The first law of thermodynamics

Recall that the equation of state (relating p, α, and T) does not define the reaction of the atmosphere to a change in one of the variables (if P decreases, how does T change?). We need more information, and this is provided by the first law of thermodynamics under a restrictive (but often realistic) set of conditions.

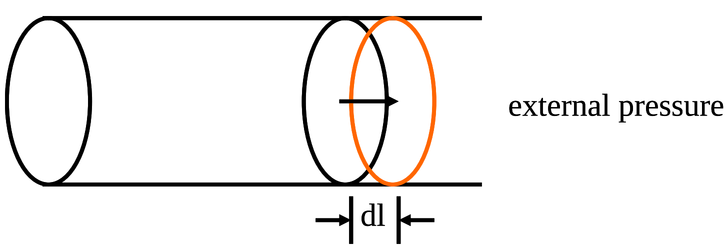
The first law of thermodynamics is a statement of the conservation of energy for a thermodynamic system. We can write it in the form

$$dQ = dE + dW$$

where dQ = an infinitesimal amount of heat added to the system
dE = the increase in internal energy, recorded as a change in temperature
dW = the work done by the system on its surroundings

Work of expansion

dW is the work performed by the system. As heat is added, a gas that is free to expand will perform work on its surroundings against the pressure of the external gas. Imagine a volume of gas contained in a cylinder – heat added forces the gas to expand and to push against a piston. We calculate the work performed in the following manner:



Let the cylinder contain unit mass of air (1 kg). The work done in the expansion is equal to the force (pA) multiplied by the distance moved by the cylinder dl.

Then work done dW = (PA)dl

Now, if A is the cross-sectional area of the cylinder, and dl is the distance moved by the piston, Adl is the increment of volume during the expansion. Since we stipulated that there would be unit mass of gas in the cylinder we can write the increment of volume as $d\alpha$ (recall the definition of specific volume). Hence

$$dW = p\,d\alpha$$

Internal energy and specific heat

To consider the heat content or internal energy of a gas, we need first to define specific heat. Specific heat is the amount of heat required to change the temperature of unit mass of gas by one degree. But heat added to a gas can be partitioned in two ways (as the first law tells us). Thus,

heat added → raise T (internal energy)

heat added → perform mechanical work (expansion)

and the specific heat will depend on how the added heat is partitioned. There are an infinite number of ways to partition the heat, but it is useful to consider two special cases:

1) the gas is allowed to expand but the pressure is kept constant (a very important process in the atmosphere). Then we define the specific heat at constant pressure C_p as

$$C_p = \left(\frac{dQ}{dT}\right)_{p=\text{constant}}$$

2) the volume is kept constant. There is no expansion so that no work is performed and all the added heat goes into increasing the internal energy of the system. Thus we define the specific heat at constant volume C_v such that

$$C_v = \left(\frac{dQ}{dT}\right)_{V=\text{constant}}$$

C_p and C_v can both be determined experimentally in the laboratory. Clearly $C_p > C_v$ because in the process defined by (1) above, not all of the heat goes towards varying the internal energy of the gas (in fact, $C_p = C_v + R$).

Now, if the gas is not allowed to expand, $dW=0$ and the first law of thermodynamics reduces to

$$dQ = dE$$

and, from the definition of C_v, we can write that

$$dE = C_v\, dT$$

and the first law of thermodynamics can be written in

$$dQ = \underbrace{C_v\, dT}_{\text{change in internal energy}} + \underbrace{p d\alpha}_{\text{work done by the gas}}$$

Thus the first law provides a second relationship between p, α, and T. Since we generally want to know how temperature changes for a given change in atmospheric pressure, an alternative from of the first law is often used:

$$dQ = C_p dT - \alpha dp$$

Note:

1) This alternative form is obtained by differentiating the equation of state and substituting for $d\alpha$. We do not need to know the details at this point but students are welcome to attempt the proof.

2) $C_p dT$ is not the change in internal energy and $-\alpha dp$ is not the work done by the system, but rather dE and dW are both involved in each term.