**9. Chemical Reactions**

**9.1 Types of Chemical Reactions**

Chemists have identified many millions of different chemical compounds that can react in many different ways to form new chemical compounds. One of the popular classification schemes is to breaks them up into few major categories or types based on the simplicity/complexity of reactants/products in chemical reactions. Some of these types have been given more than one name and is could get complicated. You need to recognize the pattern, as you may encounter different names in different places.

**Classification based on the simplicity/complexity of reactants/products**

**1) Combination**: **A + B**  **AB**

**2H2(g) + O2(g)**  →**2H2O(g)**

**C(s) + O2(g)**  **CO2(g)**

**CaO(s) + H2O(l)**  **Ca(OH)2(s)**

**Other modifications**:

**A synthesis reaction** involves two or more substances combining to make a more complex substance. The reactants may be elements or compounds, and the product will always be a compound. The general formula for **synthesis** (simple to complex): **CO2 + H2O  C6H12O6 + O2** (photosynthesis)

**Addition reaction** involves two or more substances combining to make single substance.  The general formula for **addition** (simple to complex): **C2H4 + Br2--> C2H4Br2**

Also includes many polymerization reactions such as:

 **n C2H4 (ethylene) (C2H4)n(polyethylene)**

**2) Decomposition:** One substance is broken down into two or more, simpler substances.

 **AB**  **A + B; E.g. KClO3  KCl + O2**

**C12H22O11(s)**  **12C(s) + 11H2O(g)**

**Pb(OH)2(s)**  **PbO(s) + H2O(g)**

**2Ag2O(s)**  **4Ag(s) + O2(s)**

**3) Displacement:**

**a) Single Displacement:** In this type of reaction, a neutral element metal or nonmetal become an ion as it replaces another ion in a compound.

 **M1X + M2**  **M2X + M1:**

**For metals**

Thereaction follows **Activity series**: Active metal, **M2** (Fe) at beginning of the series replaces the **M1**+ ion, and produces metal **M1**, (Cu)

**Metals**:Li> K>Ca>Na>Mg>Al>Zn>Cr>Fe>Ni>Sn>Pb>H>Cu>Hg>Ag>Pt>Au

**E.g. Fe(s) + Cu(NO3)2(aq)  Fe(NO3)2(aq) + Cu(s)**

**Zn(s) + H2SO4(aq)**  **ZnSO4(aq) + H2(g)**

**2Al(s)+ 3CuCl2(aq)**  **2AlCl3(aq) + 3Cu(s)**

**Non-metals: MX1 + X2**  **MX1 + X2:**

Thereaction follows **Activity series**: Nonmetal, **X2** (Cl2) at beginning of the series replaces the **X1**- ion, and produces nonmetal **X2**, (I2)

**Activity series:** F>Cl>Br>I

**E.g. 2 NaI(aq) + Cl2(g)**  **2 NaCl(aq) + I2(s)**

 **KBr(aq) + Cl2(g)**  **KCl(aq) + Br2(l)**

**b) Double Displacement** (exchange- metathesis) the compounds in this type of reaction exchange partners: **AB + XY  AY + XB**

**E.g. Ca(OH)2 + 2 HNO3  Ca(NO3)2(aq) + 2H2O(l)**

**AgNO3(aq) + NaCl(aq)  AgCl(s) + NaNO3(aq)**

**ZnBr2(aq) + 2AgNO3(aq)  Zn(NO3)2(aq) + 2AgBr(s)**

**H2SO4(aq) + 2NaOH(aq)  Na2SO4(aq) + 2H2O(l)**

**Classification of reactions based on types of reactants and products**.

**1) Formation Reactions:** One mole of a compound is formed by elements at 1 atm and 25°C. Notice that some stoichiometric coefficients are fractional to maintain the one mole on the compound on the product side.

**E.g. Na(s) + ½Cl2(g)  NaCl(s)**

**C(s) + O2(g)  CO2(g)**

**H2(g) + ½ O2(g)  H2O(l)**

**2Na(s) + C(s) + O2(g) + ½O2(g)  Na2CO3(s)**

**2Na(s) + H2(g) + 2C(s) + O2(g) + ½ O2(g)  2NaHCO3(s)**

**2) Combustion Reactions:** When an organic compound like butane is burned, it reacts with the oxygen in the air to form carbon dioxide and water.Normally organic compound with **O2** produce **H2O** and **CO2**

**E.g.** **2 C4H10(g) + 13O2(g)  8CO2(g) + 10H2O(g)**

**CH4(g) + 2O2(g)  CO2(g) + 2H2O(g)**

**2C2H6(g) + 7O2(g)  4CO2(g) + 6H20(g)**

**C3H8(g) + 5O2(g)  3CO2(g) + 4H2O(g)**

**3) Acid/Base (neutralization) Reactions:** When an acid and a base are placed together, they react to neutralize the acid and base properties, producing a salt. The compound formed by the cation of the base and the anion of the acid is called a salt. The combination of hydrochloric acid and sodium hydroxide produces common table salt, NaClAn acid and a base react to form water and salt.

**E.g. HCl(aq) (acid ) + NaOH(aq) (base)  NaCl(aq) (salt) + H2O(l)**

 **H2SO4(l) (acid ) + Ca(OH)2(*s*) (base)  CaSO4(s) (salt) + 2H2O(l)**

 **H2SO4 (acid) + KOH (base)  K2SO4 (salt) + H2O (water)**

**4) Precipitation Reactions:** Two soluble salt solutions mixed to produce an insoluble salt in the form of a precipitate which settles at the bottom of the reaction vessel. This is normally a double displacement. Precipitation predicted by **solubility rules** often happens with double replacement reactions or metathesis reactions, and one of the most common such reactions is the reaction between silver nitrate and sodium chloride:

**E.g. AgNO3(aq) + NaCl(aq)  AgCl(s) insoluble salt + NaNO3(aq)**

**5) Gas formation reaction:** two chemicals react to produce a gas: **CO2, SO2, SO3, H2S, H2, NH3**

**E.g. Ca(CO)3(s) + HCl(aq)  CaCl2(aq) + CO2(g) + H2O(l)**

Classify reactions based on **simplicity/complexity of reactants/products**

a) 2Fe(s)+ 2O2(g) 2FeO(s):Combination, Synthesis

c) Ca(OH)2(aq) + H3PO4(aq) Ca3(PO4)2(aq) + H2O(l): acid/base, Double Displacement

d) 2NaCl(s)  2Na(s) + Cl2(g): Decomposition

e) N2 (g) + 3H2(g) 2NH3(g): Combination, Synthesis

f) Fe(s)  + CuSO4(aq) FeSO4(aq) + Cu(s):  Single Displacement

g) 2P(s)  + 3Cl2(g) 2PCl3(l):  Combination, Synthesis

h) P4O10(s)  + 6H2O(l) 4H3PO4(aq): Combination, Synthesis

i) 3Fe(s)  + 4H2O(l) Fe3O4(s)  + 4H2(g): Single Displacement

j) 2H3PO4(aq) H4P2O7(s) + H2O(l): Decomposition

k) AgNO3(aq) + Cu(s)  CuNO3(aq) + Ag(s):  Single Displacement

Classify reactions based on **type of reactants and products**:

C2H6(g) + O2(g)  CO2(g) + H2O(g): Combustion Reactions

Ca(OH)2(aq) + H3PO4(aq)  Ca3(PO4)2(aq) + H2O(l): Acid/Base, Double Displacement

2C4H10(g) + 13O2(g)  8CO2(g) + 10H2O(g): Combustion Reactions

Na(s) + ½Cl2(g)  NaCl(s):  Combination Synthesis, Formation Reactions

2Na(s)  + H2O(l)  2NaOH(aq) + H2(g): Single Displacement

½N2 (g) + 3/2H2(g)  NH3(g): Combination, Synthesis, Formation Reactions

HCl(aq) + FeS(s)   FeCl2(aq) + H2S(g): Double Displacement

P(s)  + 3/2Cl2(g)  PCl3(l):  Combination, Synthesis, Formation Reactions

Al2(SO4)3(aq) + 3Ca(OH)2(aq)  2Al(OH)3(s) + 3CaSO4(aq): Double Displacement,Precipitation

CaC2(s)  + 2H2O(l)  C2H2(g) + Ca(OH)2(aq): Double Displacement

2As(s) + 6NaOH(aq)  2Na3AsO3(aq) + 3H2 (g): Single Displacement

**9.2 Redox and Nonredox Reactions**

**Reduction- Oxidation Reactions**

Unlike many nonredox reactions such as acid/base and precipitation reactions which involve simple exchange of groups or ions of the reactants to form water or precipitates, the redox reactions primarily involve the transfer of electrons between two elements in the reactants. Redox stands as an abbreviation for **redu**ction and **ox**idation One of the generalizations we can make is that all **single replacement reaction** are redox reactions.

**Single Displacement: AX + Y**  **YX + A:** Thereaction follows **Activity series**:

**Metals**:Li> K>Ca>Na>Mg>Al>Zn>Cr>Fe>Ni>Sn>Pb>H>Cu>Hg>Ag>Pt>Au

**E.g.** Fe + Cu(NO3)2  Fe(NO3)2 + Cu,

**Non-metals:** F>Cl>Br>I

**E.g.** Cl2 + 2 NaI  2 NaCl + I2

Ultimate test to find a chemical reaction is **redox** or not is to look at the oxidation numbers of elements in chemicals in the reactant and product side and see if they changed. Oxidation number is a way to keep track of number of electron gained or lost by an element in making a compound after a chemical reaction. Atoms of neutral elements have oxidation number of zero and there are rules that are used to calculate the oxidation number of an atom in any compound or ion as summarized below:

**Assign Oxidation Numbers to atoms in a compound or ion.**

* 1. **Elements**: Oxidation number (ON) of atoms in an element is zero (0). E.g. O2
	2. **Monoatomic ions**: ON equal to charge. E.g. Na+, ON = +1; Cl-, ON = -1
	3. **The group number in the periodic table**: could be used for main group elements. Transition metals show variable ONs E.g. Fe shows either +3 or +2.
	4. **Sum of the oxidation numbers**: In an element, compound is equal to zero.
	5. **Sum of the oxidation numbers**: In an a cation/ anion is equal to the ionic charge.
	6. **Almost most of the time**: ON of H =+1, and O=-2

**Examples:**

**O2**: Oxygen is an element. The oxidation number of an atom in an element is 0.

 O

ON 0

**S8:** Sulfur is an element. The oxidation number of an atom in an element is 0.

 S

ON 0

**H2O**, oxidation number (ON) of H is equal to +1 and oxidation number of O is equal to -2 making the ON= 2x1(2H) + (-2)= 0.

**SO42-**, oxidation number (ON) of O is equal to -2 and oxidation number of S is equal to +6 making the ON= +6(S) + 4 (-2)= -2. Notices when you are adding you have to multiply ON by the subscript for that atom.

**NaCl**: NaCl is an ionic compound made up of Na+ and Cl- ions**.**

For Na+ and Cl-, monoatomic ions, the oxidation number is equal to their charge**.**

 Na+ Cl-

ON +1 -1

**CBr4**: CBr4 is a covalent compound (non-metal + non-metal). Br is a halogen. Halogens normally have ON of -1. ON of C should be +4 since total of ON of a neutral compound such as CBr4 is 0.

 C 4Br

 +4 + 4 (-1) **=** 0

**MnO2::** MnO2 is an ionic compound composed of Mn 4+ and 2O2- ions**.** Oxygen always have an oxidation number -2. MN should have an ON of +4 since total of ON of a neutral compound such as MnO2 is 0.

 Mn 4+2O2-

ON+4 + 2(-2) = 0

 MnO

ON+4 -2

**KMnO4:** KMnO4 is an ionic compound composed of K+ and MnO4- ions**.** MnO4- ion could be considered as made up of Mn 7+ and 4O2-. The charge on Mn 7+ ion is obtained because oxygen always have an oxidation number -2 and total of ON of atoms in MnO4- should add up to -1 which is the charge on the ion. Mn should have a ON of +7 and K+  have ON of +1 since total of ONs of a neutral compound such asKMnO4 is 0.

K+ MnO4-

ON +1 + +7 + [4(-2)] = 0

 K MnO

ON+1 +7-2

**K2Cr2O7:** K2Cr2O7 is an ionic compound composed of 2K+ andCr2O72- ions**.** Cr2O72- ion could be considered as made up of 2Cr+6 and 7O2-. The charge on each Cr+6 ion is obtained because oxygen always have an oxidation number -2 and total of ON of atoms in Cr2O72- should add up to -2 which is the charge on the ion. Each Cr should have an ON of +6 and K+  have ON of +1 since total of ONs of a neutral compound such as K2Cr2O7 is 0.

2K+ Cr2O72-

ON 2(+1) + 2(+6) + [7(-2)] = 0

 K CrO

ON+1 +6-2

**What is the oxidation number or state of Cl in HClO4?**

H → +1, O → -2 neutral compound, thus sum is equal to zero

4O → 4 × -2 = -8; H → 1 × +1 = +1; 0 = +1(H) + y(Cl) + (-8)

y = +7

Answer: Oxidation number or state of Cl in HClO4 is +7.

**Assign the oxidation number to each atom of the elements in chemicals in following reactions:**

1. Zn + HCl(aq)  ZnCl2 (aq) + H2 (g)
2. H2CO3(aq) H2O(l) + CO2(g)
3. HCl(aq) + NaOH(aq)  NaCl(aq) + H2O(l)
4. Zn + HCl(aq)  ZnCl2 (aq) + H2 (g)

|  |  |
| --- | --- |
| **Reaction**: | a) Zn HCl(aq) http://www.howe.k12.ok.us/~jimaskew/arrow.jpg ZnCl2 (aq) + H2 (g) |
| **Element type** | Zn | H+(aq) | Cl-(aq)  | Zn2+(aq)  | Cl-(aq)  | H |
| **Oxidation number** | Zn =0 | H+ =+1 | Cl-= -1  | Zn2+=+2  | Cl-= -1  | H=0 |
| **Reason** | element | +1 ion | -1 ion | +2 ion | -1 ion | element |

1. H2CO3(aq)  H2O(l) + CO2(g)

|  |  |
| --- | --- |
| **Reaction**: | * + 1. H2CO3(aq) http://www.howe.k12.ok.us/~jimaskew/arrow.jpg H2O(l) + CO2(g)
 |
|  | 2H+(aq)  |  CO32-(aq)  | 2H+  | O2- | C+4 | 2O2- |
|  | 2H+(aq)  | C+4 | 3O2- | 2H+  | O2- | C+4 | 2O2- |
| **Element type** | H+  | C+4 | O2- | H+  | O2- | C+4 | O2- |
| **Oxidation number** | H+=+1  | C+4=4  | O2-=-2  | O2-=-2  | H+=+1  | C+4=+4  | O2-=-2  |

1. HCl(aq) + NaOH(aq)  NaCl(aq) + H2O(l)

|  |  |
| --- | --- |
| **Reaction**: | * + 1. HCl(aq) + NaOH(aq) http://www.howe.k12.ok.us/~jimaskew/arrow.jpg NaCl(aq) + H2O(l)
 |
|  | H+(aq)  | Cl-(aq) | Na+(aq) | OH-(aq) | Na+(aq) | Cl-(aq) | 2H+  | O2- |
|  | 2H+(aq)  | Cl-(aq) | 3O2- | 2H+  | Na+(aq)  | Cl-(aq) | 2H+  | O2- |
| **Element type** | H+  | Cl- | O2- | H+  | Na+  | Cl- | H+  | O2- |
| **Oxidation number** | H+=+1  | Cl-=-1 | O2-=-2  | H+=+  | Na+=+1  | Cl-=-1 | H+=+1  | O2-=-2  |

**Which of the following reactions are redox**:

1. Zn + HCl(aq)  ZnCl2 (aq) + H2 (g) (Redox reaction)

|  |  |
| --- | --- |
| **Reaction**: | a) Zn HCl(aq) http://www.howe.k12.ok.us/~jimaskew/arrow.jpg ZnCl2 (aq) + H2 (g) |
| **Oxidation number** | Zn =0 | H+ =+1 | Cl-= -1  | Zn2+=+2  | Cl-= -1  | H=0 |
|  | Zn =0 → Zn2+=+2 and H+ =+1 → H=0 **Redox reaction** |

1. H2CO3(aq) H2O(l) + CO2(g) **Not a Redox reaction**

|  |  |
| --- | --- |
| **Reaction**: | * + 1. H2CO3(aq) http://www.howe.k12.ok.us/~jimaskew/arrow.jpg H2O(l) + CO2(g)
 |
| **Oxidation number** | H+=+1  | C+4=4  | O2-=-2  | O2-=-2  | H+=+1  | C+4=+4  | O2-=-2  |
|  | None of oxidation numbers changed **Not a Redox reaction** |

1. HCl(aq) + NaOH(aq)  NaCl(aq) + H2O(l) **Not a Redox reaction**

|  |  |
| --- | --- |
| **Reaction**: | 1. HCl(aq) + NaOH(aq) http://www.howe.k12.ok.us/~jimaskew/arrow.jpg NaCl(aq) + H2O(l)
 |
| **Oxidation number** | H+=+1  | Cl-=-1 | O2-=-2  | H+=+  | Na+=+1  | Cl-=-1 | H+=+1  | O2-=-2  |
|  | None of oxidation numbers changed **Not a Redox reaction** |

**What is the oxidation number or state of Cl in HClO4?**

H → +1, O → -2 neutral compound, thus sum is equal to zero

4O → 4 × -2 = -8; H → 1 × +1 = +1; 0 = +1(H) + y(Cl) + (-8)

y = +7

Oxidation number or state of Cl in HClO4 is +7.

**What are the oxidation numbers, reducing agent, oxidizing agent, reduction half reaction (RHR) and oxidation half reaction (OHR) for the following reaction?**

|  |  |
| --- | --- |
| **Reaction**: | **Zn (s) + 2 HCl (aq) → ZnCl2 (aq) + H2 (g)**  |
| **Oxidation number** | Zn= 0 H = +1 Cl= -1 Zn= +2, Cl= -1 H=0 |
| **Reducing agent :**  Zn (s)  **Oxidizing agent:**  HCl (aq)  |
| **Reduction Half Reaction (RHR)** | 2H+ (aq) + 2e - → H2 (g) |
| **Oxidation Half Reaction (OHR)** | Zn (s) → Zn2+ (aq) + 2e - |

**Chemistry at a Glance: Types of Chemical Reactions
9.3 Terminology Associated with Redox Processes**

**LEO the Lion goes GER!**

**Oxidation-Loss of electron (LEO)**

In old days oxidation was considered as reactions of metals with oxygen. The metal loses electrons to oxygen forming metal a cation and an oxide ion. Taking electron transfer into account, today **oxidation** is defined as **loss of electrons** from ions, atoms, elements, or compounds.

E.g. Na  Na+ + e-

**Reduction-Gain of electrons (GER)**

In old days reduction was considered as reactions of hydrogen with metal oxide to produce metal. The metal cations of the metal oxide gain electrons from hydrogen to form neutral metal atoms or element. Taking electron transfer into account, today **reduction** is defined as **gain of electrons** by ions, atoms, elements, or compounds.

E.g. Cl2 + 2e-  2Cl-

**Oxidation number**

Oxidation number (sometimes called oxidation state) is number assigned to an atom in compounds, ions and polyatomic ions to show the number of electrons relative to an atom in the element, There are specific rules to assign oxidation numbers to atoms as given previously. Read the relevent sections and examples for more detail.

A redox reactions involves both reduction and oxidation in the process that takes place simultaneousl. As you can see yourself, reduction and oxidation cannot take place independently, because there has to be an electron giver (**reducing agent**) and electron acceptor (**oxidizing agent**). As a rule, the oxidation number of an atom **increases** during **reduction** and oxidation number of an atom **decreases** during **oxidation.**

**E.g**. 2 Na + Cl2  2NaCl

ON 0 0 +1 -1

**Oxidation** Na  Na+ + e-

 Na increase ON, 0  +1

**Reduction** Cl2 + 2e-  2Cl-

 Cl decrease ON, 0  -1

**Reducing agent**: the reactant that gives up electrons and increases oxidation number.

**Oxidizing agent:** the reactant that gains electrons and increases oxidation number.

**9.4 Collision Theory and Chemical Reactions**

Collision theory is based on the idea that reactant molecules/ions must collide for a reaction to take place. How fast a reaction take place is dependent on the fraction of collisions that get converted to products

**Rate of a chemical reaction**

Rate of a chemical reaction is calculated by dividing the change in concentration of reactants or products by time it took for the change.



**Activation Energy**

Collision theory also recognized that only a certain fraction of the total collisions have the energy to overcome the transformation energy (transition energy or **activation energy**) that is required to covert reactant to products. The minimal amount of energy needed for this to occur is known as **activation energy**.

**Rate determining step**

This theory also recognizes that some reactions could involve more than step and the observed reaction rate is only dependent of the slowest step (**rate determining step**) of multi-step reactions. This model assumes that the rate of reaction mainly depends on the frequency of collisions between the particles involved in that step.

**Transition state:** The transition state is a transient reactant-product species with sufficient energy (more than activation energy) that get converted to product(s). In the energy diagram for the rate-determining step this has the highest energy of a random reaction.

Consider a simple reaction involving a collision between two molecules - ethene, CH2=CH2, and hydrogen chloride, HCl, for example. These react to give chloroethane.



**Orientation factor of collisions**

Not only two species to collide to with enough energy for bonds to break and reaction to occur, they have to collide the right way around is called the orientation factor. For collision involving more than 2 particles the chances of all this happening are so remote that reactions with collision involving 3 or more particles are not likely to happen very often.



As a result of the collision between the two molecules, the double bond between the two carbons is converted into a single bond. A hydrogen atom can gets attached to one of the carbons and a chlorine atom to the other only when they collide in a certain way.

**9.5 Exothermic and Endothermic Reactions**

**Reaction Energy Diagrams**: A plot of potential energy changes that occur as reactants are converted to products.

**Exothermic reaction**: An exothermic reaction is a chemical reaction that produces heat. For that to happen the energy of the reactants has to be higher than the energy of the products as seen in the diagram below:

**Endothermic reaction**: An endothermic reaction is a chemical reaction that absorbs heat. For that to happen the energy of the reactants has to be lower than the energy of the products as seen in the diagram below:

**Exothermic reaction** **Endothermic reaction**



A reaction energy diagram for a chemical reaction gives information about the energy of the reactants, products, transition state, activation energy-Ea, the heat of reaction- Hrxn, and whether the reaction is endothermic or exothermic.

For each reaction energy diagram below, mark the location of the reactants, products and transition state. Identify the magnitude of Ea and Hrxn. Is each reaction endothermic or exothermic?


Exothermic reaction (Hrxn) Endothermic reaction (Hrxn)

Heat given out = -10 Heat given out = 5

Activation energy (Ea)=15 Activation energy(Ea)=20

**9.6 Factors That Influence Reaction Rates**

**Concentration**: A higher concentration of reactants leads to more effective collisions which lead to an increasing reaction rate. Increasing concentration also increases the number of collision and orientation factor.

**Temperature**: An increase in temperature of a reaction vessel is accompanied by an increase in the reaction rate. Temperature is a measure of the kinetic energy of a system, so higher temperature implies higher average kinetic energy of molecules and more collisions per unit time. **Increasing kinetic energy** also increase the fraction of molecules with enough activation energy.

**Catalysts**: A catalyst is a substance which alters the rate of a chemical reaction but is chemically unchanged at the end of the reaction. Catalyst increases the rate by **lowering the activation energy (Ea)** of the reaction by providing an alternative pathway which requires less kinetic energy. **Enzymes** are biological catalysts. They are slightly different in that they are easily denatured by heat. If you want to know more about enzymes, jump to the enzyme page. Most catalysts are made using **industrial catalysts** which make chemical reactions go faster. Chemists call such catalysts "positive catalysts" or "promoters". However, sometimes we want a chemical reaction to go more slowly then they use **inhibitors** the opposite of catalysis.

**Particle size of solid reactants**: If a solid reactant is broken into small pieces or ground into a powder:

* + its surface area is increased
	+ more particles are exposed to the other reactant
	+ there is a greater chance of the particles colliding on the surace
	+ the rate of reaction increases

**9.7 Chemical Equilibrium**

In previous discussions of chemical reactions, for simplicity we assumed that reactions run to completion indicated by an on way arrow:. However, many chemical reactions when carried out in a closed vessel, the system achieve equilibrium:. Equilibrium means when enough time is given a constant ratio between the concentration of the reactants and the products is established. Different reactions have different equilibriums. Some may appear to be favoring products: **product favored**, however, all equilibrium reactions have some reactants present in equilibrium with products. A reaction may look "finished" when equilibrium is reached, but actually the forward and reverse reactions continue to happen at the same rate. A reverse reaction is when the written reaction goes from right to left instead of the forward reaction which proceeds from left to right. This is why equilibrium is also referred to as "steady state". Examples of chemical equilibrium:

H2+ I2  2HI

N2 (g) + 3H2 (g)  2NH3 (g)

AgBr (s)  Ag+ (aq) + Br- (aq)

PCl5(g)  PCl3(g) +

H2O + CO  H2 + CO2 Cl2(g)

2 NO2  N2O4

**9.8 Equilibrium Constants**

It is possible to write an **equilibrium expression** for a reaction. This can be expressed by concentrations of the products divided by the concentration of the reactants with the coefficients of each equation acting as exponents. It is important to remember that only species in either the gas or aqueous phases are included in this expression because the concentrations for liquids and solids cannot change. For the reaction:

**J** A + **k** B  **l** C + **m** D

the equilibrium expression is:


Where:

**K** is the equilibrium constant
[A], [B], etc. are the molar concentrations of A, B, etc.
**l**, **m**, etc. are the coefficients of the balanced reaction.

[A] of pure (l) and (s) equals 1 and not written.

**Write the equilibrium expression for flowing reactions:**

a) CO(g) + Cl2(g) COCl2(g) : K = [COCl2]/[CO][Cl2]

b) N2O4(g) 2NO2(g) : K = [NO2]2/[ N2O4]

c) MgCO3(s)  MgO(s) + CO2(g) : K = [CO2] **Note:** (s) are not written

d) NaCl(s) + H2O(l) Na+(aq) + Cl-(aq): K = [Na+] [Cl-] **Note:** (s) and (l) are not written.

**What is the equilibrium constant expression and value for the reaction,**

**CH4**(g) + H2O(g) = CO(g) + 3 H2(g)?



 **Chemistry at a Glance: Factors That Influence Reaction Rates**

**9.9 Altering Equilibrium Conditions: Le Châtelier's Principle**

When a stress or change is applied to a reaction at equilibrium the equilibrium system will adjust to relieve the stress. These changes are initial ones to a system already at equilibrium.

The amounts of reactant and product must follow the equilibrium constant for the reaction.

**Shifting a Chemical Equilibrium: Le Chatelier's Principle**

Le Chatelier's principle is used to predict the shift of equilibrium. It simply states that:

If a change is imposed on a system at Equilibrium, the position of the equilibrium will

shift in a direction that tends to reduce that change.

* concentration changes
* temperature changes
* pressure changes
* addition of a catalyst
* concentration changes

**Listed below are how various "changes" that affect equilibriums:**

**Concentration changes**

a) **Adding products** cause the equilibrium to shift (left) to produce more reactants.

b) **Adding reactants** cause the equilibrium to shift (right) to produce more products.

c) **Removing reactants** cause the equilibrium to shift (left) to produce more reactants.

d) **Removing products** cause the equilibrium to shift (right) to produce more products.

**Increasing T** of the equilibrium should shift equilibrium to left and vice versa.

Exothermic (∆Hrxn = negative, shift (left-reactant side))

Endothermic (∆Hrxn = positive, shift (right-product side))

**Increasing P** will shift equilibrium to right and vice versa. It affects a reaction if there is a change in stoichiometric coefficients (∆n) of gaseous compounds going from reactant to products: (∆n) = 0, no change; (∆n) = +, shift left -reactant side); (∆n) = -,

shift (right-product side)) and vise versa. ∆n = Σ n (products) - Σ n (reactants).

**E.g. H2(g) + CO2(g) H2O(g) + CO(g); H = 40 kJ**

1) shit left, 2) ) shit right, 3) to shift (left), 4) shift (right), 5) T↓,shift (left); T↑,shift

(right); 6) (∆n) = 0, no change

Note: **volume changes** can be considered as pressure changes. Increased volume has

the same effect as a decrease in pressure.

**Concentration changes: Effect of Adding a Reactant or Product**

If we have a system which is already in equilibrium, addition of an extra amount of one of the reactants or one of the products upset the system out of equilibrium. Either the forward or the reverse reaction will then occur in order to restore equilibrium conditions. We can easily tell which of these two possibilities will happen from Le Chatelier’s principle. If we add more of one of the *products*, the system will adjust in order to offset the gain in concentration of this component. The *reverse* reaction will occur to a limited extent so that some of the added product can be consumed. Conversely, if one of the *reactants* is added, the system will adjust by allowing the *forward* reaction to occur to some extent. In either case *some of the added component will be consumed*.

Actually, we have already seen this principle in operation in the case of the decomposition of HI at high temperatures:

       2HI(*g*)  H2(*g*) + I2(*g*)

HI is heated some of the HI will decompose, producing an equilibrium mixture of 2HI(*g*) H2(*g*) and I2(*g*).

Chemical Connections: Combustion Reactions, Carbon Dioxide, and Global Warning; "Undesirable" Oxidation-Reduction Processes: Metallic Corrosion; Stratospheric Ozone: An Equilibrium Situation