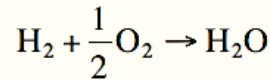


COMBUSTION STOICHIOMETRY

When molecules undergo chemical reaction, the reactant atoms are rearranged to form new combinations. For example, when hydrogen and oxygen react to form water we write



That is, two atoms of hydrogen (H) and one atom of oxygen (O) form one molecule of water (H_2O) since the number of atoms of H and O must be conserved. In the same way we can say two moles of hydrogen (H) and one mole of oxygen (O) form one mole of water (H_2O) since the number of moles of H and O must be conserved.

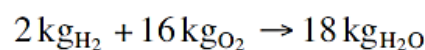
Such reaction equations represent initial and final results and do not indicate the actual path of the reaction, which may involve many intermediate steps and intermediate species. This overall or global approach is similar to thermodynamic system analysis where only end states and not path mechanisms are considered.

The relative masses of the molecules are obtained by multiplying the number of moles of each species in the molecule by their respective molecular weights. For the

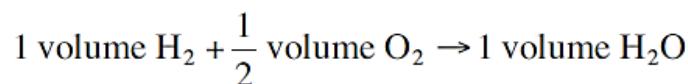
hydrogen-oxygen reaction above,

$$(1 \text{ kgmol}_{\text{H}_2}) \left(\frac{2 \text{ kg}_{\text{H}_2}}{\text{kgmol}_{\text{H}_2}} \right) + \left(\frac{1}{2} \text{ kgmol}_{\text{O}_2} \right) \left(\frac{32 \text{ kg}_{\text{O}_2}}{\text{kgmol}_{\text{O}_2}} \right) \rightarrow (1 \text{ kgmol}_{\text{H}_2\text{O}}) \left(\frac{18 \text{ kg}_{\text{H}_2\text{O}}}{\text{kgmol}_{\text{H}_2\text{O}}} \right)$$

simplifying



Thus as expected, we see that mass is conserved. The mass of the reactants equals the mass of the products, although the moles of the reactants do not equal the moles of the products. In the same way the volume may change even if ideal gases react at constant temperature and pressure. For example, consider that



In most combustion devices fuel is reacted with air rather than oxygen. Air is composed of 21% O_2 , 79% N_2 , and small amounts of argon, carbon dioxide and hydrogen. In combustion calculations it is conventional to approximate dry air as a mixture of 79% (vol) N_2 and 21% (vol) O_2 or 3.764 moles of N_2 per mole O_2 . Using $M_{\text{O}_2} = 32.00$ and $M_{\text{N}_2} = 28.01$ yields $M_{\text{air}} = 28.85$; however, the molecular weight of pure air is 28.96 because of the small amounts of other gases. The most straightforward way to correct for this difference is to use an apparent molecular weight of N,

of 28.16. This value is obtained by substitution into Equation 3.22,

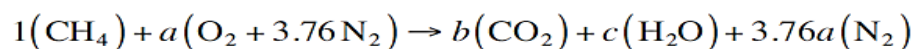
$$M_{\text{air}} = \sum_i x_i M_i = x_{\text{N}_2} M_{\text{N}_2} + x_{\text{O}_2} M_{\text{O}_2}$$

rearranging and simplifying,

$$M_{\text{N}_2} = \frac{(M_{\text{air}} - x_{\text{O}_2} M_{\text{O}_2})}{x_{\text{N}_2}} = \frac{(28.96 - 0.21 \times 32)}{0.79} = 28.16$$

In this text we assume dry air for all calculations and use a molecular weight of 29.0. In practice for certain applications the effect of water vapor in the air may need to be considered. For example, at 80°F saturated water vapor in air occupies 6.47% by volume, and hence this air contains only 19.6% O₂.

Stoichiometric air is the amount of air required to burn a fuel completely to products with no dissociation. Stoichiometric calculations are done by performing an atom balance for each of the elements in the mixture. For example, consider the combustion of methane (CH₄) with air. This can be written as



Performing an element balance for C yields

$$1 = b$$

In the same way an element balance for H yields

$$4 = 2c$$

simplifying to

$$c = 2$$

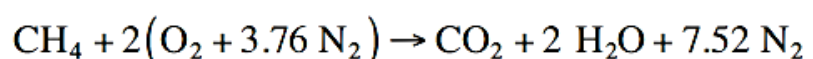
An element balance for O balance yields

$$2a = 2b + c.$$

Substituting for b and c,

$$a = 2.$$

Thus the stoichiometric equation for the combustion of CH₄ is



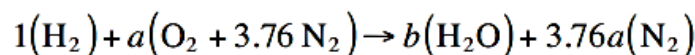
Example 3.2

For a stoichiometric hydrogen-air reaction at 1 atm pressure, find (a) the fuel-air mass ratio, f , (b) the mass of fuel per mass of reactants, and (c) the partial pressure of water vapor in the products.

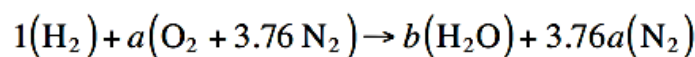
Solution

Part (a)

React 1 mole of H_2 with enough air to form the complete products H_2O and N_2 ,



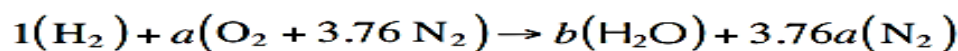
Performing a hydrogen atom balance,



$$1(2) = b(2)$$

$$b = 1$$

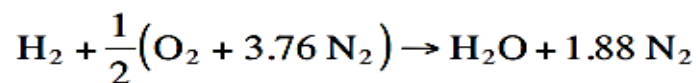
Performing an oxygen atom balance,



$$a(2) = b$$

$$a = \frac{1}{2}$$

Hence the stoichiometric equation for the combustion for H_2 is



That is, 1 kgmol of H_2 reacts with

$$\frac{1}{2}(1 + 3.76) = 2.38 \text{ kgmol}_{\text{air}}$$

On a mass basis

$$m_{H_2} = \frac{1 \text{ kgmol}_{H_2}}{1} \cdot \frac{2 \text{ kg}_{H_2}}{\text{kgmol}_{H_2}} = 2 \text{ kg}_{H_2}$$

reacts with 69.02 kg of air:

$$m_{\text{air}} = \frac{2.38 \text{ kgmol}_{\text{air}}}{1} \cdot \frac{29.0 \text{ kg}_{\text{air}}}{\text{kgmol}_{\text{air}}} = 69.02 \text{ kg}_{\text{air}}$$

Therefore

$$f = \frac{m_{\text{H}_2}}{m_{\text{air}}} = \frac{2}{69.02} = 0.029$$

Part (b)

The mass of H₂ per unit mass of reactant mixture is

$$\frac{m_f}{(m_{\text{air}} + m_f)}$$

From the definition of the fuel-air ratio,

$$m_f = m_{\text{air}} f$$

The mass of fuel to the total mass of the reactants is

$$\frac{m_f}{(m_{\text{air}} + m_f)} = \frac{m_{\text{air}} f}{(m_{\text{air}} + m_{\text{air}} f)} = \frac{f}{(1 + f)} = \frac{0.029}{1.029} = 0.0282$$

Part (c)

The partial pressure of the water vapor in the products is obtained from the mole fraction of water in the products;

$$x_{\text{H}_2\text{O}} = \frac{\text{mol}_{\text{H}_2\text{O}}}{\text{mol}_{\text{prod}}} = \frac{1}{2.88} = 0.347$$

From Equation 3.29,

$$p_{\text{H}_2\text{O}} = x_{\text{H}_2\text{O}} p = 0.347p$$

Therefore,

$$p_{\text{H}_2\text{O}} = 0.347 \text{ atm (for } T > 73^\circ\text{C)}$$

Example 3.3

Consider the stoichiometric combustion of dry pine at 1 atm pressure. Assume that the ultimate analysis of pine is 51% C, 7% H, 42% O, <0.1% N, and <0.1% S (wt %). Find (a) the fuel-air mass ratio, *f*, (b) the composition of the products on a mass basis, and (c) the partial pressure of water vapor in the products.

Solution

Part (a)

Using 100 kg of fuel as a basis for calculation,

From Equation 3.29,

$$p_{\text{H}_2\text{O}} = x_{\text{H}_2\text{O}}p = 0.347p$$

Therefore,

$$p_{\text{H}_2\text{O}} = 0.347 \text{ atm (for } T > 73^\circ\text{C)}$$

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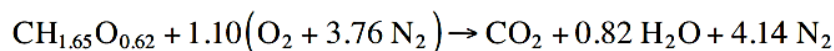
Solution

Part (a)

Using 100 kg of fuel as a basis for calculation,

	m (kg)	M (kg/kgmol)	N (kgmol)	Normalized moles
C	51	12	4.25	1.00
H	7	1	7.00	1.65
O	42	16	2.63	0.62

The stoichiometric reaction is



The mass of fuel is

$$m_f = 12 + 1.65 + 0.62(16.0) = 23.6 \text{ kg}_{\text{fuel}}$$

The mass of air is

$$m_{\text{air}} = \frac{1.1(4.76) \text{ kgmol}_{\text{air}}}{1} \cdot \frac{29.0 \text{ kg}_{\text{air}}}{\text{kgmol}_{\text{air}}} = 151.8 \text{ kg}_{\text{air}}$$

The fuel-air ratio is

$$f = \frac{m_f}{m_{\text{air}}} = \frac{23.6}{151.6} = 0.155$$

Part (b)

Referring back to the stoichiometric balance in Part a,

	N (kgmol)	M (kg/kgmol)	m (kg)	x_i
CO ₂	1.00	44.0	44.0	0.251
H ₂ O	0.82	18.0	14.8	0.084
N ₂	4.14	28.16	116.6	0.665
sum			175.4	1.000

As noted earlier we use an apparent molecular weight of 28.16 for N₂ to account for the small amounts of argon, carbon dioxide, and hydrogen in air. Based on this, the mass of products equals the mass of reactants.

Part (c)

The partial pressure of the water vapor in the products is obtained from the mole fraction of water in the products;

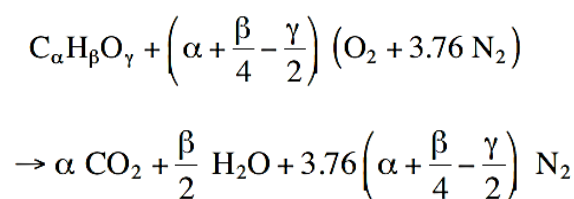
From Equation 3.29,

$$p_{\text{H}_2\text{O}} = x_{\text{H}_2\text{O}} p = 0.138 p$$

Therefore,

$$p_{\text{H}_2\text{O}} = 0.138 \text{ atm (for } T > 52^\circ\text{C)}$$

For a fuel containing carbon, hydrogen, and oxygen that is burnt to completion with a stoichiometric amount of air, atom balances on C, H, O, and N atoms yield the following general expression:



where α , β , and γ are the number of carbon, hydrogen, and oxygen atoms in a molecule of fuel. Alternatively, α , β , and γ are the mole fractions of the carbon, hydrogen, and oxygen from the ultimate analysis of the fuel. The moles of stoichiometric air, $n_{\text{air(s)}}$, per mole of fuel, is

$$\frac{n_{\text{air(s)}}}{n_f} = 4.76 \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2} \right) \quad (3.33)$$

The stoichiometric fuel-air ratio is

$$f_s = \frac{m_f}{m_{\text{air}(s)}} = \frac{n_f M_f}{n_{\text{air}(s)} M_{\text{air}}} = \frac{1(M_f)}{4.76(\alpha + \beta/4 - \gamma/2)(M_{\text{air}})}$$

substituting $M_{\text{air}} = 29.0$ and simplifying yields

$$f_s = \frac{M_f}{138.0(\alpha + \beta/4 - \gamma/2)}$$

The *percent excess air* is

$$\% \text{ excess air} = 100 \frac{(m_{\text{air}} - m_{\text{air}(s)})}{m_{\text{air}(s)}}$$

By dividing the numerator and denominator by M_{air} , this can be rewritten as

$$\% \text{ excess air} = 100 \frac{(n_{\text{air}} - n_{\text{air}(s)})}{n_{\text{air}(s)}} \tag{3.37}$$

or

$$\% \text{ excess air} = 100 \frac{(n_{\text{O}_2} - n_{\text{O}_2(s)})}{n_{\text{O}_2(s)}} \tag{3.38}$$

Percent theoretical air is the amount of air actually used divided by the stoichiometric air,

Hence,

$$\% \text{ excess air} = \% \text{ theoretical air} - 100 \tag{3.40}$$

For example, 110% theoretical air is a fuel-lean mixture (lean combustion) with 10% excess air; 85% theoretical air is a fuel-rich mixture (rich combustion) that is 15% deficient in air.

Sometimes the equivalence ratio is used instead of excess air to describe a combustible mixture. The *equivalence ratio*, F , is the actual fuel-air mass ratio, f , divided by the stoichiometric fuel-air mass ratio, f_s . That is,

$$F = \frac{f}{f_s} \quad (3.41)$$

Excess air is directly related to the equivalence ratio. Using Equation 3.38 it follows that

$$\% \text{ excess air} = \frac{100(1 - F)}{F} \quad (3.42)$$

Figure 3.1 shows percent excess air as a function of the equivalence ratio. For lean mixtures excess air tends to infinity, and this is why the use of the equivalence ratio is preferred for internal combustion engines, which often run lean.

In practice excess air is often determined by measuring the composition of the products. If combustion is complete (e.g., the products are CO_2 , H_2O , O_2 , and N_2), then we can write