**Problem solving 2**
Chemical reactions and equilibria

2.1 Altering the Atmosphere by burning fossil fuels

Problem 2.1 *In a recent year how much O_2 is removed from the atmosphere due to the combustion of fossil fuel on Earth, and how much CO_2 and H_2O is produced in the combustion process?*

The primary elemental constituents of the three major types of fossil fuel (natural gas, petroleum, and coal) are carbon and hydrogen. When fossil fuel is burned, oxygen from the atmosphere combines with the carbon to make CO_2 and with the hydrogen to make H_2O. In addition, coal contains some water (typically 10-15% by weight), which is released to the atmosphere upon combustion of the coal. All three types of fossil fuel contain various other substances such as ash, sulfur, and trace metals in even lower concentrations.

We will need to know the chemical composition of the fuel to calculate CO_2 and H_2O emission and the oxygen consumption, we need to balance the chemical combustion reactions for each fuel. Consider petroleum, first, with the approximate chemical composition $CH_{1.5}$. The combustion reaction for this fuel is

$$CH_{1.5} + xO_2 \rightarrow yCO_2 + zH_2O \tag{2.1}$$
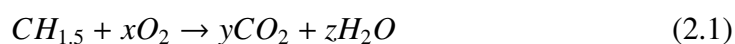
where x, y, and z are called stoichiometric constants. Their values, to be determined below, provide the answer to our problem: For each mole of petroleum consumed, x moles of oxygen are consumed, and y and z moles, respectively, of CO_2 and H_2O are produced.

Let's first determine the stoichiometric constants. Equating moles of C, H, and O on each side of the reaction gives us equations for x, y, and z. One mole of carbon in $CH_{1.5}$,for example, produces y moles of C in the form of CO_2, and so

$$y = 1. \tag{2.2}$$

Similarly, one and a half moles of H in $CH_{1.5}$ produces z moles of H_2 or $2z$ moles of H, and so

$$2z = 1.5 \tag{2.3}$$

or

$$z = 0.75. \tag{2.4}$$

Finally, $2x$ moles of O produces $2y$ moles of O in CO_2 and z moles of O in H_2O, or

$$2x = 2y + z \tag{2.5}$$

Combining Eqs. 2.2, 2.4 and 2.5, we get

$$x = 1.375 \tag{2.6}$$

The number of moles of $CH_{1.5}$ burned worldwide in a year now has to be determined. Say the energy content of the combusted petroleum in 1 year is 1.35×10^{20}J; and has a heat content of 4.3×10^{10}J/tonne. By weight, petroleum is 98% $CH_{1.5}$; thus, the amount of $CH_{1.5}$ consumed in the year is

$$0.98 \times \frac{1.35 \times 10^{20}\,\text{J}}{4.3 \times 10^{10}\,\text{J/tonne}} = 3.08 \times 10^9 \text{tonnes}(CH_{1.5}) \tag{2.7}$$

$$= 3.08 \times 10^{15}\text{g}(CH_{1.5}) \tag{2.8}$$

Since one mole of $CH_{1.5}$ has a mass of $12 + 1.5$ or 13.5 g, the number of moles of $CH_{1.5}$ consumed in the year is

$$\frac{3.08 \times 10^{15}}{13.5} = 2.28 \times 10^{14}\text{moles}(CH_{1.5}) \tag{2.9}$$

Hence $n(O_2)$, the number of moles of consumed O_2, is x times this value, or

$$n(O_2) = 1.375 \times 2.28 \times 10^{14} \tag{2.10}$$

$$= 3.14 \times 10^{14}\text{moles}(O_2) \tag{2.11}$$

The values of $n(CO_2)$ and $n(H_2O)$ can be obtained by multiplying 2.28×10^{14} moles($CH_{1.5}$) by y and z, respectively. Hence,

$$n(CO_2) = 2.28 \times 10^{14}\text{moles}(CO_2) \tag{2.12}$$

and

$$n(H_2O) = 1.71 \times 10^{14}\text{moles}(H_2O) \tag{2.13}$$

A similar procedure is used for calculating $n(O_2)$, $n(CO_2)$, and $n(H2O)$ from coal and natural gas combustion. However, now the more diverse chemical nature of the fuel must be taken into account. Say that the composition of natural gas, expressed as mole fractions, is CH_4 (75%), C_2H_6 (6%), C_3H_8 (4%), C_4H_{10}(2%), and C_5H_{12}(1%) and the remaining 12% is noncombustible. Using these mole fractions of each hydrocarbon in natural gas, first calculate an average mole fraction for each constituent and balance an equation similar to Eq 2.1.

   For coal the average formula is $CH_{0.8}$ and 75% is combustible; however, there is a subtlety in that 13% of coal is H_2O and is liberated upon combustion.

   Other information you will need is that 6.0×10^{19}J were derived from natural gas and that natural gas contains 3.9×10^7 J/m^3. For coal the numbers are 9.0×10^{19}J and 2.93×10^7 J/kg.

	$n(CO_2) \times 10^{14}$ moles	$n(H_2O) \times 10^{14}$ moles	$n(O_2) \times 10^{14}$ moles
Petroleum	2.28	1.71	3.14
Natural gas	?	?	?
Coal	?	?	?
Total	4.85	4.02	6.76

2.1.1 Notes

Follow the notes in the example.

2.1.2 Problems

1. Derive the missing results for natural gas and coal shown in the table above.

2. If all the CO_2 released to the atmosphere in a typical year from fossil-fuel burning remained there, by what percentage would that year's CO_2 emission increase the atmospheric concentration (radius of Earth= 6.4×10^6m and the thickness of atmosphere $\sim$ 10km)?

3. By what percentage does the O_2 consumed in a year by fossil-fuel burning deplete the atmosphere's stock of O_2?

4. There is great concern that the CO_2 we add to the atmosphere from fossil-fuel burning and the so-called "greenhouse" effect because this gas traps outgoing infrared radiation and thereby warms Earth's surface. Actually H_2O is a more effective absorber of infrared radiation than is CO_2. Given that emissions of H_2O were comparable to those of CO_2, why don't we worry about the effect of our H_2O emissions on the radiation balance in the atmosphere? (Hint: answering this requires only stock-flow-residence time considerations.)

2.1.3 Notes on problems

1. For this we first need to balance the equations:

   - For natural gas
     - CH_4 (75%): we need 1 mole of CO_2, 2 moles of H_2O and 2 moles of O_2.
     - C_2H_6 (6%): we need 2 moles of CO_2, 3 moles of H_2O and 3.5 moles of O_2.
     - C_3H_8 (4%): we need 3 moles of CO_2, 4 moles of H_2O and 5 moles of O_2.
     - C_4H_{10}(2%): we need 4 moles of CO_2, 5 moles of H_2O and 6.5 moles of O_2.
     - C_5H_{12}(1%): we need 5 moles of CO_2, 6 moles of H_2O and 8 moles of O_2.
     - So for 1 mole of natural gas we can use a weighted average to calculate the number of moles of CO_2, H_2O and O_2.
     - CO_2: $1 \times 0.75 + 2 \times 0.06 + 3 \times 0.04 + 4 \times 0.02 + 5 \times 0.01 = 1.12$.
     - H_2O: $2 \times 0.75 + 3 \times 0.06 + 4 \times 0.04 + 5 \times 0.02 + 6 \times 0.01 = 2$.
     - O_2: $2 \times 0.75 + 3.5 \times 0.06 + 5 \times 0.04 + 6.5 \times 0.02 + 8 \times 0.01 = 2.12$.
     - 1 mole of any gas occupies 22.4 litres (STP), so the number of m^3 burned were $\frac{6.0 \times 10^{19} \, \cancel{J}}{3.9 \times 10^7 \, \cancel{J} \, m^{-3}} \cong 1.54 \times 10^{12}$ m^3 and thus number of moles $\frac{1.54 \times 10^{15} \, \cancel{L}}{22.4 \, \cancel{L} \, mole^{-1}} \cong 6.86 \times 10^{13}$ mole. To get the number of moles of CO_2,

H_2O and O_2 multiply this number by the stochiometric constants above.

- For coal
  - $CH_{0.8}$ (75%): we need 1 mole of CO_2, 0.4 moles of H_2O and 1.2 moles of O_2.
  - Multiply all these numbers by 0.75 as only 75% is combustible: 0.75 mole of CO_2, 0.3 moles of H_2O and 0.9 moles of O_2.
  - Mass of coal: $\frac{9.0\times10^{19}\,J}{2.93\times10^7\,J\,kg^{-1}} \cong 3.07 \times 10^{12}$ kg. Therefore number of moles: $\frac{3.07\times10^{12}\,kg\times1000\,g\,kg^{-1}}{12+0.8\,g\,mole^{-1}} = 2.4 \times 10^{14}$ moles. To get the number of moles of CO_2, H_2O and O_2 multiply this number by the stoichiometric constants above.
  - However, we need to add 13% of the weight of the coal as H_2O (liberated from coal) so $3.07 \times 10^{12}\,kg \times 1000\,g\,kg^{-1} \times 0.13 = 4 \times 10^{14}$ grams, or $\frac{4\times10^{14}\,g}{18\,g\,mole^{-1}} \cong 2.21 \times 10^{13}$ moles (in addition to the $2.4 \times 10^{14} \times 0.4$ from the combustion process itself).

2. The volume that CO_2 goes into is a thin shell radius of the Earth and thickness 10 km. $V = \frac{4}{3}\pi\left((6.4 \times 10^6 + 10 \times 10^3)^3 - (6.4 \times 10^6)^3\right) \cong 5.15 \times 10^{18}\,m^3$. So number of moles (22.4 litres per mole) is $\frac{5.15\times10^{18}\,m^3\times1000\,L\,m^{-3}}{22.4\,L\,mole^{-1}} \cong 2.3 \times 10^{20}$ moles. Divide number of moles of CO_2 by this: $\frac{4.76\times10^{14}}{2.3\times10^{20}} \times 10^6 \cong 2$ ppm. Note the atmospheric CO2 conc has increased about 2 ppm per year recently.

3. Number of moles of air on earth (calculated above): 2.3×10^{20}. Multiply by percentage O_2 in air (21%): 4.83×10^{19}. So the percentage depletion: $\frac{6.58\times10^{14}}{4.83\times10^{19}} \times 100\% \cong 0.0014\%$.

4. Because the water precipitates to Earth and has a short residence time in the atmosphere, it doesn't build up like CO_2.

2.1.4 Homework and reading for next time

Background reading:

- Croft and Davison (2006, chapters on 'Simplifying algerbraic expressions', 'Factorisation' and 'Algerbraic fractions') OR 2.5 to 2.9 of the *Foundation Maths Support Pack*.

Do this weeks assessment on Blackboard:

- 'Factorising and simplifying fractions'.

- 'Altering the atmosphere by burning fossil fuels'.