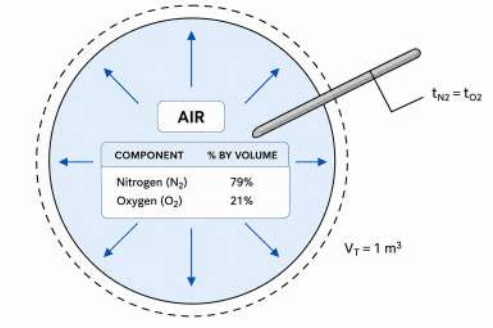
Introduction to Ideal Gas Mixtures

In engineering thermodynamics, many real-world systems involve working fluids that are mixtures of different chemical gases rather than a single pure substance. When these constituent gases operate at relatively low pressures and high temperatures relative to their critical points, they behave as an **ideal gas mixture**.



Atmospheric air is the most common example of such a mixture. For engineering calculations, dry air is modeled as an ideal gas mixture with an approximate volumetric composition of **79% Nitrogen (N_2)** and **21% Oxygen (O_2)**. Inside a fixed containment volume, each component gas expands to occupy the total volume while maintaining thermal equilibrium with the other components $\left(t_{N_2} = t_{O_2}\right)$.

Mixture Composition

To analyze the thermodynamic properties of a mixture, its composition must be precisely quantified. This is achieved using two main methods depending on whether tracking focuses on the substance's volume/molar quantities or its physical mass.

(a) Volumetric or Molar Analysis

Volumetric or Molar analysis quantifies the composition by expressing the percent by volume or percent by moles of each individual component gas with respect to the total volume or total moles of the ideal gas mixture. The volume percentage of an individual component i is mathematically defined as:

$$\%V_i = \frac{V_i}{V_m}\, x\, 100\%$$

According to **Avogadro's Law**, equal volumes of all ideal gases, when measured under identical pressure and temperature conditions, contain exactly the same number of moles. Because a direct, linear proportionality exists between volume and moles for ideal gases, the volumetric percentage is identical to the molar percentage:

$$\%V_i = \frac{n_i}{n_m}\ x\ 100\%$$

(b) Gravimetric or Ultimate Analysis

Gravimetric or Ultimate analysis quantifies a mixture by focusing strictly on its mass. It represents the percent by mass of an individual component relative to the total mass of the ideal gas mixture. The gravimetric percentage (%Gi) is expressed as:

$$\%G_i = \frac{m_i}{m_m}\ x\ 100\%$$

By the principle of conservation of mass, the total mass of the mixture (m_m) must equal the algebraic summation of the masses of its individual constituents:

$$m_m = \sum_i m_i$$

Average Molar Mass (M_m)

The apparent or average molar mass (M_m) represents the mass of the mixture per unit mole, typically expressed in units of kg/kgmol. It is determined by dividing the total mass of the mixture (m_m) by the total number of moles (n_m). Because the mass of an individual component is the product of its moles and its specific molecular weight ($m_i = n_i M_i$), the formula expands to a mole-fraction weighted sum:

$$m_m = \frac{m_m}{n_m} = \sum_i \frac{n_i M_i}{n_m}$$

Average Gas Constant (R_m)

The specific gas constant of a mixture (R_m) defines its pressure-volume-temperature limits and is expressed in units of kJ/kg·K. It can be computed using two methods: dividing the Universal Gas Constant ($\overline{R}$ = 8.314 kJ/kmol·K) by the mixture's apparent molar mass (M_m), or taking a gravimetric-weighted sum of the individual component gas constants (R_i):

$$R_m = \frac{\overline{R}}{m_m} = \sum_i \left(\%G_i\right)\left(R_i\right)$$

Note that the molar mass (M_{air}) is approximately 28.97 kg/kmol and the specific gas constant (R_{air}) is 0.287 kJ/kg·K.

Amagat's Law of Additive Volumes

In the thermodynamic analysis of gas mixtures, evaluating how individual component gases contribute to the overall volume requires understanding the relationship between volume, temperature, and pressure. **Amagat's Law of Additive Volumes** states that the total volume of an ideal gas mixture is equal to the absolute sum of the partial volumes that each individual component gas would occupy if it existed by itself at the exact same temperature and pressure as the overall mixture. Mathematically, this principle is expressed as an algebraic summation of partial volumes evaluated at the mixture's temperature (T_m) and pressure (P_m):

$$V_m = \sum_i V_i \left(T_m, P_m \right)$$

This means that if you were to isolate each component gas from a mixture and compress or expand it until its pressure and temperature matched the original mixture state, the sum of those isolated partial volumes (V_i) would perfectly equal the total volume of the mixture (V_m).

The Ideal Gas Ratios

To establish the relationship between volumetric fractions and molar quantities, we look to the ideal gas equation of state. For an isolated individual component gas i existing at the temperature and pressure of the mixture ($P_i = P_m$ and $T_i = T_m$), the equation of state is written as:

$$P_i V_i = n_i \overline{R} T_i$$

Simultaneously, the macroscopic behavior of the entire ideal gas mixture is governed by the same state equation, utilizing total mixture parameters:

$$P_m V_m = n_m \overline{R} T_m$$

Taking the ratio of these two equations allows for a major simplification. Because the individual components are evaluated under identical pressure conditions ($P_i = P_m$) and temperature conditions ($T_i = T_m$), the pressure variables, temperature variables, and the universal gas constant (R) cancel out completely.

This mathematical relationship demonstrates a core law of gas mixtures: the mole fraction $\left(\frac{n_i}{n_m} \right)$ of a gas component is exactly equal to its volume fraction $\left(\frac{V_i}{V_m} \right)$ and its pressure fraction $\left(\frac{P_i}{P_m} \right)$, all of which correspond directly to the volumetric percentage ($\%V_i$) of that component:

$$\frac{n_i}{n_m} = \frac{V_i}{V_m} = \frac{P_i}{P_m} = \%V_i$$

The Nitrogen-Oxygen Ratio of Air

Atmospheric air is standardly analyzed as a binary ideal gas mixture composed of approximately 79% Nitrogen (N_2) and 21% Oxygen (O_2) by volume. Applying the ratio derivation established above, the volumetric ratio matches the molar ratio identically:

$$\frac{n_{N_2}}{n_{O_2}} = \frac{V_{N_2}}{V_{O_2}} = \frac{0.79\ mol_{N_2}}{0.21\ mol_{O_2}} = 3.76 \frac{mol_{N_2}}{mol_{O_2}}$$

This ratio is highly important for combustion engineering calculations. It establishes that **for every 1 mole of oxygen** participating in a chemical reaction with a fuel source, there are inevitably **3.76 moles of nitrogen** accompanying it from the air supply. Consequently, for every 1 mole of O_2 consumed, 1 + 3.76 = 4.76 moles of total air must enter the combustion chamber.

Dalton's Law of Partial Pressures

Dalton's Law of Partial Pressures states that in a mixture of ideal gases occupying a vessel at a specified total volume and temperature, each constituent gas behaves independently, exerting its own characteristic pressure as if it occupied the entire vessel alone. The total pressure of the gas mixture (P_m) is equal to the absolute algebraic sum of these individual partial pressures (P_i):

$$\sum_i P_i = P_m$$

The partial pressure of any single component gas i is directly proportional to its abundance in the mixture. Specifically, it is determined by multiplying the total pressure of the mixture (P_m) by the mole fraction $\left(\frac{n_i}{n_m}\right)$ of that individual gas component:

$$P_i = P_m \frac{n_i}{n_m}$$

Because the sum of all individual mole fractions in a mixture must mathematically equal unity $\left(\Sigma \frac{n_i}{n_m} = 1\right)$ summing both sides of the partial pressure equation confirms Dalton's primary relationship:

$$\sum_i P_i = P_m \sum_i \frac{n_i}{n_m} = P_m(1) = P_m$$

Properties of Ideal Gas Mixtures

Beyond pressure and volume constraints, extensive thermodynamic properties—such as total internal energy (U_m), total enthalpy (H_m), and total entropy (S_m)—are computed by adding the individual contributions of each constituent component in the mixture. When dealing with calculations structured on a molar basis, these total mixture values are represented as follows:

- **Total Internal Energy (U_m):** The total internal energy of the mixture, measured in kilojoules (kJ), is calculated by summing the products of each component's total moles $\left(n_i\right)$ and its respective molar internal energy (u_i):

$$U_m = \sum_i n_i u_i \qquad ; \qquad \text{kJ}$$

  In this relationship, u_i represents the internal energy of the i-th component evaluated on a molar basis (kJ/kmol) at the specific temperature of the mixture.

- **Total Enthalpy (H_m):** The total enthalpy of the mixture, measured in kilojoules (kJ), is found by summing the products of each component's total moles (n_i) and its respective molar enthalpy (h_i):

$$H_m = \sum_i n_i h_i \qquad ; \qquad \text{kJ}$$

  Here, h_i represents the enthalpy of the$i$-th component evaluated on a molar basis (kJ/kmol) at the specific temperature of the mixture.

- **Total Entropy (S_m):** The total entropy of the mixture, measured in kilojoules per Kelvin (kJ/K), is determined by summing the products of each component's total moles (n_i) and its respective molar entropy (s_i):

$$S_m = \sum_i n_i s_i \qquad ; \qquad \text{kJ/K}$$

  Crucially, because entropy depends on both temperature and pressure, s_i represents the entropy of the i-th component on a molar basis (kJ/kmol-K) evaluated at the specific mixture temperature **and its individual partial pressure (P_i)**.

Gravimetric Mixture Specific Heats

When analyzing temperature changes and heat transfer rates of gas mixtures on a mass basis, it is necessary to determine the apparent specific heats of the entire mixture. The constant-pressure specific heat (C_p) and constant-volume specific heat (C_v) of a mixture are calculated using a mass-fraction weighted sum of the components' individual specific heats.

Using the gravimetric percentage ($\%G_i$) of each constituent, the mixture specific heats are defined as:

$$C_p = \sum_i \left(\%G_i\right)\left(C_{pi}\right)$$

$$C_v = \sum_i \left(\%G_i\right)\left(C_{vi}\right)$$

Where:

- $\%G_i$ = The mass fraction (gravimetric percentage expressed as a decimal) of component i.
- C_{pi} / C_{vi} = The individual constant-pressure and constant-volume specific heats of component i, respectively.

Classification of Fuels

In power plant and thermal engineering, a fuel is broadly defined as a compound containing carbon and hydrogen elements. When subjected to a rapid chemical union with oxygen, it undergoes an exothermic reaction known as combustion, releasing a significant amount of thermal energy. For engineering design and operational convenience, fuels are categorized based on their physical state and origin into four primary classifications: **liquid fuels, gaseous fuels, solid fuels, and nuclear fuels**.

Liquid Fuels

Liquid fuels are highly favored in internal combustion engines and modern thermal units due to their high energy density and ease of transport. Key examples include:

- **Gasoline:** Predominantly modeled as octane (C_8H_{18}).
- **Distilled and Blended Fuel Oils:** These encompass specialized petroleum cuts such as diesoline ($C_{16}H_{32}$) and typical diesel fuel oil, which is chemically represented by alkanes like dodecane ($C_{12}H_{26}$). Light heating oils, kerosene, and jet fuel also fall under this distinction.
- **Alcohols and Blends:** Characterized by the general formula C_xH_y,O_z, common types include ethyl and methyl alcohols. When blended as 70% gasoline and 30% anhydrous alcohol, it creates an alternative fuel known colloquially as alco-gas or green gasoline.
- **Liquefied Petroleum Gas (LPG):** Composed of a highly pressurized mixture of propane (C_3H_8) and butane (C_4H_{10}), enhanced with a specialized chemical odorizer for leak detection.

Gaseous Fuels

Gaseous fuels offer excellent mixing characteristics with air, ensuring high combustion efficiency.

- **Natural Gas:** Formed primarily of light hydrocarbons, tracking a composition cascade from methane (CH_4), ethane (C_2H_6), propane (C_3H_8), down to butane (C_4H_{10}).
- **Industrial By-product Gases:** Includes coke or oven gas, blast furnace gas, producer gas, and synthetic derivatives like enriched water gas or carburated water gas.
- **Bio-gas:** Sustainable gas mixtures emitted directly from organic or animal waste decomposition.

Solid Fuels

Solid fuels remain the backbone of heavy base-load electricity generation.

- **Coal:** The principal fuel utilized in traditional steam power plant operations.
- **Biomass and Waste:** Renewable wood barks, agricultural remains like bagasse, and fast-growing dendrothermal energy crops like ipil-ipil. It also includes general biomass derived from processing municipal garbage and organic waste products from industrial or agricultural operations.
- **Coke:** A carbonaceous solid derived from coal distillation, primarily used as blast furnace fuel.

Nuclear Fuels

Unlike chemical fuels, nuclear fuels release energy via mass-defect nuclear reactions. They are utilized in power reactors either as natural uranium containing a high proportion of stable isotope U_{238}, or artificially prepared as enriched uranium concentrated with fissile isotope U_{235}.

Principles of Combustion Chemistry and Stoichiometry

To properly design burners, furnaces, and draft systems, engineers must establish precise chemical balances for the reaction. In practical applications, the oxygen required for combustion is drawn from ambient atmospheric air. Therefore, a true combustion equation must account for the fact that fuel is reacting with moist or humid air, rather than pure oxygen. Atmospheric air is modeled as a mixture of dry air and a specific mass fraction of water vapor.

As established by the fundamental principles of gas mixtures, dry air is composed of approximately 21% Oxygen (O_2) and 79% Nitrogen (N_2) by volume. This yields a fixed molar ratio where every 1 mole of O_2 entering the system is accompanied by 3.76 moles of unreactive N_2. Consequently, the total reactant input per mole of critical oxygen is mathematically represented as:

$$[Fuel] + \left[\left(1mol\ O_2\right) + \left(3.76mol\ N_{2,\,air}\right) + \_\_ molH_2O_{air}\right] \rightarrow [Products\ of\ Combustion]$$

Stoichiometric Combustion

Stoichiometric (or theoretical) combustion represents an ideal scenario where the exact minimum amount of oxygen required to completely oxidize all the combustible elements in the fuel is supplied. In stoichiometric combustion, all carbon is converted to carbon dioxide (CO_2) and all hydrogen is converted to water (H_2O), with zero residual oxygen remaining in the exhaust stream. Assuming a dry air basis for simplicity, the theoretical balance is modeled as:

$$[Fuel] + \left[1mol\ O_2 + 3.76mol\ N_{2,\,air}\right] \rightarrow CO_2 + H_2O_F + 3.76molN_{2,\,air}$$

Actual Combustion and Excess Air Analysis

In real-world engineering systems, achieving perfect stoichiometric mixing is physically impossible due to limitations in burner turbulence, residence time, and mechanical design. If a power plant were operated using only the theoretical air volume, incomplete combustion would occur, resulting in the formation of toxic carbon monoxide (CO), unburned soot, and massive efficiency losses. To force every molecule of fuel into contact with oxygen, real systems are supplied with **excess air (e)**.

The excess air coefficient (e) represents the percentage of air supplied over and above the theoretical requirement (e.g., if 20% excess air is used, e = 0.20). When excess air is introduced, the quantity of total air entering the furnace scales by a factor of (1 + e). The complete reaction balance for actual combustion with excess air is mathematically structured as:

$$[Fuel] + (1 + e)\left[1mol\ O_2 + 3.76mol\ N_{2,\,air}\right] \rightarrow CO_2 + H_2O_F + (e)(1)molO_{2,\,excess\ air} + (1 + e)(3.76mol)N_{2,\,air}$$

Nitrogen (N_2) is entirely inert during low-to-moderate temperature combustion, meaning whatever enters the furnace must exit unchanged. Because it scales by (1 + e)(3.76), excess air significantly increases the volume of nitrogen passing through the system. This extra nitrogen acts as a thermal ballast, absorbing combustion energy and carrying it out the stack, which reduces the overall boiler efficiency. Keeping excess air minimized while ensuring complete combustion is a key balancing act in plant design.

Illustration 1: Combustion Analysis of Liquid Fuels

Combustion of octane (C_8H_{18}) occurs with 10% excess air (e = 0.10).

Formulating and Balancing the Molal Combustion Equation

To determine any air-to-fuel parameter, we must establish the balanced chemical equation. Let a represent the theoretical moles of oxygen needed for stoichiometric combustion. Using the principles of excess air, the total oxygen supplied is scaled by (1 + e), which translates to a(1.10). Since every mole of O_2 brings 3.76moles of inert N_2, our general unbalanced equation stands as:

$$C_8H_{18} + a(1.1)\left[1\,O_2 + 3.76mol\,N_2\right] \rightarrow bCO_2 + cH_2O + a(0.10)O_2 + a(1.10)(3.76)N_2$$

Performing an elemental atom balance yields the values for our stoichiometric coefficients:

- **Carbon Balance:** 8 = b ⇒ b = 8 mol of CO_2
- **Hydrogen Balance:** 18 = 2c ⇒ c = 9 mol of H_2O
- **Oxygen Balance:** To solve for a, balance the total oxygen atoms across both sides:

$$a(1.10)(2) = b(2) + c(1) + a(0.10)(2)$$
$$a(1.10)(2) = (8)(2) + (9)(1) + a(0.10)(2)$$

Substituting a = 12.5 back into the original expression determines our actual air coefficient: Actual O_2 = (12.5)(1.10) = 13.75mols. Multiplying this by the nitrogen ratio gives (13.75)(3.76) = 51.7mols of N_2, the fully balanced actual molal combustion equation is:

$$C_8H_{18} + 13.75\left[1\,O_2 + 3.76mol\,N_2\right] \rightarrow 8CO_2 + 9H_2O + 1.25O_2 + 51.7N_2$$

Mass of Fuel (m_f): Evaluated per mole of fuel using the molecular weights of Carbon (12 kg/kmol) and Hydrogen (1 kg/kmol):

$$m_f = (8)(12) + (18)(1) = 114\,kg$$

Actual Mass of Air (m'$_a$): Calculated using the actual moles of oxygen and nitrogen multiplied by their respective molecular weights ($M_{O_2} = 32$, $M_{N_2} = 28$):

$$m'_a = (13.75)(32) + (51.7)(28) = 1887.6\,kg$$

Actual Air-Fuel Ratio (A:F'):

$$A{:}\,F' = \frac{m'_a}{m_f} = \frac{1887.6\,kg}{114\,kg} = 16.5579\frac{kg_{air}}{kg_{fuel}}$$

Stoichiometric Air-Fuel Ratio (A:F): Computed by removing the excess air multiplier:

$$A{:}\,F = \frac{A{:}F'}{1+e} = \frac{16.5579 \frac{kg_{air}}{kg_{fuel}}}{1.10} = 15.0526 \frac{kg_{air}}{kg_{fuel}}$$

1. **If $A{:}\,F'$ > $A{:}\,F$ (Lean Mixture)**

   This means the actual mass of air supplied per kilogram of fuel is higher than what is chemically required for a perfect burn.

2. **If $A{:}\,F'$ < $A{:}\,F$ (Rich Mixture)**

   This means the actual mass of air supplied per kilogram of fuel falls below the baseline required for complete oxidation.

3. **If $A{:}\,F'$ = $A{:}\,F$ (Stoichiometric Mixture)**

   This represents the ideal theoretical balance where the air supplied matches the minimum chemical requirements exactly.

Theoretical Mass of Air (m_a): The minimum mass required for complete stoichiometric oxidation:

$$m_a = (A{:}\,F) m_f = \left(15.0526 \frac{kg_{air}}{kg_{fuel}}\right)(114\ kg) = 1,716\ kg$$

Amount of Excess Air (m_{excess}):

$$m_{excess} = m'_a - m_a = 1,887.6\ kg - 1,716\ kg = 171.60\ kg$$

Dilution Coefficient (DC): Defines the ratio of actual air to theoretical air:

DC = 1 + e = 1.10

Equivalence Ratio (ER): Broadly defined in this specific source material's convention as identical to the dilution factor:

$$\text{ER} = \phi = \frac{1}{1+e} = \frac{(A:F)_{stoich}}{(A:F')_{actual}} = 0.91$$

Flue Gas Composition Analysis

To conduct the product analysis, we first calculate the total moles and masses of our products:

- **Total Product Moles (n_T):** 8 + 9 + 1.25 + 51.7 = 69.95 moles
- **Total Dry Moles (n_{dry}):** n_T - n_{H_2O} = 69.95 - 9 = 60.95 moles
- **Component Masses:**

  m_{CO_2} = 8(44) = 352 kg

  m_{H_2O}= 9(18) = 162 kg

  m_{O_2} = 1.25(32) = 40 kg

  m_{N_2} = 51.7(28) = 1447.6 kg

- **Total Product Mass (m_T):** 352 + 162 + 40 + 1447.6 = 2001.6 kg

Using the standard percentage equations $\left(\%G_i = \frac{m_i}{m_T} \; and \; \%V_i = \frac{n_i}{n_T}\right)$, the composition breakdown is calculated as follows:

Flue Gas Component	(g) Gravimetric (Wet)	(h) Volumetric (Wet)	(i) Gravimetric (Dry)	(j) Volumetric (Dry)
CO_2	17.59%	11.44%	19.13%	13.13%
H_2O	8.09%	12.87%	*Excluded*	*Excluded*
O_2	2.00%	1.79%	2.17%	2.0%
N_2	72.32%	73.91%	78.69%	84.82%

Molecular Properties and Condensation Limits

- **Molecular Weight of the Mixture (M):**

$$M = \frac{m_T}{n_T} = \frac{2001.6\ kg}{69.95\ moles} = 28.6147\ \frac{kg}{kmol}$$

- **Gas Constant of the Product (R):** Divide the Universal Gas Constant ($\overline{R} = 8.314$) by the mixture's molecular weight:

$$R = \frac{\overline{R}}{M} = \frac{8.314\ kJ/kmol{-}K}{28.6147\ kg/kmol} = 0.2905\ \frac{kJ}{kg{-}K}$$

- **Water Vapor Partial Pressure (P_{H_2O}) & Dew Point:** Using Dalton's Law of Partial Pressures under standard atmospheric pressure (P_T = 101.325 kPa):

$$P_{H_2O} = P_T\left(\frac{n_{H_2O}}{n_T}\right) = 101.325\ kPa\left(\frac{9\ mols}{69.95\ mols}\right) = 13.0037\ kPa$$

Looking up $13.0037\ kPa$ in standard saturated steam tables via temperature interpolation:

$$t_{dew\ point} = t_{sat}@13.0037\ kPa = 50.85°C$$

Illustration 2: Combustion Analysis of Liquid Fuels

A natural gas mixture with a volumetric composition of 2.4%CO_2, 1.8%N_2, 64.1%CH_4, and 31.7%C_2H_6 is burned with 10% excess air e = 0.10).
Determine:
(a) The actual gravimetric air-fuel ratio (A:F' on a mass basis).
(b) The actual molal air-fuel ratio (A:F' on a molar basis).

Because a volumetric analysis is provided, we can apply Avogadro's law to treat the volume percentages directly as mole values. Assuming a convenient baseline of **100 moles of total gaseous fuel**, the composition yields:

- n_{CO_2} = 2.4 mol
- n_{N_2} = 1.8 mol
- n_{CH_4} = 64.1 mol
- $n_{C_2H_6}$ = 31.7 mol

Let a represent the theoretical moles of oxygen needed for stoichiometric combustion. Since the system utilizes 10% excess air (e = 0.10), the total oxygen supplied is scaled by (1 + e) = 1.10. The balancing framework is structured as follows:

$$\left[2.4CO_2 + 1.8N_2 + 64.1CH_4 + 31.7C_2H_6\right] + a(1.10)\left[1\,O_2 + 3.76mol\,N_2\right] \rightarrow bCO_2 + cH_2O + a(0.10)O_2 + [a(1.10)(3.76) + 1.8]N_2$$

We perform an atomic balance to determine our stoichiometric coefficients:

- **Carbon (C) Balance:** The carbon in the products (b) comes from the CO_2, CH_4, and C_2H_6 in the fuel:

$$b = 2.4(1) + 64.1(1) + 31.7(2)$$

$$b = 129.9\ moles\ of\ CO_2$$

- **Hydrogen (H) Balance:** The hydrogen forms water (H_2O), with two atoms per molecule:

$$2c = 64.1(4) + 31.7(6)$$

$$c = 223.3\ moles\ of\ H_2O$$

- **Oxygen (O) Balance:** Equating total oxygen atoms across both sides:

$$2.4(2) + 2.20a = 129.9(2) + 223.3(1) + 0.20a$$

$$a = 239.153\ moles\ of\ O_2$$

Substituting a = 239.15 determines the actual oxygen supplied: 239.15(1.10) = 263.065 moles. The accompanying nitrogen from the air is 263.065(3.76) = 989.124 moles.

Solving for the Gravimetric Air-Fuel Ratio

To find the mass-based air-fuel ratio (A:F'), we determine the absolute masses of our components based on our 100 mol fuel baseline:

- **Mass of Fuel (m_F):** Multiply the moles of each constituent by its specific molecular weight (M_{CO_2}=44, M_{N_2}=28, M_{CH_2}=16, $M_{C_2H_6}$=30):

$$m_F = 2.4(44) + 1.8(28) + 64.1(16) + 31.7(30) = 2,132.6\ kg_{fuel}$$

- **Actual Mass of Air (m'_a):** Multiply the actual moles of oxygen and nitrogen supplied by their molecular weights (32 and 28):

$$m'_a = 263.065(32) + 989.124(28) = 36,113.55\ kg_{air}$$

- **Actual Mass Air-Fuel Ratio (A:F'):**

$$A{:}\,F' = \frac{m'_a}{m_f} = \frac{36{,}113.55\ kg_{air}}{2{,}132.6\ kg_{fuel}} = 16.9341 \frac{kg_{air}}{kg_{fuel}}$$

Solving for the Molal Air-Fuel Ratio

The molal air-fuel ratio evaluates the quantitative mixture properties purely on a molar basis $\left(\frac{mol_{air}}{mol_{fuel}}\right)$.

- **Total Moles of Fuel (n_f):** Fixed at our baseline of 100 moles.

- **Total Moles of Air (n'_a):** Calculated by adding the actual moles of oxygen and nitrogen brought into the intake system:

$$n'_a = n'_{O_2} + n'_{N_2} = 263.065 + 989.124 = 1{,}252.189\ moles$$

- **Actual Molal Air-Fuel Ratio:**

$$A{:}\,F'_{molal} = \frac{n'_a}{n_f} = \frac{1{,}252.189\ moles}{100\ moles} = 12.5219 \frac{mol_{air}}{mol_{fuel}}$$

Handling Fuel Inerts (CO_2 and N_2): Notice that natural gas often contains pre-existing internal inerts like carbon dioxide (2.4%) and nitrogen (1.8%). These components do not contribute any heat energy to the combustion reaction. In fact, they act as an internal thermal ballast, absorbing combustion energy and carrying it out the stack as waste heat, which reduces the fuel's net heating value.

The Impact of Ethane (C_2H_6) on Air Demand: Methane (CH_4) requires only 2 moles of O_2 per mole of fuel, whereas ethane (C_2H_6) requires 3.5 moles of O_2. Because this natural gas has a high concentration of ethane (31.7%), its overall air requirement increases significantly. This demonstrates why power plants must continuously monitor the changing chemical composition of incoming natural gas supplies; an unexpected increase in heavier hydrocarbons like ethane requires immediate adjustments to the forced-draft fans to prevent incomplete combustion and soot formation.

Illustration 3: Combustion Analysis of Solid Fuels

Consider the combustion of a coal sample with the following gravimetric composition: 45%C, 20%H_2, 10%O_2, 15%N_2, 5%S, 3%Ash, and 2%moisture(H_2O). Combustion occurs with 10% excess air (e = 0.10).
Determine:
(a) The theoretical air-fuel ratio (A:F).
(b) The actual air-fuel ratio (A:F').
(c) The higher heating value (HHV) of the fuel in kJ/kg.

Calculating the Theoretical Air-Fuel Ratio

The theoretical air required for solid fuels is derived by aggregating the exact oxygen requirements needed to stoichiometrically oxidize each combustible element (Carbon, Hydrogen, and Sulfur) present in 1 kg of the fuel, while subtracting any inherent oxygen already bound inside the fuel matrix.

The fundamental chemical equations dictate that:

- 1 kg of Carbon requires 2.67kg of O_2 to form CO_2, which equates to 11.5 kg of air.
- 1 kg of Hydrogen requires 8.00kg of O_2 to form H_2O, which equates to 34.5 kg of air.
- 1 kg of Sulfur requires 1.00kg of O_2 to form SO_2, which equates to 4.3 kg of air.

Combining these constants yields the standard empirical equation for theoretical air-fuel ratio (A:F):

$$A{:}F = 11.5C + 34.5\left(H_2 - \frac{O_2}{8}\right) + 4.3S$$

Substituting the given gravimetric decimal fractions (C = 0.45, H_2 = 0.20, O_2 = 0.10, S = 0.05):

$$A{:}F = 11.5(0.45) + 34.5\left(0.20 - \frac{0.10}{8}\right) + 4.3(0.05)$$

$$A{:}F = 11.8588 \frac{kg_{air}}{kg_{fuel}}$$

Calculating the Actual Air-Fuel Ratio

The actual air-fuel ratio (A:F') accounts for the deliberate introduction of extra air to guarantee complete combustion in the furnace environment. It is computed directly by scaling the theoretical baseline by the dilution factor (1 + e), where e = 0.10:

A:F' = (1 + e)(A:F)

A:F' = (1 + 0.10)(11.8588) $= 13.0447 \frac{kg_{air}}{kg_{fuel}}$

Calculating the Higher Heating Value via Dulong's Formula

Dulong's formula is an empirical relationship used to approximate the total chemical energy released upon complete oxidation of a solid fuel based on its elemental mass fractions. The formula assumes the hydrogen bound to the internal oxygen yields no net heat, hence the net combustible hydrogen term $\left(H_2 - \frac{O_2}{8}\right)$. The standard formula in Imperial units (Btu/lb) is:

$$HHV_{Btu/lb} = 14,600C + 62,000\left(H_2 - \frac{O_2}{8}\right) + 4,050S$$

Substituting our elemental fractions:

$$HHV_{Btu/lb} = 14,600(0.45) + 62,000\left(0.20 - \frac{0.10}{8}\right) + 4,050(0.05)$$

$$HHV_{Btu/lb} = 18,397 \frac{Btu}{lb}$$

To convert this value cleanly into standard SI units (kJ/kg), we apply the accurate international thermodynamic conversion factor (1 Btu/lb = 2.326 kJ/kg):

$$HHV_{kJ/kg} = \left(18,397 \frac{Btu}{lb}\right)\left(\frac{2.326 \frac{kJ}{kg}}{1 \frac{Btu}{lb}}\right)$$

$$HHV_{kJ/kg} = 42,792.59 \frac{kJ}{kg}$$

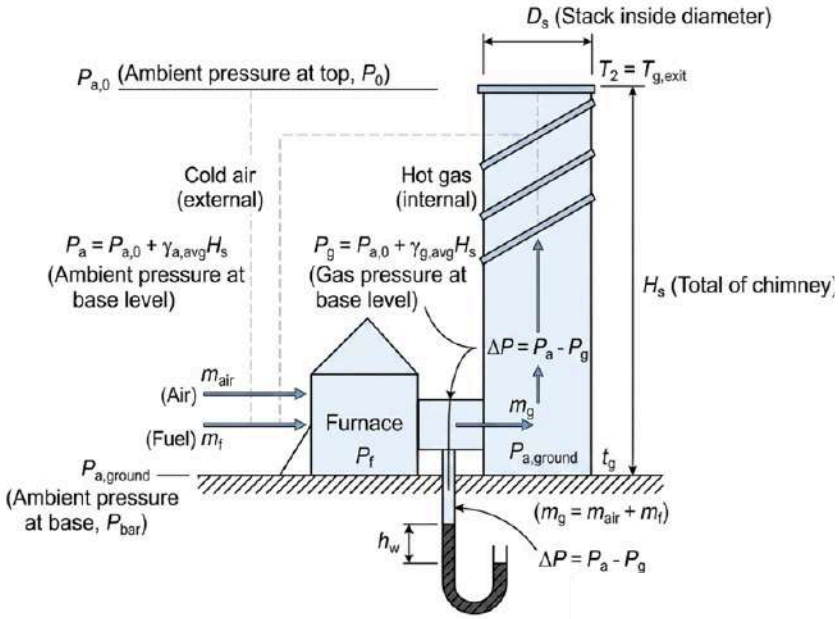
CHIMNEY

A chimney (or stack) is a vertical structural element designed to fulfill two critical industrial parameters: discharging undesirable, hazardous products of combustion away from the immediate working vicinity, and supplying the draft necessary to sustain the combustion process within a furnace.

The underlying operating mechanism relies on natural buoyancy forces. Because flue gases inside the stack are at a significantly higher temperature than the surrounding ambient air, their molecules expand, giving them a much lower density than the cold outside air. This density differential generates a pressure imbalance. The heavier, denser ambient air sinks down into the combustion zone, pushing the lighter, buoyant column of hot flue gas up through the stack.

The Mechanics of Draft

In power plant design, **draft** is defined as the small pressure differential that drives the movement of combustion air into a furnace and expels the resulting exhaust gases out through the chimney. In a natural draft system, this driving force is entirely a function of chimney height (H_s) and the fluid density difference ($\rho_a - \rho_g$).



When measuring this draft, mechanical indicators like a U-tube manometer are referenced. Because the absolute pressure difference (ΔP) is so small, it is standard practice to express the draft head not in Pascals or KiloPascals, but in **meters (or millimeters) of water column (h_w)**. Water provides a highly sensitive physical displacement that can be monitored during boiler operation.

Gas Density Formulations

The density of both the incoming atmospheric air (ρ_{air}) and the escaping flue gas (ρ_g) are governed by the Ideal Gas Law. They are calculated based on absolute local atmospheric pressure and their respective gas constants:

$$\rho_{air} = \frac{P}{R_{air} T_{air}}$$

$$\rho_g = \frac{P}{R_g T_g}$$

Where the average flue gas temperature (T_g) is taken as the arithmetic mean of the stack base temperature (T_1) and stack exit temperature (T_2):

$$T_g = \frac{T_1 + T_2}{2}$$

Note: Temperature inputs (T_{air} and T_g) must always be converted to absolute scale (K=°C+273). The gas constants used are typically R_{air} = 0.287 kJ/kg-K, and R_g is calculated based on the specific molecular properties of the exhaust components.

Total Pressure Draft Head (ΔP)

The theoretical static draft pressure created at the base of a chimney with a height H_s is the difference in hydrostatic weight between the cold external air column and the hot internal gas column:

$$\Delta P = H_s\left(\gamma_a - \gamma_g\right) = H_s\, g_o\left(\rho_a - \rho_g\right)$$

When expressing this pressure in terms of an equivalent height of a water column (h_w), we equate the hydrostatic pressure of the draft to the hydrostatic pressure of a water column $\left(\Delta P = h_w \gamma_w\right)$:

$$h_w = \frac{H_s\left(\gamma_a - \gamma_g\right)}{\gamma_w} = \frac{H_s\left(\rho_a - \rho_g\right)}{\rho_w}$$

Determining Total Chimney Height (H_S)

By rearranging the water column draft equation, a plant designer can determine the absolute structural height required to produce a specific target draft:

$$H_S = \frac{h_w \gamma_w}{\gamma_a - \gamma_g} = \frac{h_w \rho_w}{\rho_a - \rho_g}$$

Fluid Flow Dynamics and Sizing Parameters

The volumetric flow rate of the gas (Q_g or V_g) passing through a chimney is a function of its internal cross-sectional area (A) and the actual velocity of the gas (v_{actual}):

$$Q_g = A v_{actual} = \frac{\pi}{4} D_S^{\,2} v_{actual}$$

Where D_S represents the internal stack diameter. To compute the theoretical velocity of the gas $\left(v_{theoretical}\right)$ leaving the chimney, Torricelli's Law is applied using the equivalent fluid head of the flue gas (h_g):

$$v_{theoretical} = \sqrt{2 g_o h_g}$$

The fluid head in terms of meters of flue gas (h_g) is determined by translating the water column pressure or the density differential into a column of the gas itself:

Due to wall-boundary friction, structural turbulence, and internal fluid cooling, the actual velocity of the gas moving through the chimney is significantly lower than the ideal theoretical calculation. In practice, actual velocity scales between 30% to 50% of the theoretical value. For standard board problem solving, a fixed velocity coefficient (C_v) of **0.40** is applied as the default design parameter:

$$v_{actual} = C_v \cdot v_{theoretical} = 0.40\sqrt{2g_o h_g}$$

Natural draft chimneys are entirely dependent on ambient conditions. On a hot summer day, the external air density (ρ_a) decreases, which shrinks the density gap $\left(\rho_a - \rho_g\right)$. This drops the draft head (h_w), reducing air supply to the furnace. This seasonal drop-off is why modern industrial facilities rely on mechanical draft options (like forced-draft or induced-draft fans) rather than tall, expensive chimney stacks alone.

Sizing a chimney requires a careful balance between height and diameter. While height (H_S) dictates the total draft pressure available to overcome system resistance, the stack diameter (D_S) dictates the volumetric capacity. If a design diameter is restricted too much, gas velocity spikes, driving up frictional flow resistance and choking the overall capacity of the furnace.