

This note will cover a lot of ground, but there aren't too many prerequisites. You should be familiar with the notions of entropy, reversible processes, and heat engines. If you're not completely clear on what those are or need a refresher, I strongly recommend Chapter 24 from [Halliday, Resnick, Krane](#).

1. Phase Equilibrium

Any substance can take on a variety of phases, and under certain conditions two phases of a substance can coexist when they're put in contact. Consider, for example, a closed vessel with liquid water and water vapour inside, kept at some fixed temperature T . There are mechanisms through which the water molecules can pass from one state to the other. We have evaporation, where the molecules at the surface of the liquid may break away if their thermal energy happens to be large enough (hence, there is more evaporation at higher temperatures). Likewise, we also have condensation, where the molecules in the vapour rejoin the liquid – many of these molecules will actually reflect off the interface, but some will always get swallowed up. The interaction between the vapour and the liquid can be quantified by the pressure p at the interface due to both of these processes. Naturally, the push from the vapour on the liquid is the same thing as the push from the liquid on the vapour. To belabor the point, if you think about moist air above the ocean, the pressure of the water will be equal to the total atmospheric pressure p_0 . This is emphatically *not* the interaction pressure p of the two water phases. Instead, p_0 is the sum of p and the pressure due to the interaction of the liquid water and the dry air. You can define an interaction pressure p for other setups as well, like liquid water pushing on a block of ice. If this happens out in the open, p should be equal to p_0 . But if you're pressing water and ice together in the lab, p is whatever you want it to be. The upshot is, you always need to mind the external constraints on the system.

Let's now go back to the example of liquid water and vapour in a closed vessel. This situation is, in general, unstable. The value of p at our temperature T may correspond to the rate of evaporation being larger than that of condensation. For other values of p , the condensation might dominate. At any given T , there's one specific value of p for which the two rates are equal (and I'm not claiming that this is obvious!). We then say that the two phases are in equilibrium. That is, as long as you hold the system at T , it will evolve so that the interaction pressure is p , and then it will stay like that forever.

It follows from the above that there will be some curve $p(T)$ along which both phases can coexist. We will try to derive $p(T)$. Consider a system of two phases (1 and 2) with total mass m . The surroundings of this system won't matter in what follows. Assume that we've found some point of phase equilibrium (p, T) , where the densities of the phases are ρ_1 and ρ_2 , and the transition from 1 to 2 requires you to supply a latent heat¹ $Q = \lambda m$. Suppose the system is initially in phase 1 – call this state A. We will now carry out a cyclic process on this system. Here is how:

- Process A-B: First, we transfer everything to phase 2 at (p, T) . We do this very slowly, i.e. reversibly. Note that we are able to do that because the system is in equilibrium at those p and T to begin with, such that it won't spontaneously convert to phase 1 or phase 2 by itself. We have put in heat $Q = \lambda m$, and the system has done work $A_{AB} = p \left(\frac{m}{\rho_2} - \frac{m}{\rho_1} \right)$.
- Process B-C: We move adiabatically and reversibly from (p, T) to another equilibrium state $(p - dp, T - dT)$. The system remains in phase 2 throughout. This is feasible as there is no other phase to oppose us.
- Process C-D: We transfer everything back to phase 1 at this new equilibrium state. Again, we do this reversibly. The system has done work $A_{CD} = (p - dp) \left(\frac{m}{\rho_1} - \frac{m}{\rho_2} \right)$. Note that the densities ρ'_1 and ρ'_2 are the same as ρ_1 and ρ_2 up to a first-order differential. This doesn't really matter, especially considering that ρ_1 and ρ_2 are themselves markedly different.

¹ The latent heat goes towards: **1.** Changing the binding energy between the molecules. **2.** Expanding the substance in accordance with its new density. Mathematically, $Q = \Delta U + p\Delta V$. Looking at this, there doesn't seem to be any reason why λ should be constant. And indeed, it isn't! But we'll deal with this separately. You'll get to work out how λ depends on T by yourself in Problem 6.

- Process D-A: While the system is in phase 1, we move adiabatically and reversibly back to the initial state.

The processes are shown below on a pT diagram and a pV diagram.

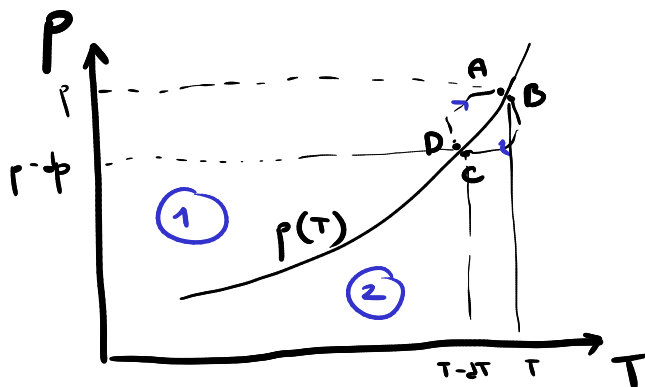


Figure 1

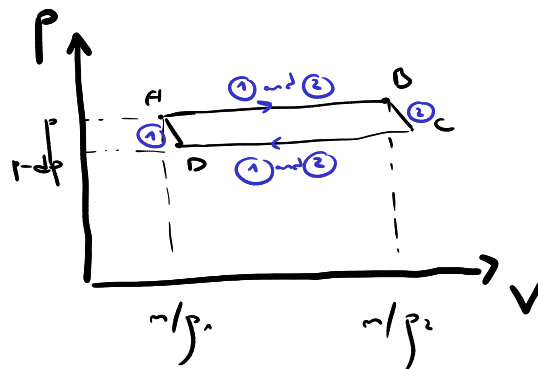


Figure 2

Let's summarise. The system has gone back to its initial state, having done work $dA = A_{AB} + A_{CD} = dp \left(\frac{1}{\rho_2} - \frac{1}{\rho_1} \right) m$. Since the entropy of the system is a function of state, its overall entropy change is $\Delta S = 0$. Then we have

$$\Delta S = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DA} = \frac{Q}{T} + 0 - \frac{Q - dA}{T - dT} + 0 = 0,$$

where we made use of the fact that all of the processes are reversible, and hence the entropy change is *exactly* $\int \frac{dQ}{T}$. We also required that all the heat we put in is either converted to work or drawn out, for otherwise the system cannot return to state A, which has a fixed internal energy. Now we can do the following:

$$\frac{dA}{Q} = \frac{dT}{T}, \quad Q = \lambda m \quad \implies \quad \frac{dp}{dT} = \frac{\lambda}{T \left(\frac{1}{\rho_2} - \frac{1}{\rho_1} \right)}.$$

This result is called the Clausius-Clapeyron equation, even though it was derived by Carnot decades earlier. Generally, λ , ρ_1 and ρ_2 are not constants, but we can nevertheless integrate this and obtain the coexistence curve $p(T)$. We have obtained something tangible through an abstract derivation. It seems as we've pulled the equation out of thin air! But this should instead convince you that entropy is as real a quantity as pressure, temperature, or internal energy.

To illustrate, the graph of $p(T)$ for liquid water and water vapour is shown on Figure 3 (note the logarithmic scale). Of course, you can study the phase boundaries of other phases as well, and this leads to phase diagrams (Figure 4).

2. Vapours

From now on we will limit ourselves to working with liquid-vapour equilibrium. Firstly, we need to introduce some terms. If the vapour is in equilibrium with the adjacent liquid, we call it *saturated vapour*. The pressure of a saturated vapour corresponds to the coexistence curve $p(T)$, meaning that it depends only on temperature.

We state without delay that in most everyday situations the vapours are not saturated. In the case of evaporation from water on a hob, there's not enough time for thermal equilibrium to settle in. The vapours are lighter than air, so they'd rather rise to the ceiling. And even if this wasn't the case, they'd get carried away by the fresh air in the room. This is the reason why vapours at a given temperature T generally have only a fraction of the pressure expected for a saturated vapour at T . In the case of water, this fraction $\varphi = p/p_{\text{sat}}$ is known as the *relative humidity*. Normally you can't get $\varphi > 100\%$, because at that point the two phases are not in equilibrium, but unlike the case of $\varphi < 100\%$, this time around external factors like air flows cannot facilitate a quasi-equilibrium state.

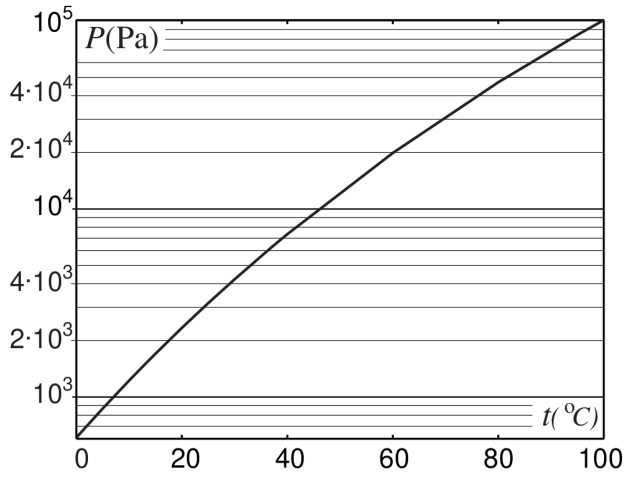


Figure 3

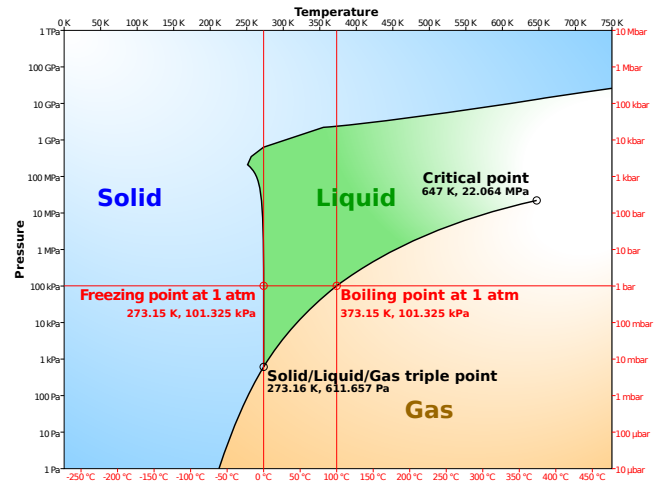


Figure 4

In contrast to the conditions in big open spaces, vapours in closed containers want to remain saturated. As you increase the temperature of the vessel, p_{sat} rises sharply (again, refer to Figure 3). If the vapours are to stay at p_{sat} , there would have to be more and more molecules in the gaseous state. These can only be supplied by the liquid, and eventually that bunch of liquid runs out of moles to give out. From that point on, there is only vapour in the vessel, and it won't be saturated.

Next, let's solve some problems to get our head around these concepts.

Example 1. Juice (Estonia 2003). A juice bottle is pasteurised at a temperature of $t_1 = 80^\circ\text{C}$ while a non-deformable light cap lies freely on the rim of the bottle (excess gas can exit freely from the bottle, but outside air cannot come in). The cap is then tightly fixed so that air can no longer enter or leave the bottle. The bottle is cooled down to $t_0 = 20^\circ\text{C}$. What is the pressure under the bottle cap at that instant? The atmospheric pressure is $p_0 = 101\text{ kPa}$. The dependence of the saturated vapour pressure on temperature is shown on Figure 3.

Solution. In the beginning, the inside of the bottle and the outside atmosphere are in mechanical equilibrium. The total pressure inside is p_0 . The vapour above the juice is saturated, so this p_0 is the sum of the saturated vapour pressure (SVP) at t_1 and the pressure of the dry air inside the bottle:

$$p_0 = p_{\text{sat}}(t_1) + p_{\text{air}}.$$

After the bottle is sealed and cooled down, there will be some condensation, because the vapours remain saturated, but the SVP has changed. Nonetheless, since the liquid is much denser than the gas, the condensation will not change the volume available to the gas significantly. Hence, from the dry air's point of view, the cooling is done at constant volume. The final pressure of the dry air is then

$$p'_{\text{air}} = p_{\text{air}} \frac{T_0}{T_1} = (p_0 - p_{\text{sat}}(t_1)) \frac{T_0}{T_1},$$

and the total pressure would be

$$p = p_{\text{sat}}(t_0) + (p_0 - p_{\text{sat}}(t_1)) \frac{T_0}{T_1} = 47\,100\text{ Pa}.$$

Example 2. Ice in a cube (Physics Brawl 2023). We enclose ice with mass $m = 15$ g and temperature $t_0 = 0^\circ\text{C}$ under normal conditions ($p_n = 101$ kPa, $t_n = 20^\circ\text{C}$) in a hermetically sealed cubic container with volume $V = 0.101$. We start heating the container until it reaches a temperature $t = 120^\circ\text{C}$. What is the pressure p in the container at that point? Use [this website](#) for any reference data that you need.

Solution. The density of the ice at 0°C is $\rho_{\text{ice}} = 916$ kg/m³, so the available volume is $V_i = V - \frac{m}{\rho_{\text{ice}}}$. The SVP at the initial temperature is negligible, so the amount of dry air inside the container can be found as

$$n_{\text{air}} = \frac{p_n V_i}{RT_n} = 3.48 \times 10^{-3} \text{ mol.}$$

Now consider the amount of water in the vessel,

$$n_w = \frac{m}{\mu_w} = 0.833 \text{ mol.}$$

If all of this has evaporated at $t = 120^\circ\text{C}$, the pressure of that vapour would be

$$p' = \frac{n_w RT}{V} = 27 \text{ MPa.}$$

This greatly exceeds the SVP at that temperature, which is $p_{\text{sat}} = 198.9$ kPa. Hence, rather than all of the water evaporating, only a small part of it has turned to gas. So, in the final state we have liquid water of mass $\approx m$ and density $\rho_{120^\circ\text{C}} = 943$ kg/m³. The remaining volume $V_f = V - \frac{m}{\rho_{120^\circ\text{C}}}$ is occupied by dry air and saturated vapour at pressure p_{sat} . And the answer is

$$p = p_{\text{sat}} + \left(\frac{V_i T}{V_f T_n} \right) p_n = 334 \text{ kPa.}$$

Example 3. Cloud formation (Russia 2017). Assuming an adiabatic atmosphere, estimate:

- (a) The total height H of Earth's atmosphere.
- (b) The lowest height h_0 at which clouds can form.

The surface temperature of the Earth is $t_0 = 27^\circ\text{C}$, and the relative humidity there is $\varphi = 80\%$. Assume $h_0 \ll H$. Also assume that air is an ideal diatomic gas of molar mass $\mu = 29$ g/mol. The dependence of the saturated vapour pressure of water p_H on the temperature t is given in the table below.

$t, ^\circ\text{C}$	6	8	10	12	14	16	18	20	22	24	26	28
$p_H, \text{ mmHg}$	7.01	8.05	9.21	10.5	12.0	13.6	15.5	17.5	19.8	22.4	25.2	28.4

Hint: In an adiabatic atmosphere, a parcel of gas moving vertically with no heat transferred to it will remain in mechanical equilibrium throughout.

Solution. (a) This is a problem on gas flows. We will examine how a column of air ('the system') can slowly rise through the atmosphere ('the surroundings'), occupying a new position where the local parameters of the atmosphere are different. Let this column of air start from the ground, $z = 0$, and end at some arbitrary z . As it rises from the ground, molecules that covered a volume V_0 at the ground will clear the space up for the surrounding atmosphere to come in. The pressure there is p_0 . Meanwhile, at the top of the column, where the pressure is p , molecules from the system will push out the surroundings and occupy a volume V :

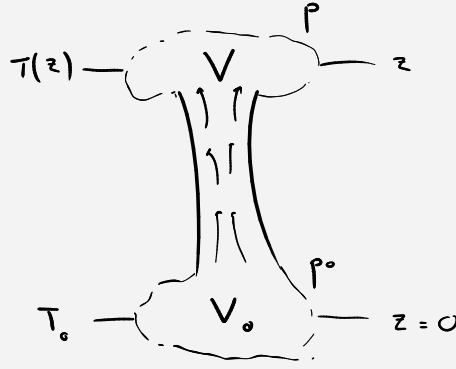


Figure 5

When this happens, the atmosphere has done work $A_{\text{ext}} = p_0 V_0 - pV$ on the air column, so the air column has done work $A_{\text{gas}} = -A_{\text{ext}} = pV - p_0 V_0$. Now let us think about how the internal energy of the air column has changed. Since the adiabatic atmosphere has a fixed temperature distribution, the final state of the column is almost the same as the initial state, the exceptions being the packets V and V_0 at the top and the bottom. The change in the internal energy ΔU comes only from the internal energies of those two packets. Note that the packets have the same mass m and the same number of moles n . This follows from mass conservation. Then, treating air as an ideal diatomic gas, we can write

$$\Delta U = \frac{5}{2}nR(T - T_0) + mg(z - 0).$$

It's more accurate to account for the gravitational potential energy change in the work term, but I don't want to dwell on formalities right now. Anyway, since the process is adiabatic, we can write the first law as

$$A_{\text{gas}} + \Delta U = 0.$$

Finally, using $pV = nRT$ and $p_0 V_0 = nRT_0$, we reach

$$\frac{7}{2}nR(T - T_0) + (\mu n)gz = 0,$$

$$T = T_0 - \frac{2\mu g}{7R}z.$$

We'll consider the height of the atmosphere to be the height z at which T turns to zero. Thus

$$H \approx \frac{7RT_0}{2\mu g} = 30 \text{ km}.$$

Of course, there's no reason why this way of estimating H is better than any other, but we got a decent numerical value, and we should leave it at that.

(b) Clouds will form at the instant when condensation becomes favourable, i.e. at phase equilibrium. This happens at a height z for which the pressure of the water vapour in the air p_{vap} equals the saturated vapour pressure p_{sat} . The latter will depend on temperature, so it certainly changes with z . We want to derive $p_{\text{vap}}(z)$. Firstly, note that $p_{\text{vap}}(0) = \varphi p_{\text{sat}}(0) = \varphi p_H(T_0) \approx 21.4 \text{ mmHg}$, where we interpolated from the table. Now, the main point here is that the vapour column must have reached mechanical equilibrium by itself (in an ideal gas mixture, all species interact separately). Balancing forces on a cylinder of height dz and cross-section S , we find

$$S dp_{\text{vap}} = -\rho_{\text{vap}} g S dz.$$

We substitute $\rho_{\text{vap}} = \frac{\mu_{\text{H}_2\text{O}} p_{\text{vap}}}{RT}$ with $T = T_0 - \frac{2\mu g}{7R}z$ to find

$$\frac{dp_{\text{vap}}}{p_{\text{vap}}} = - \left(\frac{7\mu_{\text{H}_2\text{O}}}{2\mu} \right) \frac{dT}{T} \quad \Longleftrightarrow \quad p_{\text{vap}} = p_{\text{vap}}(0) \left(\frac{T}{T_0} \right)^{\frac{7\mu_{\text{H}_2\text{O}}}{2\mu}}.$$

Since we're looking for a value of h_0 much smaller than H , we'll have $T \approx T_0$, or $\frac{2\mu g}{7R}z \ll T_0$. We can then apply the binomial approximation, which yields

$$p_{\text{vap}}(z) = \varphi p_{\text{sat}}(t_0) \left(1 - \frac{\mu_{\text{H}_2\text{O}} g}{RT_0} z \right).$$

We'll now plot this dependence on the same graph as $p_{\text{sat}}(z)$, the data points for which are taken from the table of $p_H(T)$:

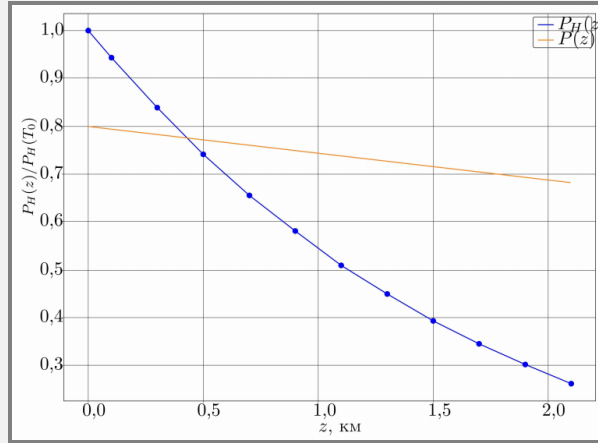


Figure 6

The intersection is at $h_0 = 0.43$ km, and we are done. Note that, indeed, $h_0 \ll H$, so our approximations above were reasonable.

3. Boiling

In a previous example, we looked at a vessel in which water was heated up to 120 °C and yet remained in a liquid state. If you're still young and innocent, you might have asked yourself, why doesn't all the water boil away when it reaches 100 °C? In reality, boiling is something entirely separate from your usual evaporation, and it plays by different rules. Conventional (nucleate) boiling is associated with bubbles which form within the liquid phase. These are filled with molecules of the substance that have transitioned to a gaseous state. This sort of phase transition requires putting in heat, and it will block the system from increasing its temperature.

Imagine that a bubble has randomly appeared in the bulk of the liquid. This is exceedingly unlikely to happen purely due to thermal fluctuations. Instead it occurs because of the uneven surface of the vessel or because of the small particles suspended in the liquid. These can act as nucleation sites which make the presence of bubbles more energetically favourable. Anyway, given that the bubble is in contact with the liquid, the vapour inside is saturated. So, at a given temperature T , the vapour pushes on the surface of the bubble with a pressure $p_{\text{sat}}(T)$. On the other hand, the surroundings want the bubble to collapse. Let the pressure above the liquid be p' . Then, if the bubble is at depth h and has a radius r , the pressure on the bubble is

$$p_{\text{out}} = p' + \rho g h + \frac{2\sigma}{r},$$

where ρ is the density of the liquid and σ is the surface tension at the liquid-vapour interface². The bubble can exist only if $p_{\text{sat}}(T)$ exceeds p_{out} . It follows that bubbles will start to appear only when

² If you're feeling underprepared on surface tension, Ashmit Dutta has made a nice [handout](#) which goes into a lot of detail.

the temperature is high enough. When it comes to p_{out} , we can usually neglect the hydrostatic term. We can do the same for the surface tension term, because the initial r of the bubbles is usually large enough. Also, in the case of a vessel open to the atmosphere (such as a pot filled with water), the pressure p' is simply the atmospheric pressure p_0 . Note that even if there's lots of vapour above the liquid, mechanical equilibrium tends to take precedence, so we still have $p' = p_0$. In conclusion, the nice and simple way to write the condition for boiling is then

$$p_{\text{sat}}(T) = p_0.$$

And as long as boiling remains possible, it will take away any heat that you put in. Only after everything has evaporated can you increase the temperature further. Still, you can get around this by purifying the liquid and smoothing out the vessel, which removes the nucleation sites. You can then go above the usual boiling point, albeit in an unstable state. This is called superheating, and you should probably try to [avoid](#) it.

Going back to the condition for boiling, notice that if the pressure of the surroundings were lower, the boiling would commence at a lower temperature. If you want to make some soup fast, you need a high temperature, though of course you also don't want the food to explode in your face, so you must stay below the boiling point. Consequently, if the boiling threshold is lower, cooking gets harder! Paying a premium for food when vacationing in the mountains is probably justified.

Now, let's see what would happen if the vessel were closed. The pressure above the liquid is simply $p_{\text{sat}}(T)$. The outside pressure near any potential bubble is therefore larger than $p_{\text{sat}}(T)$. That is why bubbles will always collapse under these circumstances. In a perfectly sealed pressure cooker, water would never boil. This allows you to cook at temperatures higher than 100°C , so you'd be done with it faster. Please understand – in general, substances *want* to remain in phase equilibrium. But in certain conditions boiling will get in the way, and you have to complete the phase transition all at once.

Example 4. Unknown liquid under a piston (Russia 2022).

A vertical cylindrical vessel of cross-section $S = 0.01 \text{ m}^2$ and height $2H$ ($H = 1 \text{ m}$) is separated from the atmosphere ($P_0 = 10^5 \text{ Pa}$) by a piston, as shown on Figure 7. The piston initially rests on narrow supports at a height H above the bottom of the vessel. The piston can slide along the walls of the vessel smoothly while maintaining a hermetic seal. The piston and the vessel do not conduct heat.

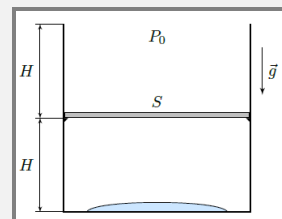


Figure 7

We drain all the air from the chamber below the piston and we put some small amount of liquid there, of negligible volume compared to SH . The temperature of the system after it has reached thermal equilibrium is $T_0 = 350 \text{ K}$. We then slowly heat up the vessel through the bottom, and we track the pressure P and the temperature T below the piston until it reaches the top of the vessel at height $2H$. The graph of $P(T)$ is given on Figure 8.

- Find the mass of the piston M .
- Find the mass m_0 of the substance in the chamber under the piston (accounting for all states of matter).
- Find the heat Q supplied to the vessel from the moment when the piston begins rising until the moment it has reached height $2H$.

The heat of vaporisation of the liquid at temperature $1.1T_0$ is equal to $L = 2.2 \text{ MJ/kg}$. The molar mass of the liquid is $\mu = 18 \text{ g/mol}$. The gas constant is $R = 8.31 \text{ J/mol K}$, and the acceleration due to gravity is $g = 9.8 \text{ m/s}^2$. The vapour of the substance can be treated as an ideal polyatomic gas.

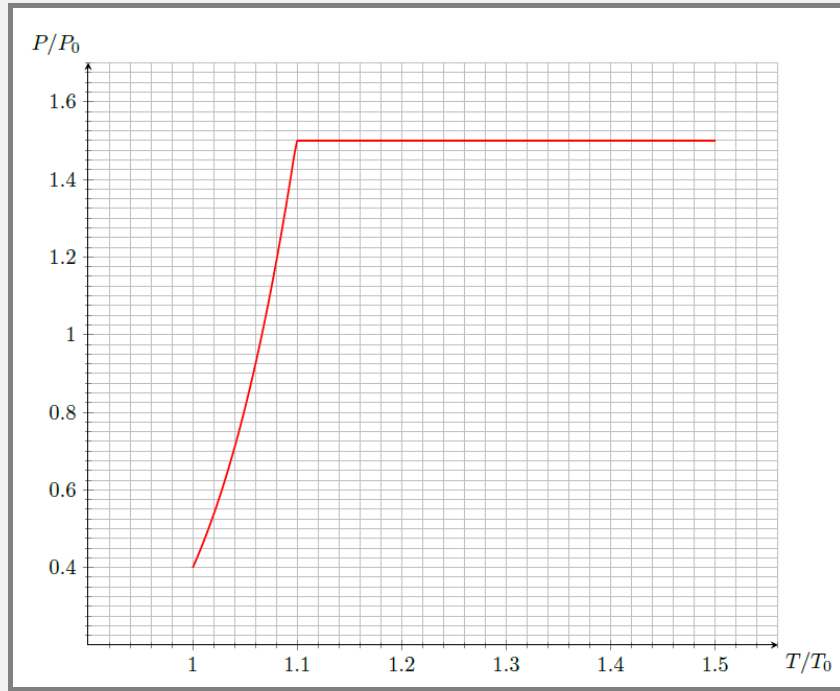


Figure 8

Solution. (a) Initially, below the piston there is the liquid and its saturated vapour, which maintains some pressure P_{sat} that depends only on the temperature. As long as this pressure is less than $P_0 + (Mg/S)$, the piston will not rise. Even when the piston does move upwards, this happens very slowly because the heat is supplied gradually too. So, as this happens, the pressure below the piston should be constant and equal to $P_0 + (Mg/S)$. On the graph, this corresponds to $1.5P_0$, so

$$M = \frac{P_0 S}{2g} = 51 \text{ kg}.$$

(b) Because of the atmosphere and the weight of the piston, the pressure in the chamber is not allowed to exceed $P_0 + (Mg/S)$. As mentioned above, this pressure initially comes from the saturated vapour of the substance. As we raise the temperature T from T_0 to $1.1T_0$, we might reach a situation where there isn't enough substance to produce a vapour of pressure $P_{\text{sat}}(T)$. After that we would only have an ideal gas beneath the piston, and it will obey

$$P = \left(\frac{m_0}{\mu} \right) \frac{RT}{SH}.$$

On the graph, this would correspond to a straight line passing through $(0,0)$, which we don't observe. Hence, when we first reach $1.1T_0$, we still have some liquid and its saturated vapour in the chamber. If this is to remain so at even higher temperatures, the pressure in the chamber must always follow the ever-increasing $P_{\text{sat}}(T)$. However, there is a constraint on the pressure, so the only option left is for the supplied heat to go towards boiling away the remaining liquid. Thus, everything is converted to vapour at $1.1T_0$, after which the temperature can actually start increasing. From that point until the end, we simply have expansion of an ideal gas under constant pressure. Note that the piston will start rising as soon as the boiling begins, because the boiling increases the amount of vapour in the chamber while the temperature and the pressure remain constant (meaning that the volume available to the vapour has to change).

One important conclusion is that there's only vapour beneath the piston at $P/P_0 = 1.5$, $T/T_0 = 1.5$, and it occupies a volume of $2SH$. Therefore,

$$(1.5P_0)(2SH) = \left(\frac{m_0}{\mu} \right) R(1.5T_0),$$

$$m_0 = \frac{2P_0SH\mu}{RT_0} = 12.4 \text{ g.}$$

(c) The mass of the vapour before right before boiling sets in can be obtained from the ideal gas equation, given that the saturated vapour is still an ideal gas:

$$m_i = \frac{(1.5P_0)(SH)\mu}{R(1.1T_0)} = 8.4 \text{ g.}$$

Then, the total heat necessary to boil the remaining liquid is

$$Q_1 = L(m_0 - m_i) = \frac{7P_0SH\mu L}{11RT_0}.$$

We also need to supply some heat in order to expand the vapour of mass m_0 isobarically from a temperature of $1.1T_0$ to a temperature of $1.5T_0$. This requires heat

$$Q_2 = \left(\frac{m_0}{\mu} \right) C_p(1.5T_0 - 1.1T_0),$$

where $C_p = \frac{i+2}{2}R = 4R$ is the molar heat capacity of the vapour at constant pressure. The vapour is polyatomic, so we used $i = 6$. In total, we have

$$Q = Q_1 + Q_2 = \left(\frac{7\mu L}{11RT_0} + \frac{4}{5} \right) P_0SH = 11.9 \text{ kJ.}$$

There's one subtle problem left to take care of, though. The latent heat, as mentioned in Footnote 1, is spent on unbinding the molecules *and* expanding the resulting vapour out in the open. The L from the problem statement is probably taken from some reference book, so it corresponds to expanding the vapour in the atmosphere, not in a closed vessel of some fixed volume. In the former case the necessary work is $P_0(V_{\text{gas, atm}} - V_{\text{liquid}})$, while in the latter it is $1.5P_0(V_{\text{gas, vessel}} - V_{\text{liquid}})$. Luckily, if the volume of the liquid is negligible compared to that of the gas (no matter if that gas is in the atmosphere or in the vessel), these turn out to be the same, because the atmosphere and the vessel have the same temperature:

$$P_0(V_{\text{gas, atm}} - V_{\text{liquid}}) \approx P_0V_{\text{gas, atm}} = \left(\frac{m_0}{\mu} \right) R(1.1T_0),$$

$$1.5P_0(V_{\text{gas, vessel}} - V_{\text{liquid}}) \approx 1.5P_0V_{\text{gas, vessel}} = \left(\frac{m_0}{\mu} \right) R(1.1T_0).$$

This means that our answer for Q is good enough. If you redo the calculations without approximating, you'd get $Q = 12.6 \text{ kJ}$, but this isn't necessary.

Example 5. Glub glub (Russia 2021). A chemical reaction in the water solution of some substance in a vat supplies heat at a constant rate of $N = 5 \text{ kW}$. In order to maintain a constant temperature, we send in air through a perforated pipe at the bottom of the vat (Figure 9). The pressure of this air is equal to the atmospheric pressure $P_0 = 10^5 \text{ Pa}$, while its temperature is equal to that of the room, $T_0 = 22^\circ\text{C}$. Find the volumetric flow rate of air q required to maintain a temperature $T < T_B$ in the vat, where $T_B = 100^\circ\text{C}$ is the boiling point of the water solution at a pressure of P_0 . Assume $T_B - T \ll T_B$. Evaluate q for $T = 95^\circ\text{C}$.

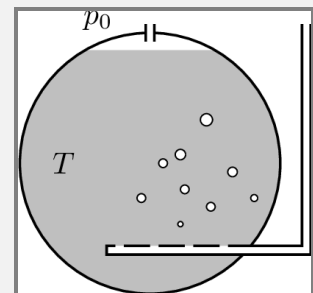


Figure 9

The molar heat of vaporisation of water at T is $\lambda = 40 \text{ kJ/mol}$. The saturated vapour pressure near T_B varies linearly with a rate of $\alpha = 3.5 \text{ kPa/}^\circ\text{C}$. The pressure of the saturated vapour above the water solution is precisely equal to the saturated vapour pressure of water. Neglect the pressure difference on both sides of the pipe connecting the vat to the atmosphere. Also neglect the heat that goes towards raising the temperature of the incoming air. The system does not exchange heat with its surroundings when air isn't flowing in.

Solution. This device carries off heat from the water by forcing the water to boil, which is associated with a latent heat. Without the air supply, we can't have boiling because the pressure above the liquid is P_0 (most of it from the saturated vapour, the rest from dry air), while the pressure of the bubbles in the bulk in the liquid would be $P_{\text{sat}} = P_0 + \alpha(T - T_B)$. This is less than P_0 , so the bubbles are immediately suppressed. However, when we send in air through the pipe, the air will take part in the bubbles, and it can provide the necessary extra pressure $\alpha(T_B - T)$ to keep them stable.

Working with partial pressures, we see that the ratio of air to vapour in the bubbles must be

$$k = \frac{\alpha(T_B - T)}{P_0 - \alpha(T_B - T)}.$$

To pump out heat at a rate $N = 5 \text{ kJ/s}$ from the water, we need the water to leave through the bubbles at a rate of $N/\lambda = 0.125 \text{ mol/s}$. The air would then need to come in at a rate of kN/λ (mol/s). All that is left is to find the volume that corresponds to a mole of gas. This is $V/n = P_0/RT_0 = 40.8 \text{ mol/m}^3$. We then obtain

$$q = \frac{NRT_0}{\lambda} \frac{\alpha(T_B - T)}{P_0(P_0 - \alpha(T_B - T))} = 6.5 \times 10^{-4} \text{ m}^3/\text{s}.$$

4. Evaporation and kinetic theory

In this section, we will proceed to estimate the rate of evaporation from a liquid in idealised conditions. Unfortunately, evaporation is a rather complicated process. Usually, right above the surface of the liquid there is a thin layer of stagnant saturated vapour. For a molecule to leave the liquid, it first needs to have enough energy to overcome the attraction from its neighbours at the surface. After that, it has to diffuse through the stagnant layer. The thinner the layer, the faster the evaporation. If we set up a flow of dry air above the liquid with a fan, the layer will thin out. The mean free path of the molecules from the liquid could then end up much larger than the width of the layer, meaning these molecules essentially don't perceive it. This is the reason why we blow on our cup of hot tea. It's not because our breath will cool the tea down directly; rather, it's mostly to speed up the evaporation (and hence the cooling, as vapours carry away heat)³. This is also why hot weather feels worse when it's humid. Your sweat evaporates slower, so its phase transition takes away heat less efficiently.

Now onto working with numbers. We'll assume that there's a dry air flow above the liquid, such that we can ignore the stagnant layer. Assume that the temperature of the system is T , at which point the saturated vapour pressure would be $p_{\text{sat}}(T)$. We'll now use a trick. Imagine that the vessel, instead of being out in the open, is placed in an enclosure, so that the liquid is in equilibrium with its saturated vapour. The evaporation occurs in the same way as before, but now there's condensation in the other direction as well. More importantly, the rate of evaporation $\frac{dN}{dt}$ is the same as the rate at which vapour molecules enter the liquid. And this latter quantity is easier to estimate.

If the surface of the liquid has area S , the molecular flux Φ of the vapour through that surface

³ Another trick is to pour the tea in a bowl, which increases the surface area available for evaporation. Likewise, you should cut your potatoes into wedges if you want them to cool down quicker. In the same vein, there's a good reason why many desert plants have spines instead of large leaves.

can be estimated from the standard formula

$$\Phi = \frac{1}{4}nS\langle v \rangle = \frac{1}{4}nS\sqrt{\frac{8RT}{\pi\mu}},$$

where n is the number density of the molecules in the vapour, and μ is their molar mass. We also need to account for the fact that only a small fraction q of the molecules actually enter the liquid, whereas the rest are reflected by the surface (for water, $q \approx 3\%$). Then, finally,

$$\frac{dN}{dt} = \frac{qp_{\text{sat}}S}{4k_B T} \sqrt{\frac{8RT}{\pi\mu}}.$$

We can then deduce the mass flow rate from the liquid from multiplying this by the mass of a single molecule:

$$\frac{dM}{dt} = \left(\frac{\mu}{N_A}\right) \frac{dN}{dt} = qp_{\text{sat}}S\sqrt{\frac{\mu}{2\pi RT}}.$$

And if the liquid has density ρ , the level of liquid in the vessel will change as

$$\frac{dh}{dt} = -\frac{qp_{\text{sat}}}{\rho} \sqrt{\frac{\mu}{2\pi RT}}.$$

Evaluating this for water at 20°C (where $p_{\text{sat}} = 2.3\text{ kPa}$), we find $\frac{dh}{dt} \approx -4\text{ mm/min}$. This seems like a lot, but bear in mind that if you remove the air flow above the liquid, the evaporation will slow down significantly.

Let's address one more question – what is the pressure on the vessel due to the evaporating molecules if we ignore the stagnant layer? To answer this, we recycle the trick from above. If we had evaporation and condensation at the same time, the pressure on the liquid would be p_{sat} . Both processes transfer an equal number of molecules, so they contribute equally to the pressure. Hence, in the case where we have evaporation only, the answer is $p_{\text{sat}}/2$.

Example 6. Ice propulsion (USSR 1980). In a science fiction novel, an astronaut of mass $M_0 = 100\text{ kg}$ is left stranded at a distance of $l = 100\text{ m}$ from his spaceship. He carries a cup full of ice, and he hopes to return to the spaceship using the sublimation of the ice. Check if this is realistic by estimating the time τ necessary for the astronaut to return. Assume that the ice sublimates at a constant temperature of $T = 272\text{ K}$. The saturated vapour pressure of water at that temperature is $p_{\text{sat}} = 550\text{ Pa}$. Estimate the dimensions of the cup and the mass of the ice by yourself.

Solution. We've essentially solved this already. When the ice sublimates in a vacuum, there isn't any condensation and there's no stagnant layer to complicate things. We estimate the cross-section of the cup as $S = 50\text{ cm}^2$ and the mass of the ice as $M = 200\text{ g}$. The ice will then evaporate in time

$$T_0 = M \left/ \frac{dM}{dt} \right. = \frac{M}{qp_{\text{sat}}S} \sqrt{\frac{2\pi RT}{\mu}} = 2150\text{ s}.$$

While the ice evaporates, there is a push on the cup equal to $p_{\text{sat}}S/2$, and the astronaut maintains a constant acceleration

$$a = \frac{p_{\text{sat}}S}{2M_0} = 0.014\text{ m/s}^2.$$

By the time all the ice has sublimated, the astronaut will have covered a distance

$$L_0 = \frac{aT_0^2}{2} = 31\text{ km} \gg l.$$

This means that the astronaut will move with a constant acceleration right until he reaches the spaceship. Thus,

$$\frac{a\tau^2}{2} = l \quad \Rightarrow \quad \tau = 2\sqrt{\frac{M_0 l}{p_{\text{sat}} S}} = 120 \text{ s.}$$

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Send comments and corrections to sivanov.mail@proton.me

Problems

The problems are chosen to go along with the handout. Starting with Problem 4, you will need to have read the section on boiling.

Problem 1. Dry ice (Estonia 2010). A disk of radius $r = 1$ cm is made out of dry ice (solid carbon dioxide). The disk is pressed against a thermally conductive plate with a force $F = 100$ N applied uniformly perpendicular to the plate. When the temperature of the plate is low, the disk cannot move laterally due to the friction between the disk and the plate. However, above some critical temperature T_0 , the friction force almost vanishes, and the disk can start to slide along the plate. Find T_0 . The atmospheric pressure is 101 kPa, and the saturated vapour pressure of CO_2 is given on Figure 10. The triple point of CO_2 corresponds to pressure $p_t = 5.1 \times 10^5$ Pa.

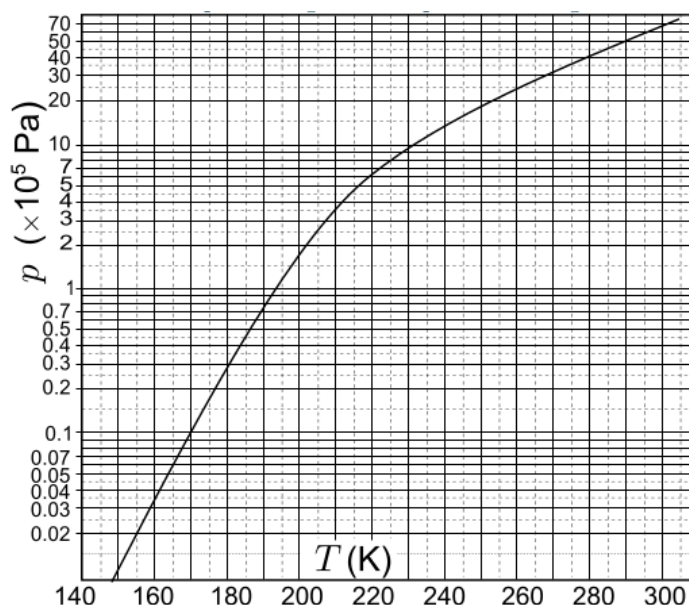


Figure 10

Problem 2. From Lord Kelvin's archives (Russia 2017). As Mr. Bug was digging through Lord Kelvin's archives, he found some graph (Figure 11) with a note scribbled on it, mentioning something about studying isochoric processes. With time, the ink has faded away, and the numbers on the vertical pressure axis and the horizontal temperature axis have disappeared. We only know that the point at the top right corner of the grid corresponds to pressure $p = 2000$ mmHg and temperature $t = 127^\circ\text{C}$.

Mr. Bug realised that the graph shows the dependence of pressure on temperature for the contents of a closed vessel. He figured that apart from air, there was some other substance in the vessel which underwent a phase transition. In order to find out what this substance was, he decided to calculate the saturated vapour pressure at the point marked with '?'.

- What are the total pressure and temperature at that point?
- Can you deduce what the unknown substance is?
- Find the temperature in the vessel at the instant when 30% of the unknown substance has evaporated.

Note: To solve this problem, you'll probably have to take a screenshot of the graph, import it in e.g. GeoGebra, and do your work there. There isn't enough space for that on this handout.

Problem 3. Physics in the mountains (IZhO 2018-2). A chunky problem on humidity in the atmosphere. See [here](#).

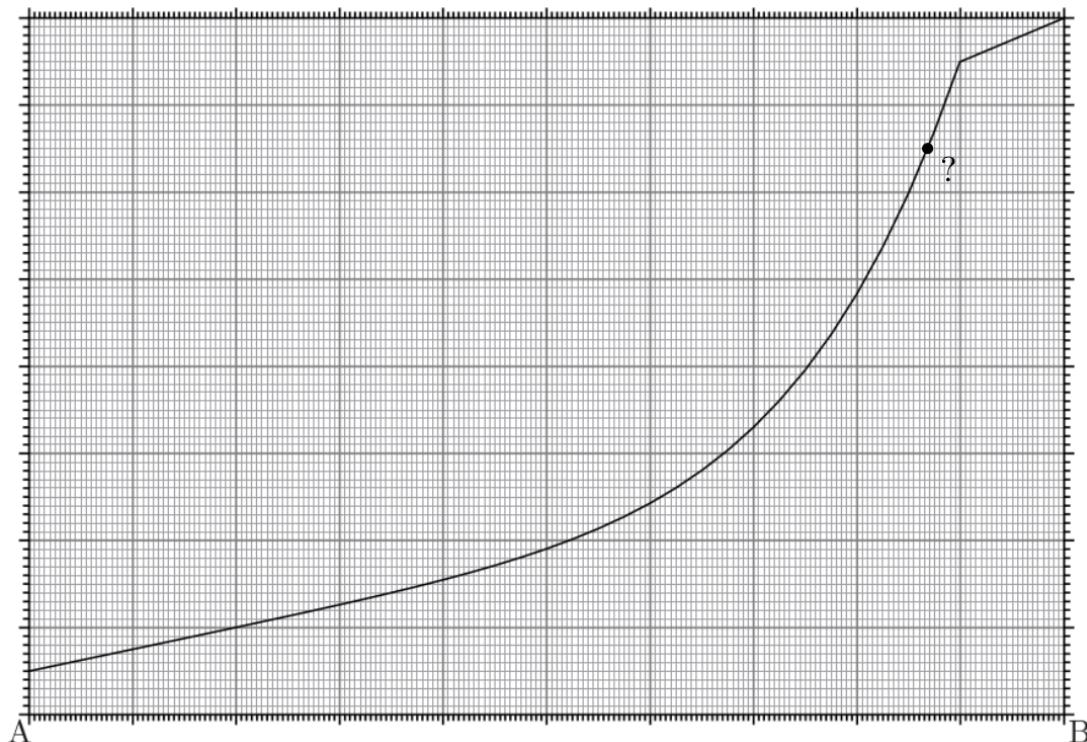


Figure 11

Problem 4. Runaway liquid (Russia 2007 Regionals). One leg of a tall U -shaped pipe of cross-section S is in contact with the atmosphere, whereas the other leg is kept closed. The pipe is filled with some liquid of density ρ such that the liquid completely fills the open leg, while its level in the other leg is lower by h , leaving an air pocket there. The pipe is heated up from the initial room temperature T_1 to the boiling temperature of the liquid T_2 at the atmospheric pressure P_0 . Find the volume of liquid ΔV that spills from the pipe by the time the liquid starts to boil.

The level of the liquid at the closed end of the pipe remains above the horizontal segment. You can neglect the evaporation from the open leg while the pipe is heated up. The saturated vapour pressure of the liquid at the initial temperature is also negligible.

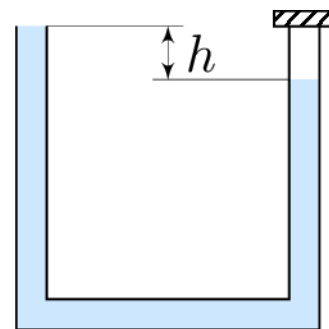


Figure 12

Problem 5. Exo-Earth (MPPP 114). At some time in the distant future, humankind makes contact with the inhabitants of an exoplanet, on which the atmospheric pressure near the surface is the same as on Earth, i.e. $1 \text{ atm} \approx 101 \text{ kPa}$. Further, the atmosphere consists of a mixture of oxygen and nitrogen gases. Because of these similarities, the planet is called Exo-Earth.

Human researchers and Exo-Earth scientists cross-check the physical and chemical data of their two atmospheres, and state that, on both planets, the boiling points of liquid nitrogen and liquid oxygen are 77.4 K and 90.2 K , respectively, at standard atmospheric pressure.

On both planets, local ‘air’ was isothermally compressed at a constant temperature of 77.4 K , and liquefaction set in when the pressure reached 113 kPa . However, on Earth oxygen, and on Exo-Earth nitrogen, condensed first.

- What is the molar ratio of oxygen to nitrogen in the atmosphere of Exo-Earth?
- For what molar ratio would the oxygen and nitrogen begin to liquefy simultaneously under isothermal compression at 77.4 K , and at what pressure would this happen?

Assume that on Earth, the molar ratio of oxygen to nitrogen is about $1 : 4$.

Problem 6. The Clausius-Clapeyron equation (IZhO 2020-2). A nice and difficult problem on border boiling. The key here is that the pressure inside the bubbles which form at the interface of the liquids is the sum of the saturated vapour pressures for those two liquids. You can find the problem statement [here](#). For extra practice on this topic, you can check out IPhO 1989-1.

Solutions

1. The answer is $T_0 \approx 212\text{K}$. If you got something markedly different, have a look at the solution [here](#) (Problem 78).
2. See the original solution [here](#). You will need to translate the text from Russian, but machine translation has become eerily good these days anyway. I use a [browser extension](#) for this, but there's probably a better way.
3. You can find the solution in the same folder as the problem statement.
4. The original solution can be found [here](#).
5. The atmosphere of Exo-Earth consists of 1 part oxygen to 8.4 parts nitrogen. Simultaneous liquefaction will happen for a molar ratio of 1 part oxygen to 4.5 parts nitrogen, at a pressure of 124 kPa. See the [book](#) for a detailed solution.
If you don't mind the open-ended style of the questions in the book (I do!), I also recommend reading through the solutions of 111, 112, and 113.
6. You can find the solution in the same folder as the problem statement.

References

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