

SOME SOLUTIONS FOR SHEET 4

A1 *Isothermal atmosphere*

Given that

$$\beta \equiv 1 - \frac{1}{\gamma},$$

when $\gamma \rightarrow 1$ then $\beta \rightarrow 0$. So

$$T = T_0 \left(1 - \beta \frac{z}{H}\right)$$

becomes $T = \text{const}$: an isothermal atmosphere. Great! The pressure, however, is tricky because $T \propto p^\beta$ or

$$p \propto T^{1/\beta},$$

which becomes unpleasant as $\beta \rightarrow 0$.

Instead imagine γ very close to 1: $\gamma = 1 + \epsilon$. Then

$$\beta = 1 - \frac{1}{1 + \epsilon} \approx 1 - (1 - \epsilon) = \epsilon.$$

So

$$\frac{T}{T_0} \approx 1 - \epsilon \frac{z}{H}$$

and

$$p \propto T^{1/\epsilon}.$$

The combination of these two results is

$$\frac{p}{p_0} \propto \left(1 - \epsilon \frac{z}{H}\right)^{1/\epsilon}.$$

This equation may not look so familiar, but look at these:

$$\begin{aligned} 1.01^{100} &\approx e, \\ 1.001^{1000} &\approx e, \\ 1.0001^{10000} &\approx e. \end{aligned}$$

The pattern for large n is:

$$\left(1 + \frac{1}{n}\right)^n \rightarrow e,$$

which gives

$$\left(1 + \frac{x}{n}\right)^n \rightarrow e^x.$$

Why?! Thus

$$\left(1 - \epsilon \frac{z}{H}\right)^{1/\epsilon} \approx e^{-z/H}.$$

Since $H = mg/kT_0$ the pressure is

$$\frac{p}{p_0} \propto e^{-mgz/kT_0}.$$

Ah, the Boltzmann factor has returned with mgz as the potential energy of a gas molecule at height z and T_0 as the temperature of the isothermal atmosphere.

A2 *Ice skating*

For the magic pressure p I'll try

$$p \sim \frac{L_{\text{vap}} \text{ for one molecule}}{\text{molecular volume}}.$$

This quantity is also the volume heat of vaporization, ρL_{vap} so

$$p \sim \rho L_{\text{vap}} \sim 10^3 \text{ kg m}^{-3} \times 2 \times 10^6 \text{ J kg}^{-1} \sim 2 \times 10^9 \text{ J m}^{-3}$$

or about 20000 atm. An ice skate blade has area

$$A \sim 20 \text{ cm} \times 0.2 \text{ cm} = 4 \times 10^{-4} \text{ m}^{-2}$$

so the pressure exerted by the ice skate blade is

$$\Delta p \sim \frac{\text{weight}}{\text{area}} \sim \frac{60 \text{ kg} \times 10 \text{ m s}^{-2}}{4 \times 10^{-4} \text{ m}^{-2}} \sim 10^6 \text{ Pa}$$

or about 10 atm.

Thus the change in freezing temperature is

$$\Delta T_{\text{freeze}} \sim T_{\text{freeze}} \times \frac{10 \text{ atm}}{20000 \text{ atm}} \sim 0.1 \text{ }^\circ\text{C}.$$

That's not enough to allow ice skating through pressure melting when the air temperature is even 1 degree below freezing. Oh, well! You can also check the pressure-melting theory by skating and then picking up one skate and looking at the blade. If pressure were keeping the water around the blade melted, as soon as you lift the blade, the water would freeze back into ice crystals. But I haven't seen that happen.

Another effect is friction. As the skate slides along, the friction means energy dissipated into the ice. This energy will melt some thickness of ice below the blade no matter how low the friction.

A3 *Fog*

As night falls, moist daytime air cools, which reduces the the vapor pressure of water. The excess water vapor condenses into tiny water droplets. From the vapor pressures at the daytime temperature and nighttime temperatures, I can work out the density of water vapor condensed out (ρ_c). That's not enough however. The water could live as one giant drop or it could be trillions of nanometer-sized droplets. To decide, I need one more equation, which comes from the other piece of information: the mean free path of a light ray. I'll guess that a light ray that hits a droplet gets well scattered. From kinetic theory, $n\sigma\ell \sim 1$, where n is the number density of droplets, σ is the cross-sectional area of a droplet, and ℓ is the mean free path.

Imagine that the droplets are cubes of side d (for diameter) separated by a distance x . Then each has mass ρd^3 and the density of condensed-out water is

$$\rho_c \sim \rho \frac{d^3}{x^3}.$$

That's the first equation for the three unknowns, ρ_c , d , and x . Another equation comes from the mean free path, since $n = 1/x^3$ and $\sigma \sim d^2$:

$$\frac{1}{x^3} \sim \frac{1}{d^2 \ell}.$$

Combining these two equations:

$$\frac{\rho_c}{\rho} \sim \frac{d}{\ell}.$$

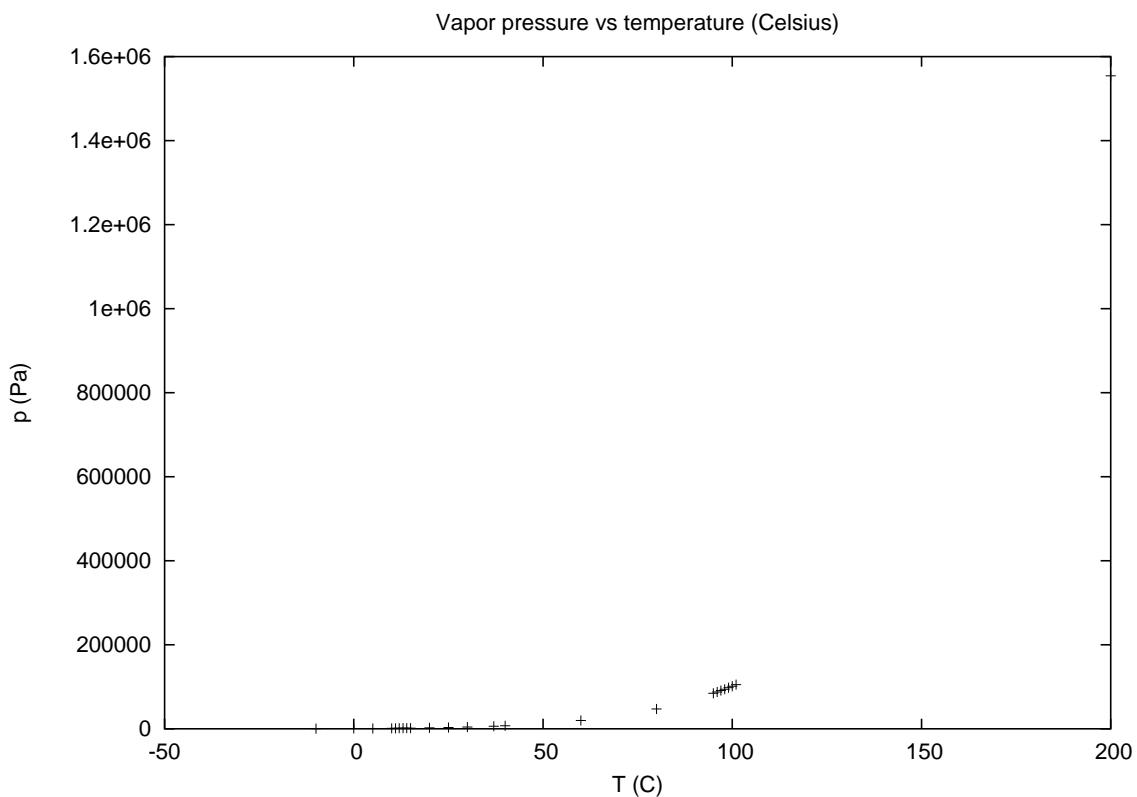
Let's say the temperature goes from a daytime 20 °C to a nighttime 10 °C. The table in question B1 says that $\Delta p_{\text{vap}} \sim 10^3$ Pa or about 10^{-2} atm. If water were air (in molar mass) then ρ_c would be 10^{-2} times the density of air. This approximation is not horrible, so I'll use it. Maybe it cancels another sloppiness in the derivation. Since ρ is 1000 times the density of air, $\rho_c/\rho \sim 10^{-5}$. In a moderate fog one can see maybe $\ell \sim 100$ m, so

$$d \sim 100 \text{ m} \times 10^{-5} = 1 \text{ mm}.$$

That's way too big (real fog droplets are about 20 to 50 times smaller), so an assumption of the analysis is badly broken. Oh, well, not every problem works out nicely.

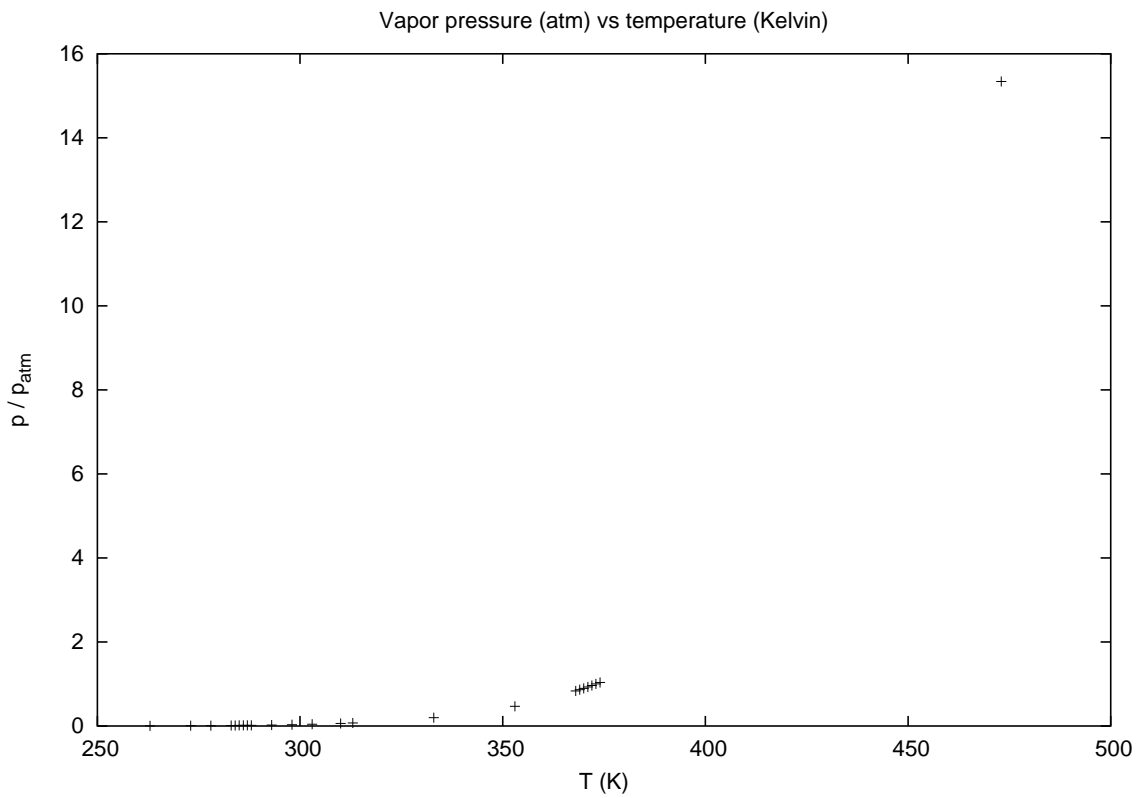
B1 Vapor pressure

(a)



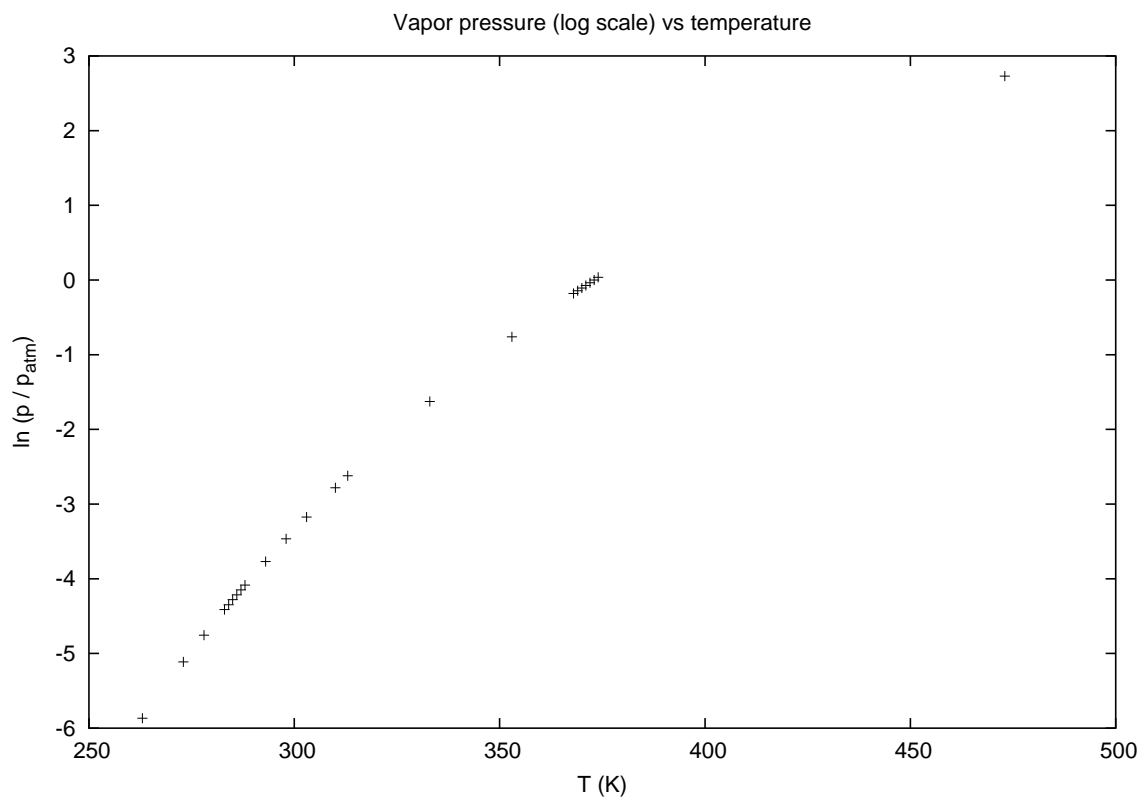
These axes are still useless! I can hardly see the points at low temperature because the high pressure at $T = 200$ °C makes the y axis span a huge range.

(b)



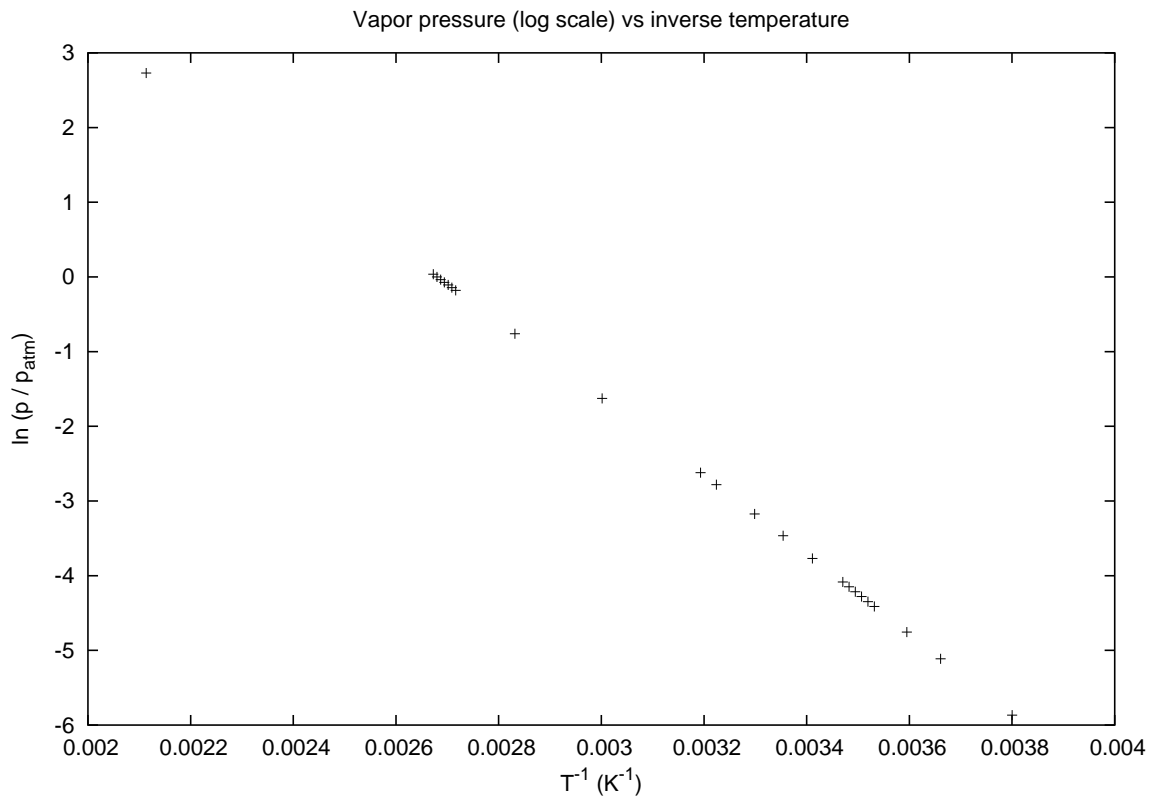
Slightly better in principle, but I still can't see anything useful.

(c)



Much better in that all the points are easy to distinguish.

(d)



And now the line is straight. Great!

(e) Since the line is straight,

$$\ln \frac{p}{p_{\text{atm}}} = -\frac{A}{T} + B,$$

where A and B are constants. The dimensions of A are temperature, so I'll use T_0 for it. B is dimensionless but its value isn't that important. Eyeballing the slope by taking the first point on the left and the penultimate point on the right:

$$\text{slope} = \frac{\text{rise}}{\text{run}} \sim \frac{-5.2 - 2.8}{(0.0036 - 0.0021) \text{ K}^{-1}} = -\frac{8}{15} \times 1000 \text{ K} \sim -5000 \text{ K}$$

So $T_0 \sim 5000 \text{ K}$. To convert it to more familiar units, I use $1 \text{ eV} \sim 10^4 \text{ K}$, so

$$\text{energy per molecule} = kT_0 \sim 0.5 \text{ eV},$$

$$\text{energy per mole} = RT_0 \sim 8 \text{ J mol}^{-1} \text{ K}^{-1} \times 5000 \text{ K} \sim 4 \times 10^4 \text{ J mol}^{-1},$$

and

$$\text{energy per mass} = 4 \times 10^4 \text{ J mol}^{-1} \times \frac{1 \text{ mol}}{1.8 \times 10^{-2} \text{ kg}} \sim 2 \times 10^6 \text{ J kg}^{-1}.$$

Especially the last value looks familiar. It's the *heat of vaporization of water*, L_{vap} .

(f) The Boltzmann factor gives the probability of finding a molecule in its different energy states. Here the states are liquid (low energy) or gas (much higher energy because all the bonds are gone). So the probabilities are:

$$P(\text{liquid}) \propto e^{-E_{\text{liquid}}/kT},$$

and

$$P(\text{vapor}) \propto e^{-E_{\text{vapor}}/kT}.$$

These probabilities are unnormalized. But their ratio is easy to compute without normalizing:

$$\frac{P(\text{vapor})}{P(\text{liquid})} = e^{-\Delta E/kT},$$

where $\Delta E = E_{\text{vapor}} - E_{\text{liquid}}$. This energy is L_{vap} . The amount of liquid is roughly constant since liquid is so much denser vapor. Then $P(\text{liquid})$ is roughly constant, and

$$P(\text{vapor}) \propto e^{-L_{\text{vap}}/kT}.$$

Since probability is proportional to density and density (by the ideal gas law) is proportional to pressure,

$$p \propto e^{-L_{\text{vap}}/kT}$$

or

$$p = p_0 e^{-L_{\text{vap}}/kT},$$

for some pressure p_0 . This pressure is not atmospheric pressure as you can see by putting in $T = 373 \text{ K}$ (boiling point of water) and $p = 1 \text{ atm}$ to solve for p_0 .

As T goes to infinity, this vapor pressure equation predicts that the pressure asymptotes to p_0 . The result seems strange. But think about the world at infinite temperature. Then everything gets huge amount of energy for free (from the heat bath), so the energy difference between liquid and gas becomes miniscule. The molecule no longer cares whether it is in the liquid or the gas. At temperatures almost as high, it cares almost as little. So as $T \rightarrow \infty$, the temperature becomes irrelevant and the vapor pressure becomes independent of temperature.

D1 Carnot cycle

The notes for 6 Feb have everything except the diagrams.