

# International Equations for the Saturation Properties of Ordinary Water Substance

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Consistent with the latest experimental data and the recent internationally recommended values for the critical parameters, we have developed compact and accurate representative equations for the following properties on the saturation line of ordinary (light) water substance: vapor pressure, density, enthalpy and entropy of both the saturated liquid and the saturated vapor. These equations form the basis of a "Supplementary Release on Saturation Properties of Ordinary Water Substance" issued by the International Association for the Properties of Steam (IAPS).

Key words: enthalpy; entropy; IAPS; orthobaric densities; saturation line; vapor pressure, water.

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## 1. Introduction

For many technical and scientific applications the knowledge of the state variables of ordinary water substance in the saturated vapor and liquid states is of essential importance. In spite of this, it is remarkable that accurate but simple correlation equations which allow the easy calculation of all thermodynamic saturation properties are not available. Each of the existing equations<sup>1-7</sup> has at least one of the following disadvantages: (a) they are not accurate enough over the whole temperature range especially in the critical region, (b) they have a large number of coefficients, (c) their structure is rather complicated, (d) they are not based on the original experimental data, (e) they do not agree with the recommended critical parameters, or (f) they do not correspond to the current international practical temperature scale (IPTS-68).

Of course, the saturation properties can be calculated from equations of state by fulfilling the condition of the vapor-liquid equilibrium, e.g., from the new IAPS Formulation 1984<sup>8</sup> developed by Haar, Gallagher and Kell,<sup>9</sup> or the Pollak equation.<sup>10</sup> However, for those applications which only require the state variables on the vapor-liquid curve, it

is much easier and quicker to use special correlation equations. In any case, the recalculation of the equilibrium properties from an equation of state would consume much less computer time if special equations for the properties on the saturation line delivered the initial values.

During the last one and a half decades new "state of the art measurements" for the property values on the coexistence line of water substance have been reported.<sup>11-14</sup> On the other hand, the development of functional structures for the properties on the saturation curve progressed, too. In addition to a new form for a vapor-pressure equation applied successfully to a large number of substances<sup>15-20</sup> accurate formulations for the orthobaric densities have been developed.<sup>21,22</sup> Furthermore, new methods in order to optimize functional structures<sup>23-27</sup> facilitated the development of improved correlating equations.

The purpose of this paper is to present equations for the following properties of ordinary water substance: vapor pressure, density, enthalpy, and entropy for both the saturated liquid and the saturated vapor. Consistent with the latest experimental data and the recently internationally recommended critical parameters<sup>28</sup> ( $T_c = 647.14$  K,  $p_c = 22.064$  MPa,  $\rho_c = 322$  kg/m<sup>3</sup>) the equations cover the entire range of the coexistence curve vapor-liquid from the triple point to the critical point.

The structure and number of coefficients in these equations has been optimized with the aid of the evolutionary

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optimization method (EOM) developed by Ewers and Wagner.<sup>26,27</sup> The new equations represent all selected data including those in the critical region within the experimental uncertainty without any systematic deviations or oscillations. In constructing the equations for the caloric properties we have started from original experimental data—which are differences between two temperatures—rather than from the mean values used by previous authors.

The equations are of importance for technical as well as for scientific applications. Hence, the equations have been used to generate the table for the thermodynamic properties of the saturation state of the new International Skeleton Tables 1984.<sup>29</sup> Furthermore, the equations are the basis of the "Supplementary Release on the Saturation Properties of Ordinary Water Substance," recently issued by IAPS. A verbatim copy of this release is presented in the Appendix.

## 2. Thermal Properties

In an earlier paper,<sup>30</sup> we have presented accurate equations for the vapor pressure  $p_s$  and the densities of the saturated

liquid  $\rho'$  and the saturated vapor  $\rho''$ , respectively. These equations are based on data sets which have been evaluated very carefully to represent the thermal properties on the saturation line of ordinary water substance. These equations are an important prerequisite in order to establish equations for the caloric properties on the saturation curve. Therefore, the equation for the vapor pressure  $p_s$

$$\ln(p_s/p_c) = (T_c/T)(a_1\tau + a_2\tau^{1.5} + a_3\tau^3 + a_4\tau^{3.5} + a_5\tau^4 + a_6\tau^{7.5}), \quad (2.1)$$

and the density of the saturated vapor  $\rho''$

$$\ln(\rho''/\rho_c) = c_1\tau^{2/6} + c_2\tau^{4/6} + c_3\tau^{8/6} + c_4\tau^{18/6} + c_5\tau^{37/6} + c_6\tau^{71/6} \quad (2.2)$$

are once again given here, where  $\tau = 1 - T/T_c$  and  $c$  refers to the corresponding property at the critical point. The numerical values of the coefficients  $a_i$  and  $c_i$  are given in the Appendix. Details of data processing and evaluation of the structure of the equations were given in the earlier publication.<sup>30</sup>

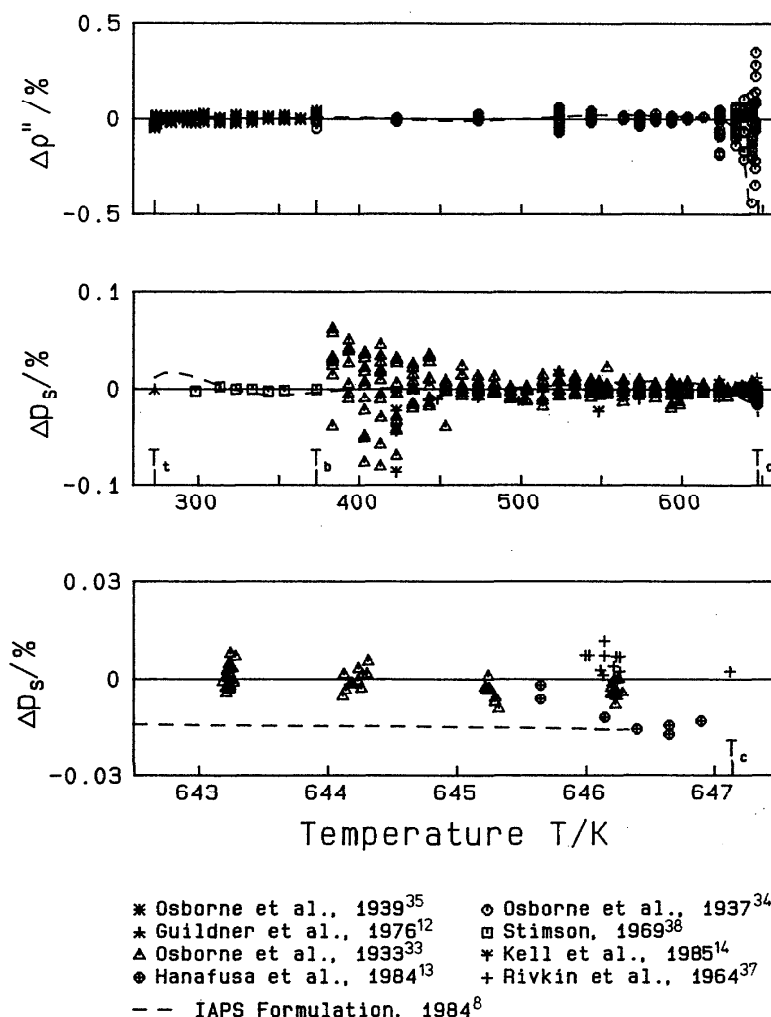


FIG. 1. Percentage deviation  $\Delta y = (y_{\text{exp}} - y_{\text{calc}})/y_{\text{exp}}$ ; ( $y = \rho'', p_s$ ) of the selected experimental data from Eqs. (2.1) and (2.2), respectively.

In Fig. 1 the quality of the two equations is illustrated by comparing the values calculated from them with the experimental data. Besides this comparison, values calculated from the IAPS Formulation 1984 are also included in the figure. The latter fundamental equation was not approved for use within an excluded range bounded by  $|T - 647.2 \text{ K}| \leq 1 \text{ K}$  and  $|\rho/(317.763 \text{ kg m}^{-3}) - 1| \leq 0.3$  near the critical point. When this region is approached, the orthobaric densities calculated from the IAPS Formulation 1984<sup>8</sup> deviate systematically from the experimental data.

Figure 1 shows that all selected experimental data of the vapor pressure and the saturated vapor density are represented by the corresponding equation within the experimental uncertainty without any systematic deviations. This statement is also valid for the critical region, cf. the deviation diagram for the vapor pressure at the bottom of Fig. 1. As a consequence the usage of equations designed especially to represent the vapor pressure in the critical region (e.g., Ref. 31) is not necessary.

We have also developed<sup>30</sup> a correlation equation for the density of the saturated liquid  $\rho'$ . For  $T > 423 \text{ K}$  this five-coefficient equation represents the experimental data within the experimental uncertainty. For  $T \approx 340 \text{ K}$  the calculated densities deviate from the data of Kell<sup>11</sup> by 22 ppm which is, however, about twice the uncertainty of these special high-quality data. The reasons for further improving this equation are discussed as follows.

A lot of scientific and technical equipment for thermodynamic measurements are calibrated with water substance as a reference fluid. Therefore, the thermodynamic properties of water substance in the compressed liquid at atmo-

spheric pressure ( $p_a = 0.101325 \text{ MPa}$ ) belong to the best known properties of any fluid. As the density along the saturation line in the region  $273.16 \text{ K} \leq T \leq 423.15 \text{ K}$  is very close to the density  $\rho_a$  at atmospheric pressure,  $\rho'$  is known in this region within the same accuracy as  $\rho_a$  (cf. Kell<sup>11</sup>). The accuracy of  $\rho_a$  is about 4 ppm at the density maximum ( $T = 277.15 \text{ K}$ ) and deteriorates to about 14 ppm at 423.15 K. Since (a) the "old"  $\rho'$  equation<sup>30</sup> is slightly outside this tight tolerance and (b) it was our intention to determine the  $\rho'$  values of the Skeleton Tables 1985<sup>29</sup> with such a  $\rho'$  equation, and (c) the equations should serve for the IAPS Supplementary Release on "The Saturation Properties of Ordinary Water Substance," the authors decided to develop a new correlation equation for  $\rho'$  that predicts values within the experimental uncertainty of the most reliable experimental data.

If proceeding in exactly the same way as it was described by Wagner and Saul,<sup>30</sup> the new equation for the saturated liquid density has the following form:

$$\rho'/\rho_c = 1 + b_1\tau^{1/3} + b_2\tau^{2/3} + b_3\tau^{5/3} + b_4\tau^{16/3} + b_5\tau^{43/3} + b_6\tau^{110/3}, \quad (2.3)$$

where  $\tau = 1 - T/T_c$  and  $c$  refers to the corresponding value at the critical point. The numerical values of the coefficients  $b_i$  are given in the Appendix.

A comparison between the selected experimental  $\rho'$  data and values calculated from Eq. (2.3) is presented in Fig. 2. For temperatures above 423 K Eq. (2.3) does not yield any significant difference in comparison with the "old"  $\rho'$  equation; all selected experimental data are represented within their uncertainty.

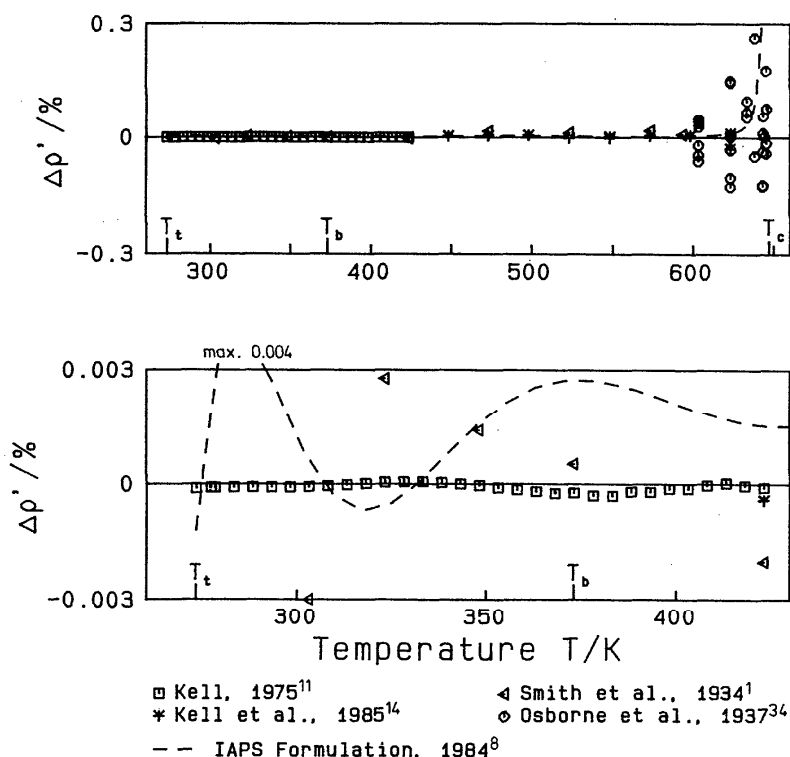


Fig. 2. Percentage deviation  $\Delta\rho' = (\rho'_{\text{exp}} - \rho'_{\text{calc}})/\rho'_{\text{exp}}$  of the selected experimental data from Eq. (2.3).

The lower diagram of Fig. 2, having an enlarged scale, shows that the experimental data of Kell<sup>11</sup> are represented by Eq. (2.3) within 3 ppm. This should be adequate for the estimated uncertainty of these data which are plotted for convenience in this figure, too. The locus of the maximum of  $\rho'$  calculated from Eq. (2.3) is  $T(\rho'_{\max}) = 277.153$  K, where  $\rho'_{\max}$  of Eq. (2.3) is  $999.9232$  kg/m<sup>3</sup>. The value of  $T(\rho'_{\max})$  is exactly the temperature where the isobaric density line crosses the saturation line (cf. Kell<sup>11</sup>). Besides the comparison with the experimental data, this figure also shows the plot of  $\rho'$  values calculated from the IAPS-Formulation 1984<sup>8</sup>; the reason for the deviation in the critical region was already given when we discussed Fig. 1.

In the following paragraphs the derivative  $dp_s/dT$  of the vapor-pressure equation is required in order to assign the various caloric properties of water substance. This derivative can be calculated with the aid of the vapor-pressure equation, Eq. (2.1), from the following expression:

$$\frac{dp_s}{dT} = -\frac{p_s}{T} \left[ \ln\left(\frac{p_s}{p_c}\right) + a_1 + 1.5a_2\tau^{0.5} + 3a_3\tau^2 + 3.5a_4\tau^{2.5} + 4a_5\tau^3 + 7.5a_6\tau^{6.5} \right], \quad (2.4)$$

where  $\tau = 1 - T/T_c$ . The numerical values for the coefficients  $a_i$  are the same as for Eq. (2.1) and are listed in the Appendix.

### 3. Enthalpy

During the period from 1930–1939 Osborne and his co-workers<sup>32–35</sup> carried out experiments of metrological quality. Besides their vapor-pressure data<sup>33</sup> which form the core of data used to establish the vapor-pressure equation, Eq. (2.1), they measured caloric properties as well.

These caloric properties

$$\beta = \frac{T}{\rho'} \frac{dp_s}{dT} \quad (3.1)$$

and

$$\gamma = \frac{T}{\rho''} \frac{dp_s}{dT} \quad (3.2)$$

were used by Wagner and Saul,<sup>30</sup> to obtain data sets for the density of saturated liquid  $\rho'$  and saturated vapor  $\rho''$ , respectively.

Because of the difficulties in converting the units of data measured by earlier researchers we did not use data published before 1930. In principle Osborne *et al.* measured the internal energy in the two-phase region of water substance. These data for the internal energy which depend on both temperature and density, can be reduced to a quantity  $\alpha$  which only depends on temperature.

The internal energy data of Baehr *et al.*<sup>36</sup> were compiled in a similar way. However, these data were found to have an experimental scatter of about  $\pm 3\%$  of the corresponding  $\alpha$  value. Furthermore, the Baehr data tend to yield  $\alpha$  values which are systematically 1% too high in comparison with the Osborne data. To avoid inconsistencies, only the data of Osborne *et al.* were used to establish the caloric equations.

During the  $\alpha$  experiments mentioned above, the change

of  $\alpha$  corresponding to

$$\alpha|_1^2 = \alpha(T_2) - \alpha(T_1) \quad (3.3)$$

is measured between the two temperatures  $T_1$  and  $T_2$ . Then the change of the enthalpy of the saturated liquid

$$h'|_1^2 = h'(T_2) - h'(T_1) \quad (3.4)$$

can be calculated using the relation

$$h'|_1^2 = \alpha|_1^2 + \beta|_1^2, \quad (3.5)$$

where

$$\beta|_1^2 = \left( \frac{T}{\rho'} \frac{dp_s}{dT} \right)_2 - \left( \frac{T}{\rho'} \frac{dp_s}{dT} \right)_1. \quad (3.6)$$

In the same way the change of the enthalpy of the saturated vapor  $h''$  is given by

$$h''|_1^2 = \alpha|_1^2 + \gamma|_1^2, \quad (3.7)$$

where

$$\gamma|_1^2 = \left( \frac{T}{\rho''} \frac{dp_s}{dT} \right)_2 - \left( \frac{T}{\rho''} \frac{dp_s}{dT} \right)_1. \quad (3.8)$$

The values of  $\beta|_1^2$  in Eq. (3.5) and of  $\gamma|_1^2$  in Eq. (3.7) are known from Eqs. (2.1)–(2.4). Thus,  $\alpha|_1^2$  is the key value for the enthalpy of the saturated liquid and vapor. We shall show below that  $\alpha$  is also a convenient quantity in describing the entropy along the saturation line. Therefore, it was decided to establish a correlation equation for  $\alpha$ .

The first step towards the development of the equation for  $\alpha$  was the selection of the  $\alpha|_1^2$  data. The  $\alpha|_1^2$  measurements can be classified by the magnitude of the temperature interval ( $T_2 - T_1$ ). In the following paragraph they will be called “small temperature interval” measurements if ( $T_2 - T_1$ )  $\leq 10$  K and “large temperature interval” measurements if ( $T_2 - T_1$ )  $> 10$  K.

The data measured in 1930,<sup>32</sup> covering the temperature range from 273 K  $\leq T \leq 543$  K, were not used because they do not have the same accuracy as the later measurements. From the data published in 1937,<sup>34</sup> which cover the temperature range 373 K  $\leq T \leq 643$  K, only the “large mass” experiments in “small temperature intervals” were used (142 data points). The “small mass” experiments are mainly important to get the calorimetric constants of the apparatus. Referring to the “large temperature interval” measurements Osborne himself said that they had less accuracy. The measurements of 1939<sup>35</sup> were carried out in the region 273 K  $\leq T \leq 373$  K; again the “small mass” data were not used. As a consequence the 256 data points of the “large mass” experiments were selected. From the two publications,<sup>34,35</sup> only the unsmoothed original data were taken and converted to SI units and to the IPTS-68.

As a second step we formulated a comprehensive expression forming a “bank of terms.” Due to the nature of the data (triplets of  $\alpha|_1^2, T_1, T_2$ ), a very special “bank of terms” never used before had to be established, namely

$$\frac{\alpha|_1^2}{\alpha_0} = \sum_{i=-120}^{120} d_i \left[ \left( \frac{T_2}{T_c} \right)^{i/2} - \left( \frac{T_1}{T_c} \right)^{i/2} \right], \quad i \neq 0, \quad (3.9)$$

where  $\alpha_0 = 1000$  J/kg.

In the third step, the most effective combination of

terms was selected from this "bank of terms" when the optimization method EOM developed by Ewers and Wagner<sup>26,27</sup> was applied. The most effective combination is the following: (1) That one which yields the smallest weighted least-square sum WLS for a given number of terms after fitting to the data. (2) Neither an increase in the number of terms would yield a significantly smaller WLS nor a decrease would be possible without substantial deterioration of the WLS. The WLS and the corresponding coefficients  $d_i$  result simultaneously from a WLS fit formulated by

$$\text{WLS} = \sum_{m=1}^M \frac{(\Delta\alpha_m)^2}{\sigma_{\Delta\alpha_m}^2} \rightarrow \text{minimum} \quad (3.10)$$

with

$$\Delta\alpha = \frac{\alpha|_1^2}{\alpha_0} - \sum_{k=1}^K n_k \left[ \left( \frac{T_2}{T_c} \right)^{\eta_k} - \left( \frac{T_1}{T_c} \right)^{\eta_k} \right],$$

where  $M$  is the number of data points,  $\sigma_{\Delta\alpha_m}^2$  is the variance of  $\Delta\alpha_m$ , and  $n_k, \eta_k$  are actual coefficients and exponents, respectively. According to the Gaussian error propagation formula, the variance  $\sigma_{\Delta\alpha}^2$  is related to the three single variances  $\sigma_{\alpha|_1^2}^2$ ,  $\sigma_{T_1}^2$ , and  $\sigma_{T_2}^2$  of each experimental  $\alpha|_1^2$  value by

$$\sigma_{\Delta\alpha}^2 = \left( \frac{\partial\Delta\alpha}{\partial\alpha|_1^2} \right)_{T_1, T_2}^2 \sigma_{\alpha|_1^2}^2 + \left( \frac{\partial\Delta\alpha}{\partial T_1} \right)_{\alpha|_1^2, T_2}^2 \sigma_{T_1}^2 + \left( \frac{\partial\Delta\alpha}{\partial T_2} \right)_{\alpha|_1^2, T_1}^2 \sigma_{T_2}^2. \quad (3.11)$$

For each experimental  $T_1, T_2, \alpha|_1^2$  point,  $\sigma_{\Delta\alpha_m}^2$  was calculated by estimating  $\sigma_{\alpha|_1^2}^2$ ,  $\sigma_{T_1}^2$ , and  $\sigma_{T_2}^2$  from the statements in the corresponding publications in connection with our own experience and judgment. The required derivative  $d\alpha|_1^2/dT$  was calculated from a preliminary equation. When we used the EOM to solve the optimization problem formulated above, the following simple equation for  $\alpha$  results:

$$\begin{aligned} \alpha|_1^2/\alpha_0 = & d_1(\theta_2^{-19} - \theta_1^{-19}) + d_2(\theta_2 - \theta_1) \\ & + d_3(\theta_2^{4.5} - \theta_1^{4.5}) + d_4(\theta_2^5 - \theta_1^5) \\ & + d_5(\theta_2^{54.5} - \theta_1^{54.5}), \end{aligned} \quad (3.12a)$$

where  $\theta = T/T_c$ . The numerical values of the coefficients  $d_i$  are listed in the Appendix.

In Fig. 3 the deviations between the experimental values of  $\alpha|_1^2$  and the values calculated from Eq. (3.12a) are plotted at the lower temperature  $T_1$  for each data point. It can be seen that Eq. (3.12a) represents all selected data within their experimental scatter. Furthermore, Fig. 3 shows the deviations between the values calculated from the IAPS Formulation 1984<sup>8</sup> and Eq. (3.12a).

In order to calculate the enthalpy with regard to a reference state it is convenient to rearrange Eq. (3.12a). According to the IAPS agreement, the reference state is the saturated liquid at the triple point where the entropy and internal energy are considered to be zero. Taking this fact into account, the enthalpy of the saturated liquid at the triple point is fixed by the relation  $h'(T_t) = p_s(T_t)/\rho'(T_t)$ . The calculation of  $p_s(T_t)$  from Eq. (2.1) and  $\rho'(T_t)$  from Eq. (2.3) yields for the enthalpy at the triple temperature

$$h'(T_t) = 6.11787 \times 10^{-4} \text{ J/g}. \quad (3.13)$$

It is obvious that  $T_t$  now is the temperature  $T_1$  of Eq. (3.5). Thus, the value of  $\beta(T_1) = \beta(T_t)$  and  $\alpha(T_1) = \alpha(T_t)$  were calculated. With regard to Eq. (3.13) a reference constant  $d_\alpha$  was assigned in a way that

$$\begin{aligned} \alpha/\alpha_0 = & d_\alpha + d_1\theta^{-19} + d_2\theta \\ & + d_3\theta^{4.5} + d_4\theta^5 + d_5\theta^{54.5} \end{aligned} \quad (3.12b)$$

enables us to calculate values for the enthalpies, namely

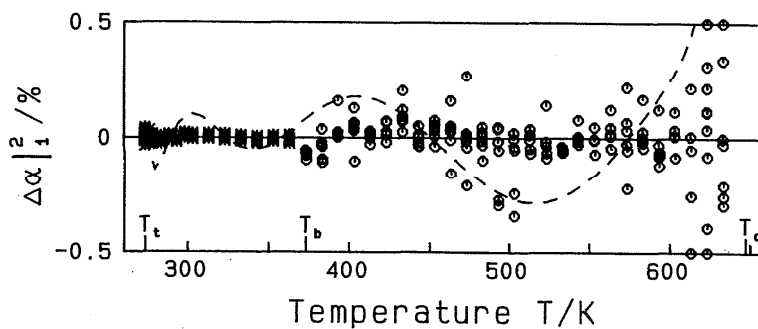
$$\frac{h'}{\text{J/g}} = \frac{\alpha}{\alpha_0} + 10^3 \frac{T/\text{K}}{\rho''/(\text{kg m}^{-3})} \left( \frac{dp_s}{dT} \right) / \left( \frac{\text{MPa}}{\text{K}} \right) \quad (3.14)$$

and

$$\frac{h''}{\text{J/g}} = \frac{\alpha}{\alpha_0} + 10^3 \frac{T/\text{K}}{\rho''/(\text{kg m}^{-3})} \left( \frac{dp_s}{dT} \right) / \left( \frac{\text{MPa}}{\text{K}} \right). \quad (3.15)$$

The numerical values of the  $d_i$  of Eq. (3.12b) are the same as for Eq. (3.12a) and are listed together with  $d_\alpha$  in the Appendix. Now the computation of  $h'$  and  $h''$  is very easy by using Eq. (3.12b) for  $\alpha$ , Eq. (2.2) for  $\rho''$ , Eq. (2.3) for  $\rho'$  and Eq. (2.4) for  $dp_s/dT$ . The value of the enthalpy at the critical point resulting from Eqs. (3.14) and (3.15), respectively, is 2086 J/g.

Due to the very small value of  $h'$  at the triple point [cf. Eq. (3.13)],  $d_\alpha$  has to be given with an accuracy of 13 signif-



\* Osborne et al., 1939<sup>35</sup>    ○ Osborne et al., 1937<sup>34</sup>  
 - - IAPS Formulation, 1984<sup>8</sup>

FIG. 3. Percentage deviation  $\Delta\alpha|_1^2 = (\alpha|_{1,exp}^2 - \alpha|_{1,IAPS}^2)/\alpha|_{1,exp}^2$  of the selected experimental data from Eq. (3.12). ( $\Delta\alpha|_1^2$  is plotted at the lower temperature  $T_1$  of the temperature interval  $T_1, T_2$ . Four data points are off scale.)

icant figures to ensure that Eq. (3.14) yields a thermodynamically consistent value at the triple point. A decrease in the number of figures of  $d_\alpha$  causes a small inconsistency with regard to the enthalpy of the saturated liquid  $h'$  only very close to the triple point.

#### 4. Entropy

As was mentioned in the preceding paragraph the quantity  $\alpha$  is also the key value for entropy calculations along the saturation line. Based on the second law of thermodynamics it can be shown, that the change of the entropy of the saturated liquid between  $T_2$  and  $T_1$  is related to  $\alpha$  by the following expression:

$$s'|_1^2 = \int_{T_1}^{T_2} \frac{1}{T} \frac{d\alpha}{dT} dT + \frac{\beta}{T}|_1^2, \quad (4.1)$$

where

$$\frac{\beta}{T}|_1^2 = \left[ \left( \frac{dp_s}{dT} \right) / \rho' \right]_2 - \left[ \left( \frac{dp_s}{dT} \right) / \rho' \right]_1. \quad (4.2)$$

When applying the Clapeyron equation the change of the entropy of the saturated vapor  $s''$  is described by

$$s''|_1^2 = \int_{T_1}^{T_2} \frac{1}{T} \frac{d\alpha}{dT} dT + \frac{\gamma}{T}|_1^2, \quad (4.3)$$

re

$$\frac{\gamma}{T}|_1^2 = \left[ \left( \frac{dp_s}{dT} \right) / \rho'' \right]_2 - \left[ \left( \frac{dp_s}{dT} \right) / \rho'' \right]_1. \quad (4.4)$$

Solving the integral in Eq. (4.1) and Eq. (4.3) under the provision that the entropy of the saturated liquid equals zero at the triple point, leads to the following expression:

$$\begin{aligned} \frac{\phi}{\phi_0} = \int \frac{1}{\theta} \frac{d(\alpha/\alpha_0)}{d\theta} d\theta = d_\phi + \frac{19}{20} d_1 \theta^{-20} + d_2 \ln \theta \\ + \frac{9}{7} d_3 \theta^{3.5} + \frac{5}{4} d_4 \theta^4 + \frac{109}{107} d_5 \theta^{53.5}, \end{aligned} \quad (4.5)$$

where  $\theta = T/T_c$ .

The numerical values for the coefficients  $d_i$  of Eq. (4.5) are the same as those for Eqs. (3.12a) and (3.12b) and are listed together with  $d_\phi$  and  $\phi_0$  in the Appendix.

Now the entropy of both the saturated liquid and the saturated vapor can be calculated very easily by the following expressions

$$\frac{s'}{J/(g K)} = \frac{\phi}{\phi_0} + 10^3 \frac{1}{\rho'/(kg m^{-3})} \left( \frac{dp_s}{dT} \right) / \left( \frac{MPa}{K} \right), \quad (4.6)$$

$$\frac{s''}{J/(g K)} = \frac{\phi}{\phi_0} + 10^3 \frac{1}{\rho''/(kg m^{-3})} \left( \frac{dp_s}{dT} \right) / \left( \frac{MPa}{K} \right). \quad (4.7)$$

Again  $\rho''$ ,  $\rho'$ ,  $dp_s/dT$ , and  $\phi$  are calculated by Eqs. (2.2)–(2.4) and (4.5), respectively. The entropy at the critical point resulting of Eqs. (4.6) and (4.7), respectively, is 4.41 J/(g K).

#### 5. Thermodynamic Consistency

The equations for  $p_s$ ,  $\rho'$ ,  $\rho''$ , and  $\alpha$  have been developed on the basis of the corresponding experimental data which were measured independently. An internal consistency be-

tween these equations has been achieved by the procedure used to establish these expressions. However, this internal consistency does not exclude completely thermodynamic inconsistencies with respect to other thermodynamic properties which have not been considered in this context. While the paper was being reviewed, such a small inconsistency was found by Hill<sup>39</sup> for the heat capacity along the phase boundary for the saturated vapor  $c_s'' = dh''/dT$  in the temperature range below 300 K. In this region the difference between  $c_s''$  and heat capacity of the ideal gas  $c_p^0$  should smoothly and continuously diminish towards zero as the vapor density decreases towards zero. In contrast to this expected behavior an increasing divergence between  $c_s''$  and  $c_p^0$  can be observed when  $c_s''$  is calculated from Eq. (3.15). This behavior is caused by extremely small inconsistencies between  $p_s$ ,  $\rho''$ , and  $\alpha$  in this low temperature region. These inconsistencies are within the experimental uncertainty and can hardly be avoided in this procedure used to establish these equations.

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## Appendix

### The International Association for the Properties of Steam

Düsseldorf, Federal Republic of Germany,  
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#### Supplementary Release on Saturation Properties of Ordinary Water Substance

Unrestricted publication allowed in all countries.  
Issued by the International Association for the Properties of Steam.

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This supplementary release has been authorized by the International Association for the Properties of Steam (IAPS) at its meeting in Düsseldorf, Federal Republic of Germany, 21–26 September 1986, for issue by its Secretariat. The members of IAPS are Canada, the Czechoslovak Socialist Republic, the Federal Republic of Germany, France, Japan, the Union of Soviet Socialist Republics, the United

Kingdom, and the United States of America.

IAPS has issued earlier a *Release on the IAPS Formulation 1984 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use* and a *Release on the IAPS Skeleton Tables 1985 for the Thermodynamic Properties of Ordinary Water Substance*. Both releases yield values for the saturation properties of ordinary water substance which are not identical but which do agree within the mutual tolerances quoted in the two releases. The present supplementary release contains a set of simple equations which yield for ordinary water substance the vapor pressure as well as the density, specific enthalpy, and specific entropy of the saturated vapor and liquid. The values calculated from these equations for the vapor pressure and for the density and specific enthalpy of the vapor and liquid at saturation are identical to the values tabulated for these properties in the IAPS Skeleton Tables 1985.

Details about the equations presented in this supplementary release can be found in an article "International Equations for the Saturation Properties of Ordinary Water Substance," by A. Saul and W. Wagner, to be submitted to the *Journal of Physical and Chemical Reference Data*.

Further information about this supplementary release and other releases issued by IAPS can be obtained from the Executive Secretary of IAPS:

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## Equations for the Thermodynamic Properties of Ordinary Water Substance at Saturation

### 1. Nomenclature

Thermodynamic quantities:

$h$  = specific enthalpy  
 $P$  = vapor pressure  
 $s$  = specific entropy  
 $T$  = temperature  
 $u$  = specific internal energy  
 $\rho$  = density (mass divided by volume)  
 $\alpha$  = auxiliary quantity for specific enthalpy  
 $\phi$  = auxiliary quantity for specific entropy  
 $\theta = T/T_c$   
 $\tau = 1 - \theta$

Subscripts:

$c$  means value at the critical point  
 $t$  means value at the triple point

Superscripts:

' means value of the saturated liquid  
 " means value of the saturated vapor

Note:  $T$  denotes absolute temperature on the International Practical Temperature Scale of 1968.

### 2. Reference constants

$T_c = 647.14$  K,       $\alpha_0 = 1000$  J/kg,  
 $P_c = 22.064 \times 10^6$  Pa,       $\phi_0 = \alpha_0/T_c$ ,  
 $\rho_c = 322$  kg/m<sup>3</sup>.

Note: The numerical values for the critical parameters  $T_c$ ,  $P_c$ ,  $\rho_c$  are identical to those given in *IAPS Statement, 1983, of the Values of the Temperature, Pressure, and Density of Pure Ordinary and Heavy Water Substances at Their Respective Critical Points*.

### 3. Vapor pressure

$$\ln(P/P_c) = T_c/T(a_1\tau + a_2\tau^{1.5} + a_3\tau^3 + a_4\tau^{3.5} + a_5\tau^4 + a_6\tau^{7.5}), \quad (1)$$

with

$$\begin{aligned} a_1 &= -7.858\ 23, & a_4 &= +22.670\ 5, \\ a_2 &= +1.839\ 91, & a_5 &= -15.939\ 3, \\ a_3 &= -11.781\ 1, & a_6 &= +1.775\ 16. \end{aligned}$$

### 4. Densities

#### 4.1 Density of the saturated liquid:

$$\rho'/\rho_c = 1 + b_1\tau^{1/3} + b_2\tau^{2/3} + b_3\tau^{5/3} + b_4\tau^{16/3} + b_5\tau^{43/3} + b_6\tau^{110/3}, \quad (2)$$

with

$$\begin{aligned} b_1 &= +1.992\ 06, & b_4 &= -1.752\ 63, \\ b_2 &= +1.101\ 23, & b_5 &= -45.448\ 5, \\ b_3 &= -5.125\ 06 \times 10^{-1}, & b_6 &= -6.756\ 15 \times 10^5. \end{aligned}$$

#### 4.2 Density of the saturated vapor:

$$\ln(\rho''/\rho_c) = c_1\tau^{2/6} + c_2\tau^{4/6} + c_3\tau^{8/6} + c_4\tau^{18/6} + c_5\tau^{37/6} + c_6\tau^{71/6}, \quad (3)$$

with

$$\begin{aligned} c_1 &= -2.029\ 57, & c_4 &= -17.3151, \\ c_2 &= -2.687\ 81, & c_5 &= -44.6384, \\ c_3 &= -5.381\ 07, & c_6 &= -64.3486. \end{aligned}$$

### 5. Specific enthalpy and entropy

#### 5.1 Auxiliary equations:

$$\alpha/\alpha_0 = d_\alpha + d_1\theta^{-19} + d_2\theta + d_3\theta^{4.5} + d_4\theta^5 + d_5\theta^{54.5}, \quad (4)$$

$$\begin{aligned} \frac{\phi}{\phi_0} &= d_\phi + \frac{19}{20}d_1\theta^{-20} + d_2\ln\theta + \frac{9}{7}d_3\theta^{3.5} \\ &+ \frac{5}{4}d_4\theta^4 + \frac{109}{107}d_5\theta^{53.5}, \end{aligned} \quad (5)$$

with

$$\begin{aligned} d_1 &= -5.717\ 56 \times 10^{-8}, & d_2 &= +2689.81, \\ d_3 &= +129.889, & d_4 &= -137.181, \\ d_5 &= +9.688\ 74 \times 10^{-1}, \\ d_\alpha &= -1135.481\ 615\ 639, & d_\phi &= +2318.9142. \end{aligned}$$

#### 5.2 Specific enthalpy of the saturated liquid:

$$h' = \alpha + \frac{T}{\rho'} \frac{dP}{dT}. \quad (6)$$

Equation (6) yields the specific enthalpy of the saturated liquid when used in conjunction with Eqs. (1), (2), and (4).

Note: The specific internal energy and the specific entropy of the liquid at the triple point  $u'_t$  and  $s'_t$ , have been set equal to zero. As a consequence, the specific enthalpy of the liquid at the triple point differs from zero and assumes the value

$$h'_t = 0.611\ 787\ \text{J/kg}.$$

In order to reproduce this numerical value for  $h'_t$ , one needs to retain 13 figures for the constant  $d_\alpha$  as quoted above. A decrease of the number of decimals in  $d_\alpha$  affects the enthalpy of the saturated liquid near the triple point, but does not affect the values of  $P$ ,  $\rho'$ ,  $\rho''$ ,  $h''$ ,  $s'$ , and  $s''$  significantly.

#### 5.3 Specific enthalpy of the saturated vapor:

$$h'' = \alpha + \frac{T}{\rho''} \frac{dP}{dT}. \quad (7)$$

Equation (7) yields the specific enthalpy of the saturated vapor when used in conjunction with Eqs. (1), (3), and (4).

#### 5.4 Specific entropy of the saturated liquid:

$$s' = \phi + \frac{1}{\rho'} \frac{dP}{dT}. \quad (8)$$

Equation (8) yields the specific entropy of the saturated liquid when used in conjunction with Eqs. (1), (2), and (5).

#### 5.5 Specific entropy of the saturated vapor:

$$s'' = \phi + \frac{1}{\rho''} \frac{dP}{dT}. \quad (9)$$

Equation (9) yields the specific entropy of the saturated vapor when used in conjunction with Eqs. (1), (3), and (5).

### 6. Range of validity of the equations

IAPS endorses the validity of the equations presented in

TABLE 1. Thermodynamic property values calculated at three selected temperatures

	$T = 273.16\ \text{K}$	$T = 373.15\ \text{K}$	$T = 647.14\ \text{K}$
$P/\text{Pa}$	611.659	$0.101\ 325 \times 10^6$	$22.064 \times 10^6$
$(dP/dT)/(\text{Pa K}^{-1})$	44.426 617	$3.616 \times 10^3$	$267.9 \times 10^3$
$\rho'/(\text{kg m}^{-3})$	999.790	958.366	322
$\rho''/(\text{kg m}^{-3})$	0.004 853 64	0.597 462	322
$\alpha/(\text{J kg}^{-1})$	-11.526 335	$417.66 \times 10^3$	$1548 \times 10^3$
$h'/(\text{J kg}^{-1})$	0.611 787	$419.07 \times 10^3$	$2086 \times 10^3$
$h''/(\text{J kg}^{-1})$	$2500.3 \times 10^3$	$2675.8 \times 10^3$	$2086 \times 10^3$
$\phi/(\text{J kg}^{-1}\ \text{K}^{-1})$	-0.04	$1.303 \times 10^3$	$3.578 \times 10^3$
$s'/(\text{J kg}^{-1}\ \text{K}^{-1})$	0	$1.307 \times 10^3$	$4.410 \times 10^3$
$s''/(\text{J kg}^{-1}\ \text{K}^{-1})$	$9.153 \times 10^3$	$7.355 \times 10^3$	$4.410 \times 10^3$



this supplementary release for the entire range of vapor-liquid equilibrium which corresponds to

$$273.16 \text{ K} \leq T \leq 647.14 \text{ K.} \quad (10)$$

#### 7. Estimates of uncertainty

Values calculated from the equations for  $P$ ,  $1/\rho'$ ,  $1/\rho''$ ,  $h'$ , and  $h''$  together with their estimated uncertainties are identical to the values in Table 3 of the *Release on the IAPS Skeleton Tables 1985 for the Thermodynamic Properties of Ordinary Water Substance*.

#### 8. Computer-program verification

To assist the user in computer-program verification, Table 1 lists values for  $P$ ,  $dP/dT$ ,  $\rho'$ ,  $\rho''$ ,  $\alpha$ ,  $h'$ ,  $h''$ ,  $\phi$ ,  $s'$ , and  $s''$  calculated at three temperatures. The results quoted in Table 1 were obtained with the aid of a computer having 14 significant figures and with the values of  $d_\alpha$  and  $d_\phi$  given in Sec. 5.1. If the calculations are performed with the aid of a computer with seven significant figures, the results will be within the estimated uncertainty of the various properties except for the enthalpy of the saturated liquid very close to the triple point.