GEOS 24705 / ENST 24705

# The physics and thermodynamics of steam – the long version

***First, a reminder on pressure***. Reviewing what we did in class: pressure is force/area, i.e.

$$P = F/a$$

(The units of pressure are the same, incidentally, as energy/volume)

Because air molecules have mass, the atmosphere is pressing down on you at all times. Atmospheric pressure is 14 pounds per square inch. If you squashed all the air molecules above 1 square inch of the Earth into a box and carried them away, your box would weigh 14 pounds. We often use units relating pressure to that at the Earth's surface, which we say is "1 atmosphere" (or sometimes, "1 bar"). In Standard International units, atmospheric pressure at the surface of the Earth is about $10^5$ Pascal, where 1 Pa = 1 (kg m/s$^2$) / m$^2$. Typically about 1 to 2% of those molecules will be water vapor (most of the rest are $N_2$ and $O_2$), so we say that the "partial pressure" of water is 0.01 to 0.02 atmospheres.

Because you're used to living under atmospheric pressure you don't really notice it. But if you dive to the bottom of a swimming pool, you definitely feel the higher pressure there. You are now feeling not just the atmosphere but also all the water above you. We calculated in class the column of water that Savery's pump could lift: about 30 feet. To get feel for atmospheric pressure, then, you can dive 30 feet under water and see what that feels like. (Then you're under 2x atmospheric pressure).

***Second, what is steam?*** The English language is a little fuzzy here. Some definitions say that any water vapor ($H_2O$ in gaseous form instead of liquid) is steam. By that definition, the atmosphere itself is a very low-temperature steam engine. Other definitions say that steam is water vapor if the water vapor happens to be boiling. (Which brings up another question: what does "boiling" mean?) Finally, a third definition says that steam is "pressurized water vapor", i.e. water vapor at a pressure higher than 1 atmosphere. Those are incompatible definitions, which makes clear thinking difficult.

Let's start with the question of what boiling is, and even before that, how vapors and liquids interact.

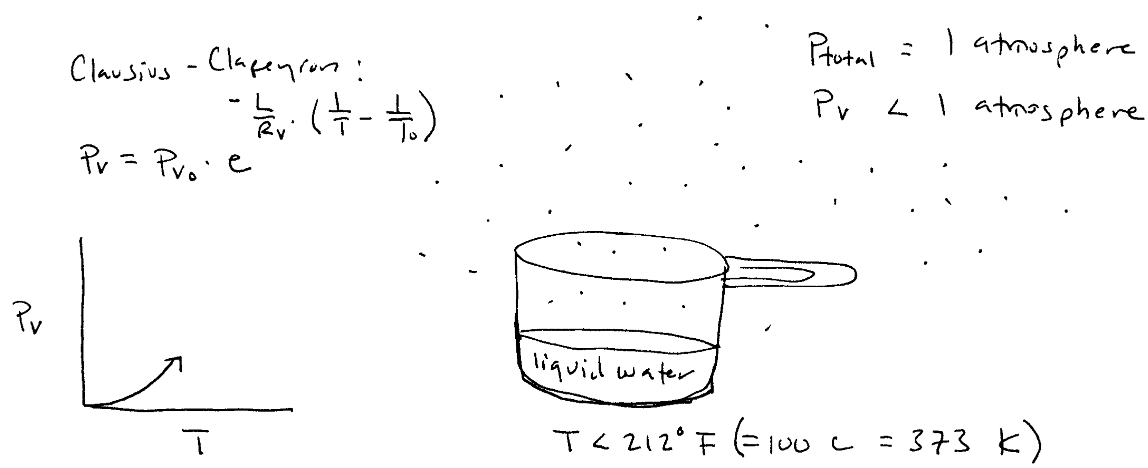
We all know from our experience that the atmosphere contains some water vapor at all times, even at temperatures well below what we might think of as the "boiling point". We talk about the humidity, and know what a humid day feels like.

In a very qualitative explanation: whenever/wherever there is liquid water, some of the water molecules "want" to be in gas phase. If you bring a pot of water into very dry air and wait, you'll find that some water from the pot evaporates (i.e. some of the molecules move into the gas phase), until eventually the liquid and vapor reach "equilibrium". At that point the liquid water and vapor are somehow in the state they "want" to be in and their proportions stay constant.

If you heat up that pot of water, however, more water "wants" to move into the gas phase. You have some intuitive sense that hot air holds more water vapor: a hot summer Chicago day feels damp to you, while cold winter air feels dry.
The amount of water that evaporates as you warm the water is described by a very simple and beautiful relationship, named after its two independent discoverers, Clausius and Clapeyron. The Clausius-Clapeyron equations states that the equilibrium "partial pressure" over liquid water -- the pressure that you'd measure if you had only water vapor and no extraneous air molecules -- is a function only of temperature. If you increase temperature by a small increment (call it dT), then the partial pressure of water (call it $p_v$) increases by a corresponding

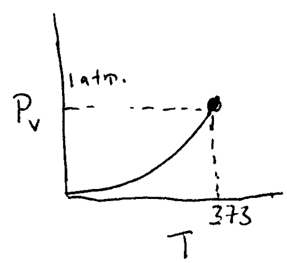
$$dp_v = p_v \cdot (L_v/R_v) \cdot dT/T^2$$

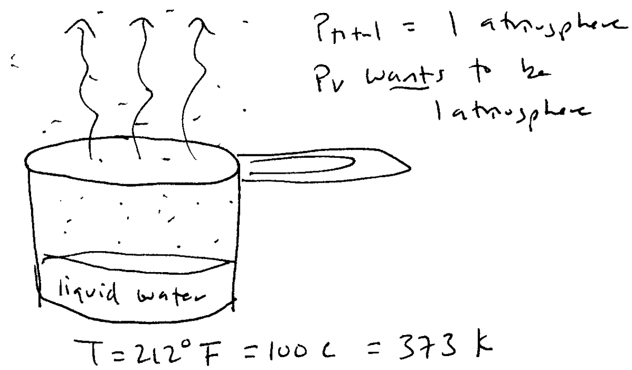
where $L_v$ is the latent heat of vaporization that we estimated in class (the J/kg required to evaporate water) and $R_v$ is the universal gas constant divided by the molecular mass of water. (See below for integrated solution. The constants are $L_v \sim 2.3 \cdot 10^6$ J/kg and $R_v \sim 460$ J / kg·K ).




***What is boiling?*** If you heat up your pot all the way to 212 degrees Fahrenheit (= 100 Celsius = 373 Kelvin), you find that so much water evaporates that the pot eventually becomes dry. "It's boiling", you might say. What does that mean? The boiling point occurs when the equilibrium vapor pressure has increased until it is the same as atmospheric pressure. That is, the pot of liquid water "wants" to be in contact with pure water vapor at a pressure of 1 atmosphere. But since the total pressure of water PLUS air can't be more than 1 atmosphere, then the liquid can never reach the condition it "wants", no matter how many water molecules evaporate. So once the water hits 212 F (=100 C = 373 K), it just keeps evaporating til all the liquid is gone.

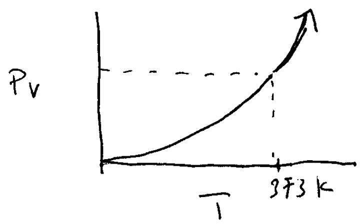
Note that once your open pot of water hits the boiling point, its temperature doesn't go up anymore (at least until it boils dry), even though you're still heating it. All the energy you transfer to the water is going into evaporating water vapor instead of into heating the liquid.

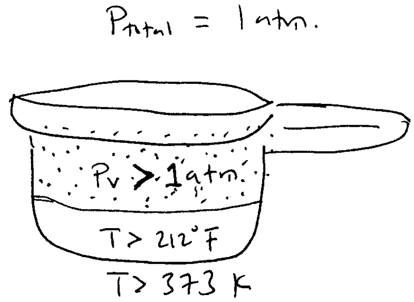


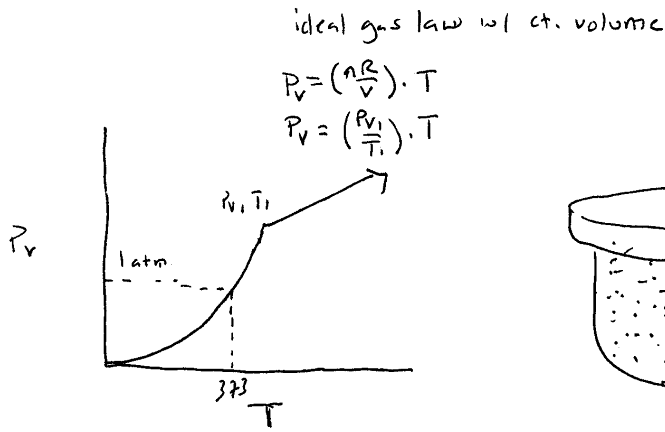

***Circumventing boiling:*** If you put a pressure-tight lid on your 212 °F pot of water, you can prevent it from boiling. The lid makes possible the condition that the liquid "wants" to be in, that it come into contact with 1 atmosphere of water vapor. The pressure in the pot simply increases til the pot holds 1 atmosphere of water vapor plus whatever pressure is due to the air trapped in the pot. In fact, you can now keep heating up the liquid, because pressure and temperature will just rise together. This how a pressure cooker works: it raises the temperature of its contents to hotter than the boiling point, so the food cooks faster.

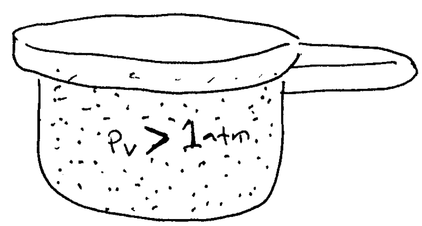
Steam engine developers adopted the same pressure-cooker strategy to raise their engine temperatures and pressures. Although the early steam engines (late 1700s) ran at pressures very close to atmospheric, a hundred years later engineers were building steam engines with pressures tens or even a hundred times atmospheric pressure (think: equivalent to the ocean at 3000 feet depth). You can imagine that it wouldn’t be pleasant to be around one of those exploding.




**Superheating steam:** If you keep raising the temperature of your pot, and you aren't somehow resupplying it with water, the number of molecules in the gas phase will keep rising, until eventually all the water you started with will have evaporated. Your pot will then be dry not because you "lost" water but because it's so hot that you can't meet the condition that liquid and vapor "want" to be in, because there simply aren't enough molecules available.  At this point you are finally free of the constraint of Clausius-Clapeyron, which describes the equilibrium between liquid and vapor. You have no more liquid, only what is termed "superheated steam", and that steam now behaves like any other gas (i.e., it follows the ideal gas relationship). Its pressure continues to rise with temperature, but less steeply than the Clausius-Clapeyron equation prescribes.




**Finally, a reminder about temperature scales:** for all problems in thermodynamics, you need to use the absolute temperature scale (Kelvin, not Fahrenheit or even Celsius). The location of what 0 degrees matters to your answers, and so does the definition of what a degree is. In Standard International units, temperature is always assumed in K.