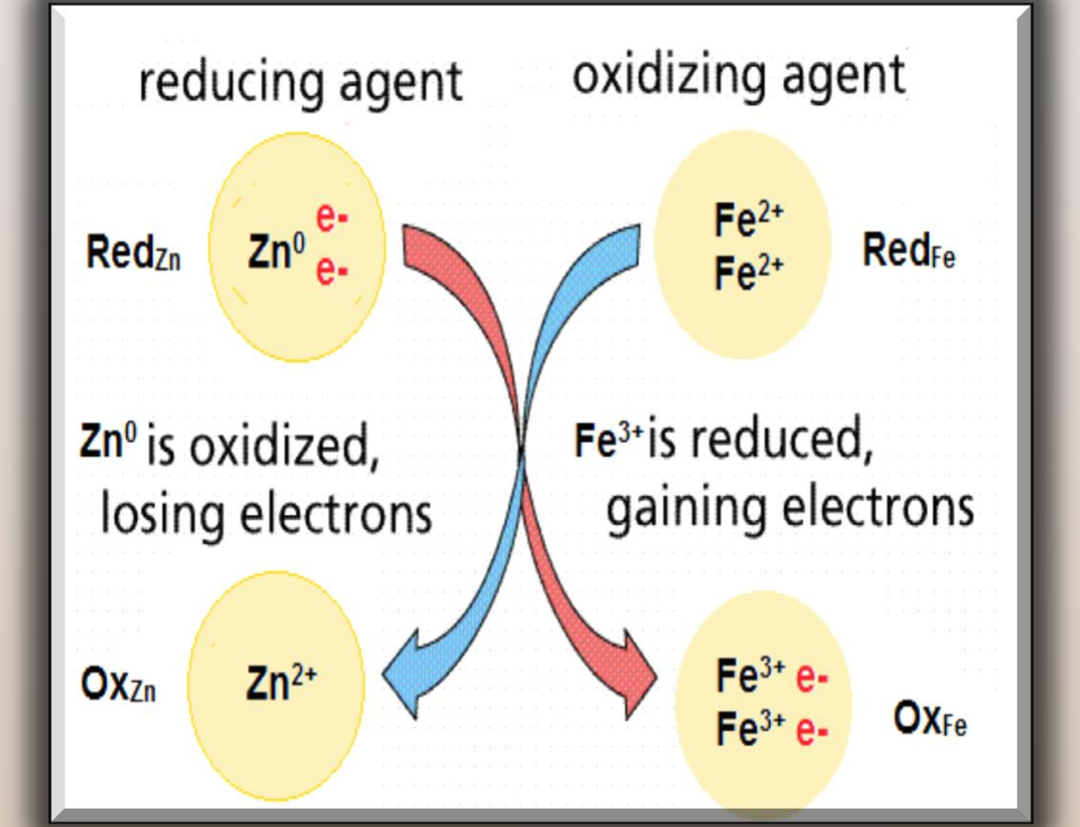
VIDEO
You Tube

VIDEO
My Channel

Definitions

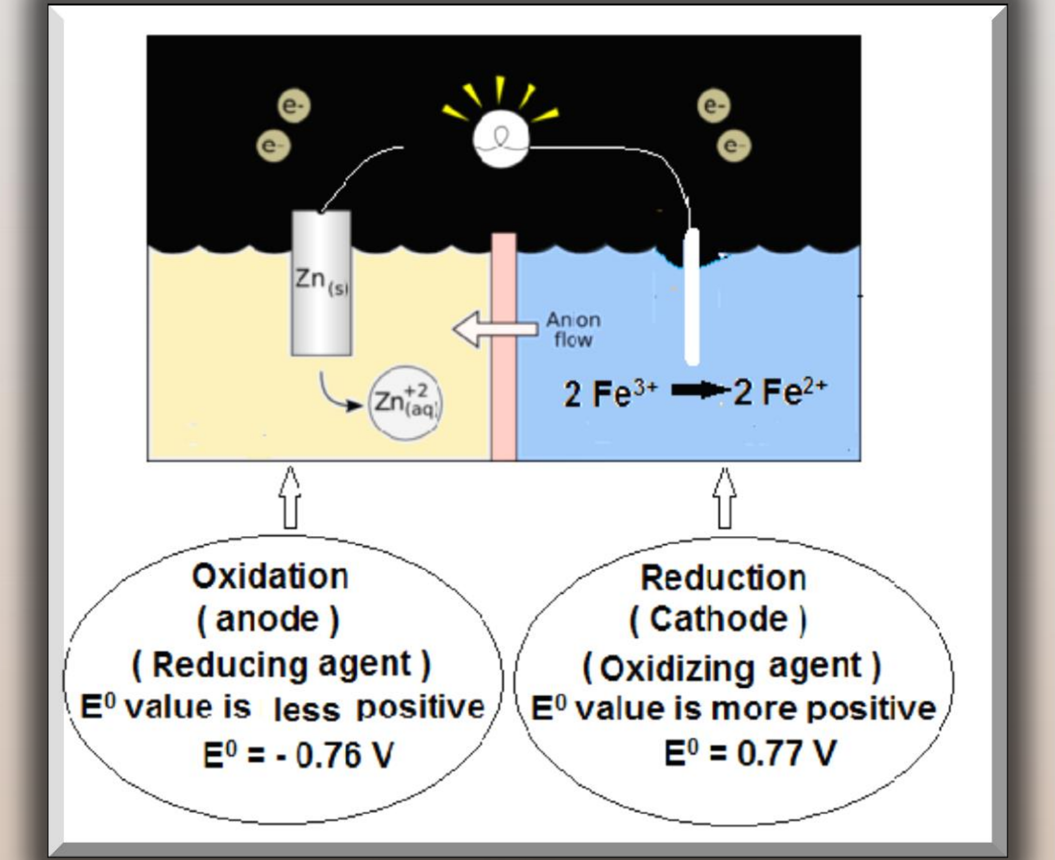
Here, two Fe^{3+} ions are being reduced through the addition of two (2) electrons to form two Fe^{2+} ions. Note that Fe^{3+} and Fe^{2+} are called iron have reaction couple. Fe^{3+} which gains electrons is called Ox form and Fe^{2+} which losses electrons is called Red form . Likewise for all other have reactions such as Zn^0 is the Red form and Zn^{2+} is the Ox form and so on. Note also that the oxidation state for the Ox form is more positive than the Red form. The full oxidation reduction is:

$$2\,Fe^{3+} + Zn^0 \rightarrow 2\,Fe^{2+} + Zn^{2+}$$

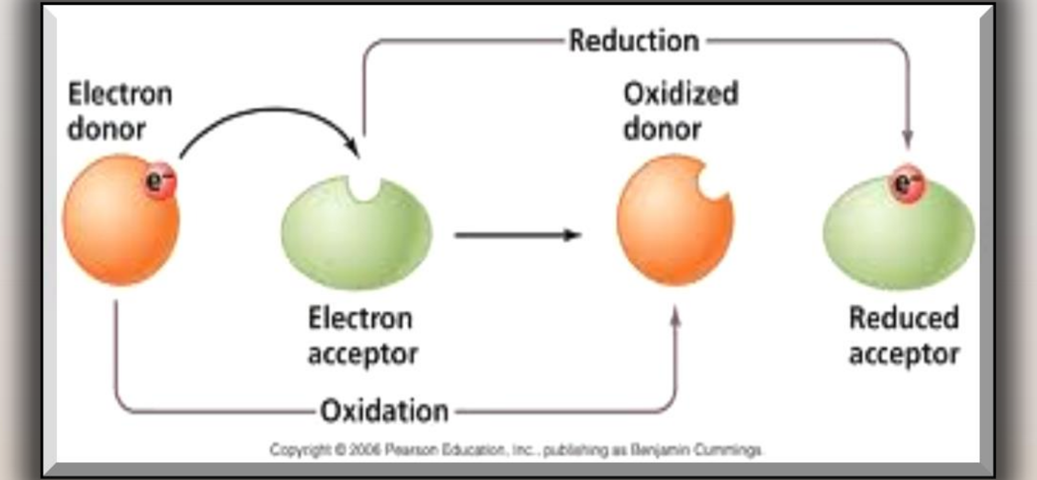


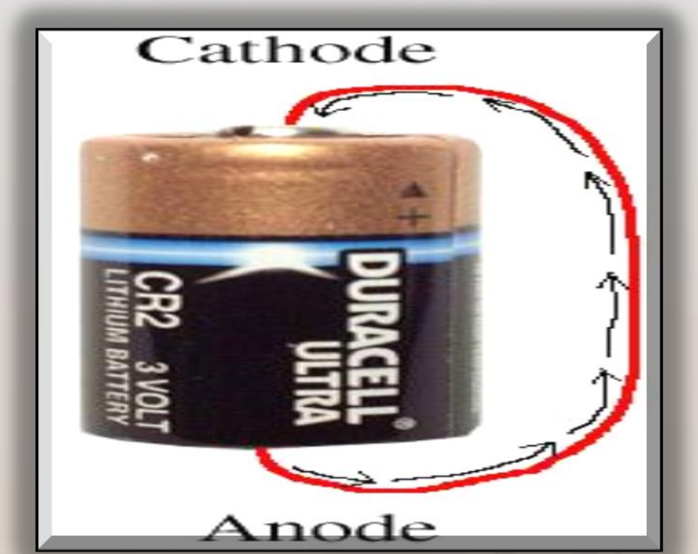
Definitions

We can also discuss the individual components of these reactions as follows. If a chemical causes another substance to be oxidized, we call it the oxidizing agent. In the equation above, Fe^{3+} is the oxidizing agent, because it causes Zn^0 to lose electrons (to be oxidized) but Fe^{3+} is reduced to Fe^{2+}. Oxidants get reduced in the process by a reducing agent. Zn^0 is, naturally, the reducing agent in this case, as it causes Fe^{3+} to gain electrons (reduced) but it is oxidized to Zn^{2+}. Reducing agents get oxidized in the process by an oxidizing agent. This is what really happens in the corresponding galvanic cell as shown in the graph.



Definitions

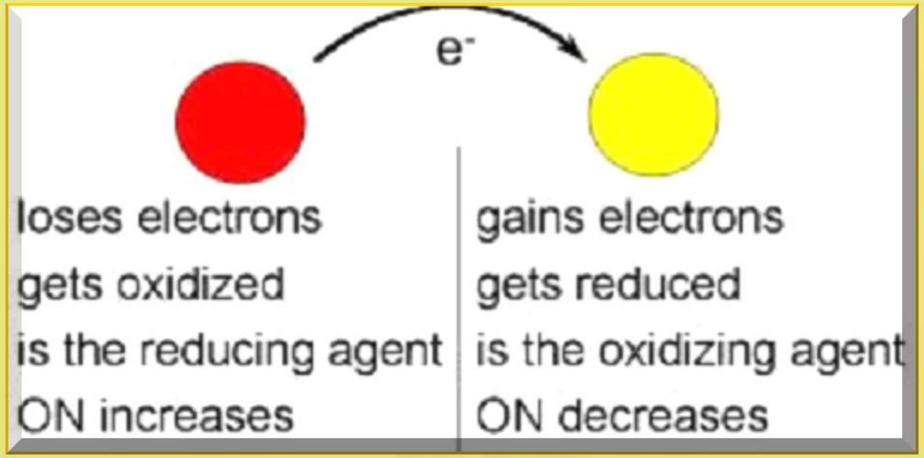




The electrons lost by the Zn^0 electrode (which is turns to Zn^{2+}) are transferred through the platinum wire to iron electrode where Fe^{3+} gains electrons, and turns to Fe^{2+} and thereby, an electric current is created . At zinc electrode an oxidation is occurred , it is called anode , it is a reducing agent and its E^0 value is less positive . while at iron electrode , reduction occurs and it is called cathode and its E^0 value is more positive . What happens in the galvanic cell is a spontaneous oxidation reduction reaction .

Rules for assigning oxidation state (OS)

We need to know which atoms are oxidized and which atoms are reduced during the redox reaction. Oxidation states OS (oxidation numbers ON) are used to keep track of how many electrons are lost or gained by each atom. In other words an increase in oxidation state corresponds to oxidation, and a decrease in oxidation state corresponds to reduction. The oxidation number tells us wither the compound is oxidized or reduced, i.e.to serve as a reducing agent or an oxidizing agent . These oxidation numbers are assigned using the following rules :



VIDEO
Galvanic , Zn , Cu

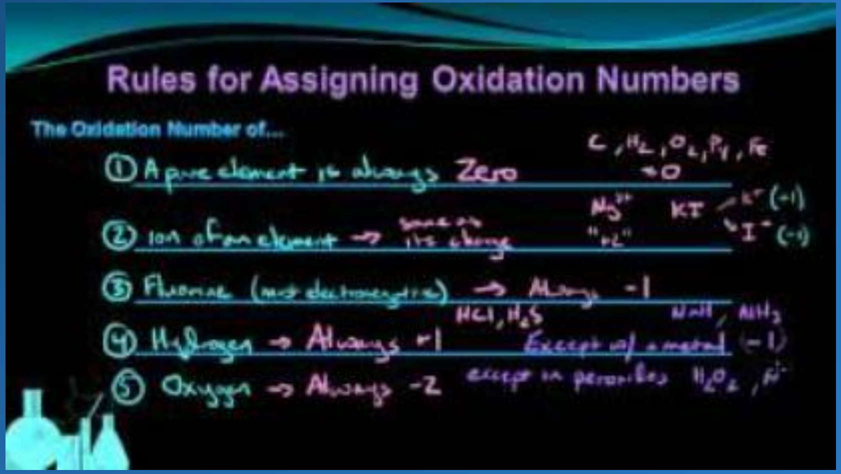
VIDEO
My Channel

Rules for assigning oxidation state (OS)

1-The convention is that the cation is written first in a formula, followed by the anion. That means if H is with metal (e.g. NaH) then H is H^- but if it is with nonmetal (e.g. HCl) then H is H^+ . However the usual oxidation number of hydrogen is +1.

2-The oxidation number of a free element is always 0. The atoms in Zn^0 and N_2, for example, have oxidation numbers of 0.

3-The oxidation number of a monatomic ion equals the charge of the ion. For example, the oxidation number of Na^+ is +1; the oxidation number of N^{3-} is -3.



Rules for Assigning Oxidation Numbers

The Oxidation Number of...

① A pure element is always Zero — C, H_2, O_2, P_4, Fe → 0

② ion of an element → same as its charge — Mg^{2+} "+2" KI → K^+ (+1), I^- (-1)

③ Fluorine (most electronegative) → Always -1

④ Hydrogen → Always +1 — HCl, H_2S — Except w/ a metal (-1) NaH, AlH_3

⑤ Oxygen → Always -2 except in peroxides H_2O_2

VIDEO
You Tube

VIDEO
My Channel

Rules for assigning oxidation state (OS)

4- The oxidation number of oxygen in compounds is usually -2.

5-The sum of the oxidation numbers of all of the atoms in a neutral compound is 0.

6-The sum of the oxidation numbers in a polyatomic ion is equal to the charge of the ion. For example, the sum of the oxidation numbers for SO_4^{2-} is -2.

7-In redox reactions, it is important to be able to identify which atoms are being oxidized and which atoms are being reduced. To identify if an atom is either oxidized or reduced, you only have to follow the electrons in the reaction.

Example : Identify the atoms that were oxidized and which atoms were reduced in the following reaction:

$$Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe$$

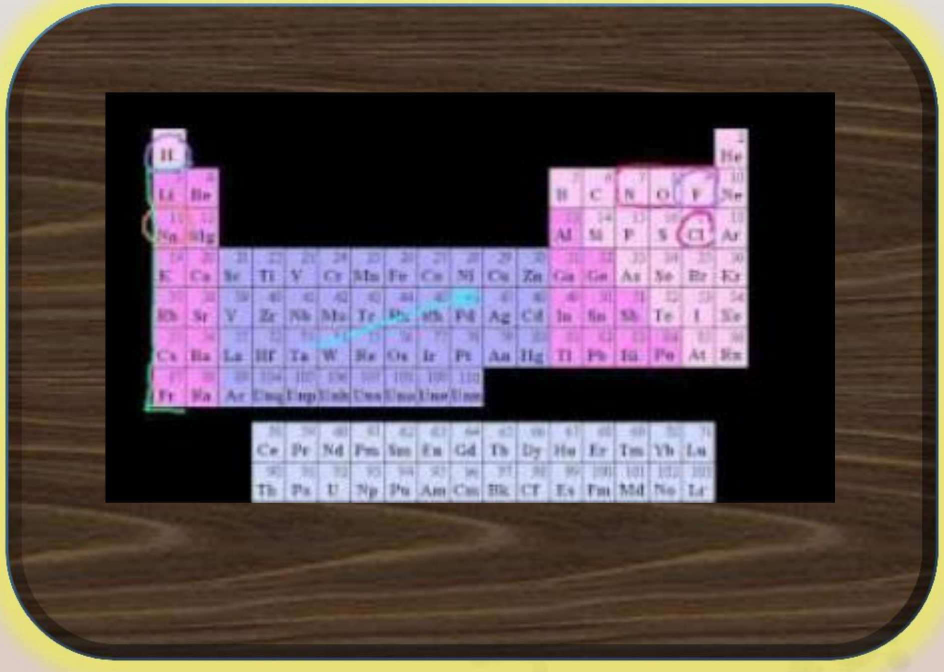
Rules for assigning oxidation state (OS)

Solution :

the first step is to assign oxidation numbers to each atom in the reaction.

Fe_2O_3:

The oxidation number of an oxygen atom is -2. 3 oxygen atoms has a total charge of -6. To balance this, the total charge of the iron atoms must be +6. Since there are two iron atoms, each iron must be in the +3 oxidation state. To summarize: -2 electrons per oxygen atom, +3 electrons for each iron atom.



VIDEO

You Tube

Rules for assigning oxidation state (OS)

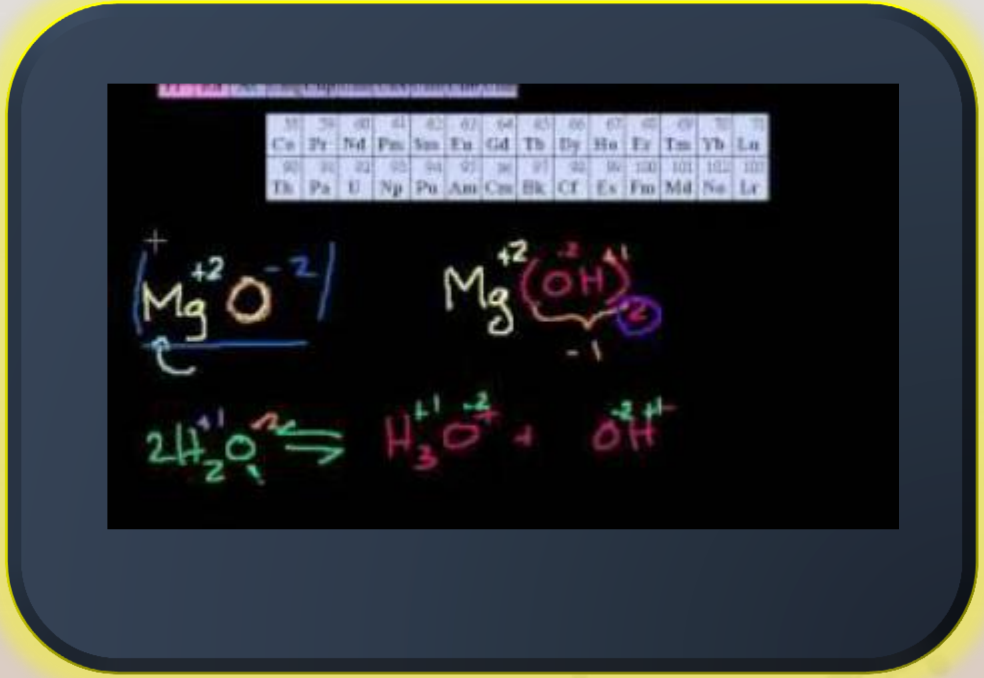
2 Al:

The oxidation number of a free element is always zero.

Al_2O_3:

Using the same rules for Fe_2O_3, we can see there are -2 electrons for each oxygen atom and +3 electrons for each aluminum atom.

http://www.youtube.com/watch?v=GA88JI4AymY&list=PL7wUg1fQdKR2s091GoRol_jyWoQJxNRcJ#t=35



VIDEO
You Tube

Rules for assigning oxidation state (OS)

2 Fe:

Again, the oxidation number of a free element is always zero.

Put all this together in the reaction, and we can see where the electrons went: Iron went from Fe^{3+} on the left side of the reaction to Fe^0 on the right. Each iron atom gained 3 electrons in the reaction.
Aluminum went from Al^0 on the left to Al^{3+} on the right. Each aluminum atom lost three electrons.Oxygen stayed the same on both sides

With this information, we can tell which atom was oxidized and which atom was reduced. Iron gained electrons so iron was oxidized. Aluminum lost electrons so aluminum was reduced.

Rules for assigning oxidation state (OS)

There is mnemonic to remember which reaction is oxidation and which reaction is reductions. It is OIL RIG:

Oxidation Is Loss of electrons (OIL)
Reduction Is Gain of electrons. (RIG)

Example: Determine the oxidation state of the colored element in each of the following:

1- Na_3PO_3
2- $H_2PO_4^-$

Rules for assigning oxidation state (OS)

Solutions:

1-The oxidation numbers of Na and O are +1 and -2. Since sodium phosphite is neutral, the sum of the oxidation numbers must be zero... Letting x be the oxidation number of phosphorus then, $0= 3(+1) + x + 3(-2)$. Then, x =oxidation number of P= +3.

2- Hydrogen and oxygen have oxidation numbers of +1 and -2. The ion has a charge of -1, so the sum of the oxidation numbers must be -1. Letting y be the oxidation number of phosphorus, $-1= y + 2(+1) +4(-2)$, then y = oxidation number of P= +5

Rules for assigning oxidation state (OS)

Example : Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the oxidation state of each):

$$Zn + 2H^{+} \rightarrow Zn^{2+} + H_2$$
$$2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$$
$$CO_3^{2-} + 2H^{+} \rightarrow CO_2 + H_2O$$

Solutions :

Zn is oxidized (Oxidation number : 0 → +2); H^{+} is reduced (Oxidation number: +1 → 0)

Al is oxidized (Oxidation number: 0 → +3); Cu^{2+} is reduced (+2 → 0)

This is not a redox type because each element has the same oxidation number

In both reactants and products: O = -2, H= +1, C= +4.

Rules for assigning oxidation state (OS)

An atom is oxidized when its oxidation number increases, i.e. the reducing agent, and an atom is reduced when its oxidation number decreases, i.e.the oxidizing agent. In other words, what is oxidized is the reducing agent and what is reduced is the oxidizing agent.

Example: Using the equations from the previous examples determine which is oxidized?

$$Zn + 2H^{+} \rightarrow Zn^{2+} + H_2$$

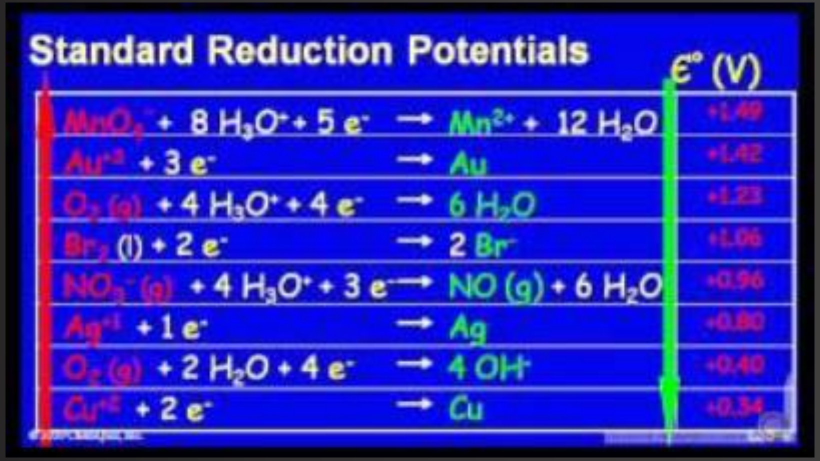
Solution :

The O.S. of H goes from +1 to 0 and the O.S. of Zn goes from 0 to 2+. Hence, Zn is oxidized and acts as the reducing agent .

Standard electrode Potential (E^0)

Standard electrode potential is given the symbol E° and it is an electrode potential measured under standard conditions; a room temperature (25°C), 1 atmosphere pressure and at 1 mole of the activity of redox participants of the half-reaction (i.e the Ox and the Red forms) Ox means the oxidized form and Red means the reduced form of a redox couple.

The Standard electrode potential of a redox couple cannot be measured alone



Standard Reduction Potentials

		ε° (V)
$MnO_4^- + 8\,H_3O^+ + 5\,e^-$	$\rightarrow Mn^{2+} + 12\,H_2O$	+1.49
$Au^{+3} + 3\,e^-$	$\rightarrow Au$	+1.42
$O_2\,(g) + 4\,H_3O^+ + 4\,e^-$	$\rightarrow 6\,H_2O$	+1.23
$Br_2\,(l) + 2\,e^-$	$\rightarrow 2\,Br^-$	+1.06
$NO_3^-\,(g) + 4\,H_3O^+ + 3\,e^-$	$\rightarrow NO\,(g) + 6\,H_2O$	+0.96
$Ag^{+1} + 1\,e^-$	$\rightarrow Ag$	+0.80
$O_2\,(g) + 2\,H_2O + 4\,e^-$	$\rightarrow 4\,OH^-$	+0.40
$Cu^{+2} + 2\,e^-$	$\rightarrow Cu$	+0.34

VIDEO
You Tube

VIDEO
My Channel

Standard electrode Potential (E^0)

(because free electrons do not exist in solution) unless is coupled to another electrode usually a standard hydrogen electrode (SHE) .

Both unknown and SHE electrodes are under standard conditions. The following graph shows the way that standard potential of the zinc couple is measured against SHE.

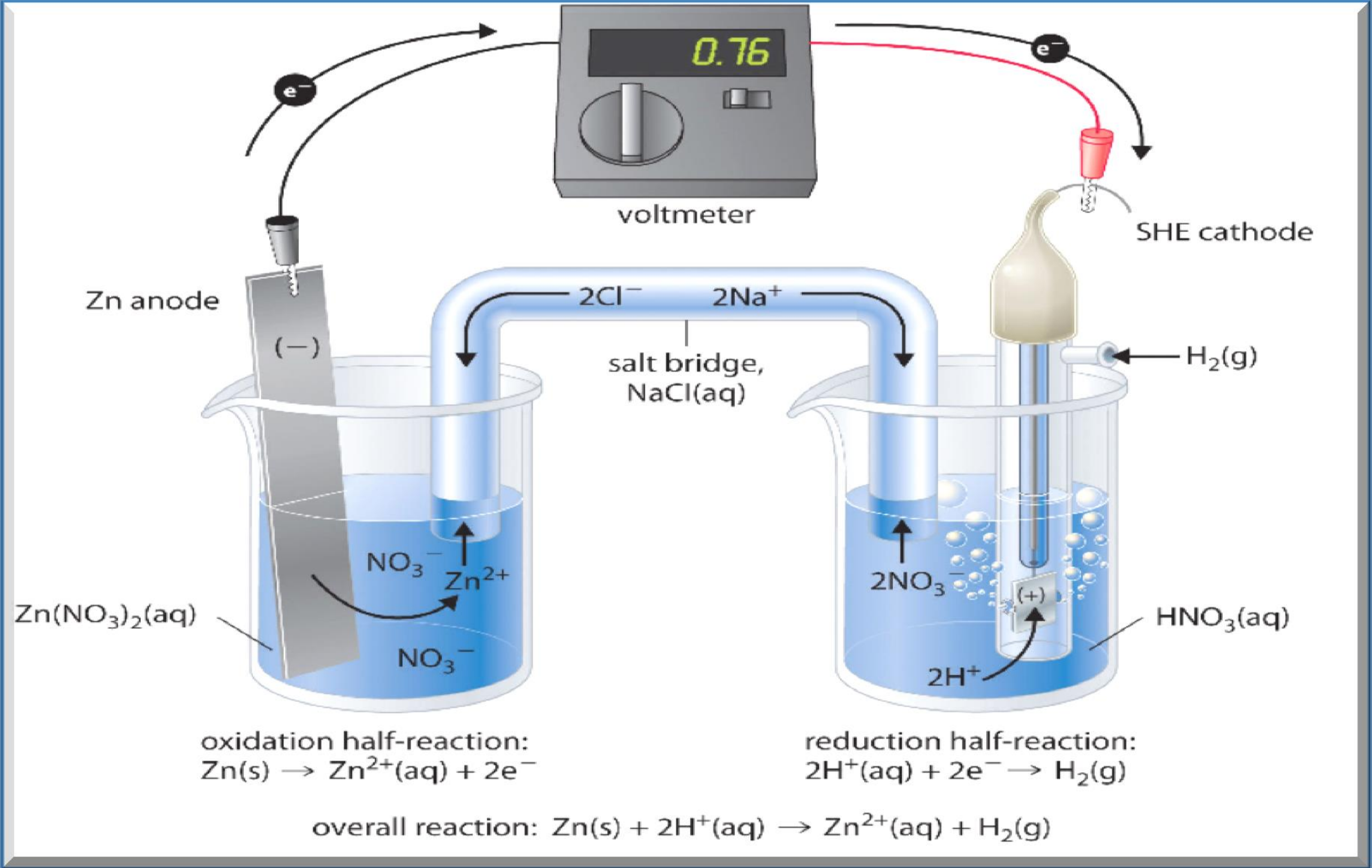
VIDEO
My Channel

VIDEO
You Tube

The E^0 values for the common redox couples are measured by the same above way .This is how we established the electrochemical series, some of which are shown in the following table .It is assumed that the E^0 for SHE under the standard conditions is equal to 0.00

Standard electrode Potential (E^0)

Measuring standard potentials using SHE



oxidation half-reaction:
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

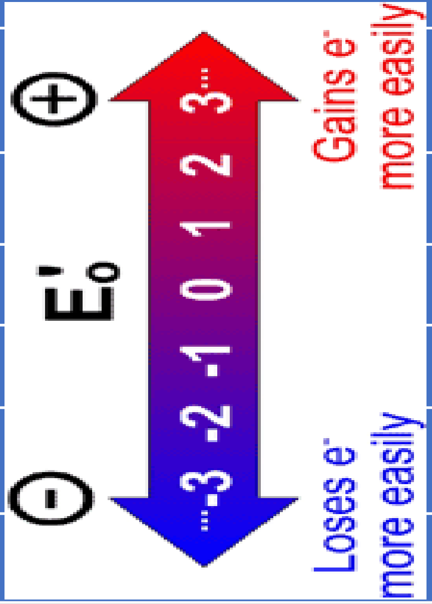
reduction half-reaction:
$2H^+(aq) + 2e^- \rightarrow H_2(g)$

overall reaction: $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

Standard electrode Potential (E^0)

This table shows small part of the electrochemical series of standard electrode potentials

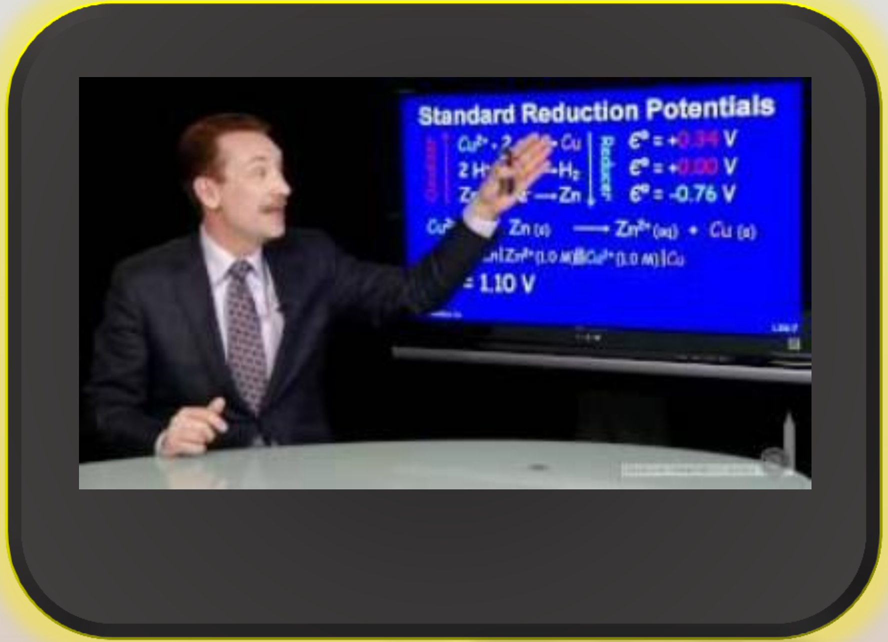
Redox couple have reaction	E^0 (V)
$Ce^{4+} + e \leftrightarrow Ce^{3+}$	1.44
$Ag^{+} + e \leftrightarrow Ag^{0}$	0.80
$Fe^{3+} + e \leftrightarrow Fe^{2+}$	0.77
$I_2 + 2e \leftrightarrow 2\,I^{-}$	0.54
$Sn^{4+} + 2e \leftrightarrow Sn^{2+}$	0.15
$H^{+} + e \leftrightarrow 1/2\,H_2$	0.00
$Cd^{2+} + 2\,e \leftrightarrow Cd^{0}$	- 0.40
$Zn^{2+} + 2\,e \leftrightarrow Zn^{0}$	- 0.76
$Al^{3+} + 3\,e \leftrightarrow Al^{0}$	- 1.66



Standard electrode Potential (E^0)

Metals at the bottom of the series are good at giving away electrons. They are good reducing agents. The reducing *ability of the metal increases as you go down the series.*

Metal ions at the top of the series are good at picking up electrons. They are good oxidizing agents. The oxidizing ability of the metal ions increases as you go up the series



VIDEO
You Tube

VIDEO
My Channel

Some important notes concerning the electrochemical series:

1-The Ox form for a couple will not react with the Ox form of another couple e.g. Fe^{3+} will not react with Sn^{4+} .

2-The Red form of a couple will usually react with the Red form of another couple e.g. Fe^{2+} will not react with Sn^{2+} .

Standard electrode Potential (E^0)

1. The Ox form of a couple will oxidize the Red form of the couple under it in series but will not oxidize the Red form of the couple over it in the series e.g. Fe^{3+} will oxidize Sn^{2+} but not Ag^0.
2. All have reactions are written as reduction whatever the direction of the have reaction.
3. The more negative the E° value, the more readily the element loses electrons and becoming a reducing agent .i.e the stronger its Red form and the weaker its Ox form.
4. The more positive (or less negative) the E° value, the more readily the element gains electrons and becomes an oxidizing agent. I.e the stronger its Ox form and the weaker its Red form.
5. Therefore, for the two have reactions of the redox reaction, the one with the more positive E^0 value is the oxidizing agent.

Standard electrode Potential (E^0)

6- The – sign of E^0 value indicates that this couple when joint with SHE under standard conditions will become reducing agent and its half reaction will proceed in the opposite direction (from right to left). In other words, the standard potential is a measure of the tendency of the oxidizing agent to be reduced. Its value is zero for $H^+ + e^- \rightarrow \frac{1}{2} H_2$ by definition, positive for oxidizing agents stronger than H^+ (e.g., +1.44 V for Ce) and negative for oxidizing agents that are weaker than H^+ (e.g., –0.76 V for Zn^{2+}).

Balancing redox reaction equation:

7-It is possible for a redox couple to be an oxidizing agent in a reaction and to be a reducing agent in another reaction e.g. Fe^{3+} will oxidize Sn^{2+} but Fe^{2+} will reduce Ag^{+} . However principal oxidising agents are: Potassium permanganate, potassium dichromate, iodine , cerium(IV) salt and potassium iodate . Also frequently used Reducing Agents are: iron (ii), tin (ii) compounds, sodium thiosulphate .

3-The oxidizing agent represents the cathode while the reducing agent represents the anode in a galvanic cell.

Balancing redox reactions :

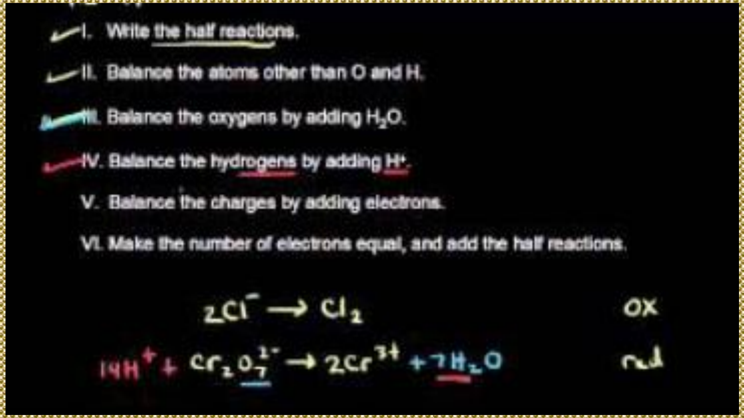
The following steps should be followed to balance a redox equation in acidic medium

(add the starred steps in a basic medium):

1. Divide the equation into an oxidation half-reaction and a reduction half-reaction

Balancing redox reaction equation:

2. Balance these
    - Balance the elements other than H and O
    - Balance the O by adding H_2O
    - Balance the H by adding H^+
    - Balance the charge by adding e^-
3. Multiply each half-reaction by an integer such that the number of e^- lost in one equals the number gained in the other
4. Combine the half-reactions and cancel
5. **Add OH^- to each side until all H^+ is gone and then cancel again**



I. Write the half reactions.

II. Balance the atoms other than O and H.

III. Balance the oxygens by adding H_2O.

IV. Balance the hydrogens by adding H^+.

V. Balance the charges by adding electrons.

VI. Make the number of electrons equal, and add the half reactions.

$2Cl^- \rightarrow Cl_2$ ox

$14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$ red

VIDEO You Tube

VIDEO My Channel

VIDEO My Channel

VIDEO You Tube

Balancing redox reaction equation:

Example : Balance the redox reaction in acidic solution:

$$MnO_4^- + 2\,I^- \rightarrow Mn^{2+} + I_2\,(s)$$

Solution :

Write and balance the half reactions:

$MnO_4^- + 2\,I^- \text{-->} Mn^{2+} + I_{2(s)}$

+7 -2 -1 +2 0

(Mn is reduced and I^- is oxidized)

Oxidation reaction : $2I^-_{(aq)} \text{-->} I_{2(s)} + 2e^-$

Reduction reaction : $MnO_4^- + 5e^- \text{-->} Mn^{2+}$

Balance oxygen, O, by adding H_2O

Oxidation reaction : $2I^-_{(aq)} \text{-->} I_{2(s)} + 2e^-$

Balancing redox reaction equation:

Reduction reaction : $MnO_4^- + 5e^- \text{-->} Mn^{2+} + 4H_2O$

Balance hydrogen, H, by adding H^+

Oxidation reaction : $2I^-_{(aq)} \text{-->} I_{2(s)} + 2e^-$

Reduction Rx : $MnO_4^- + 5e^- + 8H^+ \text{-->} Mn^{2+} + 4H_2O$

Balance charge by adding electrons through multiplying both half reactions by some integer to cancel out electrons .

Oxidation reaction : $(2I^-_{(aq)} \text{-->} I_{2(s)} + 2e^-) * 5$

Reduction reaction: $(MnO_4^- + 5e^- + 8H^+ \text{-->} Mn^{2+} + 4H_2O) *2$

Oxidation reaction : $10I^-_{(aq)} \text{-->} 5I_{2(s)} + 10e^-$

Reduction reaction : $2MnO_4^- + 10e^- + 16H^+ \text{-->} 2Mn^{2+} + 8H_2O$

Balancing redox reaction equation:

- Add the half reactions together and cancel out what appears on both sides:

  $10I^-_{(aq)} + 2MnO_4{}^-_{(aq)} + 16H^+_{(aq)} \text{-->} 2Mn^{2+}_{(aq)} + 5I_{2(s)} + 8H_2O_{(l)}$

  (Note: Don't forget the states of matter! Generally, anything with a charge is $_{(aq)}$ and H_2O is $_{(l)}$)

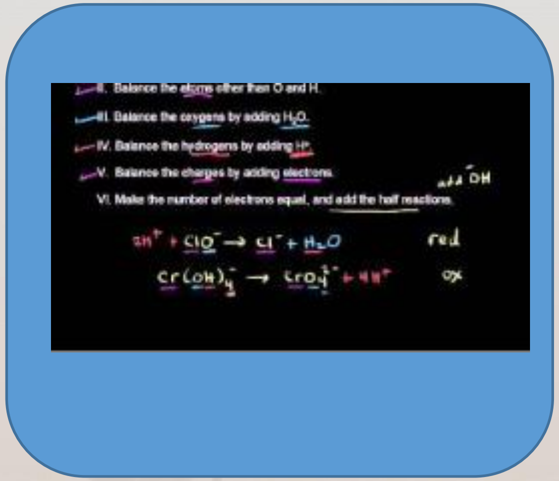
Balancing in basic solution follows balancing in acidic solutions in three steps:

- Balance the reaction in acidic solution
- Add the same amount of OH^- ions as H^+ ions to both sides of the equation. On one side, the OH^- and H^+ will react to form water (H_2O) in a 1:1 ratio. Cancel out water molecules appearing on both sides .
- Example : Balance the above redox reaction in basic solution

Balancing redox reaction equation:

VIDEO
My Channel

VIDEO
You Tube



II. Balance the atoms other than O and H.

III. Balance the oxygens by adding H_2O.

IV. Balance the hydrogens by adding H^+.

V. Balance the charges by adding electrons.

VI. Make the number of electrons equal, and add the half reactions.

Solution :

- Balance the reaction in acidic solution

  $10I^-_{(aq)} + 2MnO_4^-{}_{(aq)} + 16H^+_{(aq)} \text{-->} 2Mn^{2+}_{(aq)} + 5I_{2(s)} + 8H_2O_{(l)}$

- Add the same amount of OH^- ions as H^+ ions to both sides of the equation.

  $10I^-_{(aq)} + 2MnO_4^-{}_{(aq)} + 16H^+_{(aq)} + 16OH^- \text{-->} 2Mn^{2+}_{(aq)} + 5I_{2(s)} + 8H_2O_{(l)} + 16OH^-$

  On one side, the OH^- and H^+ will react to form water (H_2O) in a 1:1 ratio.

  $10I^-_{(aq)} + 2MnO_4^-{}_{(aq)} + 16H_2O \text{-->} 2Mn^{2+}_{(aq)} + 5I_{2(s)} + 8H_2O_{(l)} + 16OH^-$

Cancel out the water molecules appearing on both sides

$10I^-_{(aq)} + 2MnO_4^-{}_{(aq)} + 8H_2O_{(l)} \text{-->} 2Mn^{2+}_{(aq)} + 5I_{2(s)} + 16OH^-_{(aq)}$

Symbol for Galvanic Cells

Instead of drawing a cell diagram chemists have devised a shorthand way of completely describing a cell called symbol or line notation. This notation scheme places the constituents of the cathode on the right of the salt bridge [which is shown in the notation as a double line (||)] and the anode components on the left.

The phases of all reactive species are listed and their concentrations or pressures are given if those species are not in their standard states. All phase interfaces are noted with a single line (|) and multiple species in a single phase are separated by commas. For example, the previous iron – zinc cell would be written as:

$$\overbrace{Zn^0 \; / \; Zn^{2+}}^{\text{anode}} \; // \; \overbrace{Fe^{3+} , \; Fe^{2+}}^{\text{cathode}} \; / \; Pt$$

Electrode potential (Nernst equation)

Also note that Zn^0 turns to Zn^{2+} by losing electrons and Fe^{3+} turns to Fe^{2+} by gaining electrons.

One of the more useful calculations in redox reactions is the Nernst Equation. This equation allows us to calculate the electric potential of a redox reaction in "non-standard" situations :

$$E = E^{0} + \frac{RT}{nF} Ln \frac{[Ox]}{[Re\,d]}$$

By compensation for the values of the constants (R (gas constant) = 8.314510 J/K . mole , T (absolute temperature at 25 ^{0}C) , F (Faraday constant) =9.6485×10^4 J/V . mole - n the number of electrons gained or lost in have redox reaction) and converting Ln to log we obtain the simplified formula.

Electrode potential (Nernst Equation)

$$E = E^0 + \frac{0.059}{n} \log \frac{[Ox]}{[Red]}$$

It is clear from Nernest equation that an electrode potential depends on temperature, the concentration of the Ox and the Red forms of the electrode couple and the number of electrons transferred during half reaction.

The E^o values and the equilibrium constant are both measures of the tendency for a reaction to take place

Equilibrium constant in redox reactions

The following equation is for the equilibrium constant for the iron – zinc redox reaction :

$$2\,Fe^{3+} + Zn^{0} \leftrightarrow 2\,Fe^{2+} + Zn^{2+}$$

$$K_{eq} = \frac{[Fe^{2+}]^2[Zn^{2+}]}{[Fe^{3+}]^2[Zn^{0}]}$$

In this equation as we previously know we compensates for both, [solid] = 1 and also $[H_2O] = 1$. At the start of the galvanic redox reaction the cathode potential (E_c) is high and the potential of the anode (E_a) is low . During the reaction, $[Fe^{2+}]$ and $[Zn^{2+}]$ will increase while $[Fe^{3+}]$ will decrease. When the equilibrium is reached, E_c will be equal to E_a i.e the electrical current will stop

Equilibrium constant in redox reactions

and the battery will be dead ($E_{cell} = 0$) .Suppose you have two water tanks connected through pipe, one is filled with water the other is half full . The water will flow from the filled one to the half filed till the level of water in both tanks are equal, then the water flow will stop. This is what happens in galvanic cell.

$$E_{cell} = E_c - E_a = 0$$

This means:

$$E_c = E_a$$

applying Nernst equation to both cathode and anode we obtain :

Equilibrium constant in redox reactions

$$E^0{}_{Fe} + \frac{0.059}{2}\log\frac{[Fe^{3+}]^2}{[Fe^{2+}]^2} = E_{Zn}{}^0 + \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Zn^0]}$$

Rearranging this equation we get:

$$E_{Fe}{}^0 - E_{Zn}{}^{\circ} = \frac{0.059}{2}\log\frac{[Fe^{2+}]^2[Zn^{2+}]}{[Fe^{3+}]^2[Zn^0]}$$

$$E_{Fe}{}^0 - E_{Zn}{}^{\circ} = \frac{0.059}{2}\log K_{eq}$$

$$\log K_{eq} = \frac{2\,(E_{Fe}{}^0 - E_{Zn}{}^0)}{0.059}$$

Equilibrium constant in redox reactions

The general formula for calculating equilibrium constant for any redox reaction is:

$$\log K_{eq} = \frac{N\,(E_c^{\,0} - E_a^{\,0})}{0.059}$$

Where E_c^0 is the cathode standard potential , E_a^0 is the standard potential for the anode and N is the total electrons transferred in the redox reaction .Note that the more difference between E_c^0 and E_a^0 the larger the value of K_{eq} and the more complete the redox reaction will be .

The rate of redox reactions

From general observations we may say:

1. Most redox reactions particularly organic redox reactions are slow compared to acid – base or EDTA reactions.

2. If the electrons of the cathode half reaction does not equal the electrons of the anode half reaction, the overall reaction usually slow.

3. The redox reaction is usually fast if it is between cation and anion .

4. If E^0_{cell} ($E_c^0 – E_a^0$) is high, the redox reaction will be complete but not necessary fast

Summary

In this unit , the fundamentals of oxidation – reduction reactions have been investigated such as the definition of redox reactions , oxidizing agent , reducing agent , balancing redox reaction equations , standard electrode potential , electrode potential and calculation of redox reaction equilibrium constant K_{eq} . We have emphasized on the distinguish between oxidizing and reducing agents , finding the oxidation number of an element in a compound participating in a redox reaction and how to write a balanced redox reaction .The relationship between redox reaction and galvanic cell has been fully discussed .

Tutorial

Exercise 1 : 5 g of a sample containing iron (aw = 55.85) has been dissolved in water and all iron has been oxidized to Fe^{3+} . An excess of KI was added to this solution and the following reaction was occurred :

($2\ Fe^{3+} + 2I^{-} \rightarrow 2\ Fe^{2+} + I_2$) .The produced I_2 was titrated with 0.2 M $S_2O_3^{-2}$ solution according to the following reaction : ($I_2 + 2S_2O_3^{2-} \rightarrow 2\ I^{-} + S_4O_6^{2-}$) . If the volume of $S_2O_3^{2-}$ solution at the equivalent point is 20 ml , calculate the percentage of iron in the sample ?

OXIDATION REDUCTION REACTIONS

Tutorial

Your answer :

Our answer next slide

Tutorial

Answer 1 :

mmoles of $S_2O_3^{2-}$ = 20 X 0.2 = 4

mmoles of I_2 = 4 X 1/2 = 2

mmoles of Fe^{3+} = mmoles of I_2 X 2/1 = 2 X 2 = 4

weight of iron = 4 x 55.85 = 223.4 mg

% iron = [(223.4 x 10^{-3}) /5] x 100 = 4.

Tutorial

Exercise 2 : Calculate the tin electrode potential in a solution containing 0.2 M Sn^{2+} and 0.1 M Sn^{4+} ? $E^0_{Sn} = 0.15$ V

Your answer :

Our answer next slide

Tutorial

Answer 2 : direct application to Nernst equation :

$$E = 0.15 + \frac{0.059}{2}\log\frac{0.1}{0.2} = 0.14\ V$$

Tutorial

Exercise 3 : The followings are two halves of a redox reaction :

$$Sn^{4+} + 2\,e \leftrightarrow Sn^{2+} \qquad E^0 = 0.15\ V$$

$$Ag^{+} + e \leftrightarrow Ag^{0} \qquad E^0 = 1.8\ V$$

1- Write the balanced redox reaction ?

2- What is the symbol for the galvanic cell . Comment on your answer ?

3- Calculate K_{eq} for the redox reaction ?

4- Calculate the reaction standard potential E^0_{cell} . Comment on your answer ?

OXIDATION REDUCTION REACTIONS

Tutorial

Your answer :

Our answer next slide

Tutorial

Answer 3 :

(1) Ag^+ is the oxidizing agent because its standard potential is the highest so it will be reduced and will represent the cathode in the galvanic cell . Therefore the balanced reaction equation is : $2Ag^+ + Sn^{2+} \leftrightarrow 2\,Ag^0 + Sn^{4+}$.

(2) Sn^{2+}, Sn^{4+} // Ag+ / Ag^0 / Pt .

(3) $$\log K_{eq} = \frac{2\,(1.8 - 0.15\,)}{0.059} = 55.932 \quad \therefore \quad K_{eq} = 8.55\,x\,10^{55}$$

The value of K_{eq} is very high so the reaction is nearly complete .

(4) $$\Delta E^0 = E_c^{\,0} - E_a^{\,0} = 1.8 - 0.15 = 1.65\,V$$

The value of $\Delta\ E^0$ is relatively high so again the reaction is near completion .

Tutorial

Exercise 4 : You have the following galvanic cell symbol :

$$Al^0 \;/\; Al^{3+}\,(0.1\ M)\;//\;Sn^{4+}\,(0.2\ M)\;,\;Sn^{2+}\,(0.1\ M)\,/\,Pt$$

$$(\,E_{Al}^{0} = -1.76\ V \quad , \quad E_{Sn}^{0} = 0.15\ V\,)$$

(1) Write the balanced cell reaction ?

(2) Calculate the cell potential under the giving conditions ?

(3) Calculate the K_{eq} for the reaction ?

Your answer :

Our answer next slide

OXIDATION REDUCTION REACTIONS

Tutorial

Answer 4 : (1) It is clear from the cell symbol and from the values of the standard potentials that Sn^{4+} is the oxidizing agent , therefore we can write the balanced equation as follows :

$$3\ (\ Sn^{4+}\ +2\ e \leftrightarrow Sn^{2+}\ )\ ,\qquad E^0 = 0.15\ V$$

$$\underline{2\ (\ Al^0 \leftrightarrow 3\ e\ +\ Al^{3+}\ )\ ,\qquad E^0 = -\ 1.76}\ V$$

$$3\ Sn^{4+} + 2\ Al^0 \leftrightarrow 3\ Sn^{2+} + 2\ Al^{3+}\ ,\quad \Delta E^0 = 0.15-(-1.76) = 1.91\ V$$

(2) To calculate the cell potential under the giving concentrations we apply the Nernst equation to both the cathode and the anode and then we subtrsct the later from the former thus

$$E_c = 0.15 + \frac{0.059}{2}\log\frac{0.2}{0.1} \approx 0.16\ V$$

$$E_a = -1.76 + \frac{0.059}{3}\log\frac{0.1}{1} = -1.78\ V$$

$$E_{cell} = 0.16 - (-1.78) = 1.94\ V$$

(3)

$$\log\ K_{eq} = \frac{6\ [0.15-(-1.76)]}{0.059} = 32.373 \therefore K_{eq} = 2.360\ X\ 10^{32}$$

Tutorial

Exercise 5 : Determine the oxidation states:

1.$Fe(s) + O_2(g) \rightarrow Fe_2O_3(g)$

2.Fe^{2+}

3.$Ag(s) + H_2S \rightarrow Ag_2S(g) + H_2(g$

Your answer :

Our answer next slide

OXIDATION REDUCTION REACTIONS

Tutorial

Answer 5 :

1.Fe and O_2 are free elements, therefore they have an O.S. of "0". The product has a total O.S. equal to "0" , O_3 has an O.S. of -2, which means Fe_2 has an O.S. of +2.

2.The O.S. of Fe corresponds to its charge, therefore the O.S. is +2.

3.Ag has an O.S. of 0 , H_2 has an O.S. of +1 and S has an O.S. of -2 .

OXIDATION REDUCTION REACTIONS

Tutorial

Exercise 6 : Determine the oxidation state of the bold element in each of the following:

1. $Na_3\mathbf{P}O_3$
2. $H_2\mathbf{P}O_4$

Your answer :

Our answer next slide

Tutorial

Anawer 6 :

1.The oxidation numbers of Na and O are +1 and -2. Since sodium phosphite is neutral, the sum of the oxidation numbers must be zero.. Letting x be the oxidation number of phosphorus then, $0= 3(+1) + x + 3(-2)$. x=oxidation number of P= +3.

2.Hydrogen and oxygen have oxidation numbers of +1 and -2. The ion has a charge of -1, so the sum of the oxidation numbers must be -1. Letting y be the oxidation number of phosphorus, $-1= y + 2(+1) +4(-2)$, y= oxidation number of P= +5

OXIDATION REDUCTION REACTIONS

Tutorial

Exercise 7 : Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the oxidation state of each):

1. $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$
2. $2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$
3. $CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$

Your answer :

Our answer next slide

OXIDATION REDUCTION REACTIONS

Tutorial

Answer 7 :

1. Zn is oxidized (Oxidation number: 0 → +2); H^+ is reduced (Oxidation number: +1 → 0) .

2. Al is oxidized (Oxidation number: 0 → +3); Cu^{2+} is reduced (+2 → 0)

3. This is not a redox type because each element has the same oxidation number in both reactants and products: O= -2, H= +1, C= +4.

OXIDATION REDUCTION REACTIONS

Exercise 8 : determine what is oxidized?

$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

Your answer :

Our answer next slide

Tutorial

Answer 8 :

The O.S. of H goes from +1 to 0 and the O.S. of Zn goes from 0 to 2+. Hence, Zn is oxidized and acts as the reducing agent.

Tutorial

Exercise 9 : Balance the following half-equation:

$$MnO_4^- \rightarrow Mn^{2+}$$

Your answer :

Our answer next slide

Tutorial

Answer 9 :

1.Because there is one atom of Mn on both sides, no adjustment is required.

2.Because manganese is reduced from an oxidation number of +7 to +2, five electrons must be added to the left ($MnO_4^- + 5e^- \rightarrow Mn^{2+}$)

3.There is a total charge of -6 on the left versus +2 on the right. To balance, add eight H^+ to the left to give a charge of +2 on both sides. ($MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+}$)

4.To balance the eight H^+ ions on the left, add four H_2O molecules to the right.

$$\mathbf{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}$$

Tutorial

Exercise 10 : A piece of iron, e.g. an iron nail, is dropped into a solution of copper sulphate. The nail gets coated with copper metal. Write the reaction that takes place, and the redox equation. Which atom has reduced, and which was oxidized ?

Your answer :

Our answer next slide

OXIDATION REDUCTION REACTIONS

Tutorial

Answer 10 :

Fe + $CuSO_4$ ----> $FeSO_4$ + Cu

Fe + Cu^{2+} + SO_4^{2-} ----> Fe^{2+} + SO_4^{2-} + Cu

Now, the SO_4^{2-} is unchanged left and right sides of the equation, so has not been oxidized nor reduced.

Redox Reaction: Fe + Cu^{2+} ----> Fe^{2+} + Cu

Iron Fe was oxidized to Fe^{2+}, Cu^{2+} was reduced to Cu

على الراغبين الاستماع الى محاضرات الاستاذ الدكتور/ ابراهيم زامل الزامل باللغة العربية عن هذا الموضوع الرجوع الى الروابط التالية :

تفاعلات الاكسدة و الاختزال

تفاعلات الاكسدة و الاختزال ٢