The Boltzmann constant from a snifter

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Abstract
Evaporation of a small glass of ethylic alcohol is studied both experimentally
and through an elementary thermal physics approach. For a cylindrical beaker
and no air flow in the room, a simple quadratic relation is found between
the evaporation time and the mass of evaporated liquid. This problem and the
obtained results offer excellent possibilities for simple student experiments
and for testing basic principles of thermal physics. As an example, we use
the obtained results for estimating the value of the Boltzmann constant from
evaporation experiments.

(Some figures may appear in colour only in the online journal)

1. Introduction

Whenever you have left a cup of water (or any other drink) in your room, have you ever
wondered about how much time it takes to completely evaporate? Assuming you have a
large room with fixed temperature, is the evaporation rate constant, increasing or decreasing
with time? These questions are far from being rocket science, and anybody with a basic
physics education might figure out the answers. Many simple kitchen science experiments
with affordable apparatuses can be made, and with a basic thermal physics knowledge, the
problem can also be theoretically investigated. A simple rule that governs the evaporation rate
of the liquid can be easily obtained both theoretically and experimentally. By fitting this curve,
some basic microscopic parameters can be calculated or, alternatively, the value of the famous
Boltzmann constant can be approximated. This paper describes an investigation for ethylic
alcohol evaporation from a cylindrical beaker. The problem offers excellent possibilities for
further student projects and for testing some basic principles in thermal physics.

Evaporation is an everyday observable phenomenon which occurs at any temperature from
a free liquid surface. At the microscopic level, it is caused by the continuous thermal motion
of liquid molecules: a fraction of molecules with kinetic energy high enough to overcome the
attraction of other molecules will escape through the liquid's surface. These molecules are no
longer bounded to each other as they were inside the liquid; therefore, they are considered
to be in a gaseous phase and are referred to as vapours. Since predominantly the molecules
with higher energies will leave while those with lower energies remain inside the liquid,

the liquid cools while evaporating. It might be worth mentioning here that cooling atoms to ultra-low temperatures is a timely topic in modern physics, where one can investigate many quantum-mechanical and quantum-statistical phenomena. These ultra-low temperatures can be obtained either by evaporative cooling in a magnetic trap or by laser cooling and trapping (for an introductory paper on this 'hot' topic, we recommend [1]).

Studying evaporation was motivated by tangible industrial and agriculture-related problems like predicting the weather, irrigation of agricultural soil, desiccation of ponds and lakes or drying of paint (for a review see, e.g., [2]). The phenomenon of evaporation plays an important role in diverse fields of sciences like oceanography, meteorology, plant biology, chemistry and physics [2, 3]. The problem was studied both experimentally and theoretically at the beginning of the 19th century. Many investigators established empirical or thermal-physics-motivated simple formulae for the evaporation rate from a free liquid surface both in the presence and the absence of an air flow (forced convection) over the liquid surface. Dalton [4, 5] was the first who gave an empirical formula for water evaporation, based on his experimental results. He concluded that the speed of evaporation Q is proportional to the free water surface S and the difference between the saturated vapour pressure $p(T)$ measured at the temperature of the evaporating liquid water and the partial pressure of the water vapour p' in the air in which the evaporation occurred:

$$Q = \frac{dm}{dt} = S[p(T) - p']\frac{C}{p_0}. \tag{1}$$

We have denoted here by p_0 the barometric pressure of the air in which the evaporation occurred and C is a constant. Depending on the strength of the air flow (low, moderate or high) above the liquid surface, different values were proposed for the value of C (see, e.g., [6]). Stefan [7] gave a formula which is usable for describing the evaporation speed from any vessel:

$$Q = S\frac{D}{l}\ln\left(\frac{p_0 - p'}{p_0 - p(T)}\right). \tag{2}$$

In the above equation, D denotes the diffusion coefficient of the liquid molecules in air and l is the distance between the free surface of the liquid and the edge of the vessel; the other notations are the same as in Dalton's formula. Another empirical formula for the evaporation of water in still air was proposed by Himus and Hinchley [8]:

$$Q = C' \cdot S\sqrt{p(T) - p'}, \tag{3}$$

where C' is again a constant. Many other studies were published concerning the evaporation of water from pools [9, 10]. Most of the studies agree however in the basic finding that in the case of evaporation in still air and for $p' \ll p_0$ experiments show that $Q \propto S \cdot (p(T) - p')$. A detailed experimental investigation in such a sense is given in [6].

Early studies also investigated the evaporation in the presence of an air flow over the free liquid surface [8, 11–13]. Empirical formulae were given for the evaporation speed. Most of the studies agree that for not too high air velocity values, $Q = S \cdot (C_1 + C_2v)[p(T) - p']$, where C_1 and C_2 are constants and v is the air velocity over the free liquid surface. Although the results in the literature are mostly for water evaporation [14], the proposed formulae (with other values of the constants) will work reasonably well for other one-component liquids too.

As the reference list illustrates, the problem has a quite longstanding history and was studied mainly in the second half of the 19th century and first half of the 20th century. Despite being an old problem, it presents interest nowadays due to its widespread applicability. In this work, we reconsider the problem for small-size and deep cylindrical-shaped vessels, reflecting on the time dependence of the evaporation rate. A basic thermal physics approach

will be given, and its results will be compared with simple kitchen science experiments. Before proceeding however to discuss our approach, it should be mentioned that a systematic experimental investigation of this problem with a similar setup has already been made in the work of Sparrow *et al* in 1983 [15]. Although the authors of this paper consider the problem from another perspective (the effects of the geometrical parameters of the vessels on the dimensionless mass-transfer coefficient), their careful experimental investigation has to be acknowledged. The authors also consider and investigate the fact that owing to the latent heat of evaporation, the surface temperature of the liquid is depressed relative to the ambient temperature. This effect gives rise to a secondary diffusion which overpowers the oppositely directed diffusion associated with the concentration gradient of the vapours. A more careful theoretical analysis should also take into account this effect.

Our approach here is different. First, we propose a simplified theoretical description neglecting the temperature gradient which builds up in the liquid and its natural convection. Then, we test experimentally the theoretical results obtained for the evaporation speed and use it to determine some useful thermal physics quantities from experiments.

2. A simple theoretical approach

Let us first investigate the problem theoretically. Our model is based on the assumption that on the top of the liquid's surface a steady flow is formed and right above the surface there are saturated vapours. Furthermore, outside the glass the concentration of alcohol vapour is assumed to be zero due to the large room in which the experiments are performed. In case one would work with water instead of alcohol, the humidity of air should be taken into account and the vapour pressure outside of the glass should be computed from the humidity of water. A concentration gradient thus builds up, which governs the diffusion of alcohol molecules out of the glass. In this approach, we neglect the temperature gradient that might build up in the system due to the existence of the latent heat of evaporation and also the convective instability that might appear due to this temperature gradient. The experimental work of Sparrow *et al* [15] proved that the overall variation of the temperature within the liquid for small vessels is around 0.03–0.05 °C, corresponding to a temperature gradient of 1–3 °C m^{-1}. Since the temperature gradient that builds up in the case of alcohol is so small, these effects would become important only in very thin and large surface layers of liquid. However, using instead of alcohol a more quickly evaporating liquid like chloroform or ether, the temperature difference between the liquid surface and the ambient temperature would largely increase and one should also account for this in the theoretical modelling. Here, we thus consider that all parts of the system are at the same temperature.

Let H denote the height of the glass, $h(t)$ denote the height of the liquid surface measured from the bottom of the glass and z denote the coordinates on the vertical axis. According to Fick's diffusion law

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -DS\frac{\mathrm{d}n}{\mathrm{d}z}, \tag{4}$$

where N is the number of liquid molecules that escaped from the glass, S is the area of the cylindrical shaped glass, n is the concentration and D is the diffusion constant for the involved molecules.

Assuming the temperature to be homogeneous in the glass and the diffusion process stationary, we take the concentration gradient within the glass as uniform:

$$\frac{\mathrm{d}n}{\mathrm{d}z} \simeq \frac{\Delta n}{\Delta z} = \frac{n}{H - h(t)}. \tag{5}$$
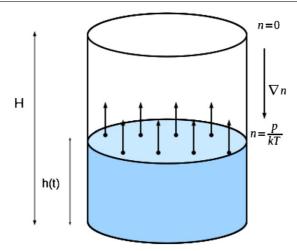
Figure 1. Schematic of the model.

Furthermore, we also assume that the liquid vapours behave as an ideal gas; therefore, the equation of state for the saturated vapours has the simple form:

$$n = \frac{p}{kT}, \tag{6}$$

where p denotes the pressure of saturated vapours, T is the absolute temperature and k is the Boltzmann constant (see figure 1). If ρ is the mass density for the liquid alcohol in the glass, its mass $m(t)$ can be expressed as

$$m(t) = \rho S h(t). \tag{7}$$

With the assumptions formulated in (5)–(7), the diffusion equation (4) can be written as

$$\frac{dN}{dT} = -DS\frac{p}{kT}\frac{\rho S}{\rho HS - m(t)}. \tag{8}$$

The above formula is in agreement with both the formula given by Dalton, (1), and the one given by Stefan, (2), in the limit of $p' \ll p(T) \ll p_0$. Now, from elementary statistical thermodynamics [16], it is well known that the diffusion constant D can be computed as

$$D = \tfrac{1}{3}V\Lambda, \tag{9}$$

where V is the average velocity of the molecules in the gas in which the diffusion takes place and Λ is the mean free path in this medium. From elementary statistical thermodynamics, it is also known that their values can be calculated as

$$V = \sqrt{\frac{8kT}{\pi m_0}}, \tag{10}$$

$$\Lambda = \frac{1}{n_0\sqrt{2}\pi d^2}. \tag{11}$$

In the above equations, n_0, m_0 and d are the concentration of the molecules, their mass and the characteristic radius for the collisions cross sections, respectively. These are again values for the gas in which the diffusion is realized. It should be mentioned here that although our approach is for an ideal gas approximation, where the molecules are assumed to be point like,

in our approach, we still consider a finite cross section for their collision. Although this might seem contradictory, this is an accepted first approximation for transport phenomena in gases, based an the real-gas model in the limit of low densities and sufficiently high temperatures. In this limit, one can use instead of the van der Waals equation the simple thermal equation of states of the ideal gases. For simplicity, this gas is assumed to be pure nitrogen at p_0 atmospheric pressure. Therefore,

$$n_0 = \frac{p_0}{kT}.$$ (12)

Assuming that m_a is the mass of one alcohol molecule

$$N = \frac{m}{m_a},$$ (13)

and one can immediately rewrite (8) for the liquid alcohol's mass variation:

$$\frac{dm(t)}{dt} = c_1 \frac{p\sqrt{T}}{c_2 - m(t)}.$$ (14)

Here, c_1 and c_2 are constants which according to (8)–(12) are computed as

$$c_1 = -\frac{2}{3}\sqrt{\frac{k}{m_0}} \pi^{-3/2} \frac{1}{d^2} \frac{1}{p_0} S^2 \rho m_a,$$ (15)

$$c_2 = \rho H S.$$ (16)

A first-order differential equation (14) is obtained which describes the time evolution of the mass of the liquid which remains in the cup. This equation can be solved analytically at constant temperature, since in such case one can assume that the saturated vapour pressure is also constant. Under such conditions, (14) can be written as

$$\frac{dm(t)}{dt} = c_3 \frac{1}{c_2 - m(t)},$$ (17)

where

$$c_3 = c_1 p\sqrt{T}.$$ (18)

From (17), we learn that the reciprocal value of the evaporation speed v_e is a linear function of the mass of liquid which remained in the glass:

$$\frac{1}{v_e} = \frac{1}{c_3} m(t) - \frac{c_2}{c_3} = a \cdot m(t) + b,$$ (19)

with a and b being constants. Since $c_3 < 0$ (because $c_1 < 0$), the evaporation speed obviously decreases during the evaporation process. The time evolution for the mass of the liquid alcohol in the glass can be obtained after the separation of the variables in (17) and integration. After integration, one obtains the quadratic equation

$$t = \frac{c_2}{c_3} m - \frac{1}{c_3} \frac{m^2}{2} + K,$$ (20)

where K is an integration constant and its value can be obtained by exploiting the initial conditions. The $m(t)$ function is then easily obtained by solving (20) for m:

$$m(t) = c_2 - \sqrt{c_2{}^2 - (2c_3 t + 2K)}.$$ (21)

Figure 2. The experimental setup.

3. Experiments

The advantage of this simple problem which allows an exact solution is that it can be tested by simple experiments.

The experimental setup is simple and quite straightforward. In order to make the experiments quicker and safer for students, ethanol was used. Using distilled water is not recommended, since the evaporation speed is much lower and also the humidity in the ambient air has to be taken into account in such experiments. In principle, it is also possible to use ether or chloroform, but these liquids are more expensive and harder to procure. Also, due to their highly volatile nature, their surface cooling is much stronger and thus the validity of our simple approach based on a homogeneous temperature is highly questionable.

A cylindrical beaker is filled with ethanol (98% pure) and it is placed on the plate of a precision digital balance. The use of a cylindrical-shape cup is crucial, since the evaporation rate depends on the liquid's surface. Thus, a recipient with a constant section is needed. In the experiments, we used a digital balance with precision of 1 mg. Due to the temperature dependence of the evaporation speed, it is also important that a constant temperature is kept in the room where the experiments are performed. In order to convince ourself that the temperature remains fixed during the evaporation, the temperature was also precisely monitored. If the temperature fluctuations during the measurement (which lasts from several hours up to 1–2 weeks in the case of total evaporation) are significant, either a new measurement has to be carried out or equation (14) has to be numerically integrated using the experimentally measured $T(t)$ variation.

For monitoring the temperature during evaporation, a digital thermometer of $0.1\,°C$ precision was used. In order not to perturb the weight measurements, this digital thermometer was immersed in another glass, similar to the one on the balance's plate, and filled to the same level with alcohol. This second recipient was placed nearby the balance.

Since evaporation in this second glass ought to be similar to the one placed on the balance, we assumed that their temperatures should also be similar. By preliminary experiments, we have convinced ourselves that the temperature of the two glasses remains the same during evaporation up to an accuracy of $0.1\,°C$, which is lower than the temperature fluctuations in the room. In figure 3, typical temperature fluctuations of the liquid are shown during the measurement.
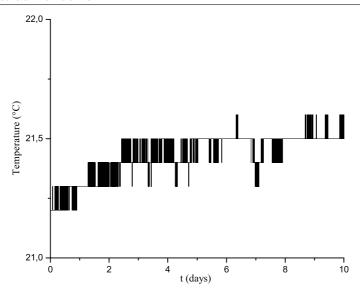
Figure 3. Typical temperature fluctuations of the sample for an acceptable measurement. Temperature data for the measurement results are presented in figure 4. Successive values are connected with a straight line. The precision of the digital thermometer is 0.1°C.

The system was checked by means of an FLIR E-50 thermal camera for the temperature gradient which could build up in the evaporating alcohol, and we found that the temperature difference between the bottom and the surface of the liquid is lower than 0.1 °C; thus, the temperature gradient is lower than 3 °C m^{-1}.

Both the thermometer and the digital balance were connected by USB ports to a PC and the measured values were recorded at each 5 s. This automatized data collection was necessary because the alcohol's evaporation rate at room temperature was quite slow. The evaporation of the whole ≈60 ml alcohol lasted approximately 10 days! If water had been used instead of ethanol, the experiment would have lasted several weeks. Finally, we placed the whole experimental setup in a corner of the lab, where the air motion was minimal. Experiments were performed during a holiday period, when the lab was not visited by students or researchers.

In the experiments, the offset value of the balance was fixed with the empty glass on the plate; therefore, the balance indicated directly the liquid alcohol's mass. Several measurements were made, all of them indicating for $m(t)$ the qualitative trend shown in the inset of figure 4. From the performed experiments, we have selected those ones where the difference between the maximal and the minimal temperature of the liquid was less than 1 °C for the whole evaporation period. A characteristic temperature variation of the liquid conforming with this criterion is shown in figure 3. Evaporation data for this experiment are represented in figure 4. As a first observation, it is clear that the evaporation speed is not constant during the evaporation, but in agreement with the predicted theoretical results, it decreases.

4. Results

In order to prove our main theoretical prediction, (19), we have plotted the inverse of the evaporation speed as a function of the amount of liquid in the glass (figure 4). For the same
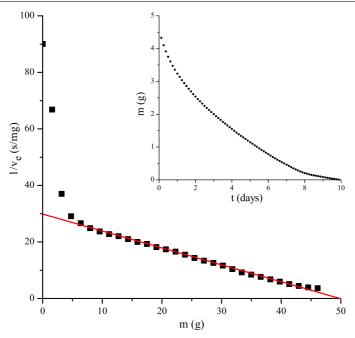
Figure 4. The inverse of the evaporation speed is plotted as a function of the mass of the liquid ethylic alcohol in the evaporation experiment. The solid line is a linear fit to the data within the range 5–46 mg. According to equation (19), its parameters are $a = 6 \cdot 10^8$ s kg^{-2} and $b = 3 \times 10^7$ s kg^{-1}, respectively. The inset shows the directly measured time-evolution of the liquid as mass measured by the balance.

evaporation experiment (with $T \approx$ const), results in such a sense are presented in the inset of figure 4. In agreement with our theoretical predictions, we find a good linear dependence for the decisive part of the evaporation. This linear dependence breaks down however for the last part of the evaporation process, when less than 10% of the initial quantity of alcohol remains in the glass. The deviation from the linear dependence at a low liquid quantity is caused mainly by the fact that the used alcohol is only 98% pure and we are dealing thus with an aqueous solution. Since the evaporation rate of water is much smaller then the one for alcohol, the proportion of water in the solution constantly increases during the experiment. This dilution becomes evident when the amounts of water and alcohol are comparable in the remaining liquid. This leads naturally to a detectable decrease in the evaporation speed of the liquid, an effect which is observable in figure 4. In order to eliminate such an effect a more pure alcohol should be used; however, this is not so simple to find.

Apart from testing our prediction (19), the experiments also allow the determination of the c_2 and c_3 constants. These values can be computed theoretically and they offer possibilities for further studies. One possibility is to use this experiment for a rough estimation of the Boltzmann constant.

5. Estimation of the Boltzmann constant

The Boltzmann constant (k) is one of the fundamental constants of physics. The first indirect estimate for the molecular size is often considered Franklin's oil spreading experiment [18] interpreted by Rayleigh [19] or the work of Loschmidt [20]. These estimates lead to the

Table 1. Values of the Boltzmann constant calculated from various measurements. Due to the theoretically estimated $\approx 80\%$ error, only the significant digits are given. For the k_{rp} values, the collision diameters were estimated by the density of liquids and considering a random packing of spherical molecules. r is the radius of the beaker and T is the average room temperature during the evaporation.

	r(m)	T(K)	p(Pa)	ρ(kg m^{-3})	c_3(kg^2 s^{-1} $\times 10^{-9}$)	k(J K^{-1} $\times 10^{-23}$)	k_{rp}(J K^{-1} $\times 10^{-23}$)
1	0.0328	297.0	7423	786	8.0	1	1
2	0.0328	297.0	7423	786	13.6	2	3
3	0.0190	294.5	6400	789	1.6	3	4
4	0.0190	295.5	6859	787	1.6	3	4

Avogadro number and, through this, to the Boltzmann constant. However, the first who introduced k and gave it a value was Max Planck [21]. Many direct and indirect methods are known to measure its value with a high precision [22–26]. Also, recently many pedagogical experiments were proposed for estimating its value in classroom experiments using video microscopy of Brownian motion [27], low-cost atomic force microscopy [28] or a simple sensitive circuit to measure Johnson's noise in a resistor [29]. Several experiments and simulations on a two-level system were proposed by Battaglia [30].

In the following, we will show that the previously discussed simple evaporation experiment can give a rough estimate for the value of k. We expect that our results are strongly biased by the simplicity of the experimental setup, so we will acknowledge the reproduction of the order of magnitude.

From equations (15) and (18), we find

$$k = \frac{9}{4} c_3^2 \pi^3 m_0 d^4 \frac{p_0^2}{S^4 \rho^2 m_a^2} \frac{1}{p^2 T}. \tag{22}$$

A pedagogical determination of the Boltzmann constant should in principle use only quantities measurable at the human scale. Unfortunately, it is not the case. Some of the quantities that are present in equation (22) are simply measurable: T, $S = \pi r^2$ (with r being the radius of the cylindrical vessel) and $p_0 = 10^5$ Pa. Knowing the value of the atomic mass unit and the relative molecular masses, one can derive $m_0 = 4.649 \times 10^{-26}$ kg and $m_a = 7.650 \times 10^{-26}$ kg for the mass of the N_2 molecule and ethylic alcohol (CH_3CH_2OH), respectively. Once the temperature is known, the p pressure of the saturated vapours and the density of the alcohol can be obtained from tables [32] by simple interpolation. The radius d for the collision cross section between the alcohol molecules and the N_2 molecules is estimated from the kinetic diameter of pure gases as $d = \frac{d_{N_2} + d_{ethanol}}{2}$. The kinetic diameter can also be estimated from the density of liquids (alcohol and liquid nitrogen) assuming spherical-shaped molecules and a random close-packing of these spheres. In such an approach, one would obtain $d_{N_2} = 0.41$ nm and $d_{ethanol} = 0.47$ nm, leading to $d = 0.44$ nm. On the other hand, one can also find better experimental estimates in the literature for the kinetic diameter of the nitrogen and ethanol: $d_{N_2} = 0.37$ nm [32] and $d_{ethanol} = 0.44$ nm [31]. Using these values, one would obtain instead $d = 0.41$ nm. According to equation (22), k depends on d^4; it is therefore extremely sensitive to errors in d. The value of c_3 can be derived from evaporation experiments plotting the value of the evaporation time t as a function of the mass of alcohol m in the beaker. A simple quadratic fit (see equation (20)) will give us the value of c_3.

Further (and shorter time evaporation) experiments with two different beakers and with different room temperatures were performed. The results obtained for the value of the Boltzmann constant are summarized in table 1. From these results, it is clear that by using the kinetic diameter values from the literature, we obtain a better approximation

for k than the values estimated from the density of the liquids. Although the spread of the data is quite strong, we conclude, from the experiments, values for the Boltzmann constant of $k = 1$–$3 \times 10^{-23}\,\mathrm{J\,K^{-1}}$, which is a reasonable approximation of the accepted $k = 1.380\,65 \times 10^{-23}\,\mathrm{J\,K^{-1}}$ value, taking into account the simplicity of our experimental setup.

Acknowledgments

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