Chapter 3: Chemical Reactions

Chemical equations describe chemical reactions – they give a great deal of information:

(1) substances that react REACTANTS
(2) substances formed PRODUCTS
(3) relative amounts of the substances involved

Note: I want to emphasize that reactions are NOT mathematical equations or equalities. Therefore

Therefore, Reactants $\neq$ Products
"are not equal"

We write Reactants $\longrightarrow$ Products
"are changing into"

The reactions as written are describing a process. At the start, only reactants are present. At the finish, only products are present (providing the reaction went 100% to completion and stoichiometric amounts of reactants are present – more later). And so, as time progresses, substances (reactants) are changed into other substances (products). This semester, we are only concerned with what is present initially and what the final products are. Next semester, we will discuss why reactions go and how fast they go, among other topics.

Recall, Law of Conservation of Matter: matter is not created or destroyed; there is no detectable change in the quantity of matter in an ordinary chemical reaction.

This law allows us to "balance" equations using stoichiometric coefficients.
For each element, # atoms on reactant side = # atoms on product side

Example: Pentane (C_5H_{12}) burns in oxygen to form carbon dioxide (CO_2) and water (H_2O).

$$C_5H_{12} + \overset{(4)}{8}O_2 \rightarrow \overset{(2)}{5}CO_2 + \overset{(3)}{6}H_2O$$

Hint: start balancing using the most complex compounds first eg C_5H_{12}. then balance the H_2O, leaving the single elements eg O_2 until the en

	Initially (1) Reactants	Products	(2) R	P	(3) R	P	(4) R	P
C	5	1	5	5	5	5	5	5
H	12	2	12	2	12	12	12	12
O	2	3	2	11	2	16	16	16

Example: Ammonia (NH_3) burns in oxygen gas to form nitrogen oxide (NO and water.

$$\overset{(2)}{2}NH_3 + \overset{(4)}{\tfrac{5}{2}}O_2 \rightarrow \overset{(3)}{2}NO + \overset{(2)}{3}H_2O$$

	(1) Reactants	Products	(2) R	P	(3) R	P	(4) R	P
N	1	1	2	1	2	2	2	2
H	3	2	6	6	6	6	6	6
O	2	2	2	4	2	5	5	5

However it is <u>more</u> correct to use whole numbers for all coefficients
$\therefore$ multiply by 2, giving

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$$

Another hint: Look for species that are the same on both sides and treat them as a unit:

Examples: NO_3^- nitrate ion — $H\underline{NO_3} \rightarrow Na\,\underline{NO_3}$
SO_4^{2-} sulfate ion — $H_2\underline{SO_4} \rightarrow Mg\,\underline{SO_4}$
NH_3 ammonia / NH_4^+ ammonium ion — $NH_3 \rightarrow NH_4Cl$

Example: $Fe(NO_3)_3 + 3NH_3 + 3H_2O \rightarrow Fe(OH)_3 + 3NH_4NO_3$

Step 1: balance Fe - OK
2: balance NO_3
3: balance NH_3 / NH_4^+
4: balance O using H_2O
5: check to see if H. is balanced.

Calculations Based on Chemical Equations

Chemical equations represent a very precise versatile language. It is possible to extract a large amount of information from them.

Let us consider:

$$\underset{\text{iron(III) oxide}}{Fe_2O_3} + 3 \underset{\text{carbon monoxide}}{CO} \rightarrow 2 \underset{\text{iron}}{Fe} + 3 \underset{\text{carbon dioxide}}{CO_2}$$

REACTANTS PRODUCTS

Meaning: for every mole (or formula unit (think: molecule)) of Fe_2O_3 3 moles (or molecules) of CO are needed to form 2 moles (or atoms) of Fe and 3 moles (or molecules) of CO_2.

∴ the equation relates moles and molecules – NOT mass!! via the stoichiometric coefficients

∴ (1) if there are 2 formula units of Fe_2O_3, how much CO is needed? 6 molecules
(2) if there are 9 moles of CO, how much CO_2 can be formed? 9 moles
(3) if 8 atoms of Fe are formed, how much CO was needed? 12 molecules.

Recall: the smallest part of an element is the atom.
the smallest part of a covalent compound is the molecule.
The smallest part of an ionic compound is the formula unit.

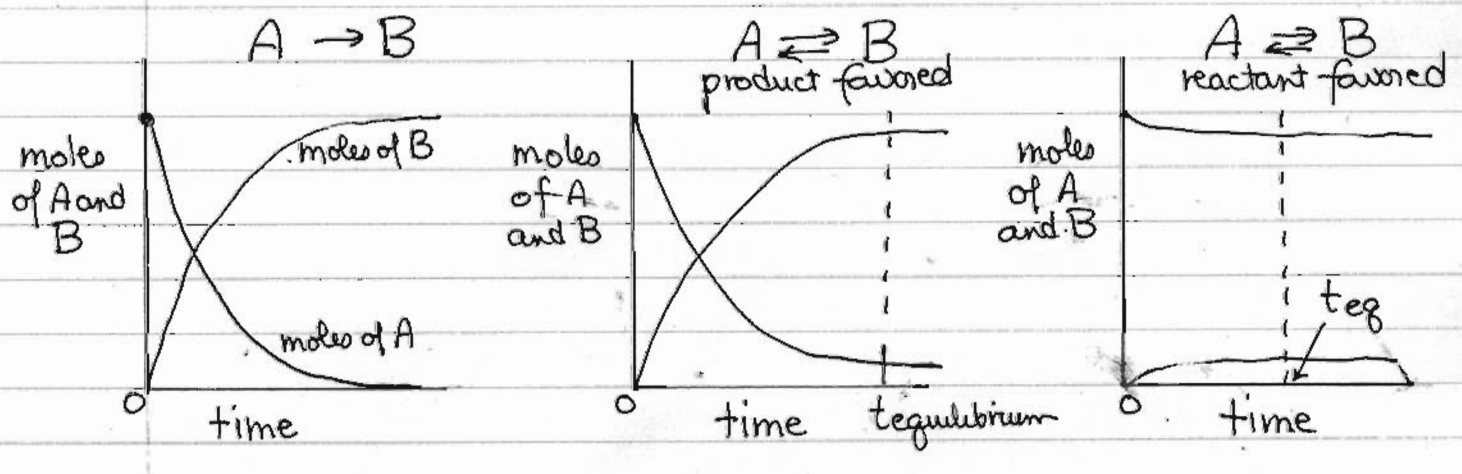
Introduction to Chemical Equilibrium:

When balancing reactions, we assumed the reactants were converted totally into products; we used a single arrow $\longrightarrow$

Most reactions do NOT turn totally into products, but rather go to equilibrium, where there is a mix of reactants and products. These reactions are called reversible since at equilibrium, reactants convert to products just as fast as products convert back to reactants. It is a very dynamic process. We represent this using 2 arrows: $\rightleftarrows$

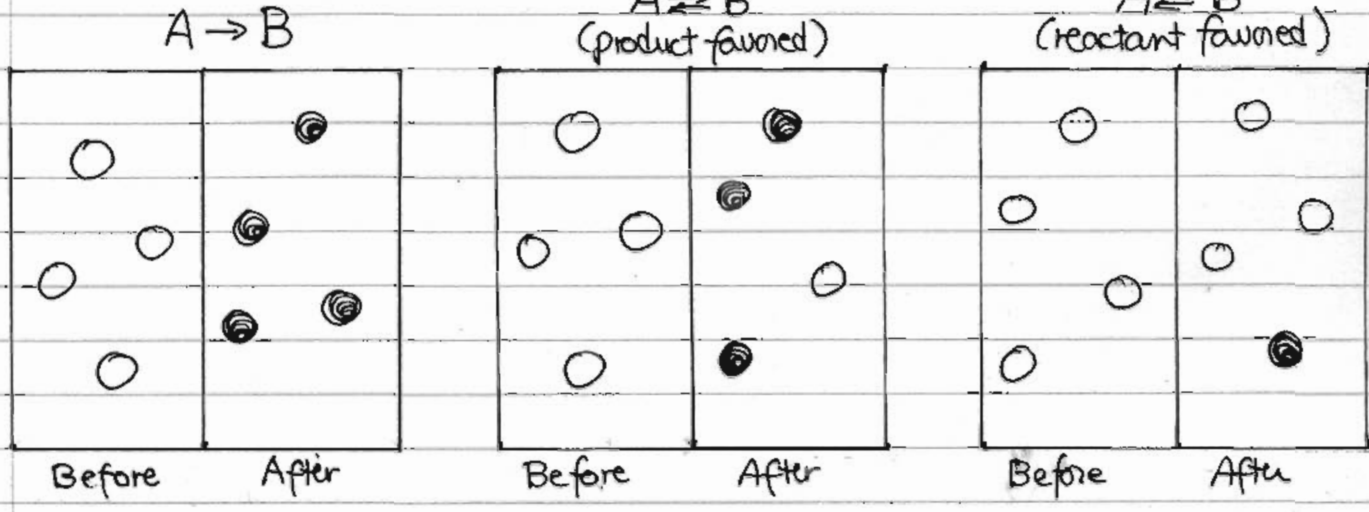
- product-favored: reactants turn mostly into products
- reactant-favored: reactants only form a small amount of product; they mainly stay as reactants.

Consider $A \rightarrow B$ The single arrow implies all of A converts to B
whereas $A \rightleftarrows B$ The double arrow implies the reaction is going to equilibrium - not all A becomes B.



- Once the system reaches equilibrium at time = t_{eq}, the amounts of product and reactant don't seem to change.
- However, at the submicroscopic level, we have a very dynamic system, with reactants converting to products and products converting to reactants!

Particle View: A = O B = ●



Aqueous Solutions

Many reactions take place in water ie in aqueous solution
Therefore, it is important to know what happens to substances when they are placed in water. (1) is it soluble in water?
(2) if it is soluble, does it break up into ions?

Terminology

acid: a substance that produces hydrogen ions, H^+, in aqueous solution
(HCl, H_2SO_4, $CH_3COO\underline{H}$, $HCOO\underline{H}$)

base: a substance that produces hydroxide ions, OH^-, in aqueous solution
($NaOH$, $Ba(OH)_2$ not CH_3OH - this is a very, very weak acid)
(NH_3, CH_3NH_2 are bases by another definition)

salt: a compound that contains a cation other than H^+ and an anion other than OH^- or O^{2-} (an oxide)
($NaCl$, $Mg(NO_3)_2$, CuS etc)

I Solubility

A compound that dissolves in water to an appreciable extent is "soluble"; if not, it is "insoluble."

No gaseous or solid substance is infinitely soluble in water.

Solubility Rules

Substance	Soluble	Insoluble
Acid	common inorganic acids and low MW organic acids	high MW organic acids
Base	IA and heavier IIA bases ($Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$) Note: $Ca(OH)_2$ and $Sr(OH)_2$ are considered by some to be insoluble. NH_3 and other organic bases	all the rest of hydroxides
Salt	common IA and NH_4^+ salts common NO_3^-, CH_3COO^-, ClO_3^-, ClO_4^-	common CO_3^{2-}, PO_4^{3-}, AsO_4^{3-} (except for IA and NH_4^+) common S^{2-} salts (except for IA, IIA, NH_4^+)

Other salts not mentioned can be either soluble or insoluble.

On the back of the exam envelope, there is a chart called "Solubility Products at 25°C." If the compound is on the chart, it is probably insoluble - but note that $Ca(OH)_2$ and $Sr(OH)_2$ are on the chart. If it is not on the chart, it may or may not be soluble.

II Once a soluble compound is dissolved in water, we can determine how well the solution conducts electricity.

electrolyte (substance whose aqueous solution conducts electricity)

strong electrolyte [conducts electricity WELL in dilute solutions]

weak electrolyte [conducts electricity POORLY in dilute solution] nonelectrolyte : substance whose aqueous solution does <u>NOT</u> conduct electricity.

Examples:

	Acid	Base	Salt
Strong electrolytes:	Strong Acids	Strong Bases	Soluble Salts
monoprotic acid (1 H)	HCl (aq)	LiOH	all soluble salts
	HBr (aq)	NaOH	
	HI (aq)	KOH	
	HNO_3	RbOH	
	$HClO_4$	CsOH	
	$HClO_3$	$Ba(OH)_2$	
diprotic acid (2H) →	H_2SO_4	$Ca(OH)_2$, $Sr(OH)_2$	
Weak electrolytes	Weak Acids	Weak Bases	—
	HF	NH_3	
	CH_3COOH	CH_3NH_2	
	HCN (aq)	+ others	
	HNO_2		
	H_2SO_3		
	H_3PO_4		
	+ others		

Nonelectrolytes : sugar, $O_2(g)$, CH_4 and other compounds that remain as molecules in water.

How do the electrolytes conduct electricity? They ionize (dissociate or separate into ions) in aqueous solution. Ions carry the electicity. since they are charged spe

in dilute aqueous solutions
- strong electrolytes dissociate (ionize) completely or nearly completely
- weak electrolytes dissociate (ionize) slightly

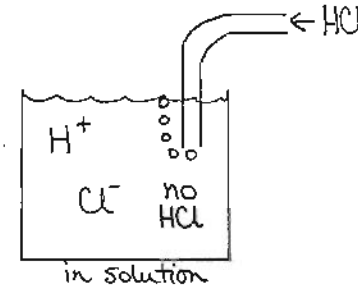
How do we represent this in an equation?

a single arrow $\rightarrow$: complete or nearly complete dissociation (ionizatio
of compound into ions

a double arrow $\rightleftarrows$: only slight dissociation (ionization)

Strong Electrolytes

(g) gas (s) solid
(l) liquid (aq) aqueous

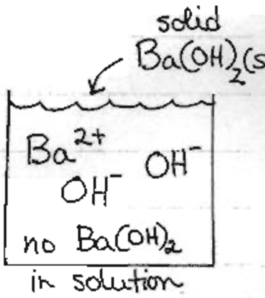


strong acid: $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

$H_2SO_4(aq) \rightarrow 2\,H^+(aq) + SO_4^{2-}(aq)$

strong base: $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

$Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2\,OH^-(aq)$



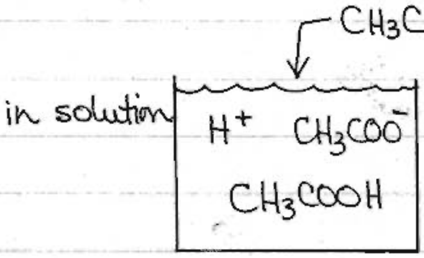
soluble salt: $Na_2SO_4(aq) \rightarrow 2\,Na^+(aq) + SO_4^{2-}(aq)$

Weak Electrolytes

weak acid: $CH_3COOH(aq) \rightleftarrows CH_3COO^-(aq) + H^+(aq)$

acetic acid — acetate ion

$\rightleftarrows$ also means the ionization reaction is reversible i.e. the reaction can occur in both directions



we have all three components in our solution
concentration of undissociated CH_3COOH is greater than concentration of H^+, CH_3COO^-

weak base: $NH_3(aq) + H_2O \rightleftarrows NH_4^+(aq) + OH^-(aq)$

Flow Chart

Substance

↓ soluble (dissolves in H_2O) — (aq)

↓ insoluble (do not dissolve appreciably in H_2O) — (S)
(1) insoluble bases $Mg(OH$
(2) insoluble salts $CaF_2($

soluble ↓

	strong electrolytes	weak electrolytes	non electrolytes
	(1) strong acids (7) (2) strong soluble bases IA and $Ba(OH)_2$ ($Ca(OH)_2$ + $Sr(OH)_2$ are slightly soluble) (3) all soluble salts	(1) weak acids all acids that are not strong (2) weak bases NH_3 and its derivatives see hand out	
Examples	$KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$ in solution, there is no $KOH(aq)$, only K^+ ions + OH^- ions	$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$ in solution, there is mostly HF molecules floating around but there are a few H^+ ions + F^- ions	sugar, O_2 only molecules are in solution — no charged particles
Electrical Conductivity	Excellent	poor	none

Now that you have been introduced to the concepts of solubility and ionization, the next step is to predict if two compounds in water will react and what will the products be.

We will consider 2 types of reactions : (I) precipitation reactions
(II) acid - base reactions

I <u>Precipitation Reactions</u> – a solid is one of the products.

Suppose we mix aqueous solutions of calcium nitrate and potassium carbonate.
calcium nitrate : $Ca(NO_3)_2\,(aq)$ since all nitrate salts are soluble
potassium carbonate: $K_2CO_3\,(aq)$ since all IA salts are soluble

and
$$Ca(NO_3)_2(aq) \xrightarrow{\text{dissociates}} Ca^{2+}(aq) + 2\,NO_3^-(aq)$$
$$K_2CO_3\,(aq) \longrightarrow 2K^+(aq) + CO_3^{2-}(aq)$$

What products can form? Switch partners! Ans. $\underset{\text{solid (see prec. rules)}}{CaCO_3}$ and $\underset{\text{aqueous for above reasons}}{KNO_3}$

Because a solid forms (ions are removed from solution), the rxn goes. There are 3 equations we can write to represent what is happening.

(1) Formula Unit Equation: $Ca(NO_3)_2(aq) + K_2CO_3(aq) \rightarrow CaCO_3(s) + 2\,KNO_3(aq)$
(Molecular) = Our Usual Equation = remember to balance

the Total Ionic Equation for this reaction is obtained by writing all the strong electrolytes (7 strong acids, 8 strong soluble bases, all soluble salts) as ions. Every other compound is written as a "molecule".

(2) Total Ionic Equation: $Ca^{2+}(aq) + \overset{\text{spectator}}{2\,NO_3^-(aq)} + \overset{\text{spectator}}{2K^+(aq)} + CO_3^{2-}(aq) \longrightarrow$

this does NOT break up because it is <u>insoluble</u> $\rightarrow CaCO_3(s) + \overset{\text{spectator}}{2\,K^+(aq)} + \overset{\text{spectator}}{2NO_3^-(aq)}$

Next we notice that some ions appear on both sides of the equation as ions. These are called SPECTATOR ions because they do not participate in the reaction. The spectators can be cancelled off both sides of the equation and the equation is reduced to the NET IONIC EQUATION.

(3) Net Ionic Equation: $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$
gives us the "nitty-gritty"

POINT of FACT: If all ions are spectators – the reaction does not occur!

II. Acid - Base Reactions (Neutralization Reactions)

In this reaction: acid + base → salt + water*

Example: Write the balanced net ionic equation for the reaction of hydrochloric acid (HCl) and barium hydroxide ($Ba(OH)_2$). Salt is soluble.

Formula Unit Equation: $\underset{\text{strong acid}}{2HCl(aq)} + \underset{\text{strong soluble base}}{Ba(OH)_2(aq)} \rightarrow \underset{\text{soluble salt}}{BaCl_2(aq)} + 2H_2O(l)$

Step (1) determine the products – salt plus water
Step (2) balance equation
Step (3) figure out what each compound is

Total Ionic Equation: $2H^+(aq) + \overset{\text{spectator}}{2Cl^-(aq)} + \overset{\text{spectator}}{Ba^{2+}(aq)} + 2OH^-(aq) \rightarrow$
Break up all strong electrolytes!

$\overset{\text{spectator}}{Ba^{2+}(aq)} + \overset{\text{spectator}}{\underset{\Uparrow \text{ not } Cl_2!}{2Cl^-(aq)}} + 2H_2O(l)$

Net Ionic Equation: $2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(l)$
remove spectator ions

OR

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

*Note: If NH_3 is the base, water does NOT form.

Example: Write the balanced net ionic equation for the reaction of phosphoric acid (H_3PO_4) and sodium hydroxide (NaOH).

Formula Unit equation:

weak acid — strong soluble base — soluble salt

$H_3PO_4(aq) + 3NaOH(aq) \rightarrow Na_3PO_4(aq) + 3H_2O(\ell)$

Total Ionic Equation:

$\underbrace{H_3PO_4(aq)}_{\text{stays together}} + \overbrace{3Na^+(aq)}^{\text{spectator}} + 3OH^-(aq) \longrightarrow$

$\overbrace{3Na^+(aq)}^{\text{spectator}} + PO_4^{3-}(aq) + 3H_2O(\ell)$

Net Ionic Equation: $H_3PO_4(aq) + 3OH^-(aq) \rightarrow PO_4^{3-}(aq) + 3H_2O(\ell)$

Example Write the balanced net ionic equation for the reaction of ammonia (NH_3) and perchloric acid ($HClO_4$).

Formula Unit Equation:

weak base — strong acid — soluble salt

$NH_3(aq) + HClO_4(aq) \rightarrow NH_4ClO_4(aq)$ NO WATER

Total Ionic Equation:

$NH_3(aq) + H^+(aq) + \overbrace{ClO_4^-(aq)}^{\text{spectator}} \rightarrow NH_4^+(aq) + \overbrace{ClO_4^-(aq)}^{\text{spectator}}$

Net Ionic Equation: $NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$

Example: Write the balanced net ionic equation for the reaction of iron(III) hydroxide and sulfuric acid (H_2SO_4). The salt is soluble

Formula Unit Equation:

insoluble base — strong acid — soluble salt

$2Fe(OH)_3(s) + 3H_2SO_4(aq) \rightarrow Fe_2(SO_4)_3(aq) + 6H_2O(\ell)$

Total Ionic Equation:

$2Fe(OH)_3(s) + 6H^+(aq) + \overbrace{3SO_4^{2-}(aq)}^{\text{spectator}} \rightarrow$

$2Fe^{3+}(aq) + \overbrace{3SO_4^{2-}(aq)}^{\text{spectator}} + 6H_2O(\ell)$

Net Ionic Equation: $2Fe(OH)_3(s) + 6H^+(aq) \rightarrow 2Fe^{3+}(aq) + 6H_2O(\ell)$

OR $Fe(OH)_3(s) + 3H^+(aq) \rightarrow Fe^{3+}(aq) + 3H_2O(\ell)$

Oxidation - Reduction (Redox) Reactions:

Many reactions, called redox, involve the transfer of electrons from 1 species to another.

- Note: the acid-base and precipitation reactions just discussed, do NOT involve redox.
- In order to keep track of the number of electrons lost or gained during a redox reaction, the concept of oxidation number is used. These are arbitrary numbers used to help writing formulas and balancing equations.

Rules for Assigning oxidation numbers:

1. The oxidation number of any free element is 0 (He, O_2, S_8, Fe etc)
2. For a compound, the sum of all the oxidation numbers of the elements = 0.
3. For an ion, the sum of all the oxidation numbers of the elements equals the charge on the ion (ox. no. of Fe in Fe^{2+} is +2)
4. Group IA: +1 (in a few cases, H can be -1; ignore for now)
5. Group IIA: +2
6. Group IIIA: +3 usually
7. oxygen: -2 (but can be -1 in H_2O_2 or even $-\frac{1}{2}$).
8. for IONIC compounds ONLY (metal + nonmetal), the nonmetals are:
   Group VA: -3   Group VIA: -2   Group VIIA: -1

Note of explanation: For stability reasons, Group A ions "want" to have the same total number of electrons as the noble gases. To do so, metals lose electrons, nonmetals gain electrons. More later.

From these rules (guidelines), you can deduce the oxidation number of any other element in a compound or polyatomic ion. The other elements can exhibit many oxidation states depending on the situation.

Examples:

(1) $H_2\underline{S}$ 2(ox. no. H) + ox. no. S = 0

$2(+1)$ + ox. no. S = 0 $\therefore$ ox. no. S = -2

(2) $KH_2\underline{P}O_4$ $\quad 0 = \text{ox. no. K} + 2(\text{ox. no. H}) + \text{ox. no. P} + 4(\text{ox. no. O})$

$0 = +1 + 2(+1) + \text{ox. no. P} + 4(-2)$

$0 = \text{ox. no. P} - 5$

$+5 = \text{ox. no. P}$

(3) $\underline{Cr}_2O_7^{2-}$ $\quad -2 = 2(\text{ox. no. Cr}) + 7(\text{ox. no. O}) = 2x + 7(-2)$

$+12 = 2(\text{ox. no. Cr})$

$+6 = \text{ox. no. Cr}$

(4) $\underline{Fe}(\underline{N}O_3)_2$ $\quad 0 = \text{ox. no. Fe} + 2(\text{charge on } NO_3^- \text{ ion}) = \text{ox. no. Fe} + 2(-1)$

$+2 = \text{ox. no. Fe}$

To determine ox. no. N, one can look at the whole compound or just the NO_3^-.

(1) $0 = \text{ox. no. Fe} + 2(\text{ox. no. N}) + 6(\text{ox. no. O})$

$0 = +2 + 2(\text{ox. no. N}) + 6(-2) = 2(\text{ox. no. N}) - 10$

$+10 = 2(\text{ox. no. N})$

$+5 = \text{ox. no. N}$

(2) $-1 = \text{ox. no. N} + 3(\text{ox. no. O})$

$-1 = \text{ox. no. N} + 3(-2)$

$+5 = \text{ox. no. N}$

More definitions

oxidation: an algebraic increase in oxidation number, or process in which e^- are lost

reduction: an algebraic decrease in oxidation number, or process in which e^- are gained

A redox reaction has both oxidation and reduction occurring simultaneously.

oxidizing agent: a substance that oxidizes another substance; it itself contains an element that gets reduced.

reducing agent: a substance that reduces another substance; it itself contains an element that gets oxidized.

Example: Write the net ionic equation for the following reaction. Is it a redox reaction? If so, label the element(s) being oxidized and reduced, the oxidizing agent and the reducing agent.

Formula unit equation: $\overset{0}{2\,Cr(s)} + 3\,\overset{+2}{Cu}(\overset{+5}{N}\overset{-2}{O_3})_2(aq) \rightarrow 2\,\overset{+3}{Cr}(\overset{+5}{N}\overset{-2}{O_3})_3(aq) + 3\,\overset{0}{Cu}(s)$

This is a redox reaction, because there are elements changing oxidation number.

element oxidized: Cr ($\overset{0}{Cr} \rightarrow \overset{+3}{Cr}$) so Cr is reducing agent

element reduced: Cu^{2+} ($\overset{+2}{Cu} \rightarrow \overset{0}{Cr}$) so $Cu(NO_3)_2$ is oxidizing agent

Total Ionic equation: $2\,Cr(s) + 3\,Cu^{2+}(aq) + 6\,NO_3^-(aq) \rightarrow$
$2\,Cr^{3+}(aq) + 6\,NO_3^-(aq) + 3\,Cu(s)$

Net Ionic equation: $2\,Cr(s) + 3\,Cu^{2+}(aq) \rightarrow 2\,Cr^{3+} + 3\,Cu(s)$

NO_3^- is a spectator ion, Cr and Cu are not

Note: If the formula unit equation is balanced, the net ionic equation is balanced, both mass-wise and charge-wise (both reactant side & product side have a net +6 charge, in above case). This must always be true.

Note: In many instances, the only equations given to you are the net ionic equations. When you see equations with charged ions present, you should recognize that the spectator ions have already been removed, leaving the essence of the reaction.

Definitions of Acids + Bases:

Arrhenius Theory:

acid: substance that has an H and produces H^+ in aqueous solution

substances with "acid" in their names are Arrhenius acids

hydrochloric acid HCl

acetic acid $CH_3COO\underline{H}$ ← acidic H

base: substance that has $-OH$ and produces OH^- ions in aqueous solution

metal hydroxides:

sodium hydroxide $NaOH$

Bronsted-Lowry Theory

acid: a proton (H^+ ion) donor

base: a proton acceptor

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \longrightarrow \underset{\text{conjugate acid}}{H_3O^+} + \underset{\text{conjugate base}}{Cl^-}$$

H_3O^+ is hydronium ion

HCl is a B-L acid since it is donating an H^+

H_2O is a B-L base since it accepted an H^+. (proton)

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \rightleftarrows \underset{\text{conjugate acid}}{NH_4^+} + \underset{\text{conjugate base}}{OH^-}$$

Note: H_2O is amphiprotic since it can accept and donate a proton

NH_3 is a B-L base since it accepted a proton (it is not an Arrhenius base - no OH)

H_2O is a B-L acid since it donated a proton.