Problem II.4 ... perpetuum mobile

7 points; (chybí statistiky)

Lego wanted to take a break from a problem in his thesis, where a quantum heat machine behaved like a perpetual motion machine. Thus, he came up with a perpetual motion machine in classical physics using the following reasoning. Somewhere in a pit (it doesn't even have to be very deep) we evaporate water (to do this we consume some latent heat). The water rises as vapor upwards, where we condense it again (releasing the latent heat). But the water now has a higher gravitational energy! Where did this energy come from? Or should Lego run to the patent office to go down in history as the inventor of the perpetual motion machine? Support your claims with calculations.

Lego was working on his thesis.

The concept behind this perpetual motion device hides two unverified assumptions. One of them concerns latent heat: at the beginning, we had to supply some latent heat to the water, and at the end, some latent heat was released. However, why should we assume that these heats are the same? Latent heat probably won't depend on the altitude *explicitly* (directly), but it may depend *implicitly*, as the pressure decreases with altitude. The same can be said for the boiling temperature; it also depends on the surrounding pressure. Therefore, when we condense water, it will likely have a lower temperature than during evaporation and, consequently, lower internal energy.

It is also important to note that the difference in the surrounding air pressure after the water ascends is inevitable. This pressure is hydrostatic pressure, meaning the difference between two heights will be equal to the air's weight per square meter. The only way to eliminate this pressure difference would be to remove the air, but then there would be no buoyancy force to push the water vapor upward.

So, we have two candidates as the source of energy for the increase in the water's gravitational potential energy – the difference in latent heat and the difference in boiling temperatures (both caused by the difference in surrounding pressure). Let's take a closer look at these. Finally, we will also examine the change in the potential energy of the air.

Temperature

Let's say we let $m=1\,\mathrm{kg}$ of water evaporate at sea level ($h_0=0\,\mathrm{m.\,a.\,s.\,l.}$) and condense it at a height of $h_2=500\,\mathrm{m.\,a.\,s.\,l.}$ This increases the gravitational potential energy by $\Delta E_\mathrm{p}=mg(h_2-h_0)=4\,905\,\mathrm{J.}$ Atmospheric pressure at h_0 is $p_0=101\,325\,\mathrm{Pa}^1$ and at height h_2 it is $p_2=95\,457\,\mathrm{Pa.}$

When we substitute the empirical formula for the dependence of the boiling point on the pressure², we get the temperature at the beginning as $T_1 = 99.97$ °C and at the end $T_2 = 98.32$ °C. Thus, the difference between the water at the beginning and the water at the end is $\Delta T = 1.6$ °C. The specific heat capacity of water is $c = 4200 \,\mathrm{J\cdot kg^{-1}\cdot °C^{-1}}$, therefore the difference of the internal energy of the water will be $\Delta U = mc\Delta T = 6900 \,\mathrm{J} > \Delta E_{\mathrm{p}}$. From where, we can start to think that the increase in potential energy could have arisen from the difference in internal energy.

Why does water vapor cool on its way up? Naturally, it cools slightly due to heat exchange with the surrounding air. However, what if we enclosed it in some intangible container that insulates it? Even in such a case, it would cool down precisely because the pressure decreases.

¹ https://www.treking.cz/pocasi/atmosfericky-tlak.htm

²http://fyzikalnipokusy.cz/1671/zavislost-teploty-varu-vody-na-tlaku

The vapor thus expands adiabatically. We can calculate the temperature that the water vapor has when it ascends using adiabatic processes, for which the following holds:

$$p_1 V_1^{\kappa} = p_2 V_2^{\kappa} \to p_1^{1-\kappa} T_1^{\kappa} = p_2^{1-\kappa} T_2^{\kappa} ,$$

$$T_2 = T_1 \left(\frac{p_1}{p_2}\right)^{\frac{1-\kappa}{\kappa}} ,$$

where $\kappa=1.33$ is the Poisson constant for water vapor. By substitution (remembering to substitute temperatures in Kelvin), we get that the temperature that the water vapor has after ascending to h_2 as $T_2=94.5\,^{\circ}\text{C}$, which is even lower than the boiling temperature at that altitude! This implies that it will be necessary to supply energy to the water on its way up to prevent it from condensing earlier. Therefore, the potential energy gained by water can also come from this heating.

Latent heat

In the case of latent heat, the situation is more complicated; nowhere have we found tabulated values, so we have to calculate the dependence ourselves. We use the Clausius-Clapeyron equation³, according to which

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T\Delta v},$$

where T is the boiling point, $\mathrm{d}P/\mathrm{d}T$ is the derivative of the pressure at which boiling occurs with respect to the boiling point temperature, and Δv is the increase in volume on evaporation. We already have boiling point T for both cases, $\mathrm{d}P/\mathrm{d}T$ is also calculated from the relationship between boiling point and pressure. Specifically, if for T we have $T=71.6\,^{\circ}\mathrm{C}+7/25\,^{\circ}\mathrm{C}\cdot\mathrm{kPa}^{-1}P$, then $\mathrm{d}P/\mathrm{d}T=25\,000/7\,\mathrm{Pa}^{\circ}\mathrm{C}^{-1}$. Volume change per mole of water Δv is obtained by neglecting the volume of liquid water and expressing the volume of vapor from the equation of state for an ideal gas

$$\Delta v \approx v = \frac{V}{n} = \frac{TR}{P}$$
.

When we substitute this relationship, we get

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{PL}{T^2R} \,.$$

When we look at this relationship, we find that the formula in this form could be already found on Wikipedia:). When we plug everything into it, we get an estimate for latent heat at sea level $L_0 = 41\,000\,\text{J}\cdot\text{mol}^{-1}$. Substituting in the values at h_2 , we get $L_2 = 43\,000\,\text{J}\cdot\text{mol}^{-1}$. Hence, we can conclude that the latent heat tends to increase rather than decrease with height. Thus, the energy required to increase potential energy cannot come from a decrease in latent heat since it doesn't seem to decrease.

³https://en.wikipedia.org/wiki/Clausius-Clapeyron_relation

The potential energy of air

It should also be mentioned that during this process, the potential energy of the air in the atmosphere decreases. But by how much? During the step in which water vapor rises, a portion of the air essentially exchanges places with the water vapor. Therefore, since air has a higher density than water vapor, its potential energy decreases more during this step than the potential energy of the rising water vapor increases. This energy exchange explains the water vapor rising in general.

However, in the given task, we are not only interested in why water vapor rises. We are concerned with the energy balance from when we have liquid water below to when we have liquid water above. In the first step, when we evaporate water, we push the air upward, significantly increasing the potential energy of the air.

In conclusion, during the entire process, only the volume of water $V = m/\rho_V = 0.001 \,\mathrm{m}^3$ is moved from the height h_0 to the height h_2 . As a result, the volume of air V is displaced from the height h_2 to the height h_0 . We can calculate how much the potential energy of the air decreases, $\Delta E_{\rm pvz} = V \rho_{\rm vz} g(h_2 - h_0) = 4.9 \,\mathrm{J}$. We can see that the potential energy of the air decreases but by less than the increase in the potential energy of the water. Therefore, this explanation is not sufficient.

Conclusion

We have looked for the energy source for the increase in the potential energy of water. We identified three suspects: the change in the water temperature, latent heat change, and the decrease in air energy. Through calculations, we showed that the water temperature decreases, causing the thermal energy of the water to decrease more than the potential energy increases. We also demonstrated that energy needs to be supplied to the water for it to rise. On the other hand, latent heat tends to increase with altitude. Furthermore, the potential energy of the air decreases, however, it does so by less than the increase in the potential energy of the water, so this explanation is insufficient. The result is that this energy comes dominantly from the difference in the thermal energy of the water at the beginning and end of the process.

Šimon Pajger legolas@fykos.org

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