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Historical Perspective

# On the temperature dependence of surface tension: Historical perspective on the Eötvös equation of capillarity, celebrating his 175th anniversary

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ABSTRACT

The Hungarian baron Roland Eötvös (Eötvös Loránd, 1848–1919) lived in the difficult period between two revolutions in Hungary, but nevertheless he achieved revolutionary results in two fields of science: capillarity (1875–1886) and gravity (after 1886). This paper describes his famous capillary equation published in 1886 in the world-language of the time (German) and in one of the most famous scientific journals of the time (Annalen der Physik und Chemie). In his paper he showed a simple equation for the temperature dependence of surface tension of one-component liquids and more importantly he showed that this quantity approaches zero as temperature tends towards the critical temperature. This result was achieved by measuring the surface tension of 160 (!) different liquids along their boiling lines as function of temperature, in a home-made high-pressure high-temperature equipment, probably the first one of this kind. In this way he extended the meaning of the critical point previously introduced by van der Waals. In this paper, also a modern model of surface tension of one-component liquids is discussed, simplified and compared to the Eötvös equation. It is also shown, how the Avogadro number and the molecular sizes can be determined from the experimental results of Eötvös (note: the Avogadro number was estimated with reasonable accuracy for the first time by Einstein in 1905 from the kinetic theory of liquids). Apparently, it was not that easy to do back in 1886: this becomes obvious from the 1911-paper by Einstein, who gave a wrong estimate for the diameter of Hg atoms (5.19 nm) using the data of Eötvös (the correct value is around 0.3 nm). The Appendix to this paper contains the summary of 1543 handwritten pages on surface tension by Eötvös, including the on-line availability of all pdf files. Note also, that Eötvös used $g = 10.0$ m/s$^2$ for acceleration due gravity and so he over-estimated his surface tension values and also his Eötvös constant by about 2.0%. The corrected Eötvös constant using his measured values but the correct $g$-value would be "0.222" vs his published value of "0.227". Probably this uncertainty in the value of $g$ was one of the motives that pushed Eötvös to study gravity after 1886.

## 1. Introduction

In probably the most influential monograph on physical chemistry of surfaces by Adamson [1], this field is described as based on 4 fundamental equations: the Young equation, the Laplace equation, the Kelvin equation and the Gibbs adsorption equation. Note, that recently it was shown by the author [2], that instead there is a single fundamental equation behind all other equations in these arts, which is the extended fundamental equation of Gibbs ($dG = \sum_i \mu_i \bullet dn_i + \sigma \bullet dA$), also mentioned by Adamson, but not called by him a fundamental equation of surface sciences. Similarly, the Eötvös capillary Eq. [3] is also described and discussed by Adamson [1] but was also not called by him a fundamental equation of surface sciences.

In this paper, the historical background of the Eötvös Eq. [3] is given and it is shown that it also follows from the extended fundamental equation of Gibbs ($dG = \sum_i \mu_i \bullet dn_i + \sigma \bullet dA$), considered by the present author the real fundamental equation of colloid and interface sciences, including "high-temperature capillarity" after Eustathopoulos [4]. Note also, that although the Eötvös equation was formally cited more than 150 times, in fact it was cited much more frequently without any formal citation in the reference list of these papers (see for example [5–9]). The Eötvös equation is discussed here in a wider perspective, including many aspects of physical chemistry, chemical thermodynamics and surface science developed in the 19th century.

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## 2. Relevant knowledge known and not known by Eötvös before 1886

Natural sciences evolved with an exponential rate during the 19th century. The Eötvös equation on capillarity can be considered as a logical consequence of the scientific developments achieved before 1886. Let us start with Thomas Young, who gave the mechanical definition of surface tension in 1805 [10]. This work was obviously known by Eötvös. Although Josiah Willard Gibbs [11] provided the more advanced thermodynamic definition of surface tension in 1878, this work, published in remoted that time Americas probably was not known by Eötvös, equally as it was not known by almost anyone in Europe before the turn of the 20th century. However, Eötvös certainly knew the equation proposed by Pierre-Simon Laplace [12], as the experimental method of Eötvös was based on this (see below).

Eötvös also knew (and used in his paper) the law of ideal gases in the form of $p \bullet V_m/T = \text{const}$, where $p$ (Pa) is the gas pressure, $T$ (K) is the absolute temperature and $V_m$ ($m^3$/mol) is the molar volume, called "molecular volume" by Eötvös.[1] The 1811 concept of Amadeo Avogadro was well known to everyone including Eötvös, claiming that equal volumes of gases at equal temperatures and at equal pressures contain equal numbers of molecules [13]. Later this number was called the Avogadro number. More specifically, the Avogadro number is the number of atoms or molecules in a mass (measured in grams) that is numerically equivalent to the value of the dimensionless relative atomic mass, while the system of relative atomic masses is based on a unit of 1 (dimensionless) for hydrogen atom, which would be 1 g/mol today.[2] From this principle a method to measure relative atomic masses followed [13]. This method was later experimentally realized by Stanislao Cannizzaro, who measured gas pressures in closed containers of known inner volumes as function of temperature and the mass of the gas in the container. Cannizzaro combined in a clever way all his measured data and was able to obtain the relative atomic masses of 30 elements in 1858 [14] (as a "side product" of his research he also clarified the stoichiometry of some molecules, such as that "hydrogen" is in fact $H_2$ and not H, etc). Note, that the definition of the Avogadro number was selected by the SI such, that the modern atomic masses ($M$, in g/mol) provide the same numerical values as the dimensionless values of the relative atomic masses measured by Cannizzaro, within ±1% of accuracy (note: modern molar masses of elements are averages over all the isotopes of the given element, but the existence of isotopes was not known in the 19th century).

The relative atomic masses helped Dmitrii Ivanovich Mendeleev to construct the first meaningful periodic table of the elements in 1863 [15]. All this was surely well known and used by Eötvös. Moreover, Eötvös was aware of the extension of the ideal gas law to real gases by Diderik van der Waals, considering the non-zero size of the molecules and the interaction between them [16]. This lead van der Waals to the hypothesis on the existence of the critical points of the liquids in 1873 [16]. This concept was developed further by Eötvös in his paper (see below).

One more comment on Cannizaro: from his measured values of the gas pressure ($p$) of 2 g of $H_2$, or 32 g of $O_2$, or 44 g of $CO_2$ etc. (all equivalent to about 1 mol of gas) in a container of known volume ($V$) at a known temperature ($T$), the universal gas constant could be found as $R = p \bullet V_m/T$. In fact, this was done only later by Mendeleev,[3] who obtained $R = 8.45$ J/molK (in the SI units) [17], being only 1.6% higher than the current value of 8.3145 J/molK.

Although Eötvös probably did not realize, but his capillarity equation could be used to estimate the value of the Avogadro number and the size of the molecules back in 1886. In the times of Eötvös even the existence of atoms and molecules was not certain, although he did not seem to care too much about this uncertainty and used the concept of atoms and molecules without any problem (see for example his term "molecular volume"). Nevertheless, according to the current history of science, the existence of atoms and molecules was "finally" proven only in one of the great 1905-papers of Albert Einstein [18]. In this paper, based on the kinetic theory of liquids, Einstein provided his best estimate of the Avogadro number as 6 $10^{23}$ 1/mol [18] (as shown above, the best expected value before 1971 was 5.97 $10^{23}$ 1/mol). However, let us note that in his Dissertation published earlier in the same year [19], a much lower value of 2.1 $10^{23}$ 1/mol is given (see also [20]), while in his paper submitted at the end of the same year, a middle value of 4 $10^{23}$ 1/mol was reported [21]. In these papers the Brownian motion is mentioned, discovered by Robert Brown in 1827 [22]. Stimulated by the papers and by the correspondence with Einstein, Jean Perrin in 1909 repeated the experiments by Brown under different conditions and excluded all other possible reasons for the Brownian motion except the constant zig-zag movement of the molecules in the liquid and in this way, he proved the existence of the molecules [23]. Further, Perrin measured also the vertical distribution of droplets in emulsions due to gravity and came up with his best value of the Avogadro number: 7.05 $10^{23}$ 1/mol [23]. Although this value appeared further from the real value of the time (5.97 $10^{23}$ 1/mol) than the "best" value by Einstein (6 $10^{23}$ 1/mol) [18], Perrin received the Noble prize in 1926 for the proof of existence of molecules and atoms (Einstein received the Nobel prize earlier, for another result). Einstein was obviously not very much certain about any of his own estimations, as in his 1911-paper he used the value of Perrin (7 $10^{23}$ 1/mol) [24].

Obviously, what Einstein and Perrin did in the first decade of the 20th century, could not be known by Eötvös before 1886. However, Josef Loschmidt already in 1865 estimated the size of the "air molecules" to be 0.969 nm from the kinetic theory of gases [25]. Of-course, there are no such things as "air molecules", but the size of the nitrogen molecules (= double of their van-der-Waals radius) is 0.310 nm, while the same for the oxygen molecules is 0.304 nm, so from the average simplified composition of air (79 mol% of $N_2$ + 21 mol% of $O_2$) their average molecular size is 0.309 nm, being 3.14 times smaller than that estimated by Loschmidt [25]. The question is left for further research whether this difference of $3.14 = \pi$ is a pure coincidence, or an indication that in the cumbersome derivation by Loschmidt parameter

[1] The quantity named „molecular volume" should have a unit of $m^3$/molecule. However, to calculate this, the value of the Avogadro constant is needed, not known by Eötvös. Before mole was introduced at the end of the 19th century and became widespread in the 20th century, the expression „gram-atom" and „gram-molecule" was used instead, so the "molar volume of a molecule" should have been called in the 19th century the „gram-molecular volume". The „molecular volume" of Eötvös is probably a short version of this „gram-molecular volume", therefore it is probably equivalent with the molar volume.

[2] Since 1971, according to the SI system, the Avogadro number is $N_{Av} = 6.02214076\ 10^{23}$ 1/mol, which follows from the SI-definition as: it is the number of atoms contained in 12 g of C-12 isotope. According to this definition, the current molar mass of H is 1.0079 g/mol, being larger by 0.79% compared to the initial definition of 1 (g/mol) of the relative atomic masses of the 19th century. Therefore, based on the relative atomic masses, the best value of the Avogadro number that could be found was 6.02214076 $10^{23}$ / 1.0079 = 5.9749 $10^{23}$ 1/mol, or 5.97 $10^{23}$ 1/mol, if rounded to the third digit, which is the best accuracy of measurements one can expect in the 19th century. Therefore, in this paper the values of the Avogadro number determined before 1971 will be taken as 5.97 $10^{23}$ 1/mol. One more comment on „atomic weights", commonly used in chemistry: scientifically atomic weight = atomic mass * the acceleration due to gravity, while the value of the latter is variable along the surface of the Earth and this variation has nothing to do with the properties of atoms; therefore, herewith the terms „mass", „atomic mass" and „molar mass" will be used.

[3] In fact, Mendeleev did not call his coefficient 8.45 as a universal gas constant and did not use the notation $R$, but he was probably the first one in 1875–77, who wrote the ideal gas law in its full form as known today: $M \bullet p \bullet V = 8.45 \bullet T \bullet m$, where $m/M = n$, the amount of matter in the gas and $8.45 = R$.

$1/\pi$ is lost by mistake. Although Loschmidt did not provide an Avogadro number, from his size of"air molecules" it can be estimated (suppose air is liquified and its molar volume is correctly measured) with an error of $\pi^{-3} = 0.032$ relative to the actual value (see Eq.3f below), so the Avogadro number after Loschmidt should be about 0.19 $10^{23}$ 1/mol. However, James Clerk Maxwell extended the derivation of Loschmidt 8 years after its publication into a different direction and came up with a value of the so-called Loschmidt constant of 1.9 $10^{25}$ 1/m$^3$. This value means the number of molecules in a unit volume at standard pressure and temperature. Interestingly, this value is lower only by 30% compared to the modern CODATA value of about 2.7 $10^{25}$ 1/m$^3$ at 0 °C and 1 bar. As the Loschmidt constant is proportional to the Avogadro number, it turns out that from the logic of Maxwell, Loschmidt predicted about 4.2 $10^{23}$ 1/mol for the Avogadro number, although without saying so. It should be noted that the estimate by Loschmidt was not widely accepted by fellow scientists, mostly because the kinetic theory of gases was published in its full only in 1896–1898 by Ludwig Boltzmann [26], a friend of Loschmidt in Vienna. At this point it is worth to mention that the ratio of the abovementioned universal gas constant and the Boltzmann constant would provide the Avogadro number, so it could be precisely determined by Boltzmann in 1896. However, Boltzmann did not provide the value of his constant. It was first done by Max Planck in 1901. By analyzing black body radiation Planck found the value of the Boltzmann constant as $k_B = 1.346\ 10^{-23}$ J/K [27], which is quite close to the current value of 1.380 $10^{-23}$ J/K. If the universal gas constant by Mendeleev ($R$ = 8.45 J/molK) is divided by the above Boltzmann constant of Planck, the Avogadro number is obtained as 6.12 $10^{23}$ 1/mol, being only 2.5% off the best expected value of 5.97 $10^{23}$ 1/mol of the time. Unfortunately, Planck in his 1901 paper [27] did not make this step. As a result, we had to wait further 4 years for the much less precise range of values of (2 … 6) $10^{23}$ 1/mol of Einstein [18–21], and 8 more years for the less precise value of 7.05 $10^{23}$ 1/mol by Perrin [23].

Summarizing: in times when the paper by Eötvös was written in 1886, the estimate by Loschmidt was the best estimate for the molecular size. Thus, there was a 40-year time-window opened for Eötvös (in his age interval of 17 … 57) between Loschmidt (1865) and Eistein (1905), in which a better and a more scientific estimate of the Avogadro number and/or the atomic-molecular size could be found. The paper of Loschmidt was probably known by Eötvös, but probably he neglected it, similarly as others did that time. Even if the Loschmidt method did not seem correct to Eötvös, at least this paper could draw the attention of Eötvös to the existence of this hot question in the Austro-Hungarian Monarchy in the second half of the 19th century. Unfortunately, Eötvös did not note (or could not use) this chance, so he never received a Nobel prize for the result he could achieve (see below) and for which Perrin received the prize much later.

## 3. The experimental setup built by Eötvös and its validation

After he finished his studies in Heidelberg (Germany), Eötvös returned to his home country Hungary and built a new equipment at the Budapest University of Technology (as called today) to measure surface tension of liquids along their boiling lines. The fact that his paper describing his equipment appeared to be paper No 1 in issue No 1 of the new journal of his university [28] probably had something to do with the fact that Eötvös was the only baron among the many co-workers of the university. Even if so, the paper is written with high scientific precision. Let me note that he wrote further two papers [29,30] in Hungarian language before his famous 1886 paper [3]. The two papers [29,30] are much more detailed compared to his first paper on the subject [28], so many details not given in [28] can be understood only from his papers [29,30].

Eötvös used a high-pressure glass container, half-filled with the liquid to be measured. One side of this container was a vertical flat glass plate. The liquid formed a curved meniscus within several millimeters from the wall of this vertical glass plate due to the equilibrium contact angle of the liquid on the plate. Two points along the curved meniscus surface were used for measurements (see Fig. 1). An incident light was reflected on selected point 1 of the surface from left top such, that it reflected horizontally from point 1 and so the vertical position of this point 1 ($z_1$, m) could be measured outside of the container by a cathetometer. Also, the angle of this incident light, closed with the same horizontal line in point 1 was measured as $\varphi_1$ by a theodolite, equipped with a telescope. The same was repeated with point 2, providing another two measured values $z_2$ (m) and $\varphi_2$. The capillary constant ($a$, m) was derived by Eötvös using the Laplace Eq. [12] as:

$$a = \left| \frac{z_1 - z_2}{\sqrt{1 - cos\varphi_1} - \sqrt{1 - cos\varphi_2}} \right| \tag{1a}$$

where the definition of the capillary constant becomes clear from his paper [29]:

$$a \equiv \sqrt{\frac{2 \bullet \sigma}{(\rho - \rho_g) \bullet g}} \tag{1b}$$

where $\sigma$ (J/m$^2$ = N/m) is the surface tension of the liquid, $\rho$ (kg/m$^3$) is the density of the liquid, $\rho_g$ (kg/m$^3$) is the density of the gas (= vapor), $g$ (m/s$^2$) is the acceleration due to gravity at the geological point where the measurements were performed (about $g$ = 9.808 m/s$^2$ in the laboratory of Eötvös, at the level of river Duna in Budapest – see Appendix). However, as follows from the Appendix, Eötvös much probably used the value of $g$ = 10.0 m/s$^2$, although he never mentioned the value of this constant. It means that when Eötvös used Eq.(1b) to calculate the value of surface tension, he over-estimated all surface tension values by about 2.0%. This also means that the value of his famous Eötvös constant is also over-estimated by about 2.0% - see below.

Note, that the current definition of the capillary length is quite similar to Eq.(1b), but without the constant 2 of Eq.(1b). Note also, that although at relatively low temperatures $\rho \gg \rho_g$, but it is certainly not the case close to the critical temperature, at which $\rho \cong \rho_g$.

The accuracy of the measured values was estimated as 5 μm for the $(z_1 - z_2)$ distance and one third of a minute of the angles $\varphi_1$ and $\varphi_2$. The measured value of the capillary constant for mercury at room temperature was found as $a = 2.44 \pm 0.10$ mm. Eötvös validated his measured value by comparing it to other measured values known before 1876 by Laplace, Hagen, Danger, Poisson, Béde, Desains and Quincke. The interval of these values (2.5 … 3.0 mm) was somewhat higher than the value of Eötvös. Substituting the current "best handbook values" for mercury at room temperature ($\sigma$ = 0.474 J/m$^2$ and $\rho - \rho_g$ = 13,540 kg/m$^3$ [31]) and $g$ = 10.0 m/s$^2$ into Eq.(1b) the theoretical value of $a$ = 2.65 mm is found. Thus, the value measured by Eötvös was lower by 8% compared to the best current value, and was also lower, than the

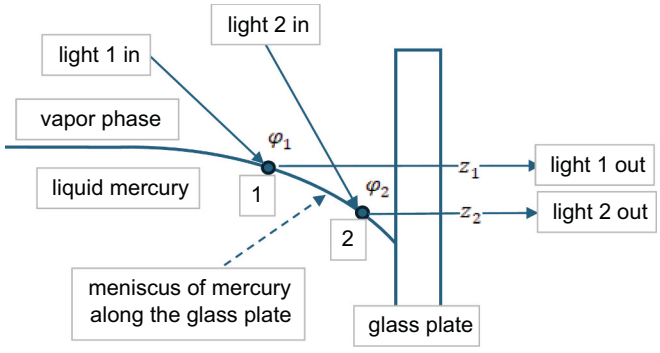


**Fig. 1.** The principle of the measurements of Eötvös [28]. Note: this figure is valid for mercury, with its meniscus curved down along the glass plate (= the poorly wetting case). The menisci of other liquids usually curve the other way up (= the wetting case, not shown here).

interval of values measured before him. This is probably due to the not very clean mercury and/or glass plate or to the partly oxidizing atmosphere used by Eötvös in 1876. Note: measured values of surface tensions of the same liquid metals at same temperatures evolve in historical time: the difference between old and new values can be up to 50% [4].

This experimental problem was realized by Eötvös in the beginning of 1883 [29], when he worked out the following procedure: he was boiling the liquid to be studied in an open container for a long time, and suddenly closed the container: in this way he started measuring time-independent capillary constants since 1883. Also, since 1883 he started to measure surface tension of liquids being in contact only with their own vapor in the gas phase.

In the text of the paper [28] an acknowledgement is given by Eötvös to his assistant Ottokar Pokorny, who helped the baron with his measurements. However, his name did not appear as a co-author of Eötvös, in accordance with the customs of the time. Probably it was his assistant, who measured the majority of $z$ and $\varphi$ values along the boiling lines of the 160 liquids during the next decade, as mentioned in the summary paper [3]. On the other hand, there is no doubt that Eq-s (1a, 2) of this paper were created by Eötvös himself.

The novelty of his method is not Fig. 1 and not Eq.(1a). The novelty was that the measurements were performed at high pressures and high temperatures along the boiling lines of the liquids, when the liquids were in equilibrium with their own vapors. In this way, Eötvös was able to observe experimentally the appearance of the critical phenomenon for many organic liquids, when the liquid seemingly "disappeared", i.e. the liquid phase was merged with the vapor phase and became a gas phase. Therefore, he could experimentally detect the critical temperatures at least for low-critical point organic liquids and could observe how his capillary constant was approaching zero as temperature was approaching the observable critical temperature. These observations lead him to his famous capillary equation (see below). From the mass of the liquid and its volume that could be measured by the cathetometer, he was also able to measure the temperature dependence of the liquid density.

## 4. The preliminary version of the capillary equation of Eötvös

The 1884–85 paper by Eötvös on the connection between surface tension and critical temperature [29] starts with the abovementioned explanation on how he ensured equilibrium between the liquids and vapors in closed containers since the beginning of 1883 (the method originally developed by Schiff). As an example, he mentions the case of water, which preserved its surface tension value identical during a year, if kept in the same closed container. He also reports his measured 6 different values of the capillary constants for water at 17 °C as (values in mm): 3.858, 3.841, 3.854, 3.840, 3.838, 3.845, with the average value of 3.846 mm. Substituting the current values of $\sigma = 73.19$ mN/m, $\rho = 998.7$ kg/m$^3$, $\rho_g = 0.016$ kg/m$^3$ at 17 °C [32] and $g = 10.0$ m/s$^2$ into Eq. (1b), the best current theoretical value is: $a = 3.828$ mm, being below the measured average value by Eötvös only by 1.00%. This indicates that the distilled water and the experimental method used by Eötvös in 1883–1885 were pure enough and precise enough to establish his famous capillary equation.

He also reported semiempirical equations for the temperature dependences of capillary constant and surface tension for water, measured in the temperature range between −3 and + 80 °C at nine different temperatures [29]:

$$a^2 \cong 15.233 - 0.02742 \bullet t - 0.000013 \bullet t^2 \quad (1c)$$

$$\sigma \cong 76.17 - 0.136 \bullet t - 0.00035 \bullet t^2 \quad (1d)$$

where $a^2$ (mm$^2$) is the square of the capillary constant of water, $\sigma$ (mN/m) is the surface tension of water, $t$ (°C) temperature between −3 and + 80 °C. Let me note, that the values calculated by Eq.(1d) should be lowered by 2.0% due to the $g = 10.0$ m/s$^2$ value, used by Eötvös (see Appendix). Let me also note, that substituting $t = 17$ °C into Eq.(1c), $a = 3.842$ mm is obtained, being close to the abovementioned values. Let me also note, that extrapolating Eq-s (1c-d) to zero values, the critical temperature can be estimated as 457 °C and 311 °C, respectively (this value is not influenced by the 2.0% reduction in the values of Eq.1d). The best current value of 374 °C [32] appears within this interval, close to the average value of 384 °C measured by Eötvös. He also found that his semi-empirical Eq-s (1c-d) are close to similar equations and values reported earlier by Frankenheim, Brunner, Wolff, Rodenbeck and Volkmann, who also paid serious attention to the purification of their samples. However, all these values differ considerably from the values measured by Quincke, who measured many surface tension values, but probably did not pay sufficient attention to the purity of his samples.

Based on his large and carefully measured empirical databank, Eötvös wanted to find a generally valid equation for the temperature dependence of surface tension of liquids. From the earlier results by van-der-Waals, he understood that it is possible only, if he searches for a relationship between surface tension and critical temperature. A similar route was followed by van-der-Waals earlier, but due to the lack of precise measured data he could not find the proper relationship. At this point it is of interest to provide different definitions of the critical temperature before 1885:

(i) this is a temperature below which matter can exist in both liquid and gaseous state, but above which matter can exist only in the gaseous state (Andrews and van der Waals),
(ii) this is a temperature at which the density of the liquid becomes identical to the density of the saturated vapor of the same liquid and at which the heat of evaporation is zero (Jamin, 1883), this definition was preferred by Eötvös, and also extended by him as:
(iii) this is a temperature at which the surface tension of the liquid in contact with its saturated vapor is nil (Eötvös [29]), with the explanation: "the (surface) tension is proportional to the density difference between a liquid and its saturated vapor, so surface tension diminishes with the disappearance of this difference". Eötvös also mentions his experiments with carbonic acid, providing clear experimental evidence supporting his idea. However, Eötvös also mentioned Wiedemann, who denied this conclusion, based on the measured values by Wolff and Clarke.

Starting from the definition of Jamin, Eötvös also worked out a method to measure critical temperature. He filled a long, closed tube half with the liquid and its vapor to be measured. Then, he made the tube hanging vertically in a way that it can freely rotate around its horizontal axis, selected just below its center of gravity when the liquid is homogeneously distributed along the length of the tube. Below the critical temperature, the stable position of this tube is vertical. However, above the critical temperature matter will be evenly distributed along the tube and so its vertical position becomes unstable and therefore the tube will somewhat turn from its previous vertical direction. This method is more advantageous compared to visual observations as it can be also applied for non-transparent containers. This is needed for example for water, which reacts with glass at elevated temperatures.

First, Eötvös checked the two theoretical equations proposed by van der Waals between surface tension, pressure, temperature, critical pressure and critical temperature. From his manuscript (see Appendix) it becomes clear that he spent years checking these equations, but eventually he declared that none of the two equations of van-der-Waals are experimentally confirmed. Then, Eötvös was looking empirically for such a combination of the absolute temperature ($T$), the value of surface tension at this temperature ($\sigma$) and the equilibrium vapor pressure at this temperature ($p$) that would have a constant value at the corresponding temperature ($T/T_{cr}$) of the given liquid. In this paper [29] Eötvös empirically found the following relationship:

$$\frac{p \bullet T^2}{\sigma^3} = const \text{ at } \frac{T}{T_{cr}} = const \tag{1e}$$

Using the measured values for ether as etalon, Eötvös estimated the critical temperature of 37 liquids by Eq.(1e). For this purpose, in addition to his own measured values, he used the measured values of Schiff, Pawlewsky, Cagniard de la Tour, Regnault, Sajotewsky, Faraday, Sarrau, Ramsay, Strauss, Hannay and Hoggart for calculations, or comparison. He found that Eq.(1e) coupled with measured values reproduces reasonably well the measured critical temperatures. Particularly, his estimated value for water is 409.3 °C = 682.5 K compared to the best current value of 374 °C = 647.2 K [32] with a difference of only 5.5%.

At the end of his paper [29] Eötvös repeated that Eq.(1e) is only empirical and only approximated, with unknown uncertainty. A year later he withdrew his Eq.(1e) [30]. This was based on his new theoretical derivation and also on the fact that his final Eq.(2) performed much better than his previous eq. (1e).

## 5. The final capillary equation of Eötvös

In the period between 1883 and 1886, the capillary constant values were measured by Eötvös (and probably by his assistants) for 160 pure liquids along their boiling lines. Unfortunately, the original values of "molecular weights", critical temperatures, and the temperature dependent values of $z$, $\varphi$, capillary constant, density, "molecular volume" and surface tension for the measured 160 liquids are missing from his papers [3,30].[4] Instead, Eötvös derived the following equation and summarized his measured values in this short and elegant form [3,30][5]:

$$\sigma \bullet V_m^{2/3} = k \bullet (T_{cr} - T) \tag{2}$$

where $\sigma$ (J/m$^2$) is the surface tension of the liquid, $V_m$ (m$^3$/mol) is the molar volume of the liquid, $T_{cr}$ (K) is the critical temperature of the liquid, $k$ (J/Kmol$^{2/3}$) is the so-called Eötvös constant. Note that Eötvös wrote his equation using $V$ (molecular volume) instead of $V_m$ (molar volume), but in [30] he specified that "molecular volume is the ratio of the molecular weight to density", in accordance with the well-known equation today:

$$V_m = \frac{M}{\rho} \tag{2a}$$

Note also, that the way to go from Eq.(1b) to Eq.(2) is not straightforward, as only the product of $\sigma \bullet V_m$ follows in a straightforward way from the measured values of the capillary constants and from the measured density values. Indeed, combining Eq-s (1b, 2a):

$$\sigma \bullet V_m = \frac{1}{2} \bullet g \bullet M \bullet a^2 \tag{2b}$$

To find his Eq.(2), he first needed to separate the expression $\sigma \bullet V_m$ first into $V_m$ by Eq.(2a), and then into $\sigma$ by dividing $\sigma \bullet V_m$ by $V_m$. After Eötvös found a good linear correlation between $\sigma \bullet V_m^{2/3}$ and $(T_{cr} - T)$ for many of the 160 liquids he studied, he believed that the coefficient $k$ between these two quantities must be a universal constant. That is why his capillary equation in his original paper is written with an average numerical slope of "0.227" (in current units it is 2.27 10$^{-7}$ J/Kmol$^{2/3}$), instead of the generally valid constant $k$. Today it is clear that the Eötvös constant depends on the type (composition) of the liquid and on temperature. Eötvös himself did not hide this experimental fact, as follows from the rare actual $k$-values reported by him in his papers [3,30] (see Table 1). Moreover, as follows from the above (see also Appendix), Eötvös overestimated his surface tension values by about 2.0% due to his $g$ = 10.0 m/s$^2$, and so also his constant is overestimated. Therefore, based on the measured values of Eötvös, but applying his later value of $g$ = 9.808 m/s$^2$ (see Appendix), the Eötvös constant can be corrected as: $k$ = 0.222 (= 2.22 10$^{-7}$ J/Kmol$^{2/3}$ in current units).

As follows from Table 1 and from Table A2 of the Appendix, Eötvös could not find from his measured values the semi-empirical value of x = 2/3 if Eq.(2) is written generally as $\sigma \bullet V_m^x = k \bullet (T_{cr} - T)$. In contrary, Eötvös derived his Eq.(2) theoretically. Let me show shortly, how he did it [3,30]. First, he considered the equilibrium of a liquid with its molar volume of $V_m$ and its vapor with its molar volume of $V_{m,g}$. Further, he declared that for similar liquids and their similar vapors at their corresponding temperatures the ratios of these molar volumes must be the same:

$$\frac{V_m}{V_{m,g}} = C_1 \tag{2c}$$

where $C_1$ is a dimensionless constant. Then, he wrote the ideal gas law as:

$$\frac{p \bullet V_{m,g}}{T} = C_2 \tag{2d}$$

where $V_{m,g}$ (m$^3$/mol) is the molar volume of the gas at pressure p ($Pa$) and at absolute temperature T ($K$), while $C_2$ is another dimensionless constant (= $R$ = 8.3145 J/molK, as we know today). Expressing $V_{m,g}$ from Eq.(2d) and substituting the resulting equation into Eq.(2c):

$$\frac{p \bullet V_m}{T} = C_1 \bullet C_2 \tag{2e}$$

Further, Eötvös supposed that the similar liquids at their corresponding temperatures are also similar in terms of forces and energies acting between their molecules (today we know that this is indeed true at least for organic liquids, in which the molecules are bonded by similar van der Waals forces – for more details see in [33]). Then, he considered the pressure of the vapor acting on a liquid surface of unit surface area as

**Table 1**
The reported $k$ values of Eq.(2) for different liquids in different $T$-intervals [3,30] (with values decreased by 2.0%) and their current critical temperatures [32].

| Liquid (formula) | $T$-interval, °C | $k$, *10$^{-7}$ J/Kmol$^{2/3}$ | $T_{cr}$, °C | confid |
|---|---|---|---|---|
| Ethyl ether ($C_4H_{10}O$) | 6 … 62 | 2.28 (2.23) | 194 | high |
| | 62 … 120 | 2.26 (2.21) | | |
| | 120 … 190 | 2.21 (2.17) | | |
| Ethylene bromide ($C_2H_5Br$) | 20 … 99 | 2.27 (2.22) | 231 | high |
| | 99 … 213 | 2.32 (2.27) | | |
| Chloroform ($CHCl_3$) | 20 … 60 | 2.30 (2.25) | 61 | high |
| Mercury methyl ($CH_3Hg$) | 20 … 99 | 2.28 (2.23) | – | – |
| Carbon oxychloride ($COCl_2$) | 3 … 63 | 2.31 (2.26) | 182 | med |
| Carbon dioxide ($CO_2$) | 3 … 31 | 2.28 (2.23) | 31 | high |
| Carbon disulfide ($CS_2$) | 22 … 78 | 2.38 (2.33) | 279 | med |
| Sulfuric acid ($H_2SO_4$) | 2 … 60 | 2.30 (2.25) | – | – |
| Ethyl alcohol ($C_2H_6O$) | 21 … 78 | 1.04 (1.02) | 270 | high |
| | 78 … 108 | 1.36 (1.33) | | |
| | 108 … 138 | 1.59 (1.56) | | |
| | 138 … 168 | 1.83 (1.79) | | |
| | 168 … 199 | 2.02 (1.98) | | |
| | 199 … 236 | 2.26 (2.21) | | |
| Water ($H_2O$) | 3 … 40 | 1.59 (1.56) | 374 | med |
| | 40 … 100 | 1.80 (1.76) | | |
| | 100 … 150 | 2.28 (2.23) | | |
| | 150 … 210 | 2.27 (2.22) | | |
| Acetic acid ($C_2H_4O_2$) | 21 … 107 | 1.32 (1.29) | 320 | med |
| | 107 … 160 | 1.32 (1.29) | | |
| | 160 … 230 | 1.38 (1.35) | | |
| Mercury (Hg) | 0 … 300 | 1.8 (1.76) | 1750 | low |

[4] Maybe someone (preferably speaking Hungarian, German and French) can find time to systematize and understand all the original notes of Eötvös in his legacy (see Appendix).

[5] Paper [30] in Hungarian language was published somewhat before the well-known paper by Eötvös published in German [3]. The latest paper [3] is a summary of earlier papers [28–30], with the latter ones providing some more details.

$p \bullet V_m^{2/3}$ and considered the surface force acting along a line of unit length as $\sigma \bullet V_m^{1/3}$ and supposed that the ratio of these two quantities must be also a constant for similar liquids at their corresponding temperatures:

$$\frac{\sigma \bullet V_m^{1/3}}{p \bullet V_m^{2/3}} = \frac{\sigma}{p \bullet V_m^{1/3}} = C_3 \tag{2f}$$

while $C_3$ ($mol^{1/3}$) is another constant ($= N_{Av}^{-1/3}$ as we know today). Now, let us express $p$ from Eq.(2e) and let us substitute the resulting equation into Eq.(2f):

$$\frac{\sigma \bullet V_m^{2/3}}{T} = C_1 \bullet C_2 \bullet C_3 \tag{2g}$$

Now, let us multiply Eq.(2g) by T and let us introduce the Eötvös constant as: $k \equiv C_1 \bullet C_2 \bullet C_3$ with the unit of $J/Kmol^{2/3}$:

$$\sigma \bullet V_m^{2/3} = k \bullet T \tag{2h}$$

From here it is clear that $\sigma \bullet V_m^{2/3}$ is proportional to $T$. Combining this result with the boundary condition deduced by Eötvös earlier (see section 4), claiming that at the critical temperature ($T_{cr}$, K) surface tension becomes zero, Eq.(2h) becomes Eq.(2), which is the Eötvös equation. Eötvös could not find theoretically the value of his constant $k$, but he found his average value for similar liquids, for which this constant was not $T$-dependent.

From the practical point of view, Eq.(2) helps to reduce the number of measured surface tension values even to a single value, and it still allows reasonable estimates for the temperature dependence of surface tension, supposing the same is known for molar volume or density and supposing the critical temperature is also known. Note that both surface tension and molar volume are thermodynamic quantities of a condensed phase, and so their values are practically pressure-independent below 100 bar. Thus, for liquids with their critical pressures below 100 bar, pressure-independent values can be used in Eq.(2) for both surface tension and molar volume at any temperature below the critical point.

For liquids with very high critical temperatures its measurement is close to impossible. In these cases the measured $T$-dependences of surface tension and molar volume, coupled with Eq.(2) can be used to estimate the critical temperature, as shown for some liquid metals in [34]. Note, however, that the order-disorder surface phase transition of liquid metals makes such estimations more difficult as it might seem [35].

The difference between maximum measured temperatures and the critical temperatures for different liquids in Table 1 helps us to classify the accuracy of the measured $k$-values in Table 1 (see remarks "high", "low" and "med" for values of high, low and medium confidence). As follows from Table 1, the lowest confidence in the reported $k$-value by Eötvös is reported for mercury. This is because of a very far extrapolation from (0 … 300) °C to 1750 °C was needed for Eötvös to estimate the reported $k$-value in Table 1. Note, that in those cases, when the critical temperature was too high, it could not be observed experimentally by Eötvös, and so it could be estimated by him only using his Eq.(2), extrapolating the $T$-dependence of $\sigma \bullet V_m^{2/3}$ linearly down to $\sigma \bullet V_m^{2/3} = 0$, at which $T = T_{cr}$ can be estimated. After this extrapolation, the $k$-value reported in Table 1 could be found by Eötvös from his Eq.(2) as the ratio $\sigma \bullet V_m^{2/3}/(T_{cr} - T)$, where $T$ is preferably selected in the middle of the measured $T$-interval.

It is important to note, that the Eötvös eq. (2) was already extended to other interfaces, claiming that "whenever two phases defining an interface merge (as the liquid and vapor phases merge into a gas phase at the critical point), the interfacial energy tends to zero at this critical temperature". This principle turned out to be valid and useful to study the $T$-dependence of the coherent solid/solid interfacial energy in Ni-based superalloys [36,37].

## 6. The modern model for surface tension and the missed chance of Eötvös: The estimation of the Avogadro number and the size of atoms-molecules

First, let me start with the general model equation valid for the surface tension of one-component liquids [36], obtained from the fundamental equation of Gibbs ($dG = \sum_i \mu_i \bullet dn_i + \sigma \bullet dA$) [11]:

$$\sigma \cong \frac{\alpha \bullet \left[ -H_{m,c,m} - \int_{Tm}^{T} C_{p,m} \bullet dT \right] - T \bullet \Delta_s S_m}{f \bullet V_m^{2/3} \bullet N_{Av}^{1/3}} \tag{3a}$$

where $\alpha$ (dimensionless) is the ratio of the broken bulk bonds along the surface, being the function of the structure of the bulk and surface layer, $H_{m,c,m}$ (J/mol) is the bulk molar cohesion energy of the liquid at its melting point with a negative value, $C_{p,m}$ (J/molK) is the molar heat capacity of the liquid, $T_m$ (K) is the melting point, $\Delta_s S_m$ (J/molK) is the excess surface molar entropy, $f$ (dimensionless) is a geometrical constant, being the function of the structure of the bulk and the surface layer. Let us note, that based on Eq.(3a) the surface tension of all organic liquids appear to be quite similar, as their molecules are bonded to each other by van-der-Waals forces, which provide quite similar bonding energies between the organic molecules per their surface area (for more details see in [33]). The same also explains why the surface tension of water is much larger compared to that of the organic liquids (because of the effect of the additional hydrogen bond connecting the water molecules), and why the surface tensions of liquid metals have the largest values among all liquid types (because the metallic bond is the strongest per atom).

Let us make the following simplifications in Eq.(3a), partly because these are more-or-less valid at least for simple liquids, and partly to simplify this equation to the level of knowledge before 1886:

(i) $\Delta_s S_m \cong 0$ [36]; although entropy was introduced in 1865 by Rudolf Clausius [38], it would be too much to expect to include it into the model equation of surface tension in the 19th century; moreover, although the Eötvös constant is routinely interpreted through $\Delta_s S_m$ in the literature (see for example [39–41] and many other papers), it is usually forgotten that the excess surface entropy has in fact two terms: the positive one due to the configurational entropy (usually considered) and the negative one due to the ordering entropy (usually forgotten), the two more-or-less cancelling each other [36]; instead, the $T$-dependence of $\sigma \bullet V_m^{2/3}$ is mostly due to the heat capacity of the liquid, describing the $T$-dependence of its cohesion energy [36],

(ii) although the molar cohesion energy of the liquid is routinely (and more-or-less correctly) estimated as the negative of the molar vaporization enthalpy, the $T$-dependence of the molar cohesion energy is wrongly taken identical to that of the molar vaporization enthalpy (which is close to zero as the molar heat capacities of liquids and vapors are similar); rather, once the cohesion energy is estimated as the negative of the vaporization enthalpy at the melting point, its temperature dependence should be described by the heat capacity term,

(iii) although molar heat capacity is a $T$-dependent quantity and therefore an integral is written in Eq.(3a), but its $T$-dependence is mostly negligible for liquids, and so in Eq.(3a) the integral can be replaced by the linear $T$-dependence of molar cohesion energy with a constant value of the molar heat capacity ($\int_{Tm}^{T} C_{p,m} \bullet dT \cong C_{p,m} \bullet (T - T_m)$),

(iv) although parameter $f$ is a difficult function of the bulk and surface structures of the liquid, but in the first approximation $f \cong 1.00$ [36] at least for simple liquids; note a usual mistake even in surface science of liquid metals: $f \cong 1.09$ is frequently applied,

although this value is valid only for the (111) surface of solid (not liquid) fcc metals [36],

(v) parameter α is also a difficult function of the bulk and surface structures of the liquid; however, in the first approximation its value $\alpha \cong 1/6$ can be used, understanding the 3D nature of the bulk liquids and the fact that only 1 out of the 6 bond directions shows out of the phase across the surface,

(vi) The simplest interpretation of the critical temperature is that it is a temperature at which the cohesion in the liquid becomes zero (see above), so $-H_{m,c,m} - C_{p,m} \bullet (T_{cr} - T_m) \cong 0$ and from here: $H_{m,c,m} \cong - C_{p,m} \bullet (T_{cr} - T_m)$; substituting this latter equation into the [] of Eq.(3a), the following expression is obtained: $-H_{m,c,m} - \int_{Tm}^{T} C_{p,m} \bullet dT \cong C_{p,m} \bullet (T_{cr} - T)$.

Substituting the above 6 simplifications into Eq.(3a), the following simple model equation is obtained:

$$\sigma \bullet V_m^{2/3} \bullet N_{Av}^{1/3} \cong \frac{C_{p,m} \bullet (T_{cr} - T)}{6} \tag{3b}$$

Eq.(3b) could be obtained logically even back in 1886, or at least it seems so to the author in 2023, using the following logic:

(i) The left hand-side of Eq.(2) $\sigma \bullet V_m^{2/3}$ has a strange unit of $J/mol^{2/3}$, so to convert it into a quantity with a reasonable unit (J/mol), it should be multiplied by $N_{Av}^{1/3}$ with a unit of $1/mol^{1/3}$ (note: although the wording "gram-molecule" was used instead of "mol" in the 19th century, but with the same meaning),

(ii) After doing so, the left hand side of Eq.(3b) has a unit of J/mol; its physical sense is the partial loss of bulk cohesive energy of the atoms / molecules when they appear in the surface layer; the ratio of the lost cohesive energy along the surface is around 1/6 in the first approximation (see explanation above); the absolute value of the cohesion energy is even not needed, but its *T*-dependence follows from the logic given above, with a reasonable boundary condition that at the critical temperature the cohesion energy of the liquid should drop to zero (the same zero value is valid for the cohesion energy in ideal gases), and the heat capacity of the liquid is the energy needed to break the bonds within bulk liquids upon their heating.

After the logical derivation of Eq.(3b), it can be re-arranged to look similar to Eq.(2):

$$\sigma \bullet V_m^{2/3} \cong \frac{C_{p,m} \bullet (T_{cr} - T)}{6 \bullet N_{Av}^{1/3}} \tag{3c}$$

Comparing Eq-s (2, 3c) one can see that their left-hand sides are identical, so their right-hand sides must be identical, too. From here:

$$k \cong \frac{C_{p,m}}{6 \bullet N_{Av}^{1/3}} \tag{3d}$$

Now, the Avogadro number can be expressed from Eq.(3d) as:

$$N_{Av} \cong \left(\frac{C_{p,m}}{6 \bullet k}\right)^3 \tag{3e}$$

Eq.(3e) is the result of our final derivation. It allows the estimation of the Avogadro number from the measured Eötvös constants *k*, if the average heat capacities of the liquids are known. At this point let us note, that heat capacities of solids and liquids were measured much before Eötvös was even born (the Dulong-Petit law (1819) and the Kopp-Neumann law (1831) were established long before 1848). Therefore, Eötvös probably had access to the heat capacities of the liquids he measured.

Once the Avogadro number is estimated by Eq.(3e), and the molar volume of the liquid calculated by Eq.(2a), the average volume of 1 molecule is obtained by dividing the molar volume by the Avogadro number. Understanding, that the 3D molecules within the condensed phase liquid probably touch each other, the effective diameter of a molecule (or atom) ($D_{at}$, m) can be obtained in the first approximation as the cubic root from this ratio, using also Eq.(2a):

$$D_{at} \cong \sqrt[3]{\frac{V_m}{N_{Av}}} \cong \sqrt[3]{\frac{M}{\rho \bullet N_{Av}}} \tag{3f}$$

Obviously, more exact expressions compared to Eq.(3f) can be obtained by considering the actual bulk structure of the liquid, but all such alternative equations would provide values with some ±10% deviations from Eq.(3f). It should be understood, that in 1886 the question of the molecular sizes was far from the accuracy of ±10% (see the estimate of Loschmidt discussed above, being out by about 300%).

Now, let me apply current literature data on molar masses, heat capacities and densities of liquids at room temperature [32] and the possible ranges of Eötvös constants from Table 1 to estimate the possible ranges of Avogadro number and the molecular (atomic) diameters by Eq-s (3e-f) (see Table 2).

As follows from Table 2, the highest deviation from the actual Avogadro number is found for Hg, rated with the lowest confidence of its *k*-value in Table 1. In 11 cases out of 12 cases in the pre-last column of Table 2 the molecular sizes range between 0.25 … 0.74 nm. Based on that, the very low value of 0.028 nm and the corresponding very high value of 57.8 $10^{23}$ 1/mol for the Avogadro number can be excluded. The other Avogadro number values estimated for 4 liquids with the *k*-values of high confidence in Table 1 equal (3.82 … 4.08 … 5.53 … 5.64 … 17.5 … 19.3) $10^{23}$ 1/mol, with the average of these six values is 9.31 $10^{23}$ 1/mol, being higher only by 56% compared to the best possible value of the time (5.97 $10^{23}$ 1/mol – see above) - if the *k*-values are reduced by 2% as explained above, the deviation increases to 65%). It also means that the average inaccuracy in molecular sizes is about $\sqrt[3]{1.56} = 1.16$ (or $\sqrt[3]{1.65} = 1.18$), i.e. about 17%. Indeed, in the pre-last column of Table 2 the molecular diameters of relatively simple organic and inorganic liquids range between 0.25 … 0.74 nm (excluding one value), which is reasonable (much better, than the 0.969 nm value of Loschmidt for the air molecules – see above). I think that if Eötvös, based on his measured capillary constant and density values and known heat capacities taken from the literature claimed the above results in 1886, this would have added to the value of his paper.

Finally, it is interesting to note that Eistein [24] used the same experimental data by Eötvös [3] to estimate the size of atoms and molecules (without a formal citation to Eötvös, "of-course"). Supposing the Avogadro number is 7 $10^{23}$ 1/mol (probably taken by Einstein from Perrin [23] but without any citation), Eistein estimated the diameter of a mercury atom to be 5.18 nm, a value being more than 17 times larger than the current atomic diameter of mercury (0.302 nm). Compared to this estimation, our estimation of 0.96 nm (see Table 2) is out only by 3.2 times, although this is called above our estimation with the lowest confidence.

Einstein in his paper [24] also estimated the molecular size of benzene ($C_6H_6$) from the data of Eötvös [3] and obtained a value of 5.31 nm. Although it is not clear where Einstein found any value for benzene (= "Benzol" in German) in the paper by Eötvös [3],[6] this is also a serious over-estimation, especially if compared to the estimated values of Table 2, all being below 0.74 nm for molecules (the actual value is around 0.3 nm, although the benzene molecule is not a 3D-symmetrical molecule, so it is hard to say exactly).

All this was written to show, that Eötvös did not have too much chance to find equations similar to Eq.(3e-f) and the values similar to

[6] Einstein and Eötvös probably corresponded (as all scientists did before the great wars), but I found no evidence of a letter with the values measured for benzene.

**Table 2**
The estimated values of the Avogadro number and the molecular (atomic) diameters by Eq-s (3e-f), using literature data [32] and the values from Table 1.

| Liquid (formula) | $k$, $*10^{-7}$ J/Kmol$^{2/3}$ [3] | $C_{p,m}$ J/molK | $M$ g/mol | $\rho$ g/cm$^3$ | $N_{Av}*10^{23}$ 1/mol | $D_{at}$ nm | conf |
|---|---|---|---|---|---|---|---|
| $C_4H_{10}O$ | 2.21 … 2.28 | 165 | 74 | 0.713 | 17.5 … 19.3 | 0.37… 0.38 | high |
| $C_2H_5Br$ | 2.27 … 2.32 | 101 | 109 | 2.18 | 3.82 … 4.08 | 0.50 … 0.51 | high |
| $CHCl_3$ | 2.30 | 114 | 120 | 1.49 | 5.64 | 0.52 | high |
| $CH_3Hg$ | 2.28 | – | 216 | – | – | – | – |
| $COCl_2$ | 2.31 | – | 99 | – | – | – | med |
| $CO_2$ | 2.28 | – | 44 | – | – | – | high |
| $CS_2$ | 2.38 | 76.4 | 76 | 1.26 | 1.5 | 0.74 | med |
| $H_2SO_4$ | 2.30 | 139 | 98 | 1.83 | 10.2 | 0.37 | – |
| $C_2H_6O$ | 1.04 … 2.26 | 112 | 46 | 0.789 | 5.63 … 57.8 | 0.028 … 0.35 | high |
| $H_2O$ | 1.59 … 2.27 | 75.3 | 18 | 1.00 | 1.69 … 4.92 | 0.33 … 0.47 | med |
| $C_2H_4O_2$ | 1.32 … 1.38 | 123 | 60 | 1.05 | 32.8 … 37.5 | 0.25 … 0.26 | med |
| Hg | 1.8 | 28.0 | 201 | 13.5 | 0.17 | 0.96 | low |

Table 2 back in 1886, if even Einstein, 25 years later, overestimated the molecular and atomic sizes by more than an order of magnitude. All this being said, the simple Eq-s (3e-f) and the values of Table 2 prove that the Eötvös constants could in principle lead to the correct magnitude of the Avogadro number and the molecular sizes back in 1886. Obviously, it is easy to be so "clever" 137 years later.

## 7. On the difficulty to make the next step in science

In this paper it was shown several times (in relation to Eötvös himself) how difficult it is for a scientist to make the next step, even if it seems obvious in retrospective (see Table 3). Only those examples are given in Table 3, which were mentioned in the paper above. The history of science obviously knows hundreds of further examples. As a lesson from Table 3 it seems that if something seems "obvious" in retrospective, it was not necessarily obvious back in time for the scientist, whose mind was full with his own problems and had no time and no free brain capacity for the next "obvious" problem. The famous saying of Newton is appropriate here: "We all stand on the shoulders of giants".

Even if a scientist understands this rule, it does not help him to avoid the same mistake. As an example: the author derived the size dependent equation for the molar Gibbs energy of nano-phases in 2012 [42]. Although he knew quite well the relationship between the molar Gibbs energy of a phase and the chemical potentials of the components in the same phase, it took him further 5 years to publish a paper on the size dependence of chemical potentials [43]. Moreover, although he also knew quite well that molar entropy and molar enthalpy are related to molar Gibbs energy, nevertheless it took him 12 years to derive the size dependence of integral and partial molar entropies and enthalpies [44].

**Table 3**
The original result of a scientist, the "obvious" next step, who did it and when.

| The original result | The "obvious" next step | Who did it and when |
|---|---|---|
| Cannizaro measured gas pressures and published relative atomic masses in 1858 | The value of the universal gas constant | Mendeleev, 1875–77 (18 years later) |
| Loschmidt estimated the size of air molecules in 1865 | The Avogadro number, or the Loschmidt number | Maxwell, 1873 (8 years later) |
| Boltzmann published kinetic theory of gases in 1896–1898 | The Boltzmann constant | Planck, 1901* (5 years later) |
| Eötvös published his capillary equation in 1886 | The Avogadro number, the size of the molecules | Einstein, 1911** (25 years later) |

*next, Planck could find the Avogadro number by dividing the gas constant of Mendeleev by his Boltzmann constant, but he did not do that. ** only the sizes of a molecule (atom) were found, but with a wrong magnitude.

## 8. Conclusions

The seminal paper by Eötvös on capillarity is discussed and celebrated here to mark his 175 years anniversary. The historical background of his results is shown in details. It is explained that although surface tension and the ways to measure it were known prior to Eötvös, probably no measurements were performed on the capillary length in a high-pressure and high-temperature equipment along the boiling lines of one-component liquids, allowing also the observation of the critical points at least for organic liquids with critical points not exceeding 300 °C. Moreover, much probably no databank on 160 liquids existed before the work of Eötvös, which allowed him to create his famous capillary equation. The most important message of his equation is that the surface tensions of liquids become zero when temperature reached the critical value and the equilibrium liquid+vapor phases merge to become a gas. This principle of Eötvös was also extended to coherent solid/solid interfacial energies in Ni-superalloys. It is also shown that in principle, the data published by Eötvös back in 1886 could be used to estimate the Avogadro number and the molecular sizes with correct order of magnitude. As these values were mostly missing in 1886, this could have some added value to the paper of Eötvös. However, it is also shown that this exercise was not that obvious, as even Einstein, 25 years after the paper of Eötvös, using his data overestimated the order of magnitude of atomic and molecular sizes. So, let us celebrate what Eötvös actually achieved: his famous capillary equation, appreciated and cited even today, although often without a formal citation (please, note citation [3] for your next paper mentioning the capillary equation by Eötvös). Note also, that Eötvös used $g = 10.0$ m/s$^2$ for the acceleration due to gravity (see Appendix) and so he over-estimated his surface tension values and also his Eötvös constant by about 2.0%. The current Eötvös constant using his measured values would be "0.222" vs his published value of "0.227".

## CRediT authorship contribution statement

**George Kaptay:** Writing – review & editing, Writing – original draft, Investigation, Data curation, Conceptualization.

## Declaration of competing interest

The author declares he has no conflict of interest in publishing this paper.

## Data availability

Data will be made available on request.

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Sciences on 20th September 2023 (organized on the same day and same place when and where the International Erdmessung started in 1906, where Eötvös presented his advanced results on gravity). The previous, short version of this paper was published in Hungarian language after this meeting, meant for general public [45]. The current paper is a largely improved scientific version of that paper. The author is also thankful to Andras Holl and Antall Babus, who helped to find 48 (!) bundles of handwritten pages of Eötvös about his experiments to measure surface tension in the Archives of the Hungarian Academy of Sciences [46] (see Appendix). The author is also grateful to János Kiss who helped to find and interpret the first paper of Eötvös on gravity [47].

## Appendix A. A short summary of the handwritten manuscripts of Eötvös on capillarity

As mentioned in the main text of the paper, Eötvös did not provide sufficient empirical information in his papers, at least according to the current publication standards. Fortunately, he was not only an ordinary researcher, but he was also a baron and later he also served as the president of the Hungarian Academy of Sciences (1889–1905) and so its Library preserved and digitalized 275 of his manuscripts [A]. Among them, there are 48 "bundles" devoted to his studies on surface tension (see Table A1). The bundles are numbered consecutively as 1–41, and then as 51–57, available online in 16 pdf files [B-Q]. These 16 files contain altogether 1543 pages of handwritten notes of Eötvös related to his studies on surface tension.

The major language of these manuscripts is Hungarian, although fragments can be also found in German and less in French languages. The manuscripts contain mostly numerical data, measured values, calculations, derivations, drawings, summary tables and copies of some papers. As follows from the manuscripts, the experimental technique described in paper [3] was far not the only one developed by Eötvös. He developed several methods, but finally used the method described here to reach his famous eq. (2).

The majority of pages of the manuscripts are written by pencil, not easy to read, and even more difficult to follow. The pages are not numbered, some of the pages are obviously confused in their sequence. Years given in Table A1 are only approximate, in some bundles different years are indicated in different pages. Some selected pages are well ordered, nicely and carefully written by a special pen, easy to read, although explanations, definitions and units are usually missing – those seem to be summary tables.

**Table A1**
Summary of the digitalized manuscripts by Eötvös devoted to surface tension.

| Bundle | Citation | Year* | Pages | Comments |
|---|---|---|---|---|
| 1-2 | B | – | 66 | mostly derivations |
| 3–5 | C | 1880 | 55 | mostly data on mercury |
| 6 | D | – | 182 | mostly on the method of Lippmann |
| 7 | E | 1882 | 108 | mostly the background of his paper [28] |
| 8–13 | F | 1883 | 117 | measured data, including critical point |
| 14–15 | G | 1882 | 26 | mostly on refractive index of liquids |
| 16–19 | H | – | 80 | measured data, including critical point |
| 20–23 | I | 1883 | 97 | soap solutions, soap bubbles + critical temperatures |
| 24–27 | J | 1885 | 91 | measurements by different methods |
| 28–31 | K | 1885 | 87 | theoretical derivations + data + plan for a dining room (?) |
| 32–36 | L | 1885 | 98 | meniscus + vapor pressure + electrocapillarity |
| 37–40 | M | 1883 | 117 | Eq-s.(1d-e), summary data + Hagen-paper-1845 |
| 41 | N | 1883 | 195 | capillary constants + refractive index |
| 51–52 | O | 1885 | 112 | tables of measured values for 89 liquids + water + Hg |
| 53–54 | P | 1893 | 71 | liquids in tubes, volume measured |
| 55–57 | Q | 1880 | 41 | capillary constants, refractive index, meniscus |
| Total 48 | 16 | – | 1543 | |

* The year of the manuscript is not always given and even if it is given, it is not always accurate.

Now, let me provide some selected data. Primary measured data in relation to Eq.(1a) are clearly visible for example in bundle 7, pp. 29–30 as: $\varphi_1 = 20^o\ 31.5'$ ($= 20.525^o$), $z_1 = 0.391$ mm, $\varphi_2 = 12^o\ 4'$ ($= 12.067^o$), $z_2 = 0.623$ mm. Substituting these values into Eq.(1a): $a = 2.24$ mm is obtained. Summary tables appear in different manuscript bundles. Some of them are summarized in Table A2 below. The following original symbols of Eötvös should be noted to compare manuscript pages with Table A2:

(i) $\mu$ is used for molecular weight (close to our molar mass, M in g/mol),
(ii) $s$ (from the Hungarian word "sűrűség") is used for density of the liquid (identical with $\rho$ in g/cm$^3$),
(iii) $\mu/s$ is used for molecular volume in agreement with Eq.(2a), but no special symbol is used by Eötvös in his manuscripts (close to our molar volume, $V_m$ in cm$^3$/mol),
(iv) $\sigma$ is used for density of the vapor (identical with $\rho_g$ in g/cm$^3$),
(v) $f$ (from the Hungarian word "feszültség") is used for surface tension (identical with $\sigma$ in mN/m, if multiplied by 10).

Table A2 lists the liquids studied, their measured temperatures, the measured square of their capillary constants, the measured densities of the liquids and the measured densities of the vapors (if their values is at least 0.001 g/cm$^3$, otherwise they are neglected). Eötvös used his eq. (1b) to calculate from here the surface tension of the liquid, also reported by him (see Table A2). However, Eötvös did not report the value of acceleration due to gravity ($g$) in none of his papers and in none of his manuscript pages on surface tension. Here, an attempt is made to recover the value of $g$ used by Eötvös, re-structuring his Eq.(1b):

$$g \cong \frac{2 \bullet \sigma}{(\rho - \rho_g) \bullet a^2} \tag{A1}$$

The values estimated by Eq.(A1) are collected in the last column of Table A2. One can see that in 15 cases out of total 17 cases $g = 9.99 \ldots 10.01$ m/s$^2$ is obtained, with two exceptions, being probably mis-calculations or mis-writings (remember: Eötvös calculated everything by hand - all those

actual calculations are visible in his manuscript pages). So, we can conclude that Eötvös used the simplified value of $g = 10.0$ m/s$^2$ in his calculations. The actual value was given by him 10 years later in one of his first papers devoted to gravity and magnetism: $g = 9.808$ m/s$^2$ [47] measured in Budapest, the same place he measured his capillary constants. Thus, his approximated value of $g = 10.0$ m/s$^2$ is higher by 2.0% from the actual value. This 2.0% inaccuracy has an influence on the actual value of the Eötvös-constant – see the main text.

One can speculate why Eötvös turned to study gravity after 1886. One of his motivations could be to find more precise surface tension values from his precise measurements of capillary constants and densities by Eq.(1b). We do not know if Eötvös ever published corrected surface tension results based on his measured values of $g$. But what we know that his studies on gravity lead him very soon to new horizons: he has become at least that famous in the field of gravity as he is famous in the field of capillarity.

Although there are many derivations of various equations found in the manuscripts, unfortunately no derivation of his most famous Eq.(2) could be detected by the present author in the studied 1543 pages.

**Table A2**
Some measured and calculated data by Eötvös and the value of acceleration of gravity calculated by Eq.(A1).

| Bundle | page | liquid<br>$M$, g/mol | $t$, °C | $a^2$, mm$^2$ | $\rho$, g/cm$^3$ | $\rho_g$, g/cm$^3$ | $\sigma$, mN/m | $g$, m/s$^2$ |
|---|---|---|---|---|---|---|---|---|
| 3–5 | 6 | Hg | 28 | 7.182 | 13.53 | – | 485.9 | 10.00 |
| | | 199.8 | 164 | 6.682 | 13.20 | – | 441.0 | 10.00 |
| | | | 300 | 6.135 | 12.88 | – | 395.1 | 10.00 |
| 7 | 108 | $CH_3COOH$ | 22 | 5.384 | 1.060 | – | 28.53 | 10.00 |
| | | 59.86 | 120 | 3.831 | 0.942 | – | 18.05 | 10.00 |
| 8–13 | 94 | $COCl_2$ | 3.7 | 3.75 | 1.424 | – | 23.8 | 8.91 (?) |
| | | 98.67 | 21 | 2.92 | 1.387 | – | 20.3 | 10.02 |
| | | | 63.7 | 2.22 | 1.295 | – | 14.4 | 10.02 |
| 24–27 | 53 | $C_2H_6O$ | 21 | 5.780 | 0.810 | – | 23.41 | 10.00 |
| | | 45.9 | 78.5 | 4.924 | 0.756 | 0.002 | 18.56 | 10.00 |
| | | | 108.3 | 4.355 | 0.724 | 0.004 | 15.67 | 9.99 |
| | | | 138 | 3.625 | 0.686 | 0.009 | 12.27 | 10.00 |
| | | | 168 | 2.762 | 0.634 | 0.021 | 8.47 | 10.01 |
| | | | 199 | 1.708 | 0.569 | 0.036 | 4.50 | 9.89 (?) |
| | | | 236.5 | 0 | – | – | 0 | – |
| 32–36 | 25 | $C_2H_6O$ | 20 | 5.731 | 0.810 | – | 23.21 | 10.00 |
| | | 45.9 | 99.2 | 4.490 | 0.734 | 0.003 | 16.41 | 10.00 |
| | | | 177 | 2.534 | 0.612 | 0.025 | 7.44 | 10.00 |

### *A.1. On-line references to the Appendix*

A. https://real-ms.mtak.hu/view/creators/E=F6tv=F6s=3ALor=E1nd=3A=3A.html
B. https://real-ms.mtak.hu/24180/1/Ms_5098_1-2.pdf
C. https://real-ms.mtak.hu/24181/1/Ms_5098_3-5.pdf
D. https://real-ms.mtak.hu/24182/1/Ms_5098_6.pdf
E. https://real-ms.mtak.hu/24183/1/Ms_5098_7.pdf
F. https://real-ms.mtak.hu/24184/1/Ms_5098_8-13.pdf
G. https://real-ms.mtak.hu/24185/1/Ms_5098_14-15.pdf
H. https://real-ms.mtak.hu/24186/1/Ms_5098_16-19.pdf
I. https://real-ms.mtak.hu/24187/1/Ms_5098_20-23.pdf
J. https://real-ms.mtak.hu/24188/1/Ms_5098_24-27.pdf
K. https://real-ms.mtak.hu/24189/1/Ms_5098_28-31.pdf
L. https://real-ms.mtak.hu/24190/1/Ms_5098_32-36.pdf
M. https://real-ms.mtak.hu/24191/1/Ms_5098_37-40.pdf
N. https://real-ms.mtak.hu/24192/1/Ms_5098_41.pdf
O. https://real-ms.mtak.hu/24177/1/Ms_5097_51_52.pdf
P. https://real-ms.mtak.hu/24178/1/Ms_5097_53_54.pdf
Q. https://real-ms.mtak.hu/24179/1/Ms_5097_55_57.pdf.

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