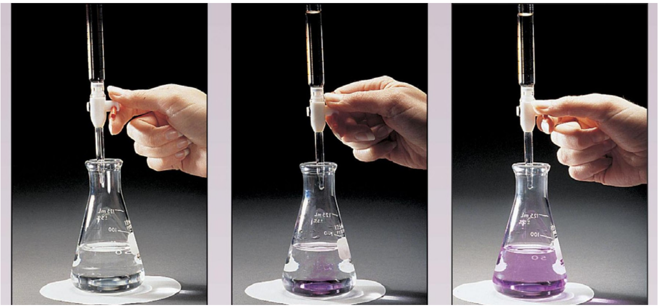
Acid-base titrations

- Titrations use measurements of volumes
- Based on stoichiometric acid-base reactions between the analyzed solution (analyte) and a solution with known concentration (titrant)
- **Equivalence point** – the amount of titrant added is stoichiometrically equivalent to the amount of analyte present in the sample
- **Indicators** – change color at the equivalence point (signal the **end point** of the titration)



- The titrant (acid or base) is added slowly to the analyte (base or acid) until the indicator changes color
- At the end point the amount of acid is equivalent to the amount of base – the concentration of the analyte is calculated from the measured volumes of the solutions and the titrant concentration

Example: A **25.0 mL H_2SO_4** solution is titrated with **16.4 mL 0.255 M KOH** solution. What is the molarity of the acid solution.

⇒**balanced equation:**

$$2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$$

⇒**mole ratio:** **[1 mol H_2SO_4/2 mol KOH]**

$$16.4 \times 10^{-3}\ \text{L} \times \left(\frac{0.255\ \text{mol KOH}}{1\ \text{L}}\right) \times \left(\frac{1\ \text{mol H}_2\text{SO}_4}{2\ \text{mol KOH}}\right) =$$

$$= 2.09 \times 10^{-3}\ \text{mol H}_2\text{SO}_4$$

$$\frac{2.09 \times 10^{-3}\ \text{mol H}_2\text{SO}_4}{25.0 \times 10^{-3}\ \text{L}} = 8.36 \times 10^{-2}\ \text{M H}_2\text{SO}_4$$

4.5 Redox Reactions

Oxidation and reduction

- **Transfer of electrons** from one species to another
- Driving force of redox reactions – movement of electrons from an atom with less to an atom with more attraction for electrons

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

NaCl is an ionic compound:

$$2Na(s) + Cl_2(g) \rightarrow 2Na^+(s) + 2Cl^-(s)$$

$Na(s) \rightarrow Na^+(s)$ ⇒ **loss of $1e^-$ by Na**

$Cl_2(g) \rightarrow 2Cl^-(s)$ ⇒ **gain of $2e^-$ by Cl_2**

Result → transfer of electrons from Na to Cl_2

- **Oxidation** - loss of electrons (Na is oxidized)
  - term originates from reactions of substances with oxygen
- **Reduction** - gain of electrons (Cl_2 is reduced)
  - term originates from reactions of metal oxides with C, CO, H_2, etc. to extract (reduce) the pure metal
- Oxidation and reduction can not occur independently
  - electrons gained by one species must be lost by another (e^- gained by Cl_2 are lost by Na)
  - Cl_2 oxidizes Na and Na reduces Cl_2

- The transfer of electrons during redox reactions is not always complete

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

H_2O is a covalent compound with polar bonds in which the electrons are not shared equally

$$H^{\delta+}\text{–}\ O^{\delta-}\text{–}\ H^{\delta+}$$

$\Rightarrow$ Electrons are shifted from H to O

$H \rightarrow H^{\delta+}$ $\quad \Rightarrow$ loss of e^- density by H

$O \rightarrow O^{\delta-}$ $\quad \Rightarrow$ gain of e^- density by O

Result $\rightarrow$ incomplete transfer of electrons from H to O

Oxidation Numbers (Ox#)

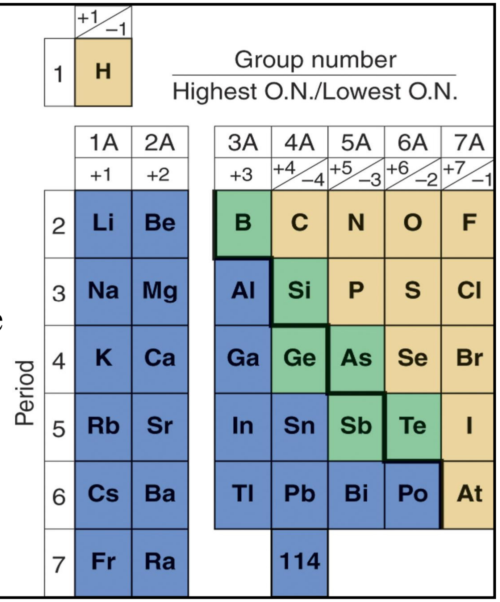
- Oxidation number (oxidation state) – the charge an atom would have if the **e**⁻s in polar bonds are not shared but are transferred completely to the atom with more attraction for **e**⁻s
  - Assigned to each element in a substance
- Oxidation numbers can help determine whether substances are oxidized or reduced
  - **Oxidation** – increase in Ox#
  - **Reduction** – decrease in Ox#

$Na(s) \rightarrow Na^+(s)$ $\quad \Rightarrow$ Ox# increases ($0 \rightarrow +1$)

$Cl_2(g) \rightarrow 2Cl^-(s)$ $\quad \Rightarrow$ Ox# decreases ($0 \rightarrow -1$)

- **Rules** for assigning Ox#
  - **Monoatomic ions $\rightarrow$ Ox# = charge of ion**
  - **Free elements $\rightarrow$ Ox# = 0**
  - **F $\rightarrow$ Ox# = -1**
  - **O $\rightarrow$ Ox# = -2** (except in combination with F and in peroxides)
  - **H $\rightarrow$ Ox# = +1** (in combination with nonmetals)
    $\rightarrow$ Ox# = -1 (in combination with metals)
  - **Halogens $\rightarrow$ Ox# = -1** (except in comb. with O or other halogen higher in the group)
  - The **sum of Ox#** of all elements in a species equals the **charge** of the species

- The highest and lowest Ox# for main group elements can be predicted from the periodic table (with some exceptions)



Example:

Assign the oxidation numbers of all elements in NO_3^- and $HClO_3$.

NO_3^- $\Rightarrow$ **O (-2) by rule**

$3\times(-2) + 1\times(X) = -1$ $\Rightarrow$ $X = +5$ $\Rightarrow$ N (+5)

$HClO_3$ $\Rightarrow$ **O (-2) by rule**

$\Rightarrow$ **H (+1) by rule**

$3\times(-2) + 1\times(+1) + 1\times(X) = 0$

$\Rightarrow$ $X = +5$ $\Rightarrow$ Cl (+5)

- **Oxidizing agent** – causes oxidation (removes electrons from the species being oxidized)
  - is the species **being reduced**
  - contains an element which undergoes a decrease in Ox# (reduction)
- **Reducing agent** – causes reduction (supplies electrons to the species being reduced)
  - is the species **being oxidized**
  - contains an element which undergoes an increase in Ox# (oxidation)