**Reflexiones**

# Does taper water boil at all temperatures?

## *¿Hierve el agua corriente a toda temperatura?*

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## Resumen

El equilibrio líquido-vapor para agua en presencia de aire involucra a una solución saturada en aire y vapor compuesto por agua y aire. El punto de ebullición es la temperatura a la cual la presión de vapor de un líquido iguala a la presión externa que actúa sobre el líquido. A cualquier temperatura entre los puntos de fusión y ebullición del agua pura, la presión de vapor de agua en equilibrio con aire (que es la suma de la presión de vapor del agua más la presión parcial de aire) obviamente es igual a la presión externa. Por lo tanto, en un sistema abierto, una solución líquida saturada agua-aire, para una dada presión externa, estará a la temperatura de ebullición a todas las temperaturas. No obstante, la experiencia cotidiana no parece sugerirlo. En este trabajo se discute diferentes aspectos de esta aparente paradoja con base en experimentación casera sencilla y la interpretación del comportamiento del sistema a partir de las teorías de la formación de burbujas.

**Palabras clave**

Ebullición, burbujeo, equilibrios de fase, disoluciones acuosas, sistemas abiertos, paradojas.

## Abstract

The liquid-vapor equilibrium for water in the presence of air involves a saturated liquid solution of air in water and a vapor phase composed of air and water vapor. The boiling point is the temperature at which the vapor pressure of a liquid system equals the external pressure acting on the liquid. At any temperature between the melting and boiling points of pure water, the vapor pressure of water in equilibrium with air (vapor pressure of water plus partial pressure of air) is obviously equal to the external pressure. Therefore, in an open system, such liquid solution would be at the boiling point for all temperatures at the same atmospheric pressure. However, our everyday experience does not seem to suggest it. Throughout this paper, different aspects of that apparent paradox are discussed based on simple home-made experimentation and the interpretation of system behaviour from bubbles formation theories.

**Keywords**

Boiling, bubbling, phase equilibria, open systems, aqueous dissolutions, paradoxes.

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# Introduction

As it is widely known, when a liquid is heated in an open vessel, it vaporizes exclusively from the free liquid surface until the saturation of the surrounding gas with the evaporating substance. In such a case, when the vapor pressure of a liquid equals the external pressure, there is a condition of free vaporization throughout the liquid. The temperature at which such a condition is reached by a pure substance is called the boiling temperature and is unique for each external pressure. When the external pressure is 1 atm (101.325 kPa) the boiling point is called normal (Silberberg and Amateis, 2018, p. 481; Atkins and de Paula, 2010, p. 138). Thus, the normal boiling point for pure liquid water is 100 °C (373.16 K).

The last statement is in agreement with our common experience in which water only boils when the temperature reaches about 100 °C, if the external pressure is 1 atm or very close to it. However, the water we use every day is not a pure substance. Tap water has dissolved salts (nonvolatile solute) that cause an increase in the boiling point (Silberberg and Amateis, 2018, p. 559), although such effect, which only causes a boiling point bias, may not be easily perceived. On the other hand, common water, but even distilled one, in equilibrium with the surrounding air, becomes a solution since it has dissolved air (volatile solute). This kind of solutions do not have a single boiling point at a given pressure, but the temperature at which it boils is fixed by the composition. Thus, even without changing the pressure, a solution has multiple boiling points and not just one as a pure substance (Atkins and de Paula, 2010, p. 179).

Water in an open vessel at equilibrium is actually a saturated air-in-water solution. Water dissolves air in a quantity given by Henry's law (Silberberg and Amateis, 2018, p. 551), i.e., $x_{air}^L = k_H \, p_{air}$, where $x_{air}^L$ is the mole fraction of dissolved air for a saturated solution, $p_{air}$ is the air partial pressure, and $k_H$ is the Henry's constant for air, which is lower at higher temperatures. At all temperatures in the range 0 °C-100 °C, the total pressure (= external pressure, $P_{ext}$) in the proximities of the liquid free surface is the sum of $p_{air}$ and $p_w$, the vapor pressure of water. This sum is the dissolution vapor pressure, $p_v$. Therefore, *at all* temperatures $p_v = P_{ext}$, which fits with the boiling condition, i.e., the liquid solution of water-air in an open vessel at constant pressure is at its boiling point (and it should boil!) at any temperature. This behavior seems to be similar to that of other liquid solutions of soluble gases such as seltzer and soda water (Goodwin, 2001).

## Relevant aspects of the air-water system

A deeper analysis of the water-air system is presented below. Considering water-air in an open vessel as a two-component system (air as an individual component), a P-T diagram would be a projection of P-T-$x^L$ diagram ($x^L$ is the mole fraction of one component at liquid phase). These diagrams are correctly represented (Andrade-Gamboa, Mártire, and Donati, 2010) by replacing P (= $P_{ext}$) by $p_v$ (there is a particular diagram for each $P_{ext}$): Figure 1 shows a $p_v$-T-$x^L$ diagram (for $P_{ext}$ = 1 atm), in the region from pure water ($x_{air}^L = 0$) up to a dissolution with the maximum mole fraction of air ($x_1^L$) corresponding to its solubility, at 0 °C.

**Figure 1.** $p_v$-T-$x_{air}^L$ diagram (curve b-c is in the plane at P = 1 atm)
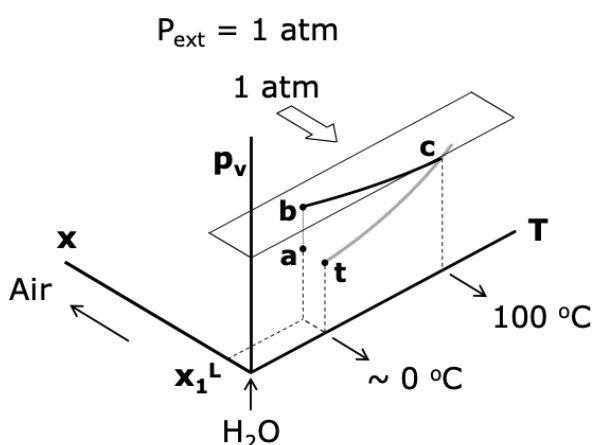
In figure 1, the gray line is the liquid-vapor curve for pure water, from triple point, t (~0 °C), up to 100 °C. For a dissolution with $x_1^L$ composition, the pressure of the system (point b) (neglecting the effect of external pressure on vapor pressure) is $p_w$ at 0 °C (point a)[1], which added to the partial pressure of air is equal to 1 atm - $p_w$. This same condition ($p_v$ = 1 atm) is fulfilled for all temperatures, as represented by black curve b-c. A projection of curve b-c on $x_{air}^L$-T plane gives the solubility of air in water as a function of temperature.

A projection onto plane $p_v$-T of the diagram of figure 1 is shown in figure 2. Such diagram allows concluding–in a redundant but more dramatic way–that for all temperatures (from point b to point c) total vapor pressure equals external pressure. As was suggested above, from 0 °C to 100 °C, saturated solutions of air in water in an open vessel are *under boiling condition*. In order to describe the system behavior, it is very useful to construct the projection of figure 1 on the T-x plane. Table 1 shows the values $x_w^{V,L}$ vs. T ($x_w$: water mole fraction; V: vapor, L: liquid), and Figure 3 is the corresponding qualitative representation.



**Figure 2.** Projection of figure 1 on the $p_v$-T plane
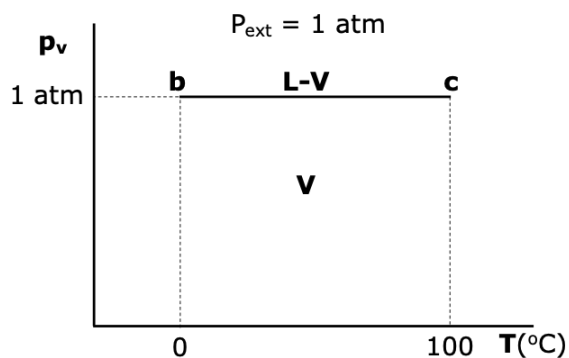
In figure 3, the black line, as mentioned, represents the solubility of air in water as a function of temperature (curve bc in figure 1), and corresponds to the liquidus line (the boiling point curve), and the gray curve gives the vapor composition (vaporus line).

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[1] The temperature of triple point t is 0.0098 °C (273.1598 K) and the temperature of point a is 0 °C (273.1500 K), so-called ice point (Andrade-Gamboa, Mártire, and Donati, 2010).

**Table 1.** Vapor (V) and liquid (L) composition for dissolutions of air in water at different temperatures ($x_w$: water mole fraction).

For calculations see Appendix 1

| T (°C) | $x_w^V$ | $x_w^L$ | T (°C) | $x_w^V$ | $x_w^L$ |
|---|---|---|---|---|---|
| 0 | 0.006021 | 0.999977 | 55 | 0.155448 | 0.999991 |
| 5 | 0.008587 | 0.999979 | 60 | 0.196704 | 0.999992 |
| 10 | 0.012140 | 0.999982 | 65 | 0.246940 | 0.999992 |
| 15 | 0.016877 | 0.999984 | 70 | 0.307738 | 0.999993 |
| 20 | 0.023095 | 0.999985 | 75 | 0.380576 | 0.999994 |
| 25 | 0.031287 | 0.999986 | 80 | 0.467529 | 0.999995 |
| 30 | 0.041946 | 0.999987 | 85 | 0.570667 | 0.999996 |
| 35 | 0.055567 | 0.999988 | 90 | 0.692065 | 0.999997 |
| 40 | 0.072839 | 0.999989 | 95 | 0.834287 | 0.999998 |
| 45 | 0.094651 | 0.999990 | 100 | 1 | 1 |
| 50 | 0.121792 | 0.999990 | | | |

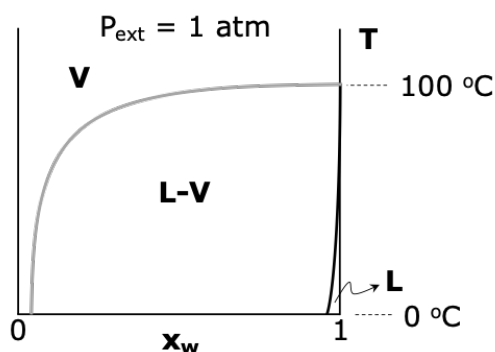**Figure 3.** Projection of figure 1 on T-$x_w$ plane (not at scale).



Table 1 and figure 1 show that vapor in equilibrium with a saturated solution of air in water is mainly composed of air at temperatures below 50 °C, decreasing up to 50% at 80 °C. Then, the air content rapidly decreases with increasing temperature until 100 °C when vapor is pure water.

## Is there boiling at the boiling point?

The arguments developed above may have convinced the reader that saturated air-in-water solutions, in an open container, are at the boiling temperature if the fixed external pressure is maintained. However, from our everyday experience, can we say that water boils at all temperatures?

Before starting a discussion about that point (the central one for this paper), we must resolve a semantic and conceptual question in a more general sense. What is the meaning of boiling and boiling temperature? Neither term is defined by IUPAC (2019), and their widespread use is not without ambiguity, since boiling is considered as either a process or a condition. Some expressions that exemplify each criterion are: "*A liquid boils when it forms bubbles against the atmospheric pressure*" (Silberberg and Amateis, 2018, p. 410) "*When the vapour pressure is equal to the external pressure, vaporization can occur throughout the bulk of the liquid and the vapour can expand freely into the surroundings. The*

*condition of free vaporization throughout the liquid is called boiling*" (Atkins and de Paula, 2010, p. 138)*.* For the first definition, a liquid at the boiling temperature can form bubbles, and for the second definition it must form bubbles (boiling is equal to bubbling, discarding bubbles formed by external causes). The title of this section could be changed to: Is there bubbling at the boiling point? The best answer should be: there may or may not be. Then, air-saturated water, in an open system at constant pressure, is at boiling temperature at all temperatures, and at those temperatures it can boil.

## The boiling process for a pure liquid

It can be curious and even contradictory that a liquid at its boiling temperature may not boil or cannot boil. Considering the boiling point as the temperature at which the vapor pressure of a liquid equals the external pressure surrounding the liquid is very accurate, and its thermodynamic nature does not give rise to doubts. Is this requirement sufficient to guarantee the boiling of the liquid? Or even more, should the boiling happen at one fixed temperature?

Some boiling temperature definitions try to make the thermodynamic vision and the occurrence of the boiling process compatible. They define boiling point as the temperature at which the vapor pressure inside bubbles in the liquid equals the external pressure (Silberberg and Amateis, 2018, p. 481) or the external pressure plus hydrostatic pressure of the liquid (Chang, 2010, p. 493). However, the equality of pressures requires thermodynamic equilibrium, while the bubbles are not usually in thermal equilibrium with the surrounding liquid. A bubble may exist if the difference in pressure inside and outside it is enough to generate and keep its place inside the liquid. The vapor phase is confined inside the bubble due to the surface tension at the liquid-gas interface because of the net attraction force on molecules towards the liquid. Even ignoring the pressure due to the depth of a bubble below the free surface of the liquid, the pressure inside (vapor pressure) must be higher than the pressure outside (external pressure that is the atmospheric pressure in an open vessel).

That is why the *boiling process* (associated with the existence of bubbles rising to the top) does not occur (or, at least, it does not necessarily take place) under the conditions the thermodynamic definition implies. A proof of that can be obtained through a simple experiment, as is indicated in figure 4.
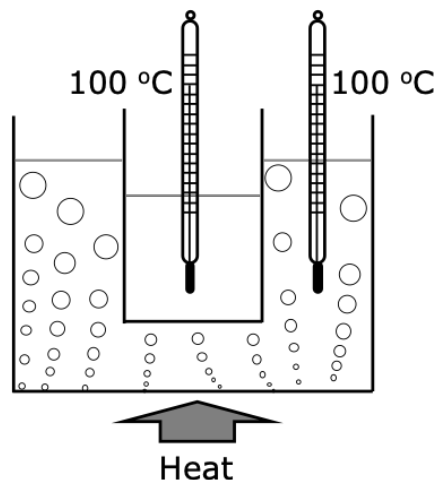


**Figure 4.** Internal vessel and external container filled with water. After enough heating and even when the temperature in both thermometers reaches the same value (boiling temperature), bubbles are only detected in the external container.

The internal vessel and the external container are filled with water, and the latter is heated to its "boiling point" (if the external pressure is 1 atm, it means 100 °C) characterized by the presence of bubbles; however, no bubbles are detected inside the internal vessel although its temperature also reaches 100 °C. Strictly speaking, it is very likely that the temperature in the external vessel is not exactly 100 °C even if the external pressure is 1 atm. There are many circumstances that may justify its variation, and here we will avoid entering into a detailed discussion, which was already raised from a historical and epistemic point of view (Chang, 2004). In any case, such experiment, among others, seems to be enough to show that even pure water (accepting that close to 100 °C, dissolved air is not present) at the boiling point is not necessarily boiling, i.e., matching pressures are necessary but not sufficient for the occurrence of boiling.

Actually, to reach the sufficient condition of boiling, a nonequilibrium condition must be imposed (Levine, 2009, p. 222). To obtain sufficient vapor pressure to form a bubble, superheating is necessary. But even uniform superheating could not cause such process; for example, very pure water can be uniformly heated as in a microwave oven (Erné and Snetsinger, 2000) even up to 300 °C (Hewitt, 1998), remaining in a metastable state of superheating without boiling.

Superheating needed for bubble formation (Çengel and Ghajar, 2015; Collier and Thome, 1994) can be easily reached when a liquid is heated over a hot plate. In this case, the temperature of the liquid close to the hot place reaches higher values than in the rest of the liquid (as for the water near the base of the external container and not for the water in the internal container, as is schematized in figure 4). In this condition, the vapor pressure is higher enough, and bubbles can be formed at the bottom of the vessel, close to the hot surface. Although bubbles can exist in such a way, it does not guarantee they can rise to the top, i.e., it is not enough for boiling. Bubbles hotter than the liquid collapse since heat would flow into the liquid causing partial vapor condensation. When the temperature of the liquid is below the thermodynamic boiling temperature (at the given external pressure) any bubble rising to the top immediately disappears; under this condition bubbles are restricted to a zone close to the hot surface, and the process is called subcooled boiling (Çengel and Ghajar, 2015).

To not collapse the bubble must be at an equal or even lower temperature than the surrounding liquid, and that occurs when the bulk liquid has achieved the maximum temperature possible at the external pressure. Heat is transferred to cooler bubbles, which allows them to grow and, due to the buoyancy forces, rise to the top. In this way, a massive and continuous escape of bubbles to the surface is produced, which is identified as the boiling process.

Although the conditions for continuous bubbling exist, a nucleation process is also needed for bubble formation (otherwise, a metastable superheated situation is achieved) and decides its kinetics. Homogeneous nucleation involves vapor formation from bulk liquid helped by a perturbation such a density fluctuation. In contrast, heterogeneous nucleation is promoted by imperfections of a surface, such as the walls of the vessel (which also explains how boiling stones or chips work). This kind of nucleation is much more probable under regular conditions because it requires lower superheating than that needed for homogeneous nucleation.

## The boiling process for an air-saturated water

As for pure substances, for solutions reaching boiling much more than the boiling equilibrium condition is needed. According to our proposal and from an equilibrium point of view, air-saturated water in an open vessel at constant external pressure is at its boiling point at any temperature from the freezing point to the boiling temperature of pure water. But daily observation does not seem to show a boiling process occurring at that temperature range, except at the temperature of 100 °C, if the external pressure is 1 atm. For this, the liquid solution should be exposed to superheating (at least only few degrees above the liquid temperature) and in such way bubbles should appear, and the boiling process would occur.

At temperatures below 80 °C, bubbles mainly contain air (Table 1) but in a very small amount in the solution; thus, even under superheating conditions, the nucleation of bubbles and their growth are seriously limited by air diffusion from the bulk liquid to the depleted region. This is why the process could be very slow and probably it could not be noticeable at very low temperatures. A glass with cold tap water allowed to stand at warmer room temperature fits with that description. In that daily situation and after 2 or 3 h, several bubbles about 1 mm in diameter attached to the walls can be observed. This is commonly interpreted as a different phenomenon in which "pure" air bubbles formed from dissolved air, although it is totally compatible with the vision presented here: the solution is boiling and the bubbles are mainly composed of air. Moreover, the explanation proposed in this work avoids the usual misconception in students who consider dissolved air as air even in a gaseous state (very small, then unobservable, bubbles).

Surely the inefficient heat transfer from the external air to the glass, the cooler surrounding liquid, among other reasons, can explain that in such home experiment, the bubbles are on the walls of the glass and rarely detach and rise to the surface as in the case of subcooled boiling. The situation can be clearly enhanced leaving the glass with cold tap over a metal surface heated just few degrees above the liquid temperature.

At temperatures higher than 80 °C, bubbles essentially contain water (which is the major component) and the processes of bubble formation and growth (now controlled by heat transfer) become faster. The rate of bubble growth in water at 100 °C is about three orders of magnitude greater than those of an air-water system at room temperature (see Appendix 2), which fits within the order of the time needed (about an hour) to achieve the formation of bubbles in the daily observation of the glass of cold tap water. Due to these reasons, bubbles are rarely observed in air-saturated water at low temperatures (except in situations similar to that described above and after some hours), which fits with the idea of a boiling point equal (or close) to the boiling point of pure water. However, giving the adequate conditions, air-saturated water in an open vessel can boil at any temperature from the freezing point to the boiling temperature of pure water at the external pressure.

## Conclusion

Since the total vapor pressure of air-saturated water in an open vessel is always equal to the external pressure, that system is at the boiling point at any temperature. Similarly, to what happens for pure substances, to achieve boiling (i.e., the process characterized by the formation of vapor bubbles that migrate into the vapor phase), the solution must be superheated just few degrees above that of the rest of the liquid. However, the formation

of bubbles (and consequently, the boiling process) that contain almost only air at low temperatures is much slower than for bubbles that contain almost exclusively water, as occurs at temperatures near the boiling point of pure water.

The introduction and discussion of the main arguments developed in this work, and the performance of extremely simple experiments could be an excellent way to discuss concepts related to the changes in the state of solutions (especially of gases in liquids) and to avoid some common misconceptions about these issues.

## Appendix 1

Solubility of gases in water can be expressed as (Lide, 2004-2005, p. 8-86)

$$\ln x(i)^L = A + B/T^* + C \ln T^* \qquad (A1.1)$$

where $x(i)^L$ is the mole fraction of dissolved gas i, at a given temperature T expressed in K, and $T^*$ is T/100 K. The Table A1.1 gives values for constants A, B and C of equation A1.1, for oxygen ($O_2$) and nitrogen ($N_2$), corresponding to 1 atm = 101.325 kPa of gas partial pressure (Lide, 2004-2005, p. 8-86).

**Table A1.1.** Constants values for equation A.1.1.

| Gas | A | B | C | Standard deviation | Temperature range (K) |
|-----|-----|-----|-----|-----|-----|
| $O_2$ | -66.7354 | 87.4755 | 24.4526 | ±0.36% | 273.15-348.15 |
| $N_2$ | -67.3877 | 86.3213 | 24.7891 | ±0.72% | 273.15-348.15 |

From equation A1.1, Henry´s constant $k_H$ can be expressed as

$$k_H(i) = \exp[\ln x(i)^L] \qquad (A1.2)$$

Then, the dissolved mole fraction at a given partial pressure p(i) is

$$x(i)^L = k_H(i)p(i) \qquad (A1.3)$$

For dry air (21% v/v $O_2$-79% v/v $N_2$) partial pressures of each gas relate to air pressure, p(air), as $p(O_2) = 0.21p(air)$; $p(N_2) = 0.79p(air)$. Because for a given water vapor pressure, $p_w$, $p(air) = P_{ext} - p_w$, the dissolved mole fraction of air is given by

$$x(air)^L = x(O_2)^L + x(N_2)^L = \qquad (A1.4)$$
$$= [0.21 \, k_H(O_2) + 0.79 \, k_H(N_2)] \, (P_{ext} - p_w)$$

Then, the mole fraction of water in liquid phase is

$$x_w^{\,L} = 1 - x(air)^L \qquad (A1.5)$$

and the mole fraction of water in vapor phase is

$$x_w^{\,V} = (p_w/P_{ext}) \qquad (A1.6)$$

Equations A1.5 and A1.6 were used for table 1, using tabulated values of vapor pressure of water as a function of temperature (Lide, 2004-2005, p. 6-8).

## Appendix 2

For a pure liquid in a beaker heated over a hot plate, it is easily observed that boiling starts at the bottom, the place at which it is at greater temperature. The liquid layer nearest to the heating plate is superheated and generates bubbles due to the heterogeneous nucleation and further growth and detachment at the beaker bottom (the model is called pool boiling). Then, boiling continues from these nucleation sites. The mechanism is complex and as the temperature of the superheated layer rises, different regimes of formation and release of bubbles are observed.

The models of bubble growth for pool boiling take into account a heat transfer control that allows vaporization in the liquid-vapor interface in each bubble. The rate, $r_1$, of bubble growth at time t is given by (Van Stralen, 1979)

$$r_1 = (dD/dt) = K_1 \, \Delta T \, t^{-1/2} \qquad\qquad (A2.1)$$

where D is the bubble diameter, $K_1 = 8(3/\pi)^{1/2} (\rho_L/\rho_V) (c/\lambda) \alpha^{1/2}$, and $\rho_L$ is the liquid density, $\rho_V$ is the vapor density, $\alpha$ is the liquid specific heat at constant pressure, $\lambda$ is the enthalpy of vaporization, a is the liquid thermal diffusivity, and $\Delta T$ is the superheating of liquid at temperature T.

The rate of growth of air bubbles in water in supersaturated condition is given by (Manley, 1960; Epstein and Plesset, 1950)

$$r_2 = (dD/dt) = K_2 \, t^{-1/2} \qquad\qquad (A2.2)$$

where $K_2 = [8 \, k(C_i - C_s)/\rho_V]^{1/2}$, and k is the diffusion coefficient of air in water, $C_i$ is, for a given temperature and pressure, the air concentration in water, and $C_s$ is the concentration for saturation condition. The concentration difference can be expressed as $C_i - C_s = \rho_L(\partial x/\partial T) \Delta T \, M_{air}/M_w$, x being the molar fraction of air in liquid phase, $M_{air}$ and $M_w$ are the molar mass of air and water respectively. Then, $K_2 = [8k\rho_L(\partial x/\partial T) \Delta T \, M_{air}/(M_w \, \rho_V)]^{1/2}$.

The quantity $(\partial x/\partial T)$ corresponds to the reciprocal of the slope of liquidus curve (figure 3) and from 20 °C (see table 1) it is practically a constant that can be calculated as $2 \times 10^{-7} \, K^{-1}$.

All values of the constants needed for pure water and air-water system are presented in table A.2, and allow obtaining the following expressions for $r_1$ and $r_2$

**Table A2.1.** Values for constants in equations A2.1 and A2.2 for t in s, r in cm/s and T in K.

\* Lide (2004-2005, p. 6-3
\*\* Calculated as ideal gas
\*\*\* (Manley, 1960)

|  | Pure water (100 °C) | Air-water (20 °C) |
|---|---|---|
| $\alpha[cm^2/s]$* | $1.7 \times 10^{-4}$ | -- |
| $\rho_L[g/L]$ * | 958 | 998 |
| $\rho_V[g/L]$** | 0.589 | 1.207 |
| c [J/g/K]* | 4.216 | -- |
| $\lambda[J/g]$* | 2460 | -- |
| $k[cm^2/s]$ | -- | $2 \times 10^{-5}$ *** |
| $M_w[g/mol]$ | -- | 18 |
| $M_{air}[g/mol]$ | -- | 29 |

$$r_1[cm/s] = (dD/dt) = 0.28\ \Delta T\ t^{-1/2} \qquad\qquad (A2.3)$$

$$r_2[cm/s] = (dD/dt) = 2 \times 10^{-4}\ (\Delta T)^{1/2}\ t^{-1/2} \qquad\qquad (A2.4)$$

For the same superheating of 5 K (5 °C) in both systems, and for a given time, $(r_1/r_2) = 3130$. The rate of bubble growth in water at 100 °C is about three orders of magnitude greater than those of an air-water system at room temperature.

In particular, integrating equation 4 (assuming $t = 0$, $D = 0$), the following expression is obtained

$$D(t)[cm] = 4 \times 10^{-4}\ (\Delta T)^{1/2}\ t^{1/2} \qquad\qquad (A2.5)$$

from which it can be estimated that for tap water at 15 °C, left in a room at 20 °C ($\Delta T = 5$ °C), the time for bubble growth up to 0.05 cm (0.5 mm) will be $t = 3125$ s $= 52$ min.

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