

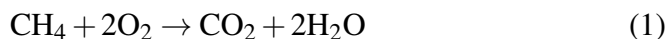
ENTHALPY IN CHEMICAL REACTIONS

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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, ΔH for the *formation* of methane from elemental carbon (solid) and hydrogen (gas) is

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

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

Similarly

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

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

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

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

ΔH for the reaction as a whole is

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

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

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

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

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

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

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

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

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

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

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

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

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

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

The change in internal energy is therefore found from

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

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

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

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

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

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 2×10^{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 are 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

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

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

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

so it would burn out after a time interval of

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

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

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