Stoichiometric Calculations

(This Chapter is good to revise. Understanding of skills involved is essential)

A balanced chemical equation may be used for calculation of the mass of reactants or products (or, in case of gases, volume may be calculated). It is also possible to calculate percentage purity of a substance or overall percentage yield, etc. Some examples are given below to illustrate the use of stoichiometric calculations.

Example

Calculate the mass and volume of hydrogen evolved at STP when 0.9 g of Al is dissolved in excess of dilute H_2SO_4.

Solution

The relevant equation is

$$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2$$

2×27 g $\qquad$ 3×2 g or 3×22.4 L at STP

$$\text{Hence, 0.9 g Al will liberate } \frac{3 \times 2 \times 0.9}{2 \times 27} = 0.1 \text{ g}$$

$$\text{or } \frac{3 \times 22.4 \times 0.9}{2 \times 27} = 1.12 \text{ L } H_2 \text{ at STP}$$

Example

1 g of an impure sample of Mg containing inert impurities reacts with excess H_2SO_4 to evolve 896 mL of H_2 at STP. Find the percentage purity of the sample.

Solution:

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$$

24 g $\qquad$ 22.4 L at STP

22.4 L H_2 at STP is given by 24 g Mg

$$\text{Hence 0.896 L } H_2 \text{ will be given by } \frac{24 \times 0.896}{22.4} = 0.96 \text{ g Mg}$$

$$\%\text{ Purity of Mg} = \frac{0.96 \times 100}{1} = 96\%$$

Example

1 g alloy of magnalium containing only Mg and Al on reaction with excess of HCl evolves 1.117 L H_2 at STP. Calculate the composition of alloy.

Solution

Both metals react with acid to produce H_2

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$

2×27 g $\qquad$ 3×22.4 L at STP

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

24 g $\qquad$ 22.4 L at STP

Suppose the mass of Al is x g, then mass of Mg will be (1 - x) g.

x g Al will evolve $\frac{3 \times 22.4 \times x}{2 \times 27}$ L H_2 at STP

and (1 - x) g Mg will evolve $\frac{22.4 \times (1-x)}{24}$ L H_2 at STP

So, $\frac{3 \times 22.4 \times x}{2 \times 27} + \frac{22.4\,(1-x)}{24} = 1.117$

or $x = 0.59$ g Al

Mass of Mg = 0.41 g

Example

1 g alloy of Cu and Al when dissolved in excess of dilute H_2SO_4 evolves 672 mL H_2 at STP. Find the percentage composition of alloy.

Solution

Here it is necessary to know that Cu being lower in activity series does not react with dilute H_2SO_4 to evolve H_2. Hence only reaction liberating H_2 is that of Al and from volume of hydrogen, mass of Al can be found.

$$\underset{2 \times 27\text{ g}}{2\,Al} + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + \underset{\substack{3 \times 22.4\text{ L}\\ \text{at STP}}}{3H_2}$$

3×22.4 L H_2 is liberated by 2×27 g Al

$\therefore$ 0.672 L H_2 will be liberated by $\frac{2 \times 27 \times 0.672}{3 \times 22.4} = 0.54$ g

Hence % Al = 54%

and % Cu = 100 - 54 = 46 %.

Example

1 g mixture of $CaCO_3$ and Na_2CO_3 when heated strongly left a residue weighing 0.67 g. Find the percentage compsotion of the mixture.

Solution

Again, here it is important to note that Na_2CO_3 is stable to heat and does not decompose or lose mass on heating. So only reaction taking place is

$$\underset{100\text{ g}}{CaCO_3} \xrightarrow{\Delta} \underset{56\text{ g}}{CaO} + \underset{\text{will escape}}{CO_2 \uparrow}$$

Suppose, mass of $CaCO_3$ is x g then mass of Na_2CO_3 is (1 - x) g.

100 g $CaCO_3$ leaves a residue of 56 g.

$\therefore$ x g $CaCO_3$ will leave a residue of (56x/100) g

x g $CaCO_3$ will leave a residue of $\frac{56x}{100}$ g

Hence mass of residue $= \frac{56x}{100} + 1 - x = 0.67$

$\Rightarrow x = 0.75$

Percentage $CaCO_3$ = 75% and Na_2CO_3 = 25%

Example

When 6.0 g of carbon reacts with 10 g of oxygen only gaseous products are formed.

Find the moles and mass of each of the product formed.
Solution
First, C reacts with O_2 to form CO, and then, any remaining O_2 reacts with CO to form CO_2.

We have $\frac{6\text{ g}}{12\text{ g mol}^{-1}}$ = 0.5 mol C and $\frac{10\text{ g}}{32\text{g mol}^{-1}}$ = 0.3125 mol O_2

First reaction : $C + \frac{1}{2}O_2 \rightarrow CO$

1 mol	0.5 mol	1 mol
0.5 mol	0.25 mol	0.5 mol

O_2 left = 0.3125 – 0.25 = 0.0625 mol

Second reaction : $CO + \frac{1}{2}O_2 \rightarrow CO_2$

1 mol	0.5 mol	1 mol

0.5 mol CO requires 0.25 mol O_2 for complete conversion to CO_2 but here oxygen is only 0.0625 mol (limiting reagent) and hence only 2 × 0.0625 = 0.125 mol CO will react.
CO left = 0.5 - 0.125 = 0.375 mol
CO_2 formed = 0.125 mol
mass of CO = 0.375 × 28 = 10.5 g
mass of CO_2 = 0.125 × 44 = 5.5 g

Example
Chromium is produced by the reaction $2\,Al + Cr_2O_3 \xrightarrow{\Delta} 2Cr + Al_2O_3$.
If 100 g Al and 100 g Cr_2O_3 are heated to start the reaction, how much chromium will be formed at the completion of the reaction?
Solution
Here it is first necessary to find which reactant is in excess. The best method for this is to find moles of reactants present.

Moles of Al= $\frac{100\text{ g}}{27\text{ g mol}^{-1}}$ = 3.7037 mol

Moles of Cr_2O_3 = $\frac{100\text{ g}}{152\text{g mol}^{-1}}$ = 0.6579 mol

For one mole of Cr_2O_3 two moles of Al are required. So according to moles given, Al is in excess and Cr_2O_3 is in the limiting quantity.
Therefore, calculations must be based on the amount of Cr_2O_3.
0.6579 mol of Cr_2O_3 will react with 2 x 0.6579 = 1.3158 mol of Al leaving 2.3879 mol of Al unreacted and 1.3158 mol of Cr will be formed.
Mass of Cr formed (atomic mass = 52) = 1.3158 × 52 = 68.4216 g

Example
What amount of H_2SO_4 in moles could be obtained from 1000 g of pure iron pyrites, FeS_2?
Solution
The equations involved are

$$4FeS_2 + 11O_2 \rightarrow 3Fe_2O_3 + 8SO_2$$
$$2SO_2 + O_2 \rightarrow 2SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

It may be noted that every atom of S in FeS_2 produces one mole of H_2SO_4. Hence, it is not necessary to use balanced equations.

Thus,

$$FeS_2 \equiv 2H_2SO_4 \text{ or } 1 \text{ mol } FeS_2 \equiv 2 \text{ mol } H_2SO_4$$

$$\text{Number of moles of } FeS_2 = \frac{\text{mass}}{\text{Molecular mass}} = \frac{1000 \text{ g}}{120 \text{ g mol}^{-1}} = 8.33 \text{ moles}$$

Hence, amount of H_2SO_4 produced = 2 $\times$ 8.33 mol = 16.66 mol.

Example

A mixture of NaCl and NaBr when heated with concentrated H_2SO_4 gave a solid residue. The mass of residue was exactly equal to that of original mixture. Find the percentage composition of the mixture.

Solution

The reactions involved are

$$\begin{array}{lcl} 2NaCl + H_2SO_4 & \rightarrow & Na_2SO_4 + 2HCl\uparrow \\ 2\,(58.5)\text{ g} & & (142)\text{ g} \\ 2NaBr + H_2SO_4 & \rightarrow & Na_2SO_4 + 2HBr\uparrow \\ 2\,(103)\text{ g} & & (142)\text{ g} \end{array}$$

Suppose, the total mass of the mixture is 1 g and that of NaCl isx g.

$$2 \times 58.5 \text{ g NaCl gives } 142 \text{ g } Na_2SO_4$$

$$x \text{ g NaCl will give} = \frac{142 \times x}{2 \times 58.5} \text{ g } Na_2SO_4$$

$$2 \times 103 \text{ g NaBr gives } 142 \text{ g } Na_2SO_4$$

$$\therefore (1 - x) \text{ g NaBr will give} = \frac{142\,(1 - x)}{2 \times 103} \text{ g } Na_2SO_4$$

$$\text{Total mass of } Na_2SO_4 = \frac{142\,x}{2 \times 58.5} + \frac{142\,(1 - x)}{2 \times 103} = 1 \text{ g (mass of mixture)}$$

$$\Rightarrow x = 0.592 \text{ g}$$

Hence, percentage composition of NaCl = 59.2 % and of NaBr = 40.8 %.

Example

A mixture of FeO and Fe_2O_3 when heated in air to a constant mass gains 5% in its weight. Find the composition of the initial mixture.

Solution

Prior knowledge of the fact that what happens when FeO and Fe_2O_3 are heated in air is necessary.

$$\begin{array}{lcl} 2FeO + \frac{1}{2}O_2 & \rightarrow & Fe_2O_3 \\ 2\,(72)\text{ g} & & (160)\text{ g} \end{array}$$

$$Fe_2O_3 + \text{Air} \rightarrow \text{No reaction}$$

So, whatever the increase in mass, it is due to FeO.
Suppose, the weight of mixture is 1 g and weight of FeO is x g.

The mass of mixture after heating will be $= \frac{105 \times 1}{100} = 1.05\,g$

Then, the mass of Fe_2O_3 produced from x g FeO $= \frac{160 \times x}{2 \times 72}$ g
Mass of Fe_2O_3 = (1 - x) g.

$$\frac{160\,x}{2 \times 72} + (1 - x) = 1.05$$

Final mass = or $x = 0.45\,g$
Hence the mixture contains 45% FeO and 55% Fe_2O_3

Example
A 1.205 g impure sample of Na_2CO_3 was dissolved and reacted with excess $CaCl_2$. The precipitate obtained was ignited and the weight of residue obtained was 0.56 g. Calculate the percentage purity of Na_2CO_3.
Solution
The reactions involved are

$$\underset{(106)\,g}{Na_2CO_3} + CaCl_2 \rightarrow \underset{(100)\,g}{CaCO_3} + 2NaCl;$$

$$\underset{(100)\,g}{CaCO_3} \rightarrow \underset{(56)\,g}{CaO + CO_2}$$

The residue obtained is of CaO. The number of moles of CaO = $\frac{0.56\,g}{56\ g\ mol^{-1}} = 0.01\,mol$
From balanced equation
1 mol CaO ≡ 1 mol $CaCO_3$ ≡ 1 mol Na_2CO_3
0.01 mol ≡ 0.01 mol ≡ 0.01mol
Hence, number of moles of Na_2CO_3 present = 0.01 mol
and 0.01 x 106 g = 1.06 g

$\therefore$ Percentage purity $= \frac{1.06 \times 100}{1.205} = 87.97\%$ Ans.

Example
How much H_2SO_4 (containing 70% by mass) is required for the production of 1000 g of HCl (containing 40% by mass) by reaction of H_2SO_4 with NaCl ?
Solution

Amount of HCl in 1000 g of 40% acid = $\frac{40}{100} \times 1000 = 400\,g$

The reaction involved: $2NaCl + \underset{(98)g}{H_2SO_4} \rightarrow Na_2SO_4 + \underset{2(36.5)g}{2HCl}$

Amount of H_2SO_4 required to produce 400 g HCl

$= \frac{98 \times 400}{2 \times 36.5} g$

Since 70 g of pure H_2SO_4 make 100 g of 70% H_2SO_4 then

$\frac{98 \times 400}{2 \times 36.5} g$ of pure H_2SO_4 will make $\frac{100 \times 98 \times 400}{2 \times 36.5 \times 70}$ g 70% H_2SO_4
= 767.1 g of 70% H_2SO_4.

Example
1 g sample of $KClO_3$ was heated so that part of it decomposed as
$2KClO_3 \rightarrow 2KCl + 3O_2$ and the remaining part as $4KClO_3 \rightarrow 3KClO_4 + KCl$. If the amount of oxygen evolved was 0.21 g, calculate the percentage by mass of $KClO_4$ in the residue.
Solution
Suppose x g of $KClO_3$ decomposed to KCl and O_2 and (1 - x) g of $KClO_4$ and KCl.
From equation
$2KClO_3 \rightarrow 2KCl + 3O_2$
2(122.5)   2(74.5)   3(32)
2 $\times$ 122.5 g $KClO_3$ gives 3 $\times$ 32 g oxygen

$\therefore$ x g $KClO_3$ will give $= \frac{3 \times 32 \times x}{2 \times 122.5}$ g oxygen

or

$\frac{3 \times 32 \times x}{2 \times 122.5} = 0.21$ (mass of Oxygen evolved)

or x = 0.5359 g (mass of $KClO_3$ decomposed as KCl and O_2)

$4KClO_3 \rightarrow 3KClO_4 + KCl$
4(122.5)   3(138.5)   2(74.5)

The remaining mass i.e. 1- 0.539 = 0.4641 g decomposes to $KClO_4$ and KCl.
4 $\times$ 122.5 g $KClO_3$ gives 3 $\times$ 138.5 g $KClO_4$.

$\therefore$ 0.4641 g $KClO_3$ will give $\frac{3 \times 138.5 \times 0.4641}{4 \times 122.5}$ g $KClO_4$
= 0.3935g $KClO_4$

Mass of residue = Original mass - mass of oxygen
= 1 - 0.21 = 0.79 g

$\therefore$ Percentage of $KClO_4$ in the residue $= \frac{0.3935 \times 100}{0.79}$
= 49.8%

Eudiometry
Molecular formula of gases
For gaseous hydrocarbons it is possible to determine their molecular formula without knowing their percentage composition.
A known volume of gaseous hydrocarbon is taken in a eudiometer tube and exploded with an excess of oxygen. The following reaction takes place:

$$C_xH_y + (x + \frac{y}{4}) O_2 \rightarrow x CO_2 + \frac{y}{2} H_2O$$

$$n \text{ Vol.} \quad n(x + \frac{y}{4}) \text{Vol} \quad n x \text{Vol} \quad n(\frac{y}{2}) \text{ Vol. (if gaseous)}$$

This volume relation follows from Avogadro's law
After explosion, the eudiometer tube is allowed to cool to room temperature when water changes to liquid and occupies negligible volume. The volume of gases left after cooling is due to carbon dioxide formed and unreacted oxygen.
The volume of carbon dioxide formed is determined by absorbing it in caustic soda or caustic potash. Corresponding contraction in volume is equal to volume of carbon dioxide formed. The gas left behind corresponds to volume of unreacted oxygen.
Knowing the volume of gaseous hydrocarbon, oxygen used and carbon dioxide formed, the molecular formula of hydrocarbon may be determined. Of course all volume measurements must be made under identical conditions of pressure and temperature.
For gaseous compounds containing oxygen, the equation becomes:

$$C_xH_yO_z + (x + \frac{y}{4} - \frac{z}{2}) O_2 \rightarrow x CO_2 + \frac{y}{2} H_2O$$

$$n \text{ Vol} \quad n(x + \frac{y}{4} - \frac{z}{2}) \text{ Vol} \quad nx \text{ Vol}$$

Example
15 mL of a gaseous hydrocarbon was exploded with 105 mL of oxygen in an eudiometer tube. After cooling, the residual gases occupied 75 mL and this volume was reduced to 30 mL on treatment with KOH solution. All volumes were measured under identical conditions. Find the molecular formula of the hydrocarbon.
Solution

$$C_xH_y + (x + \frac{y}{4}) O_2 \rightarrow x CO_2 + \frac{y}{2} H_2O$$

$$n \text{ Vol} \quad n(x + \frac{y}{4}) \text{ Vol} \quad nx \text{ Vol}$$

$$15 \text{ mL} \quad 15 \ (x + \frac{y}{4}) \text{ mL} \quad 15x \text{ mL}$$

Volume absorbed by KOH = Volume of CO_2 = 75 – 30 = 45 mL = 15x

$\therefore$ x = 3

Volume of oxygen used = 105 – 30 = 75 mL = $15(x + \frac{y}{4})$

when x = 3 , y = 8

Hence, molecular formula of hydrocarbon is C_3H_8

Example
50 mL of a mixture of methane and ethane was exploded with excess oxygen. After explosion and cooling, the remaining gases were treated with NaOH solution when a reduction of 60 mL in volume was observed. All measurements were done under identical conditions. Calculate the percentage composition of the mixture by volume.
Solution

The relevant equations are

$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

x vol x vol

$C_2H_6 + 7/2\ O_2 \rightarrow 2CO_2 + 3\ H_2O$

(50 - x) vol 2(50 - x) vol

Reduction in volume with NaOH = volume of CO_2

or, x + 2(50 - x) = 60

or, x = 40

percentage methane by volume = 40/50 $\times$ 100 = 80%

and percentage ethane by volume = 20%.

Example

10 mL mixture of ethane and another unknown gaseous hydrocarbon in equal ratio was mixed with 50 mL of oxygen and exploded. After cooling, the volume of gases was found to be 37.5 mL and there was a reduction of another 15 mL when the gases were passed in caustic potash. Find the molecular formula of unknown compound.

Answer

$$C_aH_b + (a + \frac{b}{4})\ O_2 \rightarrow aCO_2 + \frac{b}{2} H_2O$$

$$x \text{ mL} \qquad x(a + \frac{b}{4}) \text{mL} \qquad xa \text{ mL}$$

$$C_2H_6 + \frac{7}{2} O_2 \rightarrow 2CO_2 + 3H_2O$$

$$(10 - x)\text{mL} \quad (10 - x)\frac{7}{2}\text{mL} \quad (10 - x)2 \text{ mL}$$

$$\text{Volume of } CO_2 \text{ formed} = xa + (10 - x)2 = 15 \text{ mL}$$

$$\text{Volume of } O_2 \text{ used} = x(a + \frac{b}{4}) + (10 - x)\frac{7}{2}$$

$$= 50 - (37.5 - 15) = 27.5 \text{ mL}$$

Since the hydrocarbons are present in equal ratio

$x = 5$ and $10 - x = 5$

So, $5a + 5 \times 2 = 15$

So $a = 1$

and $5(1 + \frac{b}{4}) + 5 \times \frac{7}{2} = 27.5$

So, $b = 4$

Hence unknown hydrocarbon is CH_4.

Example

Gaseous benzene reacts with hydrogen gas in the presence of nickel catalyst to form gaseous cyclohexane according to the reaction.

$C_6H_6(g) + 3\ H_2 \rightarrow C_6H_{12}(g)$

A mixture of benzene with excess of hydrogen was initially at a pressure of 120 mmHg. After the gases were passed over nickel catalyst, all benzene was converted to cyclohexane and the gaseous pressure was found to be 60 mmHg under identical conditions. Find the fraction of benzene by volume in original mixture.

Answer

Here, pressure may be taken as in proportion to moles.

$$C_6H_6\ (g) + 3\ H_2 \rightarrow C_6H_{12}\ (g)$$

Initial: x mmHg   120 - x mmHg

Final: x mmHg   120 - x - 3x mmHg   xmmHg

Final pressure = 120 - x - 3x = 120 - 3x = 60 mmHg

or, x= 20 mmHg

Mole fraction of benzene in original mixture = $\frac{20}{120} = \frac{1}{6}$

Equivalent Concept

Volumetric calculations

Chemical calculations may be done using molar mass or mole as the basis of reactions (Mole concept: Here knowledge of stoichiometry and balancing of equation is required) or using equivalent mass or equivalents as the basis of reactions (Equivalent concept: Balancing of equation is not required but knowledge of equivalent mass is necessary).

On the basis of the equivalent concept, all reactions become 1:1 reaction and the number of equivalents of all reactants and products are equal in a reaction.

Equivalent mass or chemical equivalent

The mass of a substance that combines with or displaces 1 g of hydrogen or 8 g of oxygen or 35.5 g of chlorine.

Or mass of a substance that combines with or displaces 1 mole of electrons or 96,500 coulombs of charge.

(i) Gram equivalent mass or gram equivalent or equivalent

Equivalent mass expressed in grams is known as gram equivalent mass.

1 g equivalent of a substance means its mass in grams corresponding to its equivalent mass.

1 g eq. of H_2 = 1 g; 1 g eq. of O_2 = 8 g; 1 g eq. of H_2SO_4 (molecular mass = 98) = 49 g; 1 g eq. of Na_2CO_3 = 53 g

(ii) Determination of equivalent mass

a. Hydrogen displacement method

Metals react with dilute acids to evolve hydrogen. The volume of gaseous hydrogen is converted to STP from which its mass is calculated. The mass of metal which will evolve 1 g of hydrogen is its equivalent mass.

b. Oxide formation method

Substances react with oxygen to form oxides. Knowing the mass of substance and that of oxide, mass of oxygen combining with known mass of substance is found. Equivalent mass of the substance is that mass which combines with 8 g of oxygen.

c. Chloride formation method

The equivalent mass of substances that readily form chloride can be determined by finding the mass of the substance that combines with 35.5 g of chlorine.

d. Double decomposition method

Since substances react in the ratio of their equivalent mass, hence in any reaction -

$$\frac{\text{Mass of A}}{\text{Equivalent Mass of A}} = \frac{\text{Mass of B}}{\text{Equivalent Mass of B}}$$

e. Faraday's method

One gram equivalent of a substance is deposited or decomposed by 96,500 coulombs of electricity and when the same quantity of electricity is passed through different electrolytes, substances are decomposed or formed in the ratio of their equivalents.

Equivalent mass of an Acid

$$= \frac{\text{Molecular mass}}{\text{Basicity}} \text{ or } \frac{\text{Molecular mass}}{\text{Displaceable H}}$$

Equivalent mass

$$= \frac{\text{Molecular mass}}{\text{Acidity}} \text{ or } \frac{\text{Molecular mass}}{\text{Displaceable OH}}$$

Equivalent mass of Salt

$$= \frac{\text{Molecular mass of Salt}}{\text{Total number of positive or negative valencies or radicals}}$$

Equivalent mass of oxidising agents or oxidants

$$= \frac{\text{Molecular mass}}{\text{Number of moles of electrons accepted per mole}}$$

Equivalent mass of reducing agent or reductant

$$= \frac{\text{Molecular mass}}{\text{Change in oxidation number per mole}}$$

Equivalent mass of a substance is not always same. It may be different in different reactions for same substance.
On the basis of equivalent, all reactions react in 1:1 ratio.
Milliequivalent = 1000 $\times$ Equivalent or 1000 x mass/Equivalent mass
or, equivalent mass expressed in milligrams.

Strength of Solutions

Standard solution: A solution of known strength (known amount of solute in known amount of solution)

Percentage: Unless otherwise specified it is m/m i.e. in mass of solution (not solvent). 10% H_2SO_4 means 10 g H_2SO_4 in 100 g of solution (or 90 g of solvent)

Mole fraction: Amount of solute in moles divided by the total number of moles or n/(n + N)

Normality (N): Amount of gram equivalent mass of solute in one litre of solution.
N = Mass of solute in g per litre/Equivalent mass
A solution containing 1 g equivalent of substance in one litre of solution is unit Normal solution.
Decinormal solution contains one tenth of gram equivalent mass in one litre solution.
Milliequivalent (meq) = Normality $\times$ Volume in cm^3.

Molarity (M): Amount of solute in moles in one litre of a solution. A solution containing 1 mole of solute in one litre of solution is a one Molar solution.
Semimolar solution contains half gram mole in one litre solution.

Molality (m): Amount of solute in moles in one kilogram of solvent. Solution containing 1 g mol of solute in 1000 g of solvent is 1 molal. Molality is not affected by temperature.

Volumetric Calculations

Volumetric analysis is the quantitative estimation of dissolved substances in a known volume of solution. Normality and molarity are useful methods of expressing concentrations in volumetric analysis.
For a given solution, amount of solute is proportional to the volume of solution. Thus,
Normality $\times$ Volume of solution in litres
= Number of equivalents and Normality $\times$ Volume in mL
= Number of milliequivalents
Since equivalents react in 1:1 ratio,
equivalents in solution 1 or N_1V_1 = equivalents in solution 2 or N_2V_2.
Strength of a solution = Normality $\times$ equivalent mass
It is determined experimentally by titrating a known volume of unknown solution against a standard solution using an indicator to show the completion of the reaction.

Acid-Alkali Titrations

A Standard solution is prepared either using oxalic acid (equivalent mass 63) or sodium carbonate (equivalent mass 53) and indicators used are phenolphthalein or methyl orange.

Redox Titrations

In these titrations reactions are done using one oxidant and one reductant solution. Common oxidants are potassium dichromate and potassium permanganate in acidic medium.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O;$$

$$\text{equivalent mass} = \frac{\text{Molecular mass}}{6} = 49$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O;$$

$$\text{equivalent mass} = \frac{\text{Molecular mass}}{5} = 31.6$$

Common reductants are oxalic acid

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-;$$

$$\text{equivalent mass} = \frac{\text{Molecular mass}}{2}$$

and ferrous salts like ferrous ammonium sulphate.

$$\{FeSO_4\,(NH_4)_2SO_4.6H_2O\};$$

$$Fe^{2+} \rightarrow Fe^{3+} + 1e^-;$$

$$\text{equivalent mass} = \text{Molecular mass} = 392$$

In reactions involving dichromate, use potassium ferricyanide as external indicator or diphenylamine as internal indicator while potassium permanganate is self-indicator.

Iodometric titrations

In iodometric titrations, free iodine is liberated from postassium iodide by reacting it either with potassium dichromate in acidic medium

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2$$

or with copper sulphate $CuSO_4.5H_2O$

$2CuSO_4 + 4KI \rightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

Equivalent mass of $CuSO_4.5H_2O$ = molecular mass = 249 because in the reaction Cu^{2+} changes to Cu^+ .
The liberated iodine is then titrated with hypo or sodium thiosulphate solution using starch as indicator.

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$
Equivalent mass of $Na_2S_2O_3.5H_2O$ = molecular mass = 248
If iodine solution is used, then the titration is called iodimetric titration.

In calculations involving equivalent concept, it is useful to relate equivalent mass to molecular mass of the compound. The molecular mass is always same and can be calculated from its formula but the equivalent mass of same substance may be different in different reactions.
Therefore, while correlating equivalent mass to molecular mass, it is necessary to find how the substance is reacting. If it is reacting as acid or base then the molecular mass is to be divided by basicity or acidity of the substance to get the equivalent mass.
Alternately, if it is reacting as oxidant or reductant, the molecular mass is divided by change in oxidation number per mole to get the equivalent mass.
In case same substance behaves differently in different reactions, its equivalent mass may be different. Some examples are given below to explain the point.

$KMnO_4$
Formula mass = 158

It reacts in acidic medium as oxidant according to the equation.

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Change in oxidation number is 5 and hence its

$\text{Equivalent mass} = \frac{\text{Molecular mass}}{5} = 31.6$

In neutral medium, it reacts as oxidant but according to reaction

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

$\text{Hence, equivalent mass} = \frac{\text{Molecular mass}}{3} = 52.66$

In alkaline medium, the half reaction as oxidant is

$MnO_4^- + 1e^- \rightarrow MnO_4^{2-}$

$K_2Cr_2O_7$
Formula mass = 294
Acts as oxidant in acidic medium only according to half reaction.
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Though the change in oxidation state of chromium is only 3 (from +6 to +3), since there are two chromium atoms in $Cr_2O_7^{2-}$, the $\text{equivalent mass} = \frac{\text{molecular mass}}{6} = 49$.
In alkaline medium, $K_2Cr_2O_7$ does not usually act as oxidant. When it acts as

oxidising agent, it acts in the form of CrO_4^{2-}.

$$Cr_2O_7^{2-} + 2OH^{2-} \rightarrow 2CrO_4^{2-} + H_2O$$

However, if $K_2Cr_2O_7$ has to behave as a salt,

$$\text{its equivalent mass} = \frac{\text{Molecular mass}}{2} = 147$$

Mohr's salt

$FeSO_4.(NH_4)_2SO_4.6H_2O$

Formula mass = 392

As a reductant, the half reaction is

$$Fe^{2+} \rightarrow Fe^{3+} + 1e^-$$

$$\text{and equivalent mass} = \frac{\text{Formula mass}}{1} = 392$$

If it has to behave as a salt then

$$\text{Its equivalent mass} = \frac{\text{Formula mass}}{4} = 98$$

H_2O_2

Molecular mass = 34

May behave both as oxidant or reductant

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \text{ (Oxidant)}$$

$$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$$

(Reductant)

$$\text{In either case equivalent mass} = \frac{\text{Molecular mass}}{2} = 17$$

Oxalic acid

$$\begin{array}{l} COOH \\ | \\ COOH.2H_2O \end{array}$$

Molecular mass = 126

May behave as acid (has two replaceable hydrogen) or as reductant according to

$$\begin{array}{l} COO^- \rightarrow 2CO_2 + 2e^- \\ | \\ COO^- \end{array}$$

$$\text{In either case, equivalent mass} = \frac{\text{Formula mass}}{2} = 63$$

Monosodium oxalate

$$\begin{array}{l} COONa \\ | \\ COOH \end{array}$$

Molecular mass = 112

As an acid it has only one replaceable hydrogen.

$$\therefore \text{Equivalent mass} = \frac{\text{Molecular mass}}{1} = 112$$

As reductant the half reaction is

$$\begin{array}{l} COO^- \rightarrow 2CO_2 + 2e^- \\ | \\ COO^- \end{array}$$

So equivalent mass = $\frac{\text{Molecular mass}}{2}$ = 56

Hydrazine

NH_2NH_2

Molecular mass = 32

May behave as a diacid base.

Then equivalent mass = $\frac{\text{Molecular mass}}{2}$ = 16

or may act as reductant according to the reaction

$$NH_2NH_2 \rightarrow N_2 + 4H^+ + 4e^-$$

Then equivalent mass = $\frac{\text{Molecualr mass}}{4}$ = 8

$CuSO_4.5H_2O$

Formula mass = 249

In Iodometry the equation as oxidant is

$$Cu^{2+} + 1e^- \rightarrow Cu^+$$

and equivalent mass = $\frac{\text{Formula mass}}{1}$ = 249

but as salt,equivalent mass = $\frac{\text{Formula mass}}{2}$ = 124.5

Hypo

$Na_2S_2O_3.5H_2O$

Formula mass = 248

As reductant it reacts as

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$$

and equivalent mass = $\frac{\text{Formula mass}}{1}$ = 248

because 2 mol electrons are given out by 2 mole $S_2O_3^{2-}$ ion. Change in oxidation number of S is + 0.5 only but as there are two S atoms, the change in oxidation number is +1 per mole.

If it reacts as a salt then

Equivalent mass = $\frac{\text{Molecular mass}}{2}$ = 124

KIO_3

Formula mass = 214

May behave as an oxidant in several ways

e.g. $2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$

Change in oxidation number is 5 per mole

$\therefore$ Equivalent mass = $\frac{\text{Formula mass}}{5}$ = 42.8

e.g. $IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$

Change in oxidation number is 6 hence

$$\text{Equivalent mass} = \frac{\text{Formula mass}}{6} = 35.67$$

or $IO_3^- + HCl + 5H^+ + 4e^- \rightarrow ICl + 3H_2O$

Here the change in oxidation number is only 4 hence

$$\text{Equivalent mass} = \frac{\text{Formula mass}}{4} = 53.5$$

In chemical calculation when you find the same substance involved in several reactions then you must check the category of each reaction and ascertain if there is a change in the equivalent mass of the substance.

In such cases it is always advisable to change the equivalents (or milliequivalents) to moles (or millimole) after each reaction and then again change the moles (or millimoles) to equivalents (or milliequivalents) depending on the reaction. This may be done for each successive reaction.

Solved examples

Example

Find equivalent mass of substances from data given:

(a) Chloride of a metal contains 60.68% chlorine. Find its equivalent mass.

(b) 0.2 g of an acid is completely neutralised by 80 mL N/10 base. Find the equivalent mass of acid.

(c) Compound MX_2 (molecular mass = 160) on oxidation gives MO_2 and XO. Find the equivalent mass of MX_2.

(d) 5 ampere current when passed for 3.2167 minutes deposits 0.25 g of a metal from its solution. Find the equivalent mass of metal.

(e) Silver salt of an acid contains 64.67% silver. Find the equivalent mass of acid.

(f) 1.64 g. of a metal nitrate on heating leaves a residue of 0.56 g of metal oxide. Find the equivalent mass of metal.

Solution

(a) Equivalent mass of metal is that mass which combines with 35.5 g of chlorine

60.68 g Cl combines with 100 – 60.68 = 39.32 g metal

$$\therefore 35.5 \text{ g Cl will combine with } \frac{39.32 \times 35.5}{60.68} = 23 \text{ g metal}$$

Equivalent mass of metal = 23

(b) Acid and base have equal number of equivalents or mass equivalent at neutralisation point

meq of Base ≡ meq of Acid

$$80 \times \frac{1}{10} = 8$$

One equivalent has 1000 meq.

8 meq of acid weigh 0.2 g

$$\therefore 1000 \text{ meq of acid will weigh} = \frac{0.2 \times 1000}{8} = 25 \text{ g}$$

Equivalent mass of acid = 25

(c) Equivalent mass of substance is that mass which combines or displaces 8 g O_2.

$MX_2 + 2O_2 \rightarrow MO_2 + 2XO$

160 g   2x32 g

2×32 g oxygen combines with 160 g substance

$\therefore$ 8 g oxygen will combine with $\frac{160 \times 8}{2 \times 32} = 20$ g substance

Equivalent mass of MX_2 in the reaction = 20

(d) Equivalent mass of substance is the mass deposited by 96500 coulomb.

Charge = $5 \times 3.2167 \times 60 = 965$ C

965 C deposits 0.25 g of metal

$\therefore$ 96500 C will deposit $\frac{0.25 \times 96500}{965}$ = 25 g of metal

Equivalent mass of metal = 25

(e) $\frac{\text{mass of Ag Salt}}{\text{Equivalent mass of Ag Salt}} = \frac{\text{mass of Silver}}{\text{Equivalent mass of silver}}$

$\frac{100}{\text{Equivalent mass of salt}} = \frac{64.67}{108}$

$\therefore$ Equivalent mass of Ag Salt = 167

Ag salt is formed by the reaction

$HA + AgNO_3 \rightarrow HNO_3 + A\ Ag$

If E is the equivalent mass of acid then equivalent mass of silver salt will be $E - 1 + 108 = E + 107 = 167$

$\therefore E = 167 - 107 = 60$

Equivalent mass of acid = 60

(f) $\frac{\text{Mass of metal nitrate}}{\text{Equivalent mass of metal nitrate}} = \frac{\text{Mass of metal oxide}}{\text{Equivalent mass of metal oxide}}$

If x is the equivalent mass of metal, and that of oxygen and nitrate is 8 and 62 respectively, then,

$\frac{1.64}{x + 62} = \frac{0.56}{x + 8}$

$x = 20$

The equivalent mass of metal is 20

Example

1 L N/40 NaOH, 50 mL N/20 HCl and 50 mL M/5 H_2SO_4 are mixed. Find whether the resultant solution will be acidic, basic or neutral. Also find the normality of resultant solution assuming no change in volume on mixing the solutions.

Solution

No. of meq of NaOH = $\frac{1}{40} \times 1000 = 25$ meq

No. of meq of HCl = $50 \times 1/20 = 2.5$ meq

No. of meq of H_2SO_4 $(M/5 = N/2.5) = 50 \times 1/2.5 = 20$

Total meq of Acid = 20 + 2.5 = 22.5 meq

Since alkali is in excess, its meq left after reaction =

= 25 – 22.5 = 2.5 meq

Normality of alkali in resultant solution =

$$= \frac{\text{meq}}{\text{Total Volume}} = \frac{2.5}{50 + 50} = \frac{1}{40}$$

Hence resulting solution will be alkaline and its normality

= N / 40

Example

2.67 g of a metal chloride was found to contain 2.13 g of chlorine. The same metal forms a bromide whose vapour density is 133.5. Calculate the atomic mass and valency of the metal.

Solution

2.13 g chlorine combines with (2.67 – 21.3) g metal

$$\therefore 35.5 \text{ g chlorine combines with} = \frac{0.54 \times 35.5}{2.13} \text{ g metal}$$

= 9 g metal

Hence, equivalent mass of metal is 9 g. If the valency of metal is n then its atomic mass will be $9n$. Formula of its metal bromide will be MBr_n.

Or

$9n + n\,Br = 2 \times$ Vapour Density

$9n + 80n = 2 \times 133.5$

So, $n = 3$

Hence atomic mass

= valency × equivalent mass = 3×9

= 27

Example

A 1 g sample of hydrogen peroxide solution containing x% of it by mass requires x mL of $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of $KMnO_4$ solution.

Solution

$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$;

Equivalent mass of H_2O_2

$$= \frac{\text{Molecular mass}}{2} = 17$$

meq of $H_2O_2 = \frac{x}{17} \times \frac{1}{100} \times 1000$ (since it contains x in 100 g)

and meq of $KMnO_4 = N \times x$ (where N = Normality of $KMnO_4$)

$\therefore x/17 \times 1/100 \times 1000 = N \times x$

Or N = 10/17 = 0.588 N

Example

A 1.1 g sample of an organic compound containing nitrogen was digested with H_2SO_4. The resulting clear solution was boiled with NaOH and the ammonia evolved was absorbed in 60 mL of 0.09M H_2SO_4. The excess acid required 10 mL of 0.04N NaOH for complete neutralisation. Find the percentage of nitrogen in the compound.

Solution

meq of acid taken = 60 $\times$ 0.09 $\times$ 2 = 10.8

Since normality of H_2SO_4 = molarity $\times$ 2

meq of acid left = meq of NaOH used = $10 \times 0.04 = 0.4$

meq of acid used = $10.8 - 0.4 = 10.4$

meq of NH_3 = meq of N

$$\therefore \text{mass of N in 1.0 g compound} = \frac{10.4 \times 14}{1000} = 0.1456\text{ g}$$

$$\text{percentage of nitrogen} = \frac{0.1456 \times 100}{1.1} = 13.24\%$$

Example

How many grams of $KMnO_4$ should be taken to make 250 mL of a solution so that 1 mL of this solution completely oxidises 0.05 g of iron present as $FeSO_4$ in acidic medium?

Solution

meq of iron = 0.05/56 $\times$ 1000 = 0.8929

Hence, meq of $KMnO_4$ required in 1 mL = 0.8929

No. of meq required in 250 mL = 0.8929 $\times$ 250 = 223.225

Mass of $KMnO_4$ = 223.225/1000 $\times$ 31.6 = 7.05 g

Example

0.5 g of an impure sample of iron was dissolved in 100 mL sulphuric acid. 25 mL of this solution required 40 mL of a $K_2Cr_2O_7$ solution for complete oxidation. The iodine liberated by reacting excess KI with 30 mL of this dichromate solution required 50 mL of 0.027N $Na_2S_2O_3$ solution. Find the percentage purity of iron sample (Fe = 56).

Solution

meq of $Na_2S_2O_3$ solution = 50 $\times$ 0.027 = 1.35 meq of $K_2Cr_2O_7$ in 30 mL

$\therefore$ meq of $K_2Cr_2O_7$ in 40 mL = $1.35 \times 40/30 = 1.8$

= meq in 25 mL of iron solution

$\therefore$ meq of iron in 100 mL = $1.8 \times 100/25 = 7.2$

equivalent mass of iron = molecular mass because $Fe^{2+} \rightarrow Fe^{3+}$

mass of iron = $7.2 \times 56/1000 = 0.4032$ g

$\therefore$ % Purity of sample = $0.4032 \times 100/0.5 = 80.6\%$

Example

A 25 mL solution of ferrous salt was diluted to 100 mL with dilute acid. If one half of this solution required 30 mL M/100 solution of $KMnO_4$ for oxidation in acidic medium. If another half is titrated with M/100 $K_2Cr_2O_7$ solution what will be the volume of $K_2Cr_2O_7$ required?

Solution

meq of $KMnO_4$ used = 30 $\times$ 1/100 $\times$ 5

(since equivalent mass = molecular mass/5)

= 1.5 meq of Fe^{2+} in 50 mL

meq of $K_2Cr_2O_7$ required = 1.5
and volume x N = 1.5 (For $K_2Cr_2O_7$ equivalent mass = molecular mass/6
So N = 6/100)
V = 1.5 $\times$ 100/6 = 25 mL