ENTHALPY

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Reference: Daniel V. Schroeder, An Introduction to Thermal Physics, (Addison-Wesley, 2000) - Problem 1.49.

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

$$ H \equiv U + PV $$(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

$$ U = Q - PV + W_{other} $$ (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

$$ H = Q + W_{other} $$ (3)

and if no 'other' work is done,
That is, enthalpy is just the heat added to the system, separated from the compression or expansion work done.

**Example.** The enthalpy change for the reaction where one mole of hydrogen molecules combines with half a mole of oxygen molecules to produce water is $\Delta H = -2.86 \times 10^5 \text{ J}$, 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 initial volume) is

$$PV = nRT$$

We started with 1.5 moles of gas, so

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

Therefore the energy released as a result of decreasing $U$ is

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

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