

Chapter 9

Double Replacement (Metathesis) Reactions

In many reactions between two compounds in aqueous solution, the cations and anions appear to switch partners according to the following equation:



The two compounds react to form two new compounds. No changes in oxidation numbers occur. Reactions of this type are known as *double replacement* or *metathesis reactions*. An example of such a reaction would be the mixing of aqueous solutions of potassium bromide and silver nitrate forming insoluble silver bromide (precipitate) and aqueous potassium nitrate:



Note that each cation pairs up with the anion in the other compound, thus switching partners. Anions do not pair up with anions and cations do not pair up with cations. Likes repel; opposites attract!

All double replacement reactions must have a “driving force” or a reason why the reaction will occur or “go to completion.” The “driving force” in metathesis reactions is the removal of at least one pair of ions from solution.

This removal of ions can occur in one of three ways:

1. **Formation of a precipitate:** A precipitate is an insoluble substance (solid) formed by the reaction of two aqueous substances. It is the result of ions bonding together so strongly that the solvent (water) cannot pull them apart. The insoluble solid (or solids if a double precipitate occurs) will settle out (precipitate) from the solution and this results in the removal of ions from the solution.
2. **Formation of a gas:** Gases may form directly in a double replacement reaction or from the decomposition of one of the products. The gases will bubble off or evolve from the solution.
3. **Formation of primarily molecular species:** The formation of primarily unionized molecules in solution removes ions from the solution and the reaction “works” or is said to go to completion. Unionized or partially ionized molecules give solutions that are known as *nonelectrolytes* or *weak electrolytes*. The best known nonelectrolyte is water formed in acid–base neutralization reactions. Acetic acid is an example of an acid that is primarily molecular (weak electrolyte) when placed in water.

Reversible Reactions

If a double replacement reaction does not go to completion (no precipitate, gas or molecular species is formed), then the reaction is reversible (no ions have been removed). Reversible reactions are at equilibrium and have both forward and reverse reactions taking place. In a reversible reaction, evaporation of the water solvent will result in solid residues of both reactants and products. The reaction is not driven to completion (products) because no ions have been removed. A double arrow is used to designate a reversible reaction at equilibrium.



Solubility Rules Table

The solubility classification of ionic substances according to their solubility in water is difficult. Nothing is completely "insoluble" in water. The degree of solubility varies from one "soluble" substance to another. Nevertheless, a solubility classification scheme is useful even though it must be regarded as an approximate guideline.

MAINLY WATER SOLUBLE

NO_3^-	All nitrates are soluble.
CH_3COO^- or $\text{C}_2\text{H}_3\text{O}_2^-$	All acetates are soluble except $\text{AgCH}_3\text{COO}^*$.
ClO_3^-	All chlorates are soluble.
Cl^-	All chlorides are soluble except AgCl , Hg_2Cl_2 PbCl_2^* .
Br^-	All bromides are soluble except AgBr , PbBr_2^* , Hg_2Br_2 and HgBr_2^* .
I^-	All iodides are soluble except AgI , Hg_2I_2 , HgI_2 and PbI_2 .
SO_4^{2-}	All sulfates are soluble except BaSO_4 , PbSO_4 , Hg_2SO_4 , CaSO_4 , Ag_2SO_4^* and SrSO_4^* .
Alkali metal cations (Group IA) and NH_4^+	All are soluble.
H^+	All common inorganic acids and low molecular mass organic acids are soluble.

MAINLY WATER INSOLUBLE

CO_3^{2-}	All carbonates are insoluble except those of the IA elements and NH_4^+ .
CrO_4^{2-}	All chromates are insoluble except those of the IA elements, NH_4^+ , CaCrO_4^* and SrCrO_4^* .
OH^-	All hydroxides are insoluble except those of the IA elements, NH_4^+ , $\text{Ba}(\text{OH})_2$, $\text{Sr}(\text{OH})_2^*$, and $\text{Ca}(\text{OH})_2^*$.
PO_4^{3-}	All phosphates are insoluble except those of the IA elements and NH_4^+ .
SO_3^{2-}	All sulfites are insoluble except those of the IA elements and NH_4^+ .
S^{2-}	All sulfides are insoluble except those of the IA and IIA elements and NH_4^+ .

*Soluble compounds dissolve to the extent of at least 10 g/L at 25 °C. Slightly soluble compounds (marked with an *) dissolve in the range of from 1 g/L to 10 g/L at 25 °C. Those compounds that have a solubility of less than 1 g/L are considered to be insoluble. These standards are common but arbitrary.

ROUND 4

Formation of a Precipitate

In order to predict double replacement reactions yielding precipitates, one **must memorize** the solubility rules listed on page 48.

Exercise 9-1: Predict and balance the following metathesis reactions based on the solubility of the products. Use the abbreviations (aq) and (s) for the reactants and products. All reactants are aqueous.

Note: Some of these reactions do not go to completion.

1. silver nitrate + potassium chromate
2. ammonium chloride + cobalt(II) sulfate
3. lithium hydroxide + sodium chromate
4. zinc acetate + cesium hydroxide
5. ammonium sulfide + lead(II) nitrate
6. iron(III) sulfate + barium iodide
7. chromium(III) bromide + sodium nitrate
8. rubidium phosphate + titanium(IV) nitrate
9. ammonium carbonate + nickel(II) chloride
10. tin(IV) nitrate + potassium sulfite

Note: Correct molecular formulas must be written for both the reactants and products before an equation may be balanced.