# OXIDATION - REDUCTION REACTIONS

[MH5; 4.4]

- Commonly called Redox reactions, these reactions involve a transfer of electrons - one species gives them up, another receives them.
- They are easiest to deal with if we divide the overall reaction into two half - reactions.
- In one half-reaction, electrons are **LOST**; this is called the **OXIDATION** half - reaction.

EXAMPLES:

a) $\mathbf{Na \rightarrow Na^{+} + e^{-}}$ b) $\mathbf{Fe^{2+} \rightarrow Fe^{3+} + e^{-}}$

- In each case, the reactant is **losing** electrons.

- In the other half−reaction, electrons are **GAINED**; this is called the **REDUCTION** half−reaction.

EXAMPLES:

a) $\mathbf{C\ell_2 + 2\,e^{-} \rightarrow 2\,C\ell^{-}}$ b) $\mathbf{Cu^{2+} + 2\,e^{-} \rightarrow Cu}$

- In each case, the reactant is **gaining** electrons.

- It may help to remember that " **LEO says GER** " ......
  **L**oss of **E**lectrons is **O**xidation and **G**ain of **E**lectrons is **R**eduction
  OIL RIG ⇒ Oxidation is Loss, Reduction is Gain
- The reactant taking part in the **oxidation** half - reaction is called the **REDUCING AGENT** because it is reducing the other reactant.
- In doing so, it is **OXIDIZED !**
- The reactant taking part in the **reduction** half -reaction is called the **OXIDIZING AGENT** because it is oxidizing the other reactant.
- In doing so, it is **REDUCED !**

EXAMPLE: $2\ Fe^{2+} + C\ell_2 \rightarrow 2\ Fe^{3+} + 2\ C\ell^-$

- $Fe^{2+}$, the reducing agent, is reducing $C\ell_2$; the $Fe^{2+}$ is oxidized
- $C\ell_2$, the oxidizing agent, is oxidizing $Fe^{2+}$; the $C\ell_2$ is reduced
- Reduction and oxidation always go together; one cannot occur without the other.
- Notice that there are no electrons in the **"overall"** equation......
- In any **REDOX** reaction, the electrons lost in the oxidation half - reaction must exactly equal those gained in the reduction half - reaction.

# OXIDATION NUMBERS and BALANCING REDOX EQUATIONS

- Balancing Redox Reactions is a bit of a tedious process, but necessary.
- Any "method" giving the right answer may be used - use the one that you prefer!
- We shall use a modification of that described in MH5, section 4.4, the half-reaction method.
- Before beginning, it is often helpful (but not essential!!) to decide what is being oxidized, and what is being reduced.

- To do that, we use **Oxidation Numbers or States**, an artificial way of showing the "degree of oxidation" of an element.
- We assume that the more electronegative element in a compound has acquired all the shared electrons in a covalent bond.

EXAMPLE: **HBr**

| | | |
|---|---|---|
| H — | Br | Br is more **electronegative** than H; Br gets the electron |
| +1 | −1 | (and the -1 charge) |

- Recall the order of **electronegativity** of the elements.....

| |
|---|
| F > O > $C\ell$ > N > Br > C,S,I > H > ...metals<br>**high** **low** |

Values are given in **Table 6.5; MH5, p154**

**RULES FOR ASSIGNING OXIDATION NUMBERS** [MH5; page 88]

1) Oxidation Number is always zero in the pure element: ($H_2$ (g) , $C\ell_2$ (g) , Na (s) etc)

2) Oxidation Number is always equal to the charge on a monatomic ion:

   $Na^+$ is +1 $Ba^{2+}$ is +2 $C\ell^-$ is −1 etc.

3) In a neutral molecule, the total charge on the molecule must be equal to 0.

   **H - Br**: (+1) + (−1) = 0 **$PBr_5$**: (+5) + 5(−1) = 0

4) In a complex ion, the total charge must be equal to the charge on the ion.

   **$NH_4^+$**: (−3) + 4(+1) = +1 **$BF_4^-$**: (+3) + 4(−1) = −1

   **$C\ell O_4^-$**: (+7) + 4(−2) = −1

5) **Priority Rules (Memorize these!!!)**

These rules, based on the electronegativity scale are useful in assigning Oxidation Numbers in a compound:

a) **Fluorine** is always −**1**

b) **Group I** metals (Na, K, etc.) always **+1**

c) **Group II** metals (Ca, Mg, etc.) always **+2**

d) **H** is always **+1** except when combined with a metal to form a hydride .....

EXAMPLE: LiH is $[Li^+][H^-]$; therefore H is **−1**

e) **Oxygen** is always −**2** except when combined with fluorine

EXAMPLES: $OF_2$ : O is +2 (because F is -1)

**In Peroxides**, which contain the O −O bond;
such as **H - O - O - H** (Hydrogen Peroxide), where O is −1

**$Na_2O_2$:** is 2 $Na^+$ $[O - O]^{2-}$ , therefore O is −1

f)Other Halogens (**Group VII**) are always −**1**, except when combined with fluorine or oxygen.....

$BrF_5$ : Br is + 5 $Cl_2O$: Cl is + 1

$MnO_4^-$

4 O @ −2 = −8
1 Mn @ ? = +7
Overall = −1

# BALANCING REDOX EQUATIONS BY HALF REACTIONS

EXAMPLE 1:

Permanganate ion oxidizes oxalate ions in **ACIDIC** solution............

$$MnO_4^{-} + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$$

Separate the reaction into two half-reactions:

$$MnO_4^{-} \rightarrow Mn^{2+} \quad \& \quad C_2O_4^{2-} \rightarrow CO_2$$

Now, deal with each half reaction individually:

1) Balance non-O and non-H atoms as usual

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

2) Add $H_2O$ to balance oxygen

   $MnO_4^{-} \rightarrow Mn^{2+} + 4\,H_2O$

3) Add $H^+$ to balance H atoms (regardless of acidic or basic)

   $MnO_4^{-} + 8\,H^+ \rightarrow Mn^{2+} + 4\,H_2O$

   → to the more positive side

4) Add electrons to balance the charge

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

   +7 +2

5) We are told the solution is acidic, so we may use $H^+$ ions to balance H.

6) Since $e^-$ appear on the left, this is **REDUCTION** (gain of electrons).

7) Mn goes from Oxidation Number **+7** to Oxidation Number **+2** ;

   ➡ it has gained **5 e** $^-$

Now deal with the other half reaction:

$$\mathbf{C_2O_4^{2-} \rightarrow CO_2}$$

1) Balance non-O and non-H atoms as usual; in this case we must balance the C:

$$C_2O_4^{2-} \rightarrow 2\,CO_2$$

2) Add $H_2O$ to balance oxygen; oxygen is already balanced!!

3) Add $H^+$ to balance H atoms (regardless of acidic or basic); there are no H's!!

4) Add electrons to balance the charge:

$$C_2O_4^{2-} \rightarrow 2\,CO_2 + 2e^-$$

- Since $e^-$ appear on the right, this is **OXIDATION** (loss of electrons)
- Each Carbon has gone from Oxidation Number **+3** to Oxidation Number **+4** ; ➟ each C has lost one $e^-$
- In a balanced redox equation, there are no electrons; we must make the number of electrons in the two half reactions equal (then they can be cancelled)
- So.......multiply each half -reaction by the number of $e^-$ in the other half reaction!

**Red**: ×2 : $2\,MnO_4^- + 16\,H^+ + 10e^- \rightarrow 2\,Mn^{2+} + 8\,H_2O$

**Ox**: ×5 : $5\,C_2O_4^{2-} \rightarrow 10\,CO_2 + 10e^-$

- The 10 $e^-$ on each side may be cancelled; then add the two half reactions together..........

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+$$

$$\rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

- Always check that the equation is balanced for both atoms and charge

EXAMPLE 2:

The following reaction occurs in **BASIC** solution.......

| | | | | | | |
|---|---|---|---|---|---|---|
| $\mathbf{NH_3(aq)}$ | **+** | $\mathbf{C\ell O^-}$ | **→** | $\mathbf{N_2H_4}$ | **+** | $\mathbf{C\ell^-}$ |
| ammonia | | hypochlorite | | hydrazine | | |

Separate the reaction into two half reactions:

$\mathbf{NH_3 \rightarrow N_2H_4}$ & $\mathbf{C\ell O^- \rightarrow C\ell^-}$

1) Balance all non-O and non-H atoms; in this case balance N:

$$2NH_3 \rightarrow N_2H_4$$

2) Add $H_2O$ to balance oxygen; no need - as there is no oxygen present.

3) Add $H^+$ to balance H atoms; although there is no appreciable $H^+$ concentration in basic solution, we (temporarily) use $H^+$ to balance H.....

$$2NH_3 \rightarrow N_2H_4 + 2H^+$$

4) We are told the solution is basic, so use of $H^+$ is NOT really allowed......

5) We must neutralize the H+ by adding equal amounts of $OH^-$ to each side; converting all $H^+$ to $H_2O$ and retaining the balance:

$$2\,NH_3 + 2OH^- \rightarrow N_2H_4 + \underbrace{2\,H^+ + 2OH^-}$$

6) Now combine the $H^+$ and $OH^-$ on the right hand side to produce $H_2O$:

$$2\,NH_3 + 2\,OH^- \rightarrow N_2H_4 + 2H_2O$$

7) Add electrons to balance the charge:

$$2\,NH_3 + 2\,OH^- \rightarrow N_2H_4 + 2\,H_2O + 2e^-$$

8) This is the **OXIDATION** half-reaction; electrons appear on the right.

9) Each Nitrogen has gone from **-3** to **-2**;
➟ each Nitrogen has lost one electron

Now for the other half reaction:

$$\boldsymbol{C\ell O^-} \rightarrow \boldsymbol{C\ell^-}$$

1) Balance all non-O and non-H atoms; the $C\ell$ is already balanced.

2) Add $H_2O$ to balance oxygen:

$$C\ell O^- \rightarrow C\ell^- + H_2O$$

3) Add $H^+$ to balance hydrogen:

$$C\ell O^- + 2H^+ \rightarrow C\ell^- + H_2O$$

4) Add $OH^-$ to remove $H^+$:

$$ClO^- + 2H^+ + 2OH^- \rightarrow Cl^- + H_2O + 2OH^-$$

5) Combine the $H^+$ and $OH^-$ on the left hand side to produce $H_2O$:

$$ClO^- + 2H_2O \rightarrow Cl^- + H_2O + 2\,OH^-$$

6) Add electrons to balance the charge:

$$ClO^- + 2H_2O + 2e^- \rightarrow Cl^- + H_2O + 2\,OH^-$$

7) This is the **REDUCTION** half–reaction; electrons appear on the left.

8) $Cl$ has gone from **+1** to **-1**;
➟ each $Cl$ has gained **2** electrons

9) As we have 2 electrons in each half reaction; add the two half reactions together, cancelling the electrons.

10) Also cancel any $H_2O$ or $OH^-$ possible.......

$$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2\,OH^-$$
$$2\,NH_3 + 2\,OH^- \rightarrow N_2H_4 + 2H_2O + 2e^-$$

$$2NH_3 + ClO^- \rightarrow N_2H_4 + Cl^- + H_2O$$

- Check the final equation for balance in both atoms and charge.

- A **DISPROPORTIONATION** reaction is a redox reaction in which a substance in an intermediate oxidation state goes to both a higher and a lower state by $e^-$ transfer.

EXAMPLE:

Copper, Cu, may exist in the **+1** oxidation state, which is less stable than either **+2** or **0**.

It may undergo disproportionation.......

$Cu^+ \rightarrow Cu^{2+} + e^-$ Ox

$$\mathbf{2\ Cu^+ \xrightarrow[\text{1 e}^- \text{ reduction}]{\text{1 e}^- \text{ oxidation}} Cu^{2+} + Cu(s)}$$

$Cu^+ + e^- \rightarrow Cu(s)$ Red

- The opposite of disproportionation is **CONPROPORTIONATION**.
- There are two reactants; one is oxidized and one is reduced......but there is only one product.
- The oxidation state of the product is an intermediate state to those of the reactants.

EXAMPLE: $ClO_4^- + Cl^- \rightarrow ClO_3^-$

$\overset{+7}{ClO_4^-} + 2e^- \rightarrow \overset{+5}{ClO_3^-}$ Red

$\overset{-1}{Cl^-} \rightarrow \overset{+5}{ClO_3^-} + 6e^-$ Ox

EXAMPLE 1: Balance the following reaction which occurs in acidic solution. DISPROPORTIONATION

$$I_3^- \rightarrow IO_3^- + I^-$$

① $I_3^- \rightarrow I^-$

② $I_3^- \rightarrow IO_3^-$

① $I_3^- + 2e^- \rightarrow 3I^-$ Red

② $I_3^- + 9H_2O \rightarrow 3IO_3^- + 18H^+ + 16e^-$ Ox

① × ~~16~~ 8: $8I_3^- + \cancel{16e^-} \rightarrow 24I^-$

② × ~~2~~ 1: $I_3^- + 9H_2O \rightarrow 3IO_3^- + 18H^+ + \cancel{16e^-}$

add: $9I_3^- + 9H_2O \rightarrow 3IO_3^- + 24I^- + 18H^+$

÷ 3: $3I_3^- + 3H_2O \rightarrow IO_3^- + 8I^- + 6H^+$

EXAMPLE 2:

Hydrazine, $N_2H_4$, is prepared by reaction of ammonia with chloramine in basic solution, according to :

$$\overset{-3}{NH_3} + \overset{-1\ +2\ -1}{NH_2C\ell} \rightarrow \overset{-2\ +4}{N_2H_4} + \overset{-1}{C\ell^-}$$

CONPROPORTIONATION

Balance this equation.

① $NH_3 \rightarrow N_2H_4$

② $NH_2Cl \rightarrow N_2H_4 + Cl^-$

① $2NH_3 + 2OH^- \rightarrow N_2H_4 + 2H_2O$

② $2NH_2Cl \rightarrow N_2H_4 + 2Cl^-$

$$2NH_3 + 2NH_2Cl + 2OH^- \rightarrow 2N_2H_4 + 2H_2O + 2Cl^-$$

$$\div 2: \quad NH_3 + NH_2Cl + OH^- \rightarrow N_2H_4 + H_2O + Cl^-$$