

Stoichiometric Calculations

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

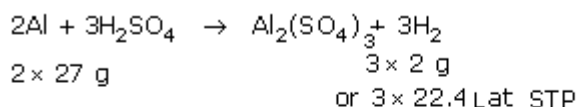
A balanced chemical equation may be used for calculation of the mass of reactants or products (or, in case of gases, volume may be calculated). It is also possible to calculate percentage purity of a substance or overall percentage yield, etc. Some examples are given below to illustrate the use of stoichiometric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

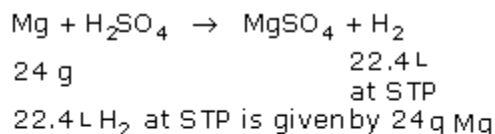


$$\begin{aligned} \text{Hence, 0.9 g Al will liberate } & \frac{3 \times 2 \times 0.9}{2 \times 27} = 0.1 \text{ g} \\ & \text{or } \frac{3 \times 22.4 \times 0.9}{2 \times 27} = 1.12 \text{ L H}_2 \text{ at STP} \end{aligned}$$

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:



$$\text{Hence 0.896 L H}_2 \text{ will be given by } \frac{24 \times 0.896}{22.4} = 0.96 \text{ g Mg}$$

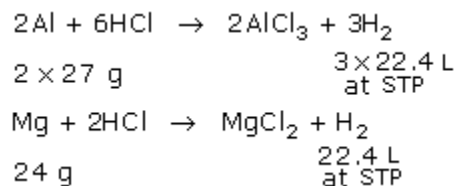
$$\% \text{ Purity of Mg} = \frac{0.96 \times 100}{1} = 96\%$$

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



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

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

or x = 0.59 g Al

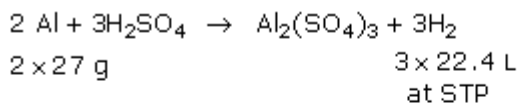
Mass of Mg = 0.41 g

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.



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

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

Hence % Al = 54%

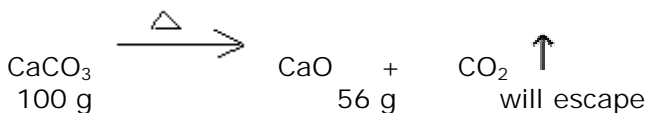
and % Cu = 100 - 54 = 46 %.

Example

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



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

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

$$\Rightarrow x = 0.75$$

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

Example

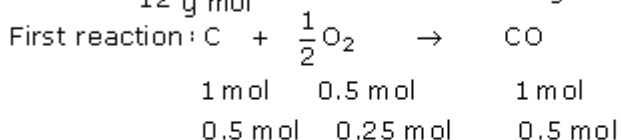
When 6.0 g of carbon reacts with 10 g of oxygen only gaseous products are formed.

Find the moles and mass of each of the product formed.

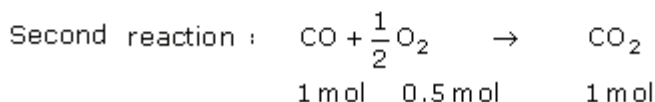
Solution

First, C reacts with O₂ to form CO, and then, any remaining O₂ reacts with CO to form CO₂.

We have $\frac{6 \text{ g}}{12 \text{ g mol}^{-1}} = 0.5 \text{ mol C}$ and $\frac{10 \text{ g}}{32 \text{ g mol}^{-1}} = 0.3125 \text{ mol O}_2$



O₂ left = 0.3125 - 0.25 = 0.0625 mol



0.5 mol CO requires 0.25 mol O₂ for complete conversion to CO₂ but here oxygen is only 0.0625 mol (limiting reagent) and hence only $2 \times 0.0625 = 0.125 \text{ mol CO}$ will react.

CO left = 0.5 - 0.125 = 0.375 mol

CO₂ formed = 0.125 mol

mass of CO = 0.375 \times 28 = 10.5 g

mass of CO₂ = 0.125 \times 44 = 5.5 g

Example



Chromium is produced by the reaction

If 100 g Al and 100 g Cr₂O₃ 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 = $\frac{100 \text{ g}}{27 \text{ g mol}^{-1}} = 3.7037 \text{ mol}$

Moles of Cr₂O₃ = $\frac{100 \text{ g}}{152 \text{ g mol}^{-1}} = 0.6579 \text{ mol}$

For one mole of Cr₂O₃ two moles of Al are required. So according to moles given, Al is in excess and Cr₂O₃ is in the limiting quantity.

Therefore, calculations must be based on the amount of Cr₂O₃.

0.6579 mol of Cr₂O₃ will react with $2 \times 0.6579 = 1.3158 \text{ mol}$ of Al leaving 2.3879 mol of Al unreacted and 1.3158 mol of Cr will be formed.

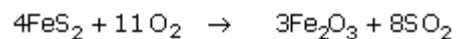
Mass of Cr formed (atomic mass = 52) = $1.3158 \times 52 = 68.4216 \text{ g}$

Example

What amount of H₂SO₄ in moles could be obtained from 1000 g of pure iron pyrites, FeS₂?

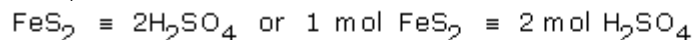
Solution

The equations involved are



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,



$$\text{Number of moles of FeS}_2 = \frac{\text{mass}}{\text{Molecular mass}} = \frac{1000 \text{ g}}{120 \text{ g mol}^{-1}} = 8.33 \text{ moles}$$

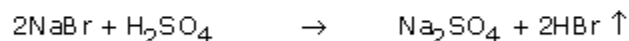
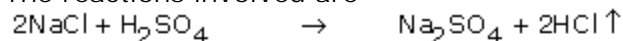
$$\text{Hence, amount of H}_2\text{SO}_4 \text{ produced} = 2 \times 8.33 \text{ mol} = 16.66 \text{ mol.}$$

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



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

$$2 \times 58.5 \text{ g NaCl gives } 142 \text{ g Na}_2\text{SO}_4$$

$$x \text{ g NaCl will give} = \frac{142 \times x}{2 \times 58.5} \text{ g Na}_2\text{SO}_4$$

$$2 \times 103 \text{ g NaBr gives } 142 \text{ g Na}_2\text{SO}_4$$

$$\therefore (1 - x) \text{ g NaBr will give} = \frac{142(1 - x)}{2 \times 103} \text{ g Na}_2\text{SO}_4$$

$$\text{Total mass of Na}_2\text{SO}_4 = \frac{142x}{2 \times 58.5} + \frac{142(1 - x)}{2 \times 103} = 1 \text{ g (mass of mixture)}$$

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

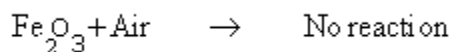
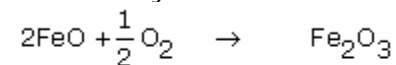
Hence, percentage composition of NaCl = 59.2 % and of NaBr = 40.8 %.

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.



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 $= \frac{105 \times 1}{100} = 1.05 \text{ g}$

Then, the mass of Fe₂O₃ produced from x g FeO $= \frac{160 \times x}{2 \times 72} \text{ g}$

Mass of Fe₂O₃ = (1 - x) g.

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

Final mass = or x = 0.45 g

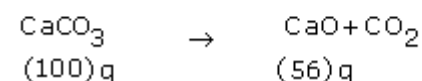
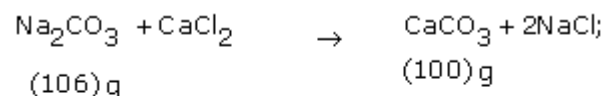
Hence the mixture contains 45% FeO and 55% Fe₂O₃

Example

A 1.205 g impure sample of Na₂CO₃ was dissolved and reacted with excess CaCl₂. The precipitate obtained was ignited and the weight of residue obtained was 0.56 g. Calculate the percentage purity of Na₂CO₃.

Solution

The reactions involved are



The residue obtained is of CaO. The number of moles of CaO = $\frac{0.56 \text{ g}}{56 \text{ g mol}^{-1}} = 0.01 \text{ mol}$

From balanced equation

1 mol CaO \equiv 1 mol CaCO₃ \equiv 1 mol Na₂CO₃

0.01 mol \equiv 0.01 mol \equiv 0.01 mol

Hence, number of moles of Na₂CO₃ present = 0.01 mol

and 0.01 x 106 g = 1.06 g

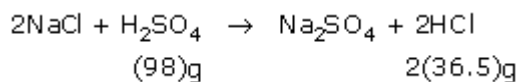
\therefore Percentage purity = $\frac{1.06 \times 100}{1.205} = 87.97\%$ Ans.

Example

How much H₂SO₄ (containing 70% by mass) is required for the production of 1000 g of HCl (containing 40% by mass) by reaction of H₂SO₄ with NaCl ?

Solution

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



The reaction involved:

Amount of H_2SO_4 required to produce 400 g HCl

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

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

$$\frac{98 \times 400}{2 \times 36.5} \text{ g of pure } \text{H}_2\text{SO}_4 \text{ will make } \frac{100 \times 98 \times 400}{2 \times 36.5 \times 70} \text{ g 70\% } \text{H}_2\text{SO}_4$$

$$= 767.1 \text{ g of 70\% } \text{H}_2\text{SO}_4.$$

Example

1 g sample of KClO_3 was heated so that part of it decomposed as $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$ and the remaining part as $4\text{KClO}_3 \rightarrow 3\text{KClO}_4 + \text{KCl}$. 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



$$2(122.5) \quad 2(74.5) \quad 3(32)$$

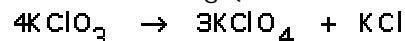
2×122.5 g KClO_3 gives 3×32 g oxygen

$$\therefore x \text{ g } \text{KClO}_3 \text{ will give } = \frac{3 \times 32 \times x}{2 \times 122.5} \text{ g oxygen}$$

or

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

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



$$4(122.5) \quad 3(138.5) \quad 2(74.5)$$

The remaining mass i.e. $1 - 0.539 = 0.4641$ g decomposes to KClO_4 and KCl.

4×122.5 g KClO_3 gives 3×138.5 g KClO_4 .

$$\therefore 0.4641 \text{ g } \text{KClO}_3 \text{ will give } \frac{3 \times 138.5 \times 0.4641}{4 \times 122.5} \text{ g } \text{KClO}_4$$

$$= 0.3935 \text{ g } \text{KClO}_4$$

Mass of residue = Original mass - mass of oxygen

$$= 1 - 0.21 = 0.79 \text{ g}$$

$$\therefore \text{Percentage of } \text{KClO}_4 \text{ in the residue} = \frac{0.3935 \times 100}{0.79}$$

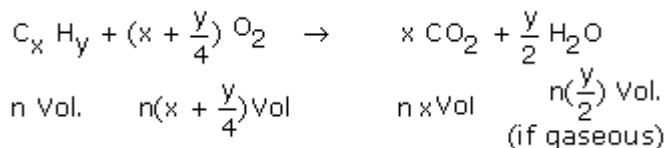
$$= 49.8\%$$

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:

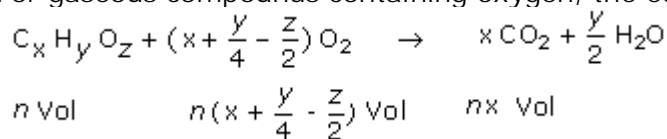


This volume relation follows from Avogadro's law

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.

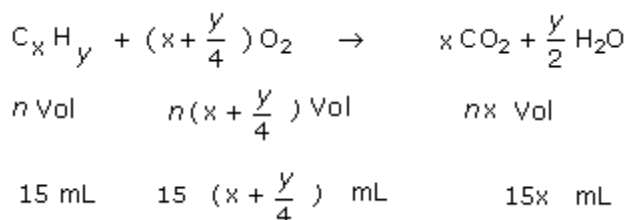
For gaseous compounds containing oxygen, the equation becomes:



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



$$\text{Volume absorbed by KOH} = \text{Volume of } CO_2 = 75 - 30 = 45 \text{ mL} = 15x$$

$$\therefore x = 3$$

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

$$\text{when } x = 3, \quad y = 8$$

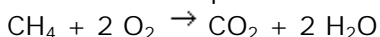
Hence, molecular formula of hydrocarbon is C_3H_8

Example

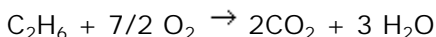
50 mL of a mixture of methane and ethane was exploded with excess oxygen. After explosion and cooling, the remaining gases were treated with NaOH solution when a reduction of 60 mL in volume was observed. All measurements were done under identical conditions. Calculate the percentage composition of the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

Solution

The relevant equations are



x vol x vol



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

Reduction in volume with NaOH = volume of CO_2

$$\text{or, } x + 2(50 - x) = 60$$

$$\text{or, } x = 40$$

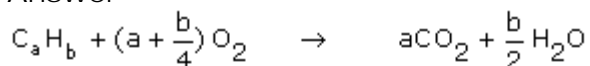
$$\text{percentage methane by volume} = 40/50 \times 100 = 80\%$$

$$\text{and percentage ethane by volume} = 20\%.$$

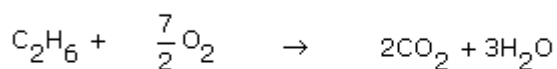
Example

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



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



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

$$\text{Volume of } \text{CO}_2 \text{ formed} = xa + (10 - x)2 = 15 \text{ mL}$$

$$\begin{aligned} \text{Volume of } \text{O}_2 \text{ used} &= x(a + \frac{b}{4}) + (10 - x)\frac{7}{2} \\ &= 50 - (37.5 - 15) = 27.5 \text{ mL} \end{aligned}$$

Since the hydrocarbons are present in equal ratio

$$x = 5 \text{ and } 10 - x = 5$$

$$\text{So, } 5a + 5 \times 2 = 15$$

$$\text{So } a = 1$$

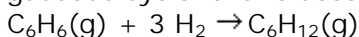
$$\text{and } 5(1 + \frac{b}{4}) + 5 \times \frac{7}{2} = 27.5$$

$$\text{So, } b = 4$$

Hence unknown hydrocarbon is CH_4 .

Example

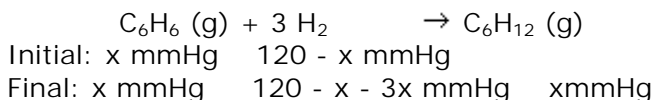
Gaseous benzene reacts with hydrogen gas in the presence of nickel catalyst to form gaseous cyclohexane according to the reaction.



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.



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

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

Equivalent mass

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

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 \times 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.

$N = \text{Mass of solute in g per litre} / \text{Equivalent mass}$

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

$$= \text{Number of equivalents and Normality} \times \text{Volume in mL}$$

$$= \text{Number of milliequivalents}$$

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

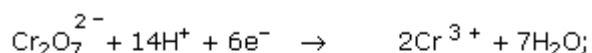
It is determined experimentally by titrating a known volume of unknown solution against a standard solution using an indicator to show the completion of the reaction.

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.

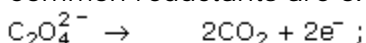


$$\text{equivalent mass} = \frac{\text{Molecular mass}}{6} = 49$$



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

Common reductants are oxalic acid



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

and ferrous salts like ferrous ammonium sulphate.

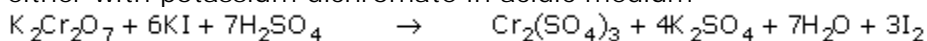


$$\text{equivalent mass} = \text{Molecular mass} = 392$$

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 potassium iodide by reacting it either with potassium dichromate in acidic medium

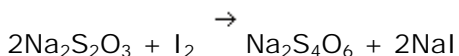


or with copper sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$



Equivalent mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 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.



Equivalent mass of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ = 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.

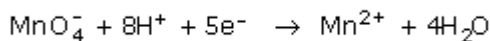
Alternately, if it is reacting as oxidant or reductant, the molecular mass is divided by change in oxidation number per mole to get the equivalent mass.

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

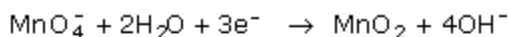
It reacts in acidic medium as oxidant according to the equation.



Change in oxidation number is 5 and hence its

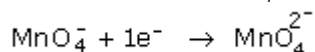
$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{5} = 31.6$$

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



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

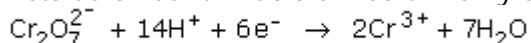
In alkaline medium, the half reaction as oxidant is



$\text{K}_2\text{Cr}_2\text{O}_7$

Formula mass = 294

Acts as oxidant in acidic medium only according to half reaction.

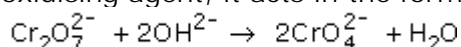


Though the change in oxidation state of chromium is only 3 (from +6 to +3), since

there are two chromium atoms in $\text{Cr}_2\text{O}_7^{2-}$, the equivalent mass = $\frac{\text{molecular mass}}{6} = 49$.

In alkaline medium, $\text{K}_2\text{Cr}_2\text{O}_7$ does not usually act as oxidant. When it acts as

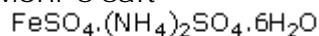
oxidising agent, it acts in the form of CrO_4^{2-} .



However, if $\text{K}_2\text{Cr}_2\text{O}_7$ has to behave as a salt,

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

Mohr's salt



Formula mass = 392

As a reductant, the half reaction is



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

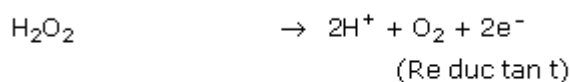
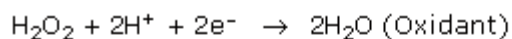
If it has to behave as a salt then

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

H_2O_2

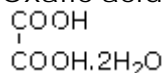
Molecular mass = 34

May behave both as oxidant or reductant



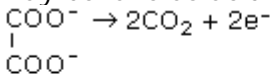
$$\text{In either case equivalent mass} = \frac{\text{Molecular mass}}{2} = 17$$

Oxalic acid



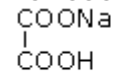
Molecular mass = 126

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



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

Monosodium oxalate

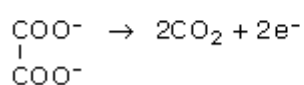


Molecular mass = 112

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



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

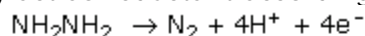
Hydrazine
 NH_2NH_2

Molecular mass = 32

May behave as a diacid base.

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

or may act as reductant according to the reaction

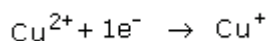


$$\text{Then equivalent mass} = \frac{\text{Molecular mass}}{4} = 8$$

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Formula mass = 249

In Iodometry the equation as oxidant is



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

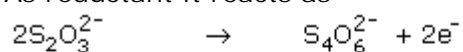
$$\text{but as salt, equivalent mass} = \frac{\text{Formula mass}}{2} = 124.5$$

Hypo

$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

Formula mass = 248

As reductant it reacts as



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

because 2 mol electrons are given out by 2 mole $\text{S}_2\text{O}_3^{2-}$ 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.

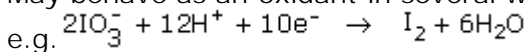
If it reacts as a salt then

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

KIO_3

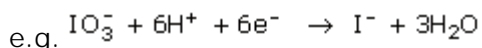
Formula mass = 214

May behave as an oxidant in several ways



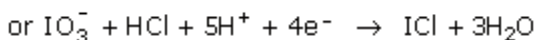
Change in oxidation number is 5 per mole

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



Change in oxidation number is 6 hence

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



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:

- Chloride of a metal contains 60.68% chlorine. Find its equivalent mass.
- 0.2 g of an acid is completely neutralised by 80 mL N/10 base. Find the equivalent mass of acid.
- Compound MX_2 (molecular mass = 160) on oxidation gives MO_2 and XO . Find the equivalent mass of MX_2 .
- 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.
- Silver salt of an acid contains 64.67% silver. Find the equivalent mass of acid.
- 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

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

$$\text{Equivalent mass of metal} = 23$$

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

$$\text{meq of Base} = \text{meq of Acid}$$

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

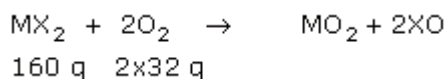
One equivalent has 1000 meq.

8 meq of acid weigh 0.2 g

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

$$\text{Equivalent mass of acid} = 25$$

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



$2 \times 32 \text{ g}$ oxygen combines with 160 g substance

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

Equivalent mass of MX_2 in the reaction = 20

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

$$\text{Charge} = 5 \times 3.2167 \times 60 = 965 \text{ C}$$

965 C deposits 0.25 g of metal

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

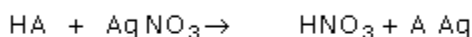
Equivalent mass of metal = 25
coulomb.

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

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

$$\therefore \text{Equivalent mass of Ag Salt} = 167$$

Ag salt is formed by the reaction



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

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

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

$$\text{No. of meq of H}_2\text{SO}_4 \text{ (M/5 = N/2.5)} = 50 \times 1/2.5 = 20$$

$$\text{Total meq of Acid} = 20 + 2.5 = 22.5 \text{ meq}$$

$$\begin{aligned} \text{Since alkali is in excess, its meq left after reaction} &= \\ &= 25 - 22.5 = 2.5 \text{ meq} \end{aligned}$$

$$\text{Normality of alkali in resultant solution} =$$

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

$$\begin{aligned} \text{Hence resulting solution will be alkaline and its normality} & \\ = \text{N/40} \end{aligned}$$

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

$$2.13 \text{ g chlorine combines with } (2.67 - 2.13) \text{ g metal}$$

$$\begin{aligned} \therefore 35.5 \text{ g chlorine combines with} &= \frac{0.54 \times 35.5}{2.13} \text{ g metal} \\ &= 9 \text{ g metal} \end{aligned}$$

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

$$9n + n\text{Br} = 2 \times \text{Vapour Density}$$

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

$$\text{So, } n = 3$$

Hence atomic mass

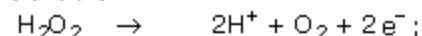
$$= \text{valency} \times \text{equivalent mass} = 3 \times 9$$

$$= 27$$

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



Equivalent mass of H_2O_2

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

$$\text{meq of H}_2\text{O}_2 = \frac{x}{17} \times \frac{1}{100} \times 1000 \text{ (since it contains } x \text{ in } 100 \text{ g)}$$

$$\text{and meq of KMnO}_4 = N \times x \text{ (where } N = \text{Normality of KMnO}_4\text{)}$$

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

$$\text{Or } N = 10/17 = 0.588 \text{ N}$$

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

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

$$\text{Since normality of } \text{H}_2\text{SO}_4 = \text{molarity} \times 2$$

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

$$\text{meq of acid used} = 10.8 - 0.4 = 10.4$$

$$\text{meq of } \text{NH}_3 = \text{meq of N}$$

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

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

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

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

$$\text{Hence, meq of } \text{KMnO}_4 \text{ required in 1 mL} = 0.8929$$

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

$$\text{Mass of } \text{KMnO}_4 = 223.225/1000 \times 31.6 = 7.05 \text{ g}$$

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 $\text{K}_2\text{Cr}_2\text{O}_7$ solution for complete oxidation. The iodine liberated by reacting excess KI with 30 mL of this dichromate solution required 50 mL of 0.027N $\text{Na}_2\text{S}_2\text{O}_3$ solution. Find the percentage purity of iron sample ($\text{Fe} = 56$).

Solution

$$\text{meq of } \text{Na}_2\text{S}_2\text{O}_3 \text{ solution} = 50 \times 0.027 = 1.35 \text{ meq of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ in 30 mL}$$

$$\therefore \text{meq of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ in 40 mL} = 1.35 \times 40/30 = 1.8$$

$$= \text{meq in 25 mL of iron solution}$$

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

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

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

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

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 $\text{K}_2\text{Cr}_2\text{O}_7$ solution what will be the volume of $\text{K}_2\text{Cr}_2\text{O}_7$ required?

Solution

$$\text{meq of } \text{KMnO}_4 \text{ used} = 30 \times 1/100 \times 5$$

$$(\text{since equivalent mass} = \text{molecular mass}/5)$$

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

meq of $\text{K}_2\text{Cr}_2\text{O}_7$ required = 1.5

and volume \times N = 1.5 (For $\text{K}_2\text{Cr}_2\text{O}_7$ equivalent mass = molecular mass/6

So N = 6/100)

$V = 1.5 \times 100/6 = 25 \text{ mL}$