The International Association for the Properties of Water and Steam

Vejle, Denmark
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Advisory Note No. 1

Uncertainties in Enthalpy
for
the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use (IAPWS-95)
and
the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam (IAPWS-IF97)

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This advisory note contains 15 pages, including this cover page.

This advisory note has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Vejle, Denmark, 24-29 August, 2003, for issue by its Secretariat. The members of IAPWS are: Argentina and Brazil, Britain and Ireland, Canada, the Czech Republic, Denmark, France, Germany, Italy, Japan, Russia, the United States of America, and associate member Greece.

IAPWS has provided two formulations to calculate the thermodynamic properties of ordinary water substance, namely "The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use" (IAPWS-95) and "The IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam" (IAPWS-IF97). In the corresponding documents, uncertainties in several properties calculated from these formulations are given, but not for the specific enthalpy. It is the purpose of this advisory note to present values for the uncertainties in specific enthalpy when this property is calculated from IAPWS-95 and IAPWS-IF97.

A minor editorial change was made to this advisory note in September 2006. The only edit was the correction of a printing error on page 3 for the value of the saturated-liquid enthalpy at the triple point.

1 Introduction

1.1 IAPWS-95 Formulation

In 1995, the International Association for the Properties of Water and Steam (IAPWS) adopted a new formulation called "The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use" (which will be referred to here as IAPWS-95). A complete description of IAPWS-95 is given in the release [1] and in the comprehensive article [2] on this formulation. The article also contains extensive details of the development of IAPWS-95 (e.g., experimental data used in the fit, numerical methods used in developing the formulation, comparison between experimental data and values calculated from IAPWS-95, and tables of thermodynamic properties).

1.2 Industrial Formulation IAPWS-IF97

In 1997, IAPWS adopted a new formulation for industrial use called "The IAPWS Industrial Formulation for the Thermodynamic Properties of Water and Steam" (IAPWS-IF97). A complete description of IAPWS-IF97 is given in the release [3] and in the comprehensive article [4] on this formulation. The article also contains extensive details of the development of IAPWS-IF97 (e.g., input data used in the fit, numerical methods used in developing the formulation, comparison between the input data and the values calculated from IAPWS-IF97). The input data used to develop IAPWS-IF97 were calculated from the scientific formulation IAPWS-95.

Previously, no estimates for the uncertainty in specific enthalpy calculated from IAPWS-IF97 have been given. However, since modern procedures of acceptance tests on energy-conversion and power plants (e.g., VDI Guideline 2048 [6]) require values for the uncertainty in specific enthalpy of H_2O, this advisory note presents the corresponding uncertainty values. Since the industrial formulation IAPWS-IF97 is based on input data calculated from IAPWS-95, the uncertainty of IAPWS-95 in specific enthalpy is estimated as a starting point.

2 Uncertainty of the IAPWS-95 Formulation in Enthalpy

For the sake of completeness, a brief statement is given in the following subsection on the uncertainties of calculations from IAPWS-95 for properties other than specific enthalpy.

2.1 Uncertainties in Properties Other than Enthalpy

The uncertainties of IAPWS-95 in the properties density ρ, speed of sound w, specific isobaric heat capacity c_p, and the thermal saturation properties vapor pressure p_σ, saturated liquid density ρ', and saturated vapor density ρ'' are given in [1, 2]. These estimates of uncertainty were derived from comparisons with the various sets of experimental data whose uncertainties had been assessed by IAPWS. An exception to this procedure is the specific isobaric heat capacity c_p, for which experimental data exist only in a limited range of pressure and temperature and with experimental uncertainties that are sometimes greater than the uncertainties of the c_p values calculated from the best equations of state. Therefore, while some comparison is made with these experimental c_p data, the uncertainty of IAPWS-95 in c_p, given in [1, 2], is mainly based on comparisons between c_p values calculated from IAPWS-95 [1, 2] and two additional equations of state for H_2O.

2.2 Uncertainty in Enthalpy

For the uncertainty in the specific enthalpy calculated from IAPWS-95, all that was said in reference [2] was that the relative uncertainty of differences in specific enthalpy Δh is smaller than the uncertainty given for c_p. However, for the reason mentioned in Sec. 1.2, results of a more accurate estimate of the uncertainty in specific enthalpy calculated from IAPWS-95 are given here.

Since these estimates could not be based on experimental data[1], they were carried out by comparisons between specific enthalpy values calculated from IAPWS-95 [1, 2], the equations of state of Hill [7] and of Saul and Wagner [8], the previous scientific formulation IAPS-84 [9, 10], and the equation of state of Pollak [11, 12]. The final estimated uncertainties presented in this advisory note are based on corresponding comparisons among the three most accurate equations of state for H_2O, namely IAPWS-95 [1, 2] and the equations of state of Hill [7] and of Saul and Wagner [8]. The comparison with the values from IAPS-84 [9, 10] and the equation of Pollak [11, 12] should convey an idea of how much these equations of state deviate from the three equations of state used. Since, except for IAPWS-95, the other four equations of state are not based on the current International Temperature Scale of 1990 (ITS-90), a corresponding temperature conversion was made for all comparisons between these equations.

2.2.1 Uncertainty in the Enthalpy of the Single-Phase Region

The reference point of all values of the specific enthalpy calculated from IAPWS-95 is the enthalpy of the saturated liquid at the triple point, namely $h'_{\mathrm{t}} = 0.611\,782\times10^{-3}$ kJ kg^{-1}, which is the value produced by IAPWS-95 when the standard convention is adopted that the specific internal energy and specific entropy are zero at this point [1, 2]. Thus, all specific enthalpies calculated from IAPWS-95 are automatically related to this reference point.

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[1] The existing experimental data of the specific isobaric heat capacity, enthalpy differences, Joule-Thomson coefficients and isothermal throttling coefficients are not suitable to estimate the uncertainty in calculated specific enthalpies, because these data relate only to small enthalpy differences in fixed directions on the thermodynamic surface. Moreover, these data cover only a small part of the range of validity of IAPWS-95 and are less accurate than IAPWS-95 for these properties in wide ranges of temperature and pressure [2].

As mentioned above, the uncertainties of the specific enthalpies calculated from IAPWS-95 have been derived from comparisons between the three equations of state for H_2O: IAPWS-95 [1, 2], Hill [7], and Saul and Wagner [8]. In addition to these direct comparisons in enthalpy calculations, the representation of experimental $p\rho T$ data (densities), speeds of sound, and isobaric heat capacities by these equations of state have also been taken into account. As a result of this entire procedure, Fig. 1 (see Sec. 2.2.4) presents the uncertainties Δh in the specific enthalpy h calculated from IAPWS-95; the values are given as absolute enthalpy uncertainties.

2.2.2 Uncertainties in Enthalpy Differences

For many applications, the uncertainty in enthalpy differences is needed. However, when calculating such uncertainties from the uncertainties of the enthalpies given in Fig. 1 (i.e., related to the enthalpy reference point of IAPWS-95), one obtains unrealistically large percentage uncertainties, particularly for relatively small enthalpy differences.

Therefore, uncertainties $\Delta(\Delta h)$ in the enthalpy differences Δh have been estimated by calculating such enthalpy differences from the three equations of state for H_2O: IAPWS-95 [1, 2], Hill [7], and Saul and Wagner [8]. Different sizes of Δh values were calculated in different directions, namely along isobars, isentropes, and differences in initial and final states corresponding to adiabatic irreversible paths representing steam turbines, boiler feed pumps, and hydroturbines. Enthalpy differences Δh between 10 kJ kg^{-1} and 1000 kJ kg^{-1} have been considered for the gas region, and between 1 kJ kg^{-1} and 10 kJ kg^{-1} for the liquid region. Apart from the uncertainties $\Delta(\Delta h)/\Delta h$ of isobaric enthalpy differences Δh in the gas region for pressures up to 1 MPa, all the other uncertainty values given do not significantly depend on the size of the enthalpy differences considered. As a result of all these comparisons, the estimated percentage uncertainties $\Delta(\Delta h)/\Delta h$ of enthalpy differences Δh calculated from the IAPWS-95 formulation are summarized in Figs. 2 and 3 (see Sec. 2.2.4).

2.2.3 Uncertainty in the Enthalpy of Vaporization

The uncertainty $\Delta(\Delta^{\mathrm{v}}h)$ in the enthalpy of vaporization $\Delta^{\mathrm{v}}h$ (the difference between the enthalpies of the saturated vapor and liquid, $h'' - h'$), has also been derived from the three equations of state for H_2O: IAPWS-95 [1, 2], Hill [7], and Saul and Wagner [8]. As a result, the uncertainty of the enthalpy of vaporization determined in this way is shown in Fig. 4 (see Sec. 2.2.4).

If one calculates $\Delta^{\mathrm{v}}h$ from the correlation equations of IAPWS for the enthalpy of the saturated vapor h'' and saturated liquid h' [13, 14] that are based on Osborne's measurements of several caloric properties [16, 17], these $\Delta^{\mathrm{v}}h$ values deviate from those calculated from IAPWS-95 by an amount that is clearly less than the uncertainty in $\Delta^{\mathrm{v}}h$ for IAPWS-95 given in Fig. 4.

2.2.4 Figures for Section 2

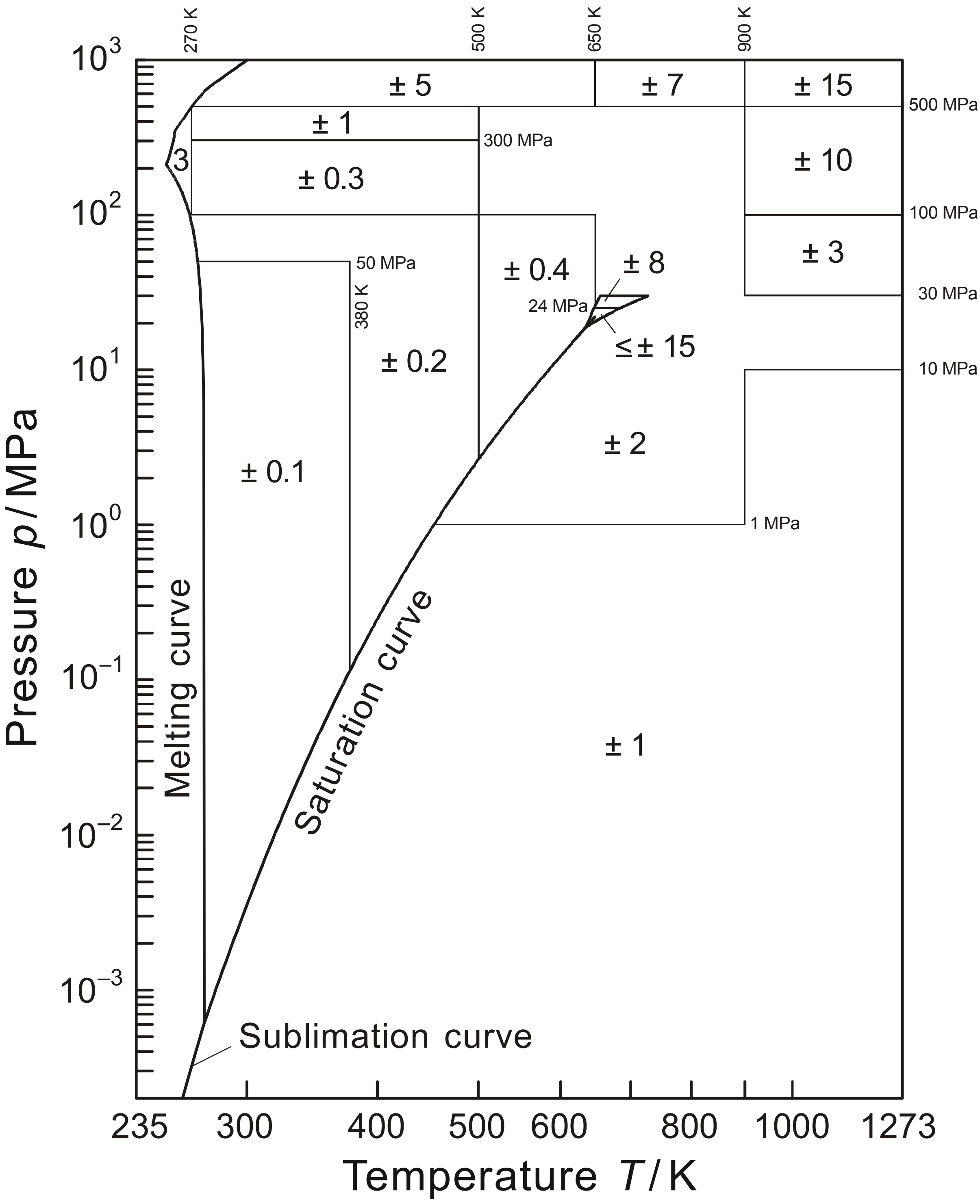

Figure 1 Absolute uncertainties Δh in the specific enthalpy h estimated for IAPWS-95 in kJ kg^{-1}. The positions of the lines separating the uncertainty regions, marked by the given values of temperature and pressure, are approximate. The enlarged critical region is bordered by the two isochors 527 kg m^{-3} and 144 kg m^{-3} and by the 30 MPa isobar.

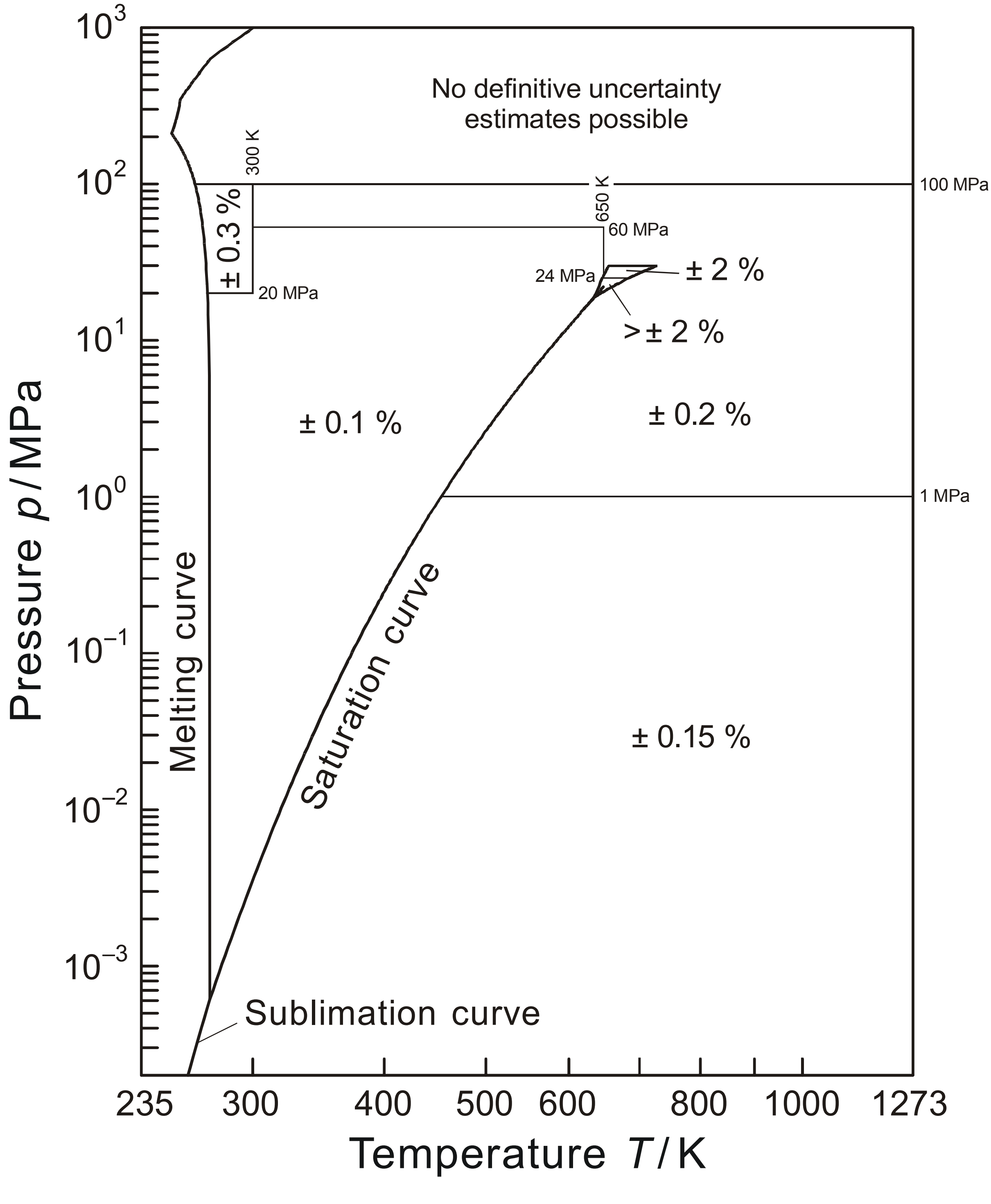

Figure 2 Percentage uncertainties $\Delta(\Delta h)/\Delta h$ in *isobaric* enthalpy differences Δh estimated for IAPWS-95. In the gas region, the uncertainty values correspond to enthalpy differences of $10 \le \Delta h/(\mathrm{kJ\ kg^{-1}}) \le 1000$. For isobaric enthalpy differences $\Delta h \ge 100\ \mathrm{kJ\ kg^{-1}}$ and $p \le 1$ MPa, the uncertainties are smaller than the values given, e.g., ± 0.1 % for $\Delta h = 500\ \mathrm{kJ\ kg^{-1}}$ and ± 0.05 % for $\Delta h = 1000\ \mathrm{kJ\ kg^{-1}}$. In the liquid region, the uncertainty values correspond to enthalpy differences of $1 \le \Delta h/(\mathrm{kJ\ kg^{-1}}) \le 10$. The positions of the lines separating the uncertainty regions, marked by the given values of temperature and pressure, are approximate. For the definition of the enlarged critical region, see Fig. 1.

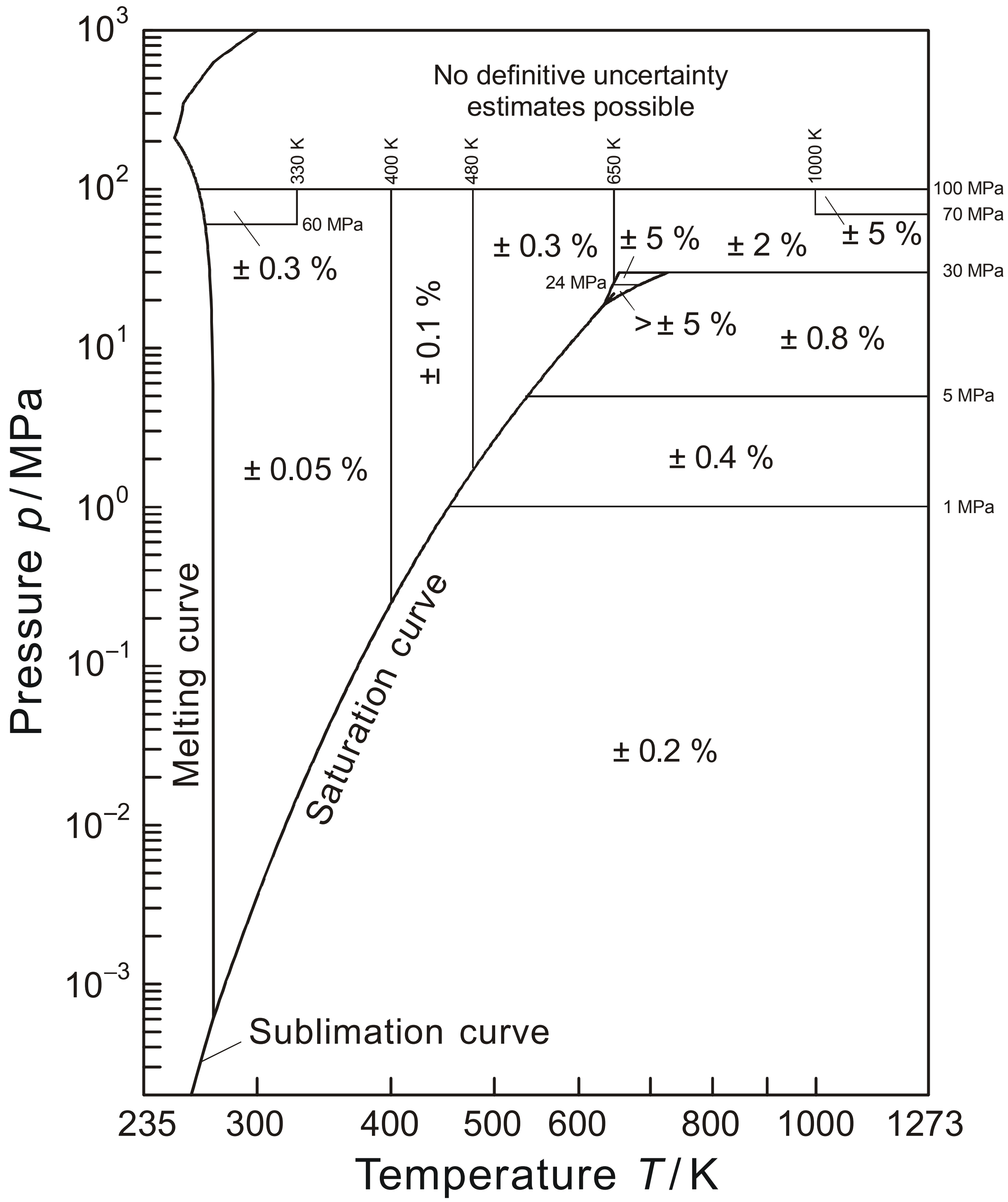

Figure 3 Percentage uncertainties $\Delta(\Delta h)/\Delta h$ in *adiabatic* enthalpy differences Δh estimated for IAPWS-95. The uncertainty values given relate to enthalpy differences along adiabatic reversible (isentropic) and adiabatic irreversible paths (steam turbines, boiler feed pumps, and hydroturbines). In the gas region, the uncertainty values correspond to enthalpy differences of $10 \le \Delta h/(\mathrm{kJ\ kg^{-1}}) \le 1000$, whereas in the liquid region, the uncertainty values correspond to enthalpy differences of $1 \le \Delta h/(\mathrm{kJ\ kg^{-1}}) \le 10$. The positions of the lines separating the uncertainty regions, marked by the given values of temperature and pressure, are approximate. For the definition of the enlarged critical region, see Fig. 1.

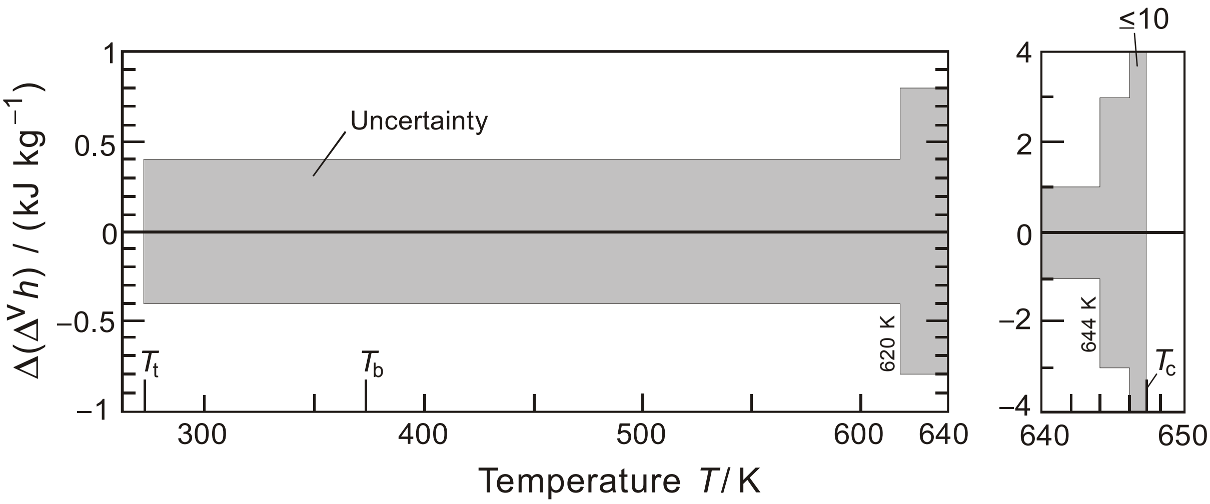

Figure 4 Absolute uncertainties $\Delta(\Delta^v h)$ in the enthalpy of vaporization $\Delta^v h$ estimated for IAPWS-95. These uncertainty values only correspond to temperatures 273.16 K $\leq T \leq$ 647 K (T_c = 647.096 K).

3 Uncertainty of the Industrial Formulation IAPWS-IF97 in Enthalpy

The industrial formulation IAPWS-IF97 was not developed based on experimental data of the various thermodynamic properties; rather, corresponding values calculated from IAPWS-95 were used as input values [4]. The deviation of enthalpy values calculated with IAPWS-IF97 from the corresponding values calculated with IAPWS-95 is very much smaller than the uncertainty of IAPWS-95 in enthalpy. Moreover, these small deviations oscillate rather regularly around the enthalpy values from IAPWS-95. Based on these facts, the uncertainty of the industrial formulation in specific enthalpy and in specific enthalpy differences has been determined by Gaussian error propagation applied to the corresponding uncertainties of IAPWS-95 and the deviations of IAPWS-IF97 values from those calculated with IAPWS-95.

3.1 Uncertainty in the Enthalpy of the Single-Phase Region

Figure 5 (see Sec. 3.4) shows the uncertainties Δh of the industrial formulation IAPWS-IF97 in the specific enthalpy h estimated as described at the beginning of Sec. 3. The enthalpy values calculated from IAPWS-IF97 relate to the same reference point as the enthalpy values from IAPWS-95, see the beginning of Sec. 2.2.1.

3.2 Uncertainties in Enthalpy Differences

For numerous technical applications, the uncertainty in enthalpy differences is needed. However, when calculating such uncertainties from the uncertainties of the enthalpies given in Fig. 5 (i.e., related to the enthalpy reference point of IAPWS-IF97), one obtains unrealistically large percentage uncertainties, particularly for relatively small enthalpy differences. Therefore, uncertainties $\Delta(\Delta h)$ of enthalpy differences Δh have been determined as described at the beginning of Sec. 3. Different sizes of Δh values were calculated in different directions, namely along isobars, isentropes, and differences in initial and final states corresponding to adiabatic irreversible paths representing steam turbines, boiler feed pumps, and hydroturbines. Enthalpy differences Δh between 10 kJ kg^{-1} and 1000 kJ kg^{-1} have been considered for the gas region, and between 1 kJ kg^{-1} and 10 kJ kg^{-1} for the liquid region. Apart from the uncertainties $\Delta(\Delta h)/\Delta h$ of isobaric enthalpy differences Δh in the gas region for pressures up to 1 MPa, all the other uncertainty values given do not significantly depend on the size of the enthalpy differences considered. As a result of all these comparisons, the estimated percentage uncertainties $\Delta(\Delta h)/\Delta h$ of enthalpy differences Δh calculated from the industrial formulation IAPWS-IF97 are summarized in Figs. 6 and 7 (see Sec. 3.4).

3.3 Uncertainties in Enthalpy of Vaporization

The uncertainty $\Delta(\Delta^{v}h)$ of the enthalpy of vaporization $\Delta^{v}h$ as the difference between the enthalpies of the saturated vapor and liquid, $h'' - h'$, has also been estimated as described at the beginning of Sec. 3. The result of estimating $\Delta(\Delta^{v}h)$ in this way is shown in Fig. 8 (see Sec. 3.4).

3.4 Figures for Section 3

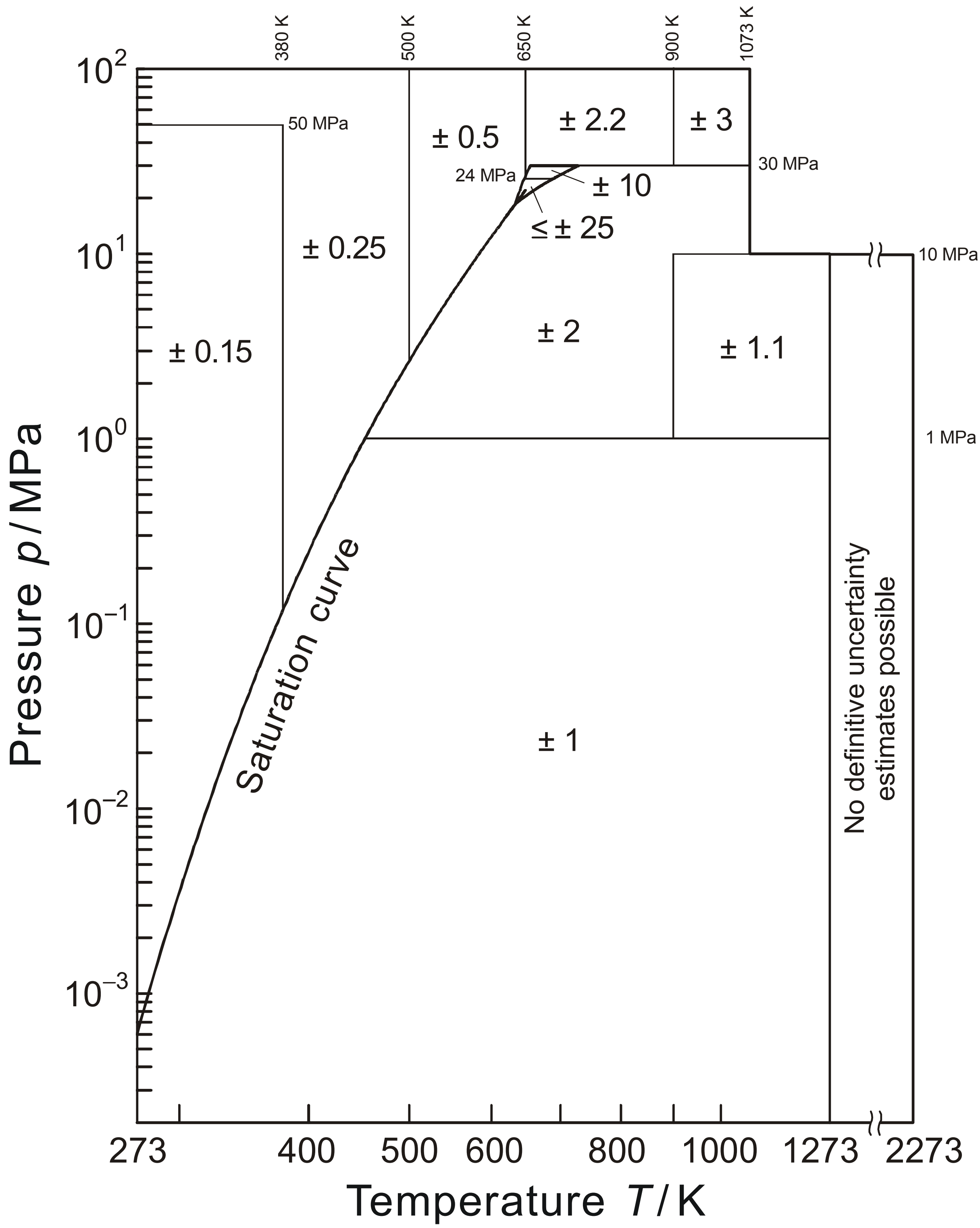

Figure 5 Absolute uncertainties Δh in the specific enthalpy h estimated for IAPWS-IF97 in kJ kg^{-1}. The positions of the lines separating the uncertainty regions, marked by the given values of temperature and pressure, are approximate. For the definition of the enlarged critical region, see Fig. 1.

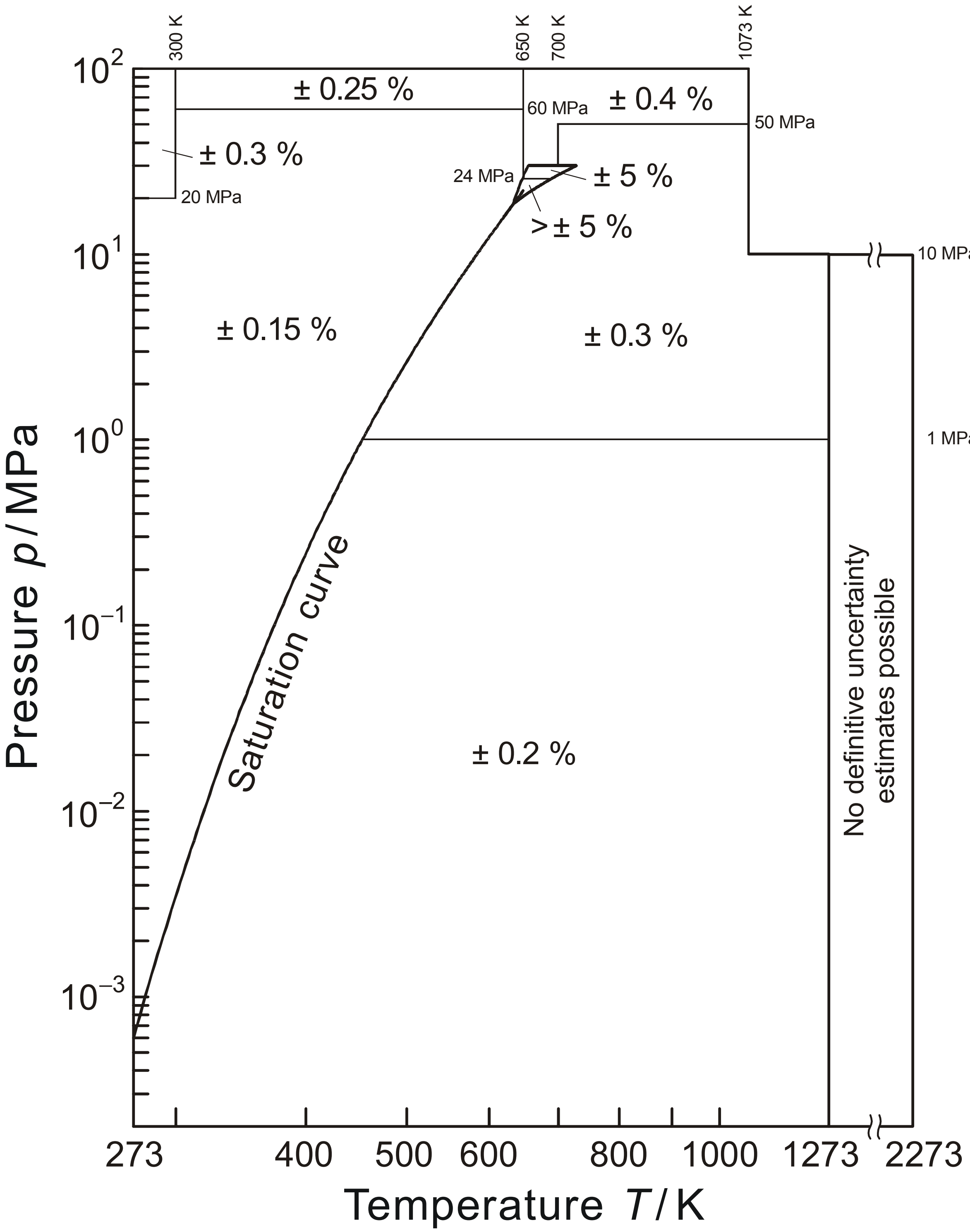

Figure 6 Percentage uncertainties $\Delta(\Delta h)/\Delta h$ in *isobaric* enthalpy differences Δh estimated for IAPWS-IF97. In the gas region, the uncertainty values correspond to enthalpy differences of $10 \leq \Delta h/(\mathrm{kJ\ kg^{-1}}) \leq 1000$. For isobaric enthalpy differences $\Delta h \geq 100\ \mathrm{kJ\ kg^{-1}}$ and $p \leq 1$ MPa, the uncertainties are smaller than the values given, e.g., ± 0.15 % for $\Delta h = 500\ \mathrm{kJ\ kg^{-1}}$ and ± 0.1 % for $\Delta h = 1000\ \mathrm{kJ\ kg^{-1}}$. In the liquid region, the uncertainty values correspond to enthalpy differences of $1 \leq \Delta h/(\mathrm{kJ\ kg^{-1}}) \leq 10$. The positions of the lines separating the uncertainty regions, marked by the given values of temperature and pressure, are approximate. For the definition of the enlarged critical region, see Fig. 1.

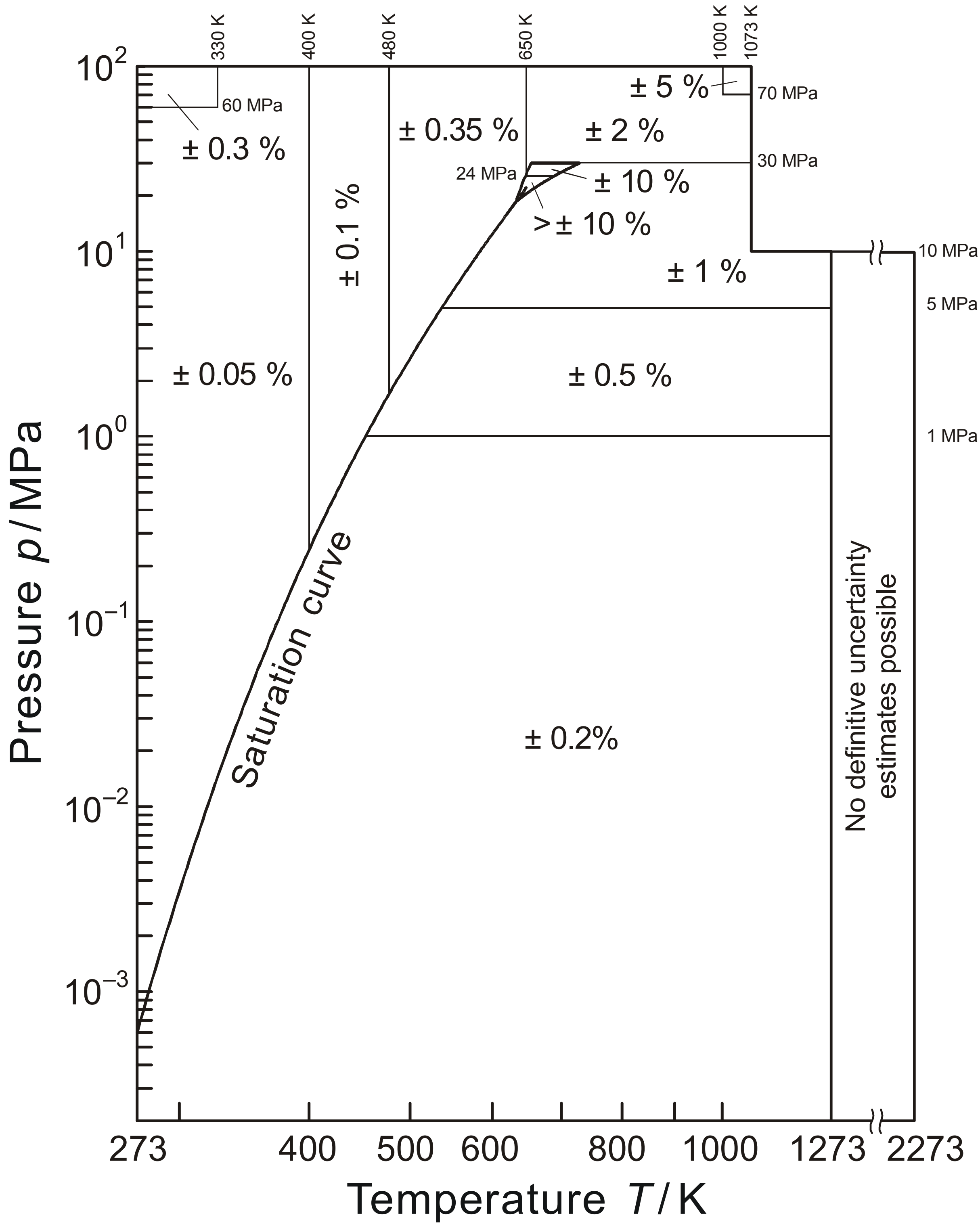

Figure 7 Percentage uncertainties $\Delta(\Delta h)/\Delta h$ in *adiabatic* enthalpy differences Δh estimated for IAPWS-IF97. The uncertainty values given relate to enthalpy differences along adiabatic reversible (isentropic) and adiabatic irreversible paths (steam turbines, boiler feed pumps, and hydroturbines). In the gas region, the uncertainty values correspond to enthalpy differences of $10 \le \Delta h/(\mathrm{kJ\ kg^{-1}}) \le 1000$, whereas in the liquid region, the uncertainty values correspond to enthalpy differences of $1 \le \Delta h/(\mathrm{kJ\ kg^{-1}}) \le 10$. The positions of the lines separating the uncertainty regions, marked by the given values of temperature and pressure, are approximate. For the definition of the enlarged critical region see, Fig. 1.

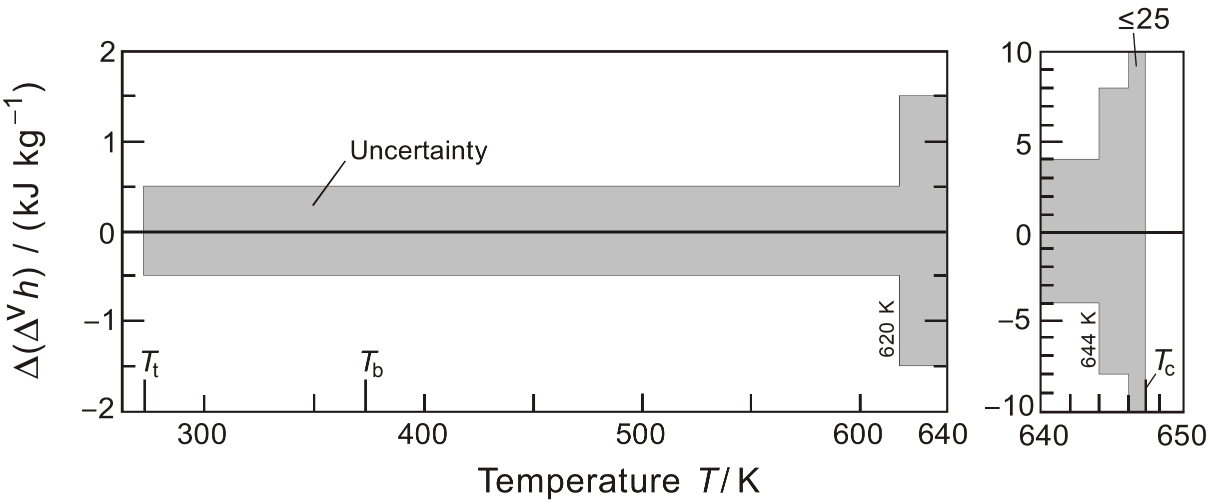

Figure 8 Absolute uncertainties $\Delta(\Delta^{\mathrm{v}}h)$ in the enthalpy of vaporization $\Delta^{\mathrm{v}}h$ estimated for IAPWS-IF97. These uncertainty values only correspond to temperatures $273.16\ \mathrm{K} \leq T \leq 647\ \mathrm{K}$ ($T_{\mathrm{c}} = 647.096\ \mathrm{K}$).

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