

Course Name: Chemistry

Course NO: CHE1203

Oxidation-Reduction reactions

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# Oxidation-Reduction reactions

## Classical Concept

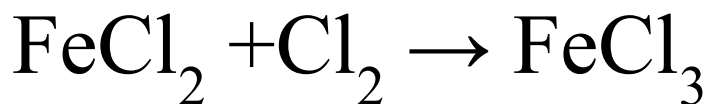
Oxidation simply means the addition of oxygen to elements or compounds. The reduction is the removal of oxygen from a compounds.

Addition of oxygen:  $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$

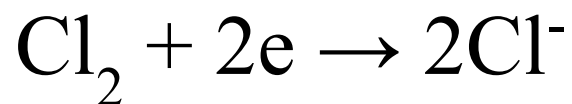
Removal of oxygen:  $2\text{CuO} \rightarrow 2\text{Cu} + \text{O}_2$

## Valence state concept

Oxidation is a chemical reaction which involves change of valence state in the positive direction.



Reduction is a chemical reaction which involves change of valence state in the negative direction.



# **Electronic concept**

## **Oxidation Reaction**

Oxidation is the loss of electrons or an increase in the oxidation state of an atom, an ion, or of certain atoms in a molecule.



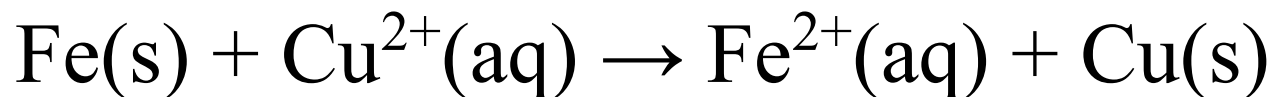
## **Reduction Reaction**

Reduction is the gain of electrons or a decrease in the oxidation state of an atom, an ion, or of certain atoms in a molecule (a reduction in oxidation state).



## **Oxidizing Agent or Oxidant**

An oxidizing agent is one that accepts electrons and is thereby reduced. Here in the following reaction,  $\text{Cu}^{2+}$  is an oxidizing agent and it is reduced because  $\text{Cu}^{2+}$  accepts two electron from Fe.

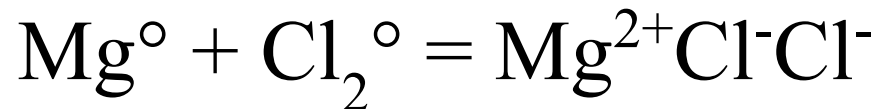


## **Reducing Agent or Reductant**

A reducing agent is one that gives off electrons and is thereby oxidized. In the upper reaction, Fe is a reducing agent and it is oxidized because  $\text{Fe}^{\circ}$  donate two electrons to  $\text{Cu}^{2+}$ .

## Oxidation state and Oxidation number

The oxidation number (or oxidation state) of an atom in a substance as the actual charge (+ve or -ve or zero) of the atom if it exists as a monoatomic ion, or a hypothetical charge assigned to the atom in the substance by simple rule.



The oxidation number of Mg undergoes a change from zero in the free state to 2+ and the oxidation number of chlorine changes from zero in the free state to 1-. Neutral molecule has zero charge e.g.  $(\text{MgCl}_2)^{\circ}$

## Rules for Assigning Oxidation Numbers

(i) The convention is that the cation is written first in a formula, followed by the anion. For example, in NaH, the H is  $\text{H}^-$  (hydride ion) in HCl, the H is  $\text{H}^+$  (hydrogen ion).

(ii) The oxidation number of a free element is always 0. The atoms in He and  $\text{N}_2$ , for example, have oxidation numbers of 0.

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

(iv) The usual oxidation number of hydrogen is 1+. The oxidation number of hydrogen is 1- in compounds containing elements that are less electronegative than hydrogen, as in  $\text{CaH}_2$ .

(v) The oxidation number of oxygen in compounds is usually 2-. Exceptions include  $\text{OF}_2$  because F is more electronegative than O, and  $\text{BaO}_2$ , due to the structure of the peroxide ion, which is  $[\text{O}-\text{O}]^{2-}$ .

(vi) The oxidation number of a Group IA element in a compound is 1+.

(vii) The oxidation number of a Group IIA element in a compound is 2+.



(viii) The oxidation number of a Group VIIA element in a compound is 1-, except when that element is combined with one having a higher Electronegativity. The oxidation number of Cl is 1- in HCl, but the oxidation number of Cl is 1+ in HOCl.

(ix) The sum of the oxidation numbers of all of the atoms in a neutral compound is 0. e.g.  $(\text{MgCl}_2)^\circ$ .

(x) 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  $\text{SO}_4^{2-}$  is 2-.

# The Half-Reaction Method of Balancing Redox Equations

A powerful technique for balancing oxidation-reduction equations involves dividing these reactions into separate oxidation and reduction half-reactions. We then balance the half-reactions, one at a time, and combine them so that electrons are neither created nor destroyed in the reaction. The steps are-

Step 1: Assign oxidation numbers to atoms on both sides of the equation.

Step 2: Write a skeleton equation for the reaction.

Step 3: Determine which atoms are oxidized and which are reduced.

Step 4: Divide the reaction into oxidation and reduction half-reactions and balance these half-reactions one at a time.

Step 5: Complete and balance each half-reaction:

- (a) Balance all atoms except O and H.
- (b) Balance O atoms by adding  $\text{H}_2\text{O}$ 's to one side of the equation
- (c) Balance H atoms by adding  $\text{H}^+$  ions to one side of equation
- (d) Balance electronic charge by adding  $e$  to more positive side.

Step 6: Combine these half-reactions so that electrons are neither created nor destroyed.

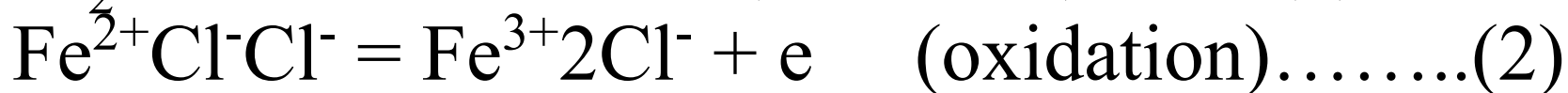
Step 7: Balance the remainder of the equation by inspection, if necessary.

Example 1: Ferrous chloride is oxidized by chlorine to ferric chloride.

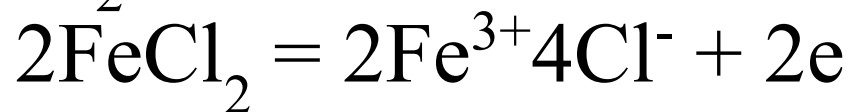
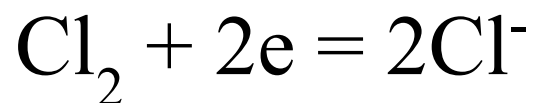
Skeleton reaction



Two half reactions:

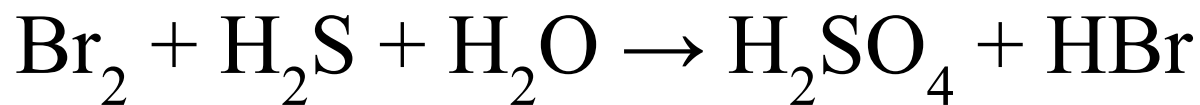


Since the loss and gain of electrons during the process must be equal, the second part has to be multiplied by 2.

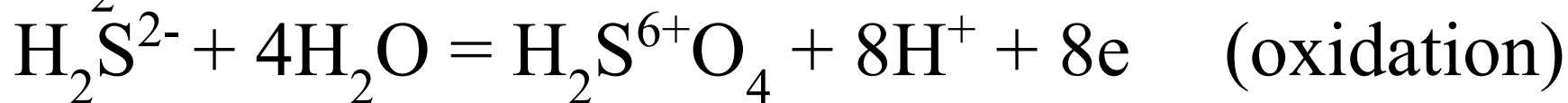


Example 2:  $\text{H}_2\text{S}$  is oxidized to  $\text{H}_2\text{SO}_4$  when passed into a concentrated aq. solution of bromine.

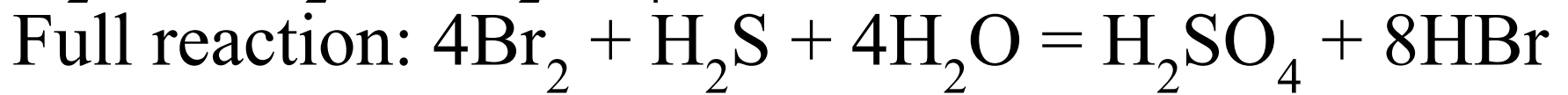
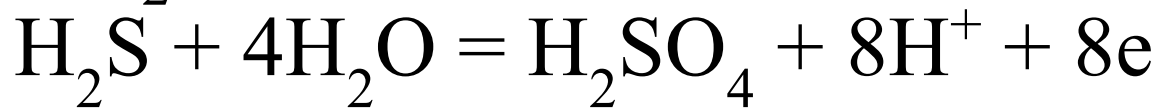
Skeleton reaction:



Two half reactions:

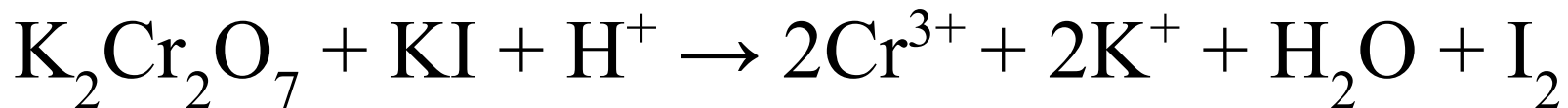


The loss and gain of electrons must be equal. Hence the upper half-reaction is to be multiplied by 4.

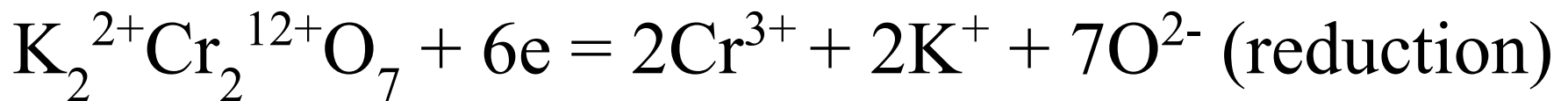


Example 3: Potassium dichromate oxidizes potassium iodide in acidic solution liberating iodine.

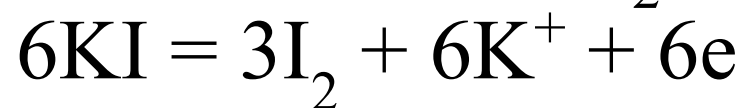
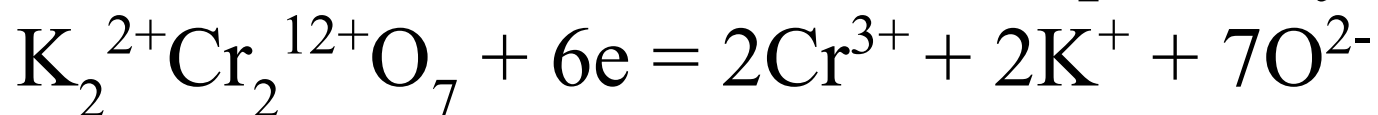
Skeleton reaction



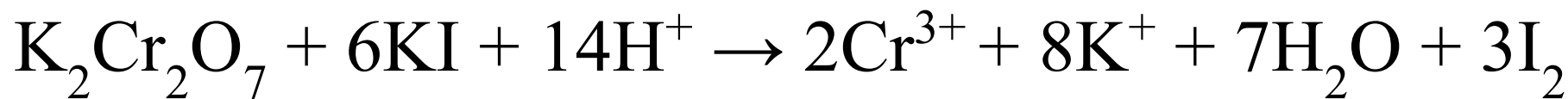
The half-reactions are



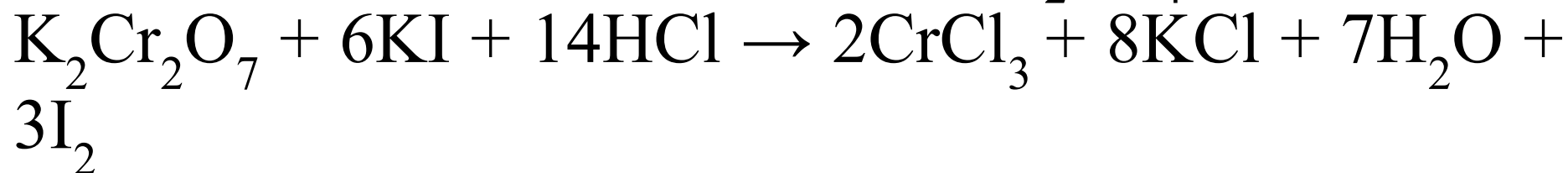
Now,  $7\text{O}^{2-}$  require  $14\text{H}^+$  ions to form  $7\text{H}_2\text{O}$ , therefore,  $14\text{H}^+$  is to introduced in the half-reaction and in order to make the number of electron lost and gained equal, the half-reactions is to be multiplied by 3.



Overall equation:

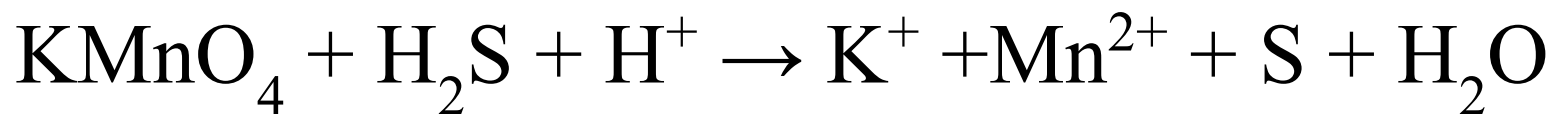


$\text{H}^+$  can come from any acid ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  etc.)

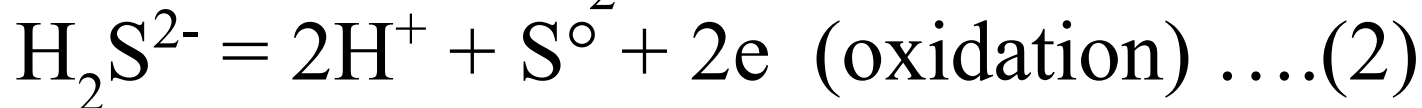


Example 4: Potassium permanganate oxidizes  $\text{H}_2\text{S}$  in aq. solution and sulphur is liberated.

Skeleton reaction:

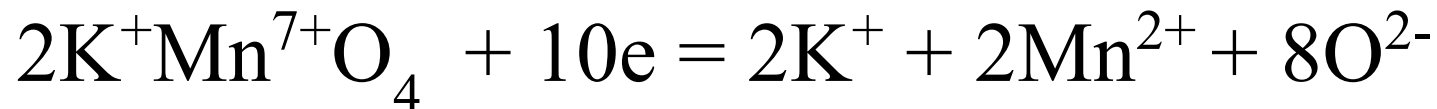


Half-reactions are

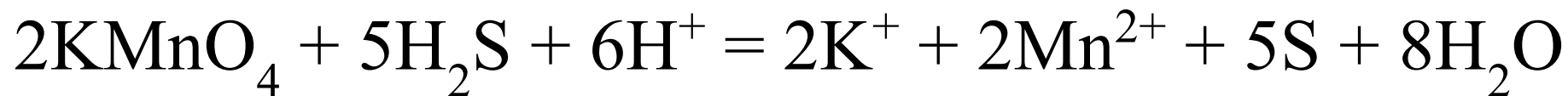


Multiplying eqn. (1) by 2 and eqn. (2) by 5 in order to make the loss and gain of electrons equal.

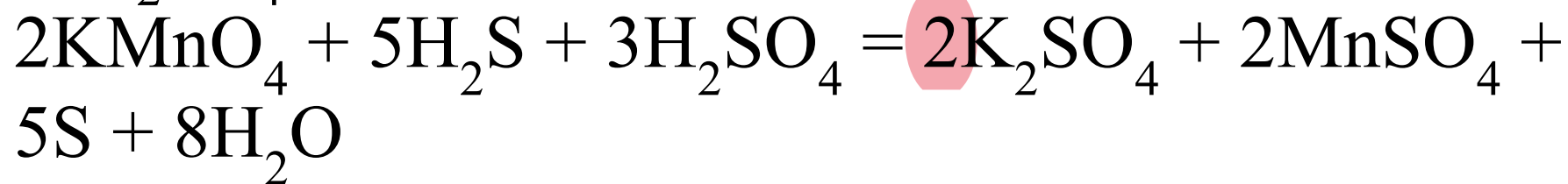




Overall reaction:

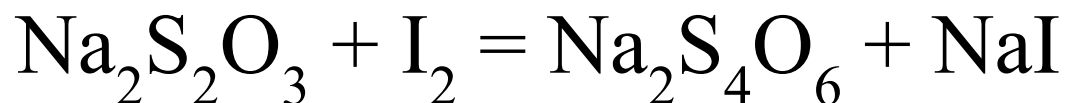


If  $\text{H}_2\text{SO}_4$  is added-



Example 5: The oxidation of sodium thiosulphate by iodine.

The skeleton reaction:



$\text{Na}_2\text{S}_2\text{O}_3$  is converted to  $\text{Na}_2\text{S}_4\text{O}_6$ ,  $\text{I}_2$  is converted to  $\text{I}^-$ .

Here  $\text{Na}_2\text{S}_2^{4+}\text{O}_3 = \text{Na}_2\text{S}_4^{10+}\text{O}_6$

Thus each S atom of thiosulphate loses  $\frac{1}{2}$  electron for oxidation to tetrathionate ( $\text{S}_4\text{O}_6^{2-}$ ). 4S atoms in tetrathionate must come from 2 molecules of thiosulphate ( $\text{S}_2\text{O}_3^{2-}$ ). Hence, the total change in oxidation number of S is from  $2(+4)=+8$  to  $4 \times 2\frac{1}{2}=+10$

$2\text{Na}_2\text{S}_2^{8+}\text{O}_3 = \text{Na}_2\text{S}_4^{10+}\text{O}_6 + 2\text{Na}^+ + 2\text{e}^-$  (oxidation)

$\text{I}_2 + 2\text{e}^- = 2\text{I}^-$  (reduction)

Overall reaction:

$2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$