

## 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:



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

$$(2) \quad \Delta H_{\text{CH}_4} = -74.81 \text{ kJ mol}^{-1}$$

$\Delta H$  for the *dissociation* of methane into its elements is therefore the negative of this.

Similarly

$$(3) \quad \Delta H_{\text{CO}_2} = -393.51 \text{ kJ mol}^{-1}$$

$$(4) \quad \Delta H_{\text{H}_2\text{O}}(\text{gas}) = -241.82 \text{ kJ mol}^{-1}$$

The total enthalpy change for the creation of the products in reaction 1 from their elements is

$$(5) \quad \Delta H_{\text{prod}} = -393.51 - 2 \times 241.82 = -877.15 \text{ kJ mol}^{-1}$$

$\Delta H$  for the reaction as a whole is

$$(6) \quad \Delta H = \Delta H_{\text{prod}} - \Delta H_{\text{react}} = -802.34 \text{ kJ mol}^{-1}$$

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

$$(7) \quad \Delta H_{\text{reac}} = H_{\text{reac}} - H_{\text{elem}}$$

$$(8) \quad \Delta H_{\text{prod}} = H_{\text{prod}} - H_{\text{elem}}$$

$$(9) \quad \Delta H = H_{\text{prod}} - H_{\text{reac}}$$

$$(10) \quad = \Delta H_{\text{prod}} - \Delta H_{\text{reac}}$$

In 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

$$(11) \quad \Delta U = \Delta H = Q = -802.34 \text{ kJ}$$

If the water is produced as liquid instead of vapour, then (from the table in Schroeder),  $\Delta H_{\text{H}_2\text{O}} = -285.83 \text{ kJ mol}^{-1}$  and

$$(12) \quad \Delta H = -890.36 \text{ kJ mol}^{-1}$$

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

$$(13) \quad -P\Delta V = -RT\Delta n$$

$$(14) \quad = -(8.31 \text{ J K}^{-1})(298 \text{ K})(-2)$$

$$(15) \quad = 4.953 \text{ kJ}$$

The change in internal energy is therefore found from

$$(16) \quad \Delta H = \Delta U + P\Delta V$$

$$(17) \quad \Delta U = -890.36 + 4.953$$

$$(18) \quad = -885.41 \text{ kJ}$$

The difference between this value and 6 should be the latent heat of vaporization at 298 K. An approximation for this is

$$(19) \quad L \approx 2500.8 - 2.36T_C$$

where  $T_C$  is the temperature in centigrade, so  $T_C = 25$  here. This gives a value of  $L = 2.442 \text{ kJ g}^{-1}$  so for 2 moles (around 36 g) of water, we have  $L = 88 \text{ kJ}$ . 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  $2 \times 10^{33}$  g and luminosity of  $3.839 \times 10^{26}$  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

$$(20) \quad n_{CH_4} = \frac{2 \times 10^{33}}{5 \times 16} = 2.5 \times 10^{31} \text{ moles}$$

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

$$(21) \quad E = 2.5 \times 10^{31} \times 802.34 = 2 \times 10^{34} \text{ kJ}$$

so it would burn out after a time interval of

$$(22) \quad t = \frac{2 \times 10^{34} \text{ kJ}}{3.839 \times 10^{23} \text{ kJ s}^{-1}} = 5.21 \times 10^{10} \text{ s} = 1651 \text{ years}$$

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

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