ENTHALPY IN CHEMICAL REACTIONS

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 1.50.

We can find how much heat is emitted or absorbed by a chemical reaction by working with the enthalpy of the reactants and products. For example, consider the combustion of methane with oxygen at a constant temperature of 298 K:

$$\mathrm{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O} \tag{0.1}$$

Using the table at the back of Schroeder's book, ΔH for the *formation* of methane from elemental carbon (solid) and hydrogen (gas) is

$$\Delta H_{CH_4} = -74.81 \text{ kJ mol}^{-1} \tag{0.2}$$

ΔH for the *dissociation* of methane into its elements is therefore the negative of this.

Similarly

$$\Delta H_{CO_2} = -393.51 \text{ kJ mol}^{-1} \tag{0.3}$$

$$\Delta H_{H_2O}\,(\text{gas}) = -241.82 \text{ kJ mol}^{-1} \tag{0.4}$$

The total enthalpy change for the creation of the products in reaction 0.1 from their elements is

$$\Delta H_{prod} = -393.51 - 2 \times 241.82 = -877.15 \text{ kJ mol}^{-1} \tag{0.5}$$

ΔH for the reaction as a whole is

$$\Delta H = \Delta H_{prod} - \Delta H_{react} = -802.34 \text{ kJ mol}^{-1} \tag{0.6}$$

We can see this as follows. Suppose the *absolute* enthalpy of the elemental components (carbon, hydrogen and oxygen) is H_{elem} and of the reactants and products H_{reac} and H_{prod}. Then

$$\Delta H_{reac} = H_{reac} - H_{elem} \tag{0.7}$$
$$\Delta H_{prod} = H_{prod} - H_{elem} \tag{0.8}$$
$$\Delta H = H_{prod} - H_{reac} \tag{0.9}$$
$$= \Delta H_{prod} - \Delta H_{reac} \tag{0.10}$$

In 0.1, if all 4 compounds are gases and the temperature is the same on both sides, there is no volume change, as there are 3 moles of gas both before and after the reaction. Therefore the entire enthalpy change is due to change in internal energy U and, assuming no 'other' work is done, all this energy is emitted as heat. That is, for one mole of methane

$$\Delta U = \Delta H = Q = -802.34 \text{ kJ} \tag{0.11}$$

If the water is produced as liquid instead of vapour, then (from the table in Schroeder), $\Delta H_{H_2O} = -285.83$ kJ mol^{-1} and

$$\Delta H = -890.36 \text{ kJ mol}^{-1} \tag{0.12}$$

This time, the final volume is $\frac{1}{3}$ of the initial volume, since the 2 moles of water has condensed out as liquid with negligible volume compared to the gases. Thus the atmosphere does work

$$-P\Delta V = -RT\Delta n \tag{0.13}$$
$$= -\left(8.31 \text{ J K}^{-1}\right)(298 \text{ K})(-2) \tag{0.14}$$
$$= 4.953 \text{ kJ} \tag{0.15}$$

The change in internal energy is therefore found from

$$\Delta H = \Delta U + P\Delta V \tag{0.16}$$
$$\Delta U = -890.36 + 4.953 \tag{0.17}$$
$$= -885.41 \text{ kJ} \tag{0.18}$$

The difference between this value and 0.6 should be the latent heat of vaporization at 298 K. An approximation for this is

$$L \approx 2500.8 - 2.36 T_C \tag{0.19}$$

where T_C is the temperature in centigrade, so $T_C = 25$ here. This gives a value of $L = 2.442$ kJ g^{-1} so for 2 moles (around 36 g) of water, we have $L = 88$ kJ. The difference from the calculations here is only about 83 kJ, but I'm not sure how accurate the various values and formulas are. At least it's close.

As a final example, suppose the Sun with a mass of around 2×10^{33} g and luminosity of 3.839×10^{26} watts used the combustion of methane and oxygen as its energy source. The molar weights of methane and molecular oxygen around 16 g and 32 g so if the Sun were composed of one part methane to two parts oxygen (by molecular number), then the mass ratio is around methane:oxygen = 1 : 4. The number of moles of methane in the Sun is therefore

$$n_{CH_4}=\frac{2\times10^{33}}{5\times16}=2.5\times10^{31}\text{ moles} \tag{0.20}$$

Assuming the water is produced as vapour, the Sun could produce a total energy of

$$E=2.5\times10^{31}\times802.34=2\times10^{34}\text{ kJ} \tag{0.21}$$

so it would burn out after a time interval of

$$t=\frac{2\times10^{34}\text{ kJ}}{3.839\times10^{23}\text{ kJ s}^{-1}}=5.21\times10^{10}\text{ s}=1651\text{ years} \tag{0.22}$$

We can be pretty sure the Sun's source of power isn't chemical reactions!

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