

The Major Classes of Chemical Reactions

4.1 The Role of Water as a Solvent

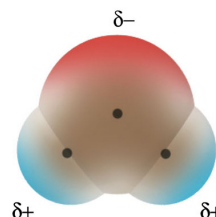
- Water participates actively in the dissolution process

The dissolution process

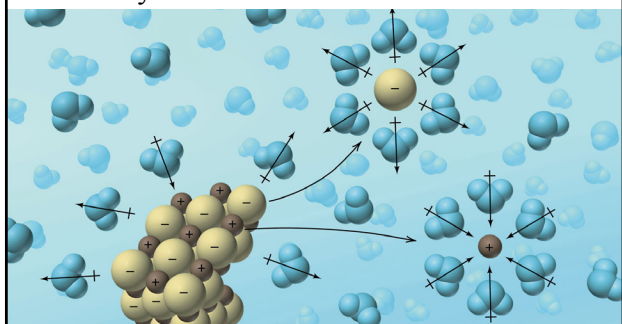
- **Hydration** (solvation) of the solute particles in solution
 - The solute particles (ions, molecules, ...) are surrounded by water (solvent) molecules
 - The solute particles are evenly spread throughout the solution

- **Electrolytes** – produce ions in solution (resulting solution conducts electricity)
 - **Strong electrolytes** – completely ionize in solution (soluble salts, strong acids and bases such as NaCl, HCl, KOH, ...)
 - **Weak electrolytes** – partially ionize in solution (weak acids and bases such as H₂S, NH₃, ...)
- **Nonelectrolytes** – do not ionize in solution (resulting solution does not conduct electricity)
 - Molecular compounds (except acids and bases) such as H₂O, sugar, acetone, methanol, ...

- The molecule of water is **polar**
 - The O atom pulls the shared electrons stronger
 - The O is partially negative and the Hs are partially positive
 - The molecule is bent
- ⇒ The molecule has a positive and a negative pole → **dipole**



- The water dipoles surround the ions on the surface of an **ionic** compound and pull them away from the crystal → hydration → electrolyte solution



- The water dipoles surround the molecules on the surface of a **covalent** compound and interact with the polar bonds in it → hydration →
 - If the molecules do not dissociate (most covalent compounds) → non-electrolytes
 - If the molecules dissociate to ions (for example in acids which contain polar X–H bonds) → electrolytes
- The **solubility** of a compound depends in large part on the relative strengths of the attractive forces between its ions or molecules and the forces of hydration

Example:

How many Na^+ ions are present in 8.2 mL of a 0.15 M $\text{Na}_2\text{SO}_4(\text{aq})$ solution?

$\text{Na}_2\text{SO}_4 \rightarrow$ strong electrolyte



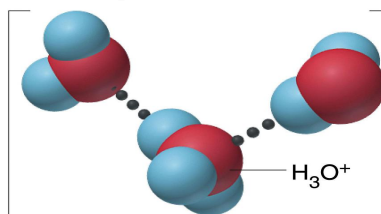
$$0.0082 \text{ L} \left(\frac{0.15 \text{ mol Na}_2\text{SO}_4}{1 \text{ L}} \right) \left(\frac{2 \text{ mol Na}^+}{1 \text{ mol Na}_2\text{SO}_4} \right)$$

$$\left(\frac{6.022 \times 10^{23} \text{ Na}^+ \text{ ions}}{1 \text{ mol Na}^+} \right) = 1.5 \times 10^{21} \text{ Na}^+ \text{ ions}$$

- The H^+ ion interacts very strongly with water and forms the **hydronium ion**, H_3O^+

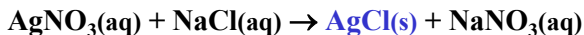


- H_3O^+ is strongly hydrated in water solutions by 1, 2 or even 3 H_2O molecules (H_5O_2^+ , H_7O_3^+ , H_9O_4^+)
- H^+ and H_3O^+ (including the hydrated forms) are equivalent expressions of the hydrogen ion

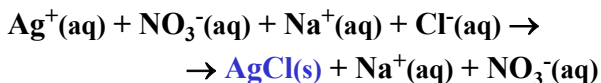
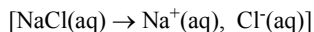


4.2 Equations for Reactions in Aqueous Solution

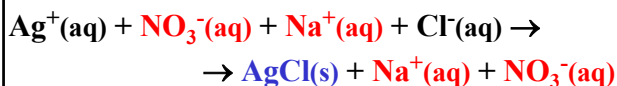
- Overall **molecular equation** (all reactants and products in their undissociated form)



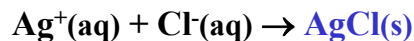
- Complete (total) ionic equation** (all strong electrolytes are completely dissociated to ions (ionized) in aqueous solutions)



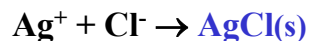
- Spectator ions** – present on both sides of the equation (can be canceled)



- Net ionic equation** – no spectator ions

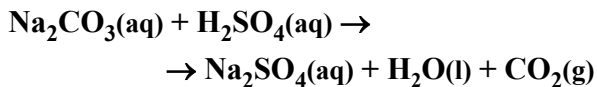


- For simplicity, we can omit **(aq)** after the symbols of all ions in aqueous solutions (assume all ions in solution as aqueous)

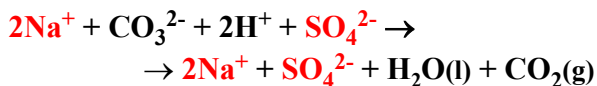


Example:

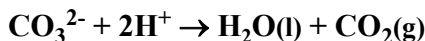
Write the net ionic equation corresponding to the following molecular equation:



\Rightarrow Complete ionic eq:

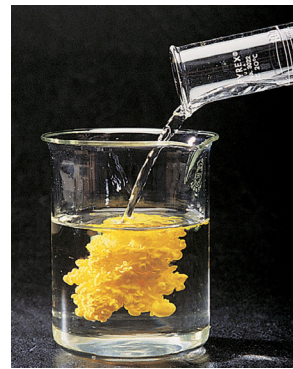


\Rightarrow Net ionic eq:



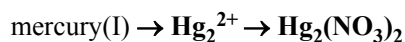
4.3 Precipitation Reactions

- Formation of an insoluble product (**precipitate**) after mixing of two electrolyte solutions
 - The driving force of precipitation reactions is the elimination of ions from the solution by formation of an insoluble product

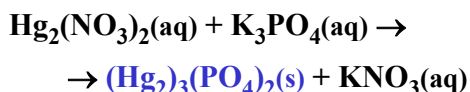


Example:

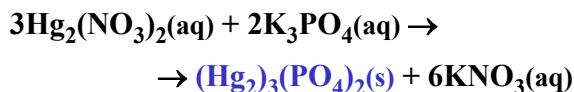
When mercury(I) nitrate and potassium phosphate solutions are mixed, mercury(I) phosphate **precipitates**. Write the net ionic equation.



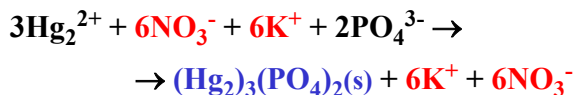
⇒Skeletal eq:



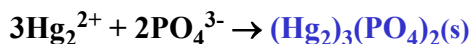
⇒Overall balanced eq:



⇒Complete ionic eq:



⇒Net ionic eq:



Predicting the outcome of precipitation

– Precipitation reactions are classified as **double replacement** (metathesis) reactions – exchange of ions leads to an insoluble combination of ions

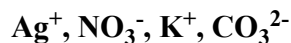
Table 4.1 Solubility Rules for Ionic Compounds in Water

Soluble Ionic Compounds	Insoluble Ionic Compounds
1. All common compounds of Group 1A(1) ions (Li^+ , Na^+ , K^+ , etc.) and ammonium ion (NH_4^+) are soluble.	1. All common metal hydroxides are insoluble, <i>except</i> those of Group 1A(1) and the larger members of Group 2A(2) (beginning with Ca^{2+}).
2. All common nitrates (NO_3^-), acetates (CH_3COO^- or $\text{C}_2\text{H}_3\text{O}_2^-$), and most perchlorates (ClO_4^-) are soluble.	2. All common carbonates (CO_3^{2-}) and phosphates (PO_4^{3-}) are insoluble, <i>except</i> those of Group 1A(1) and NH_4^+ .
3. All common chlorides (Cl^-), bromides (Br^-), and iodides (I^-) are soluble, <i>except</i> those of Ag^+ , Pb^{2+} , Cu^+ , and Hg_2^{2+} .	3. All common sulfides are insoluble <i>except</i> those of Group 1A(1), Group 2A(2), and NH_4^+ .
4. All common sulfates (SO_4^{2-}) are soluble, <i>except</i> those of Ca^{2+} , Sr^{2+} , Ba^{2+} , Ag^+ , Pb^{2+} and Hg_2^{2+} .	

Example:

Predict the outcome of the mixing of silver nitrate and potassium carbonate solutions.

⇒Ions present in the solution:



⇒consider all possible combinations of ions to find if an insoluble product can form:



⇒Net ionic eq: $2\text{Ag}^+ + \text{CO}_3^{2-} \rightarrow \text{Ag}_2\text{CO}_3(\text{s})$

Note: The net ionic equation can be predicted directly from the formula of the precipitate.

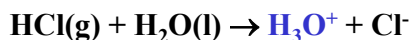
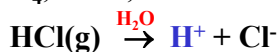
4.4 Acid-Base Reactions

– Acids - sharp, sour taste; Bases - soapy, bitter taste

- **Arrhenius acids** – release hydrogen ions, $\text{H}^+(\text{aq})$ [or $\text{H}_3\text{O}^+(\text{aq})$], in water solutions
- Acidic hydrogen atoms in molecules
 - can be released as H^+ ions
 - formulas normally begin with the acidic Hs

Examples:

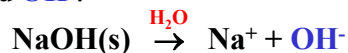
⇒ HCl , H_2SO_4 , HCN ,



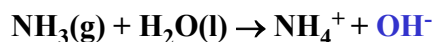
- **Arrhenius bases** – release hydroxide ions, OH^- , in water solutions

Examples:

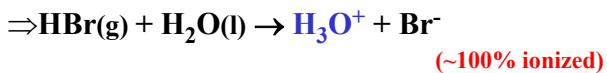
⇒ NaOH dissolves in water and dissociates to Na^+ and OH^- .



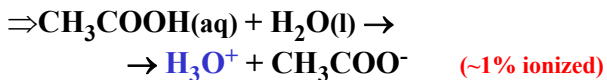
⇒Ammonia gas, NH_3 , dissolves in water and produces NH_4^+ and OH^- .



- **Strong acids** – almost completely ionized in aqueous solutions



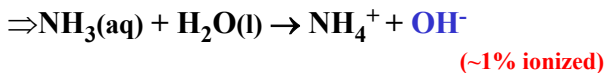
- The strong acids in aqueous solution are: HCl(aq), HBr(aq), HI(aq), HNO₃, H₂SO₄, HClO₄, and HClO₃
- **Weak acids** – only partially ionized in aqueous solutions (HF, H₂S, organic acids ...)



- **Strong bases** – almost completely ionized in aqueous solutions (oxides and hydroxides of alkali and alkaline earth metals)



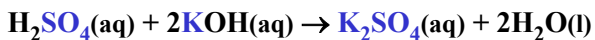
- The strong bases in aqueous solution are: Group I hydroxides, Ca(OH)₂, Sr(OH)₂, and Ba(OH)₂
- **Weak bases** – only partially ionized in aqueous solutions (ammonia, amines, ...)



Neutralization

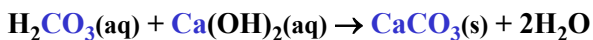
acid + base → salt + water (or other products)

- **Salt** – an ionic compound with a cation from the base and an anion from the acid



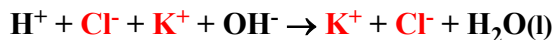
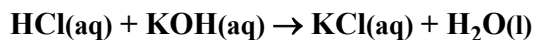
- Neutralization reactions are also viewed as **double replacement** (metathesis) reactions – exchange of ions leads to a salt and water

Example: Predict the products of the reaction between carbonic acid and calcium hydroxide.



Proton Transfer

- Net ionic equations for reactions between strong acids and bases



– H⁺ is present in the form of H₃O⁺

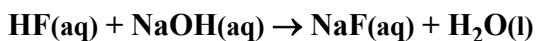


Net ionic equation for all strong acid/strong base reactions (transfer of a proton from H₃O⁺ to OH⁻)

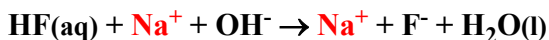
– The driving force of strong acid-base reactions is the elimination of ions (H⁺ and OH⁻) from the solution by formation of water

- Net ionic equations for reactions between weak acids and strong bases

Example:



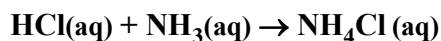
HF(aq) → weak acid (only partially ionized)



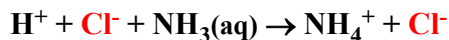
⇒ transfer of a proton from HF to OH⁻

- Net ionic equations for reactions between strong acids and weak bases

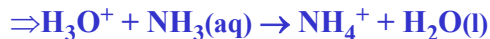
Example:



NH₃(aq) → weak base (only partially ionized)



– H⁺ is present in the form of H₃O⁺

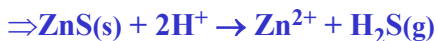
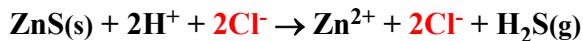
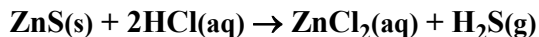


⇒ transfer of a proton from H₃O⁺ to NH₃

Gas Formation Reactions

- Reactions of salts of weak or volatile acids with strong acids

Example:



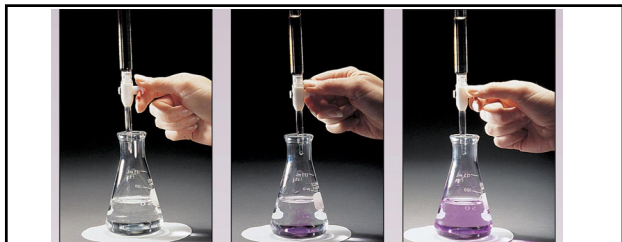
– H^+ is present in the form of H_3O^+



\Rightarrow transfer of a proton from H_3O^+ to S^{2-}

Acid-base titrations

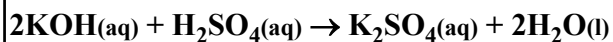
- Titrations use measurements of volumes
- Based on stoichiometric acid-base reactions between the analyzed solution (analyte) and a solution with known concentration (titrant)
- **Equivalence point** – the amount of titrant added is stoichiometrically equivalent to the amount of analyte present in the 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.

\Rightarrow balanced equation:



\Rightarrow mole ratio: [1 mol H_2SO_4 /2 mol KOH]

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

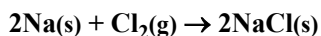
$$= 2.09 \times 10^{-3} \text{ mol H}_2\text{SO}_4$$

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

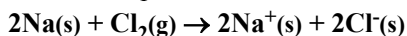
4.5 Redox Reactions

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



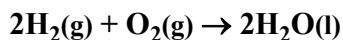
NaCl is an ionic compound:



Result \rightarrow 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



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



⇒ Electrons are shifted from H to O



Result → 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#



Rules for assigning Ox#

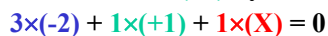
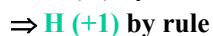
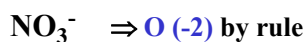
- Monoatomic ions** → Ox# = charge of ion
- Free elements** → Ox# = 0
- F** → Ox# = -1
- O** → Ox# = -2 (except in combination with F and in peroxides)
- H** → Ox# = +1 (in combination with nonmetals)
 - Ox# = -1 (in combination with metals)
- Halogens** → Ox# = -1 (except in comb. with O or other halogen 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)

		+1 -1		Group number						
				Highest O.N./Lowest O.N.						
		1A	2A	3A	4A	5A	6A	7A		
		+1	+2	+3	+4 -4	+5 -3	+6 -2	+7 -1		
1		H								
2		Li	Be	B	C	N	O	F		
3		Na	Mg	Al	Si	P	S	Cl		
4		K	Ca	Ga	Ge	As	Se	Br		
5		Rb	Sr	In	Sn	Sb	Te	I		
6		Cs	Ba	Tl	Pb	Bi	Po	At		
7		Fr	Ra			114				

Example:

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



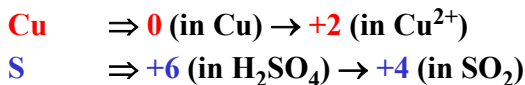
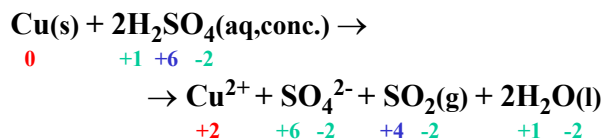
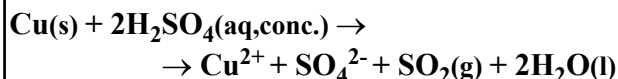
- Oxidizing agent** – causes oxidation (removes electrons from the species being oxidized)
 - is the species **being reduced**
 - contains an element which undergoes a decrease in Ox# (reduction)
- Reducing agent** – causes reduction (supplies electrons to the species being reduced)
 - is the species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

<p>X loses electron(s) X is oxidized X is the reducing agent X increases its oxidation number</p>	<p>Y gains electron(s) Y is reduced Y is the oxidizing agent Y decreases its oxidation number</p>

- Identification of Ox/Red agents – need to examine the Ox# of all elements in the reaction

Example:

Identify the Ox. and Red. agents in the reaction of **Cu** with hot, concentrated **H₂SO₄**.



⇒ Cu is oxidized ⇒ Cu is the reducing agent

⇒ S in H₂SO₄ is reduced ⇒ H₂SO₄ is the oxidizing agent

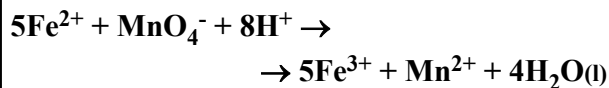
⇒ H₂SO₄ oxidizes Cu; Cu reduces H₂SO₄

Redox titrations

- Use redox reactions

Example:

A 0.202 g sample of iron ore is dissolved in HCl and all of its Fe content is converted to Fe²⁺. The resulting solution is titrated with **16.7 mL 0.0108 M KMnO₄** solution. Determine the **mass%** of Fe in the sample, if the equation of the redox reaction is:



⇒ mole ratio: [5 mol Fe²⁺/1 mol MnO₄⁻]

⇒ calculate the mass of Fe:

$$16.7 \times 10^{-3} \text{ L} \times \left(\frac{0.0108 \text{ mol MnO}_4^-}{1 \text{ L}} \right) \times \left(\frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4^-} \right) \times \left(\frac{55.85 \text{ g Fe}^{2+}}{1 \text{ mol Fe}^{2+}} \right) = 0.0504 \text{ g Fe}^{2+} \rightarrow 0.0504 \text{ g Fe}$$

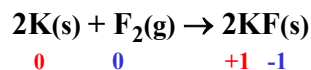
⇒ calculate the mass%:

$$\text{Mass\% Fe} = \frac{0.0504 \text{ g Fe}}{0.202 \text{ g sample}} \times 100\% = 25.0\%$$

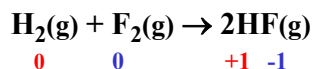
4.6 Free Elements in Redox Reactions

- If a reaction involves a free element as either reactant or product, it is a redox reaction
- Combining two elements

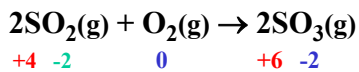
Metal + Nonmetal → Ionic compound



Nonmetal + Nonmetal → Covalent compound

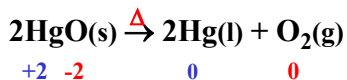


- **Combining compounds and elements**

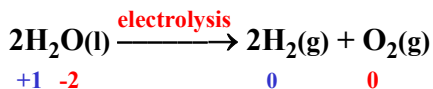


- **Decomposing compounds into elements**

– Thermal decomposition



– Electrolytic decomposition

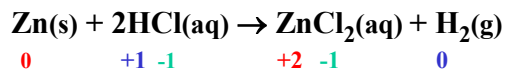


- **Displacing one element by another**

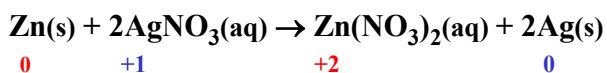


- The **activity series** of the metals – orders the metals by their ability to displace H or each other from compounds

– Metals displacing hydrogen from acids or H₂O



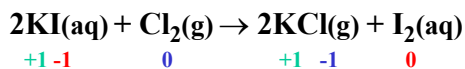
– Metals displacing each other



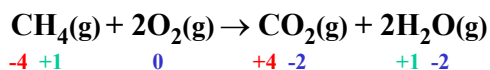
Strength as reducing agent ↑	Li	Can displace H ₂ from water	<ul style="list-style-type: none"> • Activity series – metals higher in the list are stronger reducing agents and can displace (reduce) metals lower in the list from their aqueous solutions • The most active metals are unstable in water
	K		
	Ba		
	Ca		
	Na		
	Mg		
	Al		
	Mn		
	Zn		
	Cr		
	Fe		
	Cd		
	Co		
	Ni		
	Sn		
	Pb		
H ₂			
Cu			
Hg			
Ag			
Au			

- The activity series of the halogens

– Reactivity decreases down the group (halogens higher in the group are stronger oxidizing agents and can displace (oxidize) halogens lower in the group)

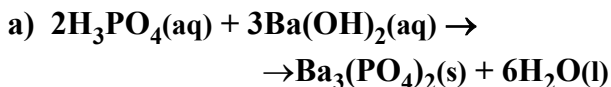


- **Combustion reactions** – combination of elements or compounds with oxygen



Example:

Classify the following reactions:



➤ H₃PO₄ is a weak acid; Ba(OH)₂ is a strong base

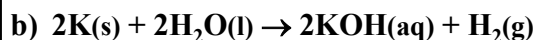
➤ Products are salt and water

⇒ **Neutralization reaction**

➤ The salt is insoluble → precipitate

⇒ **Precipitation reaction**

⇒ **Double displacement reaction**



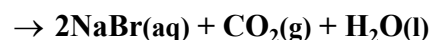
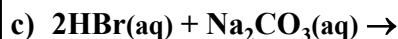
➤ Free elements involved in the reaction

➤ Change in Ox# of K and H

⇒ **Redox reaction**

➤ K displaces H from water

⇒ **Single displacement reaction**



➤ No change in Ox# of elements

➤ HBr is a strong acid, Na₂CO₃ is a salt of a weak acid

⇒ **Gas formation reaction**

⇒ **Neutralization reaction**