REDOX REACTON

Oxidation and Reduction

- Oxidation-reduction (redox) reactions involve transfer of electrons
  - Oxidation – loss of electrons
  - Reduction – gain of electrons
- Both half-reactions must happen at the same time
- Any combustion process is classified as oxidation, as it involves a gain in oxygen
  - Eg, when methane burns, the carbon atoms in the methane gain oxygen to form carbon dioxide and therefore have been oxidised.
  - Can also think of the methane as losing hydrogen, which is also oxidation.
- Substances which help oxidation to occur are called oxidising agents (oxidants)
  - eg oxygen, acidifed potassium manganate(VIII), acidified potassium dichromate
- Substances which help reduction to occur are called reducing agents (reductants)
  - Eg carbon monoxide, carbon, hydrogen

Oxidation	Reduction
Gain in oxygen	Lose of oxygen
Lose of electrons	Gain of electrons
Lose of hydrogen	Gain in hydrogen
Increase in oxidation state number	Decrease in oxidation state number

Oxidising Agents are substances that **Oxidise** another substance & **Reducing Agents** are substances that **Reduces** another substance.

Question

(a) Define oxidation in terms of electron transfer.

(b) Name a substance which is an oxidizing agent in aqueous solution. Explain how aqueous potassium iodide can be used to confirm that this named substance is an oxidizing agent.

Answers

(a) Oxidation is the transfer of electron from one particle to another. The particle that looses the electron is said to be oxidized.

(b) Chlorine is an oxidizing agent. Aqueous chlorine is added to aqueous potassium iodide with starch added. A dark blue solution is seen, indicating the presence of I2. So I- ion must have been oxidized to I2

Tests for Oxidising and reducing agents

- **Test for Oxidising agents**
  - Add potassium iodide solution
    - If it changes from colorless to brown, than an oxidising agent is present
- **Test for reducing agents**
  - Add acidified potassium dichromate(VI).
    - If it changes from orange to green, then a reducing agent is present

Oxidation States

- Oxidation number assigned to element in molecule based on distribution of electrons in molecule
- There are set rules for assigning oxidation numbers

Substance	Oxidation number
All elements, noble gases, metals	0
Group 1 ions, H+	+1
Group 2 ions	+2
Al3+	+3
Group 7 ions, Oxygen in H2O2, hydrogen in Metal hydrides e.g NaH	-1
O2-, S2-.	-2
Nitrides N3-	-3

Rules of oxidation number

Rule	Example
1. The oxidation number of any uncombined element is 0.	The oxidation number of $Na(s)$ is 0.
2. The oxidation number of a monatomic ion equals the charge on the ion.	The oxidation number of Cl^- is –1.
3. The more electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.	The oxidation number of O in NO is –2.
4. The oxidation number of fluorine in a compound is always –1.	The oxidation number of F in LiF is –1.
5. Oxygen has an oxidation number of –2 unless it is combined with F, when it is +2, or it is in a peroxide, such as H_2O_2, when it is –1.	The oxidation number of O in NO_2 is –2.
6. The oxidation state of hydrogen in most of its compounds is +1 unless it is combined with a metal, in which case it is –1.	The oxidation number of H in LiH is –1.
7. In compounds, Group 1 and 2 elements and aluminum have oxidation numbers of +1, +2, and +3, respectively.	The oxidation number of Ca in $CaCO_3$ is +2.
8. The sum of the oxidation numbers of all atoms in a neutral compound is 0.	The oxidation number of C in $CaCO_3$ is +4.
9. The sum of the oxidation numbers of all atoms in a polyatomic ion equals the charge of the ion.	The oxidation number of P in $H_2PO_4^-$ is +5.

Oxidation states and their colours

- Chromium gives great example of different oxidation numbers
- Different oxidation states of chromium have different colors
    - Chromium (II) chloride = blue
    - Chromium (III) chloride = green
    - Potassium chromate = yellow
    - Potassium dichromate = orange

Eg. Oxidation of Sodium chloride

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

- Formation of sodium ions shows oxidation because each sodium atom loses an electron to become sodium ion
- Oxidation state represented by putting oxidation number above symbol of atom and ion
- Oxidation state of sodium changed from 0 (elemental state) to +1 (state of the ion)
- **A species whose oxidation number increases is oxidized**
- Sodium atom **oxidized** to sodium ion

$$\overset{0}{Na} \longrightarrow \overset{+1}{Na^+} + e^-$$

Reduction

- reactions in which the oxidation state of an element decreases
    - Eg. Chlorine in reaction with sodium
    - Each chlorine atom accepts e- and becomes chloride ion

$$\overset{0}{Cl_2} + 2e^- \longrightarrow 2\overset{-1}{Cl^-}$$

- Oxidation state decreases from 0 to -1
- *A species that undergoes a decrease in oxidation state is* **reduced**
- The chlorine atom is reduced to the chloride ion

Oxidation and Reduction as a Process

- Electrons are made in oxidation and acquired in reduction
- For oxidation to happen during chemical reaction, reduction must happen as well
- Number of electrons made in oxidation must equal number of electrons acquired in reduction
- Transfer of e- causes changes in oxidation states of one or more elements
- **Oxidation-reduction reaction** → *any chemical process in which elements undergo changes in oxidation number*
- Eg. When copper oxidized and NO_3^- from nitric acid is reduced

Half Reactions

- *Part of the reaction involving oxidation or reduction alone can be written as a* **half-reaction**
- Overall equation is sum of two half-reactions
- Number of e- same of oxidation and reduction, they cancel and don't appear in overall equation

$$\begin{array}{lr} 3\overset{0}{Cu} \longrightarrow 3\overset{+2}{Cu^{2+}} + 6e^- & \text{(oxidation half-reaction)} \\ 2\overset{+5\,-2}{NO_3^-} + 6e^- + 8\overset{+1}{H^+} \longrightarrow 2\overset{+2\,-2}{NO} + 4\overset{+1\,-2}{H_2O} & \text{(reduction half-reaction)} \\ \hline 3\overset{0}{Cu} + 2\overset{+5}{NO_3^-} + 8H^+ \longrightarrow 3\overset{+2}{Cu^{2+}} + 2\overset{+2}{NO} + 4H_2O & \text{(redox reaction)} \end{array}$$

- Electrons lost in oxidation appear on product side of oxidation half-reaction
- Electrons gained in reduction appear as reactants in reduction half-reaction
- When copper reacts in nitric acid 3 copper atoms are oxidized to Cu^{+2} ions as two nitrogen atoms are reduced from a +5 oxidation state to a +2 oxidation state

Non-redox Reactions

- If no atoms in reaction change oxidation state, it is NOT a redox reaction
- Eg. Sulfur dioxide gas dissolves in water to form acidic solution of sulfurous acid

$$\overset{+4\,-2}{SO_2} + \overset{+1\,-2}{H_2O} \longrightarrow \overset{+1\,+4\,-2}{H_2SO_3}$$

- When solution of NaCl is added to solution of $AgNO_3$, an ion-exchange reaction occurs and white AgCl precipitates

$$\overset{+1}{Na^+} + \overset{-1}{Cl^-} + \overset{+1}{Ag^+} + \overset{+5\,-2}{NO_3^-} \longrightarrow \overset{+1}{Na^+} + \overset{+5\,-2}{NO_3^-} + \overset{+1\,-1}{AgCl}$$

Redox Reactions and Covalent Bonds

- Substances with covalent bonds also undergo redox reactions
- Unlike ionic charge, oxidation number has no physical meaning
- Oxidation number based on **electronegativity** relative to other atoms to which it is bonded in given molecule

  - NOT based on charge
- Eg. Ionic charge of -1 results from complete gain of one electron by atom
- An oxidation state of -1 means increase in attraction for a bonding electron
- Change in oxidation number does not require change in actual charge
- When hydrogen burns in chlorine a covalent bond forms from sharing of two e-
  - Two bonding e- in hydrogen chloride not shared equally
- The pair of e- is more strongly attracted to chlorine atom because of higher electronegativity
- chlorine in HCl is assigned oxidation number of -1
- Oxidation number for chlorine atoms changes from 0
- So chlorine atoms are reduced
- oxidation number of each hydrogen atom in hydrogen molecule is 0
- oxidation state of hydrogen atom in HCl is +1
- Hydrogen atom oxidized

$$\overset{0}{H_2} + \overset{0}{Cl_2} \longrightarrow 2\overset{+1}{H}\overset{-1}{Cl}$$

- No electrons totally lost or gained
- Hydrogen has donated a *share* of its bonding electron to chlorine
- It has NOT completely transferred that electron
- Assignment of oxidation numbers allows determination of partial transfer of e- in compounds that are not ionic
- Increases/decreases in oxidation number can be seen in terms of completely OR partial loss or gain of e-
- Reactants and products in redox reactions are not limited to monatomic ions and uncombined elements
- Elements in molecular compounds or polyatomic ions can also be redoxed if they have more than one non-zero oxidation state
  - Eg. copper and nitric acid
- Nitrate ion, NO_3^-, is converted to nitrogen monoxide, NO
- Nitrogen is reduced in this reaction
- Instead of saying nitrogen atom is reduced, we say nitrate ion is reduced to nitrogen monoxide

Balancing Redox Equations

- Equations for simple redox reactions can be balanced by looking at them
- Most redox equations require more systematic methods
- Equation-balancing process needs use of oxidation numbers
- Both charge and mass are conserved
- Half-reactions balanced separately then combined

Half-Reaction Method

1. Oxidation numbers assigned to all atoms and polyatomic ions to determine which species are part of redox process
2. Half-reactions balanced separately for mass and charge
3. Then added together

1. Write the equation. Then write the ionic equation

Formula equation: $H_2S + HNO_3 \longrightarrow H_2SO_4 + NO_2 + H_2O$

Ionic equation: $H_2S + H^+ + NO_3^- \longrightarrow 2H^+ + SO_4^{2-} + NO_2 + H_2O$

2. Assign oxidation numbers. Delete substances containing only elements that do not change oxidation states

$$\overset{+1\,-2}{H_2S} + \overset{+1}{H^+} + \overset{+5\,-2}{NO_3^-} \longrightarrow 2\overset{+1}{H^+} + \overset{+6\,-2}{SO_4^{2-}} + \overset{+4\,-2}{NO_2} + \overset{+1\,-2}{H_2O}$$

- Sulfur changes oxidation state from -2 to +6
- Nitrogen changes from +5 to +4
- Other substances deleted

$$\overset{+1\,-2}{H_2S} + \overset{+5\,-2}{NO_3^-} \longrightarrow \overset{+6\,-2}{SO_4^{2-}} + \overset{+4\,-2}{NO_2}$$

3. Write the half-reaction for oxidation

- In this eg, sulfur is being oxidized $\overset{-2}{H_2S} \longrightarrow \overset{+6}{SO_4^{2-}}$

a. Balance the atoms

- To balance oxygen, H_2O must be added to left side
- This gives 10 extra hydrogen atoms on that side
- So, 10 H atoms added to right side
- In basic solution, OH^- ions and water can be used to balance atoms

$$\overset{-2}{H_2S} + 4H_2O \longrightarrow \overset{+6}{SO_4^{2-}} + 10H^+$$

b. Balance the charge

- Electrons added to side having greater positive net charge
- Left side has no net charge
- Right side has +8
- Add 8 electrons to product side
- oxidation of sulfur changes from -2 to +6 involves loss of 8 e-

$$\overset{-2}{H_2S} + 4H_2O \longrightarrow \overset{+6}{SO_4^{2-}} + 10H^+ + 8e^-$$

4. Write the half-reaction for reduction

- Nitrogen reduced from +5 to +4 $\overset{+5}{NO_3^-} \longrightarrow \overset{+4}{NO_2}$

a. Balance the atoms

- H_2O added to product side to balance oxygen atoms
- 2 hydrogen ions added to reactant side to balance H atoms

$$\overset{+5}{NO_3^-} + 2H^+ \longrightarrow \overset{+4}{NO_2} + H_2O$$

b. Balance the charge

- Electrons added to side having greater positive net charge
- Left side has net charge of +1
  1 e- added to this side balancing the charge

$$\overset{+5}{NO_3^-} + 2H^+ + e^- \longrightarrow \overset{+4}{NO_2} + H_2O$$

5. Conserve charge by adjusting the coefficients in front of the electrons so that the number lost in oxidation equals the number gained in reduction. Write the ratio of the number of electrons lost to the number of electrons gained

$$\frac{e^- \text{ lost in oxidation}}{e^- \text{ gained in reduction}} = \frac{8}{1}$$

- This ratio is already in lowest terms
- If not, need to reduce
- Multiply oxidation half-reaction by 1
- Multiple reduction half-reaction by 8
- Electrons lost = electrons gained

$$1\left(\overset{-2}{H_2S} + 4H_2O \longrightarrow \overset{+6}{SO_4^{2-}} + 10H^+ + 8e^-\right)$$
$$8\left(\overset{+5}{NO_3^-} + 2H^+ + e^- \longrightarrow \overset{+4}{NO_2} + H_2O\right)$$

6. Combine the half-reactions and cancel out anything common to both sides of the equation.

$$\overset{-2}{H_2S} + 4H_2O \longrightarrow \overset{+6}{SO_4^{2-}} + 10H^+ + 8e^-$$
$$8\overset{+5}{NO_3^-} + 16H^+ + 8e^- \longrightarrow 8\overset{+4}{NO_2} + 8H_2O$$

$$8\overset{+5}{NO_3^-} + \cancelto{6}{16}H^+ + \cancel{8e^-} + \overset{-2}{H_2S} + \cancel{4H_2O} \longrightarrow$$
$$8\overset{+4}{NO_2} + \cancelto{4}{8}H_2O + \overset{+6}{SO_4^{2-}} + \cancel{10H^+} + \cancel{8e^-}$$

- Each side has $10H^+$, $8e^-$, and $4H_2O$
- They cancel out

$$8\overset{+5}{NO_3^-} + \overset{-2}{H_2S} + 6H^+ \longrightarrow 8\overset{+4}{NO_2} + 4H_2O + \overset{+6}{SO_4^{2-}}$$

7. Combine ions to form the compounds shown in the original equation. Check to ensure that all other ions balance.

- The NO3- ion appeared as nitric acid in original equation
- Only 6 H ions to pair with 8 nitrate ions
- So, 2 H ions must be added to complete this formula
- If 2 H ions added to left side, then 2 H ions must be added to the right side
- Sulfate ion appeared as sulfuric acid in original equation
- H ions added to right side used to complete formula for sulfuric acid

$$8HNO_3 + H_2S \longrightarrow 8NO_2 + 4H_2O + SO_4^{2-} + 2H^+$$
$$8HNO_3 + H_2S \longrightarrow 8NO_2 + 4H_2O + H_2SO_4$$

Oxidizing and Reducing Agents

- **Reducing agent** → *substance that has the potential to cause another substance to be reduced*
  - They love electrons
  - Attain a positive oxidation state during redox reaction
  - Reducing agent is oxidized substance
- **Oxidizing agent** → *substance that has the potential to cause another substance to be oxidized*
  - Gain electrons
  - Attain a more negative oxidation state during redox reactions
  - Oxidizing agent is reduced substance

Strength of Oxidizing and Reducing Agents

- Different substances compared and rated on relative potential as reducing/oxidizing agents
  - Eg. Activity series – related to each element's tendency to lose electrons
- Elements lose electrons to positively charged ions of any element below them in series
- The more active the element the greater its tendency to lose electrons
- Better a reducing agent it is
- Greater distance between two elements in list means more likely that a redox reaction will happen between them
- Fluorine atom most most active oxidizing agent
  - because of strong attraction for its own e-, fluoride ion is weakest reducing agent
- Negative ion of strong oxidizing agent is weak reducing agent
- Positive ion of strong reducing agent is weak oxidizing agent
  - Eg. Li
  - Strong reducing agents because Li is very active metal
  - When Li atoms oxidize they produce Li^+ ions
  - Li^+ ions unlikely to reacquire e-, so it's weak oxidizing agent
- Left column of each pair also shows relative abilities of metals listed to displace other metals
- Zinc is above copper so is more active reducing agent
  - Displaces copper ions from solutions of copper compounds
  - Copper ion is more active oxidizing agent than Zn
- **Any reducing agent is oxidized by oxidizing agents below it**
- Eg. F_2 displaces Cl^-, Br^-, and I^- from their solutions

$$Cl_2 + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2$$

$$2\overset{-1}{Br^-} \longrightarrow \overset{0}{Br_2} + 2e^- \qquad \text{(oxidation)}$$

$$\overset{0}{Cl_2} + 2e^- \longrightarrow 2\overset{-1}{Cl^-} \qquad \text{(reduction)}$$

TABLE 19-3 ***Relative Strength of Oxidizing and Reducing Agents***

Reducing agents	Oxidizing agents
Li	Li^+
K	K^+
Ca	Ca^{2+}
Na	Na^+
Mg	Mg^{2+}
Al	Al^{3+}
Zn	Zn^{2+}
Cr	Cr^{3+}
Fe	Fe^{2+}
Ni	Ni^{2+}
Sn	Sn^{2+}
Pb	Pb^{2+}
H_2	H_3O^+
H_2S	S
Cu	Cu^{2+}
I^-	I_2
MnO_4^{2-}	MnO_4^-
Fe^{2+}	Fe^{3+}
Hg	Hg_2^{2+}
Ag	Ag^+
NO_2^-	NO_3^-
Br^-	Br_2
Mn^{2+}	MnO_2
SO_2	H_2SO_4 (conc.)
Cr^{3+}	$Cr_2O_7^{2-}$
Cl^-	Cl_2
Mn^{2+}	MnO_4^-
F^-	F_2

Increasing strength ↑ (reducing agents) — Increasing strength ↓ (oxidizing agents)

Auto-oxidation

- Some substances can be both reduced and oxidized
  - Eg. Peroxide ions – O_2^{-2} has relatively unstable covalent bond
- Each O atom has oxidation number of -1
- Structure represents intermediate oxidation state between O_2 and O_2^{-2}
- So, peroxide ion is highly reactive

$$\left[:\ddot{\underset{..}{O}}:\ddot{\underset{..}{O}}:\right]^{2-}$$

- Hydrogen peroxide, H_2O_2, contains peroxide ion
- Decomposes into water and oxygen as follows

$$2H_2\overset{-1}{O_2} \longrightarrow 2H_2\overset{-2}{O} + \overset{0}{O_2}$$

$$2H_2\overset{-1}{O}_2 \longrightarrow 2H_2\overset{-2}{O} + \overset{0}{O}_2$$

- Hydrogen peroxide is both oxidized AND reduced
- Oxygen atoms that become part of gaseous oxygen molecules are oxidized (-1 → 0)
- Oxygen atoms that become part of water are reduced (-1 → -2)
- **Autooxidation →** *a process in which a substance acts as both an oxidizing agent and a reducing agent*
- The substance is *self-oxidizing* and *self-reducing*

$$2H_2\overset{-1}{O}_2 \longrightarrow 2H_2\overset{-2}{O} + \overset{0}{O}_2$$

- Hydrogen peroxide is both oxidized AND reduced
- Oxygen atoms that become part of gaseous oxygen molecules are oxidized (-1 → 0)
- Oxygen atoms that become part of water are reduced (-1 → -2)
- **Autooxidation →** *a process in which a substance acts as both an oxidizing agent and a reducing agent*
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