

Organic Compound (C, H, N)

Dumas Method

The Volumetric Approach



- **Mechanism:** Converts N to N_2 gas.



- **Key Metric:** Volume of N_2 at STP.



- **Applicability:** Universal (works for all N-containing compounds).

Kjeldahl's Method

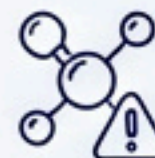
The Titrimetric Approach



- **Mechanism:** Converts N to $(NH_4)_2SO_4$ (Ammonium Sulphate).



- **Key Metric:** Volume of standard acid consumed.

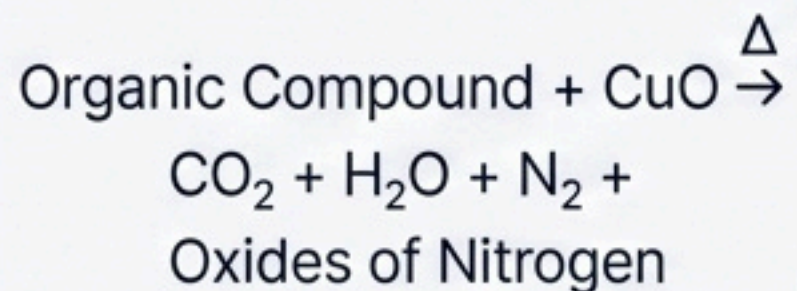
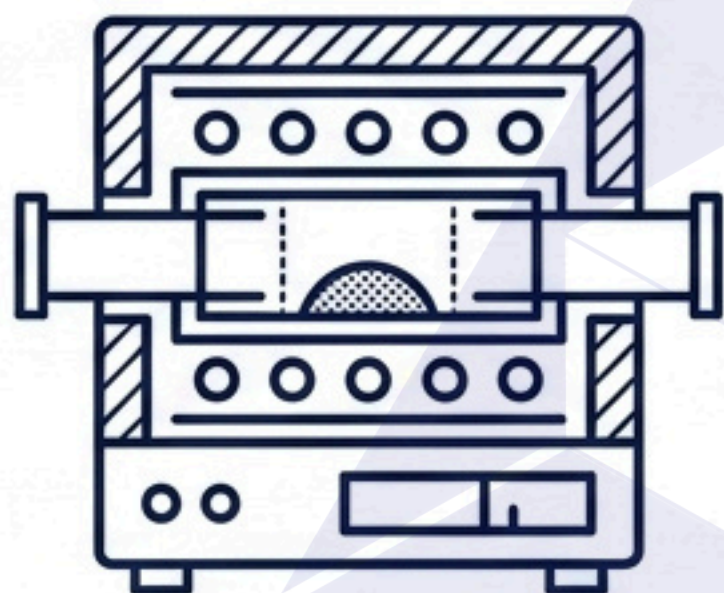


- **Applicability:** Specific (has critical structural exceptions).

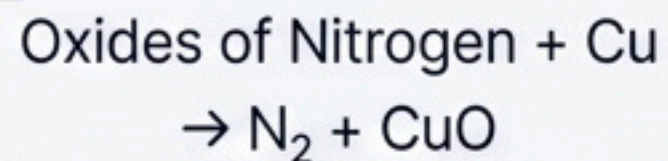
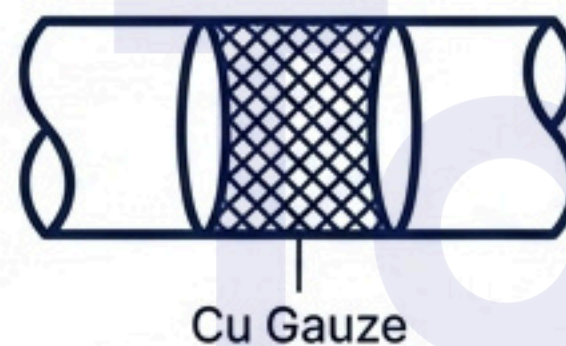
Objective: Determine the exact mass percentage of Nitrogen to derive the empirical/molecular formula.

Dumas Reaction Pipeline

1. Combustion Tube

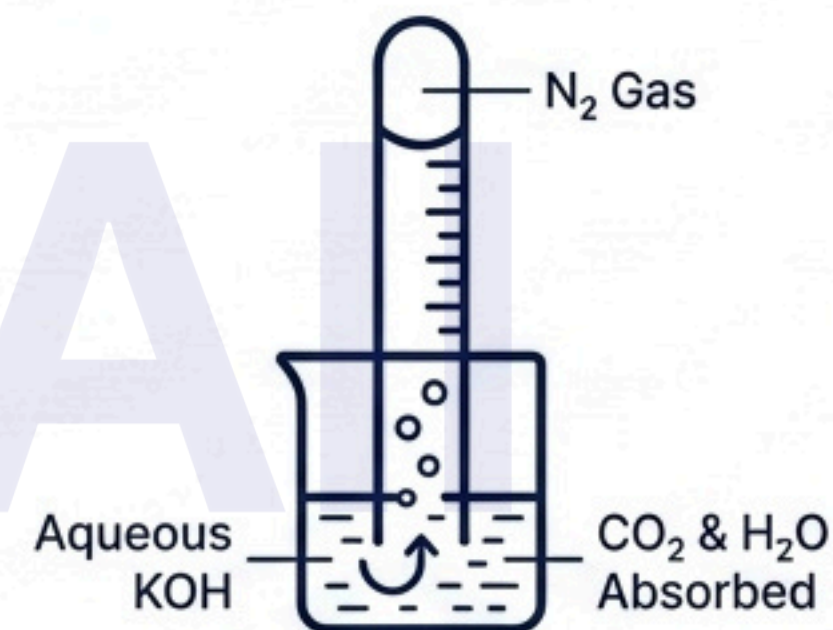


2. Reduction



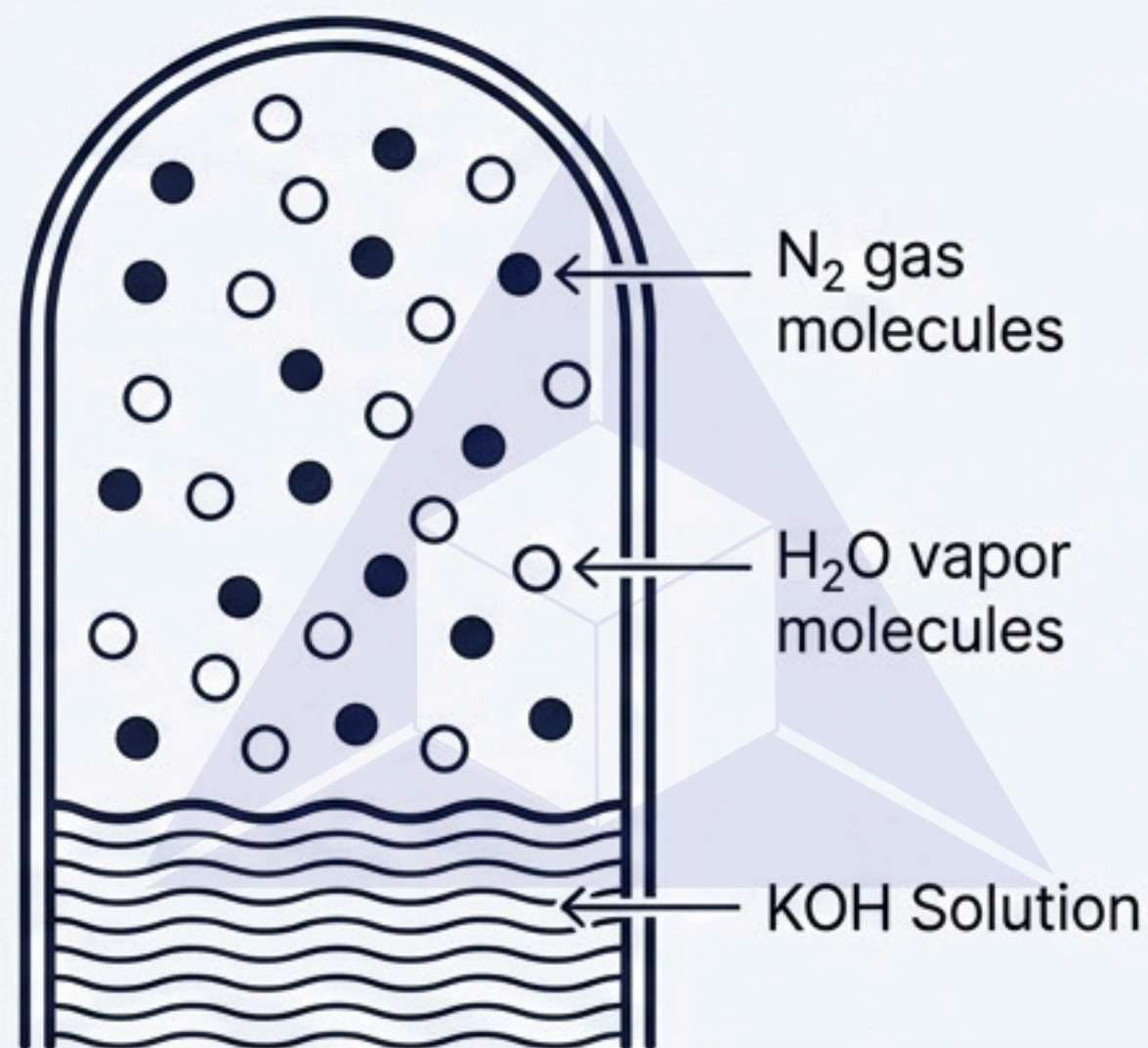
Ensures all nitrogen is uniformly in N_2 gaseous state.

3. Nitrometer Collection



- Gas mixture enters aqueous KOH.
- KOH absorbs CO_2 and H_2O . Only pure N_2 gas rises to the top.

The Physics: Aqueous Tension



Gas collected over liquid is saturated with moisture.

The Mathematical Correction

1. Isolate Dry Nitrogen Pressure

$$P(\text{dry N}_2) = P(\text{total}) - \text{Aqueous Tension}$$

2. Bridge to STP (Ideal Gas Law)

$$\frac{P_1 \times V_1}{T_1} = \frac{P_{(\text{STP})} \times V}{T_{(\text{STP})}}$$

$$P_1 = P(\text{dry N}_2)$$

$$V_1 = \text{Observed Volume}$$

$$T_1 = \text{Lab Temp (K)}$$

$$P_{(\text{STP})} = 760 \text{ mm Hg}$$

$$T_{(\text{STP})} = 273 \text{ K}$$

Solve for V: Volume of N₂ at STP



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$$E=mc^2$$



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Dumas Method: Stoichiometric Logic

Step 1: The Molar Standard

At STP, 1 mole of N_2 gas = 22,400 mL = 28 g

Step 2: The Proportional Mass

Therefore, the mass of V mL of N_2 (calculated from the previous physical correction) is:

$$\text{Mass of } \text{N}_2 = \frac{28 \times V}{22400} \text{ g}$$

Step 3: The Percentage Synthesis

$$\% \text{ N} = \left[\frac{28 \times V}{22400 \times m} \right] \times 100$$

V = Volume of N_2 at STP (mL)

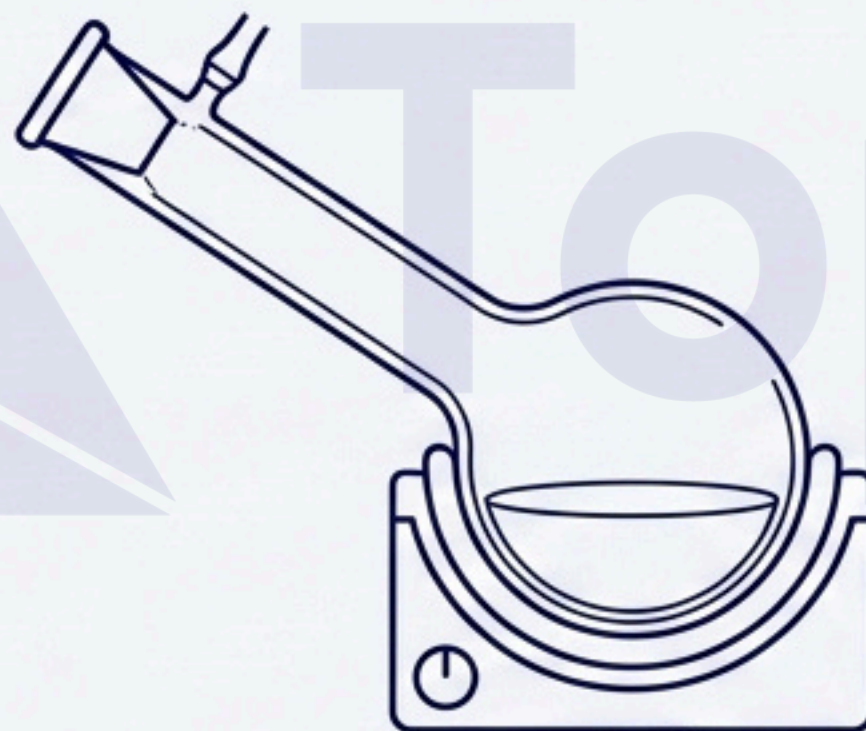
m = mass of organic sample (g)

Kjeldahl Phase 1: Acid Digestion



Carbon & Hydrogen Fate:
Oxidized to CO_2 and H_2O
and escape as gases.

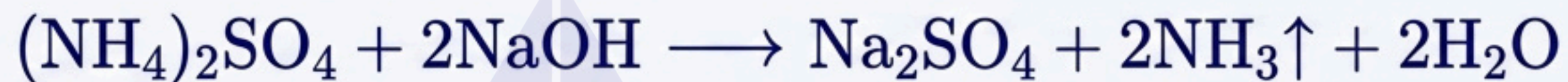
Nitrogen Fate: Converted
entirely into inorganic
Ammonium Sulphate.



Pro-Tip: Copper sulphate (CuSO_4) or
Potassium sulphate (K_2SO_4) is
added to raise the boiling point of
the acid and act as a catalyst.

Kjeldahl Phase 2 & 3: Distillation & Back-Titration

Phase 2: Liberation (Distillation)



Action: Base displaces the volatile ammonia gas.

Phase 3: Absorption & Back-Titration

Action 1: NH_3 is passed into a known excess of standard H_2SO_4 (Molarity M).

Action 2: Unreacted H_2SO_4 is titrated with standard NaOH (Volume V_1).

Volume of acid consumed by NH_3 = Total Acid Volume (V) – Acid neutralized by NaOH ($V_1 / 2$).

Note: Division by 2 accounts for stoichiometry between diprotic H_2SO_4 and monoprotic NaOH .

$$\% \text{ N} = \frac{1.4 \times M \times 2(V - V_1/2)}{m}$$

The constant 1.4 derives from Nitrogen's atomic mass (14) $\times$ 100%, divided by 1000 to convert mL to L.

Kjeldahl Limitations (High-Yield Concept)

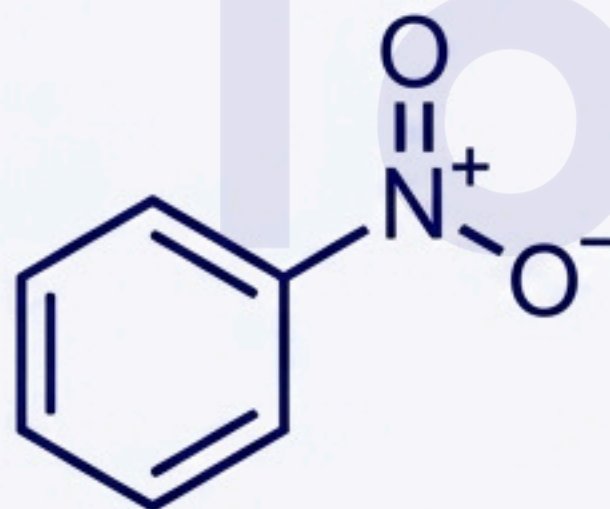
Core Rule: The method FAILS if the nitrogen cannot be converted into ammonium sulphate under standard digestion conditions.

1. Ring Nitrogen



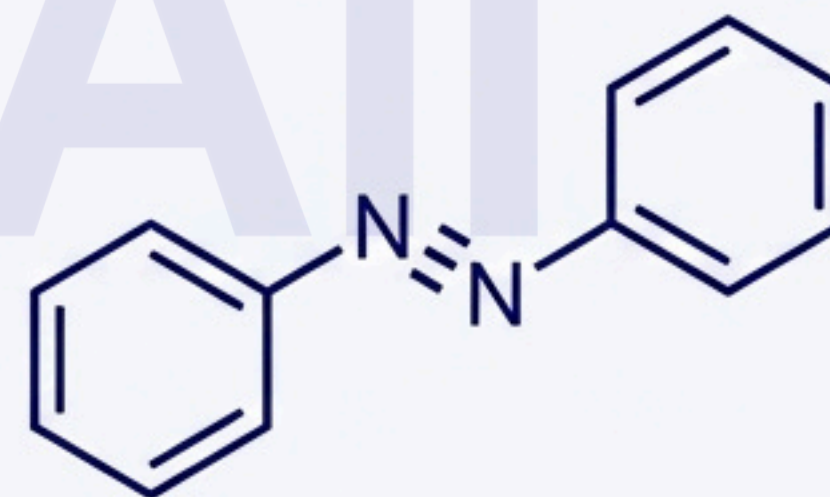
Nitrogen is too tightly bound within the highly stable aromatic ring.

2. Nitro Compounds



Nitrogen is highly oxidized; resists conversion to the reduced NH_4^+ ion.

3. Azo Compounds



N-N bonds cleave to form N_2 gas instead of ammonium ions.

Synthesis: The Revision Frame

Feature	Dumas Method	Kjeldahl's Method
Core Principle	Volumetric (N ₂ gas measured)	Titrimetric (NH ₃ gas titrated)
Chemical Intermediate	N ₂ (g)	(NH ₄) ₂ SO ₄ (aq)
Master Formula	$\% N = \frac{28 \times V \times 100}{22400 \times m}$	$\% N = \frac{1.4 \times M \times V_{\text{consumed}}}{m}$
Applicability	Universal	Fails for Pyridine, Nitro, and Azo groups
Key Error Source	Ignoring Aqueous Tension	Incomplete Digestion

Final Check: Always identify the functional groups in the organic compound before selecting a **quantitative method** for the exam.



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