

CHEM 6.2 BALANCING CHEMICAL EQUATIONS 2

Chemical reactions – balancing chemical equations/stoichiometry

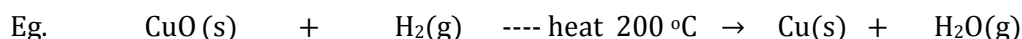
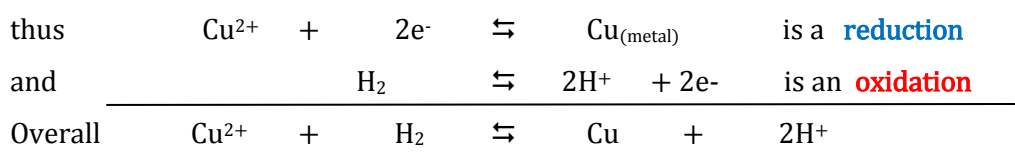
REDUCTION / OXIDATION

Redox reactions –the **key chemical event is the net movement of electron(s) from one reactant to the other**, so **REDOX REACTIONS** are concerned with chemical changes in which species are oxidized (i.e. lose electrons) or reduced (i.e. gain electrons).

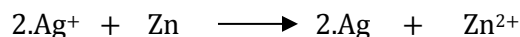
We can use the mnemonic 'OILRIG' to remember that:

OIL = oxidation is loss of electrons

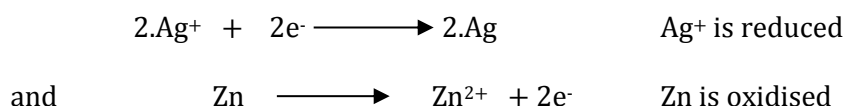
RIG = reduction is gain of electrons



The following **chemical redox reaction** :



Can be described by the two so-called **electrochemical 'half reactions'**:



(Note how the charge on the LHS of each equation must equal the charge on the RHS)

OXIDATION NUMBERS

In any discussion of redox reactions it is useful to be able to assign an **oxidation number (ON)** to any element in a given compound in order to keep track of the electrons during a reaction: **ON is defined as the apparent electrical charge on the atom** according to a set of rules like those following:

We need to recognize that:

Oxidation leads to a loss of electrons and an increase in oxidation number

Reduction is a gain of electrons, and so leads to a decrease in oxidation number

Oxidation Number Rules

1. **The oxidation number of an atom as an element is zero** (eg., O_2 , P_4 , S_8 , Fe, Mg, Br_2 are the elemental forms at room temperature, and they *all have ON's of zero*).
2. **The oxidation number of oxygen is usually (-II)** (except when bonded to F). Remember that in the element, oxygen (O_2 , $O=O$) has an oxidation number of zero, whilst in peroxides (O_2^{2-} , $\cdot O-O \cdot$) each oxygen atom has an oxidation number of (-I).
3. The oxidation number of a monatomic ion is equal to the ion's charge, eg. $Na^+ = Na(I)$, $Cl^- = Cl(-I)$, $S^{2-} = S(-II)$.
4. The algebraic sum of the oxidation numbers in a neutral polyatomic compound is zero; in a polyatomic ion the sum of the oxidation numbers is equal to the ion's overall charge.
5. In combinations of elements, the more electronegative element has its characteristic negative oxidation number (for example, (-III) for nitrogen, (-II) for oxygen, (-I) for chlorine), and the more electropositive element has a positive oxidation number (for example, (+I) for hydrogen, (+II) for calcium, (+III) for aluminium).
6. **The oxidation number of hydrogen (H) is usually (+I)** - due to its electronegativity being lower than that of the Main-group elements to which it is normally bonded. With more electropositive elements, Hydrogen has an oxidation number of (-I), eg. Na^+H^- .

Example 1. Find the oxidation number of sulfur, S, in sulfuric acid, $H_2SO_{4(aq)}$.

Using ON for oxidation number, we use rule 4 to write:

$$2[ON(H)] + [ON(S)] + 4[ON(O)] = 0$$

and rule 2 : $[ON(O) = -2]$, and rule 6 $[ON(H) = +1]$ to write :

$$2(+1) + [ON(S)] + 4(-2) = 0 \rightarrow ON(S) = +6$$

Example 2. Find the oxidation number of iodine, I, in ICl_4^- .

We use rule 4 to write $[ON(I)] + 4[ON(Cl)] = -1$

Chlorine is more electronegative than iodine, so chlorine has the conventional oxidation number of -1 (rule 3).

$$\text{Thus } [ON(I)] + 4(-1) = -1 \rightarrow ON(I) = +3$$

Predicting the Products of an Oxidation / Reduction reaction:

We can predict the outcome of the reaction between two redox couples such as $\text{MnO}_4^-/\text{Mn}^{2+}$ and $\text{H}_2\text{SO}_3/\text{SO}_4^{2-}$ in the following way:

Because each redox reaction involves the **movement of electrons**, it also has associated with it a **voltage**, called the **standard reduction potential (E^0)** defined according to:



where Ox^{n+} = oxidized form of element,

Red = reduced form of element,

n = number of electrons (e^-) transferred in the redox half-reaction

E^0 range [**+3 volt** ----- 0 ----- **-3 volt**]

Electron acceptors

Electron donors

Oxidisers = oxidizing agents **Reducers** = reducing agents

E^0 = **standard reduction potential** - which is the e.m.f. for the reaction (ie., the electron driving force for the reaction as it proceeds from left to right) when both ' Ox^{n+} ', and ' Red ' are present at 1 M concentration (or one atmosphere partial pressure for gases), and at 25°C .

NOTE: The **greater (more positive) the value of E^0** , the **greater is the tendency** for:



So, from the data in the Table below we can decide on the spontaneous (favourable) reaction:

$\text{Ox}^{n+} / \text{Red}$ couple	E^0 / volt	e- donor or e-acceptor ?	Oxidizing agent or Reducing agent ?
$\text{MnO}_4^- / \text{Mn}^{2+}$	+1.51	e- donor / e-acceptor	Oxidising agent
$\text{SO}_4^{2-} / \text{H}_2\text{SO}_3 (\text{SO}_2)$	+0.17	e- donor / e-acceptor	Reducing agent

It is crucial to note that **the redox couple with the more positive E^0 value will REMOVE electrons from a redox couple with a less positive E^0** . The oxidizing agent is the species which causes the oxidation to occur, ie. It is the agent (redox couple) which removes electrons from the other couple.

In the example above, MnO_4^- has the more positive E^0 and hence the greater affinity (liking) for electrons: therefore **MnO_4^- will behave as the electron acceptor** (ie. Oxidant = oxidizing agent) . Thus, the sulphur system must donate electrons: hence **H_2SO_3 will be the electron donor** (ie Reductant = reducing agent) .

So we predict: $\text{MnO}_4^- \longrightarrow \text{Mn}^{2+}$ and $\text{H}_2\text{SO}_3 \longrightarrow \text{SO}_4^{2-}$

REDUCTION & OXIDATION HALF-REACTIONS & THE BALANCING OF REDOX EQUATIONS

Redox equations are usually written as balanced **net ionic equations**, with spectator ions (ions that do not take part in the overall redox process) being omitted.

The determination of the stoichiometry of a redox reaction can be difficult to deduce even when the products of such a reaction are known. For this reason it is much more convenient and methodical to concentrate upon the stoichiometry of each redox "half-reaction" or "redox couple" individually.

A list of the more important redox half-reactions is presented in Section 21 of the SI data book, although you should be able to write some from memory.

Strategy for balancing redox equations:

A five step method for balancing redox equations, called the "half reaction" method, is used, and after mastering these operations, any chemical redox equation can be balanced by combining the five steps.

1. Step One is to divide the equation into the appropriate 'half-reactions' which can be balanced separately, for example :

Overall reaction $\text{H}_2\text{SO}_3 + \text{MnO}_4^- \rightarrow \text{SO}_4^{2-} + \text{Mn}^{2+}$

Assign an ON to each element in the ions or molecules of reactants and products:

MnO_4^- ON of **Mn = VII** , and in Mn^{2+} ON of **Mn = II**

Thus, Mn(VII) is being **reduced** to Mn(II).

So, Reduction half-reaction $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$ and ;

H_2SO_3 ON of **S = IV** , and in SO_4^{2-} ON of **S = VI**

So S(IV) is being **oxidised** to S(VI).

So, Oxidation half-reaction $\text{H}_2\text{SO}_3 \rightarrow \text{SO}_4^{2-}$

2. **Step Two** is to write a separate balanced **chemical equation** for each redox-active species – this is the **MASS BALANCE step** :



Note that we 'remove' oxygen (O^{2-}) as water (still O(-II)) by combination with H^+ .

And:



Note that we 'add 'oxygen (O^{2-}) as water (still O(-II)) to the appropriate side of the equation, and then add H^+ ions to balance hydrogen.

3. **Step Three** : Although we have now achieved **MASS** balance, we also need to **balance CHARGE**, by adding electrons (e^- , negative charge) as needed—this generates the balanced **electrochemical half-reaction**. The total charge on each side of a balanced reaction must be the same.



(LHS total charge = $+2$)

(RHS total charge = $+2$)



(LHS total charge = zero = 0)

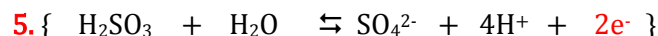
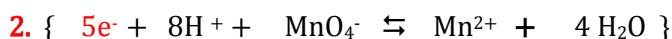
(RHS total charge = zero = 0)

If all three steps have been done correctly, one half-reaction will have electrons on the left hand side of the equation (the reduction half-reaction), while the other half-reaction will have electrons on the right hand side of the equation (the oxidation half-reaction).

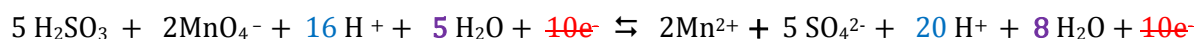
4. **Step Four** : The balanced half-reactions can be termed **electrochemical equations**, since they involve the electron. To obtain a **chemical equation** for the reaction, we need to eliminate the electron from the overall equation.

Hence, the fourth step is the addition of the two half-reactions in such a way that the electrons cancel out – this may require multiplying one equation, or both, by an appropriate integer.

For the two half-reactions above:



The **first** reaction is multiplied by **two** and the **second** reaction is multiplied by **five** and both are added to give:



Note the equal number of electrons on each side of the equation.

5. The **final step** is to **cancel the electrons** and **simplify the chemical equation** by eliminating any chemical species common to each side of the equation:



The **Reaction Stoichiometry** for the balanced chemical equation, above, is then given by :

$$\frac{\text{mol H}_2\text{SO}_3(\text{SO}_2)}{5} = \frac{\text{mol MnO}_4^-}{2} = \frac{\text{mol Mn}^{2+}}{2} = \frac{\text{mol SO}_4^{2-}}{5} = \frac{\text{mol H}_2\text{O}}{3} = \frac{\text{mol H}^+}{4}$$

So we can use these stoichiometric relationships to solve for mol or mass as required.

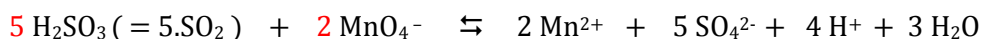
Example: Calculate the volume of a 0.0200 mol/L solution of $\text{K}^+ \text{MnO}_4^-$ required to react completely with 5 litres of sulphur dioxide gas produced at 25 °C and one atmosphere.

T = absolute temperature (Kelvin K, defined as $K = ^\circ\text{C} + 273 = 25 + 273 = 298 \text{ K}$)

R = gas constant, $8.314 \text{ J K}^{-1}\text{mol}^{-1} = 8.314 \text{ kPa.L K}^{-1}\text{mol}^{-1} = 8.314 \text{ Pa.m}^3 \text{ K}^{-1}\text{mol}^{-1}$
 $= 0.0821 \text{ L.atm K}^{-1}\text{mol}^{-1}$ and, 1 atmosphere = 101.3 kPa

Stoichiometric equations :

Since; $\text{H}_2\text{O} + \text{SO}_2 = \text{H}_2\text{SO}_3$ then the $\text{mol SO}_2 = \text{mol H}_2\text{SO}_3$,
 so we can use the balanced equation from above,



Mol SO₂ : $PV = nRT$, So, $n = PV/RT = \frac{1 \text{ atmosphere} \times 5 \text{ L}}{0.0821 \text{ L.atm K}^{-1}\text{mol}^{-1} \times 298 \text{ K}} = 0.2044 \text{ mol SO}_2$

Stoichiometric mole ratio $\frac{\text{mol SO}_2 (\text{H}_2\text{SO}_3)}{5} = \frac{\text{mol MnO}_4^-}{2}$

Now, $\text{mol MnO}_4^- = 2 \times \text{mol SO}_2 / 5 = 2 \times 0.2044 / 5 = 0.08175 \text{ mol}$
 $= \text{concentration of MnO}_4^- \times \text{volume MnO}_4^- \text{ (using } n = C \times V \text{)}$

So, $0.08175 \text{ mol} = 0.0200 \text{ mol L}^{-1} \times V \text{ L}$

Hence, $V(\text{K}^+ \text{MnO}_4^-) = 4.087 \text{ L} = 4,087 \text{ mL}$