

Stoichiometry

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CONNECTIONS

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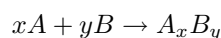
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Chapter 1

Mole concept¹

Stoichiometry is a branch of chemistry which deals with quantitative relationships of the reactants and products in a chemical reaction. The quantity of substance involved in measurement has different states (solid, liquid and gas) and forms (mixture and compound).

The stoichiometry calculations are basically arithmetic calculations, but confounded by scores of measuring terminologies. These terms are required to represent atomic or molecular level of association involved in chemical reactions. Besides chemical substance reacts or combines in definite proportion which we account by valence factor. Corresponding to valence factor, there are measurements which measures the proportion in which one element or group of elements reacts or combines with another element or group of elements.



A good part of stoichiometry is about mastering measuring terms. In this module, we seek to have a clear idea of mole and associated concept which is central to stoichiometry calculation.

1.1 Moles

Moles measure quantity of substance. There is a subtle ambiguity about treating “moles” – whether as “mass” or “number”. We take the position that it measures “amount of substance”, which can be either be expressed in terms of mass or in terms of numbers. The two approaches are equivalent and need not be a source of ambiguity any further. We only need to interpret the meaning as appropriate in a particular context.

One mole is defined as N_o entities of the substance, where N_o is equal to Avogadro’s number. N_o is generally taken as 6.022×10^{23} . If need be, then we may use still closer approximation of this number.

1.1.1 Relation between Mole and Molecular weight

The mole and molecular weight are designed to be related. Argument goes like this :

- 1: Molecular weight is arithmetic sum of atomic weights of constituent atoms.
- 2: Atomic weight is expressed in “atomic mass unit (a.m.u)”.
- 3: The atomic mass unit is the mass of $\frac{1}{12}$ th of C-12 atom. This is average weight of constituent 6 protons and 6 neutrons forming nucleus of C-12 atom. The a.m.u, therefore, is close to the mass of either a single proton or single neutron as a constituent of C-12. The a.m.u is numerically equal to :

$$1a.m.u = 1.66 \times 10^{-27} \quad kg = 1.66 \times 10^{-24} \quad gm$$

- 4: On the scale of a.m.u, the atomic weight of a carbon atom is exactly “12” and that of hydrogen is “1.008” or about “1”.

¹This content is available online at <<http://cnx.org/content/m14093/1.6/>>.

5: The number of C-12 atoms present in the quantity expressed in grams but numerically equal to atomic weight (as measured in a.m.u.) is given as :

$$N_o = \frac{\text{grams numerically equal to atomic weight}}{\text{Mass of one C-12 atom in gram}} = \frac{12}{12 \times 1.66 \times 10^{-24}}$$

The important point about this ratio is that “12” as atomic weight in the numerator and “12” as the number of a.m.u units in a single atom of C-12 cancels out, leaving us with a constant ratio :

$$\Rightarrow N_o = \frac{1}{1.66 \times 10^{-24}} = 6.022 \times 10^{23}$$

Clearly, this ratio is same for all elements. It means that the numbers of atoms in the grams numerically equal to atomic weight is N_o for all elements. Putting it equivalently, the mass of a collection N_o atoms of an element is equal to grams numerically equal to atomic weight.

6: We conclude that quantity in grams numerically equal to atomic weight contains N_o number of a particular element. This provides us with another definition of mole. In the case of an element, a mole of an atom means N_o numbers of that atom having mass in grams numerically equal to atomic weight. Important to note here is that term like "mole or moles of atoms" is a valid term. It can be emphasized that the term mole appears to be connected to molecules only, but actually it is a general concept which determines quantity of substance - atoms/molecules/ions/entities.

7: Extending the concept to molecule, a mole means N_o numbers of molecules having mass in grams numerically equal to molecular weight.

8: Further extending the concept in general, a mole of identical entities means N_o numbers of that entity having mass equal to N_o times mass of one entity.

The official SI definition of mole is :

Definition 1.1: 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.

1.1.2 Gram moles (n)

This term emphasizes the mass aspect of mole. One “gram mole” expresses mass of N_o elements, molecules, ions (as the case be) in grams. It is equal to mass in grams numerically equal to molecular weight.

If the mass of a chemical entity is “g” grams, then the given mass contains “n” gram-moles of the entity :

$$\text{gram moles}(n) = \frac{\text{Mass in gram}}{\text{Molecular weight}} = \frac{g}{M_o}$$

The gram mole or simply mole in the given grams of a sample means that there are “n” moles of substance present. This formula is widely used to express grams of substance in terms of gram moles and vice-versa.

Note that we use symbol M_o to denote molecular weight as we reserve the symbol “M” to denote molarity in the study of stoichiometry.

1.1.3 Gram atoms

It is a special case of gram moles in which chemical entity is an element. In this case, “gram atoms” substitutes “gram moles” and “atomic weight” replaces “molecular weight”.

$$\text{gram-atoms}(n_a) = \frac{\text{Mass in gram}}{\text{Atomic weight}} = \frac{g}{A}$$

The atomic and molecular weights of oxygen (O_2) are 16 and 32 respectively. If we consider a sample of 32 grams of oxygen, then

$$\text{gram moles}(n) = \frac{g}{M_o} = \frac{32}{32} = 1$$

Clearly, there are No molecules in the given 32 grams of oxygen sample. On the other hand, gram-atoms is :

$$\text{gram-atoms}(n_a) = \frac{g}{A} = \frac{32}{16} = 2$$

Thus, there are $2N_o$ atoms of oxygen in the given 32 grams of oxygen sample. These results are consistent with our understanding of the constitution of diatomic oxygen gas. The important point to keep in mind is that we need to employ the concept of “gram- atoms (g-atoms)” to elements only irrespective of whether it is mono-atomic or polyatomic.

Example 1.1

Problem : What is mass of one molecule of Calcium carbonate?

Solution : The mass of one molecule of Calcium carbonate is equal to its molecular weight (M_o)

$$m = M_o = 40 + 12 + 16 \times 3 = 100 \quad a.m.u = 100 \times 1.66 \times 10^{-24} \quad gm = 1.66 \times 10^{-22} \quad gm$$

Example 1.2

Problem : What is mass of one mole of Calcium carbonate?

Solution : The mass of one mole of Calcium carbonate is equal to grams numerically equal to molecular weight (M_o)

$$m = M_o \quad gm = (40 + 12 + 16 \times 3) \quad gm = 100 \quad gm$$

Example 1.3

Problem : Find the number of moles in 500 grams of pure Calcium carbonate?

Solution : The numbers of moles is given by :

$$n = \frac{g}{M_o} = \frac{500}{100} = 5$$

Example 1.4

Problem : Which represents greatest mass among 100 gm of calcium, 3 g-atoms of calcium , 1 mole of calcium oxide, 10^{25} molecules of oxygen?

Solution : We convert each of the given quantity in grams for comparison :

$$100 \quad gm \text{ of calcium} = 100 \quad gm$$

$$3g - \text{atoms of calcium} = 3 \times A_{Ca} = 3 \times 40 = 120 \quad gm$$

$$1 \text{mole of calcium oxide} = M_{CaO} \quad gm = 40 + 16 = 56 \quad gm$$

$$10^{25} \quad \text{molecules of oxygen} = \frac{10^{25}}{6.022 \times 10^{23}} \quad \text{moles} = 0.166 \times 10^2 \quad \text{moles}$$

$$\Rightarrow 10^{25} \text{ molecules of oxygen} = 16.6 \text{ moles} = 16.6 \times M_{O_2} \text{ gm} = 16.6 \times 32 = 531.2 \text{ gm}$$

Clearly, 10^{25} molecules of oxygen represents greatest mass.

1.1.4 Number of entities

The number of moles in a given mass of a molecule is given by :

$$\text{moles}(n) = \frac{g}{M_o}$$

Since each mole has N_o entities, the total numbers of entities in “n” moles is :

$$\text{Total number of molecules } (N) = nN_o = \frac{g}{M_o} \times N_o$$

If we are interested to count atoms in a sample of an element, then we use “gram atom” as :

$$\text{Total number of atoms } (N) = n_a N_o = \frac{g}{A} \times N_o$$

Example 1.5

Problem : If 10^{22} water molecules are removed from 100 gm of water, then find the remaining mass of water.

Solution : Here we need to find the mass of 10^{22} water molecules. We know that numbers of molecules is related to mass in gram as :

$$N = nN_o = \frac{g}{M_o} \times N_o$$

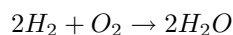
$$\Rightarrow g = \frac{NM_o}{N_o} = \frac{10^{22} \times 18}{6.022 \times 10^{23}} = 2.989 \times 0.1 = 0.2989 \text{ gm} = 2.989 \text{ mg}$$

$$\Rightarrow \text{remaining mass of water} = 100 - 2.989 = 97.011 \text{ mg}$$

1.2 Mole concept

Chemical reactions involve dissociation and association at atomic/molecular/ionic level. The measurements of constituent entities of a reaction can be carried out using conventional mass measurements in grams or kilograms. What is the need to carry out analysis in terms of moles?

Let us have a look at the chemical reaction :

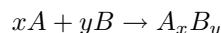


Let us further consider that there are 2 gms of hydrogen involved in the reaction. Can we interpret the given balanced equation to predict the mass of oxygen involved in the reaction? Clearly, it would not be possible unless we know the molecular mass. In terms of molecular mass, we see that 4 a.m.u of hydrogen reacts with 32 a.m.u of oxygen. This mass correlation, however, is slightly incomprehensible to our measurement sense as a.m.u is very minute mass almost incomprehensibly too small for our perceptible laboratory measurements in grams.

We can though extend the molecular mass proportion to grams. We note that the mass ratio of two elements in the reaction is 4:32 i.e. 1:8. Hence, 2 grams of hydrogen reacts with 16 grams of oxygen. This completes the picture. But, slight discomfort is that the correspondence of mass is not directly related with the numbers of molecules (coefficients of balanced chemical equation) involved in the reaction.

Mole concept simplifies the mass relation among reactants and products such that we can base our calculation on the coefficients (numbers of molecules involved in the reaction). At the same time, mass or the quantity of substance is on lab scale in grams. Looking at the equation, we can say that 2 molecules of hydrogen react with one molecule of oxygen. Extending this understanding of reaction to the moles of the substance, we come to the conclusion that “2 moles of hydrogen reacts with 1 mole of oxygen”. Here, we have simply scaled the molecular relation N_o times.

For a general reaction of the type :



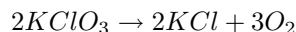
We say that “x moles of A reacts with y moles of B”.

This is a very powerful deduction popularly known as “mole concept”. It connects the measurement of mass neatly with the coefficients which are whole numbers. Further as moles are connected to mass in grams, measurement of quantities can be easily calculated in practical mass units like grams.

Example 1.6

Problem : Find the mass of KCl and oxygen liberated when 24.5 grams of $KClO_3$ is heated. Assume 100 % decomposition on heating. Given, $M_K = 39$.

Solution : On heating $KClO_3$ decomposes as :



In order to apply mole concept, we need to find the moles of $KClO_3$ in the sample.

$$\text{moles of } KClO_3 = \frac{24.5}{\text{molecular wt of } KClO_3}$$

Here, molecular weight of $KClO_3$ is :

$$\text{molecular wt of } KClO_3 = 39 + 35.5 + 3 \times 16 = 122.5$$

Putting this value in the equation of moles :

$$\Rightarrow \text{moles of } KClO_3 = \frac{24.5}{\text{molecular wt of } KClO_3} = \frac{24.5}{122.5} = 0.2$$

Applying mole concept to the equation, we have :

$$2 \text{ mole of } KClO_3 \hat{=} 2 \text{ moles of } KCl \hat{=} 3 \text{ moles of oxygen}$$

$$1 \text{ mole of } KClO_3 \hat{=} 1 \text{ moles of } KCl \hat{=} \frac{3}{2} \text{ moles of oxygen}$$

$$0.2 \text{ mole of } KClO_3 \hat{=} 0.2 \text{ moles of } KCl \hat{=} \frac{0.6}{2} \text{ moles of oxygen}$$

At this point, we need to convert the mass measurement from mole to grams,

$$m_{KCl} = n_{KCl} X M_{KCl} = 0.2 X (39 + 35.5) = 0.2 X 74.5 \text{ gm} = 14.9 \text{ gm}$$

$$m_{O_2} = n_{O_2} X M_{O_2} = \frac{0.6}{2} X 32 = 0.6 X 16 \text{ gm} = 9.6 \text{ gm}$$

1.3 Ideal gas and mole concept

The concept of mole is applicable to identical entities (atoms, molecules, ions). Thus, its direct application is restricted to pure substances – irrespective of its state (solid, liquid and gas). For all practical purposes, we treat mole as an alternative expression of mass. They are connected to each other via molecular weight for a given pure substance. However, measurement of gas is generally reported in terms of volume in stoichiometric calculation. We would, therefore, need to convert the volume of the gas to mass/mole.

If the gas in question is ideal gas, then we can easily connect volume to mole directly. Ideal gas presents a special situation. The collisions are perfectly elastic and there is no intermolecular force between molecules. The volume occupied by gas molecules is negligible with respect to the volume of ideal gas. It means that the size of molecule has no consequence as far as the volume of ideal gas is concerned. These negligibly small molecules, however, exchange momentum and kinetic energy through perfectly elastic collisions. Clearly, volume depends solely on the numbers of molecules present – not on the mass or size of molecules. This understanding leads to Avogadro's hypothesis :

All ideal gases occupy same volume at a given temperature and pressure. One mole of ideal gas occupies 22.4 litres i.e. 22,400 ml at standard temperature (273 K) and pressure (1 atmosphere) condition.

The gas volume for 1 mole is known as molar volume. The Avogadro's hypothesis provides an important relation between volume and moles of gas present. This relationship does not hold for real gas. But we are served well in our calculation by approximating real gas as ideal gas. The real gas like hydrogen, oxygen etc. may still be close to the ideal gas molar volume at normal temperature and pressure conditions.

Example 1.7

Problem : Air contains 22.4 % oxygen. How many moles of oxygen atoms are there in 1 litre of air at standard condition ?

Solution : The volume of oxygen is 0.224 litre. We know that 22.4 litres contains 1 mole of oxygen molecules. Hence, 0.21 litres contains “n” moles given by :

$$n = \frac{0.224}{22.4} = 0.01 \quad \text{moles of oxygen molecules}$$

We know that one molecule of oxygen contains 2 atoms. Therefore, numbers of moles of oxygen atoms is 0.02 moles.

Example 1.8

Problem : Calculate the numbers of molecules in 300 cc of oxygen at 27° C and 740 mm pressure.

Solution : We first need to convert the given volume at given temperature and pressure to that at standard temperature and pressure condition. Applying gas law,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\Rightarrow V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{740 \times 300 \times 273}{760 \times 300} = 265.82 \quad \text{cc}$$

Number of molecules of oxygen is :

$$\Rightarrow N = \frac{265.82 \times 6.022 \times 10^{23}}{22400} = 7.146 \times 10^{21}$$

1.4 Analysis techniques

Stoichiometric analysis is about analyzing mass of different chemical species or concentrations of solutions involved in chemical reactions. We employ varieties of different concepts and hypotheses. These principles are primarily based on molecular association of various chemical species in chemical reactions. Most important among these are mole, equivalent weight and gram equivalent weight concepts. Each of these concepts

relates amount of different species in chemical reaction in alternative ways. It means that these concepts have contextual superiority over others (suitability in a particular context), but are essentially equivalent.

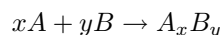
Stoichiometric analysis is broadly classified as gravimetric or volumetric analysis depending on whether calculations are mass based (gravimetric) or concentration of solution based (volumetric). There is no strict division between two approaches as we encounter reactions which require considerations of both aspects i.e. mass of species and concentration of solution.

In general, gravimetric analysis covers displacement reactions, action of acid on metals, calculations based on balanced equations, decomposition reaction etc. On the other hand, volumetric analysis covers wide ambit of titration including neutralization and redox reactions. Many of the chemical reactions, however, need combination of two analytical approaches. For example, a sequence of chemical process may involve decomposition (gravimetric analysis) and titration (volumetric analysis).

Chapter 2

Analyzing chemical equations¹

Application of mole concept requires a balanced chemical equation. The different constituents of the reaction – reactants and products – bear a simple whole number proportion same as the proportion of the coefficients associated with constituents. According to mole concept, the molar mass of constituents participates in this proportion. For a generic consideration as given :



Here, 1 mole of compound (A_xB_y) involves x mole of A and y mole of B. Using symbols :

$$x \text{ moles of A} \equiv y \text{ moles of B} \equiv 1 \text{ mole of } A_xB_y$$

The point to emphasize here is that this is a relation, which is connected by "equivalence sign (\equiv)" - not by "equal to ($=$)" sign. We know that 2 moles of hydrogen reacts with 1 mole of oxygen to form 2 moles of water. Clearly, we can not equate like $2=1=2$. We need to apply unitary method to interpret this relation of equivalence. We say that since x moles of A react with y moles of B. Hence, 1 mole of A reacts with y/x moles of "B". Similarly, 1 mole of B reacts with x/y moles of "A". Once we know the correspondence for 1 mole, we can find correspondence for any other value of participating moles of either A or B.

2.1 Mass of participating entities in a reaction

Mole concept is used to calculate mass of individual constituent of a chemical reaction. The proportion of molar mass is converted to determine proportion of mass in which entities are involved in a reaction. The symbolic mass relation for the chemical reaction as given above is :

$$xM_A \text{ gm of A} \equiv yM_B \text{ gm of B} \equiv M_{A_xB_y} \text{ gm of } A_xB_y$$

We apply unitary method on the mass relation related with equivalent sign (\equiv) to determine mass of different entities of the reaction.

Example 2.1

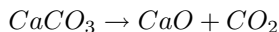
Problem : Calculate mass of lime (CaO) that can be prepared by heating 500 kg of 90 % pure limestone ($CaCO_3$).

Solution : Purity of $CaCO_3$ is 90 %. Hence,

$$\text{Mass of } CaCO_3 = 0.9 \times 500 = 450 \text{ kg}$$

The chemical reaction involved here is :

¹This content is available online at <<http://cnx.org/content/m16798/1.7/>>.



Applying mole concept :

$$\Rightarrow 1 \text{ mole of } CaCO_3 \equiv 1 \text{ mole of CaO}$$

$$\Rightarrow (40 + 12 + 3 \times 16) \text{ gm of } CaCO_3 \equiv (40 + 16) \text{ gm of CaO}$$

$$\Rightarrow 100 \text{ gm of } CaCO_3 \equiv 56 \text{ gm of CaO}$$

$$\Rightarrow 100 \text{ kg of } CaCO_3 \equiv 56 \text{ kg of CaO}$$

Applying unitary method :

$$\Rightarrow \text{mass of CaO produced} = \frac{56 \times 450}{100} = 252 \text{ kg}$$

Example 2.2

Problem : Igniting MnO_2 converts it quantitatively to Mn_3O_4 . A sample of pyrolusite contains 80% MnO_2 , 15 % SiO_2 and 5 % water. The sample is ignited in air to constant weight. What is the percentage of manganese in the ignited sample ? ($A_{Mn} = 55$)

Solution : The sample contains three components. Since this question involves percentage, we shall consider a sample of 100 gm. Water component weighing 5 gm evaporates on ignition. SiO_2 weighing 15 gm does not change. On the other hand, 80 gm of MnO_2 converts as :



Applying mole concept,

$$3 \text{ moles of } MnO_2 \equiv 1 \text{ mole of } Mn_3O_4$$

$$3 \times (55 + 2 \times 16) \text{ gm of } MnO_2 \equiv 1 \times (3 \times 55 + 4 \times 16) \text{ gm of } Mn_3O_4$$

$$261 \text{ gm of } MnO_2 \equiv 229 \text{ gm of } Mn_3O_4$$

Since sample is ignited in air to constant weight, it means that all of MnO_2 in the sample is converted. Using unitary method, we determine mass of converted mass of Mn_3O_4 for 80 gm of MnO_2 :

$$\text{Mass of } Mn_3O_4 \text{ on conversion} = \frac{229}{261} \times 80 = 70.2 \text{ gm}$$

We are required to find the percentage of Mn in the ignited sample. Thus, we need to determine the mass of the ignited sample. The ignited sample contains 70.2 gm of Mn_3O_4 and 15 gm of SiO_2 . Total mass of ignited sample is $70.2 + 15 = 85.4$ gm. On the other hand, amount of Mn in Mn_3O_4 is calculated from its molecular constitution :

$$229 \text{ gm of } Mn_3O_4 \equiv 3 \times 55 \text{ gm of Mn} \equiv 165 \text{ gm of Mn}$$

$$\text{Amount of Mn in } 70.2 \text{ gm of } Mn_3O_4 = \frac{165}{229} \times 70.2 = 0.72 \times 70.2 = 50.54 \text{ gm}$$

Clearly, 85.4 gm of ignited sample contains 50.54 gm of Mn. Hence,

$$\text{Percentage amount of manganese in the ignited sample} = \frac{50.54}{85.4} \times 100 = 59.2\%$$

2.2 Reaction involving gas

In analyzing chemical reaction involving gas, we make the assumption that gases are ideal gases. In general, there are three different situations in which we may use gas volume in chemical analysis :

- Gas volumes are given at STP.
- Gas volumes are given at other temperature and pressure condition.
- Only gas volumes are involved in calculation

In certain situation, reaction involving gas enables us to use gas volumes itself (not the moles) to analyze the reaction. We can extend the concept of molar proportions to volume proportions directly. Such is the case, when only gas volumes are involved in the calculation.

2.2.1 Gas volumes are given at STP

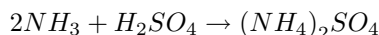
For analyzing gas volumes at STP, we make use of Avogadro's hypothesis. A volume of 22.4 litres of ideal gas contains 1 mole of gas. The number of moles present in a volume "V" at STP is :

$$n = \frac{V}{22.4}$$

Example 2.3

Problem : Determine the amount of concentrated H_2SO_4 required to neutralize 20 litres of ammonia gas at STP.

Solution : The chemical reaction involved is :



Applying mole concept :

$$2 \text{ moles of } NH_3 \equiv 1 \text{ mole of } H_2SO_4$$

$$2 \times 22.4 \text{ litres of } NH_3 \equiv 98 \text{ gm of } H_2SO_4$$

$$\text{Amount of } H_2SO_4 \text{ for 20 litres of } NH_3 = \frac{98}{44.8} \times 20 = 43.8 \text{ gm}$$

2.2.2 Gas volumes are given at other temperature and pressure condition

Under this condition, we first need to convert gas volumes to volumes at STP. We make use of ideal gas law,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

We may specify one of the suffix like "1" to represent the given condition and suffix "2" to represent the STP condition.

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