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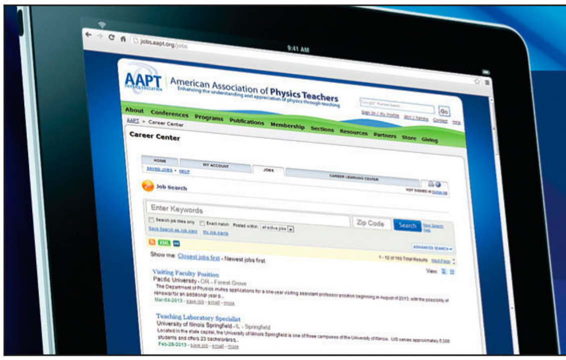

On the experimental values of the water surface tension used in some textbooks

J. Pellicer,[a] V. García-Morales, L. Guanter, M. J. Hernández, and M. Dolz
Departament de Termodinàmica, Universitat de València, E-46100 Burjassot, Spain

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A thermodynamic study of one component liquid–vapor planar interfaces and the temperature dependence of some relevant thermodynamic quantities is presented. A critical review of data for the surface tension of water found in some textbooks is given. More accurate measurements show a qualitative change in the temperature dependence of the surface tension, from the almost linear dependence of the old data to nonlinear behavior and the occurrence of an inflection point in the more accurate, more recent data.
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I. INTRODUCTION

Surface phenomena are relevant not only to physics but also to disciplines such as physical chemistry, the life and health sciences, as well as chemical engineering. The study of these phenomena has found an established place in elementary treatments of these disciplines, but not in our current introductory and intermediate physics courses. Most textbooks either present only a brief account of surface phenomena or ignore it completely. Some undergraduate physics textbooks suffer from a lack of up-to-date experimental data. Because the conclusions obtained from the older data are not correct, its use by authors can lead to conceptual errors. In this work, we discuss the thermodynamics of one-component liquid–vapor planar interfaces and the temperature dependence of some relevant thermodynamic quantities.

II. SOME SURFACE THERMODYNAMIC FUNCTIONS

Consider a closed, one-component system composed of two phases (the bulk phases), liquid and vapor, separated by a planar interface in thermodynamic equilibrium. Temperature and pressure are equal in the two phases. It has long been recognized that to produce an infinitesimal increase in the surface area Σ of the interface, while keeping the temperature T and the volume V of the entire system constant, an infinitesimal amount of reversible work,[1]

$$\delta W^{\sigma} = -\gamma d\Sigma, \tag{1}$$

is required. In Eq. (1) γ is the surface tension, which is always positive and depends only on temperature. The notation δW in Eq. (1) indicates that the work is not a total differential, and the superscript σ denotes magnitudes related to the interface.

We characterize this system by the temperature T, which is uniform throughout, the volume V of the entire system and the interfacial area, and consequently use the Helmholtz free energy F as the thermodynamic state function.[2] From the definition $F \equiv U - TS$, it follows that $dF = dU - TdS - SdT$, where U is the internal energy and S is the entropy. The first and second law of thermodynamics leads to

$$dU = TdS - PdV + \gamma d\Sigma, \tag{2}$$

and hence

$$dF = -SdT - PdV + \gamma d\Sigma, \tag{3}$$

and therefore

$$\gamma = \left(\frac{\partial F}{\partial \Sigma}\right)_{T,V}, \tag{4}$$

where P is the system pressure.

The integration of Eq. (3) gives the total free energy $F(T,V,\Sigma)$ as the sum of the interfacial contribution, $F^{\sigma}(T,\Sigma)$, and the bulk phases contribution, $F^{b}(T,V)$,

$$F(T,V,\Sigma) = F^{\sigma}(T,\Sigma) + F^{b}(T,V), \tag{5}$$

where

$$F^{\sigma}(T,\Sigma) = \gamma(T)\Sigma. \tag{6}$$

Because T and V are held constant, the contribution $F^{b}(T,V)$ is also constant.

Equation (6) now allows one to interpret γ as the interfacial specific free energy, that is,

$$\frac{F^{\sigma}(T,\Sigma)}{\Sigma} = \gamma(T). \tag{7}$$

Accurate values of the surface tension for water over the temperature range extending from the melting point to the critical point are given in Table I according to Lyklema[4] and Agrawal[10] and plotted in Fig. 1.

The Gibbs function of the system is

$$\begin{aligned} G(T,V,\Sigma) &= F(T,V,\Sigma) + PV \\ &= F^{\sigma}(T,\Sigma) + PV^{\sigma} + F^{b}(T,V) + PV^{b} \\ &= G^{\sigma}(T,\Sigma) + G^{b}(T,V), \end{aligned} \tag{8}$$

where $V = V^{\sigma} + V^{b}$, and

$$G^{\sigma}(T,\Sigma) \equiv F^{\sigma}(T,\Sigma) + PV^{\sigma}, \tag{9a}$$

$$G^{b}(T,V) \equiv F^{b}(T,V) + PV^{b}. \tag{9b}$$

Undergraduate students usually regard G as a function of T, P, Σ. In Eqs. (8) and (9) T, V, and Σ have been used as the independent variables for convenience.

If we now introduce the concept of the Gibbs dividing surface,[3] the surface region can be considered as a geometrical surface of zero volume, $V^{\sigma} = 0$, and Eq. (9a) reduces to

$$G^{\sigma}(T,\Sigma) = F^{\sigma}(T,\Sigma) = \gamma(T)\Sigma. \tag{10}$$

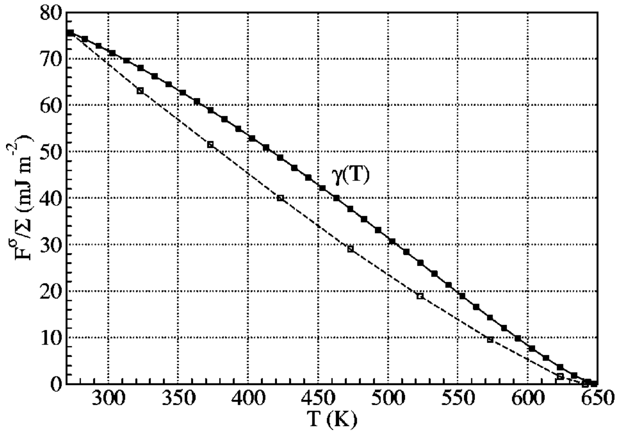

Fig. 1. The temperature dependence of the specific surface free energy of water. The solid curve represents the values calculated from recent accurate measurements—Refs. 4 and 10 (see Table I). The dashed curve is calculated from the older, erroneous values—Refs. 5 and 6 (see Table II).

Table I. Accurate values from Ref. 10 of the surface tension γ for water as a function of the temperature T. The temperature is in degrees Celsius and γ is in 10^{-3} J m^{-2}.

T	γ	T	γ	T	γ
0.01	75.64	130	52.93	260	23.67
10	74.23	140	50.85	270	21.30
20	72.75	150	48.74	280	18.94
30	71.20	160	46.58	290	16.61
40	69.60	170	44.40	300	14.30
50	67.94	180	42.19	310	12.04
60	66.24	190	39.95	320	9.81
70	64.47	200	37.69	330	7.66
80	62.67	210	35.41	340	5.59
90	60.82	220	33.10	350	3.65
100	58.91	230	30.77	360	1.90
110	56.96	240	28.42	370	0.45
120	54.96	250	26.06	380	0

Because the entropy of the system is $S(T,V,\Sigma)$, for a process conducted at constant T and V, we have

$$dS=\left(\frac{\partial S}{\partial \Sigma}\right)_{T,V} d\Sigma. \tag{11}$$

By using Eq. (3), we may deduce the Maxwell relation

$$\left(\frac{\partial S}{\partial \Sigma}\right)_{T,V} = -\frac{d\gamma}{dT}, \tag{12}$$

and hence

$$dS=-\frac{d\gamma}{dT}d\Sigma, \tag{13}$$

which after integration gives

$$S(T,V,\Sigma)=S^{\sigma}(T,\Sigma)+S^{b}(T,V), \tag{14}$$

where $S^{\sigma}(T,\Sigma)$ and $S^{b}(T,V)$ are the interfacial and bulk systems contributions to the entropy. Therefore,

$$\frac{S^{\sigma}(T,\Sigma)}{\Sigma}=-\frac{d\gamma}{dT}. \tag{15}$$

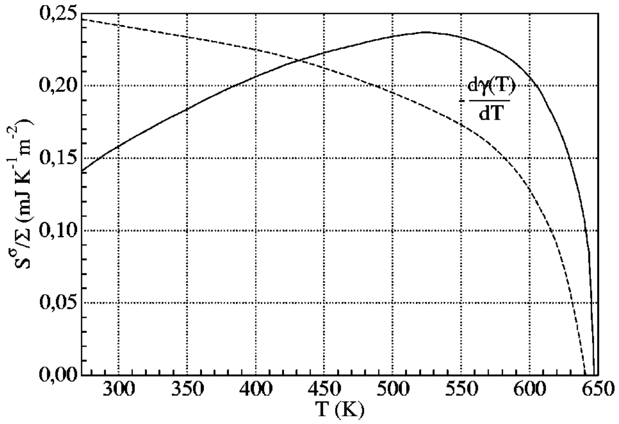

Fig. 2. The temperature dependence of the specific surface entropy of water. The solid curve represents the values obtained from Eq. (15) using recent accurate measurements—Refs. 4 and 10 (see Table I). The dashed curve is calculated from Eq. (15) for the older, erroneous values—Refs. 5 and 6 (see Table II).

The function $S^{\sigma}(T,\Sigma)/\Sigma$ for water has been plotted in Fig. 2 as a function of the temperature T as deduced from the recent more accurate measurements[4,10] (see Table I). The dashed curve is calculated from Eq. (15) from the older, erroneous values[5,6] (see Table II).

It is now easy to deduce the surface energy $U^{\sigma}(T,\Sigma)$ from Eq. (2). If we differentiate Eq. (2), with T and V constant, we obtain

$$\left(\frac{\partial U}{\partial \Sigma}\right)_{T,V} = T\left(\frac{\partial S}{\partial \Sigma}\right)_{T,V} + \gamma(T), \tag{16}$$

and using Eq. (12), we have

$$\left(\frac{\partial U}{\partial \Sigma}\right)_{T,V} = \gamma(T) - T\frac{d\gamma}{dT}. \tag{17}$$

By integrating Eq. (17), we obtain

$$U(T,V,\Sigma)=U^{\sigma}(T,\Sigma)+U^{b}(T,V), \tag{18}$$

where

$$\frac{U^{\sigma}(T,\Sigma)}{\Sigma}=\gamma(T)-T\frac{d\gamma}{dT}. \tag{19}$$

The left-hand side of Eq. (19) is interpreted as the energy per unit area of the interface and states that the creation of an interface requires an energy given by Eq. (19). Therefore, the

Table II. Obsolete values of γ and U^{σ}/Σ from Refs. 5 and 6. The temperature is in degrees Kelvin and γ and U^{σ}/Σ is in 10^{-3} J m^{-2}.

T	γ	U^{σ}/Σ
273	75.5	143
323	63.1	141
373	51.5	138
423	40.0	134
473	29.0	129
523	18.9	122
573	9.6	111
623	1.6	80
641	0	0

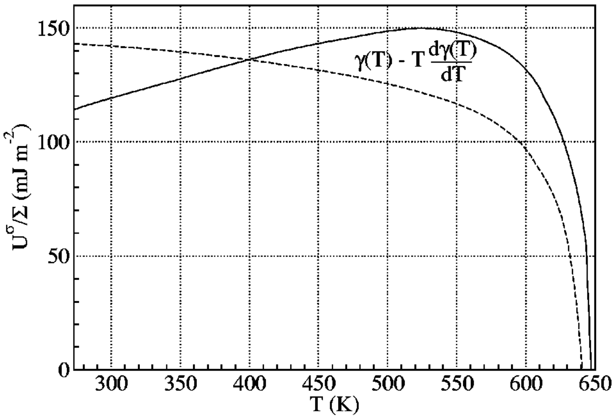

Fig. 3. The temperature dependence of the specific surface energy of water. The solid curve represents the values obtained from Eq. (19) using recent accurate measurements—Refs. 4 and 10 (see Table I). The dashed curve is calculated from the older, erroneous values—Refs. 5 and 6 (see Table II).

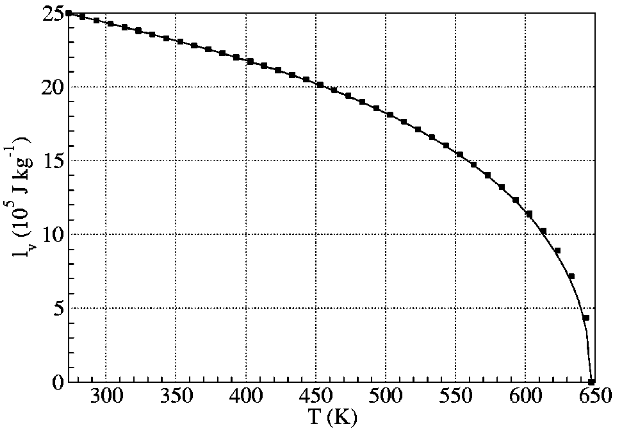

Fig. 4. The temperature dependence of the heat of vaporization of water (calculated from values given in Ref. 10).

surface energy per unit area of an interface can be calculated once the surface tension as a function of temperature is known. The quantity $U^\sigma(T,\Sigma)/\Sigma$ has been plotted in Fig. 3 as a function of the temperature T of the liquid–vapor water interface for both sets of data.

Finally, consider the surface enthalpy

$$\begin{aligned} H(T,V,\Sigma) &= U(T,V,\Sigma) + PV \\ &= U^\sigma(T,\Sigma) + PV^\sigma + U^b(T,V) + PV^b, \end{aligned} \tag{20}$$

where Eq. (18) and $V = V^\sigma + V^b$ have been used. If we define the quantities

$$H^\sigma(T,\Sigma) \equiv U^\sigma(T,\Sigma) + PV^\sigma, \tag{21a}$$

$$H^b(T,V) \equiv U^b(T,V) + PV^b, \tag{21b}$$

the system enthalpy can be written as

$$H(T,V,\Sigma) = H^\sigma(T,\Sigma) + H^b(T,V). \tag{22}$$

If we consider that the Gibbs dividing surface lacks volume $(V^\sigma = 0)$, and use Eq. (19), we find that Eq. (21a) reduces to

$$H^\sigma(T,\Sigma) = U^\sigma(T,\Sigma) = \left(\gamma(T) - T\frac{d\gamma}{dT}\right)\Sigma. \tag{23}$$

As a final remark, we point out that Eqs. (7), (15), and (19) allow us to derive the following expression:

$$\gamma(T) = \frac{U^\sigma}{\Sigma} - \frac{S^\sigma}{\Sigma}T. \tag{24}$$

If $\gamma(T)$ is linear, Eq. (24) implies that the slope is the specific surface entropy. However if $\gamma(T)$ is nonlinear, the division of γ into an energetic and entropic part becomes less obvious.[4]

III. COMPARISON OF THE EMPIRICAL VALUES OF THE SURFACE TENSION OF WATER

In Refs. 5 and 6, older, less accurate experimental values of the water surface tension and the specific surface energy of liquid–vapor water interface are given. The latter values have been calculated from Eq. (19) for various values of temperature (see Table II). In Fig. 1 we plot $F^\sigma(T,\Sigma)/\Sigma$ as a function of the temperature for the older values and for the more accurate recent ones (calculated from Table I). The curve defined by the old values is shown in many textbooks,[5–9] and suggests that the surface tension is a monotonously decreasing function of temperature, similar to most pure liquids.[3] However, the more recent experimental values of the surface tension given by Lyklema[4] and Agrawal[10] clearly differ from the older values. The accurate measurements over a wide range of temperature show that the derivative $d\gamma/dT$ is not constant (see Fig. 2), but decreases to zero at the critical point. Moreover, $d^2\gamma/dT^2$ also changes sign, which means that there must be an inflection point in the γ vs T curve. More recent measurements of γ[4] do not modify the shape of $\gamma(T)$ in Fig. 1.

The presence of a maximum around $T = 523$ K in the specific surface entropies and energies makes the existence of an inflection point in the curve based on the more accurate data of Fig. 1 evident; note that $dS^\sigma/dT = (1/T)dU^\sigma/dT = 0$ leads to $d^2\gamma/dT^2 = 0$. Therefore, the maxima in Figs. 2 and 3 deduced from the more accurate measurements correspond to the inflection point of the $\gamma(T)$ curve. As a result, there is a qualitative difference between the older and newer curves, as can be seen by comparing the older and newer curves in each plot.

The differences due to the use of the obsolete data may sometimes lead to incorrect conclusions in the analysis of different thermodynamic problems. An example can be found in the 1957 and 1968 editions of the text by Zemansky.[5] After comparing the plots of the specific surface energy and the heat of vaporization l_v (Fig. 4), Zemansky concludes that both quantities vary with the temperature in a similar way, becoming zero at the critical temperature. Certainly, a relation exists between the heat of vaporization and the surface energy.[10,11] However, l_v really is a monotonically decreasing function of the temperature while this behavior is not observed for the specific surface energy. Hence, the reader might conclude that there is a close relation between l_v and U^σ/Σ, while accurate measurements show that the relation is not so direct.

In the sixth edition of Zemansky and Dittman[12] the correct experimental values of $\gamma(T)$ are shown. However, partially erroneous information is still given. Finally, in the seventh edition,[12] the topic of surface tension has disappeared.

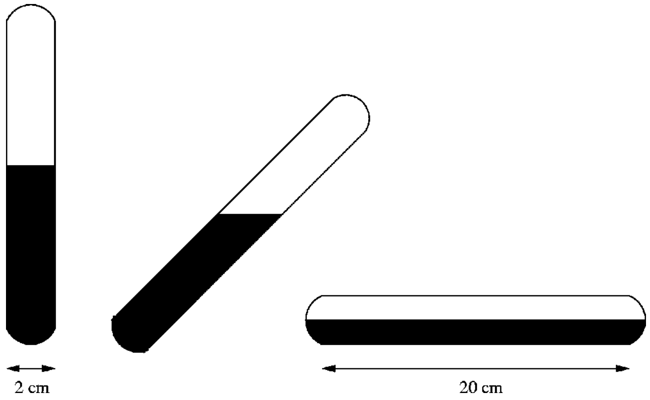

Fig. 5. Schematic view of the experiment suggested by Bruhat (Ref. 6). The water inside a closed cylindrical glass tube increases its interfacial area when the position of the tube is changed reversibly.

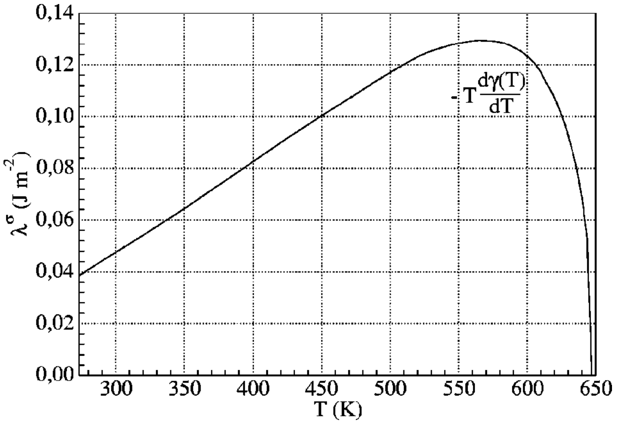

Fig. 6. Temperature dependence of the latent heat of isothermal surface growth, λ^σ for water, calculated from Eq. (32) and using the accurate values given in Table I.

IV. AN EXERCISE ON ONE COMPONENT LIQUID–VAPOR PLANAR INTERFACES

A straightforward evaluation of the surface internal energy change involved in the surface area growth of a planar interface is provided by an experiment suggested by Bruhat.[6] A more sophisticated version of the experiment is due to Wagner.[13] A cylindrical closed glass tube with a diameter of 20 mm and length 20 cm contains 10 cm of water in equilibrium with its vapor at 20 °C; the long axis is vertical (see Fig. 5). The interface is circular with an area of $\pi\times 10^2$ mm^2=3.14 cm^2. If the glass tube is horizontal, the interface is rectangular with an area of 2 cm× 20 cm=40 cm^2. Thus, after the growth of the interfacial region, the surface area has increased by approximately 37 cm^2. We neglect the energy corresponding to the contact surface between the fluid and the walls of the glass tube.

The variation of the surface internal energy of water can be evaluated easily by using Eq. (19):

$$\Delta U^\sigma(T,\Sigma)=\left(\gamma(T)-T\frac{d\gamma}{dT}\right)\Delta\Sigma. \tag{25}$$

From the accurate curve in Fig. 3 (for $T=20\,°\mathrm{C}$) and the value of the interfacial surface increment calculated above, we obtain

$$\Delta U^\sigma=117\,\mathrm{mJ\,m^{-2}}\times(37\times 10^{-4}\,\mathrm{m^2})=0.43\,\mathrm{mJ}. \tag{26}$$

Another way of evaluating the variation of the surface internal energy is by making use of the first law of thermodynamics

$$\Delta U^\sigma=Q^\sigma-W^\sigma. \tag{27}$$

The work done against surface tension can be obtained from Eq. (1) and is

$$W^\sigma=-72.75\,\mathrm{mJ\,m^{-2}}\times(37\times 10^{-4}\,\mathrm{m^2})=-0.27\,\mathrm{mJ}, \tag{28}$$

because $\gamma=72.75\,\mathrm{mJ\,m^{-2}}$ at 20 °C for water.

Because the heat exchanged in a reversible process is related to the entropy change, dS by $\delta Q=TdS$, Eq. (14) yields

$$\delta Q=TdS^\sigma(T,\Sigma)+TdS^b(T,V). \tag{29}$$

Then, by using Eq. (15), we obtain

$$\delta Q^\sigma=TdS^\sigma(T,\Sigma)=-T\frac{d\gamma}{dT}d\Sigma. \tag{30}$$

Because $d\gamma/dT$ is usually negative for pure substances, increasing the surface area ($d\Sigma>0$) implies supplying heat ($\delta Q^\sigma>0$) to the system in order to keep its temperature constant.

We define a latent heat of isothermal surface growth, λ^σ, as the heat exchanged through the interface per unit surface area at constant T:

$$\delta Q^\sigma=\lambda^\sigma d\Sigma. \tag{31}$$

By comparing Eq. (31) with Eq. (30) and taking into account Eq. (15), we obtain

$$\lambda^\sigma=-T\frac{d\gamma}{dT}=Ts^\sigma, \tag{32}$$

where $s^\sigma\equiv S^\sigma/\Sigma$ is represented in Fig. 2. In Fig. 6, λ^σ is plotted as a function of the temperature T for water.

If the growth of the interface occurs sufficiently slowly to be considered reversible and isothermal, the heat transfer is given from Eq. (31) by

$$Q^\sigma=44\,\mathrm{mJ\,m^{-2}}\times(37\times 10^{-4}\,\mathrm{m^2})=0.16\,\mathrm{mJ}, \tag{33}$$

where we have taken into account that at 20 °C, $\lambda^\sigma=44$ mJ m^{-2}, as can be deduced from Fig. 6. Finally, for the variation of the internal energy of water, we obtain

$$\Delta U^\sigma=Q^\sigma-W^\sigma=0.43\,\mathrm{mJ}. \tag{34}$$

This result agrees with that obtained in Eq. (26).

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[a] Electronic mail: juliop@uv.es

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Illustration of Pulleys and Belts. This well-preserved Illustration of Gears and Belts appears in the 1881 catalogue of E. S. Ritchie of Boston. It is in the collection of Amherst College, and dates no earlier than 1875. According to the catalogue, it ''consists of a mahogany base and pillars supporting a double metal bar, by which the frames of the systems of wheels are held, allowing them to be placed at all desired distances and positions. Three metal frames with screw pivots, holding steel axles, upon which the geared wheels or pulleys are arranged as desired. Six brass geared wheels . . . can be arranged in a great variety of combinations. A frame, with geared wheel . . . and pulley for weight, and an endless screw [at the top of the apparatus] which engages in the gear, with pulley for power. A heavy balance-wheel, grooved for belt, with crank and treadle [at the lower part of the apparatus] . . . $40.00'' (Photograph and notes by Thomas B. Greenslade, Jr., Kenyon College)