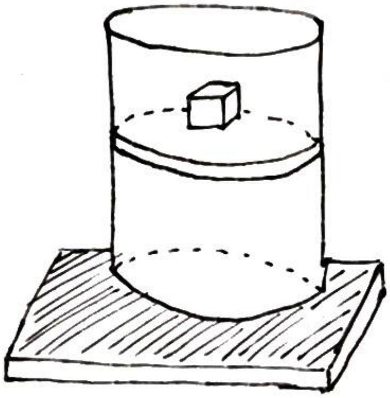
The First Law of Thermodynamics

Consider an isobaric pressure (one at constant pressure):



Here, a vessel with a piston is filled with a gas at initial temperature T_i. A weight mg pushes down on the piston such that the pressure in the gas is:

$P = P_{atm} + \frac{mg}{A}$ which is a constant throughout this process.

The vessel is placed on a thermal reservoir and the gas is heated. Using the ideal gas law: $PV = Nk_BT$, we see that if T increases and P remains constant, then the volume of the gas V must increase.

$$PV = Nk_BT \Rightarrow PV = n_M RT \quad \therefore \ \Delta V = \frac{n_M R}{P} \Delta T$$

The work done on the gas is given by:

$$W = -\int_{V_i}^{V_f} P\,dV = -P(V_f - V_i) = -P\Delta V = -n_M R \Delta T$$

So the work done by the gas is $\underline{n_M R \Delta T}$. For an increase in temperature the work done by the gas is positive. This makes sense as the gas is pushing the piston up.

So by heating up the gas, we increase its internal energy $\Delta U = C_V \Delta T = n_M c \Delta T$. But then the gas does work $W = P\Delta V = n_M R \Delta T$. So where is this energy for work coming from? The internal energy?

This question took a long time to answer and it leads to the first law of thermodynamics.

By using conservation of energy, we can say that the change in internal energy of the gas is given by the work done on the gas and the heat into the system.

$\boxed{\Delta U = Q + W}$ where Q is the heat into the system and W is work done on the gas.

So the first law of thermodynamics is:

> The change of internal energy in a system is the sum of heat added to the system and work done on the system.

Q and W here are not functions of state. A function of state is a physical quantity that depends on the equilibrium state variables P, V, N, T only.

We can also write the equation as $dU = đQ + đW$ where d is "change in" and the $đ$ is to remind us those quantities aren't state variables.

So for our isobaric experiment:

$$\Delta U = Q + W$$

$$n_m C \Delta T = Q - n_m R \Delta T$$

$$Q = n_m C \Delta T + n_m R \Delta T$$

$$= n_m \Delta T (C + R)$$

$$= n_m \Delta T (c_p)$$

$$\frac{Q}{\Delta T} = n_m c_p = C_p$$

There is a relation called "Mayer's Relation" which states $c_p - c_v = R$ i.e the specific heat capacity at constant pressure minus the one at constant volume $= R$

$$\therefore \quad C_p = \left(\frac{\partial Q}{\partial T}\right)_p \quad \text{and} \quad C_v = \left(\frac{\partial Q}{\partial T}\right)_v$$