ENTHALPY

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The *enthalpy* of a system with thermal energy U, pressure P and volume V is defined as

$$H \equiv U + PV \tag{1}$$

It can be thought of as the energy required to create the system 'from nothing', since to do this, we must provide the thermal energy U and push aside the atmosphere to create the volume V in which to place the new system. Pushing aside the atmosphere (assumed to be at constant pressure P) requires work PV, so the total energy required to create the system is its thermal energy plus the energy to push the air out of the volume the system occupies.

Note that when I say the system is created 'from nothing', I'm not saying that the actual matter itself is created, since that would require providing the relativistic energy mc^2, which is not part of the thermal energy.

The word 'enthalpy' is derived from a Greek word meaning 'to put heat into' and the symbol H is based on 'heat'. In practice, it is usually changes in enthalpy that are measured; the absolute enthalpy doesn't appear in experiments.

Enthalpy is a handy quantity in some calculations since it isolates the heat transfer from the work done. To see this, recall that the energy of a system is

$$U = Q - PV + W_{\text{other}} \tag{2}$$

That is, the energy is the heat transferred into the system plus the compression or expansion work done *on* the system (which is $-PV$ here, since the *system* does work PV on its surroundings as it is created), plus any other work (from chemical reactions, for example) done on the system. As a result

$$H = Q + W_{\text{other}} \tag{3}$$

and if no 'other' work is done,

$$H = Q \tag{4}$$

That is, enthalpy is just the heat added to the system, separated from the compression or expansion work done.

Example 1. The enthalpy change for the reaction where one mole of hydrogen molecules combines with half a mole of oxygen molecues to produce water is $\Delta H = -2.86 \times 10^5$ J, assuming that the reactant gases and the resulting water are both at 25° C and 1 atm pressure. As this is an explosive reaction producing a lot of heat, the water will initially be in the form of vapour, so it will have to give off heat to condense into a liquid and then cool off to room temperature. This results in a decrease in the thermal energy U of the system. As well, the atmosphere will fill in the volume originally occupied by the reactant gases, doing work PV on the system, which is also given off as heat. The enthalpy change is the total heat emitted by the system as a result of these two mechanisms.

The energy resulting from the PV work is (assuming that the volume of the liquid water is negligible compared to the intial volume) is

$$PV = nRT \tag{5}$$

We started with 1.5 moles of gas, so

$$PV = \frac{3}{2}\left(8.31 \text{ J K}^{-1}\right)(298 \text{ K}) = 3.71 \times 10^3 \text{ J} \tag{6}$$

Therefore the energy released as a result of decreasing U is

$$-\Delta U = 2.86 \times 10^5 - 3.71 \times 10^3 = 2.82 \times 10^5 \text{ J} \tag{7}$$

The PV contribution is just over 1% of energy released.

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