03
Stoichiometry

3.1 Chemical Engineering Calculations

3.1.1 Units and Dimensions

A measured or numbered quantity has a numerical value and a unit associated with it. It is useful and essential in most engineering calculations to specify both the parameters appearing in an equation.

A dimension is a property that can be measured, such as length, time, mass or temperature.

Alternatively, it is obtained by multiplying or dividing other dimensions; such as length/time (velocity), length^3 (volume), or mass/length^3 (density). Measurable units are specific values of dimensions that are outlined by conventions, custom or law, such as mass (grams), time (seconds), or feet (centimeters) etc.

Units are similar to algebraic variables when quantities are added, subtracted, multiplied or divided. The numerical values of two quantities may be added or subtracted only if the units are the same.

Numerical values and their corresponding units can be combined by multiplication or division.

3.1.2 Systems of Units

A system of units comprises the following components:

Base units or units

These units are to indicate the dimensions of mass, length, temperature, time, electrical current and light intensity.

Multiple units

They are defined as multiples or fractions of base units such as minutes, hours and milliseconds, all of which are defined in terms of the base unit of a second. Multiple units are defined for convenience rather than necessity.

Derived units

They are obtained in one of two ways:

- By multiplying and dividing base or multiple units (cm^2, ft/min, kg m/s^2, etc). Derived units of this type are commonly referred to as compound units
- As defined equivalents of compound units (e.g. 1 erg = 1g cm/s^2)

During the 1960's, an international conference proposed a system of metric units that is widely accepted in the scientific and engineering field. It is known as the "Systeme Internationale d'Unites," or the SI system for short.

Unit prefixes are used in the SI system to indicate powers of ten. The CGS (Centimeter, Gram, Second) system is almost identical to the SI system; the main difference being that grams (g) and centimeters (cm) are used instead of kilograms and meters as the base units of mass and length. The base units of the *American engineering system* are the foot (ft) for length, the pound mass (lb_m) for mass and the second (s) for time.

3.1.3 Conversion of Units

A measured quantity can be defined in terms of any units having the suitable dimensions. The equivalence between two expressions of a given quantity may be expressed in terms of a ratio.

For example, velocity can be expressed in terms of ft/sec, miles/hr, or any other ratio of a length unit to a time unit. The numerical value of the velocity then is based on the unit chosen.

$\frac{1\text{ ft}}{12\text{ in.}}$ (one foot per 12 inches)

$$\frac{(12\text{ in.})^2}{(1\text{ ft})^2} = \frac{144\text{in.}^2}{1\text{ ft}^2}$$

Ratios as described above are known as conversion factors.

To convert a quantity expressed in terms of one unit to its equivalent in terms of another unit, multiply the given quantity by the conversion factor (new unit /old unit).

Quantity	Conversion
Length	1(m)=100 (cm)
	=3.28084(ft)
	=39.3701 (in)
Mass	1(kg) =103 (g)
	=2.20462(ibm)
Force	1 (N) =1(kg)(m)/(s)2
	=105 (dyn)
	=0.22480923 (ib)
Pressure	1(bar)=105(kg)/(m)(s)2
	=105(N)/(m)2
	=106(dyn)/(cm)2
	=0.986923 (atm)
	=14.5038 (psia)
	=750.06(mm Hg)
Volume	1(m)3=106 (cm)2
	=103 (1)
	=35.3147(ft)
	=264.172(gal)
Density	1(g)/(cm)3=103 (kg)/(1)
	=103 (g)/(1)
	=62.4278(ibm)/(gal)
Energy	1 (J)=1(kg)(m)2/(s)2
	=1(Nm)
	=1(W.s)
	=107 (dyn cm)
	=107 (erg)
	=10 (cm)3(bar)
	=10-2 (1bar)

	=10-5 (m)3(ba)
	=0.29006(cal)
	=9.86923(cm)3(atm)
	=5.12197 x 10-3 (ft)3(psia)
	=0.737562(ft1b)
	=9.47831 x 10-4(Btu)
Power	1(kw) =103(kg)(m)2/(s)3
	=102(W)
	=103(J)/(s)
	=103(V-A)
	=239.006(cal)/(s)
	=737.562(ft-Ib)/(s)
	=56.8699(Btu)/(min)
	=1.34102(HP)

Note : atm = standard atmosphere

cal = thermochemical calorie

Btu = International Steam Table Btu.

Table 3.1
Conversion Chart

3.1.4 Force and Weight

Newton's second law of motion states that *force* is proportional to the product of mass and acceleration (length/time^2). Natural unit of force is therefore, kg m/s^2 (SI), g cm/s^2 (CGS) and lb$_m$. ft/s^2 (American engineering).

$$\mathbf{g_c = 1\ \frac{kg.m/s^2}{N} = 1\ \frac{g.cm/s^2}{dyne} = 32.174\ \frac{lb_m.ft}{lb_f\ s^2}}$$

The equation which connects force in defined units to mass and acceleration is

$$F = ma / g_c$$

The weight of an object is the force exerted on the object by the gravitational attraction of the earth. Consider an object of mass *m,* is subjected to a gravitational force W (W is by definition the weight of the object). If this object were falling freely its acceleration would be *g*. The weight, mass and free fall acceleration of the object are related by the following equation:

$$W = mg / g_c$$

The value of *g* at sea level and 45^0 latitude and corresponding value of g/g_c are given below in each system of units:

$g = 9.8066\ m/s^2 \Rightarrow g/g_c = 9.8066\ N/kg$

$g = 980.66\ cm/s^2 \Rightarrow g/g_c = 980.66\ dyne/g$

$g = 32.174\ ft / s^2 \Rightarrow g/g_c = 1\ lb_f / lb_m$

3.1.5 Dimensional Homogeneity & Dimensionless Quantities

Every valid equation must be dimensionally homogeneous which means, all additive terms on both sides of the equation must have the same units.

A dimensionless quantity can be a pure number (e.g. 2, 3.5) or a multiplicative combination of variables with no net units:

$$M (g) / M_0 (g)$$

Quantity like (M/M_0) is called a dimensionless group.

Certain important dimensionless numbers are mentioned below.

- Archimedes Number
- Arrhenius Number
- Bingham Number
- Capillary Number
- Cavitation Number
- Darcy friction factor
- Drag Coefficient
- Elasticity Number
- Fourier Number

- Heat Transfer Factor
- Mass Transfer Factor
- Reynolds Number

3.1.6 Arithmetic Calculations

- A rule of thumb is that when two or more quantities are combined by multiplication and/or division, the number of significant figures in the result should equal the lowest number of significant figures of any of the multiplicants or divisors

- The rule is that when two or more numbers are added or subtracted, the positions of the last significant figures of each number should be compared. Of these positions, the one farthest to the left is the position of the last permissible significant figure of the sum

- The logic behind rounding off numbers in which the digit to be dropped is a 5, is always to make the last digit of the rounded-off number even

e.g. 2.68 => 2.7, 5.34 =>5.3

3.2 Process Variables

A process is any operation or series of operations that results in a physical or chemical change in a material or a mixture of materials. The material that enters a process is referred to as the input or feed to the process and that which leaves is called the output or product. A process unit is a device in which one of the operations that constitutes a process is carried out. Each process unit has associated with it a set of input and output process streams, which consists of the materials that enter and leave the unit.

The process variable is a set of quantities that defines the operating conditions of a reactor or a system of reactors.

3.2.1 Mass and Volume

The density of a substance is the mass per unit volume of the substance. The specific volume of a substance is the volume per unit mass of the substance and is therefore the inverse of the density. Densities of pure solids and liquids are relatively independent of temperature and pressure and may be found in standard references (such as the Chemical Engineers' Handbook).

The specific gravity (SG) of a substance is the ratio of the density ρ of the substance to the density ρ_{ref} of a reference substance at a specific condition.

$$\mathbf{SG} = \rho / \rho_{ref}$$

3.2.2 Flow Rate

Mass and Volumetric Flow Rate

Continuous processes involve the movement of material from various process units. The rate, at which material is transported through a process line, is the flow rate of that material.

The flow rate of a process stream may be expressed as a mass flow rate (mass/time) or as a volumetric flow rate (volume/time). Consider a fluid (gas or liquid) which flows in a cylindrical pipe as shown in figure 3.1, where the shaded area represents a section perpendicular to the direction of flow.

If the mass flow rate of the fluid is m (kg/sec), then every second m kilograms of the fluid pass through the cross section. If the volumetric flow rate of the fluid at the given cross-section is V (m^3/sec), then every second V cubic meters of the fluid pass through the cross section. However, the mass m and the volume V of a fluid (in this case, the fluid that passes through the cross section each second) are not independent quantities but are related through the fluid density ρ :

$$\rho = m / V$$

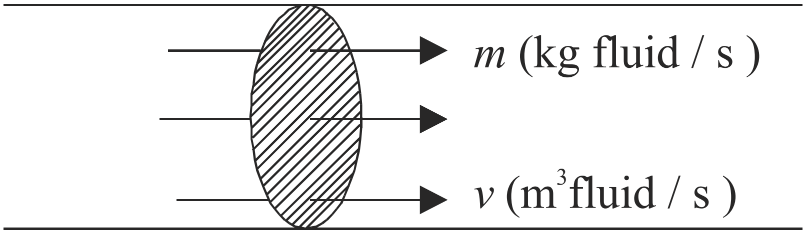

Figure 3.1
Mass and Volumetric Flow rate

3.2.3 Pressure

Fluid Pressure and Hydrostatic Head

A pressure is the ratio of a force to the area on which it acts. Accordingly, pressure units are force units divided by area units (eg N/m^2, $dynes/cm^2$....). The SI pressure unit (N/m^2) is called a Pascal (Pa).

Consider a fluid (gas or liquid) contained in a closed vessel or flowing through a pipe and suppose that a hole of area A is made in the wall of the containing vessel, as in Fig 3.2. The fluid pressure may be defined as the ratio (F/A), where F is the minimum force that would have to be exerted on a plug in the hole to keep the fluid from emerging.

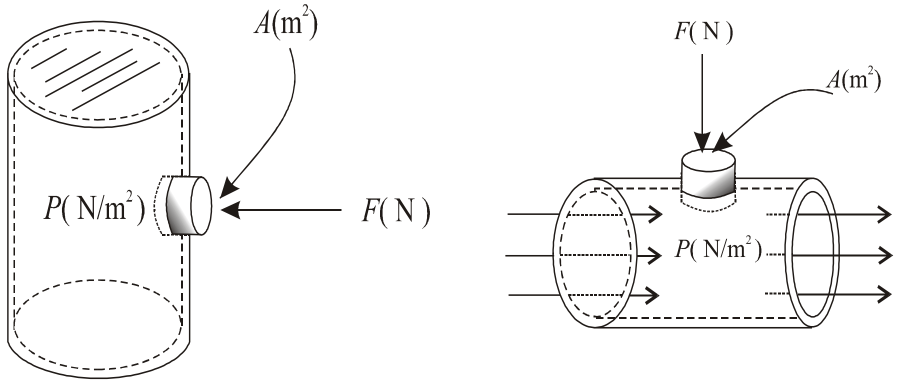

Figure 3.2
Fluid Pressure in Tank and a pipe

Consider a vertical column of fluid is *h* meters high and has a uniform cross sectional area A(m^2) Fig 3.3. Further, assume that the fluid has a density of ρ(kg / m^3) and that a pressure p_o (N/m^2) is exerted on the upper surface of the column. The pressure P of the fluid at the base of the column is called the hydrostatic pressure of the fluid (F/A). F thus equals the force on the top surface plus the weight of the fluid in the column.

$$\mathbf{P = P_0 + \rho(g/g_c)}\ h$$

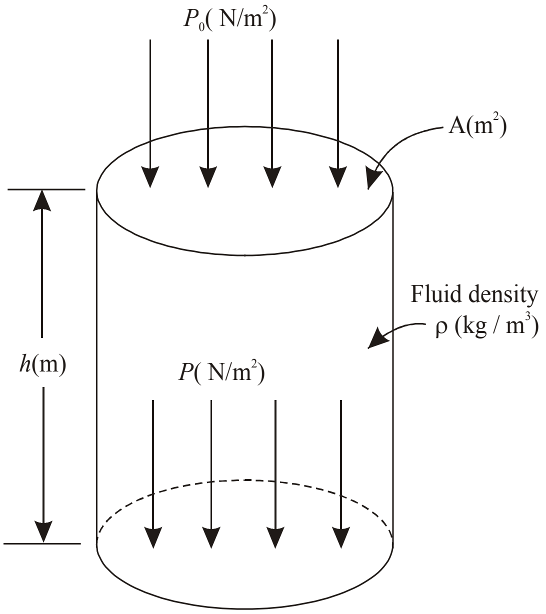

Figure 3.3
Pressure at the Base of a Fluid Column

3.2.4 Temperature

The temperature of a substance in a particular state (solid, liquid or gas) is a measure of the average kinetic energy held by the molecules.

The two most common temperature scales are defined using the freezing point (T_f) and boiling point (T_b) of water at a pressure of 1 atmosphere.

Celsius (or centigrade) scale: T_f is assigned a value of 0^0C and T_b is assigned a value of 100^0C. Absolute zero (theoretically the lowest temperature that can be reached in nature) on this scale falls at -273.15^0C.

Fahrenheit scale: T_f is assigned a value of 32^0F and T_b is assigned a value of 212^0F. Absolute zero falls at -459.67^0F.

The Kelvin and Rankine scales are defined such that absolute zero has a value of 0 and the size of a degree is the same as a Celsius degree (Kelvin scale) or a Fahrenheit degree (Rankine scale).

The following relationships may be used to convert a temperature expressed in one defined scale unit to its equivalent in another.

$$\begin{aligned} T(K) &= T(^0C) + 273.15 \\ T(^0R) &= T(^0F) + 459.67 \\ T(^0R) &= 1.8T(K) \\ T(^0F) &= 1.8T(^0C) + 32 \end{aligned}$$

A degree is to denote both a temperature and its interval.

Consider the temperature interval from 0^0C to 5^0C. There are nine Fahrenheit and Rankine degrees in this interval and only five Celsius and Kelvin degrees. An interval of 1 Celsius or Kelvin degree therefore contains 1.8 Fahrenheit or Rankine degrees, leading to these conversion factors:
1.8^0F / 1^0C
1.8^0R / 1K
1.^{0}F / 1^0R
1^0C/ 1K

3.3 What is Stoichiometry?

The word stoichiometry derives its explanation from two Greek words: *stoicheion* (meaning "element") and *metron* (meaning "measure"). Stoichiometry deals with calculations about the masses (sometimes volumes) of reactants and products involved in a chemical reaction. It is a very mathematical part of chemistry.

3.3.1 What You Should Expect?

The most simple stoichiometric problem will present you with a certain amount of a reactant and then ask how much of a product can be formed. Here is a generic chemical equation:

$2\,X + 2Y \dashrightarrow 3Z$

Here is a typically-worded problem: Given 20.0 grams of X and sufficient Y, how many grams of Z can be produced?

It is required to get familiar with the use molar ratios, molar masses, balancing and interpreting equations along with conversions between grams and moles. .This type of problem is often called "mass-mass."

3.3.2 Molecular Weight

The molecular weight of a substance is the weight in atomic mass units of all the atoms in a given formula.

An atomic mass unit is defined as 1/12 the weight of the carbon-12 isotope. The old symbol was amu, while the most correct symbol is u (a lower case letter u).

Carbon-12 is defined as weighing exactly 12 amu. This is the starting point for how much an atom weighs.

The molecular weight of a substance is needed tell us how many grams are in one mole of that substance.

The mole is the standard method in chemistry for communicating how much of a substance is present.

Four steps to calculating a substance's molecular weight are mentioned below:

Step One: Determine how many atoms of each different element are in the formula.

Step Two: Look up the atomic weight of each element in a periodic table.

Step Three: Multiply step one times step two for each element.

Step Four: Add the results of step three together and round off as necessary.

3.3.3 The Mole & Molar Mass

The mole is the standard method in chemistry for communicating how much of a substance is present.

Here is how the International Union of Pure and Applied Chemistry (IUPAC) defines "mole:"

The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

One mole contains as many entities as there are in 12 grams of carbon-12 (or 0.012 kilogram). There are 6.022 x 10^{23} atoms in 12 grams of carbon-12. This number has been very carefully measured in a number of ways over many decades.

Avogadro's Number

6.022 x 10^{23} is so important that it has a name. It is called Avogadro's Number and has the symbol N. It is so named in honor of Amedeo Avogadro, an Italian chemist, who, in 1811, made a critical contribution (recognized only in 1860 after his death) which helped greatly with the measurement of atomic weights.

3.3.4 Percent Composition

Percent composition is the percent by mass of each element present in a compound.

$$\%x = \frac{x_{mass}}{FW_{mass}} 100$$

Consider Water(H_2O) for an example.

One mole of water is 18.0152 grams.

In that compound, there are two moles of H atoms and 2 x 1.008 = 2.016 grams. That's how many grams of hydrogen are present in one mole of water.

There is also one mole of oxygen atoms weighing 16.00 grams in the mole of water.

To get the percentage of hydrogen, divide the 2.016 by 18.015 and multiply by 100, giving 11.19%.

For oxygen it is 16.00 ÷ 18.015 = 88.81%.

3.3.5 Molar Ratios

The molar ratio will assume a place of central importance in solving stoichiometry problems. The sources for these ratios are the coefficients of a balanced equation.

Consider a sample equation :

$2 H_2 + O_2 \dashrightarrow 2 H_2O$

What is the molar ratio between H_2 and O_2?

Answer: two to one. So this ratio in fractional form is: 2 / 1

What is the molar ratio between O_2 and H_2O?

Answer: one to two. As a fraction, it is: 1/ 2

3.3.6 Mole-Mole Problems

The procedure used below involves making two ratios and setting them equal to each other. This is called a proportion. One ratio will come from the coefficients of the balanced equation and the other will be constructed from the problem. The ratio set up from data in the problem will almost always be the one with an unknown in it.

It is then possible to cross-multiply and divide to get the answer.

Consider the equation:

$N_2 + 3\ H_2 \text{ ---> } 2\ NH_3$

Problem : If we have 2.00 mol of N_2 reacting with sufficient H_2, how many moles of NH_3 will be produced?

Solution

The ratio from the problem will have N_2 and NH_3 in it.

How is it possible to know which number goes on top or bottom in the ratios? Answer: it does not matter, except that you observe the next point all the time.

When making the two ratios, be 100% certain that numbers are in the same relative positions. For example, if the value associated with NH_3 is in the numerator, then MAKE SURE it is in both numerators.

Use the coefficients of the two substances to make the ratio from the equation.

Why isn't H_2 involved in the problem? Answer: The word "sufficient" removes it from consideration.

Let's use this ratio to set up the proportion: NH_3/ N_2

That means the ratio from the equation is: $2 / 1$

The ratio from the data in the problem will be: $x / 2$

The proportion (setting the two ratios equal) is: $x / 2 = 2 / 1$

Solving by cross-multiplying gives $x = 4.00$ mol of NH_3 produced.

3.3.7 Mole-Mass Problems

The solution procedure used below involves making two ratios and setting them equal to each other. This is called a proportion. One ratio will come from the coefficients of the balanced equation and the other will be constructed from the problem. The ratio set up from data in the problem will almost always be the one with an unknown in it.

It is now possible to cross-multiply and divide to get the answer.

However, there is one addition to the above technique. One of the values will need to be expressed in moles. This could be either a reactant or a product. In either case, moles will have to converted to grams or the reverse.

Suppose a specific mass is indicated in a problem. It is required to convert this to moles .

Example - If 80.0 grams of O_2 was produced, how many moles of $KClO_3$ decomposed?

The ratio from the above statement is : 3/ 2

The ratio from the data in the problem will be: 2.5 / x

The 2.50 mole came from 80.0 g ÷ 32.0 g/mol. The 32.0 g/mol is the molar mass of O_2. Be careful to keep in mind that oxygen is O_2, not just O.

Solving by cross-multiplying and dividing gives x = 1.67 mol of $KClO_3$ decomposed.

3.3.8 Mass-Mass Problems

This is the most common type of stoichiometric problem. There are four steps involved in solving these problems:

1. Make sure calculations are based on a properly balanced equation.
2. Convert grams of the substance given in the problem to moles.
3. Construct two ratios - one from the problem and one from the equation and set them equal. Solve for "x," which is usually found in the ratio from the problem.
4. Convert moles of the substance just solved for into grams.

Remarks

1. Double check the equation. Lots of students go right ahead and solve using the unbalanced equation supplied in the problem (or test question for that matter).
2. DON'T use the same molar mass in steps two and four.
3. Don't multiply the molar mass of a substance by the coefficient in the problem BEFORE using it in one of the steps above. For example, if the formula says 2 H_2O, DON'T use 36.0 g/mol, use 18.0 g/mol.
4. Don't round off until the very last answer.

A graphical representation is given below .

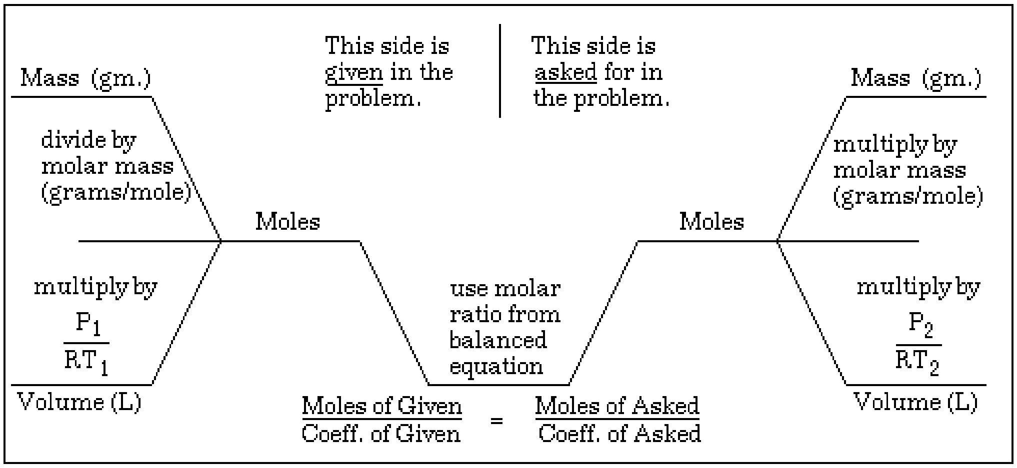

Figure 3.4
Mass-Mass Conversion Chart

3.3.9 Introduction to Solutions

A solution is a particular type of mixture. Mixtures in chemistry are combinations of different substances where each substance retains its chemical properties. Generally, mixtures can be separated by non-chemical means such as filtration, heating, or centrifugation.

A solution is a homogeneous mixture where all particles exist as individual molecules or ions. There are homogeneous mixtures where the particle size is much larger than individual molecules. However, the particle size is so small that the mixture never settles out. Terms such as colloid, sol, and gel are used to identify these mixtures.

A solution has two components: the solute and the solvent.

The solvent is the substance in greater amount.

It is usually a liquid, although it does not have to be. It is usually water, but it does not have to be. We will focus on water only and will leave non-aqueous solvents alone.

The solute is the substance in lesser amount.

Molarity

The molarity of a solution is calculated by taking the moles of solute and dividing by the liters of solution.

$$\boxed{\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}}$$

Dilution: Definition and Calculations

To dilute a solution means to add more solvent without the addition of more solute. Of course, the resulting solution is thoroughly mixed so as to ensure that all parts of the solution are identical.The fact that the solvent amount stays constant allows us to develop calculation techniques.

moles before dilution = moles after dilution

From the definition of molarity, the moles of solute equals the molarity times the volume.

Hence it is now possible to substitute MV (molarity times volume) into the above equation, like this:

$M_1V_1 = M_2V_2$

3.3.10 The Meaning of a Chemical Equation

Chemical equations give information in three major areas.

1. They tell us what substances are reacting (those being used up) and what substances are products (those being made).
2. The coefficients of a balanced equation tell us in what ratio the substances react or are produced.
3. The relative amounts of all substances involved in the reaction.

3.3.11 Balancing Chemical Equations

Chemical equations do not come already balanced. This must be done before the equation can be used in a chemically meaningful way.

A balanced equation has equal numbers of each type of atom on each side of the equation.The Law of Conservation of Mass is the rationale for balancing a chemical equation.

Here is the example equation for this lesson:

$H_2 + O_2 \text{--->} H_2O$

It is an unbalanced equation (sometimes also called a skeleton equation). This means that there are UNEQUAL numbers at least one atom on each side of the arrow.

In the example equation, there are two atoms of hydrogen on each side, But there are two atoms of oxygen on the left side and only one on the right side.

A balanced equation must have equal numbers of each type of atom on both sides of the arrow.

An equation is balanced by changing coefficients in a somewhat trial-and-error fashion. It is important to note that only the coefficients can be changed, never, a subscript. The coefficient times the subscript gives the total number of atoms.

3.4 Chemical Periodicity

Development of the Periodic Table

Lothar Meyer and Dimitri Mendeleev both discovered meaningful patterns of properties among the approximately 63 elements known in 1865.Both listed the elements in order of increasing atomic weight and saw that the properties repeat, a phenomenon called periodicity. Mendeleev offered some bold, but correct, proposals about places in the scheme that seemed inconsistent and so is generally given credit for the development of the periodic table.

Mendeleev's periodic table left holes where a known element would not properly fit. The classic example is germanium, which was unknown. There was no element that fit the properties expected of the element below silicon in the same group and to the left of arsenic. Mendeleev left that position empty and proposed that the element that belonged there, which he called eka-silicon, was simply yet to be discovered. Within a few years, it was found and its properties matched Mendeleev's predictions almost perfectly.

At the time of Mendeleev, scientists did not know about the structure of the atom and about subatomic particles and so they did knot know about atomic numbers. Now it a universal fact that the atomic number is the number of protons in the nucleus and therefore it is the charge of the nucleus. The periodic table is actually arranged in order of increasing atomic number, not increasing atomic weight, and there are only a few places where the order is affected.

A periodic table has been included in Appendix C.

Ionization Energy

The ionization energy, IE, is the energy required to remove the outermost electron from a gaseous atom or ion. The ***first ionization energy***, IE_1, is the energy for the removal of an electron from a neutral, gaseous atom: $M_{(g)}$ $M_{(g)}^{+}$ + e. Metallic atoms tend to lose enough electrons to gain the electron configuration of the proceeding noble gas.

There are periodic trends in the ionization energies, also tied to the effective nuclear charge. As the effective nuclear charge increases, it requires more energy to remove the outermost electron from an atom. Consequently, ionization energy is also related to the atomic radius, with ionization energy increasing as atomic radius decreases. therefore, the first ionization energy increases from left to right in a period and from bottom to top in a group.

Electron Affinities

Electron affinity, E, is the energy change of the reaction of adding an electron to a gaseous atom or ion.: $M_{(g)} + e\ M_{(g)}^{-}$. These reactions tend to be exothermic and so the values of E are generally negative.

In general, electron affinity tends to decrease (become more negative) from left to right in a period. Going down a group, there is little change in the electron affinities. Negative electron affinity means that the atom gains electrons easily.

Sizes of Ions

Recall that atoms increase in size going from right-to left on a period and top-to-bottom in a group.

Cations are smaller than their parent atom because the effective nuclear charge on the outermost electrons is greater in the cation. The number of protons remains the same but the number of screening electrons decreases.

Anions are larger than their parent atoms because the effective nuclear charge on the outermost electrons in smaller in the anion. The number of protons remains the same but the number of screening electrons increases.

Isoelectronic series are groups of atoms and ions which have the same electronic configuration. Within isoelectronic series, the more positive the charge, the smaller the species and the more negative the charge, the larger the species.

3.5 Classification of Chemical Reactions

In modern day chemistry, there is a great number of chemical reactions widely differing in nature. Many of them are carried out in industrial reactors and as such, they become a subject of study by chemical engineering. In order to facilitate the study of phenomena in nature, it is customary to classify them by some general attributes. These features are many and diverse and so are the classification of chemical reactions

3.5.1 Phase Composition of Feed

When designing a reactor or choosing forms of control in a given process, an important factor is the phase composition of feed.

Homogeneous reactions

The reactants and the products are in the same phase (liquid or gaseous). For example, the oxidation of nitrogen oxide by atmospheric oxygen in the manufacture of nitric acid, is a gas-phase reaction.

Heterogeneous reactions

At least one of the reactants or products is in a phase different from that of the remaining reactants or products. There are two phases (or binary) systems, such as 'gas-liquid', or 'gas-solid', 'liquid-solid', ' liquid-liquid' (involving immiscible fluids), 'solid-solid', and various combinations of three-phase (or ternary) systems.

3.5.2 Reaction Mechanisms

A simple reaction is that which can be carried to completion by overcoming only one energy barrier (a single-step reaction). Single-step reactions are an extremely rare occurrence in practice. However, some complex reactions proceed via a chain of intermediate steps which can conveniently be treated as formally simple reaction.

A complex reaction includes several concurrent (parallel) or consecutive (series) steps or both.

3.5.3 Overall Reaction Order

This is based on the sum of the powers to which all the reactant concentrations appearing in the rate equation (or expression) are raised. Accordingly, we have first-order, second-order, third-order and fractional-order reactions. The rate of reactions may or may not be changed deliberately by adding suitable substances called catalysts. Consequently, there are catalytic (or catalyzed) and non-catalytic (or uncatalyzed) reactions.

3.5.4 Thermal Effects

Exothermic reactions

They liberate heat to the surroundings. During exothermic reactions, the enthalpy of the reacting system decreases.

Endothermic reactions

They absorb heat from the surroundings. During the endothermic reaction, the enthalpy of the reacting system increases.

3.5.5 Molecularity

A further form of classification is according to the number of molecules that take part in a reaction. This is known as the Molecularity of a reaction and there may be mono-, bi- and tri- molecular series.

3.6 Efficiency Criteria of a Chemical Process

In addition to the general economic criteria, there are factors to reflect the efficiency of a chemical process.

Fractional Conversion

It is the fraction of a reactant that has undergone a chemical change at a particular stage of the reaction process.

Yield

The yield of a product is the ratio of the quantity of the product actually obtained to its maximum obtainable quantity.

Selectivity

Total or integral selectivity, is the ratio between the amount of reactant used up in a desired reaction and the total amount of the same reactant used up during the overall reaction.

Throughput and Production Rates

Throughput is the quantity of the product obtained per unit time. The maximum throughput of a chemical plant is normally referred to as its design capacity.

Production rate is defined as the throughput per unit of some quantity characterizing the standard geometry of the equipment, such as its volume, cross-sectional area etc.

3.7 Volumetric Properties of Fluids

3.7.1 Ideal Gas Law

The ideal gas law is based on the kinetic theory of gases by assuming that gas molecules have a negligible volume, exert no forces on one another and collide elastically with the walls of their container.

$$PV= nRT$$

P = absolute pressure of a gas
V = volume or volumetric flow rate of the gas
n = number of moles or molar flow rate of the gas
R = the gas constant, whose value depends on the units of P, V, n, and T
T = absolute temperature of the gas

The equation may also be written as $PV=nRT$
Where = (V/n) is the molar volume of the gas.

A gas whose P-V-T behavior is well represented by the above equation is said to behave as an idea gas or perfect gas.

3.7.2 Standard Conditions

To perform P-V-T calculations utilizing ideal gas law requires values of R with different units and it can be made easy by the following method:

$$PV = nRT$$

and for a set of arbitrarily chosen reference conditions

$$P_sV_s = n_sRT_s$$

and then to divide the first equation by the second:

$$PV / P_sV_s = nT / n_sT_s$$

Quantity	Symbol	Value	Unit
speed of light in vacuum	c; c_0	299792458	m/s
acceleration due to gravity	g	9.80665	m/s^2
Planck constant	h	6.6260687652 x 10^{-34}	J.s
Avogadro constant	N_A; L	6.0221419947 x 10^{23}	mol^{-1}
Atomic mass constant			
m_u = 1/12 m(^{12}C) = 1 u	m_u	1.6605387313 x 10^{-27}	kg
energy equivalent	m_uc^2	1.4924177812 x 10^{-10}	J
Faraday constant	F	96485.341539	C/mol
molar Planck constant	N_Ah	3.99031268930 x 10^{-10}	J.s/mol
	N_Ahc	0.1196265649291	J.m/mol
molar gas constant	R	8.314472	J/(mol.K)
Boltzmann constant	k	1.380650324 x 10^{-23}	J/K
molar volume of ideal gas RT/p	V_m		
T = 273.15 K; p = 101.325 kPa		22.41399639 x 10-3	m^3/mol
T = 273.15 K; p = 100 kPa		22.71098140 x 10^{-3}	m^3/mol
Loschmidt constant	n_0	2.686777547 x 10^{25}	m^{-3}
Sackur-Tetrode constant (absolute entropy constant)	S_0/R		
T1 = 1 K; p_0 = 101.325 kPa		- 1.164867844	
T1 = 1 K; p_0 = 100 kPa		- 1.151704844	
Stefan-Boltzmann constant	σ	5.67040040 x 10^{-8}	W/(m^2.K^4)
first radiation constant	c_1	3.7417710729 x 10^{-16}	W.m^2
second radiation constant	c_2	1.438775225 x 10^{-2}	m.K

Table 3.2
Physical Constants

3.7.3 Ideal Gas Mixtures

Suppose n_A moles of substance A, n_B moles of B, n_c moles of C, etc are contained in a volume V at a temperature T and total pressure P. The partial pressure p_A and partial volume v_A of A in the mixture are defined as follows:

p_A = The pressure that would be exerted by n_A moles of A alone in the same total Volume V at the same temperature T.

v_A = The volume that would be occupied by n_A moles of A alone at the total pressure P and temperature T of the mixture.

Consider each of the individual mixture components and that the mixture as a whole behaves in an ideal manner (this is the definition of an ideal gas mixture). If there are n moles of all species in the volume V at a pressure P and temperature T, then

$$\mathbf{PV = nRT}$$

In addition, from the definition of partial pressure,

$$\mathbf{p_A V = n_A RT}$$

Dividing the second equation by the first yields

$$\mathbf{p_A / P = n_A / n = y_A} \text{ (The Mole Fraction of A In The Gas)}$$

Or

$$\mathbf{p_A = y_A P} \quad \text{and} \quad \mathbf{v_A = y_A V}$$