Boiling, Combustion, Enthalpy

- When water boils its temperature remains fixed (100°C) and the surrounding pressure, P_0, is essentially constant. The heat required to change the water to steam is the latent heat

$$\boxed{L \equiv Q}$$ heat required to change one phase to another

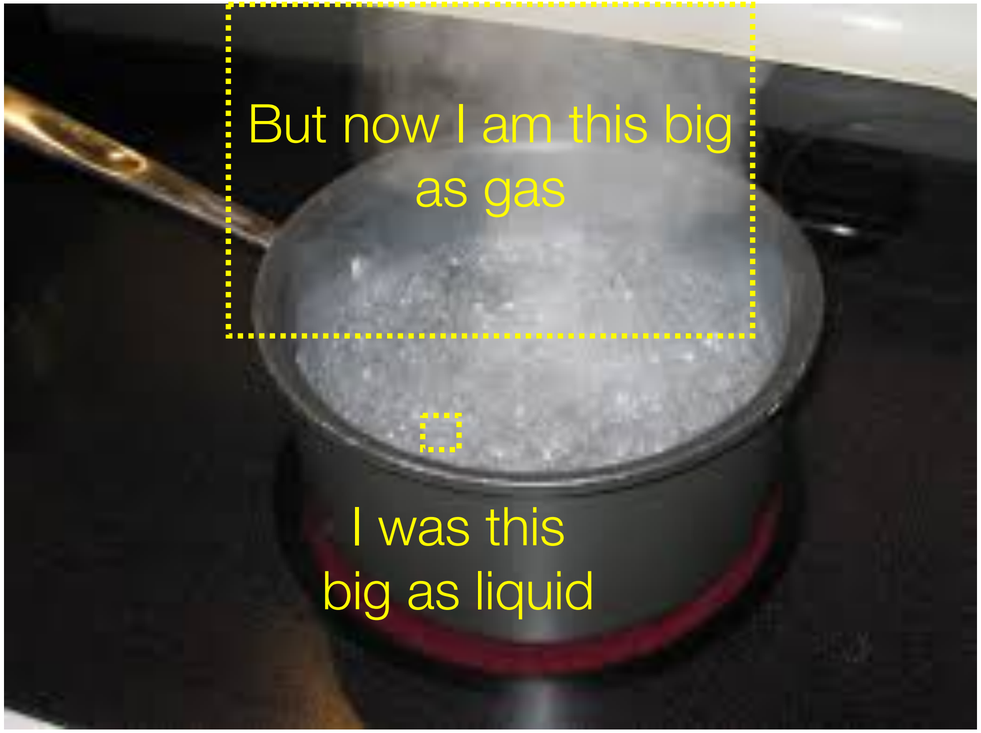
Normally we quote L for 1kg of substance or 1mol of substance, L^{1kg} or L^{1mol}. For 1mole we have for vaporization of water $L^{1mol} = 40.6$ kJ. In general $L = (N/N_A)\, L^{1mol}$. One also speaks about the latent heat of melting etc.

- The heat added is not the change in energy of the system $\Delta U = U_{steam} - U_{liquid}$.

☆ The transformation was accompanied by a change in volume, and the steam did work as it expands against the surrounding atmosphere (see slides)

$$W_{out} = P_0 \left(V_{steam} - V_{liquid}\right) > 0$$

Boiling Water



Surrounding atmosphere

the steam did work expanding against the atmospheric

So

$$Q_{in} = \Delta U + W_{out}$$

$$= (U_{steam} - U_{liquid}) + p\,(V_{steam} - V_{liquid})$$

$$= H_{steam} - H_{liquid} = \boxed{\Delta H = Q_{in} \text{ at constant pressure}}$$

Here

$\boxed{H \equiv U + pV}$ is the Enthalpy of the

of the system. It is useful whenever the pressure is constant. For gasses $H = U + NkT$.

- Another example is the combustion of hydrogen gas in atmosphere with pressure p_0

$$2H_2 + O_2 \longleftrightarrow 2H_2O + Q_{out} = 498 \frac{kJ}{mol\,O_2}$$

The heat that comes out is not (minus) the change in energy of the gasses, but (minus) the change in enthalpy of the gasses (see slide), due to W_{out}

$V_{H_2O} - V_{H_2} - V_{O_2}$

$$Q_{in} = \Delta U + W_{out} = \Delta U + p_0 \Delta V$$

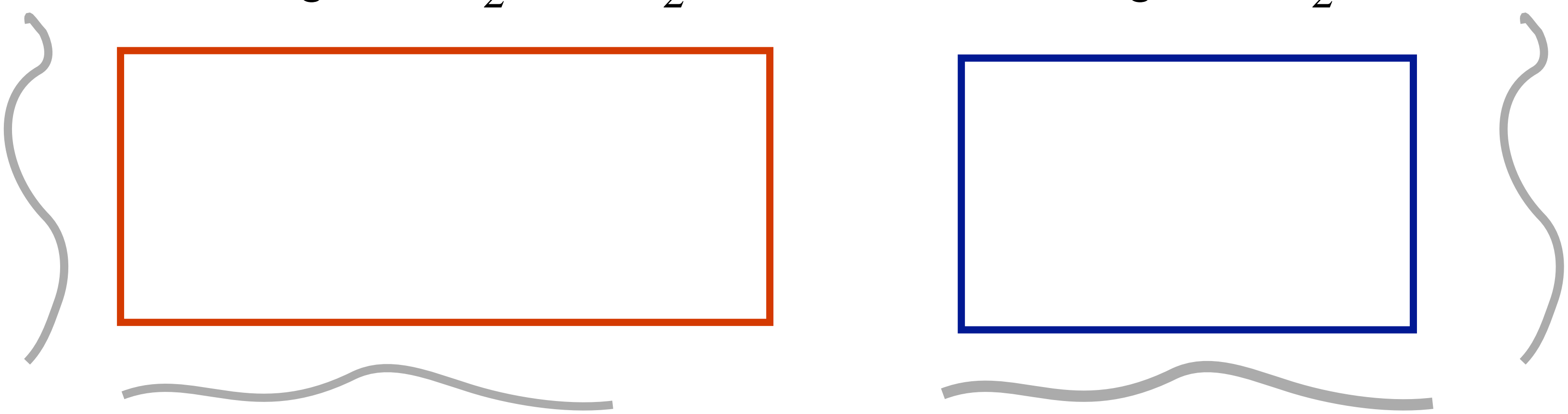
$U_{H_2O} - U_{H_2} - U_{O_2} < 0$

$Q_{in} = \Delta H < 0$ ← reaction is exothermic $Q_{in} < 0$

Combustion: $2H_2 + O_2 \rightarrow 2H_2O$

Before I was
this big as $2H_2$ and O_2

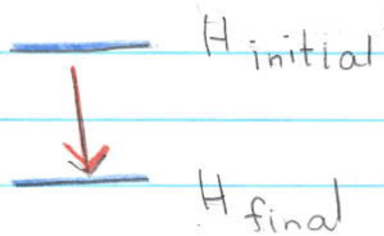
Now I am
this big as $2H_2O$



The surrounding air at atmospheric pressure
does work $p_0 \Delta V$ on system during the reaction

Now the heat that comes out is $Q_{out} = -Q_{in}$
and thus $Q_{out} = -\Delta H$

Picture:



$$\Longrightarrow \quad Q_{out} = H_{init} - H_{final} = -\Delta H$$
$$= \text{drop in enthalpy}$$

- If you want to know ΔU then in addition to measuring the heat that comes, you will need to keep track of the expansion work that was done $W_{out} = p_0(V_{final} - V_{initial})$. You will do this in HW.

- There are tables of ΔH in chemistry books. for most reactions,

<u>Math and Enthalpy</u>:

- Mathematically the enthalpy arises by integration by parts / or the chain rule

$$u\,dv = d(uv) - v\,du$$

Thus

$$dU = dQ_{in} - đW_{out} = đQ - p\,dV$$

Integrating by parts

$$dU = đQ - [\, d(pV) - V\,dp \,]$$

or

$$d(U + pV) = đQ + V\,dp$$

$H \equiv U + pV$

So

$$\boxed{dH = đQ + V\,dp}$$

If pressure is constant, $dH_p = đQ_p$, which is what we have been using.

- If the pressure is constant we can divide by dT_p

$$\boxed{\left(\frac{\partial H}{\partial T}\right)_p = \frac{dH_p}{dT_p} = C_p}$$

So we can compare

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \leftarrow \text{specific heat at const volume}$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \leftarrow \text{specific heat at const pressure}$$

- Now for an ideal gas $V = NkT/p$

$$H = U + pV = U(T) + NkT$$

not a function of volume for ideal gas.

So

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \frac{dU}{dT} + Nk$$

$$C_p = C_V + Nk$$

which we derived previously.

- This set of steps going from $dU = đQ - p\,dV$ to $dH = đQ + V\,dp$ is known as a Legendre transformation, which will appear again in this course.