18 Quantitative Estimations

Determination of percentage analysis of elements in organic compounds or quantitative estimation of elements in organic compounds :

(1) Estimation of C and H : A known mass of organic compound is burnt in oxygen (Leibig method) and the products H_2O and CO_2 formed are absorbed in conc. H_2SO_4 and $KOH_{(aq.)}$ respectively. The percentage (%) are obtained using the formulae.

$$\% \text{ H} = \frac{2}{18} \times \frac{\text{mass of } H_2O}{\text{mass of organic compound}} \times 100$$

$$\% \text{ C} = \frac{12}{44} \times \frac{\text{mass of } CO_2}{\text{mass of organic compound}} \times 100$$

(2) Estimation of nitrogen :

(i) Duma's method :

$$\% \text{ N} = \frac{28 \times \text{volume of } N_2 \text{ at NTP} \times 100}{22400 \times \text{mass of organic compound}}$$

(ii) Kjeldahl's method :

$$\% \text{ N} = \frac{1.4\, N \times V}{\text{mass of organic compound}}$$

where $(N \times V)$, *i.e.*, Meq. of NH_3 given out during Kjeldahl's method measured in terms of Meq. of acid used for NH_3 neutralisation.

(3) Estimation of sulphur :

$$\% \text{ S} = \frac{32 \times \text{mass of } BaSO_4 \times 100}{233 \times \text{mass of organic compound}}$$

(4) Estimation of halogens : Carius method

$$\% \text{ Cl} = \frac{35.5 \times \text{mass of AgCl}}{143.5 \times \text{mass of organic compound}} \times 100$$

$$\% \text{ Br} = \frac{80 \times \text{mass of AgBr}}{188 \times \text{mass of O.C.}} \times 100$$

$$\% \text{ I} = \frac{127 \times \text{mass of AgI}}{235 \times \text{mass of O.C.}} \times 100$$

(5) Estimation of phosphorus :

$$\% \text{ P} = \frac{62}{222} \times \frac{\text{mass of } Mg_2P_2O_7}{\text{mass of O.C.}} \times 100$$

(6) Estimation of oxygen : There is no direct method for estimation of oxygen in organic compounds. It is usually calculated by the difference.

$$\% \text{ O} = 100 - [\% \text{ of all other elements in organic compound}]$$

Determination of empirical formula : The empirical formula of a molecule is determined using the % of elements present in it. Following method is adopted.

Element	%	Relative no. of atoms = % /atomic mass	Simplest ratio	Empirical formula

Relative no. of atoms : Divide the percentage of each element present in compound by its atomic mass. This gives the relative no. of atoms of element in molecule.

Simplest ratio : Find out lowest value of relative no. of atoms and divide each value of relative no. of atoms by this value to get simplest ratio of elements.

If the simplest ratio obtained are not complete integers, multiply them by a common factor to get integer values of simplest ratio.

Empirical formula : Write all constitutent atoms with their respective no. of atoms derived in simplest ratio. This gives empirical formula of compound.

Molecular formula : Molecular formula

$= n \times$ empirical formula where 'n' is the whole no. obtained by

$$n = \frac{\text{molar mass of compound}}{\text{empirical formula mass of compound}}$$

molar mass of organic compound can be determined by any method for which data is given.

Some of the methods to determine molar mass are given below:

(1) Victor Meyer's method (See Problem 2)
(2) Duma's method (See Problem 3)
(3) Hofmann's method (See Problem 4)
(4) Ebullioscopic method and cryoscopic method (See Problem 13)
(5) Lowering in vapour pressure method (See Problem 10)

(6) Silver salt method (See Problem 6)
(7) Platinic chloride method (See Problem 7)
(8) Volumetric method for acid and base (See Problem 12)

Platinic chloride method : The method is based on the principle that organic bases combine with H_2PtCl_6 to form insoluble chloroplatinate which on ignition leaves metallic Pt as residue.

$$B_2 + H_2PtCl_6 \longrightarrow B_2H_2PtCl_6 \xrightarrow{\Delta} Pt$$

where B represents a monoacid base.

Let x g of $B_2H_2PtCl_6$ gives a g Pt as residue

$$\text{Mole of } B_2H_2PtCl_6 = \text{mole of Pt}$$

$$\frac{x}{\text{Molar mass of } B_2H_2PtCl_6} = \frac{a}{\text{Atomic mass of Pt}}$$

or $$\frac{x}{2 \times \text{Eq. mass of base} + \text{Molar mass of } H_2PtCl_6} = \frac{a}{195}$$

or $$\frac{x}{2 \times \text{Eq. mass of } B + 410} = \frac{a}{195}$$

$\therefore$ $$\text{Eq. mass of } B = \frac{1}{2}\left[\frac{x(195)}{a} - 410\right]$$

$\therefore$ Molar mass of base = Eq. mass of base × acidity

• NUMERICAL PROBLEMS •

1. An O.C. contains C = 40%, H = 6.6% and rest oxygen. Find out empirical formula of O.C.
2. A volatile organic compound on analysis following Victor Meyer's experiment gave as:

   Mass of organic compound = 0.1133 g
   Volume of air displaced = 22.8 mL
   Temperature = 15°C
   Pressure = 750 mm
   Vapour pressure of H_2O = 13 mm at 15°C

   Calculate vapour density and molar mass of compound.
3. A Duma's bulb full of air weighs 22.567 g at 20°C and 755 mm pressure. Full of vapours of a substance at 120°C and 755 mm pressure it weighs 22.8617 g. The capacity of bulb is 200 mL. Find the molar mass of substance. The density of air is 0.00129 g/mL.
4. During Hofmann's experiment 0.2g of an unknown compound is vaporized under reduced pressure 70 cm at 127°C and occupies 20 mL. Calculate molar mass of compound.
5. Combustion of 0.42 g of a compound gave 0.924 g CO_2 and 0.243 g H_2O. Due to distillation of 0.208 g of the compound with NaOH, ammonia evolved required 30 mL of *N*/20 H_2SO_4 for complete neutralization. Calculate the percentage composition of compound.
6. 0.607 g of silver salt of a tribasic acid on combustion gave 0.37 g pure Ag. Calculate the molar mass of acid.
7. An organic compound gave the following data : 0.236 g yielded 0.528 g CO_2 and 0.324 g H_2O on combustion. 0.295 g of the compound gave 56 mL N_2 at NTP. The compound is a monoacid base. It's platinic chloride salt contains 36.93% platinum. Calculate the molecular formula of compound.
8. 0.32g of organic compound containing sulphur on treatment with conc. HNO_3 in a Carius tube and then with excess of $BaCl_2$ produced 0.233 g of $BaSO_4$. Determine % of S in compound.
9. In Kjeldahl's method, the gas evolved from 1.325 g sample of a fertilizer is passed into 50.0 mL of 0.2030 *N* H_2SO_4. 25.32 mL of 0.1980 *N* NaOH are required for the titration of unused acid. Calculate the percentage of nitrogen in fertilizer. **(Roorkee 1991)**
10. A non-volatile hydrocarbon has 5.6% hydrogen. When 3.0 g of hydrocarbon is dissolved in 100 g of benzene, the relative lowering vapour pressure of benzene is $1.306\times10^{-2}\,Nm^{-2}$. Determine the molecular formula of non-volatile hydrocarbon. **(Punjab CET 1990)**
11. A sample of gaseous hydrocarbon occupying 1.12 litre at NTP, completely burnt in air and produced 2.2 g of CO_2 and 1.8 g H_2O. Calculate the mass of compound taken and volume of O_2 at NTP required for its burning. Also calculate molecular formula of hydrocarbon.
12. An aromatic monobasic acid contains 68.87% C and 4.9% H. 0.610 g of the acid required 25 mL of *M*/10 diacidic base for neutralization. What is molecular formula of acid?
13. The freezing point constant of C_6H_6 is 4.90 K mol^{-1} kg and its melting point is 5.51°C. A solution of 0.816 g of compound (*A*) when dissolved in 7.5 g of C_6H_6 freezes at 1.59°C. The compound (*A*) has C = 70.58% and H = 5.88%. Determine the molar mass and molecular formula of (*A*).
14. A monobasic organic acid gave on combustion the following % compositions : C = 39.9%; H = 6.69%. Also 0.2565 g of silver salt of acid gave on ignition 0.1659 g of Ag. Calculate molecular formula of acid.
15. A carbon compound containing only carbon and oxygen has an approximately molar mass of 290 g mol^{-1}. On analysis it is found to contain 50% by mass of each element. What is molecular formula of the compound?
16. Compound of C, H and N contains the three elements in the ratio 9 : 1 : 3.5, calculate empirical formula. If the molar mass is 108 g mol^{-1}, calculate molecular formula.
17. An organic compound contains 69.4% C, 5.8% H. A sample of 0.303 g of this compound was analysed for nitrogen by Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.05 *M* H_2SO_4. The excess acid required 25 mL of 0.1 *M* NaOH for neutralization. Determine molecular formula of the compound, if its molar mass is 121 g mol^{-1}. Draw possible structures of this compound.
18. An O.C., $C_xH_{2y}O_y$ was burnt with twice the oxygen needed for complete combustion to produce CO_2 and H_2O. The hot gases when cooled at 0°C and 1 atm pressure measured 2.24 litre. The water collected during cooling was 0.9 g. The vapour pressure of pure water at 20°C is 17.5 mm of Hg and it reduces by 0.104 mm when 50 g of organic compound is dissolved in 1000 g of water. What is organic compound?
19. A monoacid organic base gave the following data on analysis:

    (a) 0.2790 g of the base gave 0.7920 g CO_2 and 0.1890 g H_2O.
    (b) 0.1163 g of the base gave 14 mL of dry N_2 at NTP.
    (c) 0.2980 g of platinic chloride left 0.0975 g Pt.

    Calculate the molecular formula of base.
20. 0.2060 g of an organic compound on combustion gave 18.8 mL of moist nitrogen at 17°C and 756 mm pressure. If the vapour tension at 17°C is 14.5 mm, find the percentage of nitrogen in compound.

21. The analysis of an organic compound gave the following data:

(a) 0.4020 g gave 0.6098 g and 0.2080 g of CO_2 and H_2O respectively.

(b) 1.01 g by Kjeldahl's method produced ammonia which was neutralized by 23.2 mL of *N*/2 HCl.

(c) 0.1033 g of compound gave 0.2772 g $BaSO_4$.

(d) 0.1015 g when vaporized in Victor Meyer's apparatus displaced 27.96 mL of air at 15°C and 766 mm pressure. Calculate molecular formula (P'_{H_2O} at 15°C = 16 mm).

22. An organic monoacid base has empirical formula C_3H_3NO. 0.0563 g of platinum was left from 0.1982 g of its platinate. Find the molecular formula and molar mass of base.

23. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon : 42.86%, hydrogen : 2.40%, nitrogen : 16.67%, and oxygen : 38.07%. (i) Calculate the empirical formula of the minor product. (ii) When 5.5 g of minor product is dissolved in 45 g of benzene, the boiling point of the solution is 1.84°C higher than that of pure benzene. Calculate the molar mass of the minor product and determine its molecular and structural formula.

(Molal elevation constant of benzene is 2.53 K kg mol^{-1}). **(IIT 1999)**

24. 0.15 g of an organic compound on estimation by Carius method gave 0.12 g of AgBr. What is the percentage of bromine in organic compound?

25. 0.147 g of an organic compound on estimation by Carius method gave 0.287 g of AgCl. What is the percentage of chlorine in organic compound?

26. A sample of 0.50 g of an organic compound was estimated by Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5 *M* H_2SO_4. The residual acid required 60 mL of 0.5 *M* NaOH for neutralisation. Find out the % of nitrogen in organic compound.

27. An organic compound contains 69% carbon and 4.8% hydrogen. If the remainder is oxygen calculate the mass of CO_2 and H_2O produced on complete combustion of its 0.2 g. Also calculate the mole of oxygen for complete combustion of one mole of this compound. Molar mass of organic compound is 122 g mol^{-1}.

SOLUTIONS (Numerical Problems)

1.

Element	%	%/Atomic mass	Relative no. of atoms	Simplest ratio
C	40	40/12	3.33	$\frac{3.33}{3.33}=1$
H	6.6	6.6/1	6.6	$\frac{6.6}{3.33}=2$
O	100−[40+6.6] = 53.4	53.4/16	3.33	$\frac{3.33}{3.33}=1$

$\therefore$ Empirical formula is $\mathbf{CH_2O}$.

2. Pressure of dry air displaced = 750 − 13 = 737 mm

Organic compound occupies the same volume in gaseous phase as air displaced.

Now, $PV=\frac{w}{M}RT$

$$\frac{737}{760}\times\frac{22.8}{1000}=\frac{0.1133}{M}\times 0.0821\times 288$$

$\therefore$ $M=\mathbf{121.16\ g\ mol^{-1}}$

Now, Vapour density $=\frac{\text{molar mass}}{2}=\frac{121.16}{2}=\mathbf{60.58}$

3. Assume mass of bulb = w'

$\therefore$ Mass of air in bulb = $(22.567-w')$ g

Pressure of air $=\frac{755}{760}$ atm

Volume of air $=\frac{200}{1000}$ litre

$T=293$ K

Molar mass of air = 0.00129 × 22400 = 28.90

using $PV=\frac{w}{M}RT$ for air

$$\frac{755}{760}\times\frac{200}{1000}=\frac{(22.567-w')}{28.90}\times 0.0821\times 293$$

$\therefore$ $w'=22.3282$ g

For vapours :

Mass of vapours = 22.8617 − 22.3282 = 0.5335 g

$P_{vapour}=\frac{755}{760}$ atm

Volume of vapours = 200 mL

$T=393$ K

Again by $PV=\frac{w}{M}RT$

$$\frac{755}{760}\times\frac{200}{1000}=\frac{0.5335}{M}\times 0.0821\times 393$$

$\therefore$ $M=\mathbf{86.64\ g\ mol^{-1}}$

4. $P=\frac{70}{76}$ atm, $V=\frac{20}{1000}$ litre, $T=400$ K, $w=0.2$ g

$\because$ $PV=\frac{w}{M}RT$

$$\frac{70}{76}\times\frac{20}{1000}=\frac{0.2}{M}\times 0.0821\times 400$$

$\therefore$ $M=\mathbf{356.55\ g\ mol^{-1}}$

5. We have, % of C $=\frac{12}{44}\times\frac{\text{mass of } CO_2}{\text{mass of compound}}\times 100$

$=\frac{12}{44}\times\frac{0.924}{0.42}\times 100=60\%$

% H $=\frac{2}{18}\times\frac{\text{mass of } H_2O}{\text{mass of compound}}\times 100$

$=\frac{2}{18}\times\frac{0.243}{0.42}\times 100=6.43\%$

% N $=\frac{1.4\,NV}{W}=\frac{1.4\times\frac{1}{20}\times 30}{0.208}=10.09\%$

% O = 100 − [% C + % H + % N]

= 100 − [60 + 6.43 + 10.09] = 23.48%

$\therefore$ C = **60%**, H = **6.43%**, N = **10.09%**, O = **23.48%**

6. Meq. of silver salt = Meq. of silver

$$\frac{0.607}{E}\times 1000=\frac{0.37}{108}\times 1000$$

$\therefore$ Eq. mass of silver salt = 177.2

$\because$ Tribasic acid and thus, valence = 3

$\therefore$ Molar mass of silver salt = 177.2 × 3 = 531.6

$\therefore$ Molar mass of acid = 531.6 − 3 × atomic mass of Ag + 3 × atomic mass of H

= 531.6 − 3 × 108 + 3 = **210.6**

7. % of C $=\frac{12}{44}\times\frac{\text{mass. of } CO_2}{\text{mass of O. C.}}\times 100$

$=\frac{12}{44}\times\frac{0.528}{0.236}\times 100=61.07\%$

% of H $=\frac{2}{18}\times\frac{\text{mass of } H_2O}{\text{mass of O. C.}}\times 100$

$=\frac{2}{18}\times\frac{0.324}{0.236}\times 100=15.25\%$

% of N $=\frac{28\times\text{volume of } N_2 \text{ at NTP}\times 100}{22400\times\text{mass of compound}}$

$=\frac{28\times 56\times 100}{22400\times 0.295}=23.73\%$

$\because$ Empirical formula can be derived as;

Element	Percentage	Relative no. of atoms	Simplest ratio
C	61.07	5.09	3
H	15.25	15.25	9
N	23.73	1.695	1

$\therefore$ Empirical formula is C_3H_9N and Empirical formula mass = 59

Now, Equivalent mass of base $=\frac{1}{2}\left[\frac{x}{a}\times 195-410\right]$

where, x = mass of $PtCl_4$ salt, a = mass of Pt residue

$=\frac{1}{2}\left[\frac{100\times 195}{36.93}-410\right]=59$

$\therefore$ Molar mass of base = 59 × acidity = 59 × 1 = 59 ($\because$ monoacid base)

$\therefore$ Molecular formula = $\mathbf{C_3H_9N}$

8. $\% \text{ of } S = \frac{32 \times \text{mass of } BaSO_4}{233 \times \text{mass of O.C.}} \times 100$

$= \frac{32 \times 0.233}{0.32 \times 233} \times 100 = \mathbf{10\%}$

9. Meq. of H_2SO_4 taken to absorb $NH_3 = 50 \times 0.2030$

Meq. of H_2SO_4 left after NH_3 absorption

= Meq. of NaOH used for $H_2SO_4 = 25.32 \times 0.1980$

∴ Meq. of H_2SO_4 used for NH_3

$= 50 \times 0.2030 - (25.32 \times 0.1980)$

or (NV) used for $NH_3 = 5.137$

∴ $\% N = \frac{1.4 \times NV}{\text{mass of substance}} = \frac{1.4 \times 5.137}{1.325} = \mathbf{5.43\%}$

10. (i) Molar mass of hydrocarbon can be derived by Raoult's law

$$\frac{P^\circ - P_s}{P^\circ} = \frac{w/m}{w/m + W/M}$$

$$1.306 \times 10^{-2} = \frac{3/m}{3/m + \frac{100}{78}} \quad \therefore m = 176.83$$

(ii) For empirical formula :

Element	Percentage	Relative no. of atoms	Simplest ratio
C	94.5	7.88	1.40 or 7
H	5.6	5.60	1.0 or 5

∴ Empirical formula is C_7H_5 and molecular formula is $(C_7H_5)_n$

Empirical formula mass = 89

∵ $n = \frac{\text{molar mass}}{\text{empirical formula mass}} = \frac{176.83}{89} \approx 2$

∴ Molecular formula $= (C_7H_5)_2 = \mathbf{C_{14}H_{10}}$

11. 1.12 litre of hydrocarbon occupies mole $= \frac{1.12}{22.4} = 0.05$

Mole of CO_2 formed $= \frac{2.2}{44} = 0.05$

Mole of H_2O formed $= \frac{1.8}{18} = 0.10$

Let the hydrocarbon be C_aH_b

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

∴ 1 mole of C_aH_b gives = a mole CO_2

∴ 0.05 mole of C_aH_b will give = $0.05\,a$ mole of CO_2

∴ $0.05a = 0.05 \quad \therefore a = 1$

∴ 1 mole of C_aH_b gives $= \frac{b}{2}$ mole H_2O

∴ 0.05 mole of C_aH_b will give $= 0.05 \times \frac{b}{2}$ mole H_2O

$= 0.05 \times \frac{b}{2} = 0.10 \quad \therefore b = 4$

∴ Hydrocarbon is $\mathbf{CH_4}$.

∴ Mass of 1.12 litre CH_4 at STP $= \frac{16 \times 1.12}{22.4} = \mathbf{0.8\ g}$

Also, $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

1 mole CH_4 requires $= 2 \times 32$ g O_2

∴ 0.05 mole CH_4 requires $= 2 \times 32 \times 0.05$

$= 3.2$ g O_2 = **2.24 litre O_2**

12.

Element	Percentage	Relative no. of atoms	Simplest ratio
C	68.87	5.74	3.5 or 7
H	4.9	4.9	3.0 or 6
O	26.23	1.64	1.0 or 2

∴ Empirical formula is $C_7H_6O_2$

Empirical formula mass = 122

Now molar mass of acid can be determined as :

Meq. of acid = Meq. of alkali used

$$\frac{0.610}{M/1} \times 1000 = 25 \times \frac{1}{10} \times 2$$

∴ $M = 122$ g mol^{-1}

∴ $n = \frac{\text{molar mass of acid}}{\text{empirical formula mass}} = \frac{122}{122} = 1$

∴ Molecular formula of compound

$= (C_7H_6O_2)_n = (C_7H_6O_2)_1$

$= \mathbf{C_7H_6O_2}$

13. $\Delta T = 5.51 - 1.59 = 3.92°$ C

(i) Molar mass of compound $(A) = \frac{1000K'_f \times w}{\Delta T \times W}$

$= \frac{1000 \times 4.9 \times 0.816}{7.5 \times 3.92} = \mathbf{136}$

(ii) For empirical formula

Element	Percentage	Relative no. of atoms	Simplest ratio
C	70.58	$\frac{70.58}{12} = 5.88$	$\frac{5.88}{1.47} = 4$
H	5.88	$\frac{5.88}{1} = 5.88$	$\frac{5.88}{1.47} = 4$
O	$100 - (70.58 + 5.88) = 23.54$	$\frac{23.54}{16} = 1.47$	$\frac{1.47}{1.47} = 1$

∴ Empirical formula is C_4H_4O

Empirical formula mass = 68

Molar mass of $(A) = 136$

∴ Molecular formula of $(A) = (C_4H_4O)_n$

∵ $n = \frac{\text{molar mass}}{\text{empirical formula mass}} = \frac{136}{68} = 2$

∴ Molecular formula of $(A) = (C_4H_4O)_2 = \mathbf{C_8H_8O_2}$.

14.

Element	Percentage	Relative no. of atoms	Simplest ratio
C	39.9	3.32	1
H	6.69	6.69	2
O	$100 - (39.9 + 6.69) = 53.41$	3.34	1

∴ Empirical formula of compound = CH_2O

∴ Empirical formula mass = 30

For molar mass of acid

Meq. of Ag salt of monobasic acid = Meq. of Ag

$$\frac{0.2565}{M/1}\times 1000 = \frac{0.1659}{108}\times 1000$$

$\therefore$ Molar mass of Ag salt (RCOOAg) = 167

$\therefore$ Molar mass of acid (RCOOH) = 167 − 108 + 1 = 60

$\therefore$ Molecular formula of compound

$= (CH_2O)_2 = C_2H_4O_2 = \mathbf{CH_3COOH}$

15. (1) Molar mass of compound = 290

(2) It contains equal masses of C and H and thus,

Mass of C = 145

Mass of O = 145

$\therefore$ g-atoms of C $= \frac{145}{12} = 12$

g-atoms of O $= \frac{145}{16} = 9$

$\therefore$ Molecular formula $= \mathbf{C_{12}O_9}$

16. C : H : N :: 9 : 1 : 3.5 = 13.5

$\because$ 13.5 g contains $\frac{9}{12}$ g atom of C

$\therefore$ 108 g contains $\frac{9}{12}\times\frac{108}{13.5}$ g atom of C = 6

Similarly, g-atom of H in 1 mole $= \frac{1}{1}\times\frac{108}{13.5} = 8$

g-atom of N in 1 mole $= \frac{3.5}{14}\times\frac{108}{13.5} = 2$

$\therefore$ Molecular formula of compound is $\mathbf{C_6H_8N_2}$.

17. (i) Meq. of NH_3 evolved (NV) = Meq. of acid used for NH_3

$= 50\times 0.05\times 2 - 25\times 0.1 = 2.5$

$\because$ % of N $= \frac{1.4\times NV}{\text{mass of O.C.}} = \frac{1.4\times 2.5}{0.303} = 11.55$

(ii)

Element	Percentage	Relative no. of atoms	Simplest ratio
C	69.4	5.78	7
H	5.8	5.8	7
N	11.55	0.825	1
O	13.25	0.828	1

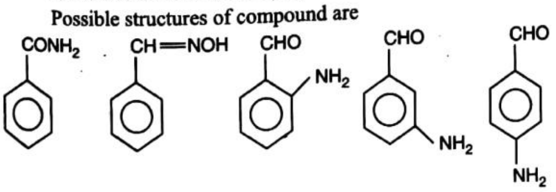
(iii) Empirical formula $= C_7H_7NO$

Empirical formula mass = 121

$\because$ Molar mass = 121 g mol^{-1}

$\therefore$ Molecular formula is $\mathbf{C_7H_7NO}$.

Possible structures of compound are



18. $$C_xH_{2y}O_y + xO_2 \longrightarrow xCO_2 + yH_2O$$

Since oxygen taken is $2x$ litre and thus x litre O_2 is left at STP after reaction. Also x litre of CO_2 is formed by 1 mole of O.C.

$\therefore$ $2x = 2.24$

$x = 1.12$ litre $CO_2 = \frac{1.12}{22.4}$ mole $CO_2 = 0.05$ mole CO_2

Mole of H_2O formed (y) $= \frac{0.9}{18} = 0.05$

$\therefore$ $x : y = 0.05 : 0.05$ $\therefore x = 1$

$y = 1$, *i.e.*, ratio of x and y

$\therefore$ Empirical formula of O.C. $= CH_2O$

and Empirical formula mass of O.C. = 30

Now Molar mass of compound is derived by Raoult's law

$$\because \quad \frac{P^\circ - P_s}{P_s} = \frac{w}{m}\times\frac{M}{W}$$

$\because$ $P^\circ - P_s = 0.104$ mm and $P^\circ = 17.5$ mm

$\frac{0.104}{17.396} = \frac{50}{m}\times\frac{18}{1000}$ $\therefore$ $m = 150.5$ g mol^{-1}

$\therefore$ Molecular formula $= (CH_2O)_5$ $\because n = \frac{150.5}{30} = 5$

$= \mathbf{C_5H_{10}O_5}$

19. % of C $= \frac{12\times 0.7920\times 100}{44\times 0.2790} = 77.42$

% of H $= \frac{2\times 0.1890\times 100}{18\times 0.2790} = 7.53$

% of N $= \frac{28\times 14\times 100}{22400\times 0.1163} = 15.05$

Element	Percentage	Relative no. of atoms	Simplest ratio
C	77.42	$\frac{77.42}{12} = 6.45$	$\frac{6.45}{1.075} = 6$
H	7.53	$\frac{7.53}{1} = 7.53$	$\frac{7.53}{1.075} = 7$
N	15.05	$\frac{15.05}{14} = 1.075$	$\frac{1.075}{1.075} = 1$

$\therefore$ Empirical formula $= C_6H_7N$

For molar mass by Platinic chloride method

Equivalent mass of base $= \frac{1}{2}\left[\frac{x}{a}\times 195 - 410\right]$

$= \frac{1}{2}\left[\frac{0.2980\times 195}{0.0975} - 410\right] = 93$

$\therefore$ Molar mass = Eq. mass × acidity = 93 × 1 = 93

$\therefore$ $n = \frac{\text{molar mass}}{\text{empirical formula mass}} = \frac{93}{93} = 1$

$\therefore$ Molecular formula $= \mathbf{C_6H_7N}$

20. $V_{N_2} = 18.8$ mL

$P_{N_2} = 756 - 14.5 = 741.5$ mm, $T = 273 + 17 = 290$ K

By $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ (at NTP)

$$\frac{741.5\times 18.8}{290} = \frac{760\times V}{273}$$

$\therefore$ V_{N_2} at STP = 17.27

$\therefore$ % of N $= \frac{28\times 17.27\times 100}{22400\times 0.2060} = \mathbf{10.5}$

21. % of C $= \frac{12\times 0.6098\times 100}{44\times 0.4020} = 41.37$

$$\% \text{ of H} = \frac{2\times 0.2080\times 100}{18\times 0.4020} = 5.75$$

$$\% \text{ of S} = \frac{32\times 0.2772\times 100}{233\times 0.1033} = 36.85$$

$$\% \text{ of N} = \frac{1.4\times 23.2\times 1}{1.01\times 2} = 16.08$$

Element	Percentage	Relative no. of atoms	Simplest ratio
C	41.37	$\frac{41.37}{12} = 3.45$	$\frac{3.45}{1.15} = 3$
H	5.75	$\frac{5.75}{1} = 5.75$	$\frac{5.75}{1.15} = 5$
S	36.85	$\frac{36.85}{32} = 1:15$	$\frac{1.15}{1.15} = 1$
N	16.08	$\frac{16.08}{14} = 1.15$	$\frac{1.15}{1.15} = 1$

∴ Empirical formula is C_3H_5NS

Empirical formula mass = 87

Molar mass $(M) = \frac{wRT}{PV}$

$$M = \frac{0.1015\times 0.0821\times 288\times 1000\times 760}{750\times 27.96}$$

$= 87 \text{ g mol}^{-1}$

∴ $n = \frac{87}{87} = 1$

∴ Molecular formula = $\mathbf{C_3H_5NS}$

22. Equivalent mass of base $= \frac{1}{2}\left[\frac{x}{a}\times 195 - 410\right]$

where x is mass of $PtCl_4$ salt and a is mass of Pt residue

Thus, $E = \frac{1}{2}\left[\frac{0.1982}{0.0563}\times 195 - 410\right] = 138.24$

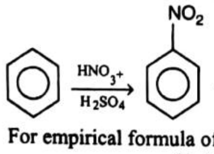
The base in monoacid, thus

molar mass = $E\times 1$ = **138.24**

Empirical formula mass (C_3H_3NO)

$= 36+3+14+16 = 69$

∴ Molecular formula = $(C_3H_3NO)_2 = \mathbf{C_6H_6N_2O_2}$

23.  + a minor product

For empirical formula of minor product

C	$\frac{42.86}{12} = 3.57$	$\frac{3.57}{1.19} = 3$
H	$\frac{2.40}{1} = 2.40$	$\frac{2.40}{1.19} = 2$
N	$\frac{16.67}{14} = 1.19$	$\frac{1.19}{1.19} = 1$
O	$\frac{38.07}{16} = 2.38$	$\frac{2.38}{1.19} = 2$

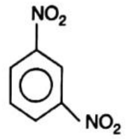
∴ Empirical formula is $C_3H_2NO_2$

Empirical formula mass = 84

Also Molar mass $= \frac{1000\times K\times w}{\Delta T\times W}$

$= \frac{1000\times 2.53\times 5.5}{1.84\times 45} = \mathbf{168 \text{ g mol}^{-1}}$

∴ Molecular formula = $(C_3H_2NO_2)_2 = \mathbf{C_6H_4N_2O_4}$,

i.e., 

24. ∴ $\% \text{ Br} = \frac{\text{Atomic mass of Br} \times \text{mass of AgBr}}{\text{Molar mass of AgBr} \times \text{mass of organic compound}}\times 100$

$= \frac{80\times 0.12\times 100}{188\times 0.15} = \mathbf{34.04\%}$

25. Percentage of Cl

$= \frac{\text{Atomic mass of Cl} \times \text{mass of AgCl}}{\text{Molar mass of AgCl} \times \text{mass of organic compound}}\times 100$

$= \frac{35.5\times 0.287\times 100}{143.5\times 0.147} = \mathbf{48.30\%}$

26. Meq. of H_2SO_4 taken = 50 × 0.5 × 2 = 50

Meq. of NaOH used after passing NH_3 = 60 × 0.5 = 30

∴ Meq. of H_2SO_4 used for NH_3 = 50 – 30 = 20 = (NV)

∴ $\% \text{ of N} = \frac{1.4\times NV}{\text{mass of organic compound}}$

$= \frac{1.4\times 20}{0.5} = \mathbf{56\%}$

27. $\% \text{ of Carbon} = \frac{12}{44}\times\frac{\text{mass of } CO_2 \text{ produced}}{\text{mass of organic compound}}\times 100$

∴ $69 = \frac{12}{44}\times\frac{\text{mass of } CO_2 \text{ formed}}{0.2}\times 100$

∴ Mass of CO_2 formed $= \frac{69\times 44\times 0.2}{12\times 100} = 0.506$ g

Now,

$\% \text{ of hydrogen} = \frac{2}{18}\times\frac{\text{mass of } H_2O \text{ formed}}{\text{mass of organic compound}}\times 100$

or $4.8 = \frac{2}{18}\times\frac{\text{mass of } H_2O \text{ formed}}{0.2}\times 100$

∴ Mass of H_2O formed $= \frac{4.8\times 18\times 0.2}{2\times 100} = 0.0864$ g

Percentage analysis (C = 69%, H = 4.8%, O = 26.2) suggest the empirical formula and molecular formula of organic compound is $C_7H_6O_2$.

$$C_7H_6O_2 + \frac{15}{2}O_2 \longrightarrow 7CO_2 + 3H_2O$$

Thus, 1 mole of $C_7H_6O_2$ requires **7.5 mole** of oxygen for complete combustion.